ISOTOPIC DETERMINATION OF PLUTONIUM, URANIUM, AND THORIUM IN WATER, SOIL, AIR, AND BIOLOGICAL TISSUE

1. Principle

1.1 Samples are decomposed utilizing techniques of nitric-hydrofluoric acid digestion or ignition. The residues are dissolved in dilute nitric acid and successive sodium and ammonium hydroxide precipitations are performed in the presence of boric acid to remove fluoride and soluble salts. The hydroxide precipitate is dissolved, the solution is adjusted to 9N in hydrochloric acid, and plutonium and uranium are adsorbed on an anion exchange column; separating them from thorium. Plutonium is eluted with hydrobromic acid. Iron is removed from the column by washing with hydriodic acid and the uranium is eluted with dilute hydrochloric acid. The thorium is converted to a nitrate form and adsorbed on the same anion exchange column, separating it from calcium and other interferences. The thorium is then eluted with 9N hydrochloric acid. The actinides are electrodeposited on stainless steel discs from an ammonium sulfate solution and subsequently counted by alpha spectrometry. Chemical yields are determined by the recovery of internal tracer standards (plutonium-236, uranium-232, and thorium-234) added at the beginning of the analysis.

2. Application

2.1 This method is appropriate for the analysis of isotopic plutonium, uranium, and thorium, together or individually, in soil, water, air filters, urine, or ashed residues of vegetation, animal tissues, and bone.

3. Range

3.1 This method is designed to detect environmental levels of activity as low as 0.02 picocuries per sample. To avoid possible cross-contamination, sample activities should be limited to 25 picocuries or less.

3.2 Optimum sample sizes for each of the sample types are listed below. Smaller samples may be analyzed with a commensurate loss in sensitivity. Larger samples may introduce interferences and insoluble residues which prevent satisfactory analysis.

3.3

Sample Type	Optimum Size
Animal tissue ash	10 grams
Bone ash	10 grams
Vegetation ash	10 grams
Soil	10 grams

Sample Type	Optimum Size
Glass-fiber filters	12-4" circles or 1-8" rectangle
Organic filters	12-4" circles
Water	1 liter
Urine	1 liter

4. Interferences

4.1 Internal tracer standards must be purified at intervals to remove progeny which might contribute to background activities or interfere with subsequent analyses. Thorium-228 will be present in aged plutonium-236 or uranium-232, which must be compensated for, if thorium-228 is to be determined.

4.2 If present, lead-210 will be co-plated with plutonium giving rise to alpha interference by ingrowing polonium-210. This can be minimized by counting the sample within a few days of separation before sufficient polonium-210 ingrowth has occurred.

4.3 Samples containing high levels of phosphate, such as fertilizer, or high levels of barium sulfate, as in glass-fiber filters, may result in low actinide yields.

5. Lower limit of detection

5.1 The lower limit of detection* (LLD) is defined as the smallest concentration of radioactive material sampled that has a 95% probability of being validly detected.

$$\text{LLD} = \frac{3.29\ S_o}{2.22 \times E \times S}$$

where 3.29 = $K_\alpha + K_\beta$

K_α = the value for the upper percentile of the standardized normal variate corresponding to the preselected risk for concluding falsely that activity is present (α) = 0.05

K_β = corresponding value for the predetermined degree of confidence for detecting the presence of activity ($1-\beta$) = 0.95

S_o = estimated standard error for the net sample activity

2.22 = dpm/pCi

E = fractional counting efficiency

S = sample size

6. Precision and accuracy

7. Shipment and storage of samples and sample stability

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* HASL procedures Manual, J. H. Harley, editor, pages D-08-01/12, August 1977.

7.1 Vegetation, urine, and animal tissue samples should be preserved by refrigeration, freezing, or the addition of formaldehyde until ashing takes place. Water should be acidified with 20 ml concentrated nitric acid per 3.7 liters of sample. Soil, air filters, and ash may be stored indefinitely.

8. Reagents

8.1 Alkaline ethyl alcohol: Adjust the pH of 95% ethanol to 8 with ammonium hydroxide.

8.2 Ammonium hydroxide, concentrated (14N): Reagent grade.

8.3 Ammonium hydroxide, (1.4N): Add 100 ml concentrated ammonium hydroxide to 800 ml distilled water. Cool and dilute to 1000 ml.

8.4 Ammonium hydroxide, (0.7N): Add 50 ml concentrated ammonium hydroxide to 900 ml distilled water. Cool and dilute to 1000 ml.

8.5 Ammonium hydroxide-ammonium nitrate solution (0.10N NH_40H-01.10N NH_4NO_3): Dissolve 8.0 g of reagent grade ammonium nitrate in 500 ml distilled water. Add 7 ml of reagent grade, concentrated ammonium hydroxide and dilute to 1000 ml.

