

Beverages: Bottled Water

Docket Number B03N-0068

Methods

A. Combined Radium-226/-228

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2. Method 7500-Ra D, "Sequential Precipitation Method"

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Combined Radium-226/-228

1. Method 7500-Ra B, "Precipitation Method"
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7500-Ra RADIUM*

7500-Ra A. Introduction

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—11.6-d radium-223, 3.6-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. Radium is a bone-seeker and high concentrations can lead to malignancies.

2. Selection of Method

The principles of the two common methods for measuring radium are (a) alpha-counting a barium-radium sulfate precipitate that has been purified, and (b) measurement of radon-222 produced from the radium-226 in a sample or in a soluble concentrate isolated from the sample.

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 ^{226}Ra plus ^{228}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 or a fusion will be necessary.

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.

Approved by Standard Methods Committee, 1993.

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.¹⁻³ The ingrowth of alpha activity from radium-226 increases at a rate 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 (H_2SO_4) is added to precipitate radium, barium, and lead as sulfates. The precipitate is purified by washing with nitric acid (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† 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.

* Fisher Filtrator or equivalent.

† Millipore Type HAWP or equivalent.

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

b. *Ammonium hydroxide*, conc and 5*N*: Verify strength of old *N* NH₄OH solution before use.

c. *Lead nitrate carrier*: Dissolve 160 g Pb(NO₃)₂ in distilled water and dilute to 1 L; 1 mL = 100 mg Pb.

d. *Stock barium chloride solution*: Dissolve 17.79 g BaCl₂·2H₂O 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 BaCl₂ 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*, H₂SO₄, 18*N*.

j. *Nitric acid*, HNO₃, conc.

k. *EDTA reagent*, 0.25*M*: 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 BaCl₂ stock solution (¶ 3a) before adding the ²²⁶Ra solution; 1 mL final standard radium solution so prepared contains 2.00 mg Ba/mL and approximately 3 pCi ²²⁶Ra/mL after the necessary correcting factors are applied.

Procedure for Radium in Drinking Water and for Dissolved Radium

a. To 1 L sample in a 1500-mL beaker, add 5 mL 1*M* citric acid, 2.5 mL conc NH₄OH, 2 mL Pb(NO₃)₂ carrier, and 3.00 mL BaCl₂ 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 18*N* H₂SO₄ 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 HNO₃, 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 5*N* NH₄OH, dropwise, until solution is definitely alkaline (red). Add

10 mL EDTA reagent and 3 mL 5*N* NH₄OH. 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).** BaSO₄ 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 PbSO₄.

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 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,⁴ 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 BaCl₂ carrier (¶ 3e above). Analyze standards as samples, beginning with ¶ 4a, but omit 3.00-mL BaCl₂ carrier.

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

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

where:

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

§ Lucite or equivalent.

|| If original concentrations of isotopes of radium other than ²²⁶Ra 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 ¶ without delay. Assuming the presence of and separation of parents, decay of ²²³Ra | ²²⁴Ra 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 not needed if the objective is to check the final precipitate for its ²²⁶Ra content only.

If solution does not clear in 10 min, cool, add another mL 5*N* NH₄OH, 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.

†† See calculation that follows.

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_4 .

5. Calculation

$$\text{Radium, pCi/L} = \frac{\text{net cpm}}{abcde \times 2.22}$$

where:

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

Ingrowth h	Alpha Activity from ^{226}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.

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^{2,3} 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.³ 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 ^{224}Ra concentration equal to that of ^{226}Ra .

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 ₄ , mg/L	30	30	150	150
MgCl ₂ ·6H ₂ O, mg/L	30	30	150	150
KCl, mg/L	5	5	10	10

* Daughter products were in substantial secular equilibrium.

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 ^{224}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}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}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 $\text{§s } 4a$ through g above.

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

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.

Recovery of Barium (Radium-226) (Optional)

If ^{133}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_3PO_4 to the latter portion before counting. The assumption that the Ba and ^{226}Ra are recovered to the same extent is valid in the method described.

