





## 7010 INTRODUCTION\*

### 7010 A. General Discussion

#### 1. Occurrence and Monitoring

The radioactivity in water and wastewater originates from both natural sources and human activities. The latter include operations concerned with the nuclear fuel cycle, from mining to reprocessing; medical uses of radioisotopes; industrial uses of radioisotopes; worldwide fallout from atmospheric testing of nuclear devices; and enhancement of the concentration of naturally occurring radionuclides. Monitoring programs for water and wastewater should be designed to assess realistically the degree of environmental radioactive contamination. In some cases, for example, compliance monitoring for drinking water, the conditions are spelled out.<sup>1</sup> In others, it may be necessary to examine the individual situation<sup>2</sup> for consideration of the critical radionuclide(s), the critical pathway by which the critical radionuclide moves through the environment, and a critical population group that is exposed to the particular radionuclide(s) moving along this particular pathway. Use of the critical nuclide-pathway-population approach will help narrow the list of possible radionuclides to monitor.

A list of the most hazardous radionuclides can be selected by examining the radioactivity concentration standards given by the International Committee on Radiation Protection (ICRP),<sup>3</sup> the Federal Radiation Council (FRC),<sup>4</sup> the National Committee on Radiation Protection and Measurement (NCRP),<sup>2</sup> the U.S. Environmental Protection Agency,<sup>1</sup> and also agencies in other countries. Individual states within the United States may have their own radioactivity concentration standards if they are Nuclear Regulatory Commission (NRC) agreement states. With few exceptions, these numerical values for radioactivity concentrations in air and water are comparable if certain qualifying assumptions are applied.

Monitoring programs should provide adequate warning of unsafe environmental conditions so that proper precautions can be taken, and of course, to assure that conditions are safe when they are indeed safe. In either circumstance, it is necessary to establish base lines for the kinds and quantities of radionuclides present naturally and to measure additions to this natural background. In this way, measurements may be made to provide information for sound judgments regarding the hazardous or nonhazardous nature of increased concentrations.

#### 2. Types of Measurement

Meaningful measurements require careful application of good scientific techniques. The types of measurements to be made are determined by the objectives of the testing. Gross alpha and gross beta measurements are relatively inexpensive, can be completed quickly, and are useful for screening to determine whether

further analysis for specific radionuclides is merited. However, gross measurements give no information about the isotopic composition of the sample, cannot be used to estimate radiation dose, and have poor sensitivity if the concentration of dissolved solids is high. Accurate gross beta and especially gross alpha measurements require careful preparation of standards to determine self-absorption and the ability to prepare samples in a similar manner.

Specific radionuclide measurements are required if dose estimates are to be made, results of gross analyses exceed a certain level, or long-term trends are being monitored. Specific analyses usually are more expensive and time-consuming than a gross analysis. Specific measurements identify radionuclides by the energy of emitted radiation, chemical techniques, half-life, or a combination of these characteristics. Gamma-emitting radionuclides can be measured rapidly and with a minimum of sample preparation by using gamma spectrometry. Measurements requiring chemical separations make it possible to increase the sensitivity by increasing the sample quantity measured.

Knowledge of the chemical and radiochemical characteristics of the radionuclide being measured is critical for satisfactory results. Gross alpha and gross beta results will not provide accurate information about radionuclides having energies significantly different from the energy of the calibration standard. During concentration of water samples by evaporation, radionuclides present in elemental form (e.g., radioiodine, polonium) or as compounds (e.g., tritium, carbon-14) may be lost by volatilization. If the sample is ignited, the chance of volatilization loss is even greater. Groundwater generally contains nuclides of the uranium and thorium series. Use special care in sampling and analyzing such samples because members of these series often are not in secular equilibrium.

#### 3. References

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2. NATIONAL COMMITTEE ON RADIATION PROTECTION AND MEASUREMENTS. 1959. Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and Water for Occupational Exposure. NBS Handbook No. 69, pp. 1, 17, 37, 38, & 93.
3. INTERNATIONAL COMMISSION ON RADIATION PROTECTION. 1979. Limits for Intakes of Radionuclides by Workers. ICRP Publ. 30, Pergamon Press, New York, N.Y.
4. FEDERAL RADIATION COUNCIL. 1961. Background Material for the Development of Radiation Protection Standards. Rep. No. 2 (Sept.), U.S. Government Printing Off., Washington, D.C.

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NATIONAL COUNCIL ON RADIATION PROTECTION AND MEASUREMENTS. 1976. Environmental Radiation Measurements. NCRP Rep. No. 50, Washington, D.C.

## 7010 B. Sample Collection and Preservation

### 1. Collection

The principles of representative sampling of water and wastewater apply to sampling for radioactivity testing (see Section 1060).

Because a radioactive element often is present in submicrogram quantities, a significant fraction may be lost by adsorption on the surface of containers used in the examination. Similarly, a radionuclide may be largely or wholly adsorbed on the surface of suspended particles.

Sample containers vary in size from 0.5 L to 18 L, depending on required analyses. Use containers of plastic (polyethylene or equivalent) or glass, except for tritium samples (use glass only). When radioactive industrial wastes or similar materials are sampled, consider the possibility of deposition of radioactivity on surfaces of glassware, plastic containers, and equipment that may cause a loss of radioactivity and possible contamination of subsequent samples collected in inadequately cleansed containers.

### 2. Preservation

For general information on sample preservation see Section 1060. Table 7010:I gives guidance for sample handling, preser-

vation, and holding times for radionuclides in drinking water. Add preservative at time of collection unless sample will be separated into suspended and dissolved fractions, but do not delay acid addition beyond 5 d. Use conc hydrochloric (HCl) or nitric (HNO<sub>3</sub>) acid to obtain a pH <2, except for radioiodine, radon, and tritium (use no preservative). Hold acidified sample at least 16 h before analysis. For further details see references.<sup>1-3</sup>

Test preservatives and reagents for radioactive content.

### 3. Wastewater Samples

Wastewater often contains larger amounts of nonradioactive suspended and dissolved solids than does water and often most of the radioactivity is in the solid phase. Generally, the use of carriers in the analysis is ineffective without prior conversion of the solid phase to the soluble phase; even then high fixed solids may interfere with radioanalytical procedures. Table 7010:II shows the usual solubility characteristics of common radioelements in wastewater.

The radioelements may exhibit unusual chemical characteristics because of the presence of complexing agents or the method of waste production. For example, tritium may be combined in an organic compound when used in the manufacture of luminous

TABLE 7010:I. SAMPLE HANDLING, PRESERVATION, AND HOLDING TIMES

Constituent	Preservative*	Container†	Maximum Holding Time‡§
Gross alpha	Conc HCl or HNO <sub>3</sub> to pH <2	P or G	1 year
Gross beta	Conc HCl or HNO <sub>3</sub> to pH <2	P or G	1 year
Radium-226	Conc HCl or HNO <sub>3</sub> to pH <2	P or G	1 year
Radium-228	Conc HCl or HNO <sub>3</sub> to pH <2	P or G	1 year
Radon-222	Cool 4°C#	G with TFE-lined septum	8 d**
Uranium, natural	Conc HCl or HNO <sub>3</sub> to pH <2	P or G	1 year
Radioactive strontium	Conc HCl or HNO <sub>3</sub> to pH <2	P or G	1 year
Radioactive iodine	None	P or G	14 d
Tritium	None	G	1 year
Photon-emitters	Conc HCl or HNO <sub>3</sub> to pH <2	P or G	1 year

\* (All except radon-222 samples). Add preservative at time of sample collection unless suspended solids activity is to be measured. If sample must be shipped to a laboratory or storage area, acidification (in original sample container) may be delayed for a period not to exceed 5 d. A minimum of 16 h must elapse between acidification and analysis.

† P = plastic, hard or soft; G = glass, hard or soft.

‡ Holding time is time from sampling to analysis. In all cases, analyze samples as soon after collection as possible.

§ A 1-year holding time allows for compositing four quarterly samples.

|| If HCl is used to acidify samples to be analyzed for gross alpha or gross beta activities, convert the acid salts to nitrate salts before transfer of samples to planchets.

# Cooling at 4°C is recommended. Large temperature changes will cause dissolved radon to outgas from sample.

\*\* Holding should not exceed regulatory maximum (4 d), if applicable.

TABLE 7010:II. USUAL DISTRIBUTION OF COMMON RADIOELEMENTS BETWEEN THE SOLID AND LIQUID PHASES OF WASTEWATER

In Solution	In Suspension
HCO <sub>3</sub>	Ce
Co	Cs
Cr	Mn
Cs	Nb
H	P
I	Pm
K	Pu
Ra	Ra
Rn	Sc
Ru	Th
Sb	U
Sr	Y
	Zn
	Zr

articles; radioiodine from hospitals may occur as complex organic compounds, compared to elemental and iodide forms found in fission products from the processing of spent nuclear

fuels; uranium and thorium progeny often exist as inorganic complexes rather than oxides after processing in uranium mills; the strontium-90 titanate waste from a radioisotope heat source is quite insoluble compared to most other strontium wastes. Valuable information on the chemical composition of wastes, the behavior of radioelements, and the quantity of radioisotopes in use appears in the literature.<sup>4,5</sup>

#### 4. References

1. U.S. GEOLOGICAL SURVEY. 1977. Methods for Determination of Radioactive Substances in Water and Fluvial Sediments. U.S. Government Printing Off., Washington, D.C.
2. U.S. DEPARTMENT OF ENERGY. 1997. EML Procedures Manual, 28th ed. (rev.). HASL-300, 28th ed., Vol. 1. Environmental Measurements Lab., U.S. Dep. Energy, New York, N.Y. Also available online at <http://www.eml.doe.gov/publications/procman/>.
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1997. Manual for the Certification of Laboratories Involved in Analyzing Public Drinking Water Supplies. EPA-815-B-97-001, Washington, D.C.
4. INTERNATIONAL ATOMIC ENERGY AGENCY. 1960. Disposal of Radioactive Wastes. International Atomic Energy Agency, Vienna, Austria.
5. NEMEROW, N.L. 1963. Industrial Waste Treatment. Addison-Wesley, Reading, Mass.

## 7020 QUALITY ASSURANCE/QUALITY CONTROL\*

### 7020 A. Basic Quality Control Program

#### 1. Introduction

Every laboratory that performs radionuclide analyses for environmental water and wastewater samples should have a written and operating quality assurance (QA) plan. This plan can be a separate document or can, by reference, use parts of existing standard operating procedures (SOPs). The quality-control (QC) portion of the QA plan addresses instrumental, background, accuracy, and precision QC. Also essential is a manual of analytical methods, or at least copies of approved methods, available to the analysts.

#### 2. Performance Criteria

For a successful QC program, select acceptable and attainable performance criteria for precision and accuracy. These criteria must reflect the capabilities of the laboratory and the purposes for which the data are to be used.

Performance criteria can be drawn up initially from experience with the analytical method or from criteria set by other laboratories using the same procedure. A tabulation of allowable deviations used by the EPA<sup>1</sup> is given in Table 7020:I. The criteria are a function of the particular analysis under study. A laboratory

might use these or other published values until enough data can be compiled to set its own criteria from experience.

#### 3. Minimum Quality Control Program

A radiochemistry QC program is composed of a number of integrated functions, including instrumental, background, precision, and accuracy QC.

A useful way of keeping track of instrument and background performance is through control charts. Certain aspects of radiochemical instrument and background QC are instrument- or method-specific and are dealt with in the individual methods.

The instrumental control charts<sup>2</sup> are prepared by plotting counts of a reference source on a graph showing time as the abscissa and count rate or total counts as the ordinate. Lines are drawn parallel to the time axis at values (corrected for decay if necessary) for the "true" count rate and for values of  $\pm 2$  and  $\pm 3$  standard deviations. The true count rate is determined by averaging at least 20 counts with acceptable individual statistics.

Interpret quality control chart data objectively. When a point goes outside the limits, determine whether instrument service is necessary or the result is simply a random occurrence by running a series of repeated measurements and applying another statistical test, such as a Chi-square test, to determine whether the variation was nonstatistical.

Trends from control charts may show other information. For example, if regular measurements of the check source show a

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TABLE 7020:I. LABORATORY PRECISION—ONE STANDARD DEVIATION VALUES FOR VARIOUS ANALYSES IN WATER SAMPLES

Analysis	Activity Level pCi/L	One Standard Deviation for Single Determination	Control Limits*
Gamma-emitters	5 to 100	5 pCi/L	$\mu \pm 8.7$ pCi/L
	>100	5% of known value	$\mu \pm 0.087 \mu$
Zinc-65, barium-133, ruthenium-106	5 to 50	5 pCi/L	$\mu \pm 8.7$ pCi/L
	>50	10% of known value	$\mu \pm 0.17 \mu$
Strontium-89, strontium-90	5 to 100	5 pCi/L	$\mu \pm 8.7$ pCi/L
	>100	5% of known value	$\mu \pm 0.087 \mu$
Gross alpha	$\leq 20$	5 pCi/L	$\mu \pm 8.7$ pCi/L
	>20	25% of known value	$\mu \pm 0.43 \mu$
Gross beta	$\leq 50$	5 pCi/L	$\mu \pm 8.7$ pCi/L
	>50 to 100	10 pCi/L	$\mu \pm 17.3$ pCi/L
	>100	15% of known value	$\mu \pm 0.26 \mu$
Tritium	<4000	$170 \times (\text{known})^{0.0933}$	$\mu \pm \times (\mu)^{0.0933}$
	$\geq 4000$	10% of known value	$\mu \pm 0.17 \mu$
Radium-226	$\geq 0.1$	15% of known value	$\mu \pm 0.26 \mu$
Radium-228	$\geq 0.1$	25% of known value	$\mu \pm 0.43 \mu$
Iodine-131	$\leq 55$	6 pCi/L	$\mu \pm 10.4$ pCi/L
	>55	10% of known value	$\mu \pm 0.17 \mu$
Uranium	$\leq 35$	3 pCi/L	$\mu \pm 5.2$ pCi/L
	>35	10% of known value	$\mu \pm 0.17 \mu$

\* Average of three determinations.  $\mu$  = known value.

movement in one direction, one can infer that some system variable is changing. This variation may not always require instrument service; instead the values of the limits or the “true” value may need to be reevaluated.

*a. Instrumental QC:* For alpha and beta counters, count check source daily (or before each use) for a predetermined time. Record count rate and plot it on the control chart for the specific system. Compare this value with the  $\pm 2 \sigma$  (warning) limits and the  $\pm 3 \sigma$  (out-of-control) limits, and repeat the procedure if the  $\pm 2 \sigma$  boundary is exceeded. Take appropriate action if repeated values are above the warning levels.

For instruments that produce spectra, such as gamma or alpha spectrometers, many parameters can be tracked, including efficiency response, i.e., count rate or total counts in a given spectral area; peak channel location of one or more spectral photopeaks; difference in channels between two specified peaks; resolution, i.e., width of peak in channels at specified peak height; and certain ratios such as “peak to compton.” It is not necessary to track all of these routinely; see specific recommendations in Section 7120. If these basic parameters are outside the limits, other parameters may need to be evaluated.

*b. Background QC:* At defined frequencies, such as daily or before each use for proportional or liquid scintillation counters, count background for each system for the standard counting time. Make background measurements with each batch of samples. Spectrometers may require specific treatment because background is determined from the sample spectrum in the analysis of activity. In this specific case, longer background counts at less frequent intervals (for example, weekly) may be needed to produce reasonable counts in specific regions of interest.

Record background counts and plot them on control charts. Obtain background “true value” by averaging at least 20 background counts. Calculate 2 and 3  $\sigma$  counting errors based on the average value and the background counting time. Take appropriate actions in the event of background or standard reference count problems.<sup>2</sup>

Background QC is specific to the type of counting instrument. For instance, gamma spectroscopy background QC represents a specific challenge depending on whether the detector is NaI(Tl) or germanium; see Section 7120.

Analyze reagent blanks often enough to ensure the absence of major interference that would bias the reported results. Ideally, results for a reagent blank will be identical to the background, e.g., for an analysis using a proportional counter, identical to the counts from a blank planchet.

*c. Precision QC:* Evaluate laboratory’s internal precision in performing an analytical procedure by analysis of blind duplicate samples, that is, duplicate portions of randomly selected samples submitted as new samples. It is important that the analyst be unaware either that a given sample will be resubmitted or that it is a reanalysis. This may be difficult in a small laboratory. It is important also that samples submitted for duplicate analysis have detectable amounts of radioactivity so that statistical treatment of data does not consist of comparing zeros or “less than” values. In some cases, it may be necessary to substitute samples with known additions for routine workload samples.

Preferably analyze 10 percent duplicate samples to verify internal laboratory precision for a specific analysis; this is a general guideline and may be varied to fit the situation. For example, for a laboratory with a heavy workload and a well-established duplicate analysis program, 5 percent duplicate samples or 20 samples per month may be sufficient to determine whether the data meet established criteria. A discussion of the statistical treatment of duplicate analysis data is given elsewhere.<sup>2,3</sup> One criterion for acceptability of duplicate measurements is given in EPA’s Drinking Water Certification Manual. The difference between duplicate measurements should be less than two times the standard deviation of the specific analysis as described in Table 7020:I.<sup>4</sup> If the difference between duplicates exceeds two standard deviations, prior measurements are suspect; examine calculations and procedures and reanalyze samples when necessary.

d. *Accuracy QC:* Analytical methods are said to be in control when they produce results that are both precise and unbiased. Evaluate accuracy by preparing or obtaining water samples of known radionuclide content, analyzing them, and comparing the results to the known values. Plot data from these standards or known-addition samples on means or individual results control charts,<sup>2,3</sup> and determine whether or not results from these samples are within the control limits and/or warning limits set on the control charts. Laboratories also can set accuracy limits for samples with known additions based on percent recovery of the known value. Preferably run a known-addition or standard sample with each batch of samples. If the known-addition value is outside the limits, investigate method bias. All sample results are suspect until the known-addition results are back within the prescribed limits.

To be certified to perform drinking water analyses under the Safe Drinking Water Act, a laboratory must participate successfully at least once each year in a proficiency testing program administered by a provider accredited by the National Institute of Standards and Technology (NIST). Acceptable performance for each parameter for which the laboratory is, or seeks to be, certified is demonstrated by the successful analysis of at least one proficiency sample. Acceptable analytical results must be within control limits established by the provider.

Laboratories are encouraged to participate in intercomparison programs such as those sponsored by International Atomic Energy Agency (IAEA),<sup>†</sup> and World Health Organization (WHO).<sup>‡</sup>

e. *Selection of radionuclide standards and sources:* Calibrated radionuclide standard solutions are prepared for storage and shipment by the supplier in flame-sealed glass ampules. Preferably perform all dilutions and storage of radionuclides in glass containers and avoid the use of polyethylene.

Standard sources are radioactive sources having adequate activity and an accurately known radionuclide content and radioactive decay rate or rate of particle or photon emission. Each radionuclide standard should have a calibration certificate containing the following information:

<i>Description:</i>	<i>Purity:</i>
Principal radionuclide	Identification of impurities
Chemical form	Activity
Solvent	Included or not included in principal activity
Carrier and content	
Mass and specific gravity or volume	
<i>Standardization:</i>	<i>Assumptions:</i>
Activity per mass or volume	Decay scheme
Date and time	Half-life
Activity of daughter	Equilibrium ratios
Method of standardization	
<i>Accuracy:</i>	<i>Production:</i>
Repeatability error	Production method
Systematic error	Date of separation
Overall error	
Confidence levels	<i>Usable lifetime</i>

<sup>†</sup> International Atomic Energy Agency, Analytical Quality Control Services, Seibersdorf, P.O. Box 100, A-1400, Vienna.

<sup>‡</sup> World Health Organization, Geneva, Switzerland.

Confirm that radionuclide standard sources are traceable to the National Institute of Standards and Technology (NIST) or equivalent. Use such standard sources, or dilutions thereof, for initial calibration. These sources may be purchased from suppliers listed in annually published buyers' guides. Before purchasing standards from commercial suppliers, inquire as to the traceability of the particular radionuclide of interest. A good discussion of NIST traceability is given elsewhere.<sup>5</sup> Example of radionuclide calibration certificates and NIST traceability certificates have been published.<sup>1</sup> At present, standardized radioisotope solutions can be purchased from the IAEA and NIST. §

Use check sources for determining changes in counting rate, counting efficiency, and/or energy calibration. These sources should be of sufficient radiochemical purity and activity to permit correction for decay, but they need not have an accurately known disintegration rate (i.e., need not be a standard source).

Standard reference materials (SRMs) are radioactive materials having adequate activity and accurately known radionuclide content and radioactive decay rate or rate of particle or photon emission. They may be used as internal laboratory control samples, internal tracers, or matrix and blind known additions. They should have calibrations traceable to NIST or equivalent.

#### 4. References

1. DILBECK, G. & P. HONSA. 1994. Environmental Radioactivity Performance Evaluation Studies Program and Radioactive Standards Distribution Program. ORD EMSL-LV, U.S. Environmental Protection Agency, Las Vegas, Nev.
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3. ROSENSTEIN, M. & A.S. GOLDIN. 1964. Statistical Techniques for Quality Control of Environmental Radioassay. AQCS Rep. Stat-1, U.S. Dep. Health, Education & Welfare, PHS, DRH, Winchester, Mass.
4. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1990. Manual for the Certification of Laboratories Analyzing Drinking Water. EPA/570/9-90/008, OGWDW (WH-550D), Office of Ground Water and Drinking Water, Washington, D.C.
5. NATIONAL COUNCIL ON RADIATION PROTECTION AND MEASUREMENTS. 1985. A Handbook of Radioactivity Measurements Procedures. NCRP Rep. No. 58, National Council on Radiation Protection and Measurements, Bethesda, Md.

§ U.S. Department of Commerce, Technology Administration, National Institute of Standards and Technology, Standard Reference Materials Program, Building 202, Room 204, Gaithersburg, MD 20899.

## 7020 B. Quality Control for Wastewater Samples

Generally it is not feasible to perform collaborative (interlaboratory) analyses of wastewater samples because of the variable composition of elements and solids from one facility to the next. The methods included herein have been evaluated by use of homogeneous samples and are useful for nonhomogeneous samples after sample preparation (wet or dry oxidation and/or fusion

and solution) resulting in homogeneity. Reference samples used for collaborative testing may be deficient in radioelements exhibiting interferences because of decay during shipment of short-half-life-radionuclides. Generally, however, analytical steps incorporated into the methods eliminate these interferences, even though they may not be necessary for the reference samples.

## 7020 C. Statistics

Section 1030 discusses statistics as applied to analysis of chemical constituents. It is applicable also to radioactivity examinations; however, certain statistical concepts peculiar to radioactivity measurements are discussed below.

### 1. Propagation of Errors

Often it is necessary to calculate the uncertainty of a quantity that is not measured directly, but is derived, by means of a mathematical formula, from directly measured quantities. The uncertainties of the latter are known or can be computed and the uncertainty of the calculated quantity derived from them. Statistically, this is known as propagation of errors. One of the more common applications of propagation of errors is in combining all the sources of error in determining pollutant concentrations in environmental samples such as soil, air, milk, or water. These data include errors from sampling, analysis, and other variables, all of which must be considered in determining the total variability or variance.

The formula for propagation of errors states that when quantities are added or subtracted, the combined error ( $\sigma_T$ ) is equal to the square root of the sum of the squares of the individual errors.

$$\sigma_T = (\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \dots + \sigma_n^2)^{1/2}$$

The propagation of errors law application is possible because variance is an additive property:

$$\sigma_T^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \dots + \sigma_n^2$$

A number of propagation-of-error formulas have possible application to the determination of radionuclide concentrations in water.<sup>1</sup> The most common of these are given in Table 7020:II. The one most widely used in nuclear counting statistics is the first formula, where  $X$  represents the activity (counts) of sample + background, and  $Y$  represents the activity of the background.

### 2. Standard Deviation and Counting Error

The variability of any measurement is described by the standard deviation, which can be obtained from replicate determinations. There is an inherent variability in radioactivity measurements, due to the random nature of radioactive decay, which is described by the Poisson distribution. This distribution is characterized by the standard deviation of a large number of events,  $N$ , that equals its square root, or:

$$\sigma(N) = N^{1/2}$$

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When  $N > 20$ , the Poisson distribution approximates the normal (Gaussian) distribution. This approximation simplifies the computation of confidence intervals and permits reasonably accurate estimates of the mean and variance of the distribution of results without performance of replicate counts.

More often, the variable of concern is the standard deviation in the counting rate (number of counts per unit time):

$$R' = \frac{N}{t}$$

where:

$t$  = duration of counting.

The standard deviation of the counting rate, when the appropriate substitutions are made, is:

$$\sigma(R') = \frac{N^{1/2}}{t} = \frac{(R't)^{1/2}}{t} = \left(\frac{R'}{t}\right)^{1/2}$$

In practice, all counting instruments have a background counting rate,  $B$ , when no sample is present. With a sample, the counting rate increases to  $R_o$ . The net counting rate,  $R$ , due to the sample is:

$$R = R_o - B$$

By propagation-of-error methods, the standard deviation of  $R$ , the net counting rate, is calculated as follows:

$$\sigma(R) = \left(\frac{R_o}{t_1} + \frac{B}{t_2}\right)^{1/2}$$

TABLE 7020:II. PROPAGATION-OF-ERROR FORMULAS

Function	Error Formula
$Q = X \pm Y$	$\sigma_Q = (\sigma_x^2 + \sigma_y^2)^{1/2}$
$Q = aX + bY$	$\sigma_Q = (a^2\sigma_x^2 + b^2\sigma_y^2)^{1/2}$
$Q = XY$	$\sigma_Q = XY \left(\frac{\sigma_x^2}{X^2} + \frac{\sigma_y^2}{Y^2}\right)^{1/2}$
$Q = \frac{X}{Y}$	$\sigma_A = \frac{X}{Y} \left(\frac{\sigma_x^2}{X^2} + \frac{\sigma_y^2}{Y^2}\right)^{1/2}$

where:

$$LLD_{95} = 4.66S_b$$

$R_o$  = gross counting rate,

$B$  = background counting rate, and

$t_1, t_2$  = elapsed counting times at which gross sample and background counting rates were measured, respectively.

Counting duration for a given set of conditions depends on the limit of detection required (see below). Preferably divide the counting time into equal periods to check constancy of observed counting rate. For low-level counting, where net count rate is of the same order of magnitude as the background, use  $t_1 = t_2$ . The error thus calculated includes only uncertainty caused by inherent variability of the radioactive disintegration process and is not the standard deviation of the total analysis. The counting uncertainty is the major portion of the total uncertainty at or near the limit of detection. As concentration levels increase, the percent counting error decreases and systematic errors become the major portion of total error.

Use a confidence level of 95%, or 1.96 standard deviations, as the counting error. Report radioactivity concentration results with the counting error as  $X \pm 1.96\sigma$ , both in pCi/L.

### 3. Limit of Detection

Various conventions have been used to estimate the lower limit of detection (LLD) or the minimum detectable activity (MDA). The procedure recommended here, used at the Environmental Measurements Laboratory,<sup>2</sup> is based on hypothesis testing.<sup>3</sup>

The LLD is defined as the smallest quantity of sample radioactivity that will yield a net count for which there is a predetermined level of confidence that radioactivity will be measured. Two errors may occur: Type I, in which a false conclusion is reached that radioactivity is present, and Type II, with a false conclusion that radioactivity is absent.

The LLD may be approximated as follows:

$$LLD = (K_\alpha + K_\beta)S_o$$

where:

$K_\alpha$  = value for upper percentile of standardized normal variate corresponding to preselected risk of concluding falsely that activity is present ( $\alpha$ ),

$K_\beta$  = corresponding value for predetermined degree of confidence for detecting presence of activity ( $1-\beta$ ), and

$S_o$  = estimated standard error of net sample counting rate.

For sample and background counting rates that are similar (as is expected at or near the LLD) and for  $\alpha$  and  $\beta$  equal to 0.05, the smallest amount of radioactivity that has a 95% probability of being detected is,

where:

$S_b$  = standard deviation of background counting rate, cpm.

To convert LLD to concentration, use the appropriate factors of sample volume, counting efficiency, etc. Note that the approximation  $LLD = 4.66S_b$  can be used only for determinations where  $S_b$  is known so that  $S_o = 2^{1/2}S_b$  and there are no counting interferences. Examples of appropriate determinations are tritium, gross alpha or beta, or any single nuclide determination.

Where tracers are added to determine yield or more than one radionuclide is counted in a sample, use the general form of the above equation, for which the 95% confidence level would be:

$$LLD_{95} = 3.29S_o$$

For the purpose of monitoring radioactivity concentrations in drinking water, the required sensitivity is defined in terms of a detection limit.<sup>4</sup> The detection limit is the amount of activity that can be counted with a precision of  $\pm 100\%$  at the 95% confidence level, i.e.,  $1.96\sigma$  where  $\sigma$  is the standard deviation of the net counting rate of the sample.

$$1.96\sigma = 1.96 \sqrt{\frac{R_o}{t_1} + \frac{B}{t_2}}$$

where:

$\sigma$  = counting error of net sample count rate,

$R_o$  = gross count rate of sample + background,

$t_1$  = count time of sample + background,

$B$  = count rate of background, and

$t_2$  = count time of background.

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## 7020 D. Calculation and Expression of Results

The results of radioactivity analyses usually are reported in terms of "activity" per unit volume or mass at 20°C. The recognized unit for activity is the Becquerel, Bq, equal to one disintegration per second. A commonly used unit for reporting environmental level concentrations is the picocurie (pCi) = 2.22

disintegrations per minute (dpm), or  $1 \times 10^{-12}$  Curie (Ci) or  $1 \times 10^{-3}$  nanocuries (nCi) or  $1 \times 10^{-6}$  microcuries ( $\mu$ Ci).

Specific formulas for the calculation of activity per volume or mass are presented in the individual methods and use the general formula:

$$C = \frac{R_{net}}{e y i v d u}$$

where:

$C$  = activity per unit volume, in units or activity/mass or volume,  
 $R_{net}$  = net counting rate, cpm  
 $e$  = counting efficiency, cpm/dpm,  
 $y$  = chemical yield,  
 $i$  = ingrowth correction factor,  
 $v$  = volume or mass or portion,  
 $d$  = decay factor, and  
 $u$  = units correction factor.

Values for variables are method-dependent. Report results in a manner that does not imply greater or lesser precision than that obtained by the method (see Section 1030).

In reporting radiochemical data, include associated random and systematic errors, as well as minimum detectable activity. For some intended data usage, it is necessary to report the result as calculated without regard to the sign of the absolute value, i.e., no "less than" values. The objective of data use, e.g., compliance

monitoring, research, dose calculation, or trend monitoring, will dictate the data reporting format.

The following formula illustrates calculation of counting uncertainty at the 95% confidence level:

$$E = \frac{1.96 \left( \frac{R_o}{t_1} + \frac{B}{t_2} \right)^{1/2}}{e y i v d u}$$

where:

$E$  = counting error,  
 $R_o$  = gross sample counting rate, cpm,  
 $t_1$  = sample count duration, min,  
 $B$  = background counting rate, cpm,  
 $t_2$  = background count duration, min, and  
 $e, y, i, v, d,$  and  $u$  are as previously defined.

## 7030 COUNTING INSTRUMENTS\*

### 7030 A. Introduction

Radiochemical analytical instruments operate on the principle that the expenditure of energy by a radiation event is detected and recorded by an instrument suitable for the type of emitted

radiation. A description of typical counting instrumentation is presented but is not intended to be all-inclusive. Instrument background and fractional counting efficiency must be measured and integrated into the sample calculations. These characteristics can be compared with historical data and used to evaluate instrument stability.

\* Approved by Standard Methods Committee, 2000.  
 Joint Task Group: 20th Edition—Ernest A. Sanchez (chair), Harry V. Summers.

### 7030 B. Description and Operation of Instruments

#### 1. Gas-Flow Proportional Counters

Gas-flow proportional counters operate on the principle that radioactive particles, e.g., alpha and beta particles, cause ionization in the gas with multiplication of resulting electrons and collection at the anode of the counter. The voltage pulse is proportional to the impressed voltage and the number of initial ion pairs formed, hence the term "proportional counter." Alpha particles produce a much higher pulse than beta particles; this provides a means to distinguish between the two.