8.6 Boric acid, powder: Reagent grade.

8.7 Calcium chloride (2N): Dissolve 111 g of calcium chloride ($CaCl_2$) in 900 ml distilled water. Cool and dilute to 1000 ml.

8.8 Dichromate cleaning solution: Dissolve 50 g sodium dichromate in 25 ml of water. Cautiously add concentrated sulfuric acid (a few drops at a time) until further additions cause little reaction. Make up to 1000 ml with concentrated sulfuric acid.

8.9 Ferric chloride 0.3N (5.6 mg Fe/ml): Dissolve 27 g of reagent grade ferric chloride ($FeCl_36H_2O$) in 300 ml of 6N hydrochloric acid. Dilute to 1000 ml with distilled water.

8.10 Hydriodic acid, concentrated (50%): Reagent grade.

8.11 Hydrobromic acid, concentrated (49%): Reagent grade.

8.12 Hydrochloric acid, concentrated (12N): Reagent grade.

8.13 Hydrochloric acid, 9N: Add 750 ml concentrated hydrochloric acid to 200 ml distilled water. Cool, then adjust the final volume to l000 ml with distilled water.

8.14 Hydrochloric acid, 6N: Add 500 ml concentrated hydrochloric acid to 450 ml distilled water. Cool, then adjust the final volume to 1000 ml with distilled water.

8.15 Hydrochloric acid, 1.2N: Add 100 ml concentrated hydrochloric acid to 850 ml distilled water. Cool, then adjust the final volume to 1000 ml with distilled water.

8.16 Hydrofluoric acid, concentrated (48%): Reagent grade.

8.17 Hydrogen peroxide, concentrated (30%): Reagent grade.

8.18 Ion exchange (anion) resin, Bio-Rad AG 1-X2, chloride form, 50-100 mesh.

8.19 Nitric acid, concentrated (16N): Reagent grade.

8.20 Nitric acid, 7.2N: Slowly add 455 ml concentrated nitric acid to 500 ml distilled water. Cool, then adjust the final volume to 1000 ml with distilled water.

8.21 Nitric acid, 4N: Slowly add 250 ml concentrated nitric acid to 800 ml distilled water. Cool, then adjust the final volume to 1000 ml with distilled water.

8.22 Potassium fluoride, anhydrous, granular: Reagent grade.

8.23 Silica sand, spherical grained, 60-200 mesh (must be free of radiochemical contaminants).

8.24 Sodium bisulfite, powder: Reagent grade.

8.25 Sodium hydroxide, pellets: Reagent grade.

8.26 Sodium hydroxide, 12.5N: Dissolve 100 g sodium hydroxide pellets in 150 ml distilled water. Cool, then adjust volume to 200 ml.

8.27 Sulfuric acid, concentrated (36N): Reagent grade.

8.28 Sulfuric acid, 3.6N: With caution, add 100 ml concentrated sulfuric acid to 850 ml distilled water. Cool, then adjust the volume to 1000 ml with distilled water.

8.29 Sulfuric acid, 0.36N: With caution, add 10 ml concentrated sulfuric acid to 900 ml distilled water. Adjust to 1000 ml with distilled water.

8.30 Thymol blue indicator, 0.02%: Dissolve 0.02 g thymol blue in 10 ml ethanol. Dilute to 100 ml with distilled water.

8.31 Tracer solutions: Purified and calibrated solutions of plutonium-236 (~5 pCi/ml), uranium-232 (~5 pCi/ml), and thorium-234 (~100 pCi/ml) dissolved in 4N nitric acid.

9. Apparatus

9.1 Alpha spectrometric analyzer: A counting system consisting of a multichannel analyzer, biasing electronics, a printer, a vacuum pump and silicon surface barrier detectors operated in vacuum chambers.

9.2 Blast burner: Adjustable. High temperature.

9.3 Caps: Black resin, poly-seal liner, 22 mm, GCMI 400-thread design.

9.4 Centrifuge: 50-m1, 250-m1, and 500-m1 capacity.

9.5 Centrifuge bottles: 50 ml plastic disposable, 250 ml Pyrex, 500 ml Pyrex.

9.6 Chromatographic column: A 250-mm by 14.5-mm i.d. tube with a 250-ml reservoir, and a stopcock with a Teflon plug, a course fritted glass disc is fused in the tube just above the stopcock to support the resin.