Note that ^{226}Ra and its decay products interfere slightly even if a gamma spectrometer is used. The technique works best when the ratio of ^{133}Ba to ^{226}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 pre-

cision (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

- HURSH, J.B. 1954. Radium-226 in water supplies of the U.S. *J. Amer. Water Works Assoc.* 46:43.
- RUSHING, D.E., W.J. GARCIA & D.A. CLARK. 1964. The analysis of effluents and environmental samples from uranium mills and of biological samples for radium, polonium, and uranium. *In Radiological Health and Safety in Mining and Milling of Nuclear Materials. International Atomic Energy Agency, Vienna, Austria, Vol. 11, p. 187.*
- LUCAS, H.F. 1957. Improved low-level alpha scintillation counter for radon. *Rev. Sci. Instrum.* 28:680.
- RUSHING, D.E. 1967. Determination of dissolved radium-226 in water. *J. Amer. Water Works Assoc.* 59:593.

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 (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- μm pore diam.†

3. Reagents

- a. Acetic acid,* conc.
- b. Acetone,* anhydrous.
- c. Ammonium hydroxide,* NH_4OH , 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 HNO_3 , and dilute to 100 mL; 1 mL = 16 mg Ba.

* Mylar or equivalent.

† Gelman Ga-6 or equivalent.

- 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 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, 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, H_2SO_4 , 18N.
- s. Yttrium carrier: Add 12.7 g Y_2O_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 HNO_3 . (About 30 mL is necessary to dissolve the Y_2O_3 . Small additions of distilled water also may be needed to replace water lost by evaporation.) After total dissolution, add 70 mL conc HNO_3 and dilute to 1 L with distilled water; 1 mL = 10 mg Y.

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 NH_4OH until a definite yellow color is obtained; add a few drops excess. Precipitate lead and barium sulfates by adding 18N H_2SO_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 HNO_3 and heat gently until the filter dissolves completely. Using conc HNO_3 transfer precipitate to a centrifuge tube. Centrifuge and discard supernatant.
- 4) Wash precipitate with 15 mL conc 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. Add 1 mL $(\text{NH}_4)_2\text{SO}_4$ solution and stir thoroughly. Add conc acetic acid until BaSO_4 precipitates; add 2 mL excess. The pH should be about 4.5. Digest in a hot water bath (80°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

BaSO_4 precipitation as zero time for ingrowth of ^{228}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 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 PbS. Centrifuge and filter supernatant through filter paper† 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 OH^-). Because of the short half-life of ^{228}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}Ra analysis, ¶s b or c below. Note time of $\text{Y}(\text{OH})_3$ precipitation; this is the end of ^{228}Ac ingrowth and beginning of ^{228}Ac decay. (t_3 = time in minutes between last BaSO_4 and first $\text{Y}(\text{OH})_3$ precipitations.) Dissolve precipitate in 2 mL 6N 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 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 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}Ra activity.

b. Radium by precipitation:

1) To the supernatant saved in ¶ a9) above add 4 mL conc HNO_3 and 2 mL $(\text{NH}_4)_2\text{SO}_4$ solution, mixing well after each addition. Add conc acetic acid until 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 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 un-

† Whatman No. 42 or equivalent.

der an infrared lamp to constant weight. If after sufficient beta decay of the actinium fraction ^{228}Ra is found to be absent, make a direct alpha count for ^{226}Ra . If ^{228}Ra is present, determine ^{226}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}Ra concentration:

$$^{228}\text{Ra}, \text{pCi/L} = \frac{C}{2.22 \times \text{EVR}} \times \frac{\lambda_2}{(1 - e^{-\lambda_2})} \times \frac{1}{(1 - e^{-\lambda_3})} \times \frac{1}{e^{-\lambda_1}}$$

where:

- C = average net count rate, cpm,
- E = counter efficiency, for ^{228}Ac ,
- V = sample volume, L,
- R = fractional chemical yield of yttrium carrier, ¶ 4a10), multiplied by fractional chemical yield of barium carrier, ¶ b3),

λ = decay constant of ^{228}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}Ac between last BaSO_4 precipitation and first $\text{Y}(\text{OH})_3$ precipitation, min.

The factor $\lambda_2/(1 - e^{-\lambda_2})$ corrects average count rate to count rate at beginning of counting time.

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

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

6. Bibliography

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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.¹⁻³

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

*Approved by Standard Methods Committee, 1996.

