Part 1000 INTRODUCTION

1010 INTRODUCTION

1010 A. Scope and Application of Methods

The procedures described in these standards are intended for the examination of waters of a wide range of quality, including water suitable for domestic or industrial supplies, surface water, ground water, cooling or circulating water, boiler water, boiler feed water, treated and untreated municipal or industrial wastewater, and saline water. The unity of the fields of water supply, receiving water quality, and wastewater treatment and disposal is recognized by presenting methods of analysis for each constituent in a single section for all types of waters.

An effort has been made to present methods that apply generally. Where alternative methods are necessary for samples of different composition, the basis for selecting the most appropriate method is presented as clearly as possible. However, samples with extreme concentrations or otherwise unusual compositions or characteristics may present difficulties that preclude the direct use of these methods. Hence, some modification of a procedure may be necessary in specific instances. Whenever a procedure is modified, the analyst should state plainly the nature of modification in the report of results.

Certain procedures are intended for use with sludges and sediments. Here again, the effort has been to present methods of the widest possible application, but when chemical sludges or slurries or other samples of highly unusual composition are encountered, the methods of this manual may require modification or may be inappropriate.

Most of the methods included here have been endorsed by regulatory agencies. Procedural modification without formal approval may be unacceptable to a regulatory body.

The analysis of bulk chemicals received for water treatment is not included herein. A committee of the American Water Works Association prepares and issues standards for water treatment chemicals.

Part 1000 contains information that is common to, or useful in, laboratories desiring to produce analytical results of known quality, that is, of known accuracy and with known uncertainty in that accuracy. To accomplish this, apply the quality assurance methods described herein to the standard methods described elsewhere in this publication. Other sections of Part 1000 address laboratory equipment, laboratory safety, sampling procedures, and method development and validation, all of which provide necessary information.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1010 B. Statistics

1. Normal Distribution

If a measurement is repeated many times under essentially identical conditions, the results of each measurement, x, will be distributed randomly about a mean value (arithmetic average) because of uncontrollable or experimental error. If an infinite number of such measurements were to be accumulated, the individual values would be distributed in a curve similar to those shown in Figure 1010:1. The left curve illustrates the Gaussian or normal distribution, which is described precisely by the mean, μ, and the standard deviation, σ. The mean, or average, of the distribution is simply the sum of all values divided by the number of values so summed, i.e., $\mu = (\sum_i x_i)/n$. Because no measurements are repeated an infinite number of times, an *estimate* of the mean is made, using the same summation procedure but with n equal to a finite number of repeated measurements (10, or 20, or. . .). This estimate of μ is denoted by $\bar{x}$. The standard deviation of the normal distribution is defined as $\sigma = [\sum(x-\mu)^2/n]^{1/2}$. Again, the analyst can only estimate the standard deviation because the number of observations made is finite; the estimate of σ is denoted by s and is calculated as follows:

$$s = [\Sigma(x-\bar{x})^2/(n-1)]^{1/2}$$

The standard deviation fixes the width, or spread, of the normal distribution, and also includes a fixed fraction of the values making up the curve. For example, 68.27% of the measurements lie between $\mu \pm 1\sigma$, 95.45% between $\mu \pm 2\sigma$, and 99.70% between $\mu \pm 3\sigma$. It is sufficiently accurate to state that 95% of the values are within $\pm 2\sigma$ and 99% within $\pm 3\sigma$. When values are assigned to the $\pm\sigma$ multiples, they are confidence limits. For example, 10 ± 4 indicates that the confidence limits are 6 and 14, while values from 6 to 14 represent the confidence interval.

Another useful statistic is the standard error of the mean, σ_μ, which is the standard deviation divided by the square root of the number of values, or $\sigma/\sqrt{n}$. This is an estimate of the accuracy of the mean and implies that another sample from the same population would have a mean within some multiple of this. Multiples of this statistic include the same fraction of the values as stated above for σ. In practice, a relatively small number of average values is available, so the confidence intervals of the mean are expressed as $\bar{x} \pm ts/\sqrt{n}$ where t has the following values for 95% confidence intervals:

n	*t*
2	12.71
3	4.30

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

n	*t*
4	3.18
5	2.78
10	2.26
∞	1.96

The use of *t* compensates for the tendency of a small number of values to underestimate uncertainty. For $n > 15$, it is common to use $t = 2$ to estimate the 95% confidence interval.

Still another statistic is the relative standard deviation, σ/μ, with its estimate s/x, also known as the coefficient of variation (*CV*), which commonly is expressed as a percentage. This statistic normalizes the standard deviation and sometimes facilitates making direct comparisons among analyses that include a wide range of concentrations. For example, if analyses at low concentrations yield a result of 10 ± 1.5 mg/L and at high concentrations 100± 8 mg/L, the standard deviations do not appear comparable. However, the percent relative standard deviations are 100 (1.5/10) = 15% and 100 (8/100) = 8%, which indicate the smaller variability obtained by using this parameter.

2. Log-Normal Distribution

In many cases the results obtained from analysis of environmental samples will not be normally distributed, i.e., a graph of the data will be obviously skewed, as shown at right in Figure 1010:1, with the mode, median, and mean being distinctly different. To obtain a nearly normal distribution, convert the results to logarithms and then calculate *x* and *s*. The antilogarithms of these two values are estimates of the geometric mean and the geometric standard deviation, x_g and s_g.

3. Rejection of Data

Quite often in a series of measurements, one or more of the results will differ greatly from the other values. Theoretically, no result should be rejected, because it may indicate either a faulty technique that casts doubt on all results or the presence of a true variant in the distribution. In practice, reject the result of any analysis in which a known error has occurred. In environmental studies, extremely high and low concentrations of contaminants may indicate the existence of areas with problems or areas with no contamination, so they should not be rejected arbitrarily.

An objective test for outliers has been described.[1] If a set of data is ordered from low to high: $x_L, x_2 \ldots x_H$, and the average and standard deviation are calculated, then suspected high or low outliers can be tested by the following procedure. First, calculate the statistic *T* :

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$T = (x_H - \bar{x})/s \text{ for a high value, or}$$
$$T = (\bar{x} - x_L)/s \text{ for a low value.}$$

Second, compare the value of T with the value from Table 1010:I for either a 5% or 1% level of significance. If the calculated T is larger than the table value for the number of measurements, n, then the x_H or x_L is an outlier at that level of significance.

Further information on statistical techniques is available elsewhere.[2,3]

4. References

1. BARNETT, V. & T. LEWIS. 1984. Outliers in Statistical Data. John Wiley & Sons, New York, N.Y.
2. NATRELLA, M.G. 1963. Experimental Statistics. National Bur. Standards Handbook 91, Washington, D.C.
3. SNEDECOR, G.W. & W.G. COCHRAN. 1980. Statistical Methods. Iowa State University Press, Ames.

1010 C. Glossary

1. Definition of Terms

The purpose of this glossary is to define concepts, not regulatory terms; it is not intended to be all-inclusive.

Accuracy—combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to a true value.

Bias—consistent deviation of measured values from the true value, caused by systematic errors in a procedure.

Calibration check standard—standard used to determine the state of calibration of an instrument between periodic recalibrations.

Confidence coefficient—the probability, %, that a measurement result will lie within the confidence interval or between the confidence limits.

Confidence interval—set of possible values within which the true value will lie with a specified level of probability.

Confidence limit—one of the boundary values defining the confidence interval.

Detection levels—Various levels in increasing order are:

Instrumental detection level (IDL)—the constituent concentration that produces a signal greater than five times the signal/ noise ratio of the instrument. This is similar, in many respects, to ‘‘critical level’’ and ‘‘criterion of detection.’’ The latter level is stated as

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1.645 times the *s* of blank analyses.

Lower level of detection (LLD)—the constituent concentration in reagent water that produces a signal 2(1.645)*s* above the mean of blank analyses. This sets both Type I and Type II errors at 5%. Other names for this level are ‘‘detection level’’ and ‘‘level of detection’’ (LOD).

Method detection level (MDL)—the constituent concentration that, when processed through the complete method, produces a signal with a 99% probability that it is different from the blank. For seven replicates of the sample, the mean must be 3.14*s* above the blank where *s* is the standard deviation of the seven replicates. Compute MDL from replicate measurements one to five times the actual MDL. The MDL will be larger than the LLD because of the few replications and the sample processing steps and may vary with constituent and matrix.

Level of quantitation (LOQ)/minimum quantitation level (MQL)—the constituent concentration that produces a signal sufficiently greater than the blank that it can be detected within specified levels by good laboratories during routine operating conditions. Typically it is the concentration that produces a signal 10*s* above the reagent water blank signal.

Duplicate—usually the smallest number of replicates (two) but specifically herein refers to duplicate samples, i.e., two samples taken at the same time from one location.

Internal standard—a pure compound added to a sample extract just before instrumental analysis to permit correction for inefficiencies.

Laboratory control standard—a standard, usually certified by an outside agency, used to measure the bias in a procedure. For certain constituents and matrices, use National Institute of Standards and Technology (NIST) Standard Reference Materials when they are available.

Precision—measure of the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation.

Quality assessment—procedure for determining the quality of laboratory measurements by use of data from internal and external quality control measures.

Quality assurance—a definitive plan for laboratory operation that specifies the measures used to produce data of known precision and bias.

Quality control—set of measures within a sample analysis methodology to assure that the process is in control.

Random error—the deviation in any step in an analytical procedure that can be treated by standard statistical techniques.

Replicate—repeated operation occurring within an analytical procedure. Two or more analyses for the same constituent in an extract of a single sample constitute replicate extract analyses.

Surrogate standard—a pure compound added to a sample in the laboratory just before processing so that the overall efficiency of a method can be determined.

Type I error—also called alpha error, is the probability of deciding a constituent is present when

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

it actually is absent.

Type II error—also called beta error, is the probability of not detecting a constituent when it actually is present.

1020 QUALITY ASSURANCE

1020 A. Introduction

This section applies primarily to chemical analyses. See Section 9020 for quality assurance and control for microbiological analyses.

Quality assurance (QA) is the definitive program for laboratory operation that specifies the measures required to produce defensible data of known precision and accuracy. This program will be defined in a documented laboratory quality system.

The laboratory quality system will consist of a QA manual, written procedures, work instructions, and records. The manual should include a quality policy that defines the statistical level of confidence used to express the precision and bias of data, as well as the method detection limits. Quality systems, which include QA policies and all quality control (QC) processes, must be in place to document and ensure the quality of analytical data produced by the laboratory and to demonstrate the competence of the laboratory. Quality systems are essential for any laboratory seeking accreditation under state or federal laboratory certification programs. Included in quality assurance are quality control (Section 1020B) and quality assessment (Section 1020C). See Section 1030 for evaluation of data quality.

1. Quality Assurance Planning

Establish a QA program and prepare a QA manual or plan. Include in the QA manual and associated documents the following items[1-4]: cover sheet with approval signatures; quality policy statement; organizational structure; staff responsibilities; analyst training and performance requirements; tests performed by the laboratory; procedures for handling and receiving samples; sample control and documentation procedures; procedures for achieving traceability of measurements; major equipment, instrumentation, and reference measurement standards used; standard operating procedures (SOPs) for each analytical method; procedures for generation, approval, and control of policies and procedures; procedures for procurement of reference materials and supplies; procedures for procurement of subcontractors' services; internal quality control activities; procedures for calibration, verification, and maintenance of instrumentation and equipment; data-verification practices including interlaboratory comparison and proficiency-testing programs; procedures to be followed for feedback and corrective action whenever testing discrepancies are detected; procedures for exceptions that permit departure from documented policies; procedures for system and performance audits and reviews; procedures for assessing data precision and accuracy and determining method detection limits;

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

procedures for data reduction, validation, and reporting; procedures for records archiving; procedures and systems for control of the testing environment; and procedures for dealing with complaints from users of the data. Also define and include the responsibility for, and frequency of, management review and updates to the QA manual and associated documents.

On the title page, include approval signatures and a statement that the manual has been reviewed and determined to be appropriate for the scope, volume, and range of testing activities at the laboratory,[4] as well as an indication that management has made a commitment to assure that the quality systems defined in the QA manual are implemented and followed at all times.

In the QA manual, clearly specify and document the managerial responsibility, authority, quality goals, objectives, and commitment to quality. Write the manual so that it is clearly understood and ensures that all laboratory personnel understand their roles and responsibilities.

Implement and follow chain-of-custody procedures to ensure that chain of custody is maintained and documented for each sample. Institute procedures to permit tracing a sample and its derivatives through all steps from collection through analysis to reporting final results to the laboratory's client and disposal of the sample. Routinely practice adequate and complete documentation, which is critical to assure data defensibility and to meet laboratory accreditation/certification requirements, and ensure full traceability for all tests and samples.

Standard operating procedures (SOPs) describe the analytical methods to be used in the laboratory in sufficient detail that a competent analyst unfamiliar with the method can conduct a reliable review and/or obtain acceptable results. Include in SOPs, where applicable, the following items[2-5]: title of referenced, consensus test method; sample matrix or matrices; method detection level (MDL); scope and application; summary of SOP; definitions; interferences; safety considerations; waste management; apparatus, equipment, and supplies; reagents and standards; sample collection, preservation, shipment, and storage requirements; specific quality control practices, frequency, acceptance criteria, and required corrective action if acceptance criteria are not met; calibration and standardization; details on the actual test procedure, including sample preparation; calculations; qualifications and performance requirements for analysts (including number and type of analyses); data assessment/data management; references; and any tables, flowcharts, and validation or method performance data. At a minimum, validate a new SOP before use by first determining the MDL and performing an initial demonstration of capability using relevant regulatory guidelines.

Use and document preventive maintenance procedures for instrumentation and equipment. An effective preventive maintenance program will reduce instrument malfunctions, maintain more consistent calibration, be cost-effective, and reduce downtime. Include measurement traceability to National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) or commercially available reference materials certified traceable to NIST SRMs in the QA manual or SOP to establish integrity of the laboratory calibration and measurement program. Formulate document-control procedures, which are essential to data defensibility, to cover the complete process of document generation, approval, distribution, storage, recall, archiving, and disposal. Maintain logbooks for each test or procedure performed

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

with complete documentation on preparation and analysis of each sample, including sample identification, associated standards and QC samples, method reference, date/time of preparation/analysis, analyst, weights and volumes used, results obtained, and any problems encountered. Keep logbooks that document maintenance and calibration for each instrument or piece of equipment. Calibration procedures, corrective actions, internal quality control activities, performance audits, and data assessments for precision and accuracy (bias) are discussed in Section 1020B and Section 1020C.

Data reduction, validation, and reporting are the final steps in the data-generation process. The data obtained from an analytical instrument must first be subjected to the data reduction processes described in the applicable SOP before the final result can be obtained. Specify calculations and any correction factors, as well as the steps to be followed in generating the sample result, in the QA manual or SOP. Also specify all of the data validation steps to be followed before the final result is made available. Report results in standard units of mass, volume, or concentration as specified in the method or SOP. Report results below the MDL in accordance with the procedure prescribed in the SOP. Ideally, include a statement of uncertainty with each result. See references and bibliography for other useful information and guidance on establishing a QA program and developing an effective QA manual.

2. References

1. STANLEY, T.T. & S.S. VERNER. 1983. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans. EPA-600/4-83-004, U.S. Environmental Protection Agency, Washington, D.C.
2. QUALITY SYSTEMS COMMITTEE, NATIONAL ENVIRONMENTAL LABORATORY ACCREDITATION CONFERENCE. 1996. National Environmental Laboratory Accreditation Conference, 2nd Annual Meeting, Washington, D.C. [available online]. U.S. Environmental Protection Agency, Washington, D.C.
3. QUALITY SYSTEMS COMMITTEE, NATIONAL ENVIRONMENTAL LABORATORY ACCREDITATION CONFERENCE. 1997. National Environmental Laboratory Accreditation Conference, 2nd Interim Meeting, Bethesda, Md. [available online]. U.S. Environmental Protection Agency, Washington, D.C.
4. INTERNATIONAL ORGANIZATION FOR STANDARDIZATION. 1996. General Requirements for the Competence of Testing and Calibration Laboratories, ISO/IEC Guide 25-Draft Four. International Org. for Standardization, Geneva, Switzerland.
5. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1995. Guidance for the Preparation of Standard Operating Procedures (SOPs) for Quality-Related Documents. EPA QA/G-6, Washington, D.C.

3. Bibliography

DELFINO, J.J. 1977. Quality assurance in water and wastewater analysis laboratories. *Water Sew. Works* 124:79.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

INHORN, S.L., ed. 1978. Quality Assurance Practices for Health Laboratories. American Public Health Assoc., Washington, D.C.

STANLEY, T.W. & S.S. VERNER. 1983. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans. EPA-600/4-83-004, U.S. Environmental Protection Agency, Washington, D.C.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1997. Manual for the Certification of Laboratories Analyzing Drinking Water. EPA-815-B-97-001, U.S. Environmental Protection Agency, Washington, D.C.

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION. 1990. General Requirements for the Competence of Testing and Calibration Laboratories, ISO/IEC Guide 25. International Org. for Standardization, Geneva, Switzerland.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. National Environmental Laboratory Accreditation Conference (NELAC) Notice of Conference and Availability of Standards. *Federal Register* 59, No. 231.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1995. Good Automated Laboratory Practices. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

AMERICAN ASSOCIATION FOR LABORATORY ACCREDITATION. 1996. General Requirements for Accreditation. A2LA, American Assoc. Laboratory Accreditation, Gaithersburg, Md.

1020 B. Quality Control

Include in each analytical method or SOP the minimum required QC for each analysis. A good quality control program consists of at least the following elements, as applicable: initial demonstration of capability, ongoing demonstration of capability, method detection limit determination, reagent blank (also referred to as method blank), laboratory-fortified blank (also referred to as blank spike), laboratory-fortified matrix (also referred to as matrix spike), laboratory-fortified matrix duplicate (also referred to as matrix spike duplicate) or duplicate sample, internal standard, surrogate standard (for organic analysis) or tracer (for radiochemistry), calibration, control charts, and corrective action, frequency of QC indicators, QC acceptance criteria, and definitions of a batch. Section 1010 and Section 1030 describe calculations for evaluating data quality.

1. Initial Demonstration of Capability

The laboratory should conduct an initial demonstration of capability (IDC) at least once, by each analyst, before analysis of any sample, to demonstrate proficiency to perform the method and obtain acceptable results for each analyte. The IDC also is used to demonstrate that modifications to the method by the laboratory will produce results as precise and accurate as results produced by the reference method. As a minimum, include a reagent blank and at least four laboratory-fortified blanks (LFBs) at a concentration between 10 times the method detection level (MDL) and the midpoint of the calibration curve or other level as specified in the method.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Run the IDC after analyzing all required calibration standards. Ensure that the reagent blank does not contain any analyte of interest at a concentration greater than half the MQL or other level as specified in the method. See Section 1010C, for definition of MQL. Ensure that precision and accuracy (percent recovery) calculated for the LFBs are within the acceptance criteria listed in the method of choice. If no acceptance criteria are provided, use 80 to 120% recovery and ≤20% relative standard deviation (RSD), as a starting point. If details of initial demonstration of capability are not provided in the method of choice, specify and reference the method or procedure used for demonstrating capability.

2. Ongoing Demonstration of Capability

The ongoing demonstration of capability, sometimes referred to as a ‘‘laboratory control sample or laboratory control standard,’’ ‘‘quality control check sample,’’ or ‘‘laboratory-fortified blank,’’ is used to ensure that the laboratory remains in control during the period when samples are analyzed, and separates laboratory performance from method performance on the sample matrix. See ¶ 5 below for further details on the laboratory-fortified blank. Preferably obtain this sample from an external source (not the same stock as the calibration standards). Analyze QC check samples on a quarterly basis, at a minimum.

3. Method Detection Level Determination and Application

Determine the method detection level (MDL) for each analyte of interest and method to be used before data from any samples are reported, using the procedure described in Section 1030C. As a starting point for determining the concentration to use in MDL determination, use an estimate of five times the estimated detection limit. Perform MDL determinations as an iterative process. If calculated MDL is not within a factor of l0 of the value for the known addition, repeat determinations at a more suitable concentration. Conduct MDL determinations at least annually (or other specified frequency) for each analyte and method in use at the laboratory. Perform or verify MDL determination for each instrument. Perform MDL determinations over a period of at least 3 d for each part of the procedure. Calculate recoveries for MDL samples. Recoveries should be between 50 and 150% and %RSD values ≤ 20% or repeat the MDL determination. Maintain MDL and IDC data and have them available for inspection.

Apply the MDL to reporting sample results as follows:

- Report results below the MDL as ‘‘not detected.’’
- Report results between the MDL and MQL with qualification for quantitation.
- Report results above the MQL with a value and its associated error.

4. Reagent Blank

A reagent blank or method blank consists of reagent water (See Section 1080) and all reagents that normally are in contact with a sample during the entire analytical procedure. The reagent blank is used to determine the contribution of the reagents and the preparative analytical steps to error in the measurement. As a minimum, include one reagent blank with each sample set (batch) or on a 5% basis, whichever is more frequent. Analyze a blank after the daily

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

calibration standard and after highly contaminated samples if carryover is suspected. Evaluate reagent blank results for the presence of contamination. If unacceptable contamination is present in the reagent blank, identify and eliminate source of contamination. Typically, sample results are suspect if analyte(s) in the reagent blank are greater than the MQL. Samples analyzed with an associated contaminated blank must be re-prepared and re-analyzed. Refer to the method of choice for specific acceptance criteria for the reagent blank. Guidelines for qualifying sample results with consideration to reagent blank results are as follows:

- If the reagent blank is less than the MDL and sample results are greater than the MQL, then no qualification is required.
- If the reagent blank is greater than the MDL but less than the MQL and sample results are greater than the MQL, then qualify the results to indicate that analyte was detected in the reagent blank.
- If the reagent blank is greater than the MQL, further corrective action and qualification is required.

5. Laboratory-Fortified Blank

A laboratory-fortified blank is a reagent water sample to which a known concentration of the analytes of interest has been added. A LFB is used to evaluate laboratory performance and analyte recovery in a blank matrix. As a minimum, include one LFB with each sample set (batch) or on a 5% basis, whichever is more frequent. The definition of a batch is typically method-specific. Process the LFB through all of the sample preparation and analysis steps. Use an added concentration of at least 10 times the MDL, the midpoint of the calibration curve, or other level as specified in the method. Prepare the addition solution from a different reference source than that used for calibration. Evaluate the LFB for percent recovery of the added analytes. If LFB results are out of control, take corrective action, including re-preparation and re-analysis of associated samples if required. Use the results obtained for the LFB to evaluate batch performance, calculate recovery limits, and plot control charts (see ¶ 12 below). Refer to the method of choice for specific acceptance criteria for the LFB.

6. Laboratory-Fortified Matrix

A laboratory-fortified matrix (LFM) is an additional portion of a sample to which known amounts of the analytes of interest are added before sample preparation. The LFM is used to evaluate analyte recovery in a sample matrix. As a minimum, include one LFM with each sample set (batch) or on a 5% basis, whichever is more frequent. Add a concentration of at least 10 times the MRL, the midpoint of the calibration curve, or other level as specified in the method to the selected sample(s). Preferably use the same concentration as for the LFB to allow the analyst to separate the effect of matrix from laboratory performance. Prepare the LFM from a reference source different from that used for calibration. Make the addition such that sample background levels do not adversely affect the recovery (preferably adjust LFM concentrations if the known sample is above five times the background level). For example, if the sample contains the analyte of interest, make the LFM sample at a concentration equivalent to the concentration found in the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

known sample. Evaluate the results obtained for LFMs for accuracy or percent recovery. If LFM results are out of control, take corrective action to rectify the effect or use another method or the method of standard addition. Refer to the method of choice for specific acceptance criteria for LFMs until the laboratory develops statistically valid, laboratory-specific performance criteria. Base sample batch acceptance on results of LFB analyses rather than LFMs alone, because the matrix of the LFM sample may interfere with the method performance.

7. Laboratory-Fortified Matrix Duplicate/Duplicate Sample

A LFM duplicate is a second portion of the sample described in ¶ 6 above to which a known amount of the analyte of interest is added before sample preparation. If sufficient sample volume is collected, this second portion of sample is added and processed in the same way as the LFM. If sufficient sample volume is not collected to analyze a LFM duplicate, use an additional portion of an alternate sample to obtain results for a duplicate sample to gather data on precision. As a minimum, include one LFM duplicate or one duplicate sample with each sample set (batch) or on a 5% basis, whichever is more frequent. Evaluate the results obtained for LFM duplicates for precision and accuracy (precision alone for duplicate samples). If LFM duplicate results are out of control, take corrective action to rectify the effect or use another method or the method of standard addition. If duplicate results are out of control, reprepare and reanalyze the sample and take additional corrective action as needed (such as reanalysis of sample batch). Refer to the method of choice for specific acceptance criteria for LFM duplicates or duplicate samples until the laboratory develops statistically valid, laboratory-specific performance criteria. If no limits are included in the method of choice, calculate preliminary limits from initial demonstration of capability. Base sample batch acceptance on results of LFB analyses rather than LFM duplicates alone, because the matrix of the LFM sample may interfere with the method performance.

8. Internal Standard

Internal standards (IS) are used for organic analyses by GC/MS, some GC analyses, and some metals analyses by ICP/MS. An internal standard is an analyte included in each standard and added to each sample or sample extract/digestate just before sample analysis. Internal standards should mimic the analytes of interest but not interfere with the analysis. Choose an internal standard having retention time or mass spectrum separate from the analytes of interest and eluting in a representative area of the chromatogram. Internal standards are used to monitor retention time, calculate relative response, and quantify the analytes of interest in each sample or sample extract/digestate. When quantifying by the internal standard method, measure all analyte responses relative to this internal standard, unless interference is suspected. If internal standard results are out of control, take corrective action, including reanalysis if required. Refer to the method of choice for specific internal standards and their acceptance criteria.

9. Surrogates and Tracers

Surrogates are used for organic analyses; tracers are used for radiochemistry analyses. Surrogates and tracers are used to evaluate method performance in each sample. A surrogate

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

standard is a compound of a known amount added to each sample before extraction. Surrogates mimic the analytes of interest and are compound(s) unlikely to be found in environmental samples, such as fluorinated compounds or stable, isotopically labeled analogs of the analytes of interest. Tracers are a different isotope of the analyte or element of interest. Surrogates and tracers are introduced to samples before extraction to monitor extraction efficiency and percent recovery in each sample. If surrogate or tracer results are out of control, take corrective action, including repreparation and reanalysis if required. Refer to the method of choice for specific surrogates or tracers and their acceptance criteria, until the laboratory develops statistically valid, laboratory-specific performance criteria.

10. Calibration

a. Instrument calibration: Perform instrument calibration, as well as maintenance, according to instrument manual instructions. Use instrument manufacturer's recommendations for calibration. Perform instrument performance checks, such as those for GC/MS analyses, according to method or SOP instructions.

b. Initial calibration: Perform initial calibration with a minimum of three concentrations of standards for linear curves, a minimum of five concentrations of standards for nonlinear curves, or as specified by the method of choice. Choose a lowest concentration at the reporting limit, and highest concentration at the upper end of the calibration range. Ensure that the calibration range encompasses the analytical concentration values expected in the samples or required dilutions. Choose calibration standard concentrations with no more than one order of magnitude between concentrations.

Use the following calibration functions as appropriate: response factor for internal standard calibration, calibration factor for external standard calibration, or calibration curve. Calibration curves may be linear through the origin, linear not through the origin, or nonlinear through or not through the origin. Some nonlinear functions can be linearized through mathematical transformations, e.g., log. The following acceptance criteria are recommended for the various calibration functions.

If response factors or calibration factors are used, the calculated %RSD for each analyte of interest must be less than the method-specified value. When using response factors (e.g., for GC/MS analysis), evaluate the performance or sensitivity of the instrument for the analyte of interest against minimum acceptance values for the response factors. Refer to the method of choice for the calibration procedure and acceptance criteria on the response factors or calibration factors for each analyte.

If linear regression is used, use the minimum correlation coefficient specified in the method. If the minimum correlation coefficient is not specified, then a minimum value of 0.995 is recommended. Compare each calibration point to the curve and recalculate. If any recalculated values are not within the method acceptance criteria, identify the source of outlier(s) and correct before sample quantitation. Alternately, a method's calibration can be judged against a reference method by measuring the method's ''calibration linearity'' or %RSD among the ''response

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

factors'' at each calibration level or concentration.[2]

Use initial calibration, with any of the above functions (response factor, calibration factor, or calibration curve), for quantitation of the analytes of interest in samples. Use calibration verification, described in the next section, only for checks on the initial calibration and not for sample quantitation, unless otherwise specified by the method of choice. Perform initial calibration when the instrument is set up and whenever the calibration verification criteria are not met.

c. Calibration verification: Calibration verification is the periodic confirmation by analysis of a calibration standard that the instrument performance has not changed significantly from the initial calibration. Base this verification on time (e.g., every 12 h) or on the number of samples analyzed (e.g., after every 10 samples). Verify calibration by analyzing a single standard at a concentration near or at the midpoint of the calibration range. The evaluation of the calibration verification analysis is based either on allowable deviations from the values obtained in the initial calibration or from specific points on the calibration curve. If the calibration verification is out of control, take corrective action, including reanalysis of any affected samples. Refer to the method of choice for the frequency of calibration verification and the acceptance criteria for calibration verification.

11. QC Calculations

The following is a compilation of equations frequently used in QC calculations.

a. Initial calibrations:

Relative response factor (RRF):

$$RRF(x) = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

where:

RRF = relative response factor,
A = peak area or height of characteristic ion measured,
C = concentration,
is = internal standard, and
x = analyte of interest.

Response factor (RF):

$$RF(x) = \frac{A_x}{C_x}$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

where:

RF = response factor,
A = peak area or height,
C = concentration, and
x = analyte of interest.

Calibration factor (CF):

$$CF = \frac{\text{peak area (or height) of standards}}{\text{mass injected}}$$

Relative standard deviation (%RSD):

$$\%\ RSD = \frac{s}{\bar{x}} \times 100\%$$

$$s = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{(n-1)}}$$

where:

s = standard deviation,
n = total number of values,
x_i = each individual value used to calculate mean, and
x = mean of n values.

b. Calibration verification:

% Difference (%D) for response factor:

$$\%\ D = \frac{\overline{RF_i} - RF_c}{RF_i} \times 100\%$$

where:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$\overline{RF_i}$ = average RF or RRF from initial calibration, and
RF_c = relative RF or RRF from calibration verification standard.

% Difference (%D) for values:

$$\%D = \frac{\text{true value} - \text{found value}}{\text{true value}} \times 100\%$$

% Recovery:

$$\%\ \text{Recovery} = \frac{\text{found value}}{\text{true value}} \times 100\%$$

c. Laboratory-fortified blank (laboratory control sample):

$$\%\ \text{Recovery} = \frac{\text{found value}}{\text{true value}} \times 100\%$$

d. Surrogates:

$$\%\ \text{Recovery} = \frac{\text{quantity measured}}{\text{quantity added}} \times 100\%$$

e. Laboratory-fortified matrix (LFM) sample (matrix spike sample):

$$\%\ \text{Recovery} = \frac{(\text{LFM sample result} - \text{sample result})}{\text{known LFM added concentration}} \times 100\%$$

f. Duplicate sample:

Relative percent difference (RPD):

$$RPD = \frac{(\text{sample result} - \text{duplicate result})}{(\text{sample result} + \text{duplicate result})/2} \times 100\%$$

g. Method of standards addition:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\text{Sample concentrations} \times \text{mg/L} = \frac{S_2 \times V_1 \times C}{(S_1 - S_2) \times V_2}$$

where:

C = concentration of the standard solution, mg/L,
S_1 = signal for fortified portion,
S_2 = signal for unfortified portion,
V_1 = volume of standard addition, L, and
V_2 = volume of sample portion used for method of standard addition, L.

12. Control Charts

Two types of control charts commonly used in laboratories are as follows: accuracy or means charts for QC samples, including reagent blanks, laboratory control standards, calibration check standards, laboratory fortified blanks, laboratory fortified matrices, and surrogates; and precision or range charts, %RSD or relative percent difference (RPD), for replicate or duplicate analyses. These charts are essential tools for quality control. Computer-generated and maintained lists or databases with values, limits, and trending may be used as an alternate to control charts.

a. Accuracy (means) chart: The accuracy chart for QC samples is constructed from the average and standard deviation of a specified number of measurements of the analyte of interest. The accuracy chart includes upper and lower warning levels (WL) and upper and lower control levels (CL). Common practice is to use ±2*s* and ±3*s* limits for the WL and CL, respectively, where *s* represents standard deviation. These values are derived from stated or measured values for reference materials. The number of measurements, *n* or *n*-1, used to determine the standard deviation, *s*, is specified relative to statistical confidence limits of 95% for WLs and 99% for CLs. Set up an accuracy chart by using either the calculated values for mean and standard deviation or the percent recovery. Percent recovery is necessary if the concentration varies. Construct a chart for each analytical method. Enter results on the chart each time the QC sample is analyzed. Examples of control charts for accuracy are given in Figure 1020:1.

b. Precision (range) chart: The precision chart also is constructed from the average and standard deviation of a specified number of measurements of the analyte of interest. If the standard deviation of the method is known, use the factors from Table 1020:I to construct the central line and warning and control limits as in Figure 1020:2. Perfect agreement between replicates or duplicates results in a difference of zero when the values are subtracted, so the baseline on the chart is zero. Therefore for precision charts, only upper warning limits and upper control limits are meaningful. The standard deviation is converted to the range so that the analyst need only subtract the two results to plot the value on the precision chart. The mean range is computed as:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\overline{R} = D_2 s$$

the control limit as

$$CL = \overline{R} \pm 3s(R) = D_4 \overline{R}$$

and the warning limit as

$$WL = \overline{R} \pm 2s(R) = \overline{R} \pm 2/3(D_4 \overline{R} - \overline{R})$$

where:

D_2 = factor to convert s to the range (1.128 for duplicates, as given in Table 1020:I),
$s(R)$ = standard deviation of the range, and
D_4 = factor to convert mean range to $3s(R)$ (3.267 for duplicates, as given in Table 1020:I).

A precision chart is rather simple when duplicate analyses of a standard are used (Figure 1020:2). For duplicate analyses of samples, the plot will appear different because of the variation in sample concentration. If a constant relative standard deviation in the concentration range of interest is assumed, then R, D_4R etc., may be computed as above for several concentrations, a smooth curve drawn through the points obtained, and an acceptable range for duplicates determined. Figure 1020:3 illustrates such a chart. A separate table, as suggested below the figure, will be needed to track precision over time.

More commonly, the range can be expressed as a function of the relative standard deviation (coefficient of variation). The range can be normalized by dividing by the average. Determine the mean range for the pairs analyzed by

$$\overline{R} = (\Sigma R_i)/n$$

and the variance (square of the standard deviation) as

$$s_R^2 = (\Sigma R_i^2 - n\overline{R}^2)/(n - 1)$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Then draw lines on the chart at $R + 2s_R$ and $R + 3s_R$ and, for each duplicate analysis, calculate normalized range and enter the result on the chart. Figure 1020:4 is an example of such a chart.

c. Chart analyses: If the warning limits (WL) are at the 95% confidence level, 1 out of 20 points, on the average, would exceed that limit, whereas only 1 out of 100 would exceed the control limits (CL). Use the following guidelines, based on these statistical parameters, which are illustrated in Figure 1020:5 :

Control limit—If one measurement exceeds a CL, repeat the analysis immediately. If the repeat measurement is within the CL, continue analyses; if it exceeds the CL, discontinue analyses and correct the problem.

Warning limit—If two out of three successive points exceed a WL, analyze another sample. If the next point is within the WL, continue analyses; if the next point exceeds the WL, evaluate potential bias and correct the problem.

Standard deviation—If four out of five successive points exceed 1*s*, or are in decreasing or increasing order, analyze another sample. If the next point is less than 1*s*, or changes the order, continue analyses; otherwise, discontinue analyses and correct the problem.

Trending—If seven successive samples are on the same side of the central line, discontinue analyses and correct the problem.

The above considerations apply when the conditions are either above or below the central line, but not on both sides, e.g., four of five values must exceed either +1*s* or –1*s*. After correcting the problem, reanalyze the samples analyzed between the last in-control measurement and the out-of-control one.

Another important function of the control chart is assessment of improvements in method precision. In the accuracy and precision charts, if measurements never or rarely exceed the WL, recalculate the WL and CL using the 10 to 20 most recent data points. Trends in precision can be detected sooner if running averages of 10 to 20 are kept. Trends indicate systematic error; random error is revealed when measurements randomly exceed warning or control limits.

13. QC Evaluation for Small Sample Sizes

Small sample sizes, such as for field blanks and duplicate samples, may not be suitable for QC evaluation with control charts. QC evaluation techniques for small sample sizes are discussed elsewhere.[3]

14. Corrective Action

Quality control data outside the acceptance limits or exhibiting a trend are evidence of unacceptable error in the analytical process. Take corrective action promptly to determine and eliminate the source of the error. Do not report data until the cause of the problem is identified and either corrected or qualified. Example data qualifiers are listed in Table 1020:II. Qualifying data does not eliminate the need to take corrective actions, but allows for the reporting of data of known quality when it is either not possible or practical to reanalyze the sample(s). Maintain

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

records of all out-of-control events, determined causes, and corrective action taken. The goal of corrective action is not only to eliminate such events, but also to reduce repetition of the causes.

Corrective action begins with the analyst, who is responsible for knowing when the analytical process is out of control. The analyst should initiate corrective action when a QC check exceeds the acceptance limits or exhibits trending and should report an out-of-control event to the supervisor. Such events include QC outliers, hold-time failures, loss of sample, equipment malfunctions, and evidence of sample contamination. Recommended corrective action to be used when QC data are unacceptable are as follows:

- Check data for calculation or transcription error. Correct results if error occurred.
- Check to see if sample(s) was prepared and analyzed according to the approved method and SOP. If it was not, prepare and/or analyze again.
- Check calibration standards against an independent standard or reference material. If calibration standards fail, reprepare calibration standards and/or recalibrate instrument and reanalyze affected sample(s).
- If a LFB fails, reanalyze another laboratory-fortified blank.
- If a second LFB fails, check an independent reference material. If the second source is acceptable, reprepare and reanalyze affected sample(s).
- If a LFM fails, check LFB. If the LFB is acceptable, qualify the data for the LFM sample or use another method or the method of standard addition.
- If a LFM and the associated LFB fail, reprepare and reanalyze affected samples.
- If reagent blank fails, analyze another reagent blank.
- If second reagent blank fails, reprepare and reanalyze affected sample(s).
- If the surrogate or internal standard known addition fails and there are no calculation or reporting errors, reprepare and reanalyze affected sample(s).

If data qualifiers are used to qualify samples not meeting QC requirements, the data may or may not be usable for the intended purposes. It is the responsibility of the laboratory to provide the client or end-user of the data with sufficient information to determine the usability of qualified data.

15. References

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1990. Quality Assurance/Quality Control Guidance for Removal Activities, Sampling QA/QC Plan and Data Validation Procedures. EPA-540/G-90/004, U.S. Environmental Protection Agency, Washington, D.C.
2. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1997. 304h Streamlining Proposal Rule. *Federal Register*, March 28, 1997 (15034).
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. National Functional Guidelines for

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Inorganic Data Review. EPA-540/R-94-013, U.S. Environmental Protection Agency, Contract Laboratory Program, Office of Emergency and Remedial Response, Washington, D.C.

1020 C. Quality Assessment

Quality assessment is the process used to ensure that quality control measures are being performed as required and to determine the quality of the data produced by the laboratory. It includes such items as proficiency samples, laboratory intercomparison samples, and performance audits. These are applied to test the precision, accuracy, and detection limits of the methods in use, and to assess adherence to standard operating procedure requirements.

1. Laboratory Check Samples (Internal Proficiency)

The laboratory should perform self-evaluation of its proficiency for each analyte and method in use by periodically analyzing laboratory check samples. Check samples with known amounts of the analytes of interest supplied by an outside organization or blind additions can be prepared independently within the laboratory to determine percent recovery of the analytes of interest by each method.

In general, method performance will have been established beforehand; acceptable percent recovery consists of values that fall within the established acceptance range. For example, if the acceptable range of recovery for a substance is 85 to 115%, then the analyst is expected to achieve a recovery within that range on all laboratory check samples and to take corrective action if results are outside of the acceptance range.

2. Laboratory Intercomparison Samples

A good quality assessment program requires participation in periodic laboratory intercomparison studies. Commercial and some governmental programs supply laboratory intercomparison samples containing one or multiple constituents in various matrices. The frequency of participation in intercomparison studies should be adjusted relative to the quality of results produced by the analysts. For routine procedures, semi-annual analyses are customary. If failures occur, take corrective action and analyze laboratory check samples more frequently until acceptable performance is achieved.

3. Compliance Audits

Compliance audits are conducted to evaluate whether the laboratory meets the applicable requirements of the SOP or consensus method claimed as followed by the laboratory. Compliance audits can be conducted by internal or external parties. A checklist can be used to document the manner in which a sample is treated from time of receipt to final reporting of the result. The goal of compliance audits is to detect any deviations from the SOP or consensus method so that corrective action can be taken on those deviations. An example format for a

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

checklist is shown in Table 1020:III.

4. Laboratory Quality Systems Audits

A quality systems audit program is designed and conducted to address all program elements and provide a review of the quality system. Quality systems audits should be conducted by a qualified auditor(s) who is knowledgeable about the section or analysis being audited. Audit all major elements of the quality system at least annually. Quality system audits may be conducted internally or externally; both types should occur on a regular scheduled basis and should be handled properly to protect confidentiality. Internal audits are used for self-evaluation and improvement. External audits are used for accreditation as well as education on client requirements and for approval of the end use of the data. Corrective action should be taken on all audit findings and its effectiveness reviewed at or before the next scheduled audit.

5. Management Review

Review and revision of the quality system, conducted by laboratory management, is vital to its maintenance and effectiveness. Management review should assess the effectiveness of the quality system and corrective action implementation, and should include internal and external audit results, performance evaluation sample results, input from end user complaints, and corrective actions.

6. Bibliography

JARVIS, A.M. & L. SIU. 1981. Environmental Radioactivity Laboratory Intercomparison Studies Program. EPA-600/4-81-004, U.S. Environmental Protection Agency, Las Vegas, Nev.

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION. 1990. General Requirements for the Competence of Testing and Calibration Laboratories, ISO/IEC Guide 25. International Org. for Standardization, Geneva, Switzerland.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1996. Standard Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water. ASTM D2777-96, American Society Testing & Materials, West Conshohocken, Pa.

1030 DATA QUALITY

1030 A. Introduction

The role of the analytical laboratory is to produce measurement-based information that is technically valid, legally defensible, and of known quality. Quality assurance is aimed at optimizing the reliability of the measurement process. All measurements contain error, which may be systematic (with an unvarying magnitude) or random (with equal probability of being positive or negative and varying in magnitude). Determination of the systematic and random error components of an analytical method uniquely defines the analytical performance of that

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

method.[1] Quality control (QC) procedures identify and control these sources of error.

1. Measures of Quality Control

Random error (precision) and systematic error (bias) are two routine indicators of measurement quality used by analysts to assess validity of the analytical process. Precision is the closeness of agreement between repeated measurements. A measurement has acceptable precision if the random errors are low. Accuracy is the closeness of a measurement to the true value. A measurement is acceptably accurate when both the systematic and random errors are low. QC results outside the acceptance limits, as set by the data quality objectives, are evidence of an analytical process that may be out of control due to determinant errors such as contaminated reagents or degraded standards.

2. Measurement Error and Data Use

Measurement error, whether random or systematic, reduces the usability of laboratory data. As a measured value decreases, its relative error (e.g., relative standard deviation) may increase and its usable information decrease. Reporting tools, such as detection or quantitation limits, frequently are used to establish a lower limit on usable information content.

Laboratory data may be used for such purposes as regulatory monitoring, environmental decision-making, and process control. The procedures used to extract information for these different purposes vary and may be diametrically opposed. For example, a measurement for regulatory monitoring may be appropriately qualified when below the detection level because the error bar is relatively large and may preclude a statistically sound decision. Data collected over a period of time, however, may be treated by statistical methods to provide a statistically sound decision even when many of the data are below detection levels.[2]

3. The Analyst's Responsibility

The analyst must understand the measures of quality control and how to apply them to the data quality objectives of process control, regulatory monitoring, and environmental field studies. It is important that the quality objectives for the data be clearly defined and detailed before sample analysis so that the data will be technically correct and legally defensible.

4. Reference

1. YOUDEN, W.J. 1975. Statistical Manual of the Association of Official Analytical Chemists. Assoc. Official Analytical Chemists, Arlington, Va.
2. OSBORN, K.E. 1995. You Can't Compute with Less Thans. *Water Environment Laboratory Solutions*, Water Environment Federation, Alexandria, Va.

1030 B. Measurement Uncertainty

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Standard Methods for the Examination of Water and Wastewater

1. Introduction

Even with the fullest possible extent of correction, every measurement has error that is ultimately unknown and unknowable. The description of this unknown error is ‘‘measurement uncertainty.’’

Reporting uncertainty along with a measurement result is good practice, and may spare the user from making unwarranted or risky decisions based only on the measurement.

Whereas measurement error (E) is the actual, unknown deviation of the measurement (M) from the unknown true value (T), measurement uncertainty (U) is the state of knowledge about this unknown deviation, and is often expressed as U, as in $M \pm U$. U may be defined as an uncertainty expression.[1,2] This section concerns the definition of U, how to compute it, a recommendation for reporting uncertainty, the interpretation and scope of uncertainty, and other ways of expressing measurement uncertainty.

2. Error

A measurement can be related to the unknown true value and unknown measurement error as follows:

$$M = T + E$$

This is a simple additive relationship. There are other plausible relationships between M and E, such as multiplicative or arbitrary functional relationships, which are not discussed here.

Because E is unknown, M must be regarded as an uncertain measurement. In some practical situations, a value may be treated as known. T^* may be, for example, a published reference value, a traceable value, or a consensus value. The purpose of the substitution may be for convenience or because the measurement process that produced T^* has less bias or variation than the one that produced M. For example, based on the average of many measurements, a vessel might be thought to contain $T^* = 50$ µg/ L of salt in water. It then may be sampled and routinely measured, resulting in a reported concentration of $M = 51$ µg/L. The actual concentration may be $T = 49.9$ µg/L, resulting in $E = 51 - 49.9 = 1.1$ µg/L.

To generalize the nature of uncertainty, measurement error may be negligible or large in absolute terms (i.e., in the original units) or relative terms (i.e., unitless, $E \div T$ or T^*). The perceived acceptability of the magnitude of an absolute error depends on its intended use. For example, an absolute error of 1.1 µg/L may be inconsequential for an application where any concentration over 30 µg/L will be sufficient. However, if it is to be used instead as a standard for precision measurement (e.g., of pharmaceutical ingredients), 1.1 µg/L too much could be unacceptable.

3. Uncertainty

Reported measurement uncertainty will contain the actual measurement error with a stated

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

level of confidence. For example, if $M \pm U$ is presented as a 95% confidence interval, approximately 95% of the time, the measurement error E will fall within the range of $\pm U$.

4. Bias

Bias is the systematic component of error. It is defined as the signed deviation between the limiting average measured value and the true value being measured as the number of measurements in the average tends to infinity and the uncertainty about the average tends to zero. For example, the reason the T = 49.9 µg/L salt solution is thought to be T^* = 50 µg/L could be a bias, B = 0.1 µg/L. The ‘‘leftover’’ error, 1.1 – 0.1 = 1.0 µg/L, is the random component. This random component (also called stochastic error) changes with each measurement. The bias is fixed, and may be related to the laboratory method used to produce T^*. Usually, a recognized method will be used to produce or certify the traceable standard, a sample with a certificate stating the accepted true value T^*. The method may be the best method available or simply the most widely accepted method. It is chosen to have very low error, both bias and random. Such a traceable standard may be purchased from a standards organization such as NIST.

5. Bias and Random Variation

Measurement error, E, (and measurement uncertainty) can be split into two components, random and systematic:

$$E = Z + B$$

Random error, Z, is the component of the measurement error that changes from one measurement to the next, under certain conditions. Random measurement errors are assumed to be independent and have a distribution, often assumed to be Gaussian (i.e., they are normally distributed). The normal distribution of Z is characterized by the distribution mean, µ, and standard deviation, σ_E. In discussion of measurement error distribution, µ is assumed to be zero because any non-zero component is part of bias, by definition. The population standard deviation, σ_E, can be used to characterize the random component of measurement error because the critical values of the normal distribution are well known and widely available. For example, about 95% of the normal distribution lies within the interval $\mu \pm 2\sigma_E$. Hence, if there is no measurement bias, and measurement errors are independent and normally distributed, $M \pm 2\sigma_E$ (95% confidence, assumed normal) is a suitable way to report a measurement and its uncertainty. More generally, normal probability tables and statistical software give the proportion of the normal distribution and thus the % confidence gained that is contained within $\pm k\sigma_E$ for any value of scalar k.

Usually, however, the population standard deviation, σ_E, is not known and must be estimated by the sample standard deviation, s_E. This estimate of the standard deviation is based on multiple observations and statistical estimation. In this case, the choice of the scalar k must be based not

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

on the normal distribution function, but on the Student's *t* distribution, taking into account the number of degrees of freedom associated with s_E.

Systematic error (*B*) is all error that is not random, and typically is equated with bias. Systematic error also can contain outright mistakes (blunders) and lack of control (drifts, fluctuations, etc.).[3] In this manual, the terms ''systematic error'' and ''bias'' are used interchangeably.

Systematic uncertainty often is more difficult to estimate and make useful than is random uncertainty. Knowledge about bias is likely to be hard to obtain, and once obtained it is appropriately and likely to be exploited to make the measurement less biased. If measurement bias is known exactly (or nearly so), the user can subtract it from *M* to reduce total measurement error.

If measurement bias is entirely unknown, and could take on any value from a wide but unknown distribution of plausible values, users may adopt a worst-case approach and report an extreme bound, or they may simply ignore the bias altogether. For example, historical data may indicate that significant interlaboratory biases are present, or that every time a measurement system is cleaned, a shift is observed in QC measurements of standards. In the absence of traceable standards, it is hard for laboratory management or analysts to do anything other than ignore the potential problem.

The recommended practice is to conduct routine QA/QC measurements with a suite of internal standards. Plot measurements on control charts, and when an out-of-control condition is encountered, recalibrate the system with traceable standards. This permits the laboratory to publish a boundary on bias, assuming that the underlying behavior of the measurement system is somewhat predictable and acceptably small in scale in between QA/QC sampling (e.g., slow drifts and small shifts).

6. Repeatability, Reproducibility, and Sources of Bias and Variation

a. Sources and measurement: The sources of bias and variability in measurements are many; they include sampling error, sample preparation, interference by matrix or other measurement quantities/qualities, calibration error variation, software errors, counting statistics, deviations from method by analyst, instrument differences (e.g., chamber volume, voltage level), environmental changes (temperature, humidity, ambient light, etc.), contamination of sample or equipment (e.g., carryover and ambient contamination), variations in purity of solvent, reagent, catalyst, etc., stability and age of sample, analyte, or matrix, and warm-up or cool-down effects, or a tendency to drift over time.

The simplest strategy for estimating typical measurement bias is to measure a traceable (known) standard, then compute the difference between the measured value *M* and the known value *T*, assumed to be the true value being measured.

$$M - T = B + Z$$

The uncertainty in the measurement of the traceable standard is assumed to be small,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

although in practice there may be situations where this is not an appropriate assumption. If random measurement uncertainty is negligible (i.e., $Z \approx 0$), the difference, $M - T$, will provide an estimate of bias (B). If random uncertainty is not negligible, it can be observed and quantified by making a measurement repeatedly on the same test specimen (if the measurement process is not destructive). This may be part of a QA/QC procedure.

b. Repeatability: As quantified by the repeatability standard deviation (σ_{RPT}), repeatability is the minimal variability of a measurement system obtained by repeatedly measuring the same specimen while allowing *no* controllable sources of variability to affect the measurement. Repeatability also can be obtained by pooling sample standard deviations of measurements of J different specimens, as follows:

$$\sigma_{RPT} = \sqrt{\frac{1}{J} \cdot \sum_{i=1}^{J} \sigma_{RPT,i}^{2}}$$

Repeatability also is called ‘‘intrinsic measurement variability,’’ and is considered an approximate lower boundary to the measurement standard deviation that will be experienced in practice. The repeatability standard deviation sometimes is used to compute uncertainty intervals, $\pm U$, that can be referred to as ultimate instrument variability, based on the Student's t distribution function ($\pm U = \pm k s_{RPT}$).

Common sense and application experience demonstrate that repeatability is an overly optimistic estimate to report as measurement uncertainty for routine measurement. In routine use, measurements will be subject to many sources of bias and variability that are intentionally eliminated or restrained during a repeatability study. In routine use, uncertainty in both bias (B) and variability (Z) are greater.

c. Reproducibility: As quantified by the reproducibility standard deviation (σ_{RPD}), reproducibility is the variability of a measurement system obtained by repeatedly measuring a sample while allowing (or requiring) selected sources of bias or variability to affect the measurement. With σ_{RPD}, provide list of known applicable sources of bias and variability, and whether or not they were varied.

Barring statistical variation (i.e., variation in estimates of variability, such as the noisiness in sample standard deviations), the reproducibility standard deviation always is greater than the repeatability standard deviation, because it has additional components. Typically, one or more of the following is varied in a reproducibility study: instrument, analyst, laboratory, or day. Preferably design a study tailored to the particular measurement system (see 1030B.7). If the sample is varied, compute reproducibility standard deviations separately for each sample, then pool results if they are homogeneous. Treat factors varied in the study as random factors and assume them to be independent normal random variables with zero mean. However, this

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

assumption often can be challenged, because the sample and possibly the target populations may be small (they may even be identical), and there may be a question of ‘‘representativeness.’’ For example, six laboratories (or analysts, or instruments) may report usable measurements out of a total population of twenty capable of doing tandem mass spectrometry for a particular analyte and matrix. It is hard to know how representative the six are of the twenty, especially after a ranking and exclusion process that can follow a study, and whether the biases of the twenty are normally distributed (probably not discernible from six measurements, even if the six are representative).

It may be more appropriate to treat each factor with few, known factor values (i.e., choices such as laboratories) as fixed factors, to use the statistical term. Fixed factors have fixed effects. That is, each laboratory has a different bias, as might each analyst, each instrument, and each day, but these biases are not assumed to have a known (or knowable) distribution. Therefore, a small sample cannot be used to estimate distribution parameters, particularly a standard deviation. For example, assuming that variables are random, normal, and have zero mean may be inappropriate in an interlaboratory round-robin study. It must be assumed that every laboratory has some bias, but it is difficult to characterize the biases because of laboratory anonymity, the small number of laboratories contributing usable data, and other factors.

Because of these concerns about assumptions and the potential ambiguity of its definition, do not report reproducibility unless it is accompanied with study design and a list of known sources of bias and variability and whether or not they were varied.

7. Gage Repeatability and Reproducibility, and the Measurement Capability Study

Combining the concepts of repeatability and reproducibility, the Gage Repeatability and Reproducibility (Gage R&R) approach has been developed.[4] It treats all factors as random (including biases), and is based on the simplest nontrivial model:

$$Z = Z_{RPT} + Z_L$$

where:

Z_{RPT} = normally distributed random variable with mean equal to zero and variance equal to σ_{RPT}^2, and

Z_L = normally distributed random variable with mean equal to zero and with the variance of the factor (e.g., interlaboratory) biases, σ_L^2.

The overall measurement variation then is quantified by

$$\sigma_E = \sigma_{RPD} = \sqrt{\sigma_{RPT}^2 + \sigma_L^2}$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Estimates for σ_{RPT} and σ_{RPD} usually are obtained by conducting a nested designed study and analyzing variance components of the results. This approach can be generalized to reflect good practice in conducting experiments. The following measurement capability study (MCS) procedure is recommended. The objective of such studies is not necessarily to quantify the contribution of every source of bias and variability, but to study those considered to be important, through systematic error budgeting.

To perform a measurement capability study to assess measurement uncertainty through systematic error budgeting, proceed as follows:

Identify sources of bias and variation that affect measurement error. This can be done with a cause-and-effect diagram, perhaps with source categories of: equipment, analyst, method (i.e., procedure and algorithm), material (i.e., aspects of the test specimens), and environment.

Select sources to study, either empirically or theoretically. Typically, study sources that are influential, that can be varied during the MCS, and that cannot be eliminated during routine measurement. Select models for the sources. Treat sources of bias as fixed factors, and sources of variation as random factors.

Design and conduct the study, allowing (or requiring) the selected sources to contribute to measurement error. Analyze the data graphically and statistically (e.g., by regression analysis, ANOVA, or variance components analysis). Identify and possibly eliminate outliers (observations with responses that are far out of line with the general pattern of the data), and leverage points (observations that exert high, perhaps undue, influence).

Refine the models, if necessary (e.g., based on residual analysis), and draw inferences for future measurements. For random effects, this probably would be a confidence interval; for fixed effects, a table of estimated biases.

8. Other Assessments of Measurement Uncertainty

In addition to the strictly empirical MCS approach to assessing measurement uncertainty, there are alternative procedures, discussed below in order of increasing empiricism.

a. Exact theoretical: Some measurement methods are tied closely to exact first-principles models of physics or chemistry. For example, measurement systems that count or track the position and velocity of atomic particles can have exact formulas for measurement uncertainty based on the known theoretical behavior of the particles.

b. Delta method (law of propagation of uncertainty): If the measurement result can be expressed as a function of input variables with known error distributions, the distribution of the measurement result sometimes can be computed exactly.

c. Linearized: The mathematics of the delta method may be difficult, so a linearized form of $M = T + E$ may be used instead, involving a first-order Taylor series expansion about key variables that influence E:

$$(M + \delta M) = T + \delta M/\delta G_1 + \delta M/\delta G_2 + \delta M/\delta G_3 + ...$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

for sources G_1, G_2, G_3, etc. of bias and variation that are continuous variables (or can be represented by continuous variables). The distribution of this expression may be simpler to determine, as it involves the linear combination of scalar multiples of the random variables.

d. Simulation: Another use of the delta method is to conduct computer simulation. Again assuming that the distributions of measurement errors in input variables are known or can be approximated, a computer (i.e., Monte Carlo) simulation can obtain empirically the distribution of measurement errors in the result. Typically, one to ten thousand sets of random deviates are generated (each set has one random deviate for each variable), and the value of M is computed and archived. The archived distribution is an empirical characterization of the uncertainty in M.

e. Sensitivity study (designed experiment): If the identities and distributions of sources of bias and variation are known and these sources are continuous factors, but the functional form of the relationship between them and M is not known, an empirical sensitivity study (i.e., MCS) can be conducted to estimate the low-order coefficients ($\delta M/\delta G$) for any factor G. This will produce a Taylor series approximation to the δM, which can be used to estimate the distribution of δM, as in ¶ c above.

f. Random effects study: This is the nested MCS and variance components analysis described in ¶ 7 above.

g. Passive empirical (QA/QC-type data): An even more empirical and passive approach is to rely solely on QA/QC or similar data. The estimated standard deviation of sample measurements taken on many different days, by different analysts, using different equipment, perhaps in different laboratories can provide a useful indication of uncertainty.

9. Statements of Uncertainty

Always report measurements with a statement of uncertainty and the basis for the statement.

Develop uncertainty statements as follows:[4-6]

Involve experts in the measurement principles and use of the measurement system, individuals familiar with sampling contexts, and potential measurement users to generate a cause-and-effect diagram for measurement error, with sources of bias and variation (‘‘factors’’) identified and prioritized. Consult literature quantifying bias and variation. If needed, conduct one or more measurement capability studies incorporating those sources thought to be most important. In some cases, Gage R&R studies may be sufficient. These studies will provide ‘‘snapshot’’ estimates of bias and variation.

Institute a QA/QC program in which traceable or internal standards are measured routinely and the results are plotted on X and R control charts (or equivalent charts). React to out-of-control signals on the control charts. In particular, re-calibrate using traceable standards when the mean control chart shows a statistically significant change. Use the control charts, relevant literature, and the MCSs to develop uncertainty statements that involve both bias and variation.

10. References

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. YOUDEN, W.J. 1972. Enduring values. *Technometrics* 14:1.
2. HENRION, M. & B. FISCHHOFF. 1986. Assessing uncertainty in physical constant. *Amer. J. Phys.* 54:791.
3. CURRIE, L. 1995. Nomenclature in evaluation of analytical methods including detection and quantification capabilities. *Pure Appl. Chem.* 67:1699.
4. MANDEL, J. 1991. Evaluation and Control of Measurements. Marcel Dekker, New York, N.Y.
5. NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY. 1994. Technical note TN 1297. National Inst. Standards & Technology.
6. INTERNATIONAL STANDARDS ORGANIZATION. 1993. Guide to the Expression of Uncertainty in Measurement. International Standards Org., Geneva, Switzerland.

1030 C. Method Detection Level

1. Introduction

Detection levels are controversial, principally because of inadequate definition and confusion of terms. Frequently, the instrumental detection level is used for the method detection level and *vice versa*. Whatever term is used, most analysts agree that the smallest amount that can be detected above the noise in a procedure and within a stated confidence level is the detection level. The confidence levels are set so that the probabilities of both Type I and Type II errors are acceptably small.

Current practice identifies several detection levels (see 1010C), each of which has a defined purpose. These are the instrument detection level (IDL), the lower level of detection (LLD), the method detection level (MDL), and the level of quantitation (LOQ). Occasionally the instrument detection level is used as a guide for determining the MDL. The relationship among these levels is approximately IDL:LLD:MDL:LOQ = 1:2:4:10.

2. Determining Detection Levels

An operating analytical instrument usually produces a signal (noise) even when no sample is present or when a blank is being analyzed. Because any QA program requires frequent analysis of blanks, the mean and standard deviation become well known; the blank signal becomes very precise, i.e., the Gaussian curve of the blank distribution becomes very narrow. The IDL is the constituent concentration that produces a signal greater than three standard deviations of the mean noise level or that can be determined by injecting a standard to produce a signal that is five times the signal-to-noise ratio. The IDL is useful for estimating the constituent concentration or amount in an extract needed to produce a signal to permit calculating an estimated method detection level.

The LLD is the amount of constituent that produces a signal sufficiently large that 99% of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

the trials with that amount will produce a detectable signal. Determine the LLD by multiple injections of a standard at near zero concentration (concentration no greater that five times the IDL). Determine the standard deviation by the usual method. To reduce the probability of a Type I error (false detection) to 5%, multiply *s* by 1.645 from a cumulative normal probability table. Also, to reduce the probability of a Type II error (false nondetection) to 5%, double this amount to 3.290. As an example, if 20 determinations of a low-level standard yielded a standard deviation of 6 μg/L, the LLD is 3.29 × 6 = 20 μg/L.[1]

The MDL differs from the LLD in that samples containing the constituent of interest are processed through the complete analytical method. The method detection level is greater than the LLD because of extraction efficiency and extract concentration factors. The MDL can be achieved by experienced analysts operating well-calibrated instruments on a nonroutine basis. For example, to determine the MDL, add a constituent to reagent water, or to the matrix of interest, to make a concentration near the estimated MDL.[2] Prepare and analyze seven portions of this solution over a period of at least 3 d to ensure that MDL determination is more representative than measurements performed sequentially. Include all sample processing steps in the determination. Calculate the standard deviation and compute the MDL. The replicate measurements should be in the range of one to five times the calculated MDL. From a table of the one-sided *t* distribution select the value of *t* for 7 – 1 = 6 degrees of freedom and at the 99% level; this value is 3.14. The product 3.14 times *s* is the desired MDL.

Although the LOQ is useful within a laboratory, the practical quantitation limit (PQL) has been proposed as the lowest level achievable among laboratories within specified limits during routine laboratory operations.[3] The PQL is significant because different laboratories will produce different MDLs even though using the same analytical procedures, instruments, and sample matrices. The PQL is about five times the MDL and represents a practical and routinely achievable detection level with a relatively good certainty that any reported value is reliable.

3. Description of Levels

Figure 1030:1 illustrates the detection levels discussed above. For this figure it is assumed that the signals from an analytical instrument are distributed normally and can be represented by a normal (Gaussian) curve.[4] The curve labeled B is representative of the background or blank signal distribution. As shown, the distribution of the blank signals is nearly as broad as for the other distributions, that is $\sigma_B = \sigma_I = \sigma_L$. As blank analyses continue, this curve will become narrower because of increased degrees of freedom.

The curve labeled I represents the IDL. Its average value is located $k\sigma_B$ units distant from the blank curve, and *k* represents the value of *t* (from the one-sided *t* distribution) that corresponds to the confidence level chosen to describe instrument performance. For a 95% level and $n = 14$, $k = 1.782$ and for a 99% limit, $k = 2.68$. The overlap of the B and I curves indicates the probability of not detecting a constituent when it is present (Type II error).

The curve at the extreme right of Figure 1030:1 represents the LLD. Because only a finite

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

number of determinations is used for calculating the IDL and LLD, the curves are broader than the blank but are similar, so it is reasonable to choose $\sigma_I = \sigma_L$. Therefore, the LLD is $k\sigma_I + k\sigma_L = 2k\sigma_L$ from the blank curve.

4. References

1. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1983. Standard Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data. Designation D4210-83, American Soc. Testing & Materials, Philadelphia, Pa.
2. GLASER, J.A., D.L. FOERST, J.D. MCKEE, S.A. QUAVE & W.L. BUDDE. 1981. Trace analyses for wastewaters. *Environ. Sci. Technol.* 15:1426.
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1985. National Primary Drinking Water Standards: Synthetic Organics, Inorganics, and Bacteriologicals. 40 CFR Part 141; *Federal Register* 50: No. 219, November 13, 1985.
4. OPPENHEIMER, J. & R. TRUSSELL. 1984. Detection limits in water quality analysis. *In* Proc. Water Quality Technology Conference (Denver, Colorado, December 2-5, 1984). American Water Works Assoc., Denver, Colo.

1030 D. Data Quality Objectives

1. Introduction

Data quality objectives are systematic planning tools based on the scientific method. They are used to develop data collection designs and to establish specific criteria for the quality of data to be collected. The process helps planners identify decision-making points for data collection activities, to determine the decisions to be made based on the data collected, and to identify the criteria to be used for making each decision. This process documents the criteria for defensible decision-making before an environmental data collection activity begins.

2. Procedure

The data quality objective process comprises the stages explained in this section.

a. Stating the issue: Sometimes the reason for performing analyses is straightforward, e.g., to comply with a permit or other regulatory requirement. However, at times the reason is far more subjective; e.g., to gather data to support remedial decisions, or to track the changes in effluent quality resulting from process changes. A clear statement of the reason for the analyses is integral to establishing appropriate data quality objectives; this should include a statement of how the data are to be used, e.g., to determine permit compliance, to support decisions as to whether additional process changes will be necessary, etc.

b. Identifying possible decisions and actions: Initially, express the principal study question. For example: Is the level of contaminant A in environmental medium B higher than regulatory

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

level C? This example is relatively straightforward.

Other questions may be more complex, for example: How is aquatic life affected by discharges into receiving waters by publicly owned treatment works (POTWs)? Break such a question down into several questions that might then be used to develop several decisions; organize these questions in order of consensus priority of all participating parties.

Identify alternative actions, including the no-action alternative, that could result from the various possible answers to the principal study questions.

In the first example above, if the level of contaminant in the environmental medium is higher than the regulatory level, some cleanup or treatment action may be indicated. If it is lower, the no-action alternative may be indicated, or the study team may wish to look at other environmental media and regulatory levels.

Finally, combine the principal study question with alternative actions into a decision statement. For the first example, the decision statement might be: Determine whether the mean level of contaminant A in environmental medium B exceeds the regulatory level C and requires remediation.

A multi-tiered decision statement might be: . . . if not, determine whether the maximum level of contaminant A in environmental medium D exceeds the regulatory level E and requires remediation.

c. Identifying inputs: Identify the information needed to make the necessary decision. Inputs may include measurements (including measurements of physical and chemical characteristics), data sources (historical), applicable action levels, or health effects concerns.

Identify and list the sources of information: previous data, historical records, regulatory guidance, professional judgment, scientific literature, and new data. Evaluate qualitatively whether any existing data are appropriate for the study. Existing data will be evaluated quantitatively later. Identify information needed to establish the action level. Define the basis for setting the action levels: they may be based on regulatory thresholds or standards or may be derived from issue-specific considerations, such as risk analysis. Determine only the criteria that will be used to set the numerical value. The actual numerical action level is determined later.

Confirm that the appropriate measurement methods exist to provide the necessary data. Assure that there are analytical methods for the parameters or contaminants of interest, and that they are appropriate for the matrix to be sampled. Consider the samples to be collected and the analytical methods to determine the potential for matrix interferences for each method. Assure that the limits of the method (e.g., detection limit, quantitation limit, reporting limit) are appropriate for the matrix (e.g., drinking water, wastewater, groundwater, leachate, soil, sediment, hazardous waste) and the parameter to be measured. Ensure that a laboratory is available to perform the analyses; determine its capacity, turn-around time, data product, and cost. Include this information as input to the decision-making process.

d. Identifying study limits: Identify both the geographical area and the time frame to which the decision will apply. Also define the scale of decision-making. Identify the smallest, most appropriate subsets of the total population for which decisions will be made. These subsets could

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

be based on spatial or temporal boundaries. For example, while spatial boundaries of the issue may be a 300-acre site, samples may be collected from, and decisions made for, each square of a grid made up of 50-ft squares drawn on a site map. Also, while temporal boundaries of the issue may be identified (as the duration of storm events), samples may be collected at, and decisions made for, 2-h increments during a storm event. A decision resulting from this type of study might be to construct a stormwater bypass structure that would carry the first flow, which might contain the highest nutrient load, but would not necessarily carry the peak flow.

Identify any practical constraints on data collection. Identify any logistical issues that might interfere with the data-collection process, including seasonal conditions, daily variations, meteorological conditions, access conditions, availability of personnel, time, equipment, project budget, regulatory limits, appropriate analytical methods, matrix interferences, detection limits, reporting limits, site access limitations, and expertise.

e. Developing a decision rule: Define the parameter of interest, specify an action level, and integrate outputs from the previous data quality objective process steps into a single statement that describes a logical basis for choosing among alternative actions. A decision rule may be worded as follows, substituting case-specific information for the underlined words:

If *the factor of interest* within *the scale of decision making* is greater than *the action level*, then take *alternative action A*; otherwise take *alternative action B.*

The factor of interest is a descriptive measure (such as an instantaneous value, a mean, a median, or a proportion) that specifies the characteristic (such as calcium level in water, PCB level in soil, radon level in air) that the decision-maker would like to know about the statistical population affected by the potential decision (such as rivers or streams within a specific watershed, the specified depth of soil within a site boundary, or in basements or crawlspaces within a metropolitan area).

The scale of decision-making is the smallest, most appropriate subset for which separate decisions will be made (such as each stream segment/river mile or each square of a grid identified on a site map, or each section of township X, range Y of county Z).

The action level is a measurement threshold value of the parameter of interest that provides the criterion for choosing among alternative actions (such as a stream standard to protect aquatic life, a published regulatory standard, or a health-effects-related level).

Alternative action A is the alternative of choice if the action level is exceeded (such as initiate non-point-source controls, initiate cleanup of the soil to a specified depth, or distribute technical information to property owners). Noncompliance with the action level is the alternative hypothesis. (Either alternative action can be labeled A without making the decision rule any less valid.)

Alternative action B is the alternative of choice if the action level is not exceeded (such as continue routine monitoring, leave the soil in place, or provide a summary of the data collection activity to potential developers). Compliance with the action level is the null hypothesis that is generally the no-action alternative or baseline condition. Either alternative action can be labeled B without making the decision rule any less valid.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

f. Specifying limits on decision errors: Establish limits on the decision error that the decision-maker will tolerate. Use these limits to establish performance goals for design of the data collection activity. Base limits on the consequences of making a wrong decision.

Decision-makers are interested in knowing the true state of some feature of the environment. Environmental data can be only an estimate of this true state; decisions therefore are based on environmental data that are in some degree of error. The goal is to develop a data-collection design that reduces the chances of making a decision error to a level that is acceptable to the decision-maker. Sources of uncertainty include sample design error and measurement error; when combined, they represent the total study error.

Sample design error refers to the error inherent in using a portion of a population to represent the whole population. It is not practical, for example, to measure and record the concentration of an analyte at every point in a stream on a continuous basis; instead, measure analyte concentration at well-defined locations and time intervals to represent this analyte concentration continuum.

Measurement error refers to the error inherent in the measurement process. A measurement system does not measure, on a molecular level, the amount of an analyte in a sample; it measures an indicator of the amount of an analyte in a sample. This indicator might be the amount of a specific wavelength of light absorbed by a sample, the change in conductivity of a solution containing the analyte, or the amount of an analyte, in a gaseous or ionized form, that passes through a membrane.

Use data to choose between the one condition of the environment (the null hypothesis, H_0) and an alternative condition (the alternative hypothesis, H_a). A decision error occurs when the decision-maker rejects the null hypothesis when it is true (false-positive decision error) or fails to reject the null hypothesis when it is false (false-negative decision error).*#(1)

The null hypothesis usually is treated as the baseline condition that is presumed to be true in the absence of strong evidence to the contrary. Either condition may be selected as the null hypothesis, but if the null hypothesis is chosen carefully, it provides a way to guard against making the decision error that the decision-maker considers to have the more undesirable consequences.

While the possibility of a decision error never can be totally eliminated, it can be controlled by various means, including collecting a large number of samples (to control sampling design error), analyzing individual samples several times, or using more precise laboratory methods (to control measurement error). Better sampling designs also can be developed to collect data that more accurately represent the population of interest. Every study will use a different method of controlling decision errors, depending on the source of the largest components of total decision error in the data set and the ease of reducing those error components.

Reducing the probability of making decision errors generally increases study costs. In many cases, however, it is not necessary to control decision error within very small limits to meet the decision-maker's needs. If the consequences of decision errors are minor, a reasonable decision could be made on the basis of relatively crude data. If, on the other hand, consequences of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

decision errors are severe, the decision-maker will want to control sampling design and measurements within very small limits.

Factors used to judge data quality include precision, bias, representativeness, completeness, and comparability. Precision, bias, and completeness can be applied to the measurement (field and laboratory) system. Most analytical laboratories have systems to quantify these factors. Laboratory precision can be estimated through the analysis of laboratory replicates. Laboratory bias can be estimated by the analysis of standards, known additions, and performance evaluation (PE) samples. There is no common system in place to estimate field bias. A combination of field and laboratory completeness can be estimated through comparison of the number of analytical results provided by the laboratory with the number of analytical results specified in the sample design. Laboratory representativeness and comparability involve the analytical method used and the performance of the laboratory as compared to the performance of other laboratories (PE studies), which are not commonly quantified.

Precision, bias, representativeness, completeness, and comparability can be applied to the sample design: Precision would indicate how precisely this sample design reflects the total population. Bias would indicate how accurately this sample design reflects the total population. Representativeness would indicate to what extent the sample design is representative of the total population. Completeness would indicate how well the sample design reflects the complete population. Comparability would indicate the similarity of the sample design to other sample designs for similar situations. None of these usually is measured.

While data quality factors provide some insight into sample measurement errors, they do not provide any indication of sample design errors. These errors are additive, so that if precision were ±90%, bias were ±90%, and representativeness were ±90%, combined uncertainty could be up to ±27%:

$$(100\% \times 0.1) + (90\% \times 0.1) + (81\% \times 0.1) = 10\% + 9\% + 8\% = 27\%$$

Because most errors are not quantifiable, a study usually is designed with a balance between acceptable decision errors and acceptable study cost.

g. Optimizing the design for collection: Identify the most resource-effective design for the study that will achieve the data quality objectives (DQOs). Use statistical techniques to develop alternative data collection designs and evaluate their efficiency in meeting the DQOs. To develop the optimal study design, it may be necessary to work through this step more than once after revisiting previous steps of the process.

Review the DQO outputs and existing environmental data, develop general data collection design alternatives, and formulate the mathematical expressions needed to solve the design issue for each data collection design alternative. Develop the following three mathematical expressions:

- A method for testing the statistical hypothesis and a sample size formula that corresponds to the method (e.g., Student's *t* test),

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

- A statistical model that describes the relationship of the measured value to the ‘‘true’’ value. Often the model will describe the components of error or bias believed to exist in the measured value, and
- A cost function that relates the number of samples to the total cost of sampling and analysis.

Select the optimal sample size that satisfies the DQOs for each data collection design alternative. Using the mathematical expressions specified above, calculate the optimal sample size that satisfies the DQOs. If no design will meet the limits on decision errors within the budget or other constraints, relax one or more constraints by, for example, increasing the budget for sampling and analysis, increasing the width of the region of uncertainty, increasing the tolerable decision error rates, relaxing other project constraints such as the schedule, or changing the boundaries; it may be possible to reduce sampling and analysis costs by changing or eliminating subgroups that will require separate decisions.

Select the most resource-effective data collection design that satisfies all of the DQOs and document the operational details and theoretical assumptions of the selected design in the sampling and analysis plan.

3. Bibliography

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Guidance for the Data Quality Objectives Process. EPA QA/G-4, Quality Assurance Management Staff, U.S. Environmental Protection Agency, Washington, D.C.

1030 E. Checking Correctness of Analyses

The following procedures for checking correctness of analyses are applicable specifically to water samples for which relatively complete analyses are made.[1] These include pH, conductivity, total dissolved solids (TDS), and major anionic and cationic constituents that are indications of general water quality.

The checks described do not require additional laboratory analyses. Three of the checks require calculation of the total dissolved solids and conductivity from measured constituents. Sum concentrations (in milligrams per liter) of constituents to calculate the total dissolved solids are as follows:

$$\text{Total dissolved solids} = 0.6\,(\text{alkalinity*\#(2)}) + Na^{+} + K^{+} + Ca^{2+} + Mg^{2+} + Cl^{-} + SO_4^{2-} + SiO_3^{2-} + NO_3^{-} + F^{-}$$

Calculate electrical conductivity from the equation:

$$G = \lambda C - (k_1\lambda + k_2)\,(C)^{3/2}$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

where:

G = conductivity of salt solution,
C = concentration of salt solution,
λ = equivalent conductance of salt solution at infinite dilution,
k_1, k_2 = constants for relaxation of ion cloud effect and electrophoretic effect relative to ion mobility.[1]

1. Anion-Cation Balance[2]

The anion and cation sums, when expressed as milliequivalents per liter, must balance because all potable waters are electrically neutral. The test is based on the percentage difference defined as follows:

$$\% \text{ difference} = 100 \frac{\Sigma \text{ cations} - \Sigma \text{ anions}}{\Sigma \text{ cations} + \Sigma \text{ anions}}$$

and the typical criteria for acceptance are as follows:

Anion Sum *meq/L*	Acceptable Difference
0–3.0	±0.2 meq/L
3.0–10.0	± 2%
10.0–800	5%

2. Measured TDS = Calculated TDS[2]

The measured total dissolved solids concentration should be higher than the calculated one because a significant contributor may not be included in the calculation. If the measured value is less than the calculated one, the higher ion sum and measured value are suspect; the sample should be reanalyzed. If the measured solids concentration is more than 20% higher than the calculated one, the low ion sum is suspect and selected constituents should be reanalyzed. The acceptable ratio is as follows:

$$1.0 < \frac{\text{measured TDS}}{\text{calculated TDS}} < 1.2$$

3. Measured EC = Calculated EC

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

If the calculated electrical conductivity (EC) is higher than the measured value, reanalyze the higher ion sum. If the calculated EC is less than the measured one, reanalyze the lower ion sum. The acceptable ratio is as follows:

$$0.9 < \frac{\text{calculated EC}}{\text{measured EC}} < 1.1$$

Some electrical conductivity values for ions commonly found in water are given in Table 1030:I.

4. Measured EC and Ion Sums

Both the anion and cation sums should be $^1/_{100}$ of the measured EC value. If either of the two sums does not meet this criterion, that sum is suspect; reanalyze the sample. The acceptable criteria are as follows:

$$100 \times \text{anion (or cation) sum, meq/L} = (0.9–1.1)\ \text{EC}$$

5. Calculated TDS to EC Ratio

If the ratio of calculated TDS to conductivity falls below 0.55, the lower ion sum is suspect; reanalyze it. If the ratio is above 0.7, the higher ion sum is suspect; reanalyze it. If reanalysis causes no change in the lower ion sum, an unmeasured constituent, such as ammonia or nitrite, may be present at a significant concentration. If poorly dissociated calcium and sulfate ions are present, the TDS may be as high as 0.8 times the EC. The acceptable criterion is as follows:

$$\text{calculated TDS/conductivity} = 0.55–0.7$$

6. Measured TDS to EC Ratio

The acceptable criteria for this ratio are from 0.55 to 0.7. If the ratio of TDS to EC is outside these limits, measured TDS or measured conductivity is suspect; reanalyze.

A more complete exposition[3] of the above quality-control checks has been published.

7. References

1. ROSSUM, J.R. 1975. Checking the accuracy of water analyses through the use of conductivity. *J. Amer. Water Works Assoc.* 67:204.
2. FRIEDMAN, L.C. & D.E. ERDMANN. 1982. Quality Assurance Practices for Analyses of Water and Fluvial Sediments. Tech. Water Resources Inc., Book 5, Chapter A6. U.S. Government Printing Off., Washington, D.C.
3. OPPENHEIMER, J. & A.D. EATON. 1986. Quality control and mineral analysis. *In* Proc. Water Quality Technology Conference (Houston, Texas, December 8-11, 1985). American Water Works Assoc., Denver, Colo.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1040 METHOD DEVELOPMENT AND EVALUATION

1040 A. Introduction

Although standard methods are available from many nationally recognized sources, there may be occasions when they cannot be used or when no standard method exists for a particular constituent or characteristic. Therefore, method development may be required. Method development is the set of experimental procedures devised for measuring a known amount of a constituent in various matrices, in the case of chemical analyses; or a known characteristic (e.g., biological or toxicological) of various matrices.

1040 B. Method Validation

Whether an entirely new method is developed by accepted research procedures or an existing method is modified to meet special requirements, validation by a three-step process is required: determination of single-operator precision and bias, analysis of independently prepared unknown samples, and determination of method ruggedness.

1. Single-Operator Characteristics

This part of the validation procedure requires determining the method detection level (MDL) as in Section 1030; the bias of the method, i.e., the systematic error of the method; and the precision obtainable by a single operator, i.e., the random error introduced in using the method. To make these determinations, analyze at least 7 but preferably 10 or more portions of a standard at each of several concentrations in each matrix that may be used. Use one concentration at, or slightly above, the MDL and one relatively high so that the range of concentrations for which the method is applicable can be specified.

The use of several concentrations to determine bias and precision will reveal the form of the relationship between these method characteristics and the concentration of the substance, the characteristic toxicity of the substance, or the biological factor of interest. This relationship may be constant, linear, or curvilinear and is a significant characteristic of the method that should be explained clearly. Table 1040:I shows calculation of precision and bias for a single concentration in a single matrix from eight replicate analyses of a standard with a known concentration of 1.30 mg/L.

The bias is 0.49/8 = 0.06 mg/L and the precision is the square root of $0.2335/(8-1) = \sqrt{0.03336}$, or 0.18 mg/L (note that this is similar to the calculation for standard deviation).

2. Analysis of Unknown Samples

This step in the method validation procedure requires analysis of independently prepared standards where the value is unknown to the analyst. Analyze each unknown in replicate by

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

following the standard operating procedure for the method. The mean amount recovered should be within three standard deviations (*s*) of the mean value of the standard but preferably within 2 *s*.

Obtain the unknowns from other personnel in the analyst's laboratory using either purchased analytical-grade reagents or standards available from National Institute of Standards and Technology (NIST). If available for the particular constituent, performance evaluation samples from EPA-Cincinnati are particularly useful.

3. Method Ruggedness

A test of the ruggedness, i.e., stability of the result produced when steps in the method are varied, is the final validation step. It is especially important to determine this characteristic of a method if it is to be proposed as a standard or reference method. A properly conducted ruggedness test will point out those procedural steps in which rigor is critical and those in which some leeway is permissible.

The Association of Official Analytical Chemists[1] has suggested a method for this test in which eight separate analyses can be used to determine the effect of varying seven different steps in an analytical procedure. To illustrate, suppose the effect of changing the factors in Table 1040:II is to be determined. To make the determination, denote the nominal factors by capital letters A through G and the variations by the corresponding lower-case letters. Then set up a table of the factors as in Table 1040:III.

If combination 1 is analyzed, the result will be s. If combination 2 is analyzed, the result will be t, and so on until all eight combinations have been analyzed. To determine the effect of varying a factor, find the four results where the factor was nominal (all caps) and the four where it was varied (all lower case) and compare the averages of the two groups. For example, to compare the effect of changing C to c, use results (s + u + w + y)/4 and (t + v + x + z)/4. Calculate all seven pairs to get seven differences, which can then be ranked to reveal those with a significant effect on the results. If there is no outstanding difference, calculate the average and standard deviation of the eight results s through z. The standard deviation is a realistic estimate of the precision of the method. This design tests main effects, not interactions.

4. Equivalency Testing

After a new method has been validated by the procedures listed above, it may be prudent to test the method for equivalency to standard methods, unless none exist. This requires analysis of a minimum of three concentrations by the alternate and by the standard method. If the range of concentration is very broad, test more concentrations. Once an initial set of analyses (five or more) has been made at each chosen concentration, apply the following statistical steps:[2]

1. Test the distribution of data for normality and transform the data if necessary (Section 1010B).
2. Select an appropriate sample size based on an estimate of the standard deviation.[3]

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3. Test the variances of the two methods using the F-ratio statistic.
4. Test the average values of the two methods using a Student-*t* statistic.

An explanation of each of these steps with additional techniques and examples has been published.[4] Because the number of analyses can be very large, the calculations become complex and familiarity with basic statistics is necessary. A listing of standard, reference, and equivalent methods for water analysis is available.[5]

5. References

1. YOUDEN, W.J. & E.H. STEINER. 1975. Statistical Manual of AOAC. Assoc. Official Analytical Chemists, Washington, D.C.
2. WILLIAMS, L.R. 1985. Harmonization of Biological Testing Methodology: A Performance Based Approach in Aquatic Toxicology and Hazard Assessment. 8th Symp. ASTM STP 891, R.C. Bahner & D.J. Hansen, eds. American Soc. Testing & Materials, Philadelphia, Pa.
3. NATRELLA, M.G. 1963. Experimental Statistics. National Bureau of Standards Handbook 91, Washington, D.C.
4. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1983. Guidelines for Establishing Method Equivalency to Standard Methods. Rep. 600/X-83-037, Environmental Monitoring Systems Lab., Las Vegas, Nev.
5. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Guidelines establishing test procedures for the analysis of pollutants under the Clean Water Act. Final rule. 40 CFR Part 136; *Federal Register* 59:20:4504.

1040 C. Collaborative Testing

Once a new or modified method has been developed and validated it is appropriate to determine whether the method should be made a standard method. The procedure to convert a method to standard status is the collaborative test.[1] In this test, different laboratories use the standard operating procedure to analyze a select number of samples to determine the method's bias and precision as would occur in normal practice.

In planning for a collaborative test, consider the following factors: a precisely written standard operating procedure, the number of variables to be tested, the number of levels to be tested, and the number of replicates required. Because method precision is estimated by the standard deviation, which itself is the result of many sources of variation, the variables that affect it must be tested. These may include the laboratory, operator, apparatus, and concentration range.

1. Variables

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Test at least the following variables: Laboratory—Involve at least three different laboratories, although more are desirable to provide a better estimate of the standard deviation; Apparatus—Because model and manufacturer differences can be sources of error, analyze at least two replicates of each concentration per laboratory; Operators—To determine overall precision, involve at least six analysts with not more than two from each laboratory; Levels—If the method development has indicated that the relative standard deviation is constant, test three levels covering the range of the method. If it is not constant, use more levels spread uniformly over the operating range.

If matrix effects are suspected, conduct the test in each medium for which the method was developed. If this is not feasible, use appropriate grades of reagent water as long as this is stipulated in the resulting statement of method characteristics.

2. Number of Replicates

Calculate the number of replicates after the number of variables to be tested has been determined by using the formula:

$$r > 1 + (30/P)$$

where:

r = number of replicates and
P = the product of several variables.

The minimum number of replicates is two. As an example, if three levels of a substance are to be analyzed by single operators in six laboratories on a single apparatus, then P is calculated as follows:

$$P = 3 \times 1 \times 6 \times 1 = 18$$

and the number of replicates is

$$r > 1 + (30/18) > 2.7 \text{ or } r = 3.$$

3. Illustrative Collaborative Test

Send each of five laboratories four concentrations of a compound (4.3, 11.6, 23.4, and 32.7 mg/L) with instructions to analyze in triplicate using the procedure provided. Tabulate results as shown in Table 1040:IV below (the results for only one concentration are shown). Because there are no obviously aberrant values (use the method in Section 1010B to reject outliers), use all the data.

Calculate the average and standard deviation for each laboratory; use all 15 results to calculate a grand average and standard deviation. The difference between the average of each laboratory and the grand average reveals any significant bias, such as that shown for Laboratories 1 and 3. The difference between the grand average and the known value is the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

method bias, e.g., 33.0 – 32.7 = 0.3 mg/L or 0.9%. The relative standard deviation of the grand average (1.5 mg/L) is 4.5%, which is the method precision, and the *s* for each laboratory is the single-operator precision.

As noted in Table 1040:IV, the sum of the deviations from the known value for the laboratories was 1.3, so the average deviation (bias) was 1.3/5 = 0.26, rounded to 0.3, which is the same as the difference between the grand average and the known value.

For all four unknowns in this test, the percentage results indicated increasing bias and decreasing precision as the concentration decreased. Therefore, to describe the method in a formal statement, the precision would be given by a straight line with the formula $y = mx + b$; where y is the relative standard deviation, m is the slope of the line, x is the concentration, and b is the relative standard deviation at concentration = 0. The values found from the collaborative test are shown in Table 1040:V.

These results indicate that the method is acceptable. However, concentrations of less than about 10 mg/L require greater care in analysis.

4. Reference

1. YOUDEN, W.J. & E.H. STEINER. 1975. Statistical Manual of the AOAC. Assoc. Official Analytical Chemists, Washington, D.C.

1050 EXPRESSION OF RESULTS

1050 A. Units

This text uses the International System of Units (SI) and chemical and physical results are expressed in milligrams per liter (mg/L). See Section 7020D for expression of radioactivity results. Record only the significant figures. If concentrations generally are less than 1 mg/L, it may be more convenient to express results in micrograms per liter (µg/L). Use µg/L when concentrations are less than 0.1 mg/L.

Express concentrations greater than 10 000 mg/L in percent, 1% being equal to 10 000 mg/L when the specific gravity is 1.00. In solid samples and liquid wastes of high specific gravity, make a correction if the results are expressed as parts per million (ppm) or percent by weight:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\text{ppm by weight} = \frac{\text{mg/L}}{\text{sp gr}}$$

$$\% \text{ by weight} = \frac{\text{mg/L}}{10\,000 \times \text{sp gr}}$$

In such cases, if the result is given as milligrams per liter, state specific gravity.

The unit equivalents per million (epm), or the identical and less ambiguous term milligram-equivalents per liter, or milliequivalents per liter (me/L), can be valuable for making water treatment calculations and checking analyses by anion-cation balance.

Table 1050:I presents factors for converting concentrations of common ions from milligrams per liter to milliequivalents per liter, and vice versa. The term milliequivalent used in this table represents 0.001 of an equivalent weight. The equivalent weight, in turn, is defined as the weight of the ion (sum of the atomic weights of the atoms making up the ion) divided by the number of charges normally associated with the particular ion. The factors for converting results from milligrams per liter to milliequivalents per liter were computed by dividing the ion charge by weight of the ion. Conversely, factors for converting results from milliequivalents per liter to milligrams per liter were calculated by dividing the weight of the ion by the ion charge.

1050 B. Significant Figures

1. Reporting Requirements

To avoid ambiguity in reporting results or in presenting directions for a procedure, it is the custom to use ‘‘significant figures.’’ All digits in a reported result are expected to be known definitely, except for the last digit, which may be in doubt. Such a number is said to contain only significant figures. If more than a single doubtful digit is carried, the extra digit or digits are not significant. If an analytical result is reported as ‘‘75.6 mg/L,’’ the analyst should be quite certain of the ‘‘75,’’ but may be uncertain as to whether the ‘‘.6’’ should be .5 or .7, or even .4 or .8, because of unavoidable uncertainty in the analytical procedure. If the standard deviation were known from previous work to be ±2 mg/L, the analyst would have, or should have, rounded off the result to ‘‘76 mg/L’’ before reporting it. On the other hand, if the method were so good that a result of ‘‘75.61 mg/L’’ could have been conscientiously reported, then the analyst should not have rounded it off to 75.6.

Report only such figures as are justified by the accuracy of the work. Do not follow the all-too-common practice of requiring that quantities listed in a column have the same number of figures to the right of the decimal point.

2. Rounding Off

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Round off by dropping digits that are not significant. If the digit 6, 7, 8, or 9 is dropped, increase preceding digit by one unit; if the digit 0, 1, 2, 3, or 4 is dropped, do not alter preceding digit. If the digit 5 is dropped, round off preceding digit to the nearest even number: thus 2.25 becomes 2.2 and 2.35 becomes 2.4.

3. Ambiguous Zeros

The digit 0 may record a measured value of zero or it may serve merely as a spacer to locate the decimal point. If the result of a sulfate determination is reported as 420 mg/L, the report recipient may be in doubt whether the zero is significant or not, because the zero cannot be deleted. If an analyst calculates a total residue of 1146 mg/L, but realizes that the 4 is somewhat doubtful and that therefore the 6 has no significance, the answer should be rounded off to 1150 mg/L and so reported but here, too, the report recipient will not know whether the zero is significant. Although the number could be expressed as a power of 10 (e.g., 11.5×10^2 or 1.15×10^3), this form is not used generally because it would not be consistent with the normal expression of results and might be confusing. In most other cases, there will be no doubt as to the sense in which the digit 0 is used. It is obvious that the zeros are significant in such numbers as 104 and 40.08. In a number written as 5.000, it is understood that all the zeros are significant, or else the number could have been rounded off to 5.00, 5.0, or 5, whichever was appropriate. Whenever the zero is ambiguous, it is advisable to accompany the result with an estimate of its uncertainty.

Sometimes, significant zeros are dropped without good cause. If a buret is read as ‘‘23.60 mL,’’ it should be so recorded, and not as ‘‘23.6 mL.’’ The first number indicates that the analyst took the trouble to estimate the second decimal place; ‘‘23.6 mL’’ would indicate a rather careless reading of the buret.

4. Standard Deviation

If, for example, a calculation yields a result of 1449 mg/L or 1451 mg/L with a standard deviation of ±100 mg/L, report as 1449 ± 100 mg/L or 1451 ± 100 mg/L, respectively. Ensure that the number of significant figures in the standard deviation is not reduced if the value is 100 ± 1. This could cause incorrect rounding of data to 1400 or 1500 mg/L, respectively.

5. Calculations

As a practical operating rule, round off the result of a calculation in which several numbers are multiplied or divided to as few significant figures as are present in the factor with the fewest significant figures. Suppose that the following calculations must be made to obtain the result of an analysis:

$$\frac{56 \times 0.003\,462 \times 43.22}{1.684}$$

A ten-place calculator yields an answer of ‘‘4.975 740 998.’’ Round off this number to ‘‘5.0’’

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

because one of the measurements that entered into the calculation, 56, has only two significant figures. It was unnecessary to measure the other three factors to four significant figures because the ‘‘56’’ is the ‘‘weakest link in the chain’’ and limits accuracy of the answer. If the other factors were measured to only three, instead of four, significant figures, the answer would not suffer and the labor might be less.

When numbers are added or subtracted, the number that has the fewest decimal places, not necessarily the fewest significant figures, puts the limit on the number of places that justifiably may be carried in the sum or difference. Thus the sum

```
  0.0072
 12.02
  4.0078
 25.9
4886
4927.9350
```

must be rounded off to ‘‘4928,’’ no decimals, because one of the addends, 4886, has no decimal places. Notice that another addend, 25.9, has only three significant figures and yet it does not set a limit to the number of significant figures in the answer.The preceding discussion is necessarily oversimplified. The reader is referred to mathematical texts for more detailed discussion.

1060 COLLECTION AND PRESERVATION OF SAMPLES

1060 A. Introduction

It is an old axiom that the result of any testing method can be no better than the sample on which it is performed. It is beyond the scope of this publication to specify detailed procedures for the collection of all samples because of varied purposes and analytical procedures. Detailed information is presented in specific methods. This section presents general considerations, applicable primarily to chemical analyses. See appropriate sections for samples to be used in toxicity testing and microbiological, biological, and radiological examinations.

The objective of sampling is to collect a portion of material small enough in volume to be transported conveniently and yet large enough for analytical purposes while still accurately representing the material being sampled. This objective implies that the relative proportions or concentrations of all pertinent components will be the same in the samples as in the material being sampled, and that the sample will be handled in such a way that no significant changes in composition occur before the tests are made.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Frequently the objective of sampling and testing is to demonstrate whether continuing compliance with specific regulatory requirements has been achieved. Samples are presented to the laboratory for specific determinations with the sampler being responsible for collecting a valid and representative sample. Because of the increasing importance placed on verifying the accuracy and representativeness of data, greater emphasis is placed on proper sample collection, tracking, and preservation techniques. Often, laboratory personnel help in planning a sampling program, in consultation with the user of the test results. Such consultation is essential to ensure selecting samples and analytical methods that provide a sound and valid basis for answering the questions that prompted the sampling and that will meet regulatory and/or project-specific requirements.

This section addresses the collection and preservation of water and wastewater samples; the general principles also apply to the sampling of solid or semisolid matrices.

1. General Requirements

Obtain a sample that meets the requirements of the sampling program and handle it so that it does not deteriorate or become contaminated or compromised before it is analyzed.

Ensure that all sampling equipment is clean and quality-assured before use. Use sample containers that are clean and free of contaminants. Bake at 450°C all bottles to be used for organic-analysis sampling.

Fill sample containers without prerinsing with sample; prerinsing results in loss of any pre-added preservative and sometimes can bias results high when certain components adhere to the sides of the container. Depending on determinations to be performed, fill the container full (most organic compound determinations) or leave space for aeration, mixing, etc. (microbiological and inorganic analyses). If a bottle already contains preservative, take care not to overfill the bottle, as preservative may be lost or diluted. Except when sampling for analysis of volatile organic compounds, leave an air space equivalent to approximately 1% of the container volume to allow for thermal expansion during shipment.

Special precautions (discussed below) are necessary for samples containing organic compounds and trace metals. Because many constituents may be present at low concentrations (micrograms or nanograms per liter), they may be totally or partially lost or easily contaminated when proper sampling and preservation procedures are not followed.

Composite samples can be obtained by collecting over a period of time, depth, or at many different sampling points. The details of collection vary with local conditions, so specific recommendations are not universally applicable. Sometimes it is more informative to analyze numerous separate samples instead of one composite so that variability, maxima, and minima can be determined.

Because of the inherent instability of certain properties and compounds, composite sampling for some analytes is not recommended where quantitative values are desired (examples include oil and grease, acidity, alkalinity, carbon dioxide, chlorine residual, iodine, hexavalent chromium, nitrate, volatile organic compounds, radon-222, dissolved oxygen, ozone,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

temperature, and pH). In certain cases, such as for BOD, composite samples are routinely required by regulatory agencies. Refrigerate composite samples for BOD and nitrite.

Sample carefully to ensure that analytical results represent the actual sample composition. Important factors affecting results are the presence of suspended matter or turbidity, the method chosen for removing a sample from its container, and the physical and chemical changes brought about by storage or aeration. Detailed procedures are essential when processing (blending, sieving, filtering) samples to be analyzed for trace constituents, especially metals and organic compounds. Some determinations can be invalidated by contamination during processing. Treat each sample individually with regard to the substances to be determined, the amount and nature of turbidity present, and other conditions that may influence the results.

Carefully consider the technique for collecting a representative sample and define it in the sampling plan. For metals it often is appropriate to collect both a filtered and an unfiltered sample to differentiate between total and dissolved metals present in the matrix. Be aware that some metals may partially sorb to filters. Beforehand, determine the acid requirements to bring the pH to <2 on a separate sample. Add the same relative amount of acid to all samples; use ultrapure acid preservative to prevent contamination. Be sure that the dilution caused by acidifying is negligible or sufficiently reproducible for a dilution correction factor. When filtered samples are to be collected, filter them, if possible, in the field, or at the point of collection before preservation with acid. Filter samples in a laboratory-controlled environment if field conditions could cause error or contamination; in this case filter as soon as possible. Often slight turbidity can be tolerated if experience shows that it will cause no interference in gravimetric or volumetric tests and that its influence can be corrected in colorimetric tests, where it has potentially the greatest interfering effect. Sample collector must state whether or not the sample has been filtered.

Make a record of every sample collected and identify every bottle with a unique sample number, preferably by attaching an appropriately inscribed tag or label. Document sufficient information to provide positive sample identification at a later date, including the unique sample identification number, the name of the sample collector, the date, hour, exact location, and, if possible, sample type (e.g., grab or composite), and any other data that may be needed for correlation, such as water temperature, weather conditions, water level, stream flow, post-collection conditions, etc. If space for all pertinent information for label or attached tag is insufficient, record information in a bound sample log book at the sampling site at the time of sample collection. Use waterproof ink to record all information (preferably with black, non-solvent-based ink). Fix sampling points by detailed description in the sampling plan, by maps, or with the aid of stakes, buoys, or landmarks in a manner that will permit their identification by other persons without reliance on memory or personal guidance. Global positioning systems (GPS) also are used and supply accurate sampling position data. Particularly when sample results are expected to be involved in litigation, use formal ‘‘chain-of-custody’’ procedures (see ¶ B.2 below), which trace sample history from collection to final reporting.

Before collecting samples from distribution systems, flush lines with three to five pipe

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

volumes (or until water is being drawn from the main source) to ensure that the sample is representative of the supply, taking into account the volume of pipe to be flushed and the flow velocity. If the distribution system volume is unavailable, flush with tap fully open for at least 2 to 3 min before sampling. An exception to these guidelines, i.e., collecting a first draw sample, is when information on areas of reduced or restricted flow is desired or when samples for lead in drinking water are being collected.

Although well pumping protocols depend on the objectives of an investigation and other factors such as well characteristics and available equipment, a general rule is to collect samples from wells only after the well has been purged sufficiently (usually with three to ten well volumes) to ensure that the sample represents the groundwater. Purging stagnant water is critical. Sometimes it will be necessary to pump at a specified rate to achieve a characteristic drawdown, if this determines the zones from which the well is supplied; record purging rate and drawdown, if necessary. By using methods with minimal drawdown, purging volumes can be reduced significantly.

When samples are collected from a river or stream, observed results may vary with depth, stream flow, and distance from each shore. Selection of the number and distribution of sites at which samples should be collected depends on study objectives, stream characteristics, available equipment, and other factors. If equipment is available, take an integrated sample from top to bottom in the middle of the main channel of the stream or from side to side at mid-depth. If only grab or catch samples can be collected, preferably take them at various points of equal distance across the stream; if only one sample can be collected, take it in the middle of the main channel of the stream and at mid-depth. Integrated samples are described further in ¶ B.1*c* below.

Rivers, streams, lakes, and reservoirs are subject to considerable variations from normal causes such as seasonal stratification, diurnal variations, rainfall, runoff, and wind. Choose location, depth, and frequency of sampling depending on local conditions and the purpose of the investigation.

Use the following examples for general guidance. Avoid areas of excessive turbulence because of potential loss of volatile constituents and of potential presence of denser-than-air toxic vapors. Avoid sampling at weirs if possible because such locations tend to favor retrieval of lighter-than-water, immiscible compounds. Generally, collect samples beneath the surface in quiescent areas and open sampling container below surface with the mouth directed toward the current to avoid collecting surface scum unless oil and grease is a constituent of interest; then collect water at the surface. If composite samples are required, ensure that sample constituents are not lost during compositing because of improper handling of portions being composited. If samples will be analyzed for organic constituents, refrigerate composited portions. Do not composite samples for VOC analysis because some of the components will be lost through volatilization.

2. Safety Considerations

Because sample constituents may be toxic, take adequate precautions during sampling and sample handling. Toxic substances can enter through the skin and eyes and, in the case of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

vapors, also through the lungs. Ingestion can occur via direct contact of toxic materials with foods or by adsorption of vapors onto foods. Precautions may be limited to wearing gloves or may include coveralls, aprons, or other protective apparel. Often, the degree of protection provided by chemical protective clothing (CPC) is specific for different manufacturers and their product models[1]; ensure that the clothing chosen will offer adequate protection. Always wear eye protection (e.g., safety glasses with side shields or goggles). When toxic vapors may be present, sample only in well-ventilated areas, or use an appropriate respirator or self-contained breathing apparatus. In a laboratory, open sample containers in a fume hood. Never have food in the laboratory, near samples, or near sampling locations; always wash hands thoroughly before handling food.[2]

Always prohibit eating, drinking, or smoking near samples, sampling locations, and in the laboratory. Keep sparks, flames, and excessive heat sources away from samples and sampling locations. If flammable compounds are suspected or known to be present and samples are to be refrigerated, use only specially designed *explosion-proof* refrigerators.[2]

Collect samples safely, avoiding situations that may lead to accidents. When in doubt as to the level of safety precautions needed, consult a knowledgeable industrial hygienist or safety professional. Samples with radioactive contaminants may require other safety considerations; consult a health physicist.

Label adequately any sample known or suspected to be hazardous because of flammability, corrosivity, toxicity, oxidizing chemicals, or radioactivity, so that appropriate precautions can be taken during sample handling, storage, and disposal.

3. References

1. FORSBERG K. & L.H. KEITH. 1998. Instant Gloves and CPC Database. Instant Reference Sources, Inc. Austin, Tex.
2. WATER POLLUTION CONTROL FEDERATION. 1986. Removal of Hazardous Wastes in Wastewater Facilities—Halogenated Organics. Manual of Practice FD-11, Water Pollution Control Fed., Alexandria, Va.

1060 B. Collection of Samples

1. Types of Samples

a. Grab samples: Grab samples are single samples collected at a specific spot at a site over a short period of time (typically seconds or minutes). Thus, they represent a ‘‘snapshot’’ in both space and time of a sampling area. Discrete grab samples are taken at a selected location, depth, and time. Depth-integrated grab samples are collected over a predetermined part or the entire depth of a water column, at a selected location and time in a given body of water.

A sample can represent only the composition of its source at the time and place of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

collection. However, when a source is known to be relatively constant in composition over an extended time or over substantial distances in all directions, then the sample may represent a longer time period and/or a larger volume than the specific time and place at which it was collected. In such circumstances, a source may be represented adequately by single grab samples. Examples are protected groundwater supplies, water supplies receiving conventional treatment, some well-mixed surface waters, but rarely, wastewater streams, rivers, large lakes, shorelines, estuaries, and groundwater plumes.

When a source is known to vary with time, grab samples collected at suitable intervals and analyzed separately can document the extent, frequency, and duration of these variations. Choose sampling intervals on the basis of the expected frequency of changes, which may vary from as little as 5 min to as long as 1 h or more. Seasonal variations in natural systems may necessitate sampling over months. When the source composition varies in space (i.e., from location to location) rather than time, collect samples from appropriate locations that will meet the objectives of the study (for example, upstream and downstream from a point source, etc.).

The same principles apply to sampling wastewater sludges, sludge banks, and muds, although these matrices are not specifically addressed in this section. Take every possible precaution to obtain a representative sample or one conforming to a sampling program.

b. Composite samples: Composite samples should provide a more representative sampling of heterogeneous matrices in which the concentration of the analytes of interest may vary over short periods of time and/or space. Composite samples can be obtained by combining portions of multiple grab samples or by using specially designed automatic sampling devices. Sequential (time) composite samples are collected by using continuous, constant sample pumping or by mixing equal water volumes collected at regular time intervals. Flow-proportional composites are collected by continuous pumping at a rate proportional to the flow, by mixing equal volumes of water collected at time intervals that are inversely proportional to the volume of flow, or by mixing volumes of water proportional to the flow collected during or at regular time intervals.

Advantages of composite samples include reduced costs of analyzing a large number of samples, more representative samples of heterogeneous matrices, and larger sample sizes when amounts of test samples are limited. Disadvantages of composite samples include loss of analyte relationships in individual samples, potential dilution of analytes below detection levels, increased potential analytical interferences, and increased possibility of analyte interactions. In addition, use of composite samples may reduce the number of samples analyzed below the required statistical need for specified data quality objectives or project-specific objectives.

Do not use composite samples with components or characteristics subject to significant and unavoidable changes during storage. Analyze individual samples as soon as possible after collection and preferably at the sampling point. Examples are dissolved gases, residual chlorine, soluble sulfide, temperature, and pH. Changes in components such as dissolved oxygen or carbon dioxide, pH, or temperature may produce secondary changes in certain inorganic constituents such as iron, manganese, alkalinity, or hardness. Some organic analytes also may be changed by changes in the foregoing components. Use time-composite samples only for

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

determining components that can be demonstrated to remain unchanged under the conditions of sample collection, preservation, and storage.

Collect individual portions in a wide-mouth bottle every hour (in some cases every half hour or even every 5 min) and mix at the end of the sampling period or combine in a single bottle as collected. If preservatives are used, add them to the sample bottle initially so that all portions of the composite are preserved as soon as collected.

Automatic sampling devices are available; however, do not use them unless the sample is preserved as described below. Composite samplers running for extended periods (weeks to months) should undergo routine cleaning of containers and sample lines to minimize sample growth and deposits.

c. Integrated (discharge-weighted) samples: For certain purposes, the information needed is best provided by analyzing mixtures of grab samples collected from different points simultaneously, or as nearly so as possible, using discharge-weighted methods such as equal-width increment (EWI) or equal discharge-increment (EDI) procedures and equipment. An example of the need for integrated sampling occurs in a river or stream that varies in composition across its width and depth. To evaluate average composition or total loading, use a mixture of samples representing various points in the cross-section, in proportion to their relative flows. The need for integrated samples also may exist if combined treatment is proposed for several separate wastewater streams, the interaction of which may have a significant effect on treatability or even on composition. Mathematical prediction of the interactions among chemical components may be inaccurate or impossible and testing a suitable integrated sample may provide more useful information.

Both lakes and reservoirs show spatial variations of composition (depth and horizontal location). However, there are conditions under which neither total nor average results are especially useful, but local variations are more important. In such cases, examine samples separately (i.e., do not integrate them).

Preparation of integrated samples usually requires equipment designed to collect a sample water uniformly across the depth profile. Knowledge of the volume, movement, and composition of the various parts of the water being sampled usually is required. Collecting integrated samples is a complicated and specialized process that must be described adequately in a sampling plan.

2. Chain-of-Custody Procedures

Properly designed and executed chain-of-custody forms will ensure sample integrity from collection to data reporting. This includes the ability to trace possession and handling of the sample from the time of collection through analysis and final disposition. This process is referred to as ‘‘chain-of-custody’’ and is required to demonstrate sample control when the data are to be used for regulation or litigation. Where litigation is not involved, chain-of-custody procedures are useful for routine control of samples.

A sample is considered to be under a person’s custody if it is in the individual’s physical possession, in the individual’s sight, secured and tamper-proofed by that individual, or secured in

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

an area restricted to authorized personnel. The following procedures summarize the major aspects of chain of custody. More detailed discussions are available.[1,2]

a. Sample labels (including bar-code labels): Use labels to prevent sample misidentification. Gummed paper labels or tags generally are adequate. Include at least the following information: a unique sample number, sample type, name of collector, date and time of collection, place of collection, and sample preservative. Also include date and time of preservation for comparison to date and time of collection. Affix tags or self-adhesive labels to sample containers before, or at the time of, sample collection.

b. Sample seals: Use sample seals to detect unauthorized tampering with samples up to the time of analysis. Use self-adhesive paper seals that include at least the following information: sample number (identical with number on sample label), collector's name, and date and time of sampling. Plastic shrink seals also may be used.

Attach seal in such a way that it is necessary to break it to open the sample container or the sample shipping container (e.g., a cooler). Affix seal to container before sample leaves custody of sampling personnel.

c. Field log book: Record all information pertinent to a field survey or sampling in a bound log book. As a minimum, include the following in the log book: purpose of sampling; location of sampling point; name and address of field contact; producer of material being sampled and address, if different from location; type of sample; and method, date, and time of preservation. If the sample is wastewater, identify process producing waste stream. Also provide suspected sample composition, including concentrations; number and volume of sample(s) taken; description of sampling point and sampling method; date and time of collection; collector's sample identification number(s); sample distribution and how transported; references such as maps or photographs of the sampling site; field observations and measurements; and signatures of personnel responsible for observations. Because sampling situations vary widely, it is essential to record sufficient information so that one could reconstruct the sampling event without reliance on the collector's memory. Protect log book and keep it in a safe place.

d. Chain-of-custody record: Fill out a chain-of-custody record to accompany each sample or group of samples. The record includes the following information: sample number; signature of collector; date, time, and address of collection; sample type; sample preservation requirements; signatures of persons involved in the chain of possession; and inclusive dates and times of possession.

e. Sample analysis request sheet: The sample analysis request sheet accompanies samples to the laboratory. The collector completes the field portion of such a form that includes most of the pertinent information noted in the log book. The laboratory portion of such a form is to be completed by laboratory personnel and includes: name of person receiving the sample, laboratory sample number, date of sample receipt, condition of each sample (i.e., if it is cold or warm, whether the container is full or not, color, if more than one phase is present, etc.), and determinations to be performed.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

f. Sample delivery to the laboratory: Deliver sample(s) to laboratory as soon as practicable after collection, typically within 2 d. Where shorter sample holding times are required, make special arrangements to insure timely delivery to the laboratory. Where samples are shipped by a commercial carrier, include the waybill number in the sample custody documentation. Insure that samples are accompanied by a completed chain-of-custody record and a sample analysis request sheet. Deliver sample to sample custodian.

g. Receipt and logging of sample: In the laboratory, the sample custodian inspects the condition and seal of the sample and reconciles label information and seal against the chain-of-custody record before the sample is accepted for analysis. After acceptance, the custodian assigns a laboratory number, logs sample in the laboratory log book and/or computerized laboratory information management system, and stores it in a secured storage room or cabinet or refrigerator at the specified temperature until it is assigned to an analyst.

h. Assignment of sample for analysis: The laboratory supervisor usually assigns the sample for analysis. Once the sample is in the laboratory, the supervisor or analyst is responsible for its care and custody.

i. Disposal: Hold samples for the prescribed amount of time for the project or until the data have been reviewed and accepted. Document the disposition of samples. Ensure that disposal is in accordance with local, state, and U.S. EPA approved methods.

3. Sampling Methods

a. Manual sampling: Manual sampling involves minimal equipment but may be unduly costly and time-consuming for routine or large-scale sampling programs. It requires trained field technicians and is often necessary for regulatory and research investigations for which critical appraisal of field conditions and complex sample collection techniques are essential. Manually collect certain samples, such as waters containing oil and grease.

b. Automatic sampling: Automatic samplers can eliminate human errors in manual sampling, can reduce labor costs, may provide the means for more frequent sampling,[3] and are used increasingly. Be sure that the automatic sampler does not contaminate the sample. For example, plastic components may be incompatible with certain organic compounds that are soluble in the plastic parts or that can be contaminated (e.g., from phthalate esters) by contact with them. If sample constituents are generally known, contact the manufacturer of an automatic sampler regarding potential incompatibility of plastic components.

Program an automatic sampler in accordance with sampling needs. Carefully match pump speeds and tubing sizes to the type of sample to be taken.

c. Sorbent sampling: Use of solid sorbents, particularly membrane-type disks, is becoming more frequent. These methods offer advantages of rapid, inexpensive sampling if the analytes of interest can be adsorbed and desorbed efficiently and the water matrix is free of particulates that plug the sorbent.

4. Sample Containers

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

The type of sample container used is of utmost importance. Test sample containers and document that they are free of analytes of interest, especially when sampling and analyzing for very low analyte levels. Containers typically are made of plastic or glass, but one material may be preferred over the other. For example, silica, sodium, and boron may be leached from soft glass but not plastic, and trace levels of some pesticides and metals may sorb onto the walls of glass containers.[4] Thus, hard glass containers*#(3) are preferred. For samples containing organic compounds, do not use plastic containers except those made of fluorinated polymers such as polytetrafluoroethylene (PTFE).[3]

Some sample analytes may dissolve (be absorbed) into the walls of plastic containers; similarly, contaminants from plastic containers may leach into samples. Avoid plastics wherever possible because of potential contamination from phthalate esters. Container failure due to breakdown of the plastic is possible. Therefore, use glass containers for all organics analyses such as volatile organics, semivolatile organics, pesticides, PCBs, and oil and grease. Some analytes (e.g., bromine-containing compounds and some pesticides, polynuclear aromatic compounds, etc.) are light-sensitive; collect them in amber-colored glass containers to minimize photodegradation. Container caps, typically plastic, also can be a problem. Do not use caps with paper liners. Use foil or PTFE liners but be aware that metal liners can contaminate samples collected for metals analysis and they may also react with the sample if it is acidic or alkaline. Serum vials with PTFE-lined rubber or plastic septa are useful.

In rare situations it may be necessary to use sample containers not specifically prepared for use, or otherwise unsuitable for the particular situation; thoroughly document these deviations. Documentation should include type and source of container, and the preparation technique, e.g., acid washed with reagent water rinse. For QA purposes the inclusion of a bottle blank may be necessary.

5. Number of Samples

Because of variability from analytical and sampling procedures (i.e., population variability), a single sample is insufficient to reach any reasonable desired level of confidence. If an overall standard deviation (i.e., the standard deviation of combined sampling and analysis) is known, the required number of samples for a mobile matrix such as water may be estimated as follows:[4]

$$N \geq \left(\frac{ts}{U}\right)^2$$

where:

N = number of samples,
t = Student-t statistic for a given confidence level,
s = overall standard deviation, and
U = acceptable level of uncertainty.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

To assist in calculations, use curves such as those in Figure 1060:1. As an example, if *s* is 0.5 mg/L, *U* is ± 0.2 mg/L, and a 95% confidence level is desired, approximately 25 to 30 samples must be taken.

The above equation assumes that total error (population variability) is known. Total variability consists of all sources of variability, including: the distribution of the analytes of interest within the sampling site, collection, preservation, preparation, and analysis of samples, and data handling and reporting. In simpler terms, error (variability) can be divided into sampling and analysis components. Sampling error due to population variability (including heterogeneous distribution of analytes in the environmental matrix) usually is much larger than analytical error components. Unfortunately, sampling error usually is not available and the analyst is left with only the published error of the measurement system (typically obtained by using a reagent water matrix under the best analytical conditions).

More accurate equations are available.[5] These are based on the Z distribution for determining the number of samples needed to estimate a mean concentration when variability is estimated in absolute terms using the standard deviation. The coefficient of variation (relative standard deviation) is used when variability is estimated in relative terms.

The number of random samples to be collected at a site can be influenced partly by the method that will be used. The values for standard deviation (SD) or relative standard deviation (RSD) may be obtained from each of the methods or in the literature.[6] However, calculations of estimated numbers of samples needed based only on this information will result in underestimated numbers of samples because only the analytical variances are considered, and the typically larger variances from the sampling operations are not included. Preferably, determine and use SDs or RSDs from overall sampling and analysis operations.

For estimates of numbers of samples needed for systematic sampling (e.g., drilling wells for sampling groundwater or for systematically sampling large water bodies such as lakes), equations are available[7] that relate number of samples to shape of grid, area covered, and space between nodes of grid. The grid spacing is a complex calculation that depends on the size and shape of any contaminated spot (such as a groundwater plume) to be identified, in addition to the geometric shape of the sampling grid.

See individual methods for types and numbers of quality assurance (QA) and quality control (QC) samples, e.g., for normal-level (procedural) or low-level (contamination) bias or for precision, involving sampling or laboratory analysis (either overall or individually). Estimates of numbers of QC samples needed to achieve specified confidence levels also can be calculated. Rates of false positives (Type I error) and false negatives (Type II error) are useful parameters for estimating required numbers of QC samples. A false positive is the incorrect conclusion that an analyte is present when it is absent. A false negative is the incorrect conclusion that an analyte is absent when it is present. If the frequency of false positives or false negatives desired to be detected is less than 10%, then

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$n = \frac{\ln \alpha}{\ln (1 - Y)}$$

where:

α = (1 – desired confidence level), and
Y = frequency to detect (<10%).

If the frequency that is desirable to detect is more than 10%, iterative solution of a binomial equation is necessary.[5,8]

Equations are available as a computer program†#(4) for computing sample number by the *Z* distribution, for estimating samples needed in systematic sampling, and for estimating required number of QC samples.

6. Sample Volumes

Collect a 1-L sample for most physical and chemical analyses. For certain determinations, larger samples may be necessary. Table 1060:I lists volumes ordinarily required for analyses, but it is strongly recommended that the laboratory that will conduct the analyses also be consulted to verify the analytical needs of sampling procedures as they pertain to the goals and data quality objective of an investigation.

Do not use samples from the same container for multiple testing requirements (e.g., organic, inorganic, radiological, bacteriological, and microscopic examinations) because methods of collecting and handling are different for each type of test. Always collect enough sample volume in the appropriate container in order to comply with sample handling, storage, and preservation requirements.

7. References

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1986. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 3rd ed. Publ. No. SW-846, Off. Solid Waste and Emergency Response, Washington, D.C.
2. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1982. NEIC Policies and Procedures. EPA-330/9/78/001/-R (rev. 1982).
3. WATER POLLUTION CONTROL FEDERATION. 1986. Removal of Hazardous Wastes in Wastewater Facilities—Halogenated Organics. Manual of Practice FD-11, Water Pollution Control Fed., Alexandria, Va.
4. Methods for the Examination of Waters and Associated Materials: General Principles of Sampling and Accuracy of Results. 1980. Her Majesty's Stationery Off., London, England.
5. KEITH, L.H., G.L. PATTON, D.L. LEWIS & P.G. EDWARDS. 1996. Determining numbers and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

kinds of analytical samples. Chapter 1 *in* Principles of Environmental Sampling, 2nd ed. ACS Professional Reference Book, American Chemical Soc., Washington, D.C.

6. KEITH, L.H. 1996. Compilation of EPA's Sampling and Analysis Methods, 2nd ed. Lewis Publ./CRC Press, Boca Raton, Fla.
7. GILBERT, R.O. 1987. Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold, New York, N.Y.
8. GRANT, E.L. & R.S. LEAVENWORTH. 1988. Statistical Quality Control, 6th ed. McGraw-Hill, Inc., New York, N.Y.
9. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1996. 40 CFR Part 136, Table II.
10. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1992. Rules and Regulations. 40 CFR Parts 100-149.

1060 C. Sample Storage and Preservation

Complete and unequivocal preservation of samples, whether domestic wastewater, industrial wastes, or natural waters, is a practical impossibility because complete stability for every constituent never can be achieved. At best, preservation techniques only retard chemical and biological changes that inevitably continue after sample collection.

1. Sample Storage before Analysis

a. Nature of sample changes: Some determinations are more affected by sample storage than others. Certain cations are subject to loss by adsorption on, or ion exchange with, the walls of glass containers. These include aluminum, cadmium, chromium, copper, iron, lead, manganese, silver, and zinc, which are best collected in a separate clean bottle and acidified with nitric acid to a pH below 2.0 to minimize precipitation and adsorption on container walls. Also, some organics may be subject to loss by adsorption to the walls of glass containers.

Temperature changes quickly; pH may change significantly in a matter of minutes; dissolved gases (oxygen, carbon dioxide) may be lost. Because changes in such basic water quality properties may occur so quickly, determine temperature, reduction-oxidation potential, and dissolved gases in situ and pH, specific conductance, turbidity, and alkalinity immediately after sample collection. Many organic compounds are sensitive to changes in pH and/or temperature resulting in reduced concentrations during storage.

Changes in the pH-alkalinity-carbon dioxide balance may cause calcium carbonate to precipitate, decreasing the values for calcium and total hardness.

Iron and manganese are readily soluble in their lower oxidation states but relatively insoluble in their higher oxidation states; therefore, these cations may precipitate or they may dissolve from a sediment, depending on the redox potential of the sample. Microbiological activity may affect the nitrate-nitrite-ammonia content, phenol or BOD concentration, or the reduction of sulfate to sulfide. Residual chlorine is reduced to chloride. Sulfide, sulfite, ferrous iron, iodide,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

and cyanide may be lost through oxidation. Color, odor, and turbidity may increase, decrease, or change in quality. Sodium, silica, and boron may be leached from the glass container. Hexavalent chromium may be reduced to trivalent chromium.

Biological activity taking place in a sample may change the oxidation state of some constituents. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well-known nitrogen and phosphorus cycles are examples of biological influences on sample composition.

Zero head-space is important in preservation of samples with volatile organic compounds and radon. Avoid loss of volatile materials by collecting sample in a completely filled container. Achieve this by carefully filling the bottle so that top of meniscus is above the top of the bottle rim. It is important to avoid spillage or air entrapment if preservatives such as HCl or ascorbic acid have already been added to the bottle. After capping or sealing bottle, check for air bubbles by inverting and gently tapping it; if one or more air bubbles are observed then, if practical, discard the sample and repeat refilling bottle with new sample until no air bubbles are observed (this cannot be done if bottle contained preservatives before it was filled).

Serum vials with septum caps are particularly useful in that a sample portion for analysis can be taken through the cap by using a syringe,[1] although the effect of pressure reduction in the head-space must be considered. Pulling a sample into a syringe under vacuum can result in low bias data for volatile compounds and the resulting headspace precludes taking further subsamples.

b. Time interval between collection and analysis: In general, the shorter the time that elapses between collection of a sample and its analysis, the more reliable will be the analytical results. For certain constituents and physical values, immediate analysis in the field is required. For composited samples it is common practice to use the time at the end of composite collection as the sample collection time.

Check with the analyzing laboratory to determine how much elapsed time may be allowed between sample collection and analysis; this depends on the character of the sample and the stability of the target analytes under the conditions of storage. Many regulatory methods limit the elapsed time between sample collection and analysis (see Table 1060:I). Changes caused by growth of microorganisms are greatly retarded by keeping the sample at a low temperature (<4°C but above freezing). When the interval between sample collection and analysis is long enough to produce changes in either the concentration or the physical state of the constituent to be measured, follow the preservation practices given in Table 1060:I. Record time elapsed between sampling and analysis, and which preservative, if any, was added.

2. Preservation Techniques

To minimize the potential for volatilization or biodegradation between sampling and analysis, keep samples as cool as possible without freezing. Preferably pack samples in crushed or cubed ice or commercial ice substitutes before shipment. Avoid using dry ice because it will freeze samples and may cause glass containers to break. Dry ice also may effect a pH change in

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

samples. Keep composite samples cool with ice or a refrigeration system set at 4°C during compositing. Analyze samples as quickly as possible on arrival at the laboratory. If immediate analysis is not possible, preferably store at 4°C.[1]

No single method of preservation is entirely satisfactory; choose the preservative with due regard to the determinations to be made. Use chemical preservatives only when they do not interfere with the analysis being made. When they are used, add them to the sample bottle initially so that all sample portions are preserved as soon as collected. Because a preservation method for one determination may interfere with another one, samples for multiple determinations may need to be split and preserved separately. All methods of preservation may be inadequate when applied to suspended matter. Do not use formaldehyde as a preservative for samples collected for chemical analysis because it affects many of the target analytes.

Methods of preservation are relatively limited and are intended generally to retard biological action, retard hydrolysis of chemical compounds and complexes, and reduce volatility of constituents.

Preservation methods are limited to pH control, chemical addition, the use of amber and opaque bottles, refrigeration, filtration, and freezing. Table 1060:I lists preservation methods by constituent. See Section 7010B for sample collection and preservation requirements for radionuclides.

The foregoing discussion is by no means exhaustive and comprehensive. Clearly it is impossible to prescribe absolute rules for preventing all possible changes. Additional advice will be found in the discussions under individual determinations, but to a large degree the dependability of an analytical determination rests on the experience and good judgment of the person collecting the sample. Numbers of samples required for confidence levels in data quality objectives, however, rely on statistical equations such as those discussed earlier.

3. Reference

1. WATER POLLUTION CONTROL FEDERATION. 1986. Removal of Hazardous Wastes in Wastewater Facilities—Halogenated Organics. Manual of Practice FD-11, Water Pollution Control Fed., Alexandria, Va.

4. Bibliography

KEITH, L.H., ed. 1996. Principles of Environmental Sampling, 2nd ed. ACS Professional Reference Book, American Chemical Soc., Washington, D.C.

1080 REAGENT WATER

1080 A. Introduction

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

One of the most important aspects of analysis is the preparation of reagent water to be used for dilution of reagents and for blank analysis. Reagent water is water with no detectable concentration of the compound or element to be analyzed at the detection limit of the analytical method. Reagent water should be free of substances that interfere with analytical methods. The quality of water required is related directly to the analysis being made. Requirements for water quality may differ for organic, inorganic, and biological constituents depending on the use(s) for which the water is intended.

Any method of preparation of reagent water is acceptable provided that the requisite quality can be met. Improperly maintained systems may add contaminants. Reverse osmosis, distillation, and deionization in various combinations all can produce reagent water when used in the proper arrangement. Ultrafiltration and/or ultraviolet treatment also may be used as part of the process. Section 1080 provides general guidelines for the preparation of reagent water. Table 1080:I lists commonly available processes for water purification and major classes of contaminants removed by purification.

For details on preparing water for microbiological tests, see Section 9020B.3*c*.

1080 B. Methods for Preparation of Reagent Water

1. Distillation

Prepare laboratory-grade distilled water by distilling water from a still of all-borosilicate glass, fused quartz, tin, or titanium. To remove ammonia distill from an acid solution. Remove CO_2 by boiling the water for 15 min and cooling rapidly to room temperature; exclude atmospheric CO_2 by using a tube containing soda lime or a commercially available CO_2-removing agent.*#(5)

Boiling the water may add other impurities by leaching impurities from the container. Freshly replaced filters, cartridges and resins initially can release impurities. Pretreat feedwater and provide periodic maintenance to minimize scale formation within the still. Pretreatment may be required where the feedwater contains significant concentrations of calcium, magnesium, and bicarbonate ions; it may involve demineralization via reverse osmosis or ion exchange.

2. Reverse Osmosis

Reverse osmosis is a process in which water is forced under pressure through a semipermeable membrane removing a portion of dissolved constituents and suspended impurities. Product water quality depends on feedwater quality.

Select the reverse osmosis membrane module appropriate to the characteristics of the feedwater. Obtain rejection data for contaminants in the feedwater at the operating pressure to be used in preparing reagent water. Set overall water production to make the most economical use of water without compromising the final quality of the permeate. Selection of spiral-wound or hollow fiber configurations depends on fouling potential of the feedwater. Regardless of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

configuration used, pretreatment may be required to minimize membrane fouling with colloids or particulates and to minimize introduction of chlorine, iron, and other oxidizing compounds that may degrade reverse osmosis membranes. Periodic flushing of the membrane modules is necessary.

3. Ion Exchange

Prepare deionized water by passing feedwater through a mixed-bed ion exchanger, consisting of strong anion and strong cation resins mixed together. When the system does not run continuously, recirculate product water through ion-exchange bed.

Use separate anion and cation resin beds in applications where resin regeneration is economically attractive. In such instances, position the anion exchanger downstream of the cation exchanger to remove leachates from the cation resin. Proper bed sizing is critical to the performance of the resins. In particular, set the length-to-diameter ratio of the bed in accordance with the maximum process flow rate to ensure that optimal face velocities are not exceeded and that sufficient residence time is provided.

In applications where the feedwater has significant quantities of organic matter, remove organics to minimize potential fouling of the resins. Possible pretreatments include prefiltration, distillation, reverse osmosis, or adsorption.

4. Adsorption

Adsorption is generally used to remove chlorine and organic impurities. It is accomplished typically with granular activated carbon. Efficiency of organics removal depends on the nature of the organic contaminants, the physical characteristics of the activated carbon, and the operating conditions. In general, organics adsorption efficiency is inversely proportional to solubility and may be inadequate for the removal of low-molecular-weight, polar compounds. Performance differences among activated carbons are attributable to the use of different raw materials and activation procedures. Select the appropriate activated carbon with regard to these differences. Even with optimum activated carbon, proper performance will not be attained unless the column is sized to give required face velocity and residence time at the maximum process flow rate.

Use of activated carbon may adversely affect resistivity. This effect may be controlled by use of reverse osmosis, mixed resins, or special adsorbents. To achieve the lowest level of organic contamination, use mixtures of polishing resins with special carbons in conjunction with additional treatment steps, such as reverse osmosis, natural carbons, ultraviolet oxidation, or ultrafiltration.

1080 C. Reagent Water Quality

1. Quality Guidelines

Several guidelines for reagent water quality, based on contaminant levels, are available, but the final test is the appropriateness for the analysis. Table 1080:II lists some characteristics of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

various qualities of reagent water.

High-quality reagent water, having a minimum resistivity of 10 megohms-cm, 25°C (in line), typically is prepared by distillation, deionization, or reverse osmosis treatment of feedwater followed by polishing with a mixed-bed deionizer and passage through a 0.2-µm-pore membrane filter. Alternatively treat by reverse osmosis followed by carbon adsorption and deionization. Determine quality at the time of production. Mixed-bed deionizers typically add small amounts of organic matter to water, especially if the beds are fresh. Resistivity should be >10 megohm-cm at 25°C, measured in-line. Resistivity measurements will not detect organics or nonionized contaminants, nor will they provide an accurate assessment of ionic contaminants at the microgram-per-liter level.

Medium-quality water typically is produced by distillation or deionization. Resistivity should be >1 megohm-cm at 25°C.

Low-quality water should have a minimum resistivity of 0.1 megohm-cm, and may be used for glassware washing, preliminary rinsing of glassware, and as feedwater for production of higher-grade waters.

The pH of high- or medium-quality water cannot be measured accurately without contaminating the water. Measure other constituents as required for individual tests.

High-quality water cannot be stored without significant degradation; produce it continuously and use it immediately after processing. Medium-quality water may be stored, but keep storage to a minimum and provide quality consistent with the intended use. Store only in materials that protect the water from contamination, such as TFE and glass for organics analysis or plastics for metals. Store low-quality water in materials that protect the water from contamination.

2. Bibliography

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1991. Annual Book of ASTM Standards, Vol. 11-01, D 1193-91. American Soc. Testing & Materials, Philadelphia, Pa.

1090 LABORATORY OCCUPATIONAL HEALTH AND SAFETY

1090 A. Introduction

1. General Discussion

Achievement of a safe and healthful workplace is the responsibility of the organization, the laboratory manager, the supervisory personnel and, finally, the laboratory personnel themselves. All laboratory employees must make every effort to protect themselves and their fellow workers by conscientiously adhering to the health and safety program that has been developed and documented specifically for their laboratory.

2. Organizing for Safety

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

a. Overall program: The responsibility for establishing and enforcing a laboratory health and safety (LH&S) program ultimately rests with the laboratory director. The LH&S program must, at the minimum, address how to protect oneself from the hazards of working with biological (1090H), chemical (1090J), and radiological (1090I) agents. Such a program is a necessary component of an overall laboratory quality system that provides for the health and safety of the entire laboratory staff. As a part of the quality system, all aspects of the LH&S program must be fully documented. Laboratory personnel must be trained. The LH&S program must be fully implemented and its application audited periodically. Appropriate records of all activities must be kept to document performance, meet appropriate regulatory requirements, and document the status of the LH&S program.

In the United States, the minimum standard of practice for health and safety activities is detailed in government documents.[1,2] Each laboratory should appoint as needed a chemical hygiene officer (CHO), a biological hygiene officer (BHO), a radiological hygiene officer (RHO), and, where appropriate or desired, a LH&S committee. The CHO, the committee, and laboratory management must develop, document, and implement a ‘‘written’’ laboratory hygiene plan (LHP), or chemical hygiene plan (CHP).

b. Specific responsibilities: Specific responsibilities applicable at various levels within the organization are as follows:

1) The chief executive officer (CEO) has ultimate responsibility for LH&S within the organization and must, with other managers and supervisors, provide continuous support for the LH&S program.

2) The supervisor has primary responsibility for the LH&S program in his or her work group.

3) The biological hygiene officer (BHO) has the responsibility to work with managers, supervisors, and other employees to develop and implement appropriate biological hygiene policies and practices; monitor procurement, use, and disposal of biological agents used in the laboratory; see that appropriate audits are conducted and that records are maintained; know the current legal requirements concerning working with biological agents; and seek ways to improve the biological hygiene program.

4) The chemical hygiene officer (CHO) has the same responsibilities as the biological hygiene officer, but with respect to chemicals, and also is responsible for helping supervisors (project directors) develop precautions and adequate facilities and for keeping material safety data sheets (MSDSs) available for review.

5) The radiological hygiene officer (RHO), referred to as radiation safety officer in most regulatory language, has the same responsibilities as the chemical hygiene officer, but with respect to radiological chemicals and exposure.

6) The laboratory supervisor has overall responsibility for chemical hygiene in the laboratory, including responsibility to ensure that workers know and follow the chemical hygiene rules, that protective equipment is available and in working order, and that appropriate

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

training has been provided; performs regular, formal chemical hygiene and housekeeping inspections, including routine inspections of emergency equipment, and maintenance of appropriate records; knows the current legal requirements concerning regulated substances; specifies the required levels of protective apparel and equipment needed to perform the work; and ensures that facilities and training for use of any material being ordered are adequate.

7) The project director (or a director of a specific operation) has primary responsibility for biological, chemical, and/or radiological hygiene procedures as appropriate for all operations under his or her control.

8) The laboratory worker has the responsibility for planning and conducting each operation in accordance with the institutional chemical hygiene, biological hygiene, and radiological hygiene procedures, and for developing good personal chemical, biological, and radiological hygiene habits.

3. Records

Maintain records of all accidents including ‘‘near-misses,’’ medical care audits, inspections, and training for specified time periods that depend on the nature of the requirement. Keep records on standardized report forms containing sufficient information to enable an investigator to determine who was involved, what happened, when and where it happened, and what injuries or exposures, if any, resulted. Most importantly, these records should enable the formulation of appropriate corrective actions where warranted. The standard of practice for LH&S activities requires that a log (record) be kept of those accidents causing major disability. Record not only all accidents, but also ‘‘near-misses,’’ to permit full evaluation of safety program effectiveness. Maintain a file detailing all of the recommendations for the LH&S program.

4. Information and Training[2]

The standard of practice for hazard communication or ‘‘right-to know’’ requires that employees be notified about hazards in the workplace.

Laboratory personnel must be under the direct supervision and regular observation of a technically qualified individual who must have knowledge of the hazards present, their health effects, and related emergency procedures. The supervisor must educate laboratory personnel in safe work practices at the time of initial assignment and when a new hazardous substance is introduced into the workplace. Personnel have a right to know what hazardous materials are present, the specific hazards created by those materials, and the required procedures to protect themselves against these hazards. The hazard communication standard [2] requires information and training on material safety data sheets (MSDSs), labeling, chemical inventory of all hazardous substances in the workplace, and informing contractors of hazardous substances.

Training dealing with health and safety techniques and work practices requires a concerted effort by management, and must be conducted on a routine basis by competent and qualified individuals to be effective. Records of training must be maintained.

5. References

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Laboratory Standard. Occupational Exposure to Hazardous Chemicals in Laboratories. 29 CFR 1910.1450.
2. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. 1985. Hazard Communication. Final Rule. *Federal Register* 48:53280. 29 CFR 1910.1200.

6. Bibliography

DUX, J.P. & R.F. STALZER. 1988. Managing Safety in the Chemical Laboratory. Van Nostrand Reinhold Co., Inc., New York, N.Y.

FURR, A.K., ed. 1990. CRC Handbook of Laboratory Safety, 3rd ed. CRC Press, Inc., Boca Raton, Fla.

1090 B. Safe Laboratory Practices

Use the information, rules, work practices, and/or procedures discussed below for essentially all laboratory work with chemicals.

1. General Rules

a. Accidents and spills:

1) Eye contact—Promptly flush eyes with water for a prolonged period (minimum of 15 min) and seek immediate medical attention.

2) Ingestion—Encourage victim to drink large amounts of water.

3) Skin contact—Promptly flush affected area with water for approximately 15 min and remove any contaminated clothing. If symptoms persist after washing, seek medical attention.

4) Clean-up—Promptly clean up spills, using appropriate protective apparel and equipment and proper disposal procedures.

5) Working alone—Avoid working alone in a building; do not work alone in a laboratory if the procedures to be conducted are hazardous.

b. Vigilance: Be alert to unsafe conditions and see that they are corrected when detected.

2. Work Practices/Rules

a. Work habits: Develop and encourage safe habits, avoid unnecessary exposure to chemicals by any route, and avoid working alone whenever possible.

b. Exhaust ventilation: Do not smell or taste chemicals. Vent any apparatus that may discharge toxic chemicals (vacuum pumps, distillation columns, etc.) into local exhaust devices.

c. Glove boxes: Inspect gloves and test glove boxes before use.

d. Cold and/or warm rooms: Do not allow release of toxic substances in cold rooms and/or warm rooms, because these rooms usually have no provisions for exhausting contaminants.

e. Use/choice of chemicals: Use only those chemicals for which the quality of the available

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

ventilation system is appropriate.

f. Eating, smoking, and related activities: DO NOT eat, drink, smoke, chew gum, or apply cosmetics in areas where laboratory chemicals are present. Always wash hands before conducting these activities.

g. Food storage: DO NOT store, handle, or consume food or beverages in storage areas, refrigerators, or glassware and utensils that also are used for laboratory operations.

h. Equipment and glassware: Handle and store laboratory glassware with care to avoid damage. Do not use damaged glassware. Use extra care with Dewar flasks and other evacuated glass apparatus; shield or wrap them to contain chemicals and fragments should implosion occur. Use equipment for its designed purpose only.

i. Washing: Wash areas of exposed skin well before leaving the laboratory.

j. Horseplay: Avoid practical jokes or other behavior that might confuse, startle, or distract another worker.

k. Mouth suction: Do not use mouth suction for pipetting or starting a siphon.

l. Personal protective equipment: Do not wear personal protective clothing or equipment in nonlaboratory areas. Remove laboratory coats immediately on significant contamination with hazardous materials.

m. Personal apparel: Confine long hair and loose clothing. Wear shoes at all times in the laboratory but do not wear sandals or perforated shoes.

n. Personal housekeeping: Keep work area clean and uncluttered, with chemicals and equipment properly labeled and stored. Clean up work area on completion of an operation or at the end of each day.

o. Unattended operations: Leave lights on, place an appropriate sign on the door, and provide for containment of toxic substances in the event of failure of a utility service (such as cooling water) to an unattended operation.

3. Personal Protective Equipment

Carefully plan a program addressing the need for, use of, and the training with personal protective equipment. Such a program includes seeking information and advice about hazards, developing appropriate protective procedures, and proper positioning of equipment before beginning any new operations.

a. Eye protection: Wear appropriate eye protection (this applies to all persons, including visitors) where chemicals are stored or handled. Avoid use of contact lenses in the laboratory unless necessary; if contact lenses are used, inform supervisor so that special precautions can be taken.

b. Skin protection: Wear appropriate gloves when the potential for contact with toxic chemicals exists. Inspect gloves before each use, wash them before removal, and replace periodically.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

c. Respiratory protection: Use appropriate respiratory equipment when engineering controls are unable to maintain air contaminant concentrations below the action levels, i.e., one half the permissible exposure limit (PEL)[1] or threshold limit value (TLV[7]), i.e., levels below which no irreversible health affects are expected. When work practices are used that are expected to cause routine exposures that exceed the PEL or TLV, respiratory protection is required to prevent overexposure to hazardous chemicals. If respirators are used or provided in the laboratory then the LH&S standard of practice requires that a complete respiratory protection plan (RPP) be in place. The minimum requirements for an RPP meeting the LH&S standard of practice are published.[1] Inspect respirators before use and check for proper fit.

d. Other protective equipment: Provide and use any other protective equipment and/or apparel as appropriate.