9.7 Electrolysis apparatus: 10-volt, 5-amp capacity.

9.8 Muffle furnace: Capable of reaching 750°C.

9.9 Neoprene sheet: 0.079-cm (1/32-inch) thickness.

9.10 Platinum or platinum-iridium anode: 1.27-cm (1/2-inch) diameter, 0.08-cm (1/32-inch) platinum or platinum-iridium disk having six 0.32-cm (1/8-inch) perforations and attached at the center to a 10-cm (4-inch) length of 0.16-cm (1/16-inch) platinum or platinum-iridium rod.

9.11 Rivets: #BS-4830 Dot Speedy rivets, solid brass, Carr Fastener Company, Cambridge, Massachusetts.

9.12 Stainless steel disks: 1.91-cm (3/4-inch) diameter, 0.38-mm (15-mil) thick, type 304 stainless steel planchets pre-polished to a mirror finish.

9.13 Teflon beakers and covers: Griffin, Chemware, 100 ml, 250 ml, and 500 ml.

9.14 Vials: Polyethylene, 25-ml screw cap, Packard #6001075.

10. Procedure

10.1 Sample Preparation

ANIMAL TISSUE ASH AND VEGETATION ASH

10.1.1 Transfer 10 g of previously ground and homogenized ash into a 250-ml graduated borosilicate beaker. Add 1 ml each of the appropriate tracers, (plutonium-236, uranium-232, or thorium-234) and 40 ml concentrated nitric acid. Cover and boil until it evaporates to dryness.

10.1.2 Wet the residue with concentrated nitric acid with intervening evaporations until a light-colored residue is obtained, then allow the nitric acid to evaporate. (If the residue is a porous black char following step 10.1.1, it will speed matters to ignite the sample in a muffle overnight at 600-700°C before proceeding with the nitric acid digestion in 10.1.2.)

10.1.3 Transfer the residue to a 100-ml Teflon beaker using concentrated nitric acid. Evaporate twice with intervening additions of 10 ml of concentrated nitric acid and 15 ml of 48% hydrofluoric acid.

10.1.4 Evaporate the contents of the Teflon beaker to dryness. Add 10 ml 6N hydrochloric acid, evaporate to dryness, then dissolve the residue in 50 ml 6N hydrochloric acid. Transfer the solution to a 1000-ml Pyrex beaker rinsing with 6N hydrochloric acid.

10.1.5 Dilute the solution to 600 ml with 6N hydrochloric acid. Add 20 ml 2N calcium chloride and heat to the boiling point. While stirring, add concentrated ammonium hydroxide until precipitation begins and then add 40 ml in excess. Set the beaker aside to cool.

10.1.6 Remove the supernatant liquid by aspiration, and transfer the remaining slurry to a 500-ml centrifuge bottle. Centrifuge and discard the supernatant liquid. Dissolve the precipitate with a volume of 12N hydrochloric acid equal to that of the precipitate.

10.1.7 Transfer the solution to a 150-ml graduated borosilicate beaker and dilute to 60 ml with 6N hydrochloric acid. Continue to step 10.3.2 of the separation procedure.

BONE ASH

10.1.8 Weigh 1 g ash into a tared 100-ml Teflon beaker. Add 60 ml 6N hydrochloric acid, a few drops 30% hydrogen peroxide, and I ml each of the appropriate tracer solutions. Cover and digest overnight on a hot plate.

10.1.9 Transfer the solution to a 50-ml centrifuge tube using 6N hydrochloric acid and centrifuge. Pour the supernatant liquid into a 150-ml graduated borosilicate beaker and set aside. Return the residue to the Teflon beaker using 10 ml 48% hydrofluoric acid and 5 ml concentrated nitric acid. Evaporate this solution to dryness.

10.1.10 Wet the residue with 30% hydrogen peroxide and evaporate to dryness. Add 10 ml 6N hydrochloric acid and evaporate to dryness. Add 5 ml 6N hydrochloric acid and one drop 30% hydrogen peroxide. Heat to dissolve the residue and add the solution to the supernatant liquid in the glass beaker.

10.1.11 Adjust the combined liquid volume to 60 ml by evaporation or by addition of 6N hydrochloric acid. Proceed to step 10.3.2 of the separation procedure.

GLASS-FIBER FILTERS

10.1.12 Place filter or filters in a 400-ml Teflon beaker, 250-ml platinum dish. Add appropriate tracers (1 ml each), then wet the sample with concentrated nitric acid. Add 10 ml 48% hydrofluoric acid and evaporate on a hot plate to dryness.

10.1.13 Repeat acid additions and evaporations until the silica has been volatilized.

10.1.14 Add 30 ml concentrated nitric acid and again evaporate to dryness. Repeat.

10.1.15 Add 30 ml concentrated nitric acid, 5 g boric acid and 1 ml 0.3N ferric chloride. Evaporate to approximately 10 ml.