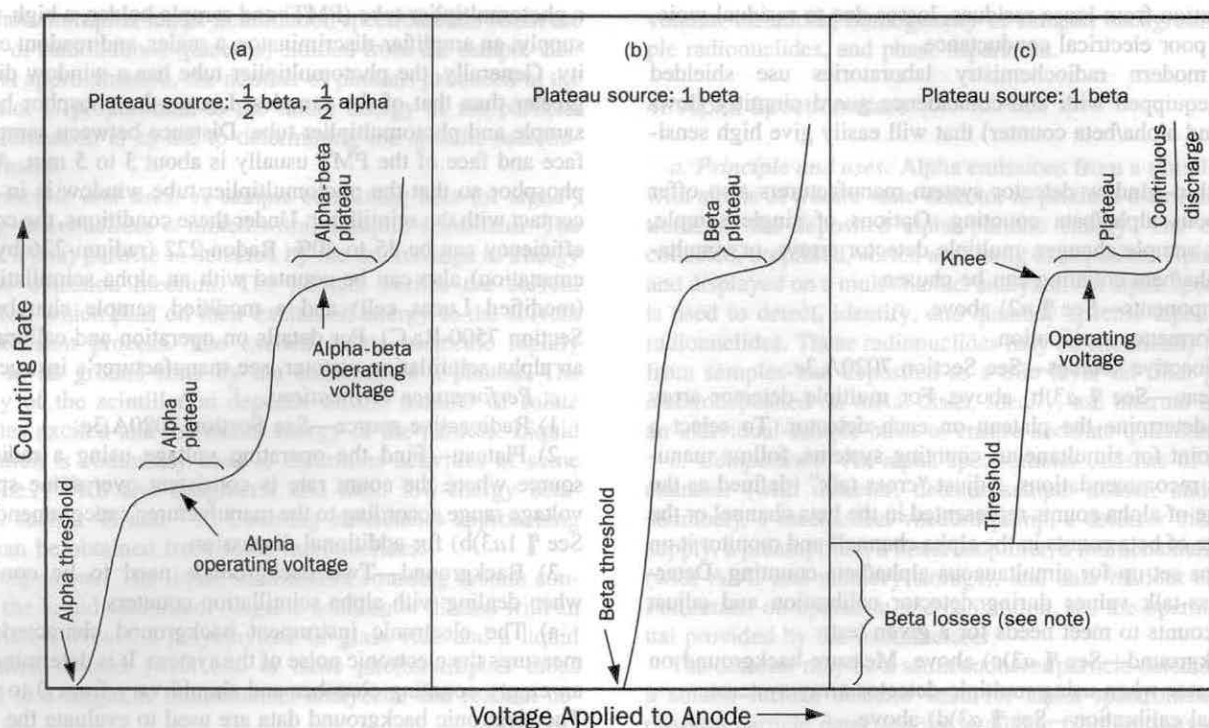
##### a. Windowless internal proportional counter:

1) Principle and uses—The internal gas-flow proportional counter accepts planchets within the counting chamber and, at the operating voltage, records the current pulses produced by the radioactive particles or photons emitted into the counting gas. Internal proportional counters are suitable for determining activity at the alpha operating plateau and alpha-plus-beta activity at the beta operating plateau. The alpha or beta activity, or both, may refer to the type of radiation produced by the radionuclides present in the sample. The energy of the activity present in the sample has an effect on the counter detection efficiency and the

counting process. These counting effects usually are accounted for during the calibration of the instrument.

Theoretically, half the radiation is emitted in the direction of the planchet and half in the direction of the detector. Depending on the energy or energies of the isotope in the sample, a percentage of the alpha or beta radiation is back-scattered into the counting gas by the sample solids, the planchet, or the walls of the counting chamber. Some of the beta radiation, but only 1 to 2% of the alpha radiation, is back-scattered into the counting gas by sample solids, the planchet, or the walls of the counting chamber, yielding in some cases greater than 50% counting efficiency. For nearly weightless samples, considerably more than 60% of the beta radiation is counted. Take considerable care in sample preparation to prevent the sample or planchet from distorting the electrical field of the counter and depressing the count rate. Avoid nonconducting surfaces, airborne dusts, and vapor from moisture or solvents, because these can damage the counter detector.

2) Components—The instrument consists of a counting chamber, a preamplifier, amplifier, scaler, high-voltage power supply, timer, and register. Use the specified counting gas and accesso-



**Figure 7030:1. Shape of counting rate–anode voltage curves.** Key: (a) and (b) are for internal proportional counter with P-10 gas; (c) is for end-window Geiger-Mueller counter with Geiger gas. (NOTE: Beta losses are dependent on energy of radiation and thickness of window and air path.)

ries, make adjustments for sensitivity, and operate in accordance with manufacturer's instruction.

### 3) Performance verification

a) Radioactive sources—See Section 7020A.3e.

b) Plateau (alpha or beta)—Find the operating voltage where the counting rate is consistent, i.e., varies less than 5% over a 150-V change in anode voltage. Check this plateau or, as a minimum, make a response check after each change of counting gas. Determine the plateau by placing a source in the counting chamber and varying the detector voltage until the count rate remains constant. Further increases in high voltage result in little change in the overall detector response until the plateau region is exceeded. **CAUTION: Instrument damage will result from continuous discharge at too high a voltage.** Plot relative counting rate (ordinate) against anode voltage (abscissa). Select an anode voltage near the center of the plateau as the detector operating voltage (see Figure 7030:1).

c) Background (alpha or beta)—Characteristic of most detectors is a background or instrument count rate usually due to cosmic radiation, radioactive contaminants in instrument parts, counting room construction material, electrical/electronic noise, and/or the proximity of radioactive sources. The background is roughly proportional to the size or mass of the counting chamber or detector, but it can be reduced by shielding or anti-coincidence guard circuitry. The instrument background count rate should not be confused with the count rate of the laboratory or reagent blanks. However, under some circumstances these count rates might be approximately equal.

Determine instrument background with an empty planchet in the counting chamber. Use a background counting duration as long as the longest sample-counting duration.

d) Initial calibration (alpha or beta)—The purpose of initial calibration is to adjust counting efficiency according to the sample thickness (which causes self-absorption of some of the alpha or beta particles within the sample matrix). Initial calibration is procedure-dependent. See individual procedures for specific initial calibration instructions. Absorption curve values do not need to be reestablished after initial calibration if check source response is monitored regularly and indicates instrument stability.

e) Continuing calibration (source check)—Verify instrument stability at the operating voltage by counting the check source routinely (see Section 7020A.3e). If source count is within two standard deviations of the previously determined average count rate, instrument reliability/stability is established. If the source count rate is not so reproduced, repeat the test. If stability is not attained, service the problem equipment.

f) Sample counting—Place prepared sample on a planchet in the counting chamber and assure electrical contact between planchet and chamber. Flush with counting gas and count for a preset duration or a preset count, to give the desired counting precision (see Section 7020D). Count samples in a geometry consistent with initial calibration.

#### b. Thin-window proportional counter:

1) Principle and uses—The thin-window proportional counter, with or without heavy shielding and/or anti-coincidence guard circuitry, has application for counting various levels of alpha and beta activity. It is approximately 50% as sensitive as an internal proportional counter because the geometry of counting is not as favorable and absorption losses (air path and window) are greater. Because the sample is outside the counting gas, this detector is less affected than the internal proportional counter by

contamination from loose residues, losses due to residual moisture, and poor electrical conductance.

Most modern radiochemistry laboratories use shielded counters equipped with anti-coincidence guard circuitry (low-background alpha/beta counter) that will easily give high sensitivity.

Some thin-window detector system manufacturers also offer simultaneous alpha/beta counting. Options of single sample, automatic sample changer, multiple detector arrays, or simultaneous alpha/beta counting can be chosen.

2) Components—See ¶ (a2) above.

3) Performance verification

a) Radioactive sources—See Section 7020A.3e.

b) Plateau—See ¶ (a3)b) above. For multiple detector array systems, determine the plateau on each detector. To select a plateau point for simultaneous counting systems, follow manufacturer's recommendations. Adjust "cross talk" (defined as the percentage of alpha counts represented in the beta channel or the percentage of beta counts in the alpha channel) and monitor it on all systems set up for simultaneous alpha/beta counting. Determine cross-talk values during detector calibration and adjust detector counts to meet needs for a given test.

c) Background—See ¶ (a3)c) above. Measure background on each detector when using multiple-detector array systems.

d) Initial calibration—See ¶ (a3)d) above.

e) Continuing calibration—See ¶ (a3)e) above. Make a check source determination on each detector in multiple-detector array systems.

f) Sample counting—Place prepared sample in sample holder according to manufacturer's instructions and set instrument for preset count or preset duration, to give the desired counting precision (see Section 7020D). Count samples in a geometry consistent with initial calibration.

## 2. Alpha Scintillation Counter

An alpha scintillation counter is used to detect and quantify alpha-emitting radionuclides. If there is more than one radionuclide in the sample, the instrument will detect and count all alpha emissions regardless of their radionuclide source or energy. However, the analysis may be made more radionuclide-specific by using a radiochemical procedure to separate the desired radionuclides. The radionuclide (e.g., naturally-occurring  $^{226}\text{Ra}$ , Th, U, etc.) is usually precipitated and mounted as a thin layer ( $\leq 5 \text{ mg/cm}^2$ ) on planchets.

a. *Principle and uses:* An alpha particle interacts with zinc sulfide phosphor (containing silver). A portion of the alpha particle's kinetic energy causes the atoms of the scintillator to become excited. When the atoms return to the ground state, they release the extra energy as visible light. This process is called scintillation. The light is further transformed into an electrical current by an attached photomultiplier tube that amplifies the electrical current into a measurable pulse. These pulses trigger a scaler and the pulse is registered as a "count." Depending on the amount of radionuclide present and required statistics, count a sample long enough to obtain required sensitivity. The counter is calibrated with a thin-layered precipitate of a radionuclide or an electrodeposited radionuclide.

b. *Components:* The alpha scintillation counter consists of a light-tight sample chamber with a phosphor detector coupled to

a photomultiplier tube (PMT) and sample holder, a high-voltage supply, an amplifier-discriminator, a scaler, and readout capability. Generally, the photomultiplier tube has a window diameter greater than that of the samples. Locate the phosphor between sample and photomultiplier tube. Distance between sample surface and face of the PMT usually is about 3 to 5 mm. Arrange phosphor so that the photomultiplier tube window is in optical contact with the scintillator. Under these conditions, the counting efficiency can be 35 to 40%. Radon-222 (radium-226 by radon emanation) also can be counted with an alpha scintillation cell (modified Lucas cell) and a modified sample chamber (see Section 7500-Ra.C). For details on operation and calibration of an alpha scintillation counter, see manufacturer's instructions.

c. *Performance verification:*

1) Radioactive source—See Section 7020A.3e.

2) Plateau—Find the operating voltage using a radioactive source where the count rate is consistent over some specified voltage range according to the manufacturer's recommendations. See ¶ (1a3)b) for additional discussion.

3) Background—Two backgrounds need to be considered when dealing with alpha scintillation counters.

a) The electronic instrument background characteristically measures the electronic noise of the system. It is determined with an empty counting chamber and should vary from 0 to 1 cpm. The electronic background data are used to evaluate the performance of the instrument.

b) The second type of background is the chamber background and is counted with the zinc sulfide phosphor in place. This background is caused by contamination of instrument parts, counting room construction material, and proximity of radioactive sources. Use a chamber background counting duration equivalent to the longest sample counting duration. Do not confuse background count rate with the count rate of the laboratory or reagent blank. Under some circumstances, these count rates might be approximately equal.

4) Initial calibration—The purpose of initial calibration is to adjust scintillation counting efficiency according to the sample thickness (which causes absorption of some of the alpha or beta particles in the sample matrix) or cell geometry in the case of scintillation cells. Initial calibration is procedure-dependent. See individual procedures for specific initial calibration instructions.

Absorption curve values do not need to be reestablished after initial calibration if check source response is monitored regularly and indicates instrument stability. Recalibrate scintillation cells periodically.

5) Continuing calibration (source check)—See ¶ (1a3)e).

6) Sample counting—Place prepared sample in the counting chamber according to manufacturer's instructions. Take the following precautions: assure that counting chamber is light-tight; assure that photomultiplier tube is not exposed to direct light while the high voltage is applied; let sample chamber dark adapt before starting count; count for a preset duration, or preset count, to give the desired counting precision; assure that the sample is in contact with the phosphor; and count samples in a geometry consistent with initial calibration.

## 3. Liquid Scintillation Counters

A liquid scintillation spectrometer system is used to detect the photons of light emitted from a scintillation solution, by one or

more photomultiplier tubes. Scintillation spectrometers count the number of scintillations (photons) emitted from the sample vial. To a first approximation, the number of photons produced in the scintillator is proportional to the initial energy of the particle. This information is an aid to determining the specific radionuclide present.

*a. Principle and uses:* A sample containing beta-(or alpha-) emitting radionuclides is mixed within a liquid scintillator. The beta (or alpha) particle is detected by the interchange of energy with the detection medium. The particle excites the solvent molecules, which pass on their excitation energy to the solvent by a collision process. The excited solute molecule rapidly returns to its ground state by the emission of a photon. The intensity of the scintillation depends on the number of solute molecules excited and the initial energy of the particle. Liquid scintillation is commonly used to determine activities of some alpha (i.e.,  $^{222}\text{Rn}$  and daughters) and most low-energy beta-emitters such as  $^3\text{H}$  and  $^{14}\text{C}$ . Counting efficiencies approaching 100% can be obtained from some radionuclides.

*b. Components:* The liquid scintillation counting system consists of the liquid scintillator (organic scintillator diluted with an appropriate solvent), a polyethylene or glass vial, and a liquid scintillation counter (with one or more photomultiplier tubes coupled to a single or multichannel analyzer), and readout device.

*c. Performance verification:*

1) Radioactive sources—See Section 7020A.3e.  
2) Background—Consider two backgrounds when dealing with liquid scintillation spectrometers.

a) Electronic or instrument background—See ¶ 2c3)a) above. Determine background with an empty counting chamber and a dark vial. Some manufacturers supply a dark or “black” vial (a counting vial filled with black material such as graphite) for this purpose.

b) Chamber background—See ¶ 2c3)b) above. Determine background using a vial (sometimes supplied by the manufacturer) containing liquid scintillator (cocktail) and an appropriate volume of low-background water (water with no detectable activity). Use a chamber background counting duration equivalent to the longest sample counting duration.

3) Initial calibration—Before sample analysis, optimize the counting conditions for the radionuclide of interest (e.g., some analysts maximize the figure of merit,  $E^2/B$  where  $E$  = efficiency and  $B$  = background count rate) for each radionuclide. Optimum counting conditions do not need to be reestablished after initial calibration if check source response is monitored regularly and indicates instrument stability. Once optimum conditions have been selected by using a pure source, determine sample counting efficiency by one of several methods (see Section 7500- $^3\text{H}$  and 7500-Rn): standard additions, quench curve, or prepared laboratory standard.

4) Continuing calibration (source check)—See ¶ 1a3)e). See Section 7500-Rn for specific calibration procedures for radon-222 by liquid scintillation counting.

5) Sample counting—Place prepared samples in the counting chamber, let samples dark adapt, and count for a preset count or preset duration necessary to obtain the desired sensitivity.

As with other counting techniques, deal with the following interferences: quenching (photon, chemical, or color), chemiluminescence/photoluminescence, static electricity, scintillation

volume variations, homogeneity of sample, background, multiple radionuclides, and phase separation.

#### 4. Alpha Spectrometers

*a. Principle and uses:* Alpha emissions from a sample interact with atoms of a solid-state detector to produce a current proportional to the deposited alpha particle energy. The current is collected, amplified, sorted according to deposited alpha energy, and displayed on a multichannel analyzer. An alpha spectrometer is used to detect, identify, and quantify specific alpha-emitting radionuclides. These radionuclides may be chemically separated from samples and deposited as a thin layer on filter papers or electrodeposited on metal disks. Ideally, use internal tracers on an individual sample basis to ensure accurate quantitation.

*b. Components:* An alpha spectrometer consists of a sample chamber (with detector, detector/sample holder, and vacuum chamber), a mechanical vacuum pump, a detector bias voltage supply, a preamplifier, a linear amplifier, a multichannel analyzer (with ADC and memory storage), and data readout capability. For details on operation and calibration, see the operation manual provided by the manufacturer.

The detector may be a semiconductor particle detector, that is, a silicon surface detector used for alpha spectrometry. Other charged particle detectors are available from various manufacturers.

*c. Performance verification:*

1) Radioactive source—See Section 7020A.3e.

2) Detector voltage—Set detector operating voltage in accordance with the manufacturer’s recommendations.

3) Background—The chamber background consists of counting a clean filter or metal disk. Use a chamber background counting duration equivalent to the longest sample counting duration. This background is caused by contamination of the sample chamber. Do not confuse the background count rate with the count rate of the laboratory or reagent blank. However, under some circumstances, these count rates might be approximately equal.

4) Initial calibration—The purpose of initial calibration is to establish a detector energy calibration and counting efficiency. Use a standard source as described in Section 7020A.3e. Before counting, for initial/continuing calibration purposes, ensure that the counting vacuum chamber is well sealed and has an adequate as well as consistent vacuum source. Inadequate vacuum will result in a distorted alpha spectrum. Inconsistent application of vacuum can cause significant drift of the alpha spectra.

5) Continuing calibration (source check)—Verify detector efficiency and energy calibration stability. A mixed alpha-emitting isotopic source (see Section 7020A.3e) allows confirmation of the energy calibration by permitting identification of specific alpha-emitting radionuclides. For standard deviation criteria, see ¶ 1a3)e).

6) Sample counting—Place prepared sample in the counting chamber according to manufacturer’s instruction. Take following precautions: assure that the air in the counting chamber is slowly evacuated to at least 500  $\mu\text{m Hg}$  or less; count for a preset duration, or preset count to give the desired counting precision; assure that the sample is properly positioned on the sample holder; and, after counting, release vacuum *slowly* to prevent contamination of chamber and detector.

## 5. Gamma Spectrometers

Gamma spectrometry identifies and quantifies specific energy photons (gamma rays), thereby quantitating specific radionuclides.

*a. Principle and uses:* Gamma rays from a sample enter the sensitive volume of the detector and interact with the detector atoms. The interactions are converted into a voltage pulse proportional to the photon energy. Pulses are stored in sequence in finite energy-equivalent increments over the desired spectrum range. After sample counting, the accumulated pulses over a certain area may result in a peak that can be identified and quantified as a specific radionuclide by its location and peak area.

*b. Components:* A gamma spectrometer consists of a detector, preamplifier and detector bias supply, pulse-height analyzer system, data readout capability, and shielded sample enclosure. The pulse-height analyzer system consists of a linear amplifier, an analog-to-digital converter (ADC), memory storage, and a logic control mechanism. The logic control capabilities allow data storage in various modes and display or recall of data. For details on operation and calibration of a gamma spectrum analyzer, see manufacturer's instructions.

Gamma detectors commonly used consist of intrinsic or high-purity germanium (Ge) or lithium drifted germanium [Ge(Li)], sodium iodide [NaI(Tl)], and silicon [Si(Li)]. Ge(Li) detectors offer good resolution and combine poor to good efficiency (depending on the application and cost). NaI(Tl) detectors offer poor resolution and good efficiency at reasonable cost. Si(Li) detectors offer good efficiency and resolution for low-energy x-rays (10 to 200 keV). Other detectors are available.

*c. Performance verification:*

- 1) Radioactive sources—See Section 7020A.3e.
- 2) Detector voltage—Set detector operating voltage according to manufacturer's recommendations.
- 3) Background—Detector background consists of counting an appropriate volume of reagent-grade water in the desired geometry. Use detector background counting duration equivalent to the longest sample counting duration. The background is caused by contamination of the sample chamber and by cosmic, natural, and worldwide fallout in the detector shielding. Do not confuse the background count rate with the count rate of the laboratory or reagent blank. Under some circumstances, these count rates may be approximately equal.
- 4) Initial calibration—Establish a detector energy calibration and counting efficiency per sample geometry. Use a standard source as described in Section 7020A.3e.
- 5) Continuing calibration (source check)—Verify detector efficiency and energy calibration stability (see Section 7020A.3e). A mixed gamma-emitting isotopic source allows confirmation of the energy calibration by permitting identification of specific gamma-emitting radionuclides. For standard deviation criteria, see ¶ 1a3e).
- 6) Sample counting—Place prepared sample in the counting chamber and proceed according to instrument manufacturer's instructions.
- 7) Resolution—Semiconductor detectors greatly improve energy resolution over other types of detectors. Energy resolution,  $R$ , refers to the ability of the detector to discriminate between two radiations of different energies. Not all detectors are capable

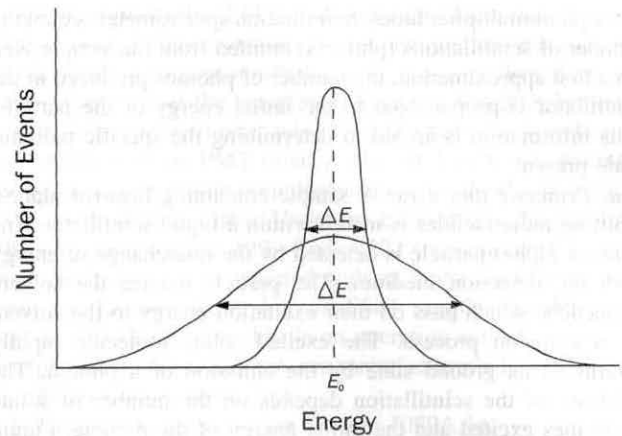


Figure 7030:2. Calculation of the energy resolution of a pulse-type detector.

of giving energy information; for such devices this characteristic is not relevant. Resolution is defined with reference to a plot of the number of radiations detected against the radiation energy, as shown in Figure 7030:2:

$$R = \frac{\Delta E}{E_0}$$

where  $E_0$  is the energy corresponding to the centroid of the peak and  $\Delta E$  refers to the width of the peak halfway between the base line and the top.  $\Delta E$  also is called the full width at half maximum (FWHM). Resolution often is expressed as a percentage (e.g.,  $R = 0.10$  or 10%). For example, if a photopeak with a maximum at 80 V had a width of 8 V at the midpoint of its amplitude, the resolution of the system would be  $100 \times (8/80) = 10\%$ . The dispersion of activities about the maximum of a peak is approximately Gaussian.

The smaller the value, the better the detector will be at separating two radiations of similar energy. Resolution is never perfect because of electronic noise and the statistical nature of the interactions of radiation with matter. Resolution varies greatly for different types of detectors (see Table 7030:I).

*d. Gamma scintillation:* A common gamma spectroscopy system is the sodium iodide, thallium-activated [NaI(Tl)] crystal system using scintillation phenomenon. The high atomic number of iodine in NaI gives good counting efficiency for a gamma-ray detector. A small amount of Tl is added to activate the crystal. The best achievable resolution is about 7% with the  $^{137}\text{Cs}$  662

TABLE 7030:I. ENERGY RESOLUTION FOR VARIOUS DETECTOR TYPES

Detector	Resolution at Given Energy		
	5.9 keV	122 keV	1332 keV
Proportional counter	1.2	—	—
X-ray NaI(Tl)	3.0	12.0	—
3 × 3 NaI(Tl)	—	12.0	60
Si(Li)	0.16	—	—
Planar Ge	0.18	0.5	—
Coaxial Ge	—	0.8	1.8

keV gamma ray [in a 3-in.- (7.6-cm) diam by 3-in.-long crystal] and slightly worse for smaller or larger detectors.

The light decay time constant in NaI is about 0.25  $\mu$ s. Typical charged sensitive pre-amplifiers translate this into an output pulse rise time of about 0.5  $\mu$ s. Fast coincidence measurements cannot achieve the very short resolving times that are possible with plastic, especially at low gamma-ray energies. Many configurations of NaI detectors are available commercially, ranging from very thin crystals for x-ray measurements to large crystals with multiple phototubes. Crystals built with a well to allow nearly spherical ( $4\pi$ ) geometry counting of weak samples also are a standard configuration.

*e. Solid state detectors:* A common high-resolution germanium detector consists of a diode of over 30 cm<sup>3</sup> sensitive volume encased in a 7.6-cm-diam sensitive volume cylinder, with a dipstick immersed in liquid nitrogen in a large cryostat, a pre-amplifier, and a detector bias voltage supply. The detector is cooled with liquid nitrogen to protect the diode and to reduce electronic noise generation. Intrinsic germanium detectors are operated at the temperature of liquid nitrogen. Maintain the detector at the temperature of liquid nitrogen. Use a linear amplifier that will maintain the pulse resolution provided by the detector.

In Ge diode detector systems, the interaction of gamma photons with the detector causes ionization of the detector atoms. A bias voltage applied to the detector allows collection of freed electrons that are proportional to the deposited photon energy with a resolving time of  $10^{-9}$  to  $10^{-13}$ s. Such a system has exceptionally high resolution.

*f. Data system:* The data systems contain one or more of the following: a visual display for the gamma spectrometer readout indicator, a digital printer, and a computer terminal with associated capabilities. An oscilloscope is helpful in aligning the instrument with standards such as <sup>60</sup>Co, <sup>137</sup>Cs, <sup>207</sup>Bi, and <sup>154</sup>Eu. Computer capability is essential in data reduction and in complex sample analysis.

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## 7040 FACILITIES\*

### 7040 A. Counting Room

The design and construction of a counting room may vary widely from one laboratory to another. Provide a room free of dust and fumes to protect the electrical stability of the instrumentation; however, a “clean room” with specific controlled access is not required. Stabilize and reduce background radiation as much as possible by careful choice of building materials for walls, floor, and ceiling as well as by assuring that samples containing appreciable activity are located distant from the instrument area. Construct floors and counter tops of a material that is easy to clean in the event of contamination.

Provide air-conditioning and/or humidity control as necessary to avoid instrument instability. Follow as closely as possible the instrument manufacturer’s recommendations for operating temperature and humidity. Most counting instruments are supplied with voltage-regulating circuitry suitable for controlling minor fluctuations in line voltage. For unusual fluctuations use an auxiliary voltage regulator/transformer. Finally, locate the counting room in an area of minimal traffic flow.

A modern chemical laboratory can be used to process routine environmental samples for radiochemical analyses. Preferably segregate nonenvironmental levels of radioactivity to preclude cross-contamination and health concerns. Provide adequate space between instruments to allow necessary access for required periodic maintenance.

\* Approved by Standard Methods Committee, 2000.  
Joint Task Group: 20th Edition—James W. Mullins (chair).

## 7040 B. Radiochemistry Laboratory

The prime consideration in the design of a radiochemistry laboratory is contamination control. Radioactivity concentration levels found in environmental samples would not normally produce cross-contamination problems if good laboratory practices are followed. In areas where radioactive standards are being prepared, take care to minimize contamination of surfaces, other samples, and personnel. Either bench surfaces of an impervious material covered with adsorbent paper or trays (stainless steel, plastic, or fiberglass) lined with adsorbent paper are acceptable.

### 1. Chemical Reagents and Reagent-Grade Water

Most reagents contain some radioactivity and other impurities that may result in a systematic error if not accounted for. Quantify the contribution of reagents by analyzing reagent blanks. A reagent blank is a sample having all of the constituents of the unknown except those being determined. Do not use reagents having a radioactivity level high enough to interfere. It is recommended that about 5% of every analysis batch be a reagent blank. In most phases of radiochemistry, it is necessary to use high-purity reagents. In such cases, use reagent-grade chemicals. For example, if barium is to be used as a carrier for radium, it is necessary to determine the radium content of the barium salt used for the analysis. Rare-earth carriers, such as yttrium or cerium, can be contaminated with thorium from the original rare-earth ores.

Distilled or deionized water is used in analytical laboratories for dilution, preparation of reagents, and final rinsing of glassware. Ordinary distilled water usually is not of sufficient purity to be used for certain applications in the environmental radio-

chemistry laboratory. These applications include background blanks for gamma spectroscopy and liquid scintillation counting. Impurities commonly present in distilled water include radon and tritium. Remove radon by aerating with aged (30 d) air or other inert gases, or aging the distilled water for 30 d to allow the radon and daughters to decay. Tritium presence, which is normal in surface water, can be avoided by using water from deep wells. Deep well water is normally old enough so that the tritium has decayed completely or at least to an acceptable level.

### 2. Apparatus and Glassware

The same considerations apply to the use and care of glassware in the radiochemistry laboratory as in any analytical laboratory. An excellent discussion is given elsewhere of the kinds of glassware available, the use of volumetric ware, and various cleaning requirements.<sup>1</sup> Certain aspects of glassware usage are peculiar to radiochemistry. Consider glassware and apparatus used in the preparation of standards or for higher-level samples as contaminated; discard or segregate for further use with samples of comparable activity. (A useful rule of thumb is to not analyze samples side by side if it is known that they differ in activity level by three orders of magnitude, i.e., pCi vs. nCi.) As available, preferably use single planchets and auxiliary supplies.

### 3. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. Chap. 4. EPA-600/4-79-019, U.S. Environmental Protection Agency, Cincinnati, Ohio.

## 7040 C. Laboratory Safety

While specific safety criteria are beyond the scope of this discussion, apply general and customary safety practices as a part of good laboratory procedure. Each laboratory should have a safety plan as part of standard operating procedure. Where safety practices are included in an approved method, follow them strictly.

Regard each chemical used as a potential health hazard and maintain exposure as low as reasonably achievable. Each labo-

ratory is responsible for maintaining a current awareness file of applicable regulations regarding the safe handling of the chemicals specified in the methods for radiochemical analysis. Make available a reference file of material data handling sheets to all personnel involved. Use fume hoods when necessary, wear safety glasses or a shield for eye protection, and wear protective clothing at all times.

## 7040 D. Pollution Prevention

### 1. Management Techniques

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, use pollution prevention techniques to address waste generation. When wastes cannot be reduced at the source, the next recom-

mended option is recycling. Further information about pollution prevention that may be applicable to laboratories and research institutions is available.<sup>1</sup>

### 2. Reference

1. AMERICAN CHEMICAL SOCIETY. 1985. Less is Better: Laboratory Chemical Management for Waste Reduction. American Chemical Soc., Washington, D.C.

## 7040 E. Waste Management

### 1. Management Techniques

Establish laboratory waste management practices consistent with all applicable rules and regulations. Protect air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the haz-

ardous waste identification rules and land disposal restrictions. Further information on waste management is available.<sup>1</sup>

### 2. Reference

1. AMERICAN CHEMICAL SOCIETY. 1990. The Waste Management Manual for Laboratory Personnel. American Chemical Soc., Washington, D.C.

## 7110 GROSS ALPHA AND GROSS BETA RADIOACTIVITY (TOTAL, SUSPENDED, AND DISSOLVED)\*

### 7110 A. Introduction

#### 1. Occurrence

*a. Natural radioactivity:* Uranium, thorium, and radium are naturally occurring radioactive elements that have a long series of radioactive daughters that emit alpha, beta, and/or gamma radiations until a stable end-element is produced. These naturally occurring elements, through their radioactive daughter gases, radon and thoron, cause airborne activity and contribute to the radioactivity of rain and groundwaters. Additional naturally radioactive elements include potassium-40, rubidium-87, samarium-147, lutetium-176, and rhenium-187.

*b. Artificial radioactivity:* With the development and operation of nuclear reactors and radionuclide-generating devices, large quantities of radioactive elements are being produced. These include almost all the elements in the periodic table.

#### 2. Significance

Regular measurements of gross alpha and gross beta activity in water may be invaluable for early detection of radioactive contamination and indicate the need for supplemental data on concentrations of more hazardous radionuclides.

With the simpler techniques for routine measurement of gross alpha and beta activity, the presence of contamination may be determined in a matter of hours, whereas days may be required to make the radiochemical analyses necessary to identify radionuclides present.

#### 3. Bibliography

- U.S. ENVIRONMENTAL PROTECTION AGENCY. 1976. Drinking Water Regulations. Radionuclides. *Fed. Reg.* 41:28402.

\* Approved by Standard Methods Committee, 2000.  
Joint Task Group: James W. Mullins (chair).

### 7110 B. Evaporation Method for Gross Alpha-Beta

#### 1. General Discussion

*a. Selection of counting instrument:* The thin-window, heavily shielded, gas-flow, anticoincidence-circuitry proportional counter is the recommended instrument for counting gross alpha and beta radioactivity because of its superior operating characteristics. These include a very low background and a high sensitivity to detect and count an alpha and beta radiation range that is reasonable but not so wide as that of internal proportional counters. Calibrate the instrument by adding standard nuclide portions to media comparable to the samples and preparing, mounting, and counting the standards exactly as the samples.

An internal proportional or Geiger counter also may be used; however, the internal proportional counter has a higher background for beta counting than the thin-window counter and alpha activity cannot be determined separately with a Geiger counter. Alpha activity can be measured with either a thin-window or internal proportional counter; counting efficiency is higher for the internal counter.

*b. Calibration standard:* When gross beta activity is assayed in samples containing mixtures of naturally radioactive elements and fission products, the choice of a calibration standard may influence the beta results significantly because self-absorption factors and counting chamber characteristics are beta-energy-dependent.

A standard solution of cesium-137, certified by the National Institute of Standards and Technology (NIST) or traceable to a certified source, is recommended for calibration of counter efficiency and self-absorption for gross beta determinations. The half-life of cesium-137 is about 30 years. The daughter products after beta decay of cesium-137 are stable barium-137 and metastable barium-137, which in turn disintegrates by gamma emission. For this reason, the standardization of cesium-137 solutions may be stated in terms of the gamma emission rate per milliliter or per gram. However, one has to consider the conversion electrons emitted by metastable barium-137 when using cesium-137 as a gross beta counting standard. It is common practice to calibrate cesium-137 on the basis of the gamma rays emitted by metastable barium-137 (85% of Cs-137 disintegrations), but a calculation of total electrons emitted must include the conversion electrons from barium-137m (9.5% of Cs-137 emissions). To convert gamma rate to equivalent beta disintegration rate, multiply calibrated gamma emission rate by  $1.095/0.85=1.29$ .

