TECHNETIUM-99 IN SOIL

1. SCOPE

1.1. This procedure describes a method to separate and measure technetium-99 in soil.

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. Technetium-99 is leached from soil samples using 1M nitric acid and separated using Eichrom TEVA Resin. After separation of the pertechnetate ion, TcO_4^-, with TEVA resin, ^{99}Tc is measured by liquid scintillation counting, adding the resin directly to liquid scintillation cocktail. Tc yield can be traced by analyzing ^{99}Tc recovery from a batch recovery standard, analyzing samples with and without a ^{99}Tc spike, spiking with the short-lived gamma emitter, ^{99m}Tc, or measuring the recovery of stable rhenium by atomic emission spectrometry. The method may also be performed using ICP-MS to measure ^{99}Tc, employing rhenium (REF 4) or ^{97}Tc (REF 1) as a yield tracer.

3. SIGNIFICANCE OF USE

3.1. This is a rapid, reliable method for measurement of ^{99}Tc in environmental samples that is more cost-effective and efficient than traditional anion exchange, solvent extraction or precipitation techniques.

4. INTERFERENCES

4.1. Beta emitting radionuclides (including ^{14}C, ^{32}P, ^{35}S, and ^{90}Sr) and components that quench the liquid scintillation counting are effectively removed using Eichrom TEVA Resin. Tritium may follow the technetium due to the absorption of tritium-labeled compounds by the resin. Possible interference by tritium can be minimized by setting the ^{99}Tc liquid scintillation counting window above the maximum energy for tritium beta particles.

4.2. Organic matter present in the sample can interfere by quenching during liquid scintillation counting. An Eichrom prefilter column is used to remove organics from the sample.

4.3. Because ^{234}Th has a beta decay with an energy in the ^{99}Tc window, it is necessary to ensure complete decontamination from thorium. For samples high in ^{234}Th it is recommended to follow procedure option #2, see 7.3.2. (Samples with high levels of natural uranium may contain significant ^{234}Th.)

5. APPARATUS

- Beakers, glass
- Centrifuge, with rotor and carriers for 50mL tubes
- Centrifuge tubes, 50mL
- Column rack, Eichrom Part: AC-103
- Extension funnels - 25 mL, Eichrom Part: AC-120
- Liquid scintillation counter
- Liquid scintillation vials
- Syringe filters, 25mm, 0.45µm
- Watch glasses

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.

Deionized water, all reagents are prepared using deionized water
Hydrofluoric acid (49%), concentrated HF **-or-** *Sodium Fluoride*, NaF
Hydrogen peroxide (30%), concentrated H_2O_2
Liquid Scintillation Cocktail
Nitric acid (70%), concentrated HNO_3
TEVA® resin, prepacked 2 mL columns, 100-150µm, Eichrom Part TE-C50-A
Optional for removal of colored compounds that can quench LSC: *Prefilter column,* prepacked 2mL column, 100-150µm, Eichrom Part PF-C50-A

6.1. *Nitric acid (0.01M)* - Add 0.63mL of nitric acid to 950mL of water. Dilute to 1L with water.

6.2. *Nitric acid (0.02M)* - Add 1.25mL of nitric acid to 950mL of water. Dilute to 1L with water.

6.3. *Nitric acid (0.02M) / hydrofluoric acid solution (0.5M*) - Add 17.8mL of concentrated HF and 1.25mL of concentrated HNO_3 to 900mL water. Dilute to 1L with water.

6.4. *Nitric acid solution (0.1M)* - Add 6.3 mL of concentrated HNO_3 to 950mL of water. Dilute to 1 liter with water.

6.5. *Nitric acid solution (1M)* - Add 62.5mL of concentrated HNO_3 to 900mL of water. Dilute to 1L with water.

7. PROCEDURE

7.1. Soil Sample Preparation:

7.1.1. If necessary, grind or use pulverizer to homogenize the soil sample.

7.1.2. Weigh up to 10 grams of the soil sample on an analytical balance.

7.1.3. Transfer the soil sample to a 250mL beaker using 10mL of 1M HNO_3.

7.1.4. Analyze each sample with and without adding Tc-99 spike to determine chemical recovery.

Note: An alternative is to use ^{99m}Tc as a tracer, measuring the short-lived gamma activity of ^{99m}Tc (6.02 hour half-life) using gamma counting, allowing the ^{99m}Tc to decay for approximately 1 week and then measure the ^{99}Tc beta using liquid scintillation counting.