4. Engineering Controls

Fume hoods: Use the hood for operations that might result in the release of toxic chemical vapors or dust. As a rule of thumb, use a hood or other local ventilation device when working with any appreciably volatile substance with a TLV of less than 50 ppm. Confirm that hood performance is adequate before use. Open hood minimally during work. Keep hood door closed at all other times except when adjustments within the hood are being made. Keep stored materials in hoods to a minimum, and do not block vents or air flow. Provide at least an 8-cm space under and around all items used in hoods, and ensure that they are at least 15 cm from the front of the hood.

5. Waste Disposal

Ensure that the plan for each laboratory operation includes plans and training for waste disposal. Deposit chemical waste in appropriately labeled receptacles and follow all other waste disposal procedures of the Chemical Hygiene Plan (see 1090J). Do not discharge any of the following contaminants to the sewer: concentrated acids or bases; highly toxic, malodorous, or lachrymatory substances; substances that might interfere with the biological activity of wastewater treatment plants; and substances that may create fire or explosion hazards, cause structural damage, or obstruct flow. For further information on waste disposal, see Section 1100.

6. Work with Chemicals of Moderate Chronic or High Acute Toxicity

Examples of chemicals in this category include diisopropylfluorophosphate, hydrofluoric acid, and hydrogen cyanide. The following rules are intended to supplement the rules listed previously for routine laboratory operations. Their purpose is to minimize exposure to these toxic substances by any exposure route using all reasonable precautions. The precautions are appropriate for substances with moderate chronic or high acute toxicity used in significant quantities.

a. Location: Use and store these substances only in areas of restricted access with special warning signs. Always use a hood (previously evaluated to confirm adequate performance with a face velocity of at least 24 m/min) or other containment device for procedures that may result in

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

the generation of aerosols or vapors containing the substance; trap released vapors to prevent their discharge with the hood exhaust.

b. Personal protection: Always avoid skin contact by use of gloves and long sleeves, and other protective apparel as appropriate. Always wash hands and arms immediately after working with these materials.

c. Records: Maintain records of the amounts of these materials on hand, amounts used, and the names of the workers involved.

d. Prevention of spills and accidents: Be prepared for accidents and spills.

Ensure that at least two people are present at all times if a compound in use is highly toxic or of unknown toxicity.

Store breakable containers of these substances in chemically resistant trays; also work and mount apparatus above such trays or cover work and storage surfaces with removable, absorbent, plastic-backed paper. If a major spill occurs outside the hood, evacuate the area; ensure that cleanup personnel wear suitable protective apparel and equipment.

e. Waste: Thoroughly decontaminate or incinerate contaminated clothing or shoes. If possible, chemically decontaminate by chemical conversion. Store contaminated waste in closed, suitably labeled, impervious containers (for liquids, in glass or plastic bottles half-filled with vermiculite).

7. Work with Chemicals of High Chronic Toxicity

Examples of chemicals in this category include (where they are used in quantities above a few milligrams, or a few grams, depending on the substance) dimethyl mercury, nickel carbonyl, benzo(a)pyrene, *N*-nitrosodiethylamine, and other substances with high carcinogenic potency. The following rules are intended to supplement the rules listed previously for routine laboratory operations.

a. Access: Conduct all transfers and work with these substances in a controlled area, i.e., a restricted-access hood, glove box, or portion of a laboratory, designated for use of highly toxic substances, for which all people with access are aware of the substances being used and necessary precautions.

b. Approvals: Prepare a plan for use and disposal of these materials and obtain the approval of the laboratory supervisor.

c. Non-contamination/decontamination: Protect vacuum pumps against contamination by scrubbers or HEPA filters and vent them into the hood. Decontaminate vacuum pumps or other contaminated equipment, including glassware, in the hood before removing them from the controlled area. Decontaminate the controlled area before routine work is resumed.

d. Exiting: On leaving a controlled area, remove any protective apparel (place it in an appropriately labeled container), and thoroughly wash hands, forearms, face, and neck.

e. Housekeeping: Use a wet mop or a vacuum cleaner equipped with a HEPA filter. Do not dry sweep if the toxic substance is a dry powder.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

f. Medical surveillance: If using toxicologically significant quantities of such a substance on a regular basis (e.g., three times per week), consult a qualified physician about desirability of regular medical surveillance.

g. Records: Keep accurate records of the amounts of these substances stored and used, the dates of use, and names of users.

h. Signs and labels: Ensure that the controlled area is conspicuously marked with warning and restricted access signs and that all containers of these substances are appropriately labeled with identity and warning labels.

i. Spills: Ensure that contingency plans, equipment, and materials to minimize exposures of people and property are available in case of accident.

j. Storage: Store containers of these chemicals only in a ventilated, limited-access area.

k. Glove boxes: For a negative-pressure glove box, ensure that the ventilation rate is at least 2 volume changes/h and the pressure drop at least 1.3 cm of water. For a positive-pressure glove box, thoroughly check for leaks before each use. In either case, trap the exit gases or filter them through a HEPA filter and then release them into the hood.

l. Waste: Ensure that containers of contaminated waste (including washings from contaminated flasks) are transferred from the controlled area in a secondary container under the supervision of authorized personnel.

8. Physical Hazards

a. Electrical: Ensure that electrical wiring, connections, and apparatus conform to the requirement of the latest National Electrical Code. Fire, explosion, power outages, and electrical shocks are all serious hazards that may result from incorrect use of electrical devices. Ground all electrical equipment or use double-insulated equipment. Use ground fault interrupter circuit breakers to the maximum extent possible. Do not locate electrical receptacles inside fume hoods, and do not use equipment near volatile flammable solvents. Use approved safety refrigerators. Disconnect electrical equipment from the power supply before service or repair is attempted and never bypass safety interlocks. Attempting to repair equipment using employees not thoroughly acquainted with electrical principles may present particularly dangerous situations.

b. Non-ionizing radiation: Non-ionizing radiation, also called electromagnetic radiation, is generally considered to be the radio frequency region of the radiation spectrum. For the purposes of dealing with personal exposures in laboratories, it also includes the microwave frequency region. Typical laboratory exposures to non-ionizing radiation usually include ultraviolet, visible, infrared, and microwave radiation.

For normal environmental conditions and for incident electromagnetic energy of frequencies from 10 MHz to 100 GHz, the radiation protection guide is 10 mW/cm^2. The radiation protection applies whether the radiation is continuous or intermittent. This means a power density of 10 mW/cm^2 for periods of 0.1 h or more, or an energy density of 1 $mW\text{-}h/cm^2$ during any 0.1-h period. These recommendations apply to both whole-body irradiation and partial body

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

irradiation.

Ultraviolet radiation (UV) and lasers are used frequently. With properly constructed and operated instruments, it is not a significant hazard but can be harmful when used for controlling microorganisms in laboratory rooms or for sterilizing objects.

When using devices that generate or use non-ionizing radiation, observe the following precautions: Wear safety glasses or goggles with solid side pieces whenever there is a possibility of exposure to harmful (UV) radiation. Provide proper shielding (shiny metal surfaces reflect this energy). Shut off all these devices (UV lamps) when not in use. Post warning signs and install indicator lights to serve as a constant reminder when these types of devices are in use (UV lamps).

c. Mechanical: Shield or guard drive belts, pulleys, chain drivers, rotating shafts, and other types of mechanical power transmission apparatus. Laboratory equipment requiring this guarding includes vacuum pumps, mixers, blenders, and grinders.

Shield portable power tools. Guard equipment such as centrifuges, which have high-speed revolving parts, against ‘‘fly-aways.’’ Securely fasten equipment that has a tendency to vibrate (e.g., centrifuges and air compressors) to prevent the tendency to ‘‘walk’’ and locate them away from bottles and other items that may fall from shelves or benches because of the vibration.

d. Compressed gases: Gas cylinders may explode or ‘‘rocket’’ if improperly handled. Leaking cylinders may present an explosion hazard if the contents are flammable; they are an obvious health hazard if the contents are toxic; and they may lead to death by suffocation if the contents are inert gases. The Compressed Gas Association has published procedures governing use and storage of compressed gases. Transfer gas cylinders only with carts, hand trucks, or dollies. Secure gas cylinders properly during storage, transport, and use, and leave valve safety covers on cylinders during storage and transport. Avoid the use of adapters or couplers with compressed gas. Properly identify cylinder contents.

9. Chemical Hazards

a. General precautions: Chemical injuries may be external or internal. External injuries may result from skin exposure to caustic or corrosive substances such as acids, bases, or reactive salts. Take care to prevent accidents, such as splashes and container spills. Internal injuries may result from the toxic or corrosive effects of substances absorbed by the body. These internal injuries may result from inhalation, skin contact, or ingestion.

Table 1090:I, Table 1090:II, and Table 1090:III list PELs, TLVs, and/or short-term exposure limits and ceilings for some chemical materials specified in *Standard Methods*, as given in various published sources.[1-8] The PEL values reported in these tables are in some instances higher than the levels that some nations believe to be appropriate. Because the health and safety program should be driven by meeting best industrial hygiene practice, always use the lowest recommended exposure values when protecting human health.

In addition, pay careful attention to equipment corrosion that ultimately may lead to safety hazards from equipment failure.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

b. Inorganic acids and bases: Many inorganic acids and bases have PELs and TLVs. Table 1090:I presents PELs (based on U.S. standards) and/or TLVs as well as short-term exposure limits and ceilings for some inorganic chemicals specified in *Standard Methods*. These PELs and TLVs indicate the maximum air concentration to which workers may be exposed. Fumes of these acids and bases are severe eye and respiratory system irritants. Liquid or solid acids and bases can quickly cause severe burns of the skin and eyes. When acids are heated to increase the rate of digestion of organic materials, they pose a significantly greater hazard because fumes are produced and the hot acid reacts very quickly with the skin.

Store acids and bases separately in well-ventilated areas and away from volatile organic and oxidizable materials. Use containers (rubber or plastic buckets) to transport acids and bases.

Work with strong acids and bases only in a properly functioning chemical fume hood. Slowly add acids and bases to water (with constant stirring) to avoid spattering. If skin contact is made, thoroughly flush the contaminated area with water and seek medical attention if irritation persists. Do not wear contaminated clothing until after it has been cleaned thoroughly. Leather items (e.g., belts and shoes) will retain acids even after rinsing with water and may cause severe burns if worn. If eye contact is made, immediately flush both eyes for at least 15 min with an eye wash and seek medical attention.

c. Perchloric acid and other highly reactive chemicals: Concentrated perchloric acid reacts violently or explosively on contact with organic material and may form explosive heavy metal perchlorates. Do not use laboratory fume hoods used with perchloric acid for organic reagents, particularly volatile solvents. In addition to these hazards, perchloric acid produces severe burns when contact is made with the skin, eyes, or respiratory tract. Preferably provide a dedicated perchloric acid hood. Follow the manufacturer's instructions for proper cleaning, because exhaust ducts become coated and must be washed down regularly.

Use extreme caution when storing and handling highly reactive chemicals, such as strong oxidizers. Improper storage can promote heat evolution and explosion. Do not store strong oxidizers and reducers in close proximity.

d. Organic solvents and reagents: Most solvents specified in *Standard Methods* have PELs and/or TLVs as well as short-term exposure limits or ceilings for workplace exposures (see Table 1090:II).

Many organic reagents, unlike most organic solvents, do not have PELs/TLVs or short-term exposure limits and ceilings, but this does not mean that they are less hazardous. Table 1090:III contains PELs/TLVs or short-term exposure limits and ceilings for some reagents specified in *Standard Methods*.

Some compounds are suspect carcinogens and should be treated with extreme caution. These compounds include solvents and reagents such as benzene, carbon tetrachloride, chloroform, dioxane, perchloroethylene, and benzidine. Lists of chemicals with special hazardous characteristics are available from the Occupational Safety and Health Administration and the National Institute for Occupational Safety and Health. In the U.S., the lists of ''Regulated Carcinogens'' and of ''Chemicals Having Substantial Evidence of Carcinogenicity'' are

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

especially important. Developing and following laboratory handling procedures for compounds on such authoritative lists should significantly reduce the potential for exposures.

Solvents used in the laboratory usually fall into several major categories: alcohols, chlorinated compounds, and hydrocarbons. Exposure to each of these classes of compounds can have a variety of health effects. Alcohols, in general, are intoxicants, capable of causing irritation of the mucous membranes and drowsiness. Chlorinated hydrocarbons cause narcosis and damage to the central nervous system and liver. Hydrocarbons, like the other two groups, are skin irritants and may cause dermatitis after prolonged skin exposure. Because of the volatility of these compounds, hazardous vapor concentrations can occur (fire or explosion hazard). Proper ventilation is essential.

The majority of organic reagents used in this manual fall into four major categories: acids, halogenated compounds, dyes and indicators, and pesticides. Most organic acids have irritant properties. They are predominantly solids from which aerosols may be produced. Dyes and indicators also present an aerosol problem. Handle pesticides with caution because they are poisons, and avoid contact with the skin. Wear gloves and protective clothing. The chlorinated compounds present much the same hazards as the chlorinated solvents (narcosis and damage to the central nervous system and liver). Proper labeling for the compound, including a date for disposal based on the manufacturer's recommendations, permits tracking chemical usage and disposal of outdated chemicals.

10. References

1. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Respiratory Protection. 29 CFR 1910.134.
2. U.S. PUBLIC HEALTH SERVICE. 1980. Annual Report on Carcinogens. National Toxicology Program, Dep. Health & Human Services, U.S. Government Printing Off., Washington, D.C.
3. INTERNATIONAL AGENCY FOR RESEARCH ON CANCER. (Various dates). IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. World Health Org. Publications Center, Albany, N.Y.
4. NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH. 1985. Occupational Health Guidelines for Chemical Hazards. NIOSH/ OSHA-NIOSH Publ. No. 85-123, U.S. Government Printing Off., Washington, D.C.
5. U.S. PUBLIC HEALTH SERVICE, CENTERS FOR DISEASE CONTROL. 1993. Registry of Toxic Effects of Chemical Substances. U.S. Government Printing Off., Washington, D.C.
6. SAX, N.I. 1989. Dangerous Properties of Industrial Materials. Van Nostrand Reinhold, New York, N.Y.
7. AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS. 1992. Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. American Conf. Governmental Industrial Hygienists, Cincinnati,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Ohio.

8. U.S. PUBLIC HEALTH SERVICE, CENTERS FOR DISEASE CONTROL. 1990. NIOSH Pocket Guide to Chemical Hazards. DHHS (NIOSH) Publ. No. 90-117, U.S. Government Printing Off., Washington, D.C.

11. Bibliography

SLINEY, D. 1980. Safety with Lasers and Other Optical Sources: A Comprehensive Handbook. Plenum Press, New York, N.Y.

COMMITTEE ON HAZARDOUS SUBSTANCES IN THE LABORATORY. 1981. Prudent Practices for Handling Hazardous Chemicals in Laboratories. National Academy Press, Washington, D.C.

COMMITTEE ON HAZARDOUS SUBSTANCES IN THE LABORATORY. 1983. Prudent Practices for Disposal of Chemicals from Laboratories. National Academy Press, Washington, D.C.

FURR, A.K., ed. 1990. CRC Handbook of Laboratory Safety, 3rd ed. CRC Press, Inc., Boca Raton, Fla.

COMPRESSED GAS ASSOCIATION, INC. 1990. Handbook of Compressed Gases. Van Nostrand Reinhold Co., New York, N.Y.

AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS. 1992. Threshold Limit Values. American Conf. Governmental Industrial Hygienists, Cincinnati, Ohio.

1090 C. Laboratory Facility/Fixed Equipment

1. Facility Design

The laboratory facility must have a general ventilation system with air intakes and exhausts located to avoid intake of contaminated air, well-ventilated stockrooms and/or storerooms, laboratory hoods and sinks, miscellaneous safety equipment including eyewash fountains and safety showers, and arrangements for the disposal of wastes and samples in accordance with applicable federal, state, and local regulations.

2. Facility and Fixed Equipment Maintenance

Maintain facilities and equipment with scheduled maintenance and continual surveillance to ensure proper operation. Give special attention to the adequacy of ventilation system.

a. Facility ventilation systems:

1) The general laboratory ventilation should provide a source of air for breathing and for input to local ventilation devices such as fume hoods. Do not rely on it for protection from exposure to toxic substances used during the working day. The system should direct air flow into the laboratory from nonlaboratory areas and then exhaust the air directly to the exterior of the building in a manner that will prevent its re-entry.

2) Laboratory fume hoods—As a minimum, provide at least 1 linear m of hood space per

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

worker if workers spend most of their time working with chemicals or if they work with chemical substances with PELs or TLVs less than 100 ppm. Equip each hood with a continuous monitoring device to allow convenient confirmation of adequate hood performance before each use. If this is not possible, avoid work with substances with PELs or TLVs less than 100 ppm or with unknown toxicity, or provide other types of local ventilation devices.

3) Other local ventilation devices—Provide ventilated chemical/biological cabinets, canopy hoods and instrument/work station snorkels as needed. Many local ventilation devices require a separate exhaust duct, as do canopy hoods and snorkels.

4) Special ventilation areas/devices—It may be necessary to pass exhaust air from special ventilation areas or devices such as radiological hoods, glove boxes, and isolation rooms through HEPA filters, scrubbers, or other treatment before release into regular exhaust system. Ensure that cool rooms and warm rooms have provisions for rapid escape and for escape in the event of electrical failure.

5) Ventilation system modifications—Make alteration in the ventilation system only in consultation with an expert qualified in laboratory ventilation system design. Thoroughly test changes in the ventilation system to demonstrate adequate worker protection.

b. Facility ventilation system performance: A ventilation system rate of 4 to 12 room air changes per hour is considered adequate where local exhaust ventilation devices such as fume hoods are used as the primary method of control. General ventilation system air flow should not be turbulent and should be relatively uniform throughout the laboratory, with no high-velocity or static areas; air flow into and within laboratory fume hoods should not be excessively turbulent; fume hood face velocity should be adequate for the intended use (for general-purpose fume hoods this is typically 18 to 30 m/min). The effective protection provided by a fume hood depends on a number of factors including hood location and design, and cannot be determined solely on the basis of the face velocity.

c. Facility ventilation system evaluation: Evaluate performance characteristics (quality and quantity) of the ventilation system on installation, re-evaluate whenever a change in local ventilation devices is made, and monitor routinely. Schedule such monitoring with a frequency dictated by the type, age, condition, and any accessories associated with the device, but at least annually; monitor hoods at least quarterly. Document all ventilation system checks or actions such as flow checks, calibration, alterations, repairs, maintenance, or any other action that may determine or change flow efficiency or characteristics.

3. Bibliography

AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS. 1982. Industrial Ventilation: A Manual of Recommended Practice, 17th ed. American Conf. Governmental Industrial Hygienists, Inc., Cincinnati, Ohio.

AMERICAN NATIONAL STANDARDS INSTITUTE & AMERICAN SOCIETY OF HEATING, REFRIGERATING, AND AIR CONDITIONING ENGINEERS. 1985. Method of Testing Performance of Laboratory Fume Hoods. ANSI/ ASHRAE 110-1985, American National Standards Inst.,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Inc., New York, N.Y.

INSTITUTE OF ENVIRONMENTAL SCIENCES. 1986. Recommended Practice for Laminar Flow Clean Devices. RP-CC-002-86, Inst. Environmental Sciences, Mount Prospect, Ill.

NATIONAL SANITATION FOUNDATION. 1987. Class II Biohazard Cabinetry (Laminar Flow). Standard 49-1987, National Sanitation Found., Ann Arbor, Mich.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1988. Standard Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water. ASTM D3856, American Soc. Testing & Materials, Philadelphia, Pa.

AMERICAN NATIONAL STANDARDS INSTITUTE & AMERICAN SOCIETY OF HEATING, REFRIGERATING, AND AIR CONDITIONING ENGINEERS. 1989. Ventilation for Acceptable Indoor Air Quality. ANSI/ASHRAE 62-1989, American National Standards Inst., Inc., New York, N.Y.

AMERICAN SOCIETY OF HEATING, REFRIGERATING, AND AIR CONDITIONING ENGINEERS. 1989. Handbook—Fundamentals. American Soc. Heating, Refrigerating & Air-Conditioning Engineers. Inc., Atlanta, Ga.

AMERICAN NATIONAL STANDARDS INSTITUTE. 1990. Emergency Eyewash and Shower Equipment. ANSI Z358.1-990, American National Standards Inst., New York, N.Y.

AMERICAN NATIONAL STANDARDS INSTITUTE. 1991. Fundamentals Governing the Design and Operation of Local Exhaust Systems. ANSI Z9.2-1979 (rev. 1991), American National Standards Inst., Inc., New York, N.Y.

AMERICAN NATIONAL STANDARDS INSTITUTE. 1991. Standard on Fire Protection for Laboratories Using Chemicals. NFPA 45, National Fire Protection Assoc., Quincy, Mass.

AMERICAN NATIONAL STANDARDS INSTITUTE & AMERICAN INDUSTRIAL HYGIENE ASSOCIATION. 1993. Standard for Laboratory Ventilation. ANSI/AIHA Z9.5, American Industrial Hygiene Assoc., Fairfax, Va.

AMERICAN NATIONAL STANDARDS INSTITUTE. 1993. Flammable and Combustible Liquids Code. NFPA 30, National Fire Protection Assoc., Quincy, Mass.

AMERICAN SOCIETY OF HEATING, REFRIGERATING, AND AIR CONDITIONING ENGINEERS. 1993. Handbook—Applications. American Soc. Heating, Refrigerating & Air-Conditioning Engineers, Inc., Atlanta, Ga.

1090 D. Hazard Evaluation

1. Hazard Evaluation

Hazard evaluation refers to the assessment of whether an employee has been overexposed to a hazardous substance or if such an exposure episode is likely to occur and to what extent.

The evaluation does not require monitoring airborne concentrations of the hazardous substances involved. Such an assessment may be informal and simply involve considering, among other factors, the chemical and physical properties of the substance and the quantity of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

substance used. In addition, the exposure assessment may be sufficient to estimate the probability of an overexposure.

Specify, document, and use hazard assessment criteria. Base such criteria on the toxicity of the substances to be used, the exposure potential of the chemical procedures to be performed, and the capacity of the available engineering control systems.

In cases where continuous monitoring devices are used, include resulting exposure data in the exposure evaluation. Air monitoring *only* provides information for inhalation exposure. Other means are required to determine whether overexposure could have occurred as a result of ingestion, or dermal or eye contact.

2. Spills of Toxic or Hazardous Substances

Spills are usually the result of loss of containment due to equipment failure or breakage (uncontrolled releases). The loss of containment can result in overexposure episodes. Calculations using data from material safety data sheets, the chemical and physical properties of the substance, known laboratory air changes, and work-station air volume will allow assessment of the possibility of an overexposure episode.

3. Work Practice Assignment

Use the information calculated from these exposure assessments to develop the written work practices needed to protect the health of the employee while conducting the procedure.

4. Documentation of Hazard Assessments

Document, validate, and authenticate all hazard assessments, preferably using a standard form.

5. Bibliography

DOULL, J., C.D. KLAASSEN & M.O. AMDUR. 1980. Casarett and Doull's Toxicology: The Basic Science of Poisons, 2nd ed. Macmillan Publishing Co., Inc., New York, N.Y.

WILLIAMS, P.L. & J.L. BURSON. 1985. Industrial Toxicology: Safety and Health Applications in the Workplace. Van Nostrand Reinhold Co., New York, N.Y.

BATTELLE MEMORIAL INSTITUTE. 1985. Guidelines for Hazard Evaluation Procedures. American Inst. Chemical Engineers, New York, N.Y.

PLOG, B.A., ed. 1988. Fundamentals of Industrial Hygiene, 3rd ed. National Safety Council, Chicago, Ill.

OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. 1988. Job Hazard Analysis. OSHA Publ. No. 3071, U.S. Dep. Labor, Occupational Safety & Health Admin., Washington, D.C.

OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. 1988. Chemical Hazard Communication. OSHA Publ. No. 3084, U.S. Dep. Labor, Occupational Safety & Health Admin., Washington, D.C.

OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. 1988. How to Prepare for Workplace Emergencies. OSHA Publ. No. 3088, U.S. Dep. Labor, Occupational Safety & Health

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Admin., Washington, D.C.

BRETHERICK, L., ed. 1990. Bretherick's Handbook of Reactive Chemical Hazards. Butterworths, London, U.K.

OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. 1990. Hazard Communication Guidelines for Compliance. OSHA Publ. No. 3111, U.S. Dep. Labor, Occupational Safety & Health Admin., Washington, D.C.

HAWKINS, N.C., S.K. NORWOOD & J.C. ROCK, eds. 1991. A Strategy for Occupational Exposure Assessment. American Industrial Hygiene Assoc., Fairfax, Va.

CLAYTON, G.D. 1991. Patty's Industrial Hygiene and Toxicology. John Wiley & Sons, New York, N.Y.

Also see references 2 through 8, Section 1090B.10.

1090 E. Personal Protective Equipment

1. Introduction

The employer must provide and maintain personal protective equipment (PPE) in condition that is sanitary and reliable against hazards in the workplace. All PPE also must be properly designed and constructed for the work to be performed. Several general references on PPE are available.[1-3] .

It is essential to select PPE based on an assessment of the hazards[3] or potential hazards to which an employee is exposed, to insure that the correct PPE will be obtained. Use personal protective equipment only when it is not possible or feasible to provide engineering controls. Such personal protective equipment includes all clothing and other work accessories designed to create a barrier against workplace hazards.

The basic element of any personal protective equipment management program must be an in-depth evaluation of the equipment needed to protect against the hazards at the workplace. Management dedicated to the safety and health of employees must use that evaluation to set a standard operating procedure for personnel, then encourage those employees to use, maintain, and clean the equipment to protect themselves against those hazards.

Using personal protective equipment requires hazard awareness and training on the part of the user. Make employees aware that the equipment does not eliminate the hazard. If the equipment fails, exposure will occur. To reduce the possibility of failure, use equipment that is properly fitted and maintained in a clean and serviceable condition.

Selection of the proper piece of personal protective equipment for the job is important. Employers and employees must understand the equipment's purpose and its limitations. Do not alter or remove equipment even though an employee may find it uncomfortable (equipment may be uncomfortable simply because it does not fit properly).

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2. Eye Protection

The LH&S standard of practice requires the use of eye and face protective equipment[3] where there is a reasonable probability of injury prevention through its use. Employers must provide a type of protector suitable for work to be performed, and employees must use the protectors. These requirements also apply to supervisors and management personnel, and to visitors while they are in hazardous areas.

Protectors must provide adequate protection against particular hazards for which they are designed, be reasonably comfortable when worn under the designated conditions, fit snugly without interfering with the movements or vision of the wearer, and be durable, easy to disinfect and clean, and kept in good repair.

In selecting the protector, consider the kind and degree of hazard. Where a choice of protectors is given, and the degree of protection required is not an important issue, worker comfort may be a deciding factor.

Persons using corrective glasses and those who are required to wear eye protection must wear glasses with protective lenses providing optical correction, goggles that can be worn over corrective glasses without disturbing the adjustment of the glasses, or goggles that incorporate corrective lenses mounted behind the protective lenses.

When limitations or precautions are indicated by the manufacturer, transmit them to the user and observe strictly. Safety glasses require special frames. Combinations of normal wire frames with safety lenses are not acceptable.

Design, construction, testing, and use of eye and face protection must be in accordance with national standards.[4]

3. Protective Work Gloves

Match glove material to the hazard: such materials as nitrile, neoprene, natural rubber, PVC, latex, and butyl rubber vary widely in chemical resistance. What may be safe with one chemical may prove harmful with another (see Table 1090:IV and Table 1090:V). Glove thickness may be as important as glove material in some cases. Many organic reagents, unlike most organic solvents, do not have PELs/TLVs but this does not mean that they are less hazardous.

Evaluate physical properties of the glove material: In addition to chemical resistance, glove materials vary in physical toughness. Select the glove that provides the abrasion, tear, flame, and puncture resistance required for the job.

Maximize comfort and dexterity. Lined gloves absorb perspiration and help insulate the hand. Unlined gloves conform to the hand. Lighter-gauge gloves improve touch sensitivity and flexibility, heavier-gauge gloves add protection and strength.

Ensure a safe grip. Nonslip grips allow for easier and safer handling. Embossed, pebbled, etched, and dotted coatings improve grip in wet or dry working conditions.

Measure proper size and length. Loose-fitting gloves affect dexterity and can be hazardous. Tight-fitting gloves may cause hand fatigue and tend to wear out faster. Gloves should fit

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

comfortably without restricting motion and they should be long enough to protect the wrist, forearm, elbow, or the entire arm, depending on the application.

4. Head Protection

Water and wastewater laboratories seldom require this kind of personal protection, but field work may require such protection.

Head injuries are caused by falling or flying objects or by bumping the head against a fixed object. Head protection, in the form of protective hats, must both resist penetration and absorb the shock of a blow. Make the shell of the hat of a material hard enough to resist the blow, and utilize a shock-absorbing lining composed of head band and crown straps to keep the shell away from the wearer's skull. Protective materials used in helmets should be water-resistant and slow burning. Helmets consist essentially of a shell and suspension. Ventilation is provided by a space between the headband and the shell. Ensure that each helmet is accompanied by instructions explaining the proper method of adjusting and replacing the suspension and headband.

Visually inspect daily all components, shells, suspensions, headbands, sweatbands, and any accessories for signs of dents, cracks, penetration or any other damage that might reduce the degree of safety originally provided.

Do not store or carry helmets on the rear window deck of an automobile because sunlight and extreme heat may adversely affect the degree of protection.

Further information is available elsewhere.[3,5]

5. Hearing Protection

Exposure to high noise levels can cause hearing loss or impairment, and it can create physical and psychological stress. There is no cure for noise-induced hearing loss, so prevention of excessive noise exposure is the only way to avoid hearing damage. Specifically designed protection is required, depending on the type of noise encountered.

Use preformed or molded ear plugs fitted individually by a professional. Waxed cotton, foam, or fiberglass wool earplugs are self-forming. When properly inserted, they work as well as most molded earplugs. Plain cotton is ineffective as protection against hazardous noise.

Some earplugs are disposable, to be used one time and then thrown away. Clean nondisposable types after each use for proper protection.

Earmuffs need to make a perfect seal around the ear to be effective. Glasses, long sideburns, long hair, and facial movements, such as chewing, can reduce protection. Special equipment is available for use with glasses or beards.

More specific information on hearing conservation is available.[3]

6. Foot and Leg Protection

According to accident reviews most workers who suffered impact injuries to the feet were not wearing protective footwear. Furthermore, most of their employers did not require them to wear safety shoes. The typical foot injury was caused by objects falling less than 1.2 m and the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

median weight was about 30 kg. Most workers were injured while performing their normal job activities at their worksites.

Safety shoes should be sturdy and have an impact-resistant toe. In some shoes, metal insoles protect against puncture wounds. Additional protection, such as metatarsal guards, may be found in some types of footwear. Safety shoes come in a variety of styles and materials, such as leather and rubber boots and oxfords.

Safety footwear is classified according to its ability to meet minimum requirements for both compression and impact test. Those requirements and testing procedures and further information may be found elsewhere.[3,6]

7. References

1. AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS. 1987. Guidelines for the Selection of Chemical Protective Clothing, 3rd ed. American Conf. Governmental Industrial Hygienists, Inc., Cincinnati, Ohio.
2. FORSBERG, K. & S.Z. MANSDORF. 1993. Quick Selection Guide To Chemical Protective Clothing, 2nd ed. Van Nostrand Reinhold, New York, N.Y.
3. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. General Requirements for Personal Protective Equipment. 29 CFR 1910.132.
4. AMERICAN NATIONAL STANDARDS INSTITUTE. 1968. Design, Construction, Testing, and Use of Eye and Face Protection. ANSI Z87 1-1968, American National Standards Inst., Inc., New York, N.Y.
5. AMERICAN NATIONAL STANDARDS INSTITUTE. 1986. Safety Requirements for Industrial Head Protection. ANSI Z89.1-1986. American National Standards Inst., Inc., New York, N.Y.
6. AMERICAN NATIONAL STANDARDS INSTITUTE. 1967 & 1983. Men's Safety-Toe Footware. ANSI Z41 1-1967 & Z41-1983, American National Standards Inst., Inc., New York, N.Y.

1090 F. Worker Protection Medical Program

1. Preventive Medicine Program

The preventive medicine program should include inoculations to provide protection from tetanus and other diseases that are associated with the types of samples received and analyzed by the laboratory. The scope of this program depends on the diseases prevalent in the area where the samples originate. The program also must comply with the appropriate regulations.

2. Medical Surveillance

Routine surveillance may be indicated for anyone whose work involves routine handling of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

hazardous chemical or biological substances. Consult a qualified occupational health physician and/or toxicologist to determine whether a regular schedule of medical surveillance is indicated.

3. Environmental Monitoring

a. General: The initiation of environmental monitoring (exposure monitoring) associated with laboratory uses of hazardous chemical substances is triggered by exposures exceeding the action level (usually defined as one-half the PEL or TLV), PEL, or TLV. The employer is responsible for ensuring that employees' exposures to such substances do not exceed the PELs specified in the regulations dealing with air contaminants.[1]

b. Employee exposure determination: Determine a worker's exposure to any hazardous chemical substance if there is reason to believe that exposure levels for that substance routinely exceed the action level. Where there is no action level for a substance the worker exposure must not exceed the PEL or TLV. If the initial monitoring confirms that an employee exposure exceeds the action level, or in the absence of an action level, the PEL, the employer must immediately comply with the exposure monitoring provisions of the relevant national standard. Monitoring may be terminated in accordance with the relevant standard (if one exists) or when the exposures are found to be below the action level (one half the PEL or TLV) or in the absence of an action level, below the PEL or TLV. The workers are to be notified in accordance with national standard; if none exists, they should at least be notified within 15 working days after any monitoring results have become available to the employer, either by contacting the employee individually or by posting the results in an appropriate location accessible to employees.

4. Medical Consultation and Medical Examinations

All employees who work with hazardous chemicals should have an opportunity to receive medical attention (at no personal cost), including any follow up examinations that the examining physician determines to be necessary, under the following circumstances:

- Whenever an employee develops signs or symptoms associated with an exposure to a hazardous chemical that the employee may have been using.
- Where exposure monitoring reveals an exposure level routinely above the action level (or in the absence of an action level, the PEL or TLV). For a national regulated substance for which there are exposure monitoring and medical surveillance requirements, establish medical surveillance for the affected employee as prescribed by the particular standard.
- Whenever an uncontrolled event, such as a spill, leak, explosion, or other occurrence, takes place in the work area, resulting in the likelihood of a hazardous exposure. Provide the affected employee an opportunity for a medical consultation to determine the need for a medical examination.

All medical examinations and consultations should be performed by, or under the direct supervision of, a licensed physician, without cost to the employee or loss of pay, and at a

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

reasonable time and place. Inform the physician of the identity of the hazardous chemical(s) to which the employee may have been exposed; the conditions under which the exposure occurred, including quantitative exposure data, if available; and the signs and symptoms of exposure that the employee is experiencing, if any. The employer must obtain from the examining physician a written opinion that includes any recommendation for further medical follow-up, the results of the medical examination and any associated tests, notice of any medical condition revealed during the examination that may place the employee at increased risk as a result of exposure to a hazardous chemical found in the workplace, and a statement that the employee has been informed by the physician of the results of the consultation or medical examination and any medical condition that may require further examination or treatment. The written opinion must not reveal specific findings or diagnoses unrelated to occupational exposure.

5. Reference

1. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Air Contaminants. 29 CFR 1910.1000.

6. Bibliography

DOULL, J., C.D. KLAASSEN & M.O. AMDUR. 1980. Casarett and Doull's Toxicology: The Basic Science of Poisons, 2nd ed. Macmillan Publishing Co., Inc., New York, N.Y.

WILLIAMS, P.L. & J.L. BURSON. 1985. Industrial Toxicology: Safety and Health Applications in the Workplace. Van Nostrand Reinhold Co., New York, N.Y.

OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Access to Employee Exposure and Medical Records. 29 CFR 1910.20.

OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Occupational Exposure to Hazardous Chemicals in Laboratories. 29 CFR 1910.1450.

1090 G. Provisions for Work with Particularly Hazardous Substances

The information outlined in the following paragraphs meets the LH&S standard of practice[1] and also represents good industrial hygiene practices.

1. Designated Area

Wherever appropriate, the employer must establish a ‘‘designated area,’’ that is, an area that may be used for work with select carcinogens, reproductive toxins, or substances having a high degree of acute toxicity. A designated area may be the entire laboratory, an area of a laboratory, or a device such as a laboratory hood.

2. Select Carcinogen

In the U.S. a ‘‘select carcinogen’’ means any substance meeting at least one of the following criteria: the substance is regulated by OSHA as a carcinogen; it is listed under the category,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

‘‘known to be carcinogenic,’’ by the U.S. National Toxicology Program (NTP);[2] it is listed under Group 1 (carcinogenic to humans) by the International Agency for Research on Cancer (IARC);[3] or it is listed in either Group 2A or 2B by IARC[3] or under the category, ‘‘reasonably anticipated to be carcinogenic’’ by NTP,[2] and causes statistically significant tumor incidence in experimental animals after inhalation exposure of 6 to 7 h/d, 5 d/week, for significant portion of a lifetime to dosages of less than 10 mg/m^3, or after repeated skin application of less than 300 mg/kg of body weight/week, or after oral dosages of less than 50 mg/kg of body weight/d.

3. Use of Containment Devices

The work conducted and its scale must be appropriate to the physical facilities available and, especially, to the quality of ventilation.

The general laboratory ventilation system must be capable of providing air for breathing and for input to local ventilation devices. It should not be relied on for protection from toxic substances released into the laboratory, but should ensure that laboratory air is continually replaced, preventing increase of air concentrations of toxic substances during the working day, and that air flows into the laboratory from nonlaboratory areas and out to the exterior of the building.

4. References

1. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Laboratory Standard. Occupational Exposure to Hazardous Chemicals in Laboratories. 29 CFR 1910.1450.
2. U.S. PUBLIC HEALTH SERVICE, NATIONAL TOXICOLOGY PROGRAM. 1980. Annual Report on Carcinogens. Dep. Health & Human Services, U.S. Government Printing Off., Washington, D.C.
3. INTERNATIONAL AGENCY FOR RESEARCH ON CANCER. (Various dates). IARC monographs on risk of chemicals to humans. World Health Org. Publications Center, Albany, N.Y.

5. Bibliography

NATIONAL INSTITUTES OF HEALTH. 1981. Guidelines for the Laboratory Use of Chemical Carcinogens. NIH Publ. No. 81-2385, U.S. Government Printing Off., Washington, D.C.

Also see Section 1090C.3.

1090 H. Biological Safety

1. Introduction

The analysis of environmental samples involves worker contact with samples that may be contaminated with agents that present microbiological hazards. The majority of these agents

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

involve exposures to pathogenic microorganisms or viruses that may produce human disease by accidental ingestion, inoculation, injection, or other means of cutaneous penetration. The primary means of exposure to these microbiological hazards involves hand-mouth contact while handling the samples, contaminated laboratory materials and/or aerosols created by incubating, pipetting, centrifuging, or blending of samples or cultures. Use the following rules, work practices and/or procedures to control or minimize exposure to these agents.

2. General Rules

Do not mix dilutions by blowing air through a pipet into a microbiological culture.

When working with grossly polluted samples, such as wastewater or high-density microbial cultures, use a pipetting device attached to a pipetting bulb to prevent accidental ingestion (never pipet by mouth).

Because untreated waters may contain waterborne pathogens, place all used pipets in a jar containing disinfectant solution for decontamination before glassware washing. Do not place used pipets on table tops, on laboratory carts, or in sinks without adequate decontamination.

3. Work Practices

Good personal hygiene practices are essential to control contact exposures. Frequently disinfect hands and working surfaces. Encourage immunization of laboratory staff against tetanus and possibly typhoid and other infectious agents to minimize risk of exposure.

Provide drinking water outside the laboratory, preferably from a foot-operated drinking fountain.

Eliminate flies and other insects to prevent contamination of sterile equipment, media, samples, and bacterial cultures and to prevent spread of infectious organisms to personnel.

Observe appropriate precautions in use of laboratory equipment. Use a leakproof blender tightly covered during operation to minimize contamination. Use a centrifuge tightly covered to minimize exposure if culture-containing tubes should shatter during centrifuging. The tube breakage produces a cleanup problem and microbiological aerosols. Conduct activities such as inserting a hot loop into a flask of broth culture in a manner that eliminates or minimizes the hazards due to aerosolized microorganisms. Sterilize contaminated materials (cultures, samples, used glassware, serological discards, etc.) by autoclaving before discarding them or processing for reuse. Preferably use specially marked biohazard bags for disposal. Dispose of contaminated broken glass in a specially marked container.

4. Procedures

Quaternary ammonium compounds that include a compatible detergent, or solutions of sodium hypochlorite are satisfactory disinfectants for pipet discard jars. Use the highest concentrations recommended for these commercial products provided that this concentration does not cause a loss of markings or fogging of pipets.

Sterilize biological waste materials to eliminate all infectious substances, and sterilize all contaminated equipment or apparatus before washing, storage, or disposal, preferably by

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

autoclaving. When decontaminating materials in the autoclave, heat them to at least 121°C under a pressure of 103 kPa for a minimum of 30 min. The contact time is measured from time the contact chamber reaches 121°C. If the waste is contained in bags, add water to the contents to insure wet heat. Dry heat and chemical treatment also may be used for sterilizing nonplastic items. After sterilization, the wastes can be handled safely and disposed of by conventional disposal systems in accordance with local regulations.

5. Waste Disposal

Sterilize contaminated materials by autoclaving (see ¶ 3 above) before discarding them.

If combustible materials cannot be decontaminated, burn them with special precautions; permits for burning may be required. Use temporary storage for decay or permanent storage for treating radioactive wastes when alternatives are not available. Collect contaminated combustible wastes and animal carcasses in impermeable containers for disposal by incineration.

6. Bibliography

NATIONAL INSTITUTES OF HEALTH. 1981. Guidelines for the Laboratory Use of Chemical Carcinogens. NIH Publ. No. 81-2385, U.S. Government Printing Off., Washington, D.C.

INSTITUTE OF ENVIRONMENTAL SCIENCES. 1986. Recommended Practice for Laminar Flow Clean Devices. RP-CC-002-86. Inst. Environmental Sciences, Mount Prospect, Ill.

NATIONAL SANITATION FOUNDATION. 1987. Class II Biohazard Cabinetry (Laminar Flow). Standard 49-1987, National Sanitation Found., Ann Arbor, Mich.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1988. Standard Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water. ASTM D3856, American Soc. Testing & Materials, Philadelphia, Pa.

FURR, A.K., ed. 1990. CRC Handbook of Laboratory Safety, 3rd ed. CRC Press, Inc., Boca Raton, Fla.

1090 I. Radiological Safety

1. Introduction

This section discusses ionizing radiation safety related to gas chromatography detectors and specific analytical procedures (see Table 1090:VI). Ionizing radiation includes alpha particles, beta particles, gamma rays, and X-rays. Non-ionizing radiation safety is discussed elsewhere (Section 1090B.8).

All persons are exposed to ionizing radiation. The average annual radiation dose to the whole body from cosmic, terrestrial, and internal sources, medical and dental X-rays, etc., is about 185 mrems/year (1.85 mSieverts/year). It is essential to prevent unnecessary continuous or intermittent occupational exposures, and to take steps to eliminate accidents that may result in dangerous radiation exposure.

Personnel who work in laboratories may be exposed to ionizing radiation sources using both

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

procedures and instruments. Evaluate potential exposures and control the associated equipment and procedures using work practices developed to minimize and/or eliminate exposures.

Users of radioactive materials are responsible for compliance with the requirements of their national nuclear regulatory body (in the United States, the Nuclear Regulatory Commission)[1] and/or related state regulations. In addition, administrative or local requirements may apply at specific facilities. The use of ‘‘exempt’’ quantities is regulated[1] even though the facility may be exempt from specific licensing requirements.

Radionuclides are used in laboratories to develop and evaluate analytical methods, to prepare counting standards, and to calibrate detectors and counting instruments (see Part 7000). Sealed sources, such as the nickel-63 detector cell used in electron capture gas chromatograph units, also are common.

2. Exposures

a. Exposure limits and control: The LH&S standard of practice[2] does not permit the use of personal protective equipment for allowing employee exposures above the limits specified by the NRC.[1] The NRC exposure limits are the maximum permissible exposures for 40 h in any workweek of 7 consecutive days.

The exposure limits may be adjusted proportionately (upward) for a period where the exposure is less than 40 h. However, the limit must be adjusted proportionately (downward) for periods where the exposure period is greater than 40 h.

Limiting exposure to ionizing radiation includes providing engineering (physical safeguards) and administrative (procedural) controls for using radioactive materials. Engineering controls include shields, barriers, and interlocks to limit external exposure, and exhaust ventilation systems and personal protective equipment to limit internal contamination. Administrative controls include conducting periodic surveys and reviews of activities, training in the use of radioactive materials, and documented procedures (see below).

Hazards associated with the use of devices, such as X-ray diffraction apparatus or an electron microscope, can be minimized or eliminated by following the manufacturer’s operating instructions and the laboratory safety procedures.

b. Monitoring procedures and equipment: Radiochemical exposure monitoring may be done by collecting and analyzing wipe samples, using portable survey instruments, and/or by collecting and analyzing air samples. More than one technique usually is required.

Survey equipment may either integrate the response over time (e.g., exposure, absorbed dose), or results may be presented as a response rate (e.g., count rate or exposure rate). Typical choices include ion chambers, G-M counters, and scintillation detectors.

Thin-windowed GM-counters are suitable for wipe samples and for monitoring skin and clothing. An alpha scintillation monitor is needed to detect alpha-emitters. An excellent discussion of monitoring techniques for radioisotopes is available.[3]

c. Facility surveys: Conduct periodic surveys to assess the effectiveness of physical and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

procedural controls. Survey procedures generally use wipe tests for removable contamination and/or portable measurement devices for locating or measuring fixed and removable radioactivity.

1) Sealed sources—Check these sources for integrity by wipe tests at least every 6 months. Electron capture detectors using ^{63}Ni or ^{3}H require counting wipes by liquid scintillation or windowless gas-flow proportional counters to measure low-energy beta radiation effectively.

2) Work and storage areas—Survey these areas periodically to assess possible contamination or external radiation fields using portable survey instruments. The frequency of the surveys is dictated by the documented contamination record for the laboratory. Usually the radioactivities presented using the methods of Part 7000 are not measurable with routine survey instruments. Therefore use blanks in the analytical process in determining the presence of low-level contamination.

3) Documentation and records—Completely document each survey, identifying the personnel involved, the location, the type, model, and serial numbers of survey instruments used, the type and energy of radiations measured, the date and time of the survey, the instrument response to a check source, the instrument background count or exposure rate, and the results of each measurement.[4]

d. Personnel surveys and monitoring: Conduct and document surveys after routine use of unsealed radionuclide sources to confirm that personnel and the work area have not been contaminated by the process. Wear monitoring devices if there is a reasonable probability of exceeding 25% of the occupational exposure dose equivalent limit. Personal monitoring devices include film badges, thermoluminescent dosimeters, and solid state electronic dosimeters. The length of time the personal monitoring badges are worn before evaluation depends on the ability of the device to integrate the exposure over long periods, the probability and magnitude of the exposure, and the need to assure that the device is available and used.

Personnel performing procedures in *Standard Methods* would not be expected to receive exposures approaching 1.25 rem/quarter and may wish to consider 3-month wear periods if dosimetry is required.

Personal (external radiation) exposure is evaluated by using a personal dosimeter, preferably the film dosimeter (badge). The dosimeter badge measures the accumulated radiation over a period of time. Pocket ionization chambers, thermoluminescent dosimeters, and thimble chambers also may be used to supplement the film dosimeter.

Whole body or gamma spectrometry radiation detectors may be used to determine the presence of radioactive substances in the body, but these instruments are expensive and require the operator to be specially trained. Evaluate equipment and supplies that have been, or are suspected to have been, in contact with radioactive substances to determine if contamination is present. Because body waste may contain radioactive contaminants evaluate it also for the presence of contamination where personal exposures have been confirmed.

3. Work Practices

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Each individual should be familiar with procedures for dealing with radiation emergencies from small spills to major accidents, depending on facility programs. Emergency procedures should include notifications required, containment methods, clean-up procedures, and survey techniques. Emergency supplies should be readily available for coping with major accidents.

Contamination is typically prevented through proper use of laboratory facilities and procedures. Procedures include the use of gloves, aprons, safety glasses, and other protective clothing to eliminate the possibility of skin contamination and transfer. Learn proper pipetting and weighing techniques before working with radioactive sources. Conduct work with unsealed radioactive sources in unobstructed work areas with adequate means of containing and absorbing potential spillage of liquids.

4. Procedures

Develop and implement a radiation safety plan and provide a copy to all persons working with radioactive materials or radiation-producing machines, and provide both lecture and practical training to all employees.

a. Safety plan elements: The recommended minimum plan should include procedures for obtaining authorization to use, order, handle, and store radionuclides; safe handling of unsealed radioactive material; safe response to radiation accidents; decontamination of personnel and facilities; personnel monitoring; laboratory monitoring; and disposal of radioactive materials.

b. Handling radioactive materials: Become knowledgeable about the hazards associated with the materials to be used. Plan work activities to minimize the time spent handling radioactive materials or in using radioactive sources. Work as far from radioactive sources as possible, use shielding appropriate for the materials to be used, and use radioactive materials only in defined work areas. Wear protective clothing and dosimeters as appropriate. Monitor work areas to ensure maximum contamination control. Minimize the accumulation of waste materials in the work area. Use appropriate personal hygiene and self-monitor after using radioactive materials and after each decontamination procedure.

c. Training of users: Train personnel working with radioactive materials in radiation safety as part of the overall occupational health program. Address at least the following topics: characteristics of ionizing radiation and radioactive contamination; radiation dose limits; environmental radiation background; acute and chronic effects; internal and external modes of exposure; basic protective measures; responsibilities of employer and employees; radiation protection program responsibilities; posting, warning signs, and alarms; radiation monitoring programs; and emergency procedures.[5]

5. Waste Disposal

Generalized disposal criteria for radioactive wastes have been developed by the U.S. National Committee on Radiation Protection and Measurements.[4] Two general philosophies govern the disposal of radioactive wastes: dilution and dispersion to reduce the concentration of radionuclide by carrier dilution or dilution in a receiving medium, and concentration and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

confinement, usually involving reduction in waste volume with subsequent storage for decay purposes.

Airborne wastes can be treated by either method. Ventilation includes discharge from hooded operations to the atmosphere. Typical radioactive gases include iodine, krypton, and xenon. Iodine can be removed by scrubbing or by reaction with silver nitrate. Noble gases can be removed by absorption; standard techniques can be used for particulate. Dilution methods are suitable for liquids with low activity. Intermediate levels may be treated by various physical-chemical processes to separate the waste into a nonradioactive portion that can be disposed of by dilution and a high-activity portion to be stored. Solid wastes may consist of equipment, glassware, and other materials. When possible, decontaminate these materials and reuse. Decontamination usually results in a liquid waste.

Dispose of all waste in conformance with the requirements of the regulatory authority having jurisdiction.

Determine the laboratory's status and obtain approval before storing, treating and/or disposing of wastes.

6. References

1. NUCLEAR REGULATORY COMMISSION. Standards for Protection Against Radiation. 10 CFR Part 20.
2. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Ionizing Radiation. 29 CFR 1910.96.
3. FURR, A.K., ed. 1990. CRC Handbook of Laboratory Safety, 3rd ed. CRC Press, Inc., Boca Raton, Fla.
4. NATIONAL COUNCIL ON RADIATION PROTECTION AND MEASUREMENTS. 1976. Environmental Radiation Measurements. Rep. No. 50, National Counc. Radiation Protection & Measurements, Washington, D.C.

7. Bibliography

NATIONAL COUNCIL ON RADIATION PROTECTION AND MEASUREMENTS. 1978. Instrumentation and Monitoring Methods for Radiation Protection. Rep. No. 57, National Counc. Radiation Protection & Measurements, Washington, D.C.

NATIONAL COUNCIL ON RADIATION PROTECTION AND MEASUREMENTS. 1978. A Handbook of Radioactivity Measurements Procedures. Rep. No. 58, National Counc. Radiation Protection & Measurements, Washington, D.C.

NATIONAL COUNCIL ON RADIATION PROTECTION AND MEASUREMENTS. 1978. Operational Radiation Safety Program. Rep. No. 59, National Counc. Radiation Protection & Measurements, Washington, D.C.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1090 J. Chemical Hygiene Plan

1. Introduction

The information presented in this section describes the intent and lists the minimum requirements and critical elements of the OSHA laboratory standard.[1] This standard is performance-based and represents good industrial hygiene practice. Any organization that chooses not to follow or use the OSHA standards to meet that standard's requirements must demonstrate that the procedures it uses meet the minimum level of employee protection afforded by the OSHA standard.

Much of the information presented in the preceding subsections of 1090 was provided as guidance and should be used in developing and finalizing the laboratory chemical hygiene plan (CHP).

2. Requirements

Develop and implement a written CHP capable of protecting employees from health hazards associated with the chemicals used in the laboratory. This CHP must be capable of keeping exposures below the permissible exposure limits (PELs/TLVs) and also must be readily available to employees. The CHP must at minimum address the following elements, and must describe specific measures the employer will undertake to ensure laboratory employee protection.

a. Standard operating procedures or work practices: Include procedures and practices relevant to safety and health considerations. These are to be followed when laboratory work involves the use of hazardous chemicals. Include the information contained in MSDSs for hazardous chemicals when conducting a hazard assessment and developing work practices. Some of the guidance presented in an MSDS is intended for use in industrial settings where material is used in large quantities for a full work shift and not for the small-volume, short-duration exposures experienced in laboratories.

b. Exposure hazard criteria and procedures: These will be used to determine and implement control measures for reducing employee exposure to hazardous chemicals while conducting laboratory operations. They include engineering controls, the use of personal protective equipment, and hygiene practices. Pay particular attention to the selection of control measures for work activities that involve chemicals known to be extremely hazardous.

c. Protective equipment performance procedures: These include procedures for evaluating the performance of fume hoods and other protective equipment and specific measures to be taken to ensure proper and adequate performance of such equipment.

d. Employee information and training: This training must be timely, be refreshed periodically, evaluated for effectiveness, and documented.

e. Approval procedures: The plan must state the circumstances under which a specific laboratory operation, procedure, or activity requires prior approval before implementation.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

f. Employee medical consultation and medical examinations.

g. Safety personnel: The plan must designate personnel responsible for implementation of the CHP. This should include the formal assignment of a Chemical Hygiene Officer and, where appropriate, the establishment of a Chemical Hygiene Committee.

h. Additional employee protection: The plan should include provisions for working with particularly hazardous substances. These substances include ‘‘select carcinogens’’ (see Section 1090G.2), reproductive toxins, and substances that have a high degree of acute toxicity. Give specific consideration to establishment of a designated area, use of containment devices such as fume hoods or glove boxes, procedures for safe removal of containment waste, decontamination procedures, emergency plans and procedure (test annually as a minimum), and employer review and evaluation of the effectiveness of the CHP at least annually and updating as necessary.

3. Reference

1. OCCUPATIONAL SAFETY AND HEALTH ADMINISTRATION. Occupational Exposure to Hazardous Chemicals in Laboratories. 29 CFR 1910.1450.

1100 WASTE MINIMIZATION AND DISPOSAL

1100 A. Introduction

Waste minimization and disposal are part of integrated hazardous materials management. It is important to become familiar with federal regulations regarding the use and disposal of hazardous materials prior to their purchase, storage, and use for water and waste-water analysis. Proper management of hazardous materials will reduce the amount of hazardous waste and associated disposal costs.

1100 B. Waste Minimization

1. General Considerations

Waste minimization or pollution prevention in the laboratory is the preferred approach in managing laboratory waste. Minimizing waste makes good economic sense: it reduces both costs and liabilities associated with waste disposal. For certain hazardous-waste generators it also is a regulatory requirement.

2. Waste Minimization Methods

Waste minimization methods include source reduction, recycling, and reclamation.[1] Waste treatment, which also may be considered a form of waste minimization, is addressed in Section 1100C.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Source reduction can be achieved through the purchase and use of smaller quantities of chemicals. While large-volume purchases may seem economical, the costs of disposing of expired-shelf-life materials also must be considered. Date chemical inventory and use oldest stock first, or if possible, use ‘‘just in time’’ material delivery. Commercial laboratories and chemical users in general can return samples or unopened chemicals to sender or supplier for recycling or disposal. Many suppliers will accept unopened containers of chemicals.

Substitute nonhazardous materials for hazardous chemicals where possible. Wherever possible use methods that do not require the use of hazardous chemicals or use micro-scale analytical methods.

Improving laboratory procedures, documentation, and training will increase awareness of waste minimization and proper disposal practices, and may allow different sections within a laboratory to share standards and stock chemicals. Evaluate hazardous materials storage and use areas for potential evaporation, spills, and leaks. Segregate waste streams where possible to keep nonhazardous waste from becoming hazardous waste through contact with hazardous waste. Segregation also facilitates treatment and disposal.

Transfer of unused stock chemicals to other areas of the laboratory where they may be used or to other institutions is a way to minimize waste.[2] Check with laboratory’s legal counsel before transferring chemicals.

Recycling/reclamation has limited potential in water and waste-water laboratories. Volumes generated are generally too small for economical reclamation and purity requirements are often too great. However, organic solvents often can be distilled and recovered for reuse and mercury and silver can be recovered.[3]

3. References

1. ASHBROOK, P.C. & P.A. REINHARDT. 1985. Hazardous wastes in academia. *Environ. Sci. Technol.* 19:1150.
2. PINE, S.H. 1984. Chemical management: A method for waste reduction. *J. Chem. Educ.* 61:A45.
3. HENDRICKSON, K.J., M.M. BENJAMIN, J.F. FERGUSON & L. GOEBEL. 1984. Removal of silver and mercury from spent COD test solutions. *J. Water Pollut. Control. Fed.* 56(5):468.

4. Bibliography

AMERICAN CHEMICAL SOCIETY. 1985. Less is Better. Dep. Public Affairs, American Chemical Soc., Washington, D.C.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. General Considerations

Stringent penalties exist for the improper disposal of hazardous wastes. Potential criminal and civil liability exists for both organizations and individuals. Specific requirements vary by state and local jurisdiction and are subject to change. Federal requirements for hazardous waste generators and transporters and for treatment, storage, and disposal facilities (TSDFs) are found in regulations pursuant to the Resource Conservation and Recovery Act of 1976 (RCRA) as amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA). Many activities, in particular treatment, storage, and disposal of hazardous wastes, require a permit or license.[1,2]

Develop a plan for the safe and legal disposal of chemical and biological substances in conjunction with the laboratory supervisor and safety coordinator. Plan should address the proper transport, storage, treatment, and disposal of hazardous waste. Properly characterize composites and document wastes. Refer to Section 1090 on Safety with regard to protective equipment in the handling of hazardous materials.

2. Waste Treatment and Disposal Methods

Treatment can be used to reduce volume, mobility, and/or toxicity of hazardous waste where expertise and facilities are available. Treatment, even on a small scale, may require a permit. Consult with federal, state, and local regulatory officials.

Waste treatment methods include thermal, chemical, physical, and biological treatment, and combinations of these methods.[1]

a. Thermal treatment: Thermal treatment methods include incineration and sterilization. They involve using high temperatures to change the chemical, physical, or biological character or composition of the waste. Incineration is often used to destroy organic solvents and is preferred for infectious wastes, although sterilization through autoclaving and/or ultraviolet light also may be allowed. Check with local health department officials.

b. Chemical treatment: Methods include chemical reaction (oxidation/reduction, neutralization, ion exchange, chemical fixation, photolysis, coagulation, precipitation) of the waste material. Neutralization of acidic or alkaline wastes is the most common form of chemical treatment. Elementary neutralization of corrosive wastes is exempt from federal RCRA permitting requirements. Before discharge of wastes to a publicly owned treatment works (POTW), ensure that they contain no pollutants (other than corrosivity) exceeding the limits set by the POTW. The oxidation of cyanide to cyanate with a strong chemical oxidant is an example of a toxicity-reducing chemical treatment.

c. Physical treatment: Methods include solidification, compaction, photo-induced reaction, distillation, flocculation, sedimentation, flotation, aeration, filtration, centrifugation, reverse osmosis, ultrafiltration, gravity thickening, and carbon or resin adsorption. Physical treatment generally reduces volume or mobility of waste materials.

d. Biological treatment: Methods include using biosolids to destroy organic compounds, composting organic-rich wastes, and using bioreactors to promote decomposition. Biological

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

treatment usually is economical on a scale larger than is possible in most water and wastewater laboratories.

e. Ultimate disposal: After waste minimization and treatment, remaining waste streams require disposal. Nonhazardous wastes that cannot be treated further can be discharged as wastewater, emitted to the atmosphere, or placed on or in the ground.

With extreme caution, it may be permissible to dispose of limited quantities (at certain concentrations) of laboratory wastes to the sanitary sewer system or to evaporate volatile wastes in chemical ventilation hoods. Obtain written permission of local, state, and federal authorities to dispose of waste in this manner. With increasing regulatory constraints imposed by RCRA, the Clean Air Act, and Clean Water Act, these disposal options are becoming increasingly limited. Wastes disposed of in this manner may contact other substances in the sewer or ventilation systems and produce hazardous reactions.

Most hazardous wastes generated in laboratories must be sent off site for further treatment and disposal. Exercise extreme care in selecting a reputable waste hauler and disposal firm. Many firms will assist laboratories in packaging and manifesting ‘‘lab packs,’’ 19- to 208-L (5- to 55-gal) drums containing several smaller containers of wastes.[1] Liability does not disappear when the waste leaves the generator’s facility. Ensure that the laboratory receives a copy of the completed manifest and certificate of treatment and/or disposal. If possible, visit the disposal facility in advance to observe how it will manage a waste.

Certain wastes require special handling. As mentioned previously, incinerate infectious waste or sterilize it before disposal. Before reuse, sterilize all nondisposable equipment that has come into contact with infectious waste.

Although most water and wastewater laboratories do not work with radiochemical wastes, some do. Handle radiochemical wastes with extreme care. Generalized disposal criteria for radioactive wastes have been developed by the National Council on Radiation Protection and Measurements.[3] Low-level radioactive waste must be in solid form for final disposal on land. Some firms will process liquid radioactive wastes into solids. Adding absorbent materials to liquid radioactive wastes is not permissible. Certain states allow low-level liquid radioactive waste to be discharged to a permitted publicly owned treatment works (POTW).

Other wastes that require special handling include polychlorinated biphenyls (PCBs), dioxin/furans and their precursors, petroleum products, and asbestos. Consult with federal and state officials before disposing of these wastes.

3. References

1. AMERICAN CHEMICAL SOCIETY. 1983. RCRA and Laboratories. Dep. Public Affairs, American Chemical Soc., Washington, D.C.
2. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1990. Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities. 40 CFR Part 264.
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. Standards for Protection Against

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Radiation. 10 CFR Part 20.

4. Bibliography

NATIONAL ACADEMY OF SCIENCES, NATIONAL ACADEMY OF ENGINEERING & INSTITUTE OF MEDICINE. 1983. Prudent Practices for the Disposal of Chemicals from Laboratories. National Academy Press, Washington, D.C.

KROFTA, M. & L.K. WANG. 1985. Hazardous Waste Management in Institutions and Colleges. PB86-194180/AS, U.S. National Technical Information Serv., Springfield, Va.

SNIDER, E.H. 1992. Waste minimization. *In* L.K. Wang & M.H.S. Wang, eds., Handbook of Industrial Waste Treatment, p.1. Marcel Dekker, Inc., New York, N.Y.

DUFOUR, J.T. 1994. Hazardous Waste Management Guide for Laboratories. Dufour Group, Sacramento, Calif.

Figures

Figure 1010:1. Normal (left) and skewed (right) distributions.

Figure 1020:1. Control charts for means.

Figure 1020:2. Duplicate analyses of a standard.

Figure 1020:3. Range chart for variable concentrations.

Figure 1020:4. Range chart for variable ranges.

Figure 1020:5. Means control chart with out-of-control data (upper half).

Figure 1030:1. Detection limit relationship.

Figure 1060:1. Approximate number of samples required in estimating a mean concentration. Source: Methods for the Examination of Waters and Associated Materials: General Principles of Sampling and Accuracy of Results. 1980. Her Majesty's Stationery Off., London, England.

TABLES

TABLE 1010:I. CRITICAL VALUES FOR 5% AND 1% TESTS OF DISCORDANCY FOR A SINGLE OUTLIER IN A NORMAL SAMPLE

Number of Measurements *n*	Critical Value 5%	1%
3	1.15	1.15
4	1.46	1.49

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Number of Measurements *n*	Critical Value 5%	1%
5	1.67	1.75
6	1.82	1.94
7	1.94	2.10
8	2.03	2.22
9	2.11	2.32
10	2.18	2.41
12	2.29	2.55
14	2.37	2.66
15	2.41	2.71
16	2.44	2.75
18	2.50	2.82
20	2.56	2.88
30	2.74	3.10
40	2.87	3.24
50	2.96	3.34
60	3.03	3.41
100	3.21	3.60
120	3.27	3.66

Source: BARNETT, V. T. LEWIS. 1984. Outliers in Statistical Data. John Wiley Sons, New York, N.Y.

TABLE 1020:I. FACTORS FOR COMPUTING LINES ON RANGE CONTROL CHARTS

Number of Observations *n*	Factor for Central Line (D_2)	Factor for Control Limits (D_4)
2	1.128	3.267
3	1.693	2.575
4	2.059	2.282
5	2.326	2.115
6	2.534	2.004

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Source: ROSENSTEIN, M. A. S. GOLDEN. 1964. Statistical Techniques for Quality Control of Environmental Radioassays. AQCS Rep. Stat-1. Public Health Serv., Winchester, Mass.

TABLE 1020:II. EXAMPLE DATA QUALIFIERS

Symbol	Explanation
B	Analyte found in reagent blank. Indicates possible reagent or background contamination.
E	Reported value exceeded calibration range.
J	Reported value is an estimate because concentration is less than reporting limit or because certain QC criteria were not met.
N	Organic constituents tentatively identified. Confirmation is needed.
PND	Precision not determined.
R	Sample results rejected because of gross deficiencies in QC or method performance. Re-sampling and/or re-analysis is necessary.
RND	Recovery not determined.
U	Compound was analyzed for, but not detected.

* Based on U.S. Environmental Protection Agency guidelines.[1]

TABLE 1020:III. AUDIT OF A SOIL ANALYSIS PROCEDURE

	Procedure	Comment	Remarks
1.a	Sample entered into logbook	yes	lab number assigned
2.a	Sample weighed	yes	dry weight
3.a	Drying procedure followed	no	maintenance of oven not done
4a.	Balance calibrated	yes	once per year
b.	Cleaned and zero adjusted	yes	weekly
5.a	Sample ground	yes	to pass 50 mesh
6.a	Ball mill cleaned	yes	should be after each sample

.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Procedure	Comment	Remarks
.		
.		

TABLE 1030:I. CONDUCTIVITY FACTORS OF IONS COMMONLY FOUND IN WATER

Ion	Conductivity (25°C) *µmhos/cm*	
	Per me/L	Per mg/L
Bicarbonate	43.6	0.715
Calcium	52.0	2.60
Carbonate	84.6	2.82
Chloride	75.9	2.14
Magnesium	46.6	3.82
Nitrate	71.0	1.15
Potassium	72.0	1.84
Sodium	48.9	2.13
Sulfate	73.9	1.54

TABLE 1040:I. PRECISION AND BIAS FOR A SINGLE CONCENTRATIONIN A SINGLE MATRIX

Result *mg/L*	Difference (–1.30)	Squared Difference
1.23	–0.07	0.0049
1.21	–0.09	0.0081
1.30	0.0	0.0000
1.59	0.29	0.0841
1.57	0.27	0.0729
1.21	–0.09	0.0081
1.53	0.23	0.0529
1.25	–0.05	0.0025
Sum	0.49	0.2335

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Result *mg/L*	Difference (–1.30)	Squared Difference

TABLE 1040:II. VARIATIONS IN FACTORS FOR METHOD RUGGEDNESS DETERMINATION

Factor	Nominal	Variation
Mixing time	10 min	12 min
Portion size	5 g	10 g
Acid concentration	1*M*	1.1*M*
Heat to	100°C	95°C
Hold heat for	5 min	10 min
Stirring	yes	no
pH adjust	6.0	6.5

TABLE 1040:III. FACTOR MATRIX FOR METHOD RUGGEDNESS DETERMINATION

	Combinations							
Factor value	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
A or a	A	A	A	A	a	a	a	a
B or b	B	B	b	b	B	B	b	b
C or c	C	c	C	c	C	c	C	c
D or d	D	D	d	d	d	d	D	D
E or e	E	e	E	e	e	E	e	E
F or f	F	f	f	F	F	f	f	F
G or g	G	g	g	G	g	G	G	g
Result	s	t	u	v	w	x	y	z

Source: YOUDEN, W. J. E. H. STEINER. 1975. Statistical Manual of AOAC. Assoc. Official Analytical Chemists, Washington, D.C.

TABLE 1040:IV. SAMPLE COLLABORATIVE TEST RESULTS

	Deviation

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 1040:IV. SAMPLE COLLABORATIVE TEST RESULTS

Laboratory	Result *mg/L*	Experimental *x* ± *s*	Deviation From Known	Deviation From Grand Average
1	32.7			
	35.2	34.7 ± 1.8	–2.0	–1.7
	36.3			
2	32.6			
	33.7	33.3 ± 0.6	–0.6	–0.3
	33.6			
3	30.6			
	30.6	31.2 ± 1.0	–1.5	–1.8
	32.4			
4	32.6			
	32.5	33.0 ± 0.8	–0.3	–0
	33.9			
5	32.4			
	33.4	32.6 ± 0.8	–0.1	–0.4
	32.9			
$(\sum x)/n$ = 33			$\sum$ = 1.3	$\sum$ = –0.2
s = 1.5				

TABLE 1040:V. METHOD PRECISION AND BIAS

Known Amount *mg/L*	Amount Found *mg/L*	CV (% Standard Deviation)	Bias %
4.3	4.8	12.5	11.5
11.6	12.2	10.2	5.6
23.4	23.8	5.4	1.9
32.7	33.0	4.5	0.9

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 1050:I. CONVERSION FACTORS* (Milligrams per Liter—Milliequivalents per Liter)

Ion (Cation)	me/L = mg/L×	mg/L = me/L×	Ion (Anion)	me/L = mg/L×	mg/L = me/L×
Al^{3+}	0.111 2	8.994	BO_2^-	0.023 36	42.81
B^{3+}	0.277 5	3.604	Br^-	0.012 52	79.90
Ba^{2+}	0.014 56	68.66	Cl^-	0.028 21	35.45
Ca^{2+}	0.049 90	20.04	CO_3^{2-}	0.033 33	30.00
Cr^{3+}	0.057 70	17.33	CrO_4^{2-}	0.017 24	58.00
			F^-	0.052 64	19.00
Cu^{2+}	0.031 47	31.77	HCO_3^-	0.016 39	61.02
Fe^{2+}	0.035 81	27.92	HPO_4^{2-}	0.020 84	47.99
Fe^{3+}	0.053 72	18.62	$H_2PO_4^-$	0.010 31	96.99
H^+	0.992 1	1.008	HS^-	0.030 24	33.07
K^+	0.025 58	39.10	HSO_3^-	0.012 33	81.07
			HSO_4^-	0.010 30	97.07
Li^+	0.144 1	6.941	I^-	0.007 880	126.9
Mg^{2+}	0.082 29	12.15	NO_2^-	0.021 74	46.01
Mn^{2+}	0.036 40	27.47	NO_3^-	0.016 13	62.00
Mn^{4+}	0.072 81	13.73	OH^-	0.058 80	17.01
Na^+	0.043 50	22.99	PO_4^{3-}	0.031 59	31.66
NH_4^+	0.055 44	18.04	S^{2-}	0.062 37	16.03
Pb^{2+}	0.009 653	103.6	SiO_3^{2-}	0.026 29	38.04
Sr^{2+}	0.022 83	43.81	SO_3^{2-}	0.024 98	40.03
Zn^{2+}	0.030 59	32.70	SO_4^{2-}	0.020 82	48.03

* Factors are based on ion charge and not on redox reactions that may be possible for certain of these ions. Cations and anions are listed separately in alphabetical order.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 1060:I. SUMMARY OF SPECIAL SAMPLING AND HANDLING REQUIREMENTS*

Determination	Container†	Minimum Sample Size *mL*	Sample Type‡	
Acidity	P, G(B)	100	g	Refrigerate
Alkalinity	P, G	200	g	Refrigerate
BOD	P, G	1000	g, c	Refrigerate
Boron	P (PTFE) or quartz	1000	g, c	HNO_3 to pH <
Bromide	P, G	100	g, c	None required
Carbon, organic, total	G (B)	100	g, c	Analyze imme H_3PO_4, or H_2S
Carbon dioxide	P, G	100	g	Analyze imme
COD	P, G	100	g, c	Analyze as so refrigerate
Chloride	P, G	50	g, c	None required
Chlorine, total, residual	P, G	500	g	Analyze imme
Chlorine dioxide	P, G	500	g	Analyze imme
Chlorophyll	P, G	500	g	Unfiltered, dar Filtered, dark, (Do not store i
Color	P, G	500	g, c	Refrigerate
Specific conductance	P, G	500	g, c	Refrigerate
Cyanide				
Total	P, G	1000	g, c	Add NaOH to
Amenable to chlorination	P, G	1000	g, c	Add 0.6 g asc refrigerate
Fluoride	P	100	g, c	None required
Hardness	P, G	100	g, c	Add HNO_3 or
Iodine	P, G	500	g	Analyze imme

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Determination	Container†	Minimum Sample Size *mL*	Sample Type‡	
Metals, general	P(A), G(A)	1000	g, c	For dissolved pH <2
Chromium VI	P(A), G(A)	1000	g	Refrigerate
Copper by colorimetry*				
Mercury	P(A), G(A)	1000	g, c	Add HNO_3 to
Nitrogen				
Ammonia	P, G	500	g, c	Analyze as so refrigerate
Nitrate	P, G	100	g, c	Analyze as so
Nitrate + nitrite	P, G	200	g, c	Add H_2SO_4 to
Nitrite	P, G	100	g, c	Analyze as so
Organic, Kjeldahl*	P, G	500	g, c	Refrigerate, ac
Odor	G	500	g	Analyze as so
Oil and grease	G, wide-mouth calibrated	1000	g	Add HCl or H_2
Organic compounds				
MBAs	P, G	250	g, c	Refrigerate
Pesticides*	G(S), PTFE-lined cap	1000	g, c	Refrigerate, ac chlorine prese
Phenols	P, G, PTFE-lined cap	500	g, c	Refrigerate, ac
Purgeables* by purge and trap	G, PTFE-lined cap	2 × 40	g	Refrigerate; ac acid/L if residu
Base/neutrals acids	G(S) amber	1000	g, c	Refrigerate
Oxygen, dissolved	G, BOD bottle	300		
Electrode				Analyze imme
Winkler				Titration may b
Ozone	G	1000	g	Analyze imme

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Determination	Container†	Minimum Sample Size *mL*	Sample Type‡	
pH	P, G	50	g	Analyze imme
Phosphate	G(A)	100	g	For dissolved
Phosphorus, total	P, G	100	g, c	Add H_2SO_4 to
Salinity	G, wax seal	240	g	Analyze imme
Silica	P (PTFE) or quartz	200	g, c	Refrigerate, d
Sludge digester gas	G, gas bottle	—	g	—
Solids[9]	P, G	200	g, c	Refrigerate
Sulfate	P, G	100	g, c	Refrigerate
Sulfide	P, G	100	g, c	Refrigerate; a NaOH to pH >
Temperature	P, G	—	g	Analyze imme
Turbidity	P, G	100	g, c	Analyze same refrigerate

* For determinations not listed, use glass or plastic containers; preferably refrigerate during storage and analyze as soon as possible.
† P = plastic (polyethylene or equivalent); G = glass; G(A) or P(A) = rinsed with 1 + 1 HNO_3; G(B) = glass, borosilicate; G(S) = glass, rinsed with organic solvents or baked.
‡ g = grab; c = composite.
§ Refrigerate = storage at 4°C ± 2°C; in the dark; analyze immediately = analyze usually within 15 min of sample collection.
‖ See citation[10] for possible differences regarding container and preservation requirements. N.S. = not stated in cited reference; stat = no storage allowed; analyze immediately.
If sample is chlorinated, see text for pretreatment.

TABLE 1080:I. WATER PURIFICATION PROCESSES

	Major Classes of Contaminants*					
Process	Dissolved Ionized Solids	Dissolved Ionized Gases	Dissolved Organics	Particulates	Bacteria	P Er
Distillation	G–E†	P	G	E	E	

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Process	Major Classes of Contaminants*					P Er
	Dissolved Ionized Solids	Dissolved Ionized Gases	Dissolved Organics	Particulates	Bacteria	
Deionization	E	E	P	P	P	
Reverse osmosis	G‡	P	G	E	E	
Carbon adsorption	P	P§	G–E ‖	P	P	
Filtration	P	P	P	E	E	
Ultrafiltration	P	P	G#	E	E	
Ultraviolet oxidation	P	P	G–E**	P	G††	

Permission to use this table from C3-A2, Vol. 11, No. 13, Aug. 1991, ‘‘Preparation and Testing of Reagent Water in the Clinical Laboratory - Second Edition’’ has been granted by the National Committee for Clinical Laboratory Standards. The complete current standard may be obtained from National Committee for Clinical Laboratory Standards, 771 E. Lancaster Ave., Villanova, PA 19085.

* E = Excellent (capable of complete or near total removal), G = Good (capable of removing large percentages), P = Poor (little or no removal).

† Resistivity of water purified by distillation is an order of magnitude less than water produced by deionization, due mainly to the presence of CO_2 and sometimes H_2S, NH_3, and other ionized gases if present in the feedwater.‡ Resistivity of dissolved ionized solids in the product water depends on original feedwater resistivity.

§ Activated carbon removes chlorine by adsorption.

‖ When used in combination with other purification processes, special grades of activated carbon and other synthetic adsorbents exhibit excellent capabilities for removing organic contaminants. Their use, however, is targeted toward specific compounds and applications.

Ultrafilters have demonstrated usefulness in reducing specific feedwater organic contaminants based on the rated molecular weight cut-off of the membrane.

** 185 nm ultraviolet oxidation (batch process systems) is effective in removing trace organic contaminants when used as post-treatment. Feedwater makeup plays a critical role in the performance of these batch processors.

†† 254 nm UV sterilizers, while not physically removing bacteria, may have bactericidal or bacteriostatic capabilities limited by intensity, contact time, and flow rate.

TABLE 1080:II. REAGENT WATER SPECIFICATIONS*

Quality Parameter	High	Medium	Low
Resistivity, megohm-cm at 25°C	>10	>1	0.1

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Quality Parameter	High	Medium	Low
Conductivity, μmho/cm at 25°C	<0.1	<1	10
SiO_2, mg/L	<0.05	<0.1	<1

TABLE 1090:I. PERMISSIBLE EXPOSURE LIMITS, THRESHOLD LIMIT VALUES, SHORT-TERM EXPOSURE LIMITS, AND/OR CEILINGS FOR SOME INORGANIC CHEMICALS SPECIFIED IN *STANDARD METHODS*

Compound	Chemical Abstract No. CAS No.	PEL/TLV STEL mg/m^3
Chromic acid and chromates†‡ (as CrO_3)	7440-47-3	0.1/0.05
Chromium, soluble chromic, chromous salts (as Cr)	7440-47-3	0.5/0.5
Chromium metal and insoluble salts	7440-47-3	1/0.5
Hydrogen chloride	7647-01-0	7.5(C)/7.5(C)
Hydrogen peroxide	7722-84-1	1.4/1.4
Lead‡	7439-92-1	–/0.15
Mercury†§	7439-97-6	0.1/0.05
Nitric acid	7697-37-2	5/5.2, 10(S)
Phosphoric acid	7664-38-2	1/1, 3(S)
Potassium hydroxide	1310-58-3	–/2(C)
Silver (metal and soluble compounds, as Ag)	7440-22-4	0.01/0.1 meta
Sodium azide	26628-22-8	–/0.29(C)
Sodium hydroxide	1310-73-2	2(C)/2(C)
Sulfuric acid	7664-93-9	1/1, 3(S)

* Short-term exposure limit. See 29 CFR 1910.1028.
† (Suspect) carcinogen.
‡ Substance has a Biological Exposure Index (BEI).
§ Skin hazard.

TABLE 1090:II. PERMISSIBLE EXPOSURE LIMITS, THRESHOLD LIMIT VALUES, SHORT-TERM EXPOSURE LIMITS, AND/OR CEILINGS FOR ORGANIC SOLVENTS SPECIFIED IN *STANDARD METHODS*

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

EXPOSURE LIMITS, AND/OR CEILINGS FOR ORGANIC SOLVENTS SPECIFIED IN *STANDARD METHODS*

Compound	Chemical Abstract No. CAS No.	PEL/TLV STEL(S)* c ppm (v/v
Acetic acid	64-19-7	10/10, 15(S)
Acetone	67-64-1	1000/750, 1000(S)
Acetonitrile	75-05-8	40/40, 60(S)
Benzene†‡	71-43-2	10, 25(C), 50 peak 10 mi
n-Butyl alcohol§	71-36-3	100/50(C)
tert-Butyl alcohol	75-65-0	100/100, 150(S)
Carbon disulfide‡	75-15-0	20, 30(C), 100 peak 30 m
Carbon tetrachloride†§	56-23-5	10, 25, 200 peak 5 min/4
Chloroform†	67-66-3	50(C)/10
Cyclohexanone§	108-94-1	50/50
Dioxane§ (diethylene dioxide)	123-91-1	100/25
Ethyl acetate	141-78-6	400/400
Ethyl alcohol	64-17-5	1000/1000
Ethyl ether (diethyl ether)	60-29-7	400/400, 500(S)
Ethylene glycol	107-21-1	–/50(C)
n-Hexane‡	110-54-3	100/50
Isoamyl alcohol (primary and secondary)	123-51-3	100/100, 125(S)
Isobutyl alcohol	78-83-1	100/50
Isopropyl alcohol	67-63-0	400/400, 500(S)
Isopropyl ether	108-20-3	500/250, 310(S)
Methyl alcohol§	67-56-1	200/200, 250(S)
2-Methoxyethanol§ (methyl cellosolve)	109-86-4	25/5
Methylene chloride†	75-09-2	500, 1000(C), 2000 peak
Pentane	109-66-0	1000/600, 750(S)
Perchloroethylene†‡ (tetrachloroethylene)	127-18-4	100, 200(C), 300 peak 5 200(S)
n-Propyl alcohol§	71-23-8	200/200, 250(S)
Pyridine	110-86-1	5/5
Toluene‡§	108-88-3	200, 300(C), 500 peak 1(

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Compound	Chemical Abstract No. CAS No.	PEL/TLV STEL(S)* c ppm (v/v
Xylenes‡ (*o*-, *m*-, *p*-isomers)	1330-20-7 (95-47-6, 108-38-3, 106-42-3)	100/100, 150(S)

* Short-term exposure limit. See 29 CFR 1910.1028.
† (Suspect) carcinogen.
‡ Substance has a Biological Exposure Index (BEI).
§ Skin hazard.

TABLE 1090:III. PERMISSIBLE EXPOSURE LIMITS, THRESHOLD LIMIT VALUES, SHORT-TERM EXPOSURE LIMITS, AND/OR CEILINGS FOR SOME OF THE REAGENTS SPECIFIED IN *STANDARD METHODS*

Compound	Chemical Abstract No. CAS No.	PEL/TLV STEL(S)* or (ppm (v/v)
2-Aminoethanol (ethanolamine)	141-43-5	3/3, 6(S)
Benzidine†‡	92-87-5	Confirmed human ca
Benzyl chloride	100-44-7	1/1
Chlorobenzene	108-90-7	75/10
Diethanolamine	111-42-2	–/3
Naphthalene	91-20-3	10/10, 15(S)
Oxalic acid	144-62-7	1/1 mg/m^3
Phenol‡	108-95-2	5/5
2-Chloro-6-(trichloromethyl) pyridine (nitrapyrin)	1929-82-4	
Total dust		15/10 mg/m^3
Respirable fraction		5/– mg/m^3

* Short-term exposure limit. See 29 CFR 1910.1028.
† (Suspect) carcinogen.
‡ Skin hazard.

TABLE 1090:IV. GLOVE SELECTION FOR ORGANIC CHEMICAL HANDLING

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 1090:IV. GLOVE SELECTION FOR ORGANIC CHEMICAL HANDLING

Compound	Chemical Abstract No. CAS No.	Chemical Class	Butyl Rubber	Neoprene
Ethers:		241		
Ethyl ether (diethyl ether)	60-29-7	241		
Isopropyl ether	108-20-3	241		
2-Methoxyethanol† (methyl cellosolve)	109-86-4	245	X	
Halogen compounds:		261		
Carbon tetrachloride*	56-23-5	261		
Chloroform*	67-66-3	261		
Methylene chloride	75-09-2	261		
Perchloroethylene* (tetrachloroethylene)	127-18-4	261		
Hydrocarbons:		291		
n-Hexane	110-54-3	291		
Pentane	109-66-0	291		
Benzene*	71-43-2	292		
Toluene	108-88-3	292		
Xylenes (*o*-, *m*-, *p*-isomers)	1330-20-7	292		
Hydroxyl compounds:		311		
n-Butyl alcohol	71-36-3	311	X	X
Ethyl alcohol	64-17-5	311	X	
Methyl alcohol	67-56-1	311	X	
n-Propyl alcohol	71-23-8	311		
Isoamyl alcohol	123-51-3	311		
Isobutyl alcohol	78-83-1	311	X	
Isopropyl alcohol	67-63-0	312		X
tert-Butyl alcohol (2,2-methylpropanol)	75-65-0	313	X	
Ethylene glycol	107-21-1	314	X	X
Ketones:		391		
Acetone	67-64-1	391	X	

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Compound	Chemical Abstract No. CAS No.	Chemical Class	Butyl Rubber	Neoprene
Cyclohexanone	108-94-1	391	X	
Heterocyclic compounds:		271		
Dioxane† (diethylene dioxide)	123-91-1	278	X	
Pyridine	110-86-1	271	X	
Miscellaneous organic compounds:				
Acetic acid	75-07-0	102	X	X
Ethyl acetate	141-78-6	222	X	
Acetonitrile	75-05-8	431	X	
Carbon disulfide	75-15-0	502		

* (Suspect) carcinogen.
† Skin hazard.

TABLE 1090:V. GLOVE SELECTION FOR INORGANIC CHEMICAL HANDLING

Compound	Chemical Abstract No. (CAS No.)	Chemical Class	Suit: Butyl Rubber	Suit: Natural Rubber	Suit: N
Inorganic acids:		370			
Chromic acid,* (Cr^{+6})	7440-47-3	370	X		
Hydrochloric acid, 30–70% solutions	10035-10-6	370	X	X	
Hydrochloric acid, <30% solutions	10035-10-6	370	X	X	
Nitric acid, 30–70% solutions	7697-37-2	370	X		
Nitric acid, <30% solutions	7697-37-2	370	X	X	
Phosphoric acid, >70% solutions	7664-38-2	370		X	
Phosphoric acid, 30–70% solutions	7664-38-2	370		X	
Sulfuric acid, >70% solutions	7664-93-9	370	X		
Sulfuric acid, 30–70% solutions	7664-93-9	370	X	X	
Sulfuric acid, <30% solutions	7664-93-9	370	X	X	
Inorganic bases:		380			

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Compound	Chemical Abstract No. (CAS No.)	Chemical Class	Suit: Butyl Rubber	Suit: Natural Rubber	Suit: N
Ammonium hydroxide, 30–70% solutions	7664-41-7	380	X		
Ammonium hydroxide, <30% solutions	7664-41-7	380	X		
Potassium hydroxide, 30–70% solutions	1310-58-3	380	X	X	
Sodium hydroxide, >70% solutions	1310-73-2	380			
Sodium hydroxide, 30–70% solutions	1310-73-2	380	X	X	
Inorganic salt solutions:		340			
Dichromate solutions, <30%,* (Cr^{+6})	7440-47-3	340			
Inorganic miscellaneous:					
Hydrogen peroxide, 30–70% solutions	7722-39-3	300		X	
Mercury†	7439-97-6	560			

* (Suspect) carcinogen.
† Skin hazard.

TABLE 1090:VI. PROCEDURES INVOLVING POTENTIAL EXPOSURE TO IONIZING RADIATION

Standard Methods Section	Radionuclide	Type of Radiation
Part 6000 methods: GC with electron capture detectors	^{63}Ni or ^{3}H	Low-energy beta (^{63}Ni, 17 ke
7110 Gross Alpha and Gross Beta Radioactivity	Alpha: Uranium, ^{230}Th, ^{239}Pu, ^{241}Am Beta: ^{137}Cs, ^{90}Sr	Alpha; beta and gamma; or b
7500-Cs Radioactive Cesium	^{134}Cs, ^{137}Cs	Beta, gamma
7500-I Radioactive Iodine	^{131}I	Beta, gamma
7500-Ra Radium	^{226}Ra	Alpha, beta, gamma
7500-Sr A Total Radioactive Strontium and Strontium-90	^{89}Sr, ^{90}Sr	Beta-emitters
7500-^{3}H Tritium	^{3}H	Low-energy beta (6 keV avg)

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Standard Methods Section	Radionuclide	Type of Radiation
7500-U Uranium	U series	Alpha, beta, gamma

Part 2000 PHYSICAL & AGGREGATE PROPERTIES

2010 INTRODUCTION

This part deals primarily with measurement of the physical properties of a sample, as distinguished from the concentrations of chemical or biological components. Many of the determinations included here, such as color, electrical conductivity, and turbidity, fit this category unequivocally. However, physical properties cannot be divorced entirely from chemical composition, and some of the techniques of this part measure aggregate properties resulting from the presence of a number of constituents. Others, for example, calcium carbonate saturation, are related to, or depend on, chemical tests. Also included here are tests for appearance, odor, and taste, which have been classified traditionally among physical properties, although the point could be argued. Finally, Section 2710, Tests on Sludges, includes certain biochemical tests. However, for convenience they are grouped with the other tests used for sludge.

With these minor exceptions, the contents of this part have been kept reasonably faithful to its name. Most of the methods included are either inherently or at least traditionally physical, as distinguished from the explicitly chemical, radiological, biological, or bacteriological methods of other parts.

2020 QUALITY ASSURANCE/QUALITY CONTROL

Part 2000 contains a variety of analytical methods, many of which are not amenable to standard quality-control techniques. General information on quality control is provided in Part 1000 and specific quality-control techniques are outlined in the individual methods. The following general guidelines may be applied to many of the methods in this part:

Evaluate analyst performance for each method. Determine competence by analyses of samples containing known concentrations.

Calibrate instruments and ensure that instrument measurements do not drift.

Assess the precision of analytical procedures by analyzing at least 10% of samples in duplicate. Analyze a minimum of one duplicate with each set of samples.

Determine bias of an analytical procedure in each sample batch by analysis of blanks, known additions with a frequency of at least 5% of samples, and, if possible, an externally provided

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

standard.

2110 APPEARANCE*#(6)

To record the general physical appearance of a sample, use any terms that briefly describe its visible characteristics. These terms may state the presence of color, turbidity, suspended solids, organisms and their immature forms, sediment, floating material, and similar particulate matter detectable by the unaided eye. Use numerical values when they are available, as for color, turbidity, and suspended solids.

2120 COLOR*#(7)

2120 A. Introduction

Color in water may result from the presence of natural metallic ions (iron and manganese), humus and peat materials, plankton, weeds, and industrial wastes. Color is removed to make a water suitable for general and industrial applications. Colored industrial wastewaters may require color removal before discharge into watercourses.

1. Definitions

The term ‘‘color’’ is used here to mean true color, that is, the color of water from which turbidity has been removed. The term ‘‘apparent color’’ includes not only color due to substances in solution, but also that due to suspended matter. Apparent color is determined on the original sample without filtration or centrifugation. In some highly colored industrial wastewaters color is contributed principally by colloidal or suspended material. In such cases both true color and apparent color should be determined.

2. Pretreatment for Turbidity Removal

To determine color by currently accepted methods, turbidity must be removed before analysis. Methods for removing turbidity without removing color vary. Filtration yields results that are reproducible from day to day and among laboratories. However, some filtration procedures also may remove some true color. Centrifugation avoids interaction of color with filter materials, but results vary with the sample nature and size and speed of the centrifuge. When sample dilution is necessary, whether it precedes or follows turbidity removal, it can alter the measured color.

Acceptable pretreatment procedures are included with each method. State the pretreatment method when reporting results.

3. Selection of Method

The visual comparison method is applicable to nearly all samples of potable water. Pollution

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

by certain industrial wastes may produce unusual colors that cannot be matched. In this case use an instrumental method. A modification of the tristimulus and the spectrophotometric methods allows calculation of a single color value representing uniform chromaticity differences even when the sample exhibits color significantly different from that of platinum cobalt standards. For comparison of color values among laboratories, calibrate the visual method by the instrumental procedures.

4. Bibliography

OPTICAL SOCIETY OF AMERICA. 1943. Committee Report. The concept of color. *J. Opt. Soc. Amer.* 33:544.

JONES, H. et al. 1952. The Science of Color. Thomas Y. Crowell Co., New York, N.Y.

2120 B. Visual Comparison Method

1. General Discussion

a. Principle: Color is determined by visual comparison of the sample with known concentrations of colored solutions. Comparison also may be made with special, properly calibrated glass color disks. The platinum-cobalt method of measuring color is the standard method, the unit of color being that produced by 1 mg platinum/L in the form of the chloroplatinate ion. The ratio of cobalt to platinum may be varied to match the hue in special cases; the proportion given below is usually satisfactory to match the color of natural waters.

b. Application: The platinum-cobalt method is useful for measuring color of potable water and of water in which color is due to naturally occurring materials. It is not applicable to most highly colored industrial wastewaters.

c. Interference: Even a slight turbidity causes the apparent color to be noticeably higher than the true color; therefore remove turbidity before approximating true color by differential reading with different color filters[1] or by differential scattering measurements.[2] Neither technique, however, has reached the status of a standard method. Remove turbidity by centrifugation or by the filtration procedure described under Method C. Centrifuge for 1 h unless it has been demonstrated that centrifugation under other conditions accomplishes satisfactory turbidity removal.

The color value of water is extremely pH-dependent and invariably increases as the pH of the water is raised. When reporting a color value, specify the pH at which color is determined. For research purposes or when color values are to be compared among laboratories, determine the color response of a given water over a wide range of pH values.[3]

d. Field method: Because the platinum-cobalt standard method is not convenient for field use, compare water color with that of glass disks held at the end of metallic tubes containing glass comparator tubes filled with sample and colorless distilled water. Match sample color with the color of the tube of clear water plus the calibrated colored glass when viewed by looking

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

toward a white surface. Calibrate each disk to correspond with the colors on the platinum-cobalt scale. The glass disks give results in substantial agreement with those obtained by the platinum-cobalt method and their use is recognized as a standard field procedure.

e. Nonstandard laboratory methods: Using glass disks or liquids other than water as standards for laboratory work is permissible only if these have been individually calibrated against platinum-cobalt standards. Waters of highly unusual color, such as those that may occur by mixture with certain industrial wastes, may have hues so far removed from those of the platinum-cobalt standards that comparison by the standard method is difficult or impossible. For such waters, use the methods in Section 2120C and Section 2120D. However, results so obtained are not directly comparable to those obtained with platinum-cobalt standards.

f. Sampling: Collect representative samples in clean glassware. Make the color determination within a reasonable period because biological or physical changes occurring in storage may affect color. With naturally colored waters these changes invariably lead to poor results.

2. Apparatus

a. Nessler tubes, matched, 50-mL, tall form.

b. pH meter, for determining sample pH (see Section 4500-H).

3. Preparation of Standards

a. If a reliable supply of potassium chloroplatinate cannot be purchased, use chloroplatinic acid prepared from metallic platinum. Do not use commercial chloroplatinic acid because it is very hygroscopic and may vary in platinum content. Potassium chloroplatinate is not hygroscopic.

b. Dissolve 1.246 g potassium chloroplatinate, K_2PtCl_6 (equivalent to 500 mg metallic Pt) and 1.00 g crystallized cobaltous chloride, $CoCl_2 \cdot 6H_2O$ (equivalent to about 250 mg metallic Co) in distilled water with 100 mL conc HCl and dilute to 1000 mL with distilled water. This stock standard has a color of 500 units.

c. If K_2PtCl_6 is not available, dissolve 500 mg pure metallic Pt in aqua regia with the aid of heat; remove HNO_3 by repeated evaporation with fresh portions of conc HCl. Dissolve this product, together with 1.00 g crystallized $CoCl_2 \cdot 6H_2O$, as directed above.

d. Prepare standards having colors of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, and 70 by diluting 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, and 7.0 mL stock color standard with distilled water to 50 mL in nessler tubes. Protect these standards against evaporation and contamination when not in use.

4. Procedure

a. Estimation of intact sample: Observe sample color by filling a matched nessler tube to the 50-mL mark with sample and comparing it with standards. Look vertically downward through tubes toward a white or specular surface placed at such an angle that light is reflected upward

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

through the columns of liquid. If turbidity is present and has not been removed, report as ‘‘apparent color.’’ If the color exceeds 70 units, dilute sample with distilled water in known proportions until the color is within the range of the standards.

b. Measure pH of each sample.

5. Calculation

a. Calculate color units by the following equation:

$$\text{Color units} = \frac{A \times 50}{B}$$

where:

A = estimated color of a diluted sample and
B = mL sample taken for dilution.

b. Report color results in whole numbers and record as follows:

Color Units	Record to Nearest
1–50	1
51–100	5
101–250	10
251–500	20

c. Report sample pH.

6. References

1. KNIGHT, A.G. 1951. The photometric estimation of color in turbid waters. *J. Inst. Water Eng.* 5:623.
2. JULLANDER, I. & K. BRUNE. 1950. Light absorption measurements on turbid solutions. *Acta Chem. Scand.* 4:870.
3. BLACK, A.P. & R.F. CHRISTMAN. 1963. Characteristics of colored surface waters. *J. Amer. Water Works Assoc.* 55:753.

7. Bibliography

HAZEN, A. 1892. A new color standard for natural waters. *Amer. Chem. J.* 14:300.

HAZEN, A. 1896. The measurement of the colors of natural waters. *J. Amer. Chem. Soc.* 18:264.

Measurement of Color and Turbidity in Water. 1902. U.S. Geol. Surv., Div. Hydrog. Circ. 8,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Washington, D.C.

RUDOLFS, W. & W.D. HANLON. 1951. Color in industrial wastes. *Sewage Ind. Wastes* 23:1125.

PALIN, A.T. 1955. Photometric determination of the colour and turbidity of water. *Water Water Eng.* 59:341.

CHRISTMAN, R.F. & M. GHASSEMI. 1966. Chemical nature of organic color in water. *J. Amer. Water Works Assoc.* 58:723.

GHASSEMI, M. & R.F. Christman. 1968. Properties of the yellow organic acids of natural waters. *Limnol. Oceanogr.* 13:583.

2120 C. Spectrophotometric Method

1. General Discussion

a. Principle: The color of a filtered sample is expressed in terms that describe the sensation realized when viewing the sample. The hue (red, green, yellow, etc.) is designated by the term ‘‘dominant wavelength,’’ the degree of brightness by ‘‘luminance,’’ and the saturation (pale, pastel, etc.) by ‘‘purity.’’ These values are best determined from the light transmission characteristics of the filtered sample by means of a spectrophotometer.

b. Application: This method is applicable to potable and surface waters and to wastewaters, both domestic and industrial.

c. Interference: Turbidity interferes. Remove by the filtration method described below.

2. Apparatus

a. Spectrophotometer, having 10-mm absorption cells, a narrow (10-nm or less) spectral band, and an effective operating range from 400 to 700 nm.

b. Filtration system, consisting of the following (see Figure 2120:1):

1) *Filtration flasks,* 250-mL, with side tubes.

2) *Walter crucible holder.*

3) *Glass Gooch filtering crucible with fritted disk,* pore size 40 to 60 μm.

4) *Calcined filter aid.**#(8)

5) *Vacuum system.*

3. Procedure

a. Preparation of sample: Bring two 50-mL samples to room temperature. Use one sample at the original pH; adjust pH of the other to 7.6 by using sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) of such concentrations that the resulting volume change does not exceed 3%. A standard pH is necessary because of the variation of color with pH. Remove excessive quantities of suspended materials by centrifuging. Treat each sample separately, as follows:

Thoroughly mix 0.1 g filter aid in a 10-mL portion of centrifuged sample and filter to form a

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

precoat in the filter crucible. Direct filtrate to waste flask as indicated in Figure 2120:1. Mix 40 mg filter aid in a 35-mL portion of centrifuged sample. With vacuum still on, filter through the precoat and pass filtrate to waste flask until clear; then direct clear-filtrate flow to clean flask by means of the three-way stopcock and collect 25 mL for the transmittance determination.

b. Determination of light transmission characteristics: Thoroughly clean 1-cm absorption cells with detergent and rinse with distilled water. Rinse twice with filtered sample, clean external surfaces with lens paper, and fill cell with filtered sample.

Determine transmittance values (in percent) at each visible wavelength value presented in Table 2120:I, using the 10 ordinates marked with an asterisk for fairly accurate work and all 30 ordinates for increased accuracy. Set instrument to read 100% transmittance on the distilled water blank and make all determinations with a narrow spectral band.

4. Calculation

a. Tabulate transmittance values corresponding to wavelengths shown in Columns *X*, *Y*, and *Z* in Table 2120:I. Total each transmittance column and multiply totals by the appropriate factors (for 10 or 30 ordinates) shown at the bottom of the table, to obtain tristimulus values *X*, *Y*, and *Z*. The tristimulus value *Y* is *percent luminance.*

b. Calculate the trichromatic coefficients *x* and *y* from the tristimulus values *X*, *Y*, and *Z* by the following equations:

$$x = \frac{X}{X + Y + Z}$$

$$y = \frac{Y}{X + Y + Z}$$

Locate point (*x*, *y*) on one of the chromaticity diagrams in Figure 2120:2 and determine the dominant wavelength (in nanometers) and the purity (in percent) directly from the diagram.

Determine hue from the dominant-wavelength value, according to the ranges in Table 2120:II.

5. Expression of Results

Express color characteristics (at pH 7.6 and at the original pH) in terms of *dominant wavelength* (nanometers, to the nearest unit), *hue* (e.g., blue, blue-green, etc.), *luminance* (percent, to the nearest tenth), and *purity* (percent, to the nearest unit). Report type of instrument (i.e., spectrophotometer), number of selected ordinates (10 or 30), and the spectral band width (nanometers) used.

6. Bibliography

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

HARDY, A.C. 1936. Handbook of Colorimetry. Technology Press, Boston, Mass.

2120 D. Tristimulus Filter Method

1. General Discussion

a. Principle: Three special tristimulus light filters, combined with a specific light source and photoelectric cell in a filter photometer, may be used to obtain color data suitable for routine control purposes.

The percentage of tristimulus light transmitted by the solution is determined for each of the three filters. The transmittance values then are converted to trichromatic coefficients and color characteristic values.

b. Application: This method is applicable to potable and surface waters and to wastewaters, both domestic and industrial. Except for most exacting work, this method gives results very similar to the more accurate Method C.

c. Interference: Turbidity must be removed.

2. Apparatus

*a. Filter photometer.**#(9)

b. Filter photometer light source: Tungsten lamp at a color temperature of 3000°C.†#(10)

c. Filter photometer photoelectric cells, 1 cm.‡#(11)

d. Tristimulus filters.§#(12)

e. Filtration system: See Section 2120C.2*b* and Figure 2120:1.

3. Procedure

a. Preparation of sample: See Section 2120C.3*a*.

b. Determination of light transmission characteristics: Thoroughly clean (with detergent) and rinse 1-cm absorption cells with distilled water. Rinse each absorption cell twice with filtered sample, clean external surfaces with lens paper, and fill cell with filtered sample.

Place a distilled water blank in another cell and use it to set the instrument at 100% transmittance. Determine percentage of light transmission through sample for each of the three tristimulus light filters, with the filter photometer lamp intensity switch in a position equivalent to 4 V on the lamp.

4. Calculation

a. Determine luminance value directly as the percentage transmittance value obtained with the No. 2 tristimulus filter.

b. Calculate tristimulus values X, Y, and Z from the percentage transmittance (T_1, T_2, T_3) for filters No. 1, 2, 3, as follows:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$X = T_3 \times 0.06 + T_1 \times 0.25$$

$$Y = T_2 \times 0.316$$

$$Z = T_3 \times 0.374$$

Calculate and determine trichromatic coefficients *x* and *y*, dominant wavelength, hue, and purity as in Section 2120C.4*b* above.

5. Expression of Results

Express results as prescribed in Section 2120C.5.

2120 E. ADMI Tristimulus Filter Method

1. General Discussion

a. Principle: This method is an extension of Tristimulus Method 2120D. By this method a measure of the sample color, independent of hue, may be obtained. It is based on use of the Adams-Nickerson chromatic value formula[1] for calculating single number color difference values, i.e., uniform color differences. For example, if two colors, A and B, are judged visually to differ from colorless to the same degree, their ADMI color values will be the same. The modification was developed by members of the American Dye Manufacturers Institute (ADMI).[2]

b. Application: This method is applicable to colored waters and wastewaters having color characteristics significantly different from platinum-cobalt standards, as well as to waters and wastewaters similar in hue to the standards.

c. Interference: Turbidity must be removed.

2. Apparatus

*a. Filter photometer**#(13) equipped with CIE tristimulus filters (see Section 2120D.2*d*).

b. Filter photometer light source: Tungsten lamp at a color temperature of 3000°C (see Section 2120D.2*b*).

c. Absorption cells and appropriate cell holders: For color values less than 250 ADMI units, use cells with a 5.0-cm light path; for color values greater than 250, use cells with 1.0-cm light path.

d. Filtration system: See Section 2120C.2*b* and Figure 2120:1; or a centrifuge capable of achieving 1000 × *g*. (See Section 2120B.)

3. Procedure

a. Instrument calibration: Establish curves for each photometer; calibration data for one instrument cannot be applied to another one. Prepare a separate calibration curve for each absorption cell path length.

1) Prepare standards as described in Section 2120B.3. For a 5-cm cell length prepare

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

standards having color values of 25, 50, 100, 200, and 250 by diluting 5.0, 10.0, 20.0, 40.0, and 50.0 mL stock color standard with distilled water to 100 mL in volumetric flasks. For the shorter pathlength, prepare appropriate standards with higher color values.

2) Determine light transmittance (see ¶ 3*c*, below) for each standard with each filter.

3) Using the calculations described in ¶ 3*d* below, calculate the tristimulus values (X_s, Y_s, Z_s) for each standard, determine the Munsell values, and calculate the intermediate value (*DE*).

4) Using the *DE* values for each standard, calculate a calibration factor F_n for each standard from the following equation:

$$F_n = \frac{(APHA)_n\,(b)}{(DE)_n}$$

where:

$(APHA)_n$ = APHA color value for standard *n*,
$(DE)_n$ = intermediate value calculated for standard *n*, and
b = cell light path, cm.

Placing $(DE)_n$ on the X axis and F_n on the Y axis, plot a curve for the standard solutions. Use calibration curve to derive the *F* value from *DE* values obtained with samples.

b. Sample preparation: Prepare two 100-mL sample portions (one at the original pH, one at pH 7.6) as described in Section 2120C.3*a*, or by centrifugation. (NOTE: Centrifugation is acceptable only if turbidity removal equivalent to filtration is achieved.)

c. Determination of light transmission characteristics: Thoroughly clean absorption cells with detergent and rinse with distilled water. Rinse each absorption cell twice with filtered sample. Clean external surfaces with lens paper and fill cell with sample. Determine sample light transmittance with the three filters to obtain the transmittance values: T_1 from Filter 1, T_2 from Filter 2, and T_3 from Filter 3. Standardize the instrument with each filter at 100% transmittance with distilled water.

d. Calculation of color values: Tristimulus values for samples are X_s, Y_s, and Z_s; for standards X_r, Y_r, and Z_r; and for distilled water X_c, Y_c, and Z_c. Munsell values for samples are V_{xs}, V_{ys}, and V_{zs}; for standards V_{xr}, V_{yr}, and V_{zr}; and for distilled water V_{xc}, Y_{yc}, and V_{zc}.

For each standard or sample calculate the tristimulus values from the following equations:

$$X = (T_3 \times 0.1899) + (T_1 \times 0.791)$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$Y = T_2$$
$$Z = T_3 \times 1.1835$$

Tristimulus values for the distilled water blank used to standardize the instrument are always:

$$X_c = 98.09$$
$$Y_c = 100.0$$
$$Z_c = 118.35$$

Convert the six tristimulus values (X_s, Y_s, Z_s, X_c, Y_c, Z_c) to the corresponding Munsell values using published tables 2, 3, 4†#(14) or by the equation given by Bridgeman.[3]

Calculate the intermediate value of *DE* from the equation:

$$DE = \{(0.23\ \Delta V_y)^2 + [\Delta(V_x - V_y)]^2 + [0.4\ \Delta(V_y - V_z)]^2\}^{1/2}$$

where:

$$V_y = V_{ys} - V_{yc}$$

$$\Delta(V_x - V_y) = (V_{xs} - V_{ys}) - (V_{xc} - V_{yc})$$

$$\Delta(V_y - V_z) = (V_{ys} - V_{zs}) - (V_{yc} - V_{zc})$$

when the sample is compared to distilled water.

With the standard calibration curve, use the *DE* value to determine the calibration factor *F*.

Calculate the final ADMI color value as follows:

$$\text{ADMI value} = \frac{(F)\ (DE)}{b}$$

where:

b = absorption cell light path, cm.

Report ADMI color values at pH 7.6 and at the original pH.

4. Alternate Method

The ADMI color value also may be determined spectrophotometrically, using a spectrophotometer with a narrow (10-nm or less) spectral band and an effective operating range

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

of 400 to 700 nm. This method is an extension of 2120C. Tristimulus values may be calculated from transmittance measurements, preferably by using the weighted ordinate method or by the selected ordinate method. The method has been described by Allen et al.,[2] who include work sheets and worked examples.

5. References

1. MCLAREN, K. 1970. The Adams-Nickerson colour-difference formula. *J. Soc. Dyers Colorists* 86:354.
2. ALLEN, W., W.B. PRESCOTT, R.E. DERBY, C.E. GARLAND, J.M. PERET & M. SALTZMAN. 1973. Determination of color of water and wastewater by means of ADMI color values. *Proc. 28th Ind. Waste Conf.*, Purdue Univ., Eng. Ext. Ser. No. 142:661.
3. BRIDGEMAN, T. 1963. Inversion of the Munsell value equation. *J. Opt. Soc. Amer.* 53:499.

6. Bibliography

JUDD, D.B. & G. WYSZECKI. 1963. Color in Business, Science, and Industry, 2nd ed. John Wiley & Sons, New York, N.Y. (See Tables A, B, and C in Appendix.)

WYSZECKI, G. & W.S. STILES. 1967. Color Science. John Wiley & Sons, New York, N.Y. (See Tables 6.4, A, B, C, pp. 462-467.)

2130 TURBIDITY*#(15)

2130 A. Introduction

1. Sources and Significance

Clarity of water is important in producing products destined for human consumption and in many manufacturing operations. Beverage producers, food processors, and potable water treatment plants drawing from a surface water source commonly rely on fluid-particle separation processes such as sedimentation and filtration to increase clarity and insure an acceptable product. The clarity of a natural body of water is an important determinant of its condition and productivity.

Turbidity in water is caused by suspended and colloidal matter such as clay, silt, finely divided organic and inorganic matter, and plankton and other microscopic organisms. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted with no change in direction or flux level through the sample. Correlation of turbidity with the weight or particle number concentration of suspended matter is difficult because the size, shape, and refractive index of the particles affect the light-scattering properties of the suspension. When present in significant concentrations, particles consisting of light-absorbing

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

materials such as activated carbon cause a negative interference. In low concentrations these particles tend to have a positive influence because they contribute to turbidity. The presence of dissolved, color-causing substances that absorb light may cause a negative interference. Some commercial instruments may have the capability of either correcting for a slight color interference or optically blanking out the color effect.

2. Selection of Method

Historically, the standard method for determination of turbidity has been based on the Jackson candle turbidimeter; however, the lowest turbidity value that can be measured directly on this device is 25 Jackson Turbidity Units (JTU). Because turbidities of water treated by conventional fluid-particle separation processes usually fall within the range of 0 to 1 unit, indirect secondary methods were developed to estimate turbidity. Electronic nephelometers are the preferred instruments for turbidity measurement.

Most commercial turbidimeters designed for measuring low turbidities give comparatively good indications of the intensity of light scattered in one particular direction, predominantly at right angles to the incident light. Turbidimeters with scattered-light detectors located at 90° to the incident beam are called nephelometers. Nephelometers are relatively unaffected by small differences in design parameters and therefore are specified as the standard instrument for measurement of low turbidities. Instruments of different make and model may vary in response.†#(16) However, interinstrument variation may be effectively negligible if good measurement techniques are used and the characteristics of the particles in the measured suspensions are similar. Poor measurement technique can have a greater effect on measurement error than small differences in instrument design. Turbidimeters of nonstandard design, such as forward-scattering devices, may be more sensitive than nephelometers to the presence of larger particles. While it may not be appropriate to compare their output with that of instruments of standard design, they still may be useful for process monitoring.

An additional cause of discrepancies in turbidity analysis is the use of suspensions of different types of particulate matter for instrument calibration. Like water samples, prepared suspensions have different optical properties depending on the particle size distributions, shapes, and refractive indices. A standard reference suspension having reproducible light-scattering properties is specified for nephelometer calibration.

Its precision, sensitivity, and applicability over a wide turbidity range make the nephelometric method preferable to visual methods. Report nephelometric measurement results as nephelometric turbidity units (NTU).

3. Storage of Sample

Determine turbidity as soon as possible after the sample is taken. Gently agitate all samples before examination to ensure a representative measurement. Sample preservation is not practical; begin analysis promptly. Refrigerate or cool to 4°C, to minimize microbiological decomposition of solids, if storage is required. For best results, measure turbidity immediately without altering the original sample conditions such as temperature or pH.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2130 B. Nephelometric Method

1. General Discussion

a. Principle: This method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same conditions. The higher the intensity of scattered light, the higher the turbidity. Formazin polymer is used as the primary standard reference suspension. The turbidity of a specified concentration of formazin suspension is defined as 4000 NTU.

b. Interference: Turbidity can be determined for any water sample that is free of debris and rapidly settling coarse sediment. Dirty glassware and the presence of air bubbles give false results. ‘‘True color,’’ i.e., water color due to dissolved substances that absorb light, causes measured turbidities to be low. This effect usually is not significant in treated water.

2. Apparatus

a. Laboratory or process nephelometer consisting of a light source for illuminating the sample and one or more photoelectric detectors with a readout device to indicate intensity of light scattered at 90° to the path of incident light. Use an instrument designed to minimize stray light reaching the detector in the absence of turbidity and to be free from significant drift after a short warmup period. The sensitivity of the instrument should permit detecting turbidity differences of 0.02 NTU or less in the lowest range in waters having a turbidity of less than 1 NTU. Several ranges may be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities. Differences in instrument design will cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, observe the following design criteria:

1) Light source—Tungsten-filament lamp operated at a color temperature between 2200 and 3000°K.

2) Distance traversed by incident light and scattered light within the sample tube—Total not to exceed 10 cm.

3) Angle of light acceptance by detector—Centered at 90° to the incident light path and not to exceed ±30° from 90°. The detector and filter system, if used, shall have a spectral peak response between 400 and 600 nm.

b. Sample cells: Use sample cells or tubes of clear, colorless glass or plastic. Keep cells scrupulously clean, both inside and out, and discard if scratched or etched. Never handle them where the instrument’s light beam will strike them. Use tubes with sufficient extra length, or with a protective case, so that they may be handled properly. Fill cells with samples and standards that have been agitated thoroughly and allow sufficient time for bubbles to escape.

Clean sample cells by thorough washing with laboratory soap inside and out followed by multiple rinses with distilled or deionized water; let cells air-dry. Handle sample cells only by

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

the top to avoid dirt and fingerprints within the light path.

Cells may be coated on the outside with a thin layer of silicone oil to mask minor imperfections and scratches that may contribute to stray light. Use silicone oil with the same refractive index as glass. Avoid excess oil because it may attract dirt and contaminate the sample compartment of the instrument. Using a soft, lint-free cloth, spread the oil uniformly and wipe off excess. The cell should appear to be nearly dry with little or no visible oil.

Because small differences between sample cells significantly impact measurement, use either matched pairs of cells or the same cell for both standardization and sample measurement.

3. Reagents

a. Dilution water: High-purity water will cause some light scattering, which is detected by nephelometers as turbidity. To obtain low-turbidity water for dilutions, nominal value 0.02 NTU, pass laboratory reagent-grade water through a filter with pore size sufficiently small to remove essentially all particles larger than 0.1 μm;*#(17) the usual membrane filter used for bacteriological examinations is not satisfactory. Rinse collecting flask at least twice with filtered water and discard the next 200 mL.

Some commercial bottled demineralized waters have a low turbidity. These may be used when filtration is impractical or a good grade of water is not available to filter in the laboratory. Check turbidity of bottled water to make sure it is lower than the level that can be achieved in the laboratory.

b. Stock primary standard formazin suspension:

1) Solution I—Dissolve 1.000 g hydrazine sulfate, $(NH_2)_2 \cdot H_2SO_4$, in distilled water and dilute to 100 mL in a volumetric flask. CAUTION: *Hydrazine sulfate is a carcinogen; avoid inhalation, ingestion, and skin contact. Formazin suspensions can contain residual hydrazine sulfate.*

2) Solution II—Dissolve 10.00 g hexamethylenetetramine, $(CH_2)_6N_4$, in distilled water and dilute to 100 mL in a volumetric flask.

3) In a flask, mix 5.0 mL Solution I and 5.0 mL Solution II. Let stand for 24 h at 25 ± 3°C. This results in a 4000-NTU suspension. Transfer stock suspension to an amber glass or other UV-light-blocking bottle for storage. Make dilutions from this stock suspension. The stock suspension is stable for up to 1 year when properly stored.

c. Dilute turbidity suspensions: Dilute 4000 NTU primary standard suspension with high-quality dilution water. Prepare immediately before use and discard after use.

d. Secondary standards: Secondary standards are standards that the manufacturer (or an independent testing organization) has certified will give instrument calibration results equivalent (within certain limits) to the results obtained when the instrument is calibrated with the primary standard, i.e., user-prepared formazin. Various secondary standards are available including: commercial stock suspensions of 4000 NTU formazin, commercial suspensions of microspheres of styrene-divinylbenzene copolymer,†#(18) and items supplied by instrument manufacturers,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

such as sealed sample cells filled with latex suspension or with metal oxide particles in a polymer gel. The U.S. Environmental Protection Agency[1] designates user-prepared formazin, commercial stock formazin suspensions, and commercial styrene-divinylbenzene suspensions as ‘‘primary standards,’’ and reserves the term ‘‘secondary standard’’ for the sealed standards mentioned above.

Secondary standards made with suspensions of microspheres of styrene-divinylbenzene copolymer typically are as stable as concentrated formazin and are much more stable than diluted formazin. These suspensions can be instrument-specific; therefore, use only suspensions formulated for the type of nephelometer being used. Secondary standards provided by the instrument manufacturer (sometimes called ‘‘permanent’’ standards) may be necessary to standardize some instruments before each reading and in other instruments only as a calibration check to determine when calibration with the primary standard is necessary.

All secondary standards, even so-called ‘‘permanent’’ standards, change with time. Replace them when their age exceeds the shelf life. Deterioration can be detected by measuring the turbidity of the standard after calibrating the instrument with a fresh formazin or microsphere suspension. If there is any doubt about the integrity or turbidity value of any secondary standard, check instrument calibration first with another secondary standard and then, if necessary, with user-prepared formazin. Most secondary standards have been carefully prepared by their manufacturer and should, if properly used, give good agreement with formazin. Prepare formazin primary standard only as a last resort. Proper application of secondary standards is specific for each make and model of nephelometer. Not all secondary standards have to be discarded when comparison with a primary standard shows that their turbidity value has changed. In some cases, the secondary standard should be simply relabeled with the new turbidity value. Always follow the manufacturer’s directions.

4. Procedure

a. General measurement techniques: Proper measurement techniques are important in minimizing the effects of instrument variables as well as stray light and air bubbles. Regardless of the instrument used, the measurement will be more accurate, precise, and repeatable if close attention is paid to proper measurement techniques.

Measure turbidity immediately to prevent temperature changes and particle flocculation and sedimentation from changing sample characteristics. If flocculation is apparent, break up aggregates by agitation. Avoid dilution whenever possible. Particles suspended in the original sample may dissolve or otherwise change characteristics when the temperature changes or when the sample is diluted.

Remove air or other entrained gases in the sample before measurement. Preferably degas even if no bubbles are visible. Degas by applying a partial vacuum, adding a nonfoaming-type surfactant, using an ultrasonic bath, or applying heat. In some cases, two or more of these techniques may be combined for more effective bubble removal. For example, it may be necessary to combine addition of a surfactant with use of an ultrasonic bath for some severe

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

conditions. Any of these techniques, if misapplied, can alter sample turbidity; *use with care*. If degassing cannot be applied, bubble formation will be minimized if the samples are maintained at the temperature and pressure of the water before sampling.

Do not remove air bubbles by letting sample stand for a period of time because during standing, turbidity-causing particulates may settle and sample temperature may change. Both of these conditions alter sample turbidity, resulting in a nonrepresentative measurement.

Condensation may occur on the outside surface of a sample cell when a cold sample is being measured in a warm, humid environment. This interferes with turbidity measurement. Remove all moisture from the outside of the sample cell before placing the cell in the instrument. If fogging recurs, let sample warm slightly by letting it stand at room temperature or by partially immersing it in a warm water bath for a short time. Make sure samples are again well mixed.

b. Nephelometer calibration: Follow the manufacturer's operating instructions. Run at least one standard in each instrument range to be used. Make certain the nephelometer gives stable readings in all sensitivity ranges used. Follow techniques outlined in ¶s 2*b* and 4*a* for care and handling of sample cells, degassing, and dealing with condensation.

c. Measurement of turbidity: Gently agitate sample. Wait until air bubbles disappear and pour sample into cell. When possible, pour well-mixed sample into cell and immerse it in an ultrasonic bath for 1 to 2 s or apply vacuum degassing, causing complete bubble release. Read turbidity directly from instrument display.

d. Calibration of continuous turbidity monitors: Calibrate continuous turbidity monitors for low turbidities by determining turbidity of the water flowing out of them, using a laboratory-model nephelometer, or calibrate the instruments according to manufacturer's instructions with formazin primary standard or appropriate secondary standard.

5. Interpretation of Results

Report turbidity readings as follows:

Turbidity Range *NTU*	Report to the Nearest *NTU*
0–1.0	0.05
1–10	0.1
10–40	1
40–100	5
100–400	10
400–1000	50
>1000	100

When comparing water treatment efficiencies, do not estimate turbidity more closely than specified above. Uncertainties and discrepancies in turbidity measurements make it unlikely that

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

results can be duplicated to greater precision than specified.

6. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1993. Methods for Determination of Inorganic Substances in Environmental Samples. EPA-600/R/93/100 - Draft. Environmental Monitoring Systems Lab., Cincinnati, Ohio.

7. Bibliography

HACH, C.C., R.D. VANOUS & J.M. HEER. 1985. Understanding Turbidity Measurement. Hach Co., Technical Information Ser., Booklet 11, Loveland, Colo.

KATZ, E.L. 1986. The stability of turbidity in raw water and its relationship to chlorine demand. *J. Amer. Water Works Assoc.* 78:72.

MCCOY, W.F. & B.H. OLSON. 1986. Relationship among turbidity, particle counts and bacteriological quality within water distribution lines. *Water Res.* 20:1023.

BUCKLIN, K.E., G.A. MCFETERS & A. AMIRTHARAJAH. 1991. Penetration of coliform through municipal drinking water filters. *Water Res.* 25: 1013.

HERNANDEZ, E., R.A. BAKER & P.C. CRANDALL. 1991. Model for evaluating turbidity in cloudy beverages. *J. Food Sci.* 56:747.

HART, V.S., C.E. JOHNSON & R.D. LETTERMAN. 1992. An analysis of low-level turbidity measurements. *J. Amer. Water Works Assoc.*, 84(12): 40.

LECHEVALLIER, M.W. & W.D. NORTON. 1992. Examining relationship between particle counts and *Giardia*, *Cryptosporidium*, and turbidity. *J. Amer. Water Works Assoc.* 84(12):54.

2150 ODOR*#(19)

2150 A. Introduction

1. Discussion

Odor, like taste, depends on contact of a stimulating substance with the appropriate human receptor cell. The stimuli are chemical in nature and the term ‘‘chemical senses’’ often is applied to odor and taste. Water is a neutral medium, always present on or at the receptors that perceive sensory response. In its pure form, water is odor-free. Man and other animals can avoid many potentially toxic foods and waters because of adverse sensory response. These senses often provide the first warning of potential hazards in the environment.

Odor is recognized[1] as a quality factor affecting acceptability of drinking water (and foods prepared with it), tainting of fish and other aquatic organisms, and esthetics of recreational waters. Most organic and some inorganic chemicals contribute taste or odor. These chemicals

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

may originate from municipal and industrial waste discharges, from natural sources such as decomposition of vegetable matter, or from associated microbial activity, and from disinfectants or their products.

The potential for impairment of the sensory quality of water has increased as a result of expansion in the variety and quantity of waste materials, demand for water disposal of captured air pollutants, and increased reuse of available water supplies by a growing population. Domestic consumers and process industries such as food, beverage, and pharmaceutical manufacturers require water essentially free of tastes and odors.

Some substances, such as certain inorganic salts, produce taste without odor and are evaluated by taste testing (Section 2160). Many other sensations ascribed to the sense of taste actually are odors, even though the sensation is not noticed until the material is taken into the mouth. Because some odorous materials are detectable when present in only a few nanograms per liter, it is usually impractical and often impossible to isolate and identify the odor-producing chemical. The human nose is the practical odor-testing device used in this method. Odor tests are performed to provide qualitative descriptions and approximate quantitative measurements of odor intensity. The method for intensity measurement presented here is the *threshold odor* test, based on a method of limits.[2] This procedure, while not universally preferred,[3] has definite strengths.[4]

Sensory tests are useful as a check on the quality of raw and finished water and for control of odor through the treatment process.[2,3,5] They can assess the effectiveness of different treatments and provide a means of tracing the source of contamination.

Section 6040B provides an analytical procedure for quantifying several organic odor-producing compounds including geosmin and methylisoborneol.

2. References

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1973. Proposed Criteria for Water Quality. Vol. 1, Washington, D.C.
2. AMERICAN SOCIETY FOR TESTING AND MATERIALS COMMITTEE E-18. 1996. Sensory Testing Methods: Second Edition. E. Chambers & M.B. Wolf, eds. American Soc. Testing & Materials, W. Conshohocken, Pa.
3. MALLEVIALLE, J. & I.H. SUFFET. 1987. Identification and Treatment of Tastes and Odors in Drinking Water. American Water Works Association Research Foundation and Lyonnaise des Eaux. AWWARF, Denver, Colo.
4. BRUVOLD, W.H. 1989. A Critical Review of Methods Used for the Sensory Evaluation of Water Quality. *CRC Crit. Rev. Environ. Control*. 19(4):291.
5. SUFFET, I., E. KAWCZYNSKI & J. MALLEVIALLE. 1995. Advances in Taste and Odor Treatment and Control. American Water Works Association Research Foundation and Lyonnaise des Eaux, AWWARF, Denver, Colo.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3. Bibliography

MONCRIEFF, R.W. 1946. The Chemical Senses. John Wiley & Sons, New York, N.Y.

BAKER, R.A. 1961. Problems of tastes and odors. *J. Water Pollut. Control Fed.* 33:1099.

BAKER, R.A. 1963. Odor effects of aqueous mixtures of organic chemicals. *J. Water Pollut. Control Fed.* 35:728.

ROSEN, A.A., R.T. SKEEL & M.B. ETTINGER. 1963. Relationship of river water odor to specific organic contaminants. *J. Water Pollut. Control Fed.* 35:777.

WRIGHT, R.H. 1964. The Science of Smell. Basic Books, New York, N.Y.

AMERINE, M.A., R.M. PANGBORN & E.B. ROESSLER. 1965. Principles of Sensory Evaluation of Food. Academic Press, New York, N.Y.

ROSEN, A.A. 1970. Report of research committee on tastes and odors. *J. Amer. Water Works Assoc.* 62:59.

GELDARD, F.A. 1972. The Human Senses. John Wiley & Sons, New York, N.Y.

MEILGAARD, M.C. 1988. Sensory evaluation techniques applied to water works samples. *Water Quality Bull.* 13(2/3):39. WHO Collaborating Centre on Surface and Groundwater Quality, Burlington, Ont., Canada

2150 B. Threshold Odor Test

1. General Discussion

a. Principle: Determine the threshold odor by diluting a sample with odor-free water until the least definitely perceptible odor is achieved. There is no absolute threshold odor concentration, because of inherent variation in individual olfactory capability. A given person varies in sensitivity over time. Day-to-day and within-day differences occur. Furthermore, responses vary as a result of the characteristic, as well as concentration, of odorant. The number of persons selected to measure threshold odor will depend on the objective of the tests, economics, and available personnel. Larger-sized panels are needed for sensory testing when the results must represent the population as a whole or when great precision is desired. Under such circumstances, panels of no fewer than five persons, and preferably ten or more, are recommended.[1] Measurement of threshold levels by one person is often a necessity at water treatment plants. Interpretation of the single tester result requires knowledge of the relative acuity of that person. Some investigators have used specific odorants, such as *m*-cresol or *n*-butanol, to calibrate a tester's response.[2] Others have used the University of Pennsylvania Smell Identification Test to assess an individual's ability to identify odors correctly.[3]

b. Application: This threshold method is applicable to samples ranging from nearly odorless natural waters to industrial wastes with threshold numbers in the thousands. There are no intrinsic difficulties with the highly odorous samples because they are reduced in concentration proportionately before being presented to the test observers.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

c. Qualitative descriptions: A fully acceptable system for characterizing odor has not been developed despite efforts over more than a century. Nevertheless, Section 2170 (Flavor Profile Analysis) specifies a set of 23 odor reference standards that may be used if qualitative descriptions are important. These descriptors can be used with the Threshold Odor Test to standardize methods for sensory analysis.

d. Sampling and storage: Collect samples for odor testing in glass bottles with glass or TFE-lined closures. Complete tests as soon as possible after sample collection. If storage is necessary, collect at least 500 mL of sample in a bottle filled to the top; refrigerate, making sure that no extraneous odors can be drawn into the sample as it cools. Do not use plastic containers.

e. Dechlorination: Most tap waters and some wastewaters are chlorinated. Often it is desirable to determine the odor of the chlorinated sample as well as that of the same sample after dechlorination. Dechlorinate with thiosulfate in exact stoichiometric quantity as described under Nitrogen (Ammonia), Section 4500-NH_3 .

f. Temperature: Threshold odor values vary with temperature. For most tap waters and raw water sources, a sample temperature of 60°C will permit detection of odors that otherwise might be missed; 60°C is the standard temperature for hot threshold odor tests. For some purposes—because the odor is too fleeting or there is excessive heat sensation—the hot odor test may not be applicable; where experience shows that a lower temperature is needed, use a standard test temperature of 40°C. For special purposes, other temperatures may be used. *Report temperature at which observations are made.*

2. Apparatus

To assure reliable threshold measurements, use odor-free glassware. Clean glassware shortly before use with nonodorous soap and acid cleaning solution and rinse with odor-free water. Reserve this glassware exclusively for threshold testing. Do not use rubber, cork, or plastic stoppers. Do not use narrow-mouth vessels.

a. Sample bottles, glass-stoppered or with TFE-lined closures.

b. Constant-temperature bath: A water bath or electric hot plate capable of temperature control of ± 1°C for odor tests at elevated temperatures. The bath must not contribute any odor to the odor flasks.

c. Odor flasks: Glass-stoppered, 500-mL (ST 32) erlenmeyer flasks, to hold sample dilutions during testing.

d. Pipets:

1) *Transfer and volumetric pipets or graduated cylinders:* 200-, 100-, 50-, and 25-mL.

2) *Measuring pipets:* 10-mL, graduated in tenths.

e. Thermometer: Zero to 110°C, chemical or metal-stem dial type.

3. Odor-Free Water

a. Sources: Prepare odor-free water by passing distilled, deionized, or tap water through

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

activated carbon. If product water is not odor-free, rebuild or purify the system. In all cases verify quality of product water daily.

b. Odor-free-water generator (Figure 2150:1):*#(20) Make the PVC generator from a 2-ft length of 4-in. PVC pipe approved for use for drinking water purposes (e.g., Schedule 80, or National Water Council-approved in U.K.). Thread pipe end to accept threaded caps. Have a small threaded nipple in the cap center for water inlet or outlet. To retain the activated carbon, place coarse glass wool in top and bottom of generator. Regulate water flow to generator by a needle valve and a pressure regulator to provide the minimum pressure for the desired flow. Use activated carbon of approximately 12 to 40 mesh grain size.†#(21)

c. Generator operation: Pass tap or purified water through odor-free-water generator at rate of 100 mL/min. When generator is started, flush to remove carbon fines and discard product, or pre-rinse carbon.

Check quality of water obtained from the odor-free-water generator daily at 40 and 60°C before use. The life of the carbon will vary with the condition and amount of water filtered. Subtle odors of biological origin often are found if moist carbon filters stand idle between test periods. Detection of odor in the water coming through the carbon indicates that a change of carbon is needed.

4. Procedure

a. Precautions: Carefully select by preliminary tests the persons to make taste or odor tests. Although extreme sensitivity is not required, exclude insensitive persons and concentrate on observers who have a sincere interest in the test. Avoid extraneous odor stimuli such as those caused by smoking and eating before the test or those contributed by scented soaps, perfumes, and shaving lotions. Insure that the tester is free from colds or allergies that affect odor response. Limit frequency of tests to a number below the fatigue level by frequent rests in an odor-free atmosphere. Keep room in which tests are conducted free from distractions, drafts, and odor.[2] If necessary, set aside a special odor-free room ventilated by air that is filtered through activated carbon and maintained at a constant comfortable temperature and humidity.[4]

For precise work use a panel of five or more testers. Do not allow persons making odor measurements to prepare samples or to know dilution concentrations being evaluated. Familiarize testers with the procedure before they participate in a panel test. Present most dilute sample first to avoid tiring the senses with the concentrated sample. Keep temperature of samples during testing within 1°C of the specified temperature.

Because many raw and waste waters are colored or have decided turbidity that may bias results, use opaque or darkly colored odor flasks, such as red actinic erlenmeyer flasks.

b. Characterization: As part of the threshold test or as a separate test, direct each observer to describe the characteristic sample odor using odor reference standards (see Section 2170). Compile the consensus that may appear among testers and that affords a clue to the origin of the odorous component. The value of the characterization test increases as observers become more experienced with a particular category of odor, e.g., earthy, musty, chlorine.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

c. Threshold measurement:‡#(22) The ‘‘threshold odor number,’’ designated by the abbreviation TON, is the greatest dilution of sample with odor-free water yielding a definitely perceptible odor. Bring total volume of sample and odor-free water to 200 mL in each test. Follow dilutions and record corresponding TON presented in Table 2150:I. These numbers have been computed thus:

$$\text{TON} = \frac{A + B}{A}$$

where:

A = mL sample and
B = mL odor-free water.

1) Place proper volume of odor-free water in the flask first, add sample to water (avoiding contact of pipet or sample with lip or neck of flask), mix by swirling, and proceed as follows:

Determine approximate range of the threshold number by adding 200 mL, 50 mL, 12 mL, and 2.8 mL sample to separate 500-mL glass-stoppered erlenmeyer flasks containing odor-free water to make a total volume of 200 mL. Use a separate flask containing only odor-free water as reference for comparison. Heat dilutions and reference to desired test temperature.

2) Shake flask containing odor-free water, remove stopper, and sniff vapors. Test sample containing least amount of odor-bearing water in the same way. If odor can be detected in this dilution, prepare more dilute samples as described in ¶ 5) below. If odor cannot be detected in first dilution, repeat above procedure using sample containing next higher concentration of odor-bearing water, and continue this process until odor is detected clearly.

3) Based on results obtained in the preliminary test, prepare a set of dilutions using Table 2150:II as a guide. Prepare the five dilutions shown on the appropriate line and the three next most concentrated on the next line in Table 2150:II. For example, if odor was first noted in the flask containing 50 mL sample in the preliminary test, prepare flasks containing 50, 35, 25, 17, 12, 8.3, 5.7, and 4.0 mL sample, each diluted to 200 mL with odor-free water. This array is necessary to challenge the range of sensitivities of the entire panel of testers.

Insert two or more blanks in the series near the expected threshold, but avoid any repeated pattern. Do not let tester know which dilutions are odorous and which are blanks. Instruct tester to smell each flask in sequence, beginning with the least concentrated sample, until odor is detected with certainty.

4) Record observations by indicating whether odor is noted in each test flask. For example:

mL Sample Diluted to 200 mL	**12**	**0**	**17**	**25**	**0**	**35**	**50**

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

mL Sample Diluted to 200 mL	12	0	17	25	0	35	50
Response	–	–	–	+	–	+	–

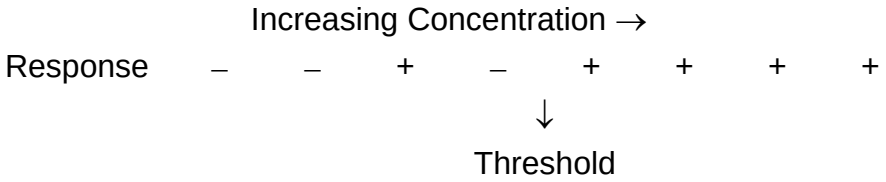
5) If the sample being tested requires more dilution than is provided by Table 2150:II, prepare an intermediate dilution consisting of 20 mL sample diluted to 200 L with odor-free water. Use this dilution for the threshold determination. Multiply TON obtained by 10 to correct for the intermediate dilution. In rare cases more than one tenfold intermediate dilution step may be required.

5. Calculation

The threshold odor number is the dilution ratio at which odor is just detectable. In the example above, 4c4), the first detectable odor occurred when 25 mL sample was diluted to 200 mL. Thus the threshold is 200 divided by 25, or 8. Table 2150:I lists the threshold numbers corresponding to common dilutions.

The smallest TON that can be observed is 1, as in the case where the odor flask contains 200 mL undiluted sample. If no odor is detected at this concentration, report ‘‘No odor observed’’ instead of a threshold number. (In special applications, fractional threshold numbers have been calculated.[6])

Anomalous responses sometimes occur; a low concentration may be called positive and a higher concentration in the series may be called negative. In such a case, designate the threshold as the point after which no further anomalies occur. For instance:



where:

– signifies negative response and
+ signifies positive response.

Occasionally a flask contains residual odor or is contaminated inadvertently. For precise testing repeat entire threshold odor test to determine if the last flask marked ‘‘ – ’’ was actually a mislabelled blank of odor-free water or if the previous ‘‘ + ’’ was a contaminated sample.

Use appropriate statistical methods to calculate the most probable average threshold from large numbers of panel results. For most purposes, express the threshold of a group as the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

geometric mean of individual thresholds.

6. Interpretation of Results

A threshold number is not a precise value. In the case of the single observer it represents a judgment at the time of testing. Panel results are more meaningful because individual differences have less influence on the result. One or two observers can develop useful data if comparison with larger panels has been made to check their sensitivity. Do not make comparisons of data from time to time or place to place unless all test conditions have been standardized carefully and there is some basis for comparison of observed intensities.

7. References

1. AMERICAN SOCIETY FOR TESTING AND MATERIALS COMMITTEE E-18. 1996. Sensory Testing Methods: Second Edition. E. Chambers & M.B. Wolf, eds. American Soc. Testing & Materials, W. Conshohocken, Pa.
2. BAKER, R.A. 1962. Critical evaluation of olfactory measurement. *J. Water Pollut. Control Fed.* 34:582.
3. DOTY, R.L., P. SHAMAN, M.S. DANN & C.P. KIMMELMAN. 1984. University of Pennsylvania smell identification test: a rapid quantitative olfactory function test for the clinic. *Laryngoscope,* 94(2):176.
4. BAKER, R.A. 1963. Odor testing laboratory. *J. Water Pollut. Control Fed.* 35:1396.
5. INTERNATIONAL ORGANIZATION FOR STANDARDIZATION. 1985. ISO 6658 Sensory Analysis–Methodology—General Guidance. International Org. for Standardization, Geneva, Switzerland.
6. ROSEN, A.A., J.B. PETER & F.M. MIDDLETON. 1962. Odor thresholds of mixed organic chemicals. *J. Water Pollut. Control Fed.* 34:7.

8. Bibliography

HULBERT, R. & D. FEBEN. 1941. Studies on accuracy of threshold odor value. *J. Amer. Water Works Assoc.* 33:1945.

SPAULDING, C.H. 1942. Accuracy and application of threshold odor test. *J. Amer. Water Works Assoc.* 34:877.

THOMAS, H.A., JR. 1943. Calculation of threshold odor. *J. Amer. Water Works Assoc.* 35:751.

CARTWRIGHT, L.C., C.T. SNELL & P.H. KELLY. 1952. Organoleptic panel testing as a research tool. *Anal. Chem.* 24:503.

LAUGHLIN, H.F. 1954. Palatable level with the threshold odor test. *Taste Odor Control J.* 20:No. 8 (Aug.).

SHELLENBERGER, R.D. 1958. Procedures for determining threshold odor concentrations in aqueous solutions. *Taste Odor Control J.* 24:No. 5 (May).

LAUGHLIN, H.F. 1962. Influence of temperature in threshold odor evaluation. *Taste Odor*

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Control J. 28:No. 10 (Oct.).

The threshold odor test. 1963. *Taste Odor Control J.* 29:Nos. 6, 7, 8 (June, July, Aug.).

SUFFET, I.H. & S. SEGALL. 1971. Detecting taste and odor in drinking water. *J. Amer. Water Works Assoc.* 63:605.

STAHL, W.H., ed. 1973. Compilation of Odor and Taste Threshold Values Data. Amer. Soc. Testing & Materials Data Ser. DS 48, Philadelphia, Pa.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1973. Annual Book of ASTM Standards. Part 23, D-1292-65, ASTM, Philadelphia, Pa.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1986. Physical Requirement Guidelines for Sensory Evaluation Laboratories. STP 913, American Soc. Testing & Materials, Philadelphia, Pa.

AMERICAN SOCIETY FOR TESTING AND MATERIALS COMMITTEE E-679. 1990. Standard Practice for Determination of Odor and Taste Thresholds by a Forced-Choice Ascending Concentration Series Method of Limits. American Soc. Testing & Materials, Philadelphia, Pa.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1991. E1432 Standard Practice for Defining and Calculating Individual and Group Sensory Thresholds from Forced Choice Data Sets of Intermediate Size. American Society for Testing and Materials, Philadelphia, Pa.

BRUVOLD, W.H. 1989. A critical review of methods used for the sensory evaluation of water quality. *Crit. Rev. Environ. Control* 19:291.

YOUNG, W.F., H. HORTH, R. CRANE, T. OGDEN & M. ARNOTT. 1996. Taste and odour threshold concentration of potential potable water contaminants. *Water Res.* 30:331.