2. References

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3. ALDRICH, L.K., III, M.K. SASSER & D.A. CONNERS, IV. 1975. Evaluation of Radon Concentrations in North Carolina Ground Water Supplies. Dept. Human Resources, Div. Facility Services, Radiation Protection Branch, Raleigh, N.C.
4. O'CONNELL, M.F. & R.F. KAUFMAN. 1976. Radioactivity Associated with Geothermal Waters in the Western United States. U.S. Environmental Protection Agency Technical Note ORP/LV-75-8A.
5. DUNCAN, D.L., T.F. GESELL & R.H. JOHNSON, JR. 1976. Radon-222 in potable water. *In Proc. Health Physics Soc. 10th Midyear Topical Symposium: Natural Radioactivity in Man's Environment.*
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Gross Alpha Particle Radioactivity

1. Method 7110 C, "Coprecipitation Method for Gross Alpha Radioactivity in Drinking Water"

onium-239) with increasing solids thickness, first on the alpha plateau, then on the beta plateau. Plot the ratios of the two counts per mg/cm² 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 alpha activity at the beta plateau is a substantial fraction of the 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 picuries 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 recom-

mended 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. Reference

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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 dis-

solved 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 HNO₃ 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.¹

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

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

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- μ 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, NH₄OH, 6N.

b. Barium carrier, 5 mg Ba²⁺/mL: Dissolve 4.4 g BaCl₂·2H₂O 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 Fe³⁺/mL: Dissolve 17.5 g Fe(NO₃)₃·9H₂O in 200 mL distilled water containing 2 mL 16N HNO₃. Dilute to 500 mL.

e. Sulfuric acid, H₂SO₄, 2N: Dilute 55 mL conc H₂SO₄ 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 H₂SO₄. Boil for 10 min to flush CO₂ (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 NH₄OH 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

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

where:

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,² 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

* Available from U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Nuclear Radiation Assessment Division, P.O. Box 93478, Las Vegas, NV 89193-3478.

† Gelman Type A/E, Millipore Type AP, or equivalent.

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

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 ^{230}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.

7120 B. Gamma Spectroscopic Method

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^{1,2} 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 spectrometry³ for a more detailed discussion.

c. Sampling and storage: See Table 7010:1.

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

Beta Particle and Photon Radioactivity

1. Method 7500-Sr B, "Precipitation Method (Strontium)"
2. Method 7500-3H B, "Liquid Scintillation Spectrophotometric Method (Tritium)"
3. Method 7120, "Gamma Spectroscopic Method (Gamma-emitting Radionuclides)"

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 2σ 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 Accuracy

A collaborative study of this method composed of 36 participants¹ 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

8. Reference

1. PIA, S.H. & P.B. HAHN. 1992. Radiation Research and Methods Validation Annual Report 1992. Environmental Monitoring Systems Laboratory—Las Vegas, Off. Research and Development, U.S. Environmental Protection Agency, Las Vegas, Nev.

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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 ⁸⁹Sr and ⁹⁰Sr. 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, 1993.

The method presented in this section is designed to measure total radioactive strontium (⁸⁹Sr and ⁹⁰Sr) or ⁹⁰Sr 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, Sr(NO₃)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

Sr(NO₃)₂ from fuming nitric acid solution. The strontium carrier, together with the radionuclides of strontium, finally is precipitated as strontium carbonate, SrCO₃, 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 ⁹⁰Y.

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}Ba , ^{140}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}Y .

d. Determination of ^{90}Sr : Because it is impossible to separate the isotopes ^{89}Sr and ^{90}Sr by any chemical procedure, the amount of ^{90}Sr is determined by separating and measuring the activity of ^{90}Y , its daughter. After equilibrium is reached, the activity of ^{90}Y is exactly equal to the activity of ^{90}Sr . Two alternate procedures are given for the separation of ^{90}Y . In the first method, ^{90}Y is separated by extraction into tributyl phosphate from concentrated nitric acid (HNO_3) solution. It is back-extracted into dilute 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).

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 ring§ on which the filter samples are mounted and covered by 0.25 mil film.

3. Reagents

a. Strontium carrier, 10 mg 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 Na_2CO_3 solution. Stir, heat in a boiling

water bath for 15 min, and cool. Filter 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 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,|| Y_2O_3 , in 30 mL conc HNO_3 by stirring and warming. Add an additional 20 mL conc 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 NH_4OH as necessary, and dilute to 1 L.

f. Acetic acid, 6N.

g. Acetone, anhydrous.

h. Ammonium hydroxide, NH_4OH , 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, 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 HNO_3 to equilibrate. Separate and discard the 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 HNO_3 and mix. Add 2.0 mL each of strontium and barium carriers and mix well. (A precipitate of 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

* Mylar, E.I. du Pont de Nemours, Wilmington, DE, or equivalent.