10.1.16 Dilute to 100 ml with distilled water and heat to dissolve salts.

10.1.17 Add 12.5N sodium hydroxide until precipitation ceases (pH 9), then add 15 g sodium hydroxide pellets. Cover and boil for 1 to 2 hours on a hot plate.

10.1.18 Continue at step 10.1.24 of the soil preparation.

SOIL

10.1.19 Weigh 10 g of soil, which has been previously ground to 100 mesh, into a porcelain crucible. Heat overnight at 700°C. Cool and transfer to a 200-ml Teflon beaker. Add 1 ml each of the tracers plus 1 ml O.3N ferric chloride. Cautiously add 60 ml 16N nitric acid and 30 ml 48% hydrofluoric acid, allowing time between additions for foaming to subside. Cover with a Teflon lid and digest on a 400°C hot plate for 1 to 2 hours. Never let volume go below 20 ml.

10.1.20 Remove from the hot plate and cool slightly before adding 30 ml each of 16N nitric acid and 48% hydrofluoric acid. Digest without the lid with intermittent stirring for 1 hour.

10.1.21 Cool, then carefully add 20 ml concentrated hydrochloric acid with stirring Digest on the hot plate for 45 minutes.

10.1.22 With stirring, add 5 g of boric acid powder. After 15 minutes digestion, add 0.2 g of sodium bisulfite crystals and continue heating until the volume is reduced to approximately 20 ml.

10.1.23 Dilute to 50 ml with distilled water. Add 50% sodium hydroxide solution until precipitation ceases (pH 9), then add 15 g of sodium hydroxide pellets. Cover and boil for 1 to 2 hours on a hot plate.

10.1.24 Transfer the solution and precipitate to a 500-m1 Pyrex centrifuge bottle using distilled water. Centrifuge for at least 15 minutes at 1500 rpm. Decant and discard the supernate. Add approximately 10 ml concentrated nitric acid to the original Teflon beaker, cover, and reflux on the hot plate to dissolve any remaining residue.

10.1.25 Add approximately 1 g boric acid to the centrifuge bottle and stir the mixture with a stream of distilled water from a wash bottle. Add the nitric acid from the Teflon beaker, rinsing with distilled water. Rinse the beaker with an additional 10 ml concentrated nitric acid and add to the bottle. Warm on a hot plate for a few minutes to complete the dissolution.

10.1.26 Add 200 ml of distilled water and adjust the pH to 9 with 14N ammonium hydroxide. Adjust the volume to 450 ml and centrifuge at 1500 rpm for 15 minutes. Decant and discard supernate.

10.1.27 Dissolve the precipitate with a minimum of concentrated hydrochloric acid. Warm on a hot plate to speed dissolution. Transfer back to the Teflon beaker with approximately 30 ml of distilled water. Add 50% sodium hydroxide until precipitation ceases, then add 15 g sodium hydroxide pellets. Cover and boil for 1 hour.

10.1.28 Transfer the solution and precipitate back to the centrifuge bottle with distilled water. Adjust the volume to 450 ml and centrifuge for 15 minutes at 1500 rpm. Decant and discard

supernate. Add 10 ml concentrated hydrochloric acid to the Teflon beaker, cover, and reflux on the hot plate for a few minutes.

10.1.29 Transfer the hydrochloric acid from the Teflon beaker to the centrifuge bottle, rinsing with distilled water. Rinse the beaker with an additional 10 ml concentrated hydrochloric acid and add to the bottle. Warm on a hot plate to aid dissolution.

10.1.30 Add 200 ml of distilled water, then adjust the pH to 9 with concentrated ammonium hydroxide. Increase the volume to 450 ml with distilled water then centrifuge at 1500 rpm for 15 minutes. Discard supernate.

10.1.31 Add a minimum volume of concentrated hydrochloric acid to the precipitate. Swirl to dissolve the precipitate, then transfer to a graduated 150-ml beaker rinsing with 6N hydrochloric acid. Adjust the solution volume to 40 ml with 6N hydrochloric acid and proceed with step (10.3.2) of the separation procedure.

URINE

10.1.32 Measure the sample volume with a graduated cylinder and transfer it into a beaker with a capacity approximately 50% larger than the sample. Rinse the sample container with concentrated hydrochloric acid, using 40 ml of acid per liter of sample. Add this rinse to the sample. Rinse the container again with 60 ml of concentrated nitric acid. Set aside this rinse for later use.

10.1.33 Add the appropriate tracers, 10 ml 2N calcium chloride, and a volume of 30% hydrogen peroxide equal to the volume of concentrated hydrochloric acid used in the previous step. Place a Teflon stirring rod in the beaker and heat to the boiling point. When foaming subsides, cover the beaker and allow the solution to simmer for I hour.