2160 TASTE*#(23)

2160 A. Introduction

1. General Discussion

Taste refers only to gustatory sensations called bitter, salty, sour, and sweet that result from chemical stimulation of sensory nerve endings located in the papillae of the tongue and soft palate. Flavor refers to a complex of gustatory, olfactory, and trigeminal sensations resulting from chemical stimulation of sensory nerve endings located in the tongue, nasal cavity, and oral cavity.[1] Water samples taken into the mouth for sensory analysis always produce a flavor, although taste, odor, or mouth-feel may predominate, depending on the chemical substances present. Methods for sensory analysis presented herein require that the sample be taken into the mouth, that is, be tasted, but technically the sensory analysis requires evaluation of the complex sensation called flavor. As used here, taste refers to a method of sensory analysis in which

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

samples are taken into the mouth but the resultant evaluations pertain to flavor.

Three methods have been developed for the sensory evaluation of water samples taken into the mouth: the flavor threshold test (FTT), the flavor rating assessment (FRA), and the flavor profile analysis (FPA) (Section 2170). The FTT is the oldest. It has been used extensively and is particularly useful for determining if the overall flavor of a sample of finished water is detectably different from a defined standard.[2] The FRA is especially valuable for determining if a sample of finished water is acceptable for daily consumption,[3] and the FPA is most useful for identifying and characterizing individual flavors in a water sample.[4]

Make flavor tests only on samples known to be safe for ingestion. Do not use samples that may be contaminated with bacteria, viruses, parasites, or hazardous chemicals, that contain dechlorinating agents such as sodium arsenite or that are derived from an unesthetic source. Do not make flavor tests on wastewaters or similar untreated effluents. Observe all sanitary and esthetic precautions with regard to apparatus and containers contacting the sample. Properly clean and sterilize containers before using them. Conduct analyses in a laboratory free from interfering background odors and if possible provide non-odorous carbon-filtered air at constant temperature and humidity. Use the procedure described in Section 2150 with respect to taste- and odor-free water to prepare dilution water and reference samples.

2. References

1. GELDARD, F.A. 1972. The Human Senses. John Wiley & Sons, New York, N.Y.
2. BAKER, R.A. 1961. Taste and Odor in Water: A Critical Review. Manufacturing Chemists' Assoc., Washington, D.C.
3. BRUVOLD, W.H. 1968. Scales for rating the taste of water. *J. Appl. Psychol.* 52:245.
4. MALLEVIALE, J. & I.H. SUFFET, eds. 1987. The Identification and Treatment of Tastes and Odors in Drinking Water. American Water Works Association Research Foundation, Denver, Colo.

2160 B. Flavor Threshold Test (FTT)

1. General Discussion

Use the FTT to measure detectable flavor quantitatively. More precisely, use the method to compare the sample flavor objectively with that of specified reference water used as diluent.

The flavor threshold number (FTN) is the greatest dilution of sample with reference water yielding a definitely perceptible difference. The FTN is computed as follows:

$$\text{FTN} = \frac{A + B}{A}$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

where:

A = sample volume, mL, and
B = reference water (diluent) volume, mL.

Table 2160:I gives the FTNs corresponding to various dilutions.

2. Procedure

a. Panel selection: Carefully select by preliminary trials interested persons to make flavor tests. Exclude insensitive persons and insure that the testers are free from colds or allergies. Familiarize testers with the procedure before they participate in a panel test, but do not let them prepare samples or know dilution concentrations being evaluated. For precise work use a panel of five or more testers.

b. Taste characterization: Have each observer describe the characteristic sample flavor of the most concentrated sample. Compile the consensus that may appear among testers. The value of characterization increases as observers become more experienced with a particular flavor category such as chlorophenolic, grassy, or musty.

c. Preliminary test: To determine approximate range of the FTN, add 200-, 50-, 12-, and 4-mL sample portions to volumes of reference water (see Section 2150) designated in Table 2160:I in separate 300-mL glass beakers to make a total of 200 mL in each beaker, and mix gently with clean stirrer. Use separate beaker containing only reference water for comparison. Keep sample temperature during testing within 1°C of specified temperature. Present samples to each taster in a uniform manner, with the reference water presented first, followed by the most dilute sample. If a flavor can be detected in this dilution, prepare an intermediate sample by diluting 20 mL sample to 200 mL with reference water. Use this dilution for threshold determination and multiply FTN obtained by 10 to correct for intermediate dilution. In rare cases a higher intermediate dilution may be required.

If no flavor is detected in the most dilute sample, repeat using the next concentration. Continue this process until flavor is detected clearly.

d. FTN determination: Based on results obtained in the preliminary test, prepare a set of dilutions using Table 2160:II as a guide. Prepare the seven dilutions shown on the appropriate line. This array is necessary to challenge the range of sensitivities of the entire panel of testers. If the sample being tested requires more dilution than is provided by Table 2160:II, make intermediate dilutions as directed in *c* above.

Use a clean 50-mL beaker filled to the 25-mL level or use an ordinary restaurant-style drinking glass for each dilution and reference sample. Do not use glassware used in sensory testing for other analyses. Between tests, sanitize containers in an automatic dishwasher supplied with water at not less than 60°C.

Maintain samples at 15± 1°C. However, if temperature of water in the distribution system is higher than 15°C, select an appropriate temperature. Specify temperature in reporting results.

Present series of samples to each tester in order of increasing concentration. Pair each

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

sample with a known reference. Have tester taste sample by taking into the mouth whatever volume is comfortable, moving sample throughout the mouth, holding it for several seconds, and discharging it without swallowing. Have tester compare sample with reference and record whether a flavor or aftertaste is detectable. Insert two or more reference blanks in the series near the expected threshold, but avoid any repeated pattern. Do not let tester know which samples have flavor and which are blanks. Instruct tester to taste each sample in sequence, beginning with the least concentrated sample, until flavor is detected with certainty.

Record observations by indicating whether flavor is noted in each test beaker. For example:

mL Sample Diluted to 200 mL	**6**	**8**	**12**	**0**	**17**	**25**	**35**	**0**	**50**
Response	–	–	–	–	–	+	+	–	+

where:

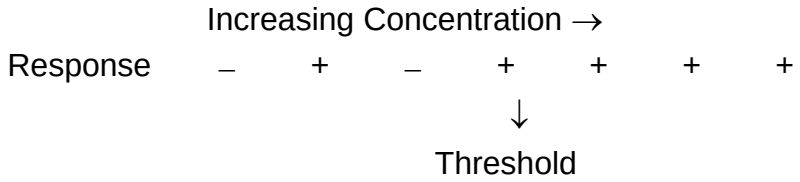
– signifies negative response and
+ signifies positive response.

3. Calculation

The flavor threshold number is the dilution ratio at which flavor is just detectable. In the example above, the first detectable flavor occurred when 25 mL sample was diluted to 200 mL yielding a threshold number of 8 (Table 2160:I). Reference blanks do not influence calculation of the threshold.

The smallest FTN that can be observed is 1, where the beaker contains 200 mL undiluted sample. If no flavor is detected at this concentration, report ‘‘No flavor observed’’ instead of a threshold number.

Anomalous responses sometimes occur; a low concentration may be called positive and a higher concentration in the series may be called negative. In such cases, designate the threshold as that point after which no further anomalies occur. The following illustrates an approach to an anomalous series (responses to reference blanks are excluded): Response:



Calculate mean and standard deviation of all FTNs if the distribution is reasonably symmetrical; otherwise, express the threshold of a group as the median or geometric mean of individual thresholds.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

4. Interpretation of Results

An FTN is not a precise value. In the case of the single observer it represents a judgment at the time of testing. Panel results are more meaningful because individual differences have less influence on the test result. One or two observers can develop useful data if comparison with larger panels has been made to check their sensitivity. Do not make comparisons of data from time to time or place to place unless all test conditions have been standardized carefully and there is some basis for comparison of observed FTNs.

5. Bibliography

HULBERT, R. & D. FEBEN. 1941. Studies on accuracy of threshold odor value. *J. Amer. Water Works Assoc.* 33:1945.

SPAULDING, C.H. 1942. Accuracy and application of threshold odor test. *J. Amer. Water Works Assoc.* 34:877.

THOMAS, H.A. 1943. Calculation of threshold odor. *J. Amer. Water Works Assoc.* 35:751.

COX, G.J. & J. W. NATHANS. 1952. A study of the taste of fluoridated water. *J. Amer. Water Works Assoc.* 44:940.

LAUGHLIN, H.F. 1954. Palatable level with the threshold odor test. *Taste Odor Control J.* 20:1.

COX, G.J., J.W. NATHANS & N. VONAU. 1955. Subthreshold-to-taste thresholds of sodium, potassium, calcium and magnesium ions in water. *J. Appl. Physiol.* 8:283.

LOCKHART, E.E., C.L. TUCKER & M.C. MERRITT. 1955. The effect of water impurities on the flavor of brewed coffee. *Food Res.* 20:598.

CAMPBELL, C.L., R.K. DAWES, S. DEOLALKAR & M.C. MERRITT. 1958. Effects of certain chemicals in water on the flavor of brewed coffee. *Food Res.* 23:575.

MIDDLETON, F.M., A.A. ROSEN & R.H. BRUTTSCHELL. 1958. Taste and odor research tools for water utilities. *J. Amer. Water Works Assoc.* 50:231.

SHELLENBERGER, R.D. 1958. Procedures for determining threshold odor concentrations in aqueous solutions. *Taste Odor Control J.* 24:1.

COHEN, J.N., L.J. KAMPHAKE, E.K. HARRIS & R.L. WOODWARD. 1960. Taste threshold concentrations of metals in drinking water. *J. Amer. Water Works Assoc.* 52:660.

BAKER, R.A. 1961. Problems of tastes and odors. *J. Water Pollut. Control Fed.* 33:1099.

ROSEN, A.A., J.B. PETER & F.M. MIDDLETON. 1962. Odor thresholds of mixed organic chemicals. *J. Water Pollut. Control Fed.* 34:7.

BAKER, R.A. 1962. Critical evaluation of olfactory measurement. *J. Water Pollut. Control Fed.* 34:582.

BAKER, R.A. 1963. Threshold odors of organic chemicals. *J. Amer. Water Works Assoc.* 55:913.

BAKER, R.A. 1963. Odor testing laboratory. *J. Water Pollut. Control Fed.* 35:1396.

BAKER, R.A. 1963. Odor effects of aqueous mixtures of organic chemicals. *J. Water Pollut. Control Fed.* 35:728.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

ROSEN, A.A., R.T. SKEEL & M.B. ETTINGER. 1963. Relationship of river water odor to specific organic contaminants. *J. Water Pollut. Control Fed.* 35:777.

BRYAN, P.E., L.N. KUZMINSKI, F.M. SAWYER & T.H. FENG. 1973. Taste thresholds of halogens in water. *J. Amer. Water Works Assoc.* 65:363.

2160 C. Flavor Rating Assessment (FRA)

1. General Discussion

When the purpose of the test is to estimate acceptability for daily consumption, use the flavor rating assessment described below. This procedure has been used with samples from public sources in laboratory research and consumer surveys to recommend standards governing mineral content in drinking water. Each tester is presented with a list of nine statements about the water ranging on a scale from very favorable to very unfavorable. The tester's task is to select the statement that best expresses his or her opinion. The individual rating is the scale number of the statement selected. The panel rating for a particular sample is an appropriate measure of central tendency of the scale numbers for all testers for that sample.

2. Samples

Sample finished water ready for human consumption or use experimentally treated water if the sanitary requirements given in Section 2160A.1 are met fully. Use taste- and odor-free water as described in Section 2150 and a solution of 2000 mg NaCl/L prepared with taste- and odor-free water as criterion samples.

3. Procedure

a. Panel selection and preparation: Give prospective testers thorough instructions and trial or orientation sessions followed by questions and discussion of procedures. In tasting samples, testers work alone. Select panel members on the basis of performance in these trial sessions. Do not let testers know the composition or source of specific samples.

b. Rating test: A single rating session may be used to evaluate up to 10 samples, including the criterion samples mentioned in ¶ 2 above. Allow at least 30 min rest between repeated rating sessions.

For glassware requirements, see Section 2160B2*d*.

Present samples at a temperature that the testers will find pleasant for drinking water; maintain this temperature throughout testing. A temperature of 15°C is recommended, but in any case, do not let the test temperature exceed tap water temperatures customary at the time of the test. Specify test temperature in reporting results.

Independently randomize sample order for each tester. Instruct each to complete the following steps: 1) Taste about half the sample by taking water into the mouth, holding it for several seconds, and discharging it without swallowing; 2) Form an initial judgment on the rating scale; 3) Make a second tasting in a similar manner; 4) Make a final rating and record

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

result on an appropriate data form; 5) Rinse mouth with reference water; 6) Rest 1 min before repeating Steps 1 through 5 on next sample.

c. Characterization: If characterization of flavor also is required, conduct a final rating session wherein each tester is asked to describe the flavor of each sample rated (see Section 2160B.2*b*).

4. Calculation

Use the following scale for rating. Record ratings as integers ranging from one to nine, with one given the highest quality rating. Calculate mean and standard deviation of all ratings if the distribution is reasonably symmetrical, otherwise express the most typical rating of a group as the median or geometric mean of individual ratings.

Action tendency scale:

1) I would be very happy to accept this water as my everyday drinking water.
2) I would be happy to accept this water as my everyday drinking water.
3) I am sure that I could accept this water as my everyday drinking water.
4) I could accept this water as my everyday drinking water.
5) Maybe I could accept this water as my everyday drinking water.
6) I don't think I could accept this water as my everyday drinking water.
7) I could not accept this water as my everyday drinking water.
8) I could never drink this water.
9) I can't stand this water in my mouth and I could never drink it.

5. Interpretation of Results

Values representing the central tendency and dispersion of quality ratings for a laboratory panel are only estimates of these values for a defined consuming population.

6. Bibliography

BRUVOLD, W.H. & R.M. PANGBORN. 1966. Rated acceptability of mineral taste in water. *J. Appl. Psychol.* 50:22.

BRUVOLD, W.H., H.J. ONGERTH & R.C. DILLEHAY. 1967. Consumer attitudes toward mineral taste in domestic water. *J. Amer. Water Works Assoc.* 59:547.

DILLEHAY, R.C., W.H. BRUVOLD & J.P. SIEGEL. 1967. On the assessment of potability. *J. Appl. Psychol.* 51:89.

BRUVOLD, W.H. 1968. Mineral Taste in Domestic Water. Univ. California Water Resources Center, Los Angeles.

BRUVOLD, W.H. & H.J. ONGERTH. 1969. Taste quality of mineralized water. *J. Amer. Water Works Assoc.* 61:170.

BRUVOLD, W.H. & W.R. GAFFEY. 1969. Rated acceptability of mineral taste in water. II: Combinatorial effects of ions on quality and action tendency ratings. *J. Appl. Psychol.*

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

53:317.

DILLEHAY, R.C., W.H. BRUVOLD & J.P. SIEGEL. 1969. Attitude, object label, and stimulus factors in response to an attitude object. *J. Personal. Social Psychol.* 11:220.

BRUVOLD, W.H. 1970. Laboratory panel estimation of consumer assessments of taste and flavor. *J. Appl Psychol.* 54:326.

PANGBORN, R.M., I.M. TRABUE & R.C. BALDWIN. 1970. Sensory examination of mineralized, chlorinated waters. *J. Amer. Water Works Assoc.* 62:572.

PANGBORN, R.M., I.M. TRABUE & A.C. LITTLE. 1971. Analysis of coffee, tea and artifically flavored drinks prepared from mineralized waters. *J. Food Sci.* 36:355.

BRUVOLD, W.H. & P.C. WARD. 1971. Consumer assessment of water quality and the cost of improvements. *J. Amer. Water Works Assoc.* 63:3.

PANGBORN, R.M. & L.L. BERTOLERO. 1972. Influence of temperature on taste intensity and degree of liking of drinking water. *J. Amer. Water Works Assoc.* 64:511.

BRUVOLD, W.H. 1975. Human perception and evaluation of water quality. *Crit. Rev. Environ. Control* 5:153.

BRUVOLD, W.H. 1976. Consumer Evaluation of the Cost and Quality of Domestic Water. Univ. California Water Resources Center, Davis.

2170 FLAVOR PROFILE ANALYSIS*#(24)

2170 A. Introduction

1. Discussion

Flavor profile analysis (FPA) is a technique for identifying sample taste(s) and odor(s). For general information on taste see Section 2160; for information on odor see Section 2150.

FPA differs from threshold odor number because the sample is not diluted and each taste or odor attribute is individually characterized and assigned its own intensity rating. The single numerical rating obtained in measuring threshold odor is controlled by the most readily perceived odorant or mixture. Sample dilution may change the odor attribute that is measured.[1,2] FPA determines the strength or intensity of each perceived taste or odor without dilution or treatment of the sample.

2. References

1. MALLEVIALLE, J. & I.H. SUFFET, eds. 1987. Identification and Treatment of Tastes and Odors in Drinking Water. American Water Works Assoc., Denver, Colo.
2. BRUCHET, A., D. KHIARI & I. SUFFET. 1995. Monitoring and analysis. *In* I. Suffet, J. Mallevialle & E. Kawczynski, eds. Advances in Taste and Odor Treatment and Control. American Water Works Assoc. Research Foundation & Lyonnaise des Eaux,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Denver, Colo.

2170 B. Flavor Profile Analysis

1. General Discussion

a. Principle: Flavor profile analysis uses a group of four or five trained panelists to examine the sensory characteristics of samples. Flavor attributes are determined by tasting; odor attributes (aroma) are determined by sniffing the sample. The method allows more than one flavor, odor attribute, or feeling factor (e.g., drying, burning) to be determined per sample and each attribute's strength to be measured.

Panelists must be able to detect and recognize various odors present. Flavor profile analysis requires well-trained panelists and data interpreters. Reproducibility of results depends on the training and experience of the panelists.

Initially, panelists record their perceptions without discussion. Once each individual has made an independent assessment of a sample, the panel discusses its findings and reaches a consensus.[1]

b. Interference: Fatigue (adaptation) denotes the decrease in the analyst's sensory acuity with continued exposure to stimulation.[1] Because odor mixtures are more complex than taste mixtures, olfactory adaptation is more serious.[2] Factors that can induce fatigue include odor intensity, type of odorants (some compounds such as geosmin and chlorine induce more fatigue than others), number of samples tested during a session, and rest interval between samples.[1] The rest interval also is important because it prevents carryover of odors between samples.

Background odors present during analysis affect results. Analyst illness, i.e., cold or allergy, can diminish or otherwise alter perception.

c. Application: Flavor profile analysis has been applied to drinking water sources, finished drinking water, sampling points within the drinking water treatment train, and bottled waters, and for investigating customer complaints.

d. Precautions: Some compounds are health hazards when inhaled or ingested. Do not use this method for industrial wastes or other samples suspected of containing high concentrations of hazardous compounds. Chemically analyze suspect samples to determine whether hazardous chemicals are present before making flavor profile analysis. Do not taste untreated drinking water unless it is certain that no health threat (biological or chemical) exists.

Because flavor profile analysis includes discussion during which panelists reach consensus description, avoid including on the panel a person with a dominating personality.[3] The opinions of a senior member or panel leader also may have this undesired effect.[3]

2. Apparatus[4-8]

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Reserve apparatus and glassware exclusively for flavor profile analysis. Prepare sample bottles by washing bottle and cap with detergent. Rinse 10 times with hot water. Optionally rinse with HCl (1:1). Rinse with odor-free water (see 2150B.3) at least three times. If there is residual odor, such as chalky, repeat cleaning.

Prepare 500-mL erlenmeyer flasks by either of the two methods described below provided that it imparts no odor to the sample. Make tests with freshly cleaned containers.

1) Without wearing rubber gloves wash flask with soapy water. Additionally, scrub outside of flask with scouring pad to remove body oils. Rinse 10 times with hot water and 3 times with odor-free water. To store flask add 100 to 200 mL odor-free water and stopper. Before use, rinse with 100 mL odor-free water. If there is residual odor, repeat cleaning.

2) Do not handle with rubber gloves. Before use, heat 200 mL odor-free water to boiling; lightly lay stopper over flask opening, permitting water vapor to escape. Discard boiled water and let flask cool to room temperature. If there is residual odor repeat or use cleaning alternative 1). After analyzing a sample, discard sample, rinse 10 times with hot tap water, add 200 mL odor-free water, stopper, and store.

For flasks with persistent odor use commercial cleaning mixture*#(25) or HCl (1:1).

a. Sample bottles: Glass, 1-L, with TFE-lined closure.

b. Containers for odor analysis:[4] Select container for odor analysis depending on panelists' preference, temperature of sample, and availability of container.

1) Panel preference[4-8]—Plastic cups, 7- or 8-ounce disposable, are convenient. Some panels have found that these plastic cups impart a plastic and/or floral aroma to samples. They prefer 500-mL erlenmeyer flasks with ST32 ground-glass stoppers. The panel should determine the acceptable, odor-free, test container.

2) Temperature[4]—If aroma samples are tested at 45°C, do not use plastic. If aroma samples are tested at 25°C, use the same plastic cup and sample for both aroma and flavor analysis.

3) Availability[4]—Containers must be consistently available because the panel responses may change when different containers are used.

c. Containers for flavor analysis:[4] Use either plastic disposable, e.g., polyethylene,†#(26) or glass containers. Do not use wax-lined or paper cups. If using glass containers verify that they contribute no taste to the sample. Wash glass containers as directed above.

d. Watch glasses.

e. Constant-temperature water bath capable of maintaining a temperature ± 1°C. The bath must not contribute any odor to the odor flasks or testing room.

f. Thermometer, graduated 0 to 110°C, chemical or metal-stem dial type.

g. Syringes.

h. Ice chest.

i. Odor-free testing room:[3,5] Hold flavor profile analysis sessions in a clean, well-lit quiet,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

aroma-free, and temperature-controlled room. Seat panel members around a common table to facilitate exchange of responses during discussion. Place a blackboard or easel pad in the room so that all panelists are able to see it. Preferably use an easel pad with odor-free markers (such as a wax, china marker).

j. Refrigerator capable of maintaining a temperature of 4°C.

3. Reagents

a. Odor-free water: See Section 2150B.3.

b. Crackers: Use salt- and flavor-free crackers‡#(27) to cleanse the palate during taste testing. Before tasting anything, use the crackers and taste-free water to cleanse the palate. Use crackers between samples to reduce carryover of perceptions.

c. Odor and flavor standards: Odor and flavor reference standards are being developed for use as a guide for qualitative descriptions (attributes). Aroma reference standards help panelists come to agreement on the description of specific aromas.[4-11] Table 2170:I, Table 2170:II, and Table 2170:III list some of the aroma references in use. New references are being added continually. A taste and odor wheel has been developed from these lists.[2] For odor identification and training, place several drops of stock solutions (producing moderately strong odors) onto sterile cotton in 25-mL amber-colored vials with TFE-lined caps. Standards can be stored until odor changes.

d. Taste standards: Chemicals used for taste standards are sucrose (sweet), citric acid (sour), sodium chloride (salt), and caffeine (bitter). Table 2170:IV lists the chemicals used and their concentrations for basic taste standards at ‘‘slight,’’ ‘‘moderate,’’ and ‘‘strong’’ levels.[4,5] The taste standards provide reference points for both taste and odor intensity ratings. The panelists compare the intensity of what they are smelling or tasting to the intensity of the standards they have tasted. Make taste standards available during panel training. Because the tastes from all but the sweet standard tend to overpower any subsequent tasting, use only the sweet taste standard during actual sample analysis. If the panel meets as seldom as once a week, make sweet standards available so that panelists can ‘‘recalibrate’’ themselves. Panels that meet more than once a week may not need to ‘‘recalibrate.’’ Make standards fresh each time they are used.[4]

4. Scale

The strength of a taste or odor is judged according to the following scale:

—	(odor-free)
T	(threshold)
2	(very weak)
4	(weak)
6	
8	(moderate)

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

10

12 (strong)

5. Procedure

a. Sample collection: Collect sample in cleaned container. When sampling from a tap, remove all screens and aerators, minimize turbulence. Flush tap at least 5 min. Reduce flow rate during sampling. Rinse bottle with sample, then fill it to the top, with no headspace. Chill or refrigerate sample immediately and analyze as soon after collection as possible, preferably within 24 h, but no longer than 48 h.

b. Sample preparation:[4] Pour samples into properly prepared glassware or acceptable disposable containers. Analyze samples at the same temperature. Adjust sample temperatures by placing samples in a water bath 15 min before analysis. Prepare a sample for each panelist. Examine odor samples before flavor samples.

1) Odor analysis—When using 500-mL erlenmeyer flasks for odor analysis, place 200 mL sample in the flask. Make transfer carefully to avoid loss of volatile components. When plastic cups are used, place 60 mL sample in cup and cover it with a watch glass.

2) Taste analysis—Bring sample to 25°C before pouring into containers for tasting. Cover with a watch glass if samples are not tasted immediately. If samples are tested at 25°C for odor, use the same sample for flavor analysis.

c. Panelists: Carefully screen and train panelists.[8]

d. Pre-test considerations: Notify panelists well in advance of panel session so a substitute can be found if necessary. Panelists who have colds or allergic attacks the day of the panel are unacceptable; they should ask the panel coordinator to find a substitute. Panelists must not smoke or eat for 15 to 30 min before the session. Wearing cologne or perfume or washing hands with scented soap before the session is not permitted.

e. Sample analysis: The panel consists of four or five members. If fewer than four panelists are available, store the sample until a full panel can meet.

1) Odor analysis—Heat samples to proper temperature. If erlenmeyer flasks are used, sample temperature is 45°C. If plastic cups are used, sample temperature is 25°C. Give each panelist his/her own sample. If a flask is used, hold it with one hand on the bottom and the other on the stopper. Do not touch flask neck. Gently swirl (do not shake) flask in a circular manner to ensure that volatile compounds are released into the headspace. Bring flask close to nose, remove stopper, and sniff at the flask opening. Record impressions of odor attributes in the order perceived and the assessment of each attribute's intensity. If a cup is used, gently swirl on the table top for a few seconds. Remove watchglass, and keeping hands away from the cup, sniff sample and record perceptions. CAUTION: *Sniff samples only if they are known to be toxicologically safe.* For both the flask and the plastic cup method, smell all samples before going on to the taste test. Do not discuss or interact with other panelists.

2) Taste analysis—When tasting, take sample into the mouth and roll it over the entire

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

surface of the tongue. Slurping enhances the odor aspect of flavor. CAUTION: *Taste only samples known to be biologically and toxicologically safe*. Do not discuss or interact with other panelists.

3) Intensity—In both taste and odor analysis, each panelist determines intensity ratings by matching intensity of the flavor or aroma perceived with the defined intensities of the basic taste standards. Initially this may be difficult. Some panels have found it helpful to make basic taste standards available throughout the analysis so that any panelist who wishes to ‘‘recalibrate’’ may do so.

4) Re-examination of samples—First impressions are most important, particularly for intensity. The intensity rating may diminish upon re-examination because of fatigue and volatility of the odorant. However, if an aroma or flavor is difficult for a panelist to describe, the panelist may go back and re-evaluate the sample before recording the results.

5) Individual results—As soon as a sample is tasted or smelled, record individual results. Information recorded includes a description of aromas or flavors perceived, their intensity, and the order in which they were perceived.

6) Rest interval—Sniff odor-free water and rest at least 2 min between samples. Fatigue is a problem[1] that can be dealt with. When samples are expected to cause fatigue, the panel leader can increase the rest interval and limit the number of samples presented. The leader also may try to arrange samples such that samples known to be fatiguing are placed near the end of the sample row. Avoid juxtaposition of such samples. Also, use taste- and odor-free blanks between samples. Five to six samples per session is the maximum.

7) Discussion—When all panelists have had an opportunity to examine the sample, hold a discussion period. Each panelist’s impression of the sample is stated and the panel leader records it to be seen by everyone. By examining the order of appearance, intensity, and description, the panel leader attempts to group responses together, soliciting comments from the panel members as to whether or not they agree. Sometimes panelists detect an aroma that they cannot describe; in the discussion they may see what another panelist called it and decide to agree with that description. With inexperienced panels, several different descriptors may be used for the same aroma. As the panel gains more experience, these differences tend to be reconciled. It is the responsibility of the panel leader to ensure that the panelists are provided with standards that duplicate the sample aromas. Descriptions that fewer than 50% of the panelists use are called ‘‘other notes’’ and are listed separately or are not included in the group results.

8) Recording panel results—Record the following: sample description; time of sampling; identity of panel member; flavor, aroma, and feeling factor descriptions; intensity rating; order of perception; range and average for each descriptor.

6. Calculation and Interpretation[1]

In early testing intensity was used to describe the strength of an odor in an ordinal scale from slight to strong.[12] If an odor was recognized, then it had an intensity. The rating scale has been modified to use numbers corresponding to the ordinal categories. Points (other than threshold) on

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

the scale can be anchored by the use of taste standards. Thus a certain concentration of a taste standard is defined as a certain point on the rating scale and numerical ratings for nonthreshold intensities are anchored. Threshold ratings are not defined by any standards. Their meaning is different from that of the other ratings and they are difficult to manipulate mathematically.

Calculate averages if at least 50% of the panelists agree on a given description. If a panelist does not give that description, assign an intensity value of zero. For example:

		Intensity								
Description	Panelist					I	II	III	IV	Average
Musty	2	4	0	2	2.0					
Chlorinous	2	4	4	4	3.5					

7. Quality Control[12]

Use odor-free samples and duplicates occasionally. The odor-free sample serves to detect guessing. Duplicates check reproducibility. A standard concentration of an odor reference standard in odor-free water also can be used to check odor recognition and reproducibility of the intensity scale.

Use counterbalancing of samples so that each panelist receives the samples in a different order. This prevents error due to order effects such as fatigue, carryover, and expectation.

8. Precision and Bias

Initial studies of precision and bias have been completed.[12,13] An odor recognition and reproducibility study by untrained panelists has rated some of the odors of Table 2170:I, Table 2170:II, and Table 2170:III as poor, fair, good, or excellent.[13]

9. References

1. SUFFET, I.H., B.M. BRADY, J.H.M. BARTELS, G.A. BURLINGAME, J. MALLEVIALLE & T. YOHE. 1988. Development of the flavor profile analysis method into a standard method for sensory analysis of water. *Water Sci. Technol.* 20:1.
2. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1968. Basic Principles of Sensory Evaluation. ASTM Spec. Tech. Publ. 433, American Soc. Testing & Materials, Philadelphia, Pa.
3. MEILGAARD, M.C. 1988. Sensory evaluation techniques applied to waterworks samples. *Water Qual. Bull.* 13(2-3):39. WHO Collaborating Centre on Surface and Groundwater Quality, Burlington, Ont., Canada.
4. BARTELS, J.H.M., B.M. BRADY & I.H. SUFFET. 1989. Appendix B *in* Taste and Odor in Drinking Water Supplies—Phases I and II. American Water Works Assoc. Research Foundation, Denver, Colo.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

5. KRASNER, S.W., M.J. MCGUIRE & V.B. FERGUSON. 1985. Tastes and odors: the flavor profile method. *J. Amer. Water Works Assoc.* 77:34.
6. BARTELS, J.H.M., B.M. BRADY & I.H. SUFFET. 1989. Appendix A i*n* Taste and Odor in Drinking Water Supplies—Phases I and II. American Water Works Assoc. Research Foundation, Denver, Colo.
7. MALLEVIALLE, J. & I.H. SUFFET, eds. 1981. Identification and Treatment of Tastes and Odors in Drinking Water. Appendix A. American Water Works Assoc., Denver, Colo.
8. BARTELS, J.H.M., B.M. BRADY & I.H. SUFFET. 1987. Training panelists for the flavor profile analysis method. *J. Amer. Water Works Assoc.* 79:26.
9. SUFFET, I.H., J. HO, D. CHIOU, D. KHIARI & J. MALLEVIALLE. 1995. Taste-and-odor problems observed during drinking water treatment. *In* I.H. Suffet, J. Mallevialle & E. Kawczynski, eds. Advances in Taste and Odor Treatment and Control. American Water Works Assoc. Research Foundation & Lyonnaise des Eaux, Denver, Colo.
10. CAUL, J.F. 1957. The profile method of flavor analysis. *In* Advances in Food Research, Vol. 7. Academic Press, New York, N.Y.
11. BURLINGAME, G.A., D. KHIARI & I.H. SUFFET. 1991. Odor reference standards: The universal language. Proc. AWWA Water Quality Technology Conf., Miami, Fla., p. 7.
12. MENG, A. & I.H. SUFFET. 1992. Assessing the quality of flavor profile analysis data. *J. Amer. Water Works Assoc.* 84:89.
13. KRASNER, S.W. 1995. The use of reference materials in sensory analysis. *Water Sci. Technol.* 31(11):265.

10. Bibliography

AMERICAN WATER WORKS ASSOCIATION. 1993. Flavor Profile Analysis: Screening and Training of Panelists. AWWA Manual. American Water Works Assoc., Denver, Colo.

2310 ACIDITY*#(28)

2310 A. Introduction

Acidity of a water is its quantitative capacity to react with a strong base to a designated pH. The measured value may vary significantly with the end-point pH used in the determination. Acidity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemcical composition of the sample is known. Strong mineral acids, weak acids such as carbonic and acetic, and hydrolyzing salts such as iron or aluminum sulfates may contribute to the measured acidity according to the method of determination.

Acids contribute to corrosiveness and influence chemical reaction rates, chemical speciation, and biological processes. The measurement also reflects a change in the quality of the source

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

water.

2310 B. Titration Method

1. General Discussion

a. Principle: Hydrogen ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard alkali. Acidity thus depends on the end-point pH or indicator used. The construction of a titration curve by recording sample pH after successive small measured additions of titrant permits identification of inflection points and buffering capacity, if any, and allows the acidity to be determined with respect to any pH of interest.

In the titration of a single acidic species, as in the standardization of reagents, the most accurate end point is obtained from the inflection point of a titration curve. The inflection point is the pH at which curvature changes from convex to concave or vice versa.

Because accurate identification of inflection points may be difficult or impossible in buffered or complex mixtures, the titration in such cases is carried to an arbitrary end-point pH based on practical considerations. For routine control titrations or rapid preliminary estimates of acidity, the color change of an indicator may be used for the end point. Samples of industrial wastes, acid mine drainage, or other solutions that contain appreciable amounts of hydrolyzable metal ions such as iron, aluminum, or manganese are treated with hydrogen peroxide to ensure oxidation of any reduced forms of polyvalent cations, and boiled to hasten hydrolysis. Acidity results may be highly variable if this procedure is not followed exactly.

b. End points: Ideally the end point of the acidity titration should correspond to the stoichiometric equivalence point for neutralization of acids present. The pH at the equivalence point will depend on the sample, the choice among multiple inflection points, and the intended use of the data.

Dissolved carbon dioxide (CO_2) usually is the major acidic component of unpolluted surface waters; handle samples from such sources carefully to minimize the loss of dissolved gases. In a sample containing only carbon dioxide-bicarbonates-carbonates, titration to pH 8.3 at 25°C corresponds to stoichiometric neutralization of carbonic acid to bicarbonate. Because the color change of phenolphthalein indicator is close to pH 8.3, this value generally is accepted as a standard end point for titration of total acidity, including CO_2 and most weak acids. Metacresol purple also has an end point at pH 8.3 and gives a sharper color change.

For more complex mixtures or buffered solutions selection of an inflection point may be subjective. Consequently, use fixed end points of pH 3.7 and pH 8.3 for standard acidity determinations via a potentiometric titration in wastewaters and natural waters where the simple carbonate equilibria discussed above cannot be assumed. Bromphenol blue has a sharp color change at its end point of 3.7. The resulting titrations are identified, traditionally, as ‘‘methyl orange acidity’’ (pH 3.7) and ‘‘phenolphthalein’’ or total acidity (pH 8.3) regardless of the actual method of measurement.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

c. Interferences: Dissolved gases contributing to acidity or alkalinity, such as CO_2, hydrogen sulfide, or ammonia, may be lost or gained during sampling, storage, or titration. Minimize such effects by titrating to the end point promptly after opening sample container, avoiding vigorous shaking or mixing, protecting sample from the atmosphere during titration, and letting sample become no warmer than it was at collection.

In the potentiometric titration, oily matter, suspended solids, precipitates, or other waste matter may coat the glass electrode and cause a sluggish response. Difficulty from this source is likely to be revealed in an erratic titration curve. Do *not* remove interferences from sample because they may contribute to its acidity. Briefly pause between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally.

In samples containing oxidizable or hydrolyzable ions such as ferrous or ferric iron, aluminum, and manganese, the reaction rates at room temperature may be slow enough to cause drifting end points.

Do not use indicator titrations with colored or turbid samples that may obscure the color change at the end point. Residual free available chlorine in the sample may bleach the indicator. Eliminate this source of interference by adding 1 drop of 0.1*M* sodium thiosulfate ($Na_2S_2O_3$).

d. Selection of procedure: Determine sample acidity from the volume of standard alkali required to titrate a portion to a pH of 8.3 (phenolphthalein acidity) or pH 3.7 (methyl orange acidity of wastewaters and grossly polluted waters). Titrate at room temperature using a properly calibrated pH meter, electrically operated titrator, or color indicators.

Use the hot peroxide procedure (¶ 4*a*) to pretreat samples known or suspected to contain hydrolyzable metal ions or reduced forms of polyvalent cation, such as iron pickle liquors, acid mine drainage, and other industrial wastes.

Color indicators may be used for routine and control titrations in the absence of interfering color and turbidity and for preliminary titrations to select sample size and strength of titrant (¶ 4*b*).

e. Sample size: The range of acidities found in wastewaters is so large that a single sample size and normality of base used as titrant cannot be specified. Use a sufficiently large volume of titrant (20 mL or more from a 50-mL buret) to obtain relatively good volumetric precision while keeping sample volume sufficiently small to permit sharp end points. For samples having acidities less than about 1000 mg as calcium carbonate ($CaCO_3$)/L, select a volume with less than 50 mg $CaCO_3$ equivalent acidity and titrate with 0.02*N* sodium hydroxide (NaOH). For acidities greater than about 1000 mg as $CaCO_3$/L, use a portion containing acidity equivalent to less than 250 mg $CaCO_3$ and titrate with 0.1*N* NaOH. If necessary, make a preliminary titration to determine optimum sample size and/or normality of titrant.

f. Sampling and storage: Collect samples in polyethylene or borosilicate glass bottles and store at a low temperature. Fill bottles completely and cap tightly. Because waste samples may be subject to microbial action and to loss or gain of CO_2 or other gases when exposed to air,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

analyze samples without delay, preferably within 1 d. If biological activity is suspected analyze within 6 h. Avoid sample agitation and prolonged exposure to air.

2. Apparatus

a. Electrometric titrator: Use any commercial pH meter or electrically operated titrator that uses a glass electrode and can be read to 0.05 pH unit. Standardize and calibrate according to the manufacturer's instructions. Pay special attention to temperature compensation and electrode care. If automatic temperature compensation is not provided, titrate at 25 ± 5°C.

b. Titration vessel: The size and form will depend on the electrodes and the sample size. Keep the free space above the sample as small as practicable, but allow room for titrant and full immersion of the indicating portions of electrodes. For conventional-sized electrodes, use a 200-mL, tall-form Berzelius beaker without a spout. Fit beaker with a stopper having three holes, to accommodate the two electrodes and the buret. With a miniature combination glass-reference electrode use a 125-mL or 250-mL erlenmeyer flask with a two-hole stopper.

c. Magnetic stirrer.

d. Pipets, volumetric.

e. Flasks, volumetric, 1000-, 200-, 100-mL.

f. Burets, borosilicate glass, 50-, 25-, 10-mL.

g. Polyolefin bottle, 1-L.

3. Reagents

a. Carbon dioxide-free water: Prepare all stock and standard solutions and dilution water for the standardization procedure with distilled or deionized water that has been freshly boiled for 15 min and cooled to room temperature. The final pH of the water should be ≥ 6.0 and its conductivity should be <2 μmhos/cm.

b. Potassium hydrogen phthalate solution, approximately 0.05*N:* Crush 15 to 20 g primary standard $KHC_8H_4O_4$ to about 100 mesh and dry at 120°C for 2 h. Cool in a desiccator. Weigh 10.0 ± 0.5 g (to the nearest mg), transfer to a 1-L volumetric flask, and dilute to 1000 mL.

c. Standard sodium hydroxide titrant, 0.1*N:* Prepare solution approximately 0.1*N* as indicated under Preparation of Desk Reagents (see inside front cover). Standardize by titrating 40.00 mL $KHC_8H_4O_4$ solution (¶ 3*b*), using a 25-mL buret. Titrate to the inflection point (¶ 1*a*), which should be close to pH 8.7. Calculate normality of NaOH:

$$\text{Normality} = \frac{A \times B}{204.2 \times C}$$

where:

A = g $KHC_8H_4O_4$ weighed into 1-L flask,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

B = mL $KHC_8H_4O_4$ solution taken for titration, and
C = mL NaOH solution used.

Use the measured normality in further calculations or adjust to 0.1000*N*; 1 mL = 5.00 mg $CaCO_3$.

d. Standard sodium hydroxide titrant, 0.02*N:* Dilute 200 mL 0.1*N* NaOH to 1000 mL and store in a polyolefin bottle protected from atmospheric CO_2 by a soda lime tube or tight cap. Standardize against $KHC_8H_4O_4$ as directed in ¶ 3*c*, using 15.00 mL $KHC_8H_4O_4$ solution and a 50-mL buret. Calculate normality as above (¶ 3*c*); 1 mL = 1.00 mg $CaCO_3$.

e. Hydrogen peroxide, H_2O_2, 30%.

f. Bromphenol blue indicator solution, pH 3.7 indicator: Dissolve 100 mg bromphenol blue, sodium salt, in 100 mL water.

g. Metacresol purple indicator solution, pH 8.3 indicator: Dissolve 100 mg metacresol purple in 100 mL water.

h. Phenolphthalein indicator solution, alcoholic, pH 8.3 indicator.

i. Sodium thiosulfate, 0.1*M:* Dissolve 25 g $Na_2S_2O_3 \cdot 5H_2O$ and dilute to 1000 mL with distilled water.

4. Procedure

If sample is free from hydrolyzable metal ions and reduced forms of polyvalent cations, proceed with analysis according to *b*, *c*, or *d*. If sample is known or suspected to contain such substances, pretreat according to *a*.

a. Hot peroxide treatment: Pipet a suitable sample (see ¶ 1*e*) into titration flasks. Measure pH. If pH is above 4.0 add 5-mL increments of 0.02*N* sulfuric acid (H_2SO_4) (Section 2320B.3*c*) to reduce pH to 4 or less. Remove electrodes. Add 5 drops 30% H_2O_2 and boil for 2 to 5 min. Cool to room temperature and titrate with standard alkali to pH 8.3 according to the procedure of 4*d*.

b. Color change: Select sample size and normality of titrant according to criteria of ¶ 1*e*. Adjust sample to room temperature, if necessary, and with a pipet discharge sample into an erlenmeyer flask, while keeping pipet tip near flask bottom. If free residual chlorine is present add 0.05 mL (1 drop) 0.1*M* $Na_2S_2O_3$ solution, or destroy with ultraviolet radiation. Add 0.2 mL (5 drops) indicator solution and titrate over a white surface to a persistent color change characteristic of the equivalence point. Commercial indicator solutions or solids designated for the appropriate pH range (3.7 or 8.3) may be used. Check color at end point by adding the same concentration of indicator used with sample to a buffer solution at the designated pH.

c. Potentiometric titration curve:

1) Rinse electrodes and titration vessel with distilled water and drain. Select sample size and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

normality of titrant according to the criteria of ¶ 1*e*. Adjust sample to room temperature, if necessary, and with a pipet discharge sample while keeping pipet tip near the titration vessel bottom.

2) Measure sample pH. Add standard alkali in increments of 0.5 mL or less, such that a change of less than 0.2 pH units occurs per increment. After each addition, mix thoroughly but gently with a magnetic stirrer. Avoid splashing. Record pH when a constant reading is obtained. Continue adding titrant and measure pH until pH 9 is reached. Construct the titration curve by plotting observed pH values versus cumulative milliliters titrant added. A smooth curve showing one or more inflections should be obtained. A ragged or erratic curve may indicate that equilibrium was not reached between successive alkali additions. Determine acidity relative to a particular pH from the curve.

d. Potentiometric titration to pH 3.7 or 8.3: Prepare sample and titration assembly as specified in ¶ 4*c*1). Titrate to preselected end-point pH (¶ 1*d*) without recording intermediate pH values. As the end point is approached make smaller additions of alkali and be sure that pH equilibrium is reached before making the next addition.

5. Calculation

$$\text{Acidity, as mg } CaCO_3/L = \frac{[(A \times B) - (C \times D)] \times 50\,000}{\text{mL sample}}$$

where:

A = mL NaOH titrant used,
B = normality of NaOH,
C = mL H_2SO_4 used (¶ 4*a*), and
D = normality of H_2SO_4.

Report pH of the end point used, as follows: ‘‘The acidity to pH _____ = _____ mg $CaCO_3$/L.’’ If a negative value is obtained, report the value as negative. The absolute value of this negative value should be equivalent to the net alkalinity.

6. Precision and Bias

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before analysis.

Forty analysts in 17 laboratories analyzed synthetic water samples containing increments of bicarbonate equivalent to 20 mg $CaCO_3$/L. Titration according to the procedure of ¶ 4*d* gave a standard deviation of 1.8 mg $CaCO_3$/L, with negligible bias. Five laboratories analyzed two

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

samples containing sulfuric, acetic, and formic acids and aluminum chloride by the procedures of ¶s 4*b* and 4*d*. The mean acidity of one sample (to pH 3.7) was 487 mg $CaCO_3$/L, with a standard deviation of 11 mg/L. The bromphenol blue titration of the same sample was 90 mg/L greater, with a standard deviation of 110 mg/L. The other sample had a potentiometric titration of 547 mg/L, with a standard deviation of 54 mg/L, while the corresponding indicator result was 85 mg/L greater, with a standard deviation of 56 mg/L. The major difference between the samples was the substitution of ferric ammonium citrate, in the second sample, for part of the aluminum chloride.

7. Bibliography

WINTER, J.A. & M.R. MIDGETT. 1969. FWPCA Method Study 1. Mineral and Physical Analyses. Federal Water Pollution Control Admin., Washington, D.C.

BROWN, E., M.W. SKOUGSTAD & M.J. FISHMAN. 1970. Methods for collection and analysis of water samples for dissolved minerals and gases. Chapter A1 *in* Book 5, Techniques of Water-Resources Investigations of United States Geological Survey. U.S. Geological Survey, Washington, D.C.

SNOEYINK, V.L. & D. JENKINS. 1980. Water Chemistry. John Wiley & Sons, New York, N.Y.

2320 ALKALINITY*#(29)

2320 A. Introduction

1. Discussion

Alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constitutents. The measured values also may include contributions from borates, phosphates, silicates, or other bases if these are present. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of a water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than, or only slightly greater than, that of the water supply. Properly operating anaerobic digesters typically have supernatant alkalinities in the range of 2000 to 4000 mg calcium carbonate ($CaCO_3$)/L.[1]

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2. Reference

1. POHLAND, F.G. & D.E. BLOODGOOD. 1963. Laboratory studies on mesophilic and thermophilic anaerobic sludge digestion. *J. Water Pollut. Control Fed.* 35:11.

2320 B. Titration Method

1. General Discussion

a. Principle: Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used. For methods of determining inflection points from titration curves and the rationale for titrating to fixed pH end points, see Section 2310B.1*a*.

For samples of low alkalinity (less than 20 mg $CaCO_3$/L) use an extrapolation technique based on the near proportionality of concentration of hydrogen ions to excess of titrant beyond the equivalence point. The amount of standard acid required to reduce pH exactly 0.30 pH unit is measured carefully. Because this change in pH corresponds to an exact doubling of the hydrogen ion concentration, a simple extrapolation can be made to the equivalence point.[1,2]

b. End points: When alkalinity is due entirely to carbonate or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide (CO_2) at that stage. CO_2 concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration. The pH values in Table 2320:I are suggested as the equivalence points for the corresponding alkalinity concentrations as milligrams $CaCO_3$ per liter. ‘‘Phenolphthalein alkalinity’’ is the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the colored indicator, if any, used in the determination. Phenolphthalein or metacresol purple may be used for alkalinity titration to pH 8.3. Bromcresol green or a mixed bromcresol green-methyl red indicator may be used for pH 4.5.

c. Interferences: Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate, or alter sample.

d. Selection of procedure: Determine sample alkalinity from volume of standard acid required to titrate a portion to a designated pH taken from ¶ 1*b*. Titrate at room temperature with a properly calibrated pH meter or electrically operated titrator, or use color indicators. If using color indicators, prepare and titrate an indicator blank.

Report alkalinity less than 20 mg $CaCO_3$/L only if it has been determined by the low-alkalinity method of ¶ 4*d*.

Construct a titration curve for standardization of reagents.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Color indicators may be used for routine and control titrations in the absence of interfering color and turbidity and for preliminary titrations to select sample size and strength of titrant (see below).

e. Sample size: See Section 2310B.1*e* for selection of size sample to be titrated and normality of titrant, substituting 0.02*N* or 0.1*N* sulfuric (H_2SO_4) or hydrochloric (HCl) acid for the standard alkali of that method. For the low-alkalinity method, titrate a 200-mL sample with 0.02*N* H_2SO_4 from a 10-mL buret.

f. Sampling and storage: See Section 2310B.1 *f*.

2. Apparatus

See Section 2310B.2.

3. Reagents

a. Sodium carbonate solution, approximately 0.05*N:* Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 h and cool in a desiccator. Weigh 2.5 ± 0.2 g (to the nearest mg), transfer to a 1-L volumetric flask, fill flask to the mark with distilled water, and dissolve and mix reagent. Do not keep longer than 1 week.

b. Standard sulfuric acid or hydrochloric acid, 0.1*N:* Prepare acid solution of approximate normality as indicated under Preparation of Desk Reagents. Standardize against 40.00 mL 0.05*N* Na_2CO_3 solution, with about 60 mL water, in a beaker by titrating potentiometrically to pH of about 5. Lift out electrodes, rinse into the same beaker, and boil gently for 3 to 5 min under a watch glass cover. Cool to room temperature, rinse cover glass into beaker, and finish titrating to the pH inflection point. Calculate normality:

$$\text{Normality, } N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1-L flask,
B = mL Na_2CO_3 solution taken for titration, and
C = mL acid used.

Use measured normality in calculations or adjust to 0.1000*N*; 1 mL 0.1000*N* solution = 5.00 mg $CaCO_3$.

c. Standard sulfuric acid or hydrochloric acid, 0.02*N:* Dilute 200.00 mL 0.1000*N* standard acid to 1000 mL with distilled or deionized water. Standardize by potentiometric titration of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

15.00 mL 0.05*N* Na_2CO_3 according to the procedure of ¶ 3*b*; 1 mL = 1.00 mg $CaCO_3$.

d. Bromcresol green indicator solution, pH 4.5 indicator: Dissolve 100 mg bromcresol green, sodium salt, in 100 mL distilled water.

e. Mixed bromcresol green-methyl red indicator solution:[3] Use either the aqueous or the alcoholic solution:

1) Dissolve 100 mg bromcresol green sodium salt and 20 mg methyl red sodium salt in 100 mL distilled water.

2) Dissolve 100 mg bromcresol green and 20 mg methyl red in 100 mL 95% ethyl alcohol or isopropyl alcohol.

f. Metacresol purple indicator solution, pH 8.3 indicator: Dissolve 100 mg metacresol purple in 100 mL water.

g. Phenolphthalein solution, alcoholic, pH 8.3 indicator.

h. Sodium thiosulfate, 0.1*N:* See Section 2310B.3*i*.

4. Procedure

a. Color change: See Section 2310B.4*b*.

b. Potentiometric titration curve: Follow the procedure for determining acidity (Section 2310B.4*c*), substituting the appropriate normality of standard acid solution for standard NaOH, and continue titration to pH 4.5 or lower. Do not filter, dilute, concentrate, or alter the sample.

c. Potentiometric titration to preselected pH: Determine the appropriate end-point pH according to ¶ 1*b*. Prepare sample and titration assembly (Section 2310B.4*c*). Titrate to the end-point pH without recording intermediate pH values and without undue delay. As the end point is approached make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant.

d. Potentiometric titration of low alkalinity: For alkalinities less than 20 mg/L titrate 100 to 200 mL according to the procedure of ¶ 4*c*, above, using a 10-mL microburet and 0.02*N* standard acid solution. Stop the titration at a pH in the range 4.3 to 4.7 and record volume and exact pH. Carefully add additional titrant to reduce the pH exactly 0.30 pH unit and again record volume.

5. Calculations

a. Potentiometric titration to end-point pH:

$$\text{Alkalinity, mg } CaCO_3/L = \frac{A \times N \times 50\,000}{\text{mL sample}}$$

where:

A = mL standard acid used and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

N = normality of standard acid

or

$$\text{Alkalinity, mg } CaCO_3/L = \frac{A \times t \times 1000}{\text{mL sample}}$$

where:

t = titer of standard acid, mg $CaCO_3$/mL.

Report pH of end point used as follows: ‘‘The alkalinity to pH _____ = _____ mg $CaCO_3$/L’’ and indicate clearly if this pH corresponds to an inflection point of the titration curve.

b. Potentiometric titration of low alkalinity:

Total alkalinity, mg $CaCO_3$/L

$$= \frac{(2B - C) \times N \times 50\,000}{\text{mL sample}}$$

where:

B = mL titrant to first recorded pH,
C = total mL titrant to reach pH 0.3 unit lower, and
N = normality of acid.

c. Calculation of alkalinity relationships: The results obtained from the phenolphthalein and total alkalinity determinations offer a means for stoichiometric classification of the three principal forms of alkalinity present in many waters. The classification ascribes the entire alkalinity to bicarbonate, carbonate, and hydroxide, and assumes the absence of other (weak) inorganic or organic acids, such as silicic, phosphoric, and boric acids. It further presupposes the incompatibility of hydroxide and bicarbonate alkalinities. Because the calculations are made on a stoichiometric basis, ion concentrations in the strictest sense are not represented in the results, which may differ significantly from actual concentrations especially at pH > 10. According to this scheme:

1) Carbonate (CO_3^{2-}) alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity.

2) Hydroxide (OH^-) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.

3) Bicarbonate (HCO_3^-) alkalinity is present if phenolphthalein alkalinity is less than half the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

total alkalinity. These relationships may be calculated by the following scheme, where *P* is phenolphthalein alkalinity and *T* is total alkalinity (¶ 1*b*):

Select the smaller value of *P* or (*T* –*P*). Then, carbonate alkalinity equals twice the smaller value. When the smaller value is *P*, the balance (*T* –2*P*) is bicarbonate. When the smaller value is (*T*–*P*), the balance (2*P*–*T*) is hydroxide. All results are expressed as $CaCO_3$. The mathematical conversion of the results is shown in Table 2320:II. (A modification of Table 2320:II that is more accurate when $P \simeq {}^1/_2T$ has been proposed.[4])

Alkalinity relationships also may be computed nomographically (see Carbon Dioxide, Section 4500-CO_2). Accurately measure pH, calculate OH^- concentration as milligrams $CaCO_3$ per liter, and calculate concentrations of CO_3^{2-} and HCO_3^- as milligrams $CaCO_3$ per liter from the OH^- concentration, and the phenolphthalein and total alkalinities by the following equations:

$$CO_3^{2-} = 2P - 2[OH^-]$$

$$HCO_3^- = T - 2P + [OH^-]$$

Similarly, if difficulty is experienced with the phenolphthalein end point, or if a check on the phenolphthalein titration is desired, calculate phenolphthalein alkalinity as $CaCO_3$ from the results of the nomographic determinations of carbonate and hydroxide ion concentrations:

$$P = 1/2\ [CO_3^{2-}] + [OH^-]$$

6. Precision and Bias

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before the analysis.

In the range of 10 to 500 mg/L, when the alkalinity is due entirely to carbonates or bicarbonates, a standard deviation of 1 mg $CaCO_3$/L can be achieved. Forty analysts in 17 laboratories analyzed synthetic samples containing increments of bicarbonate equivalent to 120 mg $CaCO_3$/L. The titration procedure of ¶ 4*b* was used, with an end point pH of 4.5. The standard deviation was 5 mg/L and the average bias (lower than the true value) was 9 mg/L.[5]

Sodium carbonate solutions equivalent to 80 and 65 mg $CaCO_3$/L were analyzed by 12 laboratories according to the procedure of ¶ 4*c*.[6] The standard deviations were 8 and 5 mg/L, respectively, with negligible bias.[6] Four laboratories analyzed six samples having total alkalinities of about 1000 mg $CaCO_3$/L and containing various ratios of carbonate/bicarbonate by the procedures of both ¶ 4*a* and ¶ 4*c*. The pooled standard deviation was 40 mg/L, with negligible difference between the procedures.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

7. References

1. LARSON, T.E. & L.M. HENLEY. 1955. Determination of low alkalinity or acidity in water. *Anal. Chem.* 27:851.
2. THOMAS, J.F.J. & J.J. LYNCH. 1960. Determination of carbonate alkalinity in natural waters. *J. Amer. Water Works Assoc.* 52:259.
3. COOPER, S.S. 1941. The mixed indicator bromocresol green-methyl red for carbonates in water. *Ind. Eng. Chem.*, Anal. Ed. 13:466.
4. JENKINS, S.R. & R.C. MOORE. 1977. A proposed modification to the classical method of calculating alkalinity in natural waters. *J. Amer. Water Works Assoc*. 69:56.
5. WINTER, J.A. & M.R. MIDGETT. 1969. FWPCA Method Study 1. Mineral and Physical Analyses. Federal Water Pollution Control Admin., Washington, D.C.
6. SMITH, R. 1980. Research Rep. No. 379, Council for Scientific and Industrial Research, South Africa.

8. Bibliography

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1982. Standard Methods for Acidity or Alkalinity of Water. Publ. D1067-70 (reapproved 1977), American Soc. Testing & Materials, Philadelphia, Pa.

SKOUGSTAD M.W., M.J. FISHMAN, L.C. FRIEDMAN, D.E. ERDMAN, & S.S. DUNCAN. 1979. Methods for determination of inorganic substances in water and fluvial sediments. *In* Techniques of Water-Resources Investigation of the United States Geological Survey. U.S. Geological Survey, Book 5, Chapter A1, Washington, D.C.

2330 CALCIUM CARBONATE SATURATION*#(30)

2330 A. Introduction

1. General Discussion

Calcium carbonate ($CaCO_3$) saturation indices commonly are used to evaluate the scale-forming and scale-dissolving tendencies of water. Assessing these tendencies is useful in corrosion control programs and in preventing $CaCO_3$ scaling in piping and equipment such as industrial heat exchangers or domestic water heaters.

Waters oversaturated with respect to $CaCO_3$ tend to precipitate $CaCO_3$. Waters undersaturated with respect to $CaCO_3$ tend to dissolve $CaCO_3$. Saturated waters, i.e., waters in equilibrium with

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$CaCO_3$, have neither $CaCO_3$-precipitating nor $CaCO_3$-dissolving tendencies. Saturation represents the dividing line between ‘‘precipitation likely’’ and ‘‘precipitation not likely.’’

Several water quality characteristics must be measured to calculate the $CaCO_3$ saturation indices described here. Minimum requirements are total alkalinity (2320), total calcium (3500-Ca), pH (4500-H^+), and temperature (2550). The ionic strength also must be calculated or estimated from conductivity (2510) or total dissolved solids (2540C) measurements. Measure pH at the system’s water temperature using a temperature-compensated pH meter. If pH is measured at a different temperature, for example in the laboratory, correct the measured pH.[1-3] In measuring pH and alkalinity, minimize CO_2 exchange between sample and atmosphere. Ideally, seal the sample from the atmosphere during measurements[4]; at a minimum, avoid vigorous stirring of unsealed samples.

There are two general categories of $CaCO_3$ saturation indices: indices that determine whether a water has a *tendency* to precipitate $CaCO_3$ (i.e., is oversaturated) or to dissolve $CaCO_3$ (i.e., is undersaturated) and indices that estimate the *quantity* of $CaCO_3$ that can be precipitated from an oversaturated water and the amount that can be dissolved by an undersaturated water. Indices in the second category generally yield more information but are more difficult to determine.

2. Limitations

It is widely assumed that $CaCO_3$ will precipitate from oversaturated waters and that it cannot be deposited from undersaturated waters. Exceptions may occur. For example, $CaCO_3$ deposition from oversaturated waters is inhibited by the presence of phosphates (particularly polyphosphates), certain naturally occurring organics, and magnesium.[5-7] These materials can act as sequestering agents or as crystal poisons. Conversely, $CaCO_3$ deposits have been found in pipes conveying undersaturated water. This apparent contradiction is caused by high pH (relative to the bulk water pH) in the immediate vicinity of certain areas (cathodes) of corroding metal surfaces. A locally oversaturated condition may occur even if the bulk water is undersaturated. A small, but significant, amount of $CaCO_3$ can be deposited.

The calculations referred to here, even the most sophisticated computerized calculations, do not adequately describe these exceptions. For this reason, do not consider saturation indices as absolutes. Rather, view them as guides to the behavior of $CaCO_3$ in aqueous systems and supplement them, where possible, with experimentally derived information.

Similarly, the effects predicted by the indices do not always conform to expectations. The relationship between the indices and corrosion rates is a case in point. Conceptually, piping is protected when $CaCO_3$ is precipitated on its surfaces. $CaCO_3$ is believed to inhibit corrosion by clogging reactive areas and by providing a matrix to retain corrosion products, thus further sealing the surfaces. Waters with positive indices traditionally have been assumed to be protective while waters with negative indices have been assumed to be not protective, or

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

corrosive. The expected relationship is observed sometimes,[8,9] but not always.[10,11] Unexpected results may be due in part to limited capability to predict $CaCO_3$ behavior. Also, water characteristics not directly involved in the calculation of the indices (e.g., dissolved oxygen, buffering intensity, chloride, sulfate, and water velocity) may influence corrosion rates appreciably.[9,12-16] Thus, do not estimate corrosion rates on the basis of $CaCO_3$ indices alone.

3. References

1. MERRILL, D.T. & R.L. SANKS. 1978, 1979. Corrosion control by deposition of $CaCO_3$ films: A practical approach for plant operators. *J. Amer. Water Works Assoc.* 70:592; 70:634 & 71:12.
2. LOEWENTHAL, R.E. & G. V. R. MARAIS. 1976. Carbonate Chemistry of Aquatic Systems: Theory and Applications. Ann Arbor Science Publishers, Ann Arbor, Mich.
3. MERRILL, D.T. 1976. Chemical conditioning for water softening and corrosion control. *In* R.L. Sanks, ed. Water Treatment Plant Design. Ann Arbor Science Publishers, Ann Arbor, Mich.
4. SCHOCK, M.R., W. MUELLER & R.W. BUELOW. 1980. Laboratory techniques for measurement of pH for corrosion control studies and water not in equilibrium with the atmosphere. *J. Amer. Water Works Assoc.* 72:304.
5. PYTKOWICZ, R.M. 1965. Rates of inorganic carbon nucleation. *J. Geol.* 73:196.
6. FERGUSON, J.F. & P.L. MCCARTY. 1969. Precipitation of Phosphate from Fresh Waters and Waste Waters. Tech. Rep. No. 120, Stanford Univ., Stanford, Calif.
7. MERRILL, D.T. & R.M. JORDEN. 1975. Lime-induced reactions in municipal wastewaters. *J. Water Pollut. Control Fed.* 47:2783.
8. DE MARTINI, F. 1938. Corrosion and the Langelier calcium carbonate saturation index. *J. Amer. Water Works Assoc.* 30:85.
9. LARSON, T.E. 1975. Corrosion by Domestic Waters. Bull. 59, Illinois State Water Survey.
10. JAMES M. MONTGOMERY, CONSULTING ENGINEERS, INC. 1985. Water Treatment Principles and Design. John Wiley & Sons, New York, N.Y.
11. STUMM, W. 1960. Investigations of the corrosive behavior of waters. *J. San. Eng. Div., Proc. Amer. Soc. Civil Eng.* 86:27.
12. PISIGAN, R.A., JR. & J.E. SINGLEY. 1985. Evaluation of water corrosivity using the Langelier index and relative corrosion rate models. *Materials Perform.* 24:26.
13. LANE, R.W. 1982. Control of corrosion in distribution and building water systems. *In* Proceedings AWWA Water Quality Technology Conf., Nashville, Tenn., Dec. 5–8, 1982.
14. SONTHEIMER, H., W. KOLLE & V.L. SNOEYINK. 1982. The siderite model of the formation of corrosion-resistant scales. *J. Amer. Water Works Assoc.* 73:572.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

15. SCHOCK, M.R. & C.H. NEFF. 1982. Chemical aspects of internal corrosion; theory, prediction, and monitoring. *In* Proceedings AWWA Water Quality Technology Conf., Nashville, Tenn., Dec. 5–8, 1982.
16. AMERICAN WATER WORKS ASSOCIATION. 1986. Corrosion Control for Plant Operators. ISBW-O-89867-350-X. Denver, Colo.

2330 B. Indices Indicating Tendency of a Water to Precipitate $CaCO_3$ or Dissolve $CaCO_3$

1. General Discussion

Indices that indicate $CaCO_3$ precipitation or dissolution tendencies define whether a water is oversaturated, saturated, or undersaturated with respect to $CaCO_3$. The most widely used indices are the Saturation Index (SI): the Relative Saturation (RS), also known as the Driving Force Index (DFI); and the Ryznar Index (RI). The SI is by far the most commonly used and will be described here. The RS and SI are related (see Equation 6, Section 2330D). The RI[1] has been used for many years, sometimes with good results. Because it is semi-empirical it may be less reliable than the SI.

2. Saturation Index by Calculation

SI is determined from Equation 1.

$$SI = pH - pH_s \qquad (1)$$

where:

pH = measured pH and
pH_s = pH of the water if it were in equilibrium with $CaCO_3$ at the existing calcium ion [Ca^{2+}] and bicarbonate ion [HCO_3^-] concentrations.

A positive SI connotes a water oversaturated with respect to $CaCO_3$. A negative SI signifies an undersaturated water. An SI of zero represents a water in equilibrium with $CaCO_3$.

a. Analytical solution for pH_s: Determine pH_s as follows[2]:

$$pH_s = pK_2 - pK_s + p[Ca^{2+}] + p[HCO_3^-] + 5\,pf_m \qquad (2)$$

where:

K_2 = second dissociation constant for carbonic acid, at the water temperature,
K_s = solubility product constant for $CaCO_3$ at the water temperature,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$[Ca^{2+}]$ = calcium ion concentration, g-moles/L,
$[HCO_3^-]$ = bicarbonate ion concentration, g-moles/L, and
f_m = activity coefficient for monovalent species at the specified temperature.

In Equation 2, *p* preceding a variable designates $-\log_{10}$ of that variable.

Calculate values of pK_2, pK_s, and pf_m required to solve Equation 2 from the equations in Table 2330:I. To save computation time, values for pK_2 and pK_s have been precalculated for selected temperatures (see Table 2330:II).

Table 2330:II gives several values for pK_s. Different isomorphs of $CaCO_3$ can form in aqueous systems, including calcite, aragonite, and vaterite. Each has somewhat different solubility properties. These differences can be accommodated when computing pH_s simply by using the pK_s for the compound most likely to form. The form of $CaCO_3$ most commonly found in fresh water is calcite. Use the pK_s for calcite unless it is clear that a different form of $CaCO_3$ controls $CaCO_3$ solubility.

Estimate calcium ion concentration from total calcium measurements with Equation 3.

$$[Ca^{2+}] = Ca_t - Ca_{ip} \qquad (3)$$

where:

Ca_t = total calcium, g-moles/L, and
Ca_{ip} = calcium associated with ion pairs such as $CaHCO_3^+$, $CaSO_4^0$, and $CaOH^+$.

Calcium associated with ion pairs is not available to form $CaCO_3$.

Estimate $[HCO_3^-]$, the bicarbonate ion concentration, from Equation 4.

$$[HCO_3^-] = \frac{Alk_t - Alk_o + 10^{(pf_m - pH)} - 10^{(pH + pf_m - pK_w)}}{1 + 0.5 \times 10^{(pH - pK_2)}} \qquad (4)$$

where:

Alk_t = total alkalinity, as determined by acid titration to the carbonic acid end point, g-equivalents/L,
K_w = dissociation constant for water, at the water temperature, and
Alk_o = alkalinity contributed by NH_3^0, $H_3SiO_4^-$, HPO_4^{2-}, $B(OH)_4^-$, CH_3COO^- (acetate), HS^-, and ion pairs such as $CaHCO_3^+$ and $MgOH^+$. These contributions usually are small compared to the contributions of components normally considered (HCO_3^-, CO_3^{2-},OH^-,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

and H^+).

Calculations can be simplified. For example, in Equation 4, terms containing exponents (e.g., $10^{(pH + pf_{m-pkw})}$) usually can be neglected for waters that are approximately neutral (pH 6.0 to 8.5) with alkalinity greater than about 50 mg/L as $CaCO_3$. The terms Ca_{ip} in Equation 3 and Alk_o in Equation 4 are difficult to calculate without computers. Therefore they usually are neglected for hand calculations. The simplified version of Equation 2 under such conditions is:

$$pH_s = pK_2 - pK_s + p[Ca_t] + p[Alk_t] + 5\,pf_m$$

1) Sample calculation—The calculation is best illustrated by working through an example. Assume that calcite controls $CaCO_3$ solubility and determine the SI for a water of the following composition:

	Concentration				
Constituent	**mg**	**÷**	**mg mole**	**=**	***g-moles/L***
Calcium	152		40 000		3.80×10^{-3}
Magnesium	39		24 312		1.60×10^{-3}
Sodium	50		22 989		2.18×10^{-3}
Potassium	5		39 102		1.28×10^{-4}
Chloride	53		35 453		1.49×10^{-3}
Alkalinity (as $CaCO_3$)	130		50 000		2.60×10^{-3}*
Sulfate	430		96 060		4.48×10^{-3}
Silica (as SiO_2)	15		60 084		2.50×10^{-4}

*g-equivalents.
Water temperature = 20°C (293.2°K); pH = 9.00.

Before evaluating pf_m in Equation 2, determine the ionic strength (I) and another constant (A). Estimate ionic strength from the first equation of Table 2330:I, assuming all the alkalinity is due to bicarbonate ion. Use the alkalinity concentration (2.60×10^{-3}) and the bicarbonate charge (–1) to calculate the contribution of alkalinity to ionic strength. Assume silica is mostly H_4SiO_4. Because H_4SiO_4 has zero charge, silica does not contribute to ionic strength.

$$I = 0.5\,[4(3.80 \times 10^{-3}) + 4(1.60 \times 10^{-3}) + 2.18 \times 10^{-3} +$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$1.28 \times 10^{-4} + 1.49 \times 10^{-3} + 2.60 \times 10^{-3} + 4(4.48 \times 10^{-3})]$$
$$= 2.29 \times 10^{-2} \text{ g-moles/L}$$

In the absence of a complete water analysis, estimate ionic strength from conductivity or total dissolved solids measurements (see alternative equations, Table 2330:I).

Estimate A from the equation in Table 2330:I, after first determining the dielectric constant E from the formula in the same table. Alternatively, use precalculated values of A in Table 2330:II. In Table 2330:II, $A = 0.506$ at 20°C.

Next estimate pf_m from the equation in Table 2330:I

$$pf_m = 0.506 \times \left[\frac{\sqrt{2.29 \times 10^{-2}}}{1 + \sqrt{2.29 \times 10^{-2}}} - 0.3\,(2.29 \times 10^{-2}) \right] = 0.063$$

Determine $[HCO_3^-]$ from Equation 4. Neglect Alk_o, but because the pH exceeds 8.5, calculate the other terms. From Table 2330:II, $pK_2 = 10.38$ and $pK_w = 14.16$.

$$[HCO_3^-] = \frac{2.60 \times 10^{-3} + 10^{(0.063 - 9.0)} - 10^{(9.0 + 0.063 - 14.16)}}{1 + 0.5 \times 10^{(9.0 - 10.38)}} = 2.54 \times 10^{-3} \text{ g-moles/L}$$

Therefore $p[HCO_3^-] = 2.60$.

Determine $[Ca^{2+}]$ from Equation 3. Neglect $Ca_{ip.}$

$$[Ca^{2+}] = Ca_t = 3.80 \times 10^{-3} \text{ g-moles/L}$$

Therefore $p[Ca^{2+}] = 2.42$.

From Table 2330:II, pK_s for calcite is 8.45.

Determine pH_s from Equation 2:

$$pH_s = 10.38 - 8.45 + 2.42 + 2.60 + 5\,(0.063) = 7.27$$

And finally, determine SI from Equation 1:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$SI = 9.00 - 7.27 = 1.73$$

The positive *SI* indicates the water is oversaturated with respect to calcite.

2) Effect of neglecting Ca_{ip} and Alk_o—If Ca_{ip} is neglected, pH_s is underestimated and *SI* is overestimated by an amount equal to $p(1 - Y_{Ca_{ip}})$, where $Y_{Ca_{ip}}$ is the fraction of total calcium in ion pairs. For example, if $Y_{Ca_{ip}} = 0.30$ then the estimate for *SI* is 0.15 units too high. Similarly, if Alk_o is neglected, *SI* is overestimated by an amount equal to $p(1-Y_{Alk_o})$, where Y_{Alk_o} is the fraction of total alkalinity contributed by species other than HCO_3^-, CO_3^{2-}, OH^-, and H^+. The effects of neglecting Ca_{ip} and Alk_o are additive.

Ca_{ip} and Alk_o may be neglected if the factors $Y_{Ca_{ip}}$ and Y_{Alk_o} are small and do not interfere with interpretation of the *SI*. The factors are small for waters of low and neutral pH, but they increase as pH values approach and exceed 9. At high pH values, however, the *SI* is typically much larger than its overestimate, so neglecting Ca_{ip} and Alk_o causes no problem. To return to the example above, when calculations were done with a computerized water chemistry code (SEQUIL) (see Table 2330:III) that considers Ca_{ip} and Alk_o, the *SI* was 1.48, i.e., 0.25 units lower than the result obtained by hand calculations. In this instance, neglecting Ca_{ip} and Alk_o did not interfere with interpreting the result. Both calculations showed the water to be strongly oversaturated.

The potential for misinterpretation is most acute in nearly-saturated waters of high sulfate concentration. Recirculating cooling water is an example. Calcium is sequestered by the robust $CaSO_4^0$ ion pair and the *SI* can be overestimated by as much as 0.3 to 0.5 units, even at neutral pH. Under these conditions, the *SI* may be thought to be zero (neither scale-forming or corrosive) when in fact it is negative.

Resolve this problem by determining pH_s using computerized water chemistry codes that consider ion pairs and the other forms of alkalinity. Section 2330D provides information about water chemistry codes. The most accurate calculations are obtained when a complete mineral analysis is provided.

An alternative but somewhat less rigorous procedure involves direct measurement of (Ca^{2+}), the calcium ion activity, with a calcium specific-ion electrode.[9] Use Equation 5 to determine $p[Ca^{2+}]$; then use $p[Ca^{2+}]$ in Equation 2.

$$p[Ca^{2+}] = p(Ca^{2+}) - 4pf_m \qquad (5)$$

This approach eliminates the need to determine Ca_{ip}. However, no equivalent procedure is available to bypass the determination of Alk_o.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

b. Graphical solutions for pH_s: Caldwell-Lawrence diagrams can be used to determine pH_s.[10-12] The diagrams are particularly useful for estimating chemical dosages needed to achieve desired water conditions. Consult the references for descriptions of how to use the diagrams; see Section 2330D for additional information about the diagrams.

3. Saturation Index by Experimental Determination

a. Saturometry: Saturometers were developed to measure the relative saturation of seawater with respect to $CaCO_3$. A water of known calcium and pH is equilibrated with $CaCO_3$ in a sealed flask containing a pH electrode. The water temperature is controlled with a constant-temperature bath. During equilibration the pH decreases if $CaCO_3$ precipitates and increases if $CaCO_3$ dissolves. When the pH stops changing, equilibrium is said to have been achieved. The initial pH and calcium values and the final pH value are used to calculate the relative saturation (RS).[13] Equation 6, Section 2330D, may then be used to determine SI.

A major advantage of this method is that the approach to equilibrium can be tracked by measuring pH, thus minimizing uncertainty about the achievement of equilibrium. The method is most sensitive in the range of minimum buffering intensity (pH 7.5 to 8.5). The calculations do not consider ion pairs or noncarbonate alkalinity, except borate. The technique has been used for *in situ* oceanographic measurements[14] as well as in the laboratory.

The saturometry calculations discussed above use K_s of the $CaCO_3$ phase assumed to control solubility. Uncertainties occur if the identity of the controlling solid is unknown. Resolve these uncertainties by measuring K_s of the controlling solid. It is equal to the $CaCO_3$ activity product, $[Ca^{2+}] \times [CO_3^{2-}]$, at equilibrium. Calculate the latter from the equilibrium pH and initial calcium, alkalinity, and pH measurements.[15]

b. Alkalinity difference technique:[16] *SI* also can be determined by equilibrating water of known pH, calcium, and alkalinity with $CaCO_3$ in a sealed, constant-temperature system. The $CaCO_3$ activity product before equilibration is determined from initial calcium, pH, and alkalinity (or total carbonate) values. The $CaCO_3$ solubility product constant (K_s) equals the $CaCO_3$ activity product after equilibration, which is determined by using the alkalinity change that occurred during equilibration. *RS* is found by dividing the initial activity product by K_s. Calculate *SI* by using Equation 6 (see Section 2330D.1). The advantage of this method is that it makes no assumptions about the identity of the $CaCO_3$ phase. However it is more difficult to determine when equilibrium is achieved with this method than with the saturometry method.

Whatever the method used, use the temperatures that are the same as the temperature of the water source. Alternatively, correct test results to the temperature of the water source.[16]

4. References

1. RYZNAR, J.W. 1944. A new index for determining the amount of calcium carbonate

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

formed by water. *J. Amer. Water Works Assoc.* 36:47.

2. SNOEYINK, V.L. & D. JENKINS. 1980. Water Chemistry. John Wiley & Sons, New York, N.Y.
3. STUMM, W. & J.J. MORGAN. 1981. Aquatic Chemistry, 2nd ed. John Wiley & Sons, New York, N.Y.
4. RUSSELL, L.L. 1976. Chemical Aspects of Groundwater Recharge with Wastewaters. Ph.D. thesis, Univ. California, Berkeley.
5. LANGELIER, W.F. 1936. The analytical control of anticorrosion water treatment. *J. Amer. Water Works Assoc.* 28:1500.
6. ROSSUM, J.R. & D.T. MERRILL. 1983. An evaluation of the calcium carbonate saturation indexes. *J. Amer. Water Works Assoc.* 75:95.
7. PLUMMER, L.N. & E. BUSENBERG. 1982. The solubilities of calcite, aragonite, and vaterite in CO_2-H_2O solutions between 0 and 90 degrees C, and an evaluation of the aqueous model for the system $CaCO_3$-CO_2-H_2O. *Geochim. Cosmochim. Acta* 46:1011.
8. ELECTRIC POWER RESEARCH INSTITUTE. 1982. Design and Operating Guidelines Manual for Cooling Water Treatment: Treatment of Recirculating Cooling Water. Section 4. Process Model Documentation and User's Manual. EPRI CS-2276, Electric Power Research Inst., Palo Alto, Calif.
9. GARRELS, R.M. & C.L. CHRIST. 1965. Solutions, Minerals, and Equilibria. Harper & Row, New York, N.Y.
10. MERRILL, D.T. & R.L. SANKS. 1978, 1979. Corrosion control by deposition of $CaCO_3$ films: A practical approach for plant operators. *J. Amer. Water Works Assoc.* 70:592; 70:634 & 71:12.
11. LOEWENTHAL, R.E. & G.V.R. MARAIS. 1976. Carbonate Chemistry of Aquatic Systems: Theory and Applications. Ann Arbor Science Publishers, Ann Arbor, Mich.
12. MERRILL, D.T. 1976. Chemical conditioning for water softening and corrosion control. *In* R.L. Sanks, ed., Water Treatment Plant Design. Ann Arbor Science Publishers, Ann Arbor, Mich.
13. BEN-YAAKOV, S. & I.R. KAPLAN. 1969. Determination of carbonate saturation of seawater with a carbonate saturometer. *Limnol. Oceanogr.* 14:874.
14. BEN-YAAKOV, S. & I.R. KAPLAN. 1971. Deep-sea in situ calcium carbonate saturometry. *J. Geophys. Res.* 76:72.
15. PLATH, D.C., K.S. JOHNSON & R.M. PYTKOWICZ. 1980. The solubility of calcite—probably containing magnesium—in seawater. *Mar. Chem.* 10:9.
16. BALZAR, W. 1980. Calcium carbonate saturometry by alkalinity difference. *Oceanol. Acta.* 3:237.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2330 C. Indices Predicting the Quantity of $CaCO_3$ That Can Be Precipitated or Dissolved

The Calcium Carbonate Precipitation Potential (CCPP) predicts both tendency to precipitate or to dissolve $CaCO_3$ and quantity that may be precipitated or dissolved. The CCPP also is known by other names, e.g., Calcium Carbonate Precipitation Capacity (CCPC).

The CCPP is defined as the quantity of $CaCO_3$ that theoretically can be precipitated from oversaturated waters or dissolved by undersaturated waters during equilibration.[1] The amount that actually precipitates or dissolves may be less, because equilibrium may not be achieved. The CCPP is negative for undersaturated waters, zero for saturated waters, and positive for oversaturated waters.

1. Calculating CCPP

The CCPP does not lend itself to hand calculations. Preferably calculate CCPP with computerized water chemistry models and Caldwell-Lawrence diagrams (see Section 2330D).

The most reliable calculations consider ion pairs and the contribution to alkalinity of other species besides HCO_3^-, CO_3^{2-}, OH^-, and H^+. Models that do not consider these factors overestimate the amount of $CaCO_3$ that can be precipitated and underestimate the amount of $CaCO_3$ that can be dissolved.

2. Experimental Determination of CCPP

Estimate CCPP by one of several experimental techniques.

a. Saturometry: See Section 2330B. The CCPP is determined as part of the RS calculation.

b. Alkalinity difference technique: See Section 2330B. The CCPP equals the difference between alkalinity (or calcium) values of the initial and equilibrated water, when they are expressed as $CaCO_3$.

c. Marble test: The marble test[1-5] is similar to the alkalinity difference technique. The CCPP equals the change in alkalinity (or calcium) values during equilibration, when they are expressed as $CaCO_3$.

d. Enslow test: The Enslow test[5] is a continuous version of the alkalinity difference or marble tests. Water is fed continuously to a leveling bulb or separatory funnel partly filled with $CaCO_3$. The effluent from this device is filtered through crushed marble so that the filtrate is assumed to be in equilibrium with $CaCO_3$. The CCPP equals the change in alkalinity (or calcium) values that occurs during passage through the apparatus.

e. Calcium carbonate deposition test:[6] The calcium carbonate deposition test (CCDT) is an electrochemical method that measures the electric current produced when dissolved oxygen is

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

reduced on a rotating electrode. When an oversaturated water is placed in the apparatus, $CaCO_3$ deposits on the electrode. The deposits interfere with oxygen transfer and the current diminishes. The rate of $CaCO_3$ deposition is directly proportional to the rate at which the current declines. The CCDT and the CCPP are related, but they are not the same. The CCDT is a rate, and the CCPP is a quantity.

For realistic assessments of the CCPP (or CCDT) keep test temperature the same as the temperature of the water source. Alternatively, correct test results to the temperature of the water source.

3. References

1. MERRILL, D.T. & R.L. SANKS. 1978, 1979. Corrosion control by deposition of $CaCO_3$ films: A practical approach for plant operators. *J. Amer. Water Works Assoc.* 70:592; 70:634 & 71:12.
2. MERRILL, D.T. 1976. Chemical conditioning for water softening and corrosion control. *In* R.L. Sanks, ed. Water Treatment Plant Design. Ann Arbor Science Publishers, Ann Arbor, Mich.
3. DE MARTINI, F. 1938. Corrosion and the Langelier calcium carbonate saturation index. *J. Amer. Water Works Assoc.* 30:85.
4. HOOVER, C.P. 1938. Practical application of the Langelier method. *J. Amer. Water Works Assoc.* 30:1802.
5. DYE, J.F. & J.L. TUEPKER. 1971. Chemistry of the Lime-Soda Process. *In* American Water Works Association. Water Quality and Treatment. McGraw-Hill Book Co., New York, N.Y.
6. MCCLELLAND, N.I. & K.H. MANCY. 1979. CCDT bests Ryzner index as pipe $CaCO_3$ film predictor. *Water Sewage Works* 126:77.

2330 D. Diagrams and Computer Codes for $CaCO_3$ Indices

1. Description

Table 2330:III lists diagrams and computer codes that can be used to determine the SI and CCPP. It also provides a brief description of their characteristics.

Many computer codes do not calculate *SI* directly, but instead calculate the relative saturation (*RS*). When *RS* data are presented, calculate the *SI* from:[1]

$$SI = \log_{10} RS \qquad (6)$$

where:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

RS = ratio of $CaCO_3$ activity product to $CaCO_3$ solubility product constant.

The diagrams and a few of the codes define pH_s as the pH the water would exhibit if it were in equilibrium with $CaCO_3$ at the existing calcium and total alkalinity concentrations.[2] This definition of pH_s differs from the definition following Equation 1 because alkalinity is used instead of bicarbonate. Within the pH range 6 to 9, alkalinity-based pH_s and bicarbonate-based pH_s are virtually equal, because total alkalinity is due almost entirely to bicarbonate ion. Above pH 9 they differ and Equation 6 no longer applies if *SI* is calculated with alkalinity-based pH_s. However, if *SI* is determined from bicarbonate-based pH, Equation 6 continues to apply.

Furthermore, calculating *SI* with alkalinity-based pH_s reverses the sign of the *SI* above pH values of approximately pK_2, i.e., a positive, not the usual negative, *SI* connotes an undersaturated water.[3] With bicarbonate-based pH_s or RS, sign reversal does not occur, thereby eliminating the confusing sign change. For these reasons, bicarbonate-based pH_s or RS is preferred. Table 2330:III lists the definition of pH_s used for each code.

Some models calculate only the amount of $CaCO_3$ that can be precipitated but not the amount of $CaCO_3$ that can be dissolved. Others calculate both.

The diagrams and codes can be used to determine many more parameters than the $CaCO_3$ saturation indices. A fee may be charged for computer software or graphs. The information in Table 2330:III describes parameters each code uses to calculate *SI*. Contact the sources listed below the table for current information.

2. References

1. SNOEYINK, V.L. & D. JENKINS. 1980. Water Chemistry. John Wiley & Sons, New York, N.Y.
2. LANGELIER, W.F. 1936. The analytical control of anticorrosion water treatment. *J. Amer. Water Works Assoc.* 28:1500.
3. LOEWENTHAL, R.E. & G.V.R. MARAIS. 1976. Carbonate Chemistry of Aquatic Systems: Theory and Applications. Ann Arbor Science Publishers, Ann Arbor, Mich.
4. MERRILL, D.T. & R.L. SANKS. 1978. Corrosion Control by Deposition of $CaCO_3$ Films: A Handbook of Practical Application and Instruction. American Water Works Assoc., Denver, Colo.
5. MERRILL, D.T. 1976. Chemical conditioning for water softening and corrosion control. *In* R.L. Sanks, ed., Water Treatment Plant Design. Ann Arbor Science Publishers, Ann Arbor, Mich.
6. ELECTRIC POWER RESEARCH INSTITUTE. 1982. Design and Operating Guidelines Manual for Cooling Water Treatment: Treatment of Recirculating Cooling Water.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Section 4. Process Model Documentation and User's Manual. EPRI CS-2276, Electric Power Research Inst., Palo Alto, Calif.

7. BROWN, D.S. & J.D. ALLISON. 1987. MINTEQA1 Equilibrium Metal Speciation Model: A User's Manual. EPA-600/3-87-012.
8. PARKHURST, D.L., D.C. THORSTENSON & L.N. PLUMMER. 1980. PHREEQE—A Computer Program for Geochemical Calculations. USGS WRI 80-96 NTIS PB 81-167801.
9. CROWE, A.S. & F.J. LONGSTAFF. 1987. Extension of Geochemical Modeling Techniques to Brines: Coupling of the Pitzer Equations to PHREEQE. *In* Proceedings of Solving Groundwater Problems With Models, National Water Well Assoc., Denver, Colo. Feb. 10–12, 1987.
10. FLEMING, G.W. & L.N. PLUMMER. 1983. PHRQINPT—An Interactive Computer Program for Constructing Input Data Sets to the Geochemical Simulation Program PHREEQE. USGS WRI 83-4236.
11. ELECTRIC POWER RESEARCH INSTITUTE. SEQUIL—An Inorganic Aqueous Chemical Equilibrium Code for Personal Computers; Volume 1, User's Manual/Workbook, Version 1.0, GS-6234-CCML. Electric Power Research Inst., Palo Alto, Calif.
12. KHARAKA, Y.K., W.D. GUNTER, P. K. AGGARWAL, E.H. PERKINS & J.D. DEBRAAL. 1988. Solmineq.88—A Computer Program for Geochemical Modeling of Water–Rock Interactions. USGS WRIR 88-4227, Menlo Park, Calif.
13. BALL, J.W., D.K. NORDSTROM & D.W. ZACHMANN. 1987. WATEQ4F—A Personal Computer Fortran Translation of the Geochemical Model WATEQ2 With Revised Data Base. USGS OFR 87-50.

2340 HARDNESS*#(31)

2340 A. Introduction

1. Definition

Originally, water hardness was understood to be a measure of the capacity of water to precipitate soap. Soap is precipitated chiefly by the calcium and magnesium ions present. Other polyvalent cations also may precipitate soap, but they often are in complex forms, frequently with organic constituents, and their role in water hardness may be minimal and difficult to define. In conformity with current practice, total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter.

When hardness numerically is greater than the sum of carbonate and bicarbonate alkalinity, that amount of hardness equivalent to the total alkalinity is called ‘‘carbonate hardness’’; the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

amount of hardness in excess of this is called ‘‘noncarbonate hardness.’’ When the hardness numerically is equal to or less than the sum of carbonate and bicarbonate alkalinity, all hardness is carbonate hardness and noncarbonate hardness is absent. The hardness may range from zero to hundreds of milligrams per liter, depending on the source and treatment to which the water has been subjected.

2. Selection of Method

Two methods are presented. Method B, hardness by calculation, is applicable to all waters and yields the higher accuracy. If a mineral analysis is performed, hardness by calculation can be reported. Method C, the EDTA titration method, measures the calcium and magnesium ions and may be applied with appropriate modification to any kind of water. The procedure described affords a means of rapid analysis.

3. Reporting Results

When reporting hardness, state the method used, for example, ‘‘hardness (calc.)’’ or ‘‘hardness (EDTA).’’

2340 B. Hardness by Calculation

1. Discussion

The preferred method for determining hardness is to compute it from the results of separate determinations of calcium and magnesium.

2. Calculation

Hardness, mg equivalent $CaCO_3$/L = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]

2340 C. EDTA Titrimetric Method

1. General Discussion

a. Principle: Ethylenediaminetetraacetic acid and its sodium salts (abbreviated EDTA) form a chelated soluble complex when added to a solution of certain metal cations. If a small amount of a dye such as Eriochrome Black T or Calmagite is added to an aqueous solution containing calcium and magnesium ions at a pH of 10.0 ± 0.1, the solution becomes wine red. If EDTA is added as a titrant, the calcium and magnesium will be complexed, and when all of the magnesium and calcium has been complexed the solution turns from wine red to blue, marking the end point of the titration. Magnesium ion must be present to yield a satisfactory end point. To insure this, a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer; this automatically introduces sufficient magnesium and obviates the need for a blank correction.

The sharpness of the end point increases with increasing pH. However, the pH cannot be

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

increased indefinitely because of the danger of precipitating calcium carbonate, $CaCO_3$, or magnesium hydroxide, $Mg(OH)_2$, and because the dye changes color at high pH values. The specified pH of 10.0 ± 0.1 is a satisfactory compromise. A limit of 5 min is set for the duration of the titration to minimize the tendency toward $CaCO_3$ precipitation.

b. Interference: Some metal ions interfere by causing fading or indistinct end points or by stoichiometric consumption of EDTA. Reduce this interference by adding certain inhibitors before titration. MgCDTA [see 2*b*3)], selectively complexes heavy metals, releases magnesium into the sample, and may be used as a substitute for toxic or malodorous inhibitors. It is useful only when the magnesium substituted for heavy metals does not contribute significantly to the total hardness. With heavy metal or polyphosphate concentrations below those indicated in Table 2340:I, use Inhibitor I or II. When higher concentrations of heavy metals are present, determine calcium and magnesium by a non-EDTA method (see Section 3500-Ca and Section 3500-Mg) and obtain hardness by calculation. The figures in Table 2340:I are intended as a rough guide only and are based on using a 25-mL sample diluted to 50 mL.

Suspended or colloidal organic matter also may interfere with the end point. Eliminate this interference by evaporating the sample to dryness on a steam bath and heating in a muffle furnace at 550°C until the organic matter is completely oxidized. Dissolve the residue in 20 mL 1*N* hydrochloric acid (HCl), neutralize to pH 7 with 1*N* sodium hydroxide (NaOH), and make up to 50 mL with distilled water; cool to room temperature and continue according to the general procedure.

c. Titration precautions: Conduct titrations at or near normal room temperature. The color change becomes impractically slow as the sample approaches freezing temperature. Indicator decomposition becomes a problem in hot water.

The specified pH may produce an environment conducive to $CaCO_3$ precipitation. Although the titrant slowly redissolves such precipitates, a drifting end point often yields low results. Completion of the titration within 5 min minimizes the tendency for $CaCO_3$ to precipitate. The following three methods also reduce precipitation loss:

1) Dilute sample with distilled water to reduce $CaCO_3$ concentration. This simple expedient has been incorporated in the procedure. If precipitation occurs at this dilution of 1 + 1 use modification 2) or 3). Using too small a sample contributes a systematic error due to the buret-reading error.

2) If the approximate hardness is known or is determined by a preliminary titration, add 90% or more of titrant to sample *before* adjusting pH with buffer.

3) Acidify sample and stir for 2 min to expel CO_2 *before* pH adjustment. Determine alkalinity to indicate amount of acid to be added.

2. Reagents

a. Buffer solution:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1) Dissolve 16.9 g ammonium chloride (NH_4Cl) in 143 mL conc ammonium hydroxide (NH_4OH). Add 1.25 g magnesium salt of EDTA (available commercially) and dilute to 250 mL with distilled water.

2) If the magnesium salt of EDTA is unavailable, dissolve 1.179 g disodium salt of ethylenediaminetetraacetic acid dihydrate (analytical reagent grade) and 780 mg magnesium sulfate ($MgSO_4 \cdot 7H_2O$) or 644 mg magnesium chloride ($MgCl_2 \cdot 6H_2O$) in 50 mL distilled water. Add this solution to 16.9 g NH_4Cl and 143 mL conc NH_4OH with mixing and dilute to 250 mL with distilled water. To attain the highest accuracy, adjust to exact equivalence through appropriate addition of a small amount of EDTA or $MgSO_4$ or $MgCl_2$.

Store Solution 1) or 2) in a plastic or borosilicate glass container for no longer than 1 month. Stopper tightly to prevent loss of ammonia (NH_3) or pickup of carbon dioxide (CO_2). Dispense buffer solution by means of a bulb-operated pipet. Discard buffer when 1 or 2 mL added to the sample fails to produce a pH of 10.0 ± 0.1 at the titration end point.

3) Satisfactory alternate ‘‘odorless buffers’’ also are available commercially. They contain the magnesium salt of EDTA and have the advantage of being relatively odorless and more stable than the NH_4Cl-NH_4OH buffer. They usually do not provide as good an end point as NH_4Cl-NH_4OH because of slower reactions and they may be unsuitable when this method is automated. Prepare one of these buffers by mixing 55 mL conc HCl with 400 mL distilled water and then, slowly and with stirring, adding 300 mL 2-aminoethanol (free of aluminum and heavier metals). Add 5.0 g magnesium salt of EDTA and dilute to 1 L with distilled water.

b. Complexing agents: For most waters no complexing agent is needed. Occasionally water containing interfering ions requires adding an appropriate complexing agent to give a clear, sharp change in color at the end point. The following are satisfactory:

1) *Inhibitor I:* Adjust acid samples to pH 6 or higher with buffer or 0.1*N* NaOH. Add 250 mg sodium cyanide (NaCN) in powder form. Add sufficient buffer to adjust to pH 10.0 ± 0.1. (CAUTION: *NaCN is extremely poisonous. Take extra precautions in its use.* Flush solutions containing this inhibitor down the drain with large quantities of water after insuring that no acid is present to liberate volatile poisonous hydrogen cyanide.)

2) *Inhibitor II:* Dissolve 5.0 g sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) or 3.7 g $Na_2S \cdot 5H_2O$ in 100 mL distilled water. Exclude air with a tightly fitting rubber stopper. This inhibitor deteriorates through air oxidation. It produces a sulfide precipitate that obscures the end point when appreciable concentrations of heavy metals are present. Use 1 mL in ¶ 3*b* below.

3) *MgCDTA:* Magnesium salt of 1, 2-cyclohexanediaminetetraacetic acid. Add 250 mg per 100 mL sample and dissolve completely before adding buffer solution. Use this complexing agent to avoid using toxic or odorous inhibitors when interfering substances are present in concentrations that affect the end point but will not contribute significantly to the hardness value.

Commercial preparations incorporating a buffer and a complexing agent are available. Such

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

mixtures must maintain pH 10.0 ± 0.1 during titration and give a clear, sharp end point when the sample is titrated.

c. Indicators: Many types of indicator solutions have been advocated and may be used if the analyst demonstrates that they yield accurate values. The prime difficulty with indicator solutions is deterioration with aging, giving indistinct end points. For example, alkaline solutions of Eriochrome Black T are sensitive to oxidants and aqueous or alcoholic solutions are unstable. In general, use the least amount of indicator providing a sharp end point. It is the analyst's responsibility to determine individually the optimal indicator concentration.

1) *Eriochrome Black T:* Sodium salt of 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulfonic acid; No. 203 in the Color Index. Dissolve 0.5 g dye in 100 g 2,2′,2″-nitrilotriethanol (also called triethanolamine) or 2-methoxymethanol (also called ethylene glycol monomethyl ether). Add 2 drops per 50 mL solution to be titrated. Adjust volume if necessary.

2) *Calmagite:* 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid. This is stable in aqueous solution and produces the same color change as Eriochrome Black T, with a sharper end point. Dissolve 0.10 g Calmagite in 100 mL distilled water. Use 1 mL per 50 mL solution to be titrated. Adjust volume if necessary.

3) Indicators 1 and 2 can be used in dry powder form if care is taken to avoid excess indicator. Prepared dry mixtures of these indicators and an inert salt are available commercially.

If the end point color change of these indicators is not clear and sharp, it usually means that an appropriate complexing agent is required. If NaCN inhibitor does not sharpen the end point, the indicator probably is at fault.

d. Standard EDTA titrant, 0.01*M*: Weigh 3.723 g analytical reagent-grade disodium ethylenediaminetetraacetate dihydrate, also called (ethylenedinitrilo)tetraacetic acid disodium salt (EDTA), dissolve in distilled water, and dilute to 1000 mL. Standardize against standard calcium solution (¶ 2*e*) as described in ¶ 3*b* below.

Because the titrant extracts hardness-producing cations from soft-glass containers, store in polyethylene (preferable) or borosilicate glass bottles. Compensate for gradual deterioration by periodic restandardization and by using a suitable correction factor.

e. Standard calcium solution: Weigh 1.000 g anhydrous $CaCO_3$ powder (primary standard or special reagent low in heavy metals, alkalis, and magnesium) into a 500-mL erlenmeyer flask. Place a funnel in the flask neck and add, a little at a time, 1 + 1 HCl until all $CaCO_3$ has dissolved. Add 200 mL distilled water and boil for a few minutes to expel CO_2. Cool, add a few drops of methyl red indicator, and adjust to the intermediate orange color by adding 3*N* NH_4OH or 1 + 1 HCl, as required. Transfer quantitatively and dilute to 1000 mL with distilled water; 1 mL = 1.00 mg $CaCO_3$.

f. Sodium hydroxide, NaOH, 0.1*N*.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3. Procedure

a. Pretreatment of polluted water and wastewater samples: Use nitric acid-sulfuric acid or nitric acid-perchloric acid digestion (Section 3030).

b. Titration of sample: Select a sample volume that requires less than 15 mL EDTA titrant and complete titration within 5 min, measured from time of buffer addition.

Dilute 25.0 mL sample to about 50 mL with distilled water in a porcelain casserole or other suitable vessel. Add 1 to 2 mL buffer solution. Usually 1 mL will be sufficient to give a pH of 10.0 to 10.1. The absence of a sharp end-point color change in the titration usually means that an inhibitor must be added at this point (¶ 2*b* et seq.) or that the indicator has deteriorated.

Add 1 to 2 drops indicator solution or an appropriate amount of dry-powder indicator formulation [¶ 2*c*3)]. Add standard EDTA titrant slowly, with continuous stirring, until the last reddish tinge disappears. Add the last few drops at 3- to 5-s intervals. At the end point the solution normally is blue. Daylight or a daylight fluorescent lamp is recommended highly because ordinary incandescent lights tend to produce a reddish tinge in the blue at the end point.

If sufficient sample is available and interference is absent, improve accuracy by increasing sample size, as described in ¶ 3*c* below.

c. Low-hardness sample: For ion-exchanger effluent or other softened water and for natural wat ers of low hardness (less than 5 mg/L), take a larger sample, 100 to 1000 mL, for titration and add proportionately larger amounts of buffer, inhibitor, and indicator. Add standard EDTA titrant slowly from a microburet and run a blank, using redistilled, distilled, or deionized water of the same volume as the sample, to which identical amounts of buffer, inhibitor, and indicator have been added. Subtract volume of EDTA used for blank from volume of EDTA used for sample.

4. Calculation

$$\text{Hardness (EDTA) as mg } CaCO_3\text{/L} = \frac{A \times B \times 1000}{\text{mL sample}}$$

where:

A = mL titration for sample and
B = mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant.

5. Precision and Bias

A synthetic sample containing 610 mg/L total hardness as $CaCO_3$ contributed by 108 mg Ca/L and 82 mg Mg/L, and the following supplementary substances: 3.1 mg K/L, 19.9 mg Na/L, 241 mg Cl^-/L, 0.25 mg NO_2^--N/L, 1.1 mg NO_3^--N/L, 259 mg SO_4^{2-}/L, and 42.5 mg total alkalinity/L (contributed by $NaHCO_3$) in distilled water was analyzed in 56 laboratories by the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

EDTA titrimetric method with a relative standard deviation of 2.9% and a relative error of 0.8%.

6. Bibliography

CONNORS, J.J. 1950. Advances in chemical and colorimetric methods. *J. Amer. Water Works Assoc.* 42:33.

DIEHL, H., C.A. GOETZ & C.C. HACH. 1950. The versenate titration for total hardness. *J. Amer. Water Works Assoc.* 42:40.

BETZ, J.D. & C.A. NOLL. 1950. Total hardness determination by direct colorimetric titration. *J. Amer. Water Works Assoc.* 42:49.

GOETZ, C.A., T.C. LOOMIS & H. DIEHL. 1950. Total hardness in water: The stability of standard disodium dihydrogen ethylenediaminetetraacetate solutions. *Anal. Chem.* 22:798.

DISKANT, E.M. 1952. Stable indicator solutions for complexometric determination of total hardness in water. *Anal. Chem.* 24:1856.

BARNARD, A.J., JR., W.C. BROAD & H. FLASCHKA. 1956 & 1957. The EDTA titration. *Chemist Analyst* 45:86 & 46:46.

GOETZ, C.A. & R.C. SMITH. 1959. Evaluation of various methods and reagents for total hardness and calcium hardness in water. *Iowa State J. Sci.* 34:81 (Aug. 15).

SCHWARZENBACH, G. & H. FLASCHKA. 1969. Complexometric Titrations, 2nd ed. Barnes & Noble, Inc., New York, N.Y.

2350 OXIDANT DEMAND/REQUIREMENT*#(32)

2350 A. Introduction

1. Significance and Chemistry

Oxidants are added to water supplies and wastewater primarily for disinfection. Other beneficial uses include slime removal, oxidation of undesirable inorganic species (e.g., ferrous ion, reduced manganese, sulfide, and ammonia) and oxidation of organic constituents (e.g., taste- and odor-producing compounds). Oxidant demand refers to the difference between the added oxidant dose and the residual oxidant concentration measured after a prescribed contact time at a given pH and temperature. Oxidant requirement refers to the oxidant dose required to achieve a given oxidant residual at a prescribed contact time, pH, and temperature.

The fate of oxidants in water and wastewater is complex. For example, chlorine reacts with sample constituents by three general pathways: oxidation, addition, and substitution. First, chlorine can oxidize reduced species, such as Fe^{2+}, Mn^{2+}, and sulfide. In these reactions, chlorine is reduced to inorganic chloride (Cl^-). Second, chlorine can add to olefins and other double-bond-containing organic compounds to produce chlorinated organic compounds. Third, chlorine can substitute onto chemical substrates. The addition and substitution reactions produce

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

organochlorine species (e.g., chlorination of phenol to chlorophenols) or active chlorine species (e.g., chlorination of ammonia to produce monochloramine). Chlorine reacts with naturally occurring organic compounds by a combination of these mechanisms to generate such products as trihalomethanes. See Section 4500-Cl (chlorine), 4500-ClO_2 (chlorine dioxide), and 4500-O_3 (ozone) for additional information.

Oxidant demand and oxidant requirement are significantly affected by the chemical and physical characteristics of the sample and the manner in which the oxidant consumption is measured. In particular, oxidant reactivity is influenced by temperature, pH, contact time, and oxidant dose. Oxidant demand and oxidant requirement are defined operationally by the analytical method used to determine the residual oxidant concentration. *Report sample temperature, pH, contact time, oxidant dose, and analytical method with oxidant demand or oxidant requirement.* Sample temperature strongly affects reaction kinetics and thus the demand exerted in a given contact time. Sample pH affects the form of the oxidant and the nature and extent of the demand. For example, ozone is unstable at high pH values and ozone demand is especially sensitive to sample pH. Oxidant demand increases with time and therefore the demand must be defined for a given contact time. Oxidant demand also is dependent on oxidant dose. Increasing oxidant dose usually will increase demand, but it is incorrect to assume that doubling the oxidant dose will double the oxidant demand. For these reasons, it is difficult to extrapolate oxidant demand data from one set of conditions to another. *Always study oxidant consumption under the range of conditions expected in the field.*

Oxidant consumption is used to evaluate oxidant demand and oxidant requirement. Report consumption values according to the objective of the study. For example, report chlorine *demand* as follows: ‘‘The sample dosed at 5.0 mg/L consumed 3.9 mg/L after 24 h at 20°C and pH 7.1, as measured by amperometric titration.’’ By contrast, report ozone *requirement* as follows: ‘‘The sample required a dose of 2.1 mg/L to achieve an ozone residual of 0.5 mg/L after 20 min at 15°C and pH 6.5, as measured by the indigo method.’’

2. Selection of Method

Select a method to measure oxidant residuals used in the demand calculation that is specific and has adequate sensitivity. Some oxidant residual measurement techniques are subject to interferences from oxidation-produced oxidants. Interferences affect oxidant demand measurements because the concentrations of the interferents may change as the oxidant residual changes. Thus, calculate free chlorine demand in municipal wastewater as the difference between free chlorine dose and free chlorine residual measured after a desired contact time at a given temperature, pH, and chlorine dose for a specified analytical method. Chlorination of non-nitrified municipal wastewater probably produces chloramines. If the analytical method for free chlorine is subject to interferences from chloramines, then the free chlorine residual measurement will be too large (see Section 4500-Cl.A.3), and the resulting free chlorine demand value will be incorrectly low. It is sometimes difficult to predict the manner in which oxidant-produced oxidants will affect the demand measurement. The best approach is to use the analytical method most specific to the oxidant of interest but always indicate the method with the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

result.

The addition of reagents may cause loss of oxidant residual or other changes in oxidant demand. The loss of total chlorine upon addition of acid and KI is discussed in Section 4500-Cl.A.3*a*.

2350 B. Chlorine Demand/Requirement

1. General Discussion

a. Principle: The sample is divided into subsamples and each is dosed with the standardized oxidant (chlorine) solution to yield a series of increasing doses. After the appropriate contact time, oxidant residual, pH, and temperature are measured and the demand/requirement determined by difference between initial and final concentrations.

b. Selection of method: Chlorine consumption tests may be made to examine the demand or requirement for total chlorine, free chlorine, combined chlorine, monochloramine, or dichloramine. Specify the chlorine species consumed in the chlorine demand/requirement test. The analytical method should exhibit minimal interferences for the species examined. For demand/ requirement studies with free chlorine, use only amperometric titration (Section 4500-Cl.D) or DPD methods (Section 4500-Cl.F and Section 4500-Cl.G).

c. Interference: Refer to Section 4500-Cl.D.1*b* (amperometric titration), Section 4500-Cl.F.1*d* (DPD ferrous titrimetric method), or Section 4500-Cl.G.1*b* (DPD colorimetric method). Pay special attention to interferences caused by oxidation products such as MnO_2, NH_2Cl, and $NHCl_2$. If the ammonia or organic nitrogen content of the water is significant, combined chlorine may form. See Section Section 4500-Cl for details. Under these conditions, expect interferences in the measurement of free chlorine by combined chlorine.

d. Minimum detectable concentration: Because it is calculated by difference, the minimum detectable chlorine demand/requirement is $\sqrt{2}$ times the minimum chlorine residual detectable by the analytical method. For minimum detectable chlorine residual, see Section 4500-Cl.F.1*e* (DPD ferrous titrimetric method) or Section 4500-Cl.G.1*c* (DPD colorimetric method). Minimum detectable demand also is influenced by amount of oxidant consumed relative to oxidant dose (see ¶ 6 below).

e. Sampling: Most reliable results are obtained on fresh samples that contain low amounts of suspended solids. If samples will be analyzed within 24 h of collection, refrigerate unacidified at 4°C immediately after collection. To preserve for up to 28 d, freeze unacidified samples at −20°C. Warm chilled samples to desired test condition before analysis.

2. Apparatus

See Section 4500-Cl.D (amperometric titration) or Section 4500-Cl.G (DPD colorimetric method).

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3. Reagents

a. Chlorine-demand-free water: See Section 4500-Cl.C.3*m*. Alternatively, prepare dilutions, blanks, and dosing solutions from high-quality distilled water (preferably carbon-filtered redistilled water).

b. Acetic acid, conc (glacial).

c. Potassium iodide, KI, crystals.

d. Standard sodium thiosulfate titrant, 0.025*N:* See Section 4500-Cl.B.2*d*.

e. Starch indicator solution: See Section 4500-Cl.B.2*e*.

f. Reagents for determining residual chlorine: See Section 4500-Cl.D.3 (amperometric titration), Section 4500-Cl.F.2 (DPD ferrous titrimetric method), or Section 4500-Cl.G.3 (DPD colorimetric method).

g. Standard chlorine solution: Prepare by bubbling chlorine gas through distilled water or by diluting commercially available 5–7% (50 000–70 000 mg/L) sodium hypochlorite. Store in the dark or in a brown, glass-stoppered bottle. Standardize each day of use. A suitable strength of chlorine solution usually will be between 100 and 1000 mg/L, preferably about 100 times estimated chlorine demand. Use a solution of sufficient concentration so that adding the chlorine solution will not increase the volume of the treated portions by more than 5%.

Standardization—Place 2 mL acetic acid and 10 to 15 mL chlorine-demand-free water in a flask. Add about 1 g KI. Measure into the flask a suitable volume of chlorine solution. In choosing a convenient volume, note that 1 mL 0.025*N* $Na_2S_2O_3$ titrant is equivalent to about 0.9 mg chlorine as Cl_2. Select volumes that will require no more than 20 mL titrant.

Titrate with standardized 0.025*N* $Na_2S_2O_3$ titrant until the yellow iodine color almost disappears. Add 1 to 2 mL starch indicator solution and continue titrating until the blue color disappears.

Determine the blank by adding identical quantities of acid, KI, and starch indicator to a volume of chlorine-demand-free water corresponding to the sample used for titration. Perform whichever blank titration applies, according to Section 4500-Cl.B.3*d*. Calculate the chlorine stock concentration as described in Section 4500-Cl.B.4.

4. Procedure

Measure sample temperature and pH. Keep sample and sample portions at desired temperature and protect from light throughout the procedure. If pH adjustment is desired, prepare a blank in distilled water containing the same amount of buffer as in the sample. Carry the blank throughout the procedure.

Measure 5*#(33) equal sample portions of 200 mL†#(34) each into glass-stoppered bottles or flasks of ample capacity to permit mixing. Add increasing amounts of standard chlorine solution (¶ 3*g*) to successive portions in the series. Try to bracket the estimated demand/requirement and satisfy criteria of ¶ 5*a*. Increase dosage between portions in increments of 0.1 mg/L for

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

determining low demands/requirements and up to 1.0 mg/L or more for higher demands. Mix while adding. Dose sample portions according to a staggered schedule that will permit determining the residual after predetermined contact times.

Conduct test over desired contact period. Record contact time. At end of contact period, measure sample temperature, sample pH, and residual chlorine. Record residual measurement method used.

5. Calculation

a. Chlorine demand: Select sample portion with a residual at the end of the contact period that satisfies the following criteria:

1) $R_s < D_s - 1.4\ R_{min}$,
2) $R_s > R_{min}$, and
3) Dose is most similar to the dosage range expected in the field

where:

R_s= residual after contact time, mg/L,
D_s= dose, mg/L, and
R_{min}= minimum residual measurable by the method, mg/L.

The first two criteria insure that the chlorine residual and demand are greater than their respective minimum detection limits. If no sample portion satisfies all criteria, repeat the test and adjust doses accordingly. Calculate chlorine demand as follows:

$$\text{Chlorine demand, mg/L} = (D_S - R_S) - (D_B - R_B)$$

where R_s and D_s are defined as above, and:

R_B= residual of blank after contact time, mg/L, and
D_B = blank dose, mg/L.

When reporting chlorine demand, include dose, contact time, sample temperature, sample pH, and analytical method.

b. Chlorine requirement: Report the chlorine dose that produced the target residual after the desired contact time. When reporting chlorine requirement, include the target residual, contact time, sample temperature, sample pH, and analytical method. Report chlorine demand of blank if it is greater than 10% of the difference between the requirement and the target residual.

6. Precision and Bias

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

For data on precision and bias of concentration measurements, see analytical method used. Because demand is calculated by difference, the uncertainty associated with the demand value will be greater than the uncertainty of the individual residual measurements. If the standard deviations of the dose measurement and residual measurements are the same, then the standard deviation and minimum detection limit of the oxidant demand will be $\sqrt{2}$ (approximately 1.4) times the standard deviation and minimum detection limit of the measurement technique, respectively.

The chlorine dose and amount consumed affect the precision and bias of demand calculation in two ways. First, the amount consumed must be sufficiently large, relative to the dose, to minimize errors associated with a value calculated from the difference of two numbers of approximately equal value. Second, the amount consumed must be small enough, relative to the dose, to prevent the residual concentration from being too small.

7. Bibliography

See Section 4500-Cl.D.7 or Section 4500-Cl.F.6, according to analytical method used.

2350 C. Chlorine Dioxide Demand/Requirement

1. General Discussion

a. Principle: See Section 2350B.1. Chlorine dioxide consumption studies are made by dosing samples from a ClO_2 stock solution.

b. Selection of method: Use the amperometric method II (Section 4500-ClO_2.E) because of its high degree of accuracy and minimal interferences.

c. Interference: See Section 4500-ClO_2.E.1*b*.

d. Minimum detectable concentration: The minimum detectable chlorine dioxide demand/requirement is $\sqrt{2}$ times the minimum chlorine dioxide residual detectable by the analytical method (see Section 2350B.1*d* and Section 2350B.6).

2. Apparatus

See Section 4500-ClO_2.E.2.

3. Reagents

See Section 4500-ClO_2.B.2 to prepare and standardize ClO_2.

See Section 4500-ClO_2.E.3 for reagents required to determine ClO_2 residual.

4. Procedure

Follow procedure of Section 2350B.4, using ClO_2 solution, rather than chlorine solution, for

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

dosing sample portions.

Follow procedure of Section 4500-ClO_2.E.4 to measure ClO_2 residual.

5. Calculation

a. Chlorine dioxide demand: See Section 2350B.5*a*.

b. Chlorine dioxide requirement: See Section 2350B.5*b*.

6. Precision and Bias

See Section 2350B.6.

7. Bibliography

See Section 4500-ClO_2.E.6 and Section 4500-ClO_2.E.7.

2350 D. Ozone Demand/Requirement—Batch Method

1. General Discussion

a. Principle: See Section 2350B.1. Samples can be ozonated in batch and semi-batch modes. In batch ozone consumption studies, an ozone stock solution is used to add ozone to the samples. In semi-batch ozone consumption studies, a stream of ozone gas is added continuously to the sample.

Ozone decomposes at high pH. Thus, even pH-buffered distilled water has a non-zero ozone demand/requirement. Analyze blanks with all ozone consumption tests. Do not subtract the ozone demand of the blank from the ozone demand of the sample, but report it separately.

b. Selection of method: Ozone produces oxidants that interfere with iodometric methods. The indigo method (Section 4500-O_3.B) is recommended for measuring ozone residuals in ozone consumption studies. The indigo method measures only the demand for ozone; it does not measure the demand for ozone-produced oxidants such as the hydroxyl radical.

c. Interference: See Section 4500-O_3.B.1*b*.

d. Minimum detectable concentration: The minimum detectable ozone demand/requirement is $\sqrt{2}$ times the minimum ozone residual detectable by the analytical method (see Section 2350B.1*d* and Section 2350B.6).

For minimum detectable ozone residuals, see Section 4500-O_3.B.1*c*.

2. Apparatus

a. Ozone generator: Use a laboratory-scale ozonator, capable of providing up to about 5% ozone in the gas phase at a gas flow of up to about 1 L/min.

b. Apparatus for measuring residual ozone: See Section 4500-O_3.B.2.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3. Reagents

a. Ozone-demand-free water: Ozonate reagent water (see Section 1080) for at least 1 h and purge with nitrogen gas for at least 1 h. CAUTION: *Conduct all laboratory ozonations under a vented hood.*

b. Standard ozone solution: Put about 800 mL of ozone-demand-free water in a 1-L flask. Bubble ozone (approximately 1 to 5% O_3 in the gas phase) through the water for about 30 min while stirring. At room temperature the ozone solution will contain about 10 to 20 mg O_3/L. If the flask is cooled in an ice bath throughout the procedure, the ozone concentration will be about 30 to 40 mg O_3/L. Standardize the ozone solution by the indigo method. Use a small sample volume (typically 1 mL) as directed in Section 4500-O_3.B.4*a*3).

4. Procedure

Follow procedure of Section 2350B.4, using standard ozone solution, rather than chlorine solution, for dosing sample portions. Carry a reagent blank through the procedure.

Follow procedure of Section 4500-O_3.B.4 to measure O_3 residual.

5. Calculation

a. Ozone demand: See Section 2350B.5*a* for selection of the proper sample portion. Calculate ozone demand in sample as follows:

$$\text{Ozone demand, mg/L} = D_S - R_S$$

where:

R_s = oxidant residual of sample after contact time, mg/L, and
D_s = sample oxidant dose, mg/L.

Calculate ozone demand in the blank separately.

$$\text{Ozone demand of blank, mg/L} = D_B - R_B$$

where:

R_B = oxidant residual of blank after contact time, mg/L, and
D_B = blank oxidant dose, mg/L.

Report the ozone demand and the ozone demand of the blank, ozone dose, contact time, sample temperature, sample pH, and analytical method.

b. Ozone requirement: See Section 2350B.5*b*.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

6. Precision and Bias

See Section 2350B.6.

7. Bibliography

See Section 4500-O_3.B.7 and Section 4500-O_3.B.8.

2350 E. Ozone Demand/Requirement—Semi-Batch Method

1. General Discussion

See Section 2350D.1.

The semi-batch method involves determination of ozone demand with the continuous addition of gaseous ozone to a batch reactor. The results obtained in this method depend on the mass-transfer characteristics of the reactor. In addition, some compounds that consume ozone may volatilize during the test.

2. Apparatus

All apparatus listed in Section 2350D.2 is required, plus:

a. Gas washing bottles, borosilicate glass, minimum volume 250 mL.

b. Tubing: Use only stainless steel or TFE tubing.

c. Glassware: Buret, 50 mL; beaker, 400 mL; graduated cylinder, 250 mL.

d. Wash bottle, 500 mL.

e. Magnetic stirrer (optional).

3. Reagents

a. Ozone-demand-free water: See Section 2350D.3*a*.

b. Sulfuric acid, H_2SO_4, 2*N*: Cautiously add 56 mL conc H_2SO_4 to 800 mL ozone-demand-free water in a 1-L volumetric flask. Mix thoroughly, cool, add up to mark with ozone-demand-free water.

c. Potassium iodide, KI: Dissolve 20 g KI in about 800 mL of ozone-demand-free water in a 1-L volumetric flask. Make up to mark with ozone-demand-free water.

d. Standard sodium thiosulfate titrant, $Na_2S_2O_3$, 0.1*N*: See Section 4500-Cl.B.2*c*.

e. Standard sodium thiosulfate titrant, $Na_2S_2O_3$, 0.005*N*: Dilute the proper volume (approximately 50 mL) of standardized 0.1*N* $Na_2S_2O_3$ to 1 L.

f. Starch indicator solution: See Section 4500-Cl.B.2*e*.

4. Procedure

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Determine the output of the ozone generator by passing the ozone gas through two serial KI traps (Traps A and B) for about 10 min. For best results, keep gas flow below approximately 1 L/min. Each trap is a gas washing bottle containing a known volume (at least 200 mL) of 2% KI. Quantitatively transfer contents of each trap into a beaker, add 10 mL of 2*N* H_2SO_4, and titrate with standardized 0.005*N* $Na_2S_2O_3$ until the yellow iodine color almost disappears. Add 1 to 2 mL starch indicator solution and continue titrating to the disappearance of blue color.

Put a known volume (at least 200 mL) of sample in a separate gas washing bottle (label gas washing bottles to avoid contaminating the reaction vessel with iodide). Direct ozone gas through this reaction vessel. For ozone demand studies, direct gas stream leaving reaction vessel through a KI trap (Trap C) prepared as above. Ozonate sample for a given contact time. For ozone demand studies, turn ozonator off at end of contact time and pour contents of Trap C into a beaker. Add 10 mL 2*N* H_2SO_4 and titrate with 0.005*N* $Na_2S_2O_3$ as described above. For ozone requirement studies, remove a portion from the reaction vessel at the end of contact time and measure residual ozone concentration by the indigo method.

5. Calculation

a. Ozone dose:

$$\text{Ozone dose, mg/min} = \frac{(A + B) \times N \times 24}{T}$$

where:

A = mL titrant for Trap A,
B = mL titrant for Trap B,
N = normality of $Na_2S_2O_3$, and
T = ozonation time, min.

b. Ozone demand:

$$\text{Ozone demand, mg/min} = \text{ozone dose, mg/min} - \frac{C \times N \times 24}{T}$$

where:

C = mL titrant for Trap C.

Report sample ozone demand and blank ozone demand, ozone dose, ozonation time, sample temperature, sample pH, sample volume, and analytical method. Because the ozone transfer rate is highly dependent on experimental conditions, also report vessel volume, vessel type, gas flow rate, and sample volume.

c. Ozone requirement: The ozone requirement in the semi-batch test is the ozone dose,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

mg/min, required to obtain the target ozone residual after the desired ozonation time. See Section 2350E.5*a* to calculate dose. When reporting ozone requirement, also include target oxidant residual as well as other experimental characteristics listed in ¶ 5*b* above.

6. Precision and Bias

See Section 2350B.6.

7. Bibliography

See Section 4500-O_3.B.7 and Section 4500-O_3.B.8.

2510 CONDUCTIVITY*#(35)

2510 A. Introduction

Conductivity, *k*, is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility, and valence; and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

1. Definitions and Units of Expression

Conductance, *G*, is defined as the reciprocal of resistance, *R*:

$$G = \frac{1}{R}$$

where the unit of *R* is ohm and *G* is ohm^{-1} (sometimes written mho). Conductance of a solution is measured between two spatially fixed and chemically inert electrodes. To avoid polarization at the electrode surfaces the conductance measurement is made with an alternating current signal.[1] The conductance of a solution, *G*, is directly proportional to the electrode surface area, *A*, cm^2, and inversely proportional to the distance between the electrodes, *L*, cm. The constant of proportionality, *k*, such that:

$$G = k\left(\frac{A}{L}\right)$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

is called ‘‘conductivity’’ (preferred to ‘‘specific conductance’’). It is a characteristic property of the solution between the electrodes. The units of k are 1/ohm-cm or mho per centimeter. Conductivity is customarily reported in micromhos per centimeter (μmho/cm).

In the International System of Units (SI) the reciprocal of the ohm is the siemens (S) and conductivity is reported as millisiemens per meter (mS/m); 1 mS/m = 10 μmhos/cm and 1 μS/cm = 1 μmho/cm. To report results in SI units of mS/m divide μmhos/cm by 10.

To compare conductivities, values of k are reported relative to electrodes with A = 1 cm^2 and L = 1 cm. Absolute conductances, G_s, of standard potassium chloride solutions between electrodes of precise geometry have been measured; the corresponding standard conductivities, k_s, are shown in Table 2510:I.

The equivalent conductivity, Λ, of a solution is the conductivity per unit of concentration. As the concentration is decreased toward zero, Λ approaches a constant, designated as Λ°. With k in units of micromhos per centimeter it is necessary to convert concentration to units of equivalents per cubic centimeter; therefore:

$$\Lambda = 0.001k/\text{concentration}$$

where the units of Λ, k, and concentration are mho-cm^2/equivalent, μmho/cm, and equivalent/L, respectively. Equivalent conductivity, Λ, values for several concentrations of KCl are listed in Table 2510:I. In practice, solutions of KCl more dilute than 0.001M will not maintain stable conductivities because of absorption of atmospheric CO_2. Protect these dilute solutions from the atmosphere.

2. Measurement

a. Instrumental measurements: In the laboratory, conductance, G_s, (or resistance) of a standard KCl solution is measured and from the corresponding conductivity, k_s, (Table 2510:I) a cell constant, C, cm^{-1}, is calculated:

$$C = \frac{k_s}{G_s}$$

Most conductivity meters do not display the actual solution conductance, G, or resistance, R; rather, they generally have a dial that permits the user to adjust the internal cell constant to match the conductivity, k_s, of a standard. Once the cell constant has been determined, or set, the conductivity of an unknown solution,

$$k_u = CG_u$$

will be displayed by the meter.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Distilled water produced in a laboratory generally has a conductivity in the range 0.5 to 3 μmhos/cm. The conductivity increases shortly after exposure to both air and the water container.

The conductivity of potable waters in the United States ranges generally from 50 to 1500 μmhos/cm. The conductivity of domestic wastewaters may be near that of the local water supply, although some industrial wastes have conductivities above 10 000 μmhos/cm. Conductivity instruments are used in pipelines, channels, flowing streams, and lakes and can be incorporated in multiple-parameter monitoring stations using recorders.

Most problems in obtaining good data with conductivity monitoring equipment are related to electrode fouling and to inadequate sample circulation. Conductivities greater than 10 000 to 50 000 μmho/cm or less than about 10 μmho/cm may be difficult to measure with usual measurement electronics and cell capacitance. Consult the instrument manufacturer's manual or published references.[1,5,6]

Laboratory conductivity measurements are used to:

- Establish degree of mineralization to assess the effect of the total concentration of ions on chemical equilibria, physiological effect on plants or animals, corrosion rates, etc.
- Assess degree of mineralization of distilled and deionized water.
- Evaluate variations in dissolved mineral concentration of raw water or wastewater. Minor seasonal variations found in reservoir waters contrast sharply with the daily fluctuations in some polluted river waters. Wastewater containing significant trade wastes also may show a considerable daily variation.
- Estimate sample size to be used for common chemical determinations and to check results of a chemical analysis.
- Determine amount of ionic reagent needed in certain precipitation and neutralization reactions, the end point being denoted by a change in slope of the curve resulting from plotting conductivity against buret readings.
- Estimate total dissolved solids (mg/L) in a sample by multiplying conductivity (in micromhos per centimeter) by an empirical factor. This factor may vary from 0.55 to 0.9, depending on the soluble components of the water and on the temperature of measurement. Relatively high factors may be required for saline or boiler waters, whereas lower factors may apply where considerable hydroxide or free acid is present. Even though sample evaporation results in the change of bicarbonate to carbonate the empirical factor is derived for a comparatively constant water supply by dividing dissolved solids by conductivity.
- Approximate the milliequivalents per liter of either cations or anions in some waters by multiplying conductivity in units of micromhos per centimeter by 0.01.

b. Calculation of conductivity: For naturally occurring waters that contain mostly Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-}, and Cl^{-} and with TDS less than about 2500 mg/L, the following procedure can be used to calculate conductivity from measured ionic concentrations.[7] The abbreviated water analysis in Table 2510:II illustrates the calculation procedure.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

At infinite dilution the contribution to conductivity by different kinds of ions is additive. In general, the relative contribution of each cation and anion is calculated by multiplying equivalent conductances, λ°_+ and λ°_-, mho-cm^2/equivalent, by concentration in equivalents per liter and correcting units. Table 2510:III contains a short list of equivalent conductances for ions commonly found in natural waters.[8] Trace concentrations of ions generally make negligible contribution to the overall conductivity. A temperature coefficient of 0.02/deg is applicable to all ions, except H^+ (0.0139/deg) and OH^- (0.018/deg).

At finite concentrations, as opposed to infinite dilution, conductivity per equivalent decreases with increasing concentration (see Table 2510:I). For solutions composed of one anion type and one cation type, e.g., KCl as in Table 2510:I, the decrease in conductivity per equivalent with concentration can be calculated, ±0.1%, using an ionic-strength-based theory of Onsager.[9] When mixed salts are present, as is nearly always the case with natural and wastewaters, the theory is quite complicated.[10] The following semiempirical procedure can be used to calculate conductivity for naturally occurring waters:

First, calculate infinite dilution conductivity (Table 2510:II, Column 4):

$$k^\circ = \sum|z_i|(\lambda^\circ_{+i})(\mathrm{m}M_i) + \sum|z_i|(\lambda^\circ_{-i})(\mathrm{m}M_i)$$

where:

$|z_i|$ = absolute value of the charge of the *i*-th ion,
$\mathrm{m}M_i$ = millimolar concentration of the *i*-th ion, and
λ°_{+i}, λ°_{-i} = equivalent conductance of the *i*-th ion.

If m*M* is used to express concentration, the product, (λ°_+) $(\mathrm{m}M_i)$ or $(\lambda^\circ_-)(\mathrm{m}M_i)$, corrects the units from liters to cm^3. In this case k° is 578.2 µmho/cm (Table 2510:II, Column 4).

Next, calculate ionic strength, *IS* in molar units:

$$IS = \sum z_i^2(\mathrm{m}M_i)/2000$$

The ionic strength is 15.33/2000 = 0.00767 *M* (Table 2510:II, Column 5).

Calculate the monovalent ion activity coefficient, *y*, using the Davies equation for IS ≤ 0.5 *M* and for temperatures from 20 to 30°C.[9,11]

$$y = 10^{-0.5[IS^{1/2}/(1 + IS^{1/2}) - 0.3IS]}$$

In the present example *IS* = 0.00767 *M* and *y* = 0.91.

Finally, obtain the calculated value of conductivity, k_{calc}, from:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$k_{calc} = k^{\circ}y^2$$

In the example being considered, $k_{calc} = 578.2 \times 0.91^2 = 478.8$ μmho/cm versus the reported value as measured by the USGS of 477 μmho/cm.

For 39 analyses of naturally occurring waters,[7,12] conductivities calculated in this manner agreed with the measured values to within 2%.

3. References

1. WILLARD, H.H., L.L. MERRITT & J.A. DEAN. 1974. Instrumental Methods of Analysis, 5th ed. D. Van Nostrand Company, New York, N.Y.
2. WU, Y.C., W.F. KOCH, W.J. HAMER & R.L. KAY. 1987. Review of electrolytic conductance standards. *J. Solution Chem.* 16:No.12.
3. JASPER, W.S. 1988. Secondary Standard Potassium Chloride Conductivity Solutions at 25°C. Corporate Metrology Laboratory, YSI Inc., Yellow Springs, Ohio.
4. ORGANISATION INTERNATIONALE DE METROLOGIE LEGALE. 1981. Standard Solutions Reproducing the Conductivity of Electrolytes, International Recommendation No. 56, 1st ed., June 1980. Bur. International de Metrologie Legale, Paris, France.
5. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1982. Standard test methods for electrical conductivity and resistivity of water. ASTM Designation D1125-82.
6. SCHOEMAKER, D.S., C.W. GARLAND & J.W. NIBLER. 1989. Experiments in Physical Chemistry, 5th ed. McGraw-Hill Book Co., New York, N.Y.
7. HAMILTON, C.E. 1978. Manual on Water. ASTM Spec. Tech. Publ. 442A, 4th ed. American Soc. Testing & Materials, Philadelphia, Pa.
8. DEAN, J.A. 1985. Lange's Handbook of Chemistry, 13th ed. McGraw-Hill Book Co., New York, N.Y.
9. ROBINSON, R.A. & R.H. STOKES. 1959. Electrolyte Solutions, 2nd ed. Academic Press, New York, N.Y.
10. HARNED, H.S. & B.B. OWEN. 1958. The Physical Chemistry of Electrolytic Solutions, 3rd ed. Reinhold Publishing Corp., New York, N.Y.
11. DAVIES, C.W. 1962. Ion Association. Elsevier Press, Amsterdam, The Netherlands.
12. TCHOBANOGLOUS, G. & E.D. SCHROEDER. 1985. Water Quality, Vol. 1. Addison-Wesley Publishing Company, Reading, Mass.

2510 B. Laboratory Method

1. General Discussion

See Section 2510A.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2. Apparatus

a. Self-contained conductivity instruments: Use an instrument capable of measuring conductivity with an error not exceeding 1% or 1 μmho/cm, whichever is greater.

b. Thermometer, capable of being read to the nearest 0.1°C and covering the range 23 to 27°C. Many conductivity meters are equipped to read an automatic temperature sensor.

c. Conductivity cell:

1) Platinum-electrode type—Conductivity cells containing platinized electrodes are available in either pipet or immersion form. Cell choice depends on expected range of conductivity. Experimentally check instrument by comparing instrumental results with true conductivities of the KCl solutions listed in Table 2510:I. Clean new cells, not already coated and ready for use, with chromic-sulfuric acid cleaning mixture [see Section 2580B.3*a*2)] and platinize the electrodes before use. Subsequently, clean and replatinize them whenever the readings become erratic, when a sharp end point cannot be obtained, or when inspection shows that any platinum black has flaked off. To platinize, prepare a solution of 1 g chloroplatinic acid, $H_2PtCl_6 \cdot 6H_2O$, and 12 mg lead acetate in 100 mL distilled water. A more concentrated solution reduces the time required to platinize electrodes and may be used when time is a factor, e.g., when the cell constant is 1.0/cm or more. Immerse electrodes in this solution and connect both to the negative terminal of a 1.5-V dry cell battery. Connect positive side of battery to a piece of platinum wire and dip wire into the solution. Use a current such that only a small quantity of gas is evolved. Continue electrolysis until both cell electrodes are coated with platinum black. Save platinizing solution for subsequent use. Rinse electrodes thoroughly and when not in use keep immersed in distilled water.

2) Nonplatinum-electrode type—Use conductivity cells containing electrodes constructed from durable common metals (stainless steel among others) for continuous monitoring and field studies. Calibrate such cells by comparing sample conductivity with results obtained with a laboratory instrument. Use properly designed and mated cell and instrument to minimize errors in cell constant. Very long meter leads can affect performance of a conductivity meter. Under such circumstances, consult the manufacturer's manual for appropriate correction factors if necessary.

3. Reagents

a. Conductivity water: Any of several methods can be used to prepare reagent-grade water. The methods discussed in Section 1080 are recommended. The conductivity should be small compared to the value being measured.

b. Standard potassium chloride solution, KCl, 0.0100*M:* Dissolve 745.6 mg anhydrous KCl in conductivity water and dilute to 1000 mL in a class A volumetric flask at 25°C and store in a CO_2-free atmosphere. This is the standard reference solution, which at 25°C has a conductivity of 1412 μmhos/cm. It is satisfactory for most samples when the cell has a constant between 1

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

and 2 cm^{-1}. For other cell constants, use stronger or weaker KCl solutions listed in Table 2510:I. Care must be taken when using KCl solutions less than 0.001*M*, which can be unstable because of the influence of carbon dioxide on pure water. For low conductivity standards, Standard Reference Material 3190, with a certified conductivity of 25.0 µS/cm ± 0.3 µS/cm, may be obtained from NIST. Store in a glass-stoppered borosilicate glass bottle.

4. Procedure

a. Determination of cell constant: Rinse conductivity cell with at least three portions of 0.01*M* KCl solution. Adjust temperature of a fourth portion to 25.0 ± 0.1°C. If a conductivity meter displays resistance, *R*, ohms, measure resistance of this portion and note temperature. Compute cell constant, *C:*

$$C, \text{ cm}^{-1} = (0.001412)(R_{\text{KCl}})[1 + 0.0191(t - 25)]$$

where:

R_{KCl} = measured resistance, ohms, and
t = observed temperature, °C.

Conductivity meters often indicate conductivity directly. Commercial probes commonly contain a temperature sensor. With such instruments, rinse probe three times with 0.0100*M* KCl, as above. Adjust temperature compensation dial to 0.0191 C^{-1}. With probe in standard KCl solution, adjust meter to read 1412 µmho/cm. This procedure automatically adjusts cell constant internal to the meter.

b. Conductivity measurement: Thoroughly rinse cell with one or more portions of sample. Adjust temperature of a final portion to about 25°C. Measure sample resistance or conductivity and note temperature to ±0.1°C.

5. Calculation

The temperature coefficient of most waters is only approximately the same as that of standard KCl solution; the more the temperature of measurement deviates from 25.0°C, the greater the uncertainty in applying the temperature correction. Report temperature-compensated conductivities as ‘‘µmho/cm 25.0°C.’’

a. When sample resistance is measured, conductivity at 25°C is:

$$k = \frac{(1\,000\,000)(C)}{R_m[1 + 0.0191(t - 25)]}$$

where:

k = conductivity, µmhos/cm,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

C = cell constant, cm^{-1},
R_m = measured resistance of sample, ohms, and
t = temperature of measurement.

b. When sample conductivity is measured without internal temperature compensation conductivity at 25°C is:

$$k, \mu mho/cm = \frac{(k_m)}{1 + 0.0191(t - 25)}$$

where:

k_m = measured conductivity in units of μmho/cm at t°C, and other units are defined as above.

For instruments with automatic temperature compensation and readout directly in μmho/cm or similar units, the readout automatically is corrected to 25.0°C. Report displayed conductivity in designated units.

6. Precision and Bias

The precision of commercial conductivity meters is commonly between 0.1 and 1.0%. Reproducibility of 1 to 2% is expected after an instrument has been calibrated with such data as is shown in Table 2510:I.

2520 SALINITY*#(36)

2520 A. Introduction

1. General Discussion

Salinity is an important unitless property of industrial and natural waters. It was originally conceived as a measure of the mass of dissolved salts in a given mass of solution. The experimental determination of the salt content by drying and weighing presents some difficulties due to the loss of some components. The only reliable way to determine the true or absolute salinity of a natural water is to make a complete chemical analysis. However, this method is time-consuming and cannot yield the precision necessary for accurate work. Thus, to determine salinity, one normally uses indirect methods involving the measurement of a physical property such as conductivity, density, sound speed, or refractive index. From an empirical relationship of salinity and the physical property detemined for a standard solution it is possible

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

to calculate salinity. The resultant salinity is no more accurate than the empirical relationship. The precision of the measurement of a physical property will determine the precision in salinity. Following are the precisions of various physical measurements and the resultant salinity presently attainable with commercial instruments:

Property	Precision of Measurement	Precision of Salinity
Conductivity	±0.0002	±0.0002
Density	$\pm 3 \times 10^{-6}$ g/cm^3	±0.004
Sound speed	±0.02 m/s	±0.01

Although conductivity has the greatest precision, it responds only to ionic solutes. Density, although less precise, responds to all dissolved solutes.

2. Selection of Method

In the past, the salinity of seawater was determined by hydrometric and argentometric methods, both of which were included in previous editions of *Standard Methods*. In recent years the conductivity (2520B) and density (2520C) methods have been used because of their high sensitivity and precision. These two methods are recommended for precise field and laboratory work.

3. Quality Assurance

Calibrate salinometer or densimeter against standards of KCl or standard seawater. Expected precision is better than ±0.01 salinity units with careful analysis and use of bracketing standards.

2520 B. Electrical Conductivity Method

1. Determination

See Conductivity, Section 2510. Because of its high sensitivity and ease of measurement, the conductivity method is most commonly used to determine salinity.[1] For seawater measurements use the Practical Salinity Scale 1978.[2-5] This scale was developed relative to a KCl solution. A seawater with a conductivity, C, at 15°C equal to that of a KCl solution containing a mass of 32.4356 g in a mass of 1 kg of solution is defined as having a practical salinity of 35. This value was determined as an average of three independent laboratory studies. The salinity dependence of the conductivity ratio, R_t, as a function of temperature (t °C, International Practical Temperature Scale 1968) of a given sample to a standard S= 35 seawater is used to determine the salinity

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$S = a_0 + a_1 R_t^{1/2} + a_2 R_t + a_3 R_t^{3/2} + a_4 R_t^2 + a_5 R_t^{5/2} + S$$

where S is given by

$$\Delta S = \left[\frac{t - 15}{1 + 0.0162\ (t - 15)}\right](b_0 + b_1 R_t^{1/2} + b_2 R_t + b_3 R_t^{3/2} + b_4 R_t^2 + b_5 R_t^{5/2})$$

and:

$a_0 = 0.0080$	$b_0 = 0.0005$
$a_1 = -0.1692$	$b_1 = -0.0056$
$a_2 = 25.3851$	$b_2 = -0.0066$
$a_3 = 14.0941$	$b_3 = -0.0375$
$a_4 = -7.0261$	$b_4 = 0.0636$
$a_5 = 2.7081$	$b_5 = -0.0144$

valid from S = 2 to 42, where:

$$R_t = \frac{C\ (\text{sample at } t)}{C\ (\text{KCl solution at } t)}.$$

To measure the conductivity, use a conductivity bridge calibrated with standard seawater*#(37) with a known conductivity relative to KCl, following manufacturer's instructions and the procedures noted in Section 2510. If the measurements are to be made in estuarine waters, make secondary calibrations of weight-diluted seawater of known conductivity to ensure that the bridge is measuring true conductivities.

