

FROM THE LAB

Simultaneous Determination of the Actinides in Small Environmental Samples

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Simultaneous determination of all alpha activity has always been and continues to be a highly desirable option in radiochemical analysis. However, the usual practice of gross alpha counting samples of raw water evaporated to dryness in planchets, air dusts collected on filters, planchets full of soils, etc., and then reporting the results quantitatively is neither accurate nor reliable, since it is virtually impossible to determine the correct counting efficiency with which the count was actually made. Attempts to calibrate empirically for a given set of conditions are also of marginal value because of wide variability in the deposition patterns. Direct gross alpha counting of samples without chemical preparation is useful when the activity present is substantially higher than that from the natural activity in its surroundings, or when a rapid order-of-magnitude indication of alpha activity is desired. All too often the results of these "screening methods" are reported with precision and accuracy that they can not possibly have. Even if excess alpha activity is indicated, a gross alpha count cannot distinguish between a man-made transuranium (TRU) radionuclide and a naturally-occurring one. The current procedure provides a true "total alpha" while eliminating the problems just discussed.

Introduction

The present spectrometric procedure is an adaptation of previous developments¹⁻³ to permit all alpha-emitting radionuclides except radium and polonium to be determined either simultaneously or sequentially. The options available in this procedure allow the chemist to customize a specific analysis scheme to a given sample based on the customer's needs. The different actinides can be separated from each other into different fractions to facilitate highly accurate measurements using tracers; or the actinides can be precipitated into one fraction providing a true "gross alpha" fraction without sacrificing complete sample dissolution, using incorrect counting efficiencies, or being time and labor intensive.

Total spectrometric alpha

This option allows the actinide activity from a given

sample to be included in a single fraction with time and effort being minimized. The alpha emitters can be identified both qualitatively and quantitatively in an alpha spectrometer. Several modifications are given to adapt to different types of samples. If little or no alpha activity is present in this gross fraction, absence of all alpha emitters will have been proven in a single analysis with known counting efficiencies and without additional separations. If activity is present and the individual peaks cannot be resolved adequately because of spectral interferences, the mounted fraction can be wet ashed and additional separations needed can be made to identify the components without redissolving another sample aliquot.

Sample types

This procedure can be used to determine the actinides in a variety of samples including soil,

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water, filter papers, sludges, ores and various types of organic samples. It is also well suited for analyses of hazardous wastes. Samples that contain high concentrations of calcium cause severe chemical interferences. No radiochemical interferences are known.

Principle

Soil and samples that contain siliceous material are dissolved completely in potassium fluoride fusions. Water samples are evaporated almost to dryness and the residues are dissolved in pyrosulfate fusions. Samples that contain organic material are treated as small soil samples after the organic material has been wet ashed. The actinides are separated from the bulk of the sample with barium sulfate. The barium sulfate is dissolved in alkaline EDTA and the actinides are precipitated as hydroxides. The actinides are then either precipitated together in one fraction which is counted to obtain a total spectrometric alpha, or the actinides are separated from each other by coprecipitation with neodymium fluoride after adjusting their oxidation states. As mentioned above, after the gross fraction is counted to determine which if any of the separations are needed, this fraction can be wet ashed, and the appropriate separations made. This saves valuable time not requiring every sample to undergo every separation. Each fraction is mounted on a 0.1- μm membrane filter and counted in an alpha spectrometer.

This method gives yields of better than 90% and is considerably less time consuming and labor intensive than methods employing solvent extraction and ion exchange. The detection limits for the actinides based on 1-g and 50-mL samples, and 1000 minute counting times are 0.03 pCi/g and 0.5 pCi/L respectively.

Apparatus

1. 60-mL platinum dishes.
2. 125-mL Erlenmeyer flasks.
3. 50-mL polymethylpentene centrifuge tubes.
4. Centrifuge.
5. 25-mm Metricell filter paper. (0.1- μm pores).
6. Gelman 25-mm filter funnel.
7. SGA filtering jar.
8. Alpha spectrometer.

Reagents

All reagents must be filtered through a 0.45- μm filter to eliminate insoluble material that will degrade the subsequent alpha spectra. All reagents should be stored in appropriately sized polypropylene (PP) bottles.

Neodymium Perchlorate 0.5 and 5 mg/mL Nd

Dissolve 0.583 g of 99.9% Nd_2O_3 in 2 mL of 72% perchloric acid with heating. Cool the solution and dilute to 100 mL with water. Dilute 10 mL of this 5 mg/mL Nd solution to 100 mL with water containing 1 mL of perchloric acid.

Ferrous Perchlorate 20%

Dissolve 1 g of ferrous perchlorate hexahydrate in 4.5 mL of water containing 2 drops of perchloric acid.

Sodium Permanganate 0.5%

Dissolve 50 mg of sodium permanganate in 10 mL of water containing 2 drops of 72% perchloric acid.

Barium Chloride 0.45%

Dissolve 2.224 g of barium chloride dihydrate in 500 mL of water.

Sodium Hydroxide 0.25 M

Dissolve 5 g of sodium hydroxide in 500 mL of water in a 500-mL wash bottle.

Ferrous Ammonium Sulfate 20%

Dissolve 10 g of ferrous ammonium sulfate in 46 mL of water and 10 drops of sulfuric acid.

