TECHNETIUM-99 IN WATER

(WITH VACUUM BOX SYSTEM)

1. SCOPE

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

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 separated from water samples using TEVA Resin. ^{99}Tc is measured by liquid scintillation counting by either adding the resin directly to liquid scintillation cocktail or by stripping the technetium from the column and adding the ^{99}Tc to the cocktail for counting. Each sample is analyzed with and without a ^{99}Tc spike to determine chemical recovery. The short-lived gamma emitter, ^{99m}Tc, can also be used as a tracer. The detection limit for this method is 1 pCi/L.

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}S) 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. One liter of solution may be passed through a 2 mL prepacked TEVA Resin column without breakthrough of ^{99}Tc.

4.4. 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

- Cartridge reservoirs, 10mL (Eichrom Part: AR-200-RV10) or 20mL (Eichrom Part: AR-200-RV20)
- Glass beakers
- Liquid scintillation counter
- Liquid scintillation vials
- Vacuum box inner liner - For collection of load and rinse fractions, Eichrom Part: AR-12-LINER or AR-24-LINER
- 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

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 cartridge, 50-100μm, Eichrom Part TE-R50-S
Optional for removal of color from samples: *Prefilter cartridge*, 2mL prepacked cartridge, 100-150μm, Eichrom Part PF-R50-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 (8M) - Add 500 mL of concentrated HNO3 to 250mL of water. Dilute to 1L with water.

6.6. Nitric acid solution (1M) - Add 62.5mL of concentrated HNO3 to 900mL of water. Dilute to 1L with water.

7. PROCEDURE

7.1. Water Sample Preparation:

7.1.1. Measure the sample volume using a graduated cylinder (or equivalent) and transfer the volume to an appropriate size beaker.

7.1.2. Analyze each sample with and without adding Tc-99 spike to determine chemical recovery, or add appropriate yield tracer.

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.

7.1.3. Add 10mL of 30wt% H_2O_2 (per liter of sample) into each beaker, stir and cover each beaker with a watch glass. Remove covers once the samples begin boiling.

7.1.4. Heat each beaker to about 90°C for 1 hour to oxidize Tc to Tc (VII), forming TcO_4^-, oxidize some of the organics present, and destroy excess H_2O_2.

7.1.5. If bubbling due to decomposition of the hydrogen peroxide has not stopped as the sample cools, continue heating until bubbling has stopped. Stir occasionally with glass stirrer rod.

7.1.6. Allow beakers to cool to room temperature.

7.1.7. If the sample contains insoluble matter, filter the sample to remove solids prior to column loading.

7.2. TEVA Resin preparation:

7.2.1. Place the inner liner into the vacuum box. Fit the lid to the vacuum system box.

7.2.2. 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.

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

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

7.2.5. 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.

7.2.6. If organics that cause quenching are known to be present or may be present, place a prefilter cartridge directly above each TEVA Resin cartridge.

7.2.7. Add 5mL of 0.1M HNO_3 into each TEVA cartridge reservoir to condition the resin. Adjust vacuum to achieve a flow rate of 2mL/min. Allow solution to completely pass through each cartridge.

7.3. TEVA Resin separation:

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 water sample from step 7.1.7 into the appropriate Prefilter cartridge (if required in step 7.2.2) and TEVA Resin cartridge reservoir. Allow solution to completely pass through each cartridge at 2-3mL/min. Empty vacuum box liner as needed.

7.3.1.2. Rinse the sample beaker or with 5-10mL of water. Transfer this rinse to the appropriate TEVA resin cartridge reservoir. Allow solution to completely pass through each cartridge at 2-3mL/min.

7.3.1.3. Add 50mL of 0.01M HNO_3 into each TEVA resin cartridge reservoir. Allow solution to completely pass through each TEVA cartridge at 2-3mL/min.

7.3.1.4. Disengage vacuum. Discard the eluate as waste. **Proceed to section 7.4**.

7.3.2. Option #2 For samples containing high levels of Th-234

7.3.2.1. Transfer each water sample from step 7.1.7 into the appropriate Prefilter cartridge (if required in step 7.2.2.) and TEVA Resin cartridge reservoir. Allow solution to completely pass through each cartridge at 2-3mL/min. Empty vacuum box inner liner as necessary.