10.1.34 Add the concentrated nitric acid rinse to the beaker and continue to simmer for another hour.

10.1.35 While stirring the hot solution, add concentrated ammonium hydroxide slowly until precipitation begins. and then add an excess equal to 60 ml of ammonium hydroxide per liter of original sample. Cover the beaker and set aside to cool.

10.1.36 Remove the supernatant liquid by aspiration and discard. Transfer the remaining slurry into a 50-ml plastic centrifuge tube using 0.7N ammonium hydroxide. Centrifuge and discard the supernate.

10.1.37 Rinse the sample beaker with approximately 10 ml of concentrated nitric acid and transfer to the residue in the centrifuge tube. Shake to dissolve the precipitate, then transfer the solution to a 250-ml beaker using about 5 ml of concentrated nitric acid as a rinse. Cover the beaker with a watch glass and boil on a hot plate until the residue is dry.

10.1.38 Wet the residue alternately with 30% hydrogen peroxide and concentrated nitric acid with intervening evaporations until a white ash is obtained and then allow all of the nitric acid to evaporate.

10.1.39 Add 50 ml 6N hydrochloric acid and boil until the volume is reduced to 25 ml. Add 6N hydrochloric acid to increase the volume to 50 ml. Proceed at step (10.3.2) of the separation procedure.

WATER

10.1.40 Add appropriate tracers, 5 ml 0.3N ferric chloride, and 20 ml of 30% hydrogen peroxide to 1 liter of sample, previously preserved by the addition of 20 ml concentrated nitric acid per gallon of water. Simmer until the hydrogen peroxide has decomposed.

10.1.41 While stirring, add concentrated ammonium hydroxide to the hot solution until precipitation begins and then add 15 ml in excess. Continue heating until the precipitate has coagulated, then allow to cool.

10.1.42 Remove the supernatant liquid by aspiration and transfer the precipitate to a centrifuge tube using 0.7N ammonium hydroxide. Add approximately 10 ml of concentrated nitric acid to the beaker, cover, and reflux on the hot plate to dissolve any remaining residue. Cool and set aside.

10.1.43 Dissolve the precipitate in the centrifuge tube by adding a volume of concentrated hydrochloric acid equal to the volume of the precipitate. Centrifuge and decant the supernate into a 150-ml Pyrex beaker.

10.1.44 Using a minimum of concentrated nitric acid, transfer any insoluble residue from the tube to a 100-ml Teflon beaker. Add the nitric acid solution from the original beaker in step (10.1.42) and evaporate to dryness on the hot plate.

10.1.45 Add 10 ml 48% hydrofluoric acid and 5 ml concentrated nitric acid. Evaporate to dryness. If any organic material remains, wet the residue with 30% hydrogen peroxide and evaporate to dryness.

10.1.46 Add 10 ml 6N hydrochloric acid and evaporate to dryness. Add 5 ml 6N hydrochloric acid and one drop 30% hydrogen peroxide. Heat to dissolve the residue and add the solution to the supernatant liquid from step (10.1.43). Evaporate the combined solutions to 60 ml and continue with step (10.3.2).

10.2 Ion Exchange Column Preparation

10.2.1 Remove fines from the resin by repeated suspension in distilled water and decantation. Add concentrated hydrochloric acid equal to 10% of the volume of slurry to shrink the resin. Transfer the resin to the column in slurry form to give a settled resin bed of 20 ml volume. Add dry 60 to 200 mesh silica sand to a depth of 15 mm through a layer of 1.2N hydrochloric acid. The sand prevents resuspension of the resin and, by its capillarity, stops the flow between additions of reagents enabling unattended operation.

10.3 Ion Exchange Separations

10.3.1 Immediately prior to use, condition the ion exchange column with 100 ml of 9N hydrochloric acid containing a drop of 30% hydrogen peroxide at a flow rate of 6.ml/min.

10.3.2 Add a volume of 12N hydrochloric acid to the sample that is equal to the volume of the 6N solution to adjust the acid concentration to 9N. Add one drop 30% hydrogen peroxide for each 10 ml of 9N solution, cover with a watch glass, and heat the solution to 80-90°C for 1-hour. Cool to room temperature.

10.3.3 Transfer the sample to the column reservoir using 9N hydrochloric acid as a rinse. If barium chloride, sodium chloride, or other solid matter is present, filter the solution into the reservoir through a plug of glass wool in the stem of a funnel.

10.3.4 Pass the 9N sample solution through the column at a flow rate of 3 ml/min. Flush the reservoir three times with 15-ml volumes of 9N hydrochloric acid and drain each rinse at 3 ml/min. Combine and save the 9N eluates for thorium analysis.