† Whatman No. 42 or equivalent.

‡ Filtron 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.

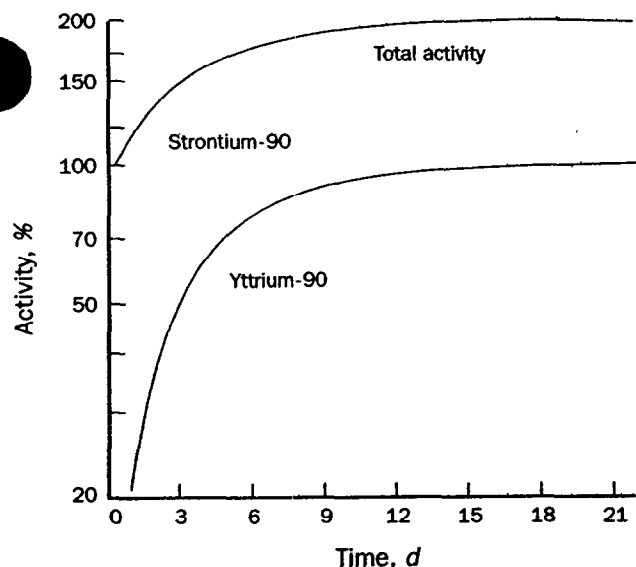


Figure 7500-Sr:1. Yttrium-90 vs. strontium-90 activity as a function of time.

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 6*N* NaOH and 20 mL 1*M* Na₂CO₃. 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

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 HNO₃. Heat to boiling, stir, then cool under running water.

6) Add 20 mL fuming HNO₃, 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 6*N* HNO₃, heat to boiling, centrifuge while hot, and combine supernate with aqueous supernate. Discard insoluble residue of SiO₂, BaSO₄, etc.

8) Cool combined supernates, then add 20 mL fuming HNO₃, 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 HNO₃ precipitation, invert tube in a beaker for about 10 min to drain off most excess HNO₃. Add 20 mL anhydrous acetone, stir thoroughly, cool, and centrifuge. Discard supernate (CAUTION).

12) Dissolve precipitate of Sr(NO₃)₂ + Ba(NO₃)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 6*N* NaOH. 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 ⁹⁰Y ingrowth period. Do not delay procedure more than a few hours after the separation; otherwise, false results will be obtained because of ingrowth of ⁹⁰Y.

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 Na₂CrO₄ 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* Na₂CO₃ 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 ⁹⁰Sr 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 SrCO₃** 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

$$\text{Total Sr activity, pCi/L} = \frac{b}{adf \times 2.22}$$

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 SrCO₃ precipitate. More precise measurements may follow a second count after substantial ingrowth of ⁹⁰Y from ⁹⁰Sr, but this precision is not warranted for the usual total radio-

Strontium-90 in thick samples is counted with low efficiency; hence, a first count within hours favors ⁸⁹Sr counting, and a recount after 3 to 6 d that exceeds the first count provides a rough estimate of the ⁹⁰Y 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 ⁹⁰Sr determination according to 14b) following.

strontium determination. When mounting samples according to Step 20b), determine self-absorption curves by separately precipitating standard solutions of ^{89}Sr and ^{90}Sr as the carbonate (see gross beta in Section 7110).

23) Correction for carrier recovery—20 mg Sr are equivalent to 33.7 mg 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 SrCO_3 precipitate, as in ¶ 4a20), for at least 2 weeks to allow ingrowth of ^{90}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 20a), in funnel and add, dropwise, 1 mL 6*N* HNO_3 (CAUTION—*effervescence*); tilt pan to empty into funnel and rinse pan twice with 2-mL portions of 6*N* HNO_3 ; or

b) Uncover precipitate from filter, as in Step 20b), 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* HNO_3 to filter, removing residual precipitate and dissolving bulk precipitate. Rinse filter and funnel twice with 2-mL portions 6*N* HNO_3 .

2) Remove filter or pan and add 10 mL fuming 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 portions 14*N* HNO_3 . Record time as the beginning of ^{90}Y decay (combine acid washings with aqueous phase in third funnel if a second ingrowth of ^{90}Y is desired).