0.1 M EDTA

Dissolve 14.6 g of EDTA acid in 485 mL of water containing 12.5 g of potassium hydroxide. Adjust the pH of the solution to 11.1.

Tellurous Acid 5mg/mL Te

Dissolve 625 mg of tellurium dioxide in 100 mL of 25% hydrochloric acid.

Seeding Suspension

Add 223 mg of barium chloride dihydrate, 6 g of anhydrous sodium sulfate and 4 mL of sulfuric acid to a 250-mL Erlenmeyer flask. Heat the flask over a blast burner until the excess sulfuric acid has been driven off and a pyrosulfate fusion has been obtained. Cool the melt to room temperature and add 100 mL of water. Heat the flask on a bare hotplate until the pyrosulfate cake has dissolved. Transfer the barium sulfate suspension to a 125-mL PP bottle. Immediately before each use shake the bottle to suspend the barium sulfate.

EDTA Cleaning Bath

Add 20 g of EDTA to a 1-L beaker containing about 600 mL of water and 2 mL of 0.04% thymol blue. Heat the suspension and add 50% sodium hydroxide with swirling until the EDTA has dissolved and the full blue color of the indicator remains. Dilute the solution to 1 L with water.

Fluoride Cleaning Bath

Add 20 g of boric acid to a 1-L beaker containing 750 mL of water and 250 mL of concentrated nitric acid.

Reprecipitating Solution

Dissolve 135 g of anhydrous potassium sulfate in 900 mL of water and 50 mL of concentrated hydrochloric acid.

Procedure: Water samples

- 1.1 Transfer up to 50 mL of water to a 125-mL Erlenmeyer flask.
- 1.2 Add 3 drops of 0.04% thymol blue (TB) and two 14 mesh carborundum boiling chips.
- 1.3 If the solution is blue or yellow, add concentrated nitric acid to the red endpoint of the TB, then add an additional 5 mL of nitric acid.
- 1.4 If the solution is red, add 5 mL of concentrated nitric acid.
- 1.5 Add an accurately known amount of ^{243}Am , ^{236}Pu (or ^{242}Pu) and ^{232}U tracers at individual activities of about 10 dpm.
→ **1.5 Note:** If a Total Spectrometric Alpha determination is to be performed, omit adding the isotopic tracers.
- 1.6 Evaporate the solution to near dryness.
- 1.7 Add 4.5 g of anhydrous potassium sulfate, 2.0 g of anhydrous sodium sulfate and 3 mL of concentrated sulfuric acid.
- 1.8 Swirl to mix and heat slowly over a blast burner until the salts dissolve.
- 1.9 Increase the temperature of the blast burner and continue to heat until the evolution of sulfuric acid fumes have slowed, the residue has dissolved and a clear pyrosulfate fusion is obtained.
- 1.10 Cool the pyrosulfate cake to room temperature and add 5 mL of concentrated hydrochloric acid and 35 mL of water.
- 1.11 Place the Erlenmeyer on a high-temperature hot plate and heat the solution to boiling. Swirl the solution occasionally to aid in the dissolution of the cake.
- 1.12 Add 10 drops of 20% ferrous ammonium sulfate and boil the solution for 10 min to ensure complete reduction of the plutonium.
→ **1.12 Note:** If uranium is to be determined, replace the 10 drops of 20% ferrous ammonium sulfate with 5 drops of 20% titanium trichloride. Continue to add titanium trichloride until the yellow iron color has been discharged and the solution exhibits a violet color. However do not use more than 15 drops of the titanium reagent or an insoluble potassium

titanium titanate will precipitate. On water samples that contain more iron than can be reduced directly by the limited amount of titanium, add 1 mL of 25% hydrazine in Step 1.10 to reduce most of the iron before the titanium reductant is used.

- 1.13 Continue under “Barium sulfate precipitation” (Step 4.1).

Procedure: Soil samples

- 2.1 Add 0.5 mL of nitric acid to 1 g of soil in a 50-mL platinum dish.
→ **2.1 Note:** Prewetting the soil with water may be necessary if the evolution of CO_2 is vigorous enough to cause some loss of the sample due to spraying.
- 2.2 Heat the dish on a hot plate until the soil is almost dry.
- 2.3 Cool and add an accurately known amount of ^{243}Am , ^{236}Pu (or ^{242}Pu) and ^{232}U tracers at individual activities of about 10 dpm.
- 2.4 Heat the platinum dish on the hot plate until the soil is almost dry, taking care not to lose any tracer by splattering.
- 2.5 Cool, and add 2 g of anhydrous potassium fluoride and 1.3 g of potassium hydrogen fluoride.
- 2.6 Mix the potassium fluoride and soil thoroughly with a Teflon stirring rod.
- 2.7 Place the dish on a ring stand and fuse over the full heat of a Fisher blast burner until a clear melt is obtained.
- 2.8 Cool the melt to room temperature and add 4 mL of sulfuric acid.
- 2.9 Heat the dish on the hot plate until the potassium fluoride cake has dissolved and the transposition has been completed.
→ **2.9 Note:** When the dissolution becomes vigorous enough for the solution to froth over the sides of the dish, cool the dish in a bath of cold running water until the reaction slows, then reheat. When most of the cake has dissolved, the vigorous reactions will subside enough so that the dish can be placed on the full heat of the bare hot plate.
- 2.10 After all of the potassium fluoride cake has transposed, add 2 g of anhydrous sodium sulfate, swirl to mix and heat over a small flame of the blast burner until the evolution of sulfuric acid fumes have slowed and a clear red pyrosulfate fusion is obtained.
- 2.11 Remove the dish from the heat and roll the melt high onto the sides of the dish while cooling.
- 2.12 Cool the dish to room temperature and gently