10.3.5 Wash the column with an additional 50 ml 9N hydrochloric acid containing one drop of 30% hydrogen peroxide. Elute at 3 ml/min and discard eluate. If plutonium analysis is not required, proceed to step 10.3.8.

PLUTONIUM

10.3.6 Elute plutonium from the column using 25 ml 49% hydrobromic acid at 3 ml/min. Collect the eluate in a 100-ml Pyrex beaker. Wash the column with an additional 50 ml 49% hydrobromic acid and combine with the 25 ml eluate.

10.3.7 Add 0.5 ml of concentrated sulfuric acid to the sample solution and evaporate at low heat to fumes of sulfuric acid. Add two drops of 30% hydrogen peroxide and again evaporate to sulfuric acid fumes. Save this fraction for electrodeposition of plutonium, step (10.4.12).

URANIUM

10.3.8 Remove iron from the column with a fresh solution prepared by mixing log ml of 12N hydrochloric acid with 31 ml of distilled water and 5 ml of 50% hydriodic acid. Rinse the column reservoir three times with 15-ml portions of this solution and elute at 3 ml/min. Add an additional 100 ml of the solution and elute at the same rate. Discard the eluates.

10.3.9 Rinse the column with two 15-ml portions of 9N hydrochloric acid followed by 5 ml 1.2N hydrochloric acid to remove residual hydriodic acid. Discard the eluates.

10.3.10 Elute uranium with 50 ml 1.2N hydrochloric acid at 3 ml/min. Collect the eluate in a 100-ml glass beaker. Add 0.5 ml concentrated sulfuric acid to the beaker and evaporate to fumes of sulfuric acid. Add 5 drops 30% hydrogen peroxide and again evaporate to sulfuric acid fumes. Save for electrodeposition of uranium, step (10.4.12).

THORIUM

10.3.11 To prepare the column for thorium, add 100 ml 1.2N hydrochloric acid to the column reservoir and elute at 3 ml/min. Discard the eluate. Add 150 ml 7.2N nitric acid and elute at 3 ml/min. Discard the eluate.

10.3.12 Evaporate the combined 9N thorium eluates (from step 10.3.4) to dryness on a hot plate. Dissolve the residue with 20 ml 7.2N nitric acid, plus 5 drops of 30% hydrogen peroxide. Cover and reflux for 45 minutes on the hot plate. Add 3 more drops 30% hydrogen peroxide and continue to heat for 15 minutes. Cool to room temperature.

10.3.13 Transfer the solution to the column reservoir, rinsing the beaker with a minimum of 7.2N nitric acid. Elute at 3 ml/min and discard the eluate. Rinse the reservoir with three 10-ml portions 7.2N nitric acid and drain at the same rate. Wash the column with 100 ml 7.2N nitric acid and discard eluate.

10.3.14 Rinse the reservoir with 5 ml 9N hydrochloric acid and drain at 3 ml/min. Discard the eluate. Elute the thorium with 100 ml 9N hydrochloric acid at 3 ml/min and collect the eluate in a 150-ml glass beaker. Add 0.5 ml concentrated sulfuric acid to the beaker and evaporate to sulfuric acid fumes. Add 5 drops 30% hydrogen peroxide and again evaporate to sulfuric acid fumes. Continue with the electrodeposition of thorium at step (10.4-12).

10.4 Electrodeposition

CONSTRUCTION OF ELECTRODEPOSITION CELLS

10.4.1 Cut a 1.43-cm (9/16-inch) hole in the bottom of the polyethylene vial with a sharp cork borer. Improve the seal by abrading the threaded end with wet #320 waterproof emery paper held against a flat surface. Finish with wet #600 emery paper.

10.4.2 Remove the polyethylene liner from a 22-mm Poly-Seal cap. With a cork borer or leather punch, cut out the polyethylene tube from the liner. The conical part of the liner is used as a cover for the cell to minimize escape of spray.

10.4.3 Drill a 0.355-cm (0.140-inch, #28 drill) hole through the center of the cap. Bevel the edge of the hole on the inside of the cap with reamer.

10.4.4 Cut a 1.91-cm (3/4-inch) disc from 0.079-cm neoprene sheeting with a cork borer or a die. Cut a 0.317-cm (1/8-inch) hole in the center of the disc with a cork borer or leather punch.

10.4.5 Place the washer in the cap and pass the shank of the rivet through the washer and the hole in the cap.

CLEANING

10.4.6 Remove any surface film of oil from the polyethylene body of the cell with acetone followed by water.

10.4.7 Completely immerse-the body of the cell in dichromate-sulfuric acid cleaning solution for 2 to 3 hours. Rinse off the cleaning solution with water and immerse the cell in 4N nitric acid for at least 1 hour. Rinse and immerse in distilled water until ready to use.

