METHOD 9320

Radium 228

1.0 SCOPE AND APPLICATION

1.1 This method covers the measurement of radium-228 in ground water and, if desired, the determination of radium-226 on the same sample. 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 of 0.404 keV) is to be calibrated with a beta source of comparable average beta energy.

2.0 SUMMARY OF METHOD

2.1 The radium in the 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-hr 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 supernatant can be reserved for coprecipitation on barium sulfate, dissolving in EDTA and storing for ingrowth in a sealed radon bubbler.

3.0 INTERFERENCES

3.1 As evidenced by 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. However, strontium-90 is not likely to be found in ground water, except possibly in monitoring wells around a radioactive burial site.

3.2 Excess barium in the water sample might result in a falsely high chemical yield.

4.0 APPARATUS

4.1 Gas-flow proportional counting system (low-background beta <3 cpm).

4.2 Electric hot plate.

4.3 Centrifuge.

4.4 Membrane filters: Matricel 47-mm.

4.5 Drying lamp.

4.6 Glassware.

4.7 Stainless steel counting planchets.

4.8 Analytical balance.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water must be monitored for impurities.

5.2 Acetic acid, 17.4 N: Glacial CH_3COOH (concentrated) sp. gr. 1.05, 99.8%.

5.3 Ammonium hydroxide, 15 N: NH_4OH (concentrated) sp gr. 0.90, 56.6%.

5.4 Ammonium oxalate, 5%: Dissolve 5g $(NH_4)_2C_2O_4 \cdot H_2O$ in Type II water and dilute to 100 mL.

5.5 Ammonium sulfate, 200 mg/mL: Dissolve 20 g $(NH_4)_2SO_4$ in Type II water and dilute to 100 mL.

5.6 Ammonium sulfide, 2%: Dilute 10 mL $(NH_4)_2S$ (20-24%), to 100 mL with Type II water.

5.7 Barium carrier, 16 mg/mL, standardized: Dissolve 2.846 g $BaCl_2 \cdot 2H_2O$ in Type II water, add 0.5 mL 16 N HNO_3, and dilute to 100 mL with Type II water.

5.8 Citric acid, 1 M: Dissolve 19.2 g $C_6H_8O_7 \cdot H_2O$ in Type II water and dilute to 100 mL.

5.9 EDTA reagent, basic (0.25 M): Dissolve 20 g NaOH in 750 mL Type II water, heat, and slowly add 93 g disodium ethylenedinitriloacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$) while stirring. After the salt is in solution, filter through coarse filter paper, and dilute to 1 liter.

5.10 Lead carrier, 15 mg/mL: Dissolve 2.397 g $Pb(NO_3)_2$ in Type II water, add 0.5 mL 16 N HNO_3, and dilute to 100 mL with Type II water.

5.11 Lead carrier, 1.5 mg/mL: Dilute 10 mL lead carrier (15 mg/mL) to 100 mL with Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected in a manner which addresses the considerations discussed in Chapter Nine of this manual.

6.2 It is recommended that samples be preserved at the time of collection by adding enough 1 N HNO_3 to the sample to bring it to pH 2 (15 mL 1 N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved, and held in the original container for a minimum of 16 hr before analysis or transfer of the sample. See also Note to Paragraph 7.2 below.

6.3 The container choice should be plastic (rather than glass) to prevent loss due to breakage during transportation and handling.

7.0 PROCEDURE

7.1 Calibrations:

7.1.1 **Counter efficiency:** The beta counter may be calibrated with actinium-228 or strontium-89 ($t_{1/2}$ = 51 d). 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 For each liter of water, add 5 mL 1 M $C_6H_8O_7 \cdot H_2O$, and a few drops of methyl orange indicator. The solution should be red.

NOTE: At the time of sample collection add 2 mL 16 N HNO_3 for each liter of water.

7.3 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. Add 15 N NH_4OH until a definite yellow color is obtained; then add a few drops excess. Heat to incipient boiling and maintain at this temperature for 30 min.

7.4 Precipitate lead and barium sulfates by adding 18 N 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 min.

7.5 Cool slightly; then filter with suction through a 47-mm matricel membrane filter (GA6,0.45-micron pore size). Make a quantitative transfer of precipitate to the filter by rinsing last particles out of beaker with a strong jet of water.

7.6 Carefully place filter with precipitate in the bottom of a 250-mL beaker. Add about 10 mL 16 N HNO_3 and heat gently until the filter completely

dissolves. Transfer the precipitate into a polypropylene centrifuge tube with additional 16 N HNO_3. Centrifuge and discard supernatant.

