

PART 2000

PHYSICAL AND AGGREGATE PROPERTIES

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SUMMARY OF MAJOR CHANGES SINCE 1998

New single-wavelength and tristimulus spectrophotometric methods were added to Color (2120), and the section's material on standard preparation, sample collection, and quality control was revised. Tests on Sludges (2710) includes a new modified settled sludge volume test using a larger-diameter settling column and stirring apparatus.

Important changes to Asbestos (2570) include reduction in pore size for filtering samples and revision of quality control information to be consistent with regulatory requirements.

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 standard.

2110 APPEARANCE

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*

2120 A. Introduction

Color in surface and ground waters results primarily from the presence of natural organic matter, particularly aquatic humic matter. Humic matter consists of humic and fulvic acids; both cause a yellow-brown color. Humic acids give a more intense color, and the presence of iron intensifies the color through the

formation of soluble ferric humates. Suspended particles, especially colloidal-size particles such as clays, algae, iron and manganese oxides, give waters an appearance of color; they should be removed before measurement. Industrial wastewaters can contain lignins, tannins, dyes, and other organic and inorganic chemicals that cause color. Humic materials and the color caused by these materials are removed from potable water supplies for aesthetic reasons and for health reasons because they are precursors in the formation of disinfection by-products.

* Approved by Standard Methods Committee, 2001.
Joint Task Group: James K. Edzwald (chair), Penny J. Bristol, Brian A. Dempsey, Darren A. Lytle, David J. Pernitsky, Mike J. Sadar, Jeff Throckmorton.

Color also is removed to make water suitable for 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. Colloidal and larger suspended particles scatter light interfering with the determination of true color measurements in Method B and in the spectrophotometric procedures of Methods C through F. 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. In some waters and wastewaters, apparent color is contributed principally by colloidal or suspended material.

2. Selection of Method

Methods B and C are applicable to measurement of color caused primarily by natural organic matter. The measurements apply to all surface and ground waters; wastewaters, both do-

mestic and industrial; and especially potable waters. While all methods (B through F) are suitable for true color measurements, for apparent color measurements use only Method B; in such cases, determine both true color and apparent color. For comparison among laboratories, calibrate Method B with Method C. Methods D through F allow color measurement for any dissolved chemical that gives the appearance of color in the visible-light wavelength range. They are especially applicable to colored waters and wastewaters having color characteristics different from, but not excluding, platinum-cobalt standards.

3. Bibliography

- BLACK, A.P. & R.F. CHRISTMAN. 1963. Characteristics of colored surface waters. *J. Amer. Water Works Assoc.* 55:753.
- CHRISTMAN, R.F. & M. GHASSEMI. 1966. Chemical nature of organic color in water. *J. Amer. Water Works Assoc.* 58:723.
- THURMAN, E.M. 1985. *Organic Geochemistry of Natural Waters*. MartinusNijhoff/Dr. W. Junk Publishers, Dordrecht, Netherlands.
- SAWYER, C.N., P.O. MCCARTY & G.F. PARKIN. 1994. *Chemistry for Environmental Engineering*, 4th ed. McGraw-Hill, Inc., 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 given (§ 3b) matches the color of natural waters.

b. Application: The platinum-cobalt method is applicable to natural waters, potable waters, and to wastewaters, both domestic and industrial.

c. Interference: Even a slight turbidity causes the apparent color to be noticeably higher than the true color; therefore remove turbidity by the filtration procedure described in Method C.

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.¹

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 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 Sections 2120C through F. However, results so obtained are not directly comparable to those obtained with platinum-cobalt standards.

2. Apparatus

- a. Nessler tubes*, matched, 50-mL, tall form.
- b. pH meter*, for determining sample pH (see Section 4500-H⁺).
- c. Filter and filter assembly* (for true color measurements): Use a 0.45- μ m-pore-diam cellulose membrane filter of 22 or 47 mm diam. Glass fiber filters also can be used. Rinse filters before use and monitor filter blanks. Smaller-pore filters of 0.2 or 0.22 μ m or even ultrafiltration may be needed to remove colloidal particles for certain samples such as Mn or Fe oxides or other colloids. Use a glass, TFE, or stainless steel assembly to hold the selected filters.

3. Reagents

- a. Organic-free water:* Type I reagent water (see Section 1080) or equivalent water. Use for all standard preparation and other procedures.
- b. Potassium chloroplatinate*, K₂PtCl₆, analytical grade.
- c. Cobaltous chloride*, CoCl₂·6H₂O, analytical grade.

d. Hydrochloric acid, HCl, analytical grade.

e. Sodium hydroxide, NaOH, analytical grade.

4. Preparation of Standards

Dissolve 1.246 g potassium chloroplatinate and 1.00 g crystallized cobaltous chloride in water with 100 mL conc HCl and dilute to 1000 mL. This stock solution has a color of 500 color units (CU). Platinum-cobalt standards of 500 CU are available commercially, and are suitable for use as the primary standard.

Prepare standards having CU of 5, 10, 15, 20, 25, 30, 40, 50, and 100 by diluting 1.0, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, and 20.0 mL stock color standard with water in 100-mL volumetric flasks. Transfer to nessler tubes for use as standards. Protect standards against evaporation and contamination when not in use. Keep in the dark when not in use, and keep only for 1 month.

5. Procedure

a. *Sample collection:* Collect samples in acid-washed amber glass bottles or plastic bottles covered to keep out light. Rinse bottles once with sample before filling bottle with sample. Preferably take a sample of at least 100 mL. Analyze sample within 24 h of collection. Keep samples cold until analysis, and warm them up to room temperature before measurement.

b. *Sample preparation:* Check sample pH. If outside the range of 4 to 10, preferably adjust sample to pH 7 and note the adjustment.

If true color is to be measured, wash membrane filter and filter assembly by passing at least 50 mL water through filter. Filter about 25 mL sample and discard filtrate. Filter a further portion of about 50 mL through the same filter and retain for analysis.

c. *Sample measurement:* 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 through the columns of liquid. If turbidity is present and has not been removed, report as "apparent color." If the color exceeds 100 units, dilute sample in known proportions until the color is within the range of the standards.

6. Calculation

a. Calculate color units (CU) by the following equation:

$$\text{Color} = \frac{A \times 50}{B}$$

where:

A = estimated color of a diluted sample and

B = mL sample taken for dilution.

b. The correct units for true color are CU. One CU is equivalent to one Hazen unit and to one Pt-Co unit. If samples are not filtered, report data as Apparent CU. Report color results in whole numbers and record as follows:

CU	Record to Nearest
1-50	1
51-100	5
101-250	10
251-500	20

c. Report sample pH.

7. Quality Control

a. *Replicate measurements:* Use at least two portions of filtered sample.

b. *Duplicate analyses:* Analyze every tenth sample in duplicate (i.e., duplicating the entire procedure) to assess method precision.

c. *Pre-programmed spectrophotometers:* For spectrophotometers with pre-programmed calibration curves, verify calibration curve regularly with the platinum-cobalt standards prepared under 2120C.4, and adjust pre-programmed curves as needed.

8. Reference

1. BLACK, A.P. & R.F. CHRISTMAN. 1963. Characteristics of colored surface waters. *J. Amer. Water Works Assoc.* 55:753.

9. Bibliography

- CHRISTMAN, R.F. & M. GHASSEMI. 1966. Chemical nature of organic color in water. *J. Amer. Water Works Assoc.* 58:723.
- SAWYER, C.N., P.L. MCCARTY & G.F. PARKIN. 1994. *Color. In Chemistry for Environmental Engineering*, 4th ed., Chap. 14. McGraw Hill, New York, N.Y.

2120 C. Spectrophotometric - Single-Wavelength Method (PROPOSED)

1. General Discussion

a. *Principle:* Color is determined spectrophotometrically at a wavelength between 450 and 465 nm, with platinum-cobalt solutions as standards.¹⁻³ True color of real samples and platinum-cobalt standards follows Beer's Law.

b. *Application:* The spectrophotometric platinum-cobalt

method is applicable to natural waters, potable waters, and wastewaters, both domestic and industrial.

c. *Interference:* The primary interference is from the presence of colloidal and suspended particles that absorb or scatter light at the wavelength of the spectrophotometric method. While in Method 2120B color measurements can be made without removal of particulate matter as long as they are reported as

“Apparent CU”, Method C requires removal of particulate matter before color determination.

Light absorbance of organic matter depends on pH; however, the variation in absorbance is small for the pH range of most waters. Because color measurements are made for aesthetic reasons, preferably do not adjust sample pH as long as it is between 4 and 10. If pH is adjusted, adjust to 7, and note. Further, pH can affect the solubility of substances, which can then interfere with the color measurement if particulate matter is formed.

d. Method detection level: The minimum detectable color depends on the cell path length. Choose a cell size that provides an absorbance within the range that results in good accuracy and linearity of response. This range depends on the quality of the spectrophotometer. If a 50-mm cell is used in the wavelength range of 450 to 465 nm, then an absorbance of 0.005 yields a minimum detectable color of 1 CU. With newer spectrophotometers, a method detection level of 2 CU can be obtained with a path length of 25 mm. Dilute samples with high color to fall within the range of the standard curve. Absorbance readings should fall within the range of 0.005 to 0.8.

2. Apparatus

a. Spectrophotometer: Choose a wavelength between 450 and 465 nm. Use matched glass cells providing a light path of at least 25 mm. Cells with path lengths of 40, 50, or 100 mm may be used. Beer's Law allows flexibility in selecting the cell path length.

b. Filter and filter assembly: See 2120B.2c.

3. Reagents

See Section 2120B.3.

4. Preparation of Standards

Prepare stock color solution of 500 CU according to 2120B.4.

Prepare standards having CU of 5, 10, 15, 20, 30, 40, 50, and 100 by diluting 1.0, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, and 20.0 mL stock color standard with water in 100-mL volumetric flasks. Protect standards against evaporation and contamination when not in use. Keep in the dark when not in use, and keep for only 1 month.

5. Spectrophotometric Standard Curve

Let spectrophotometer warm up according to manufacturer's instructions. Choose a wavelength between 450 and 465 nm to develop the standard curve; a good choice is 456 nm. The absorbance of Pt-Co has a broad maximum absorbance within this wavelength range. Use matched spectrophotometer cells. Fill one cell with water to zero the instrument. Read absorbance for each color standard, and prepare a standard curve of CU versus absorbance.

Pre-programmed color curves are available with some spectrophotometers. The curves can be verified by use of the standards prepared in 2120C.4.

6. Procedure

a. Sample collection: See 2120B.5a.

b. Sample preparation: See 2120B.5b. Always filter sample.

c. Spectrophotometric measurement: Let spectrophotometer warm up according to manufacturer's instructions. Set wavelength at same setting used to develop the standard curve; be sure that the cell path length is the same as that used for the standard curve. Fill one spectrophotometer cell with water and zero the instrument. Rinse the other cell with sample and then refill. Place cell in spectrophotometer and read absorbance. Repeat for remaining samples. Determine sample color using absorbance readings and standard curve relating absorbance and CU. For spectrophotometers with pre-programmed calibration curves for color, zero instrument and take sample measurements according to manufacturer's instructions.

7. Quality Control

See 2120B.7.

8. References

1. CROWTHER, J. & J. EVANS. 1981. Estimating color in Hazen units by spectrophotometry. *J. Amer. Water Works Assoc.* 73:265.
2. BENNETT, L. & M. DRIKAS. 1993. The evaluation of color in natural waters. *Water Res.* 27:1209.
3. HONGVE, D. & G. ÅKESSON. 1996. Spectrophotometric determination of water colour in Hazen units. *Water Res.* 30:2771.

2120 D. Spectrophotometric - Multi-Wavelength 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.

d. Interference: The primary interference is from the presence of colloidal and suspended particles that absorb or scatter light.

TABLE 2120:I. SELECTED ORDINATES FOR SPECTROPHOTOMETRIC COLOR DETERMINATIONS*

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*	444.41
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			
	0.032 69	0.033 33	0.039 38
Factors when 10 Ordinates Used			
	0.098 06	0.100 00	0.118 14

* Insert in each column the transmittance value (%) corresponding to the wavelength shown. Where limited accuracy is sufficient, use only the ordinates marked with an asterisk.

2. Apparatus

a. Spectrophotometer, having absorption cells of a minimum of 10 mm, a narrow (10-nm or less) spectral band, and an effective operating range from 400 to 700 nm.

b. Filter: See 2120B.2c.

3. Procedure

a. Sample preparation: Bring two 50-mL samples to room temperature. Use one sample at the original pH; adjust pH of the other to 7.0 by using sulfuric acid (H₂SO₄) 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 particulate matter from samples before color determination (see 2120B.5b).

b. Determination of light transmission characteristics: Thoroughly clean 1-cm absorption cells. Rinse twice with filtered sample, 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 2120:1 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 7.0 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

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 2120:1 for significance of "c".

