

Plutonium and americium analysis from soil, vegetation and sediment

Plutonium and (long) americium analysis from soil, vegetation and sediment

Samples are first digested using microwave digestion or wet ashing. Plutonium is separated with anion exchange. Americium is separated with oxalate precipitation, Fe precipitation, extractio, cation exchange and anion exchange. Pu and Am sources are prepared through electrodeposition or coprecipitation.

Digestion of the samples

- Sample size 10 – 60 g
- Weigh dried and homogenized sample into a digestion flask
- Add Pu-242 and Am-243 tracers into the digestion flask
- Samples are digested using microwave digestion (MARS5) or wet ashing with 65% HNO₃, HCl and 30% H₂O₂ (Tecator)
- If using wet ashing (Tecator), filter the digested sample through a GF-filter using Bühner-funnel with suction (figure 1). Rinse the flask and the precipitate with 8 M HNO₃ few times. Transfer the solutions into a 400 ml beaker and evaporate until salts appear.



Figure 1. filtering the digested sample using Bühner-funnel and suction

- if using microwave digestion (MARS5), transfer the digested sample from the digestion flask into a teflon beaker and evaporate to dryness (*Teflon beaker can be used max. 200-250°C*).

Plutonium separation by anion exchange

1. Dissolve the residual into 100 ml 8 M HNO₃. Heat and add 1 ml H₂O₂. Cover the beaker with a watch glass and heat at 90 oC for 1 hour. Add approx. 2 g (1 teaspoon) NaNO₂ to the hot solution. Let cool for 1 h. (*Pu³⁺ oxidises into Pu⁴⁺. Reaction is vigorous so add NaNO₂ in bit by bit*)
2. Prepare an anion exchange column: place approx. 12.5 g anion exchange resin Dowex 1 x 4 (50 – 100 mesh) in nitrate form into an anion exchange column (Ø 1 cm) using 8 M HNO₃. (*Resin, approx. 50 m, is brought in nitrate form by treating it with 50 ml conc. HNO₃ and 2 x 50 ml 8 M HNO₃*)



Figure. Anion exchange colmuns

3. Place glass wool on bottom of the column. Load the sample solution into the anion exchange column (15 cm resin in the column, \varnothing 1 cm). Wash the resin with 150 ml 8 M HNO₃. Collect the load and wash solutions for Am analysis. (*8 M HNO₃ solution contains: Am³⁺, Cm³⁺, lanthanides, Sr²⁺, Pb²⁺, Ra²⁺, Fe³⁺, U⁶⁺, Po*)
4. Wash the resin with 150 – 200 ml conc. HCl. Discard the wash solution. (*Wash solution contains Th⁴⁺*)
5. Elute Pu with freshly made 60 ml 37% HCl + 5 ml 1 M NH₄I solution. (*Pu⁴⁺ is reduced into Pu³⁺. 1M NH₄I can be preserved for one month when covered from light*)
6. Evaporate Pu eluate to dryness. Add few ml conc. HNO₃ and HCl and evaporate. Repeat this 2 – 3 times. Evaporate and add small amounts of conc. HNO₃ (< 1 ml) until no residual remains in the beaker.

Americium analysis: oxalate precipitate, iron precipitate, HDEHP-TBP-toluene extraction, anion exchange

Oxalate precipitation

1. Evaporate the Am solution (step 3 from the Pu method) to dryness, avoid baking.
2. Dissolve the residual with dist. water and conc. HCl and transfer into 1 liter beaker. Dilute with water to 600 ml. Add Ca-carrier (600 mg) and stir. Adjust pH with conc. NH₃ to 1,5 – 2. Heat the solution and add 30 g solid oxalic acid while stirring with magnetic stirrer. When precipitation forms continue stirring for ½ h. Let the precipitate settle for at least 3 h. (*Sometimes precipitate may not form until 10-20 minutes after adding oxalic acid. If the precipitate doesn't appear, add few extra drops of NH₃. pH should, however, not exceed 2.*)
3. Remove most of the solution using suction. Collect the precipitate by filtering the solution through Whatman-40- filter paper using Bühner-funnel and suction (figure 2). Wash the precipitate with 0,5 % oxalic acid. Discard the solution.