7) Back-extract ^{90}Y from combined organic phases with 10 mL 0.1*N* HNO_3 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 0.1*N* HNO_3 ; add rinsings to counting pan, evaporate to dryness, and weigh.

12) Count in an internal proportional or end-window counter and calculate ^{90}Sr as given in ¶ 4c9) following.

c. Strontium-90 by oxalate precipitation of yttrium-90:††

1) Quantitatively transfer SrCO_3 precipitate to a 40-mL centrifuge tube with 2 mL 6*N* HNO_3 . Add acid dropwise during dissolution (CAUTION—*effervescence*). Use 0.1*N* HNO_3 for rinsing.

2) Add 1 mL yttrium carrier, 2 drops methyl red indicator and, dropwise, add conc NH_4OH to the methyl red end point.

3) Add 5 mL more conc NH_4OH and record the time, which is the end of ^{90}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 6*N* HNO_3 , 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_4OH 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 ^{90}Sr as follows.

9) Calculation

$$^{90}\text{Sr}, \text{pCi/L} = \frac{\text{net cpm}}{abcdfg \times 2.22}$$

where:

a = counting efficiency for ^{90}Y ,

b = chemical yield of extracting or precipitating ^{90}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 = ^{90}Y decay factor, $e^{-\lambda t}$, and

e = base of natural logarithms,

$\lambda = 0.693/T_{1/2}$, where $T_{1/2}$ for ^{90}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 ^{90}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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†† See footnote to Step 20a) when a determination for only ^{90}Sr is required.

7500-³H TRITIUM*7500-³H 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 tritium contamination in the fu-

ture. 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.

* Approved by Standard Methods Committee, 1993.

7500-³H 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_{OR2}) 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, equivalent bottles.

POPOP = 1,4-di-2-(5-phenyloxazolyl) benzene; PPO = (2,5-diphenyloxazole).

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.

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, KMnO₄.

4. Procedure

Add three pellets NaOH and 0.1 g KMnO₄ 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, ³H, 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 7010G. 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 $\pm 10\%$.

7. Bibliography

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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.

3. Bibliography

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* Approved by Standard Methods Committee, 1996.

9%, 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 ^{230}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.
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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.

7120 B. Gamma Spectroscopic Method

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^{1,2} 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 spectrometry³ for a more detailed discussion.

c. Sampling and storage: See Table 7010:1.

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 1N HNO₃/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.⁴ 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 cm³) 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)⁴ 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: per-

form 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, HNO₃, 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.⁵

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 regions 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 λ = 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 2σ counting error term for gamma-emitters as follows:

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

here:

- 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 2σ 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. This may be freshly prepared, or it may be a previously analyzed standard sample such as a performance evaluation sample from EPA-Las Vegas. See Section 7020A.3d.

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.

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:I is a summary of the recovery, within-laboratory variance, S_w , and total-error variance, S_R , regression line equations for each gamma-emitter studied. These data are from the analysis of gamma-emitter

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

Nuclide	Recovery	S_r pCi/L	S_R pCi/L
Iodine-131*	$y = 1.013x - 0.64$	$y = 0.033x + 1.82$	$y = 0.073x + 2.66$
Cesium-137	$y = 1.004x + 0.79$	$y = 0.024x + 1.40$	$y = 0.049x + 1.93$
Cesium-134	$y = 0.919x + 0.60$	$y = 0.028x + 1.25$	$y = 0.058x + 1.67$
Barium-133	$y = 0.938x + 2.82$	$y = 0.024x + 1.49$	$y = 0.064x + 1.78$
Ruthenium-106	$y = 0.928x + 2.33$	$y = 0.051x + 3.67$	$y = 0.072x + 7.27$
Zinc-65	$y = 1.016x + 0.49$	$y = 0.029x + 2.61$	$y = 0.054x + 3.74$
Cobalt-60	$y = 0.986x + 0.79$	$y = 0.023x + 1.35$	$y = 0.045x + 1.94$
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.
 † No longer used.

ting radionuclides in standard samples by participants in the program from 1981 to 1995. 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 1995 (April 1981 through October 1995 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 σ) of the mean value of each study, $S_{\bar{x}}$; within-laboratory standard deviation (1 σ), also known as the repeatability or random error, S_r ; between-laboratory standard deviation (1 σ), 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.

$$S_{\bar{x}}^2 = S_r^2 + S_L^2$$

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

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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	31	14-148	42-119	39-115	34-105
Cesium-137	72	4-94	45-197	43-180	30-158
Cesium-134	72	2-64	17-196	15-183	8-165
Barium-133	17	49-110	118-192	107-181	94-156
Ruthenium-106	35	15-252	20-193	17-179	11-135
Zinc-65	41	10-165	61-195	55-182	46-163
Cobalt-60	62	8-69	75-196	70-183	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.