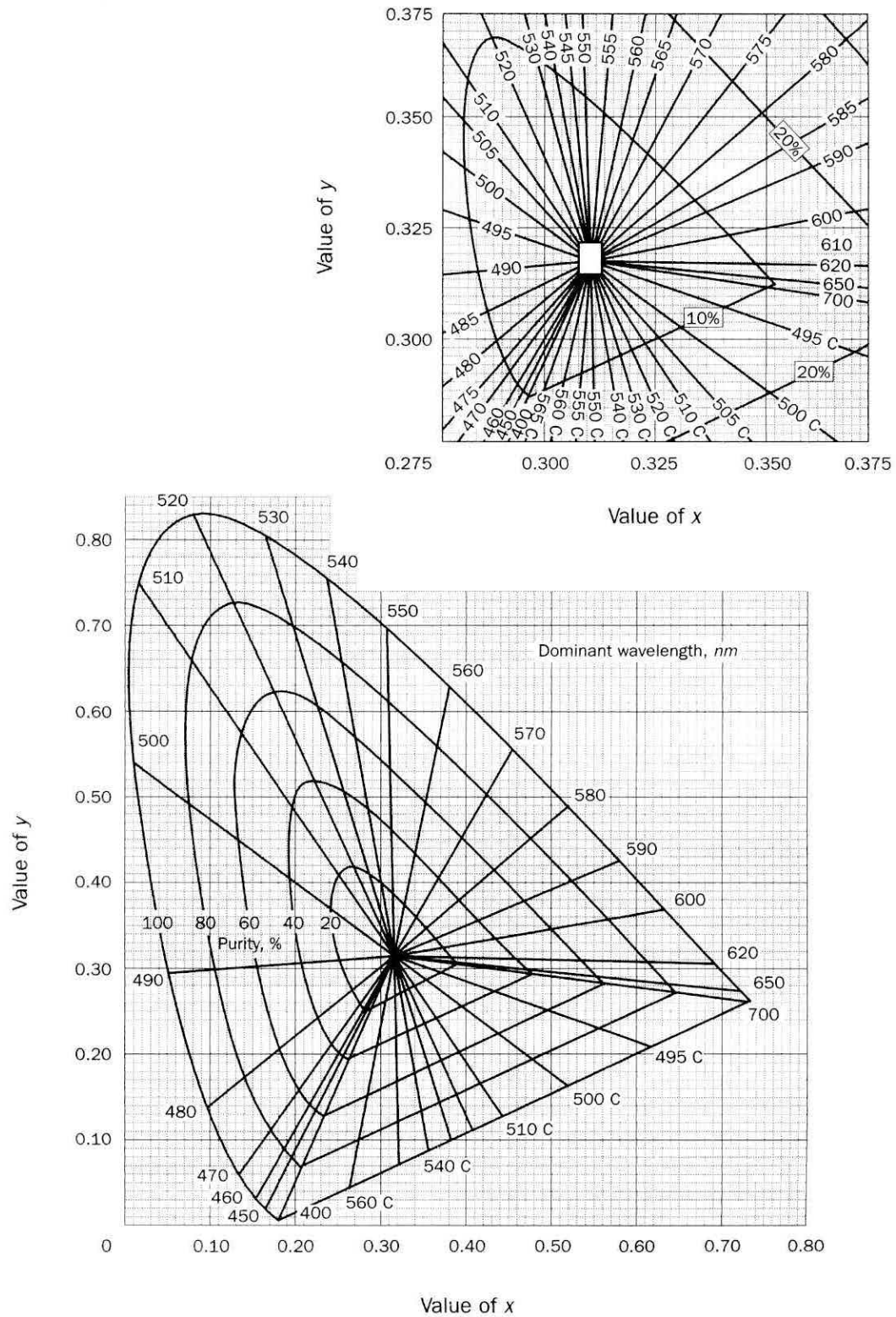


Figure 2120:1. Chromaticity diagrams.

type of instrument (i.e., spectrophotometer), number of selected ordinates (10 or 30), and the spectral band width (nanometers) used.

2120 E. Tristimulus Spectrophotometric Method

1. General Discussion

a. Principle: Tristimulus values are a set of three numbers obtained from a spectrophotometer or colorimeter that, when combined in various ways, describe how the human eye perceives a given color. Calculations using the three tristimulus values typically are used to define the color of a specimen for color matching specifications or for routine control purposes.

The percentage of tristimulus light transmitted by the solution is determined and the transmittance values are then converted to trichromatic coefficients and color characteristic values.

b. Application: This method is applicable to potable and surface waters and to domestic and industrial wastewaters.

c. Interference: See Section 2120C.1c.

2. Apparatus

a. Spectrophotometer with narrow spectral band width (10 nm or less), an effective operating range of 380 to 780 nm, and a tungsten lamp light source. Instrument must be able to obtain transmittance values at a multitude of wavelengths and calculate tristimulus values X , Y , and Z^1 to produce a final color result.* Calibrate calculation algorithm software against platinum-cobalt standard reference.

b. Spectrophotometer cells, 1 cm.

c. Filtering apparatus and filter: See 2120 B.2c.

* Hach DR/4000 Spectrophotometer, Program No. 1666, or equivalent.

6. Bibliography

HARDY, A.C. 1936. Handbook of Colorimetry. Technology Press, Boston, Mass.

3. Procedure

a. Sample collection: See 2120B.5a.

b. Sample preparation: Filter turbid samples according to 2120B.5b.

c. Spectrophotometric measurement: Let spectrophotometer warm up in accordance with manufacturer's directions. Set instrument to pre-programmed calibration curve for tristimulus color. Zero instrument and perform measurements according to manufacturer's method directions. Express results as prescribed in 2120D.5.

Alternatively, obtain tristimulus values for color by a published computation method.¹

4. Quality Control

See Section 2120B.7.

5. Reference

1. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1995. Standard practice for computing the colors of objects by using the CIE system. E308-95, ASTM Standards on Color and Appearance Measurement, 5th ed. American Soc. Testing & Materials, West Conshohocken, Pa.

6. Bibliography

HACH COMPANY. 1999. Hach DR/4000 Spectrophotometer Procedures Manual, 9th ed. Hach Co., Loveland, Colo.

2120 F. ADMI Weighted-Ordinate Spectrophotometric Method

1. General Discussion

a. Principle: Three properties describe color: hue, chroma, and value. Hue is the "color" (blue or red, for example); chroma is the intensity, brightness, or dullness of color; and value is the amount, or lightness or darkness, of color. In accordance with Adams-Nickerson chromatic value formula,¹ this method calculates 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.² Values are independent of chroma and hue. Spectrophotometrically, transmittance is measured at multiple wavelengths and converted to a set of abstract numbers, which then are converted

to a single number that indicates color value. This number is expressed on a scale used by the American Dye Manufacturers Institute (ADMI).²

b. Applications: This method is applicable to colored waters and wastewaters having color characteristics significantly different from, but not excluding, platinum-cobalt standards.

c. Interferences: See Section 2120C.1c.

2. Apparatus

a. Spectrophotometer, with narrow spectral band width (10 nm or less), an effective operating range of 400 nm to 700 nm and a tungsten lamp light source. Instrument must be able to obtain transmittance values at a multitude of wavelengths and calculate

tristimulus (ordinate) values, preferably by using the weighted-ordinate method.* Calibrate calculation algorithm software against platinum-cobalt standard reference.

b. *Spectrophotometer cells*, 1 cm.

c. *Filtering apparatus and filter*: See 2120B.2c.

3. Procedure

a. *Sample collection*: See 2120B.5a.

b. *Sample preparation*: Prepare two 100-mL sample portions, one at the original pH and one at pH 7.0. Filter turbid samples according to 2120B.5b.

c. *Spectrophotometric measurement*: Let spectrophotometer warm up in accordance with the manufacturer's instruction. Set instrument to pre-programmed calibration curve for ADMI Weighted Ordinate Method. Zero instrument and take measurements of original and pH-adjusted samples according to manu-

facturer's directions. Express results as prescribed in 2120C.6c for both original and pH-adjusted samples.

Alternatively, obtain ADMI weighted-ordinate values for color by a published computation method.²

4. Quality Control

See Section 2120B.7.

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.

6. Bibliography

HACH COMPANY. 1999. Hach DR/4000 Spectrophotometer Procedures Manual, 9th ed. Hach Co., Loveland, Colo.

* Hach DR/4000 Spectrophotometer, Program No. 1660, or equivalent.

2130 TURBIDITY*

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 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.† However, interinstrument variation may be effectively negligible

* Approved by Standard Methods Committee, 2001.

Joint Task Group: 20th Edition—Raymond D. Letterman (chair), John A. Arington, Alvin Lieberman, Kemon J. Papacosta, Theodore S. Tanaka, Brannon H. Wilder.

† 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 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.

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.

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.

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.

3) Angle of light acceptance by detector—Centered at 90° to the incident light path and not to exceed $\pm 30^\circ$ 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 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 $0.1\ \mu\text{m}$;^{*} 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, $(\text{NH}_2)_2\text{H}_2\text{SO}_4$, 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, $(\text{CH}_2)_6\text{N}_4$, 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 $25 \pm 3^\circ\text{C}$. 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,[†] and items supplied by instrument manufacturers, such as sealed sample cells filled with latex suspension or with metal oxide particles in a polymer gel. The U.S. Environmental Protection Agency¹ 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 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 out-

^{*} Nuclepore Corp., 7035 Commerce Circle, Pleasanton, CA, or equivalent.

[†] AMCO-AEPA-1 Standard, Advanced Polymer Systems, 3696 Haven Ave., Redwood City, CA, or equivalent.

lined in §§ 2b and 4a 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. Uncertain-

ties and discrepancies in turbidity measurements make it unlikely that 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*

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 recognized¹ 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 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.

* Approved by Standard Methods Committee, 1997.
Joint Task Group: 20th Edition—Irwin H. Suffet, (chair), John A. Arrington, Larry D. Benefield, Larry David Cole, Thomas S. Gittelman, James P. Kizer, Shundar Lin, Gerald L. Mahon, Morten C. Meilgaard, James R. Nugent.

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 6040 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.
- ## 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.
- 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 stoichio-

metric quantity as described under Nitrogen (Ammonia), Section 4500-NH₃.

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 $\pm 1^\circ\text{C}$ 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 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):* 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.†

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.

* For approximate metric dimensions in centimeters multiply dimensions in inches by 2.54.

† Nuchar WV-G, Westvaco, Covington, VA; Filtrasorb 200, Calgon Carbon Corporation, Pittsburgh, PA; or equivalent.

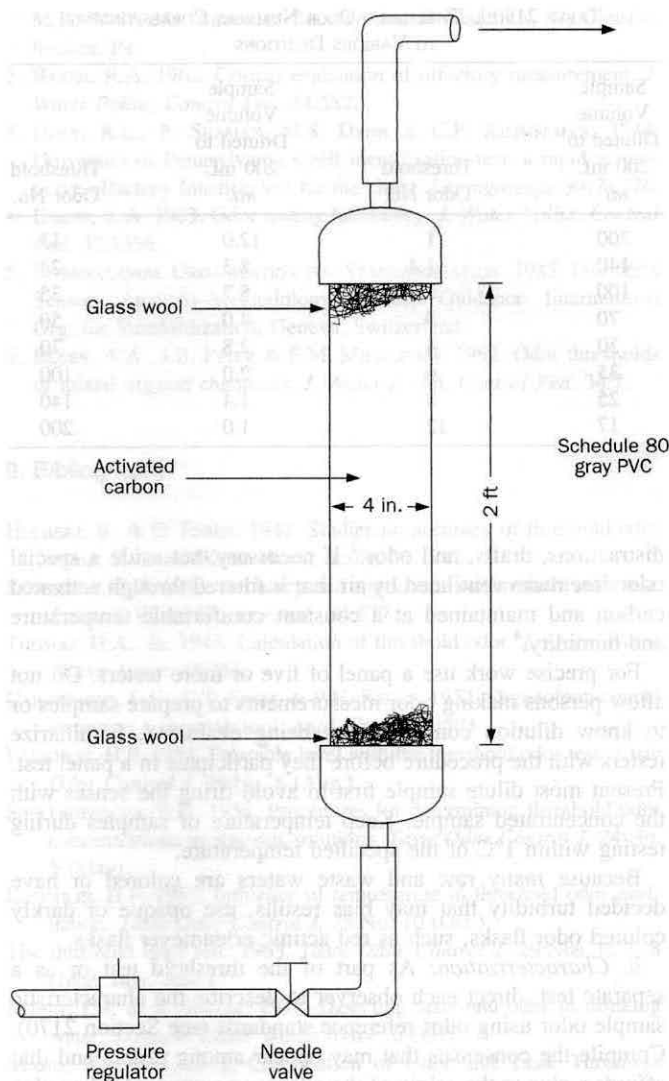


Figure 2150:1. Odor-free-water generator.

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

TABLE 2150:I. THRESHOLD ODOR NUMBERS CORRESPONDING TO VARIOUS DILUTIONS

Sample Volume Diluted to 200 mL <i>mL</i>	Threshold Odor No.	Sample Volume Diluted to 200 mL <i>mL</i>	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

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.

c. Threshold measurement:‡ 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.

‡ 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

TABLE 2150:II. DILUTIONS FOR VARIOUS ODOR INTENSITIES

Sample Volume in Which Odor Is First Noted <i>mL</i>	Volumes to Be Diluted to 200 mL <i>mL</i>
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

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
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:

[illegible]

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 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 &

- 0 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 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*

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 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

* Approved by Standard Methods Committee, 2000.

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:

$$\text{FTN} = \frac{A + B}{A}$$

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

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
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

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.

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

Present series of samples to each tester in order of increasing concentration. Pair each 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	6	8	12	0	17	25	35	0	50
Diluted to									
200 mL									
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):

	Increasing Concentration →						
Response:	—	+	—	+	+	+	+
				↓			
				Threshold			

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.

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. DEOLAKAR & 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. BRUTTSCHILL. 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.
- 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 ¶ B.2d.

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 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 ¶ B.2b).

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.* 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 artificially 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*

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, Denver, Colo.

* Approved by Standard Methods Committee, 1997.

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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

TABLE 2170:I. QUANTITATIVE ODOR REFERENCES*

Compound	Odor Characteristics	Stock Solution Concentration mg/L	Amount Placed Into 200 mL Pure Water at 25°C for Presentation
Geosmin	Earthy, red beets	0.2†	300 µL for 300 ng/L
2-Methylisoborneol	Earthy, peat-like, Brazil nut, soil	0.2†	200 µL for 200 ng/L
Free chlorine	Chlorinous	1.0@pH7	0.1 mL for 0.5 mg/L
Dichloramine	Swimming pool chlorine	1.0@pH7	0.1 mL for 0.5 mg/L
Monochloramine	Chlorinous	1.0@pH7	0.1 ml for 0.5 mg/L
<i>trans</i> -2- <i>cis</i> -6-Nonadienal	Cucumber, green vegetation	1000	1 µL for 5 µg/L
Styrene	Model airplane glue	1000	100 µL for 500 µg/L
Toluene	Glue, sweet solventy	1000	100 µL for 500 µg/L
<i>cis</i> -3-Hexenyl-1-acetate	Grassy	1000	100 µL for 500 µg/L
<i>cis</i> -3-Hexene-1-ol	Grassy, green apple	1000	100 µL for 500 µg/L
Cumene	Paste shoe polish, solventy	1000	20 µL for 100 µg/L
<i>m</i> -Xylene	Sweet solventy	1000	40 µL for 200 µg/L
Methylisobutyl ketone	Paint solventy	1000	200 µL for 1.0 mg/L
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.