Figure 2. Filtering the oxalate precipitation using Bühner-funnel and suction

4. Transfer the precipitate into quartz crucible using small amount of 0,5 % oxalic acid. Dry the sample under a heat lamp or in a heat cabinet at 105 oC (few hours). Place the crucible into the muffle oven and adjust temperature to 450 oC. Ash for 3,5 h. Increase temperature to 600 oC, ash for 30 min.

Iron precipitation

5. Transfer the cooled residual into a 250 ml centrifuge tube using 3 M HCl. Wash the empty crucible and transfer the solution into the centrifuge tube. Dilute the solution into 100 ml and add 10 mg Fe-carrier. Heat the solution and precipitate Fe(OH)₃ with carbonate free NH₃ at pH 8 while stirring at the same time. (*Precipitate should be reddish brown. If white precipitate appears (phosphates) repeat oxalic precipitation.*) Continue stirring for 10 minutes. Let the solution cool and precipitation settle down for 15 min.

6. Centrifuge and discard the solution. Wash the precipitate with an alkaline water solution (pH 7,5 – 8) and centrifuge. Discard the washing solution. Dry the precipitate at 105 oC for 1 – 2 h.

Anion exchange

7. Dissolve the residual with 20 ml of 9 M HCl. Prepare an anion exchange column: Ø 1 cm Dowex 1 x 4 (50 – 100 mesh) about 5 ml. Pretreat the resin with 10 ml conc. HCl:a and 25 ml 9 M HCl. Load the sample solution with speed 2 drops/5 s and collect the load solution into a beaker. Wash the column with 20 ml of 9 M HCl and collect the wash solution into the same beaker. (*Fe stays in resin, Am comes through the resin*)

8. Evaporate the solutions to dryness (do not bake). Repeat the evaporation few times after add-ing 2 ml of conc. HCl.

HDEHP-TBP-toluene extraction (can be skipped for air and deposition samples)

9. Evaporate after adding 5 ml conc. HNO₃, repeat. Dissolve the residual with 40 ml dist. water and adjust the pH 2-3 with 2 – 8 M HNO₃ (*Adjustment of pH must be exact so that Am is extracted into organic phase*). Pour the solution into a separation funnel and add 40 ml HDEHP-TBP-solution. Shake for 3 min. Let the phases separate and collect the organic phase (on the top). Add 30 ml of HDEHP-TBP-toluene solution into the water phase and shake for 2 minutes. Discard the water phase (lower) . Combine the organic phases and add 70 ml of 0,075 M HCl (Most of the metals in valence state +2 will stay in water phase). Shake for 3 min and discard the water phase (lower phase). Am is extracted by adding 30 ml of 4 M HNO₃ into the funnel and by shaking the funnel for 3 min. Water phase (lower phase) is collect-ed and 30 ml of 4 M HNO₃ is added into the organic phase while shaking the funnel for 3 min. Combine the water phases and discard the organic phases. Evaporate the solution to dryness. Add 2 ml conc. HNO₃ and evaporate to dryness. Add 5 ml conc. HCl:a and evaporate, repeat. (*If organic matter exists, wet ashing with conc. HNO₃ will be carried out until all org. matter is destroyed. In the end treat the sample with conc. HCl to destroy nitrates*)

Anion + cation exchange

10. Dissolve the residual with 10 ml of 9 M HCl, heat as needed. Prepare double ion exchange column: (Ø 7 mm, lower: Dowex 1 x 4 (100 – 200 mesh) anion exchange resin (7,5 cm) top: Dowex 50 W x 8 (100 – 200 mesh) cation exchange resin (7,5 cm)) Pretreat the columns with 7,5 ml conc. HCl:a and 22,5 ml of 9 M HCl. Load the sample solution and collect the eluate (1 tippa/5 s). Wash the column with 15 ml of 9 M HCl:a and collect the wash solution in the same beaker

11. Evaporate the collected solutions to dryness. Add 4 x 1 ml conc. HNO₃ and evaporate to dry-ness (*Avoid baking*).

12. Treat the residual first with mixture of conc. HNO₃ and HCl and then with conc. HNO₃ several times while heating. Carefully evaporate to dryness.