7.7 Wash the precipitate with 15 mL 16 N HNO_3, centrifuge, and discard supernatant. Repeat this washing a second time.

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

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

7.10 Add 1 mL $(NH_4)_2SO_4$ (200 mg/mL) and stir thoroughly. Add 17.4 N acetic acid until barium sulfate precipitates; then add 2 mL excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernatant.

7.11 Add 20 mL basic EDTA reagent, heat in a hot-water bath, and stir until precipitate dissolves. Repeat steps 7.9 and 7.10. (Note time of last barium sulfate precipitation; this is the beginning of the actinium-228 ingrowth time.)

7.12 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 10 N NaOH. Cap the polypropylene tube and age at least 36 hr.

7.13 Add 0.3 mL $(NH_4)_2S$ and stir well. Add 10 N NaOH dropwise with vigorous stirring until lead sulfide precipitates; then add 10 drops excess. Stir intermittently for about 10 min. Centrifuge and decant supernatant into a clean tube.

7.14 Add 1 mL lead carrier (1.5 mg/mL), 0.1 mL $(NH_4)_2S$, and a few drops 10 N 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.

7.15 Add 5 mL 18 N 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 7.20). (Note time of yttrium hydroxide precipitation; this is the end of the actinium-228 ingrowth time and beginning of actinium-228 decay time.)

7.16 Dissolve the precipitate in 2 mL 6 N HNO_3. Heat and stir in a hot water bath about 5 min. Add 5 mL water and reprecipitate yttrium hydroxide with 3 mL 10 N NaOH. Heat and stir in a hot water bath until precipitate coagulates. Centrifuge and add this supernate to the supernate produced in step 7.15 in order to determine barium yield.

7.17 Dissolve precipitate with 1 mL 1 N HNO_3 and heat in hot-water bath a few minutes. Dilute to 5 mL and add 2 mL 5% $(NH_4)_2C_2O_4 \cdot H_2O$. Heat to coagulate, centrifuge, and discard supernatant.

7.18 Add 10 mL water, 6 drops 1 N HNO_3 and 6 drops 5% $(NH_4)_2 C_2 O_4 \cdot H_2O$. Heat and stir in a hot-water bath a few minutes. Centrifuge and discard supernatant.

7.19 To determine yttrium yield, transfer quantitatively to a tared stainless steel planchet with a minimum amount of water. Dry under an infrared lamp to a constant weight and count in a low-background beta counter.

7.20 To the supernatant from step 7.15, add 4 mL 16 N HNO_3 and 2 mL $(NH_4)_2SO_4$ (200 mg/mL), stirring well after each addition. Add 17.4 N acetic acid until barium sulfate precipitates; then add 2 mL excess. Digest on a hot plate until precipitate settles. Centrifuge and discard supernatant.

7.21 Add 20 mL basic EDTA reagent, rest in a hot-water bath, and stir until precipitate dissolves. Add a few drops 10 N NaOH if precipitate does not readily dissolve.

7.22 Add 1 mL $(NH_4)_2SO_4$ (200 mg/mL) and stir thoroughly. Add 17.4 N acetic acid until barium sulfate precipitates; then add 2 mL excess. Digest in a hot-water bath until precipitate settles. Centrifuge and discard supernatant.

7.23 Wash precipitate with 10 mL water. Centrifuge and discard supernatant.

7.24 Transfer precipitate to a tared stainless steel planchet with a minimum amount of water. Dry under an infrared lamp and weigh for barium yield determination.

7.25 Calculation:

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

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

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

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 7.19) multiplied by fractional chemical yield of barrier carrier (Step 7.24);

2.22 = Conversion factor from disintegrations/minute to picocuries;

λ = The decay constant for actinium-228 (0.001884 min^{-1});

t_1 = The time interval (in min) between the first yttrium hydroxide precipitation in Step 7.15 and the start of the counting time;

t_2 = The time interval of counting in min; and

t_3 = The ingrowth time of actinium-228 in min measured from the last barium sulfate precipitation in Step 7.11 to the first yttrium hydroxide precipitation in Step 7.15.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