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. Apparatus⁴⁻⁸

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.

TABLE 2170:II. REPRESENTATIVE ODOR REFERENCE STANDARDS*

Compound	Odor Characteristics	Stock Solution Concentration mg/L	Amount Placed Into 200 mL Pure Water at 25°C for Presentation
2,3,6-Trichloroanisole	Leather, earthy	1000	4 µL for 20 µg/L
2,3-Diethylpyrazine	Mildew, damp basement	1000	2 µL for 10 µg/L
2-Isopropyl-3-methoxypyrazine	Potato bin, musty	1000	40 µL for 200 µg/L
Nonanal	Hay, sweet	1000	40 µL for 200 µg/L
Dimethyl sulfide	Decaying vegetation, canned corn	1000	1 µL for 5 µg/L
Dimethyl disulfide	Septic	1000	2 µL for 10 µg/L
Dimethyltrisulfide	Garlicky, oniony, septic	0.2	50 µL for 50 ng/L
Butyric acid	Putrid, sickening	1000	200 µL for 1 mg/L
<i>trans</i> ,2-Nonenal	Cucumber with skin	1000	40 µL for 200 µg/L
Diphenyl ether	Geranium	1000†	20 µL for 100 µg/L
D-Limonene	Citrusy	1000	400 µL for 2 mg/L
Hexanal	Lettuce heart, pumpkin, green pistachio	1000	40 µL for 200 µg/L
Benzaldehyde	Sweet almond	1000	200 µL for 1 mg/L
Ethyl-2-methyl-butylate	Fruity, pineapple	1000	1000 µL for 5 mg/L
2-Heptanone	Banana-like, sweet solventy	1000	100 µL for 500 µg/L
Hexachloro-1,3-butadiene	Sweet, minty, Vapo Rub	1000	800 µL for 4 mg/L
2-Isobutyl-3-methoxypyrazine	Green/bell pepper, musty	1000	40 µL for 200 µg/L
<i>trans</i> ,2- <i>trans</i> ,4-Decadienal	Rancid oily	1000	1000 µL for 5 mg/L
Butanol	Alcohol, solventy	1000	200 µL for 1 mg/L
Eucalyptol (cincole)	Topical ointment for chest colds	1000	40 µL for 200 µg/L
Pyridine	Sweet, alcohol, organic	1000	400 µL for 2 mg/L

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.

For flasks with persistent odor use commercial cleaning mixture* 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 preference⁴⁻⁸—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) Temperature⁴—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) Availability⁴—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,† 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 $\pm 1^\circ\text{C}$. 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, 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‡ 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 Tables 2170:I, II, and 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.

* Nochromix, Godax Laboratories, Inc., New York, NY, or equivalent.

† Plastic cup, 7- or 8-ounce, Solo or equivalent, any color except clear.

‡ Keebler Sea Toast or equivalent.

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.
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 Works Assoc., Denver, Colo.

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)
10	
12	(strong)

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
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.

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 plas-

tic 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 watch-glass, 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 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 problem¹ 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 Interpretation¹

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 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:

Description	Intensity				Average
	I	II	III	IV	
Musty	2	4	0	2	2.0
Chlorinous	2	4	4	4	3.5

7. Quality Control¹²

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 Tables 2170:I, II, and 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. MALLEVALLE & 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.
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 in 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. Mallevalle & 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*

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

chemical 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 water.

*Approved by Standard Methods Committee, 1997.

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 (CO₂) 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.

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 0.1M sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$).

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 (§ 4a) 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 (§ 4b).

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 0.02N 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 0.1N 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, 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 $25 \pm 5^\circ\text{C}$.

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 $< 2 \mu\text{mhos/cm}$.

b. Potassium hydrogen phthalate solution, approximately 0.05N: Crush 15 to 20 g primary standard $\text{KHC}_8\text{H}_4\text{O}_4$ to about 100 mesh and dry at 120°C for 2 h. Cool in a desiccator. Weigh $10.0 \pm 0.5 \text{ g}$ (to the nearest mg), transfer to a 1-L volumetric flask, and dilute to 1000 mL.

c. Standard sodium hydroxide titrant, 0.1N: Prepare solution approximately 0.1N as indicated under Preparation of Desk Reagents. Standardize by titrating 40.00 mL $\text{KHC}_8\text{H}_4\text{O}_4$ solution (3b), using a 25-mL buret. Titrate to the inflection point (§ 1a), 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 $\text{KHC}_8\text{H}_4\text{O}_4$ weighed into 1-L flask,

B = mL $\text{KHC}_8\text{H}_4\text{O}_4$ solution taken for titration, and

C = mL NaOH solution used.

Use the measured normality in further calculations or adjust to 0.1000N; 1 mL = 5.00 mg CaCO_3 .

d. *Standard sodium hydroxide titrant*, 0.02N: Dilute 200 mL 0.1N 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 $\text{KHC}_8\text{H}_4\text{O}_4$ as directed in ¶ 3c, using 15.00 mL $\text{KHC}_8\text{H}_4\text{O}_4$ solution and a 50-mL buret. Calculate normality as above (¶ 3c); 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*, 0.1M: Dissolve 25 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ 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 ¶ 1e) into titration flasks. Measure pH. If pH is above 4.0 add 5-mL increments of 0.02N sulfuric acid (H_2SO_4) (Section 2320B.3c) 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 4d.

b. *Color change*: Select sample size and normality of titrant according to criteria of ¶ 1e. 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) 0.1M $\text{Na}_2\text{S}_2\text{O}_3$ 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 normality of titrant according to the criteria of ¶ 1e. 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 ¶ 4c1). Titrate to preselected end-point pH (¶ 1d) 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

$$\text{Acidity, as mg CaCO}_3/\text{L} = \frac{[(A \times B) - (C \times D)] \times 50,000}{\text{mL sample}}$$

where:

A = mL NaOH titrant used,

B = normality of NaOH,

C = mL H_2SO_4 used (¶ 4a), 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 ¶ 4d gave a standard deviation of 1.8 mg CaCO_3/L , with negligible bias. Five laboratories analyzed two samples containing sulfuric, acetic, and formic acids and aluminum chloride by the procedures of ¶s 4b and 4d. 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*

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 constituents. The measured values also may include

* Approved by Standard Methods Committee, 1997.

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

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.1a.

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. Bromocresol green or a mixed bromocresol 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 ¶ 1b. 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 ¶ 4d.

Construct a titration curve for standardization of reagents.

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

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.1e for selection of size sample to be titrated and normality of titrant, substituting 0.02N or 0.1N 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 0.02N H_2SO_4 from a 10-mL buret.

f. Sampling and storage: See Section 2310B.1f.

2. Apparatus

See Section 2310B.2.

3. Reagents

a. Sodium carbonate solution, approximately 0.05N: 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, 0.1N: Prepare acid solution of approximate normality as indicated under Preparation of Desk Reagents. Standardize against 40.00 mL 0.05N 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 0.1000N;

1 mL 0.1000N solution = 5.00 mg CaCO_3 .

c. Standard sulfuric acid or hydrochloric acid, 0.02N: Dilute 200.00 mL 0.1000N standard acid to 1000 mL with distilled or deionized water. Standardize by potentiometric titration of 15.00 mL 0.05N Na_2CO_3 according to the procedure of ¶ 3b; 1 mL = 1.00 mg CaCO_3 .

d. Bromocresol green indicator solution, pH 4.5 indicator: Dissolve 100 mg bromocresol green, sodium salt, in 100 mL distilled water.

*e. Mixed bromocresol green-methyl red indicator solution:*³ Use either the aqueous or the alcoholic solution:

1) Dissolve 100 mg bromocresol green sodium salt and 20 mg methyl red sodium salt in 100 mL distilled water.

2) Dissolve 100 mg bromocresol 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, 0.1N: See Section 2310B.3i.

4. Procedure

a. Color change: See Section 2310B.4b.

b. Potentiometric titration curve: Follow the procedure for determining acidity (Section 2310B.4c), 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 ¶ 1b. Prepare sample and titration assembly (Section 2310B.4c). 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 ¶ 4c, above, using a 10-mL microburet and 0.02N 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:

$$\text{Alkalinity, mg CaCO}_3/\text{L} = \frac{A \times N \times 50\,000}{\text{mL sample}}$$

where:

A = mL standard acid used and

N = normality of standard acid

or

$$\text{Alkalinity, mg CaCO}_3/\text{L} = \frac{A \times t \times 1000}{\text{mL sample}}$$

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

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
$P < \frac{1}{2}T$	0	$2P$	$T - 2P$
$P = \frac{1}{2}T$	0	$2P$	0
$P > \frac{1}{2}T$	$2P - T$	$2(T - P)$	0
$P = T$	T	0	0

*Key: P —phenolphthalein alkalinity; T —total alkalinity.

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 total alkalinity. These relationships may be calculated by the following scheme, where P is phenolphthalein alkalinity and T is total alkalinity (§ 1b):

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 $(T - 2P)$ is bicarbonate. When the smaller value is $(T - P)$, the balance $(2P - T)$ 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 $P \approx \frac{1}{2}T$ 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:

$$\text{CO}_3^{2-} = 2P - 2[\text{OH}^-]$$

$$\text{HCO}_3^- = T - 2P + [\text{OH}^-]$$

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:

$$P = \frac{1}{2} [\text{CO}_3^{2-}] + [\text{OH}^-]$$

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 § 4b 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 § 4c.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 § 4a and § 4c. The pooled standard deviation was 40 mg/L, with negligible difference between the procedures.

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*

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 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 measurements⁴; 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 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.

* Approved by Standard Methods Committee, 2000.

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.
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*. ISBN-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 RI¹ 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.

$$SI = pH - pH_s \quad (1)$$

where:

pH = measured pH and

pH_s = pH of the water if it were in equilibrium with CaCO_3 at the existing calcium ion $[\text{Ca}^{2+}]$ and bicarbonate ion $[\text{HCO}_3^-]$ 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 follows²:

$$pH_s = pK_2 - pK_s + p[\text{Ca}^{2+}] + p[\text{HCO}_3^-] + 5 pf_m \quad (2)$$

where:

K_2 = second dissociation constant for carbonic acid, at the water temperature,

TABLE 2330:I. ESTIMATING EQUILIBRIUM CONSTANTS AND ACTIVITY COEFFICIENTS

Equation	Temperature Range	References
When complete mineral analysis is available: $I = 1/2 \sum [X_i] Z_i^2$	—	3
When only conductivity is available: $I = 1.6 \times 10^{-5} C$	—	4
When only TDS is available: $I = \text{TDS}/40\,000$	—	5
$pf_m = A \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right]$ (valid to $I < 0.5$) $A = 1.82 \times 10^6 (ET)^{-1.5}$	—	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
$pK_w = 4471/T + 0.017\,06T - 6.0875$	273-333	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, $\mu\text{mhos}/\text{cm}$

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, $^{\circ}\text{K}$ ($^{\circ}\text{C} + 273.2$)

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_s				pK_w	A
	pK_s	Calcite	Aragonite	Vaterite		
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 are as follows:

TDS	pf_m
100	0.024
200	0.033
400	0.044
800	0.060
1000	0.066

 K_s = solubility product constant for CaCO_3 at the water temperature, $[\text{Ca}^{2+}]$ = calcium ion concentration, g-moles/L, $[\text{HCO}_3^-]$ = 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 isoforms 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.

$$[\text{Ca}^{2+}] = \text{Ca}_t - \text{Ca}_{ip} \quad (3)$$

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 $[\text{HCO}_3^-]$, the bicarbonate ion concentration, from Equation 4.

$$[\text{HCO}_3^-] = \frac{\text{Alk}_t - \text{Alk}_o + 10^{(pf_m - pH)} - 10^{(pH + pf_m - pK_w)}}{1 + 0.5 \times 10^{(pH - pK_2)}} \quad (4)$$

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-} , $\text{B}(\text{OH})_4^-$, 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^- , and H^+).Calculations can be simplified. For example, in Equation 4, terms containing exponents (e.g., $10^{(pH + pf_m - pK_w)}$) 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:

$$pH_s = pK_2 - pK_s + p[\text{Ca}_t] + p[\text{Alk}_t] + 5 pf_m$$

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:

Constituent	Concentration		
	mg	$\div \frac{\text{mg}}{\text{mole}}$	= 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.

$$I = 0.5 [4(3.80 \times 10^{-3}) + 4(1.60 \times 10^{-3}) + 2.18 \times 10^{-3} + 1.28 \times 10^{-4} + 1.49 \times 10^{-3} + 2.60 \times 10^{-3} + 4(4.48 \times 10^{-3})] = 2.29 \times 10^{-2} \text{ g-moles/L}$$

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 $[\text{HCO}_3^-]$ 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 $pK_w = 14.16$.

$$[\text{HCO}_3^-] = \frac{2.60 \times 10^{-3} + 10^{(0.063 - 9.0)} - 10^{(9.0 + 0.063 - 14.16)}}{1 + 0.5 \times 10^{(9.0 - 10.38)}} = 2.54 \times 10^{-3} \text{ g-moles/L}$$

Therefore $p[\text{HCO}_3^-] = 2.60$.

Determine $[\text{Ca}^{2+}]$ from Equation 3. Neglect Ca_{ip} .

$$[\text{Ca}^{2+}] = Ca_t = 3.80 \times 10^{-3} \text{ g-moles/L}$$

Therefore $p[\text{Ca}^{2+}] = 2.42$.

