

SECTION 8  
RADIUM-228 IN DRINKING WATER  
METHOD 904.0

1. Scope and Application

- 1.1 This method covers the measurement of radium-228 in drinking water and, if desired, the determination of radium-226 on the same sample. The Interim Primary Drinking Water regulations state that if the alpha screening test reveals a gross alpha activity above 5 pCi/l, a radium-226 analysis must also be performed. If the level of radium-226 is above 3 pCi/l, the sample must also be measured for radium-228.
- 1.2 This technique is devised so that the beta activity from actinium-228 which is produced by decay of radium-228, can be determined and related to the radium-228 that is present in the sample.
- 1.3 To quantify actinium-228 and thus determine radium-228, the efficiency of the beta counter for measuring the very short half-lived actinium-228 (avg. beta energy-0.404 keV) is to be calibrated with a beta source of comparable average beta energy.

2. Summary of Method

- 2.1 The radium in the drinking water sample is collected by coprecipitation with barium and lead sulfate, and purified by reprecipitation from EDTA solution. Both radium-226 and radium-228 are collected in this manner. After a 36-hour ingrowth of actinium-228 from radium-228, the actinium-228 is carried on yttrium oxalate, purified and beta counted. If radium-226 is also desired, the activity in the supernate can be reserved for method 903.1 by coprecipitation on barium sulfate, dissolving in EDTA and storing for ingrowth in a sealed radon bubbler.

3. Sample Handling and Preservation - (see Sec. 3, Method 900.0)

4. Interferences

- 4.1 As evidenced from the results of the performance studies, the presence of strontium-90 in the water sample gives a positive bias to the radium-228 activity measured.

- 4.2 As in the case of method 903.0, excess barium in the drinking water sample might result in a falsely high chemical yield.
5. Apparatus - See Appendix D for details and specifications
- 5.1 Gas-flow proportional counting system. (Low-background beta < 3 cpm).
- 5.2 Electric hot plate
- 5.3 Centrifuge
- 5.4 Membrane filters, metricel 47mm
- 5.5 Drying lamp
- 5.6 Glassware
- 5.7 Stainless steel counting planchets
- 5.8 Analytical balance
6. Reagents
- 6.1 Distilled or deionized water.
- 6.2 Acetic acid, 17.4N: glacial  $\text{CH}_3\text{COOH}$  (conc.), sp. gr. 1.05, 99.8%
- 6.3 Ammonium hydroxide, 15N:  $\text{NH}_4\text{OH}$  (conc.), sp. gr. 0.90, 56.6%.
- 6.4 Ammonium oxalate, 5%: Dissolve 5g  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in water and dilute to 100 ml.
- 6.5 Ammonium sulfate, 200 mg/ml: Dissolve 20g  $(\text{NH}_4)_2\text{SO}_4$  in water and dilute to 100 ml.
- 6.6 Ammonium sulfide, 2%: Dilute 10 ml  $(\text{NH}_4)_2\text{S}$ , (20-24%), to 100 ml with water.
- 6.7 Barium carrier, 16 mg/ml, standardized: (see Sec. 6, Method 903.0).
- 6.8 Citric acid, 1M: Dissolve 19.2g  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$  in water and dilute to 100 ml.
- 6.9 EDTA reagent, basic (0.25M): Dissolve 20g NaOH in 750 ml water, heat and slowly add 93g disodium ethylenedinitriloacetate dihydrate,  $(\text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O})$  while stirring. After the salt is in solution, filter through coarse filter paper and dilute to 1 liter.