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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 in-

* Approved by Standard Methods Committee, 1993.

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

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 Cs_2PtCl_6 for counting. If total radiocesium determined by beta-counting exceeds 30 pCi/L, determine ^{134}Cs and ^{137}Cs by gamma spectrometry.

2. Apparatus

- Magnetic stirrer* with TFE-coated magnet bar.
- Centrifuge*, bench-size clinical, and centrifuge tubes.
- Filter papers** and *glass fiber filter*, 2.4 cm diam.
- pH paper*, wide range, 1 to 11 pH.
- Filtering apparatus:* See Section 7500-Sr.B.2.c.
- 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% MoO_3) in a mixture of 240 mL distilled water and 140 mL conc ammonium hydroxide (NH_4OH). When solution is complete, filter and add 60 mL conc nitric acid (HNO_3). Separately mix 400 mL conc 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 HNO_3 solution. Let stand for 24 h. Filter† and discard insoluble material.

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 (NaH_2PO_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 (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 (CsCl) in distilled water and dilute to 100 mL; 1 mL = 10 mg Cs.

d. Calcium chloride, 3M: Dissolve 330 g 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 cen-

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

† Whatman No. 42 filter paper or equivalent.

Uranium

1. Method 7500-U B, "Radiochemical Method"
2. Method 7500-U C, "Isotopic Method"

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 7010G. 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.

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* Approved by Standard Methods Committee, 1996.

7500-U B. Radiochemical Method

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 subsequently 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 HNO₃ 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*, NH₄OH, 5N, 1%.

b. *Anion-exchange resin*.*

c. *Ferric chloride carrier*: Dissolve 9.6 g FeCl₃·6H₂O in 100 mL 0.5N HCl; 1 mL = 20 mg Fe³⁺.

d. *Hydriodic acid*, HI, 47%.

e. *Hydrochloric acid*, HCl, conc, 8N, 6N, 0.1N.

f. *Iodic acid*, 1 mg/mL: Dissolve 100 mg HIO₃ in 100 mL 4N HNO₃.

g. *Nitric acid*, HNO₃, conc, 4N.

h. *Sodium hydrogen sulfite*, 1%: Dissolve 1 g NaHSO₃ in 100 mL 6N HCl.

i. *Uranium standard solution*:† Dissolve 177.3 mg natural undepleted uranyl acetate, UO₂(C₂H₃O₂)₂·2H₂O, in 1000 mL 0.2N HNO₃; 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 HIO₃ 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.

* Dowex 1×4, 100-200 mesh, chloride form, or equivalent.

† Standard radioactive solutions with uranium isotopes in equilibrium are available for participants in the performance evaluation studies program from the U.S. Environmental Protection Agency, NRA/STD, P.O. Box 93478, Las Vegas, NV 89193. A uranium oxide assay standard, CRM 129, is available for purchase from Department of Energy, Chicago Operations Office, New Brunswick Laboratory, D-350, 9800 South Cass Avenue, Argonne, IL 60439.

$$\text{Counting efficiency, } E = \frac{C - B}{D}$$

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 recovery 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 HNO₃ to 1 L sample in a 1500-mL beaker. Add 1 mL FeCl₃ 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 HNO₃ dropwise to bring pH to 1. While sample is boiling, gently add 5N NH₄OH from a polyethylene squeeze bottle with the delivery tube inserted between the watch glass and the beaker lip. Add 5N NH₄OH 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 NH₄OH 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 HNO₃, evaporating to near dryness each time. *Do not bake.* Dissolve residue (of which there may be very little visible) in 2 mL 4N HNO₃. Using a transfer pipet, transfer to a marked planchet. Complete transfer by rinsing beaker three times with 2-mL portions of 4N HNO₃. Evaporate planchet contents to dryness under a heat lamp, flame to remove traces of HIO₃, cool, and count for alpha activity.

c. To regenerate anion-exchange resin column, pass three column volumes of 1% NaHSO₃ 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.