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:

$$SI = 9.00 - 7.27 = 1.73$$

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 $p[\text{Ca}^{2+}]$; then use $p[\text{Ca}^{2+}]$ in Equation 2.

$$p[\text{Ca}^{2+}] = p(\text{Ca}^{2+}) - 4pf_m \quad (5)$$

This approach eliminates the need to determine Ca_{ip} . However, no equivalent procedure is available to bypass the determination of Alk_o .

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 measurements¹⁴ 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, $[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]$, 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 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 satumetry 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 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. LANGELEIR, 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. HARNED, H.S. & B.B. OWEN. 1958. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed. Reinhold Publishing Corp., New York, N.Y.
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 satumeter. *Limnol. Oceanogr.* 14:874.
14. BEN-YAAKOV, S. & I.R. KAPLAN. 1971. Deep-sea in situ calcium carbonate satumetry. *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 satumetry by alkalinity difference. *Oceanol. Acta.* 3:237.

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. *Satumetry*: 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 test¹⁻⁵ 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 test⁵ 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 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 Ryznar 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

$$SI = \log_{10} RS \quad (6)$$

where:

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_s , 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. 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.

TABLE 2330:III. GRAPHS AND COMPUTER SOFTWARE THAT CAN BE USED TO CALCULATE CaCO_3 SATURATION INDICES*

Item†	CaCO_3 Indices		Approximate Temperature Range °C	Approximate Limit of Ionic Strength	Ion Pairs Considered?	Alk ₀ Considered?‡	Minimum Equipment Required
	Basis for Calculation of SI	CCPP					
1. Caldwell-Lawrence diagrams ⁴	pH _{sa}	P, D	2–25	0.030	No	No	Diagrams
2. ACAPP	RS	P, D	–10–110	6+	Yes	Yes	IBM-compatible PC, 512K bytes of RAM, MS DOS or PC DOS v.2.1 or higher
3. DRIVER	RS	P	7–65	2.5	Yes	Yes	Mainframe computer
4. INDEX C	pH _{sa} , pH _{sb}	P, D	0–50	0.5	No	No	Hewlett-Packard 41C calculator, with three memory modules
5. LEQUIL	RS	No	5–90	0.5	Yes	Yes	IBM-compatible PC, 256K RAM, Lotus 1-2-3 or work-alike, PC DOS or MS DOS v.2.0 or higher
6. MINTEQA1	RS	P, D	0–100	0.5	Yes	Yes	IBM-compatible PC, 512K bytes of RAM, PC DOS v.3.0 or higher, 10 megabyte hard disk drive, math coprocessor useful but not required
7. PHREEQE Standard	RS	P, D	0–100	0.5	Yes	Yes	IBM-compatible PC, known to work with 512K RAM, PC DOS or MS DOS v.2.11 or higher. Also available for mainframe computers.
For high-salinity waters	RS	P, D	0–80	7–8	Yes	Yes	IBM-compatible PC, 640K RAM recommended, with math coprocessor, MS DOS v.3.2 or higher
8. SEQUIL	RS	P, D	7–65	2.5	Yes	Yes	IBM-compatible PC, 512K bytes of RAM, MS DOS or PC DOS v.2.1 or higher.
9. SOLMINEQ.88	RS	P, D	0–350	6	Yes	Yes	IBM-compatible PC, 640K RAM, math coprocessor, PC DOS or MS DOS v.3.0 or higher. Also available for mainframe computer.
10. WTRCHEM	pH _{sa}	P, D	0–100	0.5	No	No	Any PC equipped with a BASIC interpreter, 5K RAM.
11. WATEQ4F	RS	No	0–100	0.5	Yes	Yes	IBM-compatible PC, known to work with 512K RAM, PC DOS or MS DOS v.2.11 or higher.

*SI = saturation index

CCPP = CaCO_3 precipitation potentialpH_{sa} = alkalinity-based pH_spH_{sb} = bicarbonate-based pH_sP = calculates amount of CaCO_3 theoretically precipitatedD = calculates amount of CaCO_3 theoretically dissolved

RS = relative saturation

PC = personal computer

RAM = random access memory

† 1. Loewenthal and Marais³ provide 10.2- by 11.4-cm diagrams, with documentation; Merrill⁵ 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 documentation⁶).

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 documentation⁷).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 personal computer version of standard code); National Water Research Institute, Canada Centre for Inland Waters, 867 Lakeshore Rd., Burlington, Ont., Canada L7R 4A6 Attn: A.S. Crowe (provides software and documentation^{8,9} for personal computer versions of both standard and high-salinity codes); U.S. Geological Survey, Books and Open File Report Section, Box 25425, Federal Center, Denver, CO 80225 (provides documentation^{8,10} for mainframe and personal computer versions of standard code).8. Power Computing Company, 1930 Hi Line Dr., Dallas, TX 74207 (software and documentation¹¹).9. U.S. Geological Survey, Water Resources Division, MS 427, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: Y.K. Kharaka (software and documentation¹²).

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 File Report Section, Box 25425, Federal Center, Denver, CO 80225 (documentation¹³).‡Codes differ in the species included in Alk₀.

2340 HARDNESS*

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 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 hard-

ness 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

$$= 2.497 [\text{Ca, mg/L}] + 4.118 [\text{Mg, mg/L}]$$

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 increased indefinitely because of the

danger of precipitating calcium carbonate, CaCO_3 , or magnesium hydroxide, $\text{Mg}(\text{OH})_2$, 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 2b3)], 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 Sections 3500-Ca and 3500-Mg) and obtain hardness by calculation. The values in Table 2340:I are

*Approved by Standard Methods Committee, 1997.

TABLE 2340:I. MAXIMUM CONCENTRATIONS OF INTERFERENCES
PERMISSIBLE WITH 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.

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 1N hydrochloric acid (HCl), neutralize to pH 7 with 1N 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 CaCO₃ 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 CaCO₃ to precipitate. The following three methods also reduce precipitation loss:

1) Dilute sample with distilled water to reduce CaCO₃ 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 CO₂ *before* pH adjustment. Determine alkalinity to indicate amount of acid to be added.

2. Reagents

a. Buffer solution:

1) Dissolve 16.9 g ammonium chloride (NH₄Cl) in 143 mL conc ammonium hydroxide (NH₄OH). 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 (MgSO₄ · 7H₂O) or 644 mg magnesium chloride (MgCl₂ · 6H₂O) in 50 mL distilled water. Add this solution to 16.9 g NH₄Cl and 143 mL conc NH₄OH 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 MgSO₄ or MgCl₂.

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 (NH₃) or pickup of carbon dioxide (CO₂). 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 NH₄Cl-NH₄OH buffer. They usually do not provide as good an end point as NH₄Cl-NH₄OH 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 0.1N 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 (see Section 1090). Dispose of solutions containing this inhibitor in accordance with all applicable governmental regulations (see Section 1100C), taking special precautions to prevent its contact with acids, which can liberate volatile poisonous hydrogen cyanide.)

2) *Inhibitor II:* Dissolve 5.0 g sodium sulfide nonahydrate (Na₂S · 9H₂O) or 3.7 g Na₂S · 5H₂O 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 ¶ 3b below.

3) *MgCDA:* 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 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, 0.01M*: 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 (§ 2e) as described in § 3b 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 3N 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, 0.1N.

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 (§ 2b et seq.) or that the indicator has deteriorated.

Add 1 to 2 drops indicator solution or an appropriate amount of dry-powder indicator formulation [§ 2c3)]. 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 § 3c below.

c. *Low-hardness sample*: For ion-exchanger effluent or other softened water and for natural waters 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^-/L , 1.1 mg NO_3^-/L , 259 mg $\text{SO}_4^{2-}/\text{L}$, and 42.5 mg total alkalinity/L (contributed by NaHCO_3) in distilled water was analyzed in 56 laboratories by the 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 ethylenediamine-tetraacetate 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*

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 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 Sections 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 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.3a.

* Approved by Standard Methods Committee, 1997.

Joint Task Group: 20th Edition—Roger A. Yorton (chair), James N. Jensen, Maria T. Morsillo.

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 (Sections 4500-Cl.F and 4500-Cl.G).

c. Interference: Refer to Section 4500-Cl.D.1*b* (amperometric titration), 4500-Cl.F.1*d* (DPD ferrous titrimetric method), or 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 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 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 4500-Cl.G (DPD colorimetric method).

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 re-distilled 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), 4500-Cl.F.2 (DPD ferrous titrimetric method), or 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* $\text{Na}_2\text{S}_2\text{O}_3$ 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* $\text{Na}_2\text{S}_2\text{O}_3$ 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* equal sample portions of 200 mL† 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 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.

* 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.

† 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.

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

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 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.1b.

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.1d and B.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 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.5a.

b. Chlorine dioxide requirement: See Section 2350B.5b.

6. Precision and Bias

See Section 2350B.6.

7. Bibliography

See Section 4500- ClO_2 .E.6 and 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-O₃.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-O₃.B.1b.

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.1d and B.6).

For minimum detectable ozone residuals, see Section 4500-O₃.B.1c.

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-O₃.B.2.

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% O₃ 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 O₃/L. If the flask is cooled in an ice

bath throughout the procedure, the ozone concentration will be about 30 to 40 mg O₃/L. Standardize the ozone solution by the indigo method. Use a small sample volume (typically 1 mL) as directed in Section 4500-O₃.B.4a3).

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-O₃.B.4 to measure O₃ residual.

5. Calculation

a. Ozone demand: See Section 2350B.5a 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.5b.

6. Precision and Bias

See Section 2350B.6.

7. Bibliography

See Section 4500-O₃.B.7 and 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.3a.
- b. *Sulfuric acid*, H_2SO_4 , 2N: 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*, $\text{Na}_2\text{S}_2\text{O}_3$, 0.1N: See Section 4500-C1.B.2c.
- e. *Standard sodium thiosulfate titrant*, $\text{Na}_2\text{S}_2\text{O}_3$, 0.005N: Dilute the proper volume (approximately 50 mL) of standardized 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ to 1 L.
- f. *Starch indicator solution*: See Section 4500-C1.B.2e.

4. Procedure

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 2N H_2SO_4 , and titrate with standardized 0.005N $\text{Na}_2\text{S}_2\text{O}_3$ 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 2N H_2SO_4 and titrate with 0.005N $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_3$, 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, mg/min, required to obtain the target ozone residual after the desired ozonation time. See Section 2350E.5a to calculate dose. When reporting ozone requirement, also include target oxidant residual as well as other experimental characteristics listed in ¶ b above.

6. Precision and Bias

See Section 2350B.6.

7. Bibliography

See Section 4500-O₃.B.7 and 8.

2510 CONDUCTIVITY*

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.

* Approved by Standard Methods Committee, 1997.

Joint Task Group: 20th Edition—Robert M. Bagdikian (chair), Stephen W. Johnson, William F. Koch, Russell W. Lane, Misha Plam.

TABLE 2510:I. EQUIVALENT CONDUCTIVITY, Λ , AND CONDUCTIVITY, k , OF POTASSIUM CHLORIDE AT 25.0°C.*2-4

KCl Concentration <i>M</i> or equivalent/L	Equivalent Conductivity, Λ <i>mho-cm²/equivalent</i>	Conductivity, k_s <i>μmho/cm</i>
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
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 dm³ volume standard.² Values are accurate to $\pm 0.1\%$ or 0.1 $\mu\text{mho/cm}$, whichever is greater.

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 , cm², and inversely proportional to the distance between the electrodes, L , cm. The constant of proportionality, k , such that:

$$G = k \left(\frac{A}{L} \right)$$

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 ($\mu\text{mho/cm}$).

In the International System of Units (SI) the reciprocal of the ohm is the siemens (S) and conductivity is reported as milli-siemens per meter (mS/m); 1 mS/m = 10 $\mu\text{mhos/cm}$ and 1 $\mu\text{S/cm}$ = 1 $\mu\text{mho/cm}$. To report results in SI units of mS/m divide $\mu\text{mhos/cm}$ by 10.

To compare conductivities, values of k are reported relative to electrodes with $A = 1 \text{ cm}^2$ and $L = 1 \text{ cm}$. 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-cm²/equivalent, $\mu\text{mho/cm}$, 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 CO₂. 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.

Distilled water produced in a laboratory generally has a conductivity in the range 0.5 to 3 $\mu\text{mhos/cm}$. 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 $\mu\text{mhos/cm}$. The conductivity of domestic wastewaters may be near that of the local water supply, although some industrial wastes have conductivities above 10 000 $\mu\text{mhos/cm}$. 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

TABLE 2510:II. SAMPLE ANALYSIS ILLUSTRATING CALCULATION OF CONDUCTIVITY, k_{calc} , FOR NATURAL WATERS.⁷

Ions	mg/L	mM	$ z \lambda^\circ \text{mM}$	$z^2 \text{mM}$
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

50 000 $\mu\text{mho/cm}$ or less than about 10 $\mu\text{mho/cm}$ 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.

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-cm²/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, $\pm 0.1\%$, 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:

TABLE 2510:III. EQUIVALENT CONDUCTANCES, λ_+° AND λ_-° , (MHO-CM²/EQUIVALENT) FOR IONS IN WATER AT 25.0 C.⁸

Cation	λ_+°	Anion	λ_-°
H^+	350	OH^-	198.6
$1/2\text{Ca}^{2+}$	59.5	HCO_3^-	44.5
$1/2\text{Mg}^{2+}$	53.1	$1/2\text{CO}_3^{2-}$	72
Na^+	50.1	$1/2\text{SO}_4^{2-}$	80.0
K^+	73.5	Cl^-	76.4
NH_4^+	73.5	Ac^-	40.9
$1/2\text{Fe}^{2+}$	54	F^-	54.4
$1/3\text{Fe}^{3+}$	68	NO_3^-	71.4
		H_2PO_4^-	33
		$1/2\text{HPO}_4^{2-}$	57

First, calculate infinite dilution conductivity (Table 2510:II, Column 4):

$$k^\circ = \sum |z_i| (\lambda_{+i}^\circ)(mM_i) + \sum |z_i| (\lambda_{-i}^\circ)(mM_i)$$

where:

$|z_i|$ = absolute value of the charge of the i -th ion,

mM_i = millimolar concentration of the i -th ion, and

$\lambda_{+i}^\circ, \lambda_{-i}^\circ$ = equivalent conductance of the i -th ion.

