URANIUM IN SOIL

(2 GRAM SAMPLE, WITH VACUUM BOX SYSTEM)

1. SCOPE

1.1. This is a procedure for the separation of uranium from 2 gram soil samples. After separation of uranium with this method, source preparation for uranium measurement by alpha spectrometry is performed by electrolytic deposition onto stainless steel planchets (Eichrom Method SPA02) or by rare earth fluoride microprecipitation onto polypropylene filters (Eichrom Method SPA01).

1.2. This method does not address all aspects of safety, quality control, calibration or instrument set-up. However, enough detail is given for a trained radiochemist to achieve accurate and precise results for the analysis of the analyte(s) from the appropriate matrix, when incorporating the appropriate agency or laboratory safety, quality and laboratory control standards.

2. SUMMARY OF METHOD

2.1. Uranium is separated on Eichrom UTEVA resin prior to measurement by alpha spectrometry. Tracers are used to monitor chemical recoveries and correct results to improve precision and accuracy. A ^{232}U self-cleaning tracer is recommended for this method. Preparation of the ^{232}U self-cleaning tracer is described in Eichrom Method TP01.

3. SIGNIFICANCE OF USE

3.1. This is a rapid, reliable method for measurement of uranium in soil samples that is more cost-effective and efficient than traditional ion exchange, solvent extraction and precipitation techniques.

4. INTERFERENCES

4.1. Actinides with un-resolvable alpha energies such as ^{241}Am and ^{238}Pu or ^{237}Np and ^{234}U must be chemically separated to enable measurement. This method separates these isotopes effectively.

4.2. ^{210}Po has an alpha energy similar to ^{232}U. For samples containing very high levels of ^{210}Po (e.g., environmental samples with the natural uranium decay chain intact, or dissolved air filter samples) an additional column rinse is recommended.

4.3. This method may not adequately dissolve uranium in soils containing refractory particles. If refractory particles may be present in samples, a soil fusion method, as described in references (4) and (5), is recommended.

5. APPARATUS

- Analytical balance, 0.0001 gram sensitivity
- Beakers, glass
- Beakers, Teflon
- Cartridge reservoirs, 10mL (Eichrom Part: AR-200-RV10) or 20mL (Eichrom Part: AR-200-RV20)
- Centrifuge tubes, 50mL
- Centrifuge, with rotor and carriers for 50mL tubes
- Fume hood
- Hotplate
- Muffle Oven
- Vacuum box system, Eichrom Part: AR-12-BOX or AR-24-BOX
- Vacuum box white inner support tube-PE, Eichrom Part: AR-1000-TUBE-PE
- Vacuum box yellow outer tips, Eichrom Part: AR-1000-OT
- Vacuum pump, 115 V, 60 Hz, Fisher Part: 01-092-25 (or equivalent) or house vacuum
- Optional item for collecting load and rinse solutions:
  - o Vacuum box inner liner, Eichrom Part: AR-24-LINER or AR-12-LINER

6. REAGENTS

Note: Analytical grade or ACS grade reagents and trace metal grade (or equivalent) acids are recommended. Evaluation of key reagents, such as aluminum nitrate and ammonium hydrogen phosphate, for contribution to method background levels from naturally occurring radioactive materials is recommended.

Aluminum nitrate anhydrous, $Al(NO_3)_3$
Ammonium hydroxide(57%), concentrated NH_4OH
Appropriate tracers or standards (U-232 self-cleaning tracer).
Deionized water, All reagents are prepared with deionized water
Hydrochloric acid (37%), concentrated HCl

Hydrofluoric acid (49%), concentrated HF
Nitric acid (70%), concentrated HNO_3
Oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$
UTEVA® resin, 2mL prepacked cartridge, 50-100μm, UT-R50-S

6.1. *Hydrochloric acid (1M)* - Add 83mL of concentrated HCl to 900mL of water. Dilute to 1L with water.