Strontium-90 in equilibrium with its daughter yttrium-90 also is a suitable gross beta standard; its use is recommended by EPA.<sup>1</sup> For gross alpha activity, the recommended standards are natural uranium and thorium-230, Plutonium-239 and americium-241 also are widely used.

Note that gross alpha and beta results are meaningless unless the calibration standard also is reported.

*c. Radiation lost by self-absorption:* The radiation from alpha-emitters having an energy of 8 MeV and from beta-emitters having an energy of 60 keV will not escape from the sample if the emitters are covered by a sample thickness of  $5.5 \text{ mg/cm}^2$ . The radiation from a weak alpha-emitter will be stopped if covered by only  $4 \text{ mg/cm}^2$  of sample solids. Consequently, for low-level counting it is imperative to evaporate all moisture and preferable to destroy organic matter before depositing a thin film of sample solids from which radiation may enter the counter. In counting water samples for gross beta radioactivity, a solids thickness of  $10 \text{ mg/cm}^2$  or less on the bottom area of the counting pan is recommended. For the most accurate results, determine the self-absorption factor as outlined below.

*d. Calibration of overall counter efficiency:* Correct observed counting rate for geometry, back-scatter, and self-absorption (sample absorption).

Although it is useful to know the variation in these individual factors, determine overall efficiency by preparing standard sample sources and unknowns.

1) For measuring mixed fission products or beta radioactivity of unknown composition, use a standard solution of cesium-137 or strontium-90 in equilibrium with its daughter yttrium-90.

Prepare a standard (known disintegration rate) in an aqueous solution of sample solids similar in composition to that present in samples. Dispense increments of solution in tared pans and evaporate. Make a series of samples having a solids thickness of 1 to  $10 \text{ mg/cm}^2$  of bottom area in the counting pan. Evaporate carefully to obtain uniform solids deposition. Dry ( $103$  to  $105^\circ\text{C}$ ), weigh, and count. Calculate the ratio of counts per minute to disintegrations per minute (efficiency) for different weights of sample solids. Plot efficiency as a function of sample thickness and use the resulting calibration curve to convert counts per minute (cpm) to disintegrations per minute (dpm).

2) If other radionuclides are to be tested, repeat the above procedure, using certified solutions of each radionuclide. Avoid

unequal distribution of sample solids, particularly in the 0- to  $3\text{-mg/cm}^2$  range, in both calibration and sample preparation.

3) For alpha calibration, proceed as above, using a standard solution of natural uranium salt in secular equilibrium (not depleted uranium), thorium-230, plutonium-239, or americium-241. Recount alpha standard at the beta operating voltage and determine alpha amplification factor (§ 5b below). Report calibration standard used with results.

## 2. Apparatus

*a. Counting pans,* of metal resistant to corrosion from sample solids or reagents, about 50 mm diam, 6 to 10 mm in height, and thick enough to be serviceable for one-time use. Stainless steel planchets are recommended for acidified samples.

*b. Thin end-window proportional counter,* capable of accommodating a counting pan.

*c. Alternate counters:* Other beta counters are internal proportional and Geiger counters.

*d. Membrane filter,\**  $0.45\text{-}\mu\text{m}$  pore diam.

*e. Gooch crucibles.*

*f. Counting gas,* as recommended by the instrument manufacturer.

## 3. Reagents

*a. Methyl orange indicator solution.*

*b. Nitric acid, HNO<sub>3</sub>, 1N.*

*c. Clear acrylic solution:* Dissolve 50 mg clear acrylic† in 100 mL acetone.

*d. Ethyl alcohol, 95%.*

*e. Conducting fluid:‡* Prepare according to manufacturer's directions (for internal counters).

*f. Standard certified thorium-230, cesium-137, or strontium-90-yttrium-90 solution.*

*g. Standard certified americium-241, plutonium-239, or natural uranium solution.* For natural uranium, use material in secular equilibrium.

*h. Reagents for wet-combustion procedure:*

1) Nitric acid, HNO<sub>3</sub>, 6N.

2) Hydrogen peroxide solution: Dilute 30% H<sub>2</sub>O<sub>2</sub> with an equal volume of water.

## 4. Procedure

*a. Total sample activity:*

1) For each  $20 \text{ cm}^2$  of counting pan area, take a volume of sample containing not more than 200 mg residue for beta examination and not more than 100 mg residue for alpha examination. The specific conductance test on a nonpreserved sample helps to select the appropriate sample volume.

2) Evaporate by either of the following techniques:

a) Add sample directly to a tared counting pan in small increments, with evaporation at just below boiling temperature. This procedure is not recommended for large samples.

\* Type HA, Millipore Filter Corp., Bedford, MA, or equivalent.

† Lucite or equivalent.

‡ Anstac 2M, Chemical Development Corporation, Danvers, MA, or equivalent.

b) Place sample in a borosilicate glass beaker or evaporating dish, add a few drops of methyl orange indicator solution, add 1N HNO<sub>3</sub> dropwise to pH 4 to 6, and evaporate on a hot plate or steam bath to near dryness. Avoid baking solids on evaporation vessel. Transfer to a tared counting pan with the aid of a rubber policeman and distilled water from a wash bottle. Using a rubber policeman, thoroughly wet walls of evaporating vessel with a few drops of acid and transfer washings to counting pan. (Excess alkalinity or mineral acidity is corrosive to aluminum counting pans.)

3) Complete drying in an oven at 103 to 105°C, cool in a desiccator, weigh, and keep dry until counted.

4) Treat sample residues having particles that tend to be airborne with a few drops of clear acrylic solution, then air- and oven-dry and weigh.

5) With a thin end-window counter count alpha and/or beta activity.

6) Store sample in a desiccator and count for decay if necessary. Radionuclides that are volatile under the sample preparation conditions of this method will not be measured. In some geographic areas nitrated water solids (sample evaporated with nitric acid present) will not remain at a constant weight after being dried at 105°C for 2 h and then exposed to the atmosphere before and during counting. Other radioactive substances (such as some chemical forms of radioiodine) also may be lost during sample evaporation and drying. Heat such samples to a dull red heat for a few minutes to convert the salts to oxides. Sample weights then usually are sufficiently stable to give consistent counting rates and a correct counting efficiency can be assigned. Radioisotopes such as those of cesium may be lost when samples are heated to dull red color. Such losses are limitations of the test method.

*b. Activity of dissolved matter:* Proceed as in ¶ 4a1) above, using a sample filtered through a 0.45-µm membrane filter.

*c. Activity of suspended matter:*

1) For each 10 cm<sup>2</sup> of membrane filter area, take a volume of sample not to exceed 50 mg suspended matter for alpha assay and not to exceed 100 mg for beta assay.

2) Filter sample through membrane filter with suction; then wash sides of filter funnel with a few milliliters of distilled water.

3) Transfer filter to a tared counting pan and oven-dry.

4) If sample is to be counted in an internal counter, saturate membrane with alcohol and ignite. (When beta or alpha activity is counted with another type of counter, ignition is not necessary provided that the sample is dry and flat.) When burning has stopped, direct flame of a Meeker burner down on the partially ignited sample to fix sample to pan.

5) Cool, weigh, and count alpha and beta activities.

6) If sample particles tend to be airborne, treat sample with a few drops of clear acrylic solution, air-dry, and count.

7) Alternatively, prepare membrane filters for counting in internal counters by wetting filters with conducting fluid, drying, weighing, and counting. (Include weight of membrane filter in the tare.)

*d. Activity of suspended matter (alternate):* If it is impossible to filter sewage, highly polluted waters, or industrial wastes through membrane filters in a reasonable time, proceed as follows:

1) Determine total and dissolved activity by the procedures given in ¶s 4a and 4b and estimate suspended activity by difference.

2) Filter sample through an ashless mat or filter paper of stated porosity. Dry, ignite, and weigh suspended fixed residue. Transfer and fix a thin uniform layer of sample residue to a tared counting pan with a few drops of clear acrylic solution. Dry, weigh, and count in a thin end-window counter for alpha and beta activity.

*e. Activity of nonfatty semisolid samples:* Use the following procedure for samples of sludge, vegetation, soil, etc.:

1) Determine total and fixed solids of representative samples according to Section 2540.

2) Reduce fixed solids of a granular nature to a fine powder with pestle and mortar.

3) Transfer a maximum of 100 mg fixed solids for alpha assay and 200 mg fixed solids for beta assay for each 20 cm<sup>2</sup> of counting pan area (see NOTE below).

4) Distribute solids to uniform thickness in a tared counting pan by (a) spreading a thick aqueous cream of solids that is weighed after oven-drying, or (b) dispensing dry solids of known weight and spreading with acetone and a few drops of clear acrylic solution.

5) Oven-dry at 103 to 105°C, weigh, and count.

NOTE: The fixed residue of vegetation and similar samples usually is corrosive to aluminum counting pans. To avoid difficulty, use stainless steel pans or treat a weighed amount of fixed residue with HCl or HNO<sub>3</sub> in the presence of methyl orange indicator to pH 4 to 6, transfer to an aluminum counting pan, dry at 103 to 105°C, reweigh, and count.

*f. Alternate wet-combustion procedure for biological samples:* Some samples, such as fatty animal tissues, are difficult to process according to ¶ 4e above. An alternate procedure consists of acid digestion. Because a highly acid and oxidizing state is created, volatile radionuclides may be lost under these conditions.

1) To a 2- to 10-g sample in a tared silica dish or equivalent, add 20 to 50 mL 6N HNO<sub>3</sub> and 1 mL 15% H<sub>2</sub>O<sub>2</sub> and digest at room temperature for a few hours or overnight. Heat gently and, when frothing subsides, heat more vigorously but without spattering, until nearly dry. Add two more 6N HNO<sub>3</sub> portions of 10 to 20 mL each, heat to near boiling, and continue gentle treatment until dry.

2) Ignite in a muffle furnace for 30 min at 600°C, cool in a desiccator, and weigh.

3) Continue the test as described in ¶s 4e3)–5) above.

## 5. Calculation and Reporting

*a. Alpha activity:* Calculate alpha activity, in picocuries per liter, by the equation

$$\text{Alpha} = \frac{\text{net cpm} \times 1000}{2.22e \nu}$$

where:

*e* = calibrated overall counter efficiency (see ¶ 1d), and

*ν* = volume of sample counted, mL.

Express the counting error as described in ¶ c below. Similarly, calculate and report alpha activity in picocuries per kilogram of moist biological material or per kilogram of moist and per kilogram of dry silt.

*b. Beta activity:* Calculate and report gross beta activity and counting error in picocuries per liter of fluid, per kilogram of moist (live weight) biological material, or per kilogram of moist and per kilogram of dry silt, according to ¶s a, above, and c, below.

To calculate picocuries of beta activity per liter, determine the value of  $e$  in the above equation as described in ¶ 1d, above.

When beta activity is counted in the presence of alpha activity by gas-flow proportional counting systems (at the beta plateau) alpha particles also are counted. Because alpha particles are more readily absorbed by increased sample thickness than beta particles, alpha/beta count ratios vary. Therefore, prepare a calibration curve by counting standards (americium-241, thorium-230, or plutonium-239) with increasing solids thickness, first on the alpha plateau, then on the beta plateau. Plot the ratios of the two counts against mg/cm<sup>2</sup> thickness, determine the alpha amplification factor ( $M$ ), and correct the amplified alpha count on the beta plateau for the sample.

$$M = \frac{\text{net cpm on beta plateau}}{\text{net cpm on alpha plateau}}$$

If significant alpha activity is indicated by the sample alpha plateau count, determine beta activity by counting the sample at the beta plateau and calculating:

$$\text{Beta, pCi/L} = \frac{B - AM}{2.22 \times D \times V}$$

where:

- $B$  = net beta counts at the beta plateau,
- $A$  = net alpha counts at the alpha plateau,
- $M$  = alpha amplification factor (from ratio plot),
- 2.22 = dpm/pCi,
- $D$  = beta counting efficiency, cpm/dpm, and
- $V$  = sample volume, L.

Some gas-flow proportional counters have electronic discrimination to eliminate alpha counts at the beta operating voltage. For these instruments the alpha amplification factor will be less than 1.

Where greater precision is desired, for example, when the count of alpha activity at the beta plateau is a substantial fraction of the net counts per minute of gross beta activity, the beta counting error equals  $(E_a^2 + E_b^2)^{1/2}$ , where  $E_a$  is the alpha counting error and  $E_b$  the gross beta counting error.

*c. Counting error:* Determine the counting error,  $E$  (in picocuries per sample), at the 95% confidence level from:

$$E = \frac{1.96\sigma(R)}{2.22e}$$

where  $\sigma(R)$  is calculated as shown in Section 7020C.2, using  $t_1 = t_2$  (in minutes); and  $e$ , the counter efficiency, is defined and calculated as in ¶ 1d.

*d. Miscellaneous information to be reported:* In reporting radioactivity data, identify adequately the sample, sampling station, date of collection, volume of sample, type of test, type of activity, type of counting equipment, standard calibration solutions used (particularly when counting standards other than those recommended in ¶ 1d are used), time of counting (particularly if short-lived isotopes are involved), weight of sample solids, and kind and amount of radioactivity. So far as possible, tabulate the data for ease of interpretation and incorporate repetitious items in the table heading or in footnotes. Unless especially inconvenient, do not change quantity units within a given table. Always report the counting error to assist in interpretation of results.

## 6. Precision and Bias

In a collaborative study of two sets of paired water samples containing known additions of radionuclides, 15 laboratories determined the gross alpha activity and 16 analyzed gross beta activity. The samples contained simulated water minerals of approximately 350 mg fixed solids/L. The alpha results of one laboratory were rejected as outliers.

The average recoveries of added gross alpha activity were 86, 87, 84, and 82%. The precision (random error) at the 95% confidence level was 20 and 24% for the two sets of paired samples. The method was biased low, but not seriously.

The average recoveries of added gross beta activity were 99, 100, 100, and 100%. The precision (random error) at the 95% confidence level was 12 and 18% for the two sets of paired samples. The method showed no bias.

## 7. References

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1980. Prescribed Procedures of Measurement of Radioactivity in Drinking Water. EPA-600/4-80-032.

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## 7110 C. Coprecipitation Method for Gross Alpha Radioactivity in Drinking Water

### 1. General Discussion

The Evaporation Method for Gross Alpha-Beta, 7110B, does not separate alpha-(or beta-) emitting radionuclides from the sample's dissolved solids. For drinking water samples with high dissolved solids content, e.g., 500 mg/L or higher, Method 7110B is severely limited because of the small sample size possible and the very long counting times necessary to meet required sensitivity (3 pCi/L). The coprecipitation procedure eliminates the problem of high dissolved solids and gives increased sensitivity.

*a. Principle:* All alpha-emitting radionuclides of interest (mainly radium, uranium, and thorium isotopes) are coprecipitated with barium sulfate and iron hydroxide as carriers, thereby separating alpha-emitting radionuclides from other sample dissolved solids. The combined precipitates are filtered and counted for alpha activity. Relatively large samples can be analyzed so that sensitivity is improved and counting time is minimized.

*b. Interferences:* Allow at least 3 h for decay of radon progeny before beginning the alpha count.

Soluble ions that coprecipitate and add to the mixed barium sulfate and iron hydroxide precipitate weights result in counting efficiencies that are biased low.

Iron hydroxide precipitates collected on membrane filters without a holding agent flake when dried and are easily lost from the filter. Add 5 mg paper pulp fiber to the sample to help secure the iron hydroxide to the filter. Preferably use glass fiber filters because the surface glass fibers help to secure the precipitate.

*c. Calibration:* Add at least 100 pCi standard alpha-emitter activity to 500-mL portions of tap water in separate beakers. Add 2.5 mL conc HNO<sub>3</sub> to each beaker. Determine counting efficiency (cpm/pCi) for the alpha-emitter by taking these known additions through the procedure. Make at least six replicate determinations to determine counting efficiency.<sup>1</sup>

Use 500-mL portions with no addition for blank corrections of alpha activity in the tap water and reagents.

$$\text{Efficiency, cpm/Ci} = \frac{C_a - C_b}{\text{pCi}}$$

where:

$C_a$  = sample with added activity, mean cpm,

$C_b$  = mean blank cpm, and

pCi = activity added.

Preferably use thorium 230 (a pure alpha-emitter) for gross alpha efficiency calibration. As noted in 7110B.1b, other alpha-counting standards may be used.

### 2. Apparatus

*a. Hot plate/magnetic stirrer and stirring bars.*

*b. Filter membranes, 47-mm diam, 0.45- $\mu$ m pore size, or glass fiber filters.\**

*c. Drying lamp.*

*d. Planchets, stainless steel, 2-in. diam.*

*e. Alpha scintillation counter or low-background proportional counter.*

### 3. Reagents

*a. Ammonium hydroxide, NH<sub>4</sub>OH, 6N.*

*b. Barium carrier, 5 mg Ba<sup>2+</sup>/mL:* Dissolve 4.4 g BaCl<sub>2</sub> · 2H<sub>2</sub>O in 500 mL distilled water.

*c. Bromocresol purple, 0.1%:* Dissolve 100 mg water-soluble reagent in 100 mL distilled water.

*d. Iron carrier, 5 mg Fe<sup>3+</sup>/mL:* Dissolve 17.5 g Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O in 200 mL distilled water containing 2 mL 16N HNO<sub>3</sub>. Dilute to 500 mL.

*e. Sulfuric acid, H<sub>2</sub>SO<sub>4</sub>, 2N:* Dilute 55 mL conc H<sub>2</sub>SO<sub>4</sub> to 1 L with distilled water.

*f. Paper pulp/water mixture:* Add a 0.5-g paper pulp pellet to 500 mL distilled water in a plastic bottle. Add 5 drops diluted (1 + 4) detergent. Cap bottle and stir vigorously for 3 h before use. Stir mixture whenever a portion is taken.

*g. Detergent:* 1 part detergent + 4 parts distilled water.†

### 4. Procedure

To a sample of 500 mL to 1 L, or sample diluted to 500 mL, add 5 drops of diluted detergent. Place sample on magnetic stirrer/hot plate and, while stirring, gently add 20 mL 2N H<sub>2</sub>SO<sub>4</sub>. Boil for 10 min to flush CO<sub>2</sub> (from carbonates and bicarbonates) from sample. Radon also is flushed. Reduce temperature to below boiling, continue stirring, and add 1 mL barium carrier solution. Continue stirring for 30 min. Add 1 mL bromocresol purple indicator solution, 1 mL iron carrier solution, and 5 mL stirred paper pulp/water reagent.

Continue stirring and add 6N NH<sub>4</sub>OH dropwise until there is a distinct color change (yellow to purple). Continue warming and stirring for 30 min. Filter sample through a glass fiber filter (or membrane filter if further analysis is to be done). Quantitatively transfer all precipitate to the filter. Wash precipitate with 25 mL distilled water. Hold filter for 3 h for collected radon progeny to decay. Dry filter at 105°C or under a mild heat lamp.

Count filter for gross alpha activity.

Prepare a reagent blank precipitate to determine reagent alpha activity background.

### 5. Calculations

$$\text{Gross alpha activity, pCi/L} = \frac{C_a - C_b}{EV}$$

where:

\*Gelman Type A/E, Millipore Type AP, or equivalent.

†Rohm and Haas Triton N101 or Triton X100, or equivalent.

$E$  = counter efficiency, cpm/pCi,  
 $V$  = volume analyzed, L,  
 $C_a$  = sample counts per minute, cpm, and  
 $C_b$  = reagent blank, cpm.

## 6. Precision and Bias

In collaborative test with 18 laboratories participating,<sup>2</sup> gross alpha activities for four different samples were calculated with four different alpha-emitting radionuclide standard counting efficiencies. Thorium-230, a pure alpha-emitter, appeared to be the best standard for gross alpha counting efficiency.

Water samples A, B, C, and D contained gross alpha concentrations of 74.0, 52.6, 4.8, and 10.0 pCi/L, respectively, at 3 h after separation of alpha-emitting radionuclides by coprecipitation with iron hydroxide and barium sulfate. Test results using the thorium-230 counting efficiency showed coefficients of variation for repeatability (within laboratory precision) of 7.9, 7.8, 8.7, and 8.8%, respectively, for an average of 8.3%. Coefficients of variation for reproducibility (combined within and between

laboratory precision) of 20.4, 16.8, 18.7, and 18.5%, respectively, were obtained for an average of 18.6%.

A comparison of the 18 laboratory grand average results (calculated with the <sup>230</sup>Th counting efficiency) and known gross alpha particle concentrations showed accuracy indexes of 91.9, 99.4, 122, and 94.5%, respectively, for an average accuracy index of 102%. The *t*-test for bias showed a significant positive bias for Sample C but no significant bias for the other three samples.

## 7. References

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1984. EERF Radiochemistry Procedures Manual. 00-02 Radiochemical Determination of Gross Alpha Activity in Drinking Water by Coprecipitation. EPA-520/5-84-006, USEPA ORP-EERF, Montgomery, Ala.
2. WHITTAKER, E.L. 1986. Test Procedure for Gross Alpha Particle Activity in Drinking Water. Interlaboratory Collaborative Study. EPA-600/4-86/027 July 1986, Pre-issue copy. USEPA EMSL-Las Vegas, Las Vegas, Nev.

# 7120 GAMMA-EMITTING RADIONUCLIDES\*

## 7120 A. Introduction

For information about occurrence of natural and artificial radioactivity, see Section 7110A.1.

\* Approved by Standard Methods Committee, 1997.  
 Joint Task Group: 20th Edition — James W. Mullins (chair).

## 7120 B. Gamma Spectroscopic Method

### 1. General Discussion

*a. Application:* This method describes the use of gamma spectroscopy, using either germanium (Ge) diodes or thallium-activated sodium iodide [NaI(Tl)] crystals, for the measurement of gamma photons emitted from radionuclides present in water. The method is applicable to samples that contain radionuclides emitting gamma photons with energies ranging from about 60 to 2000 keV.

The method can be used for qualitative and quantitative determinations with Ge detectors or for screening and semi-quantitative and semi-qualitative determinations with [NaI(Tl)] detectors. Exact quantitation using NaI is possible for single nuclides or when the gamma emissions are limited to a few well-separated energies. Detection limits for typical counting systems range from a few picocuries (pCi) of gamma activity for a 100-min

count to approximately 100 pCi for a 5-min count, depending on counting geometry and gamma ray energy and abundance.

Determine energy and efficiency calibrations for each detector at several energies between 50 and 2000 keV for the geometries of interest. Gamma ray libraries<sup>1,2</sup> for Ge spectrometry should contain the nuclides and gamma ray lines most likely to be found in water samples. Have computer software available to list the contents of the library and to add more nuclides and gamma ray lines to the library for peak search routines.

*b. Principle:* Because gamma spectroscopy is nondestructive, it is possible to analyze for gamma-emitting radionuclides without separating them from the sample matrix. This technique makes it possible to identify and quantitate gamma-emitting radionuclides when the gross beta screen has been exceeded or it is otherwise necessary to define the contribution of gamma-emitters to the total radioactivity present.

A homogeneous water sample is put into a standard geometry for gamma counting. The counting efficiency for this geometry must have been determined with a mixed energy gamma standard containing known radionuclide activities. Sample portions are counted long enough to meet the required sensitivity of measurement.

The gamma spectrum is printed out and/or stored in the appropriate computer-compatible device for data processing (calculation of sample radionuclide concentrations).

Consult a good text on gamma ray spectrometry<sup>3</sup> for a more detailed discussion.

*c. Sampling and storage:* See Table 7010:I.

*d. Interferences:* Significant interference occurs when a sample is counted with a NaI(Tl) detector and the sample radionuclides emit gamma photons of nearly identical energies. Such interference is greatly reduced by counting the sample with a Ge detector. Higher-energy gammas that predominate may completely mask minor, less energetic photopeaks for both Ge and NaI detectors by increasing the baseline or Compton continuum.

Interferences can occur with Ge detectors from cascade peak summing, which results when two or more gamma rays are emitted in one disintegration, e.g., with cobalt-60, where 1172 and 1333 keV gamma rays are emitted in cascade. These can be detected together to produce a sum peak at 2505 keV or a count in the continuum between the individual peaks and the sum peak, thus causing the loss of counts from one or both of the other two peaks. Cascade summing (as distinct from random summing) is geometry/counting efficiency dependent (but not count rate dependent) with the effect, and hence error, increasing as tighter geometries and more efficient detectors are used. This problem has become more commonplace with the availability of larger, more affordable, and more efficient Ge detectors.

Sample homogeneity is important to gamma count reproducibility and counting efficiency validity. When sample radionuclides are adsorbed on the walls of the counting container, the sample is no longer homogeneous. This problem can be lessened by adding 15 mL 1M HNO<sub>3</sub>/L sample at collection.

Sample density and composition can affect data quality. Prepare efficiency calibration standards in the same geometry and density as the samples. Ensure reproducible sample geometry to limit bias.<sup>4</sup> Plexiglass spacers may be useful in producing consistent sample positions. Random noise produced by vibration or by improper grounding can increase peak width and introduce additional uncertainty.

*e. Safety:* No unusual hazards are associated with the reagents used in this procedure. Follow routine safety precautions, i.e., wear laboratory coat, plastic gloves, and safety glasses and use a hood, when transferring samples and standards and preparing standards when solutions of gamma-emitting radionuclides are used. Cool germanium diodes with liquid nitrogen when they are being used to count samples. Take care when transferring liquid nitrogen from the storage dewar to the dewar used to supply coolant for the germanium diode. Use cryogenic gloves, protective clothing, and eye protection.

## 2. Apparatus

*a. Detector,* large-volume (> 50 cm<sup>3</sup>) germanium-diode detector or 10.2-cm × 10.2-cm (4-in. × 4-in.) thallium-activated sodium iodide crystal [NaI(Tl)] detector. Smaller detectors may be acceptable if inherent limitations, such as reduced counting

efficiency, are taken into account. Be sure that large detectors can accommodate re-entrant (Marinelli) beakers. Germanium (Ge) detectors are preferred because of better photon energy resolution. Despite the possibly higher counting efficiencies of NaI(Tl) detectors, the considerably narrower peak shape from a Ge detector leads to fewer baseline counts, thereby improving peak sensitivity. Preferably do not use NaI(Tl) detectors to make both qualitative and quantitative analyses for samples containing multiple gamma-emitting radioisotopes; however, they are preferred if a single nuclide is being quantitated. Ge detectors may be of either intrinsic (pure) germanium type or lithium-drifted germanium [Ge(Li)] type. Both require use of liquid nitrogen for cooling when bias voltage is applied to the detector. Intrinsic Ge detectors can be stored or shipped at ambient temperatures; Ge(Li) detectors must be cooled with liquid nitrogen at all times to avoid damage to detector.

*b. Gamma-ray spectrometer plus analyzer* with at least 2048 channels for Ge or 256 to 512 for NaI(Tl). See Section 7030B.5.

*c. Counting container,* standard geometry for either detector, e.g., 0.5-L cylindrical container, 0.45-L or 4-L re-entrant (Marinelli)<sup>4</sup> polyethylene beaker. Counting containers of other sizes often are used.

*d. Computer:* Use a data acquisition system including a computer (PC, networked-PCs, or larger) supplied with software to automate the processing of raw spectral data as outlined in Sections 4 and 5, below. Software should contain algorithms to: perform energy and efficiency calibrations; locate peaks (deconvoluting multiplets as needed; that may require a separate routine[s] for low-resolution NaI counting data); perform peak integrations; perform nuclide searches; do activity calculations (result, uncertainty, and MDA); and manage the library reference information needed to support these actions.

*e. High-voltage power supply.*

*f. Amplifier,* suitable for spectroscopy with gain and shaping time adjustments and baseline restoration.

*g. Analog-to-digital converter and spectrum storage device.*

## 3. Reagents

*a. Distilled or deionized water,* radon-free, for standard preparation and sample dilution.

*b. Nitric acid, HNO<sub>3</sub>, 1N.*

## 4. Procedure

*a. Energy calibration:* Use NIST or NIST-traceable, or equivalent standards. For a Ge system, adjust analyzer amplifier gain and analog-to-digital converter zero offset to locate each photopeak in its appropriate channel. A 0.5- or 1.0-keV per channel calibration is recommended. If the system is calibrated for 1 keV per channel with channel zero representing 0 keV, the energy will be equal to the channel number. Check and adjust the pole zero cancellation of the amplifier output if required.<sup>5</sup>

Use a standard containing a mixture of gamma energies from about 100 to 2000 keV for energy calibration. Multiline gamma standards can be obtained commercially or can be prepared by the user. Some laboratories use radium-226 and daughters in equilibrium or europium-152 for this purpose. NIST SRM 4275 is a solid source that is useful for energy calibration and routine monitoring of instrument performance. Solid sources prepared

on plastic mounts are stable and are recommended. Count energy calibration standards long enough to minimize uncertainty due to counting statistics; as a rule of thumb accumulate 10 000 counts in each photopeak area resulting in a counting error of 1%.

For a NaI(Tl) system, a 10- or 20-keV per channel calibration is adequate. A solid multipeak standard source, e.g., bismuth-207, is satisfactory for energy calibration.

*b. Efficiency calibration:* Use NIST, NIST-traceable, or equivalent standards with minimal cascade summing concerns. Use a known amount of a multipeak standard or various radionuclides that emit gamma photons with energies well spaced and distributed over the normal range of analysis; put these into each container geometry and gamma count for a photopeak spectrum accumulation. Count efficiency calibration standards long enough to minimize uncertainty due to counting statistics; as a rule of thumb accumulate 10 000 counts in each photopeak area, resulting in a counting error of 1%.

Determine counting efficiencies for the various gamma energies (photopeaks) from the activity counts of the known-value samples as follows:

$$E = \frac{C}{A \times B}$$

where:

$E$  = efficiency (expressed as counts per minute/gamma rays emitted per minute),

$C$  = net count rate, cpm (integrated counts in the photopeak above the baseline continuum divided by the counting duration),

$A$  = activity of radionuclide added to the given geometry container, dpm (corrected for decay, if necessary), and

$B$  = gamma-ray abundance of the radionuclide being measured, gammas/disintegration.

Plot counting efficiency against gamma energy for each container geometry and for each detector that is to be used. For NaI systems, prepare a library of radionuclide spectra from counts of known radionuclide-water sample concentrations at standard sample geometries.

*c. Sample measurement:* Measure sample portion in a standard-geometry container calibrated as directed in ¶s *a* and *b* above. Place container and sample on a shielded Ge or NaI(Tl) detector and gamma count for a period of time that will meet the required sensitivity. Print gamma spectrum and/or store the spectrum on the appropriate computer-compatible device.

## 5. Calculations

The equations (Sections 4 and 5) describe the fundamental relationships between the defined variables and could be used if the calculations were to be performed manually. NaI spectral data, with their high probability for peak overlap due to low resolution, often require complex peak unfolding routines. Modern gamma spectroscopy systems rely on vendor-supplied computer software to process the 256 to 500-plus (for NaI systems) and up to 8000 (for Ge systems) data points. The supplied software should be accompanied by documentation describing the algorithms, which must incorporate the fundamental relationships presented here.

Determine isotopes indicated by the gamma spectrum as follows: Identify all photopeak energies; integrate photopeak re-

gions of the spectrum and subtract the area under the baseline continuum to determine the true photopeak area, and identify isotopes by their appropriate photopeaks, and ratios to each other when more than one gamma photon is emitted by an isotope.

Calculate the sample radionuclide concentrations as follows:

$$A' = \frac{C}{2.22 \times B \times E \times V \times e^{-\lambda t}}$$

where:

$A'$  = sample radionuclide concentration, pCi/L,

$V$  = sample volume, L,

$e^{-\lambda t}$  = decay factor (corrected to sample collection time), with  $\lambda$  = decay constant for the gamma-emitting radionuclide being analyzed, and  $t$  = duration of time from sample collection to counting,

2.22 = conversion factor from dpm to pCi,

and  $B$ ,  $C$ , and  $E$  are as defined in ¶ 4a above. Calculate the  $2\sigma$  counting error term for gamma-emitters as follows:

$$2\sigma, \text{ pCi/L} = \frac{2 \sqrt{\frac{C + 2G}{t_c}}}{2.22 \times B \times E \times V \times e^{-\lambda t}}$$

where:

$G$  = photopeak area below continuum, cpm,

$t_c$  = counting duration, min,

and other terms are as defined above.

Report the result and counting error together in the form:

$$X \pm 2\sigma, \text{ pCi/L}$$

Vendor-supplied software usually can calculate a Total Propagated Uncertainty (TPU). If so, the  $2\sigma$  value reflects the total uncertainty and not just the counting error. The vendor-supplied software also should calculate a Minimum Detectable Concentration (MDC) (see Section 7020C.3 for a general discussion). Report concentration, uncertainty, and MDC for each sample.

## 6. Quality Control

See Section 7020.

*a. Duplicates:* Make duplicate analyses for one out of every ten samples. (See Section 7020A.3c.) If it is known or strongly suspected that the sample(s) contain no detectable gamma-emitting radionuclides, do not use the sample(s) for duplicate analysis. In such a case, rely on the results of known-addition samples as described below. If desired, analyze known-addition samples in duplicate.