- flex the sides of the dish to fracture the cake and facilitate its removal.
- 2.13 Add the pyrosulfate cake to a boiling solution of 35 mL of water and 5 mL of concentrated hydrochloric acid in a 125-mL Erlenmeyer flask.
 - 2.14 Swirl the solution until the cake has dissolved.
 - 2.15 Add 1 mL of 20% ferrous ammonium sulfate.
 - 2.16 Boil the solution for 15 min to hydrolyze condensed phosphates and ensure reduction of the plutonium.
- *Note:* Uranium cannot be included in the first barium sulfate precipitation when the pyrosulfate fusion has been carried out in a platinum dish. The dissolved platinum will be reduced to the metal during the titanium reduction and carry through the procedure. The uranium fraction must be treated separately as described under "Determination of uranium from soil samples". However, if the soil or wet ashed organic sample is to be used for screening purposes, or if isotopic tracers have been omitted, uranium can be included in the first barium sulfate by using the Total Spectrometric Alpha portion (section G.X) of this procedure. Additional separations can be made on that "total" fraction as needed.
- 2.17 Continue under "Barium sulfate precipitation." (Step 4.1)

Procedure: Organic material

- 3.1 Add 1 g of organic material, 5 mL of sulfuric acid, and 5 mL of nitric acid to a 125-mL Erlenmeyer flask.
- 3.2 Heat the Erlenmeyer on a hot plate until the nitric acid has oxidized the easily oxidizable organic material.
- 3.3 Continue to heat until the excess nitric acid has been driven off and the sulfuric acid has charred the organic material.
- 3.4 While swirling the flask, add 1 mL of nitric acid dropwise to oxidize the charred organic material.
- 3.5 After the reaction subsides, continue to add 1-mL portions of nitric acid until the solution has either lightened in color or until the nitric acid has no more effect on oxidizing the organic material.
- 3.6 Continue to char the sample with sulfuric acid and to oxidize the charred material with nitric acid until the sample no longer chars when fumed with sulfuric acid (Steps 3.3 - 3.5).
- 3.7 Add 1 mL of perchloric acid dropwise to the

hot concentrated sulfuric acid to oxidize the remaining organic material.

- *3.7 Note: CAUTION!!* If the perchloric acid is added while the solution still contains carbon or while the solution is very dark in color a *VERY* vigorous reaction or *EXPLOSION* can result!! Never add perchloric acid to a sample without first pretreating the sample extensively with nitric acid. Use perchloric acid only as a last resort to oxidize the most difficult to oxidize organic material, and only after extensive treatment of repeatedly charring with sulfuric acid and then oxidizing the charred material with nitric acid!
- 3.8 Evaporate the sulfuric acid to about 5 mL and transfer the solution quantitatively to a 50-mL platinum dish.
 - 3.9 Evaporate the solution to dryness and proceed with the soil procedure (Step 2.1).

Barium sulfate precipitation

- 4.1 If necessary, add enough water to bring the total volume in the flask to about 35 mL.
 - 4.2 Reheat the solution to boiling and add 1 mL of seeding suspension.
 - 4.3 While swirling the solution, add 1 mL of 0.45% barium chloride dropwise.
 - 4.4 Place the Erlenmeyer on the hot plate and boil the solution for one minute.
 - 4.5 Repeat the 1 mL dropwise addition of barium chloride and the one minute boiling time four more times (Steps 4.3 - 4.4).
- *4.3 - 4.5 Note:* If the barium chloride solution is added at a faster rate than that specified or without swirling the solution during the addition, there will be a loss of the actinides on the barium sulfate.
- 4.6 Transfer the solution and precipitate to a 50-mL conical polymethylpentene (PMP) centrifuge tube.
 - 4.7 Centrifuge for five min while the solution is still hot to prevent calcium sulfate from precipitating.
 - 4.8 *If titanium trichloride was used* as a reducing agent in step 1.12 to include uranium in the barium sulfate, discard the supernate.
 - 4.9 *If the pyrosulfate fusion was performed in a platinum dish and uranium is to be determined, (section 2.X)* decant the supernate back into the original Erlenmeyer.
 - 4.10 Wash the precipitate with about 10 mL of water, directed in a forceful stream from a wash bottle.
 - 4.11 Centrifuge, decant and discard the wash.
 - 4.12 Treat the solution in the Erlenmeyer without

delay as described under “Determination of uranium from soil samples” (Step 5.1).

- 4.13 Continue under “EDTA dissolution” with the barium sulfate precipitate (Step 6.1).