- 6.10 Lead carrier, 15 mg/ml: Dissolve 2.397g  $\text{Pb}(\text{NO}_3)_2$  in water, add 0.5 ml 16N  $\text{HNO}_3$  and dilute to 100 ml with water.
- 6.11 Lead carrier, 1.5 mg/ml: Dilute 10 ml lead carrier, (15 mg/ml), to 100 ml with water.
- 6.12 Methyl orange indicator, 0.1%: Dissolve 0.1g methyl orange indicator in 100 ml water.
- 6.13 Nitric acid, 16N:  $\text{HNO}_3$  (conc.), sp. gr. 1.42, 70.4%.
- 6.14 Nitric acid, 6N: Mix 3 volumes 16N  $\text{HNO}_3$  (conc.) with 5 volumes of water.
- 6.15 Nitric acid, 1N: Mix 1 volume 6N  $\text{HNO}_3$  with 5 volumes of water.
- 6.16 Sodium hydroxide, 18N: Dissolve 72g NaOH in water and dilute to 100 ml.
- 6.17 Sodium hydroxide, 10N: Dissolve 40g NaOH in water and dilute to 100 ml.
- 6.18 Strontium carrier, 10 mg/ml: Dissolve 24.16 g  $\text{Sr}(\text{NO}_3)_2$  in water and dilute to 1 liter.
- 6.19 Sulfuric acid, 18N: Cautiously mix 1 volume 36N  $\text{H}_2\text{SO}_4$  (conc.) with 1 volume of water.
- 6.20 Yttrium carrier 18 mg/ml: Add 22.85g  $\text{Y}_2\text{O}_3$  to an Erlenmeyer flask containing 20 ml water. Heat to boiling and continue stirring with a magnetic stirring hot plate while adding 16N  $\text{HNO}_3$  in small amounts. Usually about 30 ml 16N  $\text{HNO}_3$  is necessary to dissolve the  $\text{Y}_2\text{O}_3$ . Small additions of water may be required to replace that lost by evaporation. After total dissolution add 70 ml 16N  $\text{HNO}_3$  and dilute to 1 liter with water.
- 6.21 Yttrium carrier, 9 mg/ml: Dilute 50 ml yttrium carrier, (18 mg/ml), to 100 ml with water.
- 6.22 Strontium-yttrium mixed carrier, 0.9 mg/ml  $\text{Sr}^{+2}$  - 0.9 mg/ml  $\text{Y}^{+3}$ :
- Solution A: Dilute 10.0 ml yttrium carrier, (18 mg/ml), to 100 ml.
  - Solution B: Dissolve 0.4348g  $\text{Sr}(\text{NO}_3)_2$  in water and dilute to 100 ml.
- Combine Solutions A and B and label.

## 7. Calibrations

7.1 Counter efficiency: It is not practical to calibrate the beta counter with actinium-228, since its half-life is only six hours. Standard strontium-89 ( $t_{1/2} = 51d$ ) may be substituted. Strontium-89 has an average beta energy of 0.589 KeV, while the average beta energy for actinium-228 is 0.404 KeV. A standard strontium-89 tracer solution can be used to determine beta efficiencies over a range of precipitate weights on the stainless steel planchet.

7.2 If radium-226 analyses are also required, see Sec. 7, Method 903.1.

## 8. Procedure(1)

8.1 For each liter of drinking water, add 5 ml 1M  $C_6H_8O_7 \cdot H_2O$  and few drops methyl orange indicator. The solution should be red.

Note: At the time of sample collection add 2 ml 16N  $HNO_3$  for each liter of water.

8.2 Add 10 ml lead carrier (15 mg/ml), 2 ml strontium carrier (10 mg/ml) 2.0 ml barium carrier (16 mg/ml), and 1 ml yttrium carrier (18 mg/ml); stir well. Heat to incipient boiling and maintain at this temperature for 30 minutes.

8.3 Add 15N  $NH_4OH$  until a definite yellow color is obtained, then add a few drops excess. Precipitate lead and barium sulfates by adding 18N  $H_2SO_4$  until the red color reappears, then add 0.25 ml excess. Add 5 ml  $(NH_4)_2SO_4$  (200 mg/ml) for each liter of sample. Stir frequently and keep at a temperature of about 90°C for 30 minutes.

8.4 Cool slightly, then filter with suction through a 47-mm metricel membrane filter (GA-6, 0.45  $\mu$ -pore size). Make a quantitative transfer of precipitate to the filter by rinsing last particles out of beaker with a strong jet of water.

8.5 Carefully place filter with precipitate in the bottom of a 250 ml beaker. Add about 10 ml 16N  $HNO_3$  and heat gently until the filter completely dissolves. Transfer the precipitate into a polypropylene centrifuge tube with additional 16N  $HNO_3$ . Centrifuge and discard supernate.

8.6 Wash the precipitate with 15 ml 16N  $HNO_3$ , centrifuge, and discard supernate.

8.7 Repeat step 8.6.

8.8 Add 25 ml basic EDTA reagent, heat in a hot water bath, and stir well. Add a few drops 10N  $NaOH$  if the precipitate does not readily dissolve.