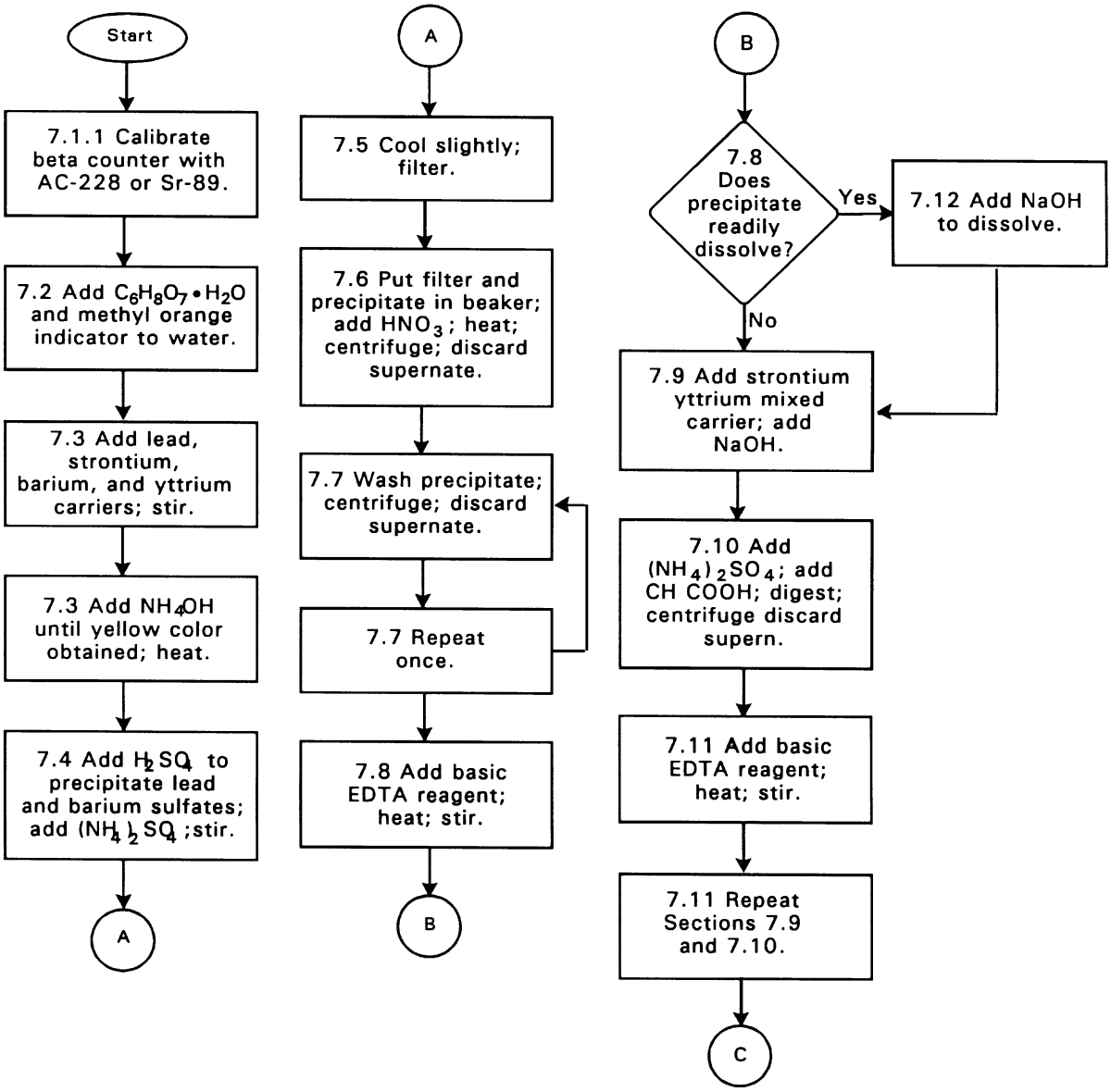
9.1 No data provided.