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 HNO₃ 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 × 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 cm². 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 7500U.B, the following are needed:

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.

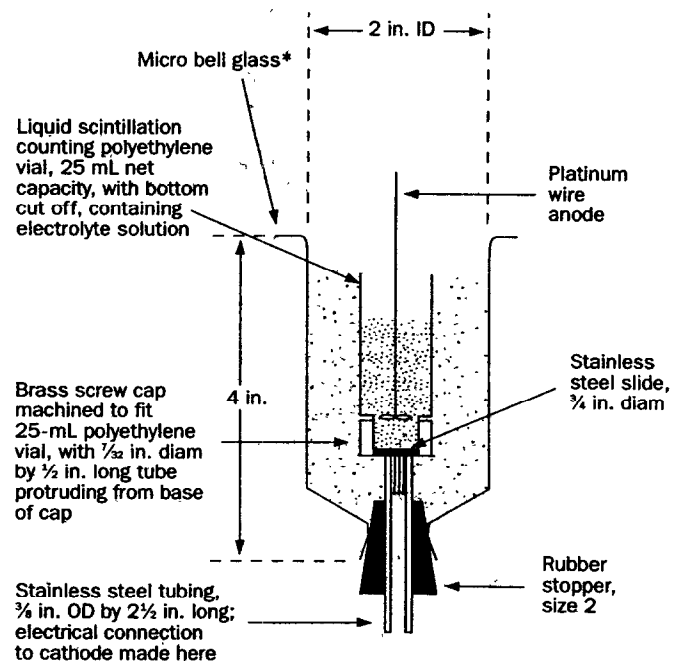


Figure 7500-U:1. Electrodeposition apparatus. To obtain dimensions in centimeters, multiply dimensions in inches by 2.54.

a. *Ammonium hydroxide,* NH₄OH, 5N, 1.5N, and 0.15N.

b. *Anion-exchange resin.**

c. *Ethyl alcohol,* made slightly basic with a few drops of conc NH₄OH/100 mL.

d. *Preadjusted electrolyte,* (NH₄)₂SO₄, 1M, adjusted to pH 3.5 with conc NH₄OH and conc H₂SO₄.

e. *Sulfuric acid,* H₂SO₄, conc, 3.6N.

* Bio Rad AGI-X4, 100-200 mesh, chloride form, or equivalent.

f. Sodium hydrogen sulfate, about 5% in 18N H₂SO₄. Dissolve 10 g NaHSO₄·H₂O in 100 mL water and carefully add 100 mL conc H₂SO₄.

g. Thymol blue indicator, sodium salt, 0.04% solution.

h. Uranium-232 tracer solution, 10 dpm/mL in 1N HNO₃; if possible use a ²³²U standard solution from, or traceable to, the National Institute for Standards and Technology (NIST). Standardize a freshly purified solution of ²³²U by thoroughly mixing a known amount with a known amount of another uranium standard such as ²³⁶U or natural uranium, and electroplating the mixture. Determine specific activity of the ²³²U solution from an alpha pulse height analysis of the electroplated mixture. Alternatively, evaporate weighed portions of a freshly purified ²³²U 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 HNO₃ to 1 L sample in a 1500-mL beaker. Mix and check pH. If pH is greater than 1, add conc HCl or HNO₃ dropwise to bring the pH to 1. Add 1.0 mL uranium-232 tracer solution and 1 mL FeCl₃ carrier. Cover, boil, add NH₄OH, cool, and let settle as directed in 7500U.B.5a. 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 8N HCl. Dilute to approximately 50 mL with 8N HCl.

b. Prepare ion-exchange column and transfer sample solution to reservoir as directed in 7500U.B.5b. Rinse centrifuge bottle twice with 25-mL portions of 8N HCl, and add rinse to the reservoir. Follow anion-exchange and uranium-elution procedures of 7500U.B.5b. Evaporate sample to about 20 mL and add 5 mL conc HNO₃. Evaporate sample to near dryness.

c. Add 2 mL 5% NaHSO₄ solution. Add 5 mL conc HNO₃, 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 3.6N H₂SO₄ (or conc NH₄OH) 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 NH₄OH 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 0.15N NH₄OH. Disassemble cell and wash slide with ethyl alcohol that has been made basic with NH₄OH. 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:

$$U_i, \text{ pCi/L} = \frac{C_i \times A_t}{2.22 \times C_t V}$$

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.

$$\text{Recovery factor, } R = \frac{C_i}{t \times A_i E}$$

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.