Determination of uranium from soil samples

- 5.1 Cool the filtrate in the Erlenmeyer to about 50°C and add 200 µL of tellurous acid.
- 5.2 Add 0.5 g of sodium metabisulfite to the solution slowly and with swirling.
- 5.3 Heat just to boiling and let stand for at least 5 min to reduce most of the iron.
- **5.3 Note:** The solution should turn black from the precipitation of elemental tellurium once most of the iron has been reduced. If the solution stays yellow more sodium metabisulfite must be added.
- 5.4 Boil the solution for at least 5 min to expel sulfur dioxide completely and to flocculate the tellurium.
- 5.5 Add 2 mL of tellurous acid, 2 drops of 1% Safranin-O indicator and heat the solution to boiling.
- 5.6 Add titanium trichloride dropwise until a dense black precipitate of elemental tellurium forms, the colorless leuco form of the indicator is obtained, and about 4 drops excess has been added.
- 5.7 Boil the solution until the tellurium has flocculated completely.
- 5.8 Transfer the solution to a 50-mL PMP centrifuge tube and centrifuge for 5 min.
- 5.9 Add about 50 mg of paper pulp directly onto the scum that will be riding on the surface of the supernate and recentrifuge for 5 min.
- 5.10 Decant the clear supernate into another 50-mL PMP centrifuge tube.
- 5.11 Discard the tellurium precipitate that contains the polonium.
- 5.12 Add one drop of Safranin-O to verify the reducing conditions of the solution.
- 5.13 If the indicator turns red, add additional drops of titanium trichloride until the leuco form is restored.
- 5.14 Reheat the solution to boiling and add 1 mL of seeding suspension.
- 5.15 While swirling the solution, add 1 mL of 0.45% barium chloride dropwise.
- 5.16 Place the Erlenmeyer on the hot plate and boil the solution for one minute.
- 5.17 Repeat the 1-mL dropwise addition of barium chloride and the 1 min boiling time four more times.
- 5.18 Transfer the solution and precipitate to a 50-mL conical polymethylpentene (PMP) centrifuge tube.

- 5.19 Centrifuge for 5 min, decant and discard the supernate.
- 5.20 Dislodge the impacted barium sulfate precipitate by flipping the centrifuge tube sharply in a downward motion.
- 5.21 Add 3 mL of water, 3 mL of 0.1 M potassium EDTA and heat in a water bath until the barium sulfate has dissolved completely.
- **5.21 Note:** It may be necessary to place the tube in an ultrasonic bath to disperse the precipitate to ensure complete dissolution.
- 5.22 With rapid swirling, add 1 drop of 20% titanium trichloride followed by 2 mL of 10 M potassium hydroxide.
- 5.23 Heat in a hot water bath for 5 min to flocculate the titanous hydroxide precipitate.
- 5.24 Centrifuge for 5 min, decant and discard the supernate.
- 5.25 Wash the precipitate with 5 mL of 0.25 M sodium hydroxide directed in a forceful stream from a wash bottle.
- 5.26 Centrifuge for 5 min, decant and discard the wash.
- 5.27 Flip the centrifuge tube sharply to dislodge the precipitate and add 15 drops of hydrochloric acid, 4 mL of water and 200 µL of 0.5 mg/mL Nd carrier.
- 5.28 Heat the centrifuge tube in a bath of boiling water until the precipitate dissolves completely.
- 5.29 Add 5 drops of 20% titanium trichloride and heat in a boiling water bath for 5 min.
- 5.30 Swirl the solution and add 1 mL of 48% hydrofluoric acid.
- 5.31 Immediately transfer the tube to a bath of cold water and let stand for 15 min to maximize the yield of uranium.
- 5.32 Mount and count as described in “Mounting fluoride precipitates” (Step 11.1).

EDTA dissolution

- 6.1 Dislodge the impacted barium sulfate precipitate by flipping the centrifuge tube sharply in a downward motion.
- 6.2 Add 3 mL of water, 3 mL of 0.1 M potassium EDTA and heat in a water bath until the barium sulfate has dissolved completely.
- **6.2 Note:** It may be necessary to place the tube in an ultrasonic bath to disperse the precipitate to ensure complete dissolution.
- 6.3 With rapid swirling, add 1 drop of 20% titanium trichloride followed by 2 mL of 10 M potassium hydroxide.
- 6.4 Heat in a hot water bath for 5 min to flocculate the titanous hydroxide precipitate.
- 6.5 Centrifuge for 5 min, decant and discard the supernate.

- 6.6 Wash the precipitate with 5 mL of 0.25 M sodium hydroxide directed in a forceful stream from a wash bottle.
- 6.7 Centrifuge for 5 min, decant and discard the wash.
- *Note:* This hydroxide precipitate contains all of the actinides and will also contain uranium (from a water sample) if uranium was included in the barium sulfate precipitate with titanium trichloride.
- 6.8 If a "Total spectrometric alpha" determination (except soils) is to be performed, continue with Step 10.1.
- 6.9 If further separations of the actinides from each other are to be performed, continue with Step 7.1.