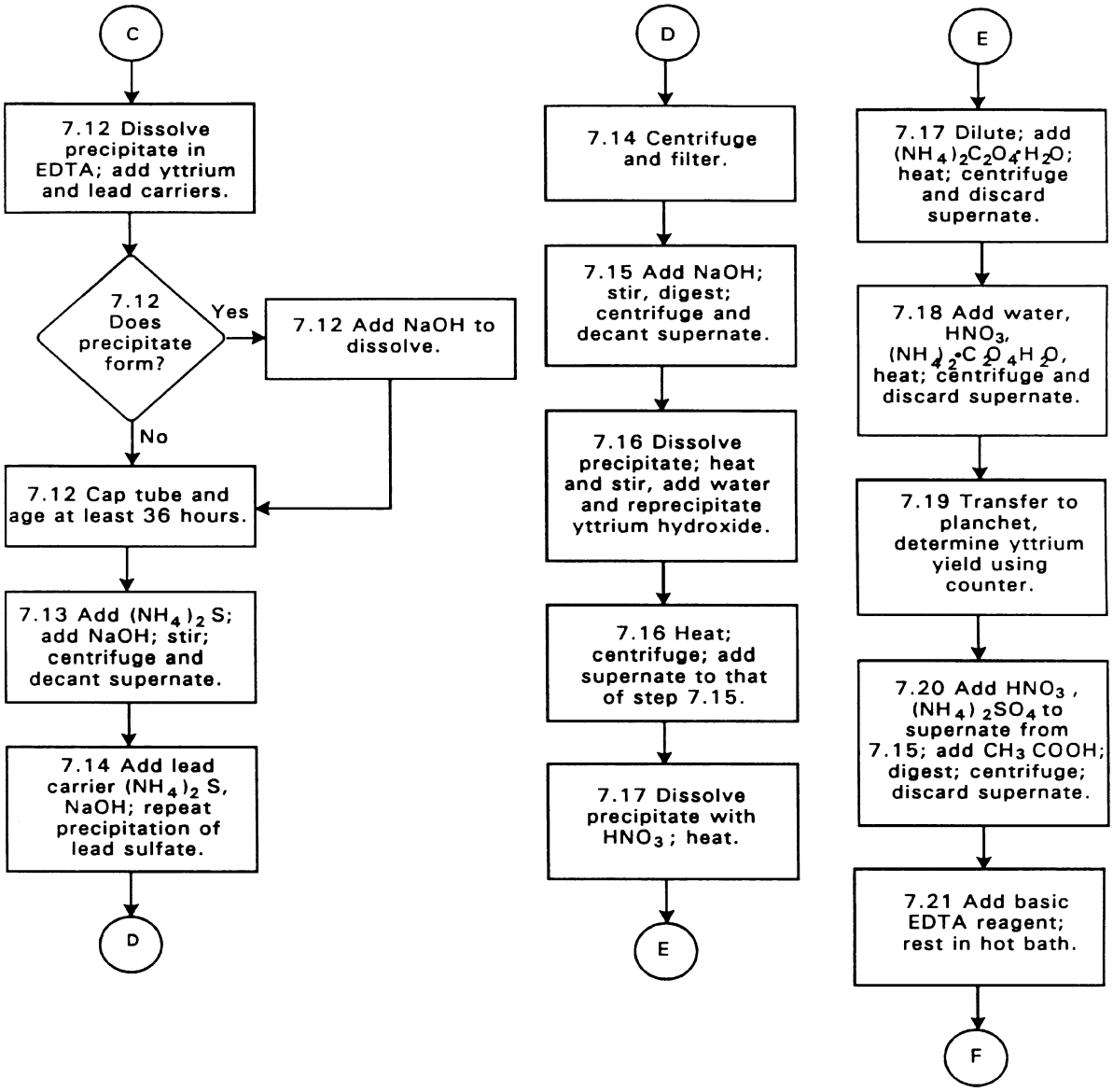
10.0 REFERENCES

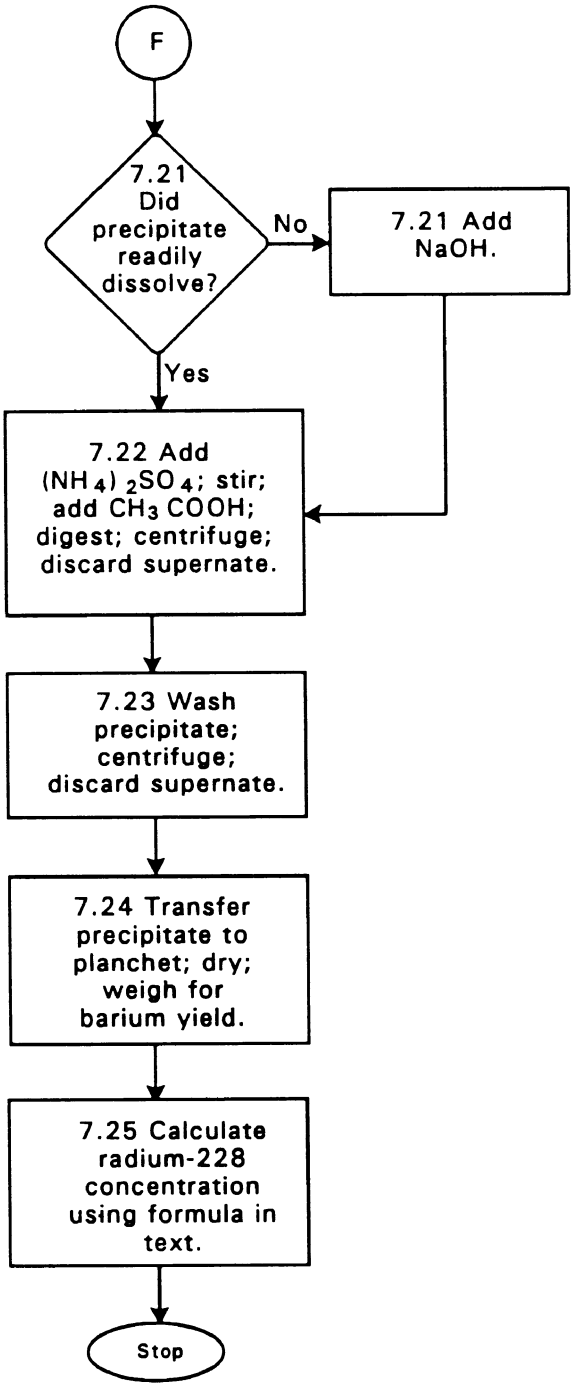
1. Greenberg, A.E., J.J. Connors, and D.J. Jenkens, eds., Standard Methods for the Examination of Water and Wastewater, 15th ed., American Public Health Assoc., Washington, D.C., Method 707, p. 600, 1980.