6.2. *Hydrochloric acid (5M) - oxalic acid (0.05M) solution* - Dissolve 6.3g oxalic acid dihydrate in 400mL of water. Add 417mL concentrated HCl. Dilute to 1L with water.

6.3. *Hydrochloric acid (9M)* - Add 750mL of concentrated HCl to 100mL of water. Dilute to 1L with water.

6.4. *Nitric acid (3M)* - add 188mL of concentrated HNO_3 to 700mL water. Dilute to 1L with water.

6.5. *Nitric acid (8M)* – add 500mL of concentrated HNO_3 to 450mL of water. Dilute to 1L with water.

6.6. Nitric acid (3M) - Aluminum nitrate (1M) solution - Dissolve 212g of anhydrous aluminum nitrate in 500mL of water, add 188mL of concentrated HNO_3. Dilute to 1L with water.

7. PROCEDURE

7.1. Sample preparation

7.1.1. Using an analytical balance, weigh up to 2g of sample into a 200mL glass beaker.

7.1.2. Heat the sample at 110°C until dry.

7.1.3. Weigh the sample again to achieve dry weight.

7.1.4. Spike samples with the appropriate yield tracer.

Note: If using a self-cleaning ^{232}U tracer, prior to removing aliquot for spiking soil samples, vortex the tracer for 1-2 minutes to suspend $BaSO_4$ precipitant and then centrifuge for 5 minutes. This will ensure that ^{228}Th and its daughters are effectively removed.

7.1.5. Place the dry sample in a muffle furnace and ash overnight at 510°C.

7.1.6. Transfer the ashed soil sample to a 125mL Teflon beaker using 10mL of concentrated HNO_3.

7.1.7. Add an additional 10mL of concentrated HNO_3 and 5mL of concentrated HCl to each beaker.

7.1.8. Place a watch glass on each beaker, and heat each sample to near boiling on a hot plate for 3 hours.

7.1.9. Cool sample and transfer, including solids, to a 50mL centrifuge tube. Complete transfer with deionized water. Dilute to 50mL with deionized water.

7.1.10. Centrifuge and decant the supernate to a clean labeled Teflon beaker, leaving the residue in the bottom of the centrifuge tube. Set the beaker aside, while the residue is treated in the following steps.

7.1.11. Transfer the residue to the original 125mL Teflon beaker using 10mL of concentrated HNO_3. Add an additional 10mL of concentrated HNO_3 and 15mL of concentrated HF to the beaker.

7.1.12. Place a Teflon cover on each beaker and heat on a hot plate until the residue is dissolved.

7.1.13. Remove the Teflon cover, and add the solution containing the dissolved residue to the supernate in the beaker from step 7.1.9. (If any residue remains, repeat the HNO_3/HF digestion from steps 7.1.11. and 7.1.12.)

7.1.14. Evaporate the combined solutions in the beaker from step 7.1.13. to dryness.

7.1.15. Remove beaker from hot plate and add 5mL of conc. $HNO_{3.}$

7.1.16. Evaporate to dryness and add 10mL of 3M HNO_3/1M $Al(NO_3)_{3.}$ Cool the solution and then transfer to a 50mL centrifuge tube.

7.1.17. Rinse the beaker with an additional 5mL of 3M HNO3/1M Al(NO3)3 solution. Add rinse to the centrifuge tube, cap the centrifuge tube, and mix by swirling. Centrifuge the solution before loading on UTEVA.

7.2. U separation using UTEVA Resin

7.2.1. Place the inner tube rack (supplied with vacuum box system) into the vacuum box with the centrifuge tubes in the rack. Fit the lid to the vacuum system box. Alternatively, the inner vacuum box liner may be used in place of the inner tube rack.

7.2.2. Place the yellow outer tips into all 12 or 24 openings in the lid of the vacuum box. Fit in the White Inner Support Tube into each yellow tip.