Separation of uranium and plutonium from americium

- 7.1 Flip the centrifuge tube sharply to dislodge the precipitate and add 15 drops of perchloric acid, 4 mL of water and 200 μ L of 0.5 mg/mL Nd carrier. Add only 100 μ L of 0.5 mg/mL Nd if the sample was a 0.5 to 1 g soil sample.
- 7.2 Heat the centrifuge tube in a bath of boiling water until the precipitate dissolves completely.
- 7.3 Add 5 drops of 0.5% sodium permanganate and continue to heat for another 5 min.
- 7.4 Swirl the solution and add 1 mL of 48% hydrofluoric acid.
- 7.5 Immediately transfer the tube to a bath of cold water and let stand for 15 min to maximize the yield of americium.
- 7.6 Wash both sides of a 25-mm 0.2- μ m Gelman HT-200 membrane filter paper with 80% ethanol and place the filter right side up in a Gelman polysulfone filter holder equipped with a stainless steel support screen.
- 7.7 Tighten the funnel against the base as tight as possible without wrinkling the filter.
- 7.8 Place the filtering assembly in the top of a bell jar that is equipped with vacuum line from a water aspirator so that the solution can be filtered directly into either a 60-mL Teflon PFA jar or a 125-mL Erlenmeyer flask.
- 7.9 If uranium (from a water sample) is to be determined, filter the solution directly into the original 125-mL Erlenmeyer flask; otherwise, filter the solution and collect the filtrate in a 60-mL PFA jar.
- 7.10 Wash the precipitate with 2 mL of water containing 5 drops of HF. (Collect the wash in the same container as the major fraction.)
- 7.11 Remove the collection container.
- 7.12 Wash the precipitate with 5 mL of 80%

ethanol. Do not collect the ethanol washes in the collection container.

- 7.13 Remove the filter containing the americium from the filtering assembly and dry under a 250-watt infrared lamp at a distance of about 4 inches for 5 min.
- 7.14 Count the americium fraction in an alpha spectrometer for a long enough period of time to obtain desired statistics. If uranium and plutonium are to be determined, continue under "Determination of uranium and plutonium from water samples" Step 8.1. If only plutonium is to be determined, continue under "Determination of plutonium" Step 9.1.

Determination of uranium and plutonium from water samples

- 8.1 Add 4.5 g of anhydrous potassium sulfate, 2.0 g of anhydrous sodium sulfate and 3 mL of concentrated sulfuric acid to the Erlenmeyer flask that contains the filtrate from the americium separation.
- 8.2 Swirl to mix and heat slowly over a blast burner until the salts dissolve.
- 8.3 Increase the temperature of the blast burner and continue to heat until the evolution of sulfuric acid fumes have slowed, the residue has dissolved and a clear pyrosulfate fusion is obtained.
- 8.4 Cool the pyrosulfate cake to room temperature and add 5 mL of concentrated hydrochloric acid and 35 mL of water.
- 8.5 Place the Erlenmeyer on a high-temperature hot plate and heat the solution to boiling.
- 8.6 Add 5 drops of 20% titanium trichloride and boil the solution for 10 min to ensure complete reduction of the uranium and plutonium.
- 8.7 If necessary, add enough water to bring the total volume in the flask to about 35 mL.
- 8.8 Reheat the solution to boiling and add 1 mL of seeding suspension.
- 8.9 While swirling the solution, add 1 mL of 0.45% barium chloride dropwise.
- 8.10 Place the Erlenmeyer on the hot plate and boil the solution for one minute.
- 8.11 Repeat the 1-mL dropwise addition of barium chloride and the one minute boiling time four more times (Steps 8.9 - 8.10).
- *8.9 - 8.11 Note:* If the barium chloride solution is added at a faster rate than that specified or without swirling the solution during the addition, there will be a loss of the actinides on the barium sulfate.
- 8.12 Transfer the solution and precipitate to a

- 50-mL conical polymethylpentene (PMP) centrifuge tube.
- 8.13 Centrifuge for 5 min, decant and discard the supernate.
 - 8.14 Dislodge the impacted barium sulfate precipitate by flipping the centrifuge tube sharply in a downward motion.
 - 8.15 Add 3 mL of water, 3 mL of 0.1 M potassium EDTA and heat in a water bath until the barium sulfate has dissolved completely.
- **8.15 Note:** It may be necessary to place the tube in an ultrasonic bath to disperse the precipitate to ensure complete dissolution.
- 8.16 With rapid swirling, add 1 drop of 20% titanium trichloride followed by 2 mL of 10 M potassium hydroxide.
 - 8.17 Heat in a hot water bath for 5 min to flocculate the titanous hydroxide precipitate.
 - 8.18 Centrifuge for 5 min, decant and discard the supernate.
 - 8.19 Wash the precipitate with 5 mL of 0.25 sodium hydroxide directed in a forceful stream from a wash bottle.
 - 8.20 Centrifuge for 5 min, decant and discard the wash.
 - 8.21 Flip the centrifuge tube sharply to dislodge the precipitate and add 15 drops of hydrochloric acid, 4 mL of water and 200 μ L of 0.5 mg/mL Nd carrier.
 - 8.22 Heat the centrifuge tube in a bath of boiling water until the precipitate dissolves completely.
 - 8.23 Add 5 drops of 20% titanium trichloride and heat in a boiling water bath for 5 min.
 - 8.24 Swirl the solution and add 1 mL of hydrofluoric acid. Immediately transfer the tube to a bath of cold water and let stand for 15 min to maximize the yield of uranium and plutonium.
 - 8.25 Mount and count as described in “Mounting fluoride precipitates” (Step 11.1).

Determination of plutonium

- 9.1 To the 60-mL PFA jar that contains the filtrate and wash from the plutonium-amercurium separation, add 1 mL of perchloric acid and evaporate the solution to 0.5 mL.
- 9.2 Add 4 mL of water, transfer the solution to a 50-mL PMP centrifuge tube, add 3 drops of 20% ferrous perchlorate, and heat for 3 min in a boiling water bath to reduce the plutonium.
- 9.3 Add 200 μ L of 0.5 mg/mL neodymium carrier solution.
- 9.4 Swirl the centrifuge tube to mix thoroughly, and add 1 mL of HF.