Anion exchange to remove lanthanides etc.

13 a **Sediment samples** :

Dissolve the residual with 20 ml of 1 M HNO₃-93 % CH₃OH-solution. It dissolves easier if let sit overnight. (*be sure not to evaporate!*). Prepare an ion exchange column Ø 7 mm, Dowex 1 x 4 (100 – 200 mesh) 6 ml = ca. 15 cm.

Pretreat the resin with 20 ml 1 M HNO₃ followed by 30 ml 1 M HNO₃ – 93 % CH₃OH

Load the sample solution (1 drop/10 s) and discard the load solution. Wash the column with 20 ml 1 M HNO₃ – 93 % CH₃OH followed by 60 ml 0,1 M HCl – 75 % CH₃OH – 1 M NH₄SCN (*solution has to be freshly made*)

Elute the Am with 45 ml of 1,5 M HCl – 86 % CH₃OH-solution (1 drop/10 s). Discard the first 10 drops.

Evaporate the eluate to dryness and beware splashing.

13 b **Other matrices than sediment:**

Dissolve the residual with 15 ml of 1 M HNO₃-93 % CH₃OH-solution. It dissolves easier if let sit overnight. (*be sure not to evaporate!*). Prepare an ion ex-change column Ø 7 mm, Dowex 1 x 4 (100 – 200 mesh) 6 ml = ca. 15 cm.

Pretreat the resin with 20 ml 1 M HNO₃ followed by 30 ml 1 M HNO₃ – 93 % CH₃OH.

Load the sample solution (1 drop/10 s) and discard the load solution. Wash the column with 20 ml 1 M HNO₃ – 93 % CH₃OH followed by 60 ml 0,1 M HCl – 75 % CH₃OH – 1 M NH₄SCN (*solution has to be freshly made*)

Elute the Am with 45 ml of 1,5 M HCl – 86 % CH₃OH-solution (1 drop/10 s). Discard the first 10 drops.

Evaporate the eluate to dryness and beware splashing.

14. Treat the residual first with conc. HNO₃ and then with a mixture of conc HNO₃ and conc. HCl-several times at hot plate. (*Thiocyanate present in the residual will be removed when evapo-rated and heated with high temperature. Sulphur will be removed by wet ashing with acids. Residual should be colourless*). Then treat with small amount (< 1 ml) conc. HNO₃ several times.

15. Prepare the Am source either using electrodeposition (1,5 h electrodeposition time) or coprecipitation as described above.

Source preparation

Pu and Am sources can be prepared by either electrodeposition or coprecipitation

Electrodeposition

1. Add 25 drops of 2 M HNO₃ into the beaker by washing the walls of the beaker at the same time. Heat and let cool. Pour the solution into an electrolysis vessel. Wash the beaker with small amount of distilled water and add wash solution into the electrolysis vessel, repeat. Volume of the solution should not exceed 4 – 5 ml.

2. Add 3 – 4 drops of methylred. Add conc. NH₃:a dropwise until colour changes from red to yellow. Add dropwise until the solution turns red (solution now acid). Add 4 drops more 2 M HNO₃.

3. Carry out the electrolysis for 45 – 90 min using 1,7 – 1,9 A (current) and 6 – 9 V (voltage) in ice water bath with Pt-spiral as an anode and steel plate as cathode. (45 min is enough for Pu but Am requires 1,5 h.) Stop the electrolysis by adding 2 ml conc.. NH₃ into the vessel, wait 1 min before taking the vessel out.

4. Wash the steel plate with distilled H₂O and ethanol. Anneal with Bunsen burner, upper part of the flame, until tinged with red. Let cool.

5. Measure Pu with -spektrometry

Co-precipitation

1. Dissolve the residual into 2-5 ml 1 M HNO₃:a. Transfer into plastic test tube and wash the beaker twice with few ml 1M HNO₃:lla. Add wash solutions into the test tube. Add 0,5 ml Ce-carrier (Ce 100 µg/ml) into the test tube and mix with Vortex mixer.

2. Co-Precipitate Pu with CeF by adding 1,5 ml 40 % HF acid. Mix the sample with Vortex and place the test tube in ice bath for 45 min.

3. Filter the precipitate