If mM is used to express concentration, the product, $(\lambda_+^\circ)(mM_i)$ or $(\lambda_-^\circ)(mM_i)$, corrects the units from liters to cm³. In this case k° is 578.2 $\mu\text{mho/cm}$ (Table 2510:II, Column 4).

Next, calculate ionic strength, IS in molar units:

$$IS = \sum z_i^2 (mM_i) / 2000$$

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 $IS \leq 0.5 M$ 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:

$$k_{\text{calc}} = k^\circ y^2$$

In the example being considered, $k_{\text{calc}} = 578.2 \times 0.91^2 = 478.8 \mu\text{mho/cm}$ versus the reported value as measured by the USGS of 477 $\mu\text{mho/cm}$.

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 MÉTROLOGIE LÉGALE. 1981. Standard Solutions Reproducing the Conductivity of Electrolytes, International Recommendation No. 56, 1st ed., June 1980. Bur. International de Métrologie Légale, 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.

2. Apparatus

a. Self-contained conductivity instruments: Use an instrument capable of measuring conductivity with an error not exceeding 1% or 1 $\mu\text{mho/cm}$, 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 platinum 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.3b2)] 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, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 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, 0.0100M: 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 $\mu\text{mhos/cm}$. It is satisfactory for most samples when the cell has a constant between 1 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 0.001M, 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 $25.0 \mu\text{S/cm} \pm 0.3 \mu\text{S/cm}$, 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 0.01M KCl solution. Adjust temperature of a fourth portion to $25.0 \pm 0.1^\circ\text{C}$. 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 0.0100M KCl, as above. Adjust temperature compensation dial to 0.0191

C^{-1} . With probe in standard KCl solution, adjust meter to read 1412 $\mu\text{mho/cm}$. 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 $\pm 0.1^\circ\text{C}$.

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 " $\mu\text{mho/cm}$ @ 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, $\mu\text{mhos/cm}$,

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:

$$k, \mu\text{mho/cm} = \frac{(k_m)}{1 + 0.0191(t - 25)}$$

where:

k_m = measured conductivity in units of $\mu\text{mho/cm}$ at $t^\circ\text{C}$, and other units are defined as above.

For instruments with automatic temperature compensation and readout directly in $\mu\text{mho/cm}$ 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 2510:1.

2520 SALINITY*

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 determined for a standard solution it is possible 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	$\pm 3 \times 10^{-6} \text{ g/cm}^3$	± 0.004
Sound speed	$\pm 0.02 \text{ m/s}$	± 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 hydro-metric and argentometric methods, both of which were included in previous editions of *Standard Methods* (see Sections 210B and C, 16th edition). 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.

* Approved by Standard Methods Committee, 2000.

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

$$S = a_0 + a_1 R_t^{1/2} + a_2 R_t + a_3 R_t^{3/2} + a_4 R_t^2 + a_5 R_t^{5/2} + \Delta S$$

where ΔS 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:

$$\begin{array}{ll} a_0 = 0.0080 & b_0 = 0.0005 \\ a_1 = -0.1692 & b_1 = -0.0056 \\ a_2 = 25.3851 & b_2 = -0.0066 \\ a_3 = 14.0941 & b_3 = -0.0375 \\ a_4 = -7.0261 & b_4 = 0.0636 \\ a_5 = 2.7081 & b_5 = -0.0144 \end{array}$$

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* 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 salinities⁶ to give an equation that is valid from 0 to 40 salinity. The equation is:

$$S = S_{PSS} - \frac{a_0}{1 + 1.5X + X^2} - \frac{b_0 f(t)}{1 + Y^{1/2} + Y^{3/2}}$$

where:

S_{PSS} = value determined from the Practical Salinity Scale given earlier,

$$a_0 = 0.008,$$

$$b_0 = 0.0005,$$

$$X = 400R_p$$

$$Y = 100R_p \text{, and}$$

$$f(t) = (t - 15) / [1 + 0.0162(t - 15)]$$

The practical salinity breaks with the old salinity-chlorinity relationship, $S = 1.80655 \text{ Cl}$. Although the scale can be used for estuarine waters⁷⁻¹⁰ and brines¹¹⁻¹³, 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. *IEEE J. 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 ‰ (Chlorinity 19.37394 ‰). *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 ‰ (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 estuaries. 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 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 ‰) 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.

* Available from Standard Seawater Services, Institute of Oceanographic Services, Warmley, Godalming, Surrey, England.

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. FORSH, 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 by passing 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).

$$\rho = A + B\tau^2$$

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

$$\rho \text{ (kg/m}^3\text{)} = \rho_0 + AS + BS^{3/2} + CS^2$$

where:

$$\begin{aligned} A &= 8.244\,93 \times 10^{-1} - 4.0899 \times 10^{-3}t \\ &\quad + 7.6438 \times 10^{-5}t^2 - 8.2467 \times 10^{-7}t^3 + 5.3875 \times 10^{-9}t^4, \\ B &= -5.724\,66 \times 10^{-3} + 1.0227 \times 10^{-4}t - 1.6546 \times 10^{-6}t^2, \\ C &= 4.8314 \times 10^{-4}, \end{aligned}$$

and the density of water is given by:

$$\begin{aligned} \rho_0 &= 999.842\,594 + 6.793\,952 \times 10^{-2}t - 9.095\,290 \times 10^{-3}t^2 \\ &\quad + 1.001\,685 \times 10^{-4}t^3 - 1.120\,083 \times 10^{-6}t^4 + 6.536\,332 \\ &\quad \times 10^{-9}t^5 \end{aligned}$$

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).

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 $S = 35$, $t = 15^\circ\text{C}$, $p = 0$ (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.,

$$R = R_p r_t R_i$$

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 $t = 15^\circ\text{C}$. From R_p and r_t calculate R_i using the *in situ* results, i.e.,

$$R_i = \frac{R}{R_p r_t}$$

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 $^\circ\text{C}$ and p in bars (10^5 Pa), as follows:

$$R_p = 1 + \frac{p(e_1 + e_2p + e_3p^2)}{1 + d_1t + d_2t^2 + (d_3 + d_4t)R}$$

where:

$$\begin{aligned} e_1 &= 2.070 \times 10^{-4}, & d_1 &= 3.426 \times 10^{-2}, \\ e_2 &= -6.370 \times 10^{-8}, & d_2 &= 4.464 \times 10^{-4}, \\ e_3 &= 3.989 \times 10^{-12}, & d_3 &= 4.215 \times 10^{-1}, \\ \text{and} & & d_4 &= -3.107 \times 10^{-3}, \end{aligned}$$

and

$$r_t = c_0 + c_1t + c_2t^2 + c_3t^3 + c_4t^4$$

where:

$$\begin{aligned} c_0 &= 0.676\,609\,7, \\ c_1 &= 2.005\,64 \times 10^{-2}, \\ c_2 &= 1.104\,259 \times 10^{-4}, \\ c_3 &= -6.9698 \times 10^{-7}, \text{ and} \\ c_4 &= 1.0031 \times 10^{-9}. \end{aligned}$$

2530 FLOATABLES*

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 bac-

teria 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.

* Approved by Standard Methods Committee, 2000.

2530 B. Particulate Floatables

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* 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.

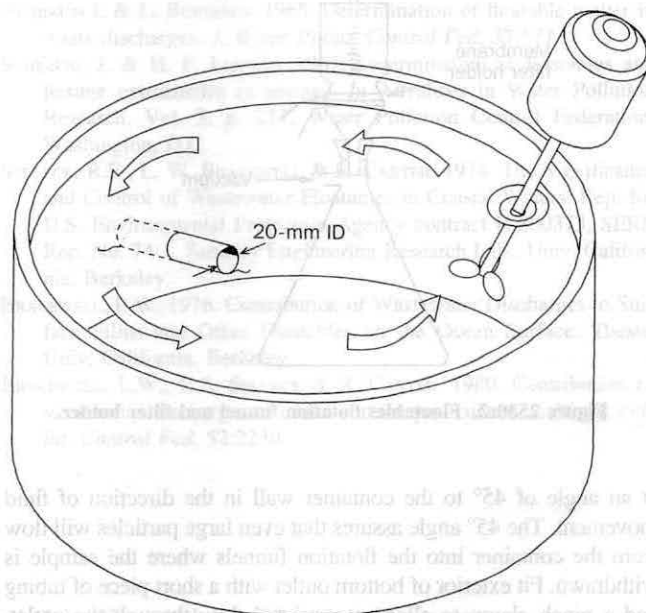


Figure 2530:1. Floatables sampler with mixer.

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

* Teflon or equivalent.

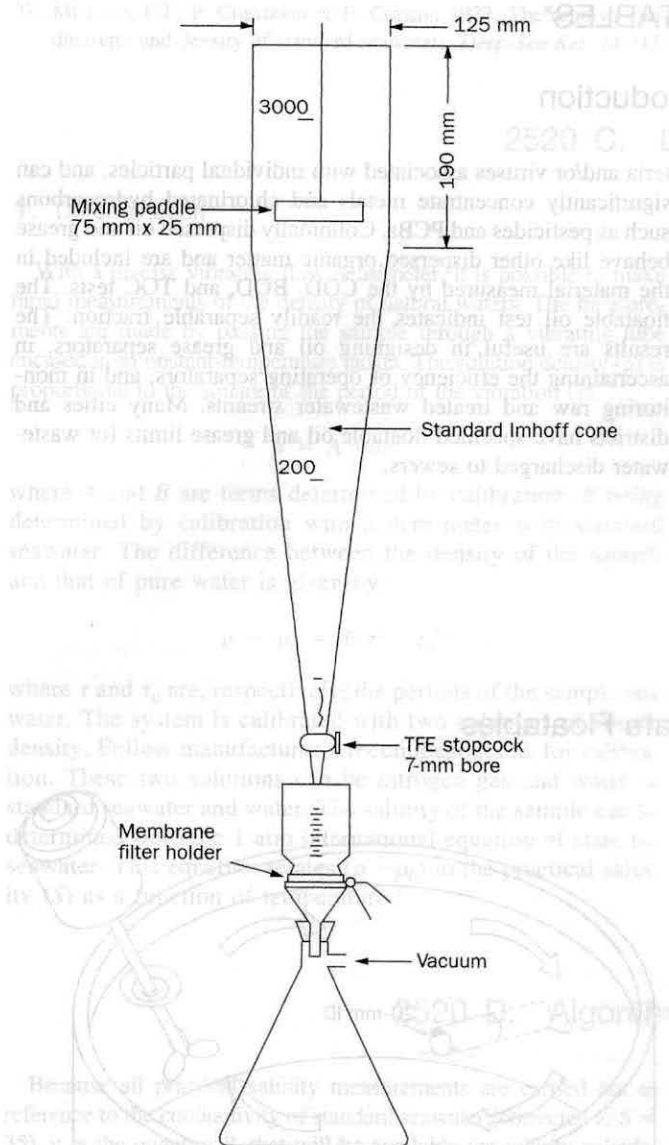


Figure 2530:2. Floatables flotation funnel and filter holder.

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.

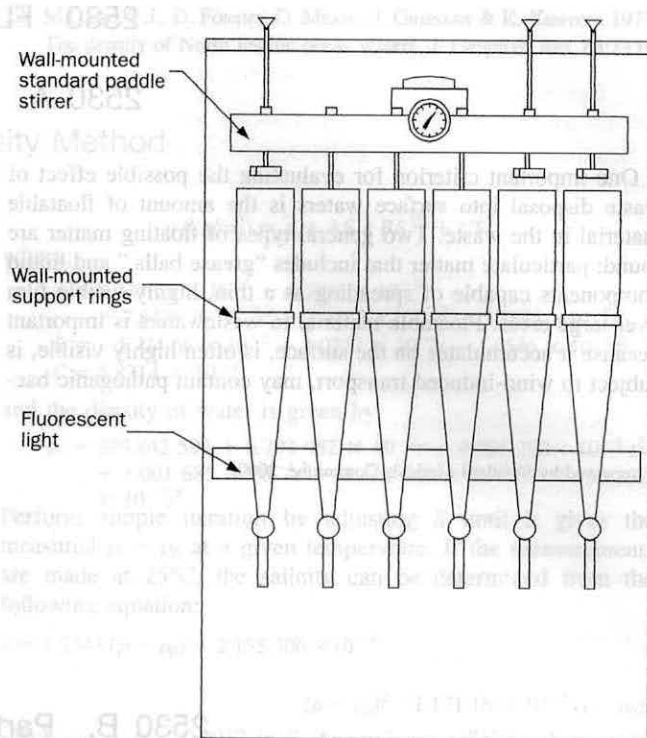


Figure 2530:3. Flotation funnels and mixing unit.

d. Filters, glass fiber, fine porosity.[†]

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 reliability of the test results, but in practice are difficult to obtain.

3. Procedure

a. Preparation of glass fiber filters: See Section 2540D.3a.

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.

[†] Whatman GF/C or equivalent.

TABLE 2530:1. 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 primary sedimentation basin.

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 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and 2.3 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. 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.3c).

4. Calculation

$$\text{mg particulate floatables/L} = \frac{(A - B)}{C}$$

where:

A = weight of filter + floatables, mg,

B = weight of filter, mg, and

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

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 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 powder. Water must form a smooth film on inside of cleaned glass. Do not use lubricant on stopcock.

b. Conical flask, 300 mL.