- 9.5 Immediately transfer the tube to a cold water bath.
- 9.6 Let the tube stand for 15 min to ensure complete precipitation of the plutonium.
- 9.7 Mount and count as described in “Mounting fluoride precipitates” (Step 11.1).

Total spectrometric alpha (except soils)

- 10.1 Flip the centrifuge tube sharply to dislodge the precipitate and add 15 drops of hydrochloric acid, 4 mL of water and 200 μ L of 0.5 mg/mL Nd carrier.
- 10.2 Heat the centrifuge tube in a bath of boiling water until the precipitate dissolves completely.
- 10.3 Add 5 drops of 20% titanium trichloride and heat in a boiling water bath for 5 min.
- 10.4 Swirl the solution and add 1 mL of 48% hydrofluoric acid.
- 10.5 Immediately transfer the tube to a bath of cold water and let stand for 15 min to maximize the yield of uranium and plutonium.
- 10.6 Mount and count as described in “Mounting fluoride precipitates” (Step 11.1).
- 10.7 After counting, the precipitate can be wet ashed if necessary (Section 12.X) and appropriate separations made.

Mounting fluoride precipitates

- 11.1 Wash both sides of a 25-mm 0.2- μ m Gelman HT-200 membrane filter paper with 80% ethanol and place the filter right side up in a Gelman polysulfone filter holder equipped with a stainless steel support screen.
 - 11.2 Tighten the funnel against the base as tight as possible without wrinkling the filter.
 - 11.3 Filter the fluoride precipitated solution through the filter paper.
 - 11.4 Wash the precipitate with 2 mL of water containing 5 drops of HF, then with 5 mL of 80% ethanol.
 - 11.5 Remove the filter from the filtering assembly and dry under a 250-watt infrared lamp at a distance of about 4 inches for 5 min.
 - 11.6 Mount and count the filter paper in an alpha spectrometer for a long enough time to obtain desired statistics.
- **NOTE:** All equipment that has been used with or contained barium sulfate and fluoride precipitates should be cleaned in the EDTA and fluoride cleaning baths respectively. These baths should be hot and equipment cleaned in the EDTA bath should be immersed in a bath containing 5% HCl to dissolve any hydrolyzed compounds.

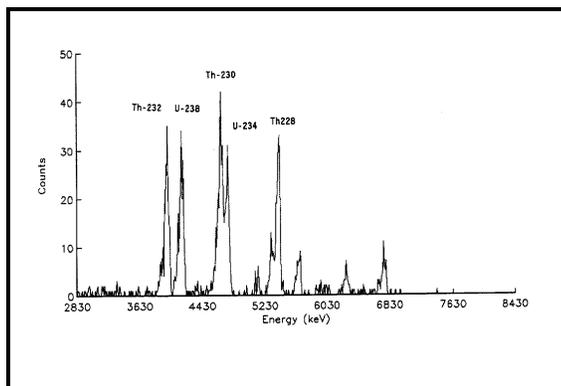


Figure 1 This spectrum was obtained by analyzing a 1-g soil sample with the total spectrometric alpha (TSA) procedure. Notice that there are no detectable transuranium nuclides present in this "blank" soil sample.

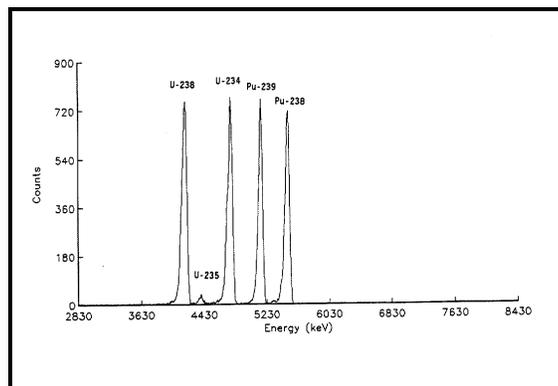


Figure 2 This spectrum is of a U-Pu fraction from a soil sample. The U and Pu were separated from Am and Th so that ^{238}Pu could be determined.

Wet ashing of mounted filter papers

- 12.1 Place the HT-200 filter paper to be wet ashed in a 60-mL PFA jar and add 0.5 mL of nitric acid and 5 mL of perchloric acid.
- 12.2 Place the jar on a clay triangle on a high temperature hotplate and evaporate to 0.5 mL of perchloric acid without swirling the solution.
- 12.3 Add 4 mL of water to the jar while still hot and transfer the solution to a 50-mL PMP centrifuge tube.
- 12.4 Continue with Step 7.3 for a uranium and plutonium separation from americium and thorium.