*b. Known-addition sample:* Analyze a known-addition sample for one out of every ten samples.

*c. Background:* See Section 7030B.5c3) and 7020A.3b. Find and identify any background lines that may be present. If present, subtract the background counts line by line from the sample photopeaks. Even if background does not significantly affect results, monitor it to ensure system integrity. Weekly background counts for durations longer than normal sample counting durations may be needed to quantify low-level activity from nuclides such as cobalt-60.

TABLE 7120:I. GAMMA-EMITTERS RECOVERY AND PRECISION ESTIMATE REGRESSION LINE EQUATIONS

Nuclide	Recovery	$S_r$ pCi/L	$S_R$ pCi/L
Iodine-131*	$y = 1.010x - 0.31$	$y = 0.033x + 1.68$	$y = 0.071x + 2.41$
Cesium-137	$y = 1.012x + 0.62$	$y = 0.018x + 1.49$	$y = 0.043x + 1.97$
Cesium-134	$y = 0.919x + 0.56$	$y = 0.023x + 1.30$	$y = 0.053x + 1.70$
Barium-133	$y = 0.966x + 0.18$	$y = 0.021x + 1.70$	$y = 0.054x + 2.35$
Ruthenium-106	$y = 0.928x + 2.33$	$y = 0.051x + 3.68$	$y = 0.072x + 7.28$
Zinc-65	$y = 1.023x + 0.11$	$y = 0.026x + 2.81$	$y = 0.052x + 3.74$
Cobalt-60	$y = 0.985x + 0.81$	$y = 0.021x + 1.40$	$y = 0.043x + 1.91$
Chromium-51	$y = 0.997x + 0.30$	$y = 0.058x + 3.99$	$y = 0.081x + 8.67$

\* Analyzed singly as a separate study from the other gamma-emitters.

d. *Energy calibration:* Check the energy calibration daily or before each use with a multi-line source as in ¶ 4a above.

e. *Efficiency check:* Check detector efficiency daily or before each use with a stable multiline source in a reproducible geometry.

f. *Records:* Collect and maintain results from duplicate pairs and check standards. Include date, results, analyst's name, and any comments relevant to the evaluation of these data.

7. Precision and Bias

The precision of an individual measurement by gamma spectrometry can be improved by increasing sample counting duration. It may be necessary to gamma count for as much as 1000 min to reach desired precision. Other ways of increasing precision of an individual measurement are to increase sample volume, use a more efficient detector, or concentrate the sample. To obtain accurate results, calibrate carefully and use standardized radionuclides at the proper activity and purity levels.

Collaborative test data for a closely defined technique or procedure were not available for gamma-emitters in water. However, data from USEPA's Environmental Radioactivity Performance Evaluation Studies Program are presented here. Table 7120:II is a summary of the recovery, within-laboratory variance,  $S_r$ , and total-error variance,  $S_R$ , regression line equations for each gamma-emitter studied. These data are from the analysis of

gamma-emitting radionuclides in standard samples by participants in the program from 1981 to 1998. It is not possible to say how many investigators used NaI(Tl) detectors in the early years of the data collection period. It is believed that most, if not all, are now using germanium detectors, and that the data are comparable among all participating laboratories. The gamma spectral data from the Gamma Performance Evaluation and Blind Samples from February 1981 through November 1998 (April 1981 through September 1998 for iodine-131) were summarized by study and the data were arrayed for analyses. See Table 7120:II.

Regression equations were generated for: recovery, grand average of each study; estimate of precision, standard deviation ( $1 \sigma$ ) of the mean value of each study,  $S_x$ ; within-laboratory standard deviation ( $1 \sigma$ ), also known as the repeatability or random error,  $S_r$ ; between-laboratory standard deviation ( $1 \sigma$ ), also known as the systematic error,  $S_L$ ; and total error from within and between labs, also known as reproducibility,  $S_R$ .  $S_R$  equals the square root of the sum of the variance of the within-laboratory error and the between-laboratory error, i.e., the reproducibility variance is equal to the sum of the random variance and the systematic variance.

$$S_R^2 = S_r^2 + S_L^2$$

$$S_R = \sqrt{S_r^2 + S_L^2}$$

TABLE 7120:II. GAMMA-EMITTERS STUDY: SUMMARY OF PARTICIPANTS

Nuclide	No. of Studies*	Concentration Range pCi/L	No. of Participants†	No. of Acceptables‡	No. where $\sigma \neq 0$ §
Iodine-131	37	6.1-148	42-119	39-115	34-105
Cesium-137	84	4-197	45-197	43-180	30-158
Cesium-134	84	2-105	17-196	15-183	8-165
Barium-133	23	25-745	118-192	107-181	94-156
Ruthenium-106	35	15-252	20-193	17-179	11-135
Zinc-65	47	10-300	61-195	55-182	50-163
Cobalt-60	74	8-99	53-196	52-183	48-165
Chromium-51	19	21-302	34-124	32-121	16-112

\* Samples with concentrations equal to 0 pCi/L were not included.

† Total number of participants in study, even though all of the data may not have been used.

‡ Number of participants used in calculating grand average and standard deviation of grand average.

§ Participants reporting within laboratory variance equal to zero were not used in calculating the study within-laboratory, between-laboratory, and total error variance.

## 8. References

1. U.S. DEPARTMENT OF ENERGY. 1992. EML Procedures Manual, 27th ed. (rev.). HASL 300, 4.5.2.3, Environmental Measurements Lab., U.S. Dep. Energy, New York, N.Y.
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5. AMERICAN NATIONAL STANDARDS INSTITUTE. 1991. Calibration and Use of Germanium Detectors for Measurements of Gamma-Ray Emission of Radionuclides. ANSI N42.14-1991 (revision of ANSI N42.14-1978). American National Standards Inst., New York, N.Y.

## 9. Bibliography

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## 7500-Cs RADIOACTIVE CESIUM\*

## 7500-Cs A. Introduction

Radioactive cesium has been considered one of the more hazardous radioactive nuclides produced in nuclear fission. Upon

ingestion, like potassium, cesium distributes itself throughout the soft tissue and has a relatively short residence time in the body. Half-lives of  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  are 2 and 30 years, respectively, both being beta- and gamma-emitters.

\* Approved by Standard Methods Committee, 2000.

## 7500-Cs B. Precipitation Method

## 1. General Discussion

*Principle:* If the activity of cesium is high, radioactive cesium can be determined directly by gamma-counting a large liquid sample (4 L) or the sample can be evaporated to dryness and counted. For lower-level environmental samples, add cesium carrier to an acidified sample and collect the cesium as phosphomolybdate. This is purified and precipitated as  $\text{Cs}_2\text{PtCl}_6$  for counting. If total radiocesium determined by beta-counting exceeds 30 pCi/L, determine  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  by gamma spectrometry.

## 2. Apparatus

- a. *Magnetic stirrer* with TFE-coated magnet bar.
- b. *Centrifuge*, bench-size clinical, and centrifuge tubes.
- c. *Filter papers\** and *glass fiber filter*, 2.4 cm diam.

d. *pH paper*, wide range, 1 to 11 pH.

e. *Filtering apparatus:* See Section 7500-Sr.B.2c.

f. *Counting instruments:* Use either a low-background beta counter (see Section 7030B.1) or a gamma spectrometer (see Section 7030B.5).

## 3. Reagents

a. *Ammonium phosphomolybdate reagent*,  $\text{H}_{12}\text{Mo}_{12}\text{N}_3\text{O}_{40}\text{P}$ : Dissolve 100 g molybdic acid (85%  $\text{MoO}_3$ ) in a mixture of 240 mL distilled water and 140 mL conc ammonium hydroxide ( $\text{NH}_4\text{OH}$ ). When solution is complete, filter and add 60 mL conc nitric acid ( $\text{HNO}_3$ ). Separately mix 400 mL conc  $\text{HNO}_3$  and 960 mL distilled water. After both solutions cool to room temperature, add, with constant stirring, the  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  solution to the  $\text{HNO}_3$  solution. Let stand for 24 h. Filter† and discard insoluble material.

\* Whatman No. 41, 9 cm diam; Whatman No. 42, 2.4 cm diam; or equivalent.

† Whatman No. 42 filter paper or equivalent.

Collect filtrate in a 3-L beaker and heat to 50 to 55°C (never above 55°C). Remove from heating unit. Add 25 g sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) dissolved in 100 mL distilled water, stir occasionally for 15 min, and let settle (approximately 30 min). Filter and wash precipitate with 1% potassium nitrate ( $\text{KNO}_3$ ) and finally with distilled water. Dry precipitate and paper at 100°C for 3 to 4 h. Transfer solid  $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$  to a weighing bottle and store in a desiccator.

b. *Chloroplatinic acid, 0.1M*: Dissolve 51.8 g  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in distilled water and dilute to 1000 mL.

c. *Cesium carrier*: Dissolve 1.267 g cesium chloride ( $\text{CsCl}$ ) in distilled water and dilute to 100 mL; 1 mL = 10 mg Cs.

d. *Calcium chloride, 3M*: Dissolve 330 g  $\text{CaCl}_2$  in distilled water and dilute to 1000 mL.

e. *Ethanol, 95%*.

f. *Hydrochloric acid, HCl, conc, 6N, 1N*.

g. *Sodium hydroxide, NaOH, 6N*.

#### 4. Procedure

a. To a 1-L sample, add 1.0 mL cesium carrier and enough conc HCl to make the solution about 0.1N HCl (about 8.6 mL). Slowly add 1 g  $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$  and stir for 30 min using a magnetic stirrer at 800 rpm. Let precipitate settle for at least 4 h and discard supernatant by decanting or using suction (provided by an inverted glass funnel connected to a vacuum source). Using a stream of 1N HCl, quantitatively transfer precipitate to a centrifuge tube. Centrifuge and discard supernatant. Wash precipitate with 20 mL 1N HCl and discard wash solution.

b. Dissolve precipitate by dropwise addition of 3 to 5 mL 6N NaOH. Heat over a flame for several minutes to remove ammonium ions. (Moist pH paper turns green as long as  $\text{NH}_3$  vapors are evolved.) Dilute to 20 mL with distilled water. Add 10 mL 3M  $\text{CaCl}_2$  and adjust to pH 7 with 6N HCl to precipitate

$\text{CaMoO}_4$ . Stir, centrifuge, and filter supernatant into a 50-mL centrifuge tube. Wash precipitate remaining in the original centrifuge tube with 10 mL distilled water, filter through the same filter paper, and combine the wash with filtrate. Discard precipitate and filter paper.

c. Add 2 mL 0.1M  $\text{H}_2\text{PtCl}_6$  and 5 mL ethanol. Cool and stir in ice bath for 10 min. Using distilled water transfer to a tared glass-fiber filter. Wash with successive portions of distilled water, 1N HCl, and ethanol.

d. Dry at 110°C for 30 min, cool, weigh, mount on a nylon disk and ring with polyester plastic cover, and beta-count or gamma-scan for  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$ .

#### 5. Calculation

Calculate the concentration of radiocesium as follows:

$$\text{Cs, pCi/L} = \frac{C}{2.22 \times E V R}$$

where:

C = net count rate, cpm,

E = counter efficiency,

V = volume of sample, L, and

R = fractional chemical yield

$$= \frac{\text{recovered Cs}_2\text{PtCl}_6, \text{ mg} \times 0.3945}{\text{added Cs carrier, mg}}$$

#### 6. Bibliography

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‡ Whatman No. 41 filter paper or equivalent.

§ Mylar or equivalent.

## 7500-I RADIOACTIVE IODINE\*

### 7500-I A. Introduction

#### 1. Occurrence and Significance

Radioiodine that results from testing nuclear devices or is released during use and processing of reactor fuels is a major concern in radioactivity monitoring. Fission products may contain iodine-129 through iodine-135. Iodine-129 has a half-life of  $1.6 \times 10^7$  years but a relatively low specific activity ( $1.73 \times 10^{-4}$  Ci/g for  $^{129}\text{I}$  as compared to  $1.24 \times 10^5$  Ci/g for  $^{131}\text{I}$ ). The

half-life of  $^{131}\text{I}$  is 8 d while for the other isotopes it is shorter (35 min to 21 h). At present, only  $^{131}\text{I}$  is likely to be found in water. When ingested or inhaled, it concentrates in the thyroid gland and may cause thyroid cancer.

#### 2. Selection of Method

Of the three methods, the precipitation method (B) is preferred because it is simple and involves the least time. Method C, in which iodide is concentrated by absorption on an anion resin, purified, and counted in a beta-gamma coincidence system, is sensitive and

\* Approved by Standard Methods Committee, 2000.

accurate. Method D uses distillation. With each method it is possible to reach the EPA recommended detection limit of 1 pCi  $^{131}\text{I}$ /L.

### 3. Bibliography

KLEINBERG, J. & G.A. COWAN. 1960. The Radiochemistry of Fluorine, Chlorine, Bromine and Iodine. Rep. NAS-NS-3005, U.S. Atomic Energy Comm.

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## 7500-I B. Precipitation Method

### 1. General Discussion

*Principle:* Iodate carrier is added to an acidified sample and, after reduction with  $\text{Na}_2\text{SO}_3$  to iodide, the  $^{131}\text{I}$  is precipitated with  $\text{AgNO}_3$ . The precipitate is dissolved and purified with zinc powder and  $\text{H}_2\text{SO}_4$  and the solution is reprecipitated as  $\text{PdI}_2$  for counting.

### 2. Apparatus

*a. Counting instrument:* Low-background beta counter (see Section 7030B.1) or gamma spectrometer (7030B.5).

*b. Fine-fritted glass funnel.*

*c. Filter apparatus:* Two-piece filter funnel with filtering equipment.\*

*d. Filter materials:* Filter paper;† glass-fiber filter, 2.4 cm diam; or 0.8- $\mu\text{m}$  pore-diam membrane filter, 4.7 cm diam.

### 3. Reagents

*a. Ammonium hydroxide,  $\text{NH}_4\text{OH}$ , 6N.*

*b. Ethanol, 95%.*

*c. Hydrochloric acid, HCl, 6N.*

*d. Iodate carrier:* Dissolve 1.685 g  $\text{KIO}_3$  in distilled water and dilute to 100 mL. Store in dark flask; 1 mL = 10 mg I.

*e. Nitric acid,  $\text{HNO}_3$ , conc.*

*f. Palladium chloride,  $\text{PdCl}_2$ :* Dissolve 3.3 g  $\text{PdCl}_2$  in 100 mL 6N HCl; 1 mL = 20 mg Pd.

*g. Silver nitrate,  $\text{AgNO}_3$ , 0.1M:* Dissolve 17 g  $\text{AgNO}_3$  in distilled water and dilute to 1000 mL. Store in dark flask.

*h. Sodium sulfite,  $\text{Na}_2\text{SO}_3$ , 1M (freshly prepared):* Dissolve 6.3 g  $\text{Na}_2\text{SO}_3$  in distilled water and dilute to 50 mL.

*i. Sulfuric acid,  $\text{H}_2\text{SO}_4$ , 2N.*

*j. Zinc, powder, reagent grade.*

### 4. Procedure

*a.* To a 2000-mL sample, add 15 mL conc  $\text{HNO}_3$  and 1.0 mL iodate carrier. Mix well. Add 4 mL freshly prepared 1M  $\text{Na}_2\text{SO}_3$  and stir for 30 min. Add 20 mL 0.1M  $\text{AgNO}_3$ , stir for 1 h, and let settle for 1 h. Decant and discard as much of the supernatant

as possible. Filter remainder through a glass-fiber filter and discard filtrate.

*b.* Transfer filter to a centrifuge tube and slurry with 10 mL distilled water. Add 1 g zinc powder and 2 mL 2N  $\text{H}_2\text{SO}_4$  and stir frequently for at least 30 min. Filter, with vacuum, through a fine-fritted glass funnel and collect filtrate in an erlenmeyer flask. Wash both residue and filter with a minimum quantity of distilled water and add wash water to filtrate. Discard residue.

*c.* Add 2 mL 6N HCl and heat in water bath at 80°C for 10 min. Add 1 mL 0.2M  $\text{PdCl}_2$  and digest for at least 5 min. Centrifuge and discard supernatant.

*d.* Dissolve precipitate in 5 mL 6N  $\text{NH}_4\text{OH}$  and heat in boiling water bath for 5 min. Filter through a glass-fiber filter and collect filtrate in a centrifuge tube. Discard filter and residue.

*e.* Neutralize filtrate with 6N HCl, add 2 mL in excess, and heat in a water bath. Add 1 mL 0.2M  $\text{PdCl}_2$  to reprecipitate  $\text{PdI}_2$  and digest for 10 min. Cool slightly and transfer to a tared filter with distilled water. Wash successively with 5-mL portions of distilled water and 95% ethanol. Dry in a vacuum oven at 60°C for 1 h, weigh precipitate, mount, and beta-count.

*f.* If final  $\text{PdI}_2$  precipitate on a glass-fiber filter is counted in a low-background beta counter, the background counting rate is relatively high (about 1.3 cpm). If precipitate is collected on a 0.8- $\mu\text{m}$  membrane filter and dried for 30 min at 70°C it may be counted in a beta-gamma coincidence scintillation system with a background rate of less than 0.1 cpm.

If a low-background counter is used, confirm identity of  $^{131}\text{I}$  by recounting precipitate after about 1 week to check the half-life.

### 5. Calculation

Calculate concentration of radioiodine as follows:

$$^{131}\text{I, pCi/L} = \frac{C}{2.22 \times \text{EVR} \times A}$$

where:

*C* = net count rate, cpm,

*E* = counting efficiency of  $^{131}\text{I}$  as function of mass of  $\text{PdI}_2$  precipitate,

*V* = volume of sample, L,

*R* = fractional chemical yield

recovered  $\text{PdI}_2 \times 0.0704$   
=  $\frac{\text{added iodine carrier}}{\text{added iodine carrier}}$ , and

*A* =  $^{131}\text{I}$  decay factor for the time interval between sample collection and measurement.

\* Fisher Filtrator or equivalent.

† Whatman No. 42 or equivalent.

## 6. Bibliography

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1980. Prescribed Procedures for Measurement of Radioactivity in Drinking Water. EPA-600/4-

80-032, Environmental Monitoring and Support Lab., Cincinnati, Ohio.

## 7500-I C. Ion-Exchange Method

## 1. General Discussion

*Principle:* A known amount of inactive iodine in the form of KI is added as a carrier and the sample is taken through an oxidation-reduction step using hydroxylamine and sodium bisulfite to convert all iodine to iodide. Iodine, as the iodide, is concentrated by absorption on an anion-exchange column. Following a NaCl wash, iodine is eluted with sodium hypochlorite. Iodine in the iodate form is reduced to  $I_2$ , extracted into  $CCl_4$ , and back-extracted as iodide into water. The iodine finally is precipitated as  $PdI_2$ .

## 2. Apparatus

- Counting instrument:* Low-background beta counter (Section 7030B.1) or gamma spectrometer (7030B.5).
- Chromatographic column,* 2 cm  $\times$  15 cm.
- Vacuum filter holder,* 2.5 cm<sup>2</sup> filter area.
- Filter paper,\** 2.4 cm diam.
- Vacuum oven.*

## 3. Reagents

- Iodine carrier:* Weigh approximately 13 g dried KI to the nearest 0.1 mg. Dissolve in a 1-L volumetric flask containing 100 mL distilled water. Add 10 mL 1M NaHSO<sub>3</sub> and dilute to mark with distilled water. Concentration of carrier I, mg/L = g KI  $\times$  0.7644.
- Ethanol,* absolute.
- Hydroxylamine hydrochloride, 1M:* Dissolve 6.95 g NH<sub>2</sub>OH  $\cdot$  HCl in distilled water and dilute to 100 mL.
- Nitric acid, HNO<sub>3</sub>, conc, 8N, 1.6N.*
- Sodium bisulfite, 1M:* Dissolve 1.04 g NaHSO<sub>3</sub> in distilled water and dilute to 10 mL.
- Sodium hydroxide, 12N:* Dissolve 480 g NaOH in distilled water and dilute to 1 L.
- Sodium hypochlorite, NaOCl, 5%:* Use available household bleach.
- Anion-exchange resin.†*
- Carbon tetrachloride, CCl<sub>4</sub>,* reagent grade.
- Hydrochloric acid, HCl, 3N, 1N.*
- Palladium chloride:* Dissolve 3.3 g PdCl<sub>2</sub> in 100 mL 6N HCl; 1 mL = 20 mg Pd.
- Sodium chloride, NaCl, 2M:* Dissolve 117 g NaCl in distilled water and dilute to 1 L.

\* Whatman No. 42 or equivalent.

† Dowex 1  $\times$  8, 50-100 mesh, chloride form, or equivalent.

*m. Hydroxylamine hydrochloride wash solution:* Add 20 mL conc HNO<sub>3</sub> and 20 mL 1M NH<sub>2</sub>OH  $\cdot$  HCl to 100 mL distilled water.

## 4. Procedure

a. To 1 L sample in a beaker add, while stirring, 2.0 mL iodine carrier and 5 mL 5% NaOCl, and heat for 2 to 3 min to complete oxidation. After the interchange reaction (2 to 3 min), slowly add 5 mL conc HNO<sub>3</sub>. Add 25 mL 1M NH<sub>2</sub>OH  $\cdot$  HCl and stir. Let reaction go on for a few seconds, add 10 mL 1M NaHSO<sub>3</sub>, and adjust pH to 6.5 with 12N NaOH or 1.6N HNO<sub>3</sub>. Stir thoroughly for a few minutes. (Stir samples containing a large amount of organic material, such as muddy water, for 45 min.) Filter through a glass-fiber filter to remove suspended matter. Discard residue.

b. Pour 20 mL anion-exchange resin into a column and wash sides down with distilled water. Pass sample through ion-exchange column at a flow rate of 20 mL/min. Discard effluent. Wash column with 200 mL distilled water and then with 100 mL 2M NaCl at a flow rate of 4 mL/min. Discard wash solutions.

c. Add 50 mL 5% NaOCl in 10- to 20-mL increments, stirring the resin as needed to eliminate gas bubbles, and maintain a flow rate of 2 mL/min. To the eluted volume of 50 to 60 mL, collected in a beaker, carefully add 10 mL conc HNO<sub>3</sub> to make sample 2 to 3N in HNO<sub>3</sub> and transfer to a separatory funnel. (Add acid slowly with stirring until vigorous reaction subsides.)

d. Add 50 mL CCl<sub>4</sub> and 10 mL 1M NH<sub>2</sub>OH  $\cdot$  HCl. Extract iodine into organic phase by shaking for about 2 min. Let phases separate and transfer organic phase to another separatory funnel. Add 25 mL CCl<sub>4</sub> and 5 mL 1M NH<sub>2</sub>OH  $\cdot$  HCl to the first separatory funnel and shake for 2 min. Combine organic phase with the one obtained from the first extraction. Discard aqueous phase. Add 20 mL NH<sub>2</sub>OH  $\cdot$  HCl wash solution to the organic phase and shake for 2 min. Let phases separate and transfer organic phase to a clean separatory funnel. Discard wash solution.

e. Add 25 mL distilled water and 10 drops 1M NaHSO<sub>3</sub> to organic phase. Shake for 2 min, let phases separate, and discard organic phase. Transfer aqueous phase to a beaker. Add 10 mL 3N HCl. Using a stirrer-hot plate, boil and stir the sample until it evaporates to 10 to 15 mL or begins to turn yellow.

f. Add 1.0 mL PdCl<sub>2</sub> solution dropwise. Rinse sides of beaker with 1N HCl and add sufficient 1N HCl to make a volume of 30 mL. Continue stirring until cool. Place beaker in a stainless steel tray and store at about 4°C overnight.

g. Filter through a tared filter mounted in a filter holder. Wash residue with 1N HCl and then with absolute alcohol. Dry in a vacuum oven at 60°C for 1 h. Cool in a desiccator, weigh

precipitate, then seal it between polyester tape and polyester plastic film,‡ with the film over the precipitate. Count with a beta-gamma coincidence system.

### 5. Calculation

Calculate  $^{131}\text{I}$ , pCi/L, as in B.5.

‡ Mylar or equivalent.

## 7500-I D. Distillation Method

### 1. General Discussion

**Principle:** Iodine carrier is added to an acidified sample and iodine is distilled into a caustic solution. The distillate is acidified and the iodine is extracted into  $\text{CCl}_4$ . After back-extraction as iodide, the iodine is purified as  $\text{PdI}_2$  for counting.

### 2. Apparatus

- Distillation apparatus and 3-L round-bottom flask.
- Separatory funnel, 60 mL.
- Filter apparatus: Two-piece filter funnel with filtering equipment.\*
- Filter paper: See B.2d.

### 3. Reagents

- Ammonium hydroxide,  $\text{NH}_4\text{OH}$ , conc.
- Carbon tetrachloride,  $\text{CCl}_4$ .
- Ethanol, 95%.
- Hydrochloric acid,  $\text{HCl}$ , 6N, 1N.
- Iodide carrier: Dissolve 2.616 g KI in distilled water, add 2 drops  $\text{NaHSO}_3$ , and dilute to 100 mL. Store in dark flask. 1 mL = 20 mg I.
- Nitric acid,  $\text{HNO}_3$ , conc.
- Palladium chloride: Dissolve 3.3 g  $\text{PdCl}_2$  in 100 mL 6N  $\text{HCl}$ ; 1 mL = 20 mg Pd.
- Sodium bisulfite,  $\text{NaHSO}_3$ , 1M: Dissolve 5.2 g  $\text{NaHSO}_3$  in distilled water and dilute to 50 mL. Prepare only in small quantities.
- Sodium hydroxide,  $\text{NaOH}$ , 0.5N.
- Sodium nitrite,  $\text{NaNO}_2$ , 1M: Dissolve 69 g  $\text{NaNO}_2$  in distilled water and dilute to 1 L.
- Sulfuric acid,  $\text{H}_2\text{SO}_4$ , 12N.
- Tartaric acid,  $\text{C}_4\text{H}_6\text{O}_6$ , 50%: Dissolve 50 g  $\text{C}_4\text{H}_6\text{O}_6$  in distilled water and dilute to 100 mL.

### 4. Procedure

- To a 2000-mL sample in a 3-L round-bottom flask, add 15 mL 50%  $\text{C}_4\text{H}_6\text{O}_6$  and 1.0 mL iodide carrier. Mix well, cautiously

\* Fisher Filtrator or equivalent.

### 6. Bibliography

- AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1972 Book of ASTM Standards. Part 23. D 2334-68, American Soc. Testing & Materials, Philadelphia, Pa.
- GABAY, J.J., C.J. PAPERIELLO, S. GOODYEAR, J.C. DALY & J.M. MATUSZEK. 1974. A method of determining  $^{129}\text{I}$  in milk and water. *Health Phys.* 26:89.

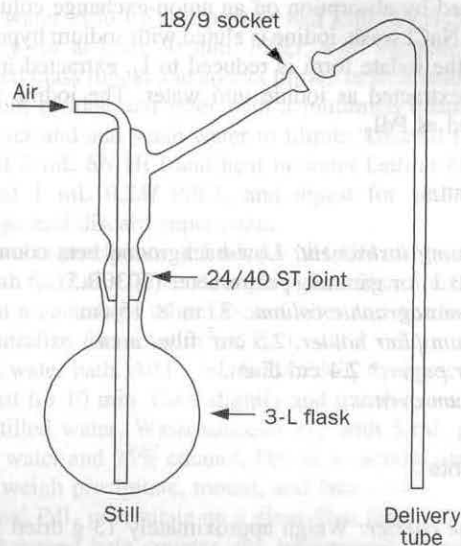


Figure 7500-I:1. Distillation apparatus for iodine analysis (not to scale).

add 25 mL cold conc  $\text{HNO}_3$ , and close distillation apparatus (Figure 7500-I:1).

- Connect an air line to still inlet, adjust flow rate to about 2 bubbles/s, and distill for at least 15 min into 15 mL 0.5N  $\text{NaOH}$ . Cool and transfer  $\text{NaOH}$  solution to a 60-mL separatory funnel. Discard still residue.

- Adjust distillate to slightly acid with 1 mL 12N  $\text{H}_2\text{SO}_4$  and oxidize with 1 mL 1M  $\text{NaNO}_2$ . Add 10 mL  $\text{CCl}_4$  and shake for 1 to 2 min. Transfer organic layer to a clean 60-mL separatory funnel containing 2 mL 1M  $\text{NaHSO}_3$ .

- Add 5 mL  $\text{CCl}_4$  and 1 mL 1M  $\text{NaNO}_2$  to original separatory funnel containing the aqueous layer and shake for 2 min. Combine organic fractions. Repeat and discard aqueous layer.

- Shake separatory funnel thoroughly until  $\text{CCl}_4$  layer is decolorized; let phases separate and transfer aqueous layer to a centrifuge tube. Add 2 mL 1M  $\text{NaHSO}_3$  to the separatory funnel containing  $\text{CCl}_4$  and shake for several minutes. When phases separate, add aqueous layer to centrifuge tube. Add 1 mL distilled water to separatory funnel and shake for several minutes. When the phases separate, add aqueous layer to centrifuge tube. Discard organic layer.

f. To combined aqueous fractions, add 2 mL 6N HCl and heat in water bath at 80°C for 10 min. Add 1.0 mL PdCl<sub>2</sub> solution dropwise, with stirring, and digest for 15 min.

g. Cool, stir precipitate, and transfer to a tared filter mounted in a two-piece funnel. Let precipitate settle by gravity for uniform deposition, then apply suction. Wash residue with 10 mL 1N HCl, 10 mL distilled water, and then with 10 mL 95% ethanol. Dry in a vacuum oven at 60°C for 1 h. Cool in desiccator, weigh, mount, and make beta count.

## 7500-Ra

### 7500-Ra A.

#### 1. Occurrence

Radium is a radioactive member of the alkaline earth family and is widely disseminated throughout the earth's crust. It has four naturally occurring isotopes—11.43-d radium-223, 3.66-d radium-224, 1600-year radium-226, and 5.75-year radium-228. Radium-223 is a member of the uranium-235 series, radium-224 and radium-228 are members of the thorium series, and radium-226 is a member of the uranium-238 series. The contribution of radium-228 (a beta-emitter) to the total radium alpha activity is negligible because of the 1.9-year half-life of its first alpha-emitting daughter product, thorium-228. The other three radium isotopes are alpha-emitters; each gives rise to a series of relatively short-lived daughter products, including three more alpha-emitters.

Because of their longer half-lives and health significance, radium-226 and radium-228 are the most important radium isotopes found in water. Even though it has a short half-life, radium-224 in groundwater is important in certain geographical areas because of the geochemistry and the short delivery time of well water to consumers. Radium is a bone-seeker and high concentrations in bone can lead to malignancies.

\* Approved by Standard Methods Committee, 2001.

Joint Task Group: Bahman Parsa (chair), Edmond J. Baratta, Loren A. Berge, John G. Griggs, Nancy E. Kinner, David E. McCurdy, James W. Mullins, Stephen H. Pia.

## 7500-Ra B. Precipitation Method

#### 1. General Discussion

a. *Application:* This method is suitable for determination of the alpha-emitting isotopes of radium.

b. *Principle:* Because of the difference in half-lives of the nuclides in the series including the alpha-emitting Ra isotopes, these isotopes can be identified by the rate of ingrowth and decay of their daughters in a barium sulfate precipitate.<sup>1-3</sup> The ingrowth of alpha activity from radium-226 increases at a rate

#### 5. Calculation

Calculate the concentration of radioiodine as given in B.5.

#### 6. Bibliography

AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1972 Book of ASTM Standards. Part 23. D 2334-68, American Soc. Testing & Materials, Philadelphia, Pa.

## RADIUM\*

### Introduction

#### 2. Selection of Method

The principles of the four common methods for measuring radium are (a) alpha counting of barium-radium sulfate precipitate that has been purified, (b) measurement of radon-222 produced from radium-226 in a sample or in a soluble concentrate isolated from the sample, (c) measurement of actinium-228 from radium-228 by beta-counting and (d) gamma counting the 238.6-keV gamma ray from the lead-212 daughter of radium-224.

The determination of radium by precipitation (Method B) includes all alpha-emitting radium isotopes; it is a screening technique particularly applicable to drinking water. As long as the concentration of radium is less than the <sup>226</sup>Ra plus <sup>228</sup>Ra drinking water standard, examination by a more specific method is seldom needed. This method also is applicable to sewage and industrial wastes, provided that steps are taken to destroy organic matter and eliminate other interfering ions (see Gross Alpha and Gross Beta Radioactivity, Section 7110). However, avoid igniting sample ash.

The emanation technique (Method C), based on measurement of radon-222, is nearly, but not absolutely, specific for radium-226. Procedures for soluble, suspended, and total radium-226 are given.

The sequential precipitation method (Method D) can be used to measure either radium-228 alone or radium-228 and radium-226.

The gamma-counting method (Method E) is used primarily to measure radium-224, but can be used to measure radium-226 and radium-228 as well.

governed primarily by the 3.8-d half-life radon-222. The ingrowth of alpha activity in radium-223 is complete by the time a radium-barium precipitate can be prepared for counting. The ingrowth of the first two alpha-emitting daughters of radium-224 is complete within a few minutes and the third alpha daughter activity increases at a rate governed by the 10.6-h half-life of lead-212. The activity of the radium-224 itself, with a 3.6-d half-life, also is decreasing, leading to a rather complicated ingrowth and decay curve.