10.4.8 The cleaning process renders the polyethylene hydrophilic, provided the cell is kept continuously wet after having been cleaned. The polyethylene parts of used cells can be rinsed and then cleaned by the directions given in 10.4.7 except that the immersion in dichromate sulfuric acid cleaning solution is limited to 1 hour. Clean the caps and neoprene washers by immersing for a few minutes in 4N nitric acid and then rinse with water.

ASSEMBLY

10.4.9 Connect one hole of a 2-hole #6 rubber stopper to an aspirator pump with a length of rubber tubing.

10. 4.10 Rinse the polyethylene cell with distilled water but do not dry. Hold the planchet centered against the threaded end of the cell and place the rubber stopper against the other end of the cell. Apply suction by placing a finger over the open hole of the stopper. The vacuum will hold the planchet in a centered position while the cap assembly is screwed on. Fill the cell halfway with water and alternately apply and release the vacuum. The flexing will cause the planchet to seat more firmly against the cell. Check to see that no stream of air bubbles rises through the water when vacuum is applied. If the vacuum is great enough, the water may boil, but the boiling is easily distinguished from air leakage.

10.4.11 Fill the assembled cell to the top with water to preserve the hydrophilic character of the cell until ready to add sample.

ELECTRODEPOSITION

10.4.12 Add 3 ml of water to the cool sulfuric acid sample solution. Replace the watch glass and warm the solution for a minute or two on a hot plate and then allow to cool.

10.4.13 Add 4 drops 0.02% thymol blue sodium salt. Neutralize the solution to the salmon-pink endpoint (pH 2) by blowing gaseous ammonia over the surface while swirling the solution. The gaseous ammonia is obtained from a polyethylene wash bottle having the inner portion of the delivery tube removed and containing concentrated ammonium hydroxide. If the endpoint is overstepped to a yellow color, add 3.6N sulfuric acid, a drop at a time, until the solution turns pink.

10.4.14 Pour the neutralized solution into the plating cell. Draw 6 ml 0.36N sulfuric acid into a pipette and use this in small increments to rinse the beaker three or more times. Add the rinses to the cell.

10.4.15 Neutralize the solution again to pH 2 with gaseous ammonia. The solution should have a straw color when viewed from the top and a slight pinkish cast when viewed through the sides of the cell. If the endpoint is overstepped, use 3.6N sulfuric acid, a drop at a time, to return the solution to the proper color.

10.4.16 Lower the platinum anode into the solution until the bottom edge of the anode is about 2 mm above the shoulder of the cell. If set too deep, gas bubbles will be trapped and cause fluctuation of the current. When the current is first turned on, it will be about 0.8 ampere. As the solution warms, the current will increase and must be readjusted to 1.2 amperes when it rises above this value. After 15 to 30 minutes, the current will stabilize and electrolysis can be allowed to continue at 1.2 ampere without attention for a total electrolysis time of 1.5 to 2 hours.

10.4.17 With current on, add 10 ml of 10% ammonium hydroxide and continue the electrolysis for 1 minute. Lift the anode out of the cell and then switch off the current. Pour the solution out of the cell and rapidly flood the cell three times with 0.1N ammonium nitrate 0.1N ammonium hydroxide solution. Disassemble the cell and quickly wash the planchet with a stream of alkaline ethyl alcohol. Touch a piece of filter paper to the edge of the planchet to adsorb the film of alcohol.

10.4.18 Place the disc in a cupped planchet and heat for 10 minutes on a hot plate. Cool and count the sample for 1000 minutes by alpha spectrometry.

11. Calibration

APPARATUS AND SUPPLIES

11.1 Windowless 27 gas flow proportional counter.

11.2 National Bureau of Standards (NBS) americium-241 point source, approximately 2 x 105 dpm deposited on platinum and certified to = 1% of its stated activity.

11.3 Stainless steel discs, 2-inch diameter; mirror finish.

CALIBRATION OF THE 2π COUNTER

11.4 Refer to manufacturer's procedure manual for calibration procedures.

11.5 Determine the counting efficiency of the 2π counter by counting the NBS americium-241 standard. Accumulate approximately 5 x 105 counts. Calculate the counting efficiency by dividing the counts per minute by the certified disintegration rate (dpm).

11.6 Correct the counting efficiency for the difference in backscatter between platinum and stainless by dividing the calculated efficiency above by 1.023.

STANDARDIZATION OF TRACERS

11.7. All tracers are checked for non-isotopic alpha-emitting contaminants by electrodeposition and alpha spectrometry. If non-isotopic contaminants are found or known to be present, the tracer must be purified before standardization (Sill, 1974).

11.8 Transfer a 100- to 250-μl aliquot of the isotopically pure stock tracer (~500 pCi/ml in a 2N nitric acid) to each of three 5-cm (2-inch) stainless steel planchets.