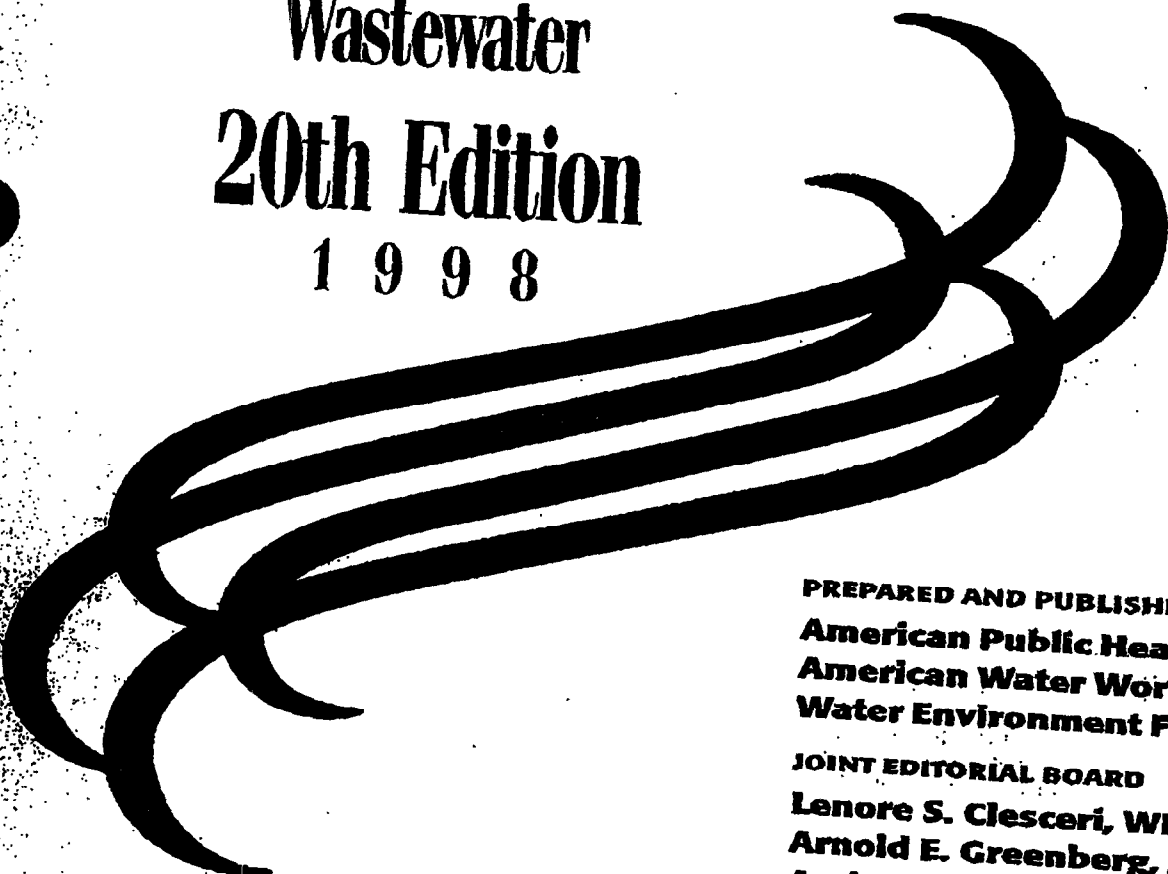
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Standard Methods

FOR THE
Examination
of Water and
Wastewater
20th Edition
1 9 9 8



PREPARED AND PUBLISHED JOINTLY BY
American Public Health Association
American Water Works Association
Water Environment Federation

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American Public Health Association
1015 Fifteenth Street, NW
Washington, DC 20005-2605

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30M12/98

ISBN 0-87553-235-7
ISSN 55-1979

Printed and bound in the United States of America.

Composition: Maryland Composition Company, Glen Burnie, MD

Set in: Times Roman

Printing: United Book Press, Inc., Baltimore, Maryland

Binding: United Book Press, Inc., Baltimore, Maryland

Cover Design: Jane Pizzini, JEP Graphics, Potomac, Maryland