Lead and barium carriers are added to the sample containing alkaline citrate, then sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is added to precipitate radium, barium, and lead as sulfates. The precipitate is purified by washing with nitric acid ( $\text{HNO}_3$ ), dissolving in alkaline EDTA, and reprecipitating as radium-barium sulfate after pH adjustment to 4.5. This slightly acidic EDTA keeps other naturally occurring alpha-emitters and the lead carrier in solution.

## 2. Apparatus

a. *Counting instruments:* One of the following is required:

1) *Internal proportional counter*, gas-flow, with scaler and register;

2) *Alpha scintillation counter*, silver-activated zinc sulfide phosphor deposited on thin polyester plastic, with photomultiplier tube, scaler, timer, and register; or

3) *Proportional counter*, thin end-window, gas-flow, with scaler and register.

b. *Membrane filter holder*, or stainless steel or TFE filter funnels, with vacuum source.\*

c. *Membrane filters*<sup>†</sup> or *glass fiber filters*.‡

## 3. Reagents

a. *Citric acid, 1M:* Dissolve 210 g  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$  in distilled water and dilute to 1 L.

b. *Ammonium hydroxide*, conc and 5N: Verify strength of old 5N  $\text{NH}_4\text{OH}$  solution before use.

c. *Lead nitrate carrier:* Dissolve 160 g  $\text{Pb}(\text{NO}_3)_2$  in distilled water and dilute to 1 L; 1 mL = 100 mg Pb.

d. *Stock barium chloride solution:* Dissolve 17.79 g  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in distilled water and dilute to 1 L in a volumetric flask; 1 mL = 10 mg Ba.

e. *Barium chloride carrier:* To a 100-mL volumetric flask, add 20.00 mL stock  $\text{BaCl}_2$  solution using a transfer pipet, dilute to 100 mL with distilled water, and mix; 1 mL = 2.00 mg Ba.

f. *Methyl orange indicator solution.*

g. *Phenolphthalein indicator solution.*

h. *Bromocresol green indicator solution:* Dissolve 0.1 g bromocresol green sodium salt in 100 mL distilled water.

i. *Sulfuric acid,  $\text{H}_2\text{SO}_4$ , 18N.*

j. *Nitric acid,  $\text{HNO}_3$ , conc.*

k. *EDTA reagent, 0.25M:* Add 93 g disodium ethylenediaminetetraacetate dihydrate to distilled water, dilute to 1 L, and mix.

l. *Acetic acid, conc.*

m. *Ethyl alcohol, 95%.*

n. *Acetone.*

o. *Clear acrylic solution:*§ Dissolve 50 mg clear acrylic in 100 mL acetone.

p. *Standard radium-226 solution:* Prepare as directed in Method C, ¶s 3d-f, except that in ¶ f (standard radium-226 solution), add 0.50 mL  $\text{BaCl}_2$  stock solution (¶ 3a) before adding the  $^{226}\text{Ra}$  solution; 1 mL final standard radium solution so prepared contains 2.00 mg Ba/mL and approximately 3 pCi  $^{226}\text{Ra}$ /mL after the necessary correcting factors are applied.

\* Fisher Filtrator or equivalent.

† Millipore Type HAWP or equivalent.

‡ No. 934-AH, diameter 2.4 cm, H. Reeve Angel and Co., or equivalent.

§ Lucite or equivalent.

## 4. Procedure for Radium in Drinking Water and for Dissolved Radium

a. To 1 L sample in a 1500-mL beaker, add 5 mL 1M citric acid, 2.5 mL conc  $\text{NH}_4\text{OH}$ , 2 mL  $\text{Pb}(\text{NO}_3)_2$  carrier, and 3.00 mL  $\text{BaCl}_2$  carrier. In each batch of samples include a distilled water blank.

b. Heat to boiling and add 10 drops methyl orange indicator.

c. While stirring, slowly add 18N  $\text{H}_2\text{SO}_4$  to obtain a permanent pink color; then add 0.25 mL acid in excess.

d. Boil gently 5 to 10 min.

e. Set beaker aside and let stand until precipitate has settled (3 to 5 h or more).||

f. Decant and discard clear supernate. Transfer precipitate to a 40-mL or larger centrifuge tube, centrifuge, decant, and discard supernate.

g. Rinse wall of centrifuge tube with a 10-mL portion of conc  $\text{HNO}_3$ , stir precipitate with a glass rod, centrifuge, and discard supernate. Repeat rinsing and washing two more times.

h. To precipitate, add 10 mL distilled water and 1 to 2 drops phenolphthalein indicator solution. Stir and loosen precipitate from bottom of tube (using a glass rod if necessary) and add 5N  $\text{NH}_4\text{OH}$ , dropwise, until solution is definitely alkaline (red). Add 10 mL EDTA reagent and 3 mL 5N  $\text{NH}_4\text{OH}$ . Stir occasionally for 2 min. Most of the precipitate should dissolve, but a slight turbidity may remain.

i. Warm in a steam bath to clear solution (about 10 min), but do not heat for an unnecessarily long period.# Add conc acetic acid dropwise until red color disappears; add 2 or 3 drops bromocresol green indicator solution and continue to add conc acetic acid dropwise, while stirring with a glass rod, until indicator turns green (aqua).\*\*  $\text{BaSO}_4$  will precipitate. Note date and time of precipitation as zero time for ingrowth of alpha activity. Digest in a steam bath for 5 to 10 min, cool, and centrifuge. Discard supernate. The final pH should be about 4.5, which is sufficiently low to destroy the Ba-EDTA complex, but not Pb-EDTA. A pH much below 4.5 will precipitate  $\text{PbSO}_4$ .

j. Wash Ba-Ra sulfate precipitate with distilled water and mount in a manner suitable for counting as given in ¶s k, l, or m following.

k. Transfer Ba-Ra sulfate precipitate to a tared stainless steel planchet with a minimum of 95% ethyl alcohol and evaporate under an infrared lamp. Add 2 mL acetone and 2 drops clear acrylic solution, disperse precipitate evenly, and evaporate under an infrared lamp. Dry in oven at 110°C, weigh, and determine alpha activity, preferably with an internal proportional counter. Calculate net counts per minute and weight of precipitate.

l. Weigh a membrane filter, a counting dish, and a weight (glass ring) as a unit. Transfer precipitate to tared membrane

|| If original concentrations of isotopes of radium other than  $^{226}\text{Ra}$  are of interest, note date and time of this original precipitation as the separation of the isotopes from their parents; use a minimal settling time and complete procedure through ¶ j without delay. Assuming the presence of and separation of parents, decay of  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  begins at the time of the first precipitation, but ingrowth of decay products is timed from the second precipitation (¶ i). The time of the first precipitation is not needed if the objective is to check the final precipitate for its  $^{226}\text{Ra}$  content only.

# If solution does not clear in 10 min, cool, add another mL 5N  $\text{NH}_4\text{OH}$ , let stand 2 min, and heat for another 10-min period.

\*\* The end point is most easily determined by comparison with a solution of similar composition that has been adjusted to pH 4.5 using a pH meter.

filter in a holder and wash with 15 to 25 mL distilled water. Place membrane filter in dish, add glass ring, and dry at 110°C. Weigh and count in one of the counters mentioned under ¶ 2a above. Calculate net counts per minute and weight of precipitate.

m. Add 20 mL distilled water to the Ba-Ra sulfate precipitate, let settle in a steam bath, cool, and filter through a special funnel with a tared glass fiber filter. Dry precipitate at 110°C to constant weight, cool, and weigh. Mount precipitate on a nylon disk and ring with an alpha phosphor on polyester plastic film,<sup>4</sup> and count in an alpha scintillation counter. Calculate net counts per minute and weight of precipitate.

n. If the isotopic composition of the precipitate is to be estimated, perform additional counting as mentioned in the calculation below.

o. *Determination of combined efficiency and self-absorption factor:* Prepare standards from 1 L distilled water and the standard radium-226 solution (¶ 3p preceding). Include at least one blank. The barium content will impose an upper limit of 3.0 mL on the volume of the standard radium-226 solution that can be used. If  $x$  is volume of standard radium-226 solution added, then add  $(3.00 - x)$  mL BaCl<sub>2</sub> carrier (¶ 3e above). Analyze standards as samples, beginning with ¶ 4a, but omit 3.00-mL BaCl<sub>2</sub> carrier.

From the observed net count rate, calculate the combined factor,  $bc$ , from the formula:

$$bc = \frac{\text{net cpm}}{ad \times 2.22 \times \text{pCi radium-226}} \dagger\dagger$$

where:

$ad$  = ingrowth factor (see below) multiplied by chemical yield.

If all chemical yields on samples and standards are not essentially equal, the factor  $bc$  will not be a constant. In this event, construct a curve relating the factor  $bc$  to varying weights of recovered BaSO<sub>4</sub>.

## 5. Calculation

$$\text{Radium, pCi/L} = \frac{\text{net cpm}}{a b c d e \times 2.22}$$

where:

$a$  = ingrowth factor (as shown in the following tabulation):

Ingrowth $h$	Alpha Activity from <sup>226</sup> Ra
0	1.000
1	1.016
2	1.036
3	1.058
4	1.080
5	1.102
6	1.124
24	1.489
48	1.905
72	2.253

$b$  = efficiency factor for alpha counting,

$c$  = self-absorption factor,

$d$  = chemical yield, and

$e$  = sample volume, L.

†† See calculation that follows.

TABLE 7500-RA:I. CHEMICAL AND RADIOCHEMICAL COMPOSITION OF SAMPLES USED TO DETERMINE BIAS AND PRECISION OF RADIUM-226 METHOD

Radionuclide Composition	Samples			
	Pair 1		Pair 2	
	A	B	C	D
Radium-226,* pCi/L	12.12	8.96	25.53	18.84
Thorium-228,* pCi/L	none	none	25.90	19.12
Uranium, natural, pCi/L	105	77.9	27.7	20.5
Lead-210,* pCi/L	11.5	8.5	23.7	17.5
Strontium-90,* pCi/L	49.1	36.3	13.9	10.2
Cesium-137, pCi/L	50.3	37.2	12.7	9.5
NaCl, mg/L	60	60	300	300
CaSO <sub>4</sub> , mg/L	30	30	150	150
MgCl <sub>2</sub> · 6H <sub>2</sub> O, mg/L	30	30	150	150
KCl, mg/L	5	5	10	10

\* Daughter products were in substantial secular equilibrium.

The calculations are based on the assumption that the radium is radium-226. If the observed concentration approaches 3 pCi/L, it may be desirable to follow the rate of ingrowth and estimate the isotopic content<sup>2,3</sup> or, preferably, to determine radium-226 by radon-222.

The optimum ingrowth periods can be selected only if the ratios and identities of the radium isotopes are known. The number of observed count rates at different ages must be equal to or greater than the number of radium isotopes present in a mixture. In the general case, suitable ages for counting are 3 to 18 h for the first count; for isotopic analysis, additional counting at 7, 14, or 28 d is suggested, depending on the number of isotopes in mixture. The amounts of the various radium isotopes can be determined by solving a set of simultaneous equations.<sup>3</sup> This approach is most satisfactory when radium-226 is the predominant isotope; in other situations, the approach suffers from statistical counting errors.

## 6. Precision and Bias

In a collaborative study, 20 laboratories analyzed four water samples for total (dissolved) radium. The radionuclide composition of these reference samples is shown in Table 7500-Ra:I. Note that Samples C and D had a <sup>224</sup>Ra concentration equal to that of <sup>226</sup>Ra.

The four results from each of two laboratories and two results from a third laboratory were rejected as outliers. The average recoveries of radium-226 from the remaining A, B, C, and D samples were 97.5, 98.7, 94.9, and 99.4%, respectively. At the 95% confidence level, the precision (random error) was 28% and 30% for the two sets of paired samples. The method is biased low for radium-226, but not seriously. The method appears satisfactory for radium-226 alone or in the presence of an equal activity of radium-224 when correction for radium-224 interference is made from a second count.

For the determination of <sup>224</sup>Ra in Samples C and D, the results of two laboratories were excluded. Hence the average recoveries were 51 and 45% for Samples C and D, respectively. At the 95%

confidence level, the precision was 46% for this pair of samples. The results indicated that the method for  $^{224}\text{Ra}$  is seriously biased low. When the recoveries for radium-224 did not agree with those for radium-226, this may have been due, in part, to incomplete instructions given in the method to account for the transitory nature of  $^{224}\text{Ra}$  activity. The method as given here contains footnotes calling attention to the importance of the time of counting. Still uncertain is the degree of separation of radium-224 from its parent, thorium-228, in ¶s 4a through g above.

Radium-223 and radium-224 analysis by this method may be satisfactory, but special refinements and further investigations are required.

## 7500-Ra C. Emanation Method

### 1. General Discussion

*a. Application:* This method is suitable for the determination of soluble, suspended, and total radium-226 in water. In this method, *total* radium-226 means the sum of suspended and dissolved radium-226. Radon means radon-222 unless otherwise specified.

*b. Principle:* Radium in water is concentrated and separated from sample solids by coprecipitation with a relatively large amount of barium as the sulfate. The precipitate is treated to remove silicates, if present, and to decompose insoluble radium compounds, fumed with phosphoric acid to remove sulfite ( $\text{SO}_3^{2-}$ ), and dissolved in hydrochloric acid (HCl). The completely dissolved radium is placed in a bubbler, which is then closed and stored for a period of several days to 4 weeks for ingrowth of radon. The bubbler is connected to an evacuated system and the radon gas is removed from the liquid by aeration, dried with a desiccant, and collected in a counting chamber. The counting chamber consists of a dome-topped scintillation cell coated inside with silver-activated zinc sulfide phosphor; a transparent window forms the bottom (Figure 7500-Ra:1). The chamber rests on a photomultiplier tube during counting. About 4 h after radon collection, the alpha-counting rate of radon and decay products is at equilibrium, and a count is obtained and related to radium-226 standards similarly treated.

The counting gas used to purge radon from the liquid to the counting chamber may be helium, nitrogen, or aged air.

Some radon (emanation) techniques employ a minimum of chemistry but require high dilution of the sample and large chambers for counting the radon-222.<sup>1</sup> Others involve more chemical separation, concentration, and purification of radium-226 before de-emanation into counting cells of either the ionization or alpha scintillation types. The method<sup>2</sup> given here requires a moderate amount of chemistry coupled with a sensitive alpha scintillation count of radon-222 plus daughter products in a small chamber.<sup>3</sup>

*c. Concentration techniques:* The chemical properties of barium and radium are similar; therefore, because barium does not interfere with de-emanation, as much as 100 mg may be used to aid in coprecipitating radium from a sample to be placed in a

### 7. References

1. KIRBY, H.W. 1954. Decay and growth tables for naturally occurring radioactive series. *Anal. Chem.* 26:1063.
2. SILL, C. 1960. Determination of radium-226, thorium-230, and thorium-232. Rep. No. TID 7616 (Oct.), U.S. Atomic Energy Comm., Washington, D.C.
3. GOLDIN, A.S. 1961. Determination of dissolved radium. *Anal. Chem.* 33:406.
4. HALLDEN, N.A. & J.H. HARLEY. 1960. An improved alpha-counting technique. *Anal. Chem.* 32:1961.

single radon bubbler. However, because some radium-226 is present in barium salts, reagent tests are necessary to account for radium-226 introduced in this way.

*d. Interferences:* Only the gaseous alpha-emitting radionuclides, radon-219 (actinon) and radon-220 (thoron), can interfere. Interference from these radionuclides would be expected to be very rare in water not contaminated by such industrial wastes as uranium mill elements.<sup>2</sup> The half-lives of these nuclides are only 3.92 and 54.5 s, respectively, so only their alpha-emitting decay products interfere.

Interference from stable chemicals is limited. Small amounts of lead, calcium, and strontium, collected by the barium sulfate, do not interfere. However, lead may cause deterioration of platinum ware. Calcium at a concentration of 300 mg/L and other dissolved solids (in brines) at 269 000 mg/L cause no difficulty.<sup>4</sup>

The formation of precipitates in excess of a few milligrams during the radon-222 ingrowth period is a warning that modifications<sup>2</sup> may be necessary because radon-222 recovery may be impaired.

*e. Minimum detectable concentration:* The minimum detectable concentration depends on counter characteristics, background-counting rate of scintillation cell, length of counting period, and contamination of apparatus and environment by radium-226. Without reagent purification, the overall reagent blank (excluding background) should be between 0.03 and 0.05 pCi radium-226, which may be considered the minimum detectable amount under routine conditions.

### 2. Apparatus

The de-emanation assembly is shown in Figure 7500-Ra:1, and its major components are described in ¶s b-e, below.

*a. Scintillation counter assembly* with a photomultiplier (PM) tube 5 cm or more in diameter, normally mounted, face up, in a light-tight housing. The photomultiplier tube, preamplifier, high-voltage supply, and scaler may be contained in one chassis; or the PM tube and preamplifier may be used as an accessory with a proportional counter or a separate scaler. A high-voltage safety

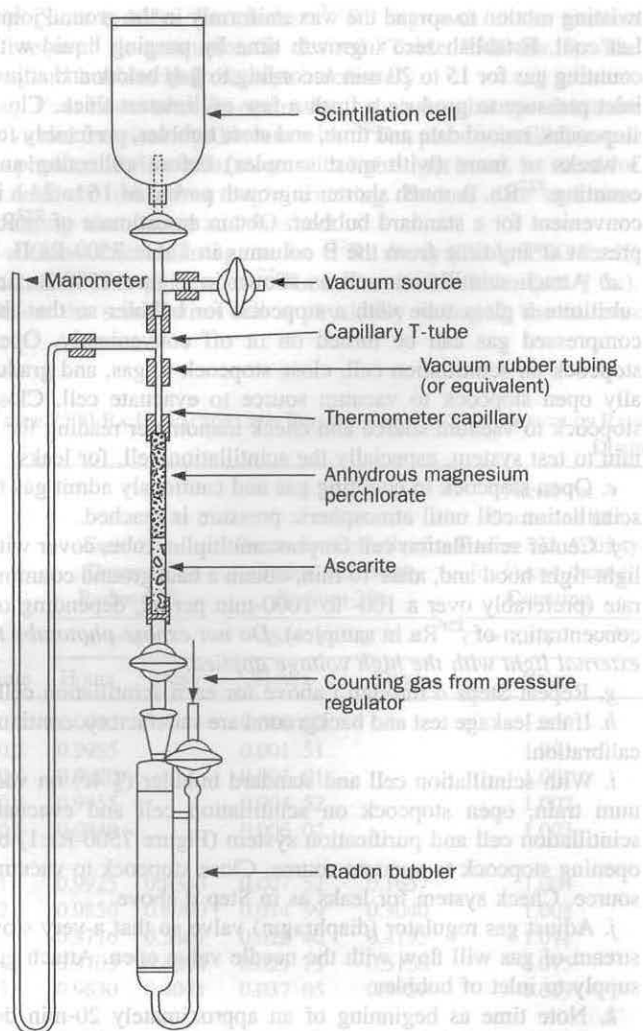


Figure 7500-Ra:1. De-emanation assembly.

switch should open automatically when the light cover is removed, to avoid damage to the photomultiplier tube.

Use a preamplifier with a variable gain adjustment. Equip counter with a flexible ground wire attached to the chassis and to the neck of the scintillation cell by an alligator clip or similar device. Ascertain operating voltage by determining a plateau using  $^{222}\text{Rn}$  in the scintillation cell as the alpha source; the slope should not exceed 2%/100 V. Calibrate and use counter and scintillation cell as a unit when more than one counter is available. The background-counting rate for the counter assembly without the scintillation cell in place should be 0.00 to 0.03 cpm.

*b. Scintillation cells,*<sup>2,3</sup> Lucas-type, preferably having a volume of 95 to 140 mL, made in the laboratory, or commercially available.\*

*c. Radon bubblers,* capacity 18 to 25 mL.† Use gas-tight glass stopcocks and a fritted glass disk of medium porosity.‡ Use one

bubbler for a standard  $^{226}\text{Ra}$  solution and one for each sample and blank in a batch.<sup>2</sup>

*d. Manometer,* open-end capillary tube or vacuum gauge having volume that is small compared to volume of scintillation cell, 0 to 760 mm Hg.

*e. Gas purification tube,* 7 to 8 mm OD standard-wall glass tubing, 100 to 120 mm long, constricted at lower end to hold glass wool plug; thermometer capillary tubing.

*f. Sample bottles,* polyethylene, 2- to 4-L capacity.

*g. Membrane filters,*§

*h. Gas supply:* Helium, nitrogen, or air aged in high-pressure cylinder with two-stage pressure regulator and needle valve. Helium is preferred.

*i. Silicone grease,* high-vacuum.

*j. Sealing wax,* low-melting. ||

*k. Laboratory glassware:* Excepting bubblers, decontaminate all glassware before and between uses by heating for 1 h in EDTA decontaminating solution at 90 to 100°C, then rinse in water, 1N HCl, and again in distilled water to dissolve barium (radium) sulfate,  $\text{Ba}(\text{Ra})\text{SO}_4$ .

Removal of previous samples from bubblers and rinsing is described in ¶ 5a17). More extensive cleaning of bubblers requires removal of wax from joints, silicone grease from stopcocks, and the last traces of barium-radium compounds.

*l. Platinum ware:* Crucibles (20 to 30 mL) or dishes (50 to 75 mL), large dish (for flux preparation), and platinum-tipped tongs (preferably Blair type). Clean platinum ware by immersion and rotation in a molten bath of potassium pyrosulfate, remove, cool, rinse in hot tap water, digest in hot 6N HCl, rinse in distilled water, and finally flame over a burner.

### 3. Reagents

*a. Stock barium chloride solution:* Dissolve 17.79 g  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in distilled water and dilute to 1 L; 1 mL = 10 mg Ba.

*b. Dilute barium chloride solution:* Dilute 200.0 mL stock barium chloride solution to 1000 mL as needed; 1 mL = 2.00 mg Ba. Let stand 24 h and filter through a membrane filter.

Optionally, add approximately 40 000 dpm of  $^{133}\text{Ba}$  to this solution before dilution. Take account of the stable barium carrier added with the  $^{133}\text{Ba}$  and with the diluting solution, so that the final barium concentration is near 2 mg/L. The use of  $^{133}\text{Ba}$  provides a convenient means of checking on the recovery of  $^{226}\text{Ra}$  from the sample; see 7, below. Use the  $\text{BaCl}_2$  solution containing  $^{133}\text{Ba}$  in steps described in ¶s 5a3), b8), and c3). Do not use in *d* below; instead, use a separate dilution of stock  $\text{BaCl}_2$  solution for preparing  $^{226}\text{Ra}$  standard solutions.

*c. Acid barium chloride solution:* To 20 mL conc HCl in a 1-L volumetric flask, add dilute  $\text{BaCl}_2$  solution to the mark and mix.

*d. Stock radium-226 solution:* Take every precaution to avoid unnecessary contamination of working area, equipment, and glassware, preferably by preparing  $^{226}\text{Ra}$  standards in a separate area or room reserved for this purpose. Obtain a National Institute of Standards and Technology (NIST) gamma ray standard containing 0.1  $\mu\text{g}$   $^{226}\text{Ra}$  as of date of standardization. Using a

\* William H. Johnston Laboratories, 3617 Woodland Ave., Baltimore, MD 21215.

† Available from Corning Glass Works, Special Sales Section, Corning, NY 14830.

‡ Corning or equivalent.

§ Type HAWP, Millipore Filter Corp., Bedford, MA, or equivalent.

|| Pyseal, Fisher Scientific Co., Pittsburgh, PA, or equivalent.

heavy glass rod, cautiously break neck of ampule, which is submerged in 300 mL acid BaCl<sub>2</sub> solution in a 600-mL beaker. Chip ampule unit until it is thoroughly broken or until hole is large enough to give complete mixing. Transfer solution to a 1-L volumetric flask, rinse beaker with acid BaCl<sub>2</sub> solution, dilute to mark with same solution, and mix; 1 mL = approximately 100 pCi <sup>226</sup>Ra.

Determine the time in years, *t*, since the NIST standardization of the original <sup>226</sup>Ra solution. Calculate pCi <sup>226</sup>Ra/mL as:

$$\text{pCi } ^{226}\text{Ra} = [1 - (4.3 \times 10^{-4})(t)] [100] [0.990]$$

*e. Intermediate radium-226 solution:* Dilute 100 mL stock radium-226 solution to 1000 mL with acid BaCl<sub>2</sub> solution; 1 mL = approximately 10 pCi <sup>226</sup>Ra.

*f. Standard radium-226 solution:* Add 30.0 mL intermediate radium-226 solution to a 100-mL volumetric flask and dilute to mark with acid BaCl<sub>2</sub> solution; 1 mL = approximately 3 pCi <sup>226</sup>Ra and contains about 2 mg Ba. See ¶ *d* et seq. above for correction factors.

*g. Hydrochloric acid,* HCl, conc, 6*N*, 1*N*, and 0.1*N*.

*h. Sulfuric acid,* H<sub>2</sub>SO<sub>4</sub>, conc and 0.1*N*.

*i. Hydrofluoric acid,* HF, 48%, in a plastic dropping bottle. (CAUTION.)

*j. Ammonium sulfate solution:* Dissolve 10 g (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in distilled water and dilute to 100 mL in a graduated cylinder.

*k. Phosphoric acid,* H<sub>3</sub>PO<sub>4</sub>, 85%.

*l. Ascarite,* 8 to 20 mesh.

*m. Magnesium perchlorate,* anhydrous desiccant.

*n. EDTA decontaminating solution:* Dissolve 10 g disodium ethylenediaminetetraacetate dihydrate and 10 g Na<sub>2</sub>CO<sub>3</sub> in distilled water and dilute to 1 L in a graduated cylinder.

*o. Special reagents for total and suspended radium:*

1) *Flux:* Add 30 mg BaSO<sub>4</sub>, 65.8 g K<sub>2</sub>CO<sub>3</sub>, 50.5 g Na<sub>2</sub>CO<sub>3</sub>, and 33.7 g Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 10H<sub>2</sub>O, to a 500-mL platinum dish. Mix thoroughly and heat cautiously to expel water, then fuse and mix thoroughly by swirling. Cool flux, grind in a porcelain mortar to pass a 10- to 12-mesh (or finer) screen, and store in an airtight bottle.

2) *Dilute hydrogen peroxide solution:* Dilute 10 mL 30% H<sub>2</sub>O<sub>2</sub> to 100 mL in a graduated cylinder. Prepare daily.

#### 4. Calibration of Scintillation Counter Assembly

*a.* Test bubblers by adding about 10 mL distilled water and passing air through them at the rate of 3 to 5 mL (free volume)/min. Air should form many fine bubbles rather than a few large ones; the latter condition indicates nonuniform pores. Do not use bubblers requiring excessive pressure to initiate bubbling. Fritted-glass disks of medium porosity (¶ 2*c*) usually are satisfactory.

*b.* Apply silicone grease to stopcocks of a bubbler and, with gas inlet stopcock closed, add 1 mL stock BaCl<sub>2</sub> solution and 10 mL (30 pCi) standard radium-226 solution, and fill bubbler two-thirds to three-fourths full with additional acid BaCl<sub>2</sub> solution.

*c.* With bubbler in a clamp or rack, dry joint with lint-free paper or cloth, warm separate parts of the joint, apply sealing wax sparingly to the male part, and make the connection with a

twisting motion to spread the wax uniformly in the ground joint. Let cool. Establish zero ingrowth time by purging liquid with counting gas for 15 to 20 min according to ¶ 4*j* below and adjust inlet pressure to produce a froth a few millimeters thick. Close stopcocks, record date and time, and store bubbler, preferably for 3 weeks or more (with most samples) before collecting and counting <sup>222</sup>Rn. A much shorter ingrowth period of 16 to 24 h is convenient for a standard bubbler. Obtain an estimate of <sup>222</sup>Rn present at any time from the B columns in Table 7500-Ra:II.

*d.* Attach scintillation cell as shown in Figure 7500-Ra:1;# substitute a glass tube with a stopcock for bubbler so that the compressed gas can be turned on or off conveniently. Open stopcock on scintillation cell, close stopcock to gas, and gradually open stopcock to vacuum source to evacuate cell. Close stopcock to vacuum source and check manometer reading for 2 min to test system, especially the scintillation cell, for leaks.

*e.* Open stopcock to counting gas and cautiously admit gas to scintillation cell until atmospheric pressure is reached.

*f.* Center scintillation cell on photomultiplier tube, cover with light-tight hood and, after 10 min, obtain a background counting rate (preferably over a 100- to 1000-min period, depending on concentration of <sup>226</sup>Ra in samples). Do not expose phototube to external light with the high voltage applied.

*g.* Repeat Steps *d* through *f* above for each scintillation cell.

*h.* If the leakage test and background are satisfactory, continue calibration.

*i.* With scintillation cell and standard bubbler (¶ 4*c*) on vacuum train, open stopcock on scintillation cell and evacuate scintillation cell and purification system (Figure 7500-Ra:1) by opening stopcock to vacuum source. Close stopcock to vacuum source. Check system for leaks as in Step *d* above.

*j.* Adjust gas regulator (diaphragm) valve so that a very slow stream of gas will flow with the needle valve open. Attach gas supply to inlet of bubbler.

*k.* Note time as beginning of an approximately 20-min de-emanation period. Very cautiously open bubbler outlet stopcock to equalize pressure and transfer all or most of the fluid in the inlet side arm to bubbler chamber.

*l.* Close outlet stopcock and very cautiously open inlet stopcock to flush remaining fluid from side arm and fritted disk. Close inlet stopcock.

*m.* Repeat Steps *h* and *l* above, four or five times, to obtain more nearly equal pressures on the two sides of bubbler.

*n.* With outlet stopcock fully open, cautiously open inlet stopcock so that gas flow produces a froth a few millimeters thick at surface of bubbler solution. Maintain flow rate by gradually increasing pressure with regulator valve and continue de-emanation until pressure in cell reaches atmospheric pressure. Total elapsed time for the de-emanation should be 15 to 25 min.

*o.* Close stopcocks to scintillation cell, close bubbler inlet and outlet, shut off and disconnect gas supply, and record date and time as the ends of the <sup>222</sup>Rn ingrowth and de-emanation periods and as the beginnings of decay of <sup>222</sup>Rn and ingrowth of decay products.

# The system as described and shown in Figure 7500-Ra:1 is considered minimal. In routine work, use manifold systems and additional, more precise needle valves. An occasional drop of solution will escape from the bubbler; provide enough free space beyond the outlet stopcock to accommodate this liquid, preventing its entrance into the gas-purifying train.

p. Store bubbler for another <sup>222</sup>Rn ingrowth in the event a subsequent de-emanation is desired (Table 7500-Ra:II). The standard bubbler may be kept indefinitely.

q. Four hours after de-emanation, when daughter products are in virtual transient equilibrium with <sup>222</sup>Rn, place scintillation cell on photomultiplier tube, cover with light-tight hood, let stand for at least 10 min, then begin counting. Record date and time counting was started and finished.

r. Correct net counting rate for <sup>222</sup>Rn decay (Table 7500-Ra:II) and relate it to picocuries <sup>226</sup>Ra in standard bubbler (see ¶ 6a). Unless the scintillation cell is physically damaged, the calibration

will remain essentially unchanged for years. Occasional calibration is recommended.

s. Repeat Steps h through r above on each scintillation cell.

t. To remove <sup>222</sup>Rn and prepare scintillation cell for reuse, evacuate and cautiously refill with counting gas. Routinely, repeat evacuation and refilling twice, and repeat process more times if the cells have contained a high <sup>222</sup>Rn activity. (Decay products with a half-life of approximately 30 min will remain in the cell. Do not check background on cells until activity of decay products has had time to decay to insignificance.)