7.1.5. Add 40mL of 1M HNO_3 to each beaker.

7.1.6. Place a watch glass on each beaker on a hot plate and heat to 80°C for 4 hours.

7.1.7. Remove each beaker from the hotplate and allow to cool.

7.1.8. Transfer the solution and solids to a centrifuge tube and centrifuge for approximately 10 minutes at 2000 rpm.

7.1.9. Decant supernate and discard solids to waste.

7.1.10. Transfer each leach solution from step 7.1.9 to a 150mL beaker.

7.1.11. Add 5mL of 30% H_2O_2 to each beaker and heat at 80°C until the effervescence and the yellow color disappears.

7.1.12. If a dark color persists, repeat step 7.1.12.

7.1.13. Allow beakers to cool to room temperature.

7.1.14. If necessary to remove residual solids, filter the sample using a 25mm, 0.45µm syringe filter or transfer sample to a centrifuge tube and centrifuge.

7.2. Eichrom TEVA Resin column preparation:

7.2.1. If necessary to remove color from samples with high organic content, pass each sample through a prefilter column.

7.2.2. For each sample aliquot analyzed, place a TEVA column in a column rack.

7.2.3. Place a beaker below each column, remove the bottom plug from each column and allow each column to drain.

7.2.4. Add 5mL of 0.1M HNO_3 into each TEVA column to condition the resin. Allow solution to drain.

7.3. Eichrom TEVA column separation:

Note: The method describes the separation of Tc using 2mL prepacked TEVA resin columns. The method may also be performed using prepacked 2mL cartridges of prefilter (PF-R50-S) and TEVA resin (TE-R50-S) and the Eichrom vacuum box system (AR-BOX-24 or AR-BOX-12).

Note: If samples have high levels of ^{234}Th (including samples high in natural uranium) then follow section 7.3.2 (Option #2).

7.3.1. Option #1

7.3.1.1. Transfer each sample from step 7.1.15 into the appropriate Prefilter (if required) and TEVA Resin columns.

7.3.1.2. Allow the sample solution to drain through each set of columns.

7.3.1.3. Rinse the original beaker or container with the minimal volume of water required (depending on beaker size) and transfer this rinse to the appropriate column.

7.3.1.4. Allow the rinse solution to drain through each column.

7.3.1.5. Add 50mL of 0.01M HNO_3 to each column.

7.3.1.6. Allow the 0.01M HNO_3 rinse solution to drain through each column. Discard the rinses. **Proceed to section 7.4**.

Note: If measuring ^{99}Tc, ^{97}Tc, or Re by ICP-MS, an additional rinse of 50mL 1M HNO_3 will help remove isobaric interferences.

7.3.2. Option #2 For samples containing high levels of natural uranium

7.3.2.1. Transfer each sample from step 7.1.15 into the appropriate Prefilter (if required) and TEVA Resin columns.

7.3.2.2. Allow the sample solution to drain through each set of columns.

7.3.2.3. Rinse the original beaker or container with the minimal volume of water required (depending on beaker size) and transfer this rinse to the appropriate column.

7.3.2.4. Allow the rinse solution to drain through each column.

7.3.2.5. Rinse each column with 25mL of 0.5M HF/0.02M HNO_3.

Note: Alternatively, 40mL of 0.25M NaF/0.02M HNO_3 or 25 mL of 1M NaF/0.02M HNO_3 may be used. This step will remove any residual ^{234}Th from the column.

7.3.2.6. Rinse column with 50mL of 0.01M HNO3 and discard the eluent. Proceed to section 7.4.

Note: If measuring ^{99}Tc, ^{97}Tc, or Re by ICP-MS, an additional rinse of 50mL 1M HNO_3 will help remove isobaric interferences.

7.4. Counting preparation

7.4.1. Transfer the TEVA resin into a liquid scintillation vial by removing the top frit, attaching a syringe to the column tip and washing the resin from each column with 3 mL of 0.1M HNO_3.

Note: Alternatively, the column can be cut near the bottom frit with a razor blade and the resin rinsed out with three 1 mL aliquots of 0.1M HNO_3.