The Practical Salinity Scale recently has been extended to low salinities[6] to give an equation that is valid from 0 to 40 salinity. The equation is:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$S = S_{PSS} - \frac{a_0}{1 + 1.5X + X^2} - \frac{b_0 f(t)}{1 + Y^{1/2} + Y^{3/2}}$$

where:

S_{PSS} = value determined from the Practical Salinity Scale given earlier,
a_0 = 0.008,
b_0 = 0.0005,
X = $400R_t$,
Y = $100R_t$, and
f(t) = (t–15)/[1 + 0.0162 (t–15)]

The practical salinity breaks with the old salinity-chlorinity relationship, S = l.806 55 Cl. Although the scale can be used for estuarine waters[7-10] and brines[11-13], there are limitations.[12,14-22]

2. References

1. LEWIS, E.L. 1978. Salinity: its definition and calculation. *J. Geophys. Res.* 83:466.
2. LEWIS, E.L. 1980. The practical salinity scale 1978 and its antecedents. *IEEEJ. Oceanic Eng.* OE-5:3.
3. BRADSHAW, A.L. & K.E. SCHLEICHER. 1980. Electrical conductivity of seawater. *IEEE J. Oceanic Eng.*OE-5:50.
4. CULKIN, F. & N.D. SMITH. 1980. Determination of the concentration of potassium chloride solution having the same electrical conductivity, at 15°C and infinite frequency, as standard seawater of salinity 35.000 $^0/_{00}$ (Chlorinity 19.37394 $^0/_{00}$.*IEEE J. Oceanic Eng*. OE-5:22.
5. DAUPHINEE, T.M., J. ANCSIN, H.P. KLEIN & M.J. PHILLIPS. 1980. The effect of concentration and temperature on the conductivity ratio of potassium chloride solutions to standard seawater of salinity 35 $^0/_{00}$ (Cl.19.3740) at 15°C and 24°. *IEEE J. Oceanic Eng.*OE-5:17.
6. HILL, K.D., T.M. DAUPHINEE & D.J. WOODS. 1986. The Extension of the Practical Salinity Scale 1978 to low salinities. *IEEE J. Oceanic Eng*. OE-11:109.
7. MILLERO, F.J. 1975. The physical chemistry of estuarines. *In* T.M. Church, ed. Marine Chemistry in the Coastal Environment. American Chemical Soc. Symposium, Ser. 18.
8. MILLERO, F.J. 1978. The physical chemistry of Baltic Sea waters. *Thalassia Jugoslavica* 14:1.
9. MILLERO, F.J. 1984. The conductivity-salinity-chlorinity relationship for estuarine

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

waters. *Limnol. Oceanogr*. 29:1318.

10. MILLERO, F.J. & K. KREMLING. 1976. The densities of Baltic Sea waters. *Deep-Sea Res*. 23:1129.
11. FERNANDEZ, F., F. VAZQUEZ & F.J. MILLERO. 1982. The density and composition of hypersaline waters of a Mexican lagoon. *Limnol. Oceanogr*. 27:315.
12. MILLERO, F.J. & P.V.CHETIRKIN. 1980. The density of Caspian Sea waters. *Deep-Sea Res*. 27:265.
13. MILLERO, F.J., A. MUCCI, J. ZULLIG & P. CHETIRKIN. 1982. The density of Red Sea brines. *Mar. Chem*. 11:477.
14. BREWER, P.G. & A. BRADSHAW. 1975. The effect of non-ideal composition of seawater on salinity and density. *J. Mar. Res*. 33:155.
15. CONNORS, D.N. & D.R. KESTER. 1974. Effect of major ion variations in the marine environment on the specific gravity-conductivity-chlorinity-salinity relationship. *Mar. Chem*. 2:301.
16. POISSON, A. 1980. The concentration of the KCl solution whose conductivity is that of standard seawater (35 $^{0}/_{00}$) at 15°C. *IEEE J. Oceanic Eng*.OE-5:24.
17. POISSON, A. 1980. Conductivity/salinity/temperature relationship of diluted and concentrated standard seawater. *IEEE J.Oceanic Eng*. OE-5:17.
18. MILLERO, F.J., A.GONZALEZ & G.K. WARD. 1976. The density of seawater solutions at one atmosphere as a function of temperature and salinity. *J. Mar. Res*. 34:61.
19. MILLERO, F.J., A. GONZALEZ, P.G. BREWER & A.BRADSHAW. 1976. The density of North Atlantic and North Pacific deep waters. *Earth Planet Sci. Lett*. 32:468.
20. MILLERO, F.J., D. LAWSON & A.GONZALEZ. 1976. The density of artificial river and estuary waters. *J. Geophys. Res*. 81:1177.
21. MILLERO, F.J., P. CHETIRKIN & F. CULKIN. 1977. The relative conductivity and density of standard seawaters. *Deep-Sea Res*. 24:315.
22. MILLERO, F.J., D. FORSHT, D. MEANS, J. GRIESKES & K. KENYON. 1977. The density of North Pacific ocean waters. *J.Geophys. Res*. 83:2359.

2520 C. Density Method

1. Determination

With a precise vibrating flow densimeter, it is possible to make rapid measurements of the density of natural waters. The measurements are made bypassing the sample through a vibrating tube encased in a constant-temperature jacket. The solution density (ρ) is proportional to the square of the period of the vibration (τ).

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\rho = A + B\tau^2$$

where *A* and *B* are terms determined by calibration, *B* being determined by calibration with a densimeter with standard seawater. The difference between the density of the sample and that of pure water is given by:

$$\rho - \rho_0 = B(\tau^2 - \tau_0^2)$$

where τ and τ_0 are, respectively, the periods of the sample and water. The system is calibrated with two solutions of known density. Follow manufacturer's recommendations for calibration. These two solutions can be nitrogen gas and water or standard seawater and water. The salinity of the sample can be determined from the 1 atm international equation of state for seawater. This equation relates $(\rho - \rho_0)$ to the practical salinity (*S*) as a function of temperature.[1]

$$\rho\ (\text{kg/m}^3) = \rho_0 + AS + BS^{3/2} + CS^2$$

where:

$$\begin{aligned} A = {} & 8.244\,93 \times 10^{-1} - 4.0899 \times 10^{-3} t \\ & + 7.6438 \times 10^{-5} t^2 - 8.2467 \times 10^{-7} t^3 + 5.3875 \times 10^{-9} t^4, \\ B = {} & -5.724\,66 \times 10^{-3} + 1.0227 \times 10^{-4} t - 1.6546 \times 10^{-6} t^2, \\ C = {} & 4.8314 \times 10^{-4}, \end{aligned}$$

and the density of water is given by:

$$\begin{aligned} \rho_0 = {} & 999.842\,594 + 6.793\,952 \times 10^{-2} t - 9.095\,290 \times 10^{-3} t^2 \\ & + 1.001\,685 \times 10^{-4} t^3 - 1.120\,083 \times 10^{-6} t^4 + 6.536\,332 \\ & \times 10^{-9} t^5 \end{aligned}$$

Perform simple iteration by adjusting *S* until it gives the measured $\rho - \rho_0$ at a given temperature. If the measurements are made at 25°C, the salinity can be determined from the following equation:

$$S = 1.3343\,(\rho - \rho_0) + 2.155\,306 \times 10^{-4}\,(\rho - \rho_0)^2 - 1.171\,16 \times 10^{-5}\,(\rho - \rho_0)^3$$

which has a $\tau = 0.0012$ in *S*. Approximate salinities also can be determined from densities or specific gravities obtained with a hydrometer at a given temperature (Section 210B, 16th edition).

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2. Reference

1. MILLERO, F.J. & A. POISSON. 1981. International one-atmosphere equation of state of seawater. *Deep Sea Res.* 28:625.

2520 D. Algorithm of Practical Salinity

Because all practical salinity measurements are carried out in reference to the conductivity of standard seawater (corrected to $S = 35$), it is the quantity R_t that will be available for salinity calculations. R_t normally is obtained directly by laboratory salinometers, but *in situ* measurements usually produce the quantity R, the ratio of the *in situ* conductivity to the standard conductivity at $S = 35$, $t = 15°C$, $p = 0$ (where p is the pressure above one standard atmosphere and the temperature is on the 1968 International Temperature Scale). R is factored into three parts, i.e.,

$$R = R_p r_t R_t$$

where:

R_p = ratio of *in situ* conductivity to conductivity of the same sample at the same temperature, but at $p = 0$ and r_t = ratio of conductivity of reference seawater, having a practical salinity of 35, at temperature t, to its conductivity at $t = 15°C$. From R_p and r_t calculate R_t using the *in situ* results, i.e.,

$$R_t = \frac{R}{R_p r_t}$$

R_p and r_t can be expressed as functions of the numerical values of the *in situ* parameters, R, t, and p, when t is expressed in °C and p in bars (10^5 Pa), as follows:

$$R_p = 1 + \frac{p(e_1 + e_2 p + e_3 p^2)}{1 + d_1 t + d_2 t^2 + (d_3 + d_4 t)R}$$

where:

$$e_1 = 2.070 \times 10^{-4}, \qquad d_1 = 3.426 \times 10^{-2},$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$e_2 = -6.370 \times 10^{-8}$, $d_2 = 4.464 \times 10^{-4}$,
$e_3 = 3.989 \times 10^{-12}$, $d_3 = 4.215 \times 10^{-1}$,
and $d_4 = -3.107 \times 10^{-3}$,

and

$$r_t = c_0 + c_1 t + c_2 t^2 + c_3 t^3 + c_4 t^4$$

where:

$c_0 = 0.676\ 609\ 7$,
$c_1 = 2.005\ 64 \times 10^{-2}$,
$c_2 = 1.104\ 259 \times 10^{-4}$,
$c_3 = -6.9698 \times 10^{-7}$, and
$c_4 = 1.0031 \times 10^{-9}$.

2530 FLOATABLES#(38)*

2530 A. Introduction

One important criterion for evaluating the possible effect of waste disposal into surface waters is the amount of floatable material in the waste. Two general types of floating matter are found: particulate matter that includes ‘‘grease balls,’’ and liquid components capable of spreading as a thin, highly visible film over large areas. Floatable material in wastewaters is important because it accumulates on the surface, is often highly visible, is subject to wind-induced transport, may contain pathogenic bacteria and/or viruses associated with individual particles, and can significantly concentrate metals and chlorinated hydrocarbons such as pesticides and PCBs. Colloidally dispersed oil and grease behave like other dispersed organic matter and are included in the material measured by the COD, BOD, and TOC tests. The floatable oil test indicates the readily separable fraction. The results are useful in designing oil and grease separators, in ascertaining the efficiency of operating separators, and in monitoring raw and treated wastewater streams. Many cities and districts have specified floatable oil and grease limits for wastewater discharged to sewers.

2530 B. Particulate Floatables (GENERAL)

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. Discussion

a. Principle: This method depends on the gravity separation of particles having densities less than that of the surrounding water. Particles that collect on the surface and can be filtered out and dried at 103 to 105°C are defined by this test as floatable particles.

b. Application: This method is applicable to raw wastewater, treated primary and secondary effluent, and industrial wastewater. Because of the limited sensitivity, it is not applicable to tertiary effluents or receiving waters, whether freshwater or seawater.

c. Precautions: Even slight differences in sampling and handling during and after collection can give large differences in the measured amount of floatable material. Additionally, uniformity of the TFE#(39)* coating of the separation funnel is critical to obtaining reliable results. For a reproducible analysis treat all samples uniformly, preferably by mixing them in a standard manner, before flotation and use consistently prepared separation funnels as much as possible. Because the procedure relies on the difference in specific gravity between the liquid and the floating particles, temperature variations may affect the results. Conduct the test at a constant temperature the same as that of the receiving water body, and report temperature with results.

d. Minimum detectable concentration: The minimum reproducible detectable concentration is approximately 1 mg/L. Although the minimum levels that can be measured are below 1 mg/ L, the results are not meaningful within the current established accuracy of the test.

2. Apparatus

a. Floatables sampler with mixer: Use a metal container of at least 5 L capacity equipped with a propeller mixer on a separate stand (Figure 2530:1), and with a 20-mm-ID bottom outlet cocked at an angle of 45° to the container wall in the direction of fluid movement. The 45° angle assures that even large particles will flow from the container into the flotation funnels where the sample is withdrawn. Fit exterior of bottom outlet with a short piece of tubing and a pinch clamp to allow unrestricted flow through the outlet. Coat inside of container with TFE as uniformly as possible, using a TFE spray to prevent oil and grease from sticking to the surface.

b. Flotation funnel: Use an Imhoff cone provided with a TFE stopcock at the bottom and extended at the top to a total volume of 3.5 L (Figure 2530:2). Coat inside of flotation funnel with TFE as uniformly as possible to prevent floatable grease particles sticking to the sides. Mount flotation funnels as shown in Figure 2530:3 with a light behind the bottom of the funnels to aid in reading levels.

c. Filter holder: Coat inside of top of a standard 500-mL membrane filter holder with TFE, again taking all possible precautions to obtain a uniform TFE coating.

d. Filters, glass fiber, fine porosity.#(40)†

e. Vacuum flask, 500 mL.

f. TFE coating: Follow instructions that accompany commercially available coating kits. Alternatively, have necessary glassware coated commercially. Uniform coatings are key to the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

reliability of the test results, but in practice are difficult to obtain.

3. Procedure

a. Preparation of glass fiber filters: See Section 2540D.3*a*.

b. Sample collection and treatment: Collect sample in the floatables sampler at a point of complete mixing, transport to the laboratory, and place 3.0 L in the flotation funnel within 2 h after sample collection to minimize changes in the floatable material. While the flotation funnel is being filled, mix sampler contents with a small propeller mixer. Adjust mixing speed to provide uniform distribution of floating particles throughout the liquid but avoid extensive air entrapment through formation of a large vortex.

c. Correction for density and for concentration effects: When a receiving water has a density and ion concentration different from that of the waste, adjust sample density and ion concentration to that of the receiving water. For example, if the receiving water is ocean water, place 1.5 L sample in flotation funnel and add 1.5 L filtered seawater from the receiving area together with mixture of 39.8 g NaCl, 8.0 g $MgCl_2 \cdot 6H_2O$, and 2.3 g $CaCl_2 \cdot 2H_2O$. The final mixture contains the amount of floatables in a 1.5-L sample in a medium of approximately the same density and ion concentration as seawater.

d. Flotation: Mix flotation funnel contents at 40 rpm for 15 min using a paddle mixer (Figure 2530:3). Let settle for 5 min, mix at 100 rpm for 1 min, and let settle for 30 min. Discharge 2.8 L through bottom stopcock at a rate of 500 mL/min. Do not disturb the sample surface in the flotation funnel during discharge. With distilled water from a wash bottle, wash down any floatable material sticking to sides of stirring paddle and funnel. Let remaining 200 mL settle for 15 min and discharge settled solids and liquid down to the 40-mL mark on the Imhoff cone. Let settle again for 10 min and discharge until only 10 mL liquid and the floating particles remain in funnel. Add 500 mL distilled water and stir by hand to separate entrapped settleable particles from the floatable particles. Let settle for 15 min, then discharge to the 40-mL mark. Let settle for 10 min, then discharge dropwise to the 10-mL mark. Filter remaining 10 mL and floating particles through a preweighed glass fiber filter. Wash sides of flotation funnel with distilled water to transfer all floatable material to filter.

e. Weighing: Dry and weigh glass fiber filter at 103 to 105° C for exactly 2 h (see Section 2540D.3*c*).

4. Calculation

$$\text{mg particulate floatables/L} = \frac{(A - B)}{C}$$

where:

A = weight of filter + floatables, mg,
B = weight of filter, mg, and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

C = sample volume, L. (Do not include volume used for density or concentration correction, if used.)

5. Precision and Bias

Precision varies with the concentration of suspended matter in the sample. There is no completely satisfactory procedure for determining the bias of the method for wastewater samples but approximate recovery can be determined by running a second test for floatables on all water discharged throughout the procedure, with the exception of the last 10 mL. Precision and bias are summarized in Table 2530:I. Experience with the method at one municipal treatment plant indicates that the practical lower limit of detection is approximately 1 mg/L.

6. Bibliography

HEUKELEKIAN, H. & J. BALMAT. 1956. Chemical composition of the particulate fractions of domestic sewage. *Sewage Ind. Wastes* 31:413.

ENGINEERING-SCIENCE, INC. 1965. Determination and Removal of Floatable Material from Waste Water. Rep. for U.S. Public Health Serv. contracts WPD 12-01 (R1)-63 and WPD 12-02-64, Engineering-Science, Inc., Arcadia & Oakland, Calif.

HUNTER, J.V. & H. HEUKELEKIAN. 1965. Composition of domestic sewage fractions. *J. Water Pollut. Control Fed.* 37:1142.

NUSBAUM I. & L. BURTMAN. 1965. Determination of floatable matter in waste discharges. *J. Water Pollut. Control Fed.* 37:577.

SCHERFIG, J. & H. F. LUDWIG. 1967. Determination of floatables and hexane extractables in sewage. *In* Advances in Water Pollution Research, Vol. 3, p. 217, Water Pollution Control Federation, Washington, D.C.

SELLECK, R.E., L. W. BRACEWELL & R. CARTER. 1974. The Significance and Control of Wastewater Floatables in Coastal Waters. Rep. for U.S. Environmental Protection Agency contract R-800373, SERL Rep. No. 74-1, Sanitary Engineering Research Lab., Univ. California, Berkeley.

BRACEWELL, L.W. 1976. Contribution of Wastewater Discharges to Surface Films and Other Floatables on the Ocean Surface. Thesis, Univ. California, Berkeley.

BRACEWELL, L.W., R.E. SELLECK & R. CARTER. 1980. Contribution of wastewater discharges to ocean surface particulates. *J. Water Pollut. Control Fed.* 52:2230.

2530 C. Trichlorotrifluoroethane-Soluble Floatable Oil and Grease (GENERAL)

1. Discussion

The floatable oil and grease test does not measure a precise class of substances; rather, the results are determined by the conditions of the test. The fraction measured includes oil and grease, both floating and adhering to the sides of the test vessel. The adhering and the floating portions are of similar practical significance because it is assumed that most of the adhering

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

portion would otherwise float under receiving water conditions. The results have been found to represent well the amount of oil removed in separators having overflow rates equivalent to test conditions.

2. Apparatus

a. Floatable oil tube (Figure 2530:4): Before use, carefully clean tube by brushing with a mild scouring power. Water must form a smooth film on inside of cleaned glass. Do not use lubricant on stopcock.

b. Conical flask, 300 mL.

3. Reagents

a. 1,1,2-trichloro-1,2,2-trifluoroethane#(41)*: See Section 5520B.3*b*.

b. Hydrochloric acid, HCl, 6*N*.

c. Filter paper.#(42)†

4. Procedure

a. Sampling: Collect samples at a place where there is a strong turbulence in the water and where floating material is not trapped at the surface. Fill floatable oil tube to mark by dipping into water. *Do not use samples taken to the laboratory in a bottle, because oil and grease cannot be redispersed to their original condition.*

b. Flotation: Support tube in a vertical position. Start flotation period at sampling site immediately after filling tube. The standard flotation time is 30 min. If a different time is used, state this variation in reporting results. At end of flotation period, discharge the first 900 mL of water carefully through bottom stopcock, stopping before any surface oil or other floating material escapes. Rotate tube slightly back and forth about its vertical axis to dislodge sludge from sides, and let settle for 5 min. Completely discharge sludge that has settled to the bottom or that comes down from the sides with the liquid. Scum on top of the liquid may mix with the water as it moves down the tube. If mixing occurs, stop drawing off water before any floatables have been lost. Let settle for 5 min before withdrawing remainder of water. After removing water, return tube to laboratory to complete test.

c. Extraction: Acidify to pH 2 or lower with a few drops of 6*N* HCl, add 50 to 100 mL trichlorotrifluoroethane, and shake vigorously. Let settle and draw off solvent into a clean dry beaker. Filter solvent through a dry filter paper into a tared 300-mL conical flask, taking care not to get any water on filter paper. Add a second 50-mL portion of trichlorotrifluoroethane and repeat extraction, settling, and filtration into the same 300-mL flask. A third extraction may be needed if the amount of floatables in sample exceeds 4 mg/L. Wash filter paper carefully with fresh solvent discharged from a wash bottle with a fine tip. Evaporate solvent from flask as described in Section 5520B.4. For each solvent batch, determine weight of residue left after evaporation from the same volume as used in the analysis.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

5. Calculations

Report results as ‘‘soluble floatable oil and grease, 30 min (or other specified) settling time, mg/L.’’

Trichlorotrifluoroethane-soluble floatable oil and grease, 30 min settling time, mg/L

$$= \frac{(A - B) \times 1000}{\text{mL sample}}$$

where:

A = total gain in weight of tared flask, mg, and
B = calculated residue from solvent blank of the same volume as that used in the test, mg.

6. Precision and Bias

There is no standard against which bias of this test can be determined. Variability of replicates is influenced by sample heterogeneity. If large grease particles are present, the element of chance in sampling may be a major factor. One municipal wastewater discharge and two meat-packing plant discharges, both containing noticeable particles of grease, were analyzed in triplicate. Averages for the three wastewaters were 48, 57, and 25 mg/L; standard deviations averaged 11%. An oil refinery made duplicate determinations of its separator effluent on 15 consecutive days, obtaining results ranging from 5.1 to 11.2 mg/L. The average difference between pairs of samples was 0.37 mg/L.

7. Bibliography

POMEROY, R.D. 1953. Floatability of oil and grease in wastewaters. *Sewage Ind. Wastes* 25:1304.

2540 SOLIDS#(43)*

2540 A. Introduction

Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. For these reasons, a limit of 500 mg dissolved solids/L is desirable for drinking waters. Highly mineralized waters also are unsuitable for many industrial applications. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. Definitions

‘‘Total solids’’ is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids includes ‘‘total suspended solids,’’ the portion of total solids retained by a filter, and ‘‘total dissolved solids,’’ the portion that passes through the filter.

The type of filter holder, the pore size, porosity, area, and thickness of the filter and the physical nature, particle size, and amount of material deposited on the filter are the principal factors affecting separation of suspended from dissolved solids. ‘‘Dissolved solids’’ is the portion of solids that passes through a filter of 2.0 μm (or smaller) nominal pore size under specified conditions. ‘‘Suspended solids’’ is the portion retained on the filter.

‘‘Fixed solids’’ is the term applied to the residue of total, suspended, or dissolved solids after heating to dryness for a specified time at a specified temperature. The weight loss on ignition is called ‘‘volatile solids.’’ Determinations of fixed and volatile solids do not distinguish precisely between inorganic and organic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts. Better characterization of organic matter can be made by such tests as total organic carbon (Section 5310), BOD (Section 5210), and COD (Section 5220).

‘‘Settleable solids’’ is the term applied to the material settling out of suspension within a defined period. It may include floating material, depending on the technique (Section 2540F.3*b*).

2. Sources of Error and Variability

Sampling, subsampling, and pipeting two-phase or three-phase samples may introduce serious errors. Make and keep such samples homogeneous during transfer. Use special handling to insure sample integrity when subsampling. Mix small samples with a magnetic stirrer. If suspended solids are present, pipet with wide-bore pipets. If part of a sample adheres to the sample container, consider this in evaluating and reporting results. Some samples dry with the formation of a crust that prevents water evaporation; special handling is required to deal with this. Avoid using a magnetic stirrer with samples containing magnetic particles.

The temperature at which the residue is dried has an important bearing on results, because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating. Each sample requires close attention to desiccation after drying. Minimize opening desiccator because moist air enters. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

Residues dried at 103 to 105°C may retain not only water of crystallization but also some mechanically occluded water. Loss of CO_2 will result in conversion of bicarbonate to carbonate. Loss of organic matter by volatilization usually will be very slight. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Residues dried at 180 ± 2°C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of CO_2 results from conversion of bicarbonates to carbonates and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost. In general, evaporating and drying water samples at 180°C yields values for dissolved solids closer to those obtained through summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.

To rinse filters and filtered solids and to clean labware use Type III water. Special samples may require a higher quality water; see Section 1080.

Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.

To aid in quality assurance, analyze samples in duplicate. Dry samples to constant weight if possible. This entails multiple drying-cooling-weighing cycles for each determination.

Analyses performed for some special purposes may demand deviation from the stated procedures to include an unusual constituent with the measured solids. Whenever such variations of technique are introduced, record and present them with the results.

3. Sample Handling and Preservation

Use resistant-glass or plastic bottles, provided that the material in suspension does not adhere to container walls. Begin analysis as soon as possible because of the impracticality of preserving the sample. Refrigerate sample at 4°C up to the time of analysis to minimize microbiological decomposition of solids. Preferably do not hold samples more than 24 h. In no case hold sample more than 7 d. Bring samples to room temperature before analysis.

4. Selection of Method

Methods B through F are suitable for the determination of solids in potable, surface, and saline waters, as well as domestic and industrial wastewaters in the range up to 20 000 mg/L.

Method G is suitable for the determination of solids in sediments, as well as solid and semisolid materials produced during water and wastewater treatment.

5. Bibliography

THERIAULT, E.J. & H.H. WAGENHALS. 1923. Studies of representative sewage plants. *Pub. Health Bull.* No. 132.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Methods for Chemical Analysis of Water and Wastes. Publ. 600/4-79-020, rev. Mar. 1983. Environmental Monitoring and Support Lab., U.S. Environmental Protection Agency, Cincinnati, Ohio.

2540 B. Total Solids Dried at 103–105°C

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. General Discussion

a. Principle: A well-mixed sample is evaporated in a weighed dish and dried to constant weight in an oven at 103 to 105°C. The increase in weight over that of the empty dish represents the total solids. The results may not represent the weight of actual dissolved and suspended solids in wastewater samples (see above).

b. Interferences: Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Exclude large, floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue (see Section 2540A.2).

2. Apparatus

a. Evaporating dishes: Dishes of 100-mL capacity made of one of the following materials:

1) Porcelain, 90-mm diam.

2) Platinum—Generally satisfactory for all purposes.

3) High-silica glass.#(44)*

b. Muffle furnace for operation at 550°C.

c. Steam bath.

d. Desiccator, provided with a desiccant containing a color indicator of moisture concentration or an instrumental indicator.

e. Drying oven, for operation at 103 to 105°C.

f. Analytical balance, capable of weighing to 0.1 mg.

g. Magnetic stirrer with TFE stirring bar.

h. Wide-bore pipets.#(45)†

i. Graduated cylinder.

j. Low-form beaker.#(46)‡

3. Procedure

a. Preparation of evaporating dish: If volatile solids are to be measured ignite clean evaporating dish at 550°C for 1 h in a muffle furnace. If only total solids are to be measured, heat clean dish to 103 to 105°C for 1 h. Store and cool dish in desiccator until needed. Weigh immediately before use.

b. Sample analysis: Choose a sample volume that will yield a residue between 2.5 and 200 mg. Pipet a measured volume of well-mixed sample, during mixing, to a preweighed dish. For homogeneous samples, pipet from the approximate midpoint of the container but not in the vortex. Choose a point both middepth and midway between wall and vortex. Evaporate to

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

dryness on a steam bath or in a drying oven. Stir sample with a magnetic stirrer during transfer. If necessary, add successive sample portions to the same dish after evaporation. When evaporating in a drying oven, lower temperature to approximately 2°C below boiling to prevent splattering. Dry evaporated sample for at least 1 h in an oven at 103 to 105°C, cool dish in desiccator to balance temperature, and weigh. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained, or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. When weighing dried sample, be alert to change in weight due to air exposure and/or sample degradation. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

4. Calculation

$$\text{mg total solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of dried residue + dish, mg, and
B = weight of dish, mg.

5. Precision

Single-laboratory duplicate analyses of 41 samples of water and wastewater were made with a standard deviation of differences of 6.0 mg/L.

6. Bibliography

SYMONS, G.E. & B. MOREY. 1941. The effect of drying time on the determination of solids in sewage and sewage sludges. *Sewage Works J.* 13:936.

2540 C. Total Dissolved Solids Dried at 180°C

1. General Discussion

a. Principle: A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures.

The results may not agree with the theoretical value for solids calculated from chemical analysis of sample (see above). Approximate methods for correlating chemical analysis with dissolved solids are available.[1] The filtrate from the total suspended solids determination (Section 2540D) may be used for determination of total dissolved solids.

b. Interferences: See Section 2540A.2 and Section 2540B.1. Highly mineralized waters

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

with a considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

2. Apparatus

Apparatus listed in Section 2540B.2*a* - h is required, and in addition:

a. Glass-fiber filter disks#(47)* without organic binder.

b. Filtration apparatus: One of the following, suitable for the filter disk selected:

1) *Membrane filter funnel.*

2) *Gooch crucible,* 25-mL to 40-mL capacity, with Gooch crucible adapter.

3) *Filtration apparatus* with reservoir and coarse (40- to 60-µm) fritted disk as filter support.#(48)†

c. Suction flask, of sufficient capacity for sample size selected.

d. Drying oven, for operation at 180 ± 2°C.

3. Procedure

a. Preparation of glass-fiber filter disk: If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up into filtration apparatus. Apply vacuum and wash disk with three successive 20-mL volumes of reagent-grade water. Continue suction to remove all traces of water. Discard washings.

b. Preparation of evaporating dish: If volatile solids are to be measured, ignite cleaned evaporating dish at 550°C for 1 h in a muffle furnace. If only total dissolved solids are to be measured, heat clean dish to 180 ± 2°C for 1 h in an oven. Store in desiccator until needed. Weigh immediately before use.

c. Selection of filter and sample sizes: Choose sample volume to yield between 2.5 and 200 mg dried residue. If more than 10 min are required to complete filtration, increase filter size or decrease sample volume.

d. Sample analysis: Stir sample with a magnetic stirrer and pipet a measured volume onto a glass-fiber filter with applied vacuum. Wash with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness on a steam bath or in a drying oven. If necessary, add successive portions to the same dish after evaporation. Dry evaporated sample for at least 1 h in an oven at 180 ± 2°C, cool in a desiccator to balance temperature, and weigh. Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

average weight. If volatile solids are to be determined, follow procedure in Section 2540E.

4. Calculation

$$\text{mg total dissolved solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of dried residue + dish, mg, and
B = weight of dish, mg.

5. Precision

Single-laboratory analyses of 77 samples of a known of 293 mg/L were made with a standard deviation of differences of 21.20 mg/L.

6. Reference

1. SOKOLOFF, V.P. 1933. Water of crystallization in total solids of water analysis. *Ind. Eng. Chem.*, Anal. Ed. 5:336.

7. Bibliography

HOWARD, C.S. 1933. Determination of total dissolved solids in water analysis. *Ind. Eng. Chem.*, Anal. Ed. 5:4.

U.S. GEOLOGICAL SURVEY. 1974. Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases. Techniques of Water-Resources Investigations, Book 5, Chap. A1. U.S. Geological Surv., Washington, D.C.

2540 D. Total Suspended Solids Dried at 103–105°C

1. General Discussion

a. Principle: A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, it may be necessary to increase the diameter of the filter or decrease the sample volume. To obtain an estimate of total suspended solids, calculate the difference between total dissolved solids and total solids.

b. Interferences: See Section 2540A.2 and Section 2540B.1. Exclude large floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not representative. Because excessive residue on the filter may form a

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

water-entrapping crust, limit the sample size to that yielding no more than 200 mg residue. For samples high in dissolved solids thoroughly wash the filter to ensure removal of dissolved material. Prolonged filtration times resulting from filter clogging may produce high results owing to increased colloidal materials captured on the clogged filter.

2. Apparatus

Apparatus listed in Section 2540B.2 and Section 2540C.2 is required, except for evaporating dishes, steam bath, and 180°C drying oven. In addition:

Aluminum weighing dishes.

3. Procedure

a. Preparation of glass-fiber filter disk: If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up in filtration apparatus. Apply vacuum and wash disk with three successive 20-mL portions of reagent-grade water. Continue suction to remove all traces of water, turn vacuum off, and discard washings. Remove filter from filtration apparatus and transfer to an inert aluminum weighing dish. If a Gooch crucible is used, remove crucible and filter combination. Dry in an oven at 103 to 105°C for 1 h. If volatile solids are to be measured, ignite at 550°C for 15 min in a muffle furnace. Cool in desiccator to balance temperature and weigh. Repeat cycle of drying or igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less. Store in desiccator until needed.

b. Selection of filter and sample sizes: Choose sample volume to yield between 2.5 and 200 mg dried residue. If volume filtered fails to meet minimum yield, increase sample volume up to 1 L. If complete filtration takes more than 10 min, increase filter diameter or decrease sample volume.

c. Sample analysis: Assemble filtering apparatus and filter and begin suction. Wet filter with a small volume of reagent-grade water to seat it. Stir sample with a magnetic stirrer at a speed to shear larger particles, if practical, to obtain a more uniform (preferably homogeneous) particle size. Centrifugal force may separate particles by size and density, resulting in poor precision when point of sample withdrawal is varied. While stirring, pipet a measured volume onto the seated glass-fiber filter. For homogeneous samples, pipet from the approximate midpoint of container but not in vortex. Choose a point both middepth and midway between wall and vortex. Wash filter with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Samples with high dissolved solids may require additional washings. Carefully remove filter from filtration apparatus and transfer to an aluminum weighing dish as a support. Alternatively, remove the crucible and filter combination from the crucible adapter if a Gooch crucible is used. Dry for at least 1 h at 103 to 105°C in an oven, cool in a desiccator to balance temperature, and weigh. Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until the weight change is less than 4% of the previous weight or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

within 5% of their average weight. If volatile solids are to be determined, treat the residue according to 2540E.

4. Calculation

$$\text{mg total suspended solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of filter + dried residue, mg, and
B = weight of filter, mg.

5. Precision

The standard deviation was 5.2 mg/L (coefficient of variation 33%) at 15 mg/L, 24 mg/L (10%) at 242 mg/L, and 13 mg/L (0.76%) at 1707 mg/L in studies by two analysts of four sets of 10 determinations each.

Single-laboratory duplicate analyses of 50 samples of water and wastewater were made with a standard deviation of differences of 2.8 mg/L.

6. Bibliography

DEGEN, J. & F.E. NUSSBERGER. 1956. Notes on the determination of suspended solids. *Sewage Ind. Wastes* 28:237.

CHANIN, G., E.H. CHOW, R.B. ALEXANDER & J. POWERS. 1958. Use of glass fiber filter medium in the suspended solids determination. *Sewage Ind. Wastes* 30:1062.

NUSBAUM, I. 1958. New method for determination of suspended solids. *Sewage Ind. Wastes* 30:1066.

SMITH, A.L. & A.E. GREENBERG. 1963. Evaluation of methods for determining suspended solids in wastewater. *J. Water Pollut. Control Fed.* 35:940.

WYCKOFF, B.M. 1964. Rapid solids determination using glass fiber filters. *Water Sewage Works* 111:277.

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT. 1975. A Preliminary Review of Analytical Methods for the Determination of Suspended Solids in Paper Industry Effluents for Compliance with EPA-NPDES Permit Terms. Spec. Rep. No. 75-01. National Council of the Paper Industry for Air & Stream Improvement, New York, N.Y.

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT. 1977. A Study of the Effect of Alternate Procedures on Effluent Suspended Solids Measurement. Stream Improvement Tech. Bull. No. 291, National Council of the Paper Industry for Air & Stream Improvement, New York, N.Y.

TREES, C.C. 1978. Analytical analysis of the effect of dissolved solids on suspended solids

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

determination. *J. Water Pollut. Control Fed.* 50:2370.

2540 E. Fixed and Volatile Solids Ignited at 550°C

1. General Discussion

a. Principle: The residue from Method B, C, or D is ignited to constant weight at 550°C. The remaining solids represent the fixed total, dissolved, or suspended solids while the weight lost on ignition is the volatile solids. The determination is useful in control of wastewater treatment plant operation because it offers a rough approximation of the amount of organic matter present in the solid fraction of wastewater, activated sludge, and industrial wastes.

b. Interferences: Negative errors in the volatile solids may be produced by loss of volatile matter during drying. Determination of low concentrations of volatile solids in the presence of high fixed solids concentrations may be subject to considerable error. In such cases, measure for suspect volatile components by another test, for example, total organic carbon (Section 5310). Highly alkaline residues may react with silica in sample or silica-containing crucibles.

2. Apparatus

See Section 2540B.2, Section 2540C.2, and Section 2540D.2.

3. Procedure

Ignite residue produced by Method 2540B, C, or D to constant weight in a muffle furnace at a temperature of 550°C. Ignite a blank glass fiber filter along with samples. Have furnace up to temperature before inserting sample. Usually, 15 to 20 min ignition are required for 200 mg residue. However, more than one sample and/or heavier residues may overtax the furnace and necessitate longer ignition times. Let dish or filter disk cool partially in air until most of the heat has been dissipated. Transfer to a desiccator for final cooling in a dry atmosphere. Do not overload desiccator. Weigh dish or disk as soon as it has cooled to balance temperature. Repeat cycle of igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight. Weight loss of the blank filter is an indication of unsuitability of a particular brand or type of filter for this analysis.

4. Calculation

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\text{mg volatile solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

$$\text{mg fixed solids/L} = \frac{(B - C) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of residue + dish before ignition, mg,
B = weight of residue + dish or filter after ignition, mg, and
C = weight of dish or filter, mg.

5. Precision

The standard deviation was 11 mg/L at 170 mg/L volatile total solids in studies by three laboratories on four samples and 10 replicates. Bias data on actual samples cannot be obtained.

2540 F. Settleable Solids

1. General Discussion

Settleable solids in surface and saline waters as well as domestic and industrial wastes may be determined and reported on either a volume (mL/L) or a weight (mg/L) basis.

2. Apparatus

The volumetric test requires only an Imhoff cone. The gravimetric test requires all the apparatus listed in Section 2540D.2 and a glass vessel with a minimum diameter of 9 cm.

3. Procedure

a. Volumetric: Fill an Imhoff cone to the 1-L mark with a well-mixed sample. Settle for 45 min, gently agitate sample near the sides of the cone with a rod or by spinning, settle 15 min longer, and record volume of settleable solids in the cone as milliliters per liter. If the settled matter contains pockets of liquid between large settled particles, estimate volume of these and subtract from volume of settled solids. The practical lower limit of measurement depends on sample composition and generally is in the range of 0.1 to 1.0 mL/L. Where a separation of settleable and floating materials occurs, do not estimate the floating material as settleable matter. Replicates usually are not required.

Where biological or chemical floc is present, the gravimetric method (3*b*) is preferred.

b. Gravimetric:

1) Determine total suspended solids as in Section 2540D.

2) Pour a well-mixed sample into a glass vessel of not less than 9 cm diam using not less

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

than 1 L and sufficient sample to give a depth of 20 cm. Alternatively use a glass vessel of greater diameter and a larger volume of sample. Let stand quiescent for 1 h and, without disturbing the settled or floating material, siphon 250 mL from center of container at a point halfway between the surface of the settled material and the liquid surface. Determine total suspended solids (milligrams per liter) of this supernatant liquor (Section 2540D). These are the nonsettleable solids.

4. Calculation

mg settleable solids/L = mg total suspended solids/L – mg nonsettleable solids/L

5. Precision and Bias

Precision and bias data are not now available.

6. Bibliography

FISCHER, A.J. & G.E. SYMONS. 1944. The determination of settleable sewage solids by weight. *Water Sewage Works* 91:37.

2540 G. Total, Fixed, and Volatile Solids in Solid and Semisolid Samples

1. General Discussion

a. Applicability: This method is applicable to the determination of total solids and its fixed and volatile fractions in such solid and semisolid samples as river and lake sediments, sludges separated from water and wastewater treatment processes, and sludge cakes from vacuum filtration, centrifugation, or other sludge dewatering processes.

b. Interferences: The determination of both total and volatile solids in these materials is subject to negative error due to loss of ammonium carbonate and volatile organic matter during drying. Although this is true also for wastewater, the effect tends to be more pronounced with sediments, and especially with sludges and sludge cakes. The mass of organic matter recovered from sludge and sediment requires a longer ignition time than that specified for wastewaters, effluents, or polluted waters. Carefully observe specified ignition time and temperature to control losses of volatile inorganic salts if these are a problem. Make all weighings quickly because wet samples tend to lose weight by evaporation. After drying or ignition, residues often are very hygroscopic and rapidly absorb moisture from the air. Highly alkaline residues may react with silica in the samples or silica-containing crucibles.

2. Apparatus

All the apparatus listed in Section 2540B.2 is required except that a magnetic stirrer and pipets are not used and a balance capable of weighing to 10 mg may be used.

3. Procedure

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

a. Total solids:

1) Preparation of evaporating dish—If volatile solids are to be measured, ignite a clean evaporating dish at 550°C for 1 h in a muffle furnace. If only total solids are to be measured, heat dish at 103 to 105°C for 1 h in an oven. Cool in desiccator, weigh, and store in desiccator until ready for use.

2) Sample analysis

a) Fluid samples—If the sample contains enough moisture to flow more or less readily, stir to homogenize, place 25 to 50 g in a prepared evaporating dish, and weigh. Evaporate to dryness on a water bath, dry at 103 to 105°C for 1 h, cool to balance temperature in an individual desiccator containing fresh desiccant, and weigh. Repeat heating, cooling, desiccating, and weighing procedure until the weight change is less than 4% or 50 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

b) Solid samples—If the sample consists of discrete pieces of solid material (dewatered sludge, for example), take cores from each piece with a No. 7 cork borer or pulverize the entire sample coarsely on a clean surface by hand, using rubber gloves. Place 25 to 50 g in a prepared evaporating dish and weigh. Place in an oven at 103 to 105°C overnight. Cool to balance temperature in a desiccator and weigh. Repeat drying (1 h), cooling, weighing, and desiccating steps until weight change is less than 4% or 50 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

b. Fixed and volatile solids: Transfer the dried residue from 2)a) above to a cool muffle furnace, heat furnace to 550°C, and ignite for 1 h. (If the residue contains large amounts of organic matter, first ignite it over a gas burner and under an exhaust hood in the presence of adequate air to lessen losses due to reducing conditions and to avoid odors in the laboratory.) Cool in desiccator to balance temperature and weigh. Repeat igniting (30 min), cooling, desiccating and weighing steps until the weight change is less than 4% or 50 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

4. Calculation

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\% \text{ total solids} = \frac{(A - B) \times 100}{C - B}$$

$$\% \text{ volatile solids} = \frac{(A - D) \times 100}{A - B}$$

$$\% \text{ fixed solids} = \frac{(D - B) \times 100}{A - B}$$

where:

A = weight of dried residue + dish, mg,
B = weight of dish,
C = weight of wet sample + dish, mg, and
D = weight of residue + dish after ignition, mg.

5. Precision and Bias

Precision and bias data are not now available.

6. Bibliography

GOODMAN, B.L. 1964. Processing thickened sludge with chemical conditioners. Pages 78 et seq. *in* Sludge Concentration, Filtration and Incineration. Univ. Michigan Continued Education Ser. No. 113, Ann Arbor.

GRATTEAU, J.C. & R.I. DICK. 1968. Activated sludge suspended solids determinations. *Water Sewage Works* 115:468.

2550 TEMPERATURE#(49)*

2550 A. Introduction

Temperature readings are used in the calculation of various forms of alkalinity, in studies of saturation and stability with respect to calcium carbonate, in the calculation of salinity, and in general laboratory operations. In limnological studies, water temperatures as a function of depth often are required. Elevated temperatures resulting from discharges of heated water may have significant ecological impact. Identification of source of water supply, such as deep wells, often is possible by temperature measurements alone. Industrial plants often require data on water temperature for process use or heat-transmission calculations.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2550 B. Laboratory and Field Methods

1. Laboratory and Other Non-Depth Temperature Measurements

Normally, temperature measurements may be made with any good mercury-filled Celsius thermometer. As a minimum, the thermometer should have a scale marked for every 0.1°C, with markings etched on the capillary glass. The thermometer should have a minimal thermal capacity to permit rapid equilibration. Periodically check the thermometer against a precision thermometer certified by the National Institute of Standards and Technology (NIST, formerly National Bureau of Standards)#(50)* that is used with its certificate and correction chart. For field operations use a thermometer having a metal case to prevent breakage.

Thermometers are calibrated for total immersion or partial immersion. One calibrated for total immersion must be completely immersed to the depth of the etched circle around the stem just below the scale level.

2. Depth Temperature Measurements

Depth temperature required for limnological studies may be measured with a reversing thermometer, thermophone, or thermistor. The thermistor is most convenient and accurate; however, higher cost may preclude its use. Calibrate any temperature measurement devices with a NIST-certified thermometer before field use. Make readings with the thermometer or device immersed in water long enough to permit complete equilibration. Report results to the nearest 0.1 or 1.0°C, depending on need.

The thermometer commonly used for depth measurements is of the reversing type. It often is mounted on the sample collection apparatus so that a water sample may be obtained simultaneously. Correct readings of reversing thermometers for changes due to differences between temperature at reversal and temperature at time of reading. Calculate as follows:

$$\Delta T = \left[\frac{(T^1 - t)(T^1 + V_0)}{K}\right] \times \left[1 + \frac{(T^1 - t)(T^1 + V_0)}{K}\right] + L$$

where:

ΔT = correction to be added algebraically to uncorrected reading,
T^1 = uncorrected reading at reversal,
t = temperature at which thermometer is read,
V_0 = volume of small bulb end of capillary up to 0°C graduation,
K = constant depending on relative thermal expansion of mercury and glass (usual

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

value of K = 6100), and

L = calibration correction of thermometer depending on T^1.

If series observations are made it is convenient to prepare graphs for a thermometer to obtain ΔT from any values of T^1 and t.

3. Bibliography

WARREN, H.F. & G.C. WHIPPLE. 1895. The thermophone—A new instrument for determining temperatures. *Mass. Inst. Technol. Quart.* 8: 125.

SVERDRUP, H.V., M.W. JOHNSON & R.H. FLEMING. 1942. The Oceans. Prentice-Hall, Inc., Englewood Cliffs, N.J.

American Society for Testing and Materials. 1949. Standard Specifications for ASTM Thermometers. No. E1-58, ASTM, Philadelphia, Pa.

REE, W.R. 1953. Thermistors for depth thermometry. *J. Amer. Water Works Assoc.* 45:259.

2560 PARTICLE COUNTING AND SIZE DISTRIBUTION (PROPOSED)#(51)*

2560 A. Introduction

1. General Discussion

Particles are ubiquitous in natural waters and in water and wastewater treatment streams. Particle counting and size distribution analysis can help to determine the makeup of natural waters, treatment plant influent, process water, and finished water. Similarly, it can aid in designing treatment processes, making decisions about changes in operations, and/or determining process efficiency. Methods for measuring particle size distribution included herein depend on electronic measurement devices because manual methods are likely to be too slow for routine analysis. However, when particle size analysis is to include size distribution of large (>500-μm) aggregates, use direct microscopic counting and sizing. Principles of various types of instruments capable of producing both size and number concentration information on particulate dispersions are included. Unless explicitly stated otherwise, the term ‘‘size distribution’’ means an absolute size distribution, i.e., one that includes the number concentration or count.

In most particle-counting instruments, particles pass though a sensing zone where they are measured individually; the only exception included is the static type of light-scattering instrument. Instruments create an electronic pulse (voltage, current, or resistance) that is proportional to a characteristic size of the particle. The instrument responses (pulse height, width, or area) are classified by magnitude and counted in each class to yield the particle size distribution.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2. Selection of Method

Three instrument types are included: electrical sensing zone instruments, light-blockage instruments, and light-scattering instruments.

Select instrument consistent with expected use of the particle size analysis. Instruments vary in the particle characteristic being sensed, lower and upper size limits of detection, degree of resolution of the size distribution, particle number concentration range that can be measured accurately, amount of shear to which a sample is subjected before measurement, amount of sample preparation, operator skill required, and the ease with which data can be obtained and manipulated into the desired forms. See Section 2560B.1, Section 2560C.1, and Section 2560D.1, and manufacturers' literature for information on characteristics of each type of instrumentation.

Some instruments can be set up for either continuous-flow or batch sampling. Others can be used only for batch analysis. For instruments usable in both modes, check that no systematic differences in particle size distributions occur between continuous-flow measurements and batch samples taken at or near the intake point for continuous-flow samples.

3. Sample Collection and Handling

a. Batch samples: Use extreme care in obtaining, handling, and preparing batch samples to avoid changing total particle count and size distribution.

Choose representative times and locations for sampling. Ensure that particles are not subjected to greater physical forces during collection than in their natural setting. Collect samples from a body of water with submerged vessels to minimize turbulence and bubble entrainment. If sampling from particular depths, use standard samplers designed for that purpose. For flowing systems, make sure that the velocity into the opening of the sampling device is the same as that of the flowing stream (isokinetic sampling) and that the opening diameter is at least 50 times as large as the particles to be measured. For sampling from a tap, let water flow slowly and continuously down the side of the collection vessel.

Minimize particle contamination from the air, dilution water (or, for electrical sensing zone instruments, electrolyte solution) (see ¶ 4 below), and any vessel or glassware that comes in contact with the sample. Minimize exposure to air by keeping sample in a closed container and by minimizing time between sampling and analysis.

Preferably use glass bottles and other vessels with bottle cap liners of TFE.

Clean all glassware scrupulously by automatic dishwashing, vigorous hand brushing, and/or ultrasonication. Rinse glassware immediately before use with particle-free water. Between samples, rinse any part of the instrument that comes in contact with samples with either clean water or the upcoming sample. Alternatively, run multiple replicates and discard the first results.

To avoid breakup of aggregates of particles or flocs, sample and make dilutions very slowly using wide-bore pipets, needles, or other sampling devices; cut off pipet tips to avoid high velocities at the entrance. If sample dilution is required, add sample to dilution water, not vice

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

versa, by submerging the pipet tip in the dilution water and releasing sample slowly. Use minimum intensity and duration of mixing adequate to dilute the suspension into the dilution water. Avoid mechanical stirrers inside the sample or ultrasonication. Simultaneously gently rotate and partially invert entire sample in a closed bottle. Use cylindrical dilution bottles to avoid sharp corners. Leave less than approximately 25% air space during mixing. To avoid sedimentation, make measurements immediately after mixing. Do not mix during measurement unless absolutely necessary to prevent sedimentation.

Most surface and ground waters contain relatively stable particles that aggregate slowly. Particle size distribution in biologically active waters or waters that have been treated with coagulants is more likely to change over short time periods. To minimize flocculation, minimize time between sampling and measurement. In highly flocculent systems, maximum holding time should be only a few minutes; for more stable samples, a few hours may be acceptable. Dilution slows flocculation kinetics and, in some cases, makes flocculation less likely. Make dilutions only immediately before measurement.

Samples measured at different temperature or pressure than when collected and those with biological activity may develop entrained air bubbles that interfere with measurement accuracy. If any gas bubbles are visible, let sample stand for a short time to degas naturally or use a mild vacuum to speed degassing. Use ultrasound to aid degassing, but only if floc breakup is not a problem.

Minimize time between sampling and analysis; if at all possible, make measurements immediately after sampling. If storage is unavoidable, refrigerate at 4°C but restore samples to room temperature, preferably in water bath, before measurement.

b. Continuous-flow: Using a particle counter as a continuous-flow monitor may be desirable. Many more samples can be processed by automated particle counting than by batch sample analysis. All the instruments mentioned in Methods B through D can be used in this mode, although instruments and samples not requiring dilution are easier to set up. For some instruments, this type of operation requires custom hardware; for others there is commercially available hardware.

Problems of batch samples are equally relevant to continuous analysis. Other critical considerations include selection of sampling point, velocity at entrance and throughout sample line, maintenance of stable sample flow rate, position of instrument's sensor in the sample line, and absence of flow-modifying devices upstream of the sensor.

Choose a sampling point that is representative and away from wall surfaces. Place entrance to sample line facing the flow, with the velocity at the opening nearly the same as the surrounding flow.

Sample preservation within the instrument is difficult because both deposition (or temporary holdup) of particles and floc breakup must be avoided. Deposition occurs by gravity settling of particles onto horizontal surfaces. Floc breakup occurs because of excessive shear forces. Minimize length of transmission lines, especially in horizontal components, and preferably have no horizontal lines. Avoid drastic changes in flow direction or velocity. Do not use

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

flow-modifying devices such as pumps, fittings with irregular surfaces, sharp angle changes, flow controllers, etc., between the sampling point and the sensor. Locate pumps after the sensor. Preferably, provide curved sample lines (e.g., flexible tubing or bent glass tubing) rather than right-angle fittings.

For most instruments, flow rate is specified. Because calibration (see ¶ 5) can change with flow rate within the range, flow control within very narrow limits is essential. Calibrate and use the sensor at the same flow rate. For continuous particle size distribution measurements, flow control, not simply flow monitoring, is necessary. Do not make measurements at a flow rate different from that used for calibration. Provide a flow control system downstream of the sensor, maintain a constant rate, and do not introduce turbulence or pulsations before or through the sensor.

4. Dilution Water

Particle-free water is virtually impossible to obtain, but it is possible to produce water containing very few particles within the size range to be measured. Produce ‘‘particle-free’’ or ‘‘clean’’ water from distilled, deionized water or water taken from the same source as the samples. If all samples are from the same source or have similar chemical characteristics, preferably filter sample water to produce ‘‘particle-free’’ water with no change in chemical environment. Distilled, deionized water produced by ion exchange and cartridge filtration may produce acceptable ‘‘particle free’’ dilution water, but preferably use continuous closed-loop membrane filtration.

Dilution water preparation systems are available from particle-counter manufacturers. Alternatively, assemble a system similar to that shown in Figure 2560:1 (or any system that produces a water of sufficient quality). In the system shown, a pump draws the water from a bottle and puts it through the in-line filter. Use membrane filters with nominal pore sizes no more than 10% of the smallest particle size expected; alternatively use cartridge filters. Pass water through the filter several times. The system lets water be passed directly from the product-water bottle to the source-water bottle by opening of the clamps and three-way stopcock. Use glass tubing in the bottles, but use flexible tubing to allow draining product-water bottle into source-water bottle. Attach a glass wool or membrane filter to air inlets. Dilute samples by drawing water directly from the three-way stopcock into the bottle to be used in sample analysis.

A simpler system with one-pass filtration directly into the sample bottle may be adequate for many samples, depending on the particle size range to be measured. Such a system would omit the product-water bottle, the connections between the two bottles and associated stopcock and clamps of Figure 2560:1. Dilution water is produced on demand and the effluent is put directly, without additional handling, into the sample container.

Guard against biological growth within filtration systems by frequent disassembly and adequate washing or replacement of components. For many samples, do not use chemical disinfectants because they might change the particle count and size distribution by their oxidizing potential.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

5. Calibration

As a particle is detected in the sensing zone of any instrument, an electrical response is generated and sorted into a channel of the instrument based on its magnitude.

Calibrate by determining the channel number into which particles of known size are sorted by the instrument. Use spherical particles manufactured for this purpose. Calibration particles are available in suspension or as dry particles. Over time, suspensions are likely to undergo some aggregation; use ultrasound to break up flocs before calibration. Calibration particles are nearly monodisperse but do exhibit a small inherent (true) variance.

The precision (see Section 1030A.1) and resolution of the instrument influence its ability to sort particles into different channels. Resolution is a measure of the ability of an instrument to distinguish between particles of similar but different sizes. An instrument with high precision and good resolution will measure monodisperse particles in a very narrow size range; some instruments have sufficient precision and resolution so that calibration particles with extremely narrow size distributions (very small variance) are sorted into a few adjacent channels. In such cases, the true variance of the particle size and the measured variance will be nearly equal. An instrument with low precision but high resolution will yield a wide distribution on the same particles (i.e., measured variance > true variance). An instrument with high precision but low resolution (e.g., few channels) may yield a narrow measured distribution (e.g., all the particles in the same channel) even though the true distribution is broader (i.e., measured variance < true variance).

Use at least three sizes of calibration particles in reasonably similar number concentrations to calibrate a sensor. To analyze different-size particles in a mixture, ensure that the different sizes do not interfere with one another. Calibrate under conditions identical with those of sample measurements, e.g., settingson the instrument, flow rate, type of sample cell, dilution water or electrolyte solution, and mixing during measurement. Do not exceed the maximum concentration for the sensor during calibration.

The calibration curve depends on the characteristic of the particle measured by the instrument (diameter, area, or volume) and whether the pulses are sorted into channels on an arithmetic or logarithmic basis. For example, if an electrical sensing zone instrument (which responds to particle volume) is used in a logarithmic mode, the calibration curve will be the logarithm of particle volume vs. channel number.

Generally, increments between channels are equal on an arithmetic or logarithmic basis. In most light-blockage and light-scattering instruments, the lower and upper limits for each channel can be set by the user. Because most samples have broad particle size distributions, spanning at least one order of magnitude, and often two or three, preferably use larger increments for larger sizes. This is consistent with equal logarithmic spacing, although other less systematic intervals that preserve the characteristic of larger increments for larger sizes are permissible. Such intervals also are consistent with the resolution capabilities of most available instruments, which respond to a characteristic particle area or volume (proportional to square or cube of diameter, respectively), and therefore require greater resolution for larger particles than for smaller ones on

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

a diameter basis.

At a given set of settings for a given sensor, each channel represents a certain average size and size increment. After measuring the channel number associated with several sizes of calibration particles, use a calibration equation to assign average sizes or, in some cases, the lower limit of size, to all other channels. Knowledge of the average size and both the arithmetic and logarithmic increment of each channel is necessary for reporting. In contrast to calibration particles, environmental particles are rarely spherical. Generally report measurements in terms of ‘‘equivalent spherical diameter,’’ i.e., size of any particle taken as that of a sphere that would give the same response in the instrument. Because most sample particles are nonspherical and different instruments respond to different characteristics of particles, different measured particle size distributions result from different instruments.

Some light-scattering instruments calculate particle size from first principles and do not require calibration per se. For those instruments, periodically adjust the system optics. Make frequent checks that the instrument response is consistent by following the calibration procedures for other instruments.

6. Data Reporting

a. Particle concentrations: Number, surface, or volume concentration over a specified size range is particularly valuable as a summary factor for particle counting and size distribution. Its variation with some changes in an independent variable in a natural or engineered system may be of interest.

When reporting the number concentration (number per milliliter) of particles, report also the size range measured (both lower and upper size limits). The lower limit is particularly important, because most samples have large number concentrations near the lower limit of detection of currently available instruments. Never state or imply a lower size limit of zero.

In some studies a surface area concentration (μm^2/mL) or volume concentration (μm^3/mL) may be more relevant; convert number concentration to these forms by multiplying by the area or volume, respectively, of a sphere with the mean diameter for each size class. (This is an approximation based on the assumption that particles are spherical.) In such cases, also report lower and upper limits of size class.

b. Tabulated size distributions: If the distribution itself (i.e., the variation of particle number, surface area, or volume concentration with particle size) is to be shown in tabular format, give for each instrument channel (or grouping of channels) the number concentration and the associated size range (lower and upper limits).

c. Graphical size distributions: For graphical reporting, preferably use the count information (on a number, surface area, or volume basis) as the ordinate and particle size as the abscissa.

For the count information, use absolute, rather than relative, scales because they indicate both concentration and size distribution. Also, preferably use differential, rather than cumulative, distributions because they show directly what size range contained the most particles. For ease of plotting, associate the number (or surface area or volume) concentration with a mean size for

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

each channel, rather than with the size range (the lower and upper limit). To account for that change without losing information, normalize the data by dividing the concentration of particles in a given size class by the size interval for that class (on either an arithmetic or a logarithmic basis). Normalization prevents creation of artificial (or apparent) peaks or valleys in a distribution and ensures that the same distribution measured by different instruments with different size increments will be the same graphically. If data are not normalized, plot size distribution data (absolute and differential) as a discrete histogram (i.e., as a bar chart with the upper limit of one channel being identical to the lower limit of the next).

Preferably show particle sizes with a logarithmic scale. Most samples have broad distributions and most analyzers use larger increments of diameter with increasing size; these characteristics are consistent with a logarithmic scale, which also intrinsically avoids showing a zero size. Produce the logarithmic scale by showing the log of diameter on an arithmetic scale or the arithmetic values of diameter on a logarithmic scale.

d. Example calculations: A calculation layout (with example data) useful for preparing either tabular or graphical presentation is shown in Table 2560:I. This format may be abbreviated or modified to suit the data presentation being developed.

Columns A through G represent calibration information. Which of these values are set (or determined from calibration by the user) and which are calculated from this primary information depends on the type of instrument. In constructing such a table, preferably place primary information first. In most light-blockage and light-scattering instruments, the lower and upper size limits for each channel are known; calculate mean diameter as the arithmetic or logarithmic (geometric) mean of these limits, depending on whether instrument channels represent arithmetic or logarithmic increments. In electrical sensing zone instruments, the mean size (or log size) is determined directly from the calibration equation and increment width (arithmetic, Δd_{pi}, or logarithmic, $\Delta \log d_{pi}$) is pre-set; calculate lower and upper limits as mean size ± one half the arithmetic or logarithmic increment.

Columns H through O represent counting information for a sample. The corrected counts (Column H) are the direct counts from the particle size analyzer minus the background count for each channel. Adjust background count for dilution and differences in sample measured and dilution water measured for background count. Adjust this figure for sample dilution and volume analyzed to obtain the number concentration of particles (Column I). For example, for corrected count n, a 1:10 dilution, and 0.5 mL analyzed, number concentration is calculated as $(n \times 10)/0.5 = 20n$/mL. Volume concentration (Column J) may be approximated as the number of particles multiplied by the volume of a spherical particle with the mean diameter for the channel ($\pi d^3_p/6$). Values in the remaining columns are calculated as shown in the table. The normalized, differential, absolute distribution functions obtained in Columns K (particle size distribution function) through O give the values needed for graphic presentations as follows:

K: particle numbers (arithmetic scale) vs. diameter (arithmetic scale)

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

L: particle volume (arithmetic scale) vs. diameter (arithmetic scale)
M: particle number (arithmetic scale) vs. diameter (logarithmic scale)
N: particle volume (arithmetic scale) vs. diameter (logarithmic scale)
O: log of particle number (arithmetic scale) vs. diameter (logarithmic scale).

(Alternatively, plot values from Column K directly on a logarithmic scale.)

If distribution K, L, M, or N is plotted, the area under the resulting graph between any two values of diameter represents the total number or volume concentration between those size limits. The logarithmic graph (O) shows the entire distribution better than other distributions, but can hide differences between similar distributions. It often is linear over specified size ranges.

7. Quality Control

See Section 1020 and Section 1030. Observe precautions for sampling and handling discussed in ¶ 3 above. Particle counting and size analysis requires experienced analysts capable of judgment in recognizing unusual behavior of an instrument. Ability to recognize partial blockage of an aperture or sensor or electronic noise is essential.

Electronic noise can be detected directly in some instruments by making a particle count when no flow is being put through a sensor. Ensure that the noise is not environmental, i.e., due to other nearby instruments, poor grounding, or inconsistent electrical supply. Noise also can be created by excessive cable length between the sensor and instrument or worn cables and connectors. Perform noise checks periodically.

Analyze sample blanks, handled identically to real samples, daily. Discard data from all channels that yield counts in the blanks greater than 5% of the counts for real samples. This procedure accounts for both particle contamination and electronic noise. Develop a maximum acceptable total count for blanks for each sensor (or for each set of standard settings for one sensor); if blanks give more than this maximum, discontinue particle counting until the contamination or noise is eliminated. Set maximum so that the 5% rule is met for all channels of interest (i.e., down to some minimum size limit acceptable in the laboratory for the sensor in use and the samples being measured). Recognize that the lower size limit of measurement for every sensor and every instrument is more likely to be dictated by electronic noise and particle contamination than by electronic settings.

Test cleaning and rinsing for sample bottles by partially filling the container with clean water, swirling the water to contact all sides, and performing a particle count. When the container has been shown to contribute negligible counts, check cleanliness of the cap similarly. Develop and document the standard washing and rinsing procedure, verify its validity as indicated, and follow the procedure without exception.

Also develop standard procedure for mixing samples and dilution water. Test mixing by varying the mixing intensity and/or duration to determine the minimum that gives adequate reproducibility (a sign of uniform concentration) and to determine if greater mixing increases the total particle counts (a sign of floc breakup). Follow an established mixing procedure without

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

exception.

To determine precision, make replicate measurements on at least 5% of the samples. Report standard deviation (or range) of the total particle number concentration for each sensor or the total of all sensors, if more than one is used. See Section 1030.

Particle counting and size distribution analyzers are calibrated for size, not concentration. Standards for calibrating (or checking) the ability of an instrument to measure particle concentration accurately are under development. Currently, only precision, not bias, can be measured well for particle concentration. Obtain an indication of bias by preparing standards of particles of known density at a known suspended solids concentration; multiply total measured particle volume concentration by the known density to estimate the suspended solids concentration from the particle measurements. Compare this estimate with the known suspended solids concentration as an indicator of the combined instrument and laboratory bias.

Periodically calibrate with particles traceable to the National Institute of Standards and Technology (NIST).

8. Bibliography

KAVANAUGH, M.C., C.H. TATE, A.R. TRUSSELL, R.R. TRUSSELL & G. TREWEEK. 1980. Use of particle size distribution measurements for selection and control of solid/liquid separation processes. *In* M.C. Kavanaugh & J. Leckie, eds. Particulates in Water. Advan. Chem. Ser. No. 189, American Chemical Soc., Washington, D.C.

LAWLER, D.F., C.R. O'MELIA & J.E. TOBIASON. 1980. Integral water treatment plant design: from particle size to plant performance. *In* M.C. Kavanaugh & J. Leckie, eds. Particulates in Water. Advan. in Chem. Ser. No. 189, American Chemical Soc., Washington, D.C.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1980. Standard method for determining the quality of calibration particles for automatic particle counters. F322-80, Annual Book of ASTM Standards. American Soc. Testing & Materials, Philadelphia, Pa.

STUMM, W. & J.J. MORGAN. 1981. Aquatic Chemistry, 2nd ed. John Wiley & Sons, New York, N.Y.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1985. Standard practice for particle size analysis of particulated substances in the range of 0.2 to 75 micrometers by optical microscopy. E20-85, Annual Book of ASTM Standards. American Soc. Testing & Materials, Philadelphia, Pa.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1987. Defining size calibration, resolution, and counting accuracy of a liquid-borne particle counter using near-monodisperse spherical particulate material. F658-87, Annual Book of ASTM Standards. American Soc. Testing & Materials, Philadelphia, Pa.

HARGESHEIMER, E.E., C.M. LEWIS & C.M. YENTSCH. 1992. Evaluation of Particle Counting as a Measure of Treatment Plant Performance. AWWA Research Foundation, Denver, Colo.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2560 B. Electrical Sensing Zone Method

1. General Discussion

a. Principle: In electrical sensing zone instruments, particles are suspended in an electrolyte solution and pass through a small orifice. A constant current or potential is applied between electrodes on either side of the orifice; the change in resistance caused by the particle taking up volume in the orifice causes a change in potential or current (whichever is not being held constant electronically). The pulse is proportional to the particle volume.

The voltage or current pulses are amplified and sorted into size classes or channels based on their maximum height. Some instruments have fixed channels; others permit selection of number of size classes, size width of each channel, and/or lowest size to be measured.

b. Interferences: Interferences are caused by contamination with particles, the presence of gas bubbles, and electronic noise. See Section 2560A.3*a* and *b* for sampling precautions, and Section 2560A.4 for particle-free water preparation. Minimize electronic noise as directed in Section 2560A.7. Increasing electrolyte strength is another method for minimizing electronic noise.

c. Detectable sizes and concentrations: The lower size limit of measurement depends on both electronic noise and aperture size. Manufacturers claim that the lower size limit (diameter) is approximately 2% of the aperture size, but not lower than approximately 0.4 μm, but values as low as approximately 0.7 μm have been reported. For the upper size limit, manufacturers state the maximum size is 40 to 60% of the aperture size, but a realistic upper limit for measuring flocs is 20% of the aperture size.

The minimum concentration limit depends on the ability to distinguish particles from background counts. For each channel, background count should be less than 5% of total count. In size ranges in which the count is very low (zero or nearly so), counts may be statistically unreliable. Determine if a larger sample volume provides more satisfactory (less scattered) data. Grouping data from several adjacent channels, thereby increasing the size increment, also can give a more accurate size distribution.

The maximum concentration limit depends on the rate at which the instrument can process different pulses and the need to avoid more than one particle in the sensing zone at the same time (coincidence). Follow manufacturers' instructions for upper limits on particle counts for each aperture size. Some instruments include a capability for correcting for overly concentrated samples, but do not use this feature because each particle is not measured individually and errors in absolute size distribution may result.

2. Apparatus

a. Particle counter and size-distribution analyzer.

b. Glassware: For glassware preparation, see Section 2560A.3*a* and Section 2560A.7.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3. Reagents

a. Particle-free electrolyte solution: Prepare an electrolyte solution of NaCl, $CaCl_2$, $NaNO_3$, $Ca(NO_3)_2$, or some other simple inorganic salt at a concentration of 1 to 10% by weight. Pass solution through a continuous-flow membrane microfiltration system (see Section 2560A.4). Alternatively, use a commercially prepared electrolyte solution (filtration also may be required).

b. Calibration particles: See Section 2560A.5.

4. Procedure

a. Preparation: Let instrument warm up according to manufacturer's instructions. Select proper size aperture for particle sizes of interest; use more than one aperture if size distribution is wider than the range that can be measured with one aperture. Rinse aperture with acid solution, distilled water, and finally clean electrolyte solution. Install aperture. Choose settings on the instrument for each type of choice, including linear or logarithmic mode (spacing of sizes for each channel; logarithmic is preferable for environmental samples), desired size width of each channel, total number of channels and which channels are to be included, and method of starting and stopping counting. Counting can be started and stopped manually, by switches built into the manometer representing set sample volumes, by a set maximum count in any one channel, or stopped by time after a manual start. For reporting absolute measurements, choose a method that measures volume sampled.

b. Calibration: See Section 2560A.5. Calibrate each aperture with at least three particle sizes, determining the channel number at which the maximum count for each size is located. Handle calibration samples identically to those used for measurement. Because calibration can change, check it at each use of the instrument. Plot results as the volume of calibration particles vs. channel number (linear mode) or as the logarithm (base 10 or e) of the volume of calibration particles vs. channel number (logarithmic mode). The results should plot as a straight line. Use an equation for that line to assign an average size to each channel. Convert results from particle volume to particle diameter for reporting.

c. Blank sample: Measure at least one blank sample of the electrolyte solution. Carry a sample bottle with only electrolyte solution through procedures identical to those used for samples. Subtract counts from the blank solution (i.e., background counts), channel by channel, from the counts of the samples. See Section 2560A.7.

d. Measurement of samples: Prepare diluted sample, ensuring that the volume of sample is no greater than the volume of the electrolyte solution (dilution water); if a more concentrated suspension is necessary, prepare dilution water with a higher electrolyte concentration. Mix gently (see Section 2560A.3*a*). Insert sample container into the instrument. Start vacuum to control the mercury column and start particle counting. During counting, continuously watch the monitor provided on the instrument to check for blockage of the aperture by oversized particles. Check that the time for the specified volume (if the count is controlled by the stop and start switches on the manometer) is consistent with that found for particle-free electrolyte solution.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

When count is complete, check that the concentration did not exceed the manufacturer's recommendations. Repeat with a greater dilution if necessary. When a series of samples with various concentrations is to be measured and sample order is not critical, measure samples in order of expected increasing particle concentration, rinsing with next sample.

5. Calculation

See Section 2560A.6.

2560 C. Light-Blockage Methods

1. General Discussion

a. Principle: In light-blockage instruments, a focused beam of light shines from one side of the measurement zone toward a photovoltaic cell on the other side. The illuminated volume of liquid constitutes the sensing zone. Particles pass through the sensing zone at a known velocity. The blockage of light by the particle creates a change in the voltage at the photovoltaic cell. In different instruments, different characteristics of the resulting signal are used to determine size: light obscuration instruments use pulse height (related to the cross-sectional area of the particle) while time-of-transition instruments use the pulse width (proportional to a characteristic length of the particle). In all cases, measurements usually are reported in terms of equivalent spherical diameter.

For light-obscuration instruments, consult manufacturer's literature to determine the relationship between height of the voltage pulse and particle size (and increment of particle size).

Time-of-transition devices typically utilize a laser beam as the light source. The beam may scan a stationary sample at a fixed velocity as it sweeps out an optical sensing zone. Alternatively, a suspension can be passed through a fixed optical sensing zone. In the latter case, the measured particle size is sensitive to flow rate through the sensor.

Devices using light blockage principles vary in the number of channels (size classes) into which particles are sorted. In some cases, these are pre-set by the manufacturer; in others, they can be set by the analyst. Different (interchangeable) sensors are available to measure different size ranges and different particle concentrations.

b. Interferences: Interferences are caused by contamination with particles, the presence of gas bubbles, and electronic noise. See Section 2560A.3*a* and *b* for sampling precautions and Section 2560A.4 for particle-free dilution water preparation. Dilution water is necessary only for samples with particle number concentrations exceeding the capacity of the sensor to distinguish different particles. If dilution water is to be used, analyze it without sample and subtract particle counts in each channel from sample counts.

For devices in which sample flows through the sensor, some electronic noise can be detected by counting with clean water in the sensor and no flow (that is, with no true particle counts). If noise is present, it is likely to occur as a very large number of counts in the smallest size range (lowest channel). Eliminate this noise by re-setting the size range of the smallest channel

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

(increasing the lowest size range to be measured) high enough to avoid significant counts in the lowest channel. For further measures to minimize electronic noise, see Section 2560A.7.

c. Detectable sizes and concentrations: The lower size limit of measurement depends on both electronic noise and sensor capability. Devices using the principle of light obscuration typically are limited to particles larger than approximately 1 μm. Devices using the time-of-transition principle can detect particles as small as 0.1 μm. The upper particle size limit usually is determined by the size of the orifice through which particles pass. Manufacturers state particle size limits (lower and upper) for each sensor. See Section 2560B.1*c*.

2. Apparatus

a. Particle counter and size distribution analyzer.

b. Glassware: See Section 2560A.3*a* and Section 2560A.7.

3. Reagents

a. Particle-free dilution water: See Section 2560A.4.

b. Calibration particles: See Section 2560A.5.

4. Procedure

a. Preparation: Let instrument warm up according to manufacturer's instructions. Select sensor to measure size and concentration ranges expected; use more than one sensor if size distribution is wider than the range that can be measured with one sensor. Rinse sensor with a volume of particle-free dilution water equivalent to at least three times that used in measuring samples.

Choose settings on the instrument for each type of choice available: including total number of channels and which channels are to be included, absolute or relative counts, cumulative or differential counts, etc. Also choose method of starting and stopping counting based on total count, maximum count in one channel, duration of counting, or analysis of a specified volume of sample. Usually, the known-volume method is preferable because it lends itself to determination of absolute size distribution.

b. Calibration: See Section 2560A.5. Initial calibration of each sensor on an instrument requires several particle sizes to determine the relationship between particle size and channel number. Either this relationship may be controlled by varying the range of millivolt responses that are sorted into each channel or it is pre-set by the manufacturer.

After initial calibration, use at least two sizes of calibration particles for each sensor each time the instrument is used. For instruments in which the sample flows through a stationary sensing zone, measure flow rate of sample and adjust it to that used during initial calibration.

c. Blank sample: See Section 2560B.4*c* but substitute particle-free dilution water for electrolyte solution.

d. Measurement of samples: Dilute sample, if necessary to keep within manufacturer's guidelines. Mix gently (see Section 2560A.3*a*). For flow-type instruments with pressure-based

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

samplers, insert sample container into the instrument; for vacuum-based samplers, insert sampler tubing into the sample container. Start counting only after sufficient sample has passed through the tubing connecting the sample and sensor to ensure that the sensor is receiving the sample. For instruments that scan a stationary sample, gently transfer sample into the measurement device and insert.

For all instruments, when the count is complete, check that the concentration did not exceed the manufacturer's recommendations. Repeat with a greater dilution if necessary.

Between samples, rinse with dilution water or the upcoming sample. When a series of samples with various concentrations is to be measured and sample order is not critical, measure samples in order of expected increasing particle concentration; preferably, rinse with the next sample.

5. Calculation

See Section 2560A.6.

2560 D. Light-Scattering Method

1. General Discussion

a. Principle: Light-scattering instruments may be either flow or static devices. In flow instruments, the direct path of the light beam through the flow cell is blocked by a particle as it flows through the measurement zone with the fluid, and light scattered over a fixed range of angles is collected and measured. Particle size is determined from the angle and intensity of scattering based on the principles of Fraunhofer diffraction and/or Mie scattering. In static instruments, the particles remain quiescent and a laser light beam scans part of the suspension. Scattered light is collected by a photovoltaic cell and the resulting response from all particles scanned is mathematically deconvoluted to generate the size distribution.

Available particle counters vary in the angle or range of angles at which scattered light is measured and in the number of channels (size classes) into which particles are sorted. For flow-type instruments, different (interchangeable) sensors are available to measure different size ranges and different particle concentrations. The particle sizes determined by these instruments are equivalent spherical diameters, i.e., they are determined from the amount of light that would have been scattered at the angle(s) built in to the instrument by a calibration sphere of that diameter.

b. Interferences: For both types of instruments, interferences are caused by contamination of the sample with particles, the presence of gas bubbles, and electronic noise. For static-type instruments, additional sources of interference can be surface contamination (particles, markings, or scratches) on the sample container and sample color. See Section 2560A.3*a* and *b* for sampling precautions and 2560A.4 for particle-free dilution water preparation. Dilution water is necessary only for samples with particle number concentrations exceeding the capacity of the sensor to distinguish different particles. If dilution water is to be used, analyze it without sample

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

and subtract particle counts in each channel from sample counts. To correct for color interference, consult the instrument manual.

In flow-type instruments, some electronic noise can be detected by counting with clean water in the sensor and no flow (that is, with no true particle counts). If noise is present, it is likely to occur as a very large number of counts in the smallest size range (lowest channel). Eliminate this noise by resetting the size range of the smallest channel (increasing the lowest size range to be measured) high enough to avoid significant counts in the lowest channel. For further measures to minimize electronic noise, see Section 2560A.7.

For static-type instruments, use a glass container that is optically clear and has no lettering or markings, at least in the light path. Minimize the effect of specific glassware by using the same sample container for all samples that will be compared and ensuring that the orientation of the sample container in the light beam is the same for every sample.

c. Detectable sizes and concentrations: The lower size limit of measurement depends on both electronic noise and sensor capability. For flow-type instruments, the upper particle size limit usually is determined by the size of the orifice through which particles pass. Manufacturers state particle size limits (lower and upper) for each sensor. See Section 2560B.1*c*.

Application of the Mie theory to the scattering data can extend the range of light-scattering instruments to as low as 0.1 μm. Alternatively, some instruments extend the lower limit of detectable diameters to 0.1 μm by augmenting Fraunhofer diffraction data with scattering intensity measurements at a fixed angle (often 90°) using two or three different wavelengths of incident light.

2. Apparatus

a. Particle counter and size distribution analyzer.

b. Glassware: See Section 2560A.3*a* and Section 2560A.7.

3. Reagents

a. Particle-free dilution water: See Section 2560A.4.

b. Calibration particles: See Section 2560A.5.

4. Procedure

a. Preparation: Let instrument warm up according to manufacturer's instructions. For flow-type instruments, select sensor to measure size and concentration ranges expected; use more than one sensor if size distribution is wider than the range that can be measured with one sensor. Preferably use a sensor designed for the concentration range of the undiluted sample rather than diluting samples into the concentration range of the sensor. For both types of instruments, place in or pass through the sensor at least three times a volume of particle-free dilution water equivalent to that used in measuring samples, before the first sample.

Choose settings on the instrument for each type of choice available, including flow rate, total number of channels and which channels are to be included, absolute or relative counts, etc.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Also choose method of starting and stopping counting: total count, maximum count in one channel, duration of counting, or analysis of a specified volume of sample. For flow-type instruments, the known-volume method is preferable because it lends itself to determination of absolute size distribution. For static-type analyzers, the analyst does not control sample size directly, but can control duration of measurement. Take care not to exceed maximum particle number concentration limits suggested by manufacturer.

Some flow-type instruments permit choice between vacuum or pressure systems for transporting the sample through the sensor. If floc preservation is essential, preferably use a vacuum system but ensure that bubbles do not form before the sensor; otherwise, use a pressure system with a pulseless gear pump.

b. Calibration: See Section 2560A.5. For flow-type instruments, initial calibration of each sensor on an instrument requires several particle sizes to determine the relationship between particle size and channel number. Either this relationship may be controlled by varying the range of millivolt responses that are sorted into each channel, or it is pre-set by the manufacturer. Static-type instruments are pre-set by the manufacturer because sizing is done by a software conversion of the light sensed. After initial calibration, use at least two sizes of calibration particles for each sensor each time the instrument is used. Although the calculation of particle sizes is based on first principles and not on this calibration, calibrate to ensure that the instrument is functioning properly. For flow-type instruments, measure flow rate through the sensor and adjust to that used during initial calibration.

c. Blank sample: See Section 2560B.4*c*, but substitute particle-free dilution water for electrolyte solution.

d. Measurement of samples: If dilution is necessary, dilute sample to keep within manufacturer's guidelines for the maximum counting rate. Mix gently (see Section 2560A.3*a*).

For flow-type instruments, initiate the flow from the sample through the sensor. Check that flow rate is the same as that used for sensor calibration. Start counting only after sufficient sample has passed through the tubing connecting the sample and sensor to ensure that the sensor is receiving the sample. When counting is complete, check that the concentration did not exceed the manufacturer's recommendations. Repeat with a greater dilution if necessary. For subsequent samples, rinse with dilution water or the next sample. When a series of samples with varying concentrations is to be measured and sample order is not critical, measure samples in order of expected increasing particle concentration; in this case, preferably rinse with next sample.

For static-type instruments, insert sample beaker or bottle and start particle counting. When counting is complete, check that the concentration did not exceed the manufacturer's recommendations by diluting and measuring again. If the second count is related to the first according to the ratio of the dilution factors of the two measurements, consider the first measurement acceptable. Repeat with a greater dilution if necessary. For subsequent samples, see directions in preceding paragraph.

5. Calculation

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

See Section 2560A.6.

2570 ASBESTOS#(52)*

2570 A. Introduction

1. Occurrence and Significance

The term ‘‘asbestos’’ describes a group of naturally occurring, inorganic, highly fibrous silicate minerals that are easily separated into long, thin, flexible fibers when crushed or processed. Included in the definition are the asbestiform (see ¶ 2 below) varieties of serpentine (chrysotile), riebeckite (crocidolite), grunerite (grunerite asbestos), anthophyllite (anthophyllite asbestos), tremolite (tremolite asbestos), and actinolite (actinolite asbestos).

Asbestos has been used widely as a thermal insulator and in filtration. The tiny, almost indestructible fibers penetrate lung tissue and linings of other body cavities, causing asbestosis and cancer in the lungs and mesothelioma in other cavity linings.

2. Definitions

Asbestiform—having a special type of fibrous habit (form) in which the fibers are separable into thinner fibers and ultimately into fibrils. This habit accounts for greater flexibility and higher tensile strength than other habits of the same mineral. More information on asbestiform mineralogy is available.[1,2]

Aspect ratio—ratio of the length of a fibrous particle to its average width.

Bundle—structure composed of three or more fibers in parallel arrangement with the fibers closer than one fiber diameter to each other.

Cluster—structure with fibers in a random arrangement such that all fibers are intermixed and no single fiber is isolated from the group; groupings of fibers must have more than two points touching.

Fiber (AHERA)—structure having a minimum length greater than or equal to 0.5 μm, an aspect ratio of 5:1 or greater, and substantially parallel sides.[3]

Fibril—single fiber that cannot be separated into smaller components without losing its fibrous properties or appearance.

Fibrous—composed of parallel, radiating, or interlaced aggregates of fibers, from which the fibers are sometimes separable. The crystalline aggregate of a mineral may be referred to as fibrous even if it is not composed of separable fibers, but has that distinct appearance. ‘‘Fibrous’’ is used in a general mineralogical way to describe aggregates of grains that crystallize in a needle-like habit and appear to be composed of fibers; it has a much more general meaning than ‘‘asbestos.’’ While all asbestos minerals are fibrous, not all minerals having fibrous habits are asbestos.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Matrix—fiber or fibers with one end free and the other end embedded in, or hidden by, a particle. The exposed fiber must meet the fiber definition.

Structures—all the types of asbestos particles, including fibers, bundles, clusters, and matrices.

3. References

1. STEEL, E. & A. WYLIE. 1981. Mineralogical characteristics of asbestos. *In* P.H. Riordon, ed. Geology of Asbestos Deposits. Soc. Mining Engineers—American Inst. Mechanical Engineers, New York, N.Y.
2. ZUSSMAN, J. 1979. The mineralogy of asbestos. *In* Asbestos: Properties, Applications and Hazards. John Wiley & Sons, New York, N.Y.
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1987. Asbestos-containing materials in schools: Final rule and notice. *Federal Register*, 40 CFR Part 763, Appendix A to Sub-part E, Oct. 30, 1987.

2570 B. Transmission Electron Microscopy Method

1. General Discussion

This method is used to determine the concentration of asbestos structures, expressed as the number of such structures per liter of water. Asbestos identification by transmission electron microscopy (TEM) is based on morphology, selected area electron diffraction (SAED), and energy dispersive X-ray analysis (EDXA). Information about structure size also is generated. Only asbestos structures containing fibers greater than or equal to 0.5 μm in length are counted. The concentrations of both fibrous asbestos structures greater than 10 μm in length and total asbestos structures per liter of water are determined. The fibrous asbestos structures greater than 10 μm in length are of specific interest for meeting the Federal Maximum Contaminant Level Goal (MCLG) for drinking water, but in many cases the total asbestos concentration provides important additional information.

a. Principle: Sample portions are filtered through a membrane filter. A section of the filter is prepared and transferred to a TEM grid using the direct transfer method. The asbestiform structures are identified, sized, and counted by transmission electron microscopy (TEM), using selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS or EDXA) at a magnification of 15 000 to 20 000×.

b. Interferences: Certain minerals have properties (i.e., chemical or crystalline structure) that are very similar to those of asbestos minerals and may interfere with the analysis by causing false positives. Maintain references for the following materials in the laboratory for comparison with asbestos minerals, so that they are not misidentified as asbestos minerals: antigorite, attapulgite (palygorskite), halloysite, hornblende, pyroxenes, sepiolite, and vermiculite scrolls.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

High concentrations of iron or other minerals in the water may coat asbestos fibers and prevent their full identification.

2. Sampling

a. Containers: Use new, pre-cleaned, capped bottles of glass or low-density (conventional) polyethylene, capable of holding at least 1 L. Do not use polypropylene bottles. Rinse bottles twice by filling approximately one-third full with fiber-free water and shaking vigorously for 30 s. Discard rinse water, fill bottles with fiber-free water, treat in ultrasonic bath (60 to 100 W) for 15 min, and rinse several times with fiber-free water.

Make blank determinations on the bottles before collecting a sample. Use one bottle in each batch or a minimum of one bottle in each 24 to test for background level when using polyethylene bottles. When sampling waters probably containing very low levels of asbestos, or for additional confidence in the bottle blanks, run additional blank determinations.

b. Collection: Follow general principles for water sampling (see Section 1060). Some specific considerations apply to asbestos fibers, which range in length from 0.1 μm to 20 μm or more. In large bodies of water, because of the range of sizes there may be a vertical distribution of particle sizes that may vary with depth. If a representative sample from a water supply tank or impoundment is required, take a carefully designated set of samples representing vertical as well as horizontal distribution and composite for analysis. When sampling from a distribution system, choose a commonly used faucet, remove all hoses or fittings, and let water run to waste for 1 to 3 min. (Often, the appropriate time to obtain a main's sample can be determined by waiting for a change in water temperature.) Because sediment may build up in valving works, do not adjust faucets or valves until all samples have been collected. Similarly, do not consider samples at hydrants and at dead ends of the distribution systems to be representative of the water in the system. As an additional precaution against contamination, rinse each bottle several times with the source water being sampled. For depth sampling, omit rinsing. Obtain a sample of approximately 800 mL from each sampling site, leaving some air space in each bottle. Using a waterproof marker, label each container with date, time, place, and sampler's initials.

c. Shipment: Ship water samples in a sealed container, but separate from any bulk or air samples intended for asbestos analysis. Preferably, ship in a cooler to retard bacterial or algal growth. Do not freeze the sample. In the laboratory, prepare sample within 48 h of collection.

3. Apparatus

a. High-efficiency particulate air (HEPA) filtered negative-flow hood.

b. Filter funnel assemblies, either 25 mm or 47 mm, of either of the following types:

1) *Disposable plastic units*, or

2) *Glass filtering unit*. With this type of unit, observe the following precautions: Never let unit dry after filtering. Immediately place it in detergent solution, scrub with a test-tube brush, and rinse several times in particle-free water. Periodically treat unit in detergent solution in an ultrasonic bath. Clean unit after each sample is filtered. Run a blank on particle-free water

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

filtered through the glass filtering unit at frequent intervals to ensure absence of residual asbestos contamination.

c. Side-arm filter flask, 1000 mL.

d. Either:

1) *Mixed cellulose ester (MCE) membrane filters,* 25- or 47-mm diam, ≤ 0.45-µm and 5-µm pore size, or

2) *Polycarbonate (PC) filters,* 25- or 47-mm diam, ≤ 0.4-µm pore size.

e. Ultrasonic bath, tabletop model, 60 to 100 W.

f. Graduated pipet, disposable glass, 1, 5, and 10 mL.

g. Cabinet-type dessicator or *low-temperature drying oven.*

h. Cork borer, 7 mm.

i. Glass slides.

j. Petri dishes, glass, approximately 90-mm diam.

k. Mesh screen, stainless steel or aluminum, 30 to 40 mesh.

l. Ashless filter paper filters, 90-mm diam.

m. Exhaust or fume hood.

n. Scalpel blades.

o. Low-temperature plasma asher.

p. High-vacuum carbon evaporator with rotating stage, capable of less than 0.013 Pa pressure. Do not use units that evaporate carbon filaments in a vacuum generated only by oil rotary pump. Use carbon rods sharpened with a carbon rod sharpener to necks about 4 mm long and 1 mm in diam. Install rods in the evaporator so that the points are approximately 100 to 120 mm from surface of microscope slide held in the rotating device.

q. Lens tissue.

r. Copper TEM finder grids, 200 mesh. Use pre-calibrated grids, or determine grid opening area by either of the following methods:

1) Measure at least 20 grid openings in each of 20 random 200-mesh grids (total of 400 grid openings for every 1000 grids used) by placing the 20 grids on a glass slide and examining them under an optical microscope. Use a calibrated reticule to measure average length and width of 20 openings from each of the individual grids. From the accumulated data, calculate the average grid opening area.

2) Measure grid area at the TEM (¶ s below) at a calibrated screen magnification of between 15 000 and 20 000×. Measure one grid opening for each grid examined. Measure grid openings in both the x and y directions and calculate area.

s. Transmission electron microscope (TEM), 80 to 120 kV, equipped with energy dispersive X-ray system (EDXA), capable of performing electron diffraction with a fluorescent screen

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

inscribed with calibrated gradations. The TEM must have a scanning transmission electron microscopy (STEM) attachment or be capable of producing a spot size of less than 250 nm diam at crossover. Calibrate routinely for magnification, camera constant, and EDXA settings according to procedures of 5*d*.

4. Reagents and Materials

a. Acetone.

b. Dimethylformamide (DMF). CAUTION: *Toxic; use only in a fume hood.*

c. Glacial acetic acid. CAUTION: *Use in a fume hood.*

d. Chloroform.

e. 1-Methyl-2-pyrrolidinone.

f. Particle-free water: Use glass-distilled water or treat by reverse osmosis; filter through a filter with pore diam 0.45 μm or smaller.

g. Non-asbestos standards for minerals listed in ¶ 1*b* above.

h. Asbestos standards for minerals listed in Section 2570A.1.

5. Procedure

a. Sample filtration: Samples with high levels of organic contaminants may require pretreatment. A process using ultraviolet light and ozone bubbling is described elsewhere.[1] Drinking water samples prepared within 48 h of collection do not require pretreatment.

Under a HEPA hood, carefully wet-wipe exterior of sample bottle to remove any possible contamination before taking bottle into a clean preparation area separated from preparation areas for bulk or air-sample handling.

Prepare specimen in a clean HEPA filtered negative-pressure hood. Measure cleanliness of preparation area hoods by cumulative process blank concentrations (see ¶ b below).

If using a disposable plastic filter funnel unit, remove funnel assembly and discard top filter supplied with the apparatus, but be sure to retain the coarse polypropylene support pad in place. Assemble unit with the adapter and a properly sized neoprene stopper, and attach funnel to the 1000-mL side-arm vacuum flask. Moisten support pad with a few milliliters distilled water, place a 5.0-μm-pore-size MCE backing filter on support pad, and place an MCE or PC filter (≤0.45-μm-pore-size) on top of backing filter. After both filters are completely wet, apply vacuum, ensuring that filters are centered and pulled flat without air bubbles. If there are any irregularities on the filter surface, discard filters and repeat process. Replace funnel assembly. Return flask to atmospheric pressure. Alternatively, use glass filtering unit, following the same procedure to set up filters.

With flask at atmospheric pressure, add 20 mL particle-free water to funnel. Cover funnel with its plastic cover if the disposable filtering unit is used.

Briefly, by hand, shake capped bottle with sample suspension, then place it in tabletop ultrasonic bath and sonicate for 3.0 min. The water level in the bath should be approximately the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

same as that of the sample. After treatment, return sample bottle to work surface of HEPA hood. Carry out all preparation steps, until filters are ready for drying, in this hood.

Shake suspension vigorously by hand for 2 to 3 s. Estimate amount of liquid to be withdrawn to produce an adequate filter preparation. Experience has shown that a light staining of the filter surface will usually yield a suitable preparation. If the sample is relatively clean, use a volumetric cylinder to measure sample. If sample has a high particulate or asbestos content, withdraw a small volume (but at least 1 mL) with disposable glass pipet, inserting pipet halfway into sample.

NOTE: If, after examination in the TEM, the smallest volume measured (1.0 mL) yields an overloaded sample, make additional serial dilutions of the suspension. Shake suspension vigorously by hand for 2 to 3 s before taking serial dilution portion. Do not re-treat in ultrasonic bath either original solution or any dilutions. Mix 10 mL sample with 90 mL particle-free water in a clean sample bottle to obtain a 1:10 serial dilution.

Uncover filter funnel and dispense mixture into the water in the funnel. Recover funnel and agitate but do not swirl the liquid. (One acceptable means of agitation is to inject 5 to 10 mL particle-free water from a squeeze bottle into the funnel.) Apply vacuum and filter. Discard pipet, if used.

Disassemble filtering unit and carefully remove filter with clean forceps. Place filter, particle side up, in a precleaned, labeled, disposable plastic petri dish or similar container.

To obtain an optimally loaded filter, make several filtrations with different sample portions. Use new disposable plastic funnel units or carefully cleaned glass units for each filtration. When additional filters are prepared, shake suspension without additional ultrasonic treatment before removing the sample portion. Each new filtration should represent at least a five-fold loading difference.

Dry MCE filters for at least 12 h (over desiccant) in airtight, cabinet-type desiccator. Alternatively, to shorten drying time for filters prepared using the acetone collapsing method, plug damp filter and attach to a glass slide as described in ¶ c1)a) below. Place the slide with filter plug(s) (up to eight plugs can be attached to one slide) on a bed of desiccant, cover, and place in desiccator for 1 to 2 h.

Place PC filters in a dessicator for at least 30 min before preparation; lengthy drying is not required.

b. Sample blank preparation: Prepare sample blanks that include both a process blank (50 mL particle-free water) for each set of samples analyzed and one unused filter from each new box of sample filters (MCE or PC). Blanks are considered contaminated if, after analysis, they are shown to contain more than 53 asbestos structures/mm^2. This corresponds to 3 or 4 asbestos structures found in 10 grid openings. Identify source of contamination before making any further analysis. Reject samples that were processed with the contaminated blanks and prepare new samples after source of contamination is found. Take special care with polycarbonate filters, because some have been shown to contain asbestos contamination.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

c. Specimen preparation:

1) Mixed cellulose ester (MCE) filters

a) Filter fusing—Use either the acetone or the DMF-acetic acid method.

(1) Acetone fusing method—Remove a section from any quadrant of the sample and blank filters with a 7-mm cork borer. Place filter section (particle side up) on a clean microscope slide. Affix filter section to slide with a gummed page reinforcement or other suitable means. Label slide with a glass scribing tool or permanent marker.

Prepare a fusing dish as follows: Make a pad from five to six ashless paper filters and place in bottom of a glass petri dish. Place metal screen bridge on top of pad and saturate filter pads with acetone. Place slide on top of bridge and cover the petri dish. Wait approximately 5 min for sample filter to fuse and clear completely.

(2) DMF-acetic acid fusing method—Place drop of clearing solution (35% dimethylformamide [DMF], 15% glacial acetic acid, and 50% particle-free water by volume) on a clean microscope slide. CAUTION: *DMF is a toxic solvent; use only in a fume hood*. Use an amount of clearing solution that just saturates the filter. Using a clean scalpel blade, cut a wedge-shaped section of filter. A one-eighth filter section is sufficient. Carefully lay filter segment, sample surface upward, on top of solution. Bring filter and solution together at an angle of about 20 deg to help exclude air bubbles. Remove excess clearing solution with filter paper. Place slide in oven, on a slide-warmer, or on hot plate, in a fume hood, at 65 to 70°C for 5 to 10 min. The filter section should fuse and clear completely.

b) Plasma etching—Place microscope slide, with attached collapsed filter pieces, in a low-temperature plasma asher. Because plasma ashers vary greatly in their performance, both from unit to unit and between different positions in the asher barrel, it is difficult to specify operating conditions. Insufficient etching will result in a failure to expose embedded fibers; too much etching may result in the loss of particles from the filter surface. Calculate time for ashing on the basis of final sample observations in transmission electron microscope. Additional information on calibration is available.[2,3]

c) Carbon coating—Using high-vacuum carbon evaporator (¶ 3 *p*), proceed as follows: Place glass slide holding filters on the rotation device and evacuate evaporator chamber to a pressure of less than 0.013 Pa. Perform evaporation in very short bursts, separated by 3 to 4 s to let electrodes cool. An experienced analyst can judge the thickness of the carbon film. Make initial tests on unused filters. If the carbon film is too thin, large particles will be lost from the TEM specimen, and there will be few complete and undamaged grid openings. A coating that is too thick will lead to a TEM image lacking in contrast and a compromised ability to obtain electron diffraction patterns. The carbon film should be as thin as possible and still remain intact on most of the grid openings of the TEM specimen.

d) Specimen washing—Prepare a Jaffe washer according to any published design.[1,4] One such washer consists of a simple stainless steel bridge contained in a glass petri dish. Place on the stainless steel bridge several pieces of lens tissue large enough to hang completely over the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

bridge and into the solvent. In a fume hood, fill petri dish with either acetone or DMF to one quarter of the level in the dish.

Place TEM grids, shiny side up, on a piece of lens tissue or filter paper so that individual grids can be easily picked up with forceps. Prepare from each sample three grids. Using a curved scalpel blade, excise three square (3-mm × 3-mm) pieces of carbon-coated MCE filter from random areas on the filter. Place each square filter piece, carbon-side up, on top of a TEM specimen grid (¶ 3*r*).

Place all three assemblies (filter/grid) for each sample on the same piece of saturated lens tissue in Jaffe washer. Place lid on the Jaffe washer and let system stand, preferably overnight.

Alternatively, place grids on a low-level (petri dish is filled only enough to wet paper on screen bridge) DMF Jaffe washer for 60 min. Then add enough solution of equal parts DMF/acetone to fill washer up to screen level. Remove grids after 30 min if they have cleared, i.e., all filter material has been removed from the carbon film, as determined by inspecting in the TEM. Let grids dry before placing in TEM.

2) Polycarbonate (PC) filters—Cover surface of a clean microscope slide with two strips of double-sided cellophane tape. Cut a strip of filter paper slightly narrower than width of slide. Position filter paper strip on center of length of slide. Using a clean, curved scalpel blade, cut a strip of the PC filter approximately 25 × 6 mm. Use a rocking motion of the scalpel blade to avoid tearing filter. Place PC strip, particle side up, on slide perpendicular to long axis of slide, making sure that the ends of the PC strip contact the double-sided cellophane tape. Each slide can hold several PC strips. Label filter paper next to each PC strip with sample number.

Carbon-coat filter strips as directed in ¶ 1)c) above. (Etching is not required.) Take special care to avoid overheating filter sections during carbon coating.

Prepare a Jaffe washer as described in ¶ 1)d) above, but fill washer with chloroform or 1-methyl-2-pyrrolidinone to the level of the screen. Using a clean curved scalpel blade, excise three 3-mm-square filter pieces from each PC strip. Place filter squares, carbon side up, on shiny side of a TEM grid (¶ 3*r*). Pick up grid and filter section together and place them on lens tissue in the Jaffe washer. Place lid on Jaffe washer and leave grids for at least 4 h. Best results are obtained with longer wicking times, up to 12 h. Carefully remove grids from the Jaffe washer and let dry in the grid box before placing them in a clean, marked grid box.

d. Instrument calibration: Calibrate instrumentation regularly, and keep a calibration record for each TEM in the laboratory, in accordance with the laboratory's quality assurance program. Record all calibrations in a log book along with dates of calibration and attached backup documentation.

Check TEM for both alignment and systems operation. Refer to manufacturer's operational manual for detailed instructions.

Calibrate camera length of TEM in electron diffraction (ED) operating mode before observing ED patterns of unknown samples. Measure camera length by using a carbon-coated grid on which a thin film of gold has been sputtered or evaporated. A thin film of gold may be evaporated directly on to a specimen grid containing asbestos fibers. This yields zone-axis ED

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

patterns from the asbestos fibers superimposed on a ring pattern from the polycrystalline gold film. Optimize thickness of gold film so that only one or two sharp rings are obtained. Thicker gold films may mask weaker diffraction spots from the fibrous particles. Because unknown d-spacings of most interest in asbestos analysis are those lying closest to the transmitted beam, multiple gold rings from thicker films are unnecessary. Alternatively, use a gold standard specimen to obtain an average camera constant calculated for that particular instrument, which can then be used for ED patterns of unknowns taken during the corresponding period.

Calibrate magnification at the fluorescent screen at magnification used for structure counting. Use a grating replica (e.g., one containing at least 2160 lines/mm). Define a field of view on the fluorescent screen; the field must be measurable or previously inscribed with a scale or concentric circles (use metric scales). Place grating replica at the same distance from the objective lens as the specimen. For instruments that incorporate a eucentric tilting specimen stage, place all specimens and the grating replica at the eucentric position. Follow the instructions provided with the grating replica to calculate magnification. Frequency of calibration depends on service history of the microscope. Check calibration after any maintenance that involves adjustment of the power supply to the lens, the high-voltage system, or the mechanical disassembly of the electron optical column (apart from filament exchange).

Check smallest spot size of the TEM. At the crossover point, photograph spot size at a magnification of 25 000× (screen magnification 20 000×). An exposure time of 1 s usually is adequate. Measured spot size must be less than or equal to 250 nm.

Verify resolution and calibration of the EDXA as follows: Collect a standard EDXA Cu peak from the Cu grid and compare X-ray energy with channel number for Cu peak to make sure readings are within ± 10 eV. Collect a standard EDXA of crocidolite asbestos; elemental analysis of the crocidolite must resolve the Na peak. Collect a standard EDXA spectrum of chrysotile asbestos; elemental analysis of chrysotile must resolve both Si and Mg on a single chrysotile fiber.

e. Sample analysis: Carefully load TEM grid with grid bars oriented parallel/perpendicular to length of specimen holder. Use a hand lens or eye loupe if necessary. This procedure will line up the grid with the x and y translation directions of the microscope. Insert specimen holder into microscope.

Scan entire grid at low magnification (250× to 1000×) to determine its acceptability for high-magnification analysis. Grids are acceptable if the following conditions are met:

- The fraction of grid openings covered by the replica section is at least 50%.
- Relative to that section of the grid covered by the carbon replica, the fraction of intact grid openings is greater than 50%.
- The fractional area of undissolved filter is less than 10%.
- The fraction of grid squares with overlapping or folded replica film is less than 50%.
- At least 20 grid squares have no overlapping or folded replica, are less than 5% covered with

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

holes, and have less than 5% opaque area due to incomplete filter dissolution.

If the grid meets these criteria, chose grid squares for analysis from various areas of the grid so that the entire grid is represented. To be suitable for analysis, an individual grid square must meet the following criteria:

- It must have less than 5% holes over its area.
- It must be less than 25% covered with particulate matter.
- It must be uniformly loaded.

Observe and record orientation of grid at 80 to 150× on a grid map record sheet along with the location of the grid squares examined. If indexed grids are used, a grid map is not needed, but record identifying coordinates of the grid square.

At a screen magnification of 15 000 to 25 000×, evaluate the grids for the most concentrated sample loading. Reject sample if it is estimated to contain more than about 25 asbestos structures per grid opening. Proceed to the next most concentrated sample until a set of grids is obtained that have less than 25 asbestos structures per grid opening.

Analyze a minimum of four grid squares for each sample.

Analyze approximately one-half of the predetermined sample area on one sample grid preparation and the remainder on a second sample grid preparation.

Use structure definitions given in Section 2570A.2 to enumerate asbestos structures. Record all data on count sheet. Record asbestos structures in two size categories: ≥0.5 μm to ≥ 10.0 μm and >10.0 μm. For fibers and bundles, record size category of greatest length of the structure. For matrices and clusters, record size category of the visible portion of the longest fiber or bundle involved with the structure, not the greatest overall dimension of the structure. No minimum or maximum width restrictions are applied to the fiber definition, as long as the minimum length and aspect ratio criteria are met. Record ‘‘NSD’’ (no structures detected) when no structures are found in the grid opening.

Record a typical electron diffraction pattern for each type of asbestos observed for each group of samples (or a minimum of every five samples) analyzed. Record micrograph number on count sheet. For chrysotile, record one X-ray spectrum for each tenth structure analyzed. For each type of amphibole, record one X-ray spectrum for each fifth structure analyzed. (More information on identification is available.[1,4]) Attach the printouts to the back of the count sheet. If the X-ray spectrum is stored, record file and disk number on count sheet.

Analytical sensitivity can be improved by increasing amount of liquid filtered, increasing number of grid openings analyzed, or decreasing size of filter used. Occasionally, because of high particle loadings or high asbestos concentration, the desired analytical sensitivity cannot be achieved in practice.

Unless a specific analytical sensitivity is desired, stop analysis on the 10th grid opening or

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

the grid opening that contains the 100th asbestos structure, whichever comes first. If the analysis is stopped at the grid opening that contains the 100th asbestos structure, count entire grid square containing the 100th structure.

After analysis, remove grids from TEM, replace them in grid storage holder, and store for a minimum of one year from the date of the analysis for legal purposes. Sample filters also may be stored in the plastic petri dishes, if necessary. Prolonged storage of the remaining water sample is not recommended, because microbial growth may cause loss of asbestos structures to the sides of the storage container.

Report the following information for each water sample analyzed: asbestos concentration in structures per liter, for total structures and fibrous asbestos structures greater than 10 μm in length; types of asbestos present; number of asbestos structures counted; effective filtration area; average size of TEM grid openings counted; number of grid openings examined; size category for each structure counted. Include a copy of the TEM count sheet, either hand-written or computer-generated.

6. Calculations

Calculate amount of asbestos in a sample as follows:

$$\text{Asbestos concentration, structures/L} = \frac{N \times A_f \times D}{G \times A_G \times V_s}$$

where:

N = number of asbestos structures counted,
A_f = effective filter area of final sampling filter, mm^2,
D = dilution factor (if applicable),
G = number of grid openings counted,
A_G = area of grid openings, mm^2, and
V_s = volume of sample, L.

The same formula may be used to calculate asbestos fibers greater than 10 μm in length per liter based on the total number of fibers and bundles greater than 10 μm in length whether free or associated with matrices and clusters. Express final results as million structures per liter (MSL) and million fibers per liter (MFL).

7. Quality Control/Quality Assurance

Use the laboratory's quality-control checks to verify that system is performing according to accuracy and consistency specifications. Because of the difficulties in preparing known quantitative asbestos samples, routine quality-control testing focuses on reanalysis of samples

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

(duplicate recounts). Reanalyze 1 out of every 10 samples, not including laboratory blanks.

In addition, set up quality assurance programs according to the criteria developed by Federal agencies.[2,3] These documents cover sample custody, sample preparation, blank checks for contamination, calibration, sample analysis, analyst qualifications, and technical facilities.

8. Precision and Bias

Precision measurements for intralaboratory comparisons have been found to have a relative standard deviation (RSD) of 13 to 22% for standard and environmental water samples, with an RSD of 8.4 to 29% for interlaboratory comparisons.[1] An earlier study found an interlaboratory reproducibility of 25 to 50% in standard samples.[5]

Accuracy measurements from inter- and intralaboratory studies have demonstrated an RSD of 17% for standard chrysotile suspensions, and an RSD of 16% for standard crocidolite suspensions.[1]

9. References

1. CHATFIELD, E.J. & M.J. DILLON. 1983. Analytical Method for the Determination of Asbestos in Water. EPA 600/4-83-043, U.S. Environmental Protection Agency, Athens, Ga.
2. NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY & NATIONAL VOLUNTARY ACCREDITATION PROGRAM. 1989. Program Handbook for Airborne Asbestos Analysis. NISTIR 89-4137, U.S. Dep. Commerce, Gaithersburg, Md.
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1987. Asbestos-containing materials in schools: Final rule and notice. *Federal Register*, 40 CFR Part 763, Appendix A to Sub-part E, Oct. 30, 1987.
4. YAMATE, G., S.C. AGARWALL & R.D. GIBBONS. 1984. Methodology for the Measurement of Airborne Asbestos by Electron Microscopy. USEPA draft report, Contract No. 68-02-3266, Research Triangle Park, N.C.
5. CHOPRA, K.S. 1977. Inter-laboratory measurements of amphibole and chrysotile fiber concentrations in water. *In* National Bureau of Standards Spec. Publ. 506, Proc. of the Workshop on Asbestos: Definitions and Measurement Methods. Gaithersburg, Md.

2580 OXIDATION-REDUCTION POTENTIAL (ORP)#(53)*

2580 A. Introduction

1. Significance

Oxidation and reduction (redox) reactions mediate the behavior of many chemical

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

constituents in drinking, process, and wastewaters as well as most aquatic compartments of the environment.[1-5] The reactivities and mobilities of important elements in biological systems (e.g., Fe, S, N, and C), as well as those of a number of other metallic elements, depend strongly on redox conditions. Reactions involving both electrons and protons are pH- and Eh-dependent; therefore, chemical reactions in aqueous media often can be characterized by pH and Eh together with the activity of dissolved chemical species. Like pH, Eh represents an intensity factor. It does not characterize the capacity (i.e., poise) of the system for oxidation or reduction.

The potential difference measured in a solution between an inert indicator electrode and the standard hydrogen electrode should not be equated to Eh, a thermodynamic property, of the solution. The assumption of a reversible chemical equilibrium, fast electrode kinetics, and the lack of interfering reactions at the electrode surface are essential for such an interpretation. These conditions rarely, if ever, are met in natural water.

Thus, although measurement of Eh in water is relatively straightforward, many factors limit the interpretation of these values. These factors include irreversible reactions, electrode poisoning, the presence of multiple redox couples, very small exchange currents, and inert redox couples. Eh values measured in the field correlate poorly with Eh values calculated from the redox couples present. Nevertheless, measurement of redox potential, when properly performed and interpreted, is useful in developing a more complete understanding of water chemistry.

2. Sampling and Storage

Do not store samples; analyze on collection. Minimize both atmospheric contact and delay in analysis.

3. References

1. BAAS-BECKING, L.G.M., I.R. KAPLAN & D. MOORE. 1960. Limits of the natural environment in terms of pH and oxidation-reduction potentials. *J. Geol.* 68:243.
2. LANGMUIR, D. 1971. Eh-pH determination. *In* R.E. Carver, ed. Procedures in Sedimentary Petrology. Wiley-Interscience, New York, N.Y.
3. GARRELS, R.M. & C.L. CHRIST. 1965. Solutions, Minerals and Equilibria. Harper and Row, New York, N.Y.
4. BRECK, W.G. 1972. Redox potentials by equilibration. *J. Mar. Res.* 30:121.
5. BRICKER, O.P. 1982. Redox potential: Its measurement and importance in water systems. *In* R.A. Minear & L.H. Keith, eds. Water Analysis, Vol. 1, Inorganic Species. Academic Press, New York, N.Y.

4. Bibliography

GARRELS, R.M. 1960. Mineral Equilibria at Low Temperature and Pressure. Harper & Brothers, New York, N.Y.

POURBAIX, M.J.N. 1966. Atlas of Electrochemical Equilibriums in Aqueous Solutions (transl.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

J.A. Franklin, Centre Belge d'Etude de la Corrosion). Pergamon Press, Ltd., Oxford, England.

STUMM, W. 1967. Redox potential as an environmental parameter; conceptual significance and operational limitation. *In* Advances in Water Pollution Research. Proc. Int. Conf. Water Pollut. Res., 3rd, 1:283.

ADAMS, R.N. 1969. Electrochemistry at Solid Electrodes. Marcel Dekker, New York, N.Y.

BATES, R.G. 1973. Determination of pH, Theory and Practice, 2nd ed. John Wiley & Sons, New York, N.Y.

LINDBERG, R.D. & D.D. RUNNELLS. 1984. Groundwater redox reactions: an analysis of equilibrium state applied to Eh measurements and geochemical modeling. *Science* 225:925.

2580 B. Oxidation-Reduction Potential Measurement in Clean Water

1. General Discussion

a. Principle: Electrometric measurements are made by potentiometric determination of electron activity (or intensity) with an inert indicator electrode and a suitable reference electrode. Ideally, the indicator electrode will serve as either an electron donor or acceptor with respect to electroactive oxidized or reduced chemical species in solution. At redox equilibrium, the potential difference between the ideal indicator electrode and the reference electrode equals the redox potential of the system. However, inert indicator electrodes that behave ideally in all aqueous systems, particularly in natural waters, do not exist. Electrodes made of platinum are most commonly used for Eh measurements. They have limitations,[1] as do alternative materials such as gold and graphite.

The standard hydrogen reference electrode is fragile and impractical for routine laboratory and field use. Therefore, silver: silver-chloride or calomel reference electrodes are used commonly. The redox potential measurement is corrected for the difference between the potential of the reference electrode and that of the standard hydrogen electrode. See Section 4500-H pH Value.

It is not possible to calibrate Eh electrodes over a range of redox potentials (as is done with pH electrodes). Instead, standard solutions that exhibit both chemical stability and known redox potentials for specific indicator electrodes are used to check electrode response at the temperature of measurement.

The potential of the platinum (Pt) Eh electrode versus the Ag/AgCl reference electrode with KCl electrolyte in ZoBell's solution ($3 \times 10^{-3}M$ potassium ferrocyanide and $3 \times 10^{-3}M$ potassium ferricyanide in $0.1M$ KCl)[2] has been measured as a function of temperature.[3] Good agreement was obtained between Eh values measured with this electrode pair in ZoBell's solution and those calculated from the stability constants at 8 to 85°C. The potential of the ZoBell's solution with this electrode configuration

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

as a function of temperature can be calculated:[4]

$$Eh, \text{ V} = 0.428 - 0.0022\ (T - 25)$$

where T = solution temperature, °C. Alternatively, select the value from Table 2580:I.

To determine the Eh of a sample relative to the standard hydrogen electrode, measure Eh of both sample and standard solution at the same temperature (within ±0.1°C). Then calculate Eh value of the sample:

$$Eh_{\text{system}} = \text{E}_{\text{observed}} + \text{Eh}_{\text{ZoBell/reference}} - \text{Eh}_{\text{ZoBell observed}}$$

where:

E_{observed} = sample potential relative to reference electrode.

$Eh_{\text{ZoBell/reference}}$ = theoretical Eh of reference electrode and ZoBell's solution, relative to the standard hydrogen electrode (see Table 2580:I), and

$Eh_{\text{ZoBellobserved}}$ = observed potential of ZoBell's solution, relative to the reference electrode.

The measurements described above can be applied analogously to other indicator electrode/reference electrode pairs and standard solutions.

b. Interferences: Specific interferences may be due to operation of either indicator or reference electrode, redox capacity or poise of the sample, sample preservation and handling, and temperature equilibration.

1) Sorption and poisoning effects on electrodes—Contamination of the electrode surface, salt bridge, or internal electrolyte in the case of reference electrodes, can lead to excessive drift, poor electrode response, and artifact potentials. Organic matter, sulfide, and bromide may cause these problems, particularly in long-term electrode use.[1,5-7] If excessive drift occurs or erratic performance of paired electrodes is observed in redox standard solutions after appropriate cleaning, refilling, or regeneration procedures, discard the faulty electrode and use a new one.

2) pH variations—Redox potential is sensitive to pH if hydrogen ion or hydroxide ion is involved in the redox half-cells. Cell potentials tend to increase as proton concentration increases (i.e., pH decreases) and Eh values drop as hydroxide concentrations increase (i.e., pH increase).

3) Sample handling and preservation—The sample poise will govern the resistance of the sample to change in redox potential; this phenomenon is analogous to the resistance to pH change afforded by buffer capacity. Except in concentrated process streams, sludges, leachates, and highly reducing or treated waters, the concentrations of oxidized or reduced species may be fairly low (i.e., $<10^{-4}M$). Under these conditions, handle reduced samples very carefully to avoid exposure to atmospheric oxygen. A closed cell sampling configuration may be used.[4,8] Samples cannot be stored or preserved; analyze at sampling.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

4) Temperature equilibration—Obtain Eh standard solution reading for the electrode pair at a temperature as close as possible to that of the sample. Temperature determines the Eh reference potential for a particular solution and electrode pair. It also may affect the reversibility of the redox reaction, the magnitude of the exchange current, and the stability of the apparent redox potential reading, particularly in poorly poised solutions. Hold temperature constant for all measurements and report it with Eh results.

2. Apparatus

a. pH or millivolt meter: Use a pH meter or other type of high-impedance potentiometer capable of reading either pH or millivolts (mV). For most applications, a meter scale readable to ±1400 mV is sufficient.

b. Reference electrode consisting of a half-cell providing a constant electrode potential. See Section 4500-H^+.B.2*b*.

c. Oxidation-reduction indicator electrode: The platinum electrode is used most commonly. A noble metal or graphite electrode may be useful for specific applications.

1) Noble metal electrode—Noble metal (i.e., gold or platinum) foil, wire, or billet types of electrode are inert and resistant to chemical reaction. Clean and polish electrode surface to insure reliable performance. Platinum electrodes may be cleaned by strong acid soaking,[9,10] hydrogen peroxide and detergent washing,[11] and anodic activation.[10] Abrasive polishing with crocus cloth, jeweler's rouge, or 400 to 600 grit wet/dry carborundum paper may be best.[5]

2) Graphite electrode—A wax-impregnated graphite (WIG) electrode may be used, especially in aqueous suspensions or soils.[12,13] The WIG electrode is more resistant to electrode poisoning than electrodes made of platinum wire.

d. Beakers: Preferably use polyethylene, TFE, or glass beakers.

e. Stirrer: Use a magnetic TFE-coated stirring-bar-type mixer.

f. Flow cell: Use for continuous flow measurements and for poorly buffered solutions.

3. Reagents

a. Standard redox solutions: Standardize the electrode system against redox solutions that provide stable known Eh values over a range of temperatures. Although standard solutions are available, they do not cover the anticipated range of Eh values. Commercially prepared solutions may be used, particularly in field testing. The composition and Eh values of standard solutions are shown in Table 2580:II. With reasonable care, these solutions are stable for several months.

b. Eh electrode cleaners: Use either:

1) Aqua regia—Mix 1 volume conc nitric acid with 3 volumes conc hydrochloric acid. Prepare fresh and dilute by at least 50% with water. Neutralize prior to discarding.

2) Chromic acid—Dissolve 5 g potassium dichromate, $K_2Cr_2O_7$, in 500 mL conc sulfuric acid. Conduct cleaning procedure in a fume hood.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

4. Procedure

a. Instrument calibration: Follow manufacturer's instructions for using pH/millivolt meter and in preparing electrodes for use. Use a shorting lead to verify the zero point on the meter's millivolt scale. Equilibrate the standard solution to the temperature of the sample. Immerse electrodes in the gently stirred, standard solution in a beaker (or flow cell). Turn on meter, placing the function switch in the millivolt mode.

After several minutes for electrode equilibration, record reading to nearest millivolt. If the reading is more than ±10 mV from the theoretical redox standard value at that temperature, replace reference electrode fluid and repeat the measurement. If that procedure fails to bring the reading to within ±10 mV of the theoretical value, polish the sensing element of the indicator electrode with carborundum paper, crocus cloth, or jeweler's rouge. Rinse electrode thoroughly and recheck reading with a fresh portion of the standard solution. If the reading is within ±10 mV of the theoretical value, record it and the temperature. If the reading is not within ±10 mV, repeat the cleaning procedure or try another electrode. Then rinse the electrode with distilled water and proceed with the sample measurement. Recalibrate daily and more frequently if turbid, organic-rich, or high-dissolved-solids solutions are being measured.

b. Electrode cleaning procedure: Useful treatments for noble metal electrodes in restoring performance after long periods of use include immersion in warm (70°C) aqua regia for 1 to 2 min or 5 min in 6*N* HNO_3 after bringing to a boil. Alternatively treat with chromic acid solution followed by 6*N* HCl and rinse with water.

c. Sample analysis: Check system for performance with the standard solution, rinse electrodes thoroughly with sample water, then immerse them in the gently stirred sample. Let equilibrate, record Eh value to the nearest millivolt, and temperature to ±0.1°C. Repeat with a second sample portion to confirm successive readings within ±10 mV. Equilibration times vary and may take many minutes in poorly poised solutions. Successive readings that vary less than ±10 mV over 10 min are adequate for most purposes. Make continuous flow or pumped sample measurements, particularly of poorly poised solutions, in a closed flow cell after external calibration of the electrode system.

See Table 2580:III for recommended combinations of electrodes, standards, and sample handling.

5. Trouble Shooting

a. Meter: Use a shorting lead to establish meter reading at zero millivolts whenever possible. If the meter cannot be zeroed, follow the manufacturer's instructions for service.

b. Electrodes: If the potentiometer is in good working order, the fault may be in the electrodes. Frequently, renewal of the filling solution for the salt bridge for the reference electrode is sufficient to restore electrode performance. Another useful check is to oppose the emf of a questionable reference electrode with that of the same type known to be in good order. Using an adapter, plug the good reference electrode into the indicator electrode jack of the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

potentiometer. Then plug the questionable electrode into the reference electrode jack. With the meter in the millivolt position, immerse electrodes in an electrolyte (e.g., KCl) solution and then into a redox standard solution. The two millivolt readings should be 0 ± 5 mV for both solutions. If different electrodes are used (e.g., silver:silver chloride versus calomel or vice versa), the reading should be 44 ± 5 mV for a good reference electrode.

Unless an indicator electrode has been poisoned, physically damaged, or shorted out, it usually is possible to restore function by proper cleaning.

6. Calculation

$$Eh_{system} = E_{observed} + E_{reference\ standard} - E_{reference\ observed}$$

Report temperature at which readings were made.

7. Precision and Bias

Standard solution measurements made at stable temperatures with a properly functioning electrode system should be accurate to within ±10 mV. Calibration precision as reflected by the agreement of dual platinum electrodes versus an Ag:AgCl reference electrode for over a 2-year period has been estimated at ±15 mV (i.e., one standard deviation) in ZoBell's solution (N = 78) at approximately 12°C. Precision on groundwater samples (N = 234) over the same period has been estimated at ±22 mV (i.e., ± one standard deviation) in a closed flow cell.[15]

8. References

1. WHITFIELD, M. 1974. Thermodynamic limitations on the use of the platinum electrode in Eh measurements. *Limnol. Oceanogr.* 19:857.
2. ZOBELL, C.E. 1946. Studies on redox potential of marine sediments. *Amer. Assoc. Petroleum Geol.* 30:447.
3. NORDSTROM, D.K. 1977. Thermochemical equilibria of ZoBell's solution. *Geochim. Cosmochim. Acta* 41:1835.
4. WOOD, W.W. 1976. Guidelines for collection and field analysis of ground water samples for selected unstable constituents. Chapter D2 *in* Techniques of Water-Resources Investigations of the United States Geological Survey, Book 1. U.S. Geological Survey, Washington, D.C.
5. BRICKER, O.P. 1982. Redox potential: Its measurement and importance in water systems. *In* R.A. Minear & L.H. Keith, eds. Water Analysis, Vol. 1, Inorganic Species. Academic Press, New York, N.Y.
6. GERISCHER, H. 1950. Messungen der Austauschstromdichte beim Gleichgewichtspotential an einer Platinelektrode in Fe^{2+}/Fe^{3+} - Losungen. *Z. Elektrochem.* 54:366.
7. BOULEGUE, J. & G. MICHARD. 1979. Sulfur speciations and redox processes in reducing environments. *In* E.A. Jenne, ed., ACS Symposium Ser., Vol. 93. American Chemical

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Soc., Washington, D.C.

8. GARSKE, E.E. & M.R. SCHOCK. 1986. An inexpensive flow-through cell and measurement system for monitoring selected chemical parameters in ground water. *Ground Water Monit. Rev.* 6:79.
9. STARKEY, R.L. & K.M. WIGHT. 1945. Anaerobic Corrosion in Soil. Tech. Rep. American Gas Assoc., New York, N.Y.
10. IVES, D.J.G. & G.J. JANZ. 1961. Reference Electrodes. Academic Press, New York, N.Y.
11. BOHN, H.L. 1971. Redox potentials. *Soil Sci.* 112:39.
12. SHAIKH, A.U., R.M. HAWK, R.A. SIMS & H.D. SCOTT. 1985. Graphite electrode for the measurement of redox potential and oxygen diffusion rate in soil. *Nucl. Chem. Waste Manage.* 5:237.
13. SHAIKH, A.U., R.M. HAWK, R.A. SIMS & H.D. SCOTT. 1985. Redox potential and oxygen diffusion rate as parameters for monitoring biodegradation of some organic wastes in soil. *Nucl. Chem. Waste Manage*. 5:337.
14. LIGHT, T.S. 1972. Standard solution for redox potential measurements. *Anal. Chem.* 44:1038.
15. BARCELONA, M.J., H.A. WEHRMANN, M.R. SCHOCK , M.E. SIEVERS & J.R. KARNY. 1989. Sampling Frequency for Ground-Water Quality Monitoring. EPA 600S4/89/032. Illinois State Water Survey-Univ. Illinois, rep. to USEPA-EMSL, Las Vegas, Nev.

2710 TESTS ON SLUDGES#(54)*

2710 A. Introduction

This section presents a series of tests uniquely applicable to sludges or slurries. The test data are useful in designing facilities for solids separation and concentration and for assessing operational behavior, especially of the activated sludge process.

2710 B. Oxygen-Consumption Rate

1. General Discussion

This test is used to determine the oxygen consumption rate of a sample of a biological suspension such as activated sludge. It is useful in laboratory and pilot-plant studies as well as in the operation of full-scale treatment plants. When used as a routine plant operation test, it often will indicate changes in operating conditions at an early stage. However, because test conditions are not necessarily identical to conditions at the sampling site, the observed measurement may

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

not be identical with actual oxygen consumption rate.

2. Apparatus

a. Oxygen-consumption rate device: Either:

1) *Probe with an oxygen-sensitive electrode* (polarographic or galvanic), or

2) *Manometric or respirometric device* with appropriate readout and sample capacity of at least 300 mL. The device should have an oxygen supply capacity greater than the oxygen consumption rate of the biological suspension, or at least 150 mg/L·h.

b. Stopwatch or other suitable timing device.

c. Thermometer to read to ± 0.5°C.

3. Procedure

a. Calibration of oxygen-consumption rate device: Either:

1) Calibrate the oxygen probe and meter according to the method given in Section 4500-O.G, or

2) Calibrate the manometric or respirometric device according to manufacturer's instructions.

b. Volatile suspended solids determination: See Section 2540.

c. Preparation of sample: Adjust temperature of a suitable sample portion to that of the basin from which it was collected or to required evaluation temperature, and maintain constant during analysis. Record temperature. Increase DO concentration of sample by shaking it in a partially filled bottle or by bubbling air or oxygen through it.

d. Measurement of oxygen consumption rate:

1) Fill sample container to overflowing with an appropriate volume of a representative sample of the biological suspension to be tested.

2) If an oxygen-sensing probe is used, immediately insert it into a BOD bottle containing a magnetic stirring bar and the biological suspension. Displace enough suspension with probe to fill flared top of bottle and isolate its contents from the atmosphere. Activate probe stirring mechanism and magnetic stirrer. (NOTE: Adequate mixing is essential. For suspensions with high concentrations of suspended solids, i.e., >5000 mg/L, more vigorous mixing than that provided by the probe stirring mechanism and magnetic stirrer may be required.) If a manometric or respirometric device is used, follow manufacturer's instructions for startup.

3) After meter reading has stabilized, record initial DO and manometric or respirometric reading, and start timing device. Record appropriate DO, manometric, or respirometric data at time intervals of less than 1 min, depending on rate of consumption. Record data over a 15-min period or until DO becomes limiting, whichever occurs first. The oxygen probe may not be accurate below 1 mg DO/L. If a manometric or respirometric device is used, refer to manufacturer's instructions for lower limiting DO value. Low DO (≤2 mg/L at the start of the test) may limit oxygen uptake by the biological suspension and will be indicated by a decreasing

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

rate of oxygen consumption as the test progresses. Reject such data as being unrepresentative of suspension oxygen consumption rate and repeat test beginning with higher initial DO levels.

The results of this determination are quite sensitive to temperature variations and poor precision is obtained unless replicate determinations are made at the same temperature. When oxygen consumption is used as a plant control test, run periodic (at least monthly) replicate determinations to establish the precision of the technique. This determination also is sensitive to the time lag between sample collection and test initiation.

4. Calculations

If an oxygen probe is used, plot observed readings (DO, milligrams per liter) versus time (minutes) on arithmetic graph paper and determine the slope of the line of best fit. The slope is the oxygen consumption rate in milligrams per liter per minute.

If a manometric or respirometric device is used, refer to manufacturer's instructions for calculating the oxygen consumption rate.

Calculate specific oxygen consumption rate in milligrams per gram per hour as follows:

Specific oxygen consumption rate, (mg/g)/h

$$= \frac{\text{oxygen consumption rate, (mg/L)/min}}{\text{volatile suspended solids, g/L}} \times \frac{60 \text{ min}}{\text{h}}$$

5. Precision and Bias

Bias is not applicable. The precision for this test has not been determined.

6. Bibliography

UMBREIT, W.W., R.H. BURRIS & J.F. STAUFFER. 1964. Manometric Techniques. Burgess Publishing Co., Minneapolis, Minn.

2710 C. Settled Sludge Volume

1. General Discussion

The settled sludge volume of a biological suspension is useful in routine monitoring of biological processes. For activated sludge plant control, a 30-min settled sludge volume or the ratio of the 15-min to the 30-min settled sludge volume has been used to determine the returned-sludge flow rate and when to waste sludge. The 30-min settled sludge volume also is used to determine sludge volume index[1] (Section 2710D).

This method is inappropriate for dilute sludges because of the small volume of settled material. In such cases, use the volumetric test for settleable solids using an Imhoff cone

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

(2540F). Results from 2540F are not comparable with those obtained with the procedure herein.

2. Apparatus

a. Settling column: Use 1-L graduated cylinder equipped with a stirring mechanism consisting of one or more thin rods extending the length of the column and positioned within two rod diameters of the cylinder wall. Provide a stirrer able to rotate the stirring rods at no greater than 4 rpm (peripheral tip speed of approximately 1.3 cm/s). See Figure 2710:1.

b. Stopwatch.

c. Thermometer.

3. Procedure

Place 1.0 L sample in settling column and distribute solids by covering the top and inverting cylinder three times. Insert stirring rods, activate stirring mechanism, start the stop watch, and let suspension settle. Continue stirring throughout test. Maintain suspension temperature during test at that in the basin from which the sample was taken.

Determine volume occupied by suspension at measured time intervals, e.g., 5, 10, 15, 20, 30, 45, and 60 min.

Report settled sludge volume of the suspension in milliliters for an indicated time interval.

Variations in suspension temperature, sampling and agitation methods, dimensions of settling column, and time between sampling and start of the determination significantly affect results.

4. Precision and Bias

Bias is not applicable. The precision for this test has not been determined.

5. Reference

1. DICK, R.I. & P.A. VESILIND. 1969. The SVI—What is It? *J. Water Pollut. Control Fed.* 41:1285.

2710 D. Sludge Volume Index

1. General Discussion

The sludge volume index (SVI) is the volume in milliliters occupied by 1 g of a suspension after 30 min settling. SVI typically is used to monitor settling characteristics of activated sludge and other biological suspensions.[1] Although SVI is not supported theoretically,[2] experience has shown it to be useful in routine process control.

2. Procedure

Determine the suspended solids concentration of a well-mixed sample of the suspension (See Section 2540D).

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Determine the 30 min settled sludge volume (See Section 2710C).

3. Calculations

$$\text{SVI} = \frac{\text{settled sludge volume (mL/L)} \times 1000}{\text{suspended solids (mg/L)}}$$

4. Precision and Bias

Precision is determined by the precision achieved in the suspended solids measurement, the settling characteristics of the suspension, and variables associated with the measurement of the settled sludge volume. Bias is not applicable.

5. References

1. DICK, R.I. & P.A. VESILIND. 1969. The SVI—What is it? *J. Water Pollut. Control Fed.* 41:1285.
2. FINCH, J. & H. IVES. 1950. Settleability indexes for activated sludge. *Sewage Ind. Wastes* 22:833.

6. Bibliography

DONALDSON, W. 1932. Some notes on the operation of sewage treatment works. *Sewage Works J.* 4:48.

MOHLMAN, F.W. 1934. The sludge index. *Sewage Works J.* 6:119.

RUDOLFS, W. & I.O. LACY. 1934. Settling and compacting of activated sludge. *Sewage Works J.* 6:647.

2710 E. Zone Settling Rate

1. General Discussion

At high concentrations of suspended solids, suspensions settle in the zone-settling regime. This type of settling takes place under quiescent conditions and is characterized by a distinct interface between the supernatant liquor and the sludge zone. The height of this distinct sludge interface is measured with time. Zone settling data for suspensions that undergo zone settling, e.g., activated sludge and metal hydroxide suspensions, can be used in the design, operation, and evaluation of settling basins.[1-3]

2. Apparatus

a. Settling vessel: Use a transparent cylinder at least 1 m high and 10 cm in diameter. To reduce the discrepancy between laboratory and full-scale thickener results, use larger diameters

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

and taller cylinders.[1,3] Attach a calibrated millimeter tape to outside of cylinder. Equip cylinder with a stirring mechanism, e.g., one or more thin rods positioned within two rod diameters of the internal wall of settling vessel. Stir suspension near vessel wall over the entire depth of suspension at a peripheral speed no greater than 1 cm/s. Greater speeds may interfere with the thickening process and yield inaccurate results.[4] Provide the settling vessel with a port in the bottom plate for filling and draining. See Figure 2710:2.

b. Stopwatch.

c. Thermometer.

3. Procedure

Maintain suspension in a reservoir in a uniformly mixed condition. Adjust temperature of suspension to that of the basin from which it was collected or to required evaluation temperature. Record temperature. Remove a well-mixed sample from reservoir and measure suspended solids concentration (Section 2540D).

Activate stirring mechanism. Fill settling vessel to a fixed height by pumping suspension from reservoir or by gravity flow. Fill at a rate sufficient to maintain a uniform suspended solids concentration throughout settling vessel at end of filling. The suspension should agglomerate, i.e., form a coarse structure with visible fluid channels, within a few minutes. If suspension does not agglomerate, test is invalid and should be repeated.

Record height of solids-liquid interface at intervals of about 1 min. Collect data for sufficient time to assure that suspension is exhibiting a constant zone-settling velocity and that any initial reflocculation period, characterized by an accelerating interfacial settling velocity, has been passed.

Zone settling rate is a function of suspended solids concentration, suspension characteristics, vessel dimensions, and laboratory artifacts. With the filling method described above and a sufficiently large cylinder, these artifacts should be minimized. However, even with careful testing suspensions often may behave erratically. Unpredictable behavior increases for sludges with high solids concentrations and poor settling characteristics, and in small cylinders.

4. Calculations

Plot interface height in centimeters vs. time in minutes.[1,3] Draw straight line through data points, ignoring initial shoulder or reflocculation period and compression shoulder. Calculate interfacial settling rate as slope of line in centimeters per minute.

5. Precision and Bias

Bias is not applicable. The precision for this test has not been determined.

6. References

1. DICK, R.I. 1972. Sludge treatment. *In* W.J. Weber, ed., Physicochemical Processes for Water Quality Control. Wiley-Interscience, New York, N.Y.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2. DICK, R.I. & K.W. YOUNG. 1972. Analysis of thickening performance of final settling tanks. *Proc. 27th Ind. Waste Conf.*, Purdue Univ., Eng. Ext. Ser. No. 141, 33.
3. VESILIND, P.A. 1975. Treatment and Disposal of Wastewater Sludges. Ann Arbor Science Publishing Co., Ann Arbor, Mich.
4. VESILIND, P.A. 1968. Discussion of Evaluation of activated sludge thickening theories. *J. San. Eng. Div., Proc. Amer. Soc. Civil Eng.* 94: SA1, 185.

7. Bibliography

DICK, R.I. & R.B. EWING. 1967. Evaluation of activated sludge thickening theories. *J. San. Eng. Div., Proc. Amer. Soc. Civil Eng.* 93:SA4, 9.

DICK, R.I. 1969. Fundamental aspects of sedimentation I & II. *Water Wastes Eng.* 3:47, 45, & 6:2.

DICK, R.I. 1970. Role of activated sludge final settling tanks. *J. San. Eng. Div., Proc. Amer. Soc. Civil Eng.* 96:SA2, 423.

2710 F. Specific Gravity

1. General Discussion

The specific gravity of a sludge is the ratio of the masses of equal volumes of a sludge and distilled water. It is determined by comparing the mass of a known volume of a homogeneous sludge sample at a specific temperature to the mass of the same volume of distilled water at 4°C.

2. Apparatus

Container: A marked flask or bottle to hold a known sludge volume during weighing.

3. Procedure

Follow either *a* or *b*.

a. Record sample temperature, *T*. Weigh empty container and record weight, *W*. Fill empty container to mark with sample, weigh, and record weight, *S*. Fill empty container to mark with water, weigh, and record weight, *R*. Measure all masses to the nearest 10 mg.

b. If sample does not flow readily, add as much of it to container as possible without exerting pressure, record volume, weigh, and record mass, *P*. Fill container to mark with distilled water, taking care that air bubbles are not trapped in the sludge or container. Weigh and record mass, *Q*. Measure all masses to nearest 10 mg.

4. Calculation

Use *a* or *b*, matching choice of procedure above.

a. Calculate specific gravity, *SG*, from the formula

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$SG_{T/4°C} = \frac{\text{weight of sample}}{\text{weight of equal volume of water at 4°C}} = \frac{S - W}{R - W} \times F$$

The values of the temperature correction factor *F* are given in Table 2710:I.

b. Calculate specific gravity, *SG*, from the formula

$$SG_{T/4°C} = \frac{\text{weight of sample}}{\text{weight of equal volume of water at 4°C}} = \frac{(P - W)}{(R - W) - (Q - P)} \times F$$

For values of *F*, see Table 2710:I.

2710 G. Capillary Suction Time

1. General Discussion

The capillary suction time (CST) test determines rate of water release from sludge. It provides a quantitative measure, reported in seconds, of how readily a sludge releases its water. The results can be used to assist in sludge dewatering processes; to evaluate sludge conditioning aids and dosages; or, when used with a jar test and the settleable solids procedure, to evaluate coagulation effects on the rate of water release from sludges.

The test consists of placing a sludge sample in a small cylinder on a sheet of chromatography paper. The paper extracts liquid from the sludge by capillary action. The time required for the liquid to travel a specified distance is recorded automatically by monitoring the conductivity change occurring at two contact points appropriately spaced and in contact with the chromatography paper. The elapsed time is indicative of the water drainage rate. The CST test has been used as a relative indicator to characterize the performance of most sludge dewatering processes.

2. Apparatus

a. Test materials and apparatus may be fabricated (see Figure 2710:3) or are commercially available.#(55)* The unit includes a paper support block, stainless steel reservoir with 18-mm ID and 25-mm height, and a digital timer.

b. CST paper.#(56)†

c. Thermometer to read ± 0.5C.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

d. Pipet, 10-mL, plastic with tip trimmed to allow free passage of sludge flocs.

3. Procedure

Turn on and reset CST meter. Dry CST test block and reservoir. Place a new CST paper on lower test block with rough side up and grain parallel to the 9-cm side. Add upper test block, insert sludge reservoir into test block, and seat it using light pressure and a quarter turn to prevent surface leaks. Measure and record temperature of sludge. Pipet 6.4 mL sludge into test cell reservoir; if pipetting is difficult because of sludge consistency, pour a representative sludge sample into the test cell until it is full. The CST device will begin time measurement as liquid being drawn into the paper reaches the inner pair of electrical contacts. Timing ends when the outer contact is reached. Record CST shown on digital display. Empty remaining sludge from reservoir and remove and discard used CST paper. Rinse and dry test block and reservoir. Repeat for a minimum of five determinations per sample to account for measurement variation and to allow identification of any faulty readings due to leaks or spills.

Variations in sludge temperature and sample volume can affect CST results. Ensure that all analyses are run under similar conditions. Sludge suspended solids concentration has a significant effect on test results. In evaluating sludge conditioners or monitoring operation of a dewatering process, avoid this effect by ensuring homogeneity among sludge samples. Comparison of CST data from different sludge samples from the same source (especially if taken on different days) cannot be made with confidence unless suspended solids concentrations are comparable. Make a rough correction for different solids contents by dividing the sludge's CST value by its corresponding solids concentration.

Characteristics of CST paper may vary between lots. If comparison of CST values for distilled water indicates such variations, subtract times for distilled water blanks from sample times to improve comparisons.

Record CST model used, paper type, sludge type, sludge temperature, and capillary suction time. Measure solids concentration and CST of distilled water using the same paper to provide useful information.

4. Precision and Bias

Ten tests conducted on an anaerobically digested pulp mill sludge resulted in a mean CST of 363.2 s with a standard deviation of 36.2 s. Twenty tests using an anaerobically digested municipal wastewater sludge gave a mean of 85.2 s with a standard deviation of 14.12 s. Triplicate analyses of 30 sample sets of conditioned and unconditioned alum sludge resulted in an average standard deviation of 1.0 s with means between 5 and 80 s. Method bias cannot be determined.

5. Bibliography

BASKERVILLE, R.C. & R.S. GALE. 1968. A simple automatic instrument for determining the filtrability of sewage sludges. *J. Inst. Water Pollut. Control* 67:233.

KAVANAGH, B.A. 1980. The dewatering of activated sludge: measurements of specific resistance

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

to filtration and capillary suction time. *Water Pollut. Control* 79:388.

VESILIND, P.A. 1988. Capillary suction time as a fundamental measure of sludge dewaterability. *J. Water Pollut. Control Fed.* 60:215.

TILLER, F.M., Y.L. SHEN & A. ADIN. 1990. Capillary suction theory for rectangular cells. *Res. J. Water Pollut. Control Fed.* 62:130.

2710 H. Time-to-Filter

1. General Discussion

The time to filter (TTF) correlates with capillary suction time (CST) and is similar to the specific resistance to filtration if sludge solids content and filtrate viscosity do not vary among compared samples. The test requires approximately 200 mL sludge and can be used to assist in the daily operation of sludge dewatering processes or to evaluate sludge-conditioning polymers and dosages.

Testing with a smaller volume is possible in applications to evaluate water drainage rate subsequent to jar tests and settleable solids determination (see Section 2540F). In this case, drain collected sludge from one or more Imhoff cones after decanting as much supernatant as possible; use a small-volume TTF apparatus.

The test consists of placing a sludge sample in a Buchner funnel with a paper support filter, applying vacuum, and measuring the time required for 100 mL filtrate (or, for reduced sample volumes, 50% of original sample) to collect. While similar to the specific resistance to filtration test, the time-to-filter test is superior because of its ease of use and simplicity.

2. Apparatus

a. Time-to-filter large-volume or small-volume (Figure 2710:4) *assembly.*

*b. Filter paper#(57)**

c. Stopwatch.

3. Procedure

Place paper filter in funnel and make a firm seal by pre-wetting with a small volume of water with vacuum on. If using large-volume apparatus, take a 200-mL sample of sludge. With vacuum pump providing a constant vacuum of 51 kPa, pour sample into funnel. Start stopwatch or timer and determine time required for 100 mL of sample to collect in graduated cylinder. This is the time to filter. Make a minimum of three replicate determinations.