11.9 Allow the solutions to evaporate to complete dryness at room temperature.

11.10 Heat each planchet over a blast burner just to the first dull red glow. Then quickly lower the temperature by placing the planchet on a cold steel surface to minimize oxidation of the plate.

11.11 Count each planchet in the 2π counter, collecting at least 10^4 counts to ensure adequate statistical precision. Verify the 2π counter counting efficiency before and after counting.

11.12 Electrodeposit approximately 250 pCi of the isotopically pure tracer as described in sections 10.3.7 and 10.4.12.

11.13 Count the electroplated source on an alpha spectrometer for 100 minutes. Calculate the fraction of the total number of counts in the spectrum that is due to the tracing nuclide ^{236}Pu or ^{243}Am. This fraction is the correction factor to be applied to the counting rates of the evaporated sources in the 2π counter.

11.14 Calculate the activity concentration of the tracer (pCi/ml) by multiplying the observed 2π counting rates of the evaporated sources by the correction factor (Step 11.13) and dividing by the 2π counter efficiency (Step 11.6) and 2.22 dpm/pCi.

CALIBRATION OF THE ALPHA SPECTROMETER

11.15 Because a point-source standard electrodeposited on platinum (the NBS americium-241 source) cannot be used to calibrate an alpha spectrometer for use with diffuse sources electrodeposited on stainless steel, a secondary standard must be employed.

11.16 Standardize a secondary source (such as one prepared in Step 11.12 or any alpha activity electrodeposited as described in Sections 10.3.7 and 10.4.12 through 10.4.18) by counting with the 2π counter until at least 104 counts have been collected.

11.17 Count the secondary source with the alpha spectrometer until at least 10^4 counts have been collected. Calculate the spectrometer efficiency by multiplying the source's counting rate on the spectrometer (summed over the entire energy range) by the 2π counting efficiency and dividing by the sources counting rate on the 2π counter.

12. Quality Control

Approximately 10% of all samples are recycled as blind duplicates. The results are evaluated by standard statistical tests, and corrective action is taken, if necessary.

Data obtained from efficiency determinations are plotted on line graphs to indicate the condition of the detectors and various electronic components.

13. Calculations

CALCULATION OF SAMPLE ACTIVITY (R)

13.1

$$\text{(R) isotope activity (pCi/unit)} = \frac{(A - A_1) \times F \times D)}{(B - B_1) \times (\text{sample size})}$$

CALCULATION OF THE TWO-SIGMA ERROR (E)

13.2

$$(E) = 2R\sqrt{\left(\frac{\frac{A}{T_S}+\frac{A_1}{T_B}}{(A-A_1)^2}+\frac{\frac{B}{T_S}+\frac{B_1}{T_B}}{(B-B_1)^2}\right)}$$

where:

A	=	gross sample counts per minute which appear in the alpha energy region characteristic of the specific nuclide being analyzed
A_1	=	background counts per minute in the same alpha energy region (channels) as “A” above
B	=	gross tracer counts per minute from the sample disc
B_1	=	background counts per minute in the same alpha energy region (channels) as “B” above
F	=	tracer activity in picocuries added to the sample
D	=	fractional decay of the tracer between the time of its standardization and the time of the sample count
T_s	=	sample counting time in minutes
T_B	=	reagent blank (background) counting time in minutes

14. References

Burney, G. A. and R. M. Harbour. Radiochemistry of Neptunium. National Academy of Sciences - National Research Council. NAS-NS-3060 (1974).

Sill, C. W., K. W. Puphal, and F. D. Hindman. Simultaneous Determination of Alpha-Emitting Nuclides of Radium Through Californium in Soil. Analytical Chemistry 46:1725 (1974).

Sill, C. W. Purification of Radioactive Tracers for Use in High Sensitivity Alpha Spectrometry. Analytical Chemistry 46:1426 (1974).

Sill, C. W. Simultaneous Determination of ^{238}U, ^{234}U, ^{23O}Th, ^{226}Ra, and ^{21O}Pb in Uranium Ores, Dusts, and Mill Tailings. Health Physics, Vol. 33, No. 5, November 1977. pp 393-404.

Talvitie, N. A. Radiochemical Determination of Plutonium in Environmental and Biological Samples by Ion Exchange. Analytical Chemistry 43:1827 (1971).

Talvitie, N. A. Electrodeposition of Actinides for Alpha Spectrometric Determination. Analytical Chemistry 44:280 (1972).

U.S. Atomic Energy Commission. Measurement of Radionuclides in the Environment - Sampling and Analysis of Plutonium in Soil. U.S. AEC Regulatory Guide 4.5 (1974).