TABLE 7500-Ra:II. FACTORS FOR DECAY OF RADON-222, GROWTH OF RADON-222 FROM RADIUM-226, AND CORRECTION OF RADON-222 ACTIVITY FOR DECAY DURING COUNTING

Time	Factor for Decay of Radon-222		Factor for Growth of Radon-222 from Radium-226		Factor for Correction of Radon-222 Activity for Decay during Counting	Time	Factor for Decay of Radon-222		Factor for Growth of Radon-222 from Radium-226		Factor for Correction of Radon-222 Activity for Decay during Counting
	$A = e^{-\lambda t}$		$B = 1 - e^{-\lambda t}$		$C = \lambda t / (1 - e^{-\lambda t})$		$A = e^{-\lambda t}$		$B = 1 - e^{-\lambda t}$		$C = \lambda t / (1 - e^{-\lambda t})$
	Hours	Days	Hours	Days	Hours		Hours	Days	Hours	Days	Hours
0.0	1.0000		0.000	00	1.000	29	0.8034	0.0052	0.1966	0.9948	1.113
0.2	0.9985		0.001	51	1.001	30	0.7973	0.0044	0.2027	0.9956	1.118
0.4	0.9970		0.003	01	1.001	31	0.7913	0.0036	0.2087	0.9964	1.122
0.6	0.9955		0.004	52	1.002	32	0.7854	0.0030	0.2146	0.9970	1.126
0.8	0.9940		0.006	02	1.003	33	0.7795	0.0025	0.2205	0.9975	1.130
1	0.9925	0.8343	0.007	52	1.004	34	0.7736	0.0021	0.2264	0.9979	1.134
2	0.9850	0.6960	0.014	99	1.008	35	0.7678	0.0018	0.2322	0.9982	1.138
3	0.9776	0.5807	0.022	40	1.011	36	0.7620	0.0015	0.2380	0.9985	1.142
4	0.9703	0.4844	0.029	75	1.015	37	0.7563	0.0012	0.2437	0.9988	1.146
5	0.9630	0.4041	0.037	05	1.019	38	0.7506	0.0010	0.2494	0.9990	1.150
6	0.9557	0.3372	0.044	29	1.023	39	0.7449	0.0009	0.2551	0.9991	1.154
7	0.9485	0.2813	0.051	48	1.027	40	0.7393	0.0007	0.2607	0.9993	1.159
8	0.9414	0.2347	0.058	61	1.031	41	0.7338	0.0006	0.2662	0.9994	1.163
9	0.9343	0.1958	0.065	69	1.034	42	0.7283	0.0005	0.2717	0.9995	1.167
10	0.9273	0.1633	0.072	72	1.038	43	0.7228	0.0004	0.2772	0.9996	1.171
11	0.9203	0.1363	0.079	69	1.042	44	0.7173	0.0003	0.2827	0.9997	1.175
12	0.9134	0.1137	0.086	62	1.046	45	0.7117	0.0003	0.2880	0.9997	1.179
13	0.9065	0.0948	0.093	49	1.050	46	0.7066	0.0002	0.2934	0.9998	1.184
14	0.8997	0.0791	0.100	31	1.054	47	0.7013	0.0002	0.2987	0.9998	1.188
15	0.8929	0.0660	0.107	07	1.058	48	0.6960	0.0002	0.3040	0.9998	1.192
16	0.8862	0.0551	0.1138		1.062	49	0.6908	0.0001	0.3092	0.9999	1.196
17	0.8795	0.0459	0.1205	0.9449	1.066	50	0.6856	0.0001	0.3144	0.9999	1.201
18	0.8729	0.0383	0.1271	0.9617	1.069	51	0.6804	0.0001	0.3196	0.9999	1.205
19	0.8664	0.0320	0.1336	0.9680	1.073	52	0.6753	0.0001	0.3247	0.9999	1.209
20	0.8598	0.0267	0.1402	0.9733	1.077	53	0.6702	0.0001	0.3298	0.9999	1.213
21	0.8534	0.0223	0.1466	0.9777	1.081	54	0.6652	0.0001	0.3348	0.9999	1.218
22	0.8470	0.0186	0.1530	0.9814	1.085	55	0.6602	0.0000	0.3398	1.0000	1.222
23	0.8406	0.0155	0.1594	0.9845	1.089	56	0.6552	0.0000	0.3448	1.0000	1.226
24	0.8343	0.0129	0.1657	0.9871	1.093	57	0.6503	0.0000	0.3497	1.0000	1.231
25	0.8280	0.0108	0.1720	0.9892	1.097	58	0.6454	0.0000	0.3546	1.0000	1.235
26	0.8218	0.0090	0.1782	0.9910	1.101	59	0.6405	0.0000	0.3595	1.0000	1.239
27	0.8156	0.0075	0.1844	0.9925	1.105	60	0.6357	0.0000	0.3643	1.0000	1.244
28	0.8095	0.0063	0.1905	0.9937	1.109						

## 5. Procedure

### a. Soluble radium-226:

1) Using a membrane filter, filter at least 1 L sample or a volume containing up to 30 pCi  $^{226}\text{Ra}$  and transfer to a polyethylene bottle as soon after sampling as possible. Save the suspended matter for determination by the procedure described in 5b, below. Record sample volume filtered if suspended solids are to be analyzed as in the procedure for  $^{226}\text{Ra}$  in suspended matter.

2) Add 20 mL conc HCl/L of filtrate and continue analysis when convenient.

3) Add 50 mL dilute  $\text{BaCl}_2$  solution, with vigorous stirring, to 1020 mL acidified filtrate [¶ 2) preceding] in a 1.5-L beaker. In each batch of samples include a reagent blank consisting of distilled water plus 20 mL conc HCl.

4) Cautiously, with vigorous stirring, add 20 mL conc  $\text{H}_2\text{SO}_4$ . Cover beaker and let precipitate overnight.

5) Filter supernate through a membrane filter, using 0.1N  $\text{H}_2\text{SO}_4$  to transfer Ba-Ra precipitate to filter, and wash precipitate twice with 0.1N  $\text{H}_2\text{SO}_4$ .

6) Place filter in a platinum crucible or dish, add 0.5 mL HF and 3 drops (0.15 mL)  $(\text{NH}_4)_2\text{SO}_4$  solution, and evaporate to dryness.

7) Carefully ignite over a small flame until carbon is burned off; cool. (After filter is charred a Meker burner may be used.)

8) Add 1 mL  $\text{H}_3\text{PO}_4$  with a calibrated dropper and heat on hot plate at about 200°C. Gradually raise temperature and maintain at about 300 to 400°C for 30 min.

9) Swirl vessel over a low Bunsen flame, adjusted to avoid spattering, while covering the walls with hot  $\text{H}_3\text{PO}_4$ . Continue to heat for a minute after precipitate fuses into a clear melt (just below redness) to insure complete removal of  $\text{SO}_3$ .

10) Fill cooled vessel one-half full with 6N HCl, heat on steam bath, then gradually add distilled water to within 2 mm of top of vessel.

11) Evaporate on boiling steam bath until there are no more vapors of HCl.

12) Add 6 mL 1N HCl, swirl, and warm to dissolve  $\text{BaCl}_2$  crystals.

13) Close gas inlet stopcock, add a drop of water to the fritted disk of the fully greased and tested radon bubbler, and transfer sample from platinum vessel to bubbler with a medicine dropper. Use dropper to rinse vessel with at least three 2-mL portions of distilled water. Add distilled water until bubbler is two-thirds to three-fourths full.

14) Dry, wax if necessary, and seal joint. Establish zero ingrowth time as instructed in ¶ 4c preceding.

15) Close stopcocks, record date and time, and store bubbler for  $^{222}\text{Rn}$  ingrowth, preferably for 3 weeks for low concentrations of radium-226.

16) De-emanate and count  $^{222}\text{Rn}$  as instructed for calibrations in ¶s 4i through r, with sample replacing standard bubbler.

17) The sample in the bubbler may be stored for a second ingrowth or it may be discarded and the bubbler cleaned for reuse. (A bubbler is readily cleaned while in an inverted position by attaching a tube from a beaker containing 100 mL 0.1N HCl to the inlet and attaching another tube from outlet to a suction flask. Alternately open and close outlet and inlet stopcocks to pass the acid rinse water sequentially through the fritted disk, accumulate in the bubbler, and flush into the suction flask. Drain

bubbler with the aid of vacuum, heat ground joint gently to melt wax, and separate joint. More extensive cleaning, as indicated in ¶ 2k above, may be necessary if the bubbler contained more than 10 pCi  $^{226}\text{Ra}$ .)

### b. Radium-226 in suspended matter:

1) Suspended matter in water usually contains siliceous materials that require fusion with an alkaline flux to insure recovery of radium. Dry suspended matter (up to 1000 mg inorganic material) retained on the membrane filter specified in ¶ 5a1) above in a tared platinum crucible and ignite as in ¶ 5a7).

2) Weigh crucible to estimate residue.

3) Add 8 g flux/g residue, but not less than 2 g flux, and mix with a glass rod.

4) Heat over a Meker burner until melting begins, being careful to prevent spattering. Continue heating for 20 min after bubbling stops, with an occasional swirl of the crucible to mix contents and achieve a uniform melt. A clear melt usually is obtained only when the suspended solids are present in small amount or have a high silica content.

5) Remove crucible from burner and rotate as melt cools to distribute it in a thin layer on crucible wall.

6) When cool, place crucible in a covered beaker containing 120 mL distilled water, 20 mL conc  $\text{H}_2\text{SO}_4$ , and 5 mL dilute  $\text{H}_2\text{O}_2$  solution for each 8 g flux. (Reduce acid and  $\text{H}_2\text{O}_2$  in proportion to flux used.) Rotate crucible to dissolve melt if necessary.

7) When melt is dissolved, remove and rinse crucible into beaker. Save crucible for Step 10) below.

8) Heat solution and slowly add 50 mL dilute  $\text{BaCl}_2$  solution with vigorous stirring. Cover beaker and let stand overnight for precipitation. (Precipitation with cool sample solution also is satisfactory.)

9) Add about 1 mL dilute  $\text{H}_2\text{O}_2$  and, if yellow color (from titanium) deepens, add more  $\text{H}_2\text{O}_2$  until there is no further color change.

10) Continue analysis according to ¶s 5a5) through 16).

11) Calculate result as directed in ¶s 6a and b, taking into account that the suspended solids possibly were contained in a sample volume other than 1 L [see ¶ 5a1)].

### c. Total radium-226:

1) Total  $^{226}\text{Ra}$  in water is the sum of soluble and suspended  $^{226}\text{Ra}$  as determined in 5a and b preceding, or it may be determined directly by examining the original water sample that has been acidified with 20 mL conc HCl/L sample and stored in a polyethylene bottle.

2) Thoroughly mix acidified sample and take 1020 mL or a measured volume containing not more than 1000 mg inorganic suspended solids.

3) Add 50 mL dilute  $\text{BaCl}_2$  solution and slowly, with vigorous stirring, add 20 mL conc  $\text{H}_2\text{SO}_4$ /L sample. Cover and let precipitate overnight.

4) Filter supernate through membrane filter and transfer solids to filter as in ¶ 5a5) preceding.

5) Place filter and precipitate in tared platinum crucible and proceed as in ¶s 5b2) through 10) above but with the following changes in the procedure given in ¶ 5b8): Omit adding dilute  $\text{BaCl}_2$  solution, digest for 1 h on a steam bath, and filter immediately after digestion without stirring up  $\text{BaSO}_4$ . (If these changes are not made, filtration will be very slow.)

6) Calculate total radium-226 concentration as directed in §§ 6a and b.

6. Calculations

a. Calculate the <sup>226</sup>Ra in a bubbler, including reagent blank, as follows:

$$^{226}\text{Ra, pCi} = \frac{R_s - R_b}{R_c} \times \frac{1}{1 - e^{-\lambda t_1}} \times \frac{1}{e^{-\lambda t_2}} \times \frac{\lambda t_3}{1 - e^{-\lambda t_3}}$$

where:

- λ = decay constant for <sup>222</sup>Rn, 0.007 55/h,
- t<sub>1</sub> = time interval allowed for ingrowth of <sup>222</sup>Rn, h,
- t<sub>2</sub> = time interval between de-emanation and counting, h,
- t<sub>3</sub> = time interval of counting, h,
- R<sub>s</sub> = observed counting rate of sample in scintillation cell, cph,
- R<sub>b</sub> = (previously) observed background counting rate of scintillation cell with counting gas, cph,
- R<sub>c</sub> = calibration constant for scintillation cell [i.e., observed net counts per hour, corrected by use of ingrowth and decay factors (C/AB from below) per picocurie of Ra in standard],

or:

$$^{226}\text{Ra, pCi} = \frac{(R_s - R_b)}{R_c} \times \frac{C}{AB}$$

where:

- A = factor for decay of <sup>222</sup>Rn (see Table 7500-Ra:II),
- B = factor for growth of <sup>222</sup>Rn from <sup>226</sup>Ra (see Table 7500-Ra: II), and
- C = factor for correction of <sup>222</sup>Rn activity for decay during counting (see Table 7500-Ra:II).

For nontabulated times, obtain decay factors for <sup>222</sup>Rn by multiplying together the appropriate tabulated "day" and "hour" decay factors, interpolating for less than 0.2 h if indicated by the precision desired. Obtain radon-222 growth factors for nontabulated times most accurately, especially for short periods (e.g., in calibrations), by calculation from <sup>222</sup>Rn decay factors given in Column A and using formula given in heading for Column B (of Table 7500-Ra:II). Linear interpolations are satisfactory for routine samples. Obtain the decay-during-counting factors by linear interpolation for all nontabulated times.

In calculating cell calibration constants, use the same equation, but picocuries of <sup>226</sup>Ra is known and R<sub>c</sub> is unknown.

b. Convert the activity into picocuries per liter of soluble, suspended, or total <sup>226</sup>Ra by the following equation:

$$^{226}\text{Ra, pCi/L} = \frac{(D - E) \times 1000}{\text{mL sample}}$$

where:

- D = pCi <sup>226</sup>Ra found in sample, and

$$E = \text{pCi } ^{226}\text{Ra found in reagent blank.}$$

7. Recovery of Barium (Radium-226) (Optional)

If <sup>133</sup>Ba was added in reagent b, check recovery of Ba by removing sample from bubbler, adjusting its volume appropriately, gamma-counting it under standardized conditions, and comparing the result with the count obtained from a 50-mL portion (evaporated if necessary to reduce volume) of dilute barium solution also counted under standardized conditions; add 1 mL H<sub>3</sub>PO<sub>4</sub> to the latter portion before counting. The assumption that the Ba and <sup>226</sup>Ra are recovered to the same extent is valid in the method described.

Note that <sup>226</sup>Ra and its decay products interfere slightly even if a gamma spectrometer is used. The technique works best when the ratio of <sup>133</sup>Ba to <sup>226</sup>Ra is high.

Determinations of recovery are particularly helpful with irreplaceable samples, both in gaining experience with the method and in applying the general method to unfamiliar media.

8. Precision and Bias

In a collaborative study, seven laboratories analyzed four water samples for dissolved radium-226 by this method. No result was rejected as an outlier. The average recoveries of added radium-226 from Samples A, B, C, and D (below) were 97.1, 97.3, 97.6, and 98.0%, respectively. At the 95% confidence level, the precision (random error) was 6% and 8% for the two sets of paired samples. Because of the small number of participating laboratories and the low values for random and total errors, there was no evidence of laboratory systematic errors. Neither radium-224 at an activity equal to that of the radium-226 nor dissolved solids up to 610 mg/L produced a detectable error in the results.

Test samples consisted of two pairs of simulated moderately hard and hard water samples containing known amounts of added radium-226 and other radionuclides. The composition of the samples with respect to nonradioactive substances was the same for a pair of samples but varied for the two pairs. The radiochemical composition of the samples is given in Table 7500-Ra:I.

9. References

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## 7500-Ra D. Sequential Precipitation Method

## 1. General Discussion

*a. Application:* This method can be used to determine soluble radium-228 alone or soluble radium-228 plus radium-226.

*b. Principle:* Radium-228 and radium-226 in water are concentrated and separated by coprecipitation with barium and lead as sulfates and purified by EDTA chelation. After 36-h ingrowth of actinium-228 from radium-228, actinium-228 is carried on yttrium oxalate, purified, and beta-counted. Radium-226 in the supernatant is precipitated as the sulfate, purified, and alpha-counted (Method B) or it is transferred to a radon bubbler and determined by the emanation procedure (Method C), which is the preferred method.

If analysis of radium-226 is not required, the procedure for radium-228 may be terminated by beta-counting the yttrium oxalate precipitate with a follow-up precipitation of barium sulfate for yield determination. If it is determined that radium-228 is absent, the radium-226 fraction may be alpha-counted directly. If radium-228 is present, radium-226 must be determined by radon emanation.

*c. Sampling and storage:* To drinking water or a filtered sample of turbid water, add 2 mL conc nitric acid ( $\text{HNO}_3$ )/L sample at the time of collection or immediately after filtration.

## 2. Apparatus

*a. Counting instruments:* One of the following is required:

1) *Internal proportional counter,* gas flow, with scaler, timer, and register; or a thin end-window (polyester plastic)\* proportional counting chamber with scaler, timer, register amplifier, and preferably having an anticoincident system (low background).

2) *Scintillation counter assembly:* See ¶ C.2a. This equipment is necessary only if radium-226 is determined sequentially with radium-228 and is analyzed by emanation of radon.

*b. Centrifuge,* bench-size clinical, with polypropylene tubes.

*c. Filter funnels,* for 2.4-cm filter paper.

*d. Stainless steel pans,* 5.1 cm.

*e. Infrared drying lamp assembly.*

*f. Magnetic stirrer hot plate.*

*g. Membrane filters,* 47-mm diam, 0.45- $\mu\text{m}$  pore diam.†

## 3. Reagents

*a. Acetic acid,* conc.

*b. Acetone,* anhydrous.

*c. Ammonium hydroxide,*  $\text{NH}_4\text{OH}$ , conc.

*d. Ammonium oxalate solution:* Dissolve 25 g  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  in distilled water and dilute to 500 mL.

*e. Ammonium sulfate solution:* Dissolve 20 g  $(\text{NH}_4)_2\text{SO}_4$  in a minimum of distilled water and dilute to 100 mL.

*f. Ammonium sulfide solution:* Dilute 10 mL  $(\text{NH}_4)_2\text{S}$  (20 to 24%) to 100 mL with distilled water.

*g. Barium carrier standardized:* Dissolve 2.846 g  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in distilled water, add 0.5 mL conc  $\text{HNO}_3$ , and dilute to 100 mL; 1 mL = 16 mg Ba.

*h. Citric acid,* 1M: See Section B.3a.

*i. EDTA reagent,* 0.25M: See Section B.3k.

*j. Ethanol,* 95%.

*k. Lead carrier: Solution A:* Dissolve 2.397 g  $\text{Pb}(\text{NO}_3)_2$  in distilled water, add 0.5 mL conc  $\text{HNO}_3$ , and dilute to 100 mL; 1 mL = 15 mg Pb. *Solution B:* Dilute 10 mL Solution A to 100 mL with distilled water; 1 mL = 1.5 mg Pb.

*l. Methyl orange indicator solution:* Dissolve 0.1 g methyl orange powder in 100 mL distilled water.

*m. Nitric acid,*  $\text{HNO}_3$ , conc, 6N, and 1N.

*n. Sodium hydroxide,* 18N: Dissolve 720 g NaOH in 500 mL distilled water and dilute to 1 L.

*o. Sodium hydroxide,* 10N: Dissolve 400 g NaOH in 500 mL distilled water and dilute to 1 L.

*p. Sodium hydroxide,* NaOH, 1N.

*q. Strontium-yttrium mixed carrier: Solution A:* Dilute 10.0 mL yttrium carrier to 100 mL. *Solution B:* Dissolve 0.4348 g  $\text{Sr}(\text{NO}_3)_2$  in distilled water and dilute to 100 mL. Combine equal volumes of Solutions A and B; 1 mL = 0.9 mg Sr and 0.9 mg Y.

*r. Sulfuric acid,*  $\text{H}_2\text{SO}_4$ , 18N.

*s. Yttrium carrier:* Add 12.7 g  $\text{Y}_2\text{O}_3$  (Section 7500-Sr.B.3d) to an erlenmeyer flask containing 20 mL distilled water. Heat to boiling and, while stirring with a magnetic stirring hot plate, add small portions of conc  $\text{HNO}_3$ . (About 30 mL is necessary to dissolve the  $\text{Y}_2\text{O}_3$ . Small additions of distilled water also may be needed to replace water lost by evaporation.) After total dissolution, add 70 mL conc  $\text{HNO}_3$  and dilute to 1 L with distilled water; 1 mL = 10 mg Y.

## 4. Procedure

*a. Radium-228:*

1) For 1 L sample add 5 mL 1M citric acid and a few drops methyl orange indicator. The solution should be red. Add 10 mL lead carrier (Solution A), 2.0 mL barium carrier, and 2 mL yttrium carrier; stir well. Heat to incipient boiling and maintain at this temperature for 30 min.

2) Add conc  $\text{NH}_4\text{OH}$  until a definite yellow color is obtained; add a few drops excess. Precipitate lead and barium sulfates by adding 18N  $\text{H}_2\text{SO}_4$  until the red color reappears; add 0.25 mL excess. Add 5 mL  $(\text{NH}_4)_2\text{SO}_4$  solution/L sample. Stir frequently and hold at about 90°C for 30 min.

3) Cool and filter with suction through a membrane filter. Quantitatively transfer precipitate to filter. Carefully place filter in a 250-mL beaker. Add about 10 mL conc  $\text{HNO}_3$  and heat gently until the filter dissolves completely. Using conc  $\text{HNO}_3$  transfer precipitate to a centrifuge tube. Centrifuge and discard supernatant.

4) Wash precipitate with 15 mL conc  $\text{HNO}_3$ , centrifuge, and discard supernatant. Repeat wash and centrifuge again. Add 25 mL EDTA reagent, heat in a hot water bath, and stir well. Add a few drops 10N NaOH if the precipitate does not dissolve readily.

5) Add 1 mL strontium-yttrium mixed carrier and stir thoroughly. Add a few drops 10N NaOH if any precipitate forms.

\* Mylar or equivalent.

† Gelman Ga-6 or equivalent.

Add 1 mL  $(\text{NH}_4)_2\text{SO}_4$  solution and stir thoroughly. Add conc acetic acid until  $\text{BaSO}_4$  precipitates; add 2 mL excess. The pH should be about 4.5. Digest in a hot water bath ( $80^\circ\text{C}$ ) until precipitate settles. Centrifuge and discard supernatant.

6) Add 20 mL EDTA reagent, heat in a hot water bath, and stir until precipitate dissolves. Repeat Step 5. Note time of last  $\text{BaSO}_4$  precipitation as zero time for ingrowth of  $^{228}\text{Ac}$ . Dissolve precipitate in 20 mL EDTA reagent, add 0.5 mL yttrium carrier and 1 mL lead carrier (Solution B). If any precipitate forms, dissolve by adding a few drops 10N NaOH. Mix well, cap tube, and age at least 36 h.

7) Add 0.3 mL  $(\text{NH}_4)_2\text{S}$  solution and mix well. Add 10N NaOH dropwise with vigorous stirring until  $\text{PbS}$  precipitates; add 10 drops excess. Stir intermittently for about 10 min. Centrifuge and decant supernatant into a clean tube.

8) Add 1 mL lead carrier (Solution B), 0.1 mL  $(\text{NH}_4)_2\text{S}$  solution, and a few drops 10N NaOH. Repeat precipitation of  $\text{PbS}$ . Centrifuge and filter supernatant through filter paper $\ddagger$  into a clean tube. Wash filter with a few milliliters of distilled water. Discard residue.

9) Add 5 mL 18N NaOH (make at least 2N in  $\text{OH}^-$ ). Because of the short half-life of  $^{228}\text{Ac}$  (6.13 h) complete the following procedure without delay. Mix well and digest in a hot water bath until  $\text{Y}(\text{OH})_3$  coagulates. Centrifuge and decant supernatant into a beaker. Cover beaker and save supernatant for  $^{226}\text{Ra}$  analysis, ¶s b or c below. Note time of  $\text{Y}(\text{OH})_3$  precipitation; this is the end of  $^{228}\text{Ac}$  ingrowth and beginning of  $^{228}\text{Ac}$  decay. ( $t_3$  = time in minutes between last  $\text{BaSO}_4$  and first  $\text{Y}(\text{OH})_3$  precipitations.) Dissolve precipitate in 2 mL 6N  $\text{HNO}_3$ . Heat and stir in a hot water bath about 5 min. Add 5 mL distilled water and reprecipitate  $\text{Y}(\text{OH})_3$  with 3 mL 10N NaOH. Heat and stir in a hot water bath until precipitate coagulates. Centrifuge and discard supernatant.

10) Dissolve precipitate with 1 mL 1N  $\text{HNO}_3$  and heat in hot water bath for several minutes. Dilute to 5 mL with distilled water and add 2 mL ammonium oxalate solution. Heat to coagulate, centrifuge, and discard supernatant. Add 10 mL distilled water, 6 drops 1N  $\text{HNO}_3$ , and 6 drops ammonium oxalate solution. Heat and stir in a hot water bath for several minutes. Centrifuge and discard supernatant. Transfer quantitatively to a tared stainless-steel planchet using a minimum quantity of distilled water. Dry under an infrared lamp to constant weight and count in a low-background beta counter. ( $t_1$  = time in minutes between first  $\text{Y}(\text{OH})_3$  precipitation and counting.)

If analysis of radium-226 is not required, complete Steps b1) and 3) below to obtain the fractional barium yield to be used in calculating  $^{228}\text{Ra}$  activity.

#### b. Radium by precipitation:

1) To the supernatant saved in ¶ a9) above add 4 mL conc  $\text{HNO}_3$  and 2 mL  $(\text{NH}_4)_2\text{SO}_4$  solution, mixing well after each addition. Add conc acetic acid until  $\text{BaSO}_4$  precipitates; add 2 mL excess. Digest on a hot plate until precipitate settles. Centrifuge and discard supernatant.

2) Add 20 mL EDTA reagent, heat in a hot water bath, and stir until precipitate dissolves. Add a few drops 10N NaOH if precipitate does not dissolve readily. Add 1 mL strontium-yttrium mixed carrier and 1 mL lead carrier (Solution B), and stir

thoroughly. Add a few drops 10N NaOH if any precipitate forms. Add 1 mL  $(\text{NH}_4)_2\text{SO}_4$  solution and stir thoroughly. Add conc acetic acid until  $\text{BaSO}_4$  precipitates; add 2 mL excess. Digest in a hot water bath until precipitate settles. Centrifuge, discard supernatant, and note time.

3) Wash precipitate with 10 mL distilled water. Centrifuge and discard supernatant. Transfer quantitatively to a tared stainless-steel planchet using a minimum quantity distilled water. Dry under an infrared lamp to constant weight. If after sufficient beta decay of the actinium fraction  $^{228}\text{Ra}$  is found to be absent, make a direct alpha count for  $^{226}\text{Ra}$ . If  $^{228}\text{Ra}$  is present, determine  $^{226}\text{Ra}$  by radon emanation, ¶ c below.

4) Count immediately in an alpha proportional counter.

c. Radium-226 by radon: Transfer the final precipitate obtained in b above to a small beaker using a rubber policeman and 14 mL EDTA reagent. Add a few drops 10N NaOH and heat on a hot plate to dissolve. Cool and transfer to a radon bubbler (Figure 7500-Ra:1) rinsing beaker with 1 mL EDTA reagent. Proceed as in Method C beginning with 5a14).

## 5. Calculation

### a. Calculation of $^{228}\text{Ra}$ concentration:

$$^{228}\text{Ra, pCi/L} = \frac{C}{2.22 \times \text{EVR}} \times \frac{\lambda t_2}{(1 - e^{-\lambda t_2})} \times \frac{1}{(1 - e^{-\lambda t_3})} \times \frac{1}{e^{-\lambda t_1}}$$

where:

C = average net count rate, cpm,

E = counter efficiency, for  $^{228}\text{Ac}$ ,

V = sample volume, L,

R = fractional chemical yield of yttrium carrier, ¶ 4a10),

multiplied by fractional chemical yield of barium carrier, ¶ b3),

$\lambda$  = decay constant of  $^{228}\text{Ac}$ , 0.001 884/min,

$t_1$  = time between first  $\text{Y}(\text{OH})_3$  precipitation and start of counting, min,

$t_2$  = counting time, min, and

$t_3$  = ingrowth time of  $^{228}\text{Ac}$  between last  $\text{BaSO}_4$  precipitation and first  $\text{Y}(\text{OH})_3$  precipitation, min.

The factor  $\lambda t_2/(1 - e^{-\lambda t_2})$  corrects average count rate to count rate at beginning of counting time.

b. Calculation of  $^{226}\text{Ra}$  (plus any  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$ ) concentration: See Section B.5.

c. Calculation of  $^{226}\text{Ra}$  (emanation) concentration: See Section C.6.

## 6. Bibliography

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‡ Whatman No. 42 or equivalent.

## 7500-Ra E. Gamma Spectroscopy Method

### 1. General Discussion

*a. Application:* This method is a gamma spectroscopy method for the measurement of radium-224 ( $^{224}\text{Ra}$ ) in ground and surface water that is, or may be, used for drinking water. Other radium isotopes ( $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ) are not the focus of this method. However, with sufficient time allowed for ingrowth of  $^{226}\text{Ra}$  progeny,  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , in addition to  $^{224}\text{Ra}$ , may be determined concurrently, in a single analysis.

Ensure that the analyst is experienced with gamma-ray measurements and the mathematics and implications of transient equilibrium, because commercial gamma software does not have the capability to calculate sample concentration for transient equilibrium.

Preferably have the analyst prepare at least three samples with known additions by the method before it is used for samples. This method also can be the basis for standard operating procedures (SOPs) that may differ with respect to the intrinsic efficiency of the detector, the method of precipitating the radium and lead, the method of yield determination, and the sample volume used with the chemistry.

*b. Principle:* Radium in water is separated from a 3-L sample by a fast  $\text{PbSO}_4$  coprecipitation technique. The gamma radiation from  $^{212}\text{Pb}$ , which is produced by the decay of  $^{224}\text{Ra}$ , is assayed by using a high-resolution intrinsic Ge detector. The 238.6-keV  $^{212}\text{Pb}$  photopeak is used to determine the  $^{212}\text{Pb}$  activity, and standard decay and growth equations are applied to determine the parent  $^{224}\text{Ra}$  activity.

Because of the short half-life of  $^{224}\text{Ra}$  and radioactive growth/decay considerations (see ¶ 5 below), the water sample must be prepared and counted during the 2- to 4-d window after sample collection. If presence of unsupported  $^{212}\text{Pb}$  ( $^{212}\text{Pb}$  not due to ingrowth from  $^{224}\text{Ra}$  parent) is suspected, at least two consecutive countings are required to assess this contribution.

*c. Interferences:* Lead-214, a  $^{226}\text{Ra}$  progeny, has a 241.9-keV gamma ray (7.5% abundance). Similarly,  $^{224}\text{Ra}$  has a 240.8-keV gamma ray (3.9% abundance). Resolve the photopeaks due to these two gamma rays correctly in the gamma-ray spectrum to minimize interference with the  $^{212}\text{Pb}$  238.6-keV peak, thus avoiding high bias for  $^{224}\text{Ra}$  determination.

The carryover of  $^{228}\text{Th}$  into the  $\text{Pb}(\text{Ra})\text{SO}_4$  precipitate has been measured to be about 5%. This is insignificant for drinking water samples because the typical range of activities for thorium radionuclides is below 0.1 pCi/L. Consequently, the  $^{224}\text{Ra}$  activity due to ingrowth, during the time span between sample preparation and counting, from the carried-over  $^{228}\text{Th}$  also is negligible and can be disregarded.

### 2. Apparatus

*a. Gamma-ray spectroscopy system* with high-resolution intrinsic Ge detector.

*b. Beakers*, 4-L.

*c. Watch glasses*.

*d. Hot plates*.

*e. Magnetic stirrer*.

*f. Stirring rods*.

*g. Stirring bar retriever*.

*h. Planchets*, stainless steel, 5-cm diam, either shallow or deep type.

*i. Membrane filters*, 47-mm diam, 0.45- $\mu\text{m}$  porosity.

*j. Suction filter apparatus*.

*k. Retaining rings or o-rings*.

*l. Snap-ring pliers* to inset retaining rings.

*m. Pipets*, 1.0- and 20-mL.

### 3. Reagents

*a. Sodium sulfate*,  $\text{Na}_2\text{SO}_4$ , anhydrous.

*b. Sulfuric acid*, 18M, 96%  $\text{H}_2\text{SO}_4$ .

*c. Lead carrier*, 100 mg  $\text{Pb}^{2+}/\text{mL}$ : Dissolve 160 g reagent-grade  $\text{Pb}(\text{NO}_3)_2$  in 800 mL distilled water and dilute to 1 L.

*d. Lead sulfate wash solution*: Dissolve 25 g anhydrous sodium sulfate in 1 L 1% sulfuric acid.

*e. Mixed-nuclide gamma-ray standard solution*, traceable to NIST.

### 4. Procedure

*a. Sample collection and preservation:* Collect water samples in plastic bottles and acidify in the field, immediately after collection, with  $\text{HNO}_3$  (or  $\text{HCl}$  if sample is to be shipped, because of DOT requirements) to a pH of 2.0 or lower. Record time and date of sample collection. If sample is not preserved in the field, acidify it in the laboratory and let it stand over 16 h before chemical separation.

*b. Chemical separation:* Measure 3 L sample by weight and transfer to a 4-L beaker. NOTE: For other sample portions, vary the concentration of chemicals used in the subsequent steps proportionally.

To the 3-L portion, add 24 g anhydrous sodium sulfate and 18 mL conc  $\text{H}_2\text{SO}_4$ . Place a magnetic stirrer bar in the beaker, cover with watch glass, and bring sample to a roiling boil on magnetic stirrer/hot plate. While stirring and boiling, add 1.0 mL lead carrier solution (100 mg/mL) dropwise to each beaker and continue boiling for 2 min. Then, add another 1.0 mL lead carrier solution similarly, and boil an additional 15 min. NOTE: In most cases, the roiling boiling water is sufficient to facilitate rapid and nearly homogeneous  $\text{PbSO}_4$  precipitation. For samples with high total dissolved solids (TDS), constant stirring of water sample is recommended to avoid bumping.

