

TECHNETIUM-99 IN SOIL

(WITH VACUUM BOX SYSTEM)

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, $^{99\text{m}}\text{Tc}$, 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
- Cartridge reservoirs, 10mL (Eichrom Part: AR-200-RV10) or 20mL (Eichrom Part: AR-200-RV20)
- Centrifuge
- Centrifuge tubes
- Liquid scintillation counter
- Liquid scintillation vials
- Syringe filters, 25mm, 0.45 μm
- 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
- Watch glasses
- Optional: vacuum box inner liner - For collection of load and rinse fractions, Eichrom Part: AR-12-LINER or AR-24-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.

Deionized water, all reagents are prepared using deionized water

Hydrofluoric acid (49%), concentrated HF -or- Sodium Fluoride, NaF

<i>Hydrogen peroxide (30%), concentrated H₂O₂</i>
<i>Liquid Scintillation Cocktail</i>
<i>Nitric acid (70%), concentrated HNO₃</i>
<i>TEVA® resin, prepacked 2 mL cartridge, 50-100µm, Eichrom Part TE-R50-S</i>
<i>Optional for removal of colored compounds that can quench LSC: Prefilter cartridge, prepacked 2mL cartridge, 50-100µm, Eichrom Part PF-R50-A</i>

- 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 HNO₃ to 900mL water. Dilute to 1L with water.
- 6.4. *Nitric acid solution (0.1M)* - Add 6.3 mL of concentrated HNO₃ to 950mL of water. Dilute to 1 liter with water.
- 6.5. *Nitric acid solution (1M)* - Add 62.5mL of concentrated HNO₃ 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 HNO₃.
 - 7.1.4. Analyze each sample with and without adding ⁹⁹Tc 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 ⁹⁹Tc beta using liquid scintillation counting.

- 7.1.5. Add 40mL of 1M HNO₃ 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% H₂O₂ 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 preparation:
- 7.2.1. If necessary to remove color from samples with high organic content, pass each sample through a prefilter cartridge.
 - 7.2.2. Place the inner tube rack (supplied with vacuum box system) into the vacuum box with centrifuge tubes in the rack. Fit the lid to the vacuum system box. Alternatively, a vacuum box inner liner may be used.
 - 7.2.3. Place yellow outer tips into all 12 or 24 openings in the lid of the vacuum box. Fit a white inner support tube into each yellow tip.
 - 7.2.4. For each sample solution, fit a TEVA cartridge on to the inner support tube.
 - 7.2.5. Add syringe barrels (funnels/reservoirs) to the top end of each TEVA cartridge.
 - 7.2.6. Connect the vacuum pump to the box. Turn the vacuum pump on and ensure proper fitting of the lid.

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.

- 7.2.7. Add 5mL of 0.1M HNO₃ into each TEVA cartridge reservoir to condition the resin. Adjust vacuum to achieve a flow rate of 1-2mL/min. Allow solution to completely drain through each cartridge.

7.3. Eichrom TEVA separation:

Note: If samples have high levels of ²³⁴Th (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 7.1.14 into the appropriate Prefilter (if required) and TEVA Resin cartridge reservoirs.
- 7.3.1.2. Allow the sample solution to completely drain through each set of cartridges at 2mL/min.
- 7.3.1.3. Rinse the sample beaker with 5-10mL of water. Transfer the beaker rinse to the appropriate TEVA resin cartridge reservoir. Allow solution to completely drain through each cartridge.
- 7.3.1.4. Disengage vacuum. Empty centrifuge tubes to waste.
- 7.3.1.5. Add 50mL of 0.01M HNO₃ to each TEVA cartridge reservoir. Engage vacuum. Allow solution to completely pass through each cartridge at 2mL/min.
- 7.3.1.6. Disengage vacuum. Discard rinse as waste. **Proceed to section 7.4.**

Note: If measuring ⁹⁹Tc, ⁹⁷Tc, or Re by ICP-MS, an additional rinse of 50mL 1M HNO₃ 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 7.1.14 into the appropriate Prefilter (if required) and TEVA Resin cartridge reservoir.

- 7.3.2.2. Allow the sample solution to completely drain through each set of cartridges at 2mL/min.
- 7.3.2.3. Rinse the original beaker with 5-10mL of water. Transfer the beaker rinse to the appropriate TEVA cartridge reservoir.
- 7.3.2.4. Allow the rinse solution to completely drain through each cartridge at 2mL/min.
- 7.3.2.5. Disengage vacuum. Empty centrifuge tubes to waste. Rinse each TEVA cartridge with 25mL of 0.5M HF/0.02M HNO₃. Engage vacuum and allow solution to completely pass through each cartridge at 1-2mL/min.

Note: Alternately, 40mL of 0.25M NaF/0.02M HNO₃ or 25 mL of 1M NaF/0.02M HNO₃ may be used. This step will remove any residual ²³Th from the column.

- 7.3.2.6. Disengage vacuum. Empty centrifuge tubes to waste. Rinse TEVA with 50mL of 0.01M HNO₃. Engage vacuum and allow solution to completely pass through each TEVA cartridge at 2mL/min. Disengage vacuum. Discard the eluent. **Proceed to section 7.4.**

Note: If measuring ⁹⁹Tc, ⁹⁷Tc, or Re by ICP-MS, an additional rinse of 50mL 1M HNO₃ 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 HNO₃.

Note: Alternately, 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 HNO₃.

- 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 ⁹⁹Tc matrix standard by adding a known amount of ⁹⁹Tc 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 = yield = $\frac{(\text{spiked sample cpm} - \text{unspiked sample cpm})}{E \times \text{Tc-99 spike activity, dpm}}$

Note: If Tc-99m 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).



A BRAND OF
EICHROM TECHNOLOGIES