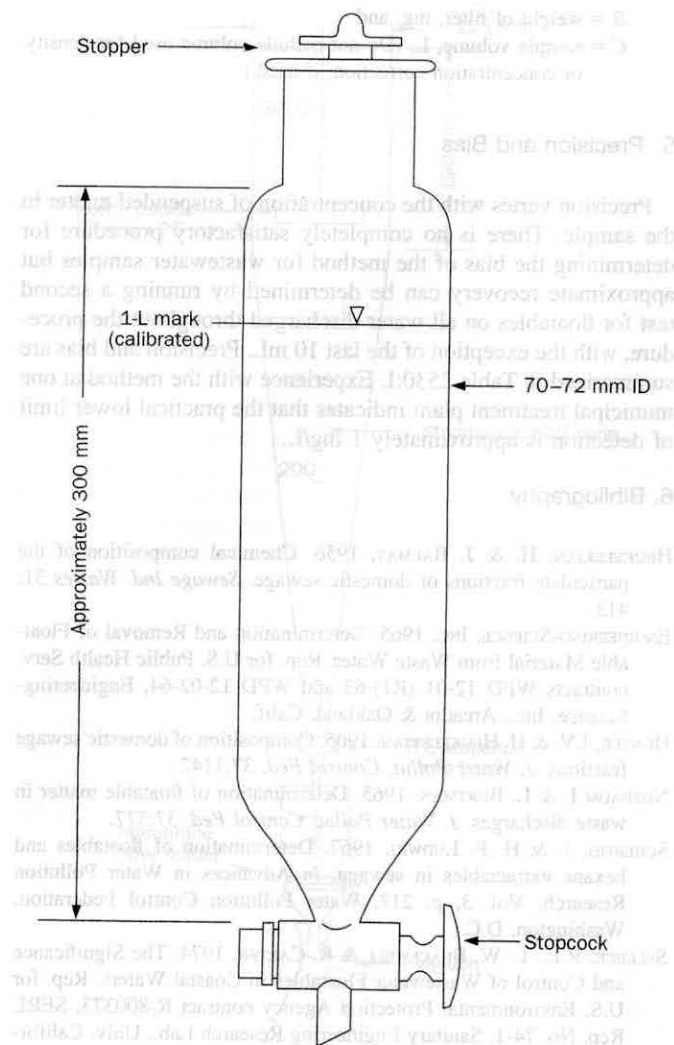


Figure 2530:4. Floatable oil tube, 1-L capacity.

3. Reagents

- 1,1,2-trichloro-1,2,2-trifluoroethane*: See Section 5520C.3b.
- Hydrochloric acid, HCl, 6N.
- Filter paper.†

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

* Freon or equivalent.

† Whatman No. 40 or equivalent.

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 6N 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.

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*

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.

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 (2540F.3b).

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.

Residues dried at $180 \pm 2^\circ\text{C}$ 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.

* Approved by Standard Methods Committee, 1997.

Joint Task Group: 20th Edition—Brannon H. Wilder (chair), Harold S. Costa, Christine M. Kosmowski, William E. Purcell.

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.

2540 B. Total Solids Dried at 103–105°C

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 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.*

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.†

i. Graduated cylinder.

j. Low-form beaker.‡

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

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.

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 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.

* Vycor, product of Corning Glass Works, Corning, NY, or equivalent.

† Kimble Nos. 37005 or 37034B, or equivalent.

‡ Class B or better.

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 2540A.2 and 2540B.1. Highly mineralized waters 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 2540B.2a-h is required, and in addition:

- Glass-fiber filter disks** without organic binder.
- Filtration apparatus:* One of the following, suitable for the filter disk selected:
 - Membrane filter funnel.*
 - Gooch crucible*, 25-mL to 40-mL capacity, with Gooch crucible adapter.
 - Filtration apparatus* with reservoir and coarse (40- to 60- μ m) fritted disk as filter support.[†]
- Suction flask*, of sufficient capacity for sample size selected.
- Drying oven*, for operation at $180 \pm 2^\circ\text{C}$.

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 $180 \pm 2^\circ\text{C}$ 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 $180 \pm 2^\circ\text{C}$, 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 average weight. If volatile solids are to be determined, follow procedure in 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

- 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.

* 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.
[†] Gelman No. 4201 or equivalent.

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 2540A.2 and 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 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 Sections 2540B.2 and 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 vol-

ume 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 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 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 Sections 2540B.2, 2540C.2, and 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

$$\text{mg volatile solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

$$\text{mg fixed solids/L} = \frac{(B - C) \times 1000}{\text{sample volume, mL}}$$

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 (3b) 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 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 nonsettleeable solids.

4. Calculation

mg settleable solids/L

$$= \text{mg total suspended solids/L} - \text{mg nonsettleeable solids/L}$$

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

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

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.

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

$$\% \text{ total solids} = \frac{(A - B) \times 100}{C - B}$$

$$\% \text{ volatile solids} = \frac{(A - D) \times 100}{A - B}$$

$$\% \text{ fixed solids} = \frac{(D - B) \times 100}{A - B}$$

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.

2550 TEMPERATURE*

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

* Approved by Standard Methods Committee, 2000.

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)* that is used with its certificate and correction chart. For field operations use a thermometer having a metal case to prevent breakage.

A total immersion thermometer is designed to indicate temperatures correctly when the bulb and the entire liquid column are exposed to the temperature being measured, except for a minimal emergent length. A partial-immersion thermometer has a line around it at the immersion distance from the bottom. It indicates correctly when the bulb and the liquid column to that line are exposed to the temperature being measured and the emergent stem is at ambient temperature.

* Some commercial thermometers may be as much as 3°C in error.

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.

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.

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 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*

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 ($>500\text{-}\mu\text{m}$) 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 through 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.

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 Sections 2560B.1, C.1, and D.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

* Approved by Standard Methods Committee, 2000.
Joint Task Group: 20th Edition—Desmond F. Lawler (chair), Erika E. Hargeshimer, Carrie M. Lewis, Nancy E. McTigue, Theodore S. Tanaka, John E. Tobiason, Mark R. Wiesner.

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 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 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.

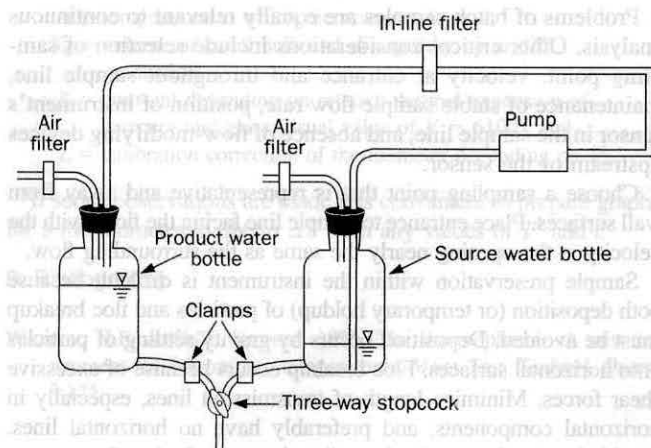


Figure 2560:1. Schematic of filtration apparatus for preparation of particle-free dilution water or electrolyte solution.

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.

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., settings on 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 diam-

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)	$\log d_{pi}$ in μm (F)	$\Delta \log d_{pi}$ (G)	Corrected Count (H)	Number Conc. ΔN_i No./mL (I)	Volume Conc. ΔV_i $\mu\text{m}^3/\text{mL}$ (J)	$\Delta N_i/\Delta d_{pi}$ No./ μm (K)	$\Delta V_i/\Delta d_{pi}$ $\text{mL}/\mu\text{m}$ (L)	$\Delta N_i/\Delta \log d_{pi}$ No./mL (M)	$\Delta V_i/\Delta \log d_{pi}$ $\mu\text{m}^3/\text{mL}$ (N)	$\log \Delta N_i/\Delta d_{pi}$ in No./mL- μm (O)
6	2.95	3.39	3.16	0.44	0.50	0.06	5125	102 500	1.69E+6	2.33E+5	3.85E+6	1.71E+6	2.83E+7	5.37
7	3.39	3.89	3.63	0.50	0.56	0.06	4568	91 360	2.29E+6	1.83E+5	4.58E+6	1.52E+6	2.82E+7	5.26
8	3.89	4.47	4.17	0.58	0.62	0.06	3888	77 760	2.95E+6	1.34E+5	5.09E+6	1.30E+6	4.92E+7	5.13
9	4.47	5.13	4.79	0.66	0.68	0.06	3088	61 760	3.55E+6	9.36E+4	5.38E+6	1.03E+6	5.91E+7	4.97
10	5.13	5.89	5.50	0.76	0.74	0.06	2289	45 780	3.99E+6	6.02E+4	5.25E+6	7.63E+5	6.63E+7	4.78
11	5.89	6.76	6.31	0.87	0.80	0.06	1584	31 680	4.17E+6	3.64E+4	4.86E+6	5.28E+5	6.94E+7	4.56
12	6.76	7.76	7.24	1.00	0.86	0.06	1023	20 460	4.07E+6	2.05E+4	4.07E+6	3.41E+5	6.79E+7	4.31
13	7.76	8.91	8.32	1.15	0.92	0.06	631	12 620	3.81E+6	1.10E+4	3.31E+6	2.10E+5	6.33E+7	4.04
14	8.91	10.23	9.55	1.32	0.98	0.06	363	7 260	3.31E+6	5.50E+3	2.51E+6	1.21E+5	5.52E+7	3.74
15	10.23	11.75	10.96	1.52	1.04	0.06	199	3 980	2.74E+6	2.62E+3	1.80E+6	6.65E+4	4.59E+7	3.42

eter, respectively), and therefore require greater resolution for larger particles than for smaller ones on 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 ($\mu\text{m}^2/\text{mL}$) or volume concentration ($\mu\text{m}^3/\text{mL}$) 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 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 $\pm$ 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 $(n \times 10)/0.5 = 20n/\text{mL}$. 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 ($\pi d_p^3/6$). 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)

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 Sections 1020 and 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 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. AWA Research Foundation, Denver, Colo.

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 be-

tween 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 Sections 2560A.3a and *b* for sampling precautions, and 2560A.4 for particle-free water preparation. Minimize electronic noise as directed in 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 Sections 2560A.3a and 2560A.7.

3. Reagents

a. Particle-free electrolyte solution: Prepare an electrolyte solution of NaCl, CaCl_2 , NaNO_3 , $\text{Ca}(\text{NO}_3)_2$, 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 parti-

cle 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.3a). 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. 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 Sections 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 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 (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 Sections 2560A.3*a* and 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 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 Sections 2560A.3a 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 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.1c.

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 Sections 2560A.3a and 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. 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.4c, 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.3a).

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

See Section 2560A.6.

2570 ASBESTOS*

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 10 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.

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.

* Approved by Standard Methods Committee, 2000.

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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 10 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 10 000 to 20 000 $\times$.

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.

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 and remove all hoses or fittings. Let the water run to waste for at least 1 to 3 min or longer to guarantee that the sample collected is representative of the water supply. (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 with ice 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 positive-pressure positive-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 filtered through the glass filtering unit at frequent intervals to ensure absence of residual asbestos contamination.

c. Side-arm filter flask, 1000 mL.

d. Filters: Use either:

1) *Mixed cellulose ester (MCE) membrane filters*, 25- or 47-mm diam, $\leq 0.22\text{-}\mu\text{m}$ and 5- μm pore size, or

2) *Polycarbonate (PC) filters*, 25- or 47-mm diam, $\leq 0.1\text{-}\mu\text{m}$ pore size.

e. Ultrasonic bath, tabletop model, 60 to 100 W.

f. Graduated pipet, disposable glass, 1, 5, and 10 mL.

g. Cabinet-type desiccator 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 evapo-

rate 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 low enough to permit the measurement of the sides of the opening. 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 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 5d.

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-pyrrolidone.

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 ¶ 1b 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.

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 positive-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 ($\leq 0.22 \mu\text{m}$ or 0.1 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.

Vigorously, by hand, shake capped bottle with sample suspension, then place it in tabletop ultrasonic bath and sonicate for 15 min. The water level in the bath should be approximately the 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.

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 in an airtight, cabinet-type desiccator, or in a HEPA filtered hood or an asbestos-free oven. 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 a process blank using ≥ 50 mL particle-free water for each set of samples analyzed. An acceptable process blank level is ≤ 0.01 million fibers/L (MFL) $> 10 \mu\text{m}$ in length.

Analyze one unused filter from each new box of MCE or PC sample filters. Filter blanks are considered acceptable if they are shown to contain ≤ 53 asbestos structures/ μm^2 , which corresponds to ≤ 3 asbestos structures / 10 grid openings analyzed.

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.

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 10 to 30 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 (§ 3p), 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 bridge and into the solvent. In a fume hood, fill petri dish with either acetone, DMF, 1-methyl-2-pyrrolidone, or chloroform to the level of the stainless steel bridge.

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 (§ 3r).

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 § 1c) above. (Etching is not required.) Take special care to avoid overheating filter sections during carbon coating.

Prepare a Jaffe washer as described in § 1d) above, but fill washer with chloroform or 1-methyl-2-pyrrolidone 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 (§ 3r). 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 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 $\times$ (screen magnification 20 000 $\times$). 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 and Al peak from a Cu grid coated with an aluminum film 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 $\times$ to 1000 $\times$) 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 holes, and have less than 5% opaque area due to incomplete filter dissolution.

If the grid meets these criteria, choose 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 $\times$ 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 10 000 to 25 000 $\times$, 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 >10.0 μm . For fibers and bundles, record greatest length of the structure. For matrices and clusters, record size of 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 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 if requested, either hand-written or computer-generated. Also include: upper and lower 95% confidence limits on the mean concentration, volume of sample filtered, and analytical sensitivity.

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, mm²,

D = dilution factor (if applicable),

G = number of grid openings counted,

A_G = area of grid openings, mm², 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 (duplicate recounts). Reanalyze 1 out of every 100 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)*

2580 A. Introduction

1. Significance

Oxidation and reduction (redox) reactions mediate the behavior of many chemical 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,

* Approved by Standard Methods Committee, 1997.
Joint Task Group: 20th Edition—Michael J. Barcelona (chair), William C. Boyle, Thomas R. Holm, Zoltan Kerekes.