7.4.2. Add 10mL of the scintillation cocktail into each vial containing the resin. Cap the vial and shake well.

Note: Ultima Gold -XR™ or Ultima Gold -AB™ is suggested. Opti-Fluor™ or Insta-Gel XF™ cocktails may also be used. Insta-Gel XF™ is less desirable from an environmental, waste disposal standpoint.

7.5. Liquid scintillation counting:

7.5.1. Prepare a blank by preparing a vial containing the same amount of resin, water and cocktail as used in the resin counting method to determine background counts.

7.5.2. Prepare a ^{99}Tc matrix standard by adding a known amount of ^{99}Tc to a vial containing the same amount of resin, water and cocktail as used in the resin counting method to determine counting efficiency.

7.5.3. Set up the scintillation counting window to measure from 25 - 290 Kev or alternate window desired.

7.5.4. If the quenching between samples and standards is not similar, prepare a quench curve.

7.5.5. Count the vials the time required to obtain the counting statistics desired (typically 30 minutes to 1 hour) and to determine beta counts per minute.

7.5.6. Analyze a blank with each set of samples analyzed.

8. CALCULATIONS

Calculate the Tc-99 activity as follows:

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

where:

S = sample counts/time in minutes, cpm
B = blank counts/time in minutes, cpm
E = counting efficiency = measured cpm/dpm of Tc-99 matrix standard, step 7.5.2.
V = sample weight, g

$$Y = \text{yield} = \frac{(\text{spiked sample cpm} - \text{unspiked sample cpm})}{E \times \text{Tc-99 spike activity, dpm}}$$

Note: If ^{99m}Tc is used as a tracer, calculate the yield as follows:

$$\text{Yield} = \frac{(C_s - B_s)}{E_s \times A_s}$$

where:

C_s = measured Tc-99m tracer, gamma cpm
B_s = background, gamma cpm
E_s = gamma counting efficiency for Tc-99m
A_s = Tc-99m tracer activity, dpm, corrected for decay from reference date

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

9. PRECISION AND BIAS

9.1. *Precision* - A relative standard deviation of 2.8% at the 10,000 dpm level has been reported for option #1 (section 7.3.1.)

9.2. *Bias* - A mean recovery of 90.2% has been reported for option #1 (section 7.3.1.) Since results are corrected based on spike recovery, no significant bias exists for the method.

10. REFERENCES

1)DOE Methods Compendium, RP550. "Technetium-99 Analysis Using Extraction Chromatography,"

2)Banavali, A.D., "The Determination of Technetium-99 in Low-Level Radioactive Waste, *Radioactivity & Radiochemistry*," 6(3), 26-35 (1995).

3)Sullivan, T., et al., "Determination of Technetium-99 in Borehole Waters Using an Extraction Chromatographic Resin," 37th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry, Ottawa, Canada. 1991.

4) Mas, J.L. "Method for the detection of Tc in seaweed samples coupling the use of Re as a chemical tracer and isotope dilution inductively coupled plasma mass spectrometry," *Analytica Chimica Acta*, 509, 83-88 (2004).

1) Weigh up to 10g of dry soil into a 200mL glass
2) Add 40mL of 1M HNO_3 and appropriate tracer.
3) Place a watch glass on beaker and heat at 80°C for 4 hours
4) Cool sample. Transfer solution and solids to a centrifuge tube.
5) Centrifuge for 10 minutes at 2000rpm.
6) Decant supernate to glass beaker. Discard solids as waste
7) Add 5mL of 30% H2O2 to each sample. Heat at 80°C until color disappears and effervescence stops. Repeat if necessary to remove color.
8) Cool sample. If necessary filter or centrifuge to remove solids.
Soil in 200 mL Glass Beaker. Leach with 40mL 1M HNO_3 at 80°C
Cool Sample. Centrifuge. Decant supernate to glass beaker.
Digest supernate in glass beaker with 30%H_2O_2
Sample in <1M HNO_3
9) Precondition TEVA column with 5mL 0.1M HNO_3.
10) Load sample on to column. Allow liquid to drain to waste. Tc is retained.
11) If sample contains Th-234/natural U, rinse column with 25mL 0.5M HF-0.02M HNO_3.
12) Rinse column with 50mL 0.01M HNO_3. Allow liquid to drain to waste.
13) Extrude resin into LSC vial or strip Tc with 20mL 8M HNO_3.
2mL TEVA Column with 25mL extension funnel
(9) (10) (11) (12)
Waste
(13)
Tc sample to preparation for measurement technique