Total spectrometric alpha for soils

- G.1 Add 1 g of soil to a 50-mL platinum dish.
 - G.2 Add 2 g of anhydrous potassium fluoride and 1.3 g of potassium hydrogen fluoride.
 - G.3 Mix the potassium fluoride and soil thoroughly with a Teflon stirring rod.
 - G.4 Place the dish on a ring stand and fuse over the full heat of a Fisher blast burner until a clear melt is obtained.
 - G.5 Cool the melt to room temperature and add 5 mL of sulfuric acid.
 - G.6 Heat the dish on the hot plate until the potassium fluoride cake has dissolved and the transposition has been completed.
- **G.6 NOTE:** If the dissolution becomes vigorous enough for the solution to froth over the sides of the dish, cool the dish in a bath of cold running water until the

reaction slows, then reheat. When most of the cake has dissolved, the vigorous reactions will subside enough so that the dish can be placed on the full heat of the bare hot plate.

- G.7 After the cake has dissolved completely, add 0.5 g of boric acid with swirling to the dish.
 - G.8 Transfer the transposed cake directly to a 125-mL Erlenmeyer flask containing 2 g of sodium sulfate.
 - G.9 Wash the platinum dish with water, heat the dish over a gentle flame to suspend the cake, and transfer the slurry to the flask.
 - G.10 Swirl the flask and heat slowly over a blast burner until fumes of sulfuric acid are being evolved strongly.
 - G.11 Increase the temperature of the blast burner and continue to heat until the evolution of sulfuric acid fumes have slowed, the residue has dissolved and a clear pyrosulfate fusion is obtained.
 - G.12 Heat the entire flask strongly while swirling the flux high onto the sides of the flask. The molten fusion should coat the entire inside of the flask (to retrieve any unfused sample that was splattered). The flask should be hot enough to keep the molten flux from solidifying on the sides.
 - G.13 Remove the flask from the heat and set on an insulated surface to cool.
 - G.14 Do not swirl the cake onto the sides of the flask while cooling.
- **NOTE:** Platinum is eliminated from the

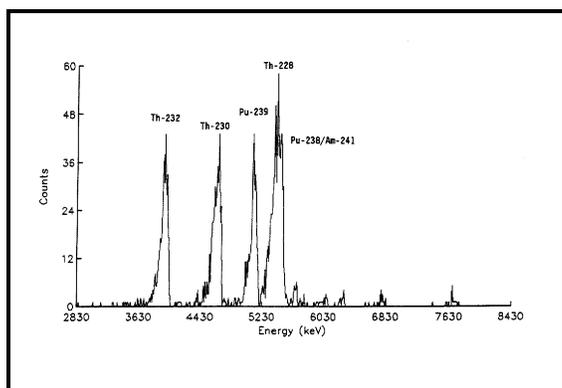


Figure 3 This spectrum is from a TSA of a soil sample without the uranium being included in the fraction. Notice that the ^{239}Pu peak is fully resolved from the other peaks; and that the high energy edge of the ^{228}Th has shifted to higher energy. Compare this ^{228}Th to the ^{228}Th in Figure 1. This shift indicates the presence of ^{238}Pu and/or ^{241}Am . To quantify the sum of the ^{238}Pu and ^{241}Am , the counts obtained from the ^{232}Th (parent of ^{228}Th) can be subtracted from this peak.

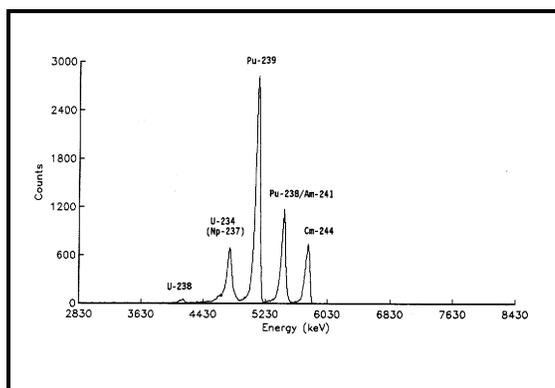


Figure 4 This spectrum is the TSA from a “sludge” sample. Notice the hump on the low energy side of the ^{234}U . This indicates the presence of ^{237}Np .

sample by performing the pyrosulfate fusion in glass instead of in the platinum dish. However, the pyrosulfate fusion in an Erlenmeyer flask solidifies much slower than in a platinum dish. This can cause a very insoluble crystalline precipitate to form in the subsequent dissolution if the pyrosulfate fusion is not heated long and hot enough. If this precipitate is present, the barium sulfate must be recrystallized (Step G.30), or the resolution of the final fraction will be badly degraded.

- G.15 After the pyrosulfate cake has cooled to room temperature, add two 14 mesh carborundum boiling chips, 5 mL of concentrated hydrochloric acid, 35 mL of water and 0.5 mL of 25% hydrazine.
 - G.16 Place the Erlenmeyer flask on a high-temperature hot plate and heat the solution to boiling.
 - G.17 Swirl the solution occasionally to aid in the dissolution of the cake.
 - G.18 Check the solution in a darken room with a flashlight. If a very crystalline needle-like precipitate is present, the barium sulfate precipitate *MUST* be reprecipitated to ensure complete dissolution in EDTA.
 - G.19 Add 5 drops of 20% titanium trichloride and boil the solution for 10 min to ensure complete reduction of the uranium and plutonium.
- **G.19 NOTE:** The yellow ferric iron color should be absent and the solution should

have a violet color from the titanium reductant. If the solution is yellow or colorless, continue to add titanium trichloride dropwise until a permanent violet color is present.