For the small-volume test, use 7 to 10 mL sludge. Record time required for 50% of sample to collect in graduated cylinder. Compare this time to filter only to other results using the same sample volume.

Sludge suspended solids concentration has a significant effect on test results. In evaluating sludge-conditioning products, compare results for which initial suspended solids concentrations

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

are comparable. Make a rough correction for different solids contents by dividing the time-to-filter value by its corresponding solids concentration. However, variations in solids concentration occur in full-scale applications, and the time-to-filter results may be interpreted as indicating the overall rate of water release from sludges, including the effect of differing solids concentrations.

4. Precision and Bias

Variations in vacuum pressure, support filter type, sludge temperature, and sample volume can affect test results. Triplicate analyses of 18 sample sets of conditioned and unconditioned alum sludge resulted in an average method precision of 19 s (approximately 4% of the average value) for the large-volume TTF test. Triplicate analyses of 9 sample sets of conditioned and unconditioned alum sludge resulted in a method precision of 9 s (approximately 6% of the average value) for the small-volume TTF test. Method bias, which refers to the agreement between the value determined by the test method and the real value, cannot be determined.

5. Bibliography

KNOCKE, W.R. & D.L. WAKELAND. 1983. Fundamental characteristics of water treatment plant sludges. *J. Amer. Water Works Assoc.* 113: 516.

DENTEL, S.K., T.A. BOBER, P.V. SHETTY & J.R. RESTA. 1986. Procedures Manual for Selection of Coagulant, Filtration, and Sludge Conditioning Aids in Water Treatment. Publ. 90515, American Water Works Assoc., Denver, Colo.

2720 ANAEROBIC SLUDGE DIGESTER GAS ANALYSIS*#(58)

2720 A. Introduction

Gas produced during the anaerobic decomposition of wastes contains methane (CH_4) and carbon dioxide (CO_2) as the major components with minor quantities of hydrogen (H_2), hydrogen sulfide (H_2S), nitrogen (N_2), and oxygen (O_2). It is saturated with water vapor. Common practice is to analyze the gases produced to estimate their fuel value and to check on the treatment process. The relative proportions of CO_2, CH_4, and N_2 are normally of most concern and the easiest to determine because of the relatively high percentages of these gases.

1. Selection of Method

Two procedures are described for gas analysis, the volumetric method (B), and the gas chromatographic method (C). The volumetric analysis is suitable for the determination of CO_2, H_2, CH_2, and O_2. Nitrogen is estimated indirectly by difference. Although the method is time-consuming, the equipment is relatively simple. Because no calibration is needed before use, the procedure is particularly appropriate when analyses are conducted infrequently.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

The principal advantage of gas chromatography is speed. Commercial equipment is designed specifically for isothermal or temperature-programmed gas analysis and permits the routine separation and measurement of CO_2, N_2, O_2, and CH_4 in less than 15 to 20 min. The requirements for a recorder, pressure-regulated bottles of carrier gas, and certified standard gas mixtures for calibration raise costs to the point where infrequent analyses by this method may be uneconomical. The advantages of this system are freedom from the cumulative errors found in sequential volumetric measurements, adaptability to other gas component analyses, adaptability to intermittent on-line sampling and analysis, and the use of samples of 1 mL or less.[1]

2. Sample Collection

When the source of gas is some distance from the apparatus used for analysis, collect samples in sealed containers and bring to the instrument. Displacement collectors are the most suitable containers. Glass sampling bulbs (or tubes) with three-way glass or TFE stopcocks at each end, as indicated in Figure 2720:1, are particularly useful. These also are available with centrally located ports provided with septa for syringe transfer of samples. Replace septa periodically to prevent contamination by atmospheric gases. Connect one end of collector to gas source and vent three-way stopcock to the atmosphere. Clear line of air by passing 10 to 15 volumes of gas through vent and open stopcock to admit sample. If large quantities of gas are available, sweep air away by passing 10 to 15 volumes of gas through tube. If the gas supply is limited, fill the gas sampling bulb (tube) with an acidic salt solution.[2] Then completely displace the acidic salt solution in the gas sampling bulb (tube) with the sample gas. Because the acidic salt solution absorbs gases to some extent, fill the gas sampling bulb completely with the gas and seal off from any contact with displacement fluid during temporary storage. When transferring gas to the gas-analyzing apparatus, do not transfer any fluid.

3. References

1. GRUNE, W.N. & C.F. CHUEH. 1962–63. Sludge gas analysis using gas chromatograph. *Water Sewage Works* 109:468; 110:43, 77, 102, 127, 171, 220, and 254.
2. CHIN, K.K. & K.K. WONG. 1983. Thermophilic anaerobic digestion of palm oil mill effluent. *Water Res.* 17:993.

2720 B. Volumetric Method

1. General Discussion

a. Principle: This method may be used for the analysis either of digester gas or of methane in water (see Section 6211, Methane). A measured volume of gas is passed first through a solution of potassium hydroxide (KOH) to remove CO_2, next through a solution of alkaline pyrogallol to remove O_2, and then over heated cupric oxide, which removes H_2 by oxidation to water. After

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

each of the above steps, the volume of gas remaining is measured; the decrease that results is a measure of the relative percentage of volume of each component in the mixture. Finally, CH_4 is determined by conversion to CO_2 and H_2O in a slow-combustion pipet or a catalytic oxidation assembly. The volume of CO_2 formed during combustion is measured to determine the fraction of methane originally present. Nitrogen is estimated by assuming that it represents the only gas remaining and equals the difference between 100% and the sum of the measured percentages of the other components.

When only CO_2 is measured, report only CO_2. No valid assumptions may be made about the remaining gases present without making a complete analysis.

Follow the equipment manufacturers' recommendations with respect to oxidation procedures.

CAUTION: *Do not attempt any slow-combustion procedure on digester gas because of the high probability of exceeding the explosive 5% by volume concentration of* CH_4.

2. Apparatus

Orsat-type gas-analysis apparatus, consisting of at least: (1) a water-jacketed gas buret with leveling bulb; (2) a CO_2-absorption pipet; (3) an O_2-absorption pipet; (4) a cupric oxide-hydrogen oxidation assembly; (5) a shielded catalytic CH_4-oxidation assembly or slow-combustion pipet assembly; and (6) a leveling bulb. With the slow-combustion pipet use a controlled source of current to heat the platinum filament electrically. Preferably use mercury as the displacement fluid; alternatively use aqueous Na_2SO_4-H_2SO_4 solution for sample collection. Use any commercially available gas analyzer having these units.

3. Reagents

a. Potassium hydroxide solution: Dissolve 500 g KOH in distilled water and dilute to 1 L.

b. Alkaline pyrogallol reagent: Dissolve 30 g pyrogallol (also called pyrogallic acid) in distilled water and make up to 100 mL. Add 500 mL KOH solution.

c. Oxygen gas: Use approximately 100 mL for each gas sample analyzed.

d. Displacement liquid (acidic salt solution): Dissolve 200 g Na_2SO_4 in 800 mL distilled water; add 30 mL conc H_2SO_4. Add a few drops of methyl orange indicator. When color fades, replace solution.

4. Procedure

a. Sample introduction: Transfer 5 to 10 mL gas sample into gas buret through a capillary-tube connection to the collector. Expel this sample to the atmosphere to purge the system. Transfer up to 100 mL gas sample to buret. Bring sample in buret to atmospheric or reference pressure by adjusting leveling bulb. Measure volume accurately and record as V_1.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

b. Carbon dioxide absorption: Remove CO_2 from sample by passing it through the CO_2-absorption pipet charged with the KOH solution. Pass gas back and forth until sample volume remains constant. Before opening stopcocks between buret and any absorption pipet, make sure that the gas in the buret is under a slight positive pressure to prevent reagent in the pipet from contaminating stopcock or manifold. After absorption of CO_2, transfer sample to buret and measure volume. Record as V_2.

c. Oxygen absorption: Remove O_2 by passing sample through O_2-absorption pipet charged with alkaline pyrogallol reagent until sample volume remains constant. Measure volume and record as V_3 . For digester gas samples, continue as directed in ¶ 4*d*. For CH_4 in water, store gas in CO_2 pipet and proceed ¶ 4*e* below.

d. Hydrogen oxidation: Remove H_2 by passing sample through CuO assembly maintained at a temperature in the range 290 to 300°C. When a constant volume has been obtained, transfer sample back to buret, cool, and measure volume. Record as V_4.

Waste to the atmosphere all but 20 to 25 mL of remaining gas. Measure volume and record as V_5. Store temporarily in CO_2-absorption pipet.

e. Methane oxidation: Purge inlet connections to buret with O_2 by drawing 5 to 10 mL into buret and expelling to the atmosphere. Oxidize CH_4 either by the catalytic oxidation process for digester gas and gas phase of water samples or by the slow-combustion process for gas phase of water samples.

1) Catalytic oxidation process—For catalytic oxidation of digester gas and gas phase of water samples, transfer 65 to 70 mL O_2 to buret and record this volume as V_6 . Pass O_2 into CO_2-absorption pipet so that it will mix with sample stored there. Return this mixture to buret and measure volume. Record as V_7. This volume should closely approximate V_5 plus V_6 . Pass O_2-sample mixture through catalytic oxidation assembly, which should be heated in accordance with the manufacturer's directions. Keep rate of gas passage less than 30 mL/min. After first pass, transfer mixture back and forth through the assembly between buret and reservoir at a rate not faster than 60 mL/min until a constant volume is obtained. Record as V_8.

2) Slow-combustion process—For slow combustion of the gas phase of water samples, transfer 35 to 40 mL O_2 to buret and record volume as V_6 . Transfer O_2 to slow-combustion pipet and then transfer sample from CO_2-absorption pipet to buret. Heat platinum coil in combustion pipet to yellow heat while controlling temperature by adjusting current. Reduce pressure of O_2 in pipet to somewhat less than atmospheric pressure by means of the leveling bulb attached to the pipet. Pass sample into slow-combustion pipet at rate of approximately 10 mL/min. After the first pass, transfer sample and O_2 mixture back and forth between pipet and buret several times at a faster rate, allowing mercury in pipet to rise to a point just below heated

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

coil. Collect sample in combustion pipet, turn off coil, and cool pipet and sample to room temperature with a jet of compressed air. Transfer sample to buret and measure volume. Record as V_8.

f. Measurement of carbon dioxide produced: Determine amount of CO_2 formed in the reaction by passing sample through CO_2-absorption pipet until volume remains constant. Record volume as V_9 . Check accuracy of determination by absorbing residual O_2 from sample. After this absorption, record final volume as V_{10}.

5. Calculation

a. CH_4 and H_2 usually are the only combustible gases present in sludge digester gas. When this is the case, determine percentage by volume of each gas as follows:

$$\% \ CO_2 = \frac{(V_1 - V_2) \times 100}{V_1}$$

$$\% \ O_2 = \frac{(V_2 - V_3) \times 100}{V_1}$$

$$\%H_2 = \frac{(V_3 - V_4) \times 100}{V_1}$$

$$\% \ CH_4 = \frac{V_4 \times (V_8 - V_9) \times 100}{V_1 \times V_5}$$

$$\% \ N_2 = 100 - (\% \ CO_2 + \%O_2 + \%H_2 + \%CH_4)$$

b. Alternatively, calculate CH_4 by either of the two following equations:

$$\%CH_4 = \frac{V_4 \times (V_6 + V_{10} - V_9) \times 100}{2 \times V_1 \times V_5}$$

$$\%CH_4 = \frac{V_4 \ (V_7 - V_8) \times 100}{2 \times V_1 \times V_5}$$

Results from the calculations for CH_4 by the three equations should be in reasonable agreement.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

If not, repeat analysis after checking apparatus for sources of error, such as leaking stopcocks or connections. Other combustible gases, such as ethane, butane, or pentane, will cause a lack of agreement among the calculations; however, the possibility that digester gas contains a significant amount of any of these is remote.

6. Precision and Bias

A gas buret measures gas volume with a precision of 0.05 mL and a probable accuracy of 0.1 mL. With the large fractions of CO_2 and CH_4 normally present in digester gas, the overall error for their determination can be made less than 1%. The error in the determination of O_2 and H_2, however, can be considerable because of the small concentrations normally present. For a concentration as low as 1%, an error as large as 20% can be expected. When N_2 is present in a similar low-volume percentage, the error in its determination would be even greater, because errors in each of the other determinations would be reflected in the calculation for N_2.

7. Bibliography

YANT, W.F. & L.B. BERGER. 1936. Sampling of Mine Gases and the Use of the Bureau of Mines Portable Orsat Apparatus in Their Analysis. Miner's Circ. No. 34, U.S. Bur. Mines, Washington, D.C.

MULLEN, P.W. 1955. Modern Gas Analysis. Interscience Publishers, New York, N.Y.

2720 C. Gas Chromatographic Method

1. General Discussion

See Section 6010C for discussions of gas chromatography.

2. Apparatus

a. Gas chromatograph: Use any instrument system equipped with a thermal conductivity detector (TCD), carrier-gas flow controllers, injector and column temperature setting dials, TCD current controller, attenuator, carrier-gas pressure gauge, injection port, signal output, and power switch. Some columns require temperature programming while others are isothermal. Preferably use a unit with a gas sampling loop and valve that allow automatic injection of a constant sample volume.

b. Sample introduction apparatus: An instrument equipped with gas-sampling valves is designed to permit automatic injection of a specific sample volume into the chromatograph. If such an instrument is not available, introduce samples with a 2-mL syringe fitted with a 27-gauge hypodermic needle. Reduce escape of gas by greasing plunger lightly with mineral oil or preferably by using a special gas-tight syringe. One-step separation of oxygen, nitrogen, methane, and carbon dioxide may be accomplished in concentric columns (column within a column) under isothermal conditions at room temperature instead of performing two column

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

analyses. These concentric columns permit the simultaneous use of two different packings for the analysis of gas samples.

*c. Chromatographic column:#(59)** Select column on the basis of manufacturer's recommendations.#(60)† Report column and packing specifications and conditions of analyses with results.

A two-column system usually is required. A molecular sieve column separates H_2, O_2, N_2, CO, and CH_4 isothermally, but because CO_2 is adsorbed by the molecular sieve, a second column is needed to complete the analysis. A commonly used two-column system utilizes a Chromosorb 102 column and a Molecular Sieve 5A or 13X column to separate H_2, O_2, N_2, CH_4, and CO_2 isothermally.[1,2]

A single-column procedure can be used; however, it requires temperature programming. Columns packed with special porous spherical or granular packing materials effect separation with sharp, well-resolved peaks.[3] With temperature programming, columns packed with Chromosorb 102,[2] Carbosphere,[4] and Carbosieve[3] separate the gases listed.†#(61) Commercial equipment specifically designed for such operations is available.[2,4-6]

d. Integrator/recorder: Use a 10–mV full-span strip chart recorder with the gas chromatograph. When minor components such as H_2 and H_2S are to be detected, a 1-mV full-span recorder is preferable.

Integrators that can easily detect very minute quantities of gases are available. Computerized data-processing systems, to record and manipulate the chromatographic signal, chromatographic base line, etc., also are available.

3. Reagents

a. Carrier gases: Preferably use helium for separating digester gases. It is impossible to detect less than 1% hydrogen when helium is used as the carrier gas.[1] Obtain linear TCD responses for molar concentrations of hydrogen between 0 and 60% by using an 8.5% hydrogen–91.5% helium carrier gas mixture.[7] To detect trace quantities of hydrogen use argon or nitrogen as carrier gas.[1]

b. Calibration gases: Use samples of CH_4, CO_2, and N_2 of known purity, or gas mixtures of certified composition, for calibration. Also use samples of O_2, H_2, and H_2S of known purity if these gases are to be measured. Preferably use custom-made gas mixtures to closely approximate digester gas composition.

c. Displacement liquids: See Section 2720B.3*d*.

4. Procedure

a. Preparation of gas chromatograph: Open main valve of carrier-gas cylinder and adjust carrier-gas flow rate to recommended values. To obtain accurate flow measurements, connect a soap-film flow meter to the TCD vent. Turn power on. Turn on oven heaters, if used, and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

detector current and adjust to desired values.

Set injection port and column temperatures as specified for the column being used. Set TCD current. Turn on recorder or data processor. Check that the injector/detector temperature has risen to the appropriate level and confirm that column temperature is stabilized. Set range and attenuation at appropriate positions.

The instrument is ready for use when the recorder yields a stable base line. Silica gel and molecular sieve columns gradually lose activity because of adsorbed moisture or materials permanently adsorbed at room temperature. If insufficient separations occur, reactivate by heating or repacking.

b. Calibration: For accurate results, prepare a calibration curve for each gas to be measured because different gas components do not give equivalent detector responses on either a weight or a molar basis. Calibrate with synthetic mixtures or with pure gases.

1) Synthetic mixtures—Use purchased gas mixtures of certified composition or prepare in the laboratory. Inject a standard volume of each mixture into the gas chromatograph and note response for each gas. Compute detector response, either as area under a peak or as height of peak, after correcting for attenuation. Read peak heights accurately and correlate with concentration of component in sample. Reproduce operating parameters exactly from one analysis to the next. If sufficient reproducibility cannot be obtained by this procedure, use peak areas for calibration. Preferably use peak areas when peaks are not symmetrical. Prepare calibration curve by plotting either peak area or peak height against volume or mole percent for each component.

Modern integrators and data-processing systems are able to generate calibration tables for certified gas mixtures.

2) Pure gases—Introduce pure gases into chromatograph individually with a syringe. Inject sample volumes of 0.25, 0.5, 1.0 mL, etc., and plot detector response, corrected for attenuation, against gas volume.

When the analysis system yields a linear detector response with increasing gas component concentration from zero to the range of interest, run standard mixtures along with samples. If the same sample size is used, calculate gas concentration by direct proportions.

c. Sample analysis: If samples are to be injected with a syringe, equip sample collection container with a port closed by a rubber or silicone septum. To take a sample for analysis, expel air from barrel of syringe by depressing plunger and force needle through the septum. Withdraw plunger to take gas volume desired, pull needle from collection container, and inject sample rapidly into chromatograph.

When samples are to be injected through a gas-sampling valve, connect sample collection container to inlet tube. Let gas flow from collection tube through the valve to purge dead air space and fill sample tube. About 15 mL normally are sufficient to clear the lines and to provide a sample of 1 to 2 mL. Transfer sample from loop into carrier gas stream by following manufacturer’s instructions. Bring samples to atmospheric pressure before injection.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

When calibration curves have been prepared with a synthetic gas mixture of certified composition, use the same sample volume as that used during calibration. When calibration curves are prepared by the procedure using varying volumes of pure gases, inject any convenient gas sample volume up to about 2 mL.

Inject sample and standard gases in sequence to permit calculation of unknown gas concentration in volume (or mole) percent by direct comparison of sample and standard gas peak heights or areas. For more accurate analysis, make duplicate or triplicate injections of sample and standard gases.

5. Calculation

a. When calibration curves have been prepared with synthetic mixtures and the volume of the sample analyzed is the same as that used in calibration, read volume percent of each component directly from calibration curve after detector response for that component is computed.

b. When calibration curves are prepared with varying volumes of pure gases, calculate the percentage of each gas in the mixture as follows:

$$\text{Volume \%} = \frac{A}{B} \times 100$$

where:

A = partial volume of component (read from calibration curve) and
B = volume sample injected.

c. Where standard mixtures are run with samples and instrument response is linear from zero to the concentration range ofinterest:

$$\text{Volume \%} = \text{volume \% (std)} \frac{C}{D}$$

where:

C = recorder value of sample and
D = recorder value of standard.

d. Digester gases usually are saturated with water vapor that is not a digestion product. Therefore, apply corrections to calculate the dry volume percent of each digester gas component as follows:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\text{Dry volume \%} = \frac{\text{volume \% as above}}{1 - P_v}$$

where:

P_v = saturated water vapor pressure at room temperature and pressure, decimal %.

The saturation water vapor pressure can be found in common handbooks. The correction factor $\frac{1}{1 - P_v}$ is usually small and is often neglected by analysts.

6. Precision and Bias

Precision and bias depend on the instrument, the column, operating conditions, gas concentrations, and techniques of operation. The upper control limits for replicate analyses of a high-methane-content standard gas mixture (65.01% methane, 29.95% carbon dioxide, 0.99% oxygen, and 4.05% nitrogen) by a single operator were as follows: 65.21% for methane, 30.36% for carbon dioxide, 1.03% for oxygen, and 4.15% for nitrogen. The lower control limits for this same standard gas mixture were: 64.67% for methane, 29.88% for carbon dioxide, 0.85% for oxygen, and 3.85% for nitrogen. The observed relative standard deviations (RSD) were: 0.14% for methane, 0.26% for carbon dioxide, 3.2% for oxygen, and 1.25% for nitrogen.

In a similar analysis of another standard gas mixture (55% methane, 35% carbon dioxide, 10% diatomic gases—2% hydrogen, 6% nitrogen, 2% oxygen), typical upper control limits for precision of duplicate determinations were: 55.21% for methane, 35.39% for carbon dioxide, and 10.26% for the diatomic gases. The lower control limits for this standard gas mixture were: 54.78% for methane, 34.62% for carbon dioxide, and 9.73% for the diatomic gases. The observed RSDs for this analysis were: 0.13% for methane, 0.36% for carbon dioxide, and 0.88% for the diatomic gases.

A low-methane-content standard gas mixture (35.70% methane, 47.70% carbon dioxide, 3.07% oxygen, 8.16% nitrogen, and 5.37% hydrogen) was analyzed as above yielding upper control limits as follows: 34.4% for methane, 49.46% for carbon dioxide, 3.07% for oxygen, and 8.2% for nitrogen. The lower control limits were: 34.18% for methane, 49.11% for carbon dioxide, 2.83% for oxygen, and 7.98% for nitrogen. The observed RSDs were: 0.11% for methane, 0.16% for carbon dioxide, 1.37% for oxygen, and 0.46% for nitrogen.

With digester gas the sum of the percent CH_4, CO_2, and N_2 should approximate 100%. If it does not, suspect errors in collection, handling, storage, and injection of gas, or in instrumental operation or calibration.

7. References

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. SUPELCO, INC. 1983. Isothermal and Temperature Programmed Analyses of Permanent Gases and Light Hydrocarbons. GC Bull. 760F. Bellefonte, Pa.
2. MINDRUP, R. 1978. The analysis of gases and light hydrocarbons by gas chromatography. *J. Chromatogr. Sci.* 16:380.
3. SUPELCO, INC. 1983. Analyzing Mixtures of Permanent Gases and Light (C1 - C3) Hydrocarbons on a Single GC Column. GC Bull. 712F. Bellefonte, Pa.
4. ALLTECH ASSOCIATES, INC. 1989. Chromatography. Catalog No. 200. Deerfield, Ill.
5. SUPELCO, INC. 1983. Column Selection for Gas and Light Hydrocarbon Analysis. GC Bull. 786C. Bellefonte, Pa.
6. SUPELCO, INC. 1989. Supelco Chromatography Products. Catalog 27. Bellefonte, Pa.
7. PURCELL, J.E. & L.S. ETTRE. 1965. Analysis of hydrogen with thermal conductivity detectors. *J. Gas Chromatogr.* 3(2):69.

8. Bibliography

LEIBRAND, R.J. 1967. Atlas of gas analyses by gas chromatography. *J. Gas Chromatogr.* 5:518.

JEFFREY, P.G. & P.J. KIPPING. 1972. Gas Analysis by Gas Chromatography, 2nd ed. Pergamon Press Inc., Elmsford, N.Y.

BURGETT, C., L. GREEN & E. BONELLI. 1977. Chromatographic Methods in Gas Analysis. Hewlett-Packard Inc., Avondale, Pa.

THOMPSON, B. 1977. Fundamentals of Gas Analysis by Gas Chromatography. Varian Associates, Inc., Palo Alto, Calif.

2810 DISSOLVED GAS SUPERSATURATION#(62)*

2810 A. Introduction

Water can become supersaturated with atmospheric gases by various means, heating and air entrainment in spilled or pumped water being the most common. The primary sign of gas supersaturation is the formation of bubbles on submerged surfaces or within the vascular systems and tissues of aquatic organisms.

Gas supersaturation can limit aquatic life and interfere with water treatment processes. Levels of supersaturation lethal to aquatic organisms have been found in springs, rivers, wells, lakes, estuaries, and seawater. Gas supersaturation can be produced in pumped or processed water intended for drinking, fish hatchery supply, and laboratory bioassays. Seasonal and other temporal variations in supersaturation may occur in surface waters as a result of solar heating and photosynthesis. Because the rate of equilibration may be slow, supersaturation may persist in flowing water for days and excessive dissolved gas levels thus may persist far from the source of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

supersaturation.

Gas bubbles form only when the total dissolved gas pressure is greater than the sum of compensating pressures. Compensating pressures include water, barometric and, for organisms, tissue or blood pressure. The total dissolved gas pressure is equal to the sum of the partial pressures of all the dissolved gases, including water vapor. Typically, only nitrogen, oxygen, argon, carbon dioxide, and water vapor pressures need to be considered in most natural waters. Gas bubble disease, of fish or other aquatic organisms, is a result of excessive uncompensated gas pressure. A single supersaturated gas such as oxygen or nitrogen may not necessarily result in gas bubble disease because bubble formation depends largely on total dissolved gas pressure. The degree of gas saturation should be described in terms of pressures rather than concentration or volume units.

2810 B. Direct-Sensing Membrane-Diffusion Method

1. General Discussion

a. Principle: This method requires an instrument with a variable length of ‘‘gas permeable’’ tubing, connected to a pressure-measuring device. Dimethyl silicone rubber tubing often is used because it is highly permeable to dissolved gases, including water vapor. At steady state, the gauge pressure inside the tubing is equal to the difference in gas pressure (ΔP) between the total dissolved gas pressure and the ambient barometric pressure. When the water is in equilibrium with the atmosphere, ΔP equals zero.

If ΔP is greater than zero, the water is supersaturated. Conversely, if ΔP is negative the water is undersaturated.

b. Working range: The working range of this method depends on the pressure-sensing device used, but typically will range from –150 to +600 mm Hg. Dissolved solids in wastewater will not interfere with this method. The practical depth range for these instruments is 1 to 10 m.

2. Apparatus

Several types of membrane-diffusion instruments are available commercially.#(63)* Alternatively, construct a unit from commercially available parts. Several units have been described, including a direct-reading instrument using pressure transducers and a digital readout,[1] an on-line unit that can activate an alarm system,[2] and an early model of the Weiss saturometer.[3] Each of these units has specific advantages and limitations; the instrument of choice will depend on the specific application. All these instruments are portable so that data collection is completed in the field.

Test the instrument for leaks according to the manufacturer’s recommendation. Even a very small leak, difficult to detect and locate, will result in useless data. Calibrate the pressure-measuring device with a mercury manometer or certified pressure gauge. If a manometer is used, include fresh mercury that flows freely in the tubing. An alternative method

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

for directly testing membrane-diffusion instruments in a small, closed chamber where induced ΔP levels can be compared against observed ΔP levels is available.[2]

Van Slyke-Neill[4] or gas chromatography methods[1] are inappropriate for calibration but they may be used to verify results. These methods measure individual gas concentrations and require further conversion to ΔP or partial pressure and suffer from sampling and sample handling problems.[5-7]

3. Procedure

At the start of each day, test the instrument for leaks and recalibrate. At a monitoring site, completely submerge the sensing element in the water, preferably below the hydrostatic compensation depth. This is the depth where the hydrostatic and total gas pressures are equal and as a result, bubbles will not form on the tubing. Bubble formation on the silicone rubber tubing seriously reduces accuracy. Compute hydrostatic compensation depth[5] as follows:

$$Z = \frac{\Delta P}{73.42}$$

where:

Z = hydrostatic compensation depth, m, and
ΔP = pressure difference between total dissolved gas pressure and the ambient barometric pressure, mm Hg.

The factor 73.42 is the hydrostatic pressure of fresh water at 20°C expressed in terms of mm Hg/m water depth. Because the variation of hydrostatic pressure with temperature and salinity is small, this equation can be used for all natural waters.

Dislodge formed bubbles on the tubing by gently striking the instrument or moving the instrument rapidly in the water. Movement of water across the silicone rubber tubing also facilitates establishing the equilibrium between gas pressure in the water and in the tubing.

Operate the instrument ‘‘bubble free’’ until a stable ΔP is observed. This may take from 5 to 30 min, depending on the ΔP, water temperature, water flow, and geometry of the system. The time response of the membrane-diffusion method is shown in Figure 2810:1 for ‘‘bubble-free’’ and ‘‘bubble’’ conditions.

If the instrument is used in heavily contaminated water containing oil or other organic compounds, clean the silicone tubing with a mild detergent according to the manufacturer’s instructions. Silicone rubber tubing has been used in uncontaminated natural water for at least eight years without being adversely affected by attached algal growth.[2] The tubing can be damaged by abrasive grit, diatoms, biting aquatic organisms, certain organic compounds, and strong acids.[2]

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Obtain the barometric pressure with each measurement by using a laboratory mercury barometer, a calibrated portable barometer, or pressure transducer. Barometric pressures reported by weather agencies (or airports) are corrected to sea level and are unusable.

4. Calculation

a. Total gas pressure: Preferably report total gas pressure as ΔP.[2,6,8] Express pressure as millimeters of mercury.

Total gas pressure also has been reported as a percentage of local barometric pressure:

$$\text{TGP } \% = \left[\frac{P_b + \Delta P}{P_b}\right] \times 100$$

where:

P_b = true local barometric pressure, mm Hg.

The reporting of total gas pressure as a percentage is not encouraged.[8]

b. Component gas pressures: When information on component gas supersaturation is needed, express data as partial pressures, differential pressures, or percent saturation.[5,8] This requires additional measurements of dissolved oxygen, temperature, and salinity#(64)† at the monitoring site. In a mixture of gases in a given volume, the partial pressure of a gas is the pressure that this gas would exert if it were the only gas present.

1) Oxygen partial pressure—Calculate partial pressure of oxygen as follows:

$$P_{O_2} = \frac{DO}{\beta_{O_2}} \times 0.5318$$

where:

P_{O_2} = partial pressure of dissolved oxygen, mm Hg,

β_{O_2} = Bunsen coefficient for oxygen (Table 2810:I), L/(L·atm), and

DO = measured concentration of oxygen, mg/L.

Bunsen coefficients for marine waters are available.[5] The factor 0.5318 equals 760/(1000 K), where K is the ratio of molecular weight to molecular volume for oxygen gas.[5]

2) Nitrogen partial pressure—Estimate the partial pressure of nitrogen by subtracting the partial pressures of oxygen and water vapor from the total gas pressure.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$P_{N_2} = P_b + \Delta P - P_{O_2} - P_{H_2O}$$

where:

P_{H_2O} = vapor pressure of water in mm Hg from Table 2810:II.

This term includes a small contribution from argon and any other gases present, including carbon dioxide and methane. The partial pressure of carbon dioxide is negligible in natural waters of pH > 7.0.

3) Nitrogen:oxygen partial pressure ratio—The ratio of the partial pressure of nitrogen to the partial pressure of oxygen (N_2:O_2) characterizes the relative contribution of the two gases to the total dissolved gas pressure. In water in equilibrium with air, this ratio is 3.77.

c. Differential pressures: The differential pressure of a gas is the difference between the partial pressures of that gas in water and air. The oxygen differential pressure may be calculated as

$$\Delta P_{O_2} = P_{O_2} - 0.209\,46(P_b - P_{H_2O})$$

and the nitrogen differential pressure as

$$\Delta P_{N_2} = \Delta P - \Delta P_{O_2}$$

d. Percent of saturation: In older literature, supersaturation values have been reported as percent saturation. This method of reporting component gases is discouraged but can be calculated as follows:

$$N_2(\%) = \left[\frac{P_{N_2}}{0.7902\ (P_b - P_{H_2O})}\right] \times 100$$

$$O_2(\%) = \left[\frac{P_{O_2}}{0.20946(P_b - P_{H_2O})}\right] \times 100$$

The following relationships are useful conversions:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\text{TGP}(\%) = 0.209\ 46\ \text{O}_2(\%) + 0.7902\ \text{N}_2(\%)$$

$$\Delta P = 0.20946\left[\frac{O_2(\%)}{100} - 1\right][P_b - P_{H_2O}] + 0.7902\left[\frac{N_2(\%)}{100} - 1\right][P_b - P_{H_2O}]$$

$$\Delta P = \frac{DO}{\beta_{O_2}}(0.5318)(1 + N_2{:}O_2) - (P_b - P_{H_2O})$$

Use care with these relationships with older data because both TGP(%) and N_2(%) have been differently defined.[5]

5. Quality Control

The precision of the membrane-diffusion method depends primarily on the pressure-sensing instrument. For an experienced operator it is approximately ±1 to 2 mm Hg with an accuracy of ±3 to 5 mm Hg.[3,6] Air leaks, bubble formation, biofilm development, incomplete equilibration, or condensation produce negative errors while direct water leaks can result in positive errors in submersible units.

For accurate work, measure water temperature to the nearest ±0.1°C.

6. Reporting of Results

In reporting results, include the following data:

Sensor depth, m,

Barometric pressure, mm Hg,

Water temperature, °C,

Dissolved oxygen, mm Hg or mg/L,

Salinity, g/kg, and

ΔP, mm Hg.

If component gas information is needed add:

Partial pressure of oxygen, mm Hg,

Partial pressure of nitrogen, mm Hg, and

Nitrogen:oxygen partial pressure ratio

or

ΔP_{O_2}, mm Hg, and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

ΔP_{N_2}, mm Hg.

7. Interpretation of Results

The biological effects of dissolved gas supersaturation depend on the species, age, depth in water column, length of exposure, temperature, and nitrogen:oxygen partial pressure ratio.[12] Safe limits generally are segregated into wild/natural circumstances, where behavior and hydrostatic pressure can modify the exposure by horizontal and vertical movements away from dangers, and captive environments such as aquaria, hatcheries, or laboratories, where conditions not only preclude escape but also include other significant stresses. Of these two realms, captive circumstances are more likely to cause illness or mortality from gas bubble disease and will do so sooner and at the lower ΔP levels.

In wild/natural circumstances, the limit of safe levels of gas supersaturation depends on the depth available to the species and/ or species behavior, but this limit usually occurs at a ΔP between 50 and 150 mm Hg. Under captive conditions, the ΔP should be as close to zero as possible. For sensitive species and life stages, sublethal and lethal effects have been observed at ΔP of 10 to 50 mm Hg.[13]

8. References

1. D'AOUST, B.G., R. WHITE & H. SIEBOLD. 1975. Direct measurement of total dissolved gas partial pressure. *Undersea Biomed. Res.* 2:141.
2. BOUCK, G.R. 1982. Gasometer: an inexpensive device for continuous monitoring of dissolved gases and supersaturation. *Trans. Amer. Fish. Soc.* 111:505.
3. FICKEISEN, D.H., M.J. SCHNEIDER & J.C. MONTGOMERY. 1975. A comparative evaluation of the Weiss saturometer. *Trans. Amer. Fish. Soc.* 104:816.
4. BEININGEN, K.T. 1973. A Manual for Measuring Dissolved Oxygen and Nitrogen Gas Concentrations in Water with the Van Slyke-Neill Apparatus. Fish Commission of Oregon, Portland.
5. COLT, J. 1984. Computation of dissolved gas concentrations in water as functions of temperature, salinity, and pressure. Spec. Publ. 14, American Fisheries Soc., Bethesda, Md.
6. D'AOUST, B.G. & M.J.R. CLARK. 1980. Analysis of supersaturated air in natural waters and reservoirs. *Trans. Amer. Fish. Soc.* 109:708.
7. PIRIE, W.R. & W.A. HUBBERT. 1977. Assumptions in statistical analysis. *Trans. Amer. Fish. Soc.* 106:646.
8. COLT, J. 1983. The computation and reporting of dissolved gas levels. *Water Res.* 17:841.
9. BENSON, B.B. & D. KRAUSE. 1980. The concentration and isotopic fractionation in freshwater in equilibrium with the atmosphere. 1. Oxygen. *Limnol. Oceanogr.* 25:662.
10. BENSON, B.B. & D. KRAUSE. 1984. The concentration and isotopic fractionation of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere. *Limnol. Oceanogr.* 29:620.

11. GREEN, E.J. & D.E. CARRITT. 1967. New tables for oxygen saturation of seawater. *J. Mar. Res.* 25:140.
12. WEITKAMP, D.E. & M. KATZ. 1980. A review of dissolved gas supersaturation literature. *Trans. Amer. Fish. Soc.* 109:659.
13. COLT, J. 1986. The impact of gas supersaturation on the design and operation of aquatic culture systems. *Aquacult. Eng.* 5:49.

Figures

Figure 2120:1. Filtration system for color determinations.

Figure 2120:2. Chromaticity diagrams.

Figure 2150:1. Odor-free-water generator.

Figure 2530:1. Floatables sampler with mixer.

Figure 2530:2. Floatables flotation funnel and filter holder.

Figure 2530:3. Flotation funnels and mixing unit.

Figure 2530:4. Floatable oil tube, 1-L capacity.

Figure 2560:1. Schematic of filtration apparatus for preparation of particle-free dilution water or electrolyte solution.

Figure 2710:1. Schematic diagram of settling vessel for settled sludge volume test.

Figure 2710:2. Schematic diagram of settling vessel for zone settling rate test.

Figure 2710:3. Capillary suction time apparatus.

Figure 2710:4. TTF equipment. Large-volume equipment requires a 9-cm- diam Buchner funnel and a 250-mL graduated cylinder. Small-volume equipment requires a 2.5-cm-diam funnel and a 10-mL cylinder.

Figure 2720:1. Gas collection apparatus.

Figure 2810:1. Time response for the membrane-diffusion method.

Tables

TABLE 2120:I. SELECTED ORDINATES FOR SPECTROPHOTOMETRIC COLOR DETERMINATIONS*

	X	*Y*	*Z*
Ordinate No.	**Wavelength *nm***		

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Ordinate No.	*X*	*Y*	*Z*
	Wavelength *nm*		
1	424.4	465.9	414.1
2*	435.5*	489.5*	422.2*
3	443.9	500.4	426.3
4	452.1	508.7	429.4
5*	461.2*	515.2*	432.0*
6	474.0	520.6	434.3
7	531.2	525.4	436.5
8*	544.3*	529.8*	438.6*
9	552.4	533.9	440.6
10	558.7	537.7	442.5
11*	564.1*	541.4*	444.4*
12	568.9	544.9	446.3
13	573.2	548.4	448.2
14*	577.4*	551.8*	450.1*
15	581.3	555.1	452.1
16	585.0	558.5	454.0
17*	588.7*	561.9*	455.9*
18	592.4	565.3	457.9
19	596.0	568.9	459.9
20*	599.6*	572.5*	462.0*
21	603.3	576.4	464.1
22	607.0	580.4	466.3
23*	610.9*	584.8*	468.7*
24	615.0	589.6	471.4
25	619.4	594.8	474.3
26*	624.2*	600.8*	477.7*
27	629.8	607.7	481.8
28	636.6	616.1	487.2
29*	645.9*	627.3*	495.2*
30	663.0	647.4	511.2

Factors When 30 Ordinates Used

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Ordinate No.	*X*	*Y*	*Z*
	Wavelength *nm*		
38	0.032 69	0.033 33	0.039
Factors When 10 Ordinates Used			
14	0.098 06	0.100 00	0.118

* Insert in each column the transmittance value (%) corresponding to the wavelengthshown. Where limited accuracy is sufficient, use only the ordinates marked with anasterisk.

TABLE 2120:II. COLOR HUES FOR DOMINANT WAVELENGTH RANGES

Wavelength Range *nm*	Hue
400–465	Violet
465–482	Blue
482–497	Blue-green
497–530	Green
530–575	Greenish yellow
575–580	Yellow
580–587	Yellowish orange
587–598	Orange
598–620	Orange-red
620–700	Red
400–530c*	Blue-purple
530c–700*	Red-purple

* See Figure 2120:2 for significance of ‘‘c’’.

TABLE 2150:I. THRESHOLD ODOR NUMBERS CORRESPONDING TO VARIOUS DILUTIONS

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

* See Figure 2120:2 for significance of ''c''.

TABLE 2150:I. THRESHOLD ODOR NUMBERS CORRESPONDING TO VARIOUS DILUTIONS

Sample Volume Diluted to 200 mL *mL*	Threshold Odor No.	Sample Volume Diluted to 200 mL *mL*	Threshold Odor No.
200	1	12.0	17
140	1.4	8.3	24
100	2	5.7	35
70	3	4.0	50
50	4	2.8	70
35	6	2.0	100
25	8	1.4	140
17	12	1.0	200

TABLE 2150:II. DILUTIONS FOR VARIOUS ODOR INTENSITIES

Sample Volume in Which Odor Is First Noted *mL*	Volumes to Be Diluted to 200 mL *mL*
200	200, 140, 100, 70, 50
50	50, 35, 25, 17, 12
12	12, 8.3, 5.7, 4.0, 2.8
2.8	Intermediate dilution

TABLE 2160:I. FLAVOR THRESHOLD NUMBERS CORRESPONDING TO VARIOUS DILUTIONS

Sample Volume *mL*	Diluent Volume *mL*	Flavor Threshold No. *FTN*
200	0	1
100	100	2
70	130	3

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Sample Volume *mL*	Diluent Volume *mL*	Flavor Threshold No. *FTN*
50	150	4
35	165	6
25	175	8
17	183	12
12	188	17
8	192	25
6	194	33
4	196	50
3	197	67
2	198	100
1	199	200

TABLE 2160:II. DILUTIONS FOR DETERMINING THE FTN

Sample Volume in Which Taste Is First Noted *mL*	Volumes to be Diluted to 200 mL *mL*
200	200, 100, 70, 50, 35, 25, 17
50	50, 35, 25, 17, 12, 8, 6
12	12, 8, 6, 4, 3, 2, 1
4	Intermediate dilution

TABLE 2170:I. QUANTITATIVE ODOR REFERENCES*

Compound	Odor Characteristics	Stock Solution Concentration *mg/L*	Amount Placed Ir 200 mL Pure Wate 25°C for Presentat
Geosmin	Earthy, red beets	0.2†	300 μL for 300 ng
2-Methylisoborneol	Earthy, peat-like, Brazil nut, soil	0.2†	200 μL for 200 ng
Free chlorine	Chlorinous	1.0	0.1 mL for 0.5 mg

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Compound	Odor Characteristics	Stock Solution Concentration *mg/L*	Amount Placed Ir 200 mL Pure Wate 25°C for Presentat
		pH = 7	
Dichloramine	Swimming pool chlorine	pH = 7	
Monochloramine	Chlorinous	pH = 7	
trans,2-*cis*,6-Nonadienal	Cucumber, green vegetation	1000	1 μL for 5 μg/L
Styrene	Model airplane glue	1000	100 μL for 500 μg
Toluene	Glue, sweet solventy	1000	100 μL for 500 μg
cis-3-Hexenyl-1-acetate	Grassy	1000	100 μL for 500 μg
cis-3-Hexene-1-ol	Grassy, green apple	1000	100 μL for 500 μg
Cumene	Paste shoe polish, solventy	1000	20 μL for 100 μg/l
m-Xylene	Sweet solventy	1000	40 μL for 200 μg/l
Methylisobutyl ketone	Paint solventy	1000	200 μL for 1.0 mg
1,2,4-Trimethylbenzene	Shoe polish, coal tar	1000	50 μL for 250 μg/l
Indene	Glue, moth balls	1000	1 μL for 5 μg/L
Indan	Varnish, coal tar	1000	5 μL for 25 μg/L
Naphthalene	Sweet solventy	1000	1 μL for 5 μg/L
Benzofuran	Shoe polish, moth balls	1000	2 μL for 10 μg/L
2-Methyl-benzofuran	Moth balls, sweet solventy	1000	50 μL for 250 μg/l

NOTE: These compounds have actually been identified as causes of odors in raw and finished drinking water.
* Adapted from AMERICAN WATER WORKS ASSOCIATION. 1993. Flavor Profile Analysis: Screening and Training of Panelists. AWWA Manual, American Water Works Assoc.,Denver, Colo.
† Compounds available only in solid form and must be dissolved in methanol.

TABLE 2170:II. REPRESENTATIVE ODOR REFERENCE STANDARDS*

Compound	Odor Characteristics	Stock Solution Concentration *mg/L*	Amou mL Pu
2,3,6-Trichloroanisole	Leather, earthy	1000	4 μL
2,3-Diethylpyrazine	Mildew, damp basement	1000	2 μL
2-Isopropyl-3-methoxypyrazine	Potato bin, musty	1000	40 μ
Nonanal	Hay, sweet	1000	40 μ
Dimethyl sulfide	Decaying vegetation, canned corn	1000	1 μL

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Compound	Odor Characteristics	Stock Solution Concentration *mg/L*	Amou mL Pu
Dimethyl disulfide	Septic	1000	2 µL
Dimethyltrisulfide	Garlicky, oniony, septic	0.2	50 µ
Butyric acid	Putrid, sickening	1000	200
trans,2-Nonenal	Cucumber with skin	1000	40 µ
Diphenyl ether	Geranium	1000†	20 µ
D-Limonene	Citrusy	1000	400
Hexanal	Lettuce heart, pumpkin, green pistachio	1000	40 µ
Benzaldehyde	Sweet almond	1000	200
Ethyl-2-methyl-butyrate	Fruity, pineapple	1000	100
2-Heptanone	Banana-like, sweet solventy	1000	100
Hexachloro-1,3-butadiene	Sweet, minty, Vapo Rub	1000	800
2-Isobutyl-3-methoxypyrazine	Green/bell pepper, musty	1000	40 µ
trans,2-*trans*,4-Decadienal	Rancid oily	1000	100
Butanol	Alcohol, solventy	1000	200
Eucalyptol (cincole)	Topical ointment for chest colds	1000	40 µ
Pyridine	Sweet, alcohol, organic	1000	400

NOTE: Possible causes of odors or chemical substitutes for causes of odors.
* Adapted from AMERICAN WATER WORKS ASSOCIATION. 1993. FLAVOR PROFILE ANALYSIS: SCREENING AND TRAINING OF PANELISTS. AWWA Manual, American Water Works Assoc., Denver, Colo.
* Compounds available only in solid form and must be dissolved in methanol.

TABLE 2170:III. SUBSTITUTE ODOR REFERENCE STANDARDS*

Compound	Odor Characteristic	Preparation
Cloves	Spicy like cloves	Use supermarket brand of dried clove buds (spice). Add 3 clove buds to 200 mL pure water and swirl 1–2 min. Allow to stand overnight at room temperature, then discard the buds.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Compound	Odor Characteristic	Preparation
Dried grass	Hay	Place dried cut grass in erlenmeyer flask until half full.
Grass	Decaying vegetation	Weigh 2 g of fresh grass and mix into 200 mL pure water and let stand at room temperature. In 1–3 d, the odor will appear.
Grass	Septic	Allow the solution above for decaying vegetation to stand for an additional 1–2 weeks.
Rubber hose	Rubber hose	Boil a short section of rubber hose in 200 mL pure water for 5 min. Allow to cool and remove the hose.
Soap	Soapy	Place 5 g of chipped nonscented bar soap in 200 mL pure water.
Pencil shavings	Woody	Instruct panel member to sharpen a wood pencil and sniff the freshly exposed wood.

NOTE: Standards made from materials rather than chemicals.* Adapted from AMERICAN WATER WORKS ASSOCIATION. 1993. Flavor Profile Analysis: Screening and Training of Panelists. AWWA Manual. American Water WorksAssoc., Denver, Colo.

TABLE 2170:IV. BASIC TASTE STANDARDS

Chemical for Basic Tastes	Food or Beverage Corresponding to Intensity	Concentration %	Intensity Scale (1 to 12)*
Sweet: sugar	Canned fruit or vegetables	5.00	4 W
	Carbonated soda	10.00	8 M
	Syrup, jelly	15.00	12 S
Sour: citric acid	Fresh fruit jelly	0.05	4 W
	Some carbonated sodas	0.10	8 M
	Lemon juice	0.20	12 S

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Chemical for Basic Tastes	Food or Beverage Corresponding to Intensity	Concentration %	Intensity Scale (1 to 12)*
Salt: sodium chloride	Level in bread	0.40	4 W
	Dehydrated soup mix	0.70	8 M
	Soy sauce	1.00	12 S
Bitter: caffeine	Strong coffee	0.05	4 W
		0.10	8 M
		0.20	12 S
	or quinine hydrochloride dihydrate	0.001	4 W
		0.002	8 M
		0.004	12 S

* W = weak; M = moderate; S = strong.

TABLE 2320:I. END-POINT pH VALUES

Test Condition	End Point pH	
	Total Alkalinity	Phenolphthalein Alkalinity
Alkalinity, mg $CaCO_3$/L:		
30	4.9	8.3
150	4.6	8.3
500	4.3	8.3
Silicates, phosphates known or suspected	4.5	8.3
Routine or automated analyses	4.5	8.3
Industrial waste or complex system	4.5	8.3

TABLE 2320:II. ALKALINITY RELATIONSHIPS*

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 2320:II. ALKALINITY RELATIONSHIPS*

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Concentration as $CaCO_3$
P = 0	0	0	T
P < *tfrac*12T	0	2P	T – 2P
P = *tfrac*12T	0	2P	0
P > *tfrac*12T	2P – T	2(T – P)	0
P = T	T	0	0

*Key: P–phenolphthalein alkalinity; T–total alkalinity.

Table 2330:I. Estimating Equilibrium Constants and Activity Coefficients

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 2330:I. ESTIMATING EQUILIBRIUM CONSTANTS AND ACTIVITY COEFFICIENTS

Equation	Temperature Range	References
When complete mineral analysis is available:		
$I = {}^1/_2 \sum_{i=1}^{i} [X_i]\, Z_i^2$	—	3
When only conductivity is available:		
$I = 1.6 \times 10^{-5} C$	—	4
When only TDS is available:		
$I = TDS/40\,000$	—	5
$pf_m = A\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right]$ (valid to $I < 0.5$)	—	3
$A = 1.82 \times 10^6\,(ET)^{-1.5}$	—	3
$E = \frac{60\,954}{T + 116} - 68.937$	—	6
$pK_2 = 107.8871 + 0.032\,528\,49T - 5151.79/T - 38.925\,61 \log_{10}T + 563\,713.9/T^2$	273–373	7
$pK_w = 4471/T + 0.017\,06T - 6.0875$	280–338	8
$pK_{sc} = 171.9065 + 0.077\,993T - 2839.319/T - 71.595 \log_{10}T$	273–363	7
$pK_{sa} = 171.9773 + 0.077\,993T - 2903.293/T - 71.595 \log_{10}T$	273–363	7
$pK_{sv} = 172.1295 + 0.077\,993T - 3074.688/T - 71.595 \log_{10}T$	273–363	7

*I = ionic strength
$[X_i]$ = concentration of component i, g-moles/L
Z_i = charge of species i
C = conductivity, µmhos/cm
TDS = total dissolved solids, mg/L
pY = $-\log_{10}$ of the value of any factor Y
f_m = activity coefficient for monovalent species
E = dielectric constant
T = temperature, °K (°C + 273.2)
K_2 = second dissociation constant for carbonic acid
K_w = dissociation constant for water
K_{sc} = solubility product constant for calcite
K_{sa} = solubility product constant for aragonite
K_{sv} = solubility product constant for vaterite

TABLE 2330:II. PRECALCULATED VALUES FOR *pK* AND *A* AT SELECTED TEMPERATURES

Temperature °C	pK_2	pK_S Calcite	pK_S Aragonite	pK_S Vaterite	pK_W	A

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Temperature °C	pK_2	pK_s Calcite	Aragonite	Vaterite	pK_w	A
5	10.55	8.39	8.24	7.77	14.73	0.494
10	10.49	8.41	8.26	7.80	14.53	0.498
15	10.43	8.43	8.28	7.84	14.34	0.502
20	10.38	8.45	8.31	7.87	14.16	0.506
25*	10.33	8.48	8.34	7.91	13.99	0.511
30	10.29	8.51	8.37	7.96	13.83	0.515
35	10.25	8.54	8.41	8.00	13.68	0.520
40	10.22	8.58	8.45	8.05	13.53	0.526
45	10.20	8.62	8.49	8.10	13.39	0.531
50	10.17	8.66	8.54	8.16	13.26	0.537
60	10.14	8.76	8.64	8.28	13.02	0.549
70	10.13	8.87	8.75	8.40	—	0.562
80	10.13	8.99	8.88	8.55	—	0.576
90	10.14	9.12	9.02	8.70	—	0.591

NOTE: All values determined from the equations of Table 2330:I.
A is used to calculate pf_m (see Table 2330:I).

* pf_m estimated from TDS values at 25°C care as follows:

TDS	pf_m
100	0.024
200	0.033
400	0.044
800	0.060
1000	0.066

TABLE 2330:III. GRAPHS AND COMPUTER SOFTWARE THAT CAN BE USED TO CALCULATE $CaCO_3$ SATURATION INDICES*

Item†	$CaCO_3$ Indices: Basis for Calculation of SI	CCPP	Approximate Temperature Range °C	Approximate Limit of Ionic Strength	Ion Pairs Considered?	C
1. Caldwell Lawrence diagrams[4]	pH_{sa}	P, D	2–25	0.030	No	

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Item†	$CaCO_3$ Indices: Basis for Calculation of SI	$CaCO_3$ Indices: CCPP	Approximate Temperature Range °C	Approximate Limit of Ionic Strength	Ion Pairs Considered?	C
2. ACAPP	RS	P, D	−10–110	6+	Yes	
3. DRIVER	RS	P	7–65	2.5	Yes	
4. INDEX C	pH_{sa} pH_{sb}	P, D	0–50	0.5	No	
5. LEQUIL	RS	No	5–90	0.5	Yes	
6. MINTEQA1	RS	P, D	0–100	0.5	Yes	

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Item†	$CaCO_3$ Indices: Basis for Calculation of SI	$CaCO_3$ Indices: CCPP	Approximate Temperature Range °C	Approximate Limit of Ionic Strength	Ion Pairs Considered?	C
7. PHREEQE Standard	RS	P, D	0–100	0.5	Yes	
For high-salinity waters	RS	P, D	0–80	7–8	Yes	
8. SEQUIL	RS	P, D	7–65	2.5	Yes	
9. SOLMINEQ.88	RS	P, D	0–350	6	Yes	
10. WTRCHEM	pH_{sa}	P, D	0–100	0.5	No	

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Item†	$CaCO_3$ Indices: Basis for Calculation of SI	$CaCO_3$ Indices: CCPP	Approximate Temperature Range °C	Approximate Limit of Ionic Strength	Ion Pairs Considered?	C
11. WATEQ4F	RS	No	0–100	0.5	Yes	

*SI = saturation index
CCPP = $CaCO_3$ precipitation potential
pH_{sa} = alkalinity-based pH
pH_{sb} = bicarbonate-based pH
P = calculates amount of $CaCO_3$ theoretically precipitated
D = calculates amount of $CaCO_3$ theoretically dissolved
RS = relative saturation
PC = personal computer
RAM = random access memory

†1. Loewenthal and Marais[3] provide 10.2- by 11.4-cm diagrams, with documentation; Merrill[5] provides 10.2- by 16.5-cm diagrams, with documentation.
2. Radian Corp., 8501 MoPac Blvd., P.O. Box 201088, Austin, TX 78720-1088 Attn: J.G. Noblett (software and documentation).
3. Power Computing Co., 1930 Hi Line Dr., Dallas, TX, 74207 (software and documentation[6]).
4. Brown and Caldwell, P.O. Box 8045, Walnut Creek, CA 94596-1220 Attn: D.T. Merrill (software and documentation).
5. Illinois State Water Survey, Aquatic Chemistry Section, 2204 Griffith Dr., Champaign, IL 61820-7495 Attn: T.R. Holm (software and documentation).
6. Center for Exposure Assessment Modeling, Environmental Research Laboratory, Office of Research and Development. U.S. Environmental Protection Agency,Athens, GA 30613 (software and documentation[7]).
7. U.S. Geological Survey, National Center, MS 437, Reston, VA 22902, Chief of WATSTORE Program (provides software for mainframe version of standard code);U.S. Geological Survey, Water Resources Division, MS 420, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: K. Nordstrom (provides software for personalcomputer version of standard code); National Water Research Institute, Canada Centre for Inland Waters, 867 Lakeshore Rd., Burlington, Ont., Canada L7R 4A6Attn: A.S. Crowe (provides software and documentation [8,9] for personal computer versions of both standard and high-salinity codes); U.S. Geological Survey, Booksand Open File Report Section, Box 25425, Federal Center, Denver, CO 80225 (provides documentation[8,10] for mainframe and personal computer versions ofstandard code).
8. Power Computing Company, 1930 Hi Line Dr., Dallas, TX 74207 (software and documentation[11]).
9. U.S. Geological Survey, Water Resources Division, MS 427, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: Y.K. Kharaka (software and documentation[12]).
10. D.T. Merrill, Brown and Caldwell, P.O. Box 8045, Walnut Creek, CA 94596-1220 (code listing and documentation).
11. U.S. Geological Survey, Water Resources Division, MS 420, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: K. Nordstrom (software), Books and Open FileReport Section, Box 25425, Federal Center, Denver, CO 80225 (documentation[13]).
‡Codes differ in the species included in Alk_0.

TABLE 2340:I. MAXIMUM CONCENTRATIONS OF INTERFERENCES PERMISSIBLEWITH VARIOUS INHIBITORS*

	Max. Interference Concentration *mg/L*

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 2340:I. MAXIMUM CONCENTRATIONS OF INTERFERENCES PERMISSIBLEWITH VARIOUS INHIBITORS*

Interfering Substance	Max. Interference Concentration *mg/L*	
	Inhibitor I	**Inhibitor II**
Aluminum	20	20
Barium	†	†
Cadmium	†	20
Cobalt	over 20	0.3
Copper	over 30	20
Iron	over 30	5
Lead	†	20
Manganese (Mn^{2+})	†	1
Nickel	over 20	0.3
Strontium	†	†
Zinc	†	200
Polyphosphate		10

* Based on 25-mL sample diluted to 50 mL.
† Titrates as hardness.

TABLE 2510:I. EQUIVALENT CONDUCTIVITY, Λ, AND CONDUCTIVITY, *k*, OF POTASSIUM CHLORIDE AT 25.0°C.*[2–4]

KCl Concentration *M or equivalent/L*	**Equivalent Conductivity, Λ** *mho-cm²/equivalent*	**Conductivity, k_S** *μmho/cm*
0	149.9	
0.0001	148.9	14.9
0.0005	147.7	73.9
0.001	146.9	146.9
0.005	143.6	717.5
0.01	141.2	1 412
0.02	138.2	2 765

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

KCl Concentration *M or equivalent/L*	Equivalent Conductivity, Λ *mho-cm²/equivalent*	Conductivity, k_S *μmho/cm*
0.05	133.3	6 667
0.1	128.9	12 890
0.2	124.0	24 800
0.5	117.3	58 670
1	111.9	111 900

* Based on the absolute ohm, the 1968 temperature standard, and the dm^3 volumestandard.[2] Values are accurate to ±0.1% or 0.1 μmho/cm, whichever is greater.

TABLE 2510:II. SAMPLE ANALYSIS ILLUSTRATING CALCULATION OF CONDUCTIVITY, k_{calc}, FOR NATURAL WATERS.[7]

Ions	mg/L	m*M*	|*z*| λ°±m*M*	z^2m*M*
Ca	55	1.38	164.2	5.52
Mg	12	0.49	52.0	1.96
Na	28	1.22	61.1	1.22
K	3.2	0.08	5.9	0.08
HCO_3	170	2.79	124.2	2.79
SO_4	77	0.80	128.0	3.20
Cl	20	0.56	42.8	0.56
			578.2	15.33

TABLE 2510:III. EQUIVALENT CONDUCTANCES, λ°+ AND λ°–, (MHO-CM^2/EQUIVALENT) FOR IONS IN WATER AT 25.0 C.[8]

Cation	λ°+	Anion	λ°–
H^+	350	OH^-	198.6
$1/2Ca^{2+}$	59.5	HCO_3^-	44.5
$1/2Mg^{2+}$	53.1	$1/2CO_3^{2-}$	72
Na^+	50.1	$1/2SO_4^{2-}$	80.0

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Cation	λ°+	Anion	λ°–
K^+	73.5	Cl^-	76.4
NH_4^+	73.5	Ac^-	40.9
$1/2Fe^{2+}$	54	F^-	54.4
$1/3Fe^{3+}$	68	NO_3^-	71.4
		$H_2PO_4^-$	33
		$1/2HPO_4^{2-}$	57

TABLE 2530:I. COEFFICIENT OF VARIATION AND RECOVERY FOR PARTICULATE FLOATABLES TEST

Type of Wastewater	Average Floatables Concentration *mg/L*	No. of Samples	Coefficient of Variation *%*	Recovery *%*
Raw*	49	5	5.7	96
Raw	1.0	5	20	92
Primary effluent	2.7	5	15	91

* Additional floatable material added from skimmings of a primarysedimentation basin.

TABLE 2560:I. EXAMPLE CALCULATIONS FOR PARTICLE SIZE DISTRIBUTION ANALYSIS

Channel No. (A)	Lower Limit d_p μm (B)	Upper Limit d_p μm (C)	Mean Diam. d_{pi} μm (D)	Δd_{pi} μm (E)	log d_{pi} d_p in μm (F)	Δ log d_{pi} (G)	Corrected Count (H)	Number Conc. ΔN_i *No./mL* (I)
6	2.95	3.39	3.16	0.44	0.50	0.06	5125	102 500
7	3.39	3.89	3.63	0.50	0.56	0.06	4568	91 360
8	3.89	4.47	4.17	0.58	0.62	0.06	3888	77 760
9	4.47	5.13	4.79	0.66	0.68	0.06	3088	61 760
10	5.13	5.89	5.50	0.76	0.74	0.06	2289	45 780
11	5.89	6.76	6.31	0.87	0.80	0.06	1584	31 680
12	6.76	7.76	7.24	1.00	0.86	0.06	1023	20 460

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Channel No. (A)	Lower Limit d_p μm (B)	Upper Limit d_p μm (C)	Mean Diam. d_{pi} μm (D)	Δd_{pi} μm (E)	log d_{pi} d_p in μm (F)	Δ log d_{pi} (G)	Corrected Count (H)	Number Conc. ΔN_i No./mL (I)
13	7.76	8.91	8.32	1.15	0.92	0.06	631	12 620
14	8.91	10.23	9.55	1.32	0.98	0.06	363	7 260
15	10.23	11.75	10.96	1.52	1.04	0.06	199	3 980

TABLE 2580:I. POTENTIAL OF ZOBELL'S SOLUTION AS FUNCTION OF TEMPERATURE

T °C	E V	T °C	E V
1	0.481	16	0.448
2	0.479	17	0.446
3	0.476	18	0.443
4	0.474	19	0.441
5	0.472	20	0.439
6	0.470	21	0.437
7	0.468	22	0.435
8	0.465	23	0.432
9	0.463	24	0.430
10	0.461	25	0.428
11	0.459	26	0.426
12	0.457	27	0.424
13	0.454	28	0.421
14	0.452	29	0.419
15	0.450	30	0.417

TABLE 2580:II. PREPARATION OF REDOX STANDARD SOLUTIONS

Standard Solution	Potentials of Pt Electrode vs. Selected Reference Electrodes at 25°C in Standard Solution			Weight of Aq
	Calomel	Silver:Silver Chloride Ag/AgCl	Standard Hydrogen	

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 2580:II. PREPARATION OF REDOX STANDARD SOLUTIONS

Standard Solution	Potentials of Pt Electrode vs. Selected Reference Electrodes at 25°C in Standard Solution					Weight of Aqu
	Calomel	Silver:Silver Chloride Ag/AgCl			Standard Hydrogen	
	Hg/Hg_2Cl_2 saturated KCl	KCl 1.00*M*	KCl 4.00*M*	KCl saturated		
Light's solution[14]	+430	+439	+475	+476	+675	39.21 g ferr $Fe(NH_4)$ 48.22 g fe Fe(NH 56.2 mL s 1.84
ZoBell's solution*[2]	+183	+192	+228	+229	+428	1.4080 g po $K_4Fe(C$ 1.0975 g $K_3Fe(C$ 7.4555 g

* Store in dark plastic bottle in a refrigerator.

TABLE 2580:III. RECOMMENDED COMBINATIONS FOR SELECTED SAMPLE TYPES

Sample Type	Indicator Electrode(s)	Reference Electrode	Type of Sample Cell
Process stream			
(low Br^-) (S^{2-})	Pt or Au	Calomel or silver: silver chloride	Closed continuous flow (dual indicator electrode)
(high Br^-)	Pt or Au	Calomel or silver: silver chloride with salt bridge (double junction reference electrode)	
Natural waters			
Surface waters	Pt or Au	Calomel or silver: silver chloride	Closed continuous flow (dual indicator electrode) or beaker
Groundwater	Pt or Au	Calomel or silver: silver chloride	Closed continuous flow (dual indicator electrode)

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Sample Type	Indicator Electrode(s)	Reference Electrode	Type of Sample Cell
Soils, sludges	WIG, Pt wire	Calomel or silver: silver chloride	Beaker or soil core

TABLE 2710:I. TEMPERATURE CORRECTION FACTOR

Temperature °C	Temperature Correction Factor
15	0.9991
20	0.9982
25	0.9975
30	0.9957
35	0.9941
40	0.9922
45	0.9903

TABLE 2810:I. BUNSEN COEFFICIENT FOR OXYGEN IN FRESH WATER

	Bunsen Coefficient at Given Temperature (to nearest 0.1°C) *L real gas at STP/(L · atmosphere)*							
Temperature °C	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
0	0.04914	0.04901	0.04887	0.04873	0.04860	0.04847	0.04833	0.0482(
1	0.04780	0.04767	0.04754	0.04741	0.04728	0.04716	0.04703	0.0468(
2	0.04653	0.04640	0.04628	0.04615	0.04603	0.04591	0.04579	0.0456[7]
3	0.04531	0.04519	0.04507	0.04495	0.04484	0.04472	0.04460	0.0444[9]
4	0.04414	0.04403	0.04392	0.04381	0.04369	0.04358	0.04347	0.0433[6]
5	0.04303	0.04292	0.04282	0.04271	0.04260	0.04250	0.04239	0.0422[9]
6	0.04197	0.04187	0.04177	0.04166	0.04156	0.04146	0.04136	0.0412[6]
7	0.04096	0.04086	0.04076	0.04066	0.04056	0.04047	0.04037	0.0402[7]
8	0.03999	0.03989	0.03980	0.03971	0.03961	0.03952	0.03943	0.0393[3]
9	0.03906	0.03897	0.03888	0.03879	0.03870	0.03861	0.03852	0.0384[3]
10	0.03817	0.03809	0.03800	0.03791	0.03783	0.03774	0.03766	0.0375[7]
11	0.03732	0.03724	0.03716	0.03707	0.03699	0.03691	0.03683	0.0367[5]
12	0.03651	0.03643	0.03635	0.03627	0.03619	0.03611	0.03604	0.0359[6]

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Temperature °C	Bunsen Coefficient at Given Temperature (to nearest 0.1°C) *L real gas at STP/(L · atmosphere)*							
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
13	0.03573	0.03565	0.03558	0.03550	0.03543	0.03535	0.03528	0.0352(
14	0.03498	0.03491	0.03448	0.03476	0.03469	0.03462	0.03455	0.0344{
15	0.03426	0.03419	0.03412	0.03406	0.03399	0.03392	0.03385	0.0337{
16	0.03358	0.03351	0.03344	0.03338	0.03331	0.03324	0.03318	0.0331:
17	0.03292	0.03285	0.03279	0.03272	0.03266	0.03260	0.03253	0.0324[
18	0.03228	0.03222	0.03216	0.03210	0.03204	0.03198	0.03192	0.0318(
19	0.03168	0.03162	0.03156	0.03150	0.03144	0.03138	0.03132	0.0312(
20	0.03109	0.03103	0.03098	0.03092	0.03086	0.03081	0.03075	0.0307(
21	0.03053	0.03048	0.03042	0.03037	0.03031	0.03026	0.03020	0.0301[
22	0.02999	0.02994	0.02989	0.02983	0.02978	0.02973	0.02968	0.0296:
23	0.02947	0.02942	0.02937	0.02932	0.02927	0.02922	0.02917	0.0291[
24	0.02897	0.02893	0.02888	0.02883	0.02878	0.02873	0.02868	0.0286{
25	0.02850	0.02845	0.02840	0.02835	0.02831	0.02826	0.02822	0.0281[
26	0.02803	0.02799	0.02794	0.02790	0.02785	0.02781	0.02777	0.0277[
27	0.02759	0.02755	0.02750	0.02746	0.02742	0.02737	0.02733	0.0272[
28	0.02716	0.02712	0.02708	0.02704	0.02700	0.02695	0.02691	0.0268[
29	0.02675	0.02671	0.02667	0.02663	0.02659	0.02655	0.02651	0.0264[
30	0.02635	0.02632	0.02628	0.02624	0.02620	0.02616	0.02612	0.0260[
31	0.02597	0.02594	0.02590	0.02586	0.02582	0.02579	0.02575	0.0257:
32	0.02561	0.02557	0.02553	0.02550	0.02546	0.02543	0.02539	0.0253(
33	0.02525	0.02522	0.02518	0.02515	0.02511	0.02508	0.02504	0.0250:
34	0.02491	0.02488	0.02484	0.02481	0.02478	0.02474	0.02471	0.0246{
35	0.02458	0.02455	0.02452	0.02448	0.02445	0.02442	0.02439	0.0243(
36	0.02426	0.02423	0.02420	0.02417	0.02414	0.02411	0.02408	0.0240[
37	0.02396	0.02393	0.02390	0.02387	0.02384	0.02381	0.02378	0.0237[
38	0.02366	0.02363	0.02360	0.02358	0.02355	0.02352	0.02349	0.0234(
39	0.02338	0.02335	0.02332	0.02329	0.02327	0.02324	0.02321	0.0231{
40	0.02310	0.02308	0.02305	0.02302	0.02300	0.02297	0.02294	0.0229[

Based on Benson and Krause.[9,10] $\beta = 9.9902 \times 10^{-4} \exp(9.7265 - 5.26895 \times 10^{3}/T + 1.00417 \times 10^{6}/T^{2})$, where $T = 273.15 + °C$.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 2810:II. VAPOR PRESSURE OF FRESH WATER

Temperature °C	Vapor Pressure at Given Temperature (to nearest 0.1°C) *mm Hg*									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	4.58	4.61	4.64	4.68	4.71	4.75	4.78	4.82	4.85	4.89
1	4.92	4.96	4.99	5.03	5.07	5.10	5.14	5.18	5.21	5.25
2	5.29	5.33	5.36	5.40	5.44	5.48	5.52	5.56	5.60	5.64
3	5.68	5.72	5.76	5.80	5.84	5.88	5.92	5.97	6.01	6.05
4	6.09	6.14	6.18	6.22	6.27	6.31	6.36	6.40	6.44	6.49
5	6.54	6.58	6.63	6.67	6.72	6.77	6.81	6.86	6.91	6.96
6	7.01	7.05	7.10	7.15	7.20	7.25	7.30	7.35	7.40	7.45
7	7.51	7.56	7.61	7.66	7.71	7.77	7.82	7.87	7.93	7.98
8	8.04	8.09	8.15	8.20	8.26	8.31	8.37	8.43	8.48	8.54
9	8.60	8.66	8.72	8.87	8.84	8.89	8.95	9.02	9.08	9.14
10	9.20	9.26	9.32	9.39	9.45	9.51	9.58	9.64	9.70	9.77
11	9.83	9.90	9.97	10.03	10.10	10.17	10.23	10.30	10.37	10.44
12	10.51	10.58	10.65	10.72	10.76	10.86	10.93	11.00	11.07	11.15
13	11.22	11.29	11.37	11.44	11.52	11.59	11.67	11.74	11.82	11.90
14	11.98	12.05	12.13	12.21	12.29	12.37	12.45	12.53	12.61	12.69
15	12.78	12.86	12.94	13.05	13.11	13.19	13.28	13.36	13.45	13.54
16	13.62	13.71	13.80	13.89	13.97	14.06	14.15	14.24	14.33	14.43
17	14.52	14.61	14.70	14.80	14.89	14.98	15.08	15.17	15.27	15.37
18	15.46	15.56	15.66	15.76	15.86	15.96	16.06	16.16	16.26	16.36
19	16.46	16.57	16.67	16.77	16.88	16.98	17.09	17.20	17.30	17.41
20	17.52	17.63	17.74	17.85	17.96	18.07	18.18	18.29	18.41	18.52
21	18.64	18.75	18.87	18.98	19.10	19.22	19.33	19.45	19.57	19.69
22	19.81	19.93	20.05	20.48	20.60	20.42	20.55	20.67	20.80	20.93
23	21.05	21.18	21.31	21.44	21.57	21.70	21.83	21.96	22.09	22.23
24	22.36	22.50	22.63	22.77	22.90	23.04	23.18	23.32	23.46	23.60
25	23.74	23.88	24.03	24.17	24.31	24.46	24.60	24.75	24.90	25.04
26	25.19	25.34	25.49	25.64	25.80	25.95	26.10	26.26	26.41	26.57
27	26.72	26.88	27.04	27.20	27.36	27.52	27.68	27.84	28.00	28.17
28	28.33	28.50	28.66	28.83	29.00	29.17	29.34	29.51	29.68	29.85

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Temperature °C	Vapor Pressure at Given Temperature (to nearest 0.1°C) *mm Hg*									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
29	30.03	30.80	30.37	30.55	30.73	30.91	31.08	31.26	31.44	31.62
30	31.81	31.99	32.17	32.36	32.54	32.73	32.92	33.11	33.30	33.49
31	33.68	33.87	34.06	34.26	34.45	34.65	34.85	35.05	35.24	35.44
32	35.65	35.85	36.05	36.25	36.46	36.67	36.87	37.08	37.29	37.50
33	37.71	37.92	38.14	38.35	38.57	38.78	39.00	39.22	39.44	39.66
34	39.88	40.10	40.33	40.55	40.78	41.01	41.23	41.46	41.69	41.92
35	42.16	42.39	42.63	42.86	43.10	43.34	43.58	43.82	44.06	44.30
36	44.55	44.79	45.04	45.28	45.53	45.78	46.03	46.29	46.54	46.79
37	47.05	47.31	47.56	47.82	48.08	48.35	48.61	48.87	49.14	49.41
38	49.67	49.94	50.21	50.49	50.76	51.03	51.31	51.59	51.87	52.14
39	52.43	52.71	52.99	53.28	53.56	53.85	54.14	54.43	54.72	55.01
40	55.31	55.60	55.90	56.20	56.50	56.80	57.10	57.41	57.71	58.02

Based on an equation presented by Green and Carritt.[11] This equation is cumbersome to use. The following equation[9] is adequate for most applications:

$P_{H_2O} = 760\{\exp(11.8571 - 3{,}840.70/T - 216{,}961/T^2)\}$, where $T = 273.15 + °C$.[5]

Part 3000 METALS

3010 INTRODUCTION

3010 A. General Discussion

1. Significance

The effects of metals in water and wastewater range from beneficial through troublesome to dangerously toxic. Some metals are essential to plant and animal growth while others may adversely affect water consumers, wastewater treatment systems, and receiving waters. The benefits versus toxicity of some metals depend on their concentrations in waters.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2. Types of Methods

Preliminary treatment is often required to present the metals to the analytical methodology in an appropriate form. Alternative methods for pretreatment of samples are presented in Section 3030.

Metals may be determined satisfactorily by a variety of methods, with the choice often depending on the precision and sensitivity required. Part 3000 describes colorimetric methods as well as instrumental methods, i.e., atomic absorption spectrometry, including flame, electrothermal (furnace), hydride, and cold vapor techniques; flame photometry; inductively coupled plasma emission spectrometry; inductively coupled plasma mass spectrometry, and anodic stripping voltammetry. Flame atomic absorption methods generally are applicable at moderate (0.1- to 10-mg/L) concentrations in clean and complex-matrix samples. Electrothermal methods generally can increase sensitivity if matrix problems do not interfere. Inductively coupled plasma emission techniques are applicable over a broad linear range and are especially sensitive for refractory elements. Inductively coupled plasma mass spectrometry offers significantly increased sensitivity for some elements (as low as 0.01 µg/L) in a variety of environmental matrices. Flame photometry gives good results at higher concentrations for several Group I and II elements. Anodic stripping offers high sensitivity for several elements in relatively clean matrices. Colorimetric methods are applicable to specific metal determinations where interferences are known not to compromise method accuracy; these methods may provide speciation information for some metals. Table 3010:I lists the methods available in Part 3000 for each metal.

3. Definition of Terms

a. Dissolved metals: Those metals in an unacidified sample that pass through a 0.45-µm membrane filter.

b. Suspended metals: Those metals in an unacidified sample that are retained by a 0.45-µm membrane filter.

c. Total metals: The concentration of metals determined in an unfiltered sample after vigorous digestion, or the sum of the concentrations of metals in the dissolved and suspended fractions. Note that total metals are defined operationally by the digestion procedure.

d. Acid-extractable metals: The concentration of metals in solution after treatment of an unfiltered sample with hot dilute mineral acid. To determine either dissolved or suspended metals, filter sample immediately after collection. Do not preserve with acid until after filtration.

3010 B. Sampling and Sample Preservation

Before collecting a sample, decide what fraction is to be analyzed (dissolved, suspended, total, or acid-extractable). This decision will determine in part whether the sample is acidified with or without filtration and the type of digestion required.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Serious errors may be introduced during sampling and storage because of contamination from sampling device, failure to remove residues of previous samples from sample container, and loss of metals by adsorption on and/or precipitation in sample container caused by failure to acidify the sample properly.

1. Sample Containers

The best sample containers are made of quartz or TFE. Because these containers are expensive, the preferred sample container is made of polypropylene or linear polyethylene with a polyethylene cap. Borosilicate glass containers also may be used, but avoid soft glass containers for samples containing metals in the microgram-per-liter range. Store samples for determination of silver in light-absorbing containers. Use only containers and filters that have been acid rinsed.

2. Preservation

Preserve samples immediately after sampling by acidifying with concentrated nitric acid (HNO_3) to pH <2. Filter samples for dissolved metals before preserving (see Section 3030). Usually 1.5 mL conc HNO_3/L sample (or 3 mL 1 + 1 HNO_3/L sample) is sufficient for short-term preservation. For samples with high buffer capacity, increase amount of acid (5 mL may be required for some alkaline or highly buffered samples). Use commercially available high-purity acid#(65)* or prepare high-purity acid by sub-boiling distillation of acid.

After acidifying sample, preferably store it in a refrigerator at approximately 4°C to prevent change in volume due to evaporation. Under these conditions, samples with metal concentrations of several milligrams per liter are stable for up to 6 months (except mercury, for which the limit is 5 weeks). For microgram-per-liter metal levels, analyze samples as soon as possible after sample collection.

Alternatively, preserve samples for mercury analysis by adding 2 mL/L 20% (w/v) $K_2Cr_2O_7$ solution (prepared in 1 + 1 HNO_3). Store in a refrigerator not contaminated with mercury. (CAUTION: Mercury concentrations may increase in samples stored in plastic bottles in mercury-contaminated laboratories.)

3. Bibliography

STRUEMPLER, A.W. 1973. Adsorption characteristics of silver, lead, calcium, zinc and nickel on borosilicate glass, polyethylene and polypropylene container surfaces. *Anal. Chem.* 45:2251.

FELDMAN, C. 1974. Preservation of dilute mercury solutions. *Anal. Chem.* 46:99.

KING, W.G., J.M. RODRIGUEZ & C.M. WAI. 1974. Losses of trace concentrations of cadmium from aqueous solution during storage in glass containers. *Anal. Chem.* 46:771.

BATLEY, G.E. & D. GARDNER. 1977. Sampling and storage of natural waters for trace metal analysis. *Water Res.* 11:745.

SUBRAMANIAN, K.S., C.L. CHAKRABARTI, J.E. SUETIAS & I.S. MAINES. 1978. Preservation of some trace metals in samples of natural waters. *Anal. Chem.* 50:444.

BERMAN, S. & P. YEATS. 1985. Sampling of seawater for trace metals. *Crit. Rev. Anal. Chem.*

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

16:1.

WENDLANDT, E. 1986. Sample containers and analytical accessories made of modern plastics for trace analysis. *Gewaess. Wass. Abwass.* 86:79.

3010 C. General Precautions

1. Sources of Contamination

Avoid introducing contaminating metals from containers, distilled water, or membrane filters. Some plastic caps or cap liners may introduce metal contamination; for example, zinc has been found in black bakelite-type screw caps as well as in many rubber and plastic products, and cadmium has been found in plastic pipet tips. Lead is a ubiquitous contaminant in urban air and dust.

2. Contaminant Removal

Thoroughly clean sample containers with a metal-free nonionic detergent solution, rinse with tap water, soak in acid, and then rinse with metal-free water. For quartz, TFE, or glass materials, use 1 + 1 HNO_3, 1 + 1 HCl, or aqua regia (3 parts conc HCl + 1 part conc HNO_3) for soaking. For plastic material, use 1 + 1 HNO_3 or 1 + 1 HCl. Reliable soaking conditions are 24 h at 70°C. Chromic acid or chromium-free substitutes#(66)* may be used to remove organic deposits from containers, but rinse containers thoroughly with water to remove traces of chromium. Do not use chromic acid for plastic containers or if chromium is to be determined. Always use metal-free water in analysis and reagent preparation (see Section 3111B.3*c*). In these methods, the word ‘‘water’’ means metal-free water.

3. Airborne Contaminants

For analysis of microgram-per-liter concentrations of metals, airborne contaminants in the form of volatile compounds, dust, soot, and aerosols present in laboratory air may become significant. To avoid contamination use ‘‘clean laboratory’’ facilities such as commercially available laminar-flow clean-air benches or custom-designed work stations and analyze blanks that reflect the complete procedure.

4. Bibliography

MITCHELL, J.W. 1973. Ultrapurity in trace analysis. *Anal. Chem.* 45:492A.

GARDNER, M., D. HUNT & G. TOPPING. 1986. Analytical quality control (AQC) for monitoring trace metals in the coastal and marine environment. *Water Sci. Technol.* 18:35.

3020 QUALITY ASSURANCE/QUALITY CONTROL

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3020 A. Introduction

General information and recommendations for quality assurance (QA) and quality control (QC) are provided in Section 1020 Quality Assurance, 1030 Data Quality, and 1040 Method Development and Evaluation. This section discusses QA/QC requirements that are common to the analytical methods presented in Part 3000. The requirements are recommended minimum QA/QC activities; refer to individual methods and regulatory program requirements for method-specific QA/QC requirements. Always consider the overall purpose of analyses. QA/QC measures and substantiation for operational-control determinations may differ significantly from those for determinations of trace metals at water quality criteria levels. Levels of trace metals in environmental samples may be orders of magnitude lower than in potential sources of contamination.

Use replicates of measurable concentration to establish precision and known-additions recovery to determine bias. Use blanks, calibrations, control charts, known additions, standards, and other ancillary measurement tools as appropriate. Provide adequate documentation and record keeping to satisfy client requirements and performance criteria established by the laboratory.

3020 B. Quality Control Practices

1. Initial Quality Control

a. Initial demonstration of capability: Verify analyst capability before analyzing any samples and repeat periodically to demonstrate proficiency with the analytical method. Verify that the method being used provides sufficient sensitivity for the purpose of the measurement. Test analyst capability by analyzing at least four reagent water portions containing known additions of the analyte of interest. Confirm proficiency by generating analytical results that demonstrate precision and bias within acceptable limits representative of the analytical method.

b. Method detection limit (MDL): Before samples are analyzed, determine the MDL for each analyte by the procedures of Section 1030, or other applicable procedure.[1] Determine MDL at least annually for each method and major matrix category. Verify MDL for a new analyst or whenever instrument hardware or method operating conditions are modified. Analyze samples for MDL determinations over a 3- to 5-d period to generate a realistic value. Preferably use pooled data from several analysts rather than data from a single analyst.

c. Dynamic range (DR): Before using a new method, determine the dynamic range, i.e., the concentration range over which a method has an increasing response (linear or second-order), for each analyte by analyzing several standard solutions that bracket the range of interest. Each standard measurement should be within 10% of the true value for acceptance into the DR determination. Take measurements at both the low and high end of the calibration range to

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

determine method suitability. Analytical instrumentation with curve-fitting features may allow utilization of nonlinear instrument response.

2. Calibration

a. Initial calibration: Calibrate initially with a minimum of a blank and three calibration standards of the analyte(s) of interest. Select calibration standards that bracket the expected concentration of the sample and that are within the method's dynamic range. The number of calibration points depends on the width of the dynamic range and the shape of the calibration curve. One calibration standard should be below the reporting limit for the method. As a general rule, differences between calibration standard concentrations should not be greater than one order of magnitude (i.e., 1, 10, 100, 1000). Apply linear or polynomial curve-fitting statistics, as appropriate, for analysis of the concentration-instrument response relationship. The appropriate linear or nonlinear correlation coefficient for standard concentration to instrument response should be ≥ 0.995. Use initial calibration for quantitation of analyte concentration in samples. Use calibration verification, ¶ b below, only for checks on the initial calibration and not for sample quantitation. Repeat initial calibration daily and whenever calibration verification acceptance criteria are not satisfied.

b. Calibration verification: Calibration verification is the periodic confirmation that instrument response has not changed significantly from the initial calibration. Verify calibration by analyzing a midpoint calibration standard (check standard) and calibration blank at the beginning and end of a sample run, periodically during a run (normally after each set of ten samples). A check standard determination outside 90 to 110% of the expected concentration indicates a potential problem. If a check standard determination is outside 80 to 120% of the expected concentration, immediately cease sample analyses and initiate corrective action. Repeat initial calibration and sample determinations since the last acceptable calibration verification. Use calculated control limits (Section 1020B) to provide better indications of system performance and to provide tighter control limits.

c. Quality control sample: Analyze an externally generated quality control sample of known concentration at least quarterly and whenever new calibration stock solutions are prepared. Obtain this sample from a source external to the laboratory or prepare it from a source different from those used to prepare working standards. Use to validate the laboratory's working standards both qualitatively and quantitatively.

3. Batch Quality Control

a. Method blank (MB): A method blank (also known as reagent blank) is a portion of reagent water treated exactly as a sample, including exposure to all equipment, glassware, procedures, and reagents. The MB is used to assess whether analytes or interference are present within the analytical process or system. No analyte of interest should be present in the MB at a warning level based on the end user's requirements. Undertake immediate corrective action for MB measurements above the MDL. Include a minimum of one MB with each set of 20 or fewer samples.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

b. Laboratory-fortified blank (LFB): The laboratory-fortified blank (also known as blank spike) is a method blank that has been fortified with a known concentration of analyte. It is used to evaluate ongoing laboratory performance and analyte recovery in a clean matrix. Prepare fortified concentrations approximating the midpoint of the calibration curve or lower with stock solutions prepared from a source different from those used to develop working standards. Calculate percent recovery, plot control charts, and determine control limits (Section 1020B) for these measurements. Ensure that the LFB meets performance criteria for the method. Establish corrective actions to be taken in the event that LFB does not satisfy acceptance criteria. Include a minimum of one LFB with each set of 20 or fewer samples.

c. Duplicates: Use duplicate samples of measurable concentration to measure precision of the analytical process. Randomly select routine samples to be analyzed twice. Process duplicate sample independently through entire sample preparation and analytical process. Include a minimum of one duplicate for each matrix type with each set of 20 or fewer samples.

d. Laboratory-fortified matrix (LFM)/laboratory-fortified matrix duplicate: Use LFM (also known as matrix spike) and LFM duplicate to evaluate the bias and precision, respectively, of the method as influenced by a specific matrix. Prepare by adding a known concentration of analytes to a randomly selected routing sample. Prepare addition concentrations to approximately double the concentration present in the original sample. If necessary, dilute sample to bring the measurement within the established calibration curve. Limit addition volume to 5% or less of sample volume. Calculate percent recovery and relative percent difference, plot control charts, and determine control limits (Section 1020B). Ensure that performance criteria for the method are satisfied. Process fortified samples independently through entire sample preparation and analytical process. Include a minimum of one LFM/LFM duplicate with each set of 20 or fewer samples.

e. Method of known additions: To analyze a new or unfamiliar matrix, use the method of known additions (Section 1020B) to demonstrate freedom from interference before reporting concentration data for the analyte. Verify absence of interferences by analyzing such samples undiluted and in a 1:10 dilution; results should be within 10% of each other. Limit known-addition volume to 10% or less of the sample volume.

4. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1995. Definition and procedure for the determination of the method detection limit, revision 1.11. 40 CFR Part 136, Appendix B. *Federal Register* 5:23703.

3030 PRELIMINARY TREATMENT OF SAMPLES*#(67)

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3030 A. Introduction

Samples containing particulates or organic material generally require pretreatment before spectroscopic analysis. ‘‘Total metals’’ includes all metals, inorganically and organically bound, both dissolved and particulate. Colorless, transparent samples (primarily drinking water) having a turbidity of <1 NTU, no odor, and single phase may be analyzed directly by atomic absorption spectroscopy (flame or electrothermal vaporization) or inductively coupled plasma spectroscopy (atomic emission or mass spectrometry) for total metals without digestion. For further verification or if changes in existing matrices are encountered, compare digested and undigested samples to ensure comparable results. On collection, acidify such samples to pH <2 with conc nitric acid (1.5 mL HNO_3/L is usually adequate for drinking water) and analyze directly. Digest all other samples before determining total metals. To analyze for dissolved metals, filter sample, acidify filtrate, and store until analyses can be performed. To determine suspended metals, filter sample, digest filter and the material on it, and analyze. To determine acid-extractable metals, extract metals as indicated in Section 3030E through K and analyze extract.

This section describes general pretreatment for samples in which metals are to be determined according to Section 3110 through 3500-Zn with several exceptions. The special digestion techniques for mercury are given in Section 3112B.4*b* and *c*, and those for arsenic and selenium in Section 3114 and Section 3500-Se.

Take care not to introduce metals into samples during preliminary treatment. During pretreatment avoid contact with rubber, metal-based paints, cigarette smoke, paper tissues, and all metal products including those made of stainless steel, galvanized metal, and brass. Conventional fume hoods can contribute significantly to sample contamination, particularly during acid digestion in open containers. Keep vessels covered with watch glasses and turn spouts away from incoming air to reduce airborne contamination. Plastic pipet tips often are contaminated with copper, iron, zinc, and cadmium; before use soak in 2*N* HCl or HNO_3 for several days and rinse with deionized water. Avoid using colored plastics, which can contain metals. Use certified metal-free plastic containers and pipet tips when possible. Avoid using glass if analyzing for aluminum or silica.

Use metal-free water (see Section 3111B.3*c*) for all operations. Check reagent-grade acids used for preservation, extraction, and digestion for purity. If excessive metal concentrations are found, purify the acids by distillation or use ultra-pure acids. Inductively coupled plasma mass spectrometry (ICP-MS) may require use of ultra-pure acids and reagents to avoid measurable contamination. Process blanks through all digestion and filtration steps and evaluate blank results relative to corresponding sample results. Either apply corrections to sample results or take other corrective actions as necessary or appropriate.

3030 B. Filtration for Dissolved and Suspended Metals

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. Filtration Procedures

If dissolved or suspended metals (see Section 3010A) are to be determined, filter sample at time of collection using a preconditioned plastic filtering device with either vacuum or pressure, containing a filter support of plastic or fluorocarbon, through a prewashed ungridded 0.4- to 0.45-μm-pore-diam membrane filter (polycarbonate or cellulose esters). Before use filter a blank consisting of metal-free (deionized) water to insure freedom from contamination. Precondition filter and filter device by rinsing with 50 mL deionized water. If the filter blank contains significant metals concentrations, soak membrane filters in approximately 0.5*N* HCl or 1*N* HNO_3 (recommended for electrothermal and ICP-MS analyses) and rinse with deionized water before use.

Before filtering, centrifuge highly turbid samples in acid-washed fluorocarbon or high-density plastic tubes to reduce loading on filters. Stirred, pressure filter units foul less readily than vacuum filters; filter at a pressure of 70 to 130 kPa. After filtration acidify filtrate to pH 2 with conc HNO_3 and store until analyses can be performed. If a precipitate forms on acidification, digest acidified filtrate before analysis as directed (see Section 3030E). Retain filter and digest it for direct determination of suspended metals.

If it is not possible to field-filter the sample without contaminating it, obtain sample in an ‘‘unpreserved’’ bottle as above and promptly cool to 4°C. Do not acid-preserve the sample. Then, without delay, filter sample under cleaner conditions in the laboratory.

Test pH of a portion of aqueous sample upon receipt in the laboratory to ensure that the sample has been properly filtered and acid-preserved.[1]

NOTE: Different filters display different sorption and filtration characteristics[2]; for trace analysis, test filter and filtration sytem to verify complete recovery of metals.

If suspended metals (see Section 3010A) are to be determined, filter sample as above for dissolved metals, but do not centrifuge before filtration. Retain filter and digest it for direct determination of suspended metals. Record sample volume filtered and include a filter in determination of the blank.

CAUTION: *Do not use perchloric acid to digest membrane filters*. (See Section 3030H for more information on handling $HClO_4$).

2. References

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, Method 200.2. Environmental Monitoring Systems Lab., Cincinnati, Ohio.
2. HOROWITZ, A.J., K.R. LUM, J.R. GARBARINO, G.E.M. HALL, C. LEMIEUX & C.R. DEMAS. 1996. Problems with using filtration to define dissolved trace element concentrations in natural water samples. *Environ. Sci. Technol.* 30, 954.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3030 C. Treatment for Acid-Extractable Metals

Extractable metals (see Section 3010A) are lightly adsorbed on particulate material. Because some sample digestion may be unavoidable use rigidly controlled conditions to obtain meaningful and reproducible results. Maintain constant sample volume, acid volume, and contact time. Express results as extractable metals and specify extraction conditions.

At collection, acidify entire sample with 5 mL conc HNO_3/L sample. To prepare sample, mix well, transfer 100 mL to a beaker or flask, and add 5 mL 1 + 1 high-purity HCl. Heat 15 min on a steam bath. Filter through a membrane filter (preconditioned as in Section 3030B) and carefully transfer filtrate to a tared volumetric flask. Adjust volume to 100 mL with metal-free water, mix, and analyze. If volume is greater than 100 mL, determine volume to nearest 0.1 mL by weight, analyze, and correct final concentration measurement by multiplying by the dilution factor (final volume ÷ 100).

3030 D. Digestion for Metals

To reduce interference by organic matter and to convert metals associated with particulates to a form (usually the free metal) that can be determined by atomic absorption spectrometry or inductively-coupled plasma spectroscopy, use one of the digestion techniques presented below. Use the least rigorous digestion method required to provide acceptable and consistent recovery compatible with the analytical method and the metal being analyzed.[1-3]

1. Selection of Acid

Nitric acid will digest most samples adequately (Section 3030E). Nitrate is an acceptable matrix for both flame and electrothermal atomic absorption and the preferred matrix for ICP-MS.[4] Some samples may require addition of perchloric, hydrochloric, hydrofluoric, or sulfuric acid for complete digestion. These acids may interfere in the analysis of some metals and all provide a poorer matrix for both electrothermal and ICP-MS analysis. Confirm metal recovery for each digestion and analytical procedure used. Use Table 3030:I as a guide in determining which acids (in addition to HNO_3) to use for complete digestion. As a general rule, HNO_3 alone is adequate for clean samples or easily oxidized materials; HNO_3-H_2SO_4 or HNO_3-HCl digestion is adequate for readily oxidizable organic matter; HNO_3-$HClO_4$ or HNO_3-$HClO_4$-HF digestion is necessary for difficult-to-oxidize organic matter or minerals containing silicates. Although dry ashing is not generally recommended because of the loss of many volatile elements, it may be helpful if large amounts of organic matter are present.

2. Digestion Procedures

Dilute samples with Ag concentrations greater than 1 mg/L to contain less than 1 mg Ag/L for flame atomic absorption methods and 25 µg/L or less for electrothermal analysis.[2,5,6] To

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

address problems with silver halide solubility in HNO_3, digest using method 3030F.3*b*.

Report digestion technique used.

Acid digestion techniques (Section 3030E through I) generally yield comparable precision and bias for most sample types that are totally digested by the technique. Because acids used in digestion will add metals to the samples and blanks, minimize the volume of acids used.

Because the acid digestion techniques (Section 3030E and F) normally are not total digestions, the microwave digestion procedure (Section 3030K) may be used as an alternative. The microwave method is a closed-vessel procedure and thus is expected to provide improved precision when compared with hot-plate techniques. Microwave digestion is recommended for samples being analyzed by ICP-MS. The microwave digestion method is recommended for the analysis of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V, and Zn. Microwave digestion may be acceptable for additional analytes provided its performance for those elements is validated.

Suggested sample volumes are indicated below for flame atomic absorption spectrometry. Lesser volumes, to a minimum of 5 mL, are appropriate for graphite furnace, ICP, and ICP-MS. Do not subsample volumes less than 5 mL, especially when particulates are present. Instead dilute samples with elevated analyte concentrations after digestion. If the recommended volume exceeds digestion vessel capacity, add sample as evaporation proceeds. For samples containing particulates, wide-bore pipets maybe useful for volume measurement and transfer.

When samples are concentrated during digestion (e.g., >100mL sample used) determine metal recovery for each matrix digested, to verify method validity. Using larger samples will require additional acid, which also would increase the concentration of impurities.

Estimated Metal Concentration *mg/L*	**Sample Volume*** *mL*
<0.1	1000
0.1–10	100
10–100+	10

*For flame atomic absorption spectrometry.

Report results as follows:

$$\text{Metal concentration, mg/L} = A \times \frac{B}{C}$$

where:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

A = concentration of metal in digested solution, mg/L,
B = final volume of digested solution, mL, and
C = sample size, mL.

Prepare solid samples or liquid sludges with high solids contents on a weight basis. Mix sample and transfer a suitable amount (typically 1 g of a sludge with 15% total solids) directly into a preweighed digestion vessel. Reweigh and calculate weight of sample. Proceed with one of the digestion techniques presented below. However, as these digestion methods are predominantly for dissolved and extractable metals in aqueous samples, other approaches may be more appropriate for solid samples. For complete mineralization of solid samples, consult methods available elsewhere.[1,4,6,7] Report results on wet- or dry-weight basis as follows:

$$\text{Metal concentration, mg/kg (wet-weight basis)} = \frac{A \times B}{\text{g sample}}$$

$$\text{Metal concentration, mg/kg (dry-weight basis)} = \frac{A \times B}{\text{g sample}} \times \frac{100}{D}$$

where:
A = concentration of metal in digested solution, mg/L,
B = final volume of digested solution, mL, and
D = total solids, % (see Section 2540G).

Always prepare acid blanks for each type of digestion performed. Although it is always best to eliminate all relevant sources of contamination, a reagent blank prepared with the same acids and subjected to the same digestion procedure as the sample can correct for impurities present in acids and reagent water. However, blank correction is not recommended for any other sources of contamination such as impurities adsorbed on glassware.

3. References

1. BOUMANS, P.W.J.M., ed. 1987. Inductively Coupled Plasma Emission Spectroscopy, Part II: Applications and Fundamentals. John Wiley & Sons, New York, N.Y.
2. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1992. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd ed. Update 1, Methods 3005A, 3010A, 3020A & 3050A. Off. Solid Waste & Emergency Response, Washington, D.C.
3. HOENIG, M. & A.M. DE KERSABIEC. 1996. Sample preparation steps for analysis by atomic spectroscopy methods: Present status. *Spectrochim. Acta.* B51:1297.
4. JARVIS, K.E., A.L. GRAY & R.S. HOUK, eds. 1992. Sample preparation for ICP-MS.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Chapter 7 *in* Handbook of Inductively Coupled Plasma Mass Spectrometry. Blackie, Glasgow & London, U.K.

5. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, Method 200.2. Environmental Monitoring Systems Lab., Cincinnati, Ohio.
6. KINGSTON, H.M. & S. HASWELL, eds. 1997. Microwave Enhanced Chemistry: Fundamentals, Sample Preparation and Applications. American Chemical Soc., Washington, D.C.
7. BOCK, R. 1979. A Handbook of Decomposition Methods in Analytical Chemistry. Blackie, Glasgow, U.K.

3030 E. Nitric Acid Digestion

Because of the wide variation in concentration levels detected by various instrumental techniques and the need to deal adequately with sources of contamination at trace levels, this method presents one approach for high-level analytes (>0.1 mg/L) and another for trace levels (≤0.1 mg/L).

1. Digestion for Flame Atomic Absorption and High-Level Concentrations

a. Apparatus:

1) *Hot plate.*

2) *Conical (erlenmeyer) flasks,* 125-mL, or *Griffin beakers,* 150-mL, acid-washed and rinsed with water.

3) *Volumetric flasks,* 100-mL.

4) *Watch glasses,* ribbed and unribbed.

b. Reagent:

Nitric acid, HNO_3, conc, analytical or trace-metals grade.

c. Procedure: Transfer a measured volume (100 mL recommended) of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see Section 3030D for sample volume). In a hood, add 5 mL conc HNO_3. If a beaker is used, cover with a ribbed watch glass to minimize contamination. Boiling chips, glass beads, or Hengar granules may be added to aid boiling and minimize spatter when high concentration levels (>10 mg/L) are being determined. Bring to a slow boil and evaporate on a hot plate to the lowest volume possible (about 10 to 20 mL) before precipitation occurs. Continue heating and adding conc HNO_3 as necessary until digestion is complete as shown by a light-colored, clear solution. Do not let sample dry during digestion.

Wash down flask or beaker walls and watch glass cover (if used) with metal-free water and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

then filter if necessary (see Section 3030B). Transfer filtrate to a 100-mL volumetric flask with two 5-mL portions of water, adding these rinsings to the volumetric flask. Cool, dilute to mark, and mix thoroughly. Take portions of this solution for required metal determinations.

2. Digestion for Trace-Level (≤0.1 mg/L) Concentrations for ICP and ICP-MS[1]

a. Apparatus:

1) *Block heater*, dry, with temperature control.

2) *Polypropylene tubes**#(68), graduated, round-bottom tubes with caps, 17 × 100 mm, acid-washed and rinsed with metal-free water. Preferably use tubes that simultaneously match the analysis instrument autosampler and the block digester. A fit with the centrifuge is secondary but also desirable.

3) *Pipetters*, assorted sizes or adjustable.

4) *Pipet tips*.

5) *Centrifuge*.

b. Reagent:

Nitric acid, HNO_3, conc, double distilled.†#(69)

c. Procedure: Soak new polypropylene tubes and caps overnight or for several days in 2*N* HNO_3. Triple rinse with metal-free water, and preferably dry in poly rackets or baskets in a low-temperature oven overnight. Store cleaned tubes in plastic bags before use. Pipet tips also may need to be cleaned; evaluate before use.

Pipet 10 mL well-mixed, acid-preserved sample into a precleaned, labeled tube with a macropipet. With a minimum volume change (<0.5 mL), add appropriate amount of analyte for matrix fortified samples. With a pipet, add 0.5 mL conc HNO_3 (or 1.0 mL 1 + 1 HNO_3) to all samples, blanks, standards, and quality control samples.

Place tubes in block heater in a hood and adjust temperature to 105°C. Drape caps over each tube to allow escape of acid vapors while preventing contamination. NOTE: Do not screw on caps at this time. Digest samples for a minimum of 2 h. Do not let samples boil. Add more conc nitric acid as necessary until digestion is complete by observation of a clear solution.

Remove tubes from heat and cool. Dilute back to original 10 mL volume with metal-free water. Adjust over-volume samples to next convenient gradation for calculations and note volume. (Apply concentration correction from Section 3030D.) If tubes contain particulates, centrifuge and decant clear portion into another precleaned tube. Tighten screw caps and store at 4°C until ready for analysis.

3. Reference

1. JARVIS, K.E., A.L. GRAY & R.S. HOUK, eds. 1992. Sample preparation for ICP-MS. Chapter 7 *in* Handbook of Inductively Coupled Plasma Mass Spectrometry. Blackie & Son, Ltd., Glasgow & London, U.K.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3030 F. Nitric Acid-Hydrochloric Acid Digestion

1. Apparatus

See Section 3030E.1*a*. The following also may be needed:

Steam bath.

2. Reagents

a. Nitric acid, HNO_3, conc, analytical grade or better (see Section 3030E).

b. Hydrochloric acid, HCl, 1 + 1.

c. Nitric acid, HNO_3, 1 + 1.

3. Procedure

a. Total HNO_3/HCl: Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see Section 3030D for sample volume). In a hood add 3 mL conc HNO_3 and cover with a ribbed watch glass. Place flask or beaker on a hot plate and cautiously evaporate to less than 5 mL, making certain that sample does not boil and that no area of the bottom of the container is allowed to go dry. Cool. Rinse down walls of beaker and watch glass with a minimum of metal-free water and add 5 mL conc HNO_3. Cover container with a nonribbed watch glass and return to hot plate. Increase temperature of hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Cool. Add 10 mL 1 + 1 HCl and 15 mL water per 100 mL anticipated final volume. Heat for an additional 15 min to dissolve any precipitate or residue. Cool, wash down beaker walls and watch glass with water, filter to remove insoluble material that could clog the nebulizer (see Section 3030B), and transfer filtrate to a 100-mL volumetric flask with rinsings. Alternatively centrifuge or let settle overnight. Adjust to volume and mix thoroughly.

b. Recoverable HNO_3/HCl: For this less rigorous digestion procedure, transfer a measured volume of well-mixed, acid-preserved sample to a flask or beaker. Add 2 mL 1 + 1 HNO_3 and 10 mL 1 + 1 HCl and cover with a ribbed watch glass. Heat on a steam bath or hot plate until volume has been reduced to near 25 mL, making certain sample does not boil. Cool and filter to remove insoluble material or alternatively centrifuge or let settle overnight. Quantitatively transfer sample to volumetric flask, adjust volume to 100 mL, and mix.

For trace-level digestion, use precautionary measures similar to those detailed in Section 3030E.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3030 G. Nitric Acid-Sulfuric Acid Digestion

1. Apparatus

See Section 3030E.1*a*.

2. Reagents

a. Nitric acid, HNO_3, conc. (See Section 3030E for acid grades.)

b. Sulfuric acid, H_2SO_4, conc.

3. Procedure

Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see Section 3030D for sample volume). Add 5 mL conc HNO_3 and cover with a ribbed watch glass. Bring to slow boil on hot plate and evaporate to 15 to 20 mL. Add 5 mL conc HNO_3 and 10 mL conc H_2SO_4, cooling flask or beaker between additions. Evaporate on a hot plate until dense white fumes of SO_3 just appear. If solution does not clear, add 10 mL conc HNO_3 and repeat evaporation to fumes of SO_3. Heat to remove all HNO_3 before continuing treatment. All HNO_3 will be removed when the solution is clear and no brownish fumes are evident. Do not let sample dry during digestion.

Cool and dilute to about 50 mL with water. Heat to almost boiling to dissolve slowly soluble salts. Filter if necessary, then complete procedure as directed in Section 3030E.1*c* beginning with, ‘‘Transfer filtrate . . .’’

3030 H. Nitric Acid-Perchloric Acid Digestion

1. Apparatus

See Section 3030E.1*a*. The following also are needed:

a. Safety shield.

b. Safety goggles.

c. Watch glasses.

2. Reagents

a. Nitric acid, HNO_3, conc.

b. Perchloric acid, $HClO_4$.

c. Ammonium acetate solution: Dissolve 500 g $NH_4C_2H_3O_2$ in 600 mL water.

3. Procedure

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

CAUTION: *Heated mixtures of $HClO_4$* and organic matter may explode violently. Avoid this hazard by taking the following precautions: (a) do not add $HClO_4$ to a hot solution containing organic matter; (b) always pretreat samples containing organic matter with HNO_3 before adding $HClO_4$; (c) avoid repeated fuming with $HClO_4$ in ordinary hoods (For routine operations, use a water pump attached to a glass fume eradicator. Stainless steel fume hoods with adequate water washdown facilities are available commercially and are acceptable for use with $HClO_4$); and (d) never let samples being digested with $HClO_4$ evaporate to dryness.

Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker (see Section 3030D for sample volume). In a hood add 5 mL conc HNO_3 and cover with a ribbed watch glass. Evaporate sample to 15 to 20 mL on a hot plate. Add 10 mL each of conc HNO_3 and $HClO_4$, cooling flask or beaker between additions. Evaporate gently on a hot plate until dense white fumes of $HClO_4$ just appear. If solution is not clear, keep solution just boiling until it clears. If necessary, add 10 mL conc HNO_3 to complete digestion. Cool, dilute to about 50 mL with water, and boil to expel any chlorine or oxides of nitrogen. Filter, then complete procedure as directed in 3030E.1*c* beginning with, ‘‘Transfer filtrate . . .’’

If lead is to be determined in the presence of high amounts of sulfate (e.g., determination of Pb in power plant fly ash samples), dissolve $PbSO_4$ precipitate as follows: Add 50 mL ammonium acetate solution to flask or beaker in which digestion was carried out and heat to incipient boiling. Rotate container occasionally to wet all interior surfaces and dissolve any deposited residue. Reconnect filter and slowly draw solution through it. Transfer filtrate to a 100-mL volumetric flask, cool, dilute to mark, mix thoroughly, and set aside for determination of lead.

3030 I. Nitric Acid-Perchloric Acid-Hydrofluoric Acid Digestion

1. Apparatus

a. Hot plate.

b. TFE beakers, 250-mL, acid-washed and rinsed with water.

c. Volumetric flasks, 100-mL, polypropylene or other suitable plastic.

2. Reagents

a. Nitric acid, HNO_3, conc and 1 + 1.

b. Perchloric acid, $HClO_4$.

c. Hydrofluoric acid, HF, 48 to 51%.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3. Procedure

CAUTION: *See precautions for using $HClO_4$* in 3030H; handle HF with extreme care and provide adequate ventilation, especially for the heated solution. Avoid all contact with exposed skin. Provide medical attention for HF burns.

Transfer a measured volume of well-mixed, acid-preserved sample appropriate for the expected metals concentrations into a 250-mL TFE beaker (see Section 3030D for sample volume). Evaporate on a hot plate to 15 to 20 mL. Add 12 mL conc HNO_3 and evaporate to near dryness. Repeat HNO_3 addition and evaporation. Let solution cool, add 20 mL $HClO_4$ and 1 mL HF, and boil until solution is clear and white fumes of $HClO_4$ have appeared. Cool, add about 50 mL water, filter, and proceed as directed in Section 3030E.1*c* beginning with, ‘‘Transfer filtrate . . .’’

3030 J. Dry Ashing

The procedure appears in the Eighteenth Edition of *Standard Methods*. It has been deleted from subsequent editions.

3030 K. Microwave-Assisted Digestion

1. Apparatus

a. Microwave unit with programmable power (minimum 545 W) to within ± 10 W of required power, having a corrosion-resistant, well-ventilated cavity and having all electronics protected against corrosion for safe operation. Use a unit having a rotating turntable with a minimum speed of 3 rpm to insure homogeneous distribution of microwave radiation. Use only laboratory-grade microwave equipment and closed digestion containers with pressure relief that are specifically designed for hot acid.[1]

b. Vessels: Construction requires an inner liner of perfluoroalkoxy (PFA) Teflon™,*#(70) other TFE, or composite fluorinated polymers,†#(71) capable of withstanding pressures of at least 760 ± 70 kPa (110 ± 10 psi), and capable of controlled pressure relief at the manufacturer’s maximum pressure rating.

Acid wash all digestion vessels and rinse with water (¶ 2*a*). For new vessels or when changing between high- and low-concentration samples, clean by leaching with hot‡#(72) hydrochloric acid (1:1) for a minimum of 2 h and then with hot nitric acid (1:1) for a minimum of 2 h; rinse with water and dry in a clean environment. Use this procedure whenever the previous use of digestion vessels is unknown or cross-contamination from vessels is suspected.

c. Temperature feedback control system, using shielded thermocouple, fiber-optic probe, or infrared detector.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

d. Bottles, polyethylene, 125-mL, with caps.

e. Thermometer, accurate to ± 0.1°C.

f. Balance, large-capacity (1500 g), accurate to 0.1 g.

g. Filtration or centrifuge equipment (optional).

h. Plastic container with cover, 1-L, preferably made of PFA Teflon™§.#(73)

2. Reagents

a. Metal-free water: See Section 3111B.3*c*.

b. Nitric acid, HNO_3, conc, sub-boiling distilled. Non-sub-boiling acids can be used if they are shown not to contribute blanks.

3. Calibration of Microwave Unit

NOTE: For microwave units equipped with temperature feedback electronic controls, calibration of the microwave unit is not required provided performance specifications can be duplicated.

For cavity-type microwave equipment, evaluate absolute power (watts) by measuring the temperature rise in 1 kg water exposed to microwave radiation for a fixed time. With this measurement, the relationship between available power (W) and the partial power setting (%) of the unit can be estimated, and any absolute power in watts may be transferred from one unit to another. The calibration format required depends on type of electronic system used by manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been used, determine calibration curve by a three-point calibration method; otherwise, use the multiple-point calibration method.

a. Three-point calibration method: Measure power at 100% and 50% power using the procedure described in ¶ 3*c* and calculate power setting corresponding to required power in watts as specified in the procedure from the two-point line. Measure absorbed power at the calculated partial power setting. If the measured absorbed power does not correspond to the calculated power within ± 10 W, use the multiple-point calibration method, ¶ 3*b*. Use this point periodically to verify integrity of calibration.

b. Multiple-point calibration method: For each microwave unit, measure the following power settings: 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in ¶ 3*c*. These data are clustered about the customary working power ranges. Nonlinearity commonly is encountered at the upper end of the calibration curve. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. Check this setting periodically to evaluate the integrity of the calibration. If a significant change (± 10 W) is detected, re-evaluate entire calibration.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

c. Equilibrate a large volume of water to room temperature (23 ± 2°C). Weigh 1 kg water (1000 g ± 1 g) or measure (1000 mL ± 1 mL) into a plastic, not glass, container, and measure the temperature to ± 0.1°C. Condition microwave unit by heating a glass beaker with 500 to 1000 mL tap water at full power for 5 min with the exhaust fan on. Loosely cover plastic container to reduce heat loss and place in normal sample path (at outer edge of rotating turntable); circulate continuously through the microwave field for 120 s at desired power setting with exhaust fan on as it will be during normal operation. Remove plastic container and stir water vigorously. Use a magnetic stirring bar inserted immediately after microwave irradiation; record maximum temperature within the first 30 s to ± 0.1°C. Use a new sample for each additional measurement. If the water is reused, return both water and beaker to 23 ± 2°C. Make three measurements at each power setting. When any part of the high-voltage circuit, power source, or control components in the unit have been serviced or replaced, recheck calibration power. If power output has changed by more than ± 10 W, re-evaluate entire calibration.

Compute absorbed power by the following relationship:

$$P = \frac{(K)\ (Cp)\ (m)\ (\Delta T)}{t}$$

where:

P = apparent power absorbed by sample, W,
K = conversion factor for thermochemical calories sec^{-1} to watts (4.184),
Cp = heat capacity, thermal capacity, or specific heat (cal g^{-1} $°C^{-1}$) of water,
m = mass of water sample, g,
ΔT = final temperature minus initial temperature, °C, and
t = time, s.

For the experimental conditions of 120 s and 1 kg water (Cp at 25°C = 0.9997), the calibration equation simplifies to:

$$P = (\Delta T)\ (34.85)$$

Stable line voltage within the manufacturer's specification is necessary for accurate and reproducible calibration and operation. During measurement and operation it must not vary by more than ± 2 V. A constant power supply may be necessary if line voltage is unstable.

4. Procedure

CAUTION: *This method is designed for microwave digestion of waters only. It is not intended for the digestion of solids, for which high concentrations of organic compounds may result in high pressures and possibly unsafe conditions.*

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

CAUTION: *As a safety measure, never mix different manufacturers' vessels in the same procedure. Vessels constructed differently will retain heat at different rates; control of heating conditions assumes that all vessels have the same heat-transfer characteristics. Inspect casements for cracks and chemical corrosion. Failure to maintain the vessels' integrity may result in catastrophic failure.*

Both prescription controls and performance controls are provided for this procedure. Performance controls are the most general and most accurate. When equipment capability permits, use the performance criterion.

a. Performance criterion: The following procedure is based on heating acidified samples in two stages where the first stage is to reach 160 ± 4° in 10 min and the second stage is to permit a slow rise to 165 to 170°C during the second 10 min. This performance criterion is based on temperature feedback control system capability that is implemented in various ways by different manufacturers. Because the temperature of the acid controls the reaction, this is the essential condition that will reproduce results in this preparation method. Verification of temperature conditions inside the vessel at these specific times is sufficient to verify the critical procedural requirements.

b. Prescription criterion: For all PFA vessels without liners, a verified program that meets the performance-based temperature-time profile is 545 W for 10 min followed by 344 W for 10 min using five single-wall PFA Teflon^{TM}‖#(74) digestion vessels.[2] Any verified program for a given microwave unit depends on unit power and operational power settings, heating times, number, type, and placement of digestion vessels within the unit, and sample and acid volumes. The change in power, time, and temperature profile is not directly proportional to the change in the number of sample vessels. Any deviations from the verified program conditions will require verification of the time-temperature profile to conform to the given two-stage profile. This may be done by laboratory personnel if suitable test equipment is available, or by the manufacturer of the microwave equipment.

c. General conditions: Weigh entire digestion vessel assembly to 0.1 g before use and record (*A*). Accurately transfer 45 mL of well-shaken sample into the digestion vessel. Pipet 5 mL conc HNO_3 into each vessel. Attach all safety equipment required for appropriate and safe vessel operation following manufacturer's specifications. Tighten cap to manufacturer's specifications. Weigh each capped vessel to the nearest 0.1 g (*B*).

Place appropriate number of vessels evenly distributed in the carousel. Treat sample blanks, known additions, and duplicates in the same manner as samples. For prescription control only, when fewer samples than the appropriate number are digested, fill remaining vessels with 45 mL water and 5 mL conc HNO_3 to obtain full complement of vessels for the particular program being used.

Place carousel in unit and seat it carefully on turntable. Program microwave unit to heat samples to 160 ± 4°C in 10 min and then, for the second stage, to permit a slow rise to 165 to 170°C for 10 min. Start microwave generator, making sure that turntable is turning and that

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

exhaust fan is on.

At completion of the microwave program, let vessels cool for at least 5 min in the unit before removal. Cool samples further outside the unit by removing the carousel and letting them cool on a bench or in a water bath. When cooled to room temperature, weigh each vessel (to 0.1 g) and record weight (*C*).

If the net weight of sample plus acid decreased by more than 10%, discard sample.

Complete sample preparation by carefully uncapping and venting each vessel in a fume hood. Follow individual manufacturer's specifications for relieving pressure in individual vessel types. Transfer to acid-cleaned noncontaminating plastic bottles. If the digested sample contains particulates, filter, centrifuge, or settle overnight and decant.

5. Calculations

a. Dilution correction: Multiply results by 50/45 or 1.11 to account for the dilution caused by the addition of 5 mL acid to 45 mL sample.

b. Discarding of sample: To determine if the net weight of sample plus acid decreased by more than 10% during the digestion process, use the following calculation

$$\frac{[(B - A) - (C - A)]}{(B - A)} \times 100 > 10\% \text{ (1\% for multilayer vessels)}$$

6. Quality Control

NOTE: When nitric acid digestion is used, recoveries of silver and antimony in some matrices may be unacceptably low. Verify recoveries using appropriate known additions.

Preferably include a quality-control sample in each loaded carousel. Prepare samples in batches including preparation blanks, sample duplicates, and pre-digestion known additions. Determine size of batch and frequency of quality-control samples by method of analysis and laboratory practice. The power of the microwave unit and batch size may prevent including one or more of the quality-control samples in each carousel. Do not group quality-control samples together but distribute them throughout the various carousels to give the best monitoring of digestion.

7. References

1. KINGSTON, H.M. & S. HASWELL, eds. 1997. Microwave Enhanced Chemistry: Fundamentals, Sample Preparation and Applications. American Chemical Soc., Washington, D.C.
2. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1990. Microwave assisted acid digestion of aqueous samples and extracts. SW-846 Method 3015, Test Methods for Evaluating Solid Waste. U.S. Environmental Protection Agency, Washington, D.C.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3110 METALS BY ATOMIC ABSORPTION SPECTROMETRY

Because requirements for determining metals by atomic absorption spectrometry vary with metal and/or concentration to be determined, the method is presented as follows:

Section 3111, Metals by Flame Atomic Absorption Spectrometry, encompasses:

- Determination of antimony, bismuth, cadmium, calcium, cesium, chromium, cobalt, copper, gold, iridium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin, and zinc by direct aspiration into an air-acetylene flame (Section 3111B),
- Determination of low concentrations of cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, and zinc by chelation with ammonium pyrrolidine dithiocarbamate (APDC), extraction into methyl isobutyl ketone (MIBK), and aspiration into an air-acetylene flame (Section 3111C),
- Determination of aluminum, barium, beryllium, calcium, molybdenum, osmium, rhenium, silicon, thorium, titanium, and vanadium by direct aspiration into a nitrous oxide-acetylene flame (Section 3111D), and
- Determination of low concentrations of aluminum and beryllium by chelation with 8-hydroxyquinoline, extraction into MIBK, and aspiration into a nitrous oxide-acetylene flame (Section 3111E).

Section 3112 covers determination of mercury by the cold vapor technique.

Section 3113 concerns determination of micro quantities of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin by electrothermal atomic absorption spectrometry.

Section 3114 covers determination of arsenic and selenium by conversion to their hydrides and aspiration into an argon-hydrogen or nitrogen-hydrogen flame.

3111 METALS BY FLAME ATOMIC ABSORPTION SPECTROMETRY*#(75)

3111 A. Introduction

1. Principle

In flame atomic absorption spectrometry, a sample is aspirated into a flame and atomized. A light beam is directed through the flame, into a monochromator, and onto a detector that

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

measures the amount of light absorbed by the atomized element in the flame. For some metals, atomic absorption exhibits superior sensitivity over flame emission. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used; this makes the method relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range. Most atomic absorption instruments also are equipped for operation in an emission mode, which may provide better linearity for some elements.

2. Selection of Method

See Section 3110.

3. Interferences

a. Chemical interference: Many metals can be determined by direct aspiration of sample into an air-acetylene flame. The most troublesome type of interference is termed ‘‘chemical’’ and results from the lack of absorption by atoms bound in molecular combination in the flame. This can occur when the flame is not hot enough to dissociate the molecules or when the dissociated atom is oxidized immediately to a compound that will not dissociate further at the flame temperature. Such interferences may be reduced or eliminated by adding specific elements or compounds to the sample solution. For example, the interference of phosphate in the magnesium determination can be overcome by adding lanthanum. Similarly, introduction of calcium eliminates silica interference in the determination of manganese. However, silicon and metals such as aluminum, barium, beryllium, and vanadium require the higher-temperature, nitrous oxide-acetylene flame to dissociate their molecules. The nitrous oxide-acetylene flame also can be useful in minimizing certain types of chemical interferences encountered in the air-acetylene flame. For example, the interference caused by high concentrations of phosphate in the determination of calcium in the air-acetylene flame is reduced in the nitrous oxide-acetylene flame.

MIBK extractions with APDC (see Section 3111C) are particularly useful where a salt matrix interferes, for example, in seawater. This procedure also concentrates the sample so that the detection limits are extended.

Brines and seawater can be analyzed by direct aspiration but sample dilution is recommended. Aspiration of solutions containing high concentrations of dissolved solids often results in solids buildup on the burner head. This requires frequent shutdown of the flame and cleaning of the burner head. Preferably use background correction when analyzing waters that contain in excess of 1% solids, especially when the primary resonance line of the element of interest is below 240 nm. Make more frequent recovery checks when analyzing brines and seawaters to insure accurate results in these concentrated and complex matrices.

Barium and other metals ionize in the flame, thereby reducing the ground state (potentially absorbing) population. The addition of an excess of a cation (sodium, potassium, or lithium) having a similar or lower ionization potential will overcome this problem. The wavelength of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

maximum absorption for arsenic is 193.7 nm and for selenium 196.0 nm—wavelengths at which the air-acetylene flame absorbs intensely. The sensitivity for arsenic and selenium can be improved by conversion to their gaseous hydrides and analyzing them in either a nitrogen-hydrogen or an argon-hydrogen flame with a quartz tube (see Section 3114).

b. Background correction: Molecular absorption and light scattering caused by solid particles in the flame can cause erroneously high absorption values resulting in positive errors. When such phenomena occur, use background correction to obtain accurate values. Use any one of three types of background correction: continuum-source, Zeeman, or Smith-Hieftje correction.

1) Continuum-source background correction—A continuum-source background corrector utilizes either a hydrogen-filled hollow cathode lamp with a metal cathode or a deuterium arc lamp. When both the line source hollow-cathode lamp and the continuum source are placed in the same optical path and are time-shared, the broadband background from the elemental signal is subtracted electronically, and the resultant signal will be background-compensated.

Both the hydrogen-filled hollow-cathode lamp and deuterium arc lamp have lower intensities than either the line source hollow-cathode lamp or electrodeless discharge lamps. To obtain a valid correction, match the intensities of the continuum source with the line source hollow-cathode or electrodeless discharge lamp. The matching may result in lowering the intensity of the line source or increasing the slit width; these measures have the disadvantage of raising the detection limit and possibly causing nonlinearity of the calibration curve. Background correction using a continuum source corrector is susceptible to interference from other absorbing lines in the spectral bandwidth. Miscorrection occurs from significant atomic absorption of the continuum source radiation by elements other than that being determined. When a line source hollow-cathode lamp is used without background correction, the presence of an absorbing line from another element in the spectral bandwidth will not cause an interference unless it overlaps the line of interest.

Continuum-source background correction will not remove direct absorption spectral overlap, where an element other than that being determined is capable of absorbing the line radiation of the element under study.

2) Zeeman background correction—This correction is based on the principle that a magnetic field splits the spectral line into two linearly polarized light beams parallel and perpendicular to the magnetic field. One is called the pi (π) component and the other the sigma (σ) component. These two light beams have exactly the same wavelength and differ only in the plane of polarization. The π line will be absorbed by both the atoms of the element of interest and by the background caused by broadband absorption and light scattering of the sample matrix. The σ line will be absorbed only by the background.

Zeeman background correction provides accurate background correction at much higher absorption levels than is possible with continuum source background correction systems. It also virtually eliminates the possibility of error from structured background. Because no additional light sources are required, the alignment and intensity limitations encountered using continuum sources are eliminated.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Disadvantages of the Zeeman method include reduced sensitivity for some elements, reduced linear range, and a ‘‘rollover’’ effect whereby the absorbance of some elements begins to decrease at high concentrations, resulting in a two-sided calibration curve.

3) Smith-Hieftje background correction—This correction is based on the principle that absorbance measured for a specific element is reduced as the current to the hollow cathode lamp is increased while absorption of nonspecific absorbing substances remains identical at all current levels. When this method is applied, the absorbance at a high-current mode is subtracted from the absorbance at a low-current mode. Under these conditions, any absorbance due to nonspecific background is subtracted out and corrected for.

Smith-Hieftje background correction provides a number of advantages over continuum-source correction. Accurate correction at higher absorbance levels is possible and error from structured background is virtually eliminated. In some cases, spectral interferences also can be eliminated. The usefulness of Smith-Hieftje background correction with electrodeless discharge lamps has not yet been established.

4. Sensitivity, Detection Limits, and Optimum Concentration Ranges

The sensitivity of flame atomic absorption spectrometry is defined as the metal concentration that produces an absorption of 1% (an absorbance of approximately 0.0044). The instrument detection limit is defined here as the concentration that produces absorption equivalent to twice the magnitude of the background fluctuation. Sensitivity and detection limits vary with the instrument, the element determined, the complexity of the matrix, and the technique selected. The optimum concentration range usually starts from the concentration of several times the detection limit and extends to the concentration at which the calibration curve starts to flatten. To achieve best results, use concentrations of samples and standards within the optimum concentration range of the spectrometer. See Table 3111:I for indication of concentration ranges measurable with conventional atomization. In many instances the concentration range shown in Table 3111:I may be extended downward either by scale expansion or by integrating the absorption signal over a long time. The range may be extended upward by dilution, using a less sensitive wavelength, rotating the burner head, or utilizing a microprocessor to linearize the calibration curve at high concentrations.

5. Preparation of Standards

Prepare standard solutions of known metal concentrations in water with a matrix similar to the sample. Use standards that bracket expected sample concentration and are within the method’s working range. Very dilute standards should be prepared daily from stock solutions in concentrations greater than 500 mg/L. Stock standard solutions can be obtained from several commercial sources. They also can be prepared from National Institute of Standards and Technology (NIST) reference materials or by procedures outlined in the following sections.

For samples containing high and variable concentrations of matrix materials, make the major ions in the sample and the dilute standard similar. If the sample matrix is complex and components cannot be matched accurately with standards, use the method of standard additions,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Section 3113B.4*d*2), to correct for matrix effects. If digestion is used, carry standards through the same digestion procedure used for samples.

6. Apparatus

a. Atomic absorption spectrometer, consisting of a light source emitting the line spectrum of an element (hollow-cathode lamp or electrodeless discharge lamp), a device for vaporizing the sample (usually a flame), a means of isolating an absorption line (monochromator or filter and adjustable slit), and a photoelectric detector with its associated electronic amplifying and measuring equipment.

b. Burner: The most common type of burner is a premix, which introduces the spray into a condensing chamber for removal of large droplets. The burner may be fitted with a conventional head containing a single slot; a three-slot Boling head, which may be preferred for direct aspiration with an air-acetylene flame; or a special head for use with nitrous oxide and acetylene.

c. Readout: Most instruments are equipped with either a digital or null meter readout mechanism. Most modern instruments are equipped with microprocessors or stand-alone control computers capable of integrating absorption signals over time and linearizing the calibration curve at high concentrations.

d. Lamps: Use either a hollow-cathode lamp or an electrodeless discharge lamp (EDL). Use one lamp for each element being measured. Multi-element hollow-cathode lamps generally provide lower sensitivity than single-element lamps. EDLs take a longer time to warm up and stabilize.

e. Pressure-reducing valves: Maintain supplies of fuel and oxidant at pressures somewhat higher than the controlled operating pressure of the instrument by using suitable reducing valves. Use a separate reducing valve for each gas.

f. Vent: Place a vent about 15 to 30 cm above the burner to remove fumes and vapors from the flame. This precaution protects laboratory personnel from toxic vapors, protects the instrument from corrosive vapors, and prevents flame stability from being affected by room drafts. A damper or variable-speed blower is desirable for modulating air flow and preventing flame disturbance. Select blower size to provide the air flow recommended by the instrument manufacturer. In laboratory locations with heavy particulate air pollution, use clean laboratory facilities (Section 3010C).

7. Quality Assurance/Quality Control

Some data typical of the precision and bias obtainable with the methods discussed are presented in Table 3111:II and Table 3111:III.

Analyze a blank between sample or standard readings to verify baseline stability. Rezero when necessary.

To one sample out of every ten (or one sample from each group of samples if less than ten are being analyzed) add a known amount of the metal of interest and reanalyze to confirm recovery. The amount of metal added should be approximately equal to the amount found. If

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

little metal is present add an amount close to the middle of the linear range of the test. Recovery of added metal should be between 85 and 115%.

Analyze an additional standard solution after every ten samples or with each batch of samples, whichever is less, to confirm that the test is in control. Recommended concentrations of standards to be run, limits of acceptability, and reported single-operator precision data are listed in Table 3111:III.

See Section 3020 for additional recommended quality control procedures.

8. References

1. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1986. Annual Book of ASTM Standards, Volume 11.01, Water and Environmental Technology. American Soc. Testing & Materials, Philadelphia, Pa.
2. U.S. DEPARTMENT HEALTH, EDUCATION AND WELFARE. 1970. Water Metals No. 6, Study No. 37. U.S. Public Health Serv. Publ. No. 2029, Cincinnati, Ohio.
3. U.S. DEPARTMENT HEALTH, EDUCATION AND WELFARE. 1968. Water Metals No. 4, Study No. 30. U.S. Public Health Serv. Publ. No. 999-UTH-8, Cincinnati, Ohio.
4. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1983. Methods for Chemical Analysis of Water and Wastes. Cincinnati, Ohio.

9. Bibliography

KAHN, H.L. 1968. Principles and Practice of Atomic Absorption. Advan. Chem. Ser. No. 73, Div. Water, Air & Waste Chemistry, American Chemical Soc., Washington, D.C.

RAMIRIZ-MUNOZ, J. 1968. Atomic Absorption Spectroscopy and Analysis by Atomic Absorption Flame Photometry. American Elsevier Publishing Co., New York, N.Y.

SLAVIN, W. 1968. Atomic Absorption Spectroscopy. John Wiley & Sons, New York, N.Y.

PAUS, P.E. 1971. The application of atomic absorption spectroscopy to the analysis of natural waters. *Atomic Absorption Newsletter* 10:69.

EDIGER, R.D. 1973. A review of water analysis by atomic absorption. *Atomic Absorption Newsletter* 12:151.

PAUS, P.E. 1973. Determination of some heavy metals in seawater by atomic absorption spectroscopy. *Fresenius Zeitschr. Anal. Chem.* 264:118.

BURRELL, D.C. 1975. Atomic Spectrometric Analysis of Heavy-Metal Pollutants in Water. Ann Arbor Science Publishers, Inc., Ann Arbor, Mich.

3111 B. Direct Air-Acetylene Flame Method

1. General Discussion

This method is applicable to the determination of antimony, bismuth, cadmium, calcium,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

cesium, chromium, cobalt, copper, gold, iridium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin, and zinc.

2. Apparatus

Atomic absorption spectrometer and associated equipment: See Section 3111A.6. Use burner head recommended by the manufacturer.

3. Reagents

a. Air, cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or commercially bottled gas.

b. Acetylene, standard commercial grade. Acetone, which always is present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 689 kPa (100 psi) acetylene.

CAUTION: *Acetylene gas represents an explosive hazard in the laboratory. Follow instrument manufacturer's directions in plumbing and using this gas. Do not allow gas contact with copper, brass with >65% copper, silver, or liquid mercury; do not use copper or brass tubing, regulators, or fittings.*

c. Metal-free water: Use metal-free water for preparing all reagents and calibration standards and as dilution water. Prepare metal-free water by deionizing tap water and/or by using one of the following processes, depending on the metal concentration in the sample: single distillation, redistillation, or sub-boiling. Always check deionized or distilled water to determine whether the element of interest is present in trace amounts. (NOTE: *If the source water contains Hg or other volatile metals, single- or redistilled water may not be suitable for trace analysis because these metals distill over with the distilled water. In such cases, use sub-boiling to prepare metal-free water).*

d. Calcium solution: Dissolve 630 mg calcium carbonate, $CaCO_3$, in 50 mL of 1 + 5 HCl. If necessary, boil gently to obtain complete solution. Cool and dilute to 1000 mL with water.

e. Hydrochloric acid, HCl, 1%, 10%, 20% (all v/v), 1 + 5, 1 + 1, and conc.

f. Lanthanum solution: Dissolve 58.65 g lanthanum oxide, La_2O_3, in 250 mL conc HCl. Add acid slowly until the material is dissolved and dilute to 1000 mL with water.

g. Hydrogen peroxide, 30%.

h. Nitric acid, HNO_3, 2% (v/v), 1 + 1, and conc.

i. Aqua regia: Add 3 volumes conc HCl to 1 volume conc HNO_3.

j. Standard metal solutions: Prepare a series of standard metal solutions in the optimum concentration range by appropriate dilution of the following stock metal solutions with water containing 1.5 mL conc HNO_3/L. Stock standard solutions are available from a number of commercial suppliers. Alternatively, prepare as described below. Thoroughly dry reagents before

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

use. In general, use reagents of the highest purity. For hydrates, use fresh reagents.

1) *Antimony:* Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in water, add 10 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Sb.

2) *Bismuth:* Dissolve 0.100 g bismuth metal in a minimum volume of 1 + 1 HNO_3. Dilute to 1000 mL with 2% (v/v) HNO_3; 1.00 mL = 100 μg Bi.

3) *Cadmium:* Dissolve 0.100 g cadmium metal in 4 mL conc HNO_3. Add 8.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Cd.

4) *Calcium:* Suspend 0.2497 g $CaCO_3$ (dried at 180° for 1 h before weighing) in water and dissolve cautiously with a minimum amount of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Ca.

5) *Cesium:* Dissolve 0.1267 g cesium chloride, CsCl, in 1000 mL water; 1.00 mL = 100 μg Cs.

6) *Chromium:* Dissolve 0.1923 g CrO_3 in water. When solution is complete, acidify with 10 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Cr.

7) *Cobalt:* Dissolve 0.1000 g cobalt metal in a minimum amount of 1 + 1 HNO_3. Add 10.0 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Co.

8) *Copper:* Dissolve 0.100 g copper metal in 2 mL conc HNO_3, add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Cu.

9) *Gold:* Dissolve 0.100 g gold metal in a minimum volume of aqua regia. Evaporate to dryness, dissolve residue in 5 mL conc HCl, cool, and dilute to 1000 mL with water; 1.00 mL = 100 μg Au.

10) *Iridium:* Dissolve 0.1147 g ammonium chloroiridate, $(NH_4)_2IrCl_6$, in a minimum volume of 1% (v/v) HCl and dilute to 100 mL with 1% (v/v) HCl; 1.00 mL = 500 μg Ir.

11) *Iron:* Dissolve 0.100 g iron wire in a mixture of 10 mL 1 + 1 HCl and 3 mL conc HNO_3. Add 5 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Fe.

12) *Lead:* Dissolve 0.1598 g lead nitrate, $Pb(NO_3)_2$, in a minimum amount of 1 + 1 HNO_3, add 10 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL = 100 μg Pb.

13) *Lithium:* Dissolve 0.5323 g lithium carbonate, Li_2CO_3, in a minimum volume of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Li.

14) *Magnesium:* Dissolve 0.1658 g MgO in a minimum amount of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Mg.

15) *Manganese:* Dissolve 0.1000 g manganese metal in 10 mL conc HCl mixed with 1 mL

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

conc HNO_3. Dilute to 1000 mL with water; 1.00 mL = 100 μg Mn.

16) *Nickel:* Dissolve 0.1000 g nickel metal in 10 mL hot conc HNO_3, cool, and dilute to 1000 mL with water; 1.00 mL = 100 μg Ni.

17) *Palladium:* Dissolve 0.100 g palladium wire in a minimum volume of aqua regia and evaporate just to dryness. Add 5 mL conc HCl and 25 mL water and warm until dissolution is complete. Dilute to 1000 mL with water; 1.00 mL = 100 μg Pd.

18) *Platinum:* Dissolve 0.100 g platinum metal in a minimum volume of aqua regia and evaporate just to dryness. Add 5 mL conc HCl and 0.1 g NaCl and again evaporate just to dryness. Dissolve residue in 20 mL of 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Pt.

19) *Potassium:* Dissolve 0.1907 g potassium chloride, KCl, (dried at 110°C) in water and make up to 1000 mL; 1.00 mL = 100 μg K.

20) *Rhodium:* Dissolve 0.386 g ammonium hexachlororhodate, $(NH_4)_3RhCl_6 \cdot 1.5H_2O$, in a minimum volume of 10% (v/v) HCl and dilute to 1000 mL with 10% (v/v) HCl; 1.00 mL = 100 μg Rh.

21) *Ruthenium:* Dissolve 0.205 g ruthenium chloride, $RuCl_3$, in a minimum volume of 20% (v/v) HCl and dilute to 1000 mL with 20% (v/v) HCl; 1.00 mL = 100 μg Ru.

22) *Silver:* Dissolve 0.1575 g silver nitrate, $AgNO_3$, in 100 mL water, add 10 mL conc HNO_3, and make up to 1000 mL; 1.00 mL = 100 μg Ag.

23) *Sodium:* Dissolve 0.2542 g sodium chloride, NaCl, dried at 140°C, in water, add 10 mL conc HNO_3 and make up to 1000 mL; 1.00 mL = 100 μg Na.

24) *Strontium:* Suspend 0.1685 g $SrCO_3$ in water and dissolve cautiously with a minimum amount of 1 + 1 HNO_3. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water: 1 mL = 100 μg Sr.

25) *Thallium:* Dissolve 0.1303 g thallium nitrate, $TlNO_3$, in water. Add 10 mL conc HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Tl.

27) *Zinc:* Dissolve 0.100 g zinc metal in 20 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 μg Zn.

4. Procedure

a. Sample preparation: Required sample preparation depends on the metal form being measured.

If dissolved metals are to be determined, see Section 3030B for sample preparation. If total or acid-extractable metals are to be determined, see Section 3030C through K. For all samples, make certain that the concentrations of acid and matrix modifiers are the same in both samples and standards.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

When determining Ca or Mg, dilute and mix 100 mL sample or standard with 10 mL lanthanum solution (¶ 3 *f*) before aspirating. When determining Fe or Mn, mix 100 mL with 25 mL of Ca solution (¶ 3*d*) before aspirating. When determining Cr, mix 1 mL 30% H_2O_2 with each 100 mL before aspirating. Alternatively use proportionally smaller volumes.

b. Instrument operation: Because of differences between makes and models of atomic absorption spectrometers, it is not possible to formulate instructions applicable to every instrument. See manufacturer's operating manual. In general, proceed according to the following: Install a hollow-cathode lamp for the desired metal in the instrument and roughly set the wavelength dial according to Table 3111:I. Set slit width according to manufacturer's suggested setting for the element being measured. Turn on instrument, apply to the hollow-cathode lamp the current suggested by the manufacturer, and let instrument warm up until energy source stabilizes, generally about 10 to 20 min. Readjust current as necessary after warmup. Optimize wavelength by adjusting wavelength dial until optimum energy gain is obtained. Align lamp in accordance with manufacturer's instructions.

Install suitable burner head and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer to give maximum sensitivity for the metal being measured. Turn on acetylene, adjust flow rate to value specified, and ignite flame. Let flame stabilize for a few minutes. Aspirate a blank consisting of deionized water containing the same concentration of acid in standards and samples. Zero the instrument. Aspirate a standard solution and adjust aspiration rate of the nebulizer to obtain maximum sensitivity. Adjust burner both vertically and horizontally to obtain maximum response. Aspirate blank again and rezero the instrument. Aspirate a standard near the middle of the linear range. Record absorbance of this standard when freshly prepared and with a new hollow-cathode lamp. Refer to these data on subsequent determinations of the same element to check consistency of instrument setup and aging of hollow-cathode lamp and standard.

The instrument now is ready to operate. When analyses are finished, extinguish flame by turning off first acetylene and then air.

c. Standardization: Select at least three concentrations of each standard metal solution (prepared as in ¶ 3 *j* above) to bracket the expected metal concentration of a sample. Aspirate blank and zero the instrument. Then aspirate each standard in turn into flame and record absorbance.

Prepare a calibration curve by plotting on linear graph paper absorbance of standards versus their concentrations. For instruments equipped with direct concentration readout, this step is unnecessary. With some instruments it may be necessary to convert percent absorption to absorbance by using a table generally provided by the manufacturer. Plot calibration curves for Ca and Mg based on original concentration of standards before dilution with lanthanum solution. Plot calibration curves for Fe and Mn based on original concentration of standards before dilution with Ca solution. Plot calibration curve for Cr based on original concentration of standard before addition of H_2O_2.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

d. Analysis of samples: Rinse nebulizer by aspirating water containing 1.5 mL conc HNO_3/L. Aspirate blank and zero instrument. Aspirate sample and determine its absorbance.

5. Calculations

Calculate concentration of each metal ion, in micrograms per liter for trace elements, and in milligrams per liter for more common metals, by referring to the appropriate calibration curve prepared according to ¶ 4*c*. Alternatively, read concentration directly from the instrument readout if the instrument is so equipped. If the sample has been diluted, multiply by the appropriate dilution factor.