Remove stirrer bar and place beaker in an ice bath to cool. (Cooling without ice bath takes several hours).

Pre-weigh a membrane filter. Isolate the lead sulfate precipitate by carefully pouring contents of beaker through filter system fitted with pre-weighed filter. Use lead sulfate wash solution to complete the transfer.

Transfer filter to a planchet. Insert a retaining ring using snap-ring pliers, and place planchet in a petri dish. Alternate means of securing the filter paper in a flat position, such as o-ring or adhesive, may be used. Retain filter after gamma-ray measurement for chemical yield determination.

*c. Instrumental analysis:*

1) Sample counting procedure — Mount petri dish containing coprecipitated sample source planchet on an intrinsic Ge detector. Analyze filter paper by gamma-ray spectroscopy for at least two consecutive counts, separated by 24 h. Follow the 238.6-keV  $^{212}\text{Pb}$  photopeak in these measurements. Select a count time to achieve a  $2\sigma$  error of 10%.

If analyzing for  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , measure activities of their respective daughter products  $^{228}\text{Ac}$  and  $^{214}\text{Pb}$  (or  $^{214}\text{Bi}$ ). Allow adequate time from the point of Ra separation to counting to establish equilibrium state (ingrowth periods of 2 d and 21 d for  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$ , respectively).

2) Chemical yield determinations — After gamma-ray spectroscopy measurements are completed, weigh filter paper containing  $\text{PbSO}_4$  precipitate for chemical yield determination.

3) Detector efficiency calibration — Distribute a portion of the standard solution (¶ 3e) uniformly as very fine droplets over a membrane filter (¶ 2i). Count prepared calibration standard on the Ge detector. Select count time to achieve a  $2\sigma$  counting error of 1% for the lowest accumulated standard photopeak.

4) Background determination — Prepare a background sample, consisting of a membrane filter on a planchet without application of standard solution, and count for 1000 min or longer. The spectrum obtained from the analysis of background sample detector is used to create distinct background files. For each sample analysis, subtract the contributions of background peaks, as determined from the background file, from the sample peaks.

## 5. Calculation

### a. Lead-212 activity:

Calculate  $^{212}\text{Pb}$  activity with the equation:

$$A_{212} = \frac{C_s - C_b}{E \times A \times V \times 2.22 \times Y} \left( \frac{\lambda_{224} t_s}{1 - e^{-\lambda_{224} t_s}} \right)$$

where:

$A_{212}$  =  $^{212}\text{Pb}$  activity at start of count time, pCi/L,

$C_s$  = sample net count rate under 238.6-keV photopeak region, cpm,

$C_b$  = background net count rate for 238.6-keV photopeak region, cpm,

$E$  = detection efficiency for 238.6-keV gamma ray,

$A$  = fractional gamma-ray abundance for 238.6-keV  $^{212}\text{Pb}$ , 0.436,

$V$  = volume of sample, L,

2.22 = conversion factor from dpm to pCi/L,

$Y$  = chemical yield,

$t_s$  = sample count time, min, and

$\lambda_{224}$  =  $^{224}\text{Ra}$  decay constant =  $1.31 \times 10^{-4}/\text{min}$ .

The multiplicative factor inside the parentheses in this equation represents the correction of  $^{212}\text{Pb}$  activity for decay during the counting period.

b. Radium-224 activity: The correlation between  $^{224}\text{Ra}$  parent and  $^{212}\text{Pb}$  decay products is expressed as:

$$A_{212} = \frac{\lambda_{212}}{\lambda_{212} - \lambda_{224}} A_{224}^0 (e^{-\lambda_{224} t} - e^{-\lambda_{212} t})$$

$$= 1.14 A_{224}^0 (e^{-\lambda_{224} t} - e^{-\lambda_{212} t})$$

where:

$A_{224}^0$  =  $^{224}\text{Ra}$  activity at sample collection time,

$\lambda_{212}$  =  $^{212}\text{Pb}$  decay constant ( $1.086 \times 10^{-3}/\text{min}$ ), and

$t$  = time from sample collection to the start of counting.

When the two equations above are combined,

$$A_{224}^0 = \frac{C_s - C_b}{1.14 \times E \times A \times V \times 2.22} \left( \frac{1}{e^{-\lambda_{224} t} - e^{-\lambda_{212} t}} \right) \left( \frac{\lambda_{224} t_s}{1 - e^{-\lambda_{224} t_s}} \right)$$

c. Minimum detectable count rate (MDR): The MDR is the mean expected count rate of samples having a 5% probability of not being detected where activity is present. The MDR may be calculated from the formula:

$$MDR = \frac{2.71}{t_b} + \left[ 3.29 \times \sqrt{\frac{(C_c + C_b)}{t_b} \times \left( 1 + \frac{t_b}{t_s} \right)} \right]$$

where:

$C_c$  = Compton continuum background count rate under 238.6-keV photopeak region, and

$t_b$  = background count time.

In the more specific case, where the sample count time is equal to background count time,  $t_b = t_s$ , this is simplified to

$$MDR = \frac{2.71}{t_s} + 4.65 \sqrt{(C_c + C_b) \div t_s}$$

d. Minimum detectable concentration (MDC): The MDC for  $^{212}\text{Pb}$  is calculated from the MDR as follows:

$$MDC_{212} = \frac{MDR}{E \times A \times V \times 2.22 \times Y} \left( \frac{\lambda_{224} t_s}{1 - e^{-\lambda_{224} t_s}} \right)$$

The MDC for  $^{224}\text{Ra}$  at sample collection time,  $MDC_{224}^0$ , can be calculated using the first equation in ¶ b above and expressed as:

$$MDC_{224}^0 = \frac{MDC_{212}}{1.14(e^{-\lambda_{224} t} - e^{-\lambda_{212} t})}$$

e. Uncertainties: If  $C_g$  represents the gross count rate in the 238.6-keV region, then:

$$C_s = C_g - C_c$$

The standard deviation associated with  $C_s$  is equal to  $\sqrt{(C_g + C_c)/t_s}$  and the standard deviation associated with the background subtracted sample count rate under the 238.6-keV photopeak region, i.e.,  $C_s - C_b$ , is given by

$$\sqrt{[(C_g + C_c)/t_s] + [C_b/t_b]}$$

and the percent error at 95% level confidence is:

TABLE 7500-Ra:III. RESULTS OF COLLABORATIVE PRECISION STUDY

Portion Size <i>L</i>	Sample Concentration <i>pCi/L*</i>	No. of Results	SD† <i>pCi/L</i>	Repeatability (Within- Laboratory SD) <i>pCi/L</i>	Between- Laboratory Error <i>pCi/L</i>	Reproducibility (Total Uncertainty) <i>pCi/L</i>
1	3.6	2	1.6	1.4	0.7	1.6
	5.8	4	1.3	1.7	0.6	1.8
	12.2	5	1.6	1.2	1.4	1.9
3	2.7	4	0.3	0.1	0.3	0.3
	5.8	8	1.0	1.2	0.9	1.5
	12.0	10	0.6	0.4	0.6	0.7
6	3.4	2	0.1	—	—	—
	6.0	4	0.2	—	—	—
	14.3	5	0.3	—	—	—

\* Mean of individual laboratory means.

† Standard deviation.

$$\%1.96 \text{ SD} = \frac{1.96 \sqrt{[(C_g + C_c)/t_s] + [C_b/t_b]} \times 100}{C_s - C_b}$$

## 6. Precision and Bias

A small collaborative study, consisting of three laboratories analyzing three New Jersey groundwater samples at three concentration levels, was conducted to determine precision. The results are summarized in Table 7500-Ra:III. The true activity concentrations were not known, but it was known that the samples were at three distinct concentration levels. The samples were analyzed by gamma spectroscopy of the original water and radiochemical analysis of 1-L, 3-L, and 6-L portions of the water. Two of the laboratories performed analyses of the 1-L and 3-L portions and the third laboratory performed analyses of the 6-L portions. The results of an analysis of variance, calculated by standard statistical methods, of the 3-L and 1-L portion data are given in the table. The precipitates from these portions were gamma-counted for various count times, but the vast majority were counted for 1000 min. The data for the 6-L portions are presented with the standard deviations for the three samples.

The chemical recoveries of lead carrier were determined by single-laboratory testing and multilab testing as described above. The chemical yields are 90% or greater and can be determined gravimetrically.

The radiochemical bias of the method was determined by single-laboratory analysis of water samples fortified at two levels with  $^{228}\text{Ra}$  standard solution, in equilibrium with its progeny, including  $^{224}\text{Ra}$ . For  $^{224}\text{Ra}$  sample concentration of 1350  $\text{pCi/L}$ ,

recovery was 98.5% and bias  $-1.5\%$ ; for concentration of 53.4  $\text{pCi/L}$ , recovery was 108.9% and bias 8.9%.

Two approaches to gamma spectroscopic determination of  $^{224}\text{Ra}$  were evaluated by comparing results of analyses of 20 randomly selected groundwater split samples between the New Jersey Department of Health and Senior Services (NJDHSS) Radiation Laboratory and U.S. Geological Survey Laboratory in Reston, Va. Aside from subtle differences, the two methods use similar approaches to the isolation of radium and its quantitation by gamma ray spectroscopy. Concentrations in the samples analyzed ranged from less than 0.5 to 12.6  $\text{pCi/L}$ , with a median of 2.7  $\text{pCi/L}$ . Results of the two-tailed paired  $t$  test indicated that the differences between concentrations in sample pairs were not different from zero at the 95% confidence level.

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## 7500-Rn RADON\*

## 7500-Rn A. Introduction

## 1. Occurrence and Significance

Radon-222 is a gaseous decay product of naturally occurring radium-226. It is an alpha-emitter with a 3.82-d half-life, and normally is of concern only in groundwater. It is considered to be carcinogenic, as are its short-lived daughters. In household air, radon may originate from radium in building materials and the surrounding soil. Where radon concentration in the water supply is high, the water also can be a major source of radon in household air. While radon dissolves readily in water and other solvents, it is easily displaced from water by air; thus, aeration of radon-bearing water in normal household uses can release a significant fraction of the dissolved radon to the air.<sup>1-3</sup>

The average <sup>222</sup>Rn concentration in community groundwater systems in the U.S. is estimated to range from 200 to 600 pCi/L,<sup>2-6</sup> with some individual wells having much higher concentrations.

\*Approved by Standard Methods Committee, 2001.

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## 7500-Rn B. Liquid Scintillation Method

## 1. General Discussion

*a. Principle:* This method is specific for radon-222 (radon) in drinking water. Radon is partitioned selectively into a mineral-oil scintillation cocktail immiscible with the water sample. The sample is dark-adapted and equilibrated, and then counted in a liquid scintillation counter using a region or window of the energy spectrum optimal for radon alpha particles. Results are reported as pCi/L.

The procedure has been developed for the analysis of radon in drinking water supplies from groundwater and surface-water sources. Applications of this analytical procedure to matrices other than drinking water have not been studied; use caution in analyzing any such samples.

*b. Interferences:* There are no known chemical interferences from species found in drinking water nor from the dilute concentration of acid that may be present in the calibration standards. Uranium, radium, or other radioactive elements would cause a positive bias, if present in quantities significantly greater than the radon.

Diffusion of radon is affected by temperature and pressure. Let samples equilibrate to room temperature before processing.

Precision and accuracy of the method are affected by the background in the energy window used for analysis. A procedure

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is provided for selection of the analytical window to minimize the background contribution to the measurement.

Some cocktails will become progressively quenched by atmospheric oxygen after opening. This problem has not been noted for the mineral-oil-based cocktail. For other than mineral-oil-based cocktails, check weekly for quenching.

Radon has an affinity for some plastics used in sample containers. Use only glass sample containers or glass scintillation vials with TFE or foil-lined caps.

*c. Sample preservation, storage, and holding time:* Collect samples from a nonaerated faucet that has been allowed to flow for sufficient time so that the sample is representative of the water in the distribution system or well. The following procedure will minimize the loss of radon from the sample during collection:

Place a glass sample vial in a 300- to 600-mL beaker or other suitable container; attach delivery tube to faucet, and start the flow. Make sure that delivery tube does not let bubbles enter the sample. Fill vial to prevent its floating, then fill beaker until vial is submerged. Place tip of delivery tube about two thirds of the way into vial and fill until approximately two or more vial volumes (50 to 100 mL) have been displaced. Carefully remove vial by hand or with a pair of 25-cm (10 in.) tweezers and cap vial with a TFE or foil-lined cap. Cap sample vials underwater,

if possible. Invert sample and check for air bubbles. If any bubbles are present, discard sample and repeat sampling procedure.

Alternatively, collect samples in containers other than scintillation vials, with similar precautions.

Record date and time of sample collection and store sample in a cooler. Transport samples to laboratory in a cooler or other suitable insulated package to avoid large temperature changes and outgassing of radon. Begin counting within 4 d or applicable regulatory specified holding time.

*d. Minimum detectable concentration:* 18 pCi/L for a 50-min count time, 6 cpm background, 2.7 cpm/dpm efficiency, and energy region optimized by the procedure in ¶ 4b.

## 2. Apparatus

- Pipet:* Precision 5-mL mechanical pipet or syringe.
- Scintillation cocktail dispenser* adjustable to deliver 5 mL.
- Liquid scintillation counter:* Preferably use a system permitting automatic spectral analysis.
- Faucet connector or universal faucet adapter.*
- Plastic tubing* for connector or adapter.
- Scintillation vials:* 23-mL glass vials with caps, TFE or foil-lined for sampling and plastic\* for counting.
- Volumetric glassware.*
- Sample storage and shipping containers,* insulated.

## 3. Reagents

- Scintillation cocktail:* Water-immiscible high-efficiency mineral oil cocktail or other commercial equivalent.
- Hydrochloric acid,* HCl, conc.
- Water,* radon-free demineralized or equivalent.
- Radium solution:* Use two dilutions for calibration and check standards. Use NIST-traceable (explicit or implicit) radium-226 standard solution.

## 4. Procedure

*a. Calibration:* Prepare 100 mL radium-226 in water standard such that the final activity will be approximately 8000 pCi/L by the procedure suggested below. Transfer standard to a scintillation vial or other suitable container, seal, and record initial mass to nearest 0.0001 g. To a 100-mL volumetric flask add 20 mL water and 0.5 mL conc HCl; stopper. Transfer with a pipet, or suitable dropper, the required mass of radium solution into flask; re-weigh vial. Obtain actual mass of radium solution added by difference of final and initial weights. Fill to mark and mix.

Transfer 15 mL diluted standard into scintillation vial, to which has been added 5 mL mineral oil cocktail. Prepare at least three standards and three backgrounds using distilled or deionized water.

Set standards and background samples aside for at least 25 d (99% ingrowth) to allow radon progeny to attain secular equilibrium with radium-226. Determine optimal analytical window as outlined in ¶ 4b below. After ingrowth period, let sample dark-adapt for 3 h if necessary and count for 50 min. Repeat

counting two additional times. From pooled results calculate a system calibration factor by the following expression:

$$CF = \frac{S - B}{C \times V}$$

where:

- CF* = calibration factor, cpm/pCi,
- S* = standard counting rate, cpm,
- B* = background counting rate, cpm,
- C* = concentration of radium-226 standard, pCi/L, and
- V* = volume of standard used, 0.015 L.

*b. Selecting optimal window:* Count a radon standard for 5 min or sufficient time to acquire several thousand counts or more in the alpha region and generate a sample spectrum. For greater clarity use a log scale for the channel number or energy axis if possible.

The alpha activity region of interest will be obvious as one or two large peaks at the higher end of the energy spectrum. The lower peak is the doublet of radon-222 and polonium-218 and the higher peak is that of polonium-214. The optimal window is formed by extending the region by approximately 10 channels on each side of the alpha peaks. Use this window for subsequent calibration and analysis. Calibration factor should be at least 6 cpm/pCi with the background not exceeding 6 cpm.

For counters not having a spectrum display, set window initially wide-open and count for sufficient time to obtain several thousand counts. Adjust energy window to a width of 5% of full scale at upper end of scale (95 to 100%) and determine count rate in the region. Repeat counts at successively lower regions using the same 5% interval (90 to 95, 85 to 90, 80 to 85, etc.). Plot count rate versus midpoint of interval and choose region of interest, which will be evident by one or two prominent peaks in the upper half of the energy scale. Background should be 6 cpm or less and conversion factor should be approximately 6 cpm/pCi.

*c. Analysis of samples:* Carefully remove by pipet 8.5 mL sample from the scintillation vial used for collection and add 5 mL water-immiscible scintillation cocktail. Alternatively, pipet, without turbulence, a 15-mL portion to a scintillation vial containing 5 mL cocktail if sample was collected in a different container.

Cap and shake sample for 30 s and set aside in the dark for a minimum of 3 h to equilibrate radon progeny and dark-adapt sample. Count all samples within the regulation specified holding time. The time of sample collection is the initial time for decay correction.

Count a standard for 5 min or longer if required and either examine spectrum or compare results to previous standards to determine if there has been any shift or quench due to changes in the cocktail or instrument drift. Count samples for 50 min or to a percent  $2\sigma$  counting error of 10% or for a period of time to achieve an uncertainty in the net counting rate corresponding to program data quality objectives using optimized window settings for alpha counting. Make sure the expression used includes the background in the uncertainty computation. This may have to be done manually because most instruments calculate the uncertainty only for the gross counting rate.

\*Polysal core liner, or equivalent.

## 5. Calculations

Calculate concentration of radon-222 in pCi/L from the following equation:

$$\text{Rn, pCi/L} = \frac{G - B}{CF \times D \times V}$$

where:

$G$  = gross counting rate of sample, cpm,

$B$  = background counting rate, cpm,

$CF$  = calibration factor (see 4a),

$V$  = volume of sample (~0.015 L), and

$D$  = decay factor for Rn-222 between time of collection and midpoint of counting period for that sample.

Calculate  $2\sigma$  (95% confidence level) counting uncertainty, as:

$$2\sigma, \text{ pCi/L} = \frac{2 \times \sqrt{\frac{G}{T_G} + \frac{B}{T_B}}}{CF \times D \times V}$$

where:

$T_G$  = duration of sample count, and

$T_B$  = duration of background count.

Report  $2\sigma$  uncertainty with each drinking water radioactivity concentration result. This term represents the uncertainty due to the random nature of radioactive decay; it is related to count time and can be used to determine whether sample been counted long enough to satisfy any required precision criteria. If percent counting error ( $2\sigma$  counting error divided by activity concentration) exceeds precision requirements, count sample longer or reduce the holding time.

Report result and counting error together in the form:

$$X \pm 2\sigma \text{ pCi/L, } 2\sigma \text{ counting error}$$

For example, for a water sample with calculated radon-222 concentration of 285 pCi/L and  $2\sigma$  counting error of 27 pCi/L, report result as:

$$^{222}\text{Rn: } 285 \pm 27 \text{ pCi/L, } 2\sigma \text{ counting error}$$

## 6. Quality Control

*a. Background samples:* Include a minimum of two background samples with each batch of 20 samples. Place backgrounds as first and next-to-last samples of batch. Use average of these backgrounds to calculate results for batch. The background should be  $\leq 6$  cpm.

For a suitable background sample, use laboratory deionized water, or prepare by boiling 2 L laboratory radium- and uranium-free tap water to remove residual radon if present. Store the cooled tap water in a capped 2-L bottle.

*b. Duplicate samples:* Collect duplicate field samples for one out of every ten samples. Preferably collect all samples in duplicate if the number of samples from an individual client represents a single source. Ensure that at least 10% of the samples analyzed daily are duplicates, and that duplicate analy-

ses have a relative percent difference (RPD) less than or equal to the percent  $2\sigma$  counting error or 10% of the decay-corrected radon concentration, whichever is greater. Relative percent difference is calculated by the following expression:

$$\text{RPD} = \frac{|\text{Analysis 1} - \text{Analysis 2}| \times 200}{\text{Analysis 1} + \text{Analysis 2}}$$

Record the RPD and note acceptability of the duplicate analysis. If RPD exceeds the limits, recount duplicates. If results still exceed limits but RPD for the quality control check standard is acceptable, a problem with the sampling procedure may exist. Resolve problem before collecting and analyzing additional samples.

*c. Quality control check standard (QCCS):* QCCSs are prepared from a dilution of radium different from that used to prepare standards and should have a nominal activity of ~8000 pCi/L. Place first QCCS immediately after first background and before first sample. Place additional QCCS after every tenth sample in batch, and final QCCS as last sample of the batch.

The relative percent difference (RPD) between sequential pairs of QCCS samples must be less than or equal to the  $2\sigma$  counting error or 10% of the known value of the QCCS sample, whichever is greater. If RPD exceeds this value, recount the pair of QCCS samples. If RPD is still unacceptable, standards and/or instrument are suspect. Resolve problem and rerun samples between suspect QCCS.

*d. Records:* Collect and maintain results from backgrounds, duplicate pairs, and QCCS standards in a bound notebook; include date, results, name of analyst, and comments relevant to data evaluation.

Plot averages of backgrounds and QCCS standards on a control chart for the counter.

## 7. Precision and Bias

A collaborative study of this method composed of 36 participants<sup>1</sup> produced the results shown below:

Sample Conc. pCi/L	Accuracy %	Repeatability pCi/L	Reproducibility pCi/L	Bias %
111	101-102	9	12	0.7-2.3
153	102-103	10	16-18	2.3-3.4

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## 7500-Sr TOTAL RADIOACTIVE STRONTIUM AND STRONTIUM-90\*

### 7500-Sr A. Introduction

The important radioactive nuclides of strontium produced in nuclear fission are  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$ . Strontium-90 is one of the most hazardous of all fission products. It decays slowly, with a half-life of 28 years. Upon ingestion, strontium is concentrated in the bone.

\* Approved by Standard Methods Committee, 2001.

The method presented in this section is designed to measure total radioactive strontium ( $^{89}\text{Sr}$  and  $^{90}\text{Sr}$ ) or  $^{90}\text{Sr}$  alone in drinking water or in filtered raw water. It is applicable to sewage and industrial wastes provided that steps are taken to destroy organic matter and eliminate other interfering ions.

### 7500-Sr B. Precipitation Method

#### 1. General Discussion

*a. Principle:* A known amount of inactive strontium ions, in the form of strontium nitrate,  $\text{Sr}(\text{NO}_3)_2$ , is added as a "carrier." The carrier, alkaline earths, and rare earths are precipitated as the carbonate to concentrate the radiostrontium. The carrier, along with the radionuclides of strontium, is separated from other radioactive elements and inactive sample solids by precipitation as  $\text{Sr}(\text{NO}_3)_2$  from fuming nitric acid solution. The strontium carrier, together with the radionuclides of strontium, finally is precipitated as strontium carbonate,  $\text{SrCO}_3$ , which is dried, weighed to determine recovery of carrier, and measured for radioactivity. The activity in the final precipitate is due to radioactive strontium only, because all other radioactive elements have been removed. A correction is applied to compensate for losses of carrier and activity during the various purification steps. A delay in the count will give an increased counting rate due to the ingrowth of  $^{90}\text{Y}$ .

*b. Concentration techniques:* Because of the very low amount of radioactivity, a large sample must be taken and the activity concentrated by precipitation.  $\text{Sr}(\text{NO}_3)_2$  and barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ , carriers are added to the sample. Sodium carbonate is then added to concentrate radiostrontium by precipitation of alkaline earth carbonates along with other radioactive elements. The supernate is discarded. The precipitate is dissolved and reprecipitated to remove interfering radionuclides.

*c. Interference:* Radioactive barium ( $^{140}\text{Ba}$ ,  $^{140}\text{La}$ ) interferes in the determination of radioactive strontium inasmuch as it precipitates with the radioactive strontium. Eliminate this interference by adding inactive  $\text{Ba}(\text{NO}_3)_2$  carrier and separating this from the strontium by precipitating barium chromate in acetate

buffer solution. Radium isotopes also are eliminated by this treatment.

In hard water, some calcium nitrate may be coprecipitated with  $\text{Sr}(\text{NO}_3)_2$  and can cause errors in recovery of the final precipitate and in measuring its activity. Eliminate this interference by repeated precipitations of strontium as the nitrate followed by leaching the  $\text{Sr}(\text{NO}_3)_2$  with acetone (CAUTION).

For total radiostrontium, count the precipitate within 3 to 4 h after the final separation and before ingrowth of  $^{90}\text{Y}$ .

*d. Determination of  $^{90}\text{Sr}$ :* Because it is impossible to separate the isotopes  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  by any chemical procedure, the amount of  $^{90}\text{Sr}$  is determined by separating and measuring the activity of  $^{90}\text{Y}$ , its daughter. After equilibrium is reached, the activity of  $^{90}\text{Y}$  is exactly equal to the activity of  $^{90}\text{Sr}$ . Two alternate procedures are given for the separation of  $^{90}\text{Y}$ . In the first method,  $^{90}\text{Y}$  is separated by extraction into tributyl phosphate from concentrated nitric acid ( $\text{HNO}_3$ ) solution. It is back-extracted into dilute  $\text{HNO}_3$  and evaporated to dryness for beta counting. The second method consists of adding yttrium carrier, separating by precipitation as yttrium hydroxide,  $\text{Y}(\text{OH})_3$ , and finally precipitating yttrium oxalate for counting.

#### 2. Apparatus

*a. Counting instruments:* Use either an internal proportional counter, gas-flow, with scaler, timer, and register; or a thin end-window (polyester plastic film\*) proportional or G-M counting chamber with scaler, timer, register amplifier, and preferably having an anticoincident system (low background).

\* Mylar, E.I. du Pont de Nemours, Wilmington, DE, or equivalent.

b. *Filter paper*,† 2.4-cm diam; or glass fiber filters, 2.4-cm diam.

c. *Two-piece filtering apparatus* for 2.4-cm filters such as TFE filter holder,‡ stainless steel filter holder, or equivalent.

d. *Stainless steel pans*, about 50 mm diam and 7 mm deep, for counting solids deposited on pan bottom. For counting precipitates on 2.4-cm filters, use nylon disk with rings§ on which the filter samples are mounted and covered by 0.25 mil film.

### 3. Reagents

a. *Strontium carrier*, 10 mg  $\text{Sr}^{2+}$ /mL, standardized: Carefully add 24.16 g  $\text{Sr}(\text{NO}_3)_2$  to a 1-L volumetric flask and dilute with distilled water to the mark. For standardization, pipet three 10.0-mL portions of strontium carrier solution into 40-mL centrifuge tubes and add 15 mL 2N  $\text{Na}_2\text{CO}_3$  solution. Stir, heat in a boiling water bath for 15 min, and cool. Filter  $\text{SrCO}_3$  precipitate through a tared fine-porosity sintered-glass crucible of 15-mL size. Wash precipitate with three 5-mL portions of water and then with three 5-mL portions of absolute ethanol (or acetone). Wipe crucible with absorbent tissue and dry to constant weight in an oven at 110°C (20 min). Cool in a desiccator and weigh.

$$\text{Sr, mg/mL} = \frac{(\text{mg SrCO}_3)(0.5935)}{10}$$

b. *Barium carrier*, 10 mg  $\text{Ba}^{2+}$ /mL: Dissolve 19.0 g  $\text{Ba}(\text{NO}_3)_2$  in distilled water and dilute to 1 L.

c. *Rare earth carrier, mixed*: Dissolve 12.8 g cerous nitrate hexahydrate,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 14 g zirconyl chloride octahydrate,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , and 25 g ferric chloride hexahydrate,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , in 600 mL distilled water containing 10 mL conc HCl, and dilute to 1 L.

d. *Yttrium carrier*: Dissolve 12.7 g yttrium oxide,||  $\text{Y}_2\text{O}_3$ , in 30 mL conc  $\text{HNO}_3$  by stirring and warming. Add an additional 20 mL conc  $\text{HNO}_3$  and dilute to 1 L with distilled water; 1 mL is equivalent to 10 mg Y, or approximately 34 mg  $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ . Determine exact equivalence by precipitating yttrium carrier in acid solution according to ¶s 4c2)–8), below or by extracting yttrium carrier in acid solution according to ¶s 4b3)–11), below.

e. *Acetate buffer solution*: Dissolve 154 g  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  in 700 mL distilled water, add 57 mL conc acetic acid, adjust pH to 5.5 by dropwise addition of conc acetic acid or 6N  $\text{NH}_4\text{OH}$  as necessary, and dilute to 1 L.

f. *Acetic acid*, 6N.

g. *Acetone*, anhydrous.

h. *Ammonium hydroxide*,  $\text{NH}_4\text{OH}$ , 6N.

i. *Hydrochloric acid*, HCl, 6N.

j. *Methyl red indicator*, 0.1%: Dissolve 0.1 g methyl red in 100 mL distilled water.

k. *Nitric acid*,  $\text{HNO}_3$ , fuming (90%), conc, 14N, 6N, and 0.1N.

l. *Oxalic acid*, saturated solution: Dissolve approximately 11 g  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in 100 mL distilled water.

m. *Sodium carbonate solution*, 1M: Dissolve 124 g  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  in distilled water and dilute to 1 L.

n. *Sodium chromate solution*, 0.5M: Dissolve 117 g  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$  in distilled water and dilute to 1 L.

o. *Sodium hydroxide*, 6N: Dissolve 240 g NaOH in distilled water and dilute to 1 L.

p. *Tributyl phosphate*, reagent grade: Shake with an equal volume of 14N  $\text{HNO}_3$  to equilibrate. Separate and discard the  $\text{HNO}_3$  washings.

### 4. Procedure

#### a. Total radiostrontium:

1) To 1 L of drinking water, or a filtered sample of raw water in a beaker, add 2.0 mL conc  $\text{HNO}_3$  and mix. Add 2.0 mL each of strontium and barium carriers and mix well. (A precipitate of  $\text{BaSO}_4$  may form if the water is high in sulfate ion, but this will cause no difficulties.) A smaller sample may be used if it contains at least 25 pCi strontium. The suspended matter that has been filtered off may be digested [see Gross Alpha and Gross Beta Radioactivity, 7110B.4f1)], diluted, and analyzed separately.

2) Heat to boiling, then add 20 mL 6N NaOH and 20 mL 1M  $\text{Na}_2\text{CO}_3$ . Stir and let simmer at 90 to 95°C for about 1 h.

3) Set beaker aside until precipitate has settled (about 1 to 3 h).

4) Decant and discard clear supernate. Transfer precipitate to a 40-mL centrifuge tube and centrifuge. Discard supernate.

5) Add, dropwise (CAUTION—effervescence), 4 mL conc  $\text{HNO}_3$ . Heat to boiling, stir, then cool under running water.

6) Add 20 mL fuming  $\text{HNO}_3$ , cool 5 to 10 min in ice bath, stir, and centrifuge. Discard supernate.

7) Add 4 mL distilled water, stir, and heat to boiling to dissolve the strontium. Centrifuge while hot to remove remaining insolubles and decant supernate to a clean centrifuge tube. Add 2 mL 6N  $\text{HNO}_3$ , heat to boiling, centrifuge while hot, and combine supernate with aqueous supernate. Discard insoluble residue of  $\text{SiO}_2$ ,  $\text{BaSO}_4$ , etc.

8) Cool combined supernates, then add 20 mL fuming  $\text{HNO}_3$ , cool 5 to 10 min in ice bath, stir, centrifuge, and discard supernate.

9) Add 4 mL distilled water and dissolve by heating. Repeat Step 8) preceding.

10) Repeat Step 9) preceding if more than 200 mg Ca were present in the sample.

11) After last  $\text{HNO}_3$  precipitation, invert tube in a beaker for about 10 min to drain off most excess  $\text{HNO}_3$ . Add 20 mL anhydrous acetone, stir thoroughly, cool, and centrifuge. Discard supernate (CAUTION).

12) Dissolve precipitate of  $\text{Sr}(\text{NO}_3)_2 + \text{Ba}(\text{NO}_3)_2$  in 10 mL distilled water and boil for 30 s to remove any remaining acetone.

13) Add 0.25 mL (5 drops) mixed rare earth carrier and precipitate rare earth hydroxides by making solution basic with 6N  $\text{NH}_4\text{OH}$ . Digest in a boiling water bath for 10 min. Cool, centrifuge, and decant supernate to a clean tube. Discard precipitate.

14) Repeat Step 13) preceding.

Note the time of rare earth precipitation, which marks the beginning of the  $^{90}\text{Y}$  ingrowth period. Do not delay procedure more than a few hours after the separation; otherwise, false results will be obtained because of ingrowth of  $^{90}\text{Y}$ .

† Whatman No. 42 or equivalent.

‡ Flurolon Laboratory, Box 305, Caldwell, NJ.

§ Control Molding Corp., Staten Island, NY, or equivalent.

|| Yttrium oxide, Code 1118, American Potash and Chemical Corp., West Chicago, IL, or equivalent. Yttrium oxide of purity less than Code 1118 may require purification because of radioactivity contamination.