- G.20 If necessary, add enough water to bring the total volume in the flask to about 35 mL.
 - G.21 Reheat the solution to boiling and add 1 mL of seeding suspension.
 - G.22 While swirling the solution, add 1 mL of 0.45% barium chloride dropwise.
 - G.23 Place the Erlenmeyer flask on the hot plate and boil the solution for 1 min.
 - G.24 Repeat the 1-mL dropwise addition of barium chloride and the 1-min boiling time four more times.
- **G.24 NOTE:** If the barium chloride solution is added at a faster rate than that specified or without swirling the solution during the addition, there will be a loss of the actinides on the barium sulfate.
- G.25 If the solution obtained from dissolving the pyrosulfate cake contained the crystalline precipitate described above, transfer the solution and precipitate to a 50-mL conical Pyrex centrifuge tube; otherwise transfer the solution and precipitate to a 50-mL conical PMP centrifuge tube.
 - G.26 Centrifuge for 5 min while the solution is still hot to prevent calcium sulfate from precipitating.
 - G.27 Wash the precipitate in the centrifuge tube

Mixture number		Activity, pCi/g		Ratio, M/K
		Known	Measured	
1	²³⁹ Pu	7.81 ± 0.04E-1	7.6 ± 0.2E-1	0.97 ± 0.03
	²³⁸ Pu	8.36 ± 0.04E-1	8.0 ± 0.2E-1	0.96 ± 0.03
	²⁴¹ Am	3.33 ± 0.02E-1	3.52 ± 0.12E-1	1.06 ± 0.04
2	²³⁹ Pu	1.983 ± 0.009E-1	1.95 ± 0.08E-1	0.99 ± 0.04
	²³⁸ Pu	1.490 ± 0.009E-1	1.44 ± 0.07E-1	0.97 ± 0.05
	²⁴¹ Am	1.241 ± 0.009E-1	1.20 ± 0.06E-1	0.97 ± 0.05
3	²³⁹ Pu	3.65 ± 0.02E-1	3.85 ± 0.15E-1	1.06 ± 0.04
	²³⁸ Pu	4.16 ± 0.02E-1	4.25 ± 0.15E-1	1.02 ± 0.04
	²⁴¹ Am	4.00 ± 0.02E-1	4.00 ± 0.15E-1	1.00 ± 0.04

Table 1 This table shows the accuracy that can be obtained with this procedure when full separations and isotopic tracers are used.

- with about 10 mL of water, directed in a forceful stream from a wash bottle.
- G.28 Add 5 drops of hydrofluoric acid with swirling to dissolve any of the titanium titanate precipitate that might have formed.
- G.29 Centrifuge, decant and discard the wash.
- G.30 If the barium sulfate needs to be reprecipitated, continue with the next step, otherwise skip to Step G.38.
- G.31 Add 2 mL of sulfuric acid to the Pyrex centrifuge tube containing the barium sulfate to be reprecipitated.
- G.32 Heat gently over a small flame of a blast burner until the precipitate has dissolved completely.
- G.33 Cool, and add 20 mL of reprecipitating solution while swirling the centrifuge tube rapidly.
- G.34 Centrifuge for 5 min, decant and discard the supernate.
- G.35 Wash the precipitate with about 10 mL of water.
- G.36 Transfer the solution and precipitate to a 50-mL conical polymethylpentene (PMP) centrifuge tube.
- G.37 Centrifuge, decant and discard the wash.
- G.38 Dislodge the impacted barium sulfate precipitate by flipping the centrifuge tube sharply in a downward motion.
- G.39 Add 3 mL of water, 3 mL of 0.1 M potassium EDTA and heat in a boiling water bath until the barium sulfate has dissolved completely.
- **G.39 NOTE:** It may be necessary to place the tube in an ultrasonic bath to disperse the precipitate to ensure complete dissolution. Quadrivalent titanium from the soil will precipitate at this point and is very flocculant. This precipitate should not be confused with undissolved barium sulfate.
- G.40 With rapid swirling, add 1 drop of 20% titanium trichloride followed by 2 mL of 10 M potassium hydroxide.
- G.41 Heat in a hot water bath for 5 min to flocculate the titanous hydroxide precipitate.
- G.42 Centrifuge for 5 min, decant and discard the supernate.
- G.43 Wash the precipitate with 5 mL of 0.25 M sodium hydroxide directed in a forceful stream from a wash bottle.
- G.44 Centrifuge for 5 min, decant and discard the wash.
- **NOTE:** This hydroxide precipitate contains uranium, thorium and all of the transuranium elements that were present in the sample.
- G.45 Flip the centrifuge tube sharply to dislodge the precipitate and add 15 drops of hydrochloric acid, 4 mL of water and 100 µL of 0.5 mg/mL Nd carrier.
- G.46 Heat the centrifuge tube in a bath of boiling water until the precipitate dissolves completely.
- G.47 Add 3 drops of 20% titanium trichloride and heat in a boiling water bath for 5 min.
- G.48 Swirl the solution and add 1 mL of 48% hydrofluoric acid.
- G.49 Immediately transfer the tube to a bath of cold water and let stand for 15 min to maximize the yield of the actinides.
- G.50 Mount the precipitate on a 25-mm Gelman HT-200 filter paper and count in an alpha spectrometer for a long enough period of time to obtain desired statistics.

After this gross fraction has been counted in an alpha spectrometer, the filter paper containing the precipitate can be wet ashed and additional separations that are necessary can be performed.

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Biographies

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