2. Johnson, J.O., Determination of Radium 228 in Natural Waters. Radiochemical Analysis of Water. U.S. Geol. Surv., Water Supply Paper 1696-G. U.S. Govt. Printing Office, Washington, D.C., 1971.

3. Krieger, H.L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Environmental Monitoring and Support Laboratory, U.S. EPA, Cincinnati, OH, EPA-600/4-75-008, 1976.


Start
7.1.1 Calibrate beta counter with AC-228 or Sr-89.
7.2 Add $C_6H_8O_7 \cdot H_2O$ and methyl orange indicator to water.
7.3 Add lead, strontium, barium, and yttrium carriers; stir.
7.3 Add NH_4OH until yellow color obtained; heat.
7.4 Add H_2SO_4 to precipitate lead and barium sulfates; add $(NH_4)_2SO_4$; stir.
A
A
7.5 Cool slightly; filter.
7.6 Put filter and precipitate in beaker; add HNO_3; heat; centrifuge; discard supernate.
7.7 Wash precipitate; centrifuge; discard supernate.
7.7 Repeat once.
7.8 Add basic EDTA reagent; heat; stir.
B
B
7.8 Does precipitate readily dissolve?
Yes
7.12 Add NaOH to dissolve.
No
7.9 Add strontium yttrium mixed carrier; add NaOH.
7.10 Add $(NH_4)_2SO_4$; add CH COOH; digest; centrifuge discard supern.
7.11 Add basic EDTA reagent; heat; stir.
7.11 Repeat Sections 7.9 and 7.10.
C


C
7.12 Dissolve precipitate in EDTA; add yttrium and lead carriers.
7.12 Does precipitate form?
Yes
7.12 Add NaOH to dissolve.
No
7.12 Cap tube and age at least 36 hours.
7.13 Add $(NH_4)_2S$; add NaOH; stir; centrifuge and decant supernate.
7.14 Add lead carrier $(NH_4)_2S$, NaOH; repeat precipitation of lead sulfate.
D
D
7.14 Centrifuge and filter.
7.15 Add NaOH; stir, digest; centrifuge and decant supernate.
7.16 Dissolve precipitate; heat and stir, add water and reprecipitate yttrium hydroxide.
7.16 Heat; centrifuge; add supernate to that of step 7.15.
7.17 Dissolve precipitate with HNO_3; heat.
E
E
7.17 Dilute; add $(NH_4)_2C_2O_4 \cdot H_2O$; heat; centrifuge and discard supernate.
7.18 Add water, HNO_3, $(NH_4)_2 \cdot C_2O_4H_2O$, heat; centrifuge and discard supernate.
7.19 Transfer to planchet, determine yttrium yield using counter.
7.20 Add HNO_3, $(NH_4)_2SO_4$ to supernate from 7.15; add CH_3COOH; digest; centrifuge; discard supernate.
7.21 Add basic EDTA reagent; rest in hot bath.
F


F
7.21 Did precipitate readily dissolve?
No
7.21 Add NaOH.
Yes
7.22 Add $(NH_4)_2SO_4$; stir; add CH_3COOH; digest; centrifuge; discard supernate.
7.23 Wash precipitate; centrifuge; discard supernate.
7.24 Transfer precipitate to planchet; dry; weigh for barium yield.
7.25 Calculate radium-228 concentration using formula in text.
Stop