- 8.9 Add 1 ml strontium-yttrium mixed carrier and stir thoroughly. Add a few drops 10N NaOH if any precipitate forms.
- 8.10 Add 1 ml  $(\text{NH}_4)_2\text{SO}_4$  (200 mg/ml) and stir thoroughly. Add 17.4N  $\text{CH}_3\text{COOH}$  until barium sulfate precipitates, then add 2 ml excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernate.
- 8.11 Add 20 ml basic EDTA reagent, heat in a hot water bath, and stir until precipitate dissolves. Repeat steps 8.9 and 8.10. (Note time of last barium sulfate precipitation; this is the beginning of the actinium-228 ingrowth time.)
- 8.12 Dissolve the precipitate in 20 ml basic EDTA reagent as before, then add 1.0 ml yttrium carrier (9 mg/ml) and 1 ml lead carrier (1.5 mg/ml). If any precipitate forms, dissolve by adding a few drops 10N NaOH. Cap the polypropylene tube and age at least 36 hours.
- 8.13 Add 0.3 ml  $(\text{NH}_4)_2\text{S}$  and stir well. Add 10N NaOH dropwise with vigorous stirring until lead sulfide precipitates, then add 10 drops excess. Stir intermittently for about 10 minutes. Centrifuge and decant supernate into a clean tube.
- 8.14 Add 1 ml lead carrier (1.5 mg/ml), 0.1 ml  $(\text{NH}_4)_2\text{S}$ , and a few drops 10N NaOH. Repeat precipitation of lead sulfide as before. Centrifuge and filter supernate through Whatman #42 filter paper into a clean tube. Wash filter with a few ml water. Discard residue.
- 8.15 Add 5 ml 18N NaOH, stir well and digest in a hot water bath until yttrium hydroxide coagulates. Centrifuge and decant supernate into a beaker. Save for barium yield determination, step 8.20 (Note time of yttrium hydroxide precipitation; this is the end of the actinium-228 ingrowth time and beginning of actinium-228 decay time.)
- 8.16 Dissolve the precipitate in 2 ml 6N  $\text{HNO}_3$ . Heat and stir in a hot water bath about 5 minutes. Add 5 ml water and reprecipitate yttrium hydroxide with 3 ml 10N NaOH. Heat and stir in a hot water bath until precipitate coagulates. Centrifuge and discard supernate.
- 8.17 Dissolve precipitate with 1 ml 1N  $\text{HNO}_3$  and heat in hot water bath a few minutes. Dilute to 5 ml and add 2 ml 5%  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . Heat to coagulate, centrifuge and discard supernate.
- 8.18 Add 10 ml water, 6 drops 1N  $\text{HNO}_3$  and 6 drops 5%  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . Heat and stir in a hot water bath a few minutes. Centrifuge and discard supernate.

- 8.19 To determine yttrium yield, transfer quantitatively to a tared stainless steel planchet with a minimum amount of water. Dry under an infra-red lamp to a constant weight and count in a low-background beta counter.
- 8.20 To the supernate from step 8.15, add 4 ml 16N HNO<sub>3</sub> and 2 ml (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (200 mg/ml), stirring well after each addition. Add 17.4N CH<sub>3</sub>COOH until barium sulfate precipitates, then add 2 ml excess. Digest on a hot plate until precipitate settles. Centrifuge and discard supernate.
- 8.21 Add 20 ml basic EDTA reagent, heat in a hot water bath, and stir until precipitate dissolves. Add a few drops 10N NaOH if precipitate does not readily dissolve.
- 8.22 Add 1 ml (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (200 mg/ml) and stir thoroughly. Add 17.4N CH<sub>3</sub>COOH until barium sulfate precipitates, then add 2 ml excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernate.
- 8.23 Wash precipitate with 10 ml water. Centrifuge and discard supernate.
- 8.24 Transfer precipitate to a tared stainless steel planchet with a minimum amount of water. Dry under an infra-red lamp and weigh for barium yield determination.

## 9. Calculation

- 9.1 Calculate the radium-228 concentration, D, in picocuries per liter as follows:

$$D = \frac{C}{2.22 \times EVR} \times \frac{\lambda t_2}{(1 - e^{-\lambda t_2})^*} \times \frac{1}{(1 - e^{-\lambda t_3})} \times \frac{1}{e^{-\lambda t_1}}$$

where:

- C = average net count rate, cpm,  
 E = counter efficiency, for actinium-228, or comparable beta energy nuclide  
 V = liters of sample used,  
 R = fractional chemical yield of yttrium carrier (step 8.19) multiplied by fractional chemical yield of barium carrier (step 8.24),  
 2.22 = conversion factor from disintegrations/minute to picocuries,  
 λ = the decay constant for actinium-228 (0.001884 min<sup>-1</sup>),

\*  $\frac{\lambda t_2}{(1 - e^{-\lambda t_2})}$  is a factor to correct the average count rate to count rate at beginning of counting time.

- $t_1$  = the time interval (in minutes) between the first yttrium hydroxide precipitation in step 8.15 and the start of the counting time,  
 $t_2$  = the time interval of counting in minutes, and  
 $t_3$  = the ingrowth time of actinium-228 in minutes measured from the last barium sulfate precipitation in step 8.11 to the first yttrium hydroxide precipitation in step 8.15.

