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Midwest Laboratory
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DETERMINATION OF SR-89 AND SR-90 IN SOIL AND BOTTOM SEDIMENTS

PROCEDURE NO. SR-06

Prepared by

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DETERMINATION OF SR-89 AND SR-90 IN SOIL AND BOTTOM SEDIMENTS

Principle of Method

The sample with stable strontium and barium carriers added is leached in hydrochloric acid. After separation from calcium, the residue is purified by adding iron and rare earth carriers and precipitating them as hydroxides. After a second strontium nitrate precipitation from 70% nitric acid, the nitrates are dissolved in acid again with addec yttrium carrier and are stored for ingrowth of yttrium-90. The yttrium is precipitated as hydroxide and separated from strontium with the strontium being in the supernate. Each fraction is precipitated separately as an oxalate (yttrium) and carbonate (strontium) and is collected on No. 42 (2.4cm) What man filter for counting.

Reagents

Ammonium acetate buffer: pH 5.0
Ammonium hydroxide, NH_4OH: concentrated (15N), 6N
Carrier solutions: Ba^{+2} as barium nitrate, $Ba(NO_3)_2$: 20mg Ba^{+2} per mL
Sr^{+2} as strontium nitrate, $Sr(NO_3)_2$: 20mg Sr^{+2} per mL
Y^{+3} as yttrium nitrate, $Y(NO_3)_3$: 10 mg Y^{+3} per mL
Hydrochloric acid, HCl: 6N
Nitric acid, HNO_3: Fuming (90%), concentrated (16N), 6N
Oxalic acid, $H_2C_2O_2 \cdot 2H_2O$: Saturated at room temperature
Scavenger solutions: 20mg Fe^{+3} per mL, 10mg each Ce^{+3} and Zr^{+4} per mL
Fe^{+3} as ferric chloride, $FeCl_3 \cdot 6H_2O$
Ce^{+3} as cerous nitrate, $Ce(NO_3)_3 \cdot 6H_2O$
Zr^{+4} as zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$
Sodium carbonate, Na_2CO_3: 3N, 0.1N
Sodium chromate, Na_2CrO_4: 3N

Apparatus

Analytical balance
Centrifuge
Hot plate
Low background beta counter
pH meter
Plastic disc and ring
Stirrer

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Procedure

1. Weigh out 5 – 50 g sample into a 1 liter beaker depending on the required LLD. Add 1mL of strontium carrier and 1mL of Ba carrier.
2. Stir mechanically while slowly adding 200mL of 6N HCl. (It may be necessary to add a few drops of octyl alcohol to prevent excessive frothing.) Continue stirring for about 3 hours. Allow a minimum of two hours for the insoluble material to settle.
3. Stir the mixture and filter with suction through a 24cm Whatman No. 42 filter paper using a Buchner funnel. Wash the residue with hot water. Wash with 6N HCl and again with hot water until the yellow color of ferric chloride is removed. Discard the residue.
4. Transfer the filtrate to a 1 liter beaker and evaporate to approximately 200mL. Cool and slowly add 200mL of concentrated HNO_3. (If there is excessive frothing, add a few drops of octyl alcohol.) Evaporate to 100-200mL.
5. Add 500mL of water and stir.
6. Add 25 grams of oxalic acid with magnetic stirring until it is completely dissolved.
7. Adjust the pH to 5.5-6.0 with concentrated NH_4OH. (If the brown color of ferric hydroxide persists, add more oxalic acid and readjust the pH.) The optimum condition is an excess of oxalic acid in solution without causing crystallization of ammonium oxalate upon cooling.
8. Allow precipitate to settle for 5-6 hours or overnight.
9. Decant most of the supernate (liquid) and transfer the precipitate to a 250mL centrifuge tube using deionized water for rinsing. Add rinsing to the tube. Centrifuge and decant supernate.
10. Wash the precipitate with 50-100mL portion of water and centrifuge again.
11. Repeat washing as needed until all the yellow color of the solution has been removed.
12. Cool the precipitate and dissolve it with 6N HNO_3 and transfer it into a 250mL beaker. Rinse the tube with 6N HNO_3, making the total volume to 50-100 mL. Add about 6 drops of H_2O_2 (30%) to facilitate dissolution.
13. Cool to room temperature. If insoluble material is present at this point, filter by suction through a glass fiber filter. Discard the filter and residue.
14. Transfer the solution to an appropriate size beaker and evaporate to dryness. The evaporation must be done slowly to avoid spattering.
15. Dissolve the salt in water and perform successive fuming nitric acid separations (the first two separations at concentration slightly greater than 75%) until the strontium has been separated from the bulk of the calcium. Samples with a high calcium content will require five or more separations.
16. The volumes of 75% HNO_3 vary (fuming solutions may be changed as required by the mass of calcium present, keeping in mind that minimum volumes are always best.)