6. Bibliography

WILLIS, J.B. 1962. Determination of lead and other heavy metals in urine by atomic absorption spectrophotometry. *Anal. Chem.* 34:614.

Also see Section 3111A.8 and Section 3111A.9.

3111 C. Extraction/Air-Acetylene Flame Method

1. General Discussion

This method is suitable for the determination of low concentrations of cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, and zinc. The method consists of chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction into methyl isobutyl ketone (MIBK), followed by aspiration into an air-acetylene flame.

2. Apparatus

a. Atomic absorption spectrometer and associated equipment: See Section 3111A.6.

b. Burner head, conventional. Consult manufacturer's operating manual for suggested burner head.

3. Reagents

a. Air: See Section 3111B.3*a*.

b. Acetylene: See Section 3111B.3*b*.

c. Metal-free water: See Section 3111B.3*c*.

d. Methyl isobutyl ketone (MIBK), reagent grade. For trace analysis, purify MIBK by redistillation or by sub-boiling distillation.

e. Ammonium pyrrolidine dithiocarbamate (APDC) solution: Dissolve 4 g APDC in 100 mL water. If necessary, purify APDC with an equal volume of MIBK. Shake 30 s in a separatory funnel, let separate, and withdraw lower portion. Discard MIBK layer.

f. Nitric acid, HNO_3, conc, ultrapure.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

g. Standard metal solutions: See Section 3111B.3 *j*.

h. Potassium permanganate solution, $KMnO_4$, 5% (w/v) aqueous.

i. Sodium sulfate, Na_2SO_4, anhydrous.

j. Water-saturated MIBK: Mix one part purified MIBK with one part water in a separatory funnel. Shake 30 s and let separate. Discard aqueous layer. Save MIBK layer.

k. Hydroxylamine hydrochloride solution, 10% (w/v). This solution can be purchased commercially.

4. Procedure

a. Instrument operation: See Section 3111B.4*b*. After final adjusting of burner position, aspirate water-saturated MIBK into flame and gradually reduce fuel flow until flame is similar to that before aspiration of solvent.

b. Standardization: Select at least three concentrations of standard metal solutions (prepared as in Section 3111B.3 *j*) to bracket expected sample metal concentration and to be, after extraction, in the optimum concentration range of the instrument. Adjust 100mL of each standard and 100 mL of a metal-free water blank to pH 3 by adding 1*N* HNO_3 or 1*N* NaOH. For individual el-ement extraction, use the following pH ranges to obtain optimum extraction efficiency:

Element	pH Range for Optimum Extraction
Ag	2–5 (complex unstable)
Cd	1–6
Co	2–10
Cr	3–9
Cu	0.1–8
Fe	2–5
Mn	2–4 (complex unstable)
Ni	2–4
Pb	0.1–6
Zn	2–6

NOTE: For Ag and Pb extraction the optimum pH value is 2.3 ± 0.2. The Mn complex deteriorates rapidly at room temperature, resulting in decreased instrument response. Chilling the extract to 0°C may preserve the complex for a few hours. If this is not possible and Mn cannot be analyzed immediately after extraction, use another analytical procedure.

Transfer each standard solution and blank to individual 200-mL volumetric flasks, add 1 mL

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

APDC solution, and shake to mix. Add 10 mL MIBK and shake vigorously for 30 s. (The maximum volume ratio of sample to MIBK is 40.) Let contents of each flask separate into aqueous and organic layers, then carefully add water (adjusted to the same pH at which the extraction was carried out) down the side of each flask to bring the organic layer into the neck and accessible to the aspirating tube.

Aspirate organic extracts directly into the flame (zeroing instrument on a water-saturated MIBK blank) and record absorbance.

Prepare a calibration curve by plotting on linear graph paper absorbances of extracted standards against their concentrations before extraction.

c. Analysis of samples: Prepare samples in the same manner as the standards. Rinse atomizer by aspirating water-saturated MIBK. Aspirate organic extracts treated as above directly into the flame and record absorbances.

With the above extraction procedure only hexavalent chromium is measured. To determine total chromium, oxidize trivalent chromium to hexavalent chromium by bringing sample to a boil and adding sufficient $KMnO_4$ solution dropwise to give a persistent pink color while the solution is boiled for 10 min. Destroy excess $KMnO_4$ by adding 1 to 2 drops hydroxylamine hydrochloride solution to the boiling solution, allowing 2 min for the reaction to proceed. If pink color persists, add 1 to 2 more drops hydroxylamine hydrochloride solution and wait 2 min. Heat an additional 5 min. Cool, extract with MIBK, and aspirate.

During extraction, if an emulsion forms at the water-MIBK interface, add anhydrous Na_2SO_4 to obtain a homogeneous organic phase. In that case, also add Na_2SO_4 to all standards and blanks.

To avoid problems associated with instability of extracted metal complexes, determine metals immediately after extraction.

5. Calculations

Calculate the concentration of each metal ion in micrograms per liter by referring to the appropriate calibration curve.

6. Bibliography

ALLAN, J.E. 1961. The use of organic solvents in atomic absorption spectrophotometry. *Spectrochim. Acta* 17:467.

SACHDEV, S.L. & P.W. WEST. 1970. Concentration of trace metals by solvent extraction and their determination by atomic absorption spectrophotometry. *Environ. Sci. Technol.* 4:749.

3111 D. Direct Nitrous Oxide-Acetylene Flame Method

1. General Discussion

This method is applicable to the determination of aluminum, barium, beryllium, calcium,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

molybdenum, osmium, rhenium, silicon, thorium, titanium, and vanadium.

2. Apparatus

a. Atomic absorption spectrometer and associated equipment: See Section 3111A.6.

b. Nitrous oxide burner head: Use special burner head as suggested in manufacturer's manual. At roughly 20-min intervals of operation it may be necessary to dislodge the carbon crust that forms along the slit surface with a carbon rod or appropriate alternative.

c. T-junction valve or other switching valve for rapidly changing from nitrous oxide to air, so that flame can be turned on or off with air as oxidant to prevent flashbacks.

3. Reagents

a. Air: See Section 3111B.3*a*.

b. Acetylene: See Section 3111B.3*b*.

c. Metal-free water: See Section 3111B.3*c*.

d. Hydrochloric acid, HCl, 1*N*, 1+1, and conc.

e. Nitric acid, HNO_3, conc.

f. Sulfuric acid, H_2SO_4, 1% (v/v).

g. Hydrofluoric acid, HF, 1*N*.

h. Nitrous oxide, commercially available cylinders. Fit nitrous oxide cylinder with a special nonfreezable regulator or wrap a heating coil around an ordinary regulator to prevent flashback at the burner caused by reduction in nitrous oxide flow through a frozen regulator. (Most modern atomic absorption instruments have automatic gas control systems that will shut down a nitrous oxide-acetylene flame safely in the event of a reduction in nitrous oxide flow rate.)

CAUTION: *Use nitrous oxide with strict adherence to manufacturer's directions. Improper sequencing of gas flows at startup and shutdown of instrument can produce explosions from flashback.*

i. Potassium chloride solution: Dissolve 250 g KCl in water and dilute to 1000 mL.

j. Aluminum nitrate solution: Dissolve 139 g $Al(NO_3)_3 \cdot 9H_2O$ in 150 mL water. Acidify slightly with conc HNO_3 to preclude possible hydrolysis and precipitation. Warm to dissolve completely. Cool and dilute to 200 mL.

k. Standard metal solutions: Prepare a series of standard metal solutions in the optimum concentration ranges by appropriate dilution of stock metal solutions with water containing 1.5 mL conc HNO_3/L. Stock standard solutions are available from a number of commercial suppliers. Alternatively, prepare as described below.

1) *Aluminum:* Dissolve 0.100 g aluminum metal in an acid mixture of 4 mL 1 + 1 HCl and 1 mL conc HNO_3 in a beaker. Warm gently to effect solution. Transfer to a 1-L flask, add 10 mL 1 + 1 HCl, and dilute to 1000 mL with water; 1.00 mL = 100 µg Al.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2) *Barium:* Dissolve 0.1516 g $BaCl_2$ (dried at 250° for 2 h), in about 10 mL water with 1 mL 1+ 1 HCl. Add 10.0 mL 1 + 1 HCl and dilute to 1000 mL with water; 1.00 mL = 100 µg Ba.

3) *Beryllium*: *Do not dry.* Dissolve 1.966 g $BeSO_4 \cdot 4H_2O$ in water, add 10.0 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL = 100 µg Be.

4) *Calcium:* See Section 3111B.3 *j*4).

5) *Molybdenum:* Dissolve 0.2043 g $(NH_4)_2\ MoO_4$ in water and dilute to 1000 mL; 1.00 mL = 100 µg Mo.

6) *Osmium:* Obtain standard 0.1*M* osmium tetroxide solution*#(76) and store in glass bottle; 1.00 mL = 19.02 mg Os. Make dilutions daily as needed using 1% (v/v) H_2SO_4. CAUTION: *OsO_4 is extremely toxic and highly volatile.*

7) *Rhenium:* Dissolve 0.1554 g potassium perrhenate, $KReO_4$, in 200 mL water. Dilute to 1000 mL with 1% (v/v) H_2SO_4; 1.00 mL = 100 µg Re.

8) *Silica: Do not dry.* Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in water. Add 10.0 mL conc HNO_3 and dilute to 1000 mL with water. 1.00 mL = 100 µg SiO_2. Store in polyethylene.

9) *Thorium:* Dissolve 0.238 g thorium nitrate, $Th(NO_3)_4 \cdot 4H_2O$ in 1000 mL water; 1.00 mL = 100 µg Th.

10) *Titanium:* Dissolve 0.3960 g pure (99.8 or 99.9%) titanium chloride, $TiCl_4$,†#(77) in a mixture of equal volumes of 1*N* HCl and 1*N* HF. Make up to 1000 mL with this acid mixture; 1.00 mL = 100 µg Ti.

11) *Vanadium:* Dissolve 0.2297 g ammonium metavanadate, NH_4VO_3, in a minimum amount of conc HNO_3. Heat to dissolve. Add 10 mL conc HNO_3, and dilute to 1000 mL with water; 1.00 mL = 100 µg V.

4. Procedure

a. Sample preparation: See Section 3111B.4*a*.

When determining Al, Ba, or Ti, mix 2 mL KCl solution into 100 mL sample or standard before aspiration. When determining Mo and V, mix 2 mL $Al(NO_3)_3 \cdot 9H_2O$ into 100 mL sample or standard before aspiration.

b. Instrument operation: See Section 3111B.4*b*. After adjusting wavelength, install a nitrous oxide burner head. Turn on acetylene (without igniting flame) and adjust flow rate to value specified by manufacturer for a nitrous oxide-acetylene flame. Turn off acetylene. With both air and nitrous oxide supplies turned on, set T-junction valve to nitrous oxide and adjust flow rate according to manufacturer's specifications. Turn switching valve to the air position and verify that flow rate is the same. Turn acetylene on and ignite to a bright yellow flame. With a rapid motion, turn switching valve to nitrous oxide. The flame should have a red cone above the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

burner. If it does not, adjust fuel flow to obtain red cone. After nitrous oxide flame has been ignited, let burner come to thermal equilibrium before beginning analysis.

Aspirate a blank consisting of deionized water containing 1.5 mL conc HNO_3/L and check aspiration rate. Adjust if necessary to a rate between 3 and 5 mL/ min. Zero the instrument. Aspirate a standard of the desired metal with a concentration near the midpoint of the optimum concentration range and adjust burner (both horizontally and vertically) in the light path to obtain maximum response. Aspirate blank again and re-zero the instrument. The instrument now is ready to run standards and samples.

To extinguish flame, turn switching valve from nitrous oxide to air and turn off acetylene. This procedure eliminates the danger of flashback that may occur on direct ignition or shutdown of nitrous oxide and acetylene. (See also discussion in Section 3111B.4*b*.)

c. Standardization: Select at least three concentrations of standard metal solutions (prepared as in ¶ 3*k*) to bracket the expected metal concentration of a sample. Aspirate each in turn into the flame and record absorbances.

Most modern instruments are equipped with microprocessors and digital readout which permit calibration in direct concentration terms. If instrument is not so equipped, prepare a calibration curve by plotting on linear graph paper absorbance of standards versus concentration. Plot calibration curves for Al, Ba, and Ti based on original concentration of standard before adding KCl solution. Plot calibration curves for Mo and V based on original concentration of standard before adding $Al(NO_3)_3$ solution.

d. Analysis of samples: Rinse atomizer by aspirating water containing 1.5 mL conc HNO_3/L and zero instrument. Aspirate a sample and determine its absorbance.

5. Calculations

Calculate concentration of each metal ion in micrograms per liter by referring to the appropriate calibration curve prepared according to ¶ 4*c*.

Alternatively, read the concentration directly from the instrument readout if the instrument is so equipped. If sample has been diluted, multiply by the appropriate dilution factor.

6. Bibliography

WILLIS, J.B. 1965. Nitrous oxide-acetylene flame in atomic absorption spectroscopy. *Nature* 207:715.

Also see Section 3111A.8 and Section 3111A.9.

3111 E. Extraction/Nitrous Oxide-Acetylene Flame Method

1. General Discussion

a. Application: This method is suitable for the determination of aluminum at concentrations

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

less than 900 µg/L and beryllium at concentrations less than 30 µg/L. The method consists of chelation with 8-hydroxyquinoline, extraction with methyl isobutyl ketone (MIBK), and aspiration into a nitrous oxide-acetylene flame.

b. Interferences: Concentrations of Fe greater than 10 mg/L interfere by suppressing Al absorption. Iron interference can be masked by addition of hydroxylamine hydrochloride/1,10-phenanthroline. Mn concentrations up to 80 mg/L do not interfere if turbidity in the extract is allowed to settle. Mg forms an insoluble chelate with 8-hydroxyquinoline at pH 8.0 and tends to remove Al complex as a coprecipitate. However, the Mg complex forms slowly over 4 to 6 min; its interference can be avoided if the solution is extracted immediately after adding buffer.

2. Apparatus

Atomic absorption spectrometer and associated equipment: See Section 3111A.6.

3. Reagents

a. Air: See Section 3111B.3*a*.

b. Acetylene: See Section 3111B.3*b*.

c. Ammonium hydroxide, NH_4OH, conc.

d. Buffer: Dissolve 300 g ammonium acetate, $NH_4C_2H_3O_2$, in water, add 105 mL conc NH_4OH, and dilute to 1 L.

e. Metal-free water: See Section 3111B.3*c*.

f. Hydrochloric acid, HCl, conc.

g. 8-Hydroxyquinoline solution: Dissolve 20 g 8-hydroxyquinoline in about 200 mL water, add 60 mL glacial acetic acid, and dilute to 1 L with water.

h. Methyl isobutyl ketone: See Section 3111C.3*d*.

i. Nitric acid, HNO_3, conc.

j. Nitrous oxide: See Section 3111D.3*h*.

k. Standard metal solutions: Prepare a series of standard metal solutions containing 5 to 1000 µg/L by appropriate dilution of the stock metal solutions prepared according to Section 3111D.3*k*.

l. Iron masking solution: Dissolve 1.3 g hydroxylamine hydrochloride and 6.58 g 1,10-phenanthroline monohydrate in about 500 mL water and dilute to 1 L with water.

4. Procedure

a. Instrument operation: See Section 3111B.4*b*, Section 3111C.4*a*, and Section 3111D.4*b*. After final adjusting of burner position, aspirate MIBK into flame and gradually reduce fuel flow until flame is similar to that before aspiration of solvent. Adjust wavelength setting according to Table 3111:I.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

b. Standardization: Select at least three concentrations of standard metal solutions (prepared as in ¶ 3*k*) to bracket the expected metal concentration of a sample and transfer 100 mL of each (and 100 mL water blank) to four different 200-mL volumetric flasks. Add 2 mL 8-hydroxyquinoline solution, 2 mL masking solution (if required), and 10 mL buffer to one flask, immediately add 10 mL MIBK, and shake vigorously. The duration of shaking affects the forms of aluminum complexed. A fast, 10-s shaking time favors monomeric Al, whereas 5 to 10 min of shaking also will complex polymeric species. Adjustment of the 8-hydroxyquinoline to sample ratio can improve recoveries of extremely high or low concentrations of aluminum. Treat each blank, standard, and sample in similar fashion. Continue as in Section 3111C.4*b*.

c. Analysis of samples: Rinse atomizer by aspirating water-saturated MIBK. Aspirate extracts of samples treated as above, and record absorbances.

5. Calculations

Calculate concentration of each metal in micrograms per liter by referring to the appropriate calibration curve prepared according to ¶ 4*b*.

3112 METALS BY COLD-VAPOR ATOMIC ABSORPTION SPECTROMETRY*#(78)

3112 A. Introduction

For general introductory material on atomic absorption spectrometric methods, see Section 3111A.

3112 B. Cold-Vapor Atomic Absorption Spectrometric Method

1. General Discussion

This method is applicable to the determination of mercury.

2. Apparatus

When possible, dedicate glassware for use in Hg analysis. Avoid using glassware previously exposed to high levels of Hg, such as those used in COD, TKN, or Cl^- analysis.

a. Atomic absorption spectrometer and associated equipment: See Section 3111A.6. Instruments and accessories specifically designed for measurement of mercury by the cold vapor technique are available commercially and may be substituted.

b. Absorption cell, a glass or plastic tube approximately 2.5 cm in diameter. An 11.4-cm-long tube has been found satisfactory but a 15-cm-long tube is preferred. Grind tube ends perpendicular to the longitudinal axis and cement quartz windows in place. Attach gas inlet and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

outlet ports (6.4 mm diam) 1.3 cm from each end.

c. Cell support: Strap cell to the flat nitrous-oxide burner head or other suitable support and align in light beam to give maximum transmittance.

d. Air pumps: Use any peristaltic pump with electronic speed control capable of delivering 2 L air/min. Any other regulated compressed air system or air cylinder also is satisfactory.

e. Flowmeter, capable of measuring an air flow of 2 L/min.

f. Aeration tubing, a straight glass frit having a coarse porosity for use in reaction flask.

g. Reaction flask, 250-mL erlenmeyer flask or a BOD bottle, fitted with a rubber stopper to hold aeration tube.

h. Drying tube, 150-mm × 18-mm-diam, containing 20 g Mg $(ClO_4)_2$. A 60-W light bulb with a suitable shade may be substituted to prevent condensation of moisture inside the absorption cell. Position bulb to maintain cell temperature at 10°C above ambient.

i. Connecting tubing, glass tubing to pass mercury vapor from reaction flask to absorption cell and to interconnect all other components. Clear vinyl plastic*#(79) tubing may be substituted for glass.

3. Reagents†#(80)

a. Metal-free water: See Section 3111B.3*c*.

b. Stock mercury solution: Dissolve 0.1354 g mercuric chloride, $HgCl_2$, in about 70 mL water, add 1 mL conc HNO_3, and dilute to 100 mL with water; 1.00 mL = 1.00 mg Hg.

c. Standard mercury solutions: Prepare a series of standard mercury solutions containing 0 to 5 µg/L by appropriate dilution of stock mercury solution with water containing 10 mL conc HNO_3/L. Prepare standards daily.

d. Nitric acid, HNO_3, conc.

e. Potassium permanganate solution: Dissolve 50 g $KMnO_4$ in water and dilute to 1 L.

f. Potassium persulfate solution: Dissolve 50 g $K_2S_2O_8$ in water and dilute to 1 L.

g. Sodium chloride-hydroxylamine sulfate solution: Dissolve 120 g NaCl and 120 g $(NH_2OH)_2 \cdot H_2SO_4$ in water and dilute to 1 L. A 10% hydroxylamine hydrochloride solution may be substituted for the hydroxylamine sulfate.

h. Stannous ion (Sn^{2+}) solution: Use either stannous chloride, ¶ 1), or stannous sulfate, ¶ 2), to prepare this solution containing about 7.0 g Sn^{2+}/100 mL.

1) Dissolve 10 g $SnCl_2$ in water containing 20 mL conc HCl and dilute to 100 mL.

2) Dissolve 11 g $SnSO_4$ in water containing 7 mL conc H_2SO_4 and dilute to 100 mL.

Both solutions decompose with aging. If a suspension forms, stir reagent continuously during use. Reagent volume is sufficient to process about 20 samples; adjust volumes prepared to

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

accommodate number of samples processed.

i. Sulfuric acid, H_2SO_4, conc.

4. Procedure

a. Instrument operation: See Section 3111B.4*b*. Set wavelength to 253.7 nm. Install absorption cell and align in light path to give maximum transmission. Connect associated equipment to absorption cell with glass or vinyl plastic tubing as indicated in Figure 3112:1. Turn on air and adjust flow rate to 2 L/min. Allow air to flow continuously. Alternatively, follow manufacturer's directions for operation. NOTE: Fluorescent lighting may increase baseline noise.

b. Standardization: Transfer 100 mL of each of the 1.0, 2.0, and 5.0 µg/L Hg standard solutions and a blank of 100 mL water to 250-mL erlenmeyer reaction flasks. Add 5 mL conc H_2SO_4 and 2.5 mL conc HNO_3 to each flask. Add 15 mL $KMnO_4$ solution to each flask and let stand at least 15 min. Add 8 mL $K_2S_2O_8$ solution to each flask and heat for 2 h in a water bath at 95°C. Cool to room temperature.

Treating each flask individually, add enough NaCl-hydroxylamine solution to reduce excess $KMnO_4$, then add 5 mL $SnCl_2$ or $SnSO_4$ solution and immediately attach flask to aeration apparatus. As Hg is volatilized and carried into the absorption cell, absorbance will increase to a maximum within a few seconds. As soon as recorder returns approximately to the base line, remove stopper holding the frit from reaction flask, and replace with a flask containing water. Flush system for a few seconds and run the next standard in the same manner. Construct a standard curve by plotting peak height versus micrograms Hg.

c. Analysis of samples: Transfer 100 mL sample or portion diluted to 100 mL containing not more than 5.0 µg Hg/L to a reaction flask. Treat as in ¶ 4*b*. Seawaters, brines, and effluents high in chlorides require as much as an additional 25 mL $KMnO_4$ solution. During oxidation step, chlorides are converted to free chlorine, which absorbs at 253 nm. Remove all free chlorine before the Hg is reduced and swept into the cell by using an excess (25 mL) of hydroxylamine reagent.

Remove free chlorine by sparging sample gently with air or nitrogen after adding hydroxylamine reducing solution. Use a separate tube and frit to avoid carryover of residual stannous chloride, which could cause reduction and loss of mercury.

5. Calculation

Determine peak height of sample from recorder chart and read mercury value from standard curve prepared according to ¶ 4*b*.

6. Precision and Bias

Data on interlaboratory precision and bias for this method are given in Table 3112:I.

7. Reference

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. KOPP, J.F., M.C. LONGBOTTOM & L.B. LOBRING. 1972. ‘‘Cold vapor’’ method for determining mercury. *J. Amer. Water Works Assoc.* 64:20.

8. Bibliography

HATCH, W.R. & W.L. OTT. 1968. Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry. *Anal. Chem.* 40:2085.

UTHE, J.F., F.A.J. ARMSTRONG & M.P. STAINTON. 1970. Mercury determination in fish samples by wet digestion and flameless atomic absorption spectrophotometry. *J. Fish. Res. Board Can.* 27:805.

FELDMAN, C. 1974. Preservation of dilute mercury solutions. *Anal. Chem.* 46:99.

BOTHNER, M.H. & D.E. ROBERTSON. 1975. Mercury contamination of sea water samples stored in polyethylene containers. *Anal. Chem.* 47: 592.

HAWLEY, J.E. & J.D. INGLE, JR. 1975. Improvements in cold vapor atomic absorption determination of mercury. *Anal. Chem.* 47:719.

LO, J.M. & C.M. WAL. 1975. Mercury loss from water during storage: Mechanisms and prevention. *Anal. Chem.* 47:1869.

EL-AWADY, A.A., R.B. MILLER & M.J. CARTER. 1976. Automated method for the determination of total and inorganic mercury in water and wastewater samples. *Anal. Chem.* 48:110.

ODA, C.E. & J.D. INGLE, JR. 1981. Speciation of mercury by cold vapor atomic absorption spectrometry with selective reduction. *Anal. Chem.* 53:2305.

SUDDENDORF, R.F. 1981. Interference by selenium or tellurium in the determination of mercury by cold vapor generation atomic absorption spectrometry. *Anal. Chem.* 53:2234.

HEIDEN, R.W. & D.A. AIKENS. 1983. Humic acid as a preservative for trace mercury (II) solutions stored in polyolefin containers. *Anal. Chem.* 55:2327.

CHOU, H.N. & C.A. NALEWAY. 1984. Determination of mercury by cold vapor atomic absorption spectrometry. *Anal. Chem.* 56:1737.

3113 METALS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY*#(81)

3113 A. Introduction

1. Applications

Electrothermal atomic absorption permits determination of most metallic elements with sensitivities and detection limits from 20 to 1000 times better than those of conventional flame techniques without extraction or sample concentration. This increase in sensitivity results from an increase in atom density within the furnace as compared to flame atomic absorption. Many

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

elements can be determined at concentrations as low as 1.0 µg/L. An additional advantage of electrothermal atomic absorption is that only a very small volume of sample is required.

The electrothermal technique is used only at concentration levels below the optimum range of direct flame atomic absorption because it is subject to more interferences than the flame procedure and requires increased analysis time. The method of standard additions may be required to insure validity of data. Because of the high sensitivity of this technique, it is extremely susceptible to contamination; extra care in sample handling and analysis may be required.

2. Principle

Electrothermal atomic absorption spectroscopy is based on the same principle as direct flame atomization but an electrically heated atomizer or graphite furnace replaces the standard burner head. A discrete sample volume is dispensed into the graphite sample tube (or cup). Typically, determinations are made by heating the sample in three or more stages. First, a low current heats the tube to dry the sample. The second, or charring, stage destroys organic matter and volatilizes other matrix components at an intermediate temperature. Finally, a high current heats the tube to incandescence and, in an inert atmosphere, atomizes the element being determined. Additional stages frequently are added to aid in drying and charring, and to clean and cool the tube between samples. The resultant ground-state atomic vapor absorbs monochromatic radiation from the source. A photoelectric detector measures the intensity of transmitted radiation. The inverse of the transmittance is related logarithmically to the absorbance, which is directly proportional to the number density of vaporized ground-state atoms (the Beer-Lambert law) over a limited concentration range.

3. Interferences

Electrothermal atomization determinations may be subject to significant interferences from molecular absorption as well as chemical and matrix effects. Molecular absorption may occur when components of the sample matrix volatilize during atomization, resulting in broadband absorption. Several background correction techniques are available commercially to compensate for this interference. A continuum source such as a deuterium arc can correct for background up to absorbance levels of about 0.8. Continuum lamp intensity diminishes at long wavelengths and use of continuum background correction is limited to analytical wavelengths below 350 nm. Zeeman effect background correctors can handle background absorbance up to 1.5 to 2.0. The Smith-Hieftje correction technique can accommodate background absorbance levels as large as 2.5 to 3.0 (see Section 3111A.3). Both Zeeman and Smith-Hieftje background corrections are susceptible to rollover (development of a negative absorbance-concentration relationship) at high absorbances. The rollover absorbance for each element should be available in the manufacturer's literature. Curvature due to rollover should become apparent during calibration; dilution produces a more linear calibration plot. Use background correction when analyzing samples containing high concentrations of acid or dissolved solids and in determining elements for which an absorption line below 350 nm is used.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Matrix modification can be useful in minimizing interference and increasing analytical sensitivity. Determine need for a modifier by evaluating recovery of a sample with a known addition. Recovery near 100% indicates that sample matrix does not affect analysis. Chemical modifiers generally modify relative volatilities of matrix and metal. Some modifiers enhance matrix removal, isolating the metal, while other modifiers inhibit metal volatilization, allowing use of higher ashing/charring temperatures and increasing efficiency of matrix removal. Chemical modifiers are added at high concentration (percent level) and can lead to sample contamination from impurities in the modifier solution. Heavy use of chemical modifiers may reduce the useful life (normally 50 to 100 firings) of the graphite tube. Some specific chemical modifiers and approximate concentrations are listed in Table 3113:I.

Addition of a chemical modifier directly to the sample before analysis is restricted to inexpensive additives (e.g. phosphoric acid). Use of palladium salts for matrix modification normally requires methods of co-addition, in which sample and modifier are added consecutively to the furnace either manually or, preferably, with an automatic sampler. Palladium salts (nitrate is preferred, chloride is acceptable) are listed in Table 3113:I as a modifier for many metals. The palladium solution (50 to 2000 mg/L) generally includes citric or ascorbic acid, which aids reduction of palladium in the furnace. Citric acid levels of 1 to 2% are typical. Use of hydrogen (5%) in the coolant gas (available commercially as a mixture) also reduces palladium, eliminating need for organic reducing acids. CAUTION: *Do not mix hydrogen and other gases in the laboratory; hydrogen gas is very flammable—handle with caution*. Use low levels of palladium (50 to 250 mg/L) for normal samples and higher levels for complex samples. Addition of excess palladium modifier may widen atomization peaks; in such cases peak area measurements may provide higher quality results. The recommended mode of modifier use is through co-addition to the furnace of about 10 µL of the palladium (or other) modifier solution. Palladium may not be the best modifier in all cases and cannot be recommended unconditionally. Test samples requiring a modifier first with palladium; test other modifiers only if palladium is unsuccessful or to minimize modifier cost. See Section 3113B.3 for preparation of modifier solution.

Temperature ramping, i.e., gradual heating, can be used to decrease background interferences and permits analysis of samples with complex matrices. Ramping permits a controlled, continuous increase of furnace temperature in any of the various steps of the temperature sequence. Ramp drying is used for samples containing mixtures of solvents or for samples with a high salt content (to avoid spattering). If spattering is suspected, develop drying ramp by visual inspection of the drying stage, using a mirror. Samples that contain a complex mixture of matrix components sometimes require ramp charring to effect controlled, complete thermal decomposition. Ramp atomization may minimize background absorption by permitting volatilization of the element being determined before the matrix. This is especially applicable in the determination of such volatile elements as cadmium and lead. Use of time-resolved absorbance profiles (available on most modern instruments) greatly aids method development. Changes in atomization, notably the element peak appearance time and magnitude of background

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

and metal absorbances, can be monitored directly.

Improve analysis by using a graphite platform, inserted into the graphite tube, as the atomization site. The platform is not heated as directly by the current flowing through the graphite tube; thus the metal atomizes later and under more uniform conditions.

Use standard additions to compensate for matrix interferences. When making standard additions, determine whether the added metal and that in the sample behave similarly under the specified conditions. [See Section 3113B.4*d*2)]. In the extreme, test every sample for recovery (85 to 115% recovery desired) to determine if standard addition is needed. Test every sample type for recovery. Recovery of only 40 to 85% generally indicates that standard addition is required. Often, as long as the samples are from sources of consistent properties, a representative recovery can be used to characterize the analysis and determine the necessity of standard addition. Test samples of unknown origin or of complex composition (digestates, for example) individually for metal recovery. Ideally, chemical modifiers and graphite platforms render the sample fit to be analyzed using a standard analytical calibration curve. Always verify this assumption; however, a properly developed method with judicious use of chemical modifiers should eliminate the necessity for standard addition in all but the most extreme samples.

Chemical interaction of the graphite tube with various elements to form refractory carbides occurs at high charring and atomization temperatures. Elements that form carbides are barium, molybdenum, nickel, titanium, vanadium, and silicon. Carbide formation is characterized by broad, tailing atomization peaks and reduced sensitivity. Using pyrolytically coated tubes for these metals minimizes the problem.

4. Sensitivity, Detection Limits, and Optimum Concentration Range

Estimated detection limits and optimum concentration ranges are listed in Table 3113:II. These values may vary with the chemical form of the element being determined, sample composition, or instrumental conditions.

For a given sample, increased sensitivity may be achieved by using a larger sample volume or by reducing flow rate of the purge gas or by using gas interrupt during atomization. Note, however, that these techniques also will increase the effects of any interferences present. Sensitivity can be decreased by diluting the sample, reducing sample volume, increasing purge-gas flow, or using a less sensitive wavelength. Use of argon, rather than nitrogen, as the purge gas generally improves sensitivity and reproducibility. Hydrogen mixed with the inert gas may suppress chemical interference and increase sensitivity by acting as a reducing agent, thereby aiding in producing more ground-state atoms. Pyrolytically coated graphite tubes can increase sensitivity for the more refractory elements and are recommended. The optical pyrometer/maximum power accessory available on some instruments also offers increased sensitivity with lower atomization temperatures for many elements.

Using the Stabilized Temperature Platform Furnace (STPF) technique, which is a combination of individual techniques, also offers significant interference reduction with improved sensitivity. Sensitivity changes with sample tube age. Discard graphite tubes when

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

significant variations in sensitivity or poor reproducibility are observed. The use of high acid concentrations, brine samples, and matrix modifiers often drastically reduces tube life. Preferably use the graphite platform in such situations.

5. References

1. PERKIN-ELMER CORP. 1991. Summary of Standard Conditions for Graphite Furnace. Perkin-Elmer Corp., Norwalk, Conn.
2. ROTHERY, E., ed. 1988. Analytical Methods for Graphite Tube Atomizers. Varian Techtron Pty, Ltd., Mulgrave, Victoria, Australia.

6. Bibliography

FERNANDEZ, F.J. & D.C. MANNING. 1971. Atomic absorption analyses of metal pollutants in water using a heated graphite atomizer. *Atomic Absorption Newsletter* 10:65.

SEGAR, D.A. & J.G. GONZALEZ. 1972. Evaluation of atomic absorption with a heated graphite atomizer for the direct determination of trace transition metals in sea water. *Anal. Chim. Acta* 58:7.

BARNARD, W.M. & M.J. FISHMAN. 1973. Evaluation of the use of heated graphite atomizer for the routine determination of trace metals in water. *Atomic Absorption Newsletter* 12:118.

KAHN, H.L. 1973. The detection of metallic elements in wastes and waters with the graphite furnace. *Int. J. Environ. Anal. Chem.* 3:121.

WALSH, P.R., J.L. FASCHING & R.A. DUCE. 1976. Matrix effects and their control during the flameless atomic absorption determination of arsenic. *Anal. Chem.* 48:1014.

HENN, E.L. 1977. Use of Molybdenum in Eliminating Matrix Interferences in Flameless Atomic Absorption. Spec. Tech. Publ. 618, American Soc. Testing & Materials, Philadelphia, Pa.

MARTIN, T.D. & J.F. KOPP. 1978. Methods for Metals in Drinking Water. U.S. Environmental Protection Agency, Environmental Monitoring and Support Lab., Cincinnati, Ohio.

HYDES, D.J. 1980. Reduction of matrix effects with a soluble organic acid in the carbon furnace atomic absorption spectrometric determination of cobalt, copper, and manganese in seawater. *Anal. Chem.* 52:289.

SOTERA, J.J. & H.L. KAHN. 1982. Background correction in AAS. *Amer. Lab.* 14:100.

SMITH, S.B. & G.M. HIEFTJE. 1983. A new background-correction method for atomic absorption spectrometry. *Appl. Spectrosc.* 37:419.

GROSSER, Z. 1985. Techniques in Graphite Furnace Atomic Absorption Spectrophotometry. Perkin-Elmer Corp., Ridgefield, Conn.

SLAVIN, W. & G.R. CARNICK. 1985. A survey of applications of the stabilized temperature platform furnace and Zeeman correction. *Atomic Spectrosc.* 6:157.

BRUEGGEMEYER, T. & F. FRICKE. 1986. Comparison of furnace & atomization behavior of aluminum from standard & thorium-treated L'vov platforms. *Anal. Chem.* 58:1143.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3113 B. Electrothermal Atomic Absorption Spectrometric Method

1. General Discussion

This method is suitable for determination of micro quantities of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin. It is also applicable to analysis of bismuth, gallium, germanium, gold, indium, mercury, tellurium, thallium, and vanadium, but precision and accuracy data are not yet available.

2. Apparatus

a. Atomic absorption spectrometer: See Section 3111A.6*a*. The instrument must have background correction capability.

b. Source lamps: See Section 3111A.6*d*.

c. Graphite furnace: Use an electrically heated device with electronic control circuitry designed to carry a graphite tube or cup through a heating program that provides sufficient thermal energy to atomize the elements of interest. Furnace heat controllers with only three heating steps are adequate only for fresh waters with low dissolved solids content. For salt waters, brines, and other complex matrices, use a furnace controller with up to seven individually programmed heating steps. Fit the furnace into the sample compartment of the spectrometer in place of the conventional burner assembly. Use argon as a purge gas to minimize oxidation of the furnace tube and to prevent the formation of metallic oxides. Use graphite tubes with platforms to minimize interferences and to improve sensitivity.

d. Readout: See Section 3111A.6*c*.

e. Sample dispensers: Use microliter pipets (5 to 100 µL) or an automatic sampling device designed for the specific instrument.

f. Vent: See Section 3111A.6 *f*.

g. Cooling water supply: Cool with tap water flowing at 1 to 4 L/min or use a recirculating cooling device.

h. Membrane filter apparatus: Use an all-glass filtering device and 0.45-µm or smaller-pore-diameter membrane filters. For trace analysis of aluminum, use polypropylene or TFE devices.

3. Reagents

a. Metal-free water: See Section 3111B.3*c*.

b. Hydrochloric acid, HCl, 1 + 1 and conc.

c. Nitric acid, HNO_3, 1 + 1 and conc.

d. Matrix modifier stock solutions:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1) *Magnesium nitrate,* 10 000 mg Mg/L: Dissolve 10.5 g $Mg(NO_3)_2 \cdot 6H_2O$ in water. Dilute to 100 mL.

2) *Nickel nitrate,* 10 000 mg Ni/L: Dissolve 4.96 g $Ni(NO_3)_2 \cdot 6H_2O$ in water. Dilute to 100 mL.

3) *Phosphoric acid,* 10% (v/v): Add 10 mL conc H_3PO_4 to water. Dilute to 100 mL.

4) *Palladium nitrate,* 4000 mg Pd/L: Dissolve 8.89 g $Pd(NO_3)_2 \cdot H_2O$ in water. Dilute to 1 L.

5) *Citric acid,* 4%: Dissolve 40 g citric acid in water. Dilute to 1 L.

NOTE: All of the modifier solutions recommended in Table 3113:I can be prepared with volumetric combination of the above solutions and water. For preparation of other matrix modifiers, see references or follow manufacturers' instructions.

e. Stock metal solutions: Refer to Section 3111B and Section 3114.

f. Chelating resin: 100 to 200 mesh#(82)* purified by heating at 60°C in 10*N* NaOH for 24 h. Cool resin and rinse 10 times each with alternating portions of 1*N* HCl, metal-free water, 1*N* NaOH, and metal-free water.

g. Metal-free seawater (or brine): Fill a 1.4-cm-ID × 20-cm-long borosilicate glass column to within 2 cm of the top with purified chelating resin. Elute resin with successive 50-mL portions of 1*N* HCl, metal-free water, 1*N* NaOH, and metal-free water at the rate of 5 mL/min just before use. Pass salt water or brine through the column at a rate of 5 mL/min to extract trace metals present. Discard the first 10 bed volumes (300 mL) of eluate.

4. Procedures

a. Sample pretreatment: Before analysis, pretreat all samples as indicated below. Rinse all glassware with 1 + 1 HNO_3 and water. Carry out digestion procedures in a clean, dust-free laboratory area to avoid sample contamination. For digestion of trace aluminum, use polypropylene or TFE utensils to avoid leachable aluminum from glassware.

1) Dissolved metals—See Section 3030B. For samples requiring arsenic and/or selenium analysis add 3 mL 30% hydrogen peroxide/100 mL sample and an appropriate volume of nickel nitrate solution (see Table 3113:I) before analysis. For all other metals no further pretreatment is required except for adding an optional matrix modifier.

2) Total recoverable metals (Al, Sb, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, and Sn)—NOTE: Sb and Sn are not recovered unless HCl is used in the digestion. See Section 3030D. Quantitatively transfer digested sample to a 100-mL volumetric flask, add an appropriate amount of matrix modifier (see Table 3113:I), and dilute to volume with water.

3) Total recoverable metals (As, Se)—Transfer 100 mL of shaken sample, 1 mL conc HNO_3, and 2 mL 30% H_2O_2 to a clean, acid-washed 250-mL beaker. Heat on a hot plate without allowing solution to boil until volume has been reduced to about 50 mL. Remove from hot plate and let cool to room temperature. Add an appropriate concentration of nickel (see Table 3113:I),

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

and dilute to volume in a 100-mL volumetric flask with water. Substitution of palladium is uneconomical. Nickel may be deleted if palladium is co-added during analysis. Simultaneously prepare a digested blank by substituting water for sample and proceed with digestion as described above.

b. Instrument operation: Mount and align furnace device according to manufacturer's instructions. Turn on instrument and data collection system. Select appropriate light source and adjust to recommended electrical setting. Select proper wavelength and set all conditions according to manufacturer's instructions, including background correction. Background correction is important when elements are determined at short wavelengths or when sample has a high level of dissolved solids. Background correction normally is not necessary at wavelengths longer than 350 nm. If background correction above 350 nm is needed deuterium arc background correction is not useful and other types must be used.

Select proper inert- or sheath-gas flow. In some cases, it is desirable to interrupt the inert-gas flow during atomization. Such interruption results in increased sensitivity by increasing residence time of the atomic vapor in the optical path. Gas interruption also increases background absorption and intensifies interference effects, but modern background correction methods usually eliminate these problems. Consider advantages and disadvantages of this option for each matrix when optimizing analytical conditions.

To optimize graphite furnace conditions, carefully adjust furnace temperature settings to maximize sensitivity and precision and to minimize interferences. Follow manufacturer's instructions.

Use drying temperatures slightly above the solvent boiling point and provide enough time and temperature for complete evaporation without boiling or spattering.

Select atomization temperature by determining the lowest temperature providing maximum sensitivity without significantly eroding precision. Optimize by a series of successive determinations at various atomization temperatures using a standard solution giving an absorbance of 0.2 to 0.5.

The charring temperature must be high enough to maximize volatilization of interfering matrix components yet too low to volatilize the element of interest. With the drying and atomization temperatures set to their optimum values, analyze a standard solution at a series of charring temperatures in increasing increments of 50 to 100°C. When the optimum charring temperature is exceeded, there will be a significant drop in sensitivity. Plot charring temperature versus sample absorbance: the optimum charring temperature is the highest temperature without reduced sensitivity. Verify optimization with major changes in sample matrix.

c. Instrument calibration: Prepare standard solutions for instrument calibration by diluting metal stock solutions. Prepare standard solutions fresh daily.

Prepare a blank and at least three calibration standards in the appropriate concentration range (see Table 3113:II) for correlating element concentration and instrument response. Match the matrix of the standard solutions to those of the samples as closely as possible. In most cases, this simply requires matching the acid background of the samples. For seawaters or brines,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

however, use the metal-free matrix (¶ 3*g*) as the standard solution diluent. In addition, add the same concentration of matrix modifier (if required for sample analysis) to the standard solutions.

Inject a suitable portion of each standard solution, in order of increasing concentration. Analyze each standard solution in triplicate to verify method precision.

Construct an analytical curve by plotting the average peak absorbances or peak areas of the standard solution versus concentration on linear graph paper. Alternatively, use electronic instrument calibration if the instrument has this capability.

d. Sample analysis: Analyze all samples except those demonstrated to be free of matrix interferences (based on recoveries of 85% to 115% for known additions) using the method of standard additions. Analyze all samples at least in duplicate or until reproducible results are obtained. A variation of ≤ 10% is considered acceptable reproducibility. Average replicate values.

1) Direct determination—Inject a measured portion of pretreated sample into the graphite furnace. Use the same volume as was used to prepare the calibration curve. Usually add modifier immediately after the sample, preferably using an automatic sampler or a micropipet. Some methods require modifier to be injected before the sample. Use the same volume and concentration of modifier for all standards and samples. Dry, char, and atomize according to the preset program. Repeat until reproducible results are obtained.

Compare the average absorbance value or peak area to the calibration curve to determine concentration of the element of interest. Alternatively, read results directly if the instrument is equipped with this capability. If absorbance (or concentration) or peak area of the sample is greater than absorbance (concentration) or peak area of the most concentrated standard solution, dilute sample and reanalyze. If very large dilutions are required, another technique (e.g., flame AA or ICP) may be more suitable for this sample. Large dilution factors magnify small errors on final calculation. Keep acid background and concentration of matrix modifier (if present in the solutions) constant. Dilute the sample in a blank solution of acid and matrix modifiers.

Proceed to ¶ 5*a* below.

2) Method of standard additions—Refer to ¶ 4*c* above. The method of standard additions is valid only when it falls in the linear portion of the calibration curve. Once instrument sensitivity has been optimized for the element of interest and the linear range for the element has been established, proceed with sample analyses.

Inject a measured volume of sample into furnace device. Dry, char or ash, and atomize samples according to preset program. Repeat until reproducible results are obtained. Record instrument response in absorbance or concentration as appropriate. Add a known concentration of the element of interest to a separate portion of sample so as not to change significantly the sample volume. Repeat the determination.

Add a known concentration (preferably twice that used in the first addition) to a separate sample portion. Mix well and repeat the determination.

Using linear graph paper, plot average absorbance or instrument response for the sample and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

the additions on the vertical axis against the concentrations of the added element on the horizontal axis, using zero as the concentration for the sample. Draw a straight line connecting the three points and extrapolate to zero absorbance. The intercept at the horizontal axis is the negative of the element concentration in the sample. The concentration axis to the left of the origin should be a mirror image of the axis to the right.

5. Calculations

a. Direct determination:

$$\mu g \text{ metal/L} = C \times F$$

where:

C = metal concentration as read directly from the instrument or from the calibration curve, µg/L, and
F = dilution factor.

b. Method of additions:

$$\mu g \text{ metal/L} = C \times F$$

where:

C = metal concentration as read from the method of additions plot, µg/L, and
F = dilution factor.

6. Precision and Bias

Data typical of the precision and bias obtainable are presented in Table 3113:III, Table 3113:IV, and Table 3113:V.

7. Quality Control

See Section 3020 for specific quality control procedures to be followed during analysis. Although previous indications were that very low optimum concentration ranges were attainable for most metals (see Table 3113:II), data in Table 3113:III using variations of these protocols show that this may not be so. Exercise extreme care when applying this method to the lower concentration ranges. Verify analyst precision at the beginning of each analytical run by making triplicate analyses. Verify autosampler precision by checking volumes (by weight) delivered by the autosampler at routinely used injection volume settings.

8. Reference

1. COPELAND, T.R. & J.P. MANEY. 1986. EPA Method Study 31: Trace Metals by Atomic Absorption (Furnace Techniques). EPA-600/S4-85-070, U.S. Environmental Protection Agency, Environmental Monitoring and Support Lab., Cincinnati, Ohio.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

9. Bibliography

RENSHAW, G.D. 1973. The determination of barium by flameless atomic absorption spectrophotometry using a modified graphite tube atomizer. *Atomic Absorption Newsletter* 12:158.

YANAGISAWA, M., T. TAKEUCHI & M. SUZUKI. 1973. Flameless atomic absorption spectrometry of antimony. *Anal. Chim. Acta* 64:381.

RATTONETTI, A. 1974. Determination of soluble cadmium, lead, silver and indium in rainwater and stream water with the use of flameless atomic absorption. *Anal. Chem.* 46:739.

HENN, E.L. 1975. Determination of selenium in water and industrial effluents by flameless atomic absorption. *Anal. Chem.* 47:428.

MARTIN, T.D. & J.F. KOPP. 1975. Determining selenium in water, wastewater, sediment and sludge by flameless atomic absorption spectrometry. *Atomic Absorption Newsletter* 14:109.

MARUTA, T., K. MINEGISHI & G. SUDOH. 1976. The flameless atomic absorption spectrometric determination of aluminum with a carbon atomization system. *Anal. Chim. Acta* 81:313.

CRANSTON, R.E. & J.W. MURRAY. 1978. The determination of chromium species in natural waters. *Anal. Chim. Acta* 99:275.

HOFFMEISTER, W. 1978. Determination of iron in ultrapure water by atomic absorption spectroscopy. *Z. Anal. Chem.* 50:289.

LAGAS, P. 1978. Determination of beryllium, barium, vanadium and some other elements in water by atomic absorption spectrometry with electrothermal atomization. *Anal. Chim. Acta* 98:261.

CARRONDO, M.J.T., J.N. LESTER & R. PERRY. 1979. Electrothermal atomic absorption determination of total aluminum in waters and waste waters. *Anal. Chim. Acta* 111:291.

NAKAHARA, T. & C.L. CHAKRABARTI. 1979. Direct determination of traces of molybdenum in synthetic sea water by atomic absorption spectrometry with electrothermal atomization and selective volatilization of the salt matrix. *Anal. Chim. Acta* 104:99.

TIMINAGA, M. & Y. UMEZAKI. 1979. Determination of submicrogram amounts of tin by atomic absorption spectrometry with electrothermal atomization. *Anal. Chim. Acta* 110:55.

3114 ARSENIC AND SELENIUM BY HYDRIDE GENERATION/ATOMIC ABSORPTION SPECTROMETRY*#(83)

3114 A. Introduction

For general introductory material on atomic absorption spectrometric methods, see Section 3111A.

Two methods are presented in this section: A manual method and a continuous-flow method

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

especially recommended for selenium. Continuous-flow automated systems are preferable to manual hydride generators because the effect of sudden hydrogen generation on light-path transparency is removed and any blank response from contamination of the HCl reagent by the elements being determined is incorporated into the background base line.

3114 B. Manual Hydride Generation/Atomic Absorption Spectrometric Method

1. General Discussion

a. Principle: This method is applicable to the determination of arsenic and selenium by conversion to their hydrides by sodium borohydride reagent and transport into an atomic absorption atomizer.

Arsenous acid and selenous acid, the As(III) and Se(IV) oxidation states of arsenic and selenium, respectively, are instantaneously converted by sodium borohydride reagent in acid solution to their volatile hydrides. The hydrides are purged continuously by argon or nitrogen into a quartz cell heated electrically or by the flame of an atomic absorption spectrometer and converted to the gas-phase atoms. The sodium borohydride reducing agent, by rapid generation of the elemental hydrides in an appropriate reaction cell, minimizes dilution of the hydrides by the carrier gas and provides rapid, sensitive determinations of arsenic and selenium.

CAUTION: *Arsenic and selenium and their hydrides are toxic. Handle with care.*

At room temperature and solution pH values of 1 or less, arsenic acid, the As(V) oxidation state of arsenic, is reduced relatively slowly by sodium borohydride to As(III), which is then instantaneously converted to arsine. The arsine atomic absorption peaks commonly are decreased by one-fourth to one-third for As(V) when compared to As(III). Determination of total arsenic requires that all inorganic arsenic compounds be in the As(III) state. Organic and inorganic forms of arsenic are first oxidized to As(V) by acid digestion. The As(V) then is quantitatively reduced to As(III) with sodium or potassium iodide before reaction with sodium borohydride.

Selenic acid, the Se(VI) oxidation state of selenium, is not measurably reduced by sodium borohydride. To determine total selenium by atomic absorption and sodium borohydride, first reduce Se(VI) formed during the acid digestion procedure to Se(IV), being careful to prevent reoxidation by chlorine. Efficiency of reduction depends on temperature, reduction time, and HCl concentration. For 4*N* HCl, heat 1 h at 100°C. For 6*N* HCl, boiling for 10 min is sufficient.[1-3] Alternatively, autoclave samples in sealed containers at 121°C for 1 h. NOTE: Autoclaving in sealed containers may result in incomplete reduction, apparently due to the buildup of chlorine gas. To obtain equal instrument responses for reduced Se(VI) and Se (IV) solutions of equal concentrations, manipulate HCl concentration and heating time. For further details, see Section 3500-Se.

b. Equipment selection:

Certain atomic absorption atomizers and hydride reaction cells are available commercially

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

for use with the sodium borohydride reagent. A functional manual system that can be constructed in the laboratory is presented in Figure 3114:1. Irrespective of the hydride reaction cell-atomizer system selected, it must meet the following quality-control considerations: (*a*) it must provide a precise and reproducible standard curve between 0 and 20 µg As or Se/L and an instrumental detection limit between 0.1 and 0.5 µg As or Se/L; (*b*) when carried through the entire procedure, oxidation state couples [As (III) - As (V) or Se (IV) - Se (VI)] must cause equal instrument response; and (*c*) sample digestion must yield 80% or greater recovery of added cacodylic acid (dimethyl arsinic acid) and 90% or greater recovery of added As(III), As(V), Se(VI), or Se(IV).

Quartz atomization cells provide for the most sensitive arsenic and selenium hydride determinations. The quartz cell can be heated electrically or by an air-acetylene flame in an atomic absorption unit.

c. Digestion techniques: Waters and wastewaters may contain varying amounts of organic arsenic compounds and inorganic compounds of As(III), As(V), Se(IV), and Se(VI). To measure total arsenic and selenium in these samples requires sample digestion to solubilize particulate forms and oxidize reduced forms of arsenic and selenium and to convert any organic compounds to inorganic ones. Organic selenium compounds rarely have been demonstrated in water. It is left to the experienced analyst's judgment whether sample digestion is required.

Various alternative digestion procedures are provided in ¶s 4*c* and 4*d* below. Consider sulfuric-nitric-perchloric acid digestion (¶ 4*c*) or sulfuric-nitric acid digestion (Section 3030F) as providing a measure of total recoverable arsenic rather than total arsenic because they do not completely convert certain organic arsenic compounds to As(V). The sulfuric-nitric-perchloric acid digestion effectively destroys organics and most particulates in untreated wastewaters or solid samples, but does not convert all organic arsenicals to As(V). The potassium persulfate digestion (¶ 4*d*) is effective for converting organic arsenic and selenium compounds to As(V) and Se(VI) in potable and surface waters and in most wastewaters.[4]

The HCl-autoclave reduction of Se(VI) described above and in ¶ 4 *f* is an effective digestion procedure for total inorganic selenium; however, it has not been found effective for converting benzene substituted selenium compounds to inorganic selenium. In all cases, verify the effectiveness of digestion methods by carrying samples with known additions of organic As or Se(IV) through the entire procedure.

d. Interferences: Interferences are minimized because the As and Se hydrides are removed from the solution containing most potential interfering substances. Slight response variations occur when acid matrices are varied. Control these variations by treating standards and samples in the same manner. Low concentrations of noble metals (approximately 100 µg/L of Ag, Au, Pt, Pd, etc.), concentrations of copper, lead, and nickel at or greater than 1 mg/L, and concentrations between 0.1 and 1 mg/L of hydride-forming elements (Bi, Sb, Sn, and Te) may suppress the response of As and Se hydrides. Interference by transition metals depends strongly on HCl concentration. Interferences are less pronounced at 4 to 6*N* HCl than at lower concentrations.[5] The presence of As or Se in each other's matrices can cause similar suppression. Reduced

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

nitrogen oxides resulting from HNO_3 digestion and nitrite also can suppress instrumental response for both elements. Large concentrations of iodide interfere with the Se determination by reducing Se to its elemental form. Do not use any glassware for determining Se that has been used for iodide reduction of As(V).

To prevent chlorine gas produced in the reduction of Se(VI) to Se(IV) from reoxidizing the Se(IV), generate the hydride within a few hours of the reduction steps or purge the chlorine from the samples by sparging.[6]

Interferences depend on system design and defy quantitative description because of their synergistic effects. Certain waters and wastewaters can contain interferences in sufficient concentration to suppress absorption responses of As and Se. For representative samples in a given laboratory and for initial analyses of unknown wastewaters, add appropriate inorganic forms of As or Se to digested sample portions and measure recovery. If average recoveries are less than 90%, consider using alternative analytical procedures.

e. Detection limit and optimum concentration range: For both arsenic and selenium, analyzed by aspiration into a nitrogen-hydrogen flame after reduction, the method detection limit is 2 μg/L or lower and the optimum concentration range 2 to 20 μg/L.

2. Apparatus

a. Atomic absorption spectrometer equipped with air-acetylene flame and quartz cell with mounting bracket or an electrically heated quartz cell, As and Se electrodeless discharge lamps with power supply, background correction at measurement wavelengths, and appropriate strip-chart recorder. A good-quality 10-mV recorder with high sensitivity and a fast response time is needed.

b. Atomizer: Use one of the following:

1) *Cylindrical quartz cell,* 10 to 20 cm long, bracket-mountable above air-acetylene burner.

2) *Cylindrical quartz cell,* 10 to 20 cm long, electrically heated by external nichrome wire to 800 to 900°C.[7]

3) *Cylindrical quartz cell* with internal fuel rich hydrogen-oxygen (air) flame.[8]

The sensitivity of quartz cells deteriorates over several months of use. Sensitivity sometimes may be restored by treatment with 40% HF. CAUTION: *HF is extremely corrosive. Avoid all contact with exposed skin. Handle with care.*

c. Reaction cell for producing As or Se hydrides: See Figure 3114:1 for an example of a manual, laboratory-made system. A commercially available system is acceptable if it utilizes liquid sodium borohydride reagents; accepts samples digested in accordance with ¶s 4*c*, *d*, and *e*; accepts 4 to 6*N* HCl; and is efficiently and precisely stirred by the purging gas and/or a magnetic stirrer.

d. Eye dropper or syringe capable of delivering 0.5 to 3.0 mL sodium borohydride reagent. Exact and reproducible addition is required so that production of hydrogen gas does not vary

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

significantly between determinations.

e. Vent: See Section 3111A.6 *f*.

3. Reagents

a. Sodium borohydride reagent: Dissolve 8 g $NaBH_4$ in 200 mL 0.1*N* NaOH. Prepare fresh daily.

b. Sodium iodide prereductant solution: Dissolve 50 g NaI in 500 mL water. Prepare fresh daily. Alternatively use an equivalent KI solution.

c. Sulfuric acid, 18*N*.

d. Sulfuric acid, 2.5*N*: Cautiously add 35 mL conc H_2SO_4 to about 400 mL water, let cool, and adjust volume to 500 mL.

e. Potassium persulfate, 5% solution: Dissolve 25 g $K_2S_2O_8$ in water and dilute to 500 mL. Store in glass and refrigerate. Prepare weekly.

f. Nitric acid, HNO_3, conc.

g. Perchloric acid, $HClO_4$, conc.

h. Hydrochloric acid, HCl, conc.

i. Argon (or nitrogen), commercial grade.

j. Arsenic(III) solutions:

1) *Stock As(III) solution:* Dissolve 1.320 g arsenic trioxide, As_2O_3, in water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As(III).

2) *Intermediate As(III) solution:* Dilute 10 mL stock As solution to 1000 mL with water containing 5 mL conc HCl; 1.00 mL = 10.0 μg As(III).

3) *Standard As(III) solution:* Dilute 10 mL intermediate As(III) solution to 1000 mL with water containing the same concentration of acid used for sample preservation (2 to 5 mL conc HNO_3); 1.00 mL = 0.100 μg As(III). Prepare diluted solutions daily.

k. Arsenic(V) solutions:

1) *Stock As(V) solution:* Dissolve 1.534 g arsenic pentoxide, As_2O_5, in distilled water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As(V).

2) *Intermediate As(V) solution:* Prepare as for As(III) above; 1.00 mL = 10.0 μg As(V).

3) *Standard As(V) solution:* Prepare as for As(III) above; 1.00 mL = 0.100 μg As(V).

l. Organic arsenic solutions:

1) *Stock organic arsenic solution:* Dissolve 1.842 g dimethylarsinic acid (cacodylic acid), $(CH_3)_2AsOOH$, in water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As. [NOTE: Check purity of cacodylic acid reagent against an intermediate arsenic standard (50 to 100 mg As/L) using flame atomic absorption.]

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2) *Intermediate organic arsenic solution:* Prepare as for As(III) above; 1.00 mL = 10.0 μg As.

3) *Standard organic arsenic solution:* Prepare as for As(III) above; 1.00 mL = 0.100 μg As.

m. Selenium(IV) solutions:

1) *Stock Se(IV) solution:* Dissolve 2.190 g sodium selenite, Na_2SeO_3, in water containing 10 mL HCl and dilute to 1 L; 1.00 mL = 1.00 mg Se(IV).

2) *Intermediate Se(IV) solution:* Dilute 10 mL stock Se(IV) to 1000 mL with water containing 10 mL conc HCl; 1.00 mL = 10.0 μg Se(IV).

3) *Standard Se(IV) solution:* Dilute 10 mL intermediate Se(IV) solution to 1000 mL with water containing the same concentration of acid used for sample preservation (2 to 5 mL conc HNO_3). Prepare solution daily when checking the equivalency of instrument response for Se(IV) and Se(VI); 1.00 mL = 0.100 μg Se(IV).

n. Selenium(VI) solutions:

1) *Stock Se(VI) solution*: Dissolve 2.393 g sodium selenate, Na_2SeO_4, in water containing 10 mL conc HNO_3. Dilute to 1 L; 1.00 mL = 1.00 mg Se(VI).

2) *Intermediate Se(VI) solution:* Prepare as for Se(IV) above; 1.00 mL = 10.0 μg Se (VI).

3) *Standard Se(VI) solution:* Prepare as for Se(IV) above; 1.00 mL = 0.100 μg Se(VI).

4. Procedure

a. Apparatus setup: Either see Figure 3114:1 or follow manufacturer's instructions. Connect inlet of reaction cell with auxiliary purging gas controlled by flow meter. If a drying cell between the reaction cell and atomizer is necessary, use only anhydrous $CaCl_2$ but not $CaSO_4$ because it may retain SeH_2. Before using the hydride generation/analysis system, optimize operating parameters. Align quartz atomizers for maximum absorbance. Aspirate a blank until memory effects are removed. Establish purging gas flow, concentration and rate of addition of sodium borohydride reagent, solution volume, and stirring rate for optimum instrument response for the chemical species to be analyzed. Optimize quartz cell temperature. If sodium borohydride reagent is added too quickly, rapid evolution of hydrogen will unbalance the system. If the volume of solution being purged is too large, the absorption signal will be decreased. Recommended wavelengths are 193.7 and 196.0 nm for As and Se, respectively.

b. Instrument calibration standards: Transfer 0.00, 1.00, 2.00, 5.00, 10.00, 15.00, and 20.00 mL standard solutions of As(III) or Se(IV) to 100-mL volumetric flasks and bring to volume with water containing the same acid concentration used for sample preservation (commonly 2 to 5 mL conc HNO_3/L). This yields blank and standard solutions of 0, 1, 2, 5, 10, 15, and 20 μg As or Se/L. Prepare fresh daily. In all cases, standards must be carried through the same digestion protocol as the samples to monitor digestion effectiveness.

c. Preparation of samples and standards for total recoverable arsenic and selenium: Use

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

digestion procedure described in 3030F for samples and standards. Alternatively, add 50 mL sample, As(III), or Se(IV) standard to 200-mL Berzelius beaker or 100-mL micro-kjeldahl flask. Add 7 mL 18*N* H_2SO_4 and 5 mL conc HNO_3. Add a small boiling chip or glass beads if necessary. Evaporate to SO_3 fumes. Maintain oxidizing conditions at all times by adding small amounts of HNO_3 to prevent solution from darkening. Maintain an excess of HNO_3 until all organic matter is destroyed. Complete digestion usually is indicated by a light-colored solution. Cool slightly, add 25 mL water and 1 mL conc $HClO_4$ and again evaporate to SO_3 fumes to expel oxides of nitrogen. CAUTION: *See Section 3030H for cautions on use of $HClO_4$*. Monitor effectiveness of either digestion procedure used by adding 5 mL of standard organic arsenic solution or 5 mL of a standard selenium solution to a 50-mL sample and measuring recovery, carrying standards and the sample with known addition through entire procedure. To report total recoverable arsenic as total arsenic, average recoveries of cacodylic acid must exceed 80%. After final evaporation of SO_3 fumes, dilute to 50 mL for arsenic measurements or to 30 mL for selenium measurements. For analysis of both elements in a single sample, increase sample volume to 100 mL and double the volumes of acids used in the digestion. Adjust final digestate volume to 100 mL. Use 50 mL for As and 30 mL for Se determinations, making appropriate volume corrections in calculating results.

d. Preparation of samples and standards for total arsenic and selenium: Add 50 mL undigested sample or standard to a 200-mL Berzelius beaker or 100-mL micro-kjeldahl flask. Add 1 mL 2.5*N* H_2SO_4 and 5 mL 5% $K_2S_2O_8$. Boil gently on a pre-heated hot plate for approximately 30 to 40 min or until a final volume of 10 mL is reached. Do not let sample go to dryness. Alternatively heat in an autoclave at 121°C for 1 h in capped containers. After manual digestion, dilute to 50 mL for subsequent arsenic measurements and to 30 mL for selenium measurements. Monitor effectiveness of digestion by measuring recovery of As or Se as above. If poor recovery of arsenic added as cacodylic acid is obtained, reanalyze using double the amount of $K_2S_2O_8$. For analysis of both elements in a single sample, increase sample volume to 100 mL and double the volumes of acids used in the digestion. Adjust final digestate volume to 100 mL. Use 50 mL for As and 30 mL for Se determinations, making appropriate volume corrections in calculating results.

e. Determination of arsenic with sodium borohydride: To 50 mL digested standard or sample in a 200-mL Berzelius beaker (see Figure 3114:1) add 5 mL conc HCl and mix. Add 5 mL NaI prereductant solution, mix, and wait at least 30 min. (NOTE: The NaI reagent has not been found necessary for certain hydride reaction cell designs if a 20 to 30% loss in instrument sensitivity is not important and variables of solution acid conditions, temperatures, and volumes for production of As(V) and arsine can be controlled strictly. Such control requires an automated delivery system; see Section 3114C.)

Attach one Berzelius beaker at a time to the rubber stopper containing the gas dispersion tube for the purging gas, the sodium borohydride reagent inlet, and the outlet to the quartz cell. Turn on strip-chart recorder and wait until the base line is established by the purging gas and all

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

air is expelled from the reaction cell. Add 0.5 mL sodium borohydride reagent. After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water, and proceed to the next sample or standard. Periodically compare standard As(III) and As(V) curves for response consistency. Check for presence of chemical interferences that suppress instrument response for arsine by treating a digested sample with 10 µg/L As(III) or As(V) as appropriate. Average recoveries should be not less than 90%.

f. Determination of selenium with sodium borohydride: To 30 mL digested standard or sample in a 200-mL Berzelius beaker or 100-mL micro-kjeldahl flask, add 15 mL conc HCl and mix. Heat for a predetermined period at 90 to 100°C. Alternatively autoclave at 121°C in capped containers for 60 min, or heat for a predetermined time in open test tubes using a 90 to 100°C hot water bath or an aluminum block digester. Check effectiveness of the selected heating time by demonstrating equal instrument responses for calibration curves prepared either from standard Se(IV) or from Se(VI) solutions. Effective heat exposure for converting Se(VI) to Se(IV), with no loss of Se(IV), ranges between 5 and 60 min when open beakers or test tubes are used. Establish a heating time for effective conversion and apply this time to all samples and standards. Do not digest standard Se(IV) and Se(VI) solutions used for this check of equivalency. After prereduction of Se(VI) to Se(IV), attach Berzelius beakers, one at a time, to the purge apparatus. For each, turn on the strip-chart recorder and wait until the base line is established. Add 0.50 mL sodium borohydride reagent. After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water, and proceed to the next sample or standard. Check for presence of chemical interferences that suppress selenium hydride instrument response by treating a digested sample with 10 µg Se (IV)/L. Average recoveries should be not less than 90%.

5. Calculation

Construct a standard curve by plotting peak heights or areas of standards versus concentration of standards. Measure peak heights or areas of samples and read concentrations from curve. If sample was diluted (or concentrated) before sample digestion, apply an appropriate factor. On instruments so equipped, read concentrations directly after standard calibration.

6. Precision and Bias

Single-laboratory, single-operator data were collected forAs(III) and organic arsenic by both manual and automated methods, and for the manual determination of selenium. Recovery values (%) from seven replicates are given below:

Method	As(III)	Org As	Se(IV)	Se(VI)
Manual with digestion	91.8	87.3	—	—
Manual without digestion	109.4	19.4	100.6	110.8
Automated with digestion	99.8	98.4	—	—

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Method	As(III)	Org As	Se(IV)	Se(VI)
Automated without digestion	92.5	10.4	—	—

7. References

1. VIJAN, P.N. & D. LEUNG. 1980. Reduction of chemical interference and speciation studies in the hydride generation-atomic absorption method for selenium. *Anal. Chim. Acta* 120:141.
2. VOTH-BEACH, L.M. & D.E. SHRADER. 1985. Reduction of interferences in the determination of arsenic and selenium by hydride generation. *Spectroscopy* 1:60.
3. JULSHAMN, K., O. RINGDAL, K.-E. SLINNING & O.R. BRAEKKAN. 1982. Optimization of the determination of selenium in marine samples by atomic absorption spectrometry: Comparison of a flameless graphite furnace atomic absorption system with a hydride generation atomic absorption system. *Spectrochim. Acta.* 37B:473.
4. NYGAARD, D.D. & J.H. LOWRY. 1982. Sample digestion procedures for simultaneous determination of arsenic, antimony, and selenium by inductively coupled argon plasma emission spectrometry with hydride generation. *Anal. Chem.* 54:803.
5. WELZ, B. & M. MELCHER. 1984. Mechanisms of transition metal interferences in hydride generation atomic-absorption spectrometry. Part 1. Influence of cobalt, copper, iron and nickel on selenium determination. *Analyst* 109:569.
6. KRIVAN, V., K. PETRICK, B. WELZ & M. MELCHER. 1985. Radiotracer error-diagnostic investigation of selenium determination by hydride-generation atomic absorption spectrometry involving treatment with hydrogen peroxide and hydrochloric acid. *Anal. Chem.* 57:1703.
7. CHU, R.C., G.P. BARRON & P.A.W. BAUMGARNER. 1972. Arsenic determination at submicrogram levels by arsine evolution and flameless atomic absorption spectrophotometric technique. *Anal. Chem.* 44: 1476.
8. SIEMER, D.D., P. KOTEEL & V. JARIWALA. 1976. Optimization of arsine generation in atomic absorption arsenic determinations. *Anal. Chem.* 48:836.

8. Bibliography

FERNANDEZ, F.J. & D.C. MANNING. 1971. The determination of arsenic at submicrogram levels by atomic absorption spectrophotometry. *Atomic Absorption Newsletter* 10:86.

JARREL-ASH CORPORATION. 1971. High Sensitivity Arsenic Determination by Atomic Absorption. Jarrel-Ash Atomic Absorption Applications Laboratory Bull. No. As-3.

MANNING, D.C. 1971. A high sensitivity arsenic-selenium sampling system for atomic absorption spectroscopy. *Atomic Absorption Newsletter* 10:123.

BRAMAN, R.S. & C.C. FOREBACK. 1973. Methylated forms of arsenic in the environment. *Science*

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

182:1247.

CALDWELL, J.S., R.J. LISHKA & E.F. MCFARREN. 1973. Evaluation of a low-cost arsenic and selenium determination of microgram-per-liter levels. *J. Amer. Water Works Assoc.*, 65:731.

AGGETT, J. & A.C. ASPELL. 1976. The determination of arsenic (III) and total arsenic by atomic-absorption spectroscopy. *Analyst* 101:341.

FIORINO, J.A., J.W. JONES & S.G. CAPAR. 1976. Sequential determination of arsenic, selenium, antimony, and tellurium in foods via rapid hydride evolution and atomic absorption spectrometry. *Anal. Chem.* 48: 120.

CUTTER, G.A. 1978. Species determination of selenium in natural waters. *Anal. Chem. Acta* 98:59.

GODDEN, R.G. & D.R. THOMERSON. 1980. Generation of covalent hydrides in atomic absorption spectroscopy. *Analyst* 105:1137.

BROWN, R.M., JR., R.C. FRY, J.L. MOYERS, S.J. NORTHWAY, M.B. DENTON & G.S. WILSON. 1981. Interference by volatile nitrogen oxides and transition-metal catalysis in the preconcentration of arsenic and selenium as hydrides. *Anal. Chem.* 53:1560.

SINEMUS, H.W., M. MELCHER & B. WELZ. 1981. Influence of valence state on the determination of antimony, bismuth, selenium, and tellurium in lake water using the hydride AA technique. *Atomic Spectrosc.* 2:81.

DEDINA, J. 1982. Interference of volatile hydride forming elements in selenium determination by atomic absorption spectrometry with hydride generation. *Anal. Chem.* 54:2097.

3114 C. Continuous Hydride Generation/Atomic Absorption Spectrometric Method

1. General Discussion

The continuous hydride generator offers the advantages of simplicity in operation, excellent reproducibility, low detection limits, and high sample volume throughput for selenium analysis following preparations as described in Section 3500-Se.B or Section 3114B.4*c* and *d*.

a. Principle: See Section 3114B.

b. Interferences: Free chlorine in hydrochloric acid is a common but difficult-to-diagnose interference. (The amount of chlorine varies with manufacturer and with each lot from the same manufacturer). Chlorine oxidizes the hydride and can contaminate the hydride generator to prevent recoveries under any conditions. When interference is encountered, or preferably before using each new bottle of HCl, eliminate chlorine from a 2.3-L bottle of conc HCl by bubbling with helium (commercial grade, 100 mL/min) for 3 h.

Excess oxidant (peroxide, persulfate, or permanganate) from the total selenium digestion can oxidize the hydride. Follow procedures in 3500-Se.B.2, 3, or 4 to ensure removal of all oxidizing agents before hydride generation.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Nitrite is a common trace constituent in natural and waste waters, and at levels as low as 10 µg/L nitrite can reduce the recovery of hydrogen selenide from Se(IV) by over 50%. Moreover, during the reduction of Se(VI) to Se(IV) by digestion with HCl (3500-Se.B.5), some nitrate is converted to nitrite, which subsequently interferes. When this interference is suspected, add sulfanilamide after sample acidification (or HCl digestion). The diazotization reaction between nitrite and sulfanilamide completely removes the interferent effect (i.e., the standard addition slope is normal).

2. Apparatus

a. Continuous hydride generator: The basic unit is composed of two parts: a precision peristaltic pump, which is used to meter and mix reagents and sample solutions, and the gas-liquid separator. At the gas-liquid separator a constant flow of argon strips out the hydrogen and metal hydride gases formed in the reaction and carries them to the heated quartz absorption cell (Section 3114B.1*b* and Section 3114B.2*b*), which is supported by a metal bracket mounted on top of the regular air acetylene burner head. The spent liquid flows out of the separator via a constant level side drain to a waste bucket. Schematics and operating parameters are shown in Figure 3114:2.

Check flow rates frequently to ensure a steady flow; an uneven flow in any tubing will cause an erratic signal. Remove tubings from pump rollers when not in use. Typical flow rates are: sample, 7 mL/min; acid, 1 mL/min; borohydride reagent, 1 mL/min. Argon flow usually is pre-fixed, typically at 90 mL/min.

b. Atomic absorption spectrometric equipment: See Section 3111A.6.

3. Reagents

a. Hydrochloric acid, HCl, 5 + 1: Handle conc HCl under a fume hood. If necessary, remove free Cl_2 by stripping conc HCl with helium as described above.

b. Borohydride reagent: Dissolve 0.6 g $NaBH_4$ and 0.5 g NaOH in 100 mL water.

CAUTION: *Sodium borohydride is toxic, flammable, and corrosive.*

c. Selenium reference standard solution, 1000 mg/L: Use commercially available standard; verify that selenium is Se(IV).

d. Intermediate standard solution, 1 mg/L: Dilute 1 mL reference standard solution to 1 L in a volumetric flask with distilled water.

e. Working standard solutions, 5, 10, 20, 30, and 40 µg/L: Dilute 0.5, 1.0, 2.0, 3.0, and 4.0 mL intermediate standard solution to 100 mL in a volumetric flask.

f. Sulfanilamide solution: Prepare a 2.5% (w/v) solution daily; add several drops conc HCl per 50 mL solution to facilitate dissolution.

4. Procedure

a. Sample preparation: See Section 3500-Se or Section 3114B.4*c* and *d* for preparation

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

steps for various Se fractions or total Se.

b. Preconditioning hydride generator: For newly installed tubing, turn on pump for at least 10 to 15 min before instrument calibration. Sample the highest standard for a few minutes to let volatile hydride react with the reactive sites in the transfer lines and on the quartz absorption cell surfaces.

c. Instrument calibration: Depending on total void volume in sample tubing, sampling time of 15 to 20 s generally is sufficient to obtain a steady signal. Between samples, submerge uptake tube in rinse water. Calibrate instrument daily after a 45-min lamp warmup time. Use either the hollow cathode or the electrodeless discharge lamp.

d. Antifoaming agents: Certain samples, particularly wastewater samples containing a high concentration of proteinaceous substances, can cause excessive foaming that could carry the liquid directly into the heated quartz absorption cell and cause splattering of salty deposits onto the windows of the spectrometer. Add a drop of antifoaming agent*#(84) to eliminate this problem.

e. Nitrite removal: After samples have been acidified, or after acid digestion, add 0.1 mL sulfanilamide solution per 10 mL sample and let react for 2 min.

f. Analysis: Follow manufacturer's instructions for operation of analytical equipment.

5. Calculation

Construct a calibration curve based on absorbance vs. standard concentration. Apply dilution factors on diluted samples.

6. Precision and Bias

Working standards were analyzed together with batches of

water samples on a routine production basis. The standards werecompounded using chemically pure sodium selenite and sodiumselenate. The values of Se(IV) + Se(VI) were determined byconverting Se(VI) to Se(IV) by digestion with HCl. Results aretabulated below.

No. Analyses	Mean Se(IV) µg/L	Rel. Dev. %	Se(IV) + Se(VI) µg/L	Rel. Del. %
21	4.3	12	10.3	7
26	8.5	12	19.7	6
22	17.2	7	39.2	8
20	52.8	5	106.0	6

7. Bibliography

REAMER, D.C. & C. VEILOON. 1981. Preparation of biological materials for determination of selenium by hydride generation-AAS. *Anal. Chem.* 53:1192.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

SINEMUS, H.W., M. MELCHER & B. WELZ. 1981. Influence of valence state on the determination of antimony, bismuth, selenium, and tellurium in lake water using the hydride AA technique. *Atomic Spectrosc.* 2:81.

RODEN, D.R. & D.E. TALLMAN. 1982. Determination of inorganic selenium species in groundwaters containing organic interferences by ion chromatography and hydride generation/atomic absorption spectrometry. *Anal. Chem.* 54:307.

CUTTER, G. 1983. Elimination of nitrite interference in the determination of selenium by hydride generation. *Anal. Chim. Acta* 149:391.

NARASAKI, H. & M. IKEDA. 1984. Automated determination of arsenic and selenium by atomic absorption spectrometry with hydride generation. *Anal. Chem.* 56:2059.

WELZ, B. & M. MELCHER. 1985. Decomposition of marine biological tissues for determination of arsenic, selenium, and mercury using hydride-generation and cold-vapor atomic absorption spectrometries. *Anal. Chem.* 57:427.

EBDON, L. & S.T. SPARKES. 1987. Determination of arsenic and selenium in environmental samples by hydride generation-direct current plasma-atomic emission spectrometry. *Microchem. J.* 36:198.

EBDON, L. & J.R. WILKINSON. 1987. The determination of arsenic and selenium in coal by continuous flow hydride-generation atomic absorption spectroscopy and atomic fluorescence spectrometry. *Anal. Chim. Acta.* 194:177.

VOTH-BEACH, L.M. & D.E. SHRADER. 1985. Reduction of interferences in the determination of arsenic and selenium by hydride generation. *Spectroscopy* 1:60.

3120 METALS BY PLASMA EMISSION SPECTROSCOPY*#(85)

3120 A. Introduction

1. General Discussion

Emission spectroscopy using inductively coupled plasma (ICP) was developed in the mid-1960's[1,2] as a rapid, sensitive, and convenient method for the determination of metals in water and wastewater samples.[3-6] Dissolved metals are determined in filtered and acidified samples. Total metals are determined after appropriate digestion. Care must be taken to ensure that potential interferences are dealt with, especially when dissolved solids exceed 1500 mg/L.

2. References

1. GREENFIELD, S., I.L. JONES & C.T. BERRY. 1964. High-pressure plasma-spectroscopic emission sources. *Analyst* 89: 713.
2. WENDT, R.H. & V.A. FASSEL. 1965. Induction-coupled plasma spectrometric excitation source. *Anal. Chem.* 37:920.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Method 200.7. Inductively coupled plasma-atomic emission spectrometric method for trace element analysis of water and wastes. Methods for the Determination of Metals in Environmental Samples–Supplement I. EPA 600/R-94-111, May 1994.
4. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1987. Annual Book of ASTM Standards, Vol. 11.01. American Soc. Testing & Materials, Philadelphia, Pa.
5. FISHMAN, M.J. & W.L. BRADFORD, eds. 1982. A Supplement to Methods for the Determination of Inorganic Substances in Water and Fluvial Sediments. Rep. No. 82-272, U.S. Geological Survey, Washington, D.C.
6. GARBARINO, J.R. & H.E. TAYLOR. 1985. Trace Analysis. Recent Developments and Applications of Inductively Coupled Plasma Emission Spectroscopy to Trace Elemental Analysis of Water. Volume 4. Academic Press, New York, N.Y.

3120 B. Inductively Coupled Plasma (ICP) Method

1. General Discussion

a. Principle: An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field typically oscillating at 27.1 MHz. This field is inductively coupled to the ionized gas by a water-cooled coil surrounding a quartz ‘‘torch’’ that supports and confines the plasma. A sample aerosol is generated in an appropriate nebulizer and spray chamber and is carried into the plasma through an injector tube located within the torch. The sample aerosol is injected directly into the ICP, subjecting the constituent atoms to temperatures of about 6000 to 8000°K.[1] Because this results in almost complete dissociation of molecules, significant reduction in chemical interferences is achieved. The high temperature of the plasma excites atomic emission efficiently. Ionization of a high percentage of atoms produces ionic emission spectra. The ICP provides an optically ‘‘thin’’ source that is not subject to self-absorption except at very high concentrations. Thus linear dynamic ranges of four to six orders of magnitude are observed for many elements.[2]

The efficient excitation provided by the ICP results in low detection limits for many elements. This, coupled with the extended dynamic range, permits effective multielement determination of metals.[3] The light emitted from the ICP is focused onto the entrance slit of either a monochromator or a polychromator that effects dispersion. A precisely aligned exit slit is used to isolate a portion of the emission spectrum for intensity measurement using a photomultiplier tube. The monochromator uses a single exit slit/photomultiplier and may use a computer-controlled scanning mechanism to examine emission wavelengths sequentially. The polychromator uses multiple fixed exit slits and corresponding photomultiplier tubes; it simultaneously monitors all configured wavelengths using a computer-controlled readout system. The sequential approach provides greater wavelength selection while the simultaneous

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

approach can provide greater sample throughput.

b. Applicable metals and analytical limits: Table 3120:I lists elements for which this method applies, recommended analytical wavelengths, and typical estimated instrument detection limits using conventional pneumatic nebulization. Actual working detection limits are sample-dependent. Typical upper limits for linear calibration also are included in Table 3120:I.

c. Interferences: Interferences may be categorized as follows:

1) Spectral interferences—Light emission from spectral sources other than the element of interest may contribute to apparent net signal intensity. Sources of spectral interference include direct spectral line overlaps, broadened wings of intense spectral lines, ion-atom recombination continuum emission, molecular band emission, and stray (scattered) light from the emission of elements at high concentrations.[4] Avoid line overlaps by selecting alternate analytical wavelengths. Avoid or minimize other spectral interference by judicious choice of background correction positions. A wavelength scan of the element line region is useful for detecting potential spectral interferences and for selecting positions for background correction. Make corrections for residual spectral interference using empirically determined correction factors in conjunction with the computer software supplied by the spectrometer manufacturer or with the calculation detailed below. The empirical correction method cannot be used with scanning spectrometer systems if the analytical and interfering lines cannot be precisely and reproducibly located. In addition, if using a polychromator, verify absence of spectral interference from an element that could occur in a sample but for which there is no channel in the detector array. Do this by analyzing single-element solutions of 100 mg/L concentration and noting for each element channel the apparent concentration from the interfering substance that is greater than the element's instrument detection limit.

2) Nonspectral interferences

a) Physical interferences are effects associated with sample nebulization and transport processes. Changes in the physical properties of samples, such as viscosity and surface tension, can cause significant error. This usually occurs when samples containing more than 10% (by volume) acid or more than 1500 mg dissolved solids/L are analyzed using calibration standards containing ≤ 5% acid. Whenever a new or unusual sample matrix is encountered, use the test described in ¶ 4*g*. If physical interference is present, compensate for it by sample dilution, by using matrix-matched calibration standards, or by applying the method of standard addition (see ¶ 5*d* below).

High dissolved solids content also can contribute to instrumental drift by causing salt buildup at the tip of the nebulizer gas orifice. Using prehumidified argon for sample nebulization lessens this problem. Better control of the argon flow rate to the nebulizer using a mass flow controller improves instrument performance.

b) Chemical interferences are caused by molecular compound formation, ionization effects, and thermochemical effects associated with sample vaporization and atomization in the plasma. Normally these effects are not pronounced and can be minimized by careful selection of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

operating conditions (incident power, plasma observation position, etc.). Chemical interferences are highly dependent on sample matrix and element of interest. As with physical interferences, compensate for them by using matrix matched standards or by standard addition (¶ 5*d*). To determine the presence of chemical interference, follow instructions in ¶ 4*g*.

2. Apparatus

a. ICP source: The ICP source consists of a radio frequency (RF) generator capable of generating at least 1.1 KW of power, torch, tesla coil, load coil, impedance matching network, nebulizer, spray chamber, and drain. High-quality flow regulators are required for both the nebulizer argon and the plasma support gas flow. A peristaltic pump is recommended to regulate sample flow to the nebulizer. The type of nebulizer and spray chamber used may depend on the samples to be analyzed as well as on the equipment manufacturer. In general, pneumatic nebulizers of the concentric or cross-flow design are used. Viscous samples and samples containing particulates or high dissolved solids content (>5000 mg/L) may require nebulizers of the Babington type.[5]

b. Spectrometer: The spectrometer may be of the simultaneous (polychromator) or sequential (monochromator) type with air-path, inert gas purged, or vacuum optics. A spectral bandpass of 0.05 nm or less is required. The instrument should permit examination of the spectral background surrounding the emission lines used for metals determination. It is necessary to be able to measure and correct for spectral background at one or more positions on either side of the analytical lines.

3. Reagents and Standards

Use reagents that are of ultra-high-purity grade or equivalent. Redistilled acids are acceptable. Except as noted, dry all salts at 105°C for 1 h and store in a desiccator before weighing. Use deionized water prepared by passing water through at least two stages of deionization with mixed bed cation/anion exchange resins.[6] Use deionized water for preparing all calibration standards, reagents, and for dilution.

a. Hydrochloric acid, HCl, conc and 1+1.

b. Nitric acid, HNO_3, conc.

c. Nitric acid, HNO_3, 1+1: Add 500 mL conc HNO_3 to 400 mL water and dilute to 1 L.

d. Standard stock solutions: See Section 3111B, Section 3111D, and Section 3114B.

CAUTION: *Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.*

1) *Aluminum:* See Section 3111D.3*k*1).

2) *Antimony:* See Section 3111B.3 *j*1).

3) *Arsenic:* See Section 3114B.3*k*1).

4) *Barium:* See Section 3111D.3*k*2).

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

5) *Beryllium:* See Section 3111D.3*k*3).

6) *Boron: Do not dry* but keep bottle tightly stoppered and store in a desiccator. Dissolve 0.5716 g anhydrous H_3BO_3 in water and dilute to 1000 mL; 1 mL = 100 μg B.

7) *Cadmium:* See Section 3111B.3 *j*3).

8) *Calcium:* See Section 3111B.3 *j*4).

9) *Chromium:* See Section 3111B.3 *j*6).

10) *Cobalt:* See Section 3111B.3 *j*7).

11) *Copper*: See Section 3111B.3 *j*8).

12) *Iron:* See Section 3111B.3 *j*11).

13) *Lead:* See Section 3111B.3 *j*12).

14) *Lithium:* See Section 3111B.3 *j*13).

15) *Magnesium:* See Section 3111B.3 *j*14).

16) *Manganese:* See Section 3111B.3 *j*15).

17) *Molybdenum:* See Section 3111D.3*k*4).

18) *Nickel:* See Section 3111B.3 *j*16).

19) *Potassium:* See Section 3111B.3 *j*19).

20) *Selenium:* See Section 3114B.3*n*1).

21) *Silica:* See Section 3111D.3*k*7).

22) *Silver:* See Section 3111B.3 *j*22).

23) *Sodium:* See Section 3111B.3 *j*23).

24) *Strontium:* See Section 3111B.3 *j*24).

25) *Thallium:* See Section 3111B.3 *j*25).

26) *Vanadium:* See Section 3111D.3*k*10).

27) *Zinc:* See Section 3111B.3 *j*27).

e. Calibration standards: Prepare mixed calibration standards containing the concentrations shown in Table 3120:I by combining appropriate volumes of the stock solutions in 100-mL volumetric flasks. Add 2 mL 1+1 HNO_3 and 10 mL 1+1 HCl and dilute to 100 mL with water. Before preparing mixed standards, analyze each stock solution separately to determine possible spectral interference or the presence of impurities. When preparing mixed standards take care that the elements are compatible and stable. Store mixed standard solutions in an FEP fluorocarbon or unused polyethylene bottle. Verify calibration standards initially using the quality control standard; monitor weekly for stability. The following are recommended combinations using the suggested analytical lines in Table 3120:I. Alternative combinations are acceptable.

1) *Mixed standard solution I:* Manganese, beryllium, cadmium, lead, selenium, and zinc.

2) *Mixed standard solution II:* Barium, copper, iron, vanadium, and cobalt.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3) *Mixed standard solution III:* Molybdenum, silica, arsenic, strontium, and lithium.

4) *Mixed standard solution IV:* Calcium, sodium, potassium, aluminum, chromium, and nickel.

5) *Mixed standard solution V:* Antimony, boron, magnesium, silver, and thallium. If addition of silver results in an initial precipitation, add 15 mL water and warm flask until solution clears. Cool and dilute to 100 mL with water. For this acid combination limit the silver concentration to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 d. Higher concentrations of silver require additional HCl.

f. Calibration blank: Dilute 2 mL 1+1 HNO_3 and 10 mL 1+1 HCl to 100 mL with water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

g. Method blank: Carry a reagent blank through entire sample preparation procedure. Prepare method blank to contain the same acid types and concentrations as the sample solutions.

h. Instrument check standard: Prepare instrument check standards by combining compatible elements at a concentration of 2 mg/L.

i. Instrument quality control sample: Obtain a certified aqueous reference standard from an outside source and prepare according to instructions provided by the supplier. Use the same acid matrix as the calibration standards.

j. Method quality control sample: Carry the instrument quality control sample (¶ 3*i*) through the entire sample preparation procedure.

k. Argon: Use technical or welder's grade. If gas appears to be a source of problems, use prepurified grade.

4. Procedure

a. Sample preparation: See Section 3030F.

b. Operating conditions: Because of differences among makes and models of satisfactory instruments, no detailed operating instructions can be provided. Follow manufacturer's instructions. Establish instrumental detection limit, precision, optimum background correction positions, linear dynamic range, and interferences for each analytical line. Verify that the instrument configuration and operating conditions satisfy the analytical requirements and that they can be reproduced on a day-to-day basis. An atom-to-ion emission intensity ratio [Cu(I) 324.75 nm/ Mn(II) 257.61 nm] can be used to reproduce optimum conditions for multielement analysis precisely. The Cu/Mn intensity ratio may be incorporated into the calibration procedure, including specifications for sensitivity and for precision.[7] Keep daily or weekly records of the Cu and Mn intensities and/or the intensities of critical element lines. Also record settings for optical alignment of the polychromator, sample uptake rate, power readings (incident, reflected), photomultiplier tube attenuation, mass flow controller settings, and system maintenance.

c. Instrument calibration: Set up instrument as directed (¶ b). Warm up for 30 min. For polychromators, perform an optical alignment using the profile lamp or solution. Check

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

alignment of plasma torch and spectrometer entrance slit, particularly if maintenance of the sample introduction system was performed. Make Cu/Mn or similar intensity ratio adjustment.

Calibrate instrument according to manufacturer's recommended procedure using calibration standards and blank. Aspirate each standard or blank for a minimum of 15 s after reaching the plasma before beginning signal integration. Rinse with calibration blank or similar solution for at least 60 s between each standard to eliminate any carryover from the previous standard. Use average intensity of multiple integrations of standards or samples to reduce random error.

Before analyzing samples, analyze instrument check standard. Concentration values obtained should not deviate from the actual values by more than ±5% (or the established control limits, whichever is lower).

d. Analysis of samples: Begin each sample run with an analysis of the calibration blank, then analyze the method blank. This permits a check of the sample preparation reagents and procedures for contamination. Analyze samples, alternating them with analyses of calibration blank. Rinse for at least 60 s with dilute acid between samples and blanks. After introducing each sample or blank let system equilibrate before starting signal integration. Examine each analysis of the calibration blank to verify that no carry-over memory effect has occurred. If carry-over is observed, repeat rinsing until proper blank values are obtained. Make appropriate dilutions and acidifications of the sample to determine concentrations beyond the linear calibration range.

e. Instrumental quality control: Analyze instrument check standard once per 10 samples to determine if significant instrument drift has occurred. If agreement is not within ± 5% of the expected values (or within the established control limits, whichever is lower), terminate analysis of samples, correct problem, and recalibrate instrument. If the intensity ratio reference is used, resetting this ratio may restore calibration without the need for reanalyzing calibration standards. Analyze instrument check standard to confirm proper recalibration. Reanalyze one or more samples analyzed just before termination of the analytical run. Results should agree to within ± 5%, otherwise all samples analyzed after the last acceptable instrument check standard analysis must be reanalyzed.

Analyze instrument quality control sample within every run. Use this analysis to verify accuracy and stability of the calibration standards. If any result is not within ± 5% of the certified value, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock solution and a new calibration standard and repeat calibration.

f. Method quality control: Analyze the method quality control sample within every run. Results should agree to within ± 5% of the certified values. Greater discrepancies may reflect losses or contamination during sample preparation.

g. Test for matrix interference: When analyzing a new or unusual sample matrix verify that neither a positive nor negative nonlinear interference effect is operative. If the element is present at a concentration above 1 mg/L, use serial dilution with calibration blank. Results from the analyses of a dilution should be within ± 5% of the original result. Alternately, or if the concentration is either below 1 mg/L or not detected, use a post-digestion addition equal to 1

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

mg/L. Recovery of the addition should be either between 95% and 105% or within established control limits of ± 2 standard deviations around the mean. If a matrix effect causes test results to fall outside the critical limits, complete the analysis after either diluting the sample to eliminate the matrix effect while maintaining a detectable concentration of at least twice the detection limit or applying the method of standard additions.

5. Calculations and Corrections

a. Blank correction: Subtract result of an adjacent calibration blank from each sample result to make a baseline drift correction. (Concentrations printed out should include negative and positive values to compensate for positive and negative baseline drift. Make certain that the calibration blank used for blank correction has not been contaminated by carry-over.) Use the result of the method blank analysis to correct for reagent contamination. Alternatively, intersperse method blanks with appropriate samples. Reagent blank and baseline drift correction are accomplished in one subtraction.

b. Dilution correction: If the sample was diluted or concentrated in preparation, multiply results by a dilution factor (*DF*) calculated as follows:

$$DF = \frac{\text{Final weight or volume}}{\text{Initial weight or volume}}$$

c. Correction for spectral interference: Correct for spectral interference by using computer software supplied by the instrument manufacturer or by using the manual method based on interference correction factors. Determine interference correction factors by analyzing single-element stock solutions of appropriate concentrations under conditions matching as closely as possible those used for sample analysis. Unless analysis conditions can be reproduced accurately from day to day, or for longer periods, redetermine interference correction factors found to affect the results significantly each time samples are analyzed.[7,8] Calculate interference correction factors (K_{ij}) from apparent concentrations observed in the analysis of the high-purity stock solutions:

$$K_{ij} = \frac{\text{Apparent concentration of element } i}{\text{Actual concentration of interfering element } j}$$

where the apparent concentration of element *i* is the difference between the observed concentration in the stock solution and the observed concentration in the blank. Correct sample concentrations observed for element *i* (already corrected for baseline drift), for spectral interferences from elements *j*, *k*, and *l*; for example:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Concentration of element i corrected for spectral interference

$$= \text{Observed concentration of } i - (K_{ij})\,\text{Observed concentration of interfering element } j - (K_{ik})\,\text{Observed concentration of interfering element } k - (K_{il})\,\text{Observed concentration of interfering element } l$$

Interference correction factors may be negative if background correction is used for element *i*. A negative K_{ij} can result where an interfering line is encountered at the background correction wavelength rather than at the peak wavelength. Determine concentrations of interfering elements *j*, *k*, and *l* within their respective linear ranges. Mutual interferences (*i* interferes with *j* and *j* interferes with *i*) require iterative or matrix methods for calculation.

d. Correction for nonspectral interference: If nonspectral interference correction is necessary, use the method of standard additions. It is applicable when the chemical and physical form of the element in the standard addition is the same as in the sample, *or* the ICP converts the metal in both sample and addition to the same form; the interference effect is independent of metal concentration over the concentration range of standard additions; and the analytical calibration curve is linear over the concentration range of standard additions.

Use an addition not less than 50% nor more than 100% of the element concentration in the sample so that measurement precision will not be degraded and interferences that depend on element/interferent ratios will not cause erroneous results. Apply the method to all elements in the sample set using background correction at carefully chosen off-line positions. Multielement standard addition can be used if it has been determined that added elements are not interferents.

e. Reporting data: Report analytical data in concentration units of milligrams per liter using up to three significant figures. Report results below the determined detection limit as not detected less than the stated detection limit corrected for sample dilution.

6. Precision and Bias

As a guide to the generally expected precision and bias, see the linear regression equations in Table 3120:II.[9] Additional interlaboratory information is available.[10]

7. References

1. FAIRES, L.M., B.A. PALMER, R. ENGLEMAN, JR. & T.M. NIEMCZYK. 1984. Temperature determinations in the inductively coupled plasma using a Fourier transform

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

spectrometer. *Spectrochim. Acta 39B:819.*

2. BARNES, R.M. 1978. Recent advances in emission spectroscopy: inductively coupled plasma discharges for spectrochemical analysis. *CRC Crit. Rev. Anal. Chem.* 7:203.
3. PARSONS, M.L., S. MAJOR & A.R. FORSTER. 1983. Trace element determination by atomic spectroscopic methods - State of the art. *Appl. Spectrosc.* 37:411.
4. LARSON, G.F., V.A. FASSEL, R. K. WINGE & R.N. KNISELEY. 1976. Ultratrace analysis by optical emission spectroscopy: The stray light problem. *Appl. Spectrosc.* 30:384.
5. GARBARINO, J.R. & H.E. TAYLOR. 1979. A Babington-type nebulizer for use in the analysis of natural water samples by inductively coupled plasma spectrometry. *Appl. Spectrosc.* 34:584.
6. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1988. Standard specification for reagent water, D1193-77 (reapproved 1983). Annual Book of ASTM Standards. American Soc. for Testing & Materials, Philadelphia, Pa.
7. BOTTO, R.I. 1984. Quality assurance in operating a multielement ICP emission spectrometer. *Spectrochim. Acta* 39B:95.
8. BOTTO, R.I. 1982. Long-term stability of spectral interference calibrations for inductively coupled plasma atomic emission spectrometry. *Anal. Chem.* 54:1654.
9. MAXFIELD, R. & B. MINDAK. 1985. EPA Method Study 27, Method 200. 7 (Trace Metals by ICP). EPA-600/S4-85/05. National Technical Information Serv., Springfield, Va.
10. GARBARINO, J.R., B.E. JONES, G. P. STEIN, W.T. BELSER & H.E. TAYLOR. 1985. Statistical evaluation of an inductively coupled plasma atomic emission spectrometric method for routine water quality testing. *Appl. Spectrosc.* 39:53.

3125 METALS BY INDUCTIVELY COUPLED PLASMA/MASS SPECTROMETRY*#(86)

3125 A. Introduction

1. General Discussion

This method is used for the determination of trace metals and metalloids in surface, ground, and drinking waters by inductively coupled plasma/mass spectrometry (ICP/MS). It may also be suitable for wastewater, soils, sediments, sludge, and biological samples after suitable digestion followed by dilution and/or cleanup.[1,2] Additional sources of information on quality assurance and other aspects of ICP/MS analysis of metals are available.[3-5]

The method is intended to be performance-based, allowing extension of the elemental analyte

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

list, implementation of ‘‘clean’’ preparation techniques as they become available, and other appropriate modifications of the base method as technology evolves. Preferably validate modifications to the base method by use of the quality control standards specified in the method.

Instrument detection limits for many analytes are between 1 and 100 ng/L. The method is best suited for the determination of metals in ambient or pristine fresh-water matrices. More complex matrices may require some type of cleanup to reduce matrix effects to a manageable level. Various cleanup techniques are available to reduce matrix interferences and/or concentrate analytes of interest.[6-10]

This method is ideally used by analysts experienced in the use of ICP/MS, the interpretation of spectral and matrix interference, and procedures for their correction. Preferably demonstrate analyst proficiency through analysis of a performance evaluation sample before the generation of data.

2. References

1. MONTASER, A. & D.W. GOLIGHTLY, eds. 1992. Inductively Coupled Plasmas in Analytical Atomic Spectrometry, 2nd ed. VCH Publishers, Inc., New York, N.Y.
2. DATE, A.R. & A.L. GRAY. 1989. Applications of Inductively Coupled Plasma Mass Spectrometry. Blackie & Son, Ltd., Glasgow, U.K.
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry, Method 200.8. U.S. Environmental Protection Agency, Environmental Monitoring Systems Lab., Cincinnati, Ohio.
4. LONGBOTTOM, J.E., T.D. MARTIN, K.W. EDGELL, S.E. LONG, M.R. PLANTZ & B.E. WARDEN. 1994. Determination of trace elements in water by inductively coupled plasma-mass spectrometry: collaborative study. *J. AOAC Internat.* 77:1004.
5. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1995. Method 1638: Determination of trace elements in ambient waters by inductively coupled plasma-mass spectrometry. U.S. Environmental Protection Agency, Off. Water, Washington, D.C.
6. MCLAREN, J.W., A.P. MYKYTIUK, S.N. WILLIE & S. S. BERMAN. 1985. Determination of trace metals in seawater by inductively coupled plasma mass spectrometry with preconcentration on silica-immobilized 8-hydroxyquinoline. *Anal. Chem.* 57:2907.
7. BURBA, P. & P.G. WILLMER. 1987. Multielement preconcentration for atomic spectroscopy by sorption of dithiocarbamate metal complexes (e.g., HMDC) on cellulose collectors. *Fresenius Z. Anal. Chem.* 329: 539.
8. WANG, X. & R.M. BARNES. 1989. Chelating resins for on-line flow injection preconcentration with inductively coupled plasma atomic emission spectroscopy. *J. Anal. Atom. Spectrom.* 4:509.
9. SIRIRAKS, A., H.M. KINGSTON & J.M. RIVIELLO. 1990. Chelation ion chromatography as a method for trace elemental analysis in complex environmental and biological samples. *Anal. Chem.* 62:1185.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

10. PUGET SOUND WATER QUALITY AUTHORITY. 1996. Recommended Guidelines for Measuring Metals in Puget Sound Marine Water, Sediment and Tissue Samples. Appendix D: Alternate Methods for the Analysis of Marine Water Samples. Puget Sound Water Quality Authority, Olympia, Wash.

3125 B. Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) Method

1. General Discussion

a. Principle: Sample material is introduced into an argon-based, high-temperature radio-frequency plasma, usually by pneumatic nebulization. Energy transfer from the plasma to the sample stream causes desolvation, atomization, and ionization of target elements. Ions generated by these energy-transfer processes are extracted from the plasma through a differential vacuum interface, and separated on the basis of their mass-to-charge ratio by a mass spectrometer. The mass spectrometer usually is of the quadrupole or magnetic sector type. The ions passing through the mass spectrometer are counted, usually by an electron multiplier detector, and the resulting information processed by a computer-based data-handling system.

b. Applicable elements and analytical limits: This method is suitable for aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, selenium, silver, strontium, thallium, uranium, vanadium, and zinc. The method is also acceptable for other elemental analytes as long as the same quality assurance practices are followed. The basic element suite and recommended analytical masses are given in Table 3125:I.

Typical instrument detection limits (IDL)[1,2] for method analytes are presented in Table 3125:I. Determine the IDL and method detection level (or limit) (MDL) for all analytes before method implementation. Section 1030 contains additional information and approaches for the evaluation of detection capabilities.

The MDL is defined in Section 1010C and elsewhere.[2] Determination of the MDL for each element is critical for complex matrices such as seawater, brines, and industrial effluents. The MDL will typically be higher than the IDL, because of background analyte in metals preparation and analysis laboratories and matrix-based interferences. Determine both IDL and MDL upon initial implementation of this method, and then yearly or whenever the instrument configuration changes or major maintenance occurs, whichever comes first.

Determine linear dynamic ranges (LDR) for all method analytes. LDR is defined as the maximum concentration of analyte above the highest calibration point where analyte response is within ±10% of the theoretical response. When determining linear dynamic ranges, avoid using unduly high concentrations of analyte that might damage the detector. Determine LDR on multielement mixtures, to account for possible interelement effects. Determine LDR on initial implementation of this method, and then yearly.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

c. Interferences: ICP/MS is subject to several types of interferences.

1) Isotopes of different elements that form ions of the same nominal mass-to-charge ratio are not resolved by the quadrupole mass spectrometer, and cause isobaric elemental interferences. Typically, ICP/MS instrument operating software will have all known isobaric interferences entered, and will perform necessary calculations automatically. Table 3125:II shows many of the commonly used corrections. Monitor the following additional masses: ^{83}Kr, ^{99}Ru, ^{118}Sn, and ^{125}Te. It is necessary to monitor these masses to correct for isobaric interference caused by ^{82}Kr on ^{82}Se, by ^{98}Ru on ^{98}Mo, by ^{114}Sn on ^{114}Cd, and by ^{123}Te on ^{123}Sb. Monitor ArCl at mass 77, to estimate chloride interferences. Verify that all elemental and molecular correction equations used in this method are correct and appropriate for the mass spectrometer used and sample matrix.

2) Abundance sensitivity is an analytical condition in which the tails of an abundant mass peak contribute to or obscure adjacent masses. Adjust spectrometer resolution to minimize these interferences.

3) Polyatomic (molecular) ion interferences are caused by ions consisting of more than one atom and having the same nominal mass-to-charge ratio as the isotope of interest. Most of the common molecular ion interferences have been identified and are listed in Table 3125:III. Because of the severity of chloride ion interference on important analytes, particularly arsenic and selenium, hydrochloric acid is not recommended for use in preparation of any samples to be analyzed by ICP/MS. The mathematical corrections for chloride interferences only correct chloride to a concentration of 0.4%. Because chloride ion is present in most environmental samples, it is critical to use chloride correction equations for affected masses. A high-resolution ICP/MS may be used to resolve interferences caused by polyatomic ions. Polyatomic interferences are strongly influenced by instrument design and plasma operating conditions, and can be reduced in some cases by careful adjustment of nebulizer gas flow and other instrument operating parameters.

4) Physical interferences include differences in viscosity, surface tension, and dissolved solids between samples and calibration standards. To minimize these effects, dissolved solid levels in analytical samples should not exceed 0.5%. Dilute water and wastewater samples containing dissolved solids at or above 0.5% before analysis. Use internal standards for correction of physical interferences. Any internal standards used should demonstrate comparable analytical behavior to the elements being determined.

5) Memory interferences occur when analytes from a previous sample or standard are measured in the current sample. Use a sufficiently long rinse or flush between samples to minimize this type of interference. If memory interferences persist, they may be indications of problems in the sample introduction system. Severe memory interferences may require disassembly and cleaning of the entire sample introduction system, including the plasma torch, and the sampler and skimmer cones.

6) Ionization interferences result when moderate (0.1 to 1%) amounts of a matrix ion change

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

the analyte signal. This effect, which usually reduces the analyte signal, also is known as ‘‘suppression.’’ Correct for suppression by use of internal standardization techniques.

2. Apparatus

a. Inductively coupled plasma/mass spectrometer: Instrumentation, available from several manufacturers, includes a mass spectrometer detector, inductively coupled plasma source, mass flow controllers for regulation of ICP gas flows, peristaltic pump for sample introduction, and a computerized data acquisition and instrument control system. An x-y autosampler also may be used with appropriate control software.

b. Laboratory ware: Use precleaned plastic laboratory ware for standard and sample preparation. Teflon,*#(87) either tetrafluoroethylene hexafluoropropylene-copolymer (FEP), polytetrafluoroethylene (PTFE), or perfluoroalkoxy PTFE (PFA) is preferred for standard preparation and sample digestion, while high-density polyethylene (HDPE) and other dense, metal-free plastics may be acceptable for internal standards, known-addition solutions, etc. Check each new lot of autosampler tubes for suitability, and preclean autosampler tubes and pipettor tips (see Section 3010C.2).

c. Air displacement pipets, 10 to 100 µL, 100 to 1000 µL, and 1 to 10 mL size.

d. Analytical balance, accurate to 0.1 mg.

e. Sample preparation apparatus, such as hot plates, microwave digestors, and heated sand baths. Any sample preparation device has the potential to introduce trace levels of target analytes to the sample.

f. Clean hood (optional), Class 100 (certified to contain less than 100 particles/m^3), for sample preparation and manipulation. Preferably perform all sample manipulations, digestions, dilutions, etc. in a certified Class 100 environment. Alternatively, handle samples in glove boxes, plastic fume hoods, or other environments where random contamination by trace metals can be minimized.

3. Reagents

a. Acids: Use ultra-high-purity grade (or equivalent) acids to prepare standards and to process sample. Redistilled acids are acceptable if each batch is demonstrated to be free from contamination by target analytes. Use extreme care in the handling of acids in the laboratory to avoid contamination of the acids with trace levels of metals.

1) *Nitric acid,* HNO_3, conc (specific gravity 1.41).

2) *Nitric acid,* 1 + 1: Add 500 mL conc HNO_3 to 500 mL reagent water.

3) *Nitric acid,* 2%: Add 20 mL conc HNO_3 to 100 mL reagent water; dilute to 1000 mL.

4) *Nitric acid,* 1%: Add 10 mL conc HNO_3 to 100 mL reagent water; dilute to 1000 mL.

b. Reagent water: Use water of the highest possible purity for blank, standard, and sample preparation (see Section 1080). Alternatively, use the procedure described below to produce

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

water of acceptable quality. Other water preparation regimes may be used, provided that the water produced is metal-free. Reagent water containing trace amounts of analyte elements will cause erroneous results.

Produce reagent water using a softener/reverse osmosis unit with subsequent UV sterilization. After the general deionization system use a dual-column strong acid/strong base ion exchange system to polish laboratory reagent water before production of metal-free water. Use a multi-stage reagent water system, with two strong acid/strong base ion exchange columns and an activated carbon filter for organics removal for final polishing of laboratory reagent water. Use only high-purity water for preparation of samples and standards.

c. Stock, standard, and other required solutions: See Section 3120B.3*d* for preparation of standard stock solutions from elemental materials (pure metals, salts). Preferably, purchase high-purity commercially prepared stock solutions and dilute to required concentrations. Single- or multi-element stock solutions (1000 mg/L) of the following elements are required: aluminum, antimony, arsenic, barium, beryllium, cerium, cadmium, chromium, cobalt, copper, germanium, indium, lead, magnesium, manganese, molybdenum, nickel, rhodium, scandium, selenium, silver, strontium, terbium, thallium, thorium, uranium, vanadium, and zinc. Prepare internal standard stock separately from target element stock solution. The potential for incompatibility between target elements and/or internal standards exists, and could cause precipitation or other solution instability.

1) *Internal standard stock solution:* Lithium, scandium, germanium, indium, and thorium are suggested as internal standards. The following masses are monitored: ^{6}Li, ^{45}Sc, ^{72}Ge, ^{115}In, and ^{232}Th. Add to all samples, standards, and quality control (QC) samples a level of internal standard that will give a suitable counts/second (cps) signal (for most internal standards, 200 000 to 500 000 cps; for lithium, 20 000 to 70 000 cps). Minimize error introduced by dilution during this addition by using an appropriately high concentration of internal standard mix solution. Maintain volume ratio for all internal standard additions.

Prepare internal standard mix as follows: Prepare a nominal 50-mg/L solution of ^{6}Li by dissolving 0.15 g $^{6}Li_2CO_3$ (isotopically pure, i.e., 95% or greater purity†#(88)) in a minimal amount of 1:1 HNO_3. Pipet 5.0 mL 1000-mg/L scandium, germanium, indium, and thorium standards into the lithium solution, dilute resulting solution to 500.0 mL, and mix thoroughly. The resultant concentration of Sc, Ge, In, and Th will be 10 mg/L. Older instruments may require higher levels of internal standard to achieve acceptable levels of precision.

Other internal standards, such as rhodium, yttrium, terbium, holmium, and bismuth may also be used in this method. Ensure that internal standard mix used is stable and that there are no undesired interactions between elements.

Screen all samples for internal standard elements before analysis. The analysis of a few representative samples for internal standards should be sufficient. Analyze samples ‘‘as received’’ or ‘‘as digested’’ (before addition of internal standard), then add internal standard mix and reanalyze. Monitor counts at the internal standard masses. If the ‘‘as received’’ or ‘‘as

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

digested'' samples show appreciable detector counts (10% or higher of samples with added internal standard), dilute sample or use an alternate internal standard. If the internal standard response of the sample with the addition is not within 70 to 125% of the response for a calibration blank with the internal standard added, either dilute the sample before analysis, or use an alternate internal standard. During actual analysis, monitor internal standard masses and note all internal standard recoveries over 125% of internal standard response in calibration blank. Interpret results for these samples with caution.

The internal standard mix may be added to blanks, standards, and samples by pumping the solution so it is mixed with the sample stream in the sample introduction process.

2) *Instrument optimization/tuning solution,* containing the following elements: barium, beryllium, cadmium, cerium, cobalt, copper, germanium, indium, magnesium, rhodium, scandium, terbium, thallium, and lead. Prepare this solution in 2% HNO_3. This mix includes all common elements used in optimization and tuning of the various ICP/MS operational parameters. It may be possible to use fewer elements in this solution, depending on the instrument manufacturer's recommendations.

3) *Calibration standards,* 0, 5, 10, 20, 50, and 100 µg/L.‡#(89) Other calibration regimes are acceptable, provided the full suite of quality assurance samples and standards is run to validate these method changes. Fewer standards may be used, and a two-point blank/mid-range calibration technique commonly used in ICP optical methods should also produce acceptable results. Calibrate all analytes using the selected concentrations. Prepare all calibration standards and blanks in a matrix of 2% nitric acid. Add internal standard mix to all calibration standards to provide appropriate count rates for interference correction. NOTE: All standards and blanks used in this method have the internal standard mix added at the same ratio.

4) *Method blank,* consisting of reagent water (¶ 3*b*) taken through entire sample preparation process. For dissolved samples, take reagent water through same filtration and preservation processes used for samples. For samples requiring digestion, process reagent water with the same digestion techniques as samples. Add internal standard mix to method blank.

5) *Calibration verification standard:* Prepare a mid-range standard, from a source different from the source of the calibration standards, in 2% HNO_3, with equivalent addition of internal standard.

6) *Calibration verification blank:* Use 2% HNO_3.

7) *Laboratory fortified blank* (optional)*:* Prepare solution with 2% nitric acid and method analytes added at about 50 µg/L. This standard, sometimes called a laboratory control sample (LCS), is used to validate digestion techniques and known-addition levels.

8) *Reference materials:* Externally prepared reference material, preferably from National Institute of Standards and Technology (NIST) 1643 series or equivalent.

9) *Known-addition solution for samples:* Add stock standard to sample in such a way that volume change is less than 5%. In the absence of information on analyte levels in the sample,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

prepare known additions at around 50 μg/L. If analyte concentration levels are known, add at 50 to 200% of the sample levels. For samples undergoing digestion, make additions before digestion. For the determination of dissolved metals, make additions after filtration, preferably immediately before analysis.

10) *Low-level standards:* Use both a 0.3- and a 1.0-μg/L standard when expected analyte concentration is below 5 μg/L. Prepare both these standards in 2% nitric acid.

Prepare volumetrically a mixed standard containing the method analytes at desired concentration(s) (0.30 μg/L, 1.0 μg/L, or both). Prepare weekly in 100-mL quantities.

d. Argon: Use a prepurified grade of argon unless it can be demonstrated that other grades can be used successfully. The use of prepurified argon is usually necessary because of the presence of krypton as an impurity in technical argon. ^{82}Kr interferes with the determination of ^{82}Se. Monitor ^{83}Kr at all times.

4. Procedures

a. Sample preparation: See Section 3010 and Section 3020 for general guidance regarding sampling and quality control. See Section 3030E for recommended sample digestion technique for all analytes except silver and antimony. If silver and antimony are target analytes, use method given in 3030F, paying special attention to interferences caused by chloride ion, and using all applicable elemental corrections. Alternative digestion techniques and additional guidance on sample preparation are available.[3,4]

Ideally use a ‘‘clean’’ environment for any sample handling, manipulation, or preparation. Preferably perform all sample manipulations in a Class 100 clean hood or room to minimize potential contamination artifacts in digested or filtered samples.

b. Instrument operating conditions: Follow manufacturer’s standard operating procedures for initialization, mass calibration, gas flow optimization, and other instrument operating conditions. Maintain complete and detailed information on the operational status of the instrument whenever it is used.

c. Analytical run sequence: A suggested analytical run sequence, including instrument tuning/optimization, checking of reagent blanks, instrument calibration and calibration verification, analysis of samples, and analysis of quality control samples and blanks, is given in Table 3125:IV.

d. Instrument tuning and optimization: Follow manufacturer’s instructions for optimizing instrument performance. The most important optimization criteria include nebulizer gas flows, detector and lens voltages, radio-frequency forward power, and mass calibration. Periodically check mass calibration and instrument resolution. Ideally, optimize the instrument to minimize oxide formation and doubly-charged species formation. Measure the CeO/Ce ratio to monitor oxide formation, and measure doubly-charged species by determination of the Ba^{2+}/Ba^{+} ratio. Both these ratios should meet the manufacturer’s criteria before instrument calibration. Monitor background counts at mass 220 after optimization and compare with manufacturer’s criteria. A

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

summary of performance criteria related to optimization and tuning, calibration, and analytical performance for this method is given in Table 3125:V.

e. Instrument calibration: After optimization and tuning, calibrate instrument using an appropriate range of calibration standards. Use appropriate regression techniques to determine calibration lines or curves for each analyte. For acceptable calibrations, correlation coefficients for regression curves are ideally 0.995 or greater.

Immediately after calibration, run initial calibration verification standard, ¶ 3*c*5); acceptance criteria are ±10% of known analyte concentration. Next run initial calibration verification blank, ¶ 3*c*6); acceptance criteria are ideally ± the absolute value of the instrument detection limit for each analyte, but in practice, ± the absolute value of the laboratory reporting limit or the laboratory method detection limit for each analyte is acceptable. Verify low-level calibration by running 0.3- and/or 1.0-µg/L standards, if analyte concentrations are less than 5 µg/L.

f. Sample analysis: Ensure that all vessels and reagents are free from contamination. During analytical run (see Table 3125:IV), include quality control analyses according to schedule of Table 3125:VI, or follow project-specific QA/QC protocols.

Internal standard recoveries must be between 70% and 125% of internal standard response in the laboratory-fortified blank; otherwise, dilute sample, add internal standard mix, and reanalyze.

Make known-addition analyses for each separate matrix in a digestion or filtration batch.

5. Calculations and Corrections

Configure instrument software to report internal standard corrected results. For water samples, preferably report results in micrograms per liter. Report appropriate number of significant figures.

a. Correction for dilutions and solids: Correct all results for dilutions, and raise reporting limit for all analytes reported from the diluted sample by a corresponding amount. Similarly, if results for solid samples are to be determined, use Method 2540B to determine total solids. Report results for solid samples as micrograms per kilogram, dry weight. Correct all results for solids content of solid samples. Use the following equation to correct solid or sediment sample results for dilution during digestion and moisture content:

$$R_{corr} = \frac{R_{uncorr} \times V}{W \times \%\ TS/100}$$

where:

R_{corr} = corrected result, µg/kg,
R_{uncorr} = uncorrected elemental result, µg/L,
V = volume of digestate (after digestion), L,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

W = mass of the wet sample, kg, and
% TS = percent total solids determined in the solid sample.

b. Compensation for interferences: Use instrument software to correct for interferences listed previously for this method. See Table 3125:III for a listing of the most common molecular ion interferences.

c. Data reporting: Establish appropriate reporting limits for method analytes based on instrument detection limits and the laboratory blank. For regulatory programs, ensure that reporting limits for method analytes are a factor of three below relevant regulatory criteria.

If method blank contamination is typically random, sporadic, or otherwise not in statistical control, do not correct results for the method blank. Consider the correction of results for laboratory method blanks only if it can be demonstrated that the concentration of analytes in the method blank is within statistical control over a period of months. Report all method blank data explicitly in a manner identical to sample reporting procedures.

d. Documentation: Maintain documentation for the following (where applicable): instrument tuning, mass calibration, calibration verification, analyses of blanks (method, field, calibration, and equipment blanks), IDL and MDL studies, analyses of samples and duplicates with known additions, laboratory and field duplicate information, serial dilutions, internal standard recoveries, and any relevant quality control charts.

Also maintain, and keep available for review, all raw data generated in support of the method.[5]

6. Method Performance

Table 3125:I presents instrument detection limit (IDL) data generated by this method; this represents optimal state-of-the-art instrument detection capabilities, not recommended method detection or reporting limits. Table 3125:VII through IX contain single-laboratory, single-operator, single-instrument performance data generated by this method for calibration verification standards, low-level standards, and known-addition recoveries for fresh-water matrices. Performance data for this method for some analytes are not currently available. However, performance data for similar ICP/MS methods are available in the literature.[1,4]

7. References

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry, Method 200.8. U.S. Environmental Protection Agency, Environmental Monitoring Systems Lab., Cincinnati, Ohio.
2. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1984. Definition and procedure for the determination of the method detection limit, revision 1.11. 40 CFR 136, Appendix B.
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1991. Methods for the determination of metals in environmental samples. U.S. Environmental Protection Agency, Off.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Research & Development, Washington D.C.

4. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1995. Method 1638: Determination of trace elements in ambient waters by inductively coupled plasma mass spectrometry. U.S. Environmental Protection Agency, Off. Water, Washington, D.C.
5. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1995. Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring. U.S. Environmental Protection Agency, Off. Water, Washington, D.C.

8. Bibliography

GRAY, A.L. 1974. A plasma source for mass analysis. *Proc. Soc. Anal. Chem.* 11:182.

HAYHURST, A.N. & N.R. TELFORD. 1977. Mass spectrometric sampling of ions from atmospheric pressure flames. I. Characteristics and calibration of the sampling system. *Combust. Flame*. 67.

HOUK, R.S., V.A. FASSEL, G.D. FLESCH, H.J. SVEC, A.L. GRAY & C.E. TAYLOR. 1980. Inductively coupled argon plasma as an ion source for mass spectrometric determination of trace elements. *Anal. Chem.* 52:2283.

DOUGLAS, D.J. & J.B. FRENCH. 1981. Elemental analysis with a microwave-induced plasma/quadrupole mass spectrometer system. *Anal. Chem.* 53:37.

HOUK, R.S., V.A. FASSEL & H.J. SVEC. 1981. Inductively coupled plasma-mass spectrometry: Sample introduction, ionization, ion extraction and analytical results. *Dyn. Mass Spectrom*. 6:234.

OLIVARES, J.A. & R.S. HOUK. 1985. Ion sampling for inductively coupled plasma mass spectrometry. *Anal. Chem.* 57:2674.

HOUK, R.S. 1986. Mass spectrometry of inductively coupled plasmas. *Anal. Chem*. 58:97.

THOMPSON, J.J. & R.S. HOUK. 1986. Inductively coupled plasma mass spectrometric detection for multielement flow injection analysis and elemental speciation by reversed-phase liquid chromatography. *Anal. Chem.* 58:2541.

VAUGHAN, M.A. & G. HORLICK. 1986. Oxide, hydroxide, and doubly charged analyte species in inductively coupled plasma/mass spectrometry. *Appl. Spectrosc.* 40:434.

GARBARINO, J.R. & H.E. TAYLOR. 1987. Stable isotope dilution analysis of hydrologic samples by inductively coupled plasma mass spectrometry. *Anal. Chem.* 59:1568.

BEAUCHEMIN, D., J.W. MCLAREN, A.P. MYKYTIUK & S.S. BERMAN. 1987. Determination of trace metals in a river water reference material by inductively coupled plasma mass spectrometry. *Anal. Chem.* 59:778.

THOMPSON, J.J. & R.S. HOUK. 1987. A study of internal standardization in inductively coupled plasma-mass spectrometry. *Appl. Spectrosc.* 41:801.

JARVIS, K.E., A.L. GRAY & R.S. HOUK. 1992. Inductively Coupled Plasma Mass Spectrometry. Blackie Academic & Professional, Chapman & Hall, New York, N.Y.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TAYLOR, D.B., H.M. KINGSTON, D.J. NOGAY, D. KOLLER & R. HUTTON. 1996. On-line solid-phase chelation for the determination of eight metals in environmental waters by ICP-MS. *JAAS* 11:187.

KINGSTON, H.M.S. & S. HASWELL, eds. 1997. Microwave Enhanced Chemistry: Fundamentals, Sample Preparation, and Applications. ACS Professional Reference Book Ser., American Chemical Soc., Washington, D.C.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1998. Inductively coupled plasma-mass spectrometry, Method 6020. *In* Solid Waste Methods. SW846, Update 4, U.S. Environmental Protection Agency, Environmental Monitoring Systems Lab., Cincinnati, Ohio.

3130 METALS BY ANODIC STRIPPING VOLTAMMETRY*#(90)

3130 A. Introduction

Anodic stripping voltammetry (ASV) is one of the most sensitive metal analysis techniques; it is as much as 10 to 100 times more sensitive than electrothermal atomic absorption spectroscopy for some metals. This corresponds to detection limits in the nanogram-per-liter range. The technique requires no sample extraction or preconcentration, it is nondestructive, and it allows simultaneous determination of four to six trace metals, utilizing inexpensive instrumentation. The disadvantages of ASV are that it is restricted to amalgam-forming metals, analysis time is longer than for spectroscopic methods, and interferences and high sensitivity can present severe limitations. The analysis should be performed only by analysts skilled in ASV methodology because of the interferences and potential for trace background contamination.

3130 B. Determination of Lead, Cadmium, and Zinc

1. General Discussion

a. Principle: Anodic stripping voltammetry is a two-step electroanalytical technique. In the preconcentration step, metal ions in the sample solution are reduced at negative potential and concentrated into a mercury electrode. The concentration of the metal in the mercury is 100 to 1000 times greater than that of the metal ion in the sample solution. The preconcentration step is followed by a stripping step applying a positive potential scan. The amalgamated metal is oxidized rapidly and the accompanying current is proportional to metal concentration.

b. Detection limits and working range: The limit of detection for metal determination using ASV depends on the metal determined, deposition time, stirring rate, solution pH, sample matrix, working electrode (hanging mercury drop electrode, HMDE, or thin mercury film electrode, TMFE), and mode of the stripping potential scan (square wave or differential pulse). Cadmium, lead, and zinc are concentrated efficiently during pre-electrolysis because of their high solubility

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

in mercury and thus have low detection limits (<1 μg/L). Long deposition times and high stirring rates increase the concentration of metal preconcentrated in the mercury phase and reduce detection limits. The effects of solution pH and matrix are more complicated. In general, add a high concentration of inert electrolyte to samples to maintain a high, constant ionic strength. Acidify sample to a low pH or add a pH buffer. If the pH buffer or other component of the sample matrix complexes the metal (3130B.1*c*), detection limits often are increased.

The choice of working electrode is determined largely by the working range of concentration required. The HMDE is best suited for analysis from approximately 1 μg/L to 10 mg/L, while the TMFE is superior for detection below 1 μg/L.

c. Interferences: Major interferences include intermetallic compound formation, overlapping stripping peaks, adsorption of organics, and complexation. Intermetallic compounds can form in the mercury phase when high concentrations of certain metals are present simultaneously. Zinc forms intermetallic compounds with cobalt and nickel, and both zinc and cadmium form intermetallic compounds with copper, silver, and gold. As a result, the stripping peak for the constituent metals may be severely depressed or shifted and additional peaks due to intermetallic compound stripping may be observed. Minimize or avoid intermetallic compound formation by use of a hanging mercury drop electrode instead of a thin film mercury electrode when metal concentrations are above 1 μg/L, application of a preconcentration potential sufficiently negative to reduce the desired but not the interfering metal, and use of a relatively short preconcentration period followed by a relatively large pulse modulation (50 mV) during the stripping stage. In general, suspect formation of intermetallic compounds if metals are present in concentrations above 1 mg/L. If metals are present at concentrations above 10 mg/L, do not use anodic stripping voltammetry. Concentrations above 10 mg/L usually can be quantitated by methods such as those given in Section 3111 and Section 3120.

Separate overlapping stripping peaks by various methods, including appropriate choice of buffer and electrolyte.[1-3] If only one of the metal peaks is of interest, eliminate interfering peaks by selective complexation with a suitable ligand, such as EDTA. Judicious choice of preconcentration potential can result in the deposition of the selected metal but not the interfering metal in the mercury electrode. Selection of buffer/ligand also may help to distinguish metals during the preconcentration step. Alternatively, use ‘‘medium exchange,’’ in which preconcentration is performed with the electrodes in the sample and stripping is performed in a different electrolyte solution. In this procedure, metals are deposited from the sample into the amalgam as usual, but they may be stripped into a medium that provides different stripping peak potentials for the overlapping metals.

Minimize interferences from adsorption of organic compounds and complexation by removal of the organic matter. Digest samples with high-purity acids as described in Section 3030. Make standard additions to determine if complexation or adsorption remains a problem. Analyze a metal-free solution with a matrix similar to that of the sample both before and after addition of known quantities of standard. Repeat procedure for sample. If the slope of the stripping current versus added metal is significantly different in the sample relative to the metal-free solution,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

digest sample further. The choice of stripping waveform also is important. While both square-wave and differential-pulse stripping attempt to minimize the contribution of adsorption currents to the total measured stripping current, square-wave stripping does this more effectively. Thus, use square-wave stripping instead of differential-pulse stripping when adsorption occurs.

2. Apparatus

a. Electrochemical analyzer: The basic electrochemical analyzer for ASV applications contains a three-electrode potentiostat, which very precisely controls potential applied to the working electrode relative to the reference electrode, and a sensitive current measuring device. It is capable of delivering potential pulses of various amplitudes and frequencies, and provides several scan rates and current ranges. More advanced ASV instruments offer automated timing, gas purge and stirring, and data processing routines including curve smoothing, baseline correction, and background subtraction.

Two variations of stripping waveforms are commonly used: differential pulse (DPASV) and square wave (SWASV) waveforms. The differential-pulse waveform consists of a series of pulses superimposed on a linear voltage ramp, while the square-wave waveform consists of a series of pulses superimposed on a staircase potential waveform. Square-wave stripping is significantly faster than differential-pulse stripping and is typically ten times more sensitive. Most commercially available ASV instruments perform both differential-pulse and square-wave stripping.

b. Electrodes and cell: Provide working, reference, and auxiliary electrodes. Working electrodes are either hanging mercury drop or thin mercury film electrodes. Hanging mercury drop electrodes must be capable of dispensing mercury in very precisely controlled drop sizes. Three types of electrodes meet this requirement: static mercury drop electrodes, controlled growth mercury drop electrodes, or Kemula-type electrodes. In any case, use a drop knocker to remove an old drop before dispensing a fresh mercury drop.

When the lowest detection limits are required, a thin mercury film electrode is preferred. This electrode consists of a rotating glassy carbon disk plated with mercury in situ during preconcentration of the analyte. A high-precision, constant-speed rotator controls the rotation rate of the electrode and provides reproducible mass transport.

Reference electrodes may be either saturated calomel or silver/ silver chloride electrodes. Use a platinum wire for the auxiliary electrode.

Use cells constructed of glass, or preferably fused silica or TFE, because they are more resistant to solution adsorption or leaching. Cover cell with a lid that provides reproducible placement of the electrodes and gas purging tubes. Provide an additional hole in the cell lid for addition of standards. Most commercially available mercury drop electrodes include electrolytic cells, reference and auxiliary electrodes, and gas purging tubes.

Use a constant-speed stirring mechanism to provide reproducible mass transport in samples and standards.

Locate the cell in an area where temperature is relatively constant. Alternatively, use a

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

constant-temperature water bath and cell jacket.

c. Oxygen-removal apparatus: Oxygen interferes in electrochemical analyses; remove it from solution before preconcentration by purging with nitrogen or argon. Provide two gas inlet tubes through the cell lid: one extends into the solution and the second purges the space above the solution. A gas outlet hole in the lid provides for removal of oxygen and excess purging gas.

d. Recording device: If the electrochemical analyzer is not equipped with a digital data acquisition system, use an XY plotter to record stripping voltammograms.

e. Timer: If preconcentration and equilibration periods are not controlled by the instrument, use an accurate timing device.

f. Polishing wheel: To obtain the high polish required for a glassy carbon disk electrode, use a motorized polishing wheel.

3. Reagents

CAUTION: *Follow proper practices for disposal of any solutions containing mercury.*

a. Metal-free water: Use deionized water to prepare buffers, electrolytes, standards, etc. Use water with at least 18 megohm-cm resistivity (see Section 1080).

b. Nitric acid, HNO_3, conc, high-purity.*#(91)

c. Nitric acid, HNO_3, 6*N*, 1.6*N* (10%), and 0.01*N*.

d. Purging gas (nitrogen or argon), high-purity. Remove traces of oxygen in nitrogen or argon gas before purging the solution. Pass gas through sequential scrubbing columns containing vanadous chloride in the first, deionized water in the second, and buffer (or electrolyte) solution in the third column.

e. Metal standards: Prepare stock solutions containing 1 mg metal/mL in polyethylene bottles. Purchase these solutions commercially or prepare as in Section 3111. Daily prepare dilutions of stock standards in a matrix similar to that of the samples to cover the concentration range desired.

f. Electrolyte/buffer: Use one of the following:

1) *Acetate buffer,* pH 4.5: Dissolve 16.4 g anhydrous sodium acetate, $NaC_2H_3O_2$, in 800 mL water. Adjust to pH 4.5 with high-purity glacial acetic acid.*#(92) Dilute to 1 L with water.

2) *Citrate buffer,* pH 3: Dissolve 42.5 g citric acid (monohydrate) in 700 mL water. Adjust to pH 3 with high-purity NH_4OH.*#(93) Dilute to 1 L with water.

3) *Phosphate buffer,* pH 6.8: Dissolve 24 g NaH_2PO_4 in 500 mL water. Adjust to pH 6.8 with 1*N* NaOH. Dilute to 1 L with water.

g. Mercury: Use commercially available triply distilled metallic mercury for hanging mercury drop electrodes. CAUTION: *Mercury vapors are highly toxic. Use only in well-ventilated area.*

h. Mercuric nitrate solution, $Hg(NO_3)_2$: For thin mercury film electrodes, dissolve 0.325 g

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$Hg(NO_3)_2$ in 100 mL 0.01*N* HNO_3.

i. Reference electrode filling solution: Available from electrode manufacturer.

j. Amalgamated zinc: Dissolve 2 g $Hg(NO_3)_2$ in 25 mL conc HNO_3; dilute to 250 mL with water. In a separate beaker, clean approximately 50 g mossy zinc by gently oxidizing the surface with 10% HNO_3 and rinse with water. Add $Hg(NO_3)_2$ solution to cleaned zinc and stir with a glass rod. If barely visible bubbles do not appear, add a small amount of 6*N* HNO_3. Zinc should rapidly acquire a shiny, metallic appearance. Decant solution and store for amalgamating future batches of zinc. Rinse amalgamated zinc copiously with water and transfer to a gas scrubbing column.

k. Hydrochloric acid, HCl, conc.

l. Vanadous chloride: Add 2 g ammonium metavanadate, NH_4VO_3, to 25 mL conc HCl and heat to boiling. Solution should turn blue-green. Dilute to 250 mL with water. Pour solution into gas scrubbing column packed with amalgamated zinc and bubble purging gas through it until the solution turns a clear violet color. When the violet color is replaced by a blue, green, or brown color, regenerate vanadous chloride by adding HCl.

m. Siliconizing solution: Preferably use commercially available solutions in sealed ampules for siliconizing capillaries used for hanging mercury drops. CAUTION: *Most commercial siliconizing reagents contain* CCl_4, a toxic and cancer-suspect agent. Handle with gloves and avoid breathing vapors.

n. Alumina suspensions, 1, 0.3, and 0.05 µm. Use commercially available alumina suspensions in water, or make a suspension by adding a small amount of water to the alumina.

o. Hydrofluoric acid, HF, 5%: Dilute 5 mL conc HF to 100 mL with water.

p. Methanol.

q. Sodium hydroxide, NaOH, 1*N*.

4. Procedure

a. Sample preparation and storage: Collect samples in pre-cleaned, acid-soaked polyethylene or TFE bottles. Add 2 mL conc HNO_3/L sample and mix well. Cap tightly and store in refrigerator or freezer until ready for analysis.

b. Cell preparation: Soak clean cell in 6*N* HNO_3 overnight and rinse well with water before use.

c. Electrode preparation:

1) HMDE—Follow manufacturer's guidance for capillary cleaning. If not available, use the following procedure. Remove all mercury from the capillary. Aspirate the following through the capillary in the order listed: 6*N* HNO_3, water, 5% HF, water, methanol, and air. Dry capillary at 100°C for 1 h. Siliconize cooled capillary using a siliconizing solution. Between uses, fill

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

capillary with clean mercury and immerse tip in clean mercury. If the capillary fails to suspend a drop of mercury, repeat cleaning.

2) TMFE—Polish glassy carbon disks used for thin mercury film electrodes to a high metallic sheen with alumina suspensions, progressively decreasing particle size from 1 μm to 0.05 μm. Use a motorized polishing wheel for best results. Completely rinse off all traces of alumina with water. Check disk frequently for etching or pitting; repolish as necessary to maintain reproducible mercury film deposition.

d. Instrumental conditions: Use the following conditions:

Variable	Value
Initial potential	−1.00 V (Pb, Cd); −1.20 V (Zn)
Final potential	0.00 V
Equilibration potential	−1.00 V (Pb, Cd); −1.20 V (Zn)
HMDE drop size	medium
TMFE rotation rate	2000 rpm
DPASV:	
Pulse amplitude	25 mV
Pulse period	0.5 s
Pulse width	50 ms
Sample width	17 ms
Scan rate	5 mV/s
SWASV:	
SW amplitude	25 mV
Step potential	4 mV
Frequency	100 Hz

e. Deoxygenation: Pipet 2 mL sample and 3 mL electrolyte/ buffer into cell. If using a TMFE, add 10 μL $Hg(NO_3)_2$ solution. Place electrodes in cell and secure cell lid. Deoxygenate solution with purified purging gas for 10 min while stirring. When solution purge is completed, purge the space above the solution with purified purging gas. Continue head-space purge throughout analysis.

f. Preconcentration: If using a HMDE, dispense a new mercury drop. Start preconcentration, stirring and timing simultaneously. Precisely control and keep constant preconcentration times and stirring rates for solutions and standards. Generally use 120 s and a rotation rate of 2000 rpm for the TMFE.

After the metal is sufficiently concentrated in the amalgam, stop stirring or TMFE rotation

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

for an equilibration period of precisely 30 s.

g. Anodic stripping: After equilibration period, begin anodic stripping without stirring and make potential at the working electrode progressively more positive as a function of time. Monitor stripping current and plot as a function of applied potential in stripping voltammograms. Use peak current to quantify metal concentration and peak potential to identify the metal.

h. Add 5 to 50 µL standard solution and repeat analysis, beginning with deoxygenation of sample. Adjust volume of added standard solution to obtain 30 to 70% increase of the stripping peak. If 50 µL addition is not sufficient, use standard solution with a higher concentration of metal. Shorten deoxygenation step to 1 min after initial gas purge.

5. Calculations

Calculate the concentration of metal in the original sample using the following equation:

$$C_o = \frac{C_s \times V_s}{V_o} \times \frac{i_o}{(i_s - i_o)}$$

where:

C_o = concentration of metal in sample, mg/ L,
C_s = concentration of metal in standard solution, mg/L,
i_o = stripping peak height in original sample,
i_s = stripping peak height in sample with standard addition,
V_o = volume of sample, mL, and
V_s = volume of standard solution added, mL.

6. Quality Control

Follow quality control guidelines outlined in Section 3020 with respect to use of additions, duplicates, and blanks for best results. Blanks are critical because of the high sensitivity of the method.

7. Precision and Bias

Table 3130:I gives precision data for analyses of samples with various matrices.

8. References

1. WANG, J. 1985. Stripping Analysis: Principles, Instrumentation, and Applications. VCH Publishers, Inc., Deerfield Beach, Fla.
2. BRAININA, K.H. & E. NEYMAN. 1993. Electroanalytical Stripping Methods. John Wiley & Sons, New York, N.Y.
3. KISSINGER, P.T. & W.R. HEINEMAN. 1996. Laboratory Techniques in Electroanalytical

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Chemistry, 2nd ed. Marcel Dekker, Inc., New York, N.Y.

4. MARTIN-GOLDBERG, M. 1989. Unpublished data. ResearchTriangle Institute, Metals Analysis Facility. ResearchTriangle Park, N.C.
5. BRULAND, K.W., K.H. COALE & L. MART. 1985. Analysis of seawater for dissolved Cd, Cu, and Pb: An intercomparison of voltammetric and atomic absorption methods. *Mar. Chem.*17:285.
6. OSTAPCZUK, P., P. VALENTA & H.W. NURNBERG. 1986. Square wave voltammetry—a rapid and reliable determination method of Zn, Cd, Pb, Ni, and Co in biological and environmental samples. *J. Electroanal. Chem.* 214:51.
7. CLARK, B.R., D.W. DEPAOLI, D.R. MCTAGGART & B.D. PATTON. 1988. An on-line voltammetric analyzer for trace metals in wastewater. *Anal. Chim. Acta* 215:13.
8. BRETT, C.M.A., A.M. OLIVEIRA-BRETT & L. TUGULEA. 1996. Anodic stripping voltammetry of trace metals by batch injection analysis. *Anal. Chim. Acta* 322:151.

9. Bibliography

E.G. & G. PRINCETON APPLIED RESEARCH CORP. 1980. Differential pulse anodic stripping voltammetry of water and wastewater. Application Note W-1. Princeton, N.J.

PETERSON, W.M. & R.V. WONG. 1981. Fundamentals of stripping voltammetry. *Amer. Lab.* 13(11):116.

E.G. & G. PRINCETON APPLIED RESEARCH CORP. 1982. Basics of voltammetry and polarography. Application Note P-2. Princeton, N.J.

NURNBERG, H.W. 1984. The voltammetric approach in trace metal chemistry of natural waters and atmospheric precipitation. *Anal. Chim. Acta* 164:1.

SHUMAN, M.S. & MARTIN-GOLDBERG, M. 1984. Electrochemical methods: Anodic stripping. *In* R. Minear & L. Keith, eds. Water Analysis: Inorganic Species. II:345. Academic Press, Orlando, Fla.

FLORENCE, T.M. 1986. Electrochemical approaches to trace element speciation in waters: A review. *Analyst* 111:489.

FLORENCE, T.M. 1992. Trace element speciation by anodic stripping voltammetry. *Analyst* 117:551.

TERCIER, M.-L. & J. BUFFLE. 1993. In situ voltammetric measurements in natural waters: Future prospects and challenges. *Electroanalysis* 5:187.