7.2.3. For each sample solution, fit a UTEVA cartridge on to the inner support tube.

7.2.4. Add syringe barrels (funnels/reservoirs) to the top end of the UTEVA cartridge.

Note: The unused openings on the vacuum box should be sealed. Vacuum manifold plugs can be used to plug unused white tips to achieve good seal during the separation. Alternatively, unused vacuum box holes can be sealed with scotch tape.

7.2.5. Connect the vacuum pump to the box. Turn the vacuum pump on and ensure proper fitting of the lid.

Note: Make sure the sample and all reagent solutions have cooled to room temperature before proceeding with the method.

7.2.6. Add 5mL of 3M HNO_3 into each UTEVA cartridge reservoir to precondition resin. Adjust vacuum to achieve a flow rate of 1-2mL/min.

7.2.7. Transfer each load solution from step 7.1.17. into the appropriate UTEVA Resin cartridge reservoir. Allow the solution to completely pass through cartridges at 1-2mL/min. Uranium will be retained by the resin.

7.2.8. Add 5mL of 3M HNO_3 to rinse to each sample tube. Transfer each rinse solution into the appropriate UTEVA Resin cartridge reservoir. Allow solution to completely pass through cartridges at 1-2mL/min.

7.2.9. Add 5mL of 3M HNO_3 into each UTEVA cartridge reservoir. Allow solution to completely pass through cartridges at 1-2mL/min. Disengage vacuum. Empty or exchange centrifuge tubes. Dispose of eluate to this point as waste.

7.2.10. Add 15mL of 8M HNO_3 to each UTEVA cartridge reservoir. Engage vacuum. Allow solution to completely pass through each cartridge at 1-2mL/min.

Note: This rinse removes Po isotopes, including ^{210}Po which can affect measurement of ^{232}U by alpha spectrometry.

7.2.11. Place a clean reservoir above each UTEVA cartridge. Add 5mL of 9M HCl into each UTEVA cartridge reservoir. Allow solution to completely pass through each cartridge at 1-2mL/min.

Note: This rinse converts the resin to the chloride system. Some Th and Np may be removed here.

7.2.12. Add 20mL of 5M HCl-0.05M oxalic acid into each UTEVA cartridge reservoir. Allow solution to pass through cartridges at 1-2mL/min. Disengage vacuum. Discard the combined eluate to this point as waste.

Note: This rinse removes plutonium, neptunium and thorium from the column.

7.2.13. Place a clean, labeled 50mL polypropylene centrifuge below each UTEVA cartridge.

7.2.14. Add 15mL of 1M HCl into each UTEVA cartridge reservoir to strip the uranium. Engage vacuum. Allow solution to completely pass through cartridges at 1-2mL/min.

7.2.15. Prepare sources for uranium measurement by alpha spectrometry using electrodeposition (Eichrom Method SPA02) or rare earth fluoride micro precipitation (Eichrom Method SPA01).

8. CALCULATIONS

Calculate the actinide activity as follows:

Calculate tracer yield:

$$\text{Yield} = \frac{(C_S - B_S)}{E_S \times A_S}$$

where:

C_S = measured actinide tracer, cpm
B_S = background, cpm
E_S = counting efficiency for tracer
A_S = tracer activity, dpm

Note: If any tracer may be present in the sample, a spiked and unspiked sample must be analyzed to determine chemical yield,

$$Y = \frac{\text{(spiked sample tracer cpm - unspiked sample tracer cpm)}}{\text{E x actinide spike activity, dpm}}$$

Percent yield =Yield x 100

Calculate actinide isotope activity:

$$\text{Sample dpm/L} = \frac{S - B}{E \times V \times Y}$$

where:

S = sample activity, cpm
B = background, cpm
E = counting efficiency
V = sample weight, g or volume, L
Y = yield