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 Equilibria in Aqueous Solutions* (transl. 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 as a function of temperature can be calculated:⁴

$$Eh, V = 0.428 - 0.0022 (T - 25)$$

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 $\pm 0.1^\circ C$). Then calculate Eh value of the sample:

$$Eh_{\text{system}} = E_{\text{observed}} + Eh_{\text{ZoBell/reference}} - Eh_{\text{ZoBell observed}}$$

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

$Eh_{\text{ZoBell observed}}$ = 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.

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

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.

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.2b.

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

TABLE 2580:II. PREPARATION OF REDOX STANDARD SOLUTIONS

Standard Solution	Potentials of Pt Electrode vs. Selected Reference Electrodes at 25°C in Standard Solution				Standard Hydrogen	Weight of Chemicals Needed/1000 mL Aqueous Solution at 25°C
	Calomel	Silver:Silver Chloride Ag/AgCl				
	Hg/Hg ₂ Cl ₂ saturated KCl	KCl 1.00M	KCl 4.00M	KCl saturated		
Light's solution ¹⁴	+430	+439	+475	+476	+675	39.21 g ferrous ammonium sulfate, Fe(NH ₄) ₂ (SO ₄) ₂ · 6H ₂ O 48.22 g ferric ammonium sulfate, Fe(NH ₄)(SO ₄) ₂ · 12H ₂ O 56.2 mL sulfuric acid, H ₂ SO ₄ , sp gr 1.84
ZoBell's solution* ²	+183	+192	+228	+229	+428	1.4080 g potassium ferrocyanide, K ₄ Fe(CN) ₆ · 3H ₂ O 1.0975 g potassium ferricyanide, K ₃ Fe(CN) ₆ 7.4555 g potassium chloride, KCl

* Store in dark plastic bottle in a refrigerator.

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.

4. Procedure

a. *Instrument calibration*: Follow manufacturer's instructions for using pH/millivolt meter and in preparing electrodes for use.

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 indi- cator 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)
Soils, sludges	WIG, Pt wire	Calomel or silver: silver chloride	Beaker or soil core

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 ($70^\circ C$) aqua regia for 1 to 2 min or 5 min in 6N HNO_3 after bringing to a boil. Alternatively treat with chromic acid solution followed by 6N 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 $\pm 0.1^\circ C$. 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 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

$$E_{h\text{ system}} = E_{\text{observed}} + E_{\text{reference standard}} - E_{\text{reference observed}}$$

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., $\pm$ 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 $\text{Fe}^{2+}/\text{Fe}^{3+}$ -Lösungen. *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 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 600/S4/89/032. Illinois State Water Survey-Univ. Illinois, rep. to USEPA-EMSL, Las Vegas, Nev.

2710 TESTS ON SLUDGES*

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.

* Approved by Standard Methods Committee, B-H, 1997; A, I, 2001. Joint Task Group: Terry E. Baxter (chair), Billie C. Byrom, Daniel D. Chen, Steven K. Dentel, Stephen R. Gelman, S. Rod Jenkins, Mesut Sezgin.

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 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 $\pm 0.5^\circ\text{C}$.

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., $>5000\text{ mg/L}$, 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 consump-

tion. 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 ($\leq 2\text{ mg/L}$ at the start of the test) may limit oxygen uptake by the biological suspension and will be indicated by a decreasing 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 index¹ (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 (2540F). Results from 2540F are not comparable with those obtained with the procedure herein.

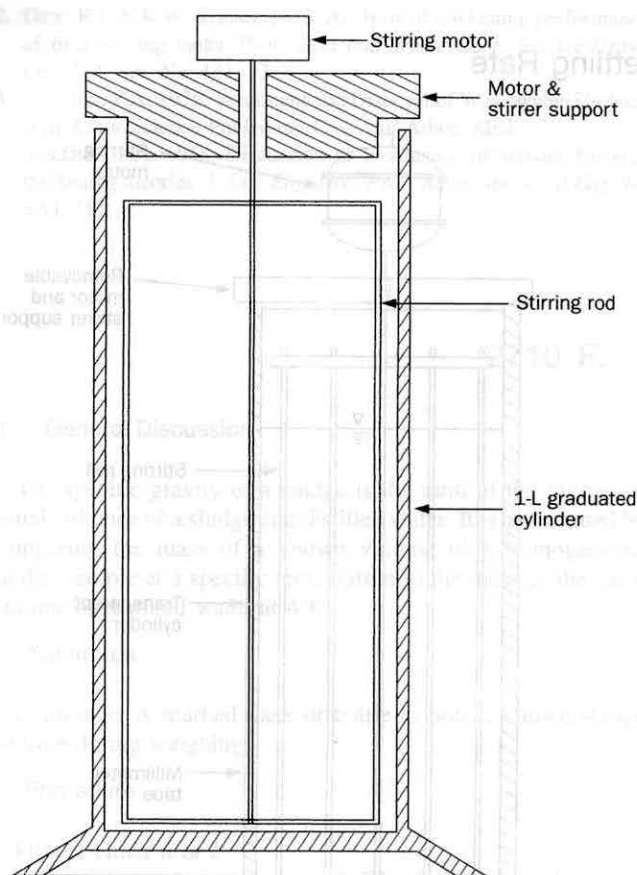


Figure 2710:1. Schematic diagram of settling vessel for settled sludge volume test.

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 stopwatch, 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

- 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).

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

- DICK, R.I. & P.A. VESILIND. 1969. The SVI—What is it? *J. Water Pollut. Control Fed.* 41:1285.
- FINCH, J. & H. IVES. 1950. Settability 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 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

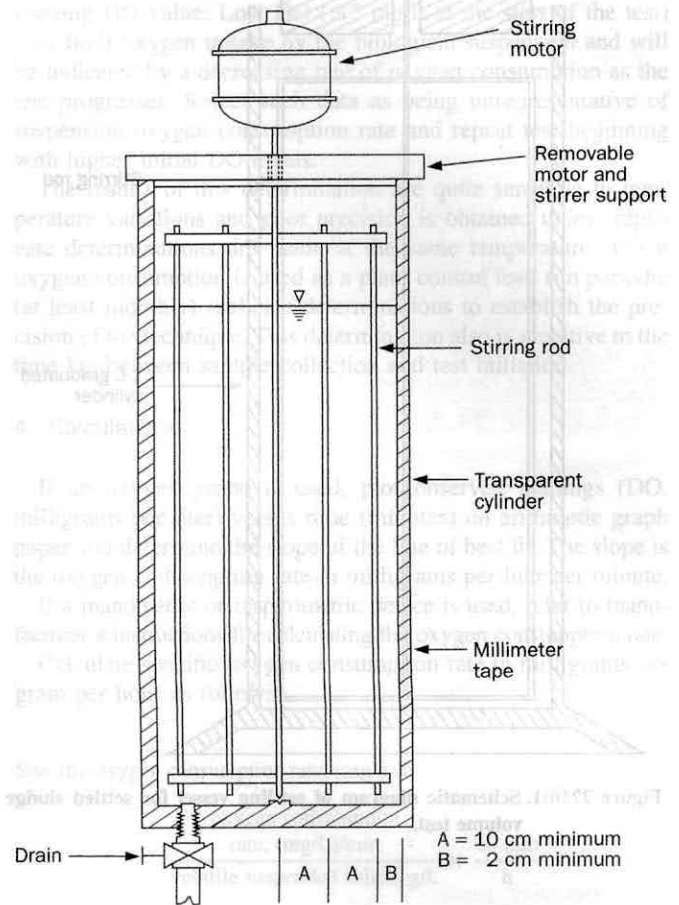


Figure 2710:2. Schematic diagram of settling vessel for zone settling rate test.

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.

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

$$SG_{T/4^{\circ}\text{C}} = \frac{\text{weight of sample}}{\text{weight of equal volume of water at } 4^{\circ}\text{C}} = \frac{S - W}{R - W} \times F$$

The values of the temperature correction factor *F* are given in Table 2710:I.

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

b. Calculate specific gravity, *SG*, from the formula

$$SG_{T/4^{\circ}\text{C}} = \frac{\text{weight of sample}}{\text{weight of equal volume of water at } 4^{\circ}\text{C}} = \frac{(P - W)}{(R - W) - (Q - P)} \times F$$

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

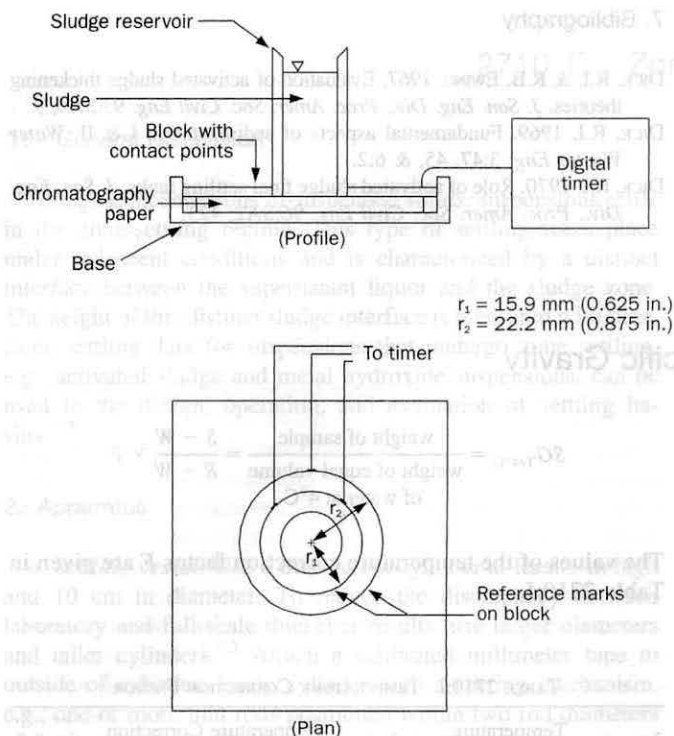


Figure 2710:3. Capillary suction time apparatus.

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.* 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*.†

c. *Thermometer* to read $\pm 0.5^\circ\text{C}$.

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 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.

* Venture Innovations, P.O. Box 53631, Lafayette, LA 70505; or Triton Electronics Ltd., Bigods Hall, Dunmow, Essex, England, CM63BE; or equivalent.

† 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.

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.

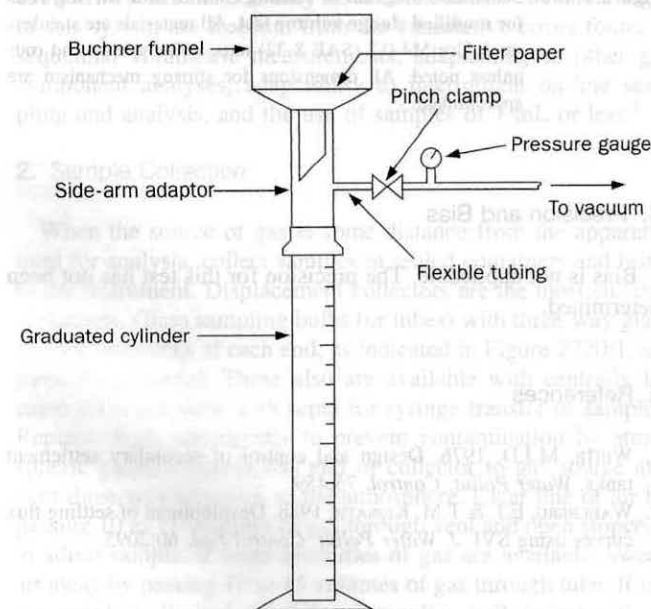


Figure 2710:4. TTF equipment. Large-volume equipment requires a 9-cm-diam Buchner funnel and a 250-mL graduated cylinder. Small-volume equipment requires a 2.5-cm-diam funnel and a 10-mL cylinder.

b. Filter paper*

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 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.

* Whatman No. 1 or 2 or equivalent.

2710 I. Modified Settled Sludge Volume

1. General Discussion

See Section 2710C.

While 2710C determines settled sludge volume using a 1-L graduated cylinder equipped with a stirring mechanism, the settling column used with the procedure herein is a wider 2-L cylindrical vessel to allow suspension volume to be determined relative to the 1-L graduated test results. Use of a settling column having a diameter wider than the 1-L graduated cylinder has been suggested¹ and the 2-L settling column is frequently used.² Results from Method 2710C are not currently considered comparable with those obtained with the procedure herein.

2. Apparatus

a. *Settling column:* Use 2-L cylindrical vessel of approximately 13 cm diam, 19 cm height (outer dimensions) equipped with a stirring mechanism consisting of four thin rods extending the length of the column, with the outer rods positioned within two rod-diameters of the cylinder wall. Provide a stirrer able to rotate the stirring rods at no more than 2 rpm (peripheral tip speed of approximately 1.2 cm/s). See Figure 2710:5.

b. *Stopwatch.*

c. *Thermometer.*

3. Procedure

Start test as soon as possible after sample collection. Distribute solids in sample without breaking flocculated particles apart by gently inverting or swirling sample container three times. Gently pour 2.0 L sample in settling column and insert stirring rods. Activate stirring mechanism, start stopwatch, 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 of the suspension occupied at measured time intervals, e.g., 5, 10, 15, 20, 30, 45 and 60 min. Take readings after stirring rod rotates past graduated scale and disturbance at top of settling suspension is minimal.

Report settled sludge volume of the suspension in milliliters for an indicated time interval.

Test results are applicable to a particular test site and are significantly affected by variables such as suspension temperature, sampling and agitation methods, dimensions of settling column and stirring rods, stirring speed, and time between sampling and start of the determination.