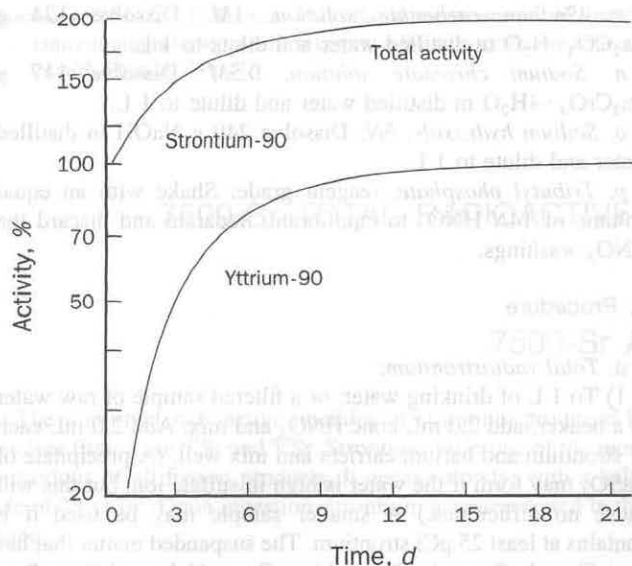


Figure 7500-Sr:1. Yttrium-90 vs. strontium-90 activity as a function of time.

15) Add 2 drops methyl red indicator and then add 6*N* acetic acid dropwise with stirring until indicator changes from yellow to red.

16) Add 5 mL acetate buffer solution, heat to boiling, and add dropwise, with stirring, 2 mL  $\text{Na}_2\text{CrO}_4$  solution. Digest in a boiling water bath for 5 min. Cool, centrifuge, and decant supernate to a clean tube. Discard residue.

17) Add 2 mL 6*N* NaOH, add 5 mL 1*M*  $\text{Na}_2\text{CO}_3$  solution, and heat to boiling. Cool in an ice bath (about 5 min) and centrifuge. Discard supernate.

18) Add 15 mL distilled water, stir, centrifuge, and discard wash water.

19) Repeat Step 18), and proceed either as in Step 20)a) or 20)b), below. *Save this precipitate if a determination of  $^{90}\text{Sr}$  is required.*

20) Either

a) Slurry precipitate with a small volume of distilled water and transfer to a tared stainless steel pan; dry under an infrared lamp, cool, weigh, and count# the precipitate of  $\text{SrCO}_3$ \*\* or

b) Transfer precipitate to a tared paper or glass filter mounted in a two-piece funnel. Allow gravity settling for uniform deposition and then apply suction. Wash precipitate with three 5-mL portions of water, three 5-mL portions of 95% alcohol, and three 5-mL portions of ethyl ether or acetone. Dry in an oven at 110 to 125°C for 15 to 30 min, cool, weigh,\*\* mount on a nylon disk and ring with polyester plastic film cover, and count.

21) Calculation

# Strontium-90 in thick samples is counted with low efficiency; hence, a first count within hours favors  $^{89}\text{Sr}$  counting, and a recount after 3 to 6 d that exceeds the first count provides a rough estimate of the  $^{90}\text{Y}$  ingrowth—see Figure 7500-Sr:1 and R.J. Velten (1966) below.

\*\* When a determination of total strontium is not required, weigh precipitate [Step 20)a) or 20)b)] for carrier recovery but do not count. Then proceed with  $^{90}\text{Sr}$  determination according to ¶ 4b) following.

$$\text{Total Sr activity, pCi/L} = \frac{b}{adf \times 2.22}$$

where:

$a$  = beta counter efficiency [see Step 22) below],

$d$  =  $\frac{\text{mg final SrCO}_3 \text{ precipitate}}{\text{mg SrCO}_3 \text{ in 2 mL of carrier}}$   
= correction for carrier recovery [see Step 23) below],

$f$  = sample volume, L,

$b$  = beta activity, net cpm =  $(i/t) - k$ ,

$i$  = total counts accumulated,

$t$  = time of counting, min, and

$k$  = background, cpm.

22) Counting efficiency—As a first estimate, when mounting sample according to Step 20)a), convert counts per minute to disintegrations per minute, based on the beta activity of cesium-137 standard solutions having a sample thickness equivalent to that of the  $\text{SrCO}_3$  precipitate. More precise measurements may follow a second count after substantial ingrowth of  $^{90}\text{Y}$  from  $^{90}\text{Sr}$ , but this precision is not warranted for the usual total radiostrontium determination. When mounting samples according to Step 20)b), determine self-absorption curves by separately precipitating standard solutions of  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  as the carbonate (see gross beta in Section 7110).

23) Correction for carrier recovery—20 mg Sr are equivalent to 33.7 mg  $\text{SrCO}_3$ . Should more than traces of stable strontium be present in the sample, it would act as carrier; hence its determination by flame photometric or atomic absorption spectrometric method would be required.

b. *Strontium-90 by extraction of yttrium-90*:†† Store  $\text{SrCO}_3$  precipitate, as in ¶ 4a20), for at least 2 weeks to allow ingrowth of  $^{90}\text{Y}$  and then proceed as directed here or in an alternate procedure in ¶ 4c) following.

1) Transfer of precipitate to separatory funnel—Either

a) Place a small funnel upright into mouth of a 60-mL separatory funnel; then place pan with precipitate, as in Step 20)a), in funnel and add, dropwise, 1 mL 6*N*  $\text{HNO}_3$  (CAUTION—*effervescence*); tilt pan to empty into funnel and rinse pan twice with 2-mL portions of 6*N*  $\text{HNO}_3$ ; or

b) Uncover precipitate from filter, as in Step 20)b), and transfer filter with forceps to upright funnel in mouth of 60-mL separatory funnel as in ¶ a) above. Dislodge bulk of precipitate into funnel stem. Dropwise, add with caution 1 mL 6*N*  $\text{HNO}_3$  to filter, removing residual precipitate and dissolving bulk precipitate. Rinse filter and funnel twice with 2-mL portions 6*N*  $\text{HNO}_3$ .

2) Remove filter or pan and add 10 mL fuming  $\text{HNO}_3$  to separatory funnel through upright funnel.

3) Remove upright funnel and add 1 mL yttrium carrier in a separatory funnel.

4) Add 5.0 mL tributyl phosphate reagent, shake thoroughly for 3 to 5 min, allow phases to separate, and transfer aqueous layer to a second 60-mL separatory funnel.

5) Add 5.0 mL tributyl phosphate reagent, shake 5 min, allow phases to separate, and transfer aqueous layer to a third 60-mL separatory funnel.

6) Combine organic extractants in the first and second funnels into one funnel and wash organic phase twice with 5-mL por-

†† See footnote to Step 20a) when a determination for only  $^{90}\text{Sr}$  is required.

tions 14N HNO<sub>3</sub>. Record time as the beginning of <sup>90</sup>Y decay (combine acid washings with aqueous phase in third funnel if a second ingrowth of <sup>90</sup>Y is desired).

7) Back-extract <sup>90</sup>Y from combined organic phases with 10 mL 0.1N HNO<sub>3</sub> for 5 min.

8) Continue as in ¶s 4c6)–8) below or transfer aqueous phase from Step 7) immediately above into a 50-mL beaker and evaporate on a hot plate to 5 to 10 mL.

9) Repeat Step 7) above and transfer aqueous phase to beaker in Step 8) preceding; evaporate to 5 to 10 mL.

10) Transfer residual solution in beaker to a tared stainless steel counting pan and evaporate.

11) Rinse beaker twice with 2-mL portions of 0.1N HNO<sub>3</sub>; add rinsings to counting pan, evaporate to dryness, and weigh.

12) Count in an internal proportional or end-window counter and calculate <sup>90</sup>Sr as given in ¶ 4c9) following.

#### c. Strontium-90 by oxalate precipitation of yttrium-90:††

1) Quantitatively transfer SrCO<sub>3</sub> precipitate to a 40-mL centrifuge tube with 2 mL 6N HNO<sub>3</sub>. Add acid dropwise during dissolution (CAUTION—effervescence). Use 0.1N HNO<sub>3</sub> for rinsing.

2) Add 1 mL yttrium carrier, 2 drops methyl red indicator and, dropwise, add conc NH<sub>4</sub>OH to the methyl red end point.

3) Add 5 mL more conc NH<sub>4</sub>OH and record the time, which is the end of <sup>90</sup>Y ingrowth and the beginning of decay; centrifuge and decant supernate to a beaker (save supernate and washings for a second ingrowth if desired).

4) Wash precipitate twice with 20-mL portions hot distilled water.

5) Add 5 to 10 drops of 6N HNO<sub>3</sub>, stir to dissolve precipitate, add 25 mL distilled water, and heat in a water bath at 90°C.

6) Gradually add 15 to 20 drops saturated oxalic acid reagent with stirring and adjust to pH 1.5 to 2.0 (pH meter or indicator paper) by adding conc NH<sub>4</sub>OH dropwise. Digest precipitate for 5 min and cool in an ice bath with occasional stirring.

7) Transfer precipitate to a tared glass fiber filter in a two-piece funnel. Let precipitate settle by gravity (for uniform deposition) and apply suction. Wash precipitate in sequence with 10 to 15 mL hot distilled water and then three times with 95% ethyl alcohol and three times with diethyl ether.

8) Air-dry precipitate with suction for 2 min, weigh, mount on a nylon disk and ring with polyester plastic film cover, count, and calculate <sup>90</sup>Sr as follows.

#### 9) Calculation

$${}^{90}\text{Sr, pCi/L} = \frac{\text{net cpm}}{a b c d f g \times 2.22}$$

where:

*a* = counting efficiency for <sup>90</sup>Y,

*b* = chemical yield of extracting or precipitating <sup>90</sup>Y,

*c* = ingrowth correction factor if not in secular equilibrium,

*d* = chemical yield of strontium determined gravimetrically or by flame photometry,

*f* = volume of original sample, L,

*g* = <sup>90</sup>Y decay factor,  $e^{-\lambda t}$ , and

*e* = base of natural logarithms,

$\lambda = 0.693/T_{1/2}$ , where  $T_{1/2}$  for <sup>90</sup>Y is 64.2 h, and

*t* = time between separation and counting, h.

#### 5. Precision and Bias

In a collaborative study of two sets of paired, moderately hard water samples containing known additions of radionuclides, 12 laboratories determined the total radiostrontium and 10 laboratories determined <sup>90</sup>Sr. The results of one sample from one laboratory were rejected as outliers.

The average recoveries of added total radiostrontium from the four samples were 99, 99, 96, and 93%. The precision (random error) at the 95% confidence level was 10 and 12% for the two sets of paired samples. The method was slightly biased on the low side.

#### 6. Bibliography

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## 7500-<sup>3</sup>H TRITIUM\*

### 7500-<sup>3</sup>H A. Introduction

Tritium exists fairly uniformly in the environment as a result of natural production by cosmic radiation and residual fallout from nuclear weapons tests. This background level

gradually is being increased by the use of nuclear reactors to generate electricity, although tritium from this source is only a small proportion of environmental tritium. Nuclear reactors and fuel-processing plants are localized sources of tritium because of discharges during normal operation. This industry is expected to become the major source of environmental

\* Approved by Standard Methods Committee, 2000.

tritium contamination in the future. Tritium is produced in light-water nuclear reactors by ternary fission, neutron capture in coolant additives, control rods and plates, and activation of deuterium. About 1% of the tritium in the primary coolant is released in gaseous form to the atmosphere; the remainder eventually is released in liquid waste discharges.

Most tritium produced in reactors remains in the fuel and is released when fuel is reprocessed.

Naturally occurring tritium is most abundant in precipitation and lowest in aged water because of its physical decay by beta emission to helium. The maximum beta energy of tritium is 0.018 MeV and its half-life is 12.26 years.

## 7500-<sup>3</sup>H B. Liquid Scintillation Spectrometric Method

### 1. General Discussion

*a. Principle:* A sample is treated by alkaline permanganate distillation to hold back most quenching materials, as well as radioiodine and radiocarbon. Complete transfer of tritiated water is assured by distillation to near dryness. A subsample of distillate is mixed with scintillation solution and the beta activity is counted on a coincidence-type liquid scintillation spectrometer. The scintillation solution consists of 1,4-dioxane, naphthalene, POPOP, and PPO.\* The spectrometer is calibrated with standard solutions of tritiated water; then background and unknown samples are prepared and counted alternately, thus nullifying errors that could result from instrument drift or from aging of the scintillation solution.

*b. Interferences:* Sample distillation effectively removes non-volatile radioactivity and the usual quenching materials. For waters containing volatile organic or radioactive materials, use wet oxidation (Section 4500-N<sub>org</sub>) to remove interference from quenching due to volatile organic material. Distillation at about pH 8.5 holds back volatile radionuclides such as iodides and bicarbonates. Double distillation with an appropriate delay (10 half-lives) between distillations may be required to eliminate interference from volatile daughters of radium isotopes. Some clear-water samples collected near nuclear facilities may be monitored satisfactorily without distillation, especially when the monitoring instrument is capable of discriminating against beta radiation energies higher than those in the tritium range.

### 2. Apparatus

*a. Liquid scintillation spectrometer,* coincidence-type.

*b. Liquid scintillation vial:* 20-mL; polyethylene, low-K glass, or equivalent bottles.

*c. Distillation apparatus:* 250-mL round-bottom distillation flask, connecting side-arm adapter, condenser, and heating mantle.

### 3. Reagents

*a. Scintillation solution:* Thoroughly mix 4 g PPO, 0.05 g POPOP, and 120 g solid naphthalene in 1 L spectroquality 1,4-dioxane. Store in dark bottle. Solution is stable for 2 months. Alternatively, use a commercially prepared scintillation solution available from suppliers of liquid scintillation materials.

\* POPOP = 1,4-di-2-(5-phenyloxazolyl) benzene; PPO = (2,5-diphenyloxazole).

*b. Low-background water:* Use water with no detectable tritium activity (most deep well waters are low in tritium).

*c. Standard tritium solution:* Dilute available tritium standard solution to approximately 1000 dpm/mL with low-background water.

*d. Sodium hydroxide,* NaOH, pellets.

*e. Potassium permanganate,* KMnO<sub>4</sub>.

### 4. Procedure

Add three pellets NaOH and 0.1 g KMnO<sub>4</sub> to 100 mL sample in 250-mL distillation flask. Distill at 100 to 105°C, discard first 10 mL distillate, and collect next 50 mL. Thoroughly mix 4 mL distillate with 16 mL scintillation solution in tightly capped vial.

Prepare low-background water and standard tritium solution in same manner as samples.

Hold samples, background, and standards in the dark for 3 h. Count samples containing less than 200 pCi/mL for 100 min and samples containing more than 200 pCi/mL for 50 min.

### 5. Calculations and Reporting

*a. Calculate and report tritium, <sup>3</sup>H, in picocuries per milliliter (pCi/mL) or its equivalent, nanocuries per liter (nCi/L) as follows:*

$${}^3\text{H} = \frac{(C - B)}{(E \times 4 \times 2.22)}$$

where:

*C* = gross counting rate for sample, cpm,

*B* = background counting rate, cpm,

*E* = counting efficiency,  $(S - B)/D$ ,

*S* = gross counting rate for standard solution, cpm, and

*D* = tritium activity in standard sample, dpm, corrected for decay to time of counting.

*b. Calculate the counting error at the 95% confidence level based on the equation for  $\sigma(R)$  given in Section 7020C. A total count of 40 000 within 1 h for a background count rate of about 50 cpm gives a counting error slightly in excess of 1% at the 95% confidence level.*

### 6. Precision and Bias

Samples with tritium activity above 200 pCi/mL can be analyzed with precision of less than  $\pm 6\%$  at the 95% confidence

level and those with 1 pCi/mL can be analyzed with a precision of less than  $\pm 10\%$ .

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## 7500-U URANIUM\*

### 7500-U A. Introduction

#### 1. Occurrence

Uranium, the heaviest naturally occurring element, is a mixture of three radioactive isotopes: uranium-238 (99.275%), uranium-235 (0.72%), and uranium-234 (0.005%). Most drinking-water sources, especially ground waters, contain soluble carbonates and bicarbonates that complex and keep uranium in solution.

#### 2. Selection of Method

Method B, a radiochemical procedure, determines total uranium alpha activity without making an isotopic uranium analysis. Method C is a radiochemical procedure that determines the isotopic content of the uranium alpha activity; it is consistent with determining the differences among naturally occurring, depleted, and enriched uranium.

\* Approved by Standard Methods Committee, 2000.  
Joint Task Group: 20th Edition—Edmond J. Baratta (chair), Paul B. Hahn.

### 7500-U B. Radiochemical Method

#### 1. General Discussion

*a. Principle:* The sample is acidified with hydrochloric or nitric acid and boiled to eliminate carbonate and bicarbonate ions. Uranium is coprecipitated with ferric hydroxide and sub-

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sequently separated. The ferric hydroxide is dissolved, passed through an anion-exchange column, and washed with acid, and the uranium is eluted with dilute hydrochloric acid. The acid eluate is evaporated to near dryness, the residual salt is converted to nitrate, and the alpha activity is counted.

*b. Interference:* The only alpha-emitting radionuclide that may be carried through this procedure is protactinium-231. However, this isotope, which is a decay product of uranium-235, causes very little interference. Check reagents for uranium contamination by analyzing a complete reagent blank.

*c. Sampling:* Preserve sample by adjusting its pH to <2 with HCl or HNO<sub>3</sub> at time of collection.

## 2. Apparatus

*a. Counting instrument,* gas-flow proportional or alpha scintillation counting system.

*b. Ion-exchange column,* approximately 13 mm ID × 150 mm long with 100-mL reservoir.

*c. Membrane filter apparatus,* 47-mm diam.

## 3. Reagents

*a. Ammonium hydroxide,* NH<sub>4</sub>OH, 5N, 1%.

*b. Anion-exchange resin.\**

*c. Ferric chloride carrier:* Dissolve 9.6 g FeCl<sub>3</sub> · 6H<sub>2</sub>O in 100 mL 0.5N HCl; 1 mL = 20 mg Fe<sup>3+</sup>.

*d. Hydriodic acid,* HI, 47%.

*e. Hydrochloric acid,* HCl, conc, 8N, 6N, 0.1N.

*f. Iodic acid,* 1 mg/mL: Dissolve 100 mg HIO<sub>3</sub> in 100 mL 4N HNO<sub>3</sub>.

*g. Nitric acid,* HNO<sub>3</sub>, conc, 4N.

*h. Sodium hydrogen sulfite,* 1%: Dissolve 1 g NaHSO<sub>3</sub> in 100 mL 6N HCl.

*i. Uranium standard solution:†* Dissolve 177.3 mg natural undepleted uranyl acetate, UO<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> · 2H<sub>2</sub>O, in 1000 mL 0.2N HNO<sub>3</sub>; 1 mL = 100 μg U = 150 dpm U = 67.6 pCi U. NOTE: Commonly available uranyl salts may be formed from depleted uranium; verify isotopic composition before use.

## 4. Calibration

Determine counting efficiency, *E*, for a known amount of uranium standard solution (about 750 dpm) evaporated from 6 to 8 mL of 1 mg/mL HIO<sub>3</sub> solution in a 50-mm-diam stainless steel planchet. After flaming planchet, count for at least 50 min. Run a reagent blank with the standard portions and count.

$$\text{Counting efficiency, } E = \frac{C - B}{D}$$

where:

*C* = gross alpha count rate of standard, cpm,

*B* = alpha background count rate, cpm, and

*D* = disintegration rate of uranium standard, dpm.

Determine uranium recovery factor by adding a measured amount of uranium standard to the same volume of sample and taking it through the entire procedure. Alpha count the separated, evaporated, and flamed uranium planchet. Determine the recov-

ery factor on at least 10% of all drinking water samples. For non-drinking water samples, it may be necessary to determine the recovery factor in every sample.

$$\text{Recovery factor, } R = \frac{C' - B'}{DE}$$

where:

*C'* = gross count rate of sample with added uranium, cpm,

*B'* = count of reagent blank, cpm,

*D* = disintegration rate of uranium standard, dpm, and

*E* = counting efficiency.

## 5. Procedure

*a.* If the sample has not been acidified, add 5 mL conc HCl or HNO<sub>3</sub> to 1 L sample in a 1500-mL beaker. Add 1 mL FeCl<sub>3</sub> carrier. In each batch of samples include a distilled-water blank. Cover with watch glass and heat to boiling for 20 min. If pH is greater than 1, add conc HCl or HNO<sub>3</sub> dropwise to bring pH to 1. While sample is boiling, gently add 5N NH<sub>4</sub>OH from a polyethylene squeeze bottle with the delivery tube inserted between the watch glass and the beaker lip. Add 5N NH<sub>4</sub>OH until turbidity persists while boiling continues; then add 10 mL more. Continue boiling for 10 min more, then set aside for 30 min to cool and settle. After sufficient settling, decant and filter supernate through a 47-mm, 0.45-μm membrane filter using a large filtering apparatus. Slurry the remaining precipitate, transfer to the filtering apparatus, and filter with suction. Complete transfer using 1% solution of NH<sub>4</sub>OH delivered from a polyethylene squeeze bottle. Place filtering apparatus over a clean 250-mL filtering flask, add 25 mL 8N HCl to dissolve precipitate, and filter. Wash filter with an additional 25 mL 8N HCl. (Alternatively, use centrifugation in place of filtration as in 7500-U.C.4a.)

*b.* Prepare an ion-exchange column by slurring the anion-exchange resin with 8N HCl and pouring it into a 13-mm-ID column to give a resin bed height of about 80 mm. Transfer solution to the 100-mL reservoir of the ion-exchange column. Rinse side-arm filtering flask twice with 25-mL portions of 8N HCl. Combine in the ion-exchange reservoir. Pass sample solution through the anion-exchange column at a flow rate of not more than 5 mL/min. After sample has passed through column, elute the iron (and plutonium if present) with six column volumes of freshly prepared 8N HCl containing 1 mL 47% HI / 9 mL 8N HCl. Wash column with two additional column volumes of 8N HCl. Discard all washes. Elute uranium into a 100-mL beaker with six column volumes of 0.1N HCl. Evaporate acid eluate to near dryness and convert residue to the nitrate form by three successive treatments with 5-mL portions of conc HNO<sub>3</sub>, evaporating to near dryness each time. *Do not bake.* Dissolve residue (of which there may be very little visible) in 2 mL 4N HNO<sub>3</sub>. Using a transfer pipet, transfer to a marked planchet. Complete transfer by rinsing beaker three times with 2-mL portions of 4N HNO<sub>3</sub>. Evaporate planchet contents to dryness under a heat lamp, flame to remove traces of HIO<sub>3</sub>, cool, and count for alpha activity.

\* Dowex 1×4, 100-200 mesh, chloride form, or equivalent.

† A uranium oxide assay standard, CRM 129, is available for purchase from U.S. Department of Energy, Chicago Operations Office, New Brunswick Laboratory, D-350, 9800 South Cass Avenue, Argonne, IL 60439.

c. To regenerate anion-exchange resin column, pass three column volumes of 1%  $\text{NaHSO}_3$  in 6N HCl through the column, follow with six column volumes of 6N HCl, and then three column volumes of distilled water. Do not let resin become dry. When ready for the next set of samples, equilibrate by passing six column volumes of 8N HCl through the column.

## 6. Calculations

$$\text{Uranium alpha activity, pCi/L} = \frac{C'' - B'}{2.22 \times ERV}$$

where:

$C''$  = gross count rate of sample, cpm,

$V$  = volume of sample, L, and other factors are as defined above.

## 7. Precision and Bias

In a collaborative study, three sets of triplicate samples with known additions of uranium were analyzed by 18 laboratories. The average recovery was 91.5%. The estimated average 95% repeatability interval was 29.3% of the uranium concentration over the range of 8 to 75 pCi/L. The estimated average 95% reproducibility interval was 37.2% over the same range.

## 7500-U C. Isotopic Method

### 1. General Discussion

a. *Principle*: The sample is acidified with hydrochloric or nitric acid and uranium-232 is added as an isotopic tracer. Uranium is separated as in the radiochemical method (see Section 7500-U.B) and is electrodeposited onto a stainless steel disk for counting by alpha pulse height analysis using a silicon surface barrier detector.

b. *Interferences*: The only alpha-emitting radionuclide that may be carried through the procedure is protactinium-231. The presence of this radionuclide can be determined from the alpha spectrum and the interference subtracted. Check reagents for uranium contamination by analyzing a complete reagent blank.

c. *Sampling*: Preserve sample by adjusting its pH to <2 with HCl or  $\text{HNO}_3$  at the time of collection.

### 2. Apparatus

a. *Counting instrument*, alpha spectrometer (see 7030B.4), giving a resolution of 50 keV (FWHM) or better and having a counting efficiency greater than 15%.

b. *Ion-exchange column*, 13 mm ID  $\times$  150 mm long with 100-mL reservoir.

c. *Electrodeposition apparatus* as shown in Figure 7500-U:1. Although the electrodeposition cell is surrounded by water the water is not circulated because cooling is unnecessary. The cathode slide has mirror finish, is 0.05 cm thick, and has an exposed electrodeposition area of 2 cm<sup>2</sup>. The anode is a 1-mm-diam platinum wire with an 8-mm-diam loop at the end above the cathode.

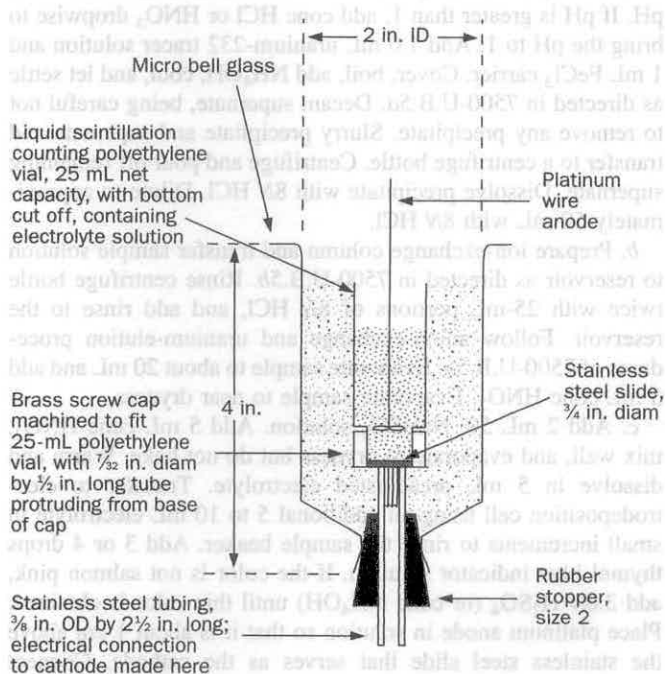
d. *DC power supply*, 0 to 12 V at 0 to 2 amp, for electrodeposition.

e. *Centrifuge*, capable of handling 100-mL or larger centrifuge bottles.

### 3. Reagents

In addition to reagents *d* through *g* from Section 7500-U.B, the following are needed:

a. *Ammonium hydroxide*,  $\text{NH}_4\text{OH}$ , 5N, 1.5N, and 0.15N.



**Figure 7500-U:1. Electrodeposition apparatus.** To obtain dimensions in centimeters, multiply dimensions in inches by 2.54.

b. *Anion-exchange resin*.\*

c. *Ethyl alcohol*, made slightly basic with a few drops of conc  $\text{NH}_4\text{OH}/100$  mL.

d. *Preadjusted electrolyte*,  $(\text{NH}_4)_2\text{SO}_4$ , 1M, adjusted to pH 3.5 with conc  $\text{NH}_4\text{OH}$  and conc  $\text{H}_2\text{SO}_4$ .

e. *Sulfuric acid*,  $\text{H}_2\text{SO}_4$ , conc, 3.6N.

f. *Sodium hydrogen sulfate*, about 5% in 18N  $\text{H}_2\text{SO}_4$ . Dissolve 10 g  $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$  in 100 mL water and carefully add 100 mL conc  $\text{H}_2\text{SO}_4$ .

g. *Thymol blue indicator*, sodium salt, 0.04% solution.

\* Bio Rad AGI-X4, 100-200 mesh, chloride form, or equivalent.

*h. Uranium-232 tracer solution*, 10 dpm/mL in 1*N* HNO<sub>3</sub>: If possible use a <sup>232</sup>U standard solution from, or traceable to, the National Institute for Standards and Technology (NIST). Standardize a freshly purified solution of <sup>232</sup>U by thoroughly mixing a known amount with a known amount of another uranium standard such as <sup>236</sup>U or natural uranium, and electroplating the mixture. Determine specific activity of the <sup>232</sup>U solution from an alpha pulse height analysis of the electroplated mixture. Alternatively, evaporate weighed portions of a freshly purified <sup>232</sup>U solution (free of HCl) on stainless steel slides and count with a 2π proportional counter. Determine efficiency of the 2π counter accurately with a NIST alpha-particle standard. When using this standard, correct for resolving time and backscattering if necessary.

#### 4. Procedure

*a.* If the sample has not been acidified, add 5 mL conc HCl or conc HNO<sub>3</sub> to 1 L sample in a 1500-mL beaker. Mix and check pH. If pH is greater than 1, add conc HCl or HNO<sub>3</sub> dropwise to bring the pH to 1. Add 1.0 mL uranium-232 tracer solution and 1 mL FeCl<sub>3</sub> carrier. Cover, boil, add NH<sub>4</sub>OH, cool, and let settle as directed in 7500-U.B.5*a*. Decant supernate, being careful not to remove any precipitate. Slurry precipitate and supernate and transfer to a centrifuge bottle. Centrifuge and pour off remaining supernate. Dissolve precipitate with 8*N* HCl. Dilute to approximately 50 mL with 8*N* HCl.

*b.* Prepare ion-exchange column and transfer sample solution to reservoir as directed in 7500-U.B.5*b*. Rinse centrifuge bottle twice with 25-mL portions of 8*N* HCl, and add rinse to the reservoir. Follow anion-exchange and uranium-elution procedures of 7500-U.B.5*b*. Evaporate sample to about 20 mL and add 5 mL conc HNO<sub>3</sub>. Evaporate sample to near dryness.

*c.* Add 2 mL 5% NaHSO<sub>4</sub> solution. Add 5 mL conc HNO<sub>3</sub>, mix well, and evaporate to dryness but do not bake. Warm and dissolve in 5 mL preadjusted electrolyte. Transfer to electrodeposition cell using an additional 5 to 10 mL electrolyte in small increments to rinse the sample beaker. Add 3 or 4 drops thymol blue indicator solution. If the color is not salmon pink, add 3.6*N* H<sub>2</sub>SO<sub>4</sub> (or conc NH<sub>4</sub>OH) until this color is obtained. Place platinum anode in solution so that it is about 1 cm above the stainless steel slide that serves as the cathode. Connect electrodes to power supply and adjust to give a current of 1.2 amp (constant current power supplies will not require further adjustments during electrodeposition). Continue electrodeposition for 1 h. When electrodeposition is to be ended, add 1 mL conc NH<sub>4</sub>OH and continue for 1 min. Remove anode from cell and then turn off power. Discard solution in cell and rinse two or three times with 0.15*N* NH<sub>4</sub>OH. Disassemble cell and wash slide with ethyl alcohol that has been made basic with NH<sub>4</sub>OH. Dry slide over a hot plate. Measure activity of the uranium isotopes using an alpha spectrometer (see 7030B.4) within a week of preparation.†

† Electrodeposition was the recommended technique for alpha spectroscopy source preparation in the collaborative test of this method. A number of laboratories are currently using a rare earth fluoride co-precipitation technique for alpha spectroscopy source preparation. If adequate resolution can be obtained, the rare earth fluoride source preparation should be adequate as an alternative to electrodeposition.

#### 5. Calculations

*a.* Determine total counts for each uranium isotope by summing the counts in the peak at the energy corresponding to the isotope. If two isotopes are close in energy, complete resolution may not be possible. Subtract background from each peak. Make a blank correction for each peak, if necessary.

*b.* Calculate concentration of each uranium isotope as follows:

where:

$$U_i, \text{ pCi/L} = \frac{C_i \times A_T}{2.22 \times C_T \times V}$$

where:

$U_i$  = concentration of uranium isotope being determined,

$C_i$  = net sample counts in the energy region corresponding to uranium isotope being measured,

$A_T$  = activity of added uranium-232 tracer, dpm,

$C_T$  = net sample counts in the energy region corresponding to uranium-232 tracer, and

$V$  = sample volume, L.

#### 6. Calibration

To calculate uranium recovery, determine absolute counting efficiency ( $E$ ) of the alpha spectrometer. To determine efficiency count a standard source of a known alpha activity having the same active area as the samples.

$$E = \frac{C_s - B}{D}$$

where:

$C_s$  = gross count rate in the energy region corresponding to the energy of the standard, cpm,

$B$  = background count rate in the energy region corresponding to the energy of the standard, cpm, and

$D$  = disintegration rate of standard, dpm.

$$\text{Recovery factor, } R = \frac{C_T}{t \times A_T E}$$

where:

$t$  = sample counting time, min.

#### 7. Precision and Bias

In a collaborative study, four sets of duplicate samples with known additions of uranium isotopes were analyzed by eight laboratories. Results agreed within 5% of the reference values, except for very low concentrations of uranium (concentrations approaching MDL due to background). Levels less than 0.1 pCi/L can be detected by this method.

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