Procedure (continued)

17. If calcium content is still thick, evaporate the solution to dryness and bake.

18. Dissolve the residue with 50mL boiling water and filter. Discard residue.

19. Evaporate the solution to dryness again.

20. Cool and dissolve the residue in a minimum amount of water and add 50 mL of fuming HNO_3.

21. Continue the fuming nitric acid separations until the strontium has been separated from the bulk of calcium.

22. Transfer the solution to a 40mL conical, heavy-duty centrifuge tube, using a minimum of concentrated HNO_3 to effect the transfer. Cool the centrifuge tube in an ice bath for about. Centrifuge and discard the supernatant.

NOTE: *The precipitate consists of calcium, strontium, and barium-radium nitrate.*

The supernatant contains part of the sample's calcium and phosphate content.

23. Add 30mL of concentrated HNO_3 to the precipitate. Heat in a hot water bath with stirring for about 10 minutes. Cool the solution in an ice bath, stirring for about 5 minutes. Centrifuge and discard the supernatant.

NOTE: *Additional calcium is removed from the sample. Nitrate precipitation with 70% HNO_3 will afford a partial decontamination from soluble calcium, while strontium, barium, and radium are completely precipitated.*

Separation of calcium is best at 60% HNO_3; however, at 60% the precipitation of strontium is not complete. Therefore, it is common practice to precipitate $(Sr(NO_3)_2$ with 70% HNO_3, which is the concentration of commercially available 16N HNO_3.

Most other fission products, induced activities, and actinides are soluble in concentrated HNO_3, affording a good "gross" decontamination step from a wide spectrum of radionuclides. The precipitation is usually repeated several times.

24. Repeat Step 23 two (2) more times.

25. Dissolve the nitrate precipitate in about 20mL distilled water. Add 1mL of scavenger solution. Adjust the pH of the mixture to 7 with 6N NH_4OH. Heat, stir, and filter through a Whatman No. 541 filter. Discard the mixed hydroxide precipitate.

26. To the filtrate, add 5mL of ammonium acetate buffer. Adjust pH with 6N HNO_3 or NH_4OH to pH 5.5.

NOTE: *The pH of the solution at this point is critical.*
Add dropwise with stirring 1mL of 3N Na_2CrO_4 solution, stir and heat in a water bath.

27. Cool and centrifuge. Decant the supernate into another 40mL centrifuge tube. (Save the precipitate for barium analysis if needed.)

Procedure (continued)

28. Heat the supernate in a water bath. Adjust the pH to 8-8.5 with NH_4OH. With continuous stirring, add 5mL 3N Na_2CO_3 solution. Heat gently for 10 minutes. Cool, centrifuge, and decant the supernate to waste. Wash the precipitate with 0.1N Na_2CO_3. Centrifuge again and decant the supernate to waste.

29. Dissolve the precipitate in no more than 4mL of 6N HNO_3. Add 20-30mL of fuming HNO_3, cover with parafilm, cool in a water bath, and centrifuge. Decant and discard the supernate.

30. Repeat Step 13. **RECORD THE TIME AND DATE AS THE BEGINNING OF YTTRIUM-90 INGROWTH.**

31. Dissolve precipitate in 4mL of 6N HNO_3 and add 1mL of yttrium carrier solution.

32. Cover with parafilm and store for 7-14 days.

NOTE: *At this point, the sample can be transferred to a glass scintillation vial for the ingrowth storage. Use several portions of 6N HNO_3 (a total of not more than 4mL); then add 1mL of yttrium carrier to the vial.*

Separation

NOTE: *If the sample was stored in the scintillation vial, transfer back into 40mL centrifuge tube using a few drops of 6N HNO_3 as a rinse.*

1. After storage (ingrowth period), heat the 40mL centrifuge tube containing the sample in the hot water bath (approximately 90°C) for 10 minutes.

2. Adjust pH to 8 with NH_4OH, stirring continuously.

3. Cool in a cold water bath and centrifuge for 5 minutes.

4. Decant the supernate into a 40 mL centrifuge tube marked with the sample number and "SR-89." **RECORD THE DATE AND TIME OF DECANTATION AS THE END OF Y-90 INGROWTH** in Sr fraction and the beginning of its decay in Y-90 fraction.