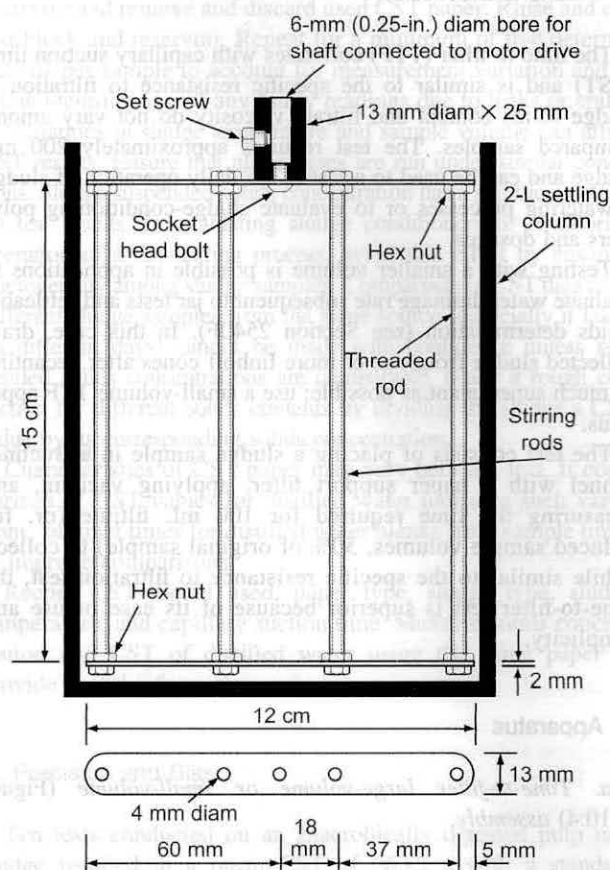


Figure 2710:5. Schematic diagram of settling column and stirring rods for modified sludge volume test. All materials are stainless steel. Use M4-0.7 (SAE 8-32) nuts, bolts, screws and rods unless noted. All dimensions for stirring mechanism are approximate.

4. Precision and Bias

Bias is not applicable. The precision for this test has not been determined.

5. References

1. WHITE, M.J.D. 1976. Design and control of secondary settlement tanks. *Water Pollut. Control*. 75:459.
2. WAHLBERG, E.J. & T.M. KEINATH. 1988. Development of settling flux curves using SVI. *J. Water Pollut. Control Fed.* 60:2095.

2720 ANAEROBIC SLUDGE DIGESTER GAS ANALYSIS*

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_4 , 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.

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

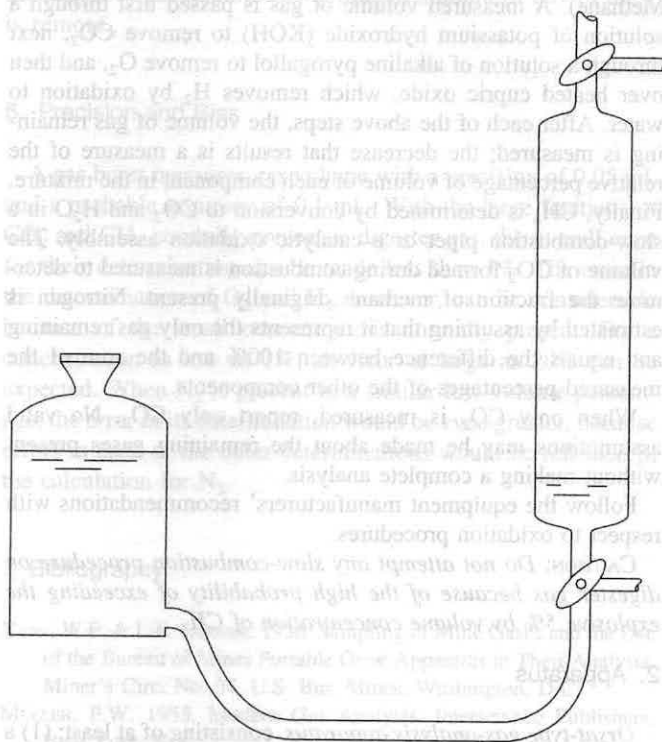


Figure 2720:1. Gas collection apparatus.

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.

* Approved by Standard Methods Committee, 1997.

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 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 pyrogalllic 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 .

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 ¶ 4d. For CH_4 in water, store gas in CO_2 pipet and proceed to ¶ 4e 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 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:

$$\% \text{CO}_2 = \frac{(V_1 - V_2) \times 100}{V_1}$$

$$\% \text{O}_2 = \frac{(V_2 - V_3) \times 100}{V_1}$$

$$\% \text{H}_2 = \frac{(V_3 - V_4) \times 100}{V_1}$$

$$\% \text{CH}_4 = \frac{V_4 \times (V_8 - V_9) \times 100}{V_1 \times V_5}$$

$$\% \text{N}_2 = 100 - (\% \text{CO}_2 + \% \text{O}_2 + \% \text{H}_2 + \% \text{CH}_4)$$

b. Alternatively, calculate CH_4 by either of the two following equations:

$$\% \text{CH}_4 = \frac{V_4 \times (V_6 + V_{10} - V_9) \times 100}{2 \times V_1 \times V_5}$$

$$\% \text{CH}_4 = \frac{V_4 (V_7 - V_8) \times 100}{2 \times V_1 \times V_5}$$

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.

Results from the calculations for CH_4 by the three equations should be in reasonable agreement. 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.

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 analyses. These concentric columns permit the simultaneous use of two different packings for the analysis of gas samples.

c. *Chromatographic column*:* Select column on the basis of manufacturer's recommendations.† 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 Carboxphere,⁴ and Carboxieve³ separate the gases listed.† 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.3d.

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 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.

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.

* 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.

† 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:

Carboxphere: 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).

Carboxieve S-II: H_2 , air ($O_2 + N_2$), CO , CH_4 , CO_2 , C_2H_6 (temperature programming required).

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 of interest:

$$\text{Volume \%} = \text{volume \% (std)} \frac{C}{D}$$

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:

$$\text{Dry volume \%} = \frac{\text{volume \% as above}}{1 - P_v}$$

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

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*

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 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.

* Approved by Standard Methods Committee, 2000.

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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.* 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 satumeter.³ Each of these units has specific advantages and limitations; the instru-

ment 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 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-Neill⁴ or gas chromatography methods¹ 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 depth⁵ as follows:

$$Z = \frac{\Delta P}{73.42}$$

* Common Sensing, Clark Fork, ID; Eco Enterprises, Seattle, WA; Novatech, Vancouver, BC, Canada; and Sweeney Aquametries, Stony Creek, CT.

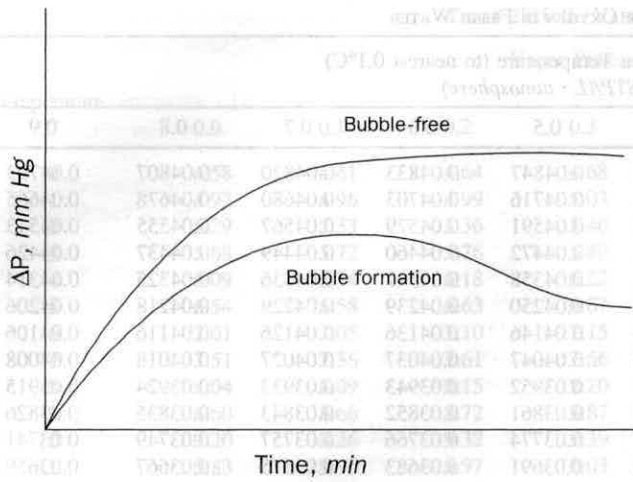


Figure 2810:1. Time response for the membrane-diffusion method.

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

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[†] 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.

$$P_{N_2} = P_b + \Delta P - P_{O_2} - P_{H_2O}$$

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

$$\Delta P_{O_2} = P_{O_2} - 0.20946(P_b - P_{H_2O})$$

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

[†] Methods for these variables may be found in Sections 4500-O, 2550, and 2520, respectively.

TABLE 2810.I. BUNSEN COEFFICIENT FOR OXYGEN IN FRESH WATER

Temperature °C	Bunsen Coefficient at Given Temperature (to nearest 0.1°C) <i>L</i> real gas at STP/(<i>L</i> · atmosphere)									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.04914	0.04901	0.04887	0.04873	0.04860	0.04847	0.04833	0.04820	0.04807	0.04793
1	0.04780	0.04767	0.04754	0.04741	0.04728	0.04716	0.04703	0.04680	0.04678	0.04665
2	0.04653	0.04640	0.04628	0.04615	0.04603	0.04591	0.04579	0.04567	0.04555	0.04543
3	0.04531	0.04519	0.04507	0.04495	0.04484	0.04472	0.04460	0.04449	0.04437	0.04426
4	0.04414	0.04403	0.04392	0.04381	0.04369	0.04358	0.04347	0.04336	0.04325	0.04314
5	0.04303	0.04292	0.04282	0.04271	0.04260	0.04250	0.04239	0.04229	0.04218	0.04206
6	0.04197	0.04187	0.04177	0.04166	0.04156	0.04146	0.04136	0.04126	0.04116	0.04106
7	0.04096	0.04086	0.04076	0.04066	0.04056	0.04047	0.04037	0.04027	0.04018	0.04008
8	0.03999	0.03989	0.03980	0.03971	0.03961	0.03952	0.03943	0.03933	0.03924	0.03915
9	0.03906	0.03897	0.03888	0.03879	0.03870	0.03861	0.03852	0.03843	0.03835	0.03826
10	0.03817	0.03809	0.03800	0.03791	0.03783	0.03774	0.03766	0.03757	0.03749	0.03741
11	0.03732	0.03724	0.03716	0.03707	0.03699	0.03691	0.03683	0.03675	0.03667	0.03659
12	0.03651	0.03643	0.03635	0.03627	0.03619	0.03611	0.03604	0.03596	0.03588	0.03581
13	0.03573	0.03565	0.03558	0.03550	0.03543	0.03535	0.03528	0.03520	0.03513	0.03505
14	0.03498	0.03491	0.03484	0.03476	0.03469	0.03462	0.03455	0.03448	0.03441	0.03433
15	0.03426	0.03419	0.03412	0.03406	0.03399	0.03392	0.03385	0.03378	0.03371	0.03364
16	0.03358	0.03351	0.03344	0.03338	0.03331	0.03324	0.03318	0.03311	0.03305	0.03298
17	0.03292	0.03285	0.03279	0.03272	0.03266	0.03260	0.03253	0.03247	0.03241	0.03235
18	0.03228	0.03222	0.03216	0.03210	0.03204	0.03198	0.03192	0.03186	0.03180	0.03174
19	0.03168	0.03162	0.03156	0.03150	0.03144	0.03138	0.03132	0.03126	0.03121	0.03115
20	0.03109	0.03103	0.03098	0.03092	0.03086	0.03081	0.03075	0.03070	0.03064	0.03059
21	0.03053	0.03048	0.03042	0.03037	0.03031	0.03026	0.03020	0.03015	0.03010	0.03004
22	0.02999	0.02994	0.02989	0.02983	0.02978	0.02973	0.02968	0.02963	0.02958	0.02952
23	0.02947	0.02942	0.02937	0.02932	0.02927	0.02922	0.02917	0.02912	0.02907	0.02902
24	0.02897	0.02893	0.02888	0.02883	0.02878	0.02873	0.02868	0.02864	0.02859	0.02854
25	0.02850	0.02845	0.02840	0.02835	0.02831	0.02826	0.02822	0.02817	0.02812	0.02808
26	0.02803	0.02799	0.02794	0.02790	0.02785	0.02781	0.02777	0.02772	0.02768	0.02763
27	0.02759	0.02755	0.02750	0.02746	0.02742	0.02737	0.02733	0.02729	0.02725	0.02720
28	0.02716	0.02712	0.02708	0.02704	0.02700	0.02695	0.02691	0.02687	0.02683	0.02679
29	0.02675	0.02671	0.02667	0.02663	0.02659	0.02655	0.02651	0.02647	0.02643	0.02639
30	0.02635	0.02632	0.02628	0.02624	0.02620	0.02616	0.02612	0.02609	0.02605	0.02601
31	0.02597	0.02594	0.02590	0.02586	0.02582	0.02579	0.02575	0.02571	0.02568	0.02564
32	0.02561	0.02557	0.02553	0.02550	0.02546	0.02543	0.02539	0.02536	0.02532	0.02529
33	0.02525	0.02522	0.02518	0.02515	0.02511	0.02508	0.02504	0.02501	0.02498	0.02494
34	0.02491	0.02488	0.02484	0.02481	0.02478	0.02474	0.02471	0.02468	0.02465	0.02461
35	0.02458	0.02455	0.02452	0.02448	0.02445	0.02442	0.02439	0.02436	0.02433	0.02429
36	0.02426	0.02423	0.02420	0.02417	0.02414	0.02411	0.02408	0.02405	0.02402	0.02399
37	0.02396	0.02393	0.02390	0.02387	0.02384	0.02381	0.02378	0.02375	0.02372	0.02369
38	0.02366	0.02363	0.02360	0.02358	0.02355	0.02352	0.02349	0.02346	0.02343	0.02341
39	0.02338	0.02335	0.02332	0.02329	0.02327	0.02324	0.02321	0.02318	0.02316	0.02313
40	0.02310	0.02308	0.02305	0.02302	0.02300	0.02297	0.02294	0.02292	0.02289	0.02286

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 $T = 273.15 + ^\circ\text{C}$.

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:

$$\text{TGP}(\%) = 0.20946 O_2(\%) + 0.7902 N_2(\%)$$

$$\Delta P = 0.20946 \left[\frac{O_2(\%)}{100} - 1 \right] [P_b - P_{H_2O}] + 0.7902 \left[\frac{N_2(\%)}{100} - 1 \right] [P_b - P_{H_2O}]$$

$$\Delta P = \frac{DO}{\beta_{O_2}} (0.5318)(1 + N_2 O_2) - (P_b - P_{H_2O})$$

Use care with these relationships with older data because both TGP(%) and $N_2(\%)$ have been differently defined.⁵

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	8.77	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
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 equation⁹ is adequate for most applications:

$$P_{H_2O} = 760\{\exp[11.8571 - 3840.70/T - 216961/T^2]\}, \text{ where } T = 273.15 + ^\circ\text{C}.$$

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 $\pm 0.1^\circ\text{C}$.

6. Reporting of Results

In reporting results, include the following data:

Sensor depth, m,
Barometric pressure, mm Hg,
Water temperature, $^\circ\text{C}$,
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
 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 satumeter. *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 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.