3500-Al ALUMINUM*#(94)

3500-Al A. Introduction

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. Occurrence and Significance

Aluminum (Al) is the second element in Group IIIA of the periodic table; it has an atomic number of 13, an atomic weight of 26.98, and a valence of 3. The average abundance in the earth's crust is 8.1%; in soils it is 0.9 to 6.5%; in streams it is 400 µg/L; in U.S. drinking waters it is 54 µg/L, and in groundwater it is <0.1 µg/L. Aluminum occurs in the earth's crust in combination with silicon and oxygen to form feldspars, micas, and clay minerals. The most important minerals are bauxite and corundum, which is used as an abrasive. Aluminum and its alloys are used for heat exchangers, aircraft parts, building materials, containers, etc. Aluminum potassium sulfate (alum) is used in water-treatment processes to flocculate suspended particles, but it may leave a residue of aluminum in the finished water.

Aluminum's occurrence in natural waters is controlled by pH and by very finely suspended mineral particles. The cation Al^{3+} predominates at pH less than 4. Above neutral pH, the predominant dissolved form is $Al(OH)_4^-$. Aluminum is nonessential for plants and animals. Concentrations exceeding 1.5 mg/L constitute a toxicity hazard in the marine environment, and levels below 200 µg/L present a minimal risk. The United Nations Food and Agriculture Organization's recommended maximum level for irrigation waters is 5 mg/L. The possibility of a link between elevated aluminum levels in brain tissues and Alzheimer's disease has been raised. The proposed U.S. EPA secondary drinking water standard MCL is 0.05 mg/L.

2. Selection of Method

The atomic absorption spectrometric methods (Section 3111D and Section 3111E, and Section 3113B) and the inductively coupled plasma methods (Section 3120 and Section 3125) are free from such common interferences as fluoride and phosphate, and are preferred. The Eriochrome cyanine R colorimetric method (B) provides a means for estimating aluminum with simpler instrumentation.

3500-Al B. Eriochrome Cyanine R Method

1. General Discussion

a. Principle: With Eriochrome cyanine R dye, dilute aluminum solutions buffered to a pH of 6.0 produce a red to pink complex that exhibits maximum absorption at 535 nm. The intensity of the developed color is influenced by the aluminum concentration, reaction time, temperature, pH, alkalinity, and concentration of other ions in the sample. To compensate for color and turbidity, the aluminum in one portion of sample is complexed with EDTA to provide a blank. The interference of iron and manganese, two elements commonly found in water when aluminum is present, is eliminated by adding ascorbic acid. The optimum aluminum range lies between 20 and 300 µg/L but can be extended upward by sample dilution.

b. Interference: Negative errors are caused by both fluoride and polyphosphates. When the fluoride concentration is constant, the percentage error decreases with increasing amounts of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

aluminum. Because the fluoride concentration often is known or can be determined readily, fairly accurate results can be obtained by adding the known amount of fluoride to a set of standards. A simpler correction can be determined from the family of curves in Figure 3500-Al:1. A procedure is given for the removal of complex phosphate interference. Orthophosphate in concentrations under 10 mg/L does not interfere. The interference caused by even small amounts of alkalinity is removed by acidifying the sample just beyond the neutralization point of methyl orange. Sulfate does not interfere up to a concentration of 2000 mg/L.

c. Minimum detectable concentration: The minimum aluminum concentration detectable by this method in the absence of fluorides and complex phosphates is approximately 6 µg/L.

d. Sample handling: Collect samples in clean, acid-rinsed bottles, preferably plastic, and examine them as soon as possible after collection. If only soluble aluminum is to be determined, filter a portion of sample through a 0.45-µm membrane filter; discard first 50 mL of filtrate and use succeeding filtrate for the determination. Do not use filter paper, absorbent cotton, or glass wool for filtering any solution that is to be tested for aluminum, because they will remove most of the soluble aluminum.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for use at 535 nm, with a light path of 1 cm or longer.

2) *Filter photometer,* providing a light path of 1 cm or longer and equipped with a green filter with maximum transmittance between 525 and 535 nm.

3) *Nessler tubes,* 50-mL, tall form, matched.

b. Glassware: Treat all glassware with warm 1 + 1 HCl and rinse with aluminum-free distilled water to avoid errors due to materials absorbed on the glass. Rinse sufficiently to remove all acid.

3. Reagents

Use reagents low in aluminum, and aluminum-free distilled water.

a. Stock aluminum solution: Use either the metal (1) or the salt (2) for preparing stock solution; 1.00 mL = 500 µg Al:

1) Dissolve 500.0 mg aluminum metal in 10 mL conc HCl by heating gently. Dilute to 1000 mL with water, or

2) Dissolve 8.791 g aluminum potassium sulfate (also called potassium alum), $AlK(SO_4)_2 \cdot 12H_2O$, in water and dilute to 1000 mL. Correct this weight by dividing by the decimal fraction of assayed $AlK(SO_4)_2 \cdot 12H_2O$ in the reagent used.

b. Standard aluminum solution: Dilute 10.00 mL stock aluminum solution to 1000 mL with water; 1.00 mL = 5.00 µg Al. Prepare daily.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

c. Sulfuric acid, H_2SO_4, 0.02*N* and 6*N*.

d. Ascorbic acid solution: Dissolve 0.1 g ascorbic acid in water and make up to 100 mL in a volumetric flask. Prepare fresh daily.

e. Buffer reagent: Dissolve 136 g sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$, in water, add 40 mL 1*N* acetic acid, and dilute to 1 L.

f. Stock dye solution: Use any of the following products:

1) *Solochrome cyanine R-200*#(95) or Eriochrome cyanine:*†#(96) Dissolve 100 mg in water and dilute to 100 mL in a volumetric flask. This solution should have a pH of about 2.9.

2) *Eriochrome cyanine R:*‡#(97) Dissolve 300 mg dye in about 50 mL water. Adjust pH from about 9 to about 2.9 with 1 + 1 acetic acid (approximately 3 mL will be required). Dilute with water to 100 mL.

3) *Eriochrome cyanine R:*§#(98) Dissolve 150 mg in about 50 mL water. Adjust pH from about 9 to about 2.9 with 1 + 1 acetic acid (approximately 2 mL will be required). Dilute with water to 100 mL.

Stock solutions have excellent stability and can be kept for at least a year.

g. Working dye solution: Dilute 10.0 mL of selected stock dye solution to 100 mL in a volumetric flask with water. Working solutions are stable for at least 6 months.

h. Methyl orange indicator solution, or bromcresol green indicator solution specified in the total alkalinity determination (Section 2320B.3*d*).

i. EDTA (sodium salt of ethylenediamine-tetraacetic acid dihydrate), 0.01*M*: Dissolve 3.7 g in water, and dilute to 1 L.

j. Sodium hydroxide, NaOH, 1*N* and 0.1*N*.

4. Procedure

a. Preparation of calibration curve:

1) Prepare a series of aluminum standards from 0 to 7 µg (0 to 280 µg/L based on a 25-mL sample) by accurately measuring the calculated volumes of standard aluminum solution into 50-mL volumetric flasks or nessler tubes. Add water to a total volume of approximately 25 mL.

2) Add 1 mL 0.02*N* H_2SO_4 to each standard and mix. Add 1 mL ascorbic acid solution and mix. Add 10 mL buffer solution and mix. With a volumetric pipet, add 5.00 mL working dye reagent and mix. Immediately make up to 50 mL with distilled water. Mix and let stand for 5 to 10 min. The color begins to fade after 15 min.

3) Read transmittance or absorbance on a spectrophotometer, using a wavelength of 535 nm or a green filter providing maximum transmittance between 525 and 535 nm. Adjust instrument to zero absorbance with the standard containing no aluminum.

Plot concentration of Al (micrograms Al in 50 mL final volume) against absorbance.

b. Sample treatment in absence of fluoride and complex phosphates: Place 25.0 mL sample,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

or a portion diluted to 25 mL, in a porcelain dish or flask, add a few drops of methyl orange indicator, and titrate with 0.02*N* H_2SO_4 to a faint pink color. Record reading and discard sample. To two similar samples at room temperature add the same amount of 0.02*N* H_2SO_4 used in the titration and 1 mL in excess.

To one sample add 1 mL EDTA solution. This will serve as a blank by complexing any aluminum present and compensating for color and turbidity. To both samples add 1 mL ascorbic acid, 10 mL buffer reagent, and 5.00 mL working dye reagent as prescribed in ¶ a2) above.

Set instrument to zero absorbance or 100% transmittance using the EDTA blank. After 5 to 10 min contact time, read transmittance or absorbance and determine aluminum concentration from the calibration curve previously prepared.

c. Visual comparison: If photometric equipment is not available, prepare and treat standards and a sample, as described above, in 50-mL nessler tubes. Make up to mark with water and compare sample color with the standards after 5 to 10 min contact time. A sample treated with EDTA is not needed when nessler tubes are used. If the sample contains turbidity or color, the use of nessler tubes may result in considerable error.

d. Removal of phosphate interference: Add 1.7 mL 6*N* H_2SO_4 to 100 mL sample in a 200-mL erlenmeyer flask. Heat on a hot plate for at least 90 min, keeping solution temperature just below the boiling point. At the end of the heating period solution volume should be about 25 mL. Add water if necessary to keep it at or above that volume.

After cooling, neutralize to a pH of 4.3 to 4.5 with NaOH, using 1*N* NaOH at the start and 0.1*N* for the final fine adjustment. Monitor with a pH meter. Make up to 100 mL with water, mix, and use a 25-mL portion for the aluminum test.

Run a blank in the same manner, using 100 mL distilled water and 1.7 mL 6*N* H_2SO_4. Subtract blank reading from sample reading or use it to set instrument to zero absorbance before reading the sample.

e. Correction for samples containing fluoride: Measure sample fluoride concentration by the SPADNS or electrode method. Either:

1) Add the same amount of fluoride as in the sample to each aluminum standard, or
2) Determine fluoride correction from the set of curves in Figure 3500-Al:1.

5. Calculation

$$\text{mg Al/L} = \frac{\mu\text{g Al (in 50 mL final volume)}}{\text{mL sample}}$$

6. Precision and Bias

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

A synthetic sample containing 520 µg Al/L and no interference in distilled water was analyzed by the Eriochrome cyanine R method in 27 laboratories. Relative standard deviation was 34.4% and relative error 1.7%.

A second synthetic sample containing 50 µg Al/L, 500 µg Ba/L, and 5 µg Be/L in distilled water was analyzed in 35 laboratories. Relative standard deviation was 38.5% and relative error 22.0%.

A third synthetic sample containing 500 µg Al/L, 50 µg Cd/L, 110 µg Cr/L, 1000 µg Cu/L, 300 µg Fe/L, 70 µg Pb/L, 50 µg Mn/L, 150 µg Ag/L, and 650 µg Zn/L in distilled water was analyzed in 26 laboratories. Relative standard deviation was 28.8% and relative error 6.2%.

A fourth synthetic sample containing 540 µg Al/L and 2.5 mg polyphosphate/L in distilled water was analyzed in 16 laboratories that hydrolyzed the sample in the prescribed manner. Relative standard deviation was 44.3% and relative error 1.3%. In 12 laboratories that applied no corrective measures, the relative standard deviation was 49.2% and the relative error 8.9%.

A fifth synthetic sample containing 480 µg Al/L and 750 µg F/L in distilled water was analyzed in 16 laboratories that relied on the curve to correct for the fluoride content. Relative standard deviation was 25.5% and relative error 2.3%. The 17 laboratories that added fluoride to the aluminum standards showed a relative standard deviation of 22.5% and a relative error of 7.1%.

7. Bibliography

SHULL, K.E. & G.R. GUTHAN. 1967. Rapid modified Eriochrome cyanine R method for determination of aluminum in water. *J. Amer. Water Works Assoc.* 59:1456.

3500-Sb ANTIMONY

Antimony (Sb) is the fourth element in Group VA in the periodic table; it has an atomic number of 51, an atomic weight of 121.75, and valences of 3 and 5. The average abundance of Sb in the earth's crust is 0.2 ppm; in soils it is 1 ppm; in streams it is 1 µg/L, and in groundwaters it is <0.1 mg/L. Antimony is sometimes found native, but more commonly in stibnite (Sb_2S_3). It is used in alloys of lead and in batteries, bullets, solder, pyrotechnics, and semiconductors.

The common aqueous species are SbO_2^-, $HSbO_2$, and complexes with carbonate and sulfate. Soluble salts of antimony are toxic. The U.S. EPA primary drinking water standard MCL is 6 µg/L.

The electrothermal atomic absorption spectrometric method (Section 3113B) or the inductively coupled plasma/mass spectrometric method (Section 3125) are the methods of choice because of their sensitivity. Alternatively use the flame atomic absorption spectrometric method (Section 3111B) or the inductively coupled plasma method (Section 3120) when high sensitivity is not required.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3500-As ARSENIC*#(99)

3500-As A. Introduction

1. Occurrence and Significance

Arsenic (As) is the third element in Group VA of the periodic table; it has an atomic number of 33, an atomic weight of 74.92, and valences of 3 and 5. The average abundance of As in the earth's crust is 1.8 ppm; in soils it is 5.5 to 13 ppm; in streams it is less than 2 µg/L, and in groundwater it is generally less than 100 µg/L. It occurs naturally in sulfide minerals such as pyrite. Arsenic is used in alloys with lead, in storage batteries, and in ammunition. Arsenic compounds are widely used in pesticides and in wood preservatives.

Arsenic is nonessential for plants but is an essential trace element in several animal species. The predominant form between pH 3 and pH 7 is $H_2AsO_4^-$, between pH 7 and pH 11 it is $HAsO_4^{2-}$, and under reducing conditions it is $HAsO_2$(aq) (or H_3AsO_3). Aqueous arsenic in the form of arsenite, arsenate, and organic arsenicals may result from mineral dissolution, industrial discharges, or the application of pesticides. The chemical form of arsenic depends on its source (inorganic arsenic from minerals, industrial discharges, and pesticides; organic arsenic from industrial discharges, pesticides, and biological action on inorganic arsenic).

Severe poisoning can arise from the ingestion of as little as 100 mg arsenic trioxide; chronic effects may result from the accumulation of arsenic compounds in the body at low intake levels. Carcinogenic properties also have been imputed to arsenic compounds. The toxicity of arsenic depends on its chemical form. Arsenite is many times more toxic than arsenate. For the protection of aquatic life, the average concentration of As^{3+} in water should not exceed 72 µg/L and the maximum should not exceed 140 µg/L. The United Nations Food and Agriculture Organization's recommended maximum level for irrigation waters is 100 µg/L. The U.S. EPA primary drinking water standard MCL is 0.05 mg/L.

2. Selection of Method

Methods are available to identify and determine total arsenic, arsenite, and arsenate. Unpolluted fresh water normally does not contain organic arsenic compounds, but may contain inorganic arsenic compounds in the form of arsenate and arsenite. The electrothermal atomic absorption spectrometric method (Section 3113B) is the method of choice in the absence of overwhelming interferences. The hydride generation-atomic absorption method (Section 3114B) is preferred when interferences are present that cannot be overcome by standard electrothermal techniques (e.g., matrix modifiers, background correction). The silver diethyldithiocarbamate method (B), in which arsine is generated by reaction with sodium borohydride in acidic solution, is applicable to the determination of total inorganic arsenic when interferences are absent and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

when the sample contains no methylarsenic compounds. This method also provides the advantage of being able to identify and quantify arsenate and arsenite separately by generating arsine at different pHs. The inductively coupled plasma (ICP) emission spectroscopy method (Section 3120) is useful at higher concentrations (greater than 50 µg/L) while the ICP-mass spectrometric method (Section 3125) is applicable at lower concentrations if chloride does not interfere. When measuring arsenic species, document that speciation does not change over time. No universal preservative for speciation measurements has been identified.

3500-As B. Silver Diethyldithiocarbamate Method

1. General Discussion

a. Principle: Arsenite, containing trivalent arsenic, is reduced selectively by aqueous sodium borohydride solution to arsine, AsH_3, in an aqueous medium of pH 6. Arsenate, methylarsonic acid, and dimethylarsenic acid are not reduced under these conditions. The generated arsine is swept by a stream of oxygen-free nitrogen from the reduction vessel through a scrubber containing glass wool or cotton impregnated with lead acetate solution into an absorber tube containing silver diethyldithiocarbamate and morpholine dissolved in chloroform. The intensity of the red color that develops is measured at 520 nm. To determine total inorganic arsenic in the absence of methylarsenic compounds, a sample portion is reduced at a pH of about l. Alternatively, arsenate is measured in a sample from which arsenite has been removed by reduction to arsine gas at pH 6 as above. The sample is then acidified with hydrochloric acid and another portion of sodium borohydride solution is added. The arsine formed from arsenate is collected in fresh absorber solution.

b. Interferences: Although certain metals—chromium, cobalt, copper, mercury, molybdenum, nickel, platinum, silver, and selenium—influence the generation of arsine, their concentrations in water are seldom high enough to interfere, except in the instance of acid rock drainage. H_2S interferes, but the interference is removed with lead acetate. Antimony is reduced to stibine, which forms a colored complex with an absorption maximum at 510 nm and interferes with the arsenic determination. Methylarsenic compounds are reduced at pH l to methylarsines, which form colored complexes with the absorber solution. If methylarsenic compounds are present, measurements of total arsenic and arsenate are unreliable. The results for arsenite are not influenced by methylarsenic compounds.

c. Minimum detectable quantity: 1 µg arsenic.

2. Apparatus

a. Arsine generator, scrubber, and absorption tube: See Figure 3500-As:1. Use a 200-mL three-necked flask with a sidearm (19/ 22 or similar size female ground-glass joint) through which the inert gas delivery tube reaching almost to the bottom of the flask is inserted; a 24/40 female ground-glass joint to carry the scrubber; and a second side arm closed with a rubber

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

septum, or preferably by a screw cap with a hole in its top for insertion of a TFE-faced silicone septum. Place a small magnetic stirring bar in the flask. Fit absorber tube (20 mL capacity) to the scrubber and fill with silver diethyldithiocarbamate solution. Do not use rubber or cork stoppers because they may absorb arsine. Clean glass equipment with concentrated nitric acid.

b. Fume hood: Use apparatus in a well-ventilated hood with flask secured on top of a magnetic stirrer.

c. Photometric equipment:

1) *Spectrophotometer,* for use at 520 nm.

2) *Filter photometer,* with green filter having a maximum transmittance in the 500- to 540-nm range.

3) *Cells,* for spectrophotometer or filter photometer, 1-cm, clean, dry, and each equipped with a tightly fitting cover (TFE stopper) to prevent chloroform evaporation.

3. Reagents

a. Reagent water: See Section 1080A.

b. Acetate buffer, pH 5.5: Mix 428 mL 0.2*M* sodium acetate, $NaC_2H_3O_2$, and 72 mL 0.2*M* acetic acid, CH_3COOH.

c. Sodium acetate, 0.2*M*: Dissolve 16.46 g anhydrous sodium acetate or 27.36 g sodium acetate trihydrate, $NaC_2H_3O_2 \cdot 3H_2O$, in water. Dilute to 1000 mL with water.

d. Acetic acid, 0.2*M*: Dissolve 11.5 mL glacial acetic acid in water. Dilute to 1000 mL.

e. Sodium borohydride solution, 1%: Dissolve 0.4 g sodium hydroxide, NaOH (4 pellets), in 400 mL water. Add 4.0 g sodium borohydride, $NaBH_4$ (check for absence of arsenic). Shake to dissolve and to mix. Prepare fresh every few days.

f. Hydrochloric acid, HCl, 2*M*: Dilute 165 mL conc HCl to 1000 mL with water.

g. Lead acetate solution: Dissolve 10.0 g $Pb(CH_3COO)_2 \cdot 3H_2O$ in 100 mL water.

h. Silver diethyldithiocarbamate solution: Dissolve 1.0 mL morpholine (CAUTION: *Corrosive—avoid contact with skin*) in 70 mL chloroform, $CHCl_3$. Add 0.30 g silver diethyldithiocarbamate, $AgSCSN(C_2H_5)_2$; shake in a stoppered flask until most is dissolved. Dilute to 100 mL with chloroform. Filter and store in a tightly closed brown bottle in a refrigerator.

i. Standard arsenite solution: Dissolve 0.1734 g $NaAsO_2$ in water and dilute to 1000 mL with water. CAUTION: *Toxic—avoid contact with skin and do not ingest.* Dilute 10.0 mL to 100 mL with water; dilute 10.0 mL of this intermediate solution to 100 mL with water; 1.00 mL = 1.00 μg As.

j. Standard arsenate solution: Dissolve 0.416 g $Na_2HAsO_4 \cdot 7H_2O$ in water and dilute to 1000 mL. Dilute 10.0 mL to 100 mL with water; dilute 10 mL of this intermediate solution to

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

100 mL; 1.00 mL = 1.00 μg As.

4. Procedure

a. Arsenite:

1) Preparation of scrubber and absorber—Dip glass wool into lead acetate solution; remove excess by squeezing glass wool. Press glass wool between pieces of filter paper, then fluff it. Alternatively, if cotton is used treat it similarly but dry in a desiccator and fluff thoroughly when dry. Place a plug of loose glass wool or cotton in scrubber tube. Add 4.00 mL silver diethyldithiocarbamate solution to absorber tube (5.00 mL may be used to provide enough volume to rinse spectrophotometer cell).

2) Loading of arsine generator—Pipet not more than 70 mL sample containing not more than 20.0 μg As (arsenite) into the generator flask. Add 10 mL acetate buffer. If necessary, adjust total volume of liquid to 80 mL. Flush flask with nitrogen at the rate of 60 mL/min.

3) Arsine generation and measurement—While nitrogen is passing through the system, use a 30-mL syringe to inject through the septum 15 mL 1% sodium borohydride solution within 2 min. Stir vigorously with magnetic stirrer. Pass nitrogen through system for an additional 15 min to flush arsine into absorber solution. Pour absorber solution into a clean and dry spectrophotometric cell and measure absorbance at 520 nm against chloroform. Determine concentration from a calibration curve obtained with arsenite standards. If arsenate also is to be determined for this sample by using the same sample portion, save the liquid in the generator flask.

4) Preparation of standard curves—Treat standard arsenite solution containing 0.0, 1.0, 2.0, 5.0, 10.0, and 20.0 μg As described in ¶s 1) through 3) above. Plot absorbance versus micrograms arsenic in the standard.

b. Arsenate: After removal of arsenite as arsine, treat sample to convert arsenate to arsine:

If the lead acetate-impregnated glass wool has become ineffective in removing hydrogen sulfide (if it has become gray to black) replace glass wool [see ¶ a1)]. Pass nitrogen through system at the rate of 60 mL/min. Cautiously add 10 mL 2.0*N* HCl. Generate arsine as directed in ¶ 4*a*3) and prepare standard curves with standard solutions of arsenate according to procedure of ¶ 4*a*4).

c. Total inorganic arsenic: Prepare scrubber and absorber as directed in ¶ 4*a*1) and load arsine generator as directed in ¶ 4*a*2) using 10 mL 2.0*N* HCl instead of acetate buffer. Generate arsine and measure as directed in ¶ 4*a*3). Prepare standard curves according to ¶ 4*a*4). Curves obtained with standard arsenite solution are almost identical to those obtained with arsenate standard solutions. Therefore, use either arsenite or arsenate standards.

5. Calculation

Calculate arsenite, arsenate, and total inorganic arsenic from readings and calibration curves obtained in 4*a*, *b*, and *c*, respectively, as follows:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\text{mg As/L} = \frac{\mu\text{g As (from calibration curve)}}{\text{mL sample in generator flask}}$$

6. Precision and Bias

Interlaboratory comparisons are not available. The relative standard deviation of results obtained with arsenite/arsenate mixtures containing approximately 10 µg arsenic was less than 10%.

7. Bibliography

PEOPLES, S.A., J. LAKSO & T. LAIS. 1971. The simultaneous determination of methylarsonic acid and inorganic arsenic in urine. *Proc. West. Pharmacol. Soc.* 14:178.

AGGETT, J. & A.C. ASPELL. 1976. Determination of arsenic (III) and total arsenic by the silver diethyldithiocarbamate method. *Analyst* 101:912.

HOWARD, A.G. & M.H. ARBAB-ZAVAR. 1980. Sequential spectrophotometric determination of inorganic arsenic (III) and arsenic (V) species. *Analyst* 105:338.

PANDE, S.P. 1980. Morpholine as a substitute for pyridine in determination of arsenic in water. *J. Inst. Chem. (India)* 52:256.

IRGOLIC, K.J. 1986. Arsenic in the environment. *In* A. V. Xavier, ed. Frontiers in Bioinorganic Chemistry. VCH Publishers, Weinheim, Germany.

IRGOLIC, K.J. 1987. Analytical procedures for the determination of organic compounds of metals and metalloids in environmental samples. *Sci. Total Environ.* 64:61.

3500-Ba BARIUM

Barium (Ba) is the fifth element in Group IIA in the periodic table; it has an atomic number of 56, an atomic weight of 137.33, and a valence of 2. The average abundance of Ba in the earth's crust is 390 ppm; in soils it is 63 to 810 ppm; in streams it is 10 mg/L; in U.S. drinking waters it is 49 µg/L; and in groundwaters it is 0.05 to 1 mg/L. It is found chiefly in barite ($BaSO_4$) or in witherite ($BaCO_3$). Barium's main use is in mud slurries used in drilling oil and exploration wells, but it is also used in pigments, rat poisons, pyrotechnics, and in medicine.

The solubility of barium in natural waters is controlled by the solubility of $BaSO_4$, and somewhat by its adsorption on hydroxides. High concentrations of barium occur in some brines. Concentrations exceeding 1 mg/L constitute a toxicity hazard in the marine environment. The U.S. EPA primary drinking water standard MCL is 1 mg/L.

Perform analyses by the atomic absorption spectrometric methods (Section 3111D or Section 3111E), the electrothermal atomic absorption method (Section 3113B), or the inductively

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

coupled plasma methods (Section 3120 or Section 3125).

3500-Be BERYLLIUM

Beryllium (Be) is the first element in Group IIA of the periodic table; it has an atomic number of 4, an atomic weight of 9.01, and a valence of 2. The average abundance of Be in the earth's crust is 2 ppm; in soils it is 0.8 to 1.3 ppm; in streams it is 0.2 μg/L, in U.S. drinking waters and in groundwaters it is typically <0.1 μg/L. Beryllium occurs in nature in deposits of beryls in granitic rocks. Beryllium is used in high-strength alloys of copper and nickel, windows in X-ray tubes, and as a moderator in nuclear reactors.

Beryllium solubility is controlled in natural waters by the solubility of beryllium hydroxides. The solubility at pH 6.0 is approximately 0.1 μg/L. It is nonessential for plants and animals. Acute toxicity occurs at 130 μg/L, and chronic toxicity at 5 μg/L in freshwater species. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 100 μg/L. The U.S. EPA primary drinking water standard MCL for beryllium is 4 μg/L.

The atomic absorption spectrometric methods (Section 3111D and Section 3111E, and Section 3113B) and the inductively coupled plasma (ICP) methods (Section 3120 and Section 3125) are the methods of choice. If atomic absorption or ICP instrumentation is not available, the aluminon colorimetric method detailed in the 19th Edition of *Standard Methods* may be used. This method has poorer precision and bias than the methods of choice.

3500-Bi BISMUTH

Bismuth (Bi) is the fifth element in Group VA in the periodic table; it has an atomic number of 83, an atomic weight of 208.98, and valences of 3 and 5. The average abundance of Bi in the earth's crust in 0.08 ppm; in streams it is <0.02 mg/L, and in groundwaters it is <0.1 mg/L. Bismuth occurs in association with lead and silver ores, and occasionally as the native element. ^{210}Bi, ^{212}Bi, and ^{214}Bi are naturally occuring radioisotopes produced in the decay of uranium and thorium. The metal is used in alloys of lead, tin, and cadmium, and in some pharmaceuticals.

In natural water, Bi^{3+} ion will occur, and complex ions with nitrate and chloride also might be expected. The iodide and telluride compounds are toxic by ingestion or inhalation.

Perform analyses by the atomic absorption spectrometric method (Section 3111B) or by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though bismuth is not specifically listed as an analyte in the method.

3500-B BORON

See Section 4500-B.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3500-Cd CADMIUM

Cadmium (Cd) is the second element in Group IIB of the periodic table; it has an atomic number of 48, an atomic weight of 112.41, and a valence of 2. The average abundance of Cd in the earth's crust is 0.16 ppm; in soils it is 0.1 to 0.5 ppm; in streams it is 1 μg/L, and in groundwaters it is from 1 to 10 μg/L. Cadmium occurs in sulfide minerals that also contain zinc, lead, or copper. The metal is used in electroplating, batteries, paint pigments, and in alloys with various other metals. Cadmium is usually associated with zinc at a ratio of about 1 part cadmium to 500 parts zinc in most rocks and soils.

The solubility of cadmium is controlled in natural waters by carbonate equilibria. Guidelines for maximum cadmium concentrations in natural water are linked to the hardness or alkalinity of the water (i.e., the softer the water, the lower the permitted level of cadmium). It is nonessential for plants and animals. Cadmium is extremely toxic and accumulates in the kidneys and liver, with prolonged intake at low levels sometimes leading to dysfunction of the kidneys. The United Nations Food and Agriculture Organization recommended maximum level for cadmium in irrigation waters is 10 μg/L. The U.S. EPA primary drinking water standard MCL is 10 μg/L.

The electrothermal atomic absorption spectrometric method (Section 3113B) is preferred. The flame atomic absorption methods (Section 3111B and Section 3111C) and inductively coupled plasma methods (Section 3120 and Section 3125) provide acceptable precision and bias, with higher detection limits. Anodic stripping voltammetry (Section 3130B) can achieve superior detection limits, but is susceptible to interferences from copper, silver, gold, and organic compounds. When atomic absorption spectrometric or inductively coupled plasma apparatus is unavailable and the desired precision is not as great, the dithizone method detailed in the 19th Edition of *Standard Methods* is suitable.

3500-Ca CALCIUM*#(100)

3500-Ca A. Introduction

1. Occurrence and Significance

Calcium (Ca) is the third element in Group IIA of the periodic table; it has an atomic number of 20, an atomic weight of 40.08, and a valence of 2. The average abundance of Ca in the earth's crust is 4.9%; in soils it is 0.07 to 1.7%; in streams it is about 15 mg/L; and in groundwaters it is from 1 to >500 mg/L. The most common forms of calcium are calcium carbonate (calcite) and calcium-magnesium carbonate (dolomite). Calcium compounds are widely used in pharmaceuticals, photography, lime, de-icing salts, pigments, fertilizers, and plasters. Calcium carbonate solubility is controlled by pH and dissolved CO_2. The CO_2 , HCO_3^-,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

and CO_3^{2-} equilibrium is the major buffering mechanism in fresh waters. Hardness is based on the concentration of calcium and magnesium salts, and often is used as a measure of potable water quality.

NOTE: Calcium is necessary in plant and animal nutrition and is an essential component of bones, shells, and plant structures. The presence of calcium in water supplies results from passage over deposits of limestone, dolomite, gypsum, and gypsiferous shale. Small concentrations of calcium carbonate combat corrosion of metal pipes by laying down a protective coating. Because precipitation of calcite in pipes and in heat-exchangers can cause damage, the amount of calcium in domestic and industrial waters is often controlled by water softening (e.g., ion exchange, reverse osmosis). Calcium carbonate saturation and water hardness are discussed in Section 2330 and Section 2340, respectively.

Calcium contributes to the total hardness of water. Chemical softening treatment, reverse osmosis, electrodialysis, or ion exchange is used to reduce calcium and the associated hardness.

2. Selection of Method

The atomic absorption methods (Section 3111B, Section 3111D, and Section 3111E) and inductively coupled plasma method (Section 3120) are accurate means of determining calcium. The EDTA titration method gives good results for control and routine applications, but for samples containing high P levels (>50 mg/L) only the atomic absorption or atomic emission methods are recommended because of interferences often encountered with EDTA indicators.

3. Storage of Samples

The customary precautions are sufficient if care is taken to redissolve any calcium carbonate that may precipitate on standing.

3500-Ca B. EDTA Titrimetric Method

1. General Discussion

a. Principle: When EDTA (ethylenediaminetetraacetic acid or its salts) is added to water containing both calcium and magnesium, it combines first with the calcium. Calcium can be determined directly, with EDTA, when the pH is made sufficiently high that the magnesium is largely precipitated as the hydroxide and an indicator is used that combines with calcium only. Several indicators give a color change when all of the calcium has been complexed by the EDTA at a pH of 12 to 13.

b. Interference: Under conditions of this test, the following concentrations of ions cause no interference with the calcium hardness determination: Cu^{2+}, 2 mg/L; Fe^{2+}, 20 mg/L; Fe^{3+}, 20 mg/L; Mn^{2+}, 10 mg/L; Zn^{2+}, 5 mg/L; Pb^{2+}, 5 mg/L; Al^{3+}, 5 mg/L; and Sn^{4+}, 5 mg/L. Orthophosphate precipitates calcium at the pH of the test. Strontium and barium give a positive interference and alkalinity in excess of 300 mg/L may cause an indistinct end point in hard

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

waters.

2. Reagents

a. Sodium hydroxide, NaOH, 1*N*.

b. Indicators: Many indicators are available for the calcium titration. Some are described in the literature (see Bibliography ¶ 6); others are commercial preparations and also may be used. Murexide (ammonium purpurate) was the first indicator available for detecting the calcium end point; directions for its use are presented in this procedure. Individuals who have difficulty recognizing the murexide end point may find the indicator Eriochrome Blue Black R (color index number 202) or Solochrome Dark Blue an improvement because of the color change from red to pure blue. Eriochrome Blue Black R is sodium-1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid. Other indicators specifically designed for use as end-point detectors in EDTA titration of calcium may be used.

1) *Murexide (ammonium purpurate) indicator:* This indicator changes from pink to purple at the end point. Prepare by dissolving 150 mg dye in 100 g absolute ethylene glycol. Water solutions of the dye are not stable for longer than 1 d. A ground mixture of dye powder and sodium chloride (NaCl) provides a stable form of the indicator. Prepare by mixing 200 mg murexide with 100 g solid NaCl and grinding the mixture to 40 to 50 mesh. Titrate immediately after adding indicator because it is unstable under alkaline conditions. Facilitate end-point recognition by preparing a color comparison blank containing 2.0 mL NaOH solution, 0.2 g solid indicator mixture (or 1 to 2 drops if a solution is used), and sufficient standard EDTA titrant (0.05 to 0.10 mL) to produce an unchanging color.

2) *Eriochrome Blue Black R indicator:* Prepare a stable form of the indicator by grinding together in a mortar 200 mg powdered dye and 100 g solid NaCl to 40 to 50 mesh. Store in a tightly stoppered bottle. Use 0.2 g of ground mixture for the titration in the same manner as murexide indicator. During titration the color changes from red through purple to bluish purple to a pure blue with no trace of reddish or purple tint. The pH of some (not all) waters must be raised to 14 (rather than 12 to 13) by the use of 8*N* NaOH to get a good color change.

c. Standard EDTA titrant, 0.01*M:* Prepare standard EDTA titrant and standardize against standard calcium solution as described in Section 2340C to obtain EDTA/$CaCO_3$ equivalence. Standard EDTA titrant, 0.0100*M*, is equivalent to 1000 mg $CaCO_3$/1.00 mL; use titrated equivalent for *B* in the calculations in 4.

3. Procedure

a. Pretreatment of water and wastewater samples: Follow the procedure described in Section 3030E or I if samples require preliminary digestion.

b. Sample preparation: Because of the high pH used in this procedure, titrate immediately after adding alkali and indicator. Use 50.0 mL sample, or a smaller portion diluted to 50 mL so that the calcium content is about 5 to 10 mg. Analyze hard waters with alkalinity higher than 300

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

mg $CaCO_3$/L by taking a smaller portion and diluting to 50 mL. Alternatively, adjust sample pH into the acid range (pH <6), boil for 1 min to dispel CO_2, and cool before beginning titration.

c. Titration: Add 2.0 mL NaOH solution or a volume sufficient to produce a pH of 12 to 13. Stir. Add 0.1 to 0.2 g indicator mixture selected (or 1 to 2 drops if a solution is used). Add EDTA titrant slowly, with continuous stirring to the proper end point. When using murexide, check end point by adding 1 to 2 drops of titrant in excess to make certain that no further color change occurs.

4. Calculation

$$\text{mg Ca/L} = \frac{A \times B \times 400.8}{\text{mL sample}}$$

$$\text{Calcium hardness as mg } CaCO_3\text{/L} = \frac{A \times B \times 1000}{\text{mL sample}}$$

where:

A = mL titrant for sample and
B = mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant at the calcium indicator end point.

5. Precision and Bias

A synthetic sample containing 108 mg Ca/L, 82 mg Mg/L, 3.1 mg K/L, 19.9 mg Na/L, 241 mg Cl^-/L, 1.1 mg NO_3^--N/L, 0.25 mg NO_2^--N/L, 259 mg SO_4^{2-}/L, and 42.5 mg total alkalinity/L (contributed by $NaHCO_3$) in distilled water was analyzed in 44 laboratories by the EDTA titrimetric method, with a relative standard deviation of 9.2% and a relative error of 1.9%.

6. Bibliography

DIEHL, H. & J.L. ELLINGBOE. 1956. Indicator for titration of calcium in the presence of magnesium using disodium dihydrogen ethylenediamine tetraacetate. *Anal. Chem.* 28:882.

HILDEBRAND, G.P. & C.N. REILLEY. 1957. New indicator for complexometric titration of calcium in the presence of magnesium. *Anal. Chem.* 29:258.

PATTON, J. & W. REEDER. 1956. New indicator for titration of calcium with (ethylenedinitrilo) tetraacetate. *Anal. Chem.* 28:1026.

SCHWARZENBACH, G. 1957. Complexometric Titrations. Interscience Publishers, New York, N.Y.

FURMAN, N.H. 1962. Standard Methods of Chemical Analysis, 6th ed. D. Van Nostrand Co., Inc., Princeton, N.J.

KATZ, H. & R. NAVONE. 1964. Method for simultaneous determination of calcium and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

magnesium. *J. Amer. Water Works Assoc.* 56:121.

3500-Cs CESIUM

Cesium (Cs) is the sixth element in Group IA of the periodic table; it has an atomic number of 55, an atomic weight of 132.90, and a valence of 1. The average abundance of Cs in the earth's crust is 2.6 ppm; in soils it is 1 to 5 ppm; in streams it is 0.02 mg/L; and in groundwaters it is generally <0.1 mg/L. Cesium is found in lepidolite and in the water of certain mineral springs. ^{137}Cs, with a 33-year half-life, is widely dispersed on the earth's surface as a result of the radioactive fallout from the atmospheric testing of nuclear weapons. Cesium compounds are used in photoelectric cells, as a catalyst, and in brewing. Some cesium compounds are fire hazards.

Perform analyses by the flame atomic absorption spectrometric method (Section 3111B). The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though cesium is not specifically listed as an analyte in the method.

3500-Cr CHROMIUM*#(101)

3500-Cr A. Introduction

1. Occurrence and Significance

Chromium (Cr) is the first element in Group VIB in the periodic table; it has an atomic number of 24, an atomic weight of 51.99, and valences of 1 through 6. The average abundance of Cr in the earth's crust is 122 ppm; in soils Cr ranges from 11 to 22 ppm; in streams it averages about 1 μg/L, and in groundwaters it is generally 100 μg/L. Chromium is found chiefly in chrome-iron ore ($FeO{\cdot}Cr_2O_3$). Chromium is used in alloys, in electroplating, and in pigments. Chromate compounds frequently are added to cooling water for corrosion control.

In natural waters trivalent chromium exists as Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2^{+}$, and $Cr(OH)_4^{-}$; in the hexavalent form chromium exists as CrO_4^{2-} and as $Cr_2O_7^{2-}$. Cr^{3+} would be expected to form strong complexes with amines, and would be adsorbed by clay minerals. Chromium may exist in water supplies in both the hexavalent and the trivalent state although the trivalent form rarely occurs in potable water.

Chromium is considered nonessential for plants, but an essential trace element for animals. Hexavalent compounds have been shown to be carcinogenic by inhalation and are corrosive to tissue. The chromium guidelines for natural water are linked to the hardness or alkalinity of the water (i.e., the softer the water, the lower the permitted level for chromium). The United Nations

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Food and Agriculture Organization recommended maximum level for irrigation waters is 100 µg/L. The U.S. EPA primary drinking water standard MCL is 0.1 mg/L for total chromium.

2. Selection of Method

The colorimetric method (B) is useful for the determination of hexavalent chromium in a natural or treated water in the range from 100 to 1000 µg/L. This range can be extended by appropriate sample dilution or concentration and/or use of longer cell paths. The ion chromatographic method with photometric detection (C) is suitable for determining dissolved hexavalent chromium in drinking water, groundwater, and industrial wastewater effluents. The electrothermal atomic absorption spectrometric method (Section 3113B) is suitable for determining low levels of total chromium (< 50 µg/L) in water and wastewater, and the flame atomic absorption spectrometric methods (Section 3111B and Section 3111C) and the inductively coupled plasma methods (Section 3120 and Section 3125) are appropriate for measuring concentrations up to milligram-per-liter levels.

3. Sample Handling

If only the dissolved metal content is desired, filter sample through a 0.45-µm membrane filter at time of collection, and after filtration acidify filtrate with conc nitric acid (HNO_3) to pH <2. If only dissolved hexavalent chromium is desired, adjust pH of filtrate to 8 or above with 1*N* sodium hydroxide solution and refrigerate. If the total chromium content is desired, acidify unfiltered sample at time of collection with conc HNO_3 to pH <2. If total hexavalent chromium is desired, adjust the pH of unfiltered sample to 8 or above with 1*N* sodium hydroxide and refrigerate.

3500-Cr B. Colorimetric Method

1. General Discussion

a. Principle: This procedure measures only hexavalent chromium (Cr^{6+}). Therefore, to determine total chromium convert all the chromium to the hexavalent state by oxidation with potassium permanganate. NOTE: The oxidation process may not provide total conversion of all chromium species to Cr^{6+}.[1-3] For total chromium determination, acid-digest the sample (see Section 3030) and follow with a suitable instrumental analysis technique. The hexavalent chromium is determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet colored complex of unknown composition is produced. The reaction is very sensitive, the molar absorptivity based on chromium being about 40 000 L g^{-1} cm^{-1} at 540 nm. To determine total chromium, digest the sample with a sulfuric-nitric acid mixture and then oxidize with potassium permanganate before reacting with the diphenylcarbazide.

b. Interferences: The reaction with diphenylcarbazide is nearly specific for chromium. Hexavalent molybdenum and mercury salts will react to form color with the reagent but the

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

intensities are much lower than that for chromium at the specified pH. Concentrations as high as 200 mg Mo or Hg/L can be tolerated. Vanadium interferes strongly but concentrations up to 10 times that of chromium will not cause trouble. Potential interference from permanganate is eliminated by prior reduction with azide. Iron in concentrations greater than 1 mg/L may produce a yellow color but the ferric ion (Fe^{3+}) color is not strong and no difficulty is encountered normally if the absorbance is measured photometrically at the appropriate wavelength. Interfering amounts of molybdenum, vanadium, iron, and copper can be removed by extraction of the cupferrates of these metals into chloroform ($CHCl_3$). A procedure for this extraction is provided but do not use it unless necessary, because residual cupferron and $CHCl_3$ in the aqueous solution complicate the later oxidation. Therefore, follow the extraction by additional treatment with acid fuming to decompose these compounds.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for use at 540 nm, with a light path of 1 cm or longer.

2) *Filter photometer,* providing a light path of 1 cm or longer and equipped with a greenish yellow filter having maximum transmittance near 540 nm.

b. Separatory funnels, 125-mL, Squibb form, with glass or TFE stopcock and stopper.

c. Acid-washed glassware: New and unscratched glassware will minimize chromium adsorption on glass surfaces during the oxidation procedure. Do not use glassware previously treated with chromic acid. Thoroughly clean other used glassware and new glassware with nitric or hydrochloric acid to remove chromium traces.

3. Reagents

Use reagent water (see Section 1080) for reagent preparation and analytical procedure.

a. Stock chromium solution: Dissolve 141.4 mg $K_2Cr_2O_7$ in water and dilute to 100 mL; 1.00 mL = 500 μg Cr.

b. Standard chromium solution: Dilute 1.00 mL stock chromium solution to 100 mL; 1.00 mL = 5.00 μg Cr.

c. Nitric acid, HNO_3, conc.

d. Sulfuric acid, H_2SO_4, conc, 18*N*, and 6*N*.

e. Sulfuric acid, H_2SO_4, 0.2*N*: Dilute 17 mL 6*N* H_2SO_4 to 500 mL with water.

f. Phosphoric acid, H_3PO_4, conc.

g. Methyl orange indicator solution.

h. Hydrogen peroxide, H_2O_2, 30%.

i. Ammonium hydroxide, NH_4OH, conc.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

j. Potassium permanganate solution: Dissolve 4 g $KMnO_4$ in 100 mL water.

k. Sodium azide solution: Dissolve 0.5 g NaN_3 in 100 mL water.

l. Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide (1,5-diphenylcarbohydrazide) in 50 mL acetone. Store in a brown bottle. Discard when solution becomes discolored.

m. Chloroform, $CHCl_3$: Avoid or redistill material that comes in containers with metal or metal-lined caps.

n. Cupferron solution: Dissolve 5 g cupferron, $C_6H_5N(NO)ONH_4$, in 95 mL water.

o. Sodium hydroxide,1N: Dissolve 40 g NaOH in 1 L water. Store in plastic bottle.

4. Procedure

a. Preparation of calibration curve: To compensate for possible slight losses of chromium during digestion or other analytical operations, treat standards by the same procedure as the sample. Accordingly, pipet measured volumes of standard chromium solution (5 µg/mL) ranging from 2.00 to 20.0 mL, to give standards for 10 to 100 µg Cr, into 250-mL beakers or conical flasks. Depending on pretreatment used in ¶ b below, proceed with subsequent treatment of standards as if they were samples, also carrying out cupferron treatment of standards if this is required for samples.

Develop color as for samples, transfer a suitable portion of each colored solution to a 1-cm absorption cell, and measure absorbance at 540 nm, using reagent water as reference. Correct absorbance readings of standards by subtracting absorbance of a reagent blank carried through the method.

Construct a calibration curve by plotting corrected absorbance values against micrograms chromium in 102 mL final volume.

b. Treatment of sample: If sample has been filtered and/or only hexavalent chromium is desired, start analysis within 24 h of collection and proceed to ¶ 4*e*. NOTE: Recent evidence[4] suggests that preserved samples can be held for 30 d without substantial changes to Cr^{6+} concentrations. If total dissolved chromium is desired and there are interfering amounts of molybdenum, vanadium, copper, or iron present, proceed to ¶ 4*c*. If interferences are not present, proceed to ¶ 4*d*.

If sample is unfiltered and total chromium is desired, digest with HNO_3 and H_2SO_4 as in Section 3030G. If interferences are present, proceed to ¶ 4*c*, ¶ 4*d*, and ¶ 4*e*. If there are no interferences, proceed to ¶ 4*d* and ¶ 4*e*.

c. Removal of molybdenum, vanadium, iron, and copper with cupferron: Pipet a portion of sample containing 10 to 100 µg Cr into a 125-mL separatory funnel. Dilute to about 40 mL with water and chill in an ice bath. Add 5 mL ice-cold cupferron solution, shake well, and let stand in ice bath for 1 min. Extract in separatory funnel with three successive 5-mL portions of $CHCl_3$;

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

shake each portion thoroughly with aqueous solution, let layers separate, and withdraw and discard $CHCl_3$ extract. Transfer extracted aqueous solution to a 125-mL conical flask. Wash separatory funnel with a small amount of water and add wash water to flask. Boil for about 5 min to volatilize $CHCl_3$ and cool. Add 5 mL HNO_3 and 3 mL H_2SO_4. Boil samples to the appearance of SO_3 fumes. Cool slightly, carefully add 5 mL HNO_3, and again boil to fumes to complete decomposition of organic matter. Cool, wash sides of flask, and boil once more to SO_3 fumes, assuming elimination of all HNO_3. Cool and add 25 mL water.

d. Oxidation of trivalent chromium: Pipet a portion of digested sample with or without interferences removed, and containing 10 to 100 µg Cr, into a 125-mL conical flask. Add several drops of methyl orange indicator, then add conc NH_4OH until solution just begins to turn yellow. Add 1 + 1 H_2SO_4 dropwise until it is acidic, plus 1 mL (20 drops) in excess. Adjust volume to about 40 mL, add two or more acid-washed glass beads, and heat to boiling. Add 2 drops $KMnO_4$ solution to give a dark red color. If fading occurs, add $KMnO_4$ dropwise to maintain an excess of about 2 drops. Boil for 2 min longer. Add 1 mL NaN_3 solution and continue boiling gently. If red color does not fade completely after boiling for approximately 30 s, add another 1 mL NaN_3 solution. Continue boiling for 1 min after color has faded completely, then cool.

e. Color development and measurement: Add 0.25 mL (5 drops) H_3PO_4. Use 0.2*N* H_2SO_4 and a pH meter to adjust solution to pH 1.0 ± 0.3. NOTE: Recent work[5] identifies the optimum pH range for color development to be 1.6 to 2.2; the matter of optimum pH range is currently being considered by *Standard Methods*. Transfer solution to a 100-mL volumetric flask, dilute to 100 mL, and mix. Add 2.0 mL diphenylcarbazide solution, mix, and let stand 5 to 10 min for full color development. Transfer an appropriate portion to a 1-cm absorption cell and measure its absorbance at 540 nm, using reagent water as reference. Correct absorbance reading of sample by subtracting absorbance of a blank carried through the method (see also note below). From the corrected absorbance, determine micrograms chromium present by reference to the calibration curve.

NOTE: If the solution is turbid after dilution to 100 mL in ¶ e above, take an absorbance reading before adding carbazide reagent and correct absorbance reading of final colored solution by subtracting the absorbance measured previously.

5. Calculation

For digested samples:

$$\text{mg Cr/L} = \frac{\text{µg Cr (in 102 mL final volume)}}{A \times B} \times 100$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

where:

A = mL original sample, and
B = mL portion from 100 mL digested sample.

For undigested samples:

$$\text{mg Cr/L} = \frac{\mu\text{g Cr (in 102 mL final volume)}}{A}$$

6. Precision and Bias

Collaborative test data from 16 laboratories were obtained on reagent water, tap water, 10% NaCl solution, treated water from synthetic organic industrial waste, EPA extraction leachate, process water, lake water, and effluent from a steel pickle liquor treatment plant.[6] The test data yielded the following relationships:

Reagent water:

$$S_t = 0.037x + 0.006$$

$$S_o = 0.022x + 0.004$$

Drinking or wastewater:

$$S_t = 0.067x + 0.004$$

$$S_o = 0.037x + 0.002$$

Leachate:

$$S_t = 0.032x + 0.007$$

$$S_o = 0.017x + 0.004$$

where:

S_t = overall precision,
S_o = single-operator precision, and
x = chromium concentration, mg/L.

7. References

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. BARTLETT, R. & B. JAMES. 1988. Mobility and bioavailability of chromium in soils. *In* J.O. Nriagu & E. Noeboer, eds. Chromium in the Natural and Human Environments, p. 267. Wiley-Interscience, New York, N.Y.
2. VITALE, R.J., G.R. MUSSOLINE, J.C. PETURA & B.R. JAMES. 1994. Hexavalent chromium extraction from soils: Evaluation of an alkaline digestion method. *J. Environ. Qual.* 23:1249.
3. VITALE, R.J., G.R. MUSSOLINE, K.A. RINEHIMER, J.C. PETURA & B.R. JAMES. 1997. Extraction of sparingly soluble chromate from soils: Evaluation of methods and Eh-pH effects. *Environ. Sci. Technol.* 31: 390.
4. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1996. Determination of hexavalent chromium by ion chromatography. Method 1636. EPA 821-R-96-003, U.S. Environmental Protection Agency, Washington, D.C.
5. VITALE, R.J., G.R. MUSSOLINE & K.A. RINEHIMER. 1997. Environmental monitoring of chromium in air, soil, and water. *Regul. Toxicol. Pharmac.* 26:S80.
6. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1986. Chromium, total. ASTM D1687-86, Annual Book of ASTM Standards, Vol. 11.01. American Soc. Testing & Materials, Philadelphia, Pa.

8. Bibliography

ROWLAND, G.P., JR. 1939. Photoelectric colorimetry—Optical study of permanganate ion and of chromium-diphenylcarbazide system. *Anal. Chem.* 11:442.

SALTZMAN, B.E. 1952. Microdetermination of chromium with diphenylcarbazide by permanganate oxidation. *Anal. Chem.* 24:1016.

URONE, P.F. 1955. Stability of colorimetric reagent for chromium, 5-diphenylcarbazide, in various solvents. *Anal. Chem.* 27:1354.

ALLEN, T.L. 1958. Microdetermination of chromium with 1,5-diphenylcarbohydrazide. *Anal. Chem.* 30:447.

SANDELL, E.B. 1959. Colorimetric Determination of Traces of Metals, 3rd ed. Interscience Publishers, New York, N.Y.

3500-Cr C. Ion Chromatographic Method

1. General Discussion

a. Principle: This method is applicable to determination of dissolved hexavalent chromium in drinking water, groundwater, and industrial wastewater effluents. An aqueous sample is filtered and its pH adjusted to 9 to 9.5 with a concentrated buffer. This pH adjustment reduces the solubility of trivalent chromium and preserves the hexavalent chromium oxidation state. The sample is introduced into the instrument's eluent stream of ammonium sulfate and ammonium

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

hydroxide. Trivalent chromium in solution is separated from the hexavalent chromium by the column. After separation, hexavalent chromium reacts with an azide dye to produce a chromogen that is measured at 530 nm. Hexavalent chromium is identified on the basis of retention time.

Although this method was developed using specific commercial equipment, use of another manufacturer's equipment should be acceptable if appropriate adjustments are made.

b. Interferences: Interferences may come from several sources. Use a good grade of salts for the buffer because trace amounts of chromium may be included.

Several soluble species of trivalent chromium in the sample may be oxidized to the hexavalent form in an alkaline medium in the presence of such oxidants as hydrogen peroxide, ozone, and manganese dioxide. The hexavalent form can be reduced to the trivalent in the presence of reducing species in an acid medium.

High ionic concentration may cause column overload. Samples high in chloride and/or sulfate might show this phenomenon, which is characterized by a change in peak geometry.

Interfering organic compounds are removed by the guard column.

c. Minimum detectable concentrations: The method detection limits obtained in a single laboratory with a 250-µL loop were as follows:

Reagent water	0.4 µg/L
Drinking water	0.3 µg/L
Groundwater	0.3 µg/L
Primary wastewater effluent	0.3 µg/L
Electroplating waste	0.3 µg/L

d. Sample preservation and holding time: Filter sample through a 0.45-µm filter. Use a portion of sample to rinse syringe filter unit and filter, then collect the required volume of filtrate. Adjust pH to 9 to 9.5 by adding buffer solution dropwise while checking pH with a pH meter.

Ship and store sample at 4°C. Bring to room temperature before analysis. Analyze samples within 24 h of collection.

2. Apparatus

a. Ion chromatograph equipped with a pump capable of precisely delivering a flow of 1 to 5 mL/min. The metallic parts of the pump must not contact sample, eluent, or reagent. Sample loops should be available or the instrument should be capable of delivering from 50 to 250-µL injections of sample. The visible absorption cell should not contain metallic parts that contact the eluent-sample flow. The cell must be usable at 530 nm. Use plastic pressurized containers to deliver eluent and post-column reagent. Use high-purity helium (99.995%) to pressurize the eluent and post-column reagent vessel.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

b. Guard column, to be placed before the separator column, containing an adsorbent capable of adsorbing organic compounds and particulates that would damage or interfere with the analysis or equipment.*#(102)

c. Separator column, packed with a high-capacity anion-exchange resin capable of resolving chromate from other sample constituents.†#(103)

d. Recorder, integrator, or computer for receiving signals from the detector as a function of time.

e. Labware: Soak all reusable labware (glass, plastic, etc.) including sample containers, overnight in laboratory-grade detergent, rinse, and soak for 4 h in a mixture of nitric acid (1 part), hydrochloric acid (2 parts), and reagent water (9 parts). Rinse with tap water and reagent water. NOTE: Never use chromic acid cleaning solution.

f. Syringe, equipped with male luer-type fitting and a capacity of at least 3 mL.

3. Reagents

a. Reagent water: Deionized or distilled water free from interferences at the minimum detection limit of each constituent, filtered through a 0.2-µm membrane filter and having a conductance of less than 0.1 µS/cm. Use for preparing all reagents.

b. Cr(VI) stock solution, 100 mg Cr^{6+}/L: Prepare from primary standard grade potassium dichromate. Dissolve 0.1414 g $K_2Cr_2O_7$ in water and dilute to 500 mL in a volumetric flask. pH adjustment is not required. Store in plastic. CAUTION: *Hexavalent chromium is toxic and a suspected carcinogen; handle with care.*

c. Eluent: Dissolve 33 g ammonium sulfate $(NH_4)_2SO_4$, in 500 mL water and add 6.5 mL conc ammonium hydroxide, NH_4OH. Dilute to 1 L with water.

d. Post-column reagent: Dissolve 0.5 g 1,5-diphenylcarbazide in 100 mL HPLC-grade methanol. Add with stirring to 500 mL water containing 28 mL conc H_2SO_4. Dilute to 1 L with water. Reagent is stable for 4 or 5 d; prepare only as needed.

e. Buffer solution: Dissolve 33 g ammonium sulfate, $(NH_4)_2SO_4$, in 75 mL water and add 6.5 mL conc ammonium hydroxide, NH_4OH. Dilute to 100 mL with water.

4. Procedure

a. Instrument setup: Establish ion chromatograph operating conditions as indicated in Table 3500-Cr:I. Set flow rate of the eluent pump at 1.5 mL/min and adjust pressure of reagent delivery module so that the system flow rate, measured after the detector, is 2.0 mL/min. Measure system flow rate using a graduated cylinder and stopwatch. Allow approximately 30 min after adjustment before measuring flow.

Use an injection loop size based on required sensitivity. A 50-µL loop is sufficient, although a 250-µL loop was used to determine the method detection limit.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

b. Calibration: Before sample analysis, construct a calibration curve using a minimum of a blank and three standards that bracket the expected sample concentration range. Prepare calibration standards from the stock standard (3*b*) by appropriate dilution with water in volumetric flasks. Adjust to pH 9 to 9.5 with buffer solution (3*e*) before final dilution. Injection volumes of standards should be about 10 times the injection loop volume to insure complete loop flushing.

c. Sample analysis: Bring chilled, pH-adjusted sample to ambient temperature. Fill a clean syringe with sample, attach a 0.45-µm syringe filter, and inject 10 times the sample loop volume into the instrument. Dilute any sample that has a concentration greater than the highest calibration standard.

5. Calculation

Determine area or height of the Cr(VI) peak in the calibration standard chromatograms. Calculate a calibration line by regressing peak area (or height) against standard concentration in mg/L. A correlation coefficient less than 0.995 may indicate a problem with the analysis.

For samples, measure area (or height) of Cr(VI) peak in sample chromatogram, as determined by retention time. Calculate Cr(VI) concentration by interpolating from the calibration line. Correct data for any dilutions made.

Currently available instrumentation automates the entire measurement process (peak measurement, calibration, and sample measurements and calculations). Ensure that enough quality control samples are analyzed to monitor the instrumental processes.

6. Quality Control

a. Initial demonstration of performance: Before sample analysis, set up instrument and analyze enough known samples to determine estimates for the method detection limit and linear calibration range. Use the initial demonstration of performance to characterize instrument performance, i.e., method detection levels (MDLs) and linear calibration range.

b. Initial and continuing calibration performance: Initially, after every 10 samples, and after the final sample, analyze an independent check sample and a calibration blank. The concentration of the calibration check sample should be near the mid-calibration range; prepare from a source independent of the calibration standards. Use acceptance criteria for check standard recovery and calibration standard concentration based on project goals for precision and accuracy. Typical values for recovery of the check standard range from 90 to 110%. The acceptance criteria for the calibration blank are typically set at ± the nominal MDL.

c. Reagent blank analysis: Analyze one laboratory reagent blank with each batch of samples. Significant Cr(VI) detected in the reagent blank is a sign of contamination. Identify source and eliminate contamination.

d. Laboratory-fortified matrix (also known as matrix spike) analysis: To a portion of a sample, add a known quantity of Cr(VI). After analysis, calculate percent recovery of the known addition. If the recovery falls outside the control limits (typically 75 to 125%), the matrix may be

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

interfering with the results. Perform additional testing to determine whether analysis by the method of standard additions will overcome the interference. Analyze fortified matrix samples as frequently as dictated by project goals and anticipated similarity of matrices in the sample set.

e. Laboratory control sample: Analyze a laboratory control sample (LCS) from an external source with every sample batch. Process LCS and samples identically, including filtering and pH adjustment. Base acceptance criteria for LCS recovery on project goals for precision and bias. Typical values for acceptable recovery range from 90 to 110%.

7. Precision and Bias

The instrument operating conditions and data from a single- laboratory test of the method are shown in Table 3500-Cr:I and Table 3500-Cr:II, respectively.

Multilaboratory test data are shown in Table 3500-Cr:III.‡#(104) Fifteen laboratories analyzed samples ranging from 1.2 to 960 μg Cr/L.

For reagent water matrix:

$$S_o = 0.033x + 0.106$$

$$S_t = 0.050x + 0.559$$

$$\text{Mean recovery} = 1.04x + 0.183$$

where:

S_o = single-operator precision,
S_t = overall precision, and
x = added amount.

For wastewater matrix:

$$S_o = 0.041x + 0.039$$

$$S_t = 0.059x + 1.05$$

$$\text{Mean recovery} = 0.989x - 0.41$$

The eleven water samples consisted of a reagent water blank and five Youden pairs. The nine wastewater samples consisted of a wastewater blank and four Youden pairs.

8. Bibliography

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1991. Methods for the Determination of Metals in Environmental Samples. Method 218.6, EPA-600/4-91-010, Environmental Monitoring Systems Lab., Cincinnati, Ohio.

DIONEX. 1990. Technical Note No. 26. Dionex, Sunnyvale, Calif.

EDGEL, K.W., J.A. LONGBOTTOM & R.A. JOYCE. 1994. Determination of dissolved hexavalent chromium in drinking water, ground water, and industrial wastewater effluents by ion chromatography: Collaborative study. *J. Assoc. Offic. Anal. Chem.* 77:994.

3500-Co COBALT

Cobalt (Co) is the second element in Group VIII in the periodic table; it has an atomic number of 27, an atomic weight of 58.93, and valences of 1, 2, and 3. The average abundance of Co in the earth's crust is 29 ppm; in soils it is 1.0 to 14 ppm; in streams it is 0.2 μg/L; and in groundwaters it is 1 to 10 μg/L. Cobalt occurs only sparingly in ores, usually as the sulfide or the arsenide. It is widely used in alloys of various steels, in electroplating, in fertilizers, and in porcelain and glass.

The solubility of cobalt is controlled by coprecipitation or adsorption by oxides or manganese and iron, by carbonate precipitation, and by the formation of complex ions. Cobalt dust is flammable and is toxic by inhalation. Cobalt is considered essential for algae and some bacteria, nonessential for higher plants, and an essential trace element for animals. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 100 μg/L.

Perform analyses by the flame atomic absorption spectrometric methods (Section 3111B and Section 3111C), by the electrothermal atomic absorption method (Section 3113B), or by the inductively coupled plasma methods (Section 3120 and Section 3125).

3500-Cu COPPER*#(105)

3500-Cu A. Introduction

1. Occurrence and Significance

Copper (Cu) is the first element in Group IB in the periodic table; it has an atomic number of 29, an atomic weight of 63.54, and valences of 1 and 2. The average abundance of Cu in the earth's crust is 68 ppm; in soils it is 9 to 33 ppm; in streams it is 4 to 12 μg/L; and in groundwater it is <0.1 mg/L. Copper occurs in its native state, but is also found in many minerals, the most important of which are those containing sulfide compounds (e.g., chalcopyrite), but also those with oxides and carbonates. Copper is widely used in electrical wiring, roofing, various alloys, pigments, cooking utensils, piping, and in the chemical industry.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Copper salts are used in water supply systems to control biological growths in reservoirs and distribution pipes and to catalyze the oxidation of manganese. Copper forms a number of complexes in natural waters with inorganic and organic ligands. Among the common aqueous species are Cu^{2+}, $Cu(OH)_2$, and $CuHCO_3^+$. Corrosion of copper-containing alloys in pipe fittings may introduce measurable amounts of copper into the water in a pipe system.

Copper is considered an essential trace element for plants and animals. Some compounds are toxic by ingestion or inhalation. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 200 µg/L. Under the lead-copper rule, the U.S. EPA drinking water 90th percentile action level is 1.3 mg/L.

2. Selection of Method

The atomic absorption spectrometric methods (Section 3111B and Section 3111C), the inductively coupled plasma methods (Section 3120 and Section 3125), and the neocuproine method (B) are recommended because of their freedom from interferences. The electrothermal atomic absorption method (Section 3113B) also may be used with success with an appropriate matrix modifier. The bathocuproine method (C) may be used for potable waters.

3. Sampling and Storage

Copper ion tends to be adsorbed on the surface of sample containers. Therefore, analyze samples as soon as possible after collection. If storage is necessary, use 0.5 mL 1 + 1 HCl/100 mL sample, or acidify to pH <2 with HNO_3, to prevent this adsorption.

3500-Cu B. Neocuproine Method

1. General Discussion

a. Principle: Cuprous ion (Cu^+) in neutral or slightly acidic solution reacts with 2,9-dimethyl-1,10-phenanthroline (neocuproine) to form a complex in which 2 moles of neocuproine are bound by 1 mole of Cu^+ ion. The complex can be extracted by a number of organic solvents, including a chloroform-methanol ($CHCl_3$-CH_3OH) mixture, to give a yellow solution with a molar absorptivity of about 8000 at 457 nm. The reaction is virtually specific for copper; the color follows Beer's law up to a concentration of 0.2 mg Cu/25 mL solvent; full color development is obtained when the pH of the aqueous solution is between 3 and 9; the color is stable in $CHCl_3$-CH_3OH for several days.

The sample is treated with hydroxylamine-hydrochloride to reduce cupric ions to cuprous ions. Sodium citrate is used to complex metallic ions that might precipitate when the pH is raised. The pH is adjusted to 4 to 6 with NH_4OH, a solution of neocuproine in methanol is added, and the resultant complex is extracted into $CHCl_3$. After dilution of the $CHCl_3$ to an exact volume with CH_3OH, the absorbance of the solution is measured at 4571 nm.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

b. Interference: Large amounts of chromium and tin may interfere. Avoid interference from chromium by adding sulfurous acid to reduce chromate and complex chromic ion. In the presence of much tin or excessive amounts of other oxidizing ions, use up to 20 mL additional hydroxylamine-hydrochloride solution.

Cyanide, sulfide, and organic matter interfere but can be removed by a digestion procedure.

c. Minimum detectable concentration: The minimum detectable concentration, corresponding to 0.01 absorbance or 98% transmittance, is 3 µg Cu when a 1-cm cell is used and 0.6 µg Cu when a 5-cm cell is used.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for use at 4571 nm, providing a light path of 1 cm or longer.

2) *Filter photometer,* providing a light path of 1 cm or longer and equipped with a narrow-band violet filter having maximum transmittance in the range 450 to 460 nm.

b. Separatory funnels, 125-mL, Squibb form, with glass or TFE stopcock and stopper.

3. Reagents

a. Redistilled water, copper-free: Because most ordinary distilled water contains detectable amounts of copper, use redistilled water, prepared by distilling singly distilled water in a resistant-glass still, or distilled water passed through an ion-exchange unit, to prepare all reagents and dilutions.

b. Stock copper solution: To 200.0 mg polished electrolytic copper wire or foil in a 250-mL conical flask, add 10 mL water and 5 mL conc HNO_3. After the reaction has slowed, warm gently to complete dissolution of the copper and boil to expel oxides of nitrogen, using precautions to avoid loss of copper. Cool, add about 50 mL water, transfer quantitatively to a 1-L volumetric flask, and dilute to the mark with water; 1 mL = 200 µg Cu.

c. Standard copper solution: Dilute 50.00 mL stock copper solution to 500 mL with water; 1.00 mL = 20.0 µg Cu.

d. Sulfuric acid, H_2SO_4, conc.

e. Hydroxylamine-hydrochloride solution: Dissolve 50 g $NH_2OH{\cdot}HCl$ in 450 mL water.

f. Sodium citrate solution: Dissolve 150 g $Na_3C_6H_5O_7{\cdot}2H_2O$ in 400 mL water. Add 5 mL $NH_2OH{\cdot}HCl$ solution and 10 mL neocuproine reagent. Extract with 50 mL $CHCl_3$ to remove copper impurities and discard $CHCl_3$ layer.

g. Ammonium hydroxide, NH_4OH, 5*N*: Dilute 330 mL conc NH_4OH (28-29%) to 1000 mL with water. Store in a polyethylene bottle.

h. Congo red paper, or other pH test paper showing a color change in the pH range of 4 to 6.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

i. Neocuproine reagent: Dissolve 100 mg 2,9-dimethyl-1,10-phenanthroline hemihydrate*#(106) in 100 mL methanol. This solution is stable under ordinary storage conditions for a month or more.

j. Chloroform, $CHCl_3$: Avoid or redistill material that comes in containers with metal-lined caps.

k. Methanol, CH_3OH, reagent grade.

l. Nitric acid, HNO_3, conc.

m. Hydrochloric acid, HCl, conc.

4. Procedure

a. Preparation of calibration curve: Pipet 50 mL water into a 125-mL separatory funnel for use as a reagent blank. Prepare standards by pipetting 1.00 to 10.00 mL (20.0 to 200 µg Cu) standard copper solution into a series of 125-mL separatory funnels, and dilute to 50 mL with water. Add 1 mL conc H_2SO_4 and use the extraction procedure given in ¶ 4*b* below.

Construct a calibration curve by plotting absorbance versus micrograms of copper.

To prepare a calibration curve for smaller amounts of copper, dilute 10.0 mL standard copper solution to 100 mL. Carry 1.00-to 10.00-mL volumes of this diluted standard through the previously described procedure, but use 5-cm cells to measure absorbance.

b. Treatment of sample: Transfer 100 mL sample to a 250-mL beaker, add 1 mL conc H_2SO_4 and 5 mL conc HNO_3. Add a few boiling chips and cautiously evaporate to dense white SO_3 fumes on a hot plate. If solution remains colored, cool, add another 5 mL conc HNO_3, and again evaporate to dense white fumes. Repeat, if necessary, until solution becomes colorless.

Cool, add about 80 mL water, and bring to a boil. Cool and filter into a 100-mL volumetric flask. Make up to 100 mL with water using mostly beaker and filter washings.

Pipet 50.0 mL or other suitable portion containing 4 to 200 µg Cu, from the solution obtained from preliminary treatment, into a 125-mL separatory funnel. Dilute, if necessary, to 50 mL with water. Add 5 mL $NH_2OH{\cdot}HCl$ solution and 10 mL sodium citrate solution, and mix thoroughly. Adjust pH to approximately 4 by adding 1-mL increments of NH_4OH until Congo red paper is just definitely red (or other suitable pH test paper indicates a value between 4 and 6).

Add 10 mL neocuproine reagent and 10 mL $CHCl_3$. Stopper and shake vigorously for 30 s or more to extract the copper-neocuproine complex into the $CHCl_3$. Let mixture separate into two layers and withdraw lower $CHCl_3$ layer into a 25-mL volumetric flask, taking care not to transfer any of the aqueous layer. Repeat extraction of the water layer with an additional 10 mL $CHCl_3$ and combine extracts. Dilute combined extracts to 25 mL with CH_3OH, stopper, and mix thoroughly.

Transfer an appropriate portion of extract to a suitable absorption cell (1 cm for 40 to 200 µg

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Cu; 5 cm for lesser amounts) and measure absorbance at 4571 nm or with a 450- to 460-nm filter. Use a sample blank prepared by carrying 50 mL water through the complete digestion and analytical procedure.

Determine micrograms copper in final solution by reference to the appropriate calibration curve.

5. Calculation

$$\text{mg Cu/L} = \frac{\mu\text{g Cu (in 25 mL final volume)}}{\text{mL portion taken for extraction}}$$

6. Bibliography

SMITH, G.F. & W.H. MCCURDY. 1952. 2,9-Dimethyl-1,10-phenanthroline: New specific in spectrophotometric determination of copper. *Anal. Chem.* 24:371.

LUKE, C.L. & M.E. CAMPBELL. 1953. Determination of impurities in germanium and silicon. *Anal. Chem.* 25:1586.

GAHLER, A.R. 1954. Colorimetric determination of copper with neocuproine. *Anal. Chem.* 26:577.

FULTON, J.W. & J. HASTINGS. 1956. Photometric determinations of copper in aluminum and lead-tin solder with neocuproine. *Anal. Chem.* 28:174.

FRANK, A.J., A.B. GOULSTON & A.A. DEACUTIS. 1957. Spectrophotometric determination of copper in titanium. *Anal. Chem.* 29:750.

3500-Cu C. Bathocuproine Method

1. General Discussion

a. Principle: Cuprous ion forms a water-soluble orange-colored chelate with bathocuproine disulfonate (2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid, disodium salt). While the color forms over the pH range 3.5 to 11.0, the recommended pH range is between 4 and 5. The sample is buffered at a pH of about 4.3 and reduced with hydroxylamine hydrochloride. The absorbance is measured at 4841 nm. The method can be applied to copper concentrations up to at least 5 mg/L with a sensitivity of 20 µg/L.

b. Interference: The following substances can be tolerated with an error of less than ±2%:

Substance	Concentration *mg/L*
Cations	

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Substance	Concentration *mg/L*
Aluminum	100
Beryllium	10
Cadmium	100
Calcium	1000
Chromium (III)	10
Cobalt (II)	5
Iron (II)	100
Iron (III)	100
Lithium	500
Magnesium	100
Manganese (II)	500
Nickel (II)	500
Sodium	1000
Strontium	200
Thorium (IV)	100
Zinc	200
Anions	
Chlorate	1000
Chloride	1000
Fluoride	500
Nitrate	200
Nitrite	200
Orthophosphate	1000
Perchlorate	1000
Sulfate	1000
Compounds	
Residual chlorine	1
Linear alkylate sulfonate (LAS)	40

Cyanide, thiocyanate, persulfate, and EDTA also can interfere.

c. Minimum detectable concentration: 20 µg/L with a 5-cm cell.

2. Apparatus

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

a. Colorimetric equipment: One of the following, with a light path of 1 to 5 cm (unless nessler tubes are used):

1) *Spectrophotometer,* for use at 4841 nm.

2) *Filter photometer,* equipped with a blue-green filter exhibiting maximum light transmission near 4841 nm.

3) *Nessler tubes,* matched, 100-mL, tall form.

b. Acid-washed glassware: Rinse all glassware with conc HCl and then with copper-free water.

3. Reagents

a. Copper-free water: See Method B, ¶ 3*a*.

b. Stock copper solution: Prepare as directed in Method B, ¶ 3*b*, but use 20.00 mg copper wire or foil; 1.00 mL = 20.00 µg Cu.

c. Standard copper solution: Dilute 250 mL stock copper solution to 1000 mL with water; 1.00 mL = 5.00 µg Cu. Prepare daily.

d. Hydrochloric acid, HCl, 1 + 1.

e. Hydroxylamine hydrochloride solution: See Method B, ¶ 3*e*.

f. Sodium citrate solution: Dissolve 300 g $Na_3C_6H_5O_7 \cdot 2H_2O$ in water and make up to 1000 mL.

g. Disodium bathocuproine disulfonate solution: Dissolve 1.000 g $C_{12}H_4N_2(CH_3)_2(C_6H_4)_2(SO_3Na)_2$ in water and make up to 1000 mL.

4. Procedure

Pipet 50.0 mL sample, or a suitable portion diluted to 50.0 mL, into a 250-mL erlenmeyer flask. In separate 250-mL erlenmeyer flasks, prepare a 50.0-mL water blank and a series of 50.0-mL copper standards containing 5.0, 10.0, 15.0, 20.0, and 25.0 µg Cu. To sample, blank, and standards add, mixing after each addition, 1.00 mL 1 + 1 HCl, 5.00 mL $NH_2OH \cdot HCl$ solution, 5.00 mL sodium citrate solution, and 5.00 mL disodium bathocuproine disulfonate solution. Transfer to cells and read sample absorbance against the blank at 4841 nm. Plot absorbance against micrograms Cu in standards for the calibration curve. Estimate concentration from the calibration curve.

5. Calculation

$$\text{mg Cu/L} = \frac{\text{µg Cu (in 66 mL final volume)}}{\text{mL sample}}$$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

6. Precision and Bias

A synthetic sample containing 1000 µg Cu/L, 500 µg Al/L, 50 µg Cd/L, 110 µg Cr/L, 300 µg Fe/L, 70 µg Pb/L, 50 µg Mn/ L, 150 µg Ag/L, and 650 µg Zn/L was analyzed in 33 laboratories by the bathocuproine method, with a relative standard deviation of 4.1% and a relative error of 0.3%.

7. Bibliography

SMITH, G.F. & D.H. WILKINS. 1953. New colorimetric reagent specific for copper. *Anal. Chem.* 25:510.

BORCHARDT, L.G. & J.P. BUTLER. 1957. Determination of trace amounts of copper. *Anal. Chem.* 29:414.

ZAK, B. 1958. Simple procedure for the single sample determination of serum copper and iron. *Clinica Chim. Acta* 3:328.

BLAIR, D. & H. DIEHL. 1961. Bathophenanthrolinedisulfonic acid and bathocuproinedisulfonic acid, water soluble reagents for iron and copper. *Talanta* 7:163.

3500-Ga GALLIUM

Gallium (Ga) is the third element in Group IIIA in the periodic table; it has an atomic number of 31, an atomic weight of 67.72, and valences of 1, 2, and 3. The average abundance of Ga in the earth's crust is 19 ppm; in soils it is 1.9 to 29 ppm; in streams it is 0.09 µg/L; and in groundwaters it is <0.1 mg/L. Gallium occurs in many zinc ores, and nearly always in bauxite. Gallium compounds are used in semiconducting devices.

The element exists as Ga^{3+} in natural water, and its solubility is controlled by formation of the hydroxide. It is considered nonessential for plants and animals.

Perform analyses by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though gallium is not specifically listed as an analyte in the method.

3500-Ge GERMANIUM

Germanium (Ge) is the third element in Group IVA in the periodic table; it has an atomic number of 32, an atomic weight bnof 72.59, and valences of 2 and 4. The average abundance of Ge in the earth's crust is 1.5 ppm; in streams it is 0.03 to 0.1 µg/ L; and in groundwaters it is <0.1 mg/L. Germanium is found in germanite, in certain zinc ores, and in elevated levels in certain

hot spring waters. Germanium alloys are used in transistors, gold alloys, phosphors, and semiconducting devices.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Germanium is present in natural waters in the tetravalent state, and its distribution in natural waters probably is controlled by adsorption on clay mineral surfaces. It is nonessential for plants and animals.

Perform analyses by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though germanium is not specifically listed as an analyte in the method.

3500-Au GOLD

Gold (Au) is the third element in Group IB in the periodic table; it has an atomic number of 79, an atomic weight of 196.97, and valences of 1 and 3. The average abundance of Au in the earth's crust is 0.004 ppm; in streams it is 2 μg/L; and in groundwater it is <0.1 mg/L. Gold occurs in the native form, and is associated with quartz or pyrite. The main uses of gold are in jewelry, dentistry, electronics, and the aerospace industry.

Gold solubility is restricted to acidic waters in the presence of oxidizing agents and chloride, or in alkaline solutions in the presence of hydrogen sulfide. Its solubility may be influenced by natural organic acids. Compounds of gold containing thiosulfate and cyanide have some human toxicity.

Perform analyses by the atomic absorption spectrometric method (Section 3111B) or by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though gold is not specifically listed as an analyte in the method.

3500-In INDIUM

Indium (In) is the fourth element in Group IIIA in the periodic table; it has an atomic number of 49, an atomic weight of 114.82, and valences of 1, 2, and 3. The average abundance of indium in the earth's crust is 0.19 ppm; in streams it is <0.01 μg/L; and in groundwaters it is <0.1 mg/L. Indium often occurs in combination with zinc ores, and sometimes with pyrites and siderite. Indium is used in alloys for bearings, brazing, solder, and in electrical devices.

Indium exists as In^{3+} and as a number of complex ions. Its solubility is controlled by the formation of the insoluble hydroxide. The metal and its compounds are toxic by inhalation.

Perform analyses by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though indium is not specifically listed as an analyte in the method.

3500-Ir IRIDIUM

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Iridium (Ir) is the eighth element in Group VIII of the periodic table; it has an atomic number of 77, an atomic weight of 192.2, and valences of 1, 3, and 4. The average abundance of Ir in the earth's crust is probably <0.001 ppm, and in groundwaters it is <0.1 mg/L. Iridium occurs uncombined with platinum and other metals. It is used in alloys with platinum in catalysts, thermocouples, electrodes, and wires.

The aqueous chemistry is controlled by complex compounds, although the solubility in natural waters is relatively unknown.

Perform analyses by the flame atomic absorption spectrometric method (Section 3111B). The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though iridium is not specifically listed as an analyte in the method.

3500-Fe IRON*#(107)

3500-Fe A. Introduction

1. Occurrence and Significance

Iron (Fe) is the first element in Group VIII of the periodic table; it has an atomic number of 26, an atomic weight of 55.85, and common valences of 2 and 3 (and occasionally valences of 1, 4, and 6). The average abundance of Fe in the earth's crust is 6.22%; in soils Fe ranges from 0.5 to 4.3%; in streams it averages about 0.7 mg/L; and in groundwater it is 0.1 to 10 mg/L. Iron occurs in the minerals hematite, magnetite, taconite, and pyrite. It is widely used in steel and in other alloys.

The solubility of ferrous ion (Fe^{2+}) is controlled by the carbonate concentration. Because groundwater is often anoxic, any soluble iron in groundwater is usually in the ferrous state. On exposure to air or addition of oxidants, ferrous iron is oxidized to the ferric state (Fe^{3+}) and may hydrolyze to form red, insoluble hydrated ferric oxide. In the absence of complex-forming ions, ferric iron is not significantly soluble unless the pH is very low.

Elevated iron levels in water can cause stains in plumbing, laundry, and cooking utensils, and can impart objectionable tastes and colors to foods. The United Nations Food and Agriculture Organization recommended level for irrigation waters is 5 mg/L. The U.S. EPA secondary drinking water standard MCL is 0.3 mg/L.

2. Selection of Method

Sensitivity and detection limits for the atomic absorption spectrometric methods (Section 3111B and Section 3111C), the inductively coupled plasma method (Section 3120), and the phenanthroline colorimetric procedure described here (B) are similar and generally adequate for analysis of natural or treated waters. Lower detection limits can be achieved with electrothermal

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

atomic absorption spectrometry (Section 3113B) when an appropriate matrix modifier is used. The complexing reagents used in the colorimetric procedures are specific for ferrous iron but the atomic absorption procedures are not. However, because of the instability of ferrous iron, which is changed easily to the ferric form in solutions in contact with air, determination of ferrous iron requires special precautions and may need to be done in the field at the time of sample collection.

The procedure for determining ferrous iron using 1,10-phenanthroline (Section 3500-Fe.B.4*c*) has a somewhat limited applicability; avoid long storage time or exposure of samples to light. A rigorous quantitative distinction between ferrous and ferric iron can be obtained with a special procedure using bathophenanthroline. Spectrophotometric methods using bathophenanthroline[1-6] and other organic complexing reagents such as ferrozine[7] or TPTZ[8] are capable of determining iron concentrations as low as 1 µg/L. A chemiluminescence procedure[9] is stated to have a detection limit of 5 ng/L. Additional procedures are described elsewhere.[10-13]

3. Sampling and Storage

Plan in advance the methods of collecting, storing, and pretreating samples. Clean sample container with acid and rinse with reagent water. Equipment for membrane filtration of samples in the field may be required to determine iron in solution (dissolved iron). Dissolved iron, considered to be that passing through a 0.45-µm membrane filter, may include colloidal iron. The value of the determination depends greatly on the care taken to obtain a representative sample. Iron in well or tap water samples may vary in concentration and form with duration and degree of flushing before and during sampling. When taking a sample portion for determining iron in suspension, shake the sample bottle often and vigorously to obtain a uniform suspension of precipitated iron. Use particular care when colloidal iron adheres to the sample bottle. This problem can be acute with plastic bottles.

For a precise determination of total iron, use a separate container for sample collection. Treat with acid at the time of collection to place the iron in solution and prevent adsorption or deposition on the walls of the sample container. Take account of the added acid in measuring portions for analysis. The addition of acid to the sample may eliminate the need for adding acid before digestion (Section 3500-Fe.B.4*a*).

4. References

1. LEE, G.F. & W. STUMM. 1960. Determination of ferrous iron in the presence of ferric iron using bathophenanthroline. *J. Amer. Water Works Assoc.* 52:1567.
2. GHOSH, M.M., J.T. O'CONNOR & R.S. ENGELBRECHT. 1967. Bathophenanthroline method for the determination of ferrous iron. *J. Amer. Water Works Assoc.* 59:897.
3. BLAIR, D. & H. DIEHL. 1961. Bathophenanthroline-disulfonic acid and bathocuproine-disulfonic acid, water soluble reagents for iron and copper. *Talanta* 7:163.
4. SHAPIRO, J. 1966. On the measurement of ferrous iron in natural waters. *Limnol.*

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Oceanogr. 11:293.

5. MCMAHON, J.W. 1967. The influence of light and acid on the measurement of ferrous iron in lake water. *Limnol. Oceanogr.* 12:437.
6. MCMAHON, J.W. 1969. An acid-free bathophenanthroline method for measuring dissolved ferrous iron in lake water. *Water Res.* 3:743.
7. GIBBS, C. 1976. Characterization and application of ferrozine iron reagent as a ferrous iron indicator. *Anal. Chem.* 48:1197.
8. DOUGAN, W.K. & A.L. WILSON. 1973. Absorbtiometric determination of iron with TPTZ. *Water Treat. Exam.* 22:110.
9. SEITZ, W.R. & D.M. HERCULES. 1972. Determination of trace amounts of iron (II) using chemiluminescence analysis. *Anal. Chem.* 44:2143.
10. MOSS, M.L. & M.G. MELLON. 1942. Colorimetric determination of iron with 2,2′-bipyridine and with 2,2′,2″-tripyridine. *Ind. Eng. Chem.,* Anal. Ed. 14:862.
11. WELCHER, F.J. 1947. Organic Analytical Reagents. D. Van Nostrand Co., Princeton, N.J., Vol. 3, pp. 100–104.
12. MORRIS, R.L. 1952. Determination of iron in water in the presence of heavy metals. *Anal. Chem.* 24:1376.
13. DOIG, M.T., III & D.F. MARTIN. 1971. Effect of humic acids on iron analyses in natural water. *Water Res.* 5:689.

3500-Fe B. Phenanthroline Method

1. General Discussion

a. Principle: Iron is brought into solution, reduced to the ferrous state by boiling with acid and hydroxylamine, and treated with 1,10-phenanthroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The colored solution obeys Beer's law; its intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 insures rapid color development in the presence of an excess of phenanthroline. Color standards are stable for at least 6 months.

b. Interference: Among the interfering substances are strong oxidizing agents, cyanide, nitrite, and phosphates (polyphosphates more so than orthophosphate), chromium, zinc in concentrations exceeding 10 times that of iron, cobalt and copper in excess of 5 mg/L, and nickel in excess of 2 mg/L. Bismuth, cadmium, mercury, molybdate, and silver precipitate phenanthroline. The initial boiling with acid converts polyphosphates to orthophosphate and removes cyanide and nitrite that otherwise would interfere. Adding excess hydroxylamine eliminates errors caused by excessive concentrations of strong oxidizing reagents. In the presence of interfering metal ions, use a larger excess of phenanthroline to replace that complexed by the interfering metals. Where excessive concentrations of interfering metal ions

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

are present, the extraction method may be used.

If noticeable amounts of color or organic matter are present, it may be necessary to evaporate the sample, gently ash the residue, and redissolve in acid. The ashing may be carried out in silica, porcelain, or platinum crucibles that have been boiled for several hours in 6*N* HCl. The presence of excessive amounts of organic matter may necessitate digestion before use of the extraction procedure.

c. Minimum detectable concentration: Dissolved or total concentrations of iron as low as 10 µg/L can be determined with a spectrophotometer using cells with a 5 cm or longer light path.

Carry a blank through the entire procedure to allow for correction.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for use at 510 nm, providing a light path of 1 cm or longer.

2) *Filter photometer,* providing a light path of 1 cm or longer and equipped with a green filter having maximum transmittance near 510 nm.

3) *Nessler tubes,* matched, 100-mL, tall form.

b. Acid-washed glassware: Wash all glassware with conc hydrochloric acid (HCl) and rinse with reagent water before use to remove deposits of iron oxide.

c. Separatory funnels: 125-mL, Squibb form, with ground-glass or TFE stopcocks and stoppers.

3. Reagents

Use reagents low in iron. Use reagent water (see Section 1080 and Section 3111B.3*c*) in preparing standards and reagent solutions and in procedure. Store reagents in glass-stoppered bottles. The HCl and ammonium acetate solutions are stable indefinitely if tightly stoppered. The hydroxylamine, phenanthroline, and stock iron solutions are stable for several months. The standard iron solutions are not stable; prepare daily as needed by diluting the stock solution. Visual standards in nessler tubes are stable for several months if sealed and protected from light.

a. Hydrochloric acid, HCl, conc, containing less than 0.5 ppm iron.

b. Hydroxylamine solution: Dissolve 10 g $NH_2OH{\cdot}HCl$ in 100 mL water.

c. Ammonium acetate buffer solution: Dissolve 250 g $NH_4C_2H_3O_2$ in 150 mL water. Add 700 mL conc (glacial) acetic acid. Because even a good grade of $NH_4C_2H_3O_2$ contains a significant amount of iron, prepare new reference standards with each buffer preparation.

d. Sodium acetate solution: Dissolve 200 g $NaC_2H_3O_2{\cdot}3H_2O$ in 800 mL water.

e. Phenanthroline solution: Dissolve 100 mg 1,10-phenanthroline monohydrate, $C_{12}H_8N_2{\cdot}H_2O$, in 100 mL water by stirring and heating to 80°C. Do not boil. Discard the solution if it darkens. Heating is unnecessary if 2 drops conc HCl are added to the water. (NOTE:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

One milliliter of this reagent is sufficient for no more than 100 µg Fe.)

f. Potassium permanganate, 0.1*M:* Dissolve 0.316 $KMnO_4$ in reagent water and dilute to 100 mL.

g. Stock iron solution: Use metal (1) or salt (2) for preparing the stock solution.

1) Use electrolytic iron wire, or ''iron wire for standardizing,'' to prepare the solution. If necessary, clean wire with fine sandpaper to remove any oxide coating and to produce a bright surface. Weigh 200.0 mg wire and place in a 1000-mL volumetric flask. Dissolve in 20 mL 6*N* sulfuric acid (H_2SO_4) and dilute to mark with water; 1.00 mL = 200 µg Fe.

2) If ferrous ammonium sulfate is preferred, slowly add 20 mL conc H_2SO_4 to 50 mL water and dissolve 1.404 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Add 0.1*M* potassium permanganate ($KMnO_4$) dropwise until a faint pink color persists. Dilute to 1000 mL with water and mix; 1.00 mL = 200 µg Fe.

h. Standard iron solutions: Prepare daily for use.

1) Pipet 50.00 mL stock solution into a 1000-mL volumetric flask and dilute to mark with water; 1.00 mL = 10.0 µg Fe.

2) Pipet 5.00 mL stock solution into a 1000-mL volumetric flask and dilute to mark with water; 1.00 mL = 1.00 µg Fe.

i. Diisopropyl or isopropyl ether. CAUTION: *Ethers may form explosive peroxides; test before using.*

4. Procedure

a. Total iron: Mix sample thoroughly and measure 50.0 mL into a 125-mL erlenmeyer flask. If this sample volume contains more than 200 µg iron use a smaller accurately measured portion and dilute to 50.0 mL. Add 2 mL conc HCl and 1 mL $NH_2OH \cdot HCl$ solution. Add a few glass beads and heat to boiling. To insure dissolution of all the iron, continue boiling until volume is reduced to 15 to 20 mL. (If the sample is ashed, take up residue in 2 mL conc HCl and 5 mL water.) Cool to room temperature and transfer to a 50- or 100-mL volumetric flask or nessler tube. Add 10 mL $NH_4C_2H_3O_2$ buffer solution and 4 mL phenanthroline solution, and dilute to mark with water. Mix thoroughly and allow a minimum of 10 min for maximum color development.

b. Dissolved iron: Immediately after collection filter sample through a 0.45-µm membrane filter into a vacuum flask containing 1 mL conc HCl/100 mL sample. Analyze filtrate for total dissolved iron (¶ 4*a*) and/or dissolved ferrous iron (¶ 4*c*). (This procedure also can be used in the laboratory if it is understood that normal sample exposure to air during shipment may result in precipitation of iron.)

Calculate suspended iron by subtracting dissolved from total iron.

c. Ferrous iron: Determine ferrous iron at sampling site because of the possibility of change

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

in the ferrous-ferric ratio with time in acid solutions. To determine ferrous iron only, acidify a separate sample with 2 mL conc HCl/100 mL sample at time of collection. Fill bottle directly from sampling source and stopper. Immediately withdraw a 50-mL portion of acidified sample and add 20 mL phenanthroline solution and 10 mL $NH_4C_2H_3O_2$ solution with vigorous stirring. Dilute to 100 mL and measure color intensity within 5 to 10 min. Do not expose to sunlight. (Color development is rapid in the presence of excess phenanthroline. The phenanthroline volume given is suitable for less than 50 μg total iron; if larger amounts are present, use a correspondingly larger volume of phenanthroline or a more concentrated reagent.)

Calculate ferric iron by subtracting ferrous from total iron.

d. Color measurement: Prepare a series of standards by accurately pipetting calculated volumes of standard iron solutions [use solution described in ¶ 3*h*2) to measure 1- to 10-μg portions] into 125-mL erlenmeyer flasks, diluting to 50 mL by adding measured volumes of water, and carrying out the steps in ¶ 4*a* beginning with transfer to a 100-mL volumetric flask or nessler tube.

For visual comparison, prepare a set of at least 10 standards, ranging from 1 to 100 μg Fe in the final 100-mL volume. Compare colors in 100-mL tall-form nessler tubes.

For photometric measurement, use Table 3500-Fe:I as a rough guide for selecting proper light path at 510 nm. Read standards against water set at zero absorbance and plot a calibration curve, including a blank (see ¶ 3*c* and General Introduction).

If samples are colored or turbid, carry a second set of samples through all steps of the procedure without adding phenanthroline. Instead of water, use the prepared blanks to set photometer to zero absorbance and read each sample developed with phenanthroline against the corresponding blank without phenanthroline. Translate observed photometer readings into iron values by means of the calibration curve. This procedure does *not* compensate for interfering ions.

e. Samples containing organic interferences: Digest samples containing substantial amounts of organic substances according to the directions given in Section 3030G or Section 3030H.

1) If a digested sample has been prepared according to the directions given in Section 3030G or Section 3030H, pipet 10.0 mL or other suitable portion containing 20 to 500 μg Fe into a 125-mL separatory funnel. If the volume taken is less than 10 mL, add water to make up to 10 mL. To the separatory funnel add 15 mL conc HCl for a 10-mL aqueous volume; or, if the portion taken was greater than 10.0 mL, add 1.5 mL conc HCl/mL sample. Mix, cool, and proceed with ¶ 4*e*3) below.

2) To prepare a sample solely for determining iron, measure a suitable volume containing 20 to 500 μg Fe and carry it through the digestion procedure described in either Section 3030G or Section 3030H. However, use only 5 mL H_2SO_4 or $HClO_4$ and omit H_2O_2. When digestion is complete, cool, dilute with 10 mL water, heat almost to boiling to dissolve slowly soluble salts, and, if the sample is still cloudy, filter through a glass-fiber, sintered-glass, or porcelain filter, washing with 2 to 3 mL water. Quantitatively transfer filtrate or clear solution to a 25-mL

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

volumetric flask and make up to 25 mL with water. Empty flask into a 125-mL separatory funnel, rinse flask with 5 mL conc HCl and add to the funnel. Add 25 mL conc HCl measured with the same flask. Mix and cool to room temperature.

3) Extract the iron from the HCl solution in the separatory funnel by shaking for 30 s with 25 mL isopropyl ether (CAUTION). Draw off lower acid layer into a second separatory funnel. Extract acid solution again with 25 mL isopropyl ether, drain acid layer into a suitable clean vessel, and add ether layer to the ether in the first funnel. Pour acid layer back into second separatory funnel and re-extract with 25 mL isopropyl ether. Withdraw and discard acid layer and add ether layer to first funnel. Persistence of a yellow color in the HCl solution after three extractions does not signify incomplete separation of iron because copper, which is not extracted, gives a similar yellow color.

Shake combined ether extracts with 25 mL water to return iron to aqueous phase and transfer lower aqueous layer to a 100-mL volumetric flask. Repeat extraction with a second 25-mL portion of water, adding this to the first aqueous extract. Discard ether layer.

4) Add 1 mL $NH_2OH{\cdot}HCl$ solution, 10 mL phenanthroline solution, and 10 mL $NaC_2H_3O_2$ solution. Dilute to 100 mL with water, mix thoroughly, and let stand for a minimum of 10 min. Measure absorbance at 510 nm using a 5-cm absorption cell for amounts of iron less than 100 µg or 1-cm cell for quantities from 100 to 500 µg. As reference, use either water or a sample blank prepared by carrying the specified quantities of acids through the entire analytical procedure. If water is used as reference, correct sample absorbance by subtracting absorbance of a sample blank.

Determine micrograms of iron in the sample from the absorbance (corrected, if necessary) by reference to the calibration curve prepared by using a suitable range of iron standards containing the same amounts of phenanthroline, hydroxylamine, and sodium acetate as the sample.

5. Calculation

When the sample has been treated according to ¶ 4*a*, ¶ 4*b*, ¶ 4*c*, or ¶ 4*e*2):

$$\text{mg Fe/L} = \frac{\text{µg Fe (in 100 mL final volume)}}{\text{mL sample}}$$

When the sample has been treated according to ¶ 4*e*1):

$$\text{mg Fe/L} = \frac{\text{µg Fe (in 100 mL final volume)}}{\text{mL sample}} \times \frac{100}{\text{mL portion}}$$

Report details of sample collection, storage, and pretreatment if they are pertinent to interpretation of results.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

6. Precision and Bias

Precision and bias depend on the method of sample collection and storage, the method of color measurement, the iron concentration, and the presence of interfering color, turbidity, and foreign ions. In general, optimum reliability of visual comparison in nessler tubes is not better than 5% and often only 10%, whereas, under optimum conditions, photometric measurement may be reliable to 3% or 3 µg, whichever is greater. The sensitivity limit for visual observation in nessler tubes is approximately 1 µg Fe. Sample variability and instability may affect precision and bias of this determination more than will the errors of analysis. Serious divergences have been found in reports of different laboratories because of variations in methods of collecting and treating samples.

A synthetic sample containing 300 µg Fe/L, 500 µg Al/L, 50 µg Cd/L, 110 µg Cr/L, 470 µg Cu/L, 70 µg Pb/L, 120 µg Mn/L, 150 µg Ag/L, and 650 µg Zn/L in distilled water was analyzed in 44 laboratories by the phenanthroline method, with a relative standard deviation of 25.5% and a relative error of 13.3%.

7. Bibliography

CHRONHEIM, G. & W. WINK. 1942. Determination of divalent iron (by o-nitrosophenol). *Ind. Eng. Chem.*, Anal. Ed. 14:447.

MEHLIG, R.P. & R.H. HULETT. 1942. Spectrophotometric determination of iron with o-phenanthroline and with nitro-o-phenanthroline. *Ind. Eng. Chem.*, Anal. Ed. 14:869.

CALDWELL, D.H. & R.B. ADAMS. 1946. Colorimetric determination of iron in water with o-phenanthroline. *J. Amer. Water Works Assoc.* 38: 727.

WELCHER, F.J. 1947. Organic Analytical Reagents. D. Van Nostrand Co., Princeton, N.J., Vol. 3, pp. 85–93.

KOLTHOFF, I.M., T.S. LEE & D.L. LEUSSING. 1948. Equilibrium and kinetic studies on the formation and dissociation of ferroin and ferrin. *Anal. Chem.* 20:985.

RYAN, J.A. & G.H. BOTHAM. 1949. Iron in aluminum alloys: Colorimetric determination using 1,10-phenanthroline. *Anal. Chem.* 21:1521.

REITZ, L.K., A.S. O'BRIEN & T.L. DAVIS. 1950. Evaluation of three iron methods using a factorial experiment. *Anal. Chem.* 22:1470.

SANDELL, E.B. 1959. Chapter 22 *in* Colorimetric Determination of Traces of Metals, 3rd ed. Interscience Publishers, New York, N.Y.

SKOUGSTAD, M.W., M.J. FISHMAN, L.C. FRIEDMAN, D.E. ERDMANN & S.S. DUNCAN. 1979. Methods for Determination of Inorganic Substances in Water and Fluvial Sediment. Chapter A1 *in* Book 5, Techniques of Water Resources Investigations of the United States Geological Survey. U.S. Geological Surv., Washington, D.C.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3500-Pb A. Introduction

1. Occurrence and Significance

Lead (Pb) is the fifth element in Group IVA in the periodic table; it has an atomic number of 82, an atomic weight of 207.19, and valences of 2 and 4. The average abundance of Pb in the earth's crust is 13 ppm; in soils it ranges from 2.6 to 25 ppm; in streams it is 3 μg/L, and in groundwaters it is generally <0.1 mg/L. Lead is obtained chiefly from galena (PbS). It is used in batteries, ammunition, solder, piping, pigments, insecticides, and alloys. Lead also was used in gasoline for many years as an anti-knock agent in the form of tetraethyl lead.

The common aqueous species are Pb^{2+} and hydroxide and carbonate complexes. Lead in a water supply may come from industrial, mine, and smelter discharges or from the dissolution of plumbing and plumbing fixtures. Tap waters that are inherently noncorrosive or not suitably treated may contain lead resulting from an attack on lead service pipes, lead interior plumbing, brass fixtures and fittings, or solder pipe joints.

Lead is nonessential for plants and animals. It is toxic by ingestion and is a cumulative poison. The Food and Drug Administration regulates lead content in food and in house paints. Under the lead-copper rule, the U.S. EPA drinking water 90th percentile action level is 15 μg/L.

2. Selection of Method

The atomic absorption spectrometric method (Section 3111B) has a relatively high detection limit in the flame mode and requires an extraction procedure (Section 3111C) for the low concentrations common in potable water. The electrothermal atomic absorption (AA) method (Section 3113B) is more sensitive for low concentrations and does not require extraction. The inductively coupled plasma/mass spectrometric method (Section 3125) is even more sensitive than the electrothermal AA method. The inductively coupled plasma method (Section 3120) has a sensitivity similar to that of the flame atomic absorption method. Anodic stripping voltammetry (Section 3130B) can achieve superior detection limits, but is susceptible to interferences from copper, silver, gold, and organic compounds. The dithizone method (B) is sensitive and specific as a colorimetric procedure.

3500-Pb B. Dithizone Method

1. General Discussion

a. Principle: An acidified sample containing microgram quantities of lead is mixed with ammoniacal citrate-cyanide reducing solution and extracted with dithizone in chloroform ($CHCl_3$) to form a cherry-red lead dithizonate. The color of the mixed color solution is measured photometrically.[1,2] Sample volume taken for analysis may be 2 L when digestion is used.

b. Interference: In a weakly ammoniacal cyanide solution (pH 8.5 to 9.5) dithizone forms

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

colored complexes with bismuth, stannous tin, and monovalent thallium. In strongly ammoniacal citrate-cyanide solution (pH 10 to 11.5) the dithizonates of these ions are unstable and are extracted only partially.[3] This method uses a high pH, mixed color, single dithizone extraction. Interference from stannous tin and monovalent thallium is reduced further when these ions are oxidized during preliminary digestion. A modification of the method allows detection and elimination of bismuth interference. Excessive quantities of bismuth, thallium, and tin may be removed.[4]

Dithizone in $CHCl_3$ absorbs at 510 nm; control its interference by using nearly equal concentrations of excess dithizone in samples, standards, and blank.

The method is without interference for the determination of 0.0 to 30.0 μg Pb in the presence of 20 μg Tl^+, 100 μg Sn^{2+}, 200 μg In^{3+}, and 1000 μg each of Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Hg^{2+}, Sr^{2+}, Zn^{2+}, Al^{3+}, Sb^{3+}, As^{3+}, Cr^{3+}, Fe^{3+}, V^{3+}, PO_4^{3-}, and SO_4^{2-}. Gram quantities of alkali metals do not interfere. A modification is provided to avoid interference from excessive quantities of bismuth or tin.

c. Preliminary sample treatment: At time of collection acidify with conc HNO_3 to pH <2 but avoid excess HNO_3. Add 5 mL 0.1*N* iodine solution to avoid losses of volatile organo-lead compounds during handling and digesting of samples. Prepare a blank of lead-free water and carry through the procedure.

d. Digestion of samples: Unless digestion is shown to be unnecessary, digest all samples for dissolved or total lead as described in 3030H or K.

e. Minimum detectable concentration: 1.0 μg Pb/10 mL dithizone solution.

2. Apparatus

a. Spectrophotometer for use at 510 nm, providing a light path of 1 cm or longer.

b. pH meter.

c. Separatory funnels: 250-mL Squibb type. Clean all glassware, including sample bottles, with 1 + 1 HNO_3. Rinse thoroughly with reagent water.

d. Automatic dispensing burets: Use for all reagents to minimize indeterminate contamination errors.

3. Reagents

Prepare all reagents in lead-free water.

a. Stock lead solution: Dissolve 0.1599 g lead nitrate, $Pb(NO_3)_2$ (minimum purity 99.5%), in approximately 200 mL water. Add 10 mL conc HNO_3 and dilute to 1000 mL with water. Alternatively, dissolve 0.1000 g pure Pb metal in 20 mL 1 + 1 HNO_3 and dilute to 1000 mL with water; 1.00 mL = 100 μg Pb.

b. Working lead solution: Dilute 2.0 mL stock solution to 100 mL with water; 1 mL = 2.00

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

μg Pb.

c. Nitric acid, HNO_3, 1 + 4: Dilute 200 mL conc HNO_3 to 1 L with water.

d. Ammonium hydroxide, NH_4OH, 1 + 9: Dilute 10 mL conc NH_4OH to 100 mL with water.

e. Citrate-cyanide reducing solution: Dissolve 400 g dibasic ammonium citrate, $(NH_4)_2HC_6H_5O_7$, 20 g anhydrous sodium sulfite, Na_2SO_3, 10 g hydroxylamine hydrochloride, $NH_2OH{\cdot}HCl$, and 40 g potassium cyanide, KCN (CAUTION: *Poison*) in water and dilute to 1 L. Mix this solution with 2 L conc NH_4OH. *Do not pipet by mouth. Prepare solution in a fume hood.*

f. Stock dithizone solution: The dithizone concentration in the stock dithizone solutions is based on having a 100% pure dithizone reagent. Some commercial grades of dithizone are contaminated with the oxidation product diphenylthiocarbodiazone or with metals. Purify dithizone as directed below. For dithizone solutions not stronger than 0.001% (w/v), calculate the exact concentration by dividing the absorbance of the solution in a 1.00-cm cell at 606 nm by 40.6×10^3, the molar absorptivity.

In a fume hood, dissolve 100 mg dithizone in 50 mL $CHCl_3$ in a 150-mL beaker and filter through a 7-cm-diam paper.*#(109) Receive filtrate in a 500-mL separatory funnel or in a 125-mL erlenmeyer flask under slight vacuum; use a filtering device designed to handle the $CHCl_3$ vapor. Wash beaker with two 5-mL portions $CHCl_3$, and filter. Wash the paper with three 5-mL portions $CHCl_3$, adding final portion dropwise to edge of paper. If filtrate is in flask, transfer with $CHCl_3$ to a 500-mL separatory funnel.

Add 100 mL 1 + 99 NH_4OH to separatory funnel and shake moderately for 1 min; excessive agitation produces slowly breaking emulsions. Let layers separate, swirling funnel gently to submerge $CHCl_3$ droplets held on surface of aqueous layer. Transfer $CHCl_3$ layer to 250-mL separatory funnel, retaining the orange-red aqueous layer in the 500-mL funnel. Repeat extraction, receiving $CHCl_3$ layer in another 250-mL separatory funnel and transferring aqueous layer, using 1 + 99 NH_4OH, to the 500-mL funnel holding the first extract. Repeat extraction, transferring the aqueous layer to 500-mL funnel. Discard $CHCl_3$ layer.

To combined extracts in the 500-mL separatory funnel add 1 + 1 HCl in 2-mL portions, mixing after each addition, until dithizone precipitates and solution is no longer orange-red. Extract precipitated dithizone with three 25-mL portions $CHCl_3$. Dilute combined extracts to 1000 mL with $CHCl_3$; 1.00 mL = 100 μg dithizone.

g. Dithizone working solution: Dilute 100 mL stock dithizone solution to 250 mL with $CHCl_3$; 1 mL = 40 μg dithizone.

h. Special dithizone solution: Dissolve 250 mg dithizone in 250 mL $CHCl_3$. This solution may be prepared without purification because all extracts using it are discarded.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

i. Sodium sulfite solution: Dissolve 5 g anhydrous Na_2SO_3 in 100 mL water.

j. Iodine solution: Dissolve 40 g KI in 25 mL water, add 12.7 g resublimed iodine, and dilute to 1000 mL.

4. Procedure

a. With sample digestion: CAUTION: *Perform the following procedure (excluding use of spectrophotometer) in a fume hood.* To a digested sample containing not more than 1 mL conc acid add 20 mL 1 + 4 HNO_3 and filter through lead-free filter paper†#(110) and filter funnel directly into a 250-mL separatory funnel. Rinse digestion beaker with 50 mL water and add to filter. Add 50 mL ammoniacal citrate-cyanide solution, mix, and cool to room temperature. Add 10 mL dithizone working solution, shake stoppered funnel vigorously for 30 s, and let layers separate. Insert lead-free cotton in stem of separatory funnel and draw off lower layer. Discard 1 to 2 mL $CHCl_3$ layer, then fill absorption cell. Measure absorbance of extract at 510 nm, using dithizone working solution, ¶ 3*g*, to zero spectrophotometer.

b. Without sample digestion: To 100 mL acidified sample (pH 2) in a 250-mL separatory funnel add 20 mL 1 + 4 HNO_3 and 50 mL citrate-cyanide reducing solution; mix. Add 10 mL dithizone working solution and proceed as in ¶ 4*a*.

c. Calibration curve: Plot concentration of at least five standards and a blank against absorbance. Determine concentration of lead in extract from curve. All concentrations are µg Pb/10 mL final extract.

d. Removal of excess interferences: The dithizonates of bismuth, tin, and thallium differ from lead dithizonate in maximum absorbance. Detect their presence by measuring sample absorbance at 510 nm and at 465 nm. Calculate corrected absorbance of sample at each wavelength by subtracting absorbance of blank at same wavelength. Calculate ratio of corrected absorbance at 510 nm to corrected absorbance at 465 nm. The ratio of corrected absorbances for lead dithizonate is 2.08 and for bismuth dithizonate is 1.07. If the ratio for the sample indicates interference, i.e., is markedly less than 2.08, proceed as follows with a new 100-mL sample: If the sample has not been digested, add 5 mL Na_2SO_3 solution to reduce iodine preservative. Adjust sample to pH 2.5 using a pH meter and 1 + 4 HNO_3 or 1 + 9 NH_4OH as required. Transfer sample to 250-mL separatory funnel, extract with a minimum of three 10-mL portions special dithizone solution, or until the $CHCl_3$ layer is distinctly green. Extract with 20-mL portions $CHCl_3$ to remove dithizone (absence of green). Add 20 mL 1 + 4 HNO_3, 50 mL citrate-cyanide reducing solution, and 10 mL dithizone working solution. Extract as in ¶ 4*a* and measure absorbance.

5. Calculation

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\text{mg Pb/L} = \frac{\mu\text{g Pb (in 10 mL, from calibration curve)}}{\text{mL sample}}$$

6. Precision and Bias

Single-operator precision in recovering 0.0104 mg Pb/L from Mississippi River water was 6.8% relative standard deviation and −1.4% relative error. At the level of 0.026 mg Pb/L, recovery was made with 4.8% relative standard deviation and 15% relative error.

7. References

1. SNYDER, L.J. 1947. Improved dithizone method for determination of lead—mixed color method at high pH. *Anal. Chem.* 19:684.
2. SANDELL, E.B. 1959. Colorimetric Determination of Traces of Metals, 3rd ed. Interscience, New York, N.Y.
3. WICHMANN, H.J. 1939. Isolation and determination of trace metals— the dithizone system. *Ind. Eng. Chem.*, Anal. Ed. 11:66.
4. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1977. Annual Book of ASTM Standards. Part 26, Method D3112-77, American Soc. Testing & Materials, Philadelphia, Pa.

3500-Li LITHIUM*#(111)

3500-Li A. Introduction

1. Occurrence and Significance

Lithium (Li) is the second element in Group IA of the periodic table; it has an atomic number of 3, an atomic weight of 6.94, and a valence of 1. The average abundance of Li in the earth's crust is 18 ppm; in soils it is 14 to 32 ppm; in streams it is 3 µg/ L, and in groundwaters it is <0.1 mg/L. The more important minerals containing lithium are lepidolite, spodumene, petalite, and amblygonite. Lithium compounds are used in pharmaceuticals, soaps, batteries, welding flux, ceramics, reducing agents (e.g., lithium aluminum hydride), and cosmetics.

Many lithium salts are only slightly soluble, and the metal's concentration in water is controlled by incorporation in clay minerals of soils. Lithium is considered nonessential for plants and animals, but it is essential for some microorganisms. Some lithium salts are toxic by ingestion. The United Nations Food and Agriculture Organization recommended maximum level for lithium in irrigation waters is 2.5 mg/L.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2. Selection of Method

The atomic absorption spectrometric method (Section 3111B) and the inductively coupled plasma method (Section 3120) are preferred. The flame emission photometric method (B) also is available for laboratories not equipped to use preferred methods. The inductively coupled plasma/mass spectrometric method (Section 3125) may be applied successfully in most cases (with lower detection limits), even though lithium is not specifically listed as an analyte in the method.

3500-Li B. Flame Emission Photometric Method

1. General Discussion

a. Principle: Lithium can be determined in trace amounts by flame photometric methods at a wavelength of 670.8 nm.

b. Interference: A molecular band of strontium hydroxide with an absorption maximum at 671.0 nm interferes in the flame photometric determination of lithium. Ionization of lithium can be significant in both the air-acetylene and nitrous oxide-acetylene flames and can be suppressed by adding potassium. See Section 3500-NaB.1*a* for additional information on minimizing interferences in flame photometry.

c. Minimum detectable concentration: The minimum lithium concentration detectable is approximately 0.1 µg/L for reagent water analyzed on an atomic absorption spectrophotometer in the emission mode with an air-acetylene flame, or 0.03 µg/L with a nitrous oxide-acetylene flame.

d. Sampling and storage: Preferably collect sample in a polyethylene bottle, although borosilicate glass containers also may be used. At time of collection adjust sample to pH <2 with nitric acid (HNO_3).

2. Apparatus

Flame photometer: A flame photometer or an atomic absorption spectrometer operating in the emission mode using a lean air-acetylene flame is recommended.

3. Reagents

Use reagent water (see Section 3111B.3*c*) in reagent preparation and analysis.

a. Potassium ionization suppressant: Dissolve 95.35 g KCl dried at 110°C and dilute to 1000 mL with water; 1.00 mL = 50 mg K.

b. Stock lithium solution: Dissolve 152.7 mg anhydrous lithium chloride, LiCl, in water and dilute to 250 mL; 1.00 mL = 100 µg Li. Dry salt overnight in an oven at 105°C. Cool in a desiccator and weigh immediately after removal from desiccator. Alternatively, purchase prepared stock from a reputable supplier.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

c. Standard lithium solution: Dilute 10.00 mL stock LiCl solution to 500 mL with water; 1.00 mL = 2.0 µg Li.

4. Procedure

a. Pretreatment of polluted water and wastewater samples: Choose digestion method appropriate to matrix (see Section 3030).

b. Suppressing ionization: If necessary, filter sample through medium-porosity paper, add 1.0 mL potassium ionization suppressant to 50 mL volumetric flask, and dilute with sample for flame photometric determination. Sample solution will be in a 0.1% K matrix.

c. Treatment of standard solutions: Prepare dilutions of the Li standard solution to bracket sample concentration or to establish at least three points on a calibration curve of emission intensity against Li concentration. Prepare standards by adding appropriate volumes of standard lithium solution to 25 mL water + 1.0 mL potassium ionization suppressant reagent in a 50-mL volumetric flask. Dilute to 50.0 mL and mix. Both samples and standards will be in a 0.1% K matrix to suppress ionization of lithium.

d. Flame photometric measurement: Determine lithium concentration by direct intensity measurements at a wavelength of 670.8 nm. The bracketing method (Section 3500-NaB.4*d*) can be used with some photometric instruments, while the construction of a calibration curve is necessary with others. Run sample, water, and lithium standard as nearly simultaneously as possible. For best results, average several readings on each solution.

Follow the manufacturer's instructions for instrument operation.

5. Calculation

$$\mu g\ Li/L = (\mu g\ Li/L \text{ in portion analyzed}) \times D$$

where:

$$D = \text{dilution ratio} = \frac{\text{mL sample} + \text{mL water}}{\text{mL sample}}$$

6. Quality Control

Process a QC standard through entire analytical protocol as a way of determining systematic bias. The control limits for precision of duplicate determinations at concentrations (in water) of 4.0 µg/L and 10.0 µg/L were 4.09 ± 0.056 µg/L and 9.96 ± 0.094 µg/L, respectively. The single-operator RSD was 1.38% for a lithium solution containing 10 µg/L.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

7. Bibliography

FISHMAN, M.J. 1962. Flame photometric determination of lithium in water. *J. Amer. Water Works Assoc.* 54:228.

PICKETT, E.E. & S.R. KOIRTYOHANN. 1968. The nitrous oxide-acetylene flame in emission analysis-I. General characteristics. *Spectrochem. Acta.* 23B:235.

KOIRTYOHANN, S.R. & E.E. PICKETT. 1968. The nitrous oxide-acetylene flame in emission analysis-II. Lithium and the alkaline earths. *Spectrochem. Acta*, 23B:673.

URE, A.M. & R.L. MITCHELL. 1975. Lithium, sodium, potassium, rubidium, and cesium. *In* J.A. Dean & T.C. Rains, eds. Flame Emission and Atomic Absorption Spectrometry. Dekker, New York, N.Y.

THOMPSON, K.C. & R.J. REYNOLDS. 1978. Atomic Absorption Fluorescence, and Flame Spectroscopy—A Practical Approach, 2nd ed. John Wiley & Sons, New York, N.Y.

WILLARD, H.H., L.L. MERRIT, J.A. DEAN & F.A. SETTLE., JR. 1981. Instrumental Methods of Analysis, 6th ed. Wadsworth Publishing Co., Belmont, Calif.

3500-Mg MAGNESIUM*#(112)

3500-Mg A. Introduction

1. Occurrence and Significance

Magnesium (Mg) is the second element in Group IIA of the periodic table; it has an atomic number of 12, an atomic weight of 24.30, and a valence of 2. The average abundance of Mg in the earth's crust is 2.1%; in soils it is 0.03 to 0.84%; in streams it is 4 mg/L, and in groundwaters it is >5 mg/L. Magnesium occurs commonly in the minerals magnesite and dolomite. Magnesium is used in alloys, pyrotechnics, flash photography, drying agents, refractories, fertilizers, pharmaceuticals, and foods.

The common aqueous species is Mg^{2+}. The carbonate equilibrium reactions for magnesium are more complicated than for calcium, and conditions for direct precipitation of dolomite in natural waters are not common. Important contributors to the hardness of a water, magnesium salts break down when heated, forming scale in boilers. Chemical softening, reverse osmosis, or ion exchange reduces magnesium and associated hardness to acceptable levels.

Magnesium is an essential element in chlorophyll and in red blood cells. Some salts of magnesium are toxic by ingestion or inhalation. Concentrations greater than 125 mg/L also can have a cathartic and diuretic effect.

2. Selection of Method

The methods presented are applicable to waters and wastewaters. Direct determinations can

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

be made with the atomic absorption spectrometric method (Section 3111B) and inductively coupled plasma method (Section 3120). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though magnesium is not specifically listed as an analyte in the method. These methods can be applied to most concentrations encountered, although sample dilution may be required. Choice of method is largely a matter of personal preference and analyst experience. A calculation method (B) also is available.

3500-Mg B. Calculation Method

Magnesium may be estimated as the difference between hardness and calcium as $CaCO_3$ if interfering metals are present in noninterfering concentrations in the calcium titration (Section 3500-Ca.B) and suitable inhibitors are used in the hardness titration (Section 2340C).

$$\text{mg Mg/L} = [\text{total hardness (as mg } CaCO_3\text{/L)} - \text{calcium hardness (as mg } CaCO_3\text{/L)}] \times 0.243$$

3500-Mn MANGANESE*#(113)

3500-Mn A. Introduction

1. Occurrence and Significance

Manganese (Mn) is the first element in Group VIIB in the periodic table; it has an atomic number of 25, an atomic weight of 54.94, and common valences of 2, 4, and 7 (and more rarely, valences of 1, 3, 5, and 6). The average abundance of Mn in the earth's crust is 1060 ppm; in soils it is 61 to 1010 ppm; in streams it is 7 µg/L, and in groundwaters it is <0.1 mg/L. Manganese is associated with iron minerals, and occurs in nodules in ocean, fresh waters, and soils. The common ores are pyrolusite (MnO_2) and psilomelane. Manganese is used in steel alloys, batteries, and food additives.

The common aqueous species are the reduced Mn^{2+} and the oxidized Mn^{4+}. The aqueous chemistry of manganese is similar to that of iron. Since groundwater is often anoxic, any soluble manganese in groundwater is usually in the reduced state (Mn^{2+}). Upon exposure to air or other oxidants, groundwater containing manganese usually will precipitate black MnO_2. Elevated manganese levels therefore can cause stains in plumbing/laundry, and cooking utensils. It is considered an essential trace element for plants and animals. The United Nations Food and Agriculture Organization recommended maximum level for manganese in irrigation waters is 0.2 mg/L. The U.S. EPA secondary drinking water standard MCL is 50 µg/L.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2. Selection of Method

The atomic absorption spectrometric methods (Section 3111B and Section 3111C), the electrothermal atomic absorption method (Section 3113B), and the inductively coupled plasma methods (Section 3120 and Section 3125) permit direct determination with acceptable sensitivity and are the methods of choice. Of the various colorimetric methods, the persulfate method (B) is preferred because the use of mercuric ion can control interference from a limited chloride ion concentration.

3. Sampling and Storage

Manganese may exist in a soluble form in a neutral water when first collected, but it oxidizes to a higher oxidation state and precipitates or becomes adsorbed on the container walls. Determine manganese very soon after sample collection. When delay is unavoidable, total manganese can be determined if the sample is acidified at the time of collection with HNO_3 to pH <2. See Section 3010B.

3500-Mn B. Persulfate Method

1. General Discussion

a. Principle: Persulfate oxidation of soluble manganous compounds to form permanganate is carried out in the presence of silver nitrate. The resulting color is stable for at least 24 h if excess persulfate is present and organic matter is absent.

b. Interference: As much as 0.1 g chloride (Cl^-) in a 50-mL sample can be prevented from interfering by adding 1 g mercuric sulfate ($HgSO_4$) to form slightly dissociated complexes. Bromide and iodide still will interfere and only trace amounts may be present. The persulfate procedure can be used for potable water with trace to small amounts of organic matter if the period of heating is increased after more persulfate has been added.

For wastewaters containing organic matter, use preliminary digestion with nitric and sulfuric acids (HNO_3 and H_2SO_4) (see Section 3030G). If large amounts of Cl^- also are present, boiling with HNO_3 helps remove it. Interfering traces of Cl^- are eliminated by $HgSO_4$ in the special reagent.

Colored solutions from other inorganic ions are compensated for in the final colorimetric step.

Samples that have been exposed to air may give low results due to precipitation of manganese dioxide (MnO_2). Add 1 drop 30% hydrogen peroxide (H_2O_2) to the sample, after adding the special reagent, to redissolve precipitated manganese.

c. Minimum detectable concentration: The molar absorptivity of permanganate ion is about 2300 L g^{-1} cm^{-1}. This corresponds to a minimum detectable concentration (98% transmittance)

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

of 210 µg Mn/L when a 1-cm cell is used or 42 µg Mn/L when a 5-cm cell is used.

2. Apparatus

Colorimetric equipment: One of the following is required:

a. Spectrophotometer, for use at 525 nm, providing a light path of 1 cm or longer.

b. Filter photometer, providing a light path of 1 cm or longer and equipped with a green filter having maximum transmittance near 525 nm.

c. Nessler tubes, matched, 100-mL, tall form.

3. Reagents

a. Special reagent: Dissolve 75 g $HgSO_4$ in 400 mL conc HNO_3 and 200 mL distilled water. Add 200 mL 85% phosphoric acid (H_3PO_4), and 35 mg silver nitrate ($AgNO_3$). Dilute the cooled solution to 1 L.

b. Ammonium persulfate, $(NH_4)_2S_2O_8$, solid.

c. Standard manganese solution: Prepare a 0.1*N* potassium permanganate ($KMnO_4$) solution by dissolving 3.2 g $KMnO_4$ in distilled water and making up to 1 L. Age for several weeks in sunlight or heat for several hours near the boiling point, then filter through a fine fritted-glass filter crucible and standardize against sodium oxalate as follows:

Weigh several 100- to 200-mg samples of $Na_2C_2O_4$ to 0.1 mg and transfer to 400-mL beakers. To each beaker, add 100 mL distilled water and stir to dissolve. Add 10 mL 1 + 1 H_2SO_4 and heat rapidly to 90 to 95°C. Titrate rapidly with the $KMnO_4$ solution to be standardized, while stirring, to a slight pink end-point color that persists for at least 1 min. Do not let temperature fall below 85°C. If necessary, warm beaker contents during titration; 100 mg $Na_2C_2O_4$ will consume about 15 mL permanganate solution. Run a blank on distilled water and H_2SO_4.

$$\text{Normality of } KMnO_4 = \frac{\text{g } Na_2C_2O_4}{(A - B) \times 0.067\ 01}$$

where:

A = mL titrant for sample and
B = mL titrant for blank.

Average results of several titrations. Calculate volume of this solution necessary to prepare 1 L of solution so that 1.00 mL = 50.0 µg Mn, as follows:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\text{mL } KMnO_4 = \frac{4.55}{\text{normality } KMnO_4}$$

To this volume add 2 to 3 mL conc H_2SO_4 and $NaHSO_3$ solution dropwise, with stirring, until the permanganate color disappears. Boil to remove excess SO_2, cool, and dilute to 1000 mL with distilled water. Dilute this solution further to measure small amounts of manganese.

d. Standard manganese solution (alternate): Dissolve 1.000 g manganese metal (99.8% min.) in 10 mL redistilled HNO_3. Dilute to 1000 mL with 1% (v/v) HCl; 1 mL = 1.000 mg Mn. Dilute 10 mL to 200 mL with distilled water; 1 mL = 0.05 mg Mn. Prepare dilute solution daily.

e. Hydrogen peroxide, H_2O_2, 30%.

f. Nitric acid, HNO_3, conc.

g. Sulfuric acid, H_2SO_4, conc.

h. Sodium nitrite solution: Dissolve 5.0 g $NaNO_2$ in 95 mL distilled water.

i. Sodium oxalate, $Na_2C_2O_4$, primary standard.

j. Sodium bisulfite: Dissolve 10 g $NaHSO_3$ in 100 mL distilled water.

4. Procedure

a. Treatment of sample: If a digested sample has been prepared according to directions for reducing organic matter and/or excessive chlorides in Section 3030G, pipet a portion containing 0.05 to 2.0 mg Mn into a 250-mL conical flask. Add distilled water, if necessary, to 90 mL and proceed as in ¶ b.

b. To a suitable sample portion add 5 mL special reagent and 1 drop H_2O_2. Concentrate to 90 mL by boiling or dilute to 90 mL. Add 1 g $(NH_4)_2S_2O_8$, bring to a boil, and boil for 1 min. Do not heat on a water bath. Remove from heat source, let stand 1 min, then cool under the tap. (Boiling too long results in decomposition of excess persulfate and subsequent loss of permanganate color; cooling too slowly has the same effect.) Dilute to 100 mL with distilled water free from reducing substances and mix. Prepare standards containing 0, 5.00, . . . 1500 µg Mn by treating various amounts of standard Mn solution in the same way.

c. Nessler tube comparison: Use standards prepared as in ¶ 4*b* and containing 5 to 100 µg Mn/100 mL final volume. Compare samples and standards visually.

d. Photometric determination: Use a series of standards from 0 to 1500µg Mn/100mL final volume. Make photometric measurements against a distilled water blank. The following table shows light path length appropriate for various amounts of manganese in 100mL final volume:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

shows light path length appropriate for various amounts of manganese in 100mL final volume:

Mn Range *µg*	Light Path *cm*
5–200	15
20–400	5
50–1000	2
100–1500	1

Prepare a calibration curve of manganese concentration vs. absorbance from the standards and determine Mn in the samples from the curve. If turbidity or interfering color is present, make corrections as in 4e.

e. Correction for turbidity or interfering color: Avoid filtration because of possible retention of some permanganate on the filter paper. If visual comparison is used, the effect of turbidity only can be estimated and no correction can be made for interfering colored ions. When photometric measurements are made, use the following ‘‘bleaching’’ method, which also corrects for interfering color: As soon as the photometer reading has been made, add 0.05 mL H_2O_2 solution directly to the sample in the optical cell. Mix and, as soon as the permanganate color has faded completely and no bubbles remain, read again. Deduct absorbance of bleached solution from initial absorbance to obtain absorbance due to Mn.

5. Calculation

a. When all of the original sample is taken for analysis:

$$\text{mg Mn/L} = \frac{\mu\text{g Mn/100 mL}}{\text{mL sample}} \times \frac{100}{\text{mL portion}}$$

b. When a portion of the digested sample (100 mL final volume) is taken for analysis:

$$\text{mg Mn/L} = \frac{\mu\text{g Mn (in 100 mL final volume)}}{\text{mL sample}}$$

6. Precision and Bias

A synthetic sample containing 120 µg Mn/L, 500 µg Al/L, 50 µg Cd/L, 110 µg Cr/L, 470 µg Cu/L, 300 µg Fe/L, 70 µg Pb/L, 150 µg Ag/L, and 650 µg Zn/L in distilled water was analyzed in 33 laboratories by the persulfate method, with a relative standard deviation of 26.3% and a

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

relative error of 0%.

A second synthetic sample, similar in all respects except for 50 µg Mn/L and 1000 µg Cu/L, was analyzed in 17 laboratories by the persulfate method, with a relative standard deviation of 50.3% and a relative error of 7.2%.

7. Bibliography

RICHARDS, M.D. 1930. Colorimetric determination of manganese in biological material. *Analyst* 55:554.

NYDAHL, F. 1949. Determination of manganese by the persulfate method. *Anal. Chem. Acta.* 3:144.

MILLS, S.M. 1950. Elusive manganese. *Water Sewage Works* 97:92.

SANDELL, E.B. 1959. Colorimetric Determination of Traces of Metals, 3rd ed. Interscience Publishers, New York, N.Y., Chapter 26.

3500-Hg MERCURY

Mercury (Hg) is the third element in Group IIB in the periodic table; it has an atomic number of 80, an atomic weight of 200.59, and valences of 1 and 2. The average abundance of Hg in the earth's crust is 0.09 ppm; in soils it is 30 to 160 ppb; in streams it is 0.07 µg/L, and in groundwaters it is 0.5 to 1 µg/L. Mercury occurs free in nature, but the chief source is cinnibar (HgS). Mercury is used in amalgams, mirror coatings, vapor lamps, paints, measuring devices (thermometers, barometers, manometers), pharmaceuticals, pesticides, and fungicides. It is often used in paper mills as a mold retardant for paper.

The common aqueous species are Hg^{2+}, $Hg(OH)_2^0$, Hg^0, and stable complexes with organic ligands. Inorganic mercury can be methylated in sediments when sulfides are present to form dimethyl mercury, $(CH_3)_2Hg$, which is very toxic and can concentrate in the aquatic food chain. Mercury poisoning occurred in Japan in the 1950s as the result of consumption of shellfish that had accumulated mercury. In times past, mercury was used in the haberdashery industry to block hats (the cause of the ''mad hatter'' syndrome).

Mercury is considered nonessential for plants and animals. The U.S. EPA primary drinking water standard MCL is 2 µg/L.

The cold-vapor atomic absorption method (Section 3112B) is the method of choice for all samples. The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in some cases, even though mercury is not specifically listed as an analyte in the method. The dithizone method detailed in the 19th edition of *Standard Methods* can be used for determining high levels of mercury (>2 µg/L) in potable waters.

Because mercury can be lost readily from samples, preserve them by treating with HNO_3 to reduce the pH to <2 (see Section 1060). Glass storage containers are preferred to plastic, because they can extend the holding time to 30 d, rather than only the 14 d allowed in plastic containers.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3500-Mo MOLYBDENUM

Molybdenum (Mo) is the second element in Group VIB in the periodic table; it has an atomic number of 42, and atomic weight of 95.95, and valences of 2, 3, 4, 5, and 6. The average abundance of Mo in the earth's crust is 1.2 ppm; in soils it is 2.5 ppm; in streams it is 1 μg/L, and in groundwaters it is <0.1 mg/L. Molybdenum occurs naturally as molybdenite (MoS_2) and wulfenite

($PbMoO_4$). It is used in alloys, ink pigments, catalysts, and lubricants.

The common aqueous species are $HMoO_4^-$, MoO_4^{2-}, and organic complexes. It is considered an essential trace element for plants and animals. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 0.01 mg/L.

Use one of the flame atomic absorption spectrometric methods (Section 3111D or Section 3111E), the electrothermal atomic absorption spectrometric method (Section 3113B), or one of the inductively coupled plasma methods (Section 3120 or Section 3125).

3500-Ni NICKEL

Nickel (Ni) is the third element in Group VIII in the periodic table; it has an atomic number of 28, an atomic weight of 58.69, and a common valence of 2 and less commonly 1, 3, or 4. The average abundance of Ni in the earth's crust is 1.2 ppm; in soils it is 2.5 ppm; in streams it is 1 μg/L, and in groundwaters it is <0.1 mg/L. Nickel is obtained chiefly from pyrrhotite and garnierite. Nickel is used in alloys, magnets, protective coatings, catalysts, and batteries.

The common aqueous species is Ni^{2+}. In reducing conditions insoluble sulfides can form, while in aerobic conditions nickel complexes with hydroxide, carbonates, and organic ligands can form. It is suspected to be an essential trace element for some plants and animals. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 200 μg/L. The U.S. EPA primary drinking water standard MCL is 0.1 mg/L.

The atomic absorption spectrometric methods (Section 3111B and Section 3111C), the inductively coupled plasma methods (Section 3120 and Section 3125), and the electrothermal atomic absorption spectrometric method (Section 3113B) are the methods of choice for all samples.

3500-Os OSMIUM

Osmium (Os) is the seventh element in Group VIII in the periodic table; it has an atomic number of 76, an atomic weight of 190.2, and valences of 3, 4, and 6, and less commonly 1, 2, 5, 7, and 8. The average abundance of Os in the earth's crust is probably <0.005 ppm, and in groundwaters it is <0.01 mg/L. Osmium occurs in iridosime and in platinum-bearing river sands.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Osmium is used as a hardener with iridium and as a catalyst with platinum.

The aqueous chemistry is controlled by complex compounds, although the solubility in natural waters is relatively unknown.

Analyze by flame atomic absorption methods (Section 3111D and Section 3111E).

3500-Pd PALLADIUM

Palladium (Pd) is the sixth element in Group VIII of the periodic table; it has an atomic number of 46, an atomic weight of 106.42, and valences of 2 and 4. Palladium occurs with platinum in nature. It is used in alloys to make electrical relays, catalysts, in the making of ‘‘white gold,’’ and in protective coatings.

Palladium has no known toxic effects. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 5 mg/L.

Preferably analyze by flame atomic absorption method (Section 3111B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though palladium is not specifically listed as an analyte in the method.

3500-Pt PLATINUM

Platinum (Pt) is the ninth element in Group VIII of the periodic table; it has an atomic number of 78, an atomic weight of 195.1, and valences of 2 and 4. The average abundance of Pt in the earth’s crust is probably <0.01 ppm, and in groundwaters it is <0.1 mg/L. Platinum is usually found in its native state, but also may be found as sperrylite ($PtAs_2$). Platinum is used as a catalyst and in laboratoryware, jewelry, and surgical wire.

The aqueous chemistry in natural waters is relatively unknown, although its solubility is probably controlled by complex compounds. In powder form, platinum can be flammable, and its soluble salts are toxic by inhalation.

Preferably analyze by flame atomic absorption method (Section 3111B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though platinum is not specifically listed as an analyte in the method.

3500-K POTASSIUM*#(114)

3500-K A. Introduction

1. Occurrence and Significance

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Potassium (K) is the fourth element in Group IA of the periodic table; it has an atomic number of 19, an atomic weight of 39.10, and a valence of 1. The average abundance of K in the earth's crust is 1.84%; in soils it has a range of 0.1 to 2.6%; in streams it is 2.3 mg/L, and in groundwaters it has a range of 0.5 to 10 mg/L. Potassium is commonly associated with aluminosilicate minerals such as feldspars. ^{40}K is a naturally occurring radioactive isotope with a half-life of 1.3×10^9 years. Potassium compounds are used in glass, fertilizers, baking powder, soft drinks, explosives, electroplating, and pigments. Potassium is an essential element in both plant and human nutrition, and occurs in groundwaters as a result of mineral dissolution, from decomposing plant material, and from agricultural runoff.

The common aqueous species is K^+. Unlike sodium, it does not remain in solution, but is assimilated by plants and is incorporated into a number of clay-mineral structures.

2. Selection of Method

Methods for the determination of potassium include flame atomic absorption (Section 3111B), inductively coupled plasma (Section 3120), flame photometry (B), and selective ion electrode (C). The inductively coupled plasma/mass spectrometric method (Section 3125) usually may be applied successfully (with lower detection limits), even though potassium is not specifically listed as an analyte in the method. The preferred methods are rapid, sensitive, and accurate; selection depends on instrument availability and analyst choice.

3. Storage of Samples

Do not store samples in soft-glass bottles because of the possibility of contamination from leaching of the glass. Use acid-washed polyethylene or borosilicate glass bottles. Adjust sample to pH < 2 with nitric acid. This will dissolve potassium salts and reduce adsorption on vessel walls.

3500-K B. Flame Photometric Method

1. General Discussion

a. Principle: Trace amounts of potassium can be determined in either a direct-reading or internal-standard type of flame photometer at a wavelength of 766.5 nm. Because much of the information pertaining to sodium applies equally to the potassium determination, carefully study the entire discussion dealing with the flame photometric determination of sodium (Section 3500-Na.B) before making a potassium determination.

b. Interference: Interference in the internal-standard method may occur at sodium-to-potassium ratios of 5:1 or greater. Calcium may interfere if the calcium-to-potassium ratio is 10:1 or more. Magnesium begins to interfere when the magnesium-to-potassium ratio exceeds 100:1.

c. Minimum detectable concentration: Potassium levels of approximately 0.1 mg/L can be

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

determined.

2. Apparatus

See Section 3500-Na.B.2.

3. Reagents

To minimize potassium pickup, store all solutions in plastic bottles. Shake each container thoroughly to dissolve accumulated salts from walls before pouring.

a. Reagent water: See Section 1080. Use this water for preparing all reagents and calibration standards, and as dilution water.

b. Stock potassium solution: Dissolve 1.907 g KCl dried at 110°C and dilute to 1000 mL with water; 1 mL = 1.00 mg K.

c. Intermediate potassium solution: Dilute 10.0 mL stock potassium solution with water to 100 mL; 1.00 mL = 0.100 mg K.

Use this solution to prepare calibration curve in potassium range of 1 to 10 mg/L.

d. Standard potassium solution: Dilute 10.0 mL intermediate potassium solution with water to 100 mL; 1.00 mL = 0.010 mg K. Use this solution to prepare calibration curve in potassium range of 0.1 to 1.0 mg/L.

4. Procedure

Make determination as described in Section 3500-Na.B.4, but measure emission intensity at 766.5 nm.

5. Calculation

See Section 3500-Na.B.5.

6. Precision and Bias

A synthetic sample containing 3.1 mg K^+/L, 108 mg Ca^{2+}/L, 82 mg Mg^{2+}/L, 19.9 mg Na^+/L, 241 mg Cl^-/L, 0.25 mg NO_2^--N/L, 1.1 mg NO_3^--N/L, 259 mg SO_4^{2-}/L, and 42.5 mg total alkalinity/L (contributed by $NaHCO_3$) was analyzed in 33 laboratories by the flame photometric method, with a relative standard deviation of 15.5% and a relative error of 2.3%.

7. Bibliography

MEHLICH, A. & R.J. MONROE. 1952. Report on potassium analyses by means of flame photometer methods. *J. Assoc. Offic. Agr. Chem.* 35:588.

Also see Section 3500-Na.B.7.

3500-K C. Potassium-Selective Electrode Method

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. General Discussion

a. Principle: Potassium ion is measured potentiometrically by using a potassium ion-selective electrode and a double-junction, sleeve-type reference electrode. The analysis is performed with either a pH meter having an expanded millivolt scale capable of being read to the nearest 0.1 mV or a specific ion meter having a direct concentration scale for potassium.

Before measurement, an ionic strength adjustor reagent is added to both standards and samples to maintain a constant ionic strength. The electrode response is measured in standard solutions with potassium concentrations spanning the range of interest using a calibration line derived either by the instrument meter or manually. The electrode response in sample solutions is measured following the same procedure and potassium concentration determined from the calibration line or instrument direct readout.

b. Interferences: Although most sensitive to potassium, the potassium electrode will respond to other cations at high concentrations; this can result in a positive bias. Table 3500-K:I lists the concentration of common cations causing a 10% error at various concentrations of potassium chloride with a background ionic strength of 0.12*N* sodium chloride. Of the cations listed, ammonium ion is most often present in samples at concentrations high enough to result in a significant bias. It can be converted to gaseous ammonia by adjusting to pH > 10.

An electrode exposed to interfering cations tends to drift and respond sluggishly. To restore normal performance soak electrode for 1 h in distilled water and then for several hours in a standard potassium solution.

c. Detection limits: Samples containing from 0.1 to 1000 mg K^+/L may be analyzed. To measure higher concentrations dilute the sample.

2. Apparatus

a. Expanded-scale or digital pH meter or ion-selective meter.

b. Potassium ion-selective electrode.

c. Sleeve-type double-junction reference electrode: Fill outer sleeve with reference electrode filling solution (see ¶ 3*b*). Fill inner sleeve with inner filling solution provided with the electrode.

d. pH electrode.

e. Mixer, magnetic, with a TFE-coated stirring bar.

3. Reagents

a. Ionic strength adjustor (ISA): Dissolve 29.22 g NaCl in reagent water and dilute to 100 mL.

b. Reference electrode outer sleeve filling solution: Dilute 2 mL ISA solution to 100 mL with reagent water.

c. Stock potassium solution: See Section 3500-K.B.3*b*.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

d. Sodium hydroxide, NaOH, 6*N*.

e. Reagent water: See Section 1080.