5. Redissolve the precipitate by adding 3-4 drops of 6N HCl. Add 5-10mL of deionized water with stirring.

6. Repeat Steps 1, 2, and 3.

7. Combine supernate with the one in Step 4.

Determination

A. Strontium-90 (Yttrium-90)

1. Add 3 drops of 6N HCl to dissolve the precipitate; then add 5-10mL of water. Heat in a water bath at approximately 90°C. Add 1mL of saturated oxalic acid solution dropwise with vigorous stirring. Adjust to a pH of 2-3 with NH_4OH. Allow the precipitate to digest for about an hour.

NOTE: *Do Part "B" while precipitate is digesting.*

2. Cool to room temperature in a cold water bath. Filter by suction on a weighed 2.5cm filter paper. Wash precipitate with water and alcohol.

3. Dry the precipitate under the lamp for 30 minutes. Cool and weigh. Mount and count without delay in a proportional counter. (See Part C for mounting.)

B. Strontium-89 (Total Strontium)

1. Heat the solution from Step 7 in water bath.

2. Adjust the pH to 8-8.5 using NH_4OH.

3. With continuous stirring, add 5mL of 3N Na_2CO_3 solution. Stir until precipitate appears. Heat gently for 10 minutes.

4. Cool and filter on a weighed No. 42 (2.4cm) Whatman filter paper.

5. Wash thoroughly with water and alcohol.

6. Mount and count without delay its beta activity as "total radiostrontium" in a proportional counter.

C. Filtering and Mounting

1. Place filters under heat lamps for 30 minutes before weighing.

2. Use an analytical balance for weighing (accuracy 0.01 mg).

3. Label a clean petri dish with the weight of the filter paper. (After samples are filtered, the filter paper will again be dried and weighed to determine weight of precipitate before mounting.)

4. Mount weighed filter paper and precipitate on nylon disc using 1" transparent tape to hold filter paper and 2" mylar foil placed over precipitate and held in place with slip-ring. Trim off excess mylar foil and place the mounted sample in a labeled petri dish.

5. Fill out corresponding loading sheets and place samples in counting room.

Calculations

Part A

Strontium-90 Concentration (pCi/g dry) = $\frac{A}{2.22BCDEF} \pm \frac{2\sqrt{E_{sb}^2 + E_b^2}}{2.22BCDEF}$

Where:

A = Net beta count rate of yttrium-90 (cpm)
B = Recovery of yttrium carrier
C = Counter efficiency for counting yttrium-90 or yttrium oxalate mounted on a 2.4cm diameter filter paper (cpm/pCi)
D = Sample weight (grams), dry
E = Correction factor $e^{-\lambda t}$ for yttrium-90 decay, where t is the time from the time of decantation (Step 4, Separation) to the time of counting
F = Correction factor $1 - e^{-\lambda t}$ for the degree of equilibrium attained during the yttrium-90 ingrowth period, where t is the time from the collection of the water sample to the time of decantation (Step 4, Separation)
E_{sb} = Counting error of sample plus background
E_b = Counting error of background

Part B

Strontium-89 Concentration (pCi/g dry) $= \frac{1}{BxC}\left[\frac{A}{2.22xDxE} - F(H + IxJ)\right] \pm 2\sigma$

Where:

A = Net beta count rate of "total radiostrontium" (cpm)
B = Counter efficiency for counting strontium-89 as strontium carbonate mounted on a 2.4cm diameter filter paper (cpm/pCi)
C = Correction factor $e^{-\lambda t}$ for strontium-89 decay, where t is the time from sample collection to the time of counting
D = Recovery of strontium carrier
E = Sample weight (grams, dry)
F = Strontium-90 concentration (pCi/g) from Part A
H = Counter efficiency for counting strontium-90 as strontium carbonate mounted on a 2.4cm diameter filter paper (cpm/pCi)
I = Counter efficiency for counting yttrium-90 as yttrium oxalate mounted on a 2.4cm diameter filter paper (cpm/pCi)
J = Correction factor $1 - e^{-\lambda t}$ for yttrium-90 ingrowth, where t is the time from the last decantation of the nitric acid (Step 4, Separation)

REFERENCE: Radioassay Procedures for Environmental Samples, U. S. Department of Health, Education, and Welfare. Environmental Health Series, January 1967.