## 10. Precision and Accuracy

- 10.1 In a single laboratory evaluation, an EMSL-Las Vegas Performance Sample was analyzed in replicate for radium-228. The known value of the water sample was  $12.7 \pm 1.9$  pCi per liter. The grand average reported by 33 laboratories was  $17.1 \pm 8.8$  pCi per liter indicating a positive bias reflecting the presence of other beta emitters in the sample.

The result of the nine replicate analyses for radium-228 expressed in pCi/l were:

16.5	16.1	16.6
16.5	16.4	16.6
15.5	16.7	16.8

The average and standard deviation of the method was  $16.4 \pm 0.4$  pCi/l.

The accuracy of the method based on the known value was +29%.

The accuracy of the method based on the reported grand average was -4%.

The precision of the method was  $\pm 2.5\%$ .

- 10.2 A number of laboratories which participate in the EPA, EMSL-Las Vegas intercomparison program for radium-228 in water used this method in their analyses of water samples received in that program for the period 9/78 to 6/79. During that period five studies for radium-228 in water were conducted. Three of the studies were crosscheck samples which contained only radium-228 and radium-226 in water. The other two studies were performance (blind) samples which contained other radionuclides, including strontium-90. Data from the five studies were used for this precision and accuracy statement of the method. However, data from the two types of studies (crosscheck and performance) are treated separately because there appears to be a bias in the performance sample studies.

The number of laboratories used for this data ranged from 8 to 15 laboratories per study. All laboratories reported triplicate analyses for each study (one test sample per study). The total number of analyses for the three cross check studies was 78, of which 60 were acceptable results (within 3 sigma of the known value, 1 sigma being 15% of the known value). This calculates to

be 77% acceptability of results as determined by this method. The total number of analyses for the two performance studies was 72, of which 36 were acceptable for a 50% acceptability of results.

A statistical evaluation of the three cross check studies and the two performance studies was done according to the methods of Youden(2) and Steiner(3). The coefficient of variation for within-laboratory error was 15%, 19%, and 18% for the three cross check studies; and was 21% for the two performance studies. The coefficient of variation for systematic error between laboratories was 23%, 23%, and 21% for the three cross check studies; and was 23% and 25% for the two performance studies. The coefficient of variation for the total error between laboratories based on a single analysis was 28%, 29%, and 28% for the three crosscheck studies; and was 31% and 27% for the two performance studies.

A comparison of the grand average values with the known values in a test for systematic error in a method gave a value for one of the cross check studies higher than the critical value, indicating a bias (low) for the method. However, values for the other two crosscheck studies were well below the critical values, indicating no bias for the method. On the other hand, when the same test was applied to the data from the two performance studies, a high bias was indicated for both studies (see Sec. 10.3 below).

### 10.3 Test for Method Bias

<u>Study</u>	<u>R(pCi/l)</u>	<u>x (pCi/l)</u>	<u>Calculated t</u>	<u>Critical t</u>
<u>Crosscheck</u>				
9/78	20.8	17.0	2.56	2.32
12/78	8.9	8.6	0.43	2.23
3/79	13.6	12.6	1.05	2.32
<u>Performance</u>				
10/78	5.4	6.8	3.01	2.15
4/79	6.2	10.7	5.00	2.28

This is a standard t-test with (n-1) degrees of freedom

$$t = \frac{(\bar{x}-R) \sqrt{n}}{S_x}$$



where:

- $\bar{x}$  = mean value of reported averages
- R = known value
- n = number of reported averages
- $S_x$  = standard deviation for the set of n reported averages.

Although the addition of man-made radionuclides to the performance samples may be creating samples that are somewhat unreal it is desirable that an approved EPA reference method for radium-228 in drinking water would not be biased by those radionuclides.

The radium-228 concentrations in the test samples for the three crosschecks and two performance studies are given in the above table (the R values). These are all relatively low level and should relate well to drinking water supplies.

#### References

1. Johnson, J.O. Determination of Radium-228 in Natural Waters. Radiochemical Analysis of Water, Geological Survey Water - Supply Paper 1696-G., U.S. Govt. Printing Office, Washington, D.C. (1971).
2. Youden, W. J. "Statistical Techniques for Collaborative Test," Statistical Manual of the AOAC, Association of Official Analytical Chemists, Washington, D.C. (1975).
3. Steiner, E.H. "Planning and Analysis of Results of Collaborative Tests," Statistical Manual of the AOAC, Association of Official Analytical Chemists, Washington, D.C. (1975).