4. Procedure

a. Preparation of standards: Prepare a series of standards containing 100.0, 10.0, 1.0, and 0.1 mg K^+/L by making serial dilutions of the stock potassium solution as in Section 3500-K.B.3*c* and Section 3500-K.B.3*d*.

b. Instrument calibration: Fill reference electrode according to the manufacturer's instructions using reference electrode filling solution. Transfer 100 mL 0.1 mg K^+/L standard into a 150-mL beaker and add 2 mL ISA. Raise pH to about 11. Stir gently with magnetic mixer. Immerse electrodes, wait approximately 2 min for potential stabilization and record meter reading. Thoroughly rinse electrodes and blot dry. Repeat for each standard solution in order of increasing concentration. Prepare calibration curve on semilogarithmic graph paper by plotting observed potential in millivolts (linear scale) against concentration (log scale). Alternatively, calculate calibration line by regression analysis.

c. Analysis of samples: Transfer 100 mL sample into a 150-mL beaker and follow procedure applied to standards in ¶ 4*b* above. From the measured response, calculate K^+ concentration from calibration curve.

5. Precision

Reproducibility of potential measured, over the method's range, can be expected to be ± 0.4 mV, corresponding to about ± 2.5% in concentration.

6. Quality Assurance

The slope of the calibration line should be –56 mV/10-fold concentration change. If the slope is outside the range of –56 ±3 mV, the electrode may require maintenance (replace filling solutions). If the proper electrode response cannot be obtained, replace electrode.

Analyze an independent check standard with a mid-range potassium concentration throughout analysis of a series, initially, every ten samples, and after final sample. If the value has changed by more than 5%, recalibrate electrode. Analyze a reagent blank at the same frequency. Readings must represent a lower concentration than the lowest concentration standard (0.1 mg/L).

7. Bibliography

PIODA, L., V. STANKOVA & W. SIMON. 1969. Highly selective potassium ion responsive liquid membrane electrode. *Anal. Lett.* 2 (12): 665.

MIDGLEY, D. & K. TORRANCE. 1978. Potentiometric Water Analysis. John Wiley & Sons, New York, N.Y.

BAILEY, P.L. 1980. Analysis with Ion-Selective Electrodes. Heyden & Son Ltd., Philadelphia, Pa.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3500-Re RHENIUM

Rhenium (Re) is the third element in Group VIIB in the periodic table; it has an atomic number of 75, an atomic weight of 186.21, and valences of 1 through 7, with 7 being the most stable. The average abundance of Re in the earth's crust is 7 ppm, and in groundwaters it is <0.1 mg/L. Rhenium is found in columbite, tantalite, and wolframite, as well as in molybdenum ore concentrates. It is used in tungsten-molybdenum-based alloys, thermocouples, filaments, and flash bulbs. Rhenium in the powderform can be flammable.

For analysis methods, see flame atomic absorption methods (Section 3111D and Section 3111E). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though rhenium is not specifically listed as an analyte in the method.

3500-Rh RHODIUM

Rhodium (Rh) is the fifth element in Group VIII in the periodic table; it has an atomic number of 45, an atomic weight of 102.91, and valences of 1 through 6, the most common being 1 and 3. Rhodium is found in its native state in platinum-bearing sands. It is used in platinum alloys for thermocouples, electrical contacts, and jewelry.

The aqueous chemistry in natural waters is relatively unknown. The metal is flammable in the powder form, and its salts are toxic by inhalation.

For analysis see flame atomic absorption method (Section 3111B). The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though rhodium is not specifically listed as an analyte in the method.

3500-Ru RUTHENIUM

Ruthenium (Ru) is the fourth element in Group VIII in the periodic table; it has an atomic number of 44, an atomic weight of 101.07, and valences of 1 through 7, the most common being 2, 3, and 4. The average abundance of Ru in the earth's crust is probably <0.01 ppm, and in groundwaters it is <0.1 mg/L. It occurs in its native state in platinum-bearing river sands. It is used in jewelry with platinum, in electrical contacts, and as a catalyst.

The aqueous chemistry in natural waters is relatively unknown. Ruthenium has no known toxic effects.

For analysis see flame atomic absorption method (Section 3111B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though ruthenium is not specifically listed as an analyte in the method.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3500-Se SELENIUM*#(115)

3500-Se A. Introduction

1. Occurrence and Significance

Selenium (Se) is the third element in Group VIA in the periodic table; it has an atomic number of 34, an atomic weight of 78.96, and valences of 2, 4, or 6. The average abundance of Se in the earth's crust is 0.2 ppm; in soils it is 0.27 to 0.74 ppm; in streams it is 0.2 µg/L, and in groundwaters it is <0.1 mg/L. Selenium is used in electronics, ceramics, and shampoos.

The inorganic fraction of dissolved selenium consists predominantly of selenium as the selenate ion (SeO_4^{2-}), designated here as Se(VI), and selenium as the selenite ion (SeO_3^{2-}), Se(IV). Other common aqueous species include Se^{2-}, HSe^-, and Se^0. Selenium is considered a nonessential trace element for most plants, but is an essential trace nutrient for most animals, and selenium deficiency diseases are well known in veterinary medicine. Above trace levels, ingested selenium is toxic to animals and may be toxic to humans. While the selenium concentration of most natural waters is low, the pore water in seleniferous soils in semiarid areas may contain up to hundreds or thousands of micrograms dissolved selenium per liter. Certain plants that grow in such areas accumulate large concentrations of selenium and may poison livestock that graze on them. Water drained from such soil may cause severe environmental pollution and wildlife toxicity. Selenopolysulfide ions (SSe^{2-}) may occur in the presence of hydrogen sulfide in waterlogged, anoxic soils. Selenium derived from microbial degradation of seleniferous organic matter includes selenite, selenate, and the volatile organic compounds dimethylselenide and dimethyldiselenide. Nonvolatile organic selenium compounds may be released to water by microbial processes. Soluble selenium may be leached from coal ash and fly ash at electric power plants that burn seleniferous coal.

The United Nations Food and Agriculture Organization recommended maximum level for selenium in irrigation waters is 20 µg/L. The U.S. EPA primary drinking water standard MCL is 50 µg/L.

2. Selection of Method

The selenium methods using hydride generation atomic absorption (Section 3114B and Section 3114C), electrothermal atomic absorption (Section 3113B), and derivatization colorimetry (C) are the most sensitive currently available. For determination of selenium at higher concentrations, the inductively coupled plasma methods (Section 3120 and Section 3125) may be used.

By using suitable preparatory steps to convert other chemical species to Se(IV), it is possible to distinguish the chemical species in the sample. In drinking water and most surface and ground

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

waters, Se(IV), Se(VI), and particulate selenium frequently are the only significant species. However, when speciation is important, for example, when a new matrix is being analyzed, the general analytical scheme shown in Figure 3500-Se:1 may be carried out as follows: Determine volatile selenium by stripping sample with nitrogen or air and collecting selenium in alkaline hydrogen peroxide (see Method D). To obtain an estimate of selenium in suspended particles, determine total selenium, filter sample, and make a second determination of total selenium. In any case, filter sample. Occasionally, a filtered sample may have the odor of hydrogen sulfide and a yellow color; such a sample may contain selenopolysulfides, which may be estimated by comparing results of total selenium analyses before and after acidification, stripping with nitrogen, settling for 10 min, and refiltration. Determine selenite, Se(IV), by analyzing filtered water sample directly by Methods 3114B or C, or by Section 3500-Se.C or Section 3500-Se.E. In principle, sample digestion with HCl will convert Se(VI) to Se(IV), and the value determined will equal the sum of the two species. In practice, samples frequently contain an unknown masking agent that produces an unduly low result. Test for this effect by analyzing samples with known additions of both species. If recovery is good, the HCl digestion followed by analyses will yield reliable results. If recovery is poor and organic selenium is to be determined subsequently, attempt to remove the interference by sample pretreatment with resin (B.1). Interference also can be eliminated by digestion with an oxidizing agent (B.2, 3, and 4), but these procedures prevent distinguishing of Se(VI) and organic selenium and also oxidize many organic selenium compounds. To measure nonvolatile organic selenium compounds, use Method E.

The choice of digestion method for oxidizing interferences and organic selenium depends on sample matrix. The methods described in B.2, 3, and 4, in order of increasing complexity and digestive ability, use ammonium (or potassium) persulfate, hydrogen peroxide, and potassium permanganate. Ammonium persulfate digestion is adequate for most filtered ground, drinking, and surface water. Hydrogen peroxide digestion may be required if organic selenium compounds are present, and potassium permanganate digestion may be needed with unfiltered samples or those containing refractory organic selenium compounds. Confirm results obtained with one digestion method by using a more rigorous method when characterizing a new matrix.

3. Interferences

Interferences are found in certain reagents, as well as in samples. Recognition of the presence of an interferant is critical, especially when unknown sample matrices are being analyzed. Routinely add Se(IV) and Se(VI) to test for interference. If present, characterize the interference and correct by the method of standard additions. A slope less than one indicates interference. In cases of mild interference (recoveries reduced by 25% or less), the standard additions method will largely correct determined values.

Because the hydride atomic absorption method is extremely sensitive, samples frequently need to be diluted to bring them within the linear range of the instrument. Diluting a filtered water sample frequently will eliminate sample-related interferences. Include full reagent blanks in each run to ensure absence of contamination from reagents. Hydride generator atomic absorption is susceptible to common interference problems related to nitrite in the sample or free

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

chlorine in the reagent HCl (see Methods Section 3114B and Section 3114C).

4. Bibliography

U.S. NATIONAL ACADEMY OF SCIENCES. 1976. Selenium: Medical and Biological Effects of Environmental Pollutants. National Academy of Sciences, Washington, D.C.

CUTTER, G.A. 1978. Species determination of selenium in natural waters. *Anal. Chim. Acta* 98:59.

ROBBERECHT, H. & R. VAN GRIEKEN. 1982. Selenium in environmental waters: Determination, speciation and concentration levels. *Talanta* 29:823.

KUBOTA, J. & E.E. CARY. 1982. Cobalt, molybdenum and selenium. *In* A.L. Page et al., eds. Methods of soil analysis, Part 2, 2nd ed. *Agronomy* 9:485.

RAPTIS, S. et al. 1983. A survey of selenium in the environment and a critical review of its determination at trace levels. *Fresenius Z. Anal. Chem.* 316:105.

CUTTER, G. 1983. Elimination of nitrite interference in the determination of selenium by hydride generation. *Anal. Chim. Acta* 149:391.

CAMPBELL, A. 1984. Critical evaluation of analytical methods for the determination of trace elements in various matrices. Part 1. Determination of selenium in biological materials and water. *Anal. Chem.* 56:645.

LEMLY, A.D. 1985. Ecological basis for regulating aquatic emissions from the power industry: The case with selenium. *Regul. Toxic. Pharm.* 5:465.

OHLENDORF, H.M., D.J. HOFFMAN, M.K. SAIKI & T.W. ALDRICH. 1986. Embryonic mortality and abnormalities of aquatic birds: Apparent impacts of selenium from irrigation drainwater. *Sci. Total Environ.* 52:49.

3500-Se B. Sample Preparation

1. Removal of Organic and Iron Interference by Resin Pretreatment

Interferences are common in selenium analysis, particularly when chemical speciation is attempted. Routine pretreatment of water samples as described here is not necessary. The methods in this section should be tried when poor recovery of standard additions indicates a problem.

Many waters contain iron and/or dissolved organic matter (humic acid) in quantities sufficient to interfere. Reduction of Se(VI) to Se(IV) usually is nonquantitative. When Se(VI) standard additions show poor recovery, treat the sample before analysis. To remove dissolved organic compounds, pass an acidified sample through a resin. Because dissolved organic selenium compounds also may be removed by this treatment, also determine total selenium in the untreated water sample (see 2, 3, or 4 below). To remove iron use a strong base ion exchange resin.*#(116) Iron is removed as the anionic chloro complex. In this treatment the acidity and ion exchanger do not alter speciation; complete speciation of selenium is possible.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

a. Apparatus:

1) *Chromatography column* for organics removal, glass, about 0.8 cm ID ×30 cm long, with fluorocarbon metering valve.

2) *Chromatography column* for ion exchange, disposable polyethylene.†#(117)

3) *pH meter.*

b. Reagents:

1) *Organics-removal resin:* Thoroughly rinse 16 to 50 mesh resin‡#(118) with deionized water and remove resin fines by decanting. Rinse three times with pH 12 solution. Store resin in pH 12 solution and refrigerate to prevent bacterial growth.

2) *Anion exchange resin:* Add 100 to 200 mesh anion exchange resin*#(119) to a beaker and thoroughly rinse with deionized water. Cover resin with 4*N* HCl, stir, and let settle. Decant and repeat acid rinse twice more. Store resin in 4*N* HCl.

3) *Hydrochloric acid,* conc: Before use, bubble helium through the acid for 3 h at rate of 100 mL/min. (CAUTION*: Use a fume hood.*)

4) *pH 1.6 solution:* Adjust pH of deionized water to 1.6 with HCl.

5) *pH 12 solution:* Adjust pH of deionized water to 12 with KOH.

c. Procedure:

1) Organic removal—Place 5 cm washed resin in a 0.8-cm-ID column. Precondition column, at 1 mL/min, with 30 mL pH 12 solution and 20 mL pH 1.6 solution. Using HCl and a pH meter adjust sample to pH 1.6 to 1.8. Pass sample through preconditioned column at rate of 1 mL/min. Discard first 10 mL and use next 11 to 50 mL collected for Se(IV) determinations by Methods 3114B or C, or 3500-Se.C preceded, if Se(VI) also is to be determined, by preparatory step B.5. If more than 50 mL sample are needed, use another column or use a column with twice as much resin.

2) Iron removal—Place 4 cm prepared resin in a small chromatographic column (add resin to column filled with 4*N* HCl to avoid air bubbles). Rinse column with 10 mL 4*N* HCl at flow rate < 6 mL/min. Let solution drain to top of resin, but do not let the column run dry. Adjust sample to 4*N* HCl and pour into column. Discard first 10 mL and collect the next 11 to 100 mL for Se(IV) analysis by Methods 3114B or C, or 3500-Se.C preceded, if necessary, by preparatory step B.2 and if Se(VI) also is to be determined, by preparatory step B.5 below.

2. Removal of Interference by Persulfate Digestion

The combination of this procedure with step B.5 below and Methods Section 3114B or Section 3114C, or Section 3500-Se.C is, in most cases, the preferred method for determining total selenium in filtered water. A small amount of ammonium or potassium persulfate is added to the mixture of sample and HCl to remove interference from reducing agents and to oxidize relatively labile organic selenium compounds such as selenoamino acids and methaneseleninic acid.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

If the sample contains hydrogen sulfide or a large concentration of organic matter or is otherwise suspect or to confirm method accuracy, reanalyze sample using digestion procedure 3 or 4 below.

Prepare 2% potassium or ammonium persulfate solution by dissolving 2.0 g in 100 mL deionized water (prepare weekly). Add 0.2 mL persulfate solution to the mixed sample and HCl of ¶ B.5*c* before heating and proceeding with pretreatment and analysis.

After completing analysis multiply concentration of selenium determined in the acidified sample by 2.04 to obtain total selenium in original sample.

3. Removal of Interference by Alkaline Hydrogen Peroxide Digestion

Occasionally, digestion with persulfate gives incomplete recovery of total selenium. In this case, digestion with hydrogen peroxide is used to remove all reducing agents that might interfere and to fully oxidize organic selenium to Se(VI). The resulting solution can be analyzed for total selenium after pretreatment according to step B.5 below.

This method is suitable for determining total selenium in unfiltered water samples, where particulate selenium is present. When working with a new matrix, confirm results obtained by reanalyzing the sample using digestion procedure 4, below.

a. Apparatus:

1) *Beakers,* 150-mL.

2) *Watch glasses.*

3) *Hot plate.*

4) *Pipetter,* 1-mL, and tips.

5) *Graduated cylinder,* 25-mL.

b. Reagents:

1) *Hydrogen peroxide,* H_2O_2, 30%. Keep refrigerated.

2) *Sodium hydroxide,* NaOH, 1*N*.

3) *Hydrochloric acid,* HCl, 1.5*N*: Dilute 125 mL conc HCl to 1 L with deionized water.

c. Procedure: Add 2 mL 30% H_2O_2 and 1 mL 1 *N* NaOH to 25 mL sample in a beaker. Cover beaker to control spattering and simmer on hot plate until fine bubbles characteristic of H_2O_2 decomposition subside and are replaced by ordinary boiling. Add 1 mL 1.5*N* HCl to redissolve any precipitate that may have formed, let cool, and pour into graduated cylinder. Rinse beaker with deionized water into graduated cylinder and make volume up to 25 mL. Proceed to B.5 and chosen analytical method.

4. Removal of Interference by Permanganate Digestion

This digestion method utilizes potassium permanganate to oxidize selenium and remove interfering organic compounds. Excess $KMnO_4$ and MnO_2 are removed by reaction with hydroxylamine. HCl digestion is included here, because it is conveniently performed in the same

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

reaction vial. Selenite may then be determined directly by Methods Section 3114B or Section 3114C, or Section 3500-Se.C.

Verify recovery for the given matrix. This method gives good recovery even with heavily contaminated water samples that contain organic selenium compounds, dissolved organic matter, and visible suspended material.

Permanganate may oxidize chloride ion to free chlorine. Part of the chlorine (which interferes with hydride analysis) is removed by reaction with hydroxylamine, but the best way to eliminate free chlorine is by prolonged heating in an open vial during the digestion step. Excess hydroxylamine may reduce recovery by reducing selenium to Se(0).

a. Apparatus:

1) *Oven with thermostat,* for continuous operation at 110 ± 5°C.

2) *Digestion vials,* 40-mL, with fluorocarbon-lined screw caps.

3) *Metal support rack* to hold 40 digestion vials.

b. Reagents:

1) *Hydrochloric acid,* HCl, conc. [See ¶ B.1*b*3)].

2) *Hydrochloric acid,* HCl, 10*N:* Dilute 1000 mL conc HCl to 1200 mL with deionized water.

3) *Sulfuric acid,* H_2SO_4, conc and 25%. NOTE: Many brands of H_2SO_4 are contaminated with selenium. Run reagent blanks when starting a new bottle. Make 25% v/v solution by adding 250 mL conc H_2SO_4 to 500 mL deionized water, and diluting to 1 L.

4) *Potassium permanganate solution,* $KMnO_4$, 5% (w/v): Dissolve 50 g $KMnO_4$ in 1000 mL deionized water.

5) *Hydroxylamine hydrochloride solution:* Dissolve 100 g $NH_2OH{\cdot}HCl$ in 1000 mL deionized water.

c. Procedure: Pipe 5 mL sample into digestion vial, add 5 mL 25% H_2SO_4 and 1 mL $KMnO_4$ solution. Screw cap on and place in preheated oven at 110°C for 1 h. Remove tray with vials from the oven and cool to room temperature. Open vial, carefully add a few drops hydroxylamine hydrochloride solution, mix, and wait until sample is decolorized and residual manganese dioxide is dissolved. Avoid excess hydroxylamine solution, which can cause a low reading. Add 10 mL conc HCl to the sample and heat vial 60 min at 95°C without cap. Let cool to room temperature. Transfer sample to a 25-mL volumetric flask or graduated cylinder, rinse vial into flask, dilute to mark, and mix well. Proceed to analyze by Methods Section 3114B or Section 3114C, or Section 3500-Se.C. If Method Section 3114B or Section 3114C is used, multiply spectrometer readings by the dilution factor as follows:

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

$$\text{Concentration, } \mu g/L = \frac{\text{final volume}}{\text{volume of sample}} \times \text{reading}$$

5. Reduction of Se(VI) to Se(IV) by Hydrochloric Acid Digestion

Se(VI) is reduced to Se(IV) by digestion with HCl. Determine Se(IV) + Se(VI) by either hydride generation atomic absorption spectrometer (Method Section 3114B or Section 3114C) or as an organic derivative (Method C).

Test any given sample matrix to ensure recovery of added Se(VI). If recovery is poor, try to remove interference by the procedure of ¶ B.1, above, or if at least 75% recovery is achieved, use the method of standard additions. The method described here is of limited utility for direct analysis of water samples, but is useful as a step in determining total selenium in a sample where selenium has been oxidized to Se(VI).

a. Apparatus:

1) *Dispenser,* bottle type, 5-mL, suitable for dispensing concentrated HCl.

2) *Pipetters,* 0.2- and 5-mL.

3) *Screw-cap culture tubes,* borosilicate glass, 25- × 150-mm.

4) *Boiling water bath,* suitable for heating culture tubes; a 1-L beaker on a hot plate is suitable.

b. Reagents:

1) *Sodium selenate additions solution:* Dilute 1000 mg/L stock selenate solution with deionized water to prepare a solution of 1 to 10 mg/L, such that the concentration of the additions solution will be approximately 50 times greater than anticipated total selenium in the sample to be analyzed.

2) *Hydrochloric acid,* HCl, conc: See ¶ B.1*b*3).

c. Procedure: Calibrate acid dispenser using water. Preheat water bath. Pipet 5 mL filtered sample into a culture tube. Add 5 mL conc HCl. Loosely cap tube (do not tighten) and place in boiling water bath for 20 min. Let tube cool and tighten cap. Determine total Se(IV) by Methods Section 3114B or C, or Section 3500-Se.C.

Add 0.200 mL additions solution with a microliter pipet to sample and proceed as above. Analyze a deionized water blank and a blank with the addition to ensure absence of contamination and to determine the true value of the addition.

Multiply the concentration of selenium determined in the acidified sample by 2.00 to obtain total concentration of Se(IV) + Se(VI). Multiply reading obtained for sample with addition by 2.04.

6. Bibliography

JANGHORBANI, M., B. TING, A. NAHAPETLAN & R. YOUNG. 1982. Conversion of urinary selenium

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

to selenium IV by wet oxidation. *Anal. Chem.* 54:1188.

ADELOJU, S.B. & A.M. BOND. 1984. Critical evaluation of some wet digestion methods for the stripping voltammetric determination of selenium in biological materials. *Anal. Chem.* 56:2397.

BRIMMER, S.P., W.R. FAWCETT & K.A. KULHAVY. 1987. Quantitative reduction of selenate ion to selenite in aqueous samples. *Anal. Chem.* 59:1470.

3500-Se C. Colorimetric Method

1. General Discussion

a. Principle: This method is specific to determining selenite ion in aqueous solution. Selenite ion reacts with 2,3-diaminonaphthalene to produce a brightly colored and strongly fluorescent piazselenol compound, which is extracted in cyclohexane and measured colorimetrically.

The optimum pH for formation of the piazselenol complex is approximately 1.5 but should not be above 2.5 because above pH 2, the rate of formation of the colored compound is critically dependent on pH. When indicators are used to adjust pH, results frequently are erratic; results can be improved when pH is monitored electrochemically.

b. Interference: No inorganic compounds are known to give a positive interference. Colored organic compounds extractable by cyclohexane may be encountered, but usually they are absent or can be removed by oxidizing the sample (see B.2, 3, or 4) or by treating it to remove dissolved organics (see B.1). Negative interference results from compounds that reduce the concentration of diaminonaphthalene by oxidizing it. Addition of EDTA eliminates negative interference from at least 2.5 mg Fe^{2+}.

c. Minimum detectable quantity: 10 µg Se/L.

2. Apparatus

a. Colorimetric equipment: A spectrophotometer, for use at 480 nm, providing a light path of 1 cm or longer.

b. Separatory funnel, 250-mL, preferably with a fluorocarbon stopcock.

c. Thermostatically controlled water bath (50°C) with cover.

d. pH meter.

e. Centrifuge, with rotor for 50-mL tubes (optional).

f. Centrifuge bottles, 60-mL, screw-capped, fluorocarbon.

g. Shaker, suitable for separatory funnel (optional).

3. Reagents

Use reagent water (see Section 1080) in preparing reagents.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

a. Selenium standard reference solution: Dissolve 2.190 g sodium selenite, Na_2SeO_3, in water containing 10 mL HCl and dilute to 1 L. 1.00 mL = 1.00 mg Se(IV).

b. Working standard selenium solutions: Dilute selenium reference standard solution with water or suitable background solution to produce a series of working standards spanning the concentration range of interest.

c. Hydrochloric acid: HCl, conc and 0.1*N*.

d. Ammonium hydroxide, NH_4OH, 50% v/v.

e. Cyclohexane, C_6H_{12}.

f. 2,3-Diaminonaphthalene (DAN) solution: Dissolve 200 mg DAN in 200 mL 0.1*N* HCl. Shake 5 min. Extract three times with 25-mL portions of cyclohexane, retaining aqueous phase and discarding organic portions. Filter into opaque container*#(120) and store in cool, dark place for no longer than 8 h. CAUTION*: Toxic, handle with extreme care.*

g. Hydroxylamine-EDTA solution (HA-EDTA): Dissolve 4.5 g Na_2EDTA in approximately 450 mL water. Add 12.5 g hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) and adjust volume to 500 mL.

4. Procedure

a. Formation of piazselenol: Add 2 mL HA-EDTA solution to 10 mL sample in 60-mL centrifuge bottle (filtered if Se(IV) is to be determined; oxidized using Method B.2, 3, or 4, then reduced using Method B.5 for total Se). Adjust to pH 1.5 ± 0.3 with 0.1*N* HCl and 50% NH_4OH, using a pH meter. Add 5 mL DAN solution and heat in a covered water bath at 50°C for 30 min.

b. Extraction of piazselenol: Cool and add 2.0 mL cyclohexane. Cap container securely and shake vigorously for 5 min. Let solution stand for 5 min or until cyclohexane layer becomes well separated. If separation is slow, centrifuge for 5 min at 2000 rpm. Place bottle in a clamp on a ringstand at a 45° angle to the vertical. Remove aqueous phase using a disposable pipet attached to a vacuum line. Transfer organic phase to a small capped container using a clean disposable pipet, or to the spectrophotometer cuvette if absorbance is to be read immediately.

c. Determination of absorbance: Read absorbance at 480 nm using a zero standard. The piazselenol color is very stable but evaporation of the cyclohexane concentrates the color unless the container is capped. CAUTION*: Avoid inhaling cyclohexane vapors*. Beer's Law is obeyed up to 2 mg/L.

5. Calculation

Construct calibration curve using at least a three-point standard curve to bracket the expected sample concentration. Plot absorbance vs. concentration. Correct for digestion blank and any reagent blank.

6. Precision and Bias

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Three standard reference materials (wheat flour, water, and a commercial standard) were used to evaluate Se recovery.[1] The wheat flour sample was digested using HNO_3 and $HClO_4$ to convert total selenium to Se(VI), digested with HCl to convert Se(VI) to Se(IV) and finally, the colorimetric method was used. Results were as follows:

	Selenium Concentration *µg Se/L*	
Standard	**Expected**	**Recovered***
NBS, SRM 1567, wheat flour†	1097 ± 197	1113 ± 8
NBS, SRM 1543ib, water	9.7 ± 0.5	8.7 ± 0
Fisher Certified AAS Standard	1002 ± 8	1002 ± 0

* Analyses in triplicate.
† Dry weight basis.

7. Reference

1. HOLTZCLAW, K.M., R.H. NEAL, G. SPOSITO & S.J. TRAINA. 1987. A sensitive colorimetric method for the quantitation of selenite in soil solutions and natural waters. *Soil Sci. Soc. Amer. J.* 51:75.

8. Bibliography

HOSTE, J. & J. GILLIS. 1955. Spectrophotometric determination of traces of selenium with 3,3′-diaminobenzidine. *Anal. Chim. Acta*. 12:158.

CHENG, K. 1956. Determination of traces of selenium. *Anal. Chem.* 28:1738.

MAGIN, G.B. et al. 1960. Suggested modified method for colorimetric determination of selenium in natural waters. *J. Amer. Water Works Assoc.* 52:1199.

ROSSUM, J.R. & P.A. VILLARRUZ. 1962. Suggested methods for determining selenium in water. *J. Amer. Water Works Assoc.* 54:746.

OLSEN, O.E. 1973. Simplified spectrophotometric analysis of plants for selenium. *J. Assoc. Offic. Anal. Chem.* 56:1073.

3500-Se D. Determination of Volatile Selenium

1. General Discussion

Dimethylselenide and dimethyldiselenide are low boiling, extremely malodorous organic compounds sparingly soluble in water. They are produced by microbial processes in seleniferous soil and decaying seleniferous organic matter, and occasionally are present in natural waters. They are readily air stripped from a water sample and can be collected with high efficiency in an

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

alkaline solution of hydrogen peroxide, which oxidizes them quantitatively to Se(VI). Total selenium is determined by digestion with HCl and analysis by the hydride atomic absorption (Section 3114B or Section 3114C) or colorimetric (Section 3500-Se.C) methods.

Either nitrogen or air may be used to strip the sample. Preferably use nitrogen if air-sensitive compounds (e.g., selenopolysulfides) are suspected.

Because volatile selenium can be lost in the course of sample collection and handling, preferably air-strip the sample in the field immediately after it is collected. After boiling to decompose H_2O_2, return the alkaline peroxide solution to the laboratory for analysis.

2. Apparatus

All apparatus required for selenate reduction (¶ B.5) and Methods Section 3114B or Section 3114C, or Section 3500-Se.C, plus:

a. Gas washing bottles, borosilicate glass, 250-mL, with coarse porous glass gas dispersion frit. Mark 100-mL level on side of bottle.

b. Rotameter, to measure 3 L/min air flow.

c. Gas flow regulator

d. Hot plate.

e. Graduated cylinder, 100-mL.

f. Beakers, 250-mL.

g. Rubber tubing, to interconnect gas washing bottles and other gas equipment.

h. Rubber gloves.

3. Reagents

All reagents required for selenate reduction (¶ B.5) and Methods Section 3114B or Section 3114C, or Section 3500-Se.C, plus:

a. Hydrogen peroxide, 30%. Refrigerate.

b. Sodium hydroxide solution, NaOH, 1*N*.

c. Compressed air or nitrogen.

4. Procedure

Set up air-flow train in this order: Regulated air supply→rotameter→gas washing bottle 1→gas washing bottle 2.

Prepare alkaline peroxide solution immediately before use by pouring 20 mL 30% H_2O_2 into a 100-mL graduated cylinder, adding 50 to 60 mL deionized water and 5 mL 1*N* NaOH, and making up to 100 mL. CAUTION: *Alkaline* H_2O_2 is unstable. Do not keep in glass bottle; hold at about 0 °C in oversized plastic bottle. Solution is corrosive; protect eyes and skin. Pour into gas washing bottle 2. Pour approximately 100 mL freshly collected sample into gas washing bottle 1. Do not attempt to measure sample volume accurately before volatile selenium determination, as

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

unnecessary handling may cause volatile selenium to be lost.

Connect and check all air lines, turn on air and adjust flow to 3 L/min. Strip for 30 min or more. After 30 min, turn off air, disconnect gas washing bottle 2, and place it on the hot plate. Adjust heat to produce a gentle simmering of oxygen bubbles from decomposition of H_2O_2. Continue heating until the characteristic effervescence of oxygen subsides and is replaced by ordinary boiling. Remove from hot plate and let cool. Pour solution into beaker. (Volume will be very near to 100 mL, and correction will usually be unnecessary.) Analyze for total selenium using HCl digestion (B.5) and Methods Section 3114B or Section 3114C, or Section 3500-Se.C. Once boiled, this solution may be safely stored and transported in plastic bottles. Measure volume of sample in gas washing bottle 1.

5. Calculation

The concentration of volatile selenium compounds in the original water sample can be calculated as:

$$C = \frac{100}{\text{volume of original sample}} \times \text{conc of Se in solution}$$

6. Precision and Bias

Approximately 90% of dimethylselenide in samples will be recovered with 30 min air stripping. The recovery of dimethyldiselenide is not known. Loss of gases to the atmosphere during sampling and handling that precede analysis may cause a significant negative error.

3500-Se E. Determination of Nonvolatile Organic Selenium Compounds

1. General Discussion

In principle, the total amount of dissolved organic selenium plus polysulfidic selenium may be estimated by comparing ‘‘total Se,’’ determined by oxidation and HCl digestion (¶ B.2 or ¶ B.3 and ¶ B.5, or ¶ B.4), followed by Methods Section 3114B or Section 3114C, or Section 3500-Se.C, with Se(IV) + Se(VI) determined by HCl digestion (¶ B.5) and Method Section 3114C, or Section 3500-Se.C. In practice, this will give a meaningful estimate only if a known addition of Se(VI) is fully recovered. Even if recovery is good, this estimate may be unreliable, because it is the difference of two (frequently larger) numbers determined by slightly different methods. Comparing total Se before and after treatment with resin [¶ B.1*c*1)] gives a similarly unreliable estimate of nonvolatile organic Se.

It is preferable to separate and directly determine nonvolatile organic selenium. One method involves adsorption of dissolved organic matter onto a C-18 reverse phase HPLC resin, elution

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

with an organic solvent, and determination of selenium in this fraction. While this technique is relatively simple, it is affected by pH and small organic molecules (e.g., individual selenium containing amino acids) are not retained by the resins. Adjust sample pH to 1.5 to 2.0 before using the column, but because the latter problem cannot be solved easily, the use of organic adsorbents provides only an estimate of organic selenium concentration.

Alternatively, isolate specific compounds and determine their selenium content. In some natural waters selenium may be associated with dissolved polypeptides or small proteins, and even small amounts of free selenoamino acids may be present. Because selenoamino acids are the most toxic form of the element, a direct determination is sometimes desirable.

To determine selenium in dissolved peptides, hydrolyze with acid and isolate the free amino acids via ligand exchange chromatography. Elute the selenoamino acids from the column and determine selenium. Selenoamino acids are unstable during acid hydrolysis and even using nonoxidizing methyl sulfonic acid and nitrogen-purged glass ampules, selenoamino acid recoveries are only 50 to 80%. This method is good only for estimating protein-bound selenium. A somewhat more reliable estimate of free selenoamino acids and selenium associated with small oligopeptides is obtained by performing a similar procedure without the hydrolysis step.

While these methods are too intricate for routine use, semiquantitative, and sensitive only to certain classes of organic compounds, at present they are the only ones available with any practical experience.

Imperfect separation of organic selenium compounds from inorganic forms of selenium may cause interference. In parallel with the actual determination, always perform the procedure using a solution compounded to resemble the actual matrix and containing a similar amount of selenium, but in the form of Se(IV) and Se(VI) to determine degree of interference.

2. Apparatus

a. Rotary evaporator, with temperature-control bath and 30-mL pear-shaped flasks.

b. Glass ampule sealing apparatus, or oxygen-gas torch.

c. Heating block, 100°C, or pressure cooker.

d. Glass chromatography columns, 15 cm long, 0.7 cm ID.*#(121)

e. Glass syringe, 50-mL.

f. Glass ampules, 10- or 20- mL. Clean by heating in a muffle furnace at 400°C for 24 h.

g. pH meter.

3. Reagents

a. Hydrochloric acid, HCl, 1*N*.

b. Methyl sulfonic acid, conc.

c. Ammonium hydroxide, NH_4OH, 1.5*N:* Dilute 100 mL conc NH_4OH to 1 L with deionized water.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

d. Sodium hydroxide, NaOH pellets and 1*N* solution.

e. pH 1.6 solution: Adjust pH of deionized water to 1.6 using HCl.

f. pH 9.0 solution: Adjust pH of deionized water to 9.0 using NaOH.

g. Copper sulfate solution, $CuSO_4$, 1*M:* Dissolve 25 g $CuSO_4 \cdot 5H_2O$ in deionized water and dilute to 100 mL.

h. Methanol, purified.

i. C-18 cartridges†#(122) Using a glass syringe, pass the following sequence of reagents through the cartridge to clean the resin (6 mL/min or less): 10 mL deionized water; 20 mL 1*N* HCl; 10 mL deionized water; 20 mL methanol; 10 mL deionized water; and 20 mL pH 1.6 solution. Refrigerate but do not freeze cleaned cartridges.

j. Ligand-exchange chromatographic resin, 100/200 mesh: Rinse resin‡#(123) with deionized water to remove fines. Then rinse resin three times in the following sequence: 1*N* HCl; 1.5*N* NH_4OH; and deionized water. Store resin wet.

k. Copper-treated ligand-exchange chromatographic resin, 100/200 mesh: Rinse resin‡ with deionized water to remove fines. Then rinse three times with 1*N* HCl, followed by deionized water. Using NaOH adjust pH of supernatant above the resin to about 7. Add $CuSO_4$ solution to the resin and stir. After settling, decant supernatant and add more $CuSO_4$ solution. Decant $CuSO_4$ solution and rinse with deionized water until no copper is noticeable in the supernatant. Rinse resin three times with 1.5*N* NH_4OH and three times with deionized water. Store resin wet.

4. Procedures

a. Extractable organic selenium: Adjust sample (5 to 50 mL) to pH 1.5 to 2.0 using HCl and place in a clean glass syringe with an attached cleaned C-18 cartridge. Push sample through the cartridge at a rate of 6 mL/min. After removing the cartridge, draw 2 mL pH 1.6 solution into syringe as a rinse, reattach cartridge, and push the rinse through the cartridge. Repeat two additional times. The cartridge can be refrigerated for storage. To elute organic selenium, push 10 mL methanol through the cartridge at rate of 2 mL/min and collect eluate in a 30 mL pear-shaped flask. Remove methanol by rotary evaporation, with the water bath temperature less than 40°C. Use deionized water to solubilize and transfer the residue into the vessel used for total selenium digestions. Determine total dissolved selenium by digestion with persulfate (pG; B.2) or peroxide (pG; B.3), reduction of Se(VI) (pG; B.5), and analysis by Methods Section 3114B or Section 3114C, or Section 3500-Se.C.

b. Hydrolysis of protein-bound selenium: Place filtered sample in a 10- or 20-mL glass ampule (depending on desired volume), and add conc methyl sulfonic acid to adjust concentration to 4*M*. Purge acidified sample with nitrogen for 10 min and seal top with a torch. Heat sealed vial at 100°C for 24 h in a heating block or pressure cooker. Transfer cooled hydrolysis solution with deionized water rinses to a 50-mL beaker and place in an ice bath. Using NaOH pellets and 1*N* NaOH, adjust to pH 9.0, taking care not to allow solution to heat to

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

boiling.

c. Determination of selenoamino acids: If sample is not hydrolyzed as in ¶ 4*b*, filter, and adjust pH to 9.0 using 1*N* NaOH.

Fill an empty chromatographic column with deionized water and add ammonium-form resin to a depth of 2 cm. Add copper-treated resin to form a 12-cm length of resin. (The ammonium-form resin removes any copper that bleeds from the copper-treated resin above it). Rinse with deionized water until the pH of the effluent is 9.0; maintain flow through the column by gravity. Pass sample through column, rinse sample beaker with 5 mL pH 9 solution, and place the rinse on column (after the last of the sample reaches the top of the resin). Rinse beaker twice more. Discard flow through column.

Place clean beaker under column and add 20 mL 1.5*N* NH_4OH to the column. Neutralize NH_4OH eluate with 2.5 mL conc HCl. Determine total dissolved selenium by digestion with persulfate (¶ B.2) or peroxide (¶ B.3), reduction of Se(VI) (¶ B.5) and analysis by Methods Section 3114B or Section 3114C, or Section 3500-Se.C.

5. Precision and Bias

These procedures are only semiquantitative. Typical relative standard deviation is 12% for the C-18 isolation of dissolved organic selenium, and 15% for protein-bound selenium.

6. Bibliography

CUTTER, G. 1982. Selenium in reducing waters. *Science* 217:829.

COOKE, T.D. & K.W. BRULAND. 1987. Aquatic chemistry of selenium: evidence of biomethylation. *Environ. Sci. Technol.* 21:1214.

3500-Ag SILVER

Silver (Ag) is the second element in Group IB of the periodic table; it has an atomic number of 47, an atomic weight of 107.87, and valences of 1 and 2. The average abundance of Ag in the earth's crust is 0.08 ppm; in soils it is <0.01 to 0.5 ppm; in streams it is 0.3 µg/L; in U.S. drinking waters it is 0.23 µg/L, and in groundwater it is <0.1 µg/L. Silver occurs in its native state and in combination with many nonmetallic elements such as argentite (Ag_2S) and horn silver (AgCl). Lead and copper ores also may yield considerable silver. Silver is widely used in photography, silverware, jewelry, mirrors, and batteries. Silver iodide has been used in the seeding of clouds, and silver oxide to a limited extent is used as a disinfectant for water.

In acidic water Ag^+ would predominate, and in high-chloride water a series of complexes would be expected. Silver is nonessential for plants and animals. Silver can cause argyria, a permanent, blue-gray discoloration of the skin and eyes that imparts a ghostly appearance. Concentrations in the range of 0.4 to 1 mg/ L have caused pathological changes in the kidneys, liver, and spleen of rats. Toxic effects on fish in fresh water have been observed at concentrations as low as 0.17 µg/L. For freshwater aquatic life, total recoverable silver should

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

not exceed 1.2 mg/L.

The atomic absorption spectrometric methods (Section 3111B and Section 3111C) and the inductively coupled plasma methods (Section 3120 and Section 3125) are preferred. The electrothermal atomization method (Section 3113B) is the most sensitive for determining silver in natural waters. The dithizone method detailed in the 19th edition of *Standard Methods* can be used when an atomic absorption spectrometer is unavailable. A method suitable for analysis of silver in industrial or other wastewaters at levels above 1 mg/L is available.[1]

If total silver is to be determined, acidify sample with conc nitric acid (HNO_3) to pH <2 at time of collection. If sample contains particulate matter and only the ‘‘dissolved’’ metal content is to be determined, filter through a 0.45-µm membrane filter at time of collection. After filtration, acidify filtrate with HNO_3 to pH <2. Complete analysis as soon after collection as possible. Some samples may require special storage and digestion; see Section 3030D.

Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1994. Approved Inorganic Test Procedures. *Federal Register* 59(20):4504.

3500-Na SODIUM*#(124)

3500-Na A. Introduction

1. Occurrence and Significance

Sodium (Na) is the third element in Group IA of the periodic table; it has an atomic number of 11, an atomic weight of 22.99, and a valence of 1. The average abundance of Na in the earth’s crust is 2.5%; in soils it is 0.02 to 0.62%; in streams it is 6.3 mg/L, and in groundwaters it is generally >5 mg/L. Sodium occurs with silicates and with salt deposits. Sodium compounds are used in many applications, including caustic soda, salt, fertilizers, and water treatment chemicals.

Sodium is very soluble, and its monovalent ion Na^+ can reach concentrations as high as 15 000 mg/L in equilibrium with sodium bicarbonate. The ratio of sodium to total cations is important in agriculture and human physiology. Soil permeability can be harmed by a high sodium ratio. In large concentrations it may affect persons with cardiac difficulties. A limiting concentration of 2 to 3 mg/L is recommended in feedwaters destined for high-pressure boilers. When necessary, sodium can be removed by the hydrogen-exchange process or by distillation. The U.S. EPA advisory limit for sodium in drinking water is 20 mg/L.

2. Selection of Method

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Method Section 3111B uses an atomic absorption spectrometer in the flame absorption mode. Method Section 3120B uses inductively coupled plasma; this method is not as sensitive as the other methods, but usually this is not important. Method Section 3500-Na.B uses either a flame photometer or an atomic absorption spectrometer in the flame emission mode. The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though sodium is not specifically listed as an analyte in the method. When all of these instruments are available, the choice will depend on factors including relative quality of the instruments, precision and sensitivity required, number of samples and analytes per sample, matrix effects, and relative ease of instrument operation. If an atomic absorption spectrometer is used, operation in the emission mode is preferred.

3. Storage of Sample

Store alkaline samples or samples containing low sodium concentrations in polyethylene bottles to eliminate the possibility of sample contamination due to leaching of the glass container.

3500-Na B. Flame Emission Photometric Method

1. General Discussion

a. Principle: Trace amounts of sodium can be determined by flame emission photometry at 589 nm. Sample is nebulized into a gas flame under carefully controlled, reproducible excitation conditions. The sodium resonant spectral line at 589 nm is isolated by interference filters or by light-dispersing devices such as prisms or gratings. Emission light intensity is measured by a phototube, photomultiplier, or photodiode. The light intensity at 589 nm is approximately proportional to the sodium concentration. Alignment of the wavelength dispersing device and wavelength readout may not be precise. The appropriate wavelength setting, which may be slightly more or less than 589 nm, can be determined from the maximum emission intensity when aspirating a sodium standard solution, and then used for emission measurements. The calibration curve may be linear but has a tendency to level off or even reverse at higher concentrations. Work in the linear to near-linear range.

b. Interferences: Minimize interference by incorporation of one or more of the following:

1) Operate at the lowest practical concentration range.

2) Add releasing agents, such as strontium or lanthanum at 1000 mg/L, to suppress ionization and anion interference. Among common anions capable of causing interference are Cl^-, SO_4^{2-} and HCO_3^- in relatively large amounts.

3) Matrix-match standards and samples by adding identical amounts of interfering substances present in the sample to calibration standards.

4) Apply an experimentally determined correction in those instances where the sample

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

contains a single important interference.

5) Remove interfering ions.

6) Remove burner-clogging particulate matter from the sample by filtration through a filter paper of medium retentiveness.

7) Use the standard addition technique as described in the flame photometric method for strontium (Section 3500-Sr.B). The method involves preparing a calibration curve using the sample matrix as a diluent, and determining the sample concentration either mathematically or graphically.

8) Use the internal standard technique. Potassium and calcium interfere with sodium determination by the internal-standard method if the potassium-to-sodium ratio is ≥5:1 and the calcium-to-sodium ratio is ≥10:1. When these ratios are exceeded, determine calcium and potassium concentrations and matrix-match sodium calibration standards by addition of approximately equivalent concentrations of interfering ions. Interference from magnesium is not significant until the magnesium-to-sodium ratio exceeds 100, a rare occurrence.

b. Minimum detectable concentration: Better flame photometers or atomic absorption spectrometers operating in the emission mode can be used to determine sodium levels approximating 5 µg/L.

2. Apparatus

a. Flame photometer (either direct-reading or internal-standard type) or atomic absorption spectrometer operating in the flame emission mode.

b. Glassware: Rinse all glassware with 1 + 15 HNO_3 followed by several portions of reagent water (¶ 3*a*).

3. Reagents

To minimize sodium contamination, store all solutions in plastic bottles. Use small containers to reduce the amount of dry element that may be picked up from the bottle walls when the solution is poured. Shake each container vigorously to wash accumulated salts from walls before pouring solution.

a. Reagent water: See Section 1080. Use reagent water to prepare all reagents and calibration standards, and as dilution water.

b. Stock sodium solution: Dissolve 2.542 g NaCl dried at 140°C to constant weight and dilute to 1000 mL with water; 1.00 mL = 1.00 mg Na.

c. Intermediate sodium solution: Dilute 10.00 mL stock sodium solution with water to 100.0 mL; 1.00 mL = 0.10 mg Na (1.00 mL = 100 µg Na). Use this intermediate solution to prepare calibration curve in sodium range of 1 to 10 mg/L.

d. Standard sodium solution: Dilute 10.00 mL intermediate sodium solution with water to 100 mL; 1.00 mL = 10.0 µg Na. Use this solution to prepare calibration curve in sodium range of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

0.1 to 1.0 mg/L.

4. Procedure

a. Pretreatment of polluted water and wastewater samples: Follow the procedures described in Section 3030.

b. Instrument operation: Because of differences between makes and models of instruments, it is impossible to formulate detailed operating instructions. Follow manufacturer's recommendation for selecting proper photocell and wavelength, adjusting slit width and sensitivity, appropriate fuel and oxidant gas pressures, and the steps for warm-up, correcting for interferences and flame background, rinsing of burner, igniting flame, and measuring emission intensity.

c. Direct-intensity measurement: Prepare a blank and sodium calibration standards in stepped amounts in any of the following applicable ranges: 0 to 1.0, 0 to 10, or 0 to 100 mg/L. Determine emission intensity at 589 nm. Aspirate calibration standards and samples enough times to secure a reliable average reading for each. Construct a calibration curve from the sodium standards. Determine sodium concentration of sample from the calibration curve. Where a large number of samples must be run routinely, the calibration curve provides sufficient accuracy. If greater precision and less bias are desired and time is available, use the bracketing approach described in ¶ 4*d* below.

d. Bracketing approach: From the calibration curve, select and prepare sodium standards that immediately bracket the emission intensity of the sample. Determine emission intensities of the bracketing standards (one sodium standard slightly less and the other slightly greater than the sample) and the sample as nearly simultaneously as possible. Repeat the determination on bracketing standards and sample. Calculate the sodium concentration by the equation in ¶ 5*b* and average the findings.

5. Calculation

a. For direct reference to the calibration curve:

$$\text{mg Na/L} = (\text{mg Na/L in portion}) \times D$$

b. For the bracketing approach:

$$\text{mg Na/L} = \left[\frac{(B - A)(s - a)}{(b - a)} + A\right] D$$

where:

B = mg Na/L in upper bracketing standard,
A = mg Na/L in lower bracketing standard,
b = emission intensity of upper bracketing standard,

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

a = emission intensity of lower bracketing standard,
s = emission intensity of sample, and
D = dilution ratio,

$$= \frac{\text{mL sample + mL water}}{\text{mL sample}}$$

6. Precision and Bias

A synthetic sample containing 19.9 mg Na^+/L, 108 mg Ca^{2+}/L, 82 mg Mg^{2+}/L, 3.1 mg K^+/L, 241 mg Cl^-/L, 0.25 mg NO_2^--N/L, 1.1 mg NO_3^--N/L, 259 mg SO_4^{2-}/L, and 42.5 mg total alkalinity/L (as $CaCO_3$) was analyzed in 35 laboratories by the flame photometric method, with a relative standard deviation of 17.3% and a relative error of 4.0%.

7. Bibliography

WEST, P.W., P. FOLSE & D. MONTGOMERY. 1950. Application of flame spectrophotometry to water analysis. *Anal. Chem.* 22:667.

COLLINS, C.G. & H. POLKINHORNE. 1952. An investigation of anionic interference in the determination of small quantities of potassium and sodium with a new flame photometer. *Analyst* 77:430.

MELOCHE, V.W. 1956. Flame photometry. *Anal. Chem.* 28:1844.

BURRIEL-MARTI, F. & J. RAMIREZ-MUNOZ. 1957. Flame Photometry: A Manual of Methods and Applications. D. Van Nostrand Co., Princeton, N.J.

DEAN, J.A. 1960. Flame Photometry. McGraw-Hill Publishing Co., New York, N.Y.

URE, A.M. & R.L. MITCHELL. 1975. Lithium, sodium, potassium, rubidium, and cesium. *In* J.A. Dean & T.C. Rains, eds. Flame Emission and Atomic Absorption Spectrometry. Dekker, New York, N.Y.

THOMPSON, K.C. & REYNOLDS, R.J. 1978. Atomic Absorption, Fluorescence, and Flame Spectroscopy—A Practical Approach, 2nd ed. John Wiley & Sons, New York, N.Y.

WILLARD, H.H., L.L. MERRIT, JR., J.A. DEAN & F.A. SETTLE, JR. 1981. Instrumental Methods of Analysis, 6th ed. Wadsworth Publishing Co., Belmont, Calif.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1988. Method D 1428-82: Standard test methods for sodium and potassium in water and water-formed deposits by flame photometry. Annual Book of ASTM Standards, Vol. 11.01. American Soc. Testing & Materials, Philadelphia, Pa.

3500-Sr STRONTIUM*#(125)

3500-Sr A. Introduction

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

1. Occurrence and Significance

Strontium (Sr) is the fourth element in Group IIA of the periodic table; it has an atomic number of 38, an atomic weight of 87.62, and a valence of 2. The average abundance of Sr in the earth's crust is 384 ppm; in soils Sr ranges from 3.6 to 160 ppm; in streams it averages 50 μg/L, and in groundwaters it ranges from 0.01 to 10 mg/L. Strontium is found chiefly in celestite ($SrSO_4$) and in strontianite ($SrCO_3$). Strontium compounds are used in pigments, pyrotechnics, ceramics, and flares. ^{90}Sr is a fission product of nuclear reactor fuels, and was widely distributed on the earth's surface as a result of fallout from nuclear weapons testing.

The common aqueous species is Sr^{2+}. The solubility of strontium is controlled by carbonate and sulfate. Some compounds are toxic by ingestion and inhalation. Although there is no U.S. EPA drinking water standard MCL for concentration of strontium, strontium-90 measurements are required when the gross beta activity of a water sample is greater than 50 pCi/L. The U.S. EPA primary drinking water standard MCL for ^{90}Sr is 8 pCi/L.

A method for determination of ^{90}Sr is found in Section 7500-Sr.

2. Selection of Method

The atomic absorption spectrometric method (Section 3111B) and inductively coupled plasma methods (Section 3120 and Section 3125) are preferred. The flame emission photometric method (B) also is available for those laboratories that do not have the equipment needed for one of the preferred methods.

3. Sampling and Storage

Polyethylene bottles are preferable for sample storage, although borosilicate glass containers also may be used. At time of collection adjust sample to pH <2 with nitric acid (HNO_3).

3500-Sr B. Flame Emission Photometric Method

1. General Discussion

a. Principle: The flame photometric method can be used for the determination of strontium in the concentration range prevalent in natural waters. The strontium emission is measured at a wavelength of 460.7 nm, while the background intensity is measured at a wavelength of 466 nm. The difference in readings obtained at these two wavelengths measures the light intensity emitted by strontium.

b. Interference: Emission intensity is a linear function of strontium concentration and concentration of other constituents. The standard addition technique distributes the same ions throughout the standards and the sample, thereby equalizing the radiation effect of possible interfering substances. A very low pH (<1) could produce an interference, but sample dilution should eliminate this interference.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

c. Minimum detectable concentration: Strontium levels of about 0.2 mg/L can be detected by the flame photometric method without prior sample concentration.

2. Apparatus

Spectrophotometer, equipped with photomultiplier tube and flame accessories; or an atomic absorption spectrophotometer capable of operation in flame emission mode.

3. Reagents

a. Stock strontium solution: Dissolve 2.415 g strontium nitrate, $Sr(NO_3)_2$, dried to constant weight at 140°C, in 1000 mL 1% (v/v) HNO_3; 1.00 mL = 1.00 mg Sr.

b. Standard strontium solution: Dilute 25.00 mL stock strontium solution to 1000 mL with water; 1.00 mL = 25.0 µg Sr. Use this solution for preparing Sr standards in the 0.2- to 25-mg/L range.

c. Nitric acid, HNO_3, conc.

4. Procedure

a. Pretreatment of polluted water and wastewater samples: Select an appropriate procedure from Section 3030.

b. Preparation of strontium standards: Dilute samples, if necessary, to contain less than 400 mg Ca or Ba/L and less than 40 mg Sr/L. Add 25.0 mL sample (or a lesser but consistent volume to keep all standards in the linear range of the instrument) to 25.0 mL of each of a series of four or more strontium standards containing from 0 mg/L to a concentration exceeding that of the sample. For most natural waters 0, 2.0, 5.0, and 10.0 mg Sr/L standards are sufficient. A broader range curve might be preferable for brines. Dilute the brine sufficiently to eliminate burner splatter and clogging.

c. Concentration of low-level strontium samples: Concentrate samples containing less than 2 mg Sr/L. Polluted water or wastewater samples can be concentrated during digestion by starting with a larger volume (see Section 3030D). For other samples, add 3 to 5 drops conc HNO_3 to 250 mL sample and evaporate to about 25 mL. Cool and make up to 50.0 mL with distilled water. Proceed as in ¶ b. The HNO_3 concentration in the sample prepared for atomization can approach 0.4 mL/50 mL without producing interference.

d. Flame photometric measurement: Measure emission intensity of prepared samples (standards plus sample) at wavelengths of 460.7 and 466 nm. Follow manufacturer's instructions for correct instrument operation. Use a fuel-rich nitrous oxide-acetylene flame, if possible.

5. Calculation

a. Using a calculator or computer with linear regression capability, enter the net intensity (reading at 460.7 nm minus reading at 466 nm) versus concentration added to the sample and solve the equation for zero emissions. The negative of this number multiplied by any dilution

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

factor is the sample concentration.

b. Plot net intensity (reading at 460.7 nm minus reading at 466 nm) against strontium concentration added to the sample. Because the plot forms a straight calibration line that intersects the ordinate, strontium concentration can be calculated from the equation:

$$\text{mg Sr/L} = \frac{A - B}{C} \times \frac{D}{E}$$

where:

A = sample emission-intensity reading of sample plus 0 mg/L at 460.7 nm,
B = background radiation reading at 466 nm, and
C = slope of calibration line.

Use the ratio D/E only when E mL of sample are concentrated to a final volume D mL (typically 50 mL).

c. Graphical method: Strontium concentration also can be evaluated by the graphical method illustrated in Figure 3500-Sr:1. Plot net intensity against strontium concentration added to sample. If the line intersects the ordinate at Y emissions, the strontium concentration is where the abscissa value of the point on the calibration line has an ordinate value of $2Y$ emissions due to the two-fold dilution with standards (if sample and standards are mixed in equal volumes). The calibration line in the example intersects the ordinate at 12. Thus, $Y = 12$ and $2Y = 24$. The strontium concentration of the sample is the abscissa value of the point on the calibration line having an ordinate value of 24. In the example, the strontium concentration is 9.0 mg/L.

d. Report strontium concentrations below 10 mg/L to the nearest 0.1 mg/L and above 10 mg/L to the nearest whole number.

6. Quality Control

See Part 1000 and Section 3020 for specific quality control procedures to be followed during sample preparation and analysis.

7. Precision and Bias

Strontium concentrations in the range 12.0 to 16.0 mg/L can be determined with an accuracy within ±1 to 2 mg/L.

8. Bibliography

CHOW, T.J. & T.G. THOMPSON. 1955. Flame photometric determination of strontium in sea water. *Anal. Chem.* 27:18.

NICHOLS, M.S. & D.R. MCNALL. 1957. Strontium content of Wisconsin municipal waters. *J. Amer. Water Works Assoc.* 49:1493.

HORR, C.A. 1959. A survey of analytical methods for the determination of strontium in natural

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

water. U.S. Geol. Surv. Water Supply Pap. No. 1496A.

3500-Te TELLURIUM

Tellurium (Te) is the fourth element in Group VIA in the periodic table; it has an atomic number of 52, an atomic weight of 127.60, and valences of 2, 4, and 6. The average abundance of Te in the earth's crust is 0.002 ppm; in soils it is 0.001 to 0.01 ppm; and in groundwaters it is <0.1 mg/L. Tellurium is found in its native state and as the telluride of gold and other metals. It is used in alloys, catalysts, batteries, and as a coloring agent in glass and ceramics.

The common aqueous species is TeO_3^{2-}. The metal and its compounds are toxic by inhalation.

Perform analyses by the electrothermal atomic absorption method (Section 3113B). The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though tellurium is not specifically listed as an analyte in the method.

3500-Tl THALLIUM

Thallium (Tl) is the fifth element in Group IIIA in the periodic table; it has an atomic number of 81, an atomic weight of 204.38, and valences of 1 and 3. The average abundance in the earth's crust is 0.07 ppm, and in groundwaters it is <0.1 mg/L. The metal occurs chiefly in pyrites. Thallium is used in the production of glasses and rodenticides, in photoelectric applications, and in electrodes for dissolved oxygen meters.

The common aqueous species is Tl^+. It is nonessential for plants and animals. Compounds of thallium are toxic on contact with moisture, and by inhalation. The U.S. EPA primary drinking water standard MCL is 2 μg/L.

For analysis, use one of the atomic absorption spectrometric methods (Section 3111B or Section 3113B), or one of the inductively coupled plasma methods (Section 3120 or Section 3125), depending upon sensitivity requirements.

3500-Th THORIUM

Thorium (Th) is the first element in the actinium series of the periodic table; it has an atomic number of 90, an atomic weight of 232.04, and a valence of 4. The average abundance in the earth's crust is 8.1 ppm; in soils it is 13 ppm; in streams it is 0.1 μg/L, and in groundwaters it is <0.1 mg/L. Thorium is a radioactive element, with ^{232}Th having a half-life of 1.4×10^{10} years. It is widely distributed in the earth, with the principal mineral being monazite. Thorium is used in sun lamps, photoelectric cells, incandescent lighting, and gas mantles.

The aqueous chemistry of thorium is controlled by the Th^{4+} ion, which forms a set of

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

complex species with hydroxides. Thorium's radioactive decay isotopes are dangerous when inhaled or ingested as thorium dust particles.

Either of the flame atomic absorption spectrometric methods (Section 3111D or Section 3111E) may be used for analysis. The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though thorium is not specifically listed as an analyte in the method.

3500-Sn TIN

Tin (Sn) is the fourth element in Group IVA in the periodic table; it has an atomic number of 50, an atomic weight of 118.69, and valences of 2 and 4. The average abundance in the earth's crust is 2.1 ppm; in soils it is 10 ppm; in streams it is 0.1 μg/L, and in groundwaters it is <0.1 mg/L. Tin is found mostly in the mineral cassiterite (SnO_2), in association with granitic rocks. Tin is used in reducing agents, solder, bronze, pewter, and coatings for various metals.

The common aqueous species are Sn^{4+}, $Sn(OH)_4$, $SnO(OH)_2$, and $SnO(OH)_3^-$. Tin is adsorbed to suspended solids, sulfides, and hydroxides. Tin can be methylated in sediments. Tributyl tin undergoes biodegradation quickly. Organo-tin compounds are toxic. Tin is considered nonessential for plants and animals.

Either the flame atomic absorption method (Section 3111B) or the electrothermal atomic absorption method (Section 3113B) may be used successfully for analyses, depending upon the sensitivity desired. The inductively coupled plasma/mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though tin is not specifically listed as an analyte in the method.

3500-Ti TITANIUM

Titanium (Ti) is the first element in Group IVB in the periodic table; it has an atomic number of 22, an atomic weight of 47.88, and valences of 2, 3, and 4. The average abundance of Ti in the earth's crust is 0.6%; in soils it is 1700 to 6600 ppm; in streams it is 3 μg/L, and in groundwaters it is <0.1 mg/L. The element is commonly associated with iron minerals. Titanium is used in alloys for aircraft, marine, and food-handling equipment. Compounds of the metal are used in pigments and as a reducing agent.

Titanium species are usually insoluble in natural waters, with the Ti^{4+} species being the most common ion when found. Some compounds are toxic by ingestion and the pure metal is flammable.

Either of the flame atomic absorption spectrometric methods (Section 3111D or Section 3111E) may be used. The inductively coupled plasma mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though titanium is not specifically listed as an analyte in the method.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

3500-U URANIUM

Uranium (U) is the third element in the actinide series of the periodic table; it has an atomic number of 92, an atomic weight of 238.04, and valences of 3, 4, and 6. The average abundance of U in the earth's crust is 2.3 ppm, and in soils it is 1.8 ppm. Concentrations of uranium in drinking waters usually are expressed in terms of picocuries per liter, but that is now being replaced by Becquerel per liter (Bq/L). The approximate conversion factor, assuming equilibrium between ^{234}U and ^{238}U, is 1 μg uranium equals 0.67 pCi. The mean concentration of uranium in drinking water is 1.8 pCi/L. The chief ore is uraninite, or pitchblende, uranous uranate [$U(UO_4)_2$]. Uranium is known mainly for its use in the nuclear industry, but has also been used in glass, ceramics, and photography.

Uranium compounds are radioactive and are thereby toxic by inhalation and ingestion. There are three natural radioisotopes of uranium. Uranium-238 has a half-life of 4.5×10^9 years, represents 99% of uranium's natural abundance, and is not fissionable, but can be used to form plutonium-239, which is fissionable. Uranium-235 has a half-life of 7.1×10^8 years, represents 0.75% of uranium's natural abundance, is readily fissionable, and was the energy source in the original atomic bombs. Uranium-234 has a half-life of 2.5×10^5 years and represents only 0.006% of uranium's natural abundance.

The common forms in natural water are U^{4+} and UO_2^{2+}. In natural waters below pH 5, UO_2^{2+} would dominate; in the pH range of 5 to 10, soluble carbonate complexes predominate. Although there is no U.S. EPA drinking water standard MCL for uranium, an analysis for uranium is required if the gross alpha activity of a water sample is greater than 15 pCi/L.

Perform analyses by the inductively coupled plasma/mass spectrometry method (Section 3125) or by one of the methods in Section 7500-U (for regulatory compliance purposes).

3500-V VANADIUM*#(126)

3500-V A. Introduction

1. Occurrence and Significance

Vanadium (V) is the first element in Group VB in the periodic table; it has an atomic number of 23, an atomic weight of 50.94, and valences of 2, 3, 4, and 5. The average abundance of V in the earth's crust is 136 ppm; in soils it ranges from 15 to 110 ppm; in streams it averages about 0.9 μg/L, and in groundwaters it is generally <0.1 mg/L. Though relatively rare, vanadium is found in a variety of minerals; most important among these are vanadinite [$Pb_5(VO_4)_3Cl$], and patronite (possibly VS_4), occurring chiefly in Peru. Vanadium complexes have been noted in

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

coal and petroleum deposits. Vanadium is used in steel alloys and as a catalyst in the production of sulfuric acid and synthetic rubber.

The dominant form in natural waters is V^{5+}. It is associated with organic complexes and is insoluble in reducing environments. It is considered nonessential for most higher plants and animals, although it may be an essential trace element for some algae and microorganisms. Laboratory and epidemiological evidence suggests that vanadium may play a beneficial role in the prevention of heart disease. In water supplies in New Mexico, which has a low incidence of heart disease, vanadium has been found in concentrations of 20 to 150 µg/L. In a state where incidence of heart disease is high, vanadium was not found in water supplies. However, vanadium pentoxide dust causes gastrointestinal and respiratory disturbances. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 0.1 mg/L.

2. Selection of Method

The atomic absorption spectrometric methods (Section 3111D and Section 3111E), the electrothermal atomic absorption method (Section 3113B), the inductively coupled plasma methods (Section 3120 and Section 3125), and gallic acid method (Section 3500-V.B) are suitable for potable water samples. The atomic absorption spectrometric and inductively coupled plasma methods are preferred for polluted samples. The electrothermal atomic absorption method also may be used successfully with an appropriate matrix modifier.

3500-V B. Gallic Acid Method

1. General Discussion

a. Principle: The concentration of trace amounts of vanadium in water is determined by measuring the catalytic effect it exerts on the rate of oxidation of gallic acid by persulfate in acid solution. Under the given conditions of concentrations of reactants, temperature, and reaction time, the extent of oxidation of gallic acid is proportional to the concentration of vanadium. Vanadium is determined by measuring the absorbance of the sample at 415 nm and comparing it with that of standard solutions treated identically.

b. Interference: The substances listed in Table 3500-V:I will interfere in the determination of vanadium if the specified concentrations are exceeded. This is not a serious problem for Cr^{6+}, Co^{2+}, Mo^{6+}, Ni^{2+}, Ag^{+}, and U^{6+} because the tolerable concentration is greater than that commonly encountered in fresh water. However, in some samples the tolerable concentration of Cu^{2+}, Fe^{2+}, and Fe^{3+} may be exceeded. Because of the high sensitivity of the method, interfering substances in concentrations only slightly above tolerance limits can be rendered harmless by dilution.

Traces of Br^{-} and I^{-} interfere seriously and dilution alone will not always reduce the concentration below tolerance limits. Mercuric ion may be added to complex these halides and

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

minimize their interference; however, mercuric ion itself interferes if in excess. Adding 350 µg mercuric nitrate, $Hg(NO_3)_2$, per sample permits determination of vanadium in the presence of up to 100 mg Cl^-/L, 250 µg Br^-/L, and 250 µg I^-/L. Dilute samples containing high concentrations of these ions to concentrations below the values given above and add $Hg(NO_3)_2$.

c. Minimum detectable concentration: 0.025 µg V in approximately 13 mL final volume or approximately 2 µg V/L.

2. Apparatus

a. Water bath, capable of being operated at 25 ± 0.5°C.

b. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for measurements at 415 nm, with a light path of 1 to 5 cm.

2) *Filter photometer,* providing a light path of 1 to 5 cm and equipped with a violet filter with maximum transmittance near 415 nm.

3. Reagents

Use reagent water (see Section 1080) in preparation of reagents, for dilutions, and as blanks.

a. Stock vanadium solution: Dissolve 229.6 mg ammonium metavanadate, NH_4VO_3, in a volumetric flask containing approximately 800 mL water and 15 mL 1 + 1 nitric acid (HNO_3). Dilute to 1000 mL; 1.00 mL = 100 µg V.

b. Intermediate vanadium solution: Dilute 1.00 mL stock vanadium solution with water to 100 mL; 1.00 mL = 1.00 µg V.

c. Standard vanadium solution: Dilute 1.00 mL intermediate vanadium solution with water to 100 mL; 1.00 mL = 0.010 µg V.

d. Mercuric nitrate solution: Dissolve 350 mg $Hg(NO_3)_2 \cdot H_2O$ in 1000 mL water.

e. Ammonium persulfate-phosphoric acid reagent: Dissolve 2.5 g $(NH_4)_2S_2O_8$ in 25 mL water. Bring just to a boil, remove from heat, and add 25 mL conc H_3PO_4. Let stand approximately 24 h before use. Discard after 48 h.

f. Gallic acid solution: Dissolve 2 g $H_6C_7O_5$ in 100 mL warm water, heat to a temperature just below boiling, and filter through filter paper.*#(127) Prepare a fresh solution for each set of samples.

4. Procedure

a. Preparation of standards and sample: Prepare both blank and sufficient standards by diluting 0- to 8.0-mL portions (0 to 0.08 µg V) of standard vanadium solution to 10 mL with water. Pipet sample (10.00 mL maximum) containing less than 0.08 µg V into a suitable container and adjust volume to 10.0 mL with water. Filter colored or turbid samples. Add 1.0 mL $Hg(NO_3)_2$ solution to each blank, standard, and sample. Place containers in a water bath

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

regulated to 25 ± 0.5°C and allow 30 to 45 min for samples to come to the bath temperature.

b. Color development and measurement: Add 1.0 mL ammonium persulfate-phosphoric acid reagent (temperature equilibrated), swirl to mix thoroughly, and return to water bath. Add 1.0 mL gallic acid solution (temperature equilibrated), swirl to mix thoroughly, and return to water bath. Add gallic acid to successive samples at intervals of 30 s or longer to permit accurate control of reaction time. Exactly 60 min after adding gallic acid, remove sample from water bath and measure its absorbance at 415 nm, using water as a reference. Subtract absorbance of blank from absorbance of each standard and sample. Construct a calibration curve by plotting absorbance values of standards versus micrograms vanadium. Determine amount of vanadium in a sample by referring to the corresponding absorbance on the calibration curve. Prepare a calibration curve with each set of samples.

5. Calculation

$$\text{mg V/L} = \frac{\mu\text{g V (in 13 mL final volume)}}{\text{original sample volume, mL}}$$

6. Precision and Bias

In a synthetic sample containing 6 µg V/L, 40 µg As/L, 250 µg Be/L, 240 µg B/L, and 20 µg Se/L in distilled water, vanadium was measured in 22 laboratories with a relative standard deviation of 20% and no relative error.

7. Bibliography

FISHMAN, M.J. & M.V. SKOUGSTAD. 1964. Catalytic determination of vanadium in water. *Anal. Chem.* 36:1643.

3500-Zn ZINC*#(128)

3500-Zn A. Introduction

1. Occurrence and Significance

Zinc (Zn) is the first element in Group IIB in the periodic table; it has an atomic number of 30, an atomic weight of 65.38, and a valence of 2. The average abundance of Zn in the earth's crust is 76 ppm; in soils it is 25 to 68 ppm; in streams it is 20 µg/L, and in groundwaters it is <0.1 mg/L. The solubility of zinc is controlled in natural waters by adsorption on mineral surfaces, carbonate equilibrium, and organic complexes. Zinc is used in a number of alloys such as brass and bronze, and in batteries, fungicides, and pigments. Zinc is an essential growth element for plants and animals but at elevated levels it is toxic to some species of aquatic life.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

The United Nations Food and Agriculture Organization recommended level for zinc in irrigation waters is 2 mg/L. The U.S. EPA secondary drinking water standard MCL is 5 mg/L. Concentrations above 5 mg/L can cause a bitter astringent taste and an opalescence in alkaline waters. Zinc most commonly enters the domestic water supply from deterioration of galvanized iron and dezincification of brass. In such cases lead and cadmium also may be present because they are impurities of the zinc used in galvanizing. Zinc in water also may result from industrial waste pollution.

2. Selection of Method

The atomic absorption spectrometric methods (Section 3111B and Section 3111C) and inductively coupled plasma methods (Section 3120 and Section 3125) are preferred. The zincon method (B), suitable for analysis of both potable and polluted waters, may be used if instrumentation for the preferred methods is not available..

3. Sampling and Storage

See Section 3010B.2 for sample handling and storage.

3500-Zn B. Zincon Method

1. General Discussion

a. Principle: Zinc forms a blue complex with 2-carboxy-2′-hydroxy-5′-sulfoformazyl benzene (zincon) in a solution buffered to pH 9.0. Other heavy metals likewise form colored complexes with zincon. Cyanide is added to complex zinc and heavy metals. Cyclohexanone is added to free zinc selectively from its cyanide complex so that it can be complexed with zincon to form a blue color. Sodium ascorbate reduces manganese interference. The developed color is stable except in the presence of copper (see table below).

b. Interferences: The following ions interfere at concentrations exceeding those listed:

Ion	*mg/L*	Ion	*mg/L*
Cd^{2+}	1	Cr^{3+}	10
Al^{3+}	5	Ni^{2+}	20
Mn^{2+}	5	Cu^{2+}	30
Fe^{3+}	7	Co^{2+}	30
Fe^{2+}	9	CrO_4^{2-}	50

c. Minimum detectable concentration: 0.02 mg Zn/L.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* for measurements at 620 nm, providing a light path of 1 cm or longer.

2) *Filter photometer,* providing a light path of 1 cm or longer and equipped with a red filter having maximum transmittance near 620 nm. Deviation from Beer's Law occurs when the filter band pass exceeds 20 nm.

b. Graduated cylinders, 50-mL, with ground-glass stoppers, Class B or better.

c. Erlenmeyer flasks, 50-mL.

d. Filtration apparatus: 0.45-μm filters and filter holders.

3. Reagents

a. Metal-free water: See Section 3111B.3*c*. Use water for rinsing apparatus and preparing solutions and dilutions.

b. Stock zinc solution: Dissolve 1000 mg (1.000 g) zinc metal in 10 mL 1 + 1 HNO_3. Dilute and boil to expel oxides of nitrogen. Dilute to 1000 mL; 1.00 mL = 1.00 mg Zn.

c. Standard zinc solution: Dilute 10.00 mL stock zinc solution to 1000 mL; 1.00 mL = 10.00 μg Zn.

d. Sodium ascorbate, fine granular powder, USP.

e. Potassium cyanide solution: Dissolve 1.00 g KCN in approximately 50 mL water and dilute to 100 mL. CAUTION: *Potassium cyanide is a deadly poison. Avoid skin contact or inhalation of vapors. Do not pipet by mouth or bring in contact with acids.*

f. Buffer solution, pH 9.0: Dissolve 8.4 g NaOH pellets in about 500 mL water. Add 31.0 g H_3BO_3 and swirl or stir to dissolve. Dilute to 1000 mL with water and mix thoroughly.

g. Zincon reagent: Dissolve 100 mg zincon (2-carboxy-2′-hydroxy-5′-sulfoformazyl benzene) in 100 mL methanol. Because zincon dissolves slowly, stir and/or let stand overnight.

h. Cyclohexanone, purified.

i. Hydrochloric acid, HCl, conc and 1*N*.

j. Sodium hydroxide, NaOH, 6*N* and 1*N*.

4. Procedure

a. Preparation of colorimetric standards: Accurately deliver 0, 0.5, 1.0, 3.0, 5.0, 10.0, and 14.0 mL standard zinc solution to a series of 50-mL graduated mixing cylinders. Dilute each to 20.0 mL to yield solutions containing 0, 0.25, 0.5, 1.5, 2.5, 5.0, and 7.0 mg Zn/L, respectively. (Lower-range standards may be prepared to extend the quantitation range. Longer optical path cells can be used. Verify linearity of response in this lower concentration range.) Add the following to each solution in sequence, mixing thoroughly after each addition: 0.5 g sodium ascorbate, 5.0 mL buffer solution, 2.0 mL KCN solution, and 3.0 mL zincon solution. Pipet 20.0

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

mL of the solution into a clean 50-mL erlenmeyer flask. Reserve remaining solution to zero the instrument. Add 1.0 mL cyclohexanone to the erlenmeyer flask. Swirl for 10 s and note time. Transfer portions of both solutions to clean sample cells. Use solution without cyclohexanone to zero colorimeter. Read and record absorbance for solution with cyclohexanone after 1 min. The calibration curve does not pass through zero because of the color enhancement effect of cyclohexanone on zincon.

b. Treatment of samples: To determine readily acid-extractable total zinc, add 1 mL conc HCl to 50 mL sample and mix thoroughly. Filter and adjust to pH 7. To determine dissolved zinc, filter sample through a 0.45-µm membrane filter. Adjust to pH 7 with 1*N* NaOH or 1*N* HCl if necessary after filtering.

c. Sample analysis: Cool samples to less than 30°C if necessary. Analyze 20.0 mL of prepared sample as described in ¶ 4*a* above, beginning with ‘‘Add the following to each solution . . .’’ If the zinc concentration exceeds 7 mg Zn/L prepare a sample dilution and analyze a 20.0-mL portion.

5. Calculation

Read zinc concentration (in milligrams per liter) directly from the calibration curve.

6. Precision and Bias

A synthetic sample containing 650 µg Zn/L, 500 µg Al/L, 50 µg Cd/L, 110 µg Cr/L, 470 µg Cu/L, 300 µg Fe/L, 70 µg Pb/L, 120 µg Mn/L, and 150 µg Ag/L in doubly demineralized water was analyzed in a single laboratory. A series of 10 replicates gave a relative standard deviation of 0.96% and a relative error of 0.15%. A wastewater sample from an industry in Standard Industrial Classification (SIC) No. 3333, primary smelting and refining of zinc, was analyzed by 10 different persons. The mean zinc concentration was 3.36 mg Zn/L and the relative standard deviation was 1.7%. The relative error compared to results from an atomic absorption analysis of the same sample was −1.0%.

7. Bibliography

PLATTE, J.A. & V.M. MARCY. 1959. Photometric determination of zinc with zincon. *Anal. Chem.* 31:1226.

RUSH, R.M. & J.H. YOE. 1954. Colorimetric determination of zinc and copper with 2-carboxy-2′-hydroxy-5′-sulfoformazyl-benzene. *Anal. Chem.* 26:1345.

MILLER, D.G. 1979. Colorimetric determination of zinc with zincon and cyclohexanone. *J. Water Pollut. Control Fed.* 51:2402.

PANDE, S.P. 1980. Study on the determination of zinc in drinking water. *J. IWWA XII* (3):275.

Figures

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Figure 3112:1. Schematic arrangement of equipment for measurement of mercury by cold-vapor atomic absorption technique.

Figure 3114:1. Manual reaction cell for producing As and Se hydrides.

Figure 3114:2. Schematic of a continuous hydride generator.

Figure 3500-Al:1. Correction curves for estimation of aluminum in the presence of fluoride. Above the mg F^-/L present, locate the point corresponding to the apparent mg Al/L measured. From this point interpolate between the curves shown, if the point does not fall directly on one of the curves, to read the true mg Al/L on the ordinate, which corresponds to 0.00 mg F^-/L. For example, an apparent 0.20 mg Al/L in a sample containing 1.00 mg F^-/L would actually be 0.30 mg Al/L if no fluoride were present to interfere.

Figure 3500-As:1. Arsine generator and absorber assembly.

Figure 3500-Se:1. General scheme for speciation of selenium in water.

Figure 3500-Sr:1. Graphical method of computing strontium concentration.

Tables

TABLE 3010:I. APPLICABLE METHODS FOR ELEMENTAL ANALYSIS

Element	Flame Atomic Absorption (Direct)	Flame Atomic Absorption (Extracted)	Flame Photometry	Electrothermal Atomic Absorption	Hydride/Cold Vapor Atomic Absorption	Inductively Coupled Plasma (ICP)	ICP/ Spect (ICF
Aluminum	3111D	3111E		3113B		3120A	3
Antimony	3111B			3113B		3120A	31
Arsenic				3113B	3114B	3120A	31
Barium	3111D	3111E		3113B		3120A	31
Beryllium	3111D	3111E		3113B		3120A	31
Bismuth	3111B			3113B			31
Boron						3120A	31
Cadmium	3111B	3111C		3113B		3120A	31
Calcium	3111B,D	3111E				3120A	31
Cesium	3111B						31
Chromium	3111B	3111C		3113B		3120A	31
Cobalt	3111B	3111C		3113B		3120A	31
Copper	3111B	3111C		3113B		3120A	31
Gallium				3113B			31
Germanium				3113B			31
Gold	3111B			3113B			31
Indium				3113B			31

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Element	Flame Atomic Absorption (Direct)	Flame Atomic Absorption (Extracted)	Flame Photometry	Electrothermal Atomic Absorption	Hydride/Cold Vapor Atomic Absorption	Inductively Coupled Plasma (ICP)	ICP/ Spect (ICF
Iridium	3111B						31
Iron	3111B	3111C		3113B		3120A	31
Lead	3111B	3111C		3113B		3120A	31
Lithium	3111B		3500-Li.B			3120A	31
Magnesium	3111B					3120A	31
Manganese	3111B	3111C		3113B		3120A	31
Mercury					3112B		31
Molybdenum	3111D	3111E		3113B		3120A	31
Nickel	3111B	3111C		3113B		3120A	31
Osmium	3111D	3111E					31
Palladium	3111B						31
Platinum	3111B						31
Potassium	3111B		3500-K.B			3120A	31
Rhenium	3111D	3111E					31
Rhodium	3111B						31
Ruthenium	3111B						31
Selenium				3113B	3114B,C	3120A	31
Silicon	3111D	3111E				3120A	31
Silver	3111B	3111C		3113B		3120A	31
Sodium	3111B		3500-Na.B			3120A	31
Strontium	3111B		3500-Sr.B			3120A	31
Tellurium				3113B			31
Thallium	3111B			3113B		3120A	31
Thorium	3111D	3111E					31
Tin	3111B			3113B			31
Titanium	3111D	3111E					31
Uranium							31
Vanadium	3111D	3111E		3113B		3120A	31
Zinc	3111B	3111C		3113B		3120A	31

* Metal is not specifically mentioned in the method, but 3125 may be used successfully in most cases.
† Additional alternative methods for aluminum, beryllium, cadmium, mercury, selenium, silver, and zinc may be found in the 19th Edition of *Standard Methods*.

TABLE 3030:I. ACIDS USED IN CONJUNCTION WITH HNO_3 for SAMPLE PREPARATION

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 3030:I. ACIDS USED IN CONJUNCTION WITH HNO_3 FOR SAMPLE PREPARATION

Acid	Recommended for	May Be Helpful for	Not Recommended for
HCl	Ag	Sb, Ru, Sn	Th, Pb
H_2SO_4	Ti	—	Ag, Pb, Ba
$HClO_4$	—	Organic materials	—
HF	—	Siliceous materials	—

TABLE 3111:I. ATOMIC ABSORPTION CONCENTRATION RANGES WITH DIRECT ASPIRATION ATOMIC ABSORPTION

Element	Wave-length *nm*	Flame Gases*	Instrument Detection Limit *mg/L*	Sensitivity *mg/L*	Optimum Concentration Range *mg/L*
Ag	328.1	A–Ac	0.01	0.06	0.1–4
Al	309.3	N–Ac	0.1	1	5–100
Au	242.8	A–Ac	0.01	0.25	0.5–20
Ba	553.6	N–Ac	0.03	0.4	1–20
Be	234.9	N–Ac	0.005	0.03	0.05–2
Bi	223.1	A–Ac	0.06	0.4	1–50
Ca	422.7	A–Ac	0.003	0.08	0.2–20
Cd	228.8	A–Ac	0.002	0.025	0.05–2
Co	240.7	A–Ac	0.03	0.2	0.5–10
Cr	357.9	A–Ac	0.02	0.1	0.2–10
Cs	852.1	A–Ac	0.02	0.3	0.5–15
Cu	324.7	A–Ac	0.01	0.1	0.2–10
Fe	248.3	A–Ac	0.02	0.12	0.3–10
Ir	264.0	A–Ac	0.6	8	—
K	766.5	A–Ac	0.005	0.04	0.1–2
Li	670.8	A–Ac	0.002	0.04	0.1–2
Mg	285.2	A–Ac	0.0005	0.007	0.02–2
Mn	279.5	A–Ac	0.01	0.05	0.1–10
Mo	313.3	N–Ac	0.1	0.5	1–20
Na	589.0	A–Ac	0.002	0.015	0.03–1
Ni	232.0	A–Ac	0.02	0.15	0.3–10

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Element	Wave-length *nm*	Flame Gases*	Instrument Detection Limit *mg/L*	Sensitivity *mg/L*	Optimum Concentration Range *mg/L*
Os	290.9	N–Ac	0.08	1	—
Pb†	283.3	A–Ac	0.05	0.5	1–20
Pt	265.9	A–Ac	0.1	2	5–75
Rh	343.5	A–Ac	0.5	0.3	—
Ru	349.9	A–Ac	0.07	0.5	—
Sb	217.6	A–Ac	0.07	0.5	1–40
Si	251.6	N–Ac	0.3	2	5–150
Sn	224.6	A–Ac	0.8	4	10–200
Sr	460.7	A–Ac	0.03	0.15	0.3–5f
Ti	365.3	N–Ac	0.3	2	5–100
V	318.4	N–Ac	0.2	1.5	2–100
Zn	213.9	A–Ac	0.005	0.02	0.05–2

* A–Ac = air-acetylene; N–Ac = nitrous oxide-acetylene.

† The more sensitive 217.0 nm wavelength is recommended for instruments with background correction capabilities.Copyright ASTM. Reprinted with permission.

TABLE 3111:II. INTERLABORATORY PRECISION AND BIAS DATA FOR ATOMIC ABSORPTION METHODS—DIRECT ASPIRATION AND EXTRACTED METALS

Metal	Conc.*	SD*	Relative SD *%*	Relative Error *%*	No. of Participants
Direct determination:					
Aluminum[1]	4.50	0.19	4.2	8.4	5
Barium[2]	1.00	0.089	8.9	2.7	11
Beryllium[1]	0.46	0.0213	4.6	23.0	11
Cadmium[3]	0.05	0.0108	21.6	8.2	26
Cadmium[1]	1.60	0.11	6.9	5.1	16
Calcium[1]	5.00	0.21	4.2	0.4	8
Chromium[1]	3.00	0.301	10.0	3.7	9

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Metal	Conc.*	SD*	Relative SD %	Relative Error %	No. of Participants
Cobalt[1]	4.00	0.243	6.1	0.5	14
Copper[3]	1.00	0.112	11.2	3.4	53
Copper[1]	4.00	0.331	8.3	2.8	15
Iron[1]	4.40	0.260	5.8	2.3	16
Iron[3]	0.30	0.0495	16.5	0.6	43
Lead[1]	6.00	0.28	4.7	0.2	14
Magnesium[3]	0.20	0.021	10.5	6.3	42
Magnesium[1]	1.10	0.116	10.5	10.0	8
Manganese[1]	4.05	0.317	7.8	1.3	16
Manganese[3]	0.05	0.0068	13.5	6.0	14
Nickel[1]	3.93	0.383	9.8	2.0	14
Silver[3]	0.05	0.0088	17.5	10.6	7
Silver[1]	2.00	0.07	3.5	1.0	10
Sodium[1]	2.70	0.122	4.5	4.1	12
Strontium[1]	1.00	0.05	5.0	0.2	12
Zinc[3]	0.50	0.041	8.2	0.4	48
Extracted determination:					
Aluminum[2]	300	32	10.7	0.7	15
Beryllium[2]	5	1.7	34.0	20.0	9
Cadmium[3]	50	21.9	43.8	13.3	12
Cobalt[1]	300	28.5	9.5	1.0	6
Copper[1]	100	71.7	71.7	12.0	8
Iron[1]	250	19.0	7.6	3.6	4
Manganese[1]	21.5	2.4	11.2	7.4	8
Molybdenum[1]	9.5	1.1	11.6	1.3	5
Nickel[1]	56.8	15.2	26.8	13.6	14
Lead[3]	50	11.8	23.5	19.0	8

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Metal	Conc.*	SD*	Relative SD %	Relative Error %	No. of Participants
Silver[1]	5.2	1.4	26.9	3.0	7

* For direct determinations, mg/L; for extracted determinations, µg/L.

Superscripts refer to reference numbers.

Source: AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1986. Annual Book of ASTM Standards. Volume 11.01, Water and Environmental Technology. American Soc. Testing Materials, Philadelphia, Pa. Copyright ASTM. Reprinted with permission.

TABLE 3111:III. SINGLE-OPERATOR PRECISION AND RECOMMENDED CONTROL RANGES FOR ATOMIC ABSORPTION METHODS—DIRECT ASPIRATIONAND EXTRACTED METALS

Metal	Conc.*	SD*	Relative SD %	No. of Participants	QC Std.*	Acceptable Range*
Direct determination:						
Aluminum[1]	4.50	0.23	5.1	15	5.00	4.3–5.7
Beryllium[1]	0.46	0.012	2.6	10	0.50	0.46–0.54
Calcium[1]	5.00	0.05	1.0	8	5.00	4.8–5.2
Chromium[1]	7.00	0.69	9.9	9	5.00	3.3–6.7
Cobalt[1]	4.00	0.21	5.3	14	4.00	3.4–4.6
Copper[1]	4.00	0.115	2.9	15	4.00	3.7–4.3
Iron[1]	5.00	0.19	3.8	16	5.00	4.4–5.6
Magnesium[1]	1.00	0.009	0.9	8	1.00	0.97–1.03
Nickel[4]	5.00	0.04	0.8	—	5.00	4.9–5.1
Silver[1]	2.00	0.25	12.5	10	2.00	1.2–2.8
Sodium[4]	8.2	0.1	1.2	—	5.00	4.8–5.2
Strontium[1]	1.00	0.04	4.0	12	1.00	0.87–1.13
Potassium[4]	1.6	0.2	12.5	—	1.6	1.0–2.2
Molybdenum[4]	7.5	0.07	0.9	—	10.0	9.7–10.3
Tin[4]	20.0	0.5	2.5	—	20	.018.5–21.5
Titanium[4]	50.0	0.4	0.8	—	50.0	48.8–51.2
Vanadium	50.0	0.2	0.4	—	50.0	49.4–50.6

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Metal	Conc.*	SD*	Relative SD %	No. of Participants	QC Std.*	Acceptable Range*
Extracted determination:						
Aluminum[1]	300	12	4.0	15	300	264–336
Cobalt[1]	300	20	6.7	6	300	220–380
Copper[1]	100	21	21	8	100	22–178
Iron[1]	250	12	4.8	4	250	180–320
Manganese[1]	21.5	202	10.2	8	25	17–23
Molybdenum[1]	9.5	1.0	10.5	5	10	5.5–14.5
Nickel[1]	56.8	9.2	16.2	14	50	22–78
Silver[1]	5.2	1.2	23.1	7	5.0	0.5–9.5

* For direct determinations, mg/L; for extracted determinations, µg/L.

Superscripts refer to reference numbers.

Source: AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1986. Annual Book of ASTM Standards. Volume 11.01, Water and Environmental Technology. American Soc. Testing Materials, Philadelphia, Pa. Copyright ASTM. Reprinted with permission.

TABLE 3112:I. INTERLABORATORY PRECISION AND BIAS OF COLD-VAPOR ATOMIC ABSORPTION SPECTROMETRIC METHOD FOR MERCURY[1]

Form	Conc. µg/L	SD µg/L	Relative SD %	Relative Error %	No. of Participants
Inorganic	0.34	0.077	22.6	21.0	23
Inorganic	4.2	0.56	13.3	14.4	21
Organic	4.2	0.36	8.6	8.4	21

TABLE 3113:I. POTENTIAL MATRIX MODIFIERS FOR ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY*

Modifier	Analyses for Which Modifier May Be Useful

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Modifier	Analyses for Which Modifier May Be Useful
1500 mg Pd/L + 1000 mg $Mg(NO_3)_2$/L[1]	Ag, As, Au, Bi, Cu, Ge, Mn, Hg, In, Sb, Se, Sn, Te, Tl
500–2000 mg Pd/L + reducing agent[2]†	Ag, As, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb
5000 mg $Mg(NO_3)_2$/L[1]	Be, Co, Cr, Fe, Mn, V
100–500 mg Pd/L[2]	As, Ga, Ge, Sn
50 mg Ni/L[2]	As, Se, Sb
2% PO_4^{3-} + 1000 mg Mg $(NO_3)_2$/L[1]	Cd, Pb

*Assumes 10 μL modifier/10 μL sample.†Citric acid (1–2%) preferred; ascorbic acid or H_2 acceptable.

TABLE 3113:II. DETECTION LEVELS AND CONCENTRATION RANGES FOR ELECTROTHERMAL ATOMIZATION ATOMIC ABSORPTION SPECTROMETRY

Element	Wavelength *nm*	Estimated Detection Limit *μg/L*	Optimum Concentration Range *μg/L*
Al	309.3	3	20–200
Sb	217.6	3	20–300
As	193.7	1	5–100
Ba	553.6	2	10–200
Be	234.9	0.2	1–30
Cd	228.8	0.1	0.5–10
Cr	357.9	2	5–100
Co	240.7	1	5–100
Cu	324.7	1	5–100
Fe	248.3	1	5–100
Pb*	283.3	1	5–100
Mn	279.5	0.2	1–30
Mo	313.3	1	3–60
Ni	232.0	1	5–100

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Element	Wavelength *nm*	Estimated Detection Limit *µg/L*	Optimum Concentration Range *µg/L*
Se	196.0	2	5–100
Ag	328.1	0.2	1–25
Sn	224.6	5	20–300

*The more sensitive 217.0-nm wavelength is recommended for instruments with background correction capabilities.

TABLE 3113:III. INTERLABORATORY SINGLE-ANALYST PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Single-Analyst Precision *% RSD*					
Element	Concentration *µg/L*	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28	66	108	70	—	—	66
	125	27	35	24	—	—	34
	11 000	11	—	—	22	—	—
	58 300	27	—	—	19	—	—
	460	9	—	—	—	30	—
	2 180	28	—	—	—	4	—
	10.5	20	13	13	13	56	18
	230	10	18	13	21	94	14
As	9.78	40	25	15	74	23	11
	227	10	6	8	11	15	6
Ba	56.5	36	21	29	59	23	27
	418	14	12	20	24	24	18
Be	0.45	18	27	15	30	2	11
	10.9	14	4	9	7	12	12
Cd	0.43	72	49	1	121	35	27
	12	11	17	22	14	11	15
Cr	9.87	24	33	10	23	15	10
	236	16	7	11	13	16	7

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Element	Concentration μg/L	Single-Analyst Precision % RSD					
		Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Co	29.7	10	17	10	19	24	12
	420	8	11	13	14	9	5
Cu	10.1	49	47	17	17	—	30
	234	8	15	6	21	—	11
	300	6	—	—	—	11	—
	1 670	11	—	—	—	6	—
Fe	26.1	144	52	153	—	—	124
	455	48	37	45	—	—	31
	1 030	17	—	—	30	—	—
	5 590	6	—	—	32	—	—
	370	14	—	—	—	19	—
	2 610	9	—	—	—	18	—
Pb	10.4	6	19	17	21	19	33
	243	17	7	17	18	12	16
Mn	0.44	187	180	—	—	—	275
	14.8	32	19	—	—	—	18
	91.0	15	—	—	48	—	—
	484.0	4	—	—	12	—	—
	111.0	12	—	—	—	21	—
	666.0	6	—	—	—	20	—
Ni	26.2	20	26	25	24	18	9
	461.0	15	11	9	8	11	4
Se	10.0	12	27	16	35	41	13
	235.0	6	6	15	6	13	14
Ag	8.48	10	—	—	15	27	16
	56.5	14	—	—	7	16	23
	0.45	27	166	48	—	—	—
	13.6	15	4	10	—	—	—

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 3113:IV. INTERLABORATORY OVERALL PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Overall Precision% *RSD*					
Element	**Concentration μg/L**	**Lab Pure Water**	**Drinking Water**	**Surface Water**	**Effluent 1**	**Effluent 2**	**Effluent 3**
Al	28	99	114	124	—	—	131
	125	45	47	49	—	—	40
	11 000	19	—	—	43	—	—
	58 300	31	—	—	32	—	—
	460	20	—	—	—	47	—
	2 180	30	—	—	—	15	—
	10.5	37	19	22	50	103	39
	230	26	16	16	17	180	21
As	9.78	43	26	37	72	50	39
	227	18	12	13	20	15	14
Ba	56.5	68	38	43	116	43	65
	418	35	35	28	38	48	16
Be	0.45	28	31	15	67	50	35
	10.9	33	15	26	20	9	19
Cd	0.43	73	60	5	88	43	65
	12	19	25	41	26	20	27
Cr	9.87	30	53	24	60	41	23
	236	18	14	24	20	14	20
Co	29.7	13	26	17	18	21	17
	420	21	21	17	18	13	13
Cu	10.1	58	82	31	32	—	74
	234	12	33	19	21	—	26
	300	13	—	—	—	14	—
	1 670	12	—	—	—	13	—
Fe	26.1	115	93	306	—	—	204
	455	53	46	53	—	—	44
	1 030	32	—	—	25	—	—

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

		Overall Precision% *RSD*					
Element	Concentration μg/L	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
	5 590	10	—	—	43	—	—
	370	28	—	—	—	22	—
	2 610	13	—	—	—	22	—
Pb	10.4	27	42	31	23	28	47
	243	18	19	17	19	19	25
Mn	0.44	299	272	—	—	—	248
	14.8	52	41	—	—	—	29
	91.0	16	—	—	45	—	—
	484.0	5	—	—	17	—	—
	111.0	15	—	—	—	17	—
	666.0	8	—	—	—	24	—
Ni	26.2	35	30	49	35	37	43
	461.0	23	22	15	12	21	17
Se	10.0	17	48	32	30	44	51
	235.0	16	18	18	17	22	34
Ag	8.48	23	—	—	16	35	34
	56.5	15	—	—	24	32	28
	0.45	57	90	368	—	—	—
	13.6	19	19	59	—	—	—

TABLE 3113:V. INTERLABORATORY RELATIVE ERROR DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Relative Error %					
Element	Concentration μg/L	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28.0	86	150	54	—	—	126
	125.0	4	41	39	—	—	30
	11 000.0	2	—	—	14	—	—

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

		Relative Error %					
Element	Concentration µg/L	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
	58 300.0	12	—	—	7	—	—
	460.0	2	—	—	—	11	—
	2 180.0	11	—	—	—	9	—
Sb	10.5	30	32	28	24	28	36
	230.0	35	14	19	13	73	39
As	9.78	36	1	22	106	13	16
	227.0	3	7	10	19	6	13
Ba	56.5	132	54	44	116	59	40
	418.0	4	0	0	13	6	60
Be	0.45	40	16	11	16	10	15
	10.9	13	2	9	7	8	8
Cd	0.43	58	45	37	66	16	19
	12.0	4	6	5	22	18	3
Cr	9.87	10	9	4	2	5	15
	236.0	11	0	9	13	5	8
Co	29.7	7	7	1	6	3	13
	420.0	12	8	8	11	5	18
Cu	10.1	16	48	2	5	—	15
	234.0	8	7	0	4	—	19
	300.0	4	—	—	—	21	—
	1 670.0	6	—	—	—	2	—
Fe	26.1	85	60	379	—	—	158
	455.0	43	22	31	—	—	18
	1 030.0	8	—	—	8	—	—
	5 590.0	2	—	—	12	—	—
	370.0	4	—	—	—	11	—
	2 610.0	35	—	—	—	2	—
Pb	10.4	16	10	17	1	34	14
	243.0	5	15	8	18	15	29
Mn	0.44	332	304	—	—	—	556

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

		Relative Error %					
Element	Concentration μg/L	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
	14.8	10	1	—	—	—	36
	91.0	31	—	—	10	—	—
	484.0	42	—	—	4	—	—
	111.0	1	—	—	—	29	—
	666.0	6	—	—	—	23	—
Ni	26.2	9	16	10	7	33	54
	461.0	15	19	18	31	16	18
Se	10.0	12	9	6	36	17	37
	235.0	7	7	0	13	10	17
Ag	8.48	12	—	—	1	51	20
	56.5	16	—	—	8	51	22
	0.45	34	162	534	—	—	—
	13.6	3	12	5	—	—	—

TABLE 3120:I. SUGGESTED WAVELENGTHS, ESTIMATED DETECTION LIMITS, ALTERNATE WAVELENGTHS, CALIBRATION CONCENTRATIONS, AND UPPER LIMITS

Element	Suggested Wavelength nm	Estimated Detection Limit μg/L	Alternate Wavelength* nm	Calibration Concentration mg/L	Upper Limit Concentration† mg/L
Aluminum	308.22	40	237.32	10.0	100
Antimony	206.83	30	217.58	10.0	100
Arsenic	193.70	50	189.04‡	10.0	100
Barium	455.40	2	493.41	1.0	50
Beryllium	313.04	0.3	234.86	1.0	10
Boron	249.77	5	249.68	1.0	50
Cadmium	226.50	4	214.44	2.0	50
Calcium	317.93	10	315.89	10.0	100
Chromium	267.72	7	206.15	5.0	50
Cobalt	228.62	7	230.79	2.0	50

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Element	Suggested Wavelength *nm*	Estimated Detection Limit *µg/L*	Alternate Wavelength* *nm*	Calibration Concentration *mg/L*	Upper Limit Concentration† *mg/L*
Copper	324.75	6	219.96	1.0	50
Iron	259.94	7	238.20	10.0	100
Lead	220.35	40	217.00	10.0	100
Lithium	670.78	4§	—	5.0	100
Magnesium	279.08	30	279.55	10.0	100
Manganese	257.61	2	294.92	2.0	50
Molybdenum	202.03	8	203.84	10.0	100
Nickel	231.60	15	221.65	2.0	50
Potassium	766.49	100§	769.90	10.0	100
Selenium	196.03	75	203.99	5.0	100
Silica (SiO_2)	212.41	20	251.61	21.4	100
Silver	328.07	7	338.29	2.0	50
Sodium	589.00	30§	589.59	10.0	100
Strontium	407.77	0.5	421.55	1.0	50
Thallium	190.86‡	40	377.57	10.0	100
Vanadium	292.40	8	—	1.0	50
Zinc	213.86	2	206.20	5.0	100

* Other wavelengths may be substituted if they provide the needed sensitivity and are corrected for spectral interference.† Defines the top end of the effective calibration range. Do not extrapolate to concentrations beyond highest standard.‡ Available with vacuum or inert gas purged optical path.§ Sensitive to operating conditions.

TABLE 3120:II. ICP PRECISION AND BIAS DATA

Element	Concentration Range *µg/L*	Total Digestion* *µg/L*	Recoverable Digestion* *µg/L*
Aluminum	4792 69–	$X = 0.9273C + 3.6$	$X = 0.9380C + 22.1$
		$S = 0.0559X + 18.6$	$S = 0.0873X + 31.7$
		$SR = 0.0507X + 3.5$	$SR = 0.0481X + 18.8$
Antimony	1406 77–	$X = 0.7940C - 17.0$	$X = 0.8908C + 0.9$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Element	Concentration Range µg/L	Total Digestion* µg/L	Recoverable Digestion* µg/L
		$S = 0.1556X - 0.6$	$S = 0.0982X + 8.3$
		$SR = 0.1081X + 3.9$	$SR = 0.0682X + 2.5$
Arsenic	69–1887	$X = 1.0437C - 12.2$	$X = 1.0175C + 3.9$
		$S = 0.1239X + 2.4$	$S = 0.1288X + 6.1$
		$SR = 0.0874X + 6.4$	$SR = 0.0643X + 10.3$
Barium	9–377	$X = 0.7683C + 0.47$	$X = 0.8380C + 1.68$
		$S = 0.1819X + 2.78$	$S = 0.2540X + 0.30$
		$SR = 0.1285X + 2.55$	$SR = 0.0826X + 3.54$
Beryllium	3–1906	$X = 0.9629C + 0.05$	$X = 1.0177C - 0.55$
		$S = 0.0136X + 0.95$	$S = 0.0359X + 0.90$
		$SR = 0.0203X - 0.07$	$SR = 0.0445X - 0.10$
Boron	19–5189	$X = 0.8807C + 9.0$	$X = 0.9676C + 18.7$
		$S = 0.1150X + 14.1$	$S = 0.1320X + 16.0$
		$SR = 0.0742X + 23.2$	$SR = 0.0743X + 21.1$
Cadmium	9–1943	$X = 0.9874C - 0.18$	$X = 1.0137C - 0.65$
		$S = 0.0557X + 2.02$	$S = 0.0585X + 1.15$
		$SR = 0.0300X + 0.94$	$SR = 0.0332X + 0.90$
Calcium	17–47 170	$X = 0.9182C - 2.6$	$X = 0.9658C + 0.8$
		$S = 0.1228X + 10.1$	$S = 0.0917X + 6.9$
		$SR = 0.0189X + 3.7$	$SR = 0.0327X + 10.1$
Chromium	13–1406	$X = 0.9544C + 3.1$	$X = 1.0049C - 1.2$
		$S = 0.0499X + 4.4$	$S = 0.0698X + 2.8$
		$SR = 0.0009X + 7.9$	$SR = 0.0571X + 1.0$
Cobalt	17–2340	$X = 0.9209C - 4.5$	$X = 0.9278C - 1.5$
		$S = 0.0436X + 3.8$	$S = 0.0498X + 2.6$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Element	Concentration Range µg/L	Total Digestion* µg/L	Recoverable Digestion* µg/L
		$SR = 0.0428X + 0.5$	$SR = 0.0407X + 0.4$
Copper	8–1887	$X = 0.9297C - 0.30$	$X = 0.9647C - 3.64$
		$S = 0.0442X + 2.85$	$S = 0.0497X + 2.28$
		$SR = 0.0128X + 2.53$	$SR = 0.0406X + 0.96$
Iron	13–9359	$X = 0.8829C + 7.0$	$X = 0.9830C + 5.7$
		$S = 0.0683X + 11.5$	$S = 0.1024X + 13.0$
		$SR = -0.0046X + 10.0$	$SR = 0.0790X + 11.5$
Lead	42–4717	$X = 0.9699C - 2.2$	$X = 1.0056C + 4.1$
		$S = 0.0558X + 7.0$	$S = 0.0799X + 4.6$
		$SR = 0.0353X + 3.6$	$SR = 0.0448X + 3.5$
Magnesium	34–13 868	$X = 0.9881C - 1.1$	$X = 0.9879C + 2.2$
		$S = 0.0607X + 11.6$	$S = 0.0564X + 13.2$
		$SR = 0.0298X + 0.6$	$SR = 0.0268X + 8.1$
Manganese	4–1887	$X = 0.9417C + 0.13$	$X = 0.9725C + 0.07$
		$S = 0.0324X + 0.88$	$S = 0.0557X + 0.76$
		$SR = 0.0153X + 0.91$	$SR = 0.0400X + 0.82$
Molybdenum	17–1830	$X = 0.9682C + 0.1$	$X = 0.9707C - 2.3$
		$S = 0.0618X + 1.6$	$S = 0.0811X + 3.8$
		$SR = 0.0371X + 2.2$	$SR = 0.0529X + 2.1$
Nickel	17–47 170	$X = 0.9508C + 0.4$	$X = 0.9869C + 1.5$
		$S = 0.0604X + 4.4$	$S = 0.0526X + 5.5$
		$SR = 0.0425X + 3.6$	$SR = 0.0393X + 2.2$
Potassium	347–14 151	$X = 0.8669C - 36.4$	$X = 0.9355C - 183.1$
		$S = 0.0934X + 77.8$	$S = 0.0481X + 177.2$
		$SR = -0.0099X + 144.2$	$SR = 0.0329X + 60.9$

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Element	Concentration Range µg/L	Total Digestion* µg/L	Recoverable Digestion* µg/L
Selenium	14–15	$X = 0.9363C - 2.5$	$X = 0.9737C - 1.0$
	69–170	$S = 0.0855X + 17.8$	$S = 0.1523X + 7.8$
		$SR = 0.0284X + 9.3$	$SR = 0.0443X + 6.6$
Silicon	189–9434	$X = 0.5742C - 35.6$	$X = 0.9737C - 60.8$
		$S = 0.4160X + 37.8$	$S = 0.3288X + 46.0$
		$SR = 0.1987X + 8.4$	$SR = 0.2133X + 22.6$
Silver	1–89	$X = 0.4466C + 5.07$	$X = 0.3987C + 8.25$
	8–170	$S = 0.5055X - 3.05$	$S = 0.5478X - 3.93$
		$SR = 0.2086X - 1.74$	$SR = 0.1836X - 0.27$
Sodium	47–1170	$X = 0.9581C + 39.6$	$X = 1.0526C + 26.7$
	35–170	$S = 0.2097X + 33.0$	$S = 0.1473X + 27.4$
		$SR = 0.0280X + 105.8$	$SR = 0.0884X + 50.5$
Thallium	14–34	$X = 0.9020C - 7.3$	$X = 0.9238C + 5.5$
	79–170	$S = 0.1004X + 18.3$	$S = 0.2156X + 5.7$
		$SR = 0.0364X + 11.5$	$SR = -0.0106X + 48.0$
Vanadium	46–98	$X = 0.9615C - 2.0$	$X = 0.9551C + 0.4$
	13–170	$S = 0.0618X + 1.7$	$S = 0.0927X + 1.5$
		$SR = 0.0220X + 0.7$	$SR = 0.0472X + 0.5$
Zinc	70–76	$X = 0.9356C - 0.30$	$X = 0.9500C + 1.22$
	7–170	$S = 0.0914X + 3.75$	$S = 0.0597X + 6.50$
		$SR = -0.0130X + 10.07$	$SR = 0.0153X + 7.78$

*X=mean recovery, µg/L,C=true value, µg/L,S=multi-laboratory standard deviation, µg/L,SR=single-an

TABLE 3125:I. RECOMMENDED ANALYTE MASSES, INSTRUMENTAL DETECTION LIMITS (IDL), and INTERNAL STANDARDS

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

TABLE 3125:I. RECOMMENDED ANALYTE MASSES, INSTRUMENTAL DETECTION LIMITS (IDL), and INTERNAL STANDARDS

Element	Analytical Mass	IDL µg/L	Recommended Internal Standard
Be	9	0.025	Li
Al	27	0.03	Sc
V	51	0.02	Sc
Cr	52	0.04	Sc
Cr	53	0.03	Sc
Mn	55	0.002	Sc
Co	59	0.002	Sc
Ni	60	0.004	Sc
Ni	62	0.025	Sc
Cu	63	0.003	Sc
Cu	65	0.004	Sc
Zn	66	0.017	Ge
Zn	68	0.020	Ge
As	75	0.025	Ge
Se	77	0.093	Ge
Se	82	0.064	Ge
Ag	107	0.003	In
Ag	109	0.002	In
Cd	111	0.006	In
Cd	114	0.003	In
Sb	121	0.07	In
Sb	123	0.07	In
Tl	203	0.03	Th
Tl	205	0.03	Th
Pb	208	0.005	Th
U	235	0.032	Th
U	238	0.001	Th
Mo	98	0.003†	In
Ba	135	0.008†	In
Sr	88	0.001‡	In

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

* IDLs were determined on a Perkin Elmer Elan 6000 ICP/MS using seven replicate analyses of a 1% nitric acid solution, at Manchester Environmental Laboratory, July 1996.† From EPA Method 200.8 for the Analysis of Drinking Waters-Application Note, Order No. ENVA-300A, The Perkin Elmer Corporation, 1996.‡ From Perkin Elmer Technical Summary TSMS-12.

TABLE 3125:II. ELEMENTAL ABUNDANCE EQUATIONS AND COMMON MOLECULAR ION CORRECTION EQUATIONS

Elemental and Molecular Equations*†
Li 6 = *C* 6
Be 9 = *C* 9
Al 27 = *C* 27
Sc 45 = *C* 45
V 51 = *C* 51 – (3.127)[(*C* 53) – (0.113 × *C* 52)]
Cr 52 = *C* 52
Cr 53 = *C* 53
Mn 55 = *C* 55
Co 59 = *C* 59
Ni 60 = *C* 60
Ni 62 = *C* 62
Cu 63 = *C* 63
Cu 65 = *C* 65
Zn 66 = *C* 66
Zn 68 = *C* 68
As 75 = *C* 75 – (3.127)[(*C* 77) – (0.815 × *C* 82)]
Se 77 = *C* 77
Se 82 = *C* 82 – (1.008696 × *C* 83)
Sr 88 = *C* 88
Mo 98 = *C* 98 – (0.110588 × *C* 101)
Rh 103 = *C* 103
Ag 107 = *C* 107
Ag 109 = *C* 109
Cd 111 = *C* 111 – (1.073)[(*C* 108) – (0.712 × *C* 106)]
Cd 114 = *C* 114 – (0.02686 × *C* 118)
Sb 121 = *C* 121
Sb 123 = *C* 123 – (0.127189 × *C* 125)

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Elemental and Molecular Equations*†
Ba 135 = *C* 135
Ho 165 = *C* 165
Tl 203 = *C* 203
Tl 205 = *C* 205
Pb 208 = *C* 208 + (1 × *C* 206) + (1 × *C* 207)
Th 232 = *C* 232
U 238 = *C* 238

* *C* = calibration blank corrected counts at indicated mass.† From EPA Method 200.8 for the Analysis of Drinking Waters – Application Note, Order No. ENVA-300A, The Perkin Elmer Corporation, 1996.

TABLE 3125:III. COMMON MOLECULAR ION INTERFERENCES IN ICP/MS[1]

Molecular Ion	Mass	Element Measurement Affected by Interference
Background molecular ions:		
NH^+	15	—
OH^+	17	—
OH_2^+	18	—
C_2^+	24	Mg
CN^+	26	Mg
CO^+	28	Si
N_2^+	28	Si
N_2H^+	29	Si
NO^+	30	—
NOH^+	31	P
O_2^+	32	S
O_2H^+	33	—
$^{36}ArH^+$	37	Cl
$^{38}ArH^+$	39	K
$^{40}ArH^+$	41	—
CO_2^+	44	Ca

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Molecular Ion	Mass	Element Measurement Affected by Interference
CO_2^+H	45	Sc
ArC^+, ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	Fe
ArH^+	57	Fe
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar$	78	Se
$^{40}Ar_2^+$	80	Se
Matrix molecular ions:		
Bromide:		
$^{81}BrH^+$	82	Se
$^{79}BrO^+$	95	Mo
$^{81}BrO^+$	97	Mo
$^{81}BrOH^+$	09	Mo
$Ar^{81}Br^+$	121	Sb
Chloride:		
$^{35}ClO^+$	51	V
$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar^{35}Cl^+$	75	As
$Ar^{37}Cl^+$	77	Se
Sulfate:		
$^{32}SO^+$	48	Ti
$^{32}SOH^+$	49	—
$^{34}SO^+$	50	V, Cr
$^{34}SOH^+$	51	V
SO_2^+, S_2^+	64	Zn

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Molecular Ion	Mass	Element Measurement Affected by Interference
$Ar^{32}S^+$	72	Ge
$Ar^{34}S^+$	74	Ge
Phosphate:		
PO^+	47	Ti
POH^+	48	Ti
PO_2^+	63	Cu
ArP^+	71	Ga
Group I II metals:		
$pArNa^+$	63	Cu
ArK^+	79	Br
$ArCa^+$	80	Se
Matrix oxides*		
TiO	62–66	Ni, Cu, Zn
ZrO	106–112	Ag, Cd
MoO	108–116	Cd
NbO	109	Ag

* Oxide interferences normally will be very small and will affect the method elements only when oxide-producing elements are present at relatively high concentrations, or when the instrument is improperly tuned or maintained. Preferably monitor Ti and Zr isotopes for soil, sediment, or solid waste samples, because these samples potentially contain high levels of these interfering elements.

TABLE 3125:IV. SUGGESTED ANALYTICAL RUN SEQUENCE

Sample Type	Comments
Tuning/optimization standard	Check mass calibration and resolution
Tuning/optimization standard	Optimize instrument for maximum rhodium counts while keeping oxides, double charged ions, and background within instrument specifications
Rinse	—
Reagent blank	Check for contamination

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Sample Type	Comments
Reagent blank	Calibration standard blank
5-μg/L standard	—
10-μg/L standard	—
20-μg/L standard	—
50-μg/L standard	—
100-μg/L standard	—
Rinse	—
Initial calibration verification, 50 μg/L	—
Initial calibration blank	—
0.30-μg/L standard	Low-level calibration verification
1.0-μg/L standard	Low-level calibration verification
External reference material	NIST 1643c or equivalent
Continuing calibration verification	—
Continuing blank calibration	—
Project sample method blank	—
Project sample laboratory-fortified blank	—
Project sample 1–4	—
Project sample 5	—
Project sample 5 with known addition	—
Project sample 5 duplicate with known addition	—
Continuing calibration verification	—
Continuing calibration blank	—

TABLE 3125:V. SUMMARY OF PERFORMANCE CRITERIA

Performance Characteristic	Criteria
Mass resolution	Manufacturer's specification
Mass calibration	Manufacturer's specification
Ba^{2+}/Ba^{+}	Manufacturer's specification
CeO/Ce	Manufacturer's specification
Background counts at mass 220	Manufacturer's specification
Correlation coefficient	$\geq$0.995

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Performance Characteristic	Criteria
Calibration blanks	< Reporting limit
Calibration verification standards	±10% of true value
Laboratory fortified blank (control sample)	±30% of true value
Precision	±20% relative percent difference for lab duplicates
Known-addition recovery	75–125%
0.3 and 1.0 μg/L standards	Dependent on data quality objectives
Reference materials	Dependent on data quality objectives
Internal standard response	70–125% of response in calibration blank with known addition

TABLE 3125:VI. QUALITY CONTROL ANALYSES FOR ICP/MS METHOD

Analysis	Frequency	Acceptance Criteria
Reference material [¶3*c*9)]	Greater of: once per sample batch, or 5%	Dependent on data quality objectives
Preparatory/method blank [¶ 3*c*4)]	Greater of: once per sample batch, or 5%	± Absolute value of instrument detection limit; ± absolute value of laboratory reporting limit or MDL is acceptable
Laboratory fortified blank [¶ 3*c*7)]	Greater of: once per sample batch, or 5%	± 30% of true value
Duplicate known-addition samples	Greater of: once per sample batch, or 5%	± 20% relative percent difference
Continuing calibration verification standards [¶ 3*c*5)]	10%	± 10% of known concentration

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Analysis	Frequency	Acceptance Criteria
Continuing calibration verification blank [¶ 3*c*6)]	10%	± Absolute value of instrument detection limit; ± absolute value of laboratory reporting limit or MDL is acceptable

TABLE 3125:VII. METHOD PERFORMANCE WITH CALIBRATION VERIFICATION STANDARDS*

		Continuing Calibration Verification Standard (*N* = 44)				Initial Calibration Verifi (*N* = 12)		
Element	Mass	Mean Recovery %	Mean	Standard Deviation	Relative Standard Deviation %	Mean Recovery %	Mean	Stan Devi
Be	9	98.71	49.35	3.43	6.94	100.06	50.03	1.
Al	27	99.62	49.81	2.99	6.01	98.42	49.21	1.
V	51	100.97	50.48	1.36	2.68	99.91	49.96	1.
Cr	52	101.39	50.70	1.86	3.66	99.94	49.97	1.
Cr	53	100.68	50.34	1.91	3.79	99.13	49.56	1.
Mn	55	101.20	50.60	1.98	3.91	99.48	49.74	1.
Co	59	101.67	50.83	2.44	4.79	99.44	49.72	1.
Ni	60	99.97	49.99	2.14	4.28	97.98	48.99	1.
Ni	62	99.79	49.89	2.09	4.18	97.57	48.79	1.
Cu	63	100.51	50.25	2.19	4.36	97.87	48.93	1.
Cu	65	100.39	50.19	2.26	4.51	98.34	49.17	1.
Zn	66	101.07	50.53	1.93	3.82	98.75	49.38	0.
Zn	68	100.42	50.21	1.89	3.77	97.75	48.87	0.
As	75	100.76	50.38	1.15	2.28	98.83	49.41	0.
Se	77	101.71	50.85	1.43	2.81	99.54	49.77	1.
Se	82	101.97	50.98	1.50	2.95	99.76	49.88	0.
Ag	107	101.50	50.75	1.68	3.30	99.27	49.63	1.
Ag	109	101.65	50.83	1.68	3.31	99.66	49.83	1.
Cd	111	100.92	50.46	1.94	3.84	98.61	49.30	1.
Cd	114	100.90	50.45	2.07	4.10	99.20	49.60	1.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Element	Mass	Continuing Calibration Verification Standard (*N* = 44) Mean Recovery %	Mean	Standard Deviation	Relative Standard Deviation %	Initial Calibration Verifi (*N* = 12) Mean Recovery %	Mean	Stan Devi
Sb	121	100.14	50.07	2.39	4.77	99.38	49.69	1.
Sb	123	99.98	49.99	2.48	4.97	99.09	49.54	1.
Tl	203	101.36	50.68	1.64	3.23	100.05	50.02	1.
Tl	205	102.40	51.20	1.93	3.78	101.23	50.62	1.
Pb	208	101.21	50.61	1.65	3.25	99.33	49.67	0.
U	238	101.54	50.77	1.93	3.80	99.80	49.90	1.

* Single-laboratory, single-operator, single-instrument data, determined using a 50-μg/L standard prepared from sources independent of calibration standard source. Data acquired January-November 1996 during actual sample determinations. Performance of continuing calibration verification standards at different levels may vary. Perkin-Elmer Elan 6000 ICP/MS used for determination.

TABLE 3125:VIII. METHOD PERFORMANCE FOR RECOVERY OF KNOWN ADDITION IN NATURAL WATERS*

Element	Mass	Total Recoverable Metals† Mean Recovery %	Relative Standard Deviation %	Dissolved Metals‡ Mean Recovery %	Relative Standard Deviation %
Be	9	89.09	5.77	—	—
V	51	87.00	8.82	—	—
Cr	52	87.33	8.42	88.38	6.43
Cr	53	86.93	7.90	88.52	5.95
Mn	55	91.81	10.12	—	—
Co	59	87.67	8.92	—	—
Ni	60	85.07	8.42	89.31	5.70
Ni	62	84.67	8.21	89.00	5.82
Cu	63	84.13	8.46	88.55	8.33
Cu	65	84.37	8.05	88.26	7.80
Zn	66	86.14	23.01	95.59	13.81
Zn	68	81.95	20.31	91.94	13.27
As	75	90.43	4.46	97.30	8.84

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

		Total Recoverable Metals†		Dissolved Metals‡	
Element	Mass	Mean Recovery %	Relative Standard Deviation %	Mean Recovery %	Relative Standard Deviation %
Se	77	83.09	4.76	105.36	10.80
Se	82	83.42	4.73	105.36	10.75
Ag	107	—	—	91.98	5.06
Ag	109	—	—	92.25	4.96
Cd	111	91.37	5.47	96.91	6.03
Cd	114	91.47	6.04	97.03	5.42
Sb	121	94.40	5.24	—	—
Sb	123	94.56	5.36	—	—
Tl	203	97.24	5.42	—	—
Tl	205	98.14	6.21	—	—
Pb	208	96.09	7.08	100.69	7.28

* Single-laboratory, single-operator, single-instrument data. Samples were Washington State surface waters from various locations. Data acquired January-November 1996 during actual sample determinations. Performance of known additions at different levels may vary. Perkin-Elmer Elan 6000 ICP/MS used for determination.
† Known-addition level 20 μg/L. Additions made before preparation according to Section 3030E (modified by cleanhood digestion in TFE beakers). *N* = 20.
‡ Known-addition level for Cd and Pb 1 μg/L; for other analytes 10 μg/L. Additions made after filtration through 1;NO1 HNO_3 precleaned 0.45-μm filters. *N* = 28.

TABLE 3125:IX. METHOD PERFORMANCE WITH LOW-LEVEL CHECK STANDARDS*

		1.0-μg/L Standard				0.3-μg/L Stan		
Element	Mass	Mean Recovery %	Mean	Standard Deviation	Relative Standard Deviation %	Mean Recovery %	Mean	Stan Devi
Be	9	97	0.97	0.06	6.24	95	0.284	0.
Al	27	121	1.21	0.32	26.49	196	0.588	0.
V	51	104	1.04	0.06	5.83	111	0.332	0.
Cr	52	119	1.19	0.34	28.62	163	0.490	0.
Cr	53	102	1.02	0.36	35.54	113	0.338	0.
Mn	55	103	1.03	0.07	6.55	110	0.329	0.
Co	59	103	1.03	0.07	6.42	102	0.307	0.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

		1.0-μg/L Standard				0.3-μg/L Stan		
Element	Mass	Mean Recovery %	Mean	Standard Deviation	Relative Standard Deviation %	Mean Recovery %	Mean	Stan Devi
Ni	60	101	1.01	0.05	5.24	107	0.321	0.
Ni	62	102	1.02	0.06	5.42	109	0.326	0.
Cu	63	107	1.07	0.09	8.78	118	0.355	0.
Cu	65	107	1.07	0.10	9.05	117	0.352	0.
Zn	66	117	1.17	0.51	43.52	182	0.547	0.
Zn	68	116	1.16	0.50	42.90	179	0.537	0.
As	75	97	0.97	0.05	5.23	101	0.302	0.
Se	77	89	0.89	0.08	8.72	88	0.265	0.
Se	82	92	0.92	0.14	15.50	106	0.317	0.
Ag	107	101	1.01	0.05	4.53	94	0.282	0.
Ag	109	103	1.03	0.07	6.57	92	0.277	0.
Cd	111	98	0.98	0.04	3.80	96	0.288	0.
Cd	114	100	1.00	0.03	3.39	98	0.293	0.
Sb	121	94	0.94	0.05	5.28	93	0.280	0.
Sb	123	94	0.94	0.05	5.36	93	0.278	0.
T1	203	101	1.01	0.04	3.57	98	0.294	0.
Tl	205	104	1.04	0.05	5.15	100	0.300	0.
Pb	208	104	1.04	0.04	3.65	104	0.312	0.
U	238	106	1.06	0.05	4.64	102	0.307	0.

* Single-laboratory, single-operator, single-instrument data. *N* = 24 for both standards.

TABLE 3130:I. PRECISION OF Cd, Pb, AND Zn ANALYSIS BY ASV

			Metal Concentration μg/L			RSD %		
Sample	Electrode	ASV Mode	Cd	Pb	Zn	Cd	Pb	Zn
Tap water #1[4]	HMDE	SW	0.068	0.57	—	4.2	4.8	—
Tap water #2[4]	HMDE	SW	—	2.50	—	—	5.1	—
Seawater #1[5]	TFME	DP	0.0121	0.0086	—	10.7	8.1	—

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Sample	Electrode	ASV Mode	Metal Concentration µg/L			RSD %		
			Cd	Pb	Zn	Cd	Pb	Zn
Seawater #2[5]	TFME	DP	0.032	0.032	—	6.3	6.3	—
Soil extract #1[6]	HMDE	SW	189	11.8	—	2.5	5.6	—
Soil extract #1[6]	HMDE	DP	186	11.9	—	2.5	4.0	—
Deionized water[4]	HMDE	SW	0.13	0.79	—	5.5	2.2	—
Wastewater #1[7]	HMDE	DP	—	74	26	—	4.3	4.5
Wastewater #2[7]	HMDE	DP	—	47	86	—	5.2	6.3
Wastewater #3[7]	HMDE	DP	—	46	65	—	4.6	6.2
Wastewater #4[8]	TFME	SW	5.2	60	12	5.2	6.1	7.4

TABLE 3500-Cr:I. ION CHROMATOGRAPHIC CONDITIONS

Variable	Value
Guard column	Dionex IonPac NG1
Separator column	Dionex IonPac AS7
Eluent	250 m*M* $(NH_4)_2SO_4$ 100 m*M* NH_4OH
Eluent flow rate	1.5 mL/min
Post-column reagent	2 m*M* diphenylcarbohydrazide 10% v/v CH_3OH 1*N* H_2SO_4
Post-column reagent flow rate	0.5 mL/min
Detector	Visible 530 nm
Retention time	3.8 min

TABLE 3500-Cr:II. SINGLE-LABORATORY PRECISION AND BIAS

Simple Type	Conc.* µg/L	Mean Recovery %	RPD†

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Simple Type	Conc.* µg/L	Mean Recovery %	RPD†
Reagent water	100	100	0.8
	1000	100	0.0
Drinking water	100	105	6.7
	1000	98	1.5
Groundwater	100	98	0.0
	1000	96	0.8
Primary wastewater effluent	100	100	0.7
	1000	104	2.7
Electroplating effluent	100	99	0.4
	1000	101	0.4

*Sample fortified at this concentration level.
†RPD - relative percent difference between fortified duplicates.

TABLE 3500-Cr:III. MULTILABORATORY DETERMINATION OF BIAS FOR HEXAVALENT CHROMIUM*

Water	Amount Added µg/L	Amount Found µg/L	S_t	S_o	Bias %
Reagent	6.00	6.68	1.03	0.53	+11.3
	8.00	8.64	1.10		+8.0
	16.0	17.4	2.25	0.77	+8.8
	20.0	21.4	2.31		+7.0
	100	101	1.91	3.76	+1.0
	140	143	5.52		+2.1
	800	819	24.3	12.7	+2.4
	960	966	18.5		+7.3
Waste	6.0	5.63	1.17	0.55	–6.2
	8.0	7.31	1.91		–8.6
	16.0	15.1	2.70	1.85	–5.6
	20.0	19.8	1.01		–1.0
	100	98.9	4.36	3.31	–1.1
	140	138	8.39		–1.4

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Water	Amount Added µg/L	Amount Found µg/L	S_t	S_o	Bias %
	800	796	60.6	27.1	–0.5
	960	944	72.1		–1.7

*Each Youden pair was used to calculate one laboratory data point (S_o).

TABLE 3500-FE:I. SELECTION OF LIGHT PATH LENGTH FOR VARIOUS IRON CONCENTRATIONS

Fe µg		
50-mL Final Volume	100-mL Final Volume	Light Path *cm*
50–200	100–400	1
25–100	50–200	2
10–40	20–80	5
5–20	10–40	10

TABLE 3500-K:I. CONCENTRATION OF CATIONS INTERFERING AT VARIOUS CONCENTRATIONS OF POTASSIUM

	Concentration Causing 10% Error *mg/L*		
Cation	K conc = 1 mg/L	K conc = 10 mg/L	K conc = 100 mg/L
Cs^+	1.0	10	100
NH_4^+	2.7	27	270
Tl^+	31.4	314	3 140
Ag^+	2 765	27 650	276 500
$Tris^+$	3 105	31 050	310 500
Li^+	356	3 560	35 600
Na^+	1 179	11 790	117 900

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

	Concentration Causing 10% Error *mg/L*		
Cation	**K conc = 1 mg/L**	**K conc = 10 mg/L**	**K conc = 100 mg/L**
H^+	3.6*	2.6*	1.6*

* pH.

TABLE 3500-V:I. CONCENTRATION AT WHICH VARIOUS IONS INTERFERE IN THE DETERMINATION OF VANADIUM

Ion	**Concentration *mg/L***
Cr^{6+}	1.0
Co^{2+}	1.0
Cu^{2+}	0.05
Fe^{2+}	0.3
Fe^{3+}	0.5
Mo^{6+}	0.1
Ni^{2+}	3.0
Ag^{+}	2.0
U^{6+}	3.0
Br^{-}	0.1
Cl^{-}	100.0
I^{-}	0.001

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Endnotes

1 (Popup - Footnote)
* Note that these definitions are not the same as false-positive or false-negative instrument readings, where similar terms commonly are used by laboratory or field personnel to describe a fault in a single result; false-positive and false-negative decision errors are defined in the context of hypothesis testing, where the terms are defined with respect to the null hypothesis.

2 (Popup - Footnote)
* As $CaCO_3$.

3 (Popup - Footnote)
* Pyrex or equivalent.

4 (Popup - Footnote)
† DQO-PRO, available (free) by downloading from American Chemical Society Division of Environmental Chemistry home page at http:// acs.environmental.duq.edu/acsenv/envchem.htm, and also as part of the tutorial, Reliable Environmental Sampling and Analysis, Instant Reference Sources, Inc., http://instantref.com/inst.ref.htm.

5 (Popup - Footnote)
* Ascarite II, Fisher Scientific Co., or equivalent.

6 (Popup - Footnote)
*APPROVED BY STANDARD METHODS COMMITTEE, 1993.

7 (Popup - Footnote)
*APPROVED BY STANDARD METHODS COMMITTEE, 1993.

8 (Popup - Footnote)
* Celite No. 505, Manville Corp., or equivalent.

9 (Popup - Footnote)
* Fisher Electrophotometer or equivalent.

10 (Popup - Footnote)
† General Electric lamp No. 1719 (at 6 V) or equivalent.

11 (Popup - Footnote)
‡ General Electric photovoltaic cell, Type PV-1, or equivalent.

12 (Popup - Footnote)
§ Corning CS-3-107 (No. 1), CS-4-98 (No. 2), and CS-5-70 (No. 3), or equivalent.

13 (Popup - Footnote)
* Fisher Electrocolorimeter, Model 181, or equivalent.

14 (Popup - Footnote)
† Instrumental Colour Systems, Ltd., 7 Bucklebury Place, Upper Woolhampton, Berkshire RG7 5UD, England.

15 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1994.

16 (Popup - Footnote)
† Nephelometers that instrument manufacturers claim meet the design specifications of this method may not give the same reading for a given suspension, even when each instrument has

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

been calibrated using the manufacturer's manual. This differential performance is especially important when measurements are made for regulatory purposes. Consult regulatory authorities when selecting a nephelometer to be used for making measurements that will be reported for regulatory purposes.

17 (Popup - Footnote)
* Nuclepore Corp., 7035 Commerce Circle, Pleasanton, CA, or equivalent.

18 (Popup - Footnote)
† AMCO-AEPA-1 Standard, Advanced Polymer Systems, 3696 Haven Ave., Redwood City, CA, or equivalent.

19 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

20 (Popup - Footnote)
* For approximate metric dimensions in centimeters multiply dimensions in inches by 2.54.

21 (Popup - Footnote)
† Nuchar WV-G, Westvaco, Covington, VA; Filtrasorb 200, Calgon Carbon Corporation, Pittsburgh, PA; or equivalent.

22 (Popup - Footnote)
‡ There are numerous methods of arranging and presenting samples for odor determinations. The methods offered here are practical and economical of time and personnel. If extensive tests are planned and statistical analysis of data is required, become familiar with the more accurate methods that have been used extensively by flavor and allied industries.[5]

23 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.

24 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

25 (Popup - Footnote)
* Nochromix, Godax Laboratories, Inc., New York, NY, or equivalent.

26 (Popup - Footnote)
† Plastic cup, 7- or 8-ounce, Solo or equivalent, any color except clear.

27 (Popup - Footnote)
‡ Keebler Sea Toast or equivalent.

28 (Popup - Footnote)
*APPROVED BY STANDARD METHODS COMMITTEE, 1997.

29 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

30 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.

31 (Popup - Footnote)
*APPROVED BY STANDARD METHODS COMMITTEE, 1997.

32 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

33 (Popup - Footnote)
* The number of sample portions can be increased when working with samples of unknown demand and may be decreased when working with samples of familiar origin.
34 (Popup - Footnote)
† Size of sample portions is not critical, but must be large enough to ensure reproducible results as well as provide volume sufficient to measure chlorine residual, pH, and temperature.
35 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
36 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
37 (Popup - Footnote)
* Available from Standard Seawater Services, Institute of Oceanographic Services, Warmley, Godalming, Surrey, England.
38 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
39 (Popup - Footnote)
* Teflon or equivalent.
40 (Popup - Footnote)
† Whatman GF/C or equivalent.
41 (Popup - Footnote)
* Freon or equivalent.
42 (Popup - Footnote)
† Whatman No. 40 or equivalent.
43 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
44 (Popup - Footnote)
* Vycor, product of Corning Glass Works, Corning, N.Y., or equivalent.
45 (Popup - Footnote)
† Kimble Nos. 37005 or 37034B, or equivalent.
46 (Popup - Footnote)
‡ Class B or better.
47 (Popup - Footnote)
* Whatman grade 934AH; Gelman type A/E; Millipore type AP40; E-D Scientific Specialties grade 161; Environmental Express Pro Weigh; or other products that give demonstrably equivalent results. Practical filter diameters are 2.2 to 12.5 cm.
48 (Popup - Footnote)
† Gelman No. 4201 or equivalent.
49 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
50 (Popup - Footnote)
* Some commercial thermometers may be as much as 3°C in error.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

51 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
52 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
53 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
54 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
55 (Popup - Footnote)
* Venture Innovations, P.O. Box 53631, Lafayette, LA 70505; or Triton Electronics Ltd., Bigods Hall, Dunmow, Essex, England, CM63BE; or equivalent.
56 (Popup - Footnote)
† Available from CST apparatus supplier or use Whatman No. 17 chromatography grade paper cut into 7- × 9-cm sections with grain parallel to long side.
57 (Popup - Footnote)
* Whatman No. 1 or 2 or equivalent.
58 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
59 (Popup - Footnote)
* Gas chromatographic methods are extremely sensitive to the materials used. Use of trade names in *Standard Methods* does not preclude the use of other existing or as-yet-undeveloped products that give *demonstrably* equivalent results.
60 (Popup - Footnote)
† Commercially available columns and gases they will separate include: Silica gel and activated alumina: Silica gel: H_2, air (O_2 + N_2), CO, CH_4, C_2H_6.

Activated alumina: air (O_2 + N_2), CH_4, C_2H_6, C_3H_8. Molecular sieves (zeolites):

Molecular sieve 5A: H_2, O_2 – Ar, N_2, CH_4, CO.

Molecular sieve 13X: O_2, N_2, CH_4, CO. Porous polymers:

Chromosorb 102: air (H_2, O_2, N_2, CO), CH_4, CO_2. Porapak Q: air - CO, CO_2.

HayeSep Q: H_2, air (O_2 + N_2), CH_4, CO_2, C_2H_6, H_2S. Carbon molecular sieves:

Carbosphere: O_2, N_2, CO, CH_4, CO_2, C_2H_6 (these gases can be eluted isothermally at various temperatures or by temperature programming).

Carbosieve S-II: H_2, air (O_2 + N_2), CO, CH_4, CO_2, C_2H_6 (temperature programming required).

61 (Popup - Footnote)
† Commercially available columns and gases they will separate include: Silica gel and activated alumina: Silica gel: H_2, air (O_2 + N_2), CO, CH_4, C_2H_6.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

Activated alumina: air (O_2 + N_2), CH_4, C_2H_6, C_3H_8. Molecular sieves (zeolites):

Molecular sieve 5A: H_2, O_2 – Ar, N_2, CH_4, CO.

Molecular sieve 13X: O_2, N_2, CH_4, CO. Porous polymers:

Chromosorb 102: air (H_2, O_2, N_2, CO), CH_4, CO_2. Porapak Q: air - CO, CO_2.

HayeSep Q: H_2, air (O_2 + N_2), CH_4, CO_2, C_2H_6, H_2S. Carbon molecular sieves:

Carbosphere: O_2, N_2, CO, CH_4, CO_2, C_2H_6 (these gases can be eluted isothermally at various temperatures or by temperature programming).

Carbosieve S-II: H_2, air (O_2 + N_2), CO, CH_4, CO_2, C_2H_6 (temperature programming required).

62 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1996.
63 (Popup - Footnote)
* Common Sensing, Clark Fork, ID; Eco Enterprises, Seattle, WA; Novatech, Vancouver, B.C., Canada; and Sweeney Aquametrics, Stony Creek, CT
64 (Popup - Footnote)
† Methods for these variables may be found in Section 4500-O, 2550, and Section 2520, respectively.
65 (Popup - Footnote)
* Ultrex, J.T. Baker, or equivalent.
66 (Popup - Footnote)
* Nochromix, Godax Laboratories, or equivalent.
67 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
68 (Popup - Footnote)
* Falcon tubes or equivalent.
69 (Popup - Footnote)
† Ultrex, Optima grade or equivalent.
70 (Popup - Footnote)
* Or equivalent.
71 (Popup - Footnote)
† Such as TFM™ or equivalent.
72 (Popup - Footnote)
‡ At temperatures greater than 80°C, but not boiling.
73 (Popup - Footnote)
§ Or equivalent.
74 (Popup - Footnote)
‖ Or equivalent.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

75 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993
76 (Popup - Footnote)
* GFS Chemicals, Inc., Columbus, OH, Cat. No. 64, or equivalent.
77 (Popup - Footnote)
† Alpha Ventron, P.O. Box 299, 152 Andover St., Danvers, MA 01923, or equivalent.
78 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITEE, 1993.
79 (Popup - Footnote)
* Tygon or equivalent.
80 (Popup - Footnote)
† Use specially prepared reagents low in mercury.
81 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
82 (Popup - Footnote)
* Chelex 100, or equivalent, available from Bio-Rad Laboratories, Richmond, CA.
83 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
84 (Popup - Footnote)
* Dow Corning or equivalent.
85 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
86 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
87 (Popup - Footnote)
* Or equivalent.
88 (Popup - Footnote)
† Cambridge Isotope Laboratories or equivalent.
89 (Popup - Footnote)
‡ Performance data for the method were obtained with these concentrations.
90 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
91 (Popup - Footnote)
* Ultrex, Suprapur, Aristar, or equivalent.
92 (Popup - Footnote)
* Ultrex, Suprapur, Aristar, or equivalent.
93 (Popup - Footnote)
* Ultrex, Suprapur, Aristar, or equivalent.
94 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
95 (Popup - Footnote)

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

* Arnold Hoffman & Co., Providence, RI.
96 (Popup - Footnote)
† K & K Laboratories, K & K Lab. Div., Life Sciences Group, Plainview, NY.
97 (Popup - Footnote)
‡ Pfaltz & Bauer, Inc., Stamford, CT.
98 (Popup - Footnote)
§ EM Science, Gibbstown, NJ.
99 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
100 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
101 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
102 (Popup - Footnote)
* IonPac NGl, Dionex, 4700 Lakeside Drive, Sunnyvale, CA 94086, or equivalent.
103 (Popup - Footnote)
† IonPac AS7, Dionex, or equivalent.
104 (Popup - Footnote)
‡ The multilaboratory precision and bias data cited in this method were the result of a collaborative study carried out jointly between U.S. EPA Environmental Monitoring Systems Laboratory (Cincinnati) and Committee D-19 of ASTM.
105 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
106 (Popup - Footnote)
* GFS Chemicals, Inc., Columbus, OH, or equivalent.
107 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
108 (Popup - Footnote)
*APPROVED BY STANDARD METHODS COMMITTEE, 1997.
109 (Popup - Footnote)
* Whatman No. 42 or equivalent.
110 (Popup - Footnote)
† Whatman No. 541 or equivalent.
111 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
112 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
113 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
114 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation

115 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1993.
116 (Popup - Footnote)
* Bio-Rad AG1-X8 or equivalent.
117 (Popup - Footnote)
† Bio-Rad Econo-Columns or equivalent.
118 (Popup - Footnote)
‡ Amberlite XAD-8, Supelco, or equivalent.
119 (Popup - Footnote)
* Bio-Rad AG1-X8 or equivalent.
120 (Popup - Footnote)
* Use Whatman No. 42 filter paper, or equivalent.
121 (Popup - Footnote)
* Bio-Rad glass Econo-Columns or equivalent.
122 (Popup - Footnote)
† Sep-Pak, Waters Associates, or equivalent.
123 (Popup - Footnote)
‡ Chelex 100 (ammonium form) Bio Rad, or equivalent.
124 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
125 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
126 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
127 (Popup - Footnote)
* Whatman No. 42 or equivalent.
128 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

© Copyright 1999 by American Public Health Association, American Water Works Association, Water Environment Federation