Conversion of dpm/g to pCi/gram: pCi/g=(dpm/g) /2.22

9. REFERENCES

1) ASTM Method C1000-11, "Standard Method for the Radiochemical Determination of Uranium Isotopes in Soil by Alpha Spectrometry."
2) Horwitz, E.P., Chiarizia, R., Dietz, M.L., Diamond, H., Essling, A.M., and Gracyk, D.W. "Separation and Preconcentration of Uranium from Acidic Media by Extraction Chromatography," Analytica Chimica Acta, 266, 25-37 (1992).
3) ASTM Method D3648-14, "Standard Practices for the Measurement of Radioactivity."
4) Maxwell, S.L., Hutchinson J.B., McAlister D.R. "Rapid Fusion Method for the determination of refractory Th and U in soil samples," Journal of Radioanalytical and Nuclear Chemistry, in press, (2015).
5) Eichrom Application Note AN-1430, "Rapid Determination of Actinides in Soil Samples".
6) Eichrom Method TP01, "Self-cleaning U-232 Tracer".

1) Weigh up to 2.0g of soil in to a 200mL glass beaker

2) Heat sample at 110ºC unitl dry

3) Cool sample and weigh. Record dry weight. Spike samples with yield tracer.

4) Ash sample overnight in muffle furnace at 510ºC.

5) Transfer ashed soil to 125mL teflon beaker with 10mL conc. HNO_3.

6) Add 10mL conc. HNO_3 and 5 mL conc. HCl. Cover with watchglass and heat to near boiling for 3 hrs.

7) Transfer sample, including solids, to 50mL centrifuge tube with DI water. Dilute sample to 50mL with DI water.

8) Centrifuge. Decant liquid to clean 125mL teflon beaker and set aside.

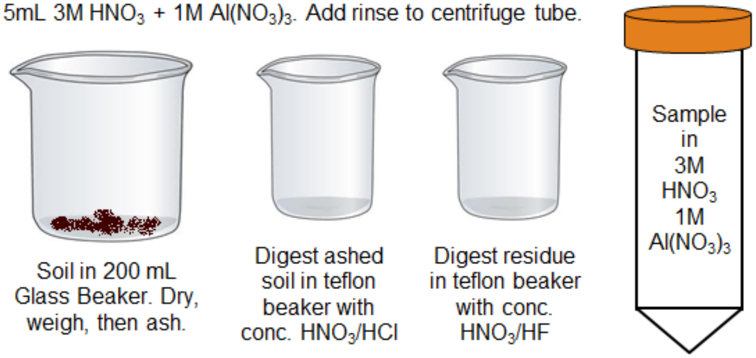
9) Transfer solids to original 125mL teflon beaker with 10mL conc. HNO_3. Add 10mL conc. HNO_3 and 15mL conc. HF. Cover beaker with teflon cover. Digest solids on hotplate until dissolved. Add more HNO_3-HF if solids persist.

10) Add digested solids to teflon beaker from step 8. Evaporate to dryness on hotplate.

11) Add 5mL conc. HNO_3. Evaporate to dryness.

12) Add 10mL 3M HNO_3 + 1M $Al(NO_3)_3$.

13) Transfer to a 50mL centrifuge tube. Rinse beaker with 5mL 3M HNO_3 + 1M $Al(NO_3)_3$. Add rinse to centrifuge tube.



14) Precondition UTEVA cartridge with 5mL 3M HNO_3.

15) Load sample on to UTEVA. Allow liquid to drain to waste. Uranium is retained.

16) Rinse sample tube with 5mL 3M HNO_3. Add rinse to UTEVA. Allow liquid to drain to waste.

17) Rinse UTEVA with 5mL 3M HNO_3. Allow liquid to drain to waste.

18) Rinse UTEVA with 15mL 8M HNO_3 for additional Po removal. Allow liquid to drain to waste.

19) Rinse UTEVA with 5mL 9M HCl. Allow liquid to drain to waste.

20) Rinse UTEVA with 20mL 5M HCl + 0.05M Oxalic acid. Allow liquid to drain to waste.

21) Place clean 50mL centrifuge tube below each UTEVA cartridge. Strip Uranium with 15mL 1M HCl.