7.3.2.2. Rinse the sample beaker with 5-10mL of water. Transfer the rinse to the appropriate TEVA resin cartridge. Allow solution to completely pass through each cartridge at 2-3mL/min.

7.3.2.3. Add 5mL of 0.01M HNO_3 into each TEVA cartridge reservoir. Allow solution to completely pass through each cartridge at 2-3mL/min.

7.3.2.4. Add 25mL of 0.5M HF/0.02M HNO_3 to each TEVA cartridge reservoir. Allow solution to completely pass through each cartridge at 2mL/min.

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.

7.3.2.5. Add 5mL of 0.1M HNO_3 to each TEVA cartridge reservoir. Allow solution to completely pass through each cartridge at 2mL/min. Disengage vacuum. Dispose of eluate as waste. **Proceed to section 7.4.**

7.4. Counting preparation options:

7.4.1. Resin counting option (most rapid)

7.4.1.1. Remove the top frit and extrude the resin with a minimum volume of water into an LSC vial. Rinse each cartridge body with 3mL water to complete resin transfer.

7.4.1.2. Add 10mL of the scintillation cocktail into each vial containing the resin. Cap the vial and shake well. GOTO 7.5.1.

Note: Ultima Gold - XR™ or Ultima Gold - AB™ is suggested. Opti-Fluor™ or Insta-Gel XF™ or Ultima gold-LLT cocktails may also be used. Insta-Gel XF™ is less desirable from an environmental, waste disposal standpoint and is not required to fix the geometry since the extractant is stripped from the resin and homogeneously dispersed throughout the cocktail.

7.4.2. Tc-99 column stripping option:

7.4.2.1. Place a clean, labeled centrifuge tube below each TEVA Resin cartridge.

7.4.2.2. Add 20mL of 8M HNO_3 into each TEVA cartridge reservoir to elute the Tc-99. Allow to drain at 1mL/min. GOTO 7.4.2.3 or 7.4.2.4.

7.4.2.3. *Direct Addition of Strip Solution to Cocktail option:*

7.4.2.3.1. Add 1mL of the 8M HNO_3 from step 7.4.2.2 into a liquid scintillation vial.

7.4.2.3.2. Add 2mL of water, swirl to mix and add 10 mL of Ultima-Gold XR™ or Ultima-Gold AB™ scintillation cocktail.

Note: Ultima-Gold XR™ and Ultima-Gold AB™ are much more tolerant of acid than Opti-Fluor™, tolerating up to approximately 2 mL of 4M HNO_3 per 10 mL of cocktail.

7.4.2.3.3. Cap each vial, mix well and GOTO step 7.5.2.

7.4.2.4. Evaporation of strip solution option:

7.4.2.4.1. Transfer ^{99}Tc samples in 8M HNO3 to appropriately sized glass beakers. Heat the beakers gently, not greater than 80°C, until the volume in each beaker is about 10 mL.

7.4.2.4.2. Transfer each solution from step 7.4.2.4.1 into a glass liquid scintillation vial.

7.4.2.4.3. Add two 2mL volumes of water to each beaker and transfer each rinse solution to the appropriate glass liquid scintillation vial.

7.4.2.4.4. Heat the vial gently (not greater than 80°C) until the solution volume is <1mL. Allow to cool, add 2mL of water and swirl to mix.

Note: Use a separate glass scintillation vial filled to exactly 0.5 mL for volume comparison. If necessary, adjust the volume back up to 0.5 mL with water. Do not go to dryness to avoid volatilizing Tc-99. If quenching problems occur, evaporate to a volume less than 0.5 mL.

7.4.2.4.5. Add 10mL of liquid scintillation cocktail (or more volume, if desired) into each vial. Cap each vial, mix well and GOTO step 7.5.2.

7.5. Liquid scintillation counting:

7.5.1. Resin counting option:

7.5.1.1. 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.

7.5.1.2. 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. GOTO step 7.5.3.

7.5.2. ^{99}Tc column stripping option:

7.5.2.1. Prepare a blank by preparing a vial containing the same amount of 8M HNO_3 and scintillation cocktail as used in the column stripping method to determine background counts.

7.5.2.2. Prepare a ^{99}Tc matrix standard by adding a known amount of ^{99}Tc to a vial containing the same amount of 8M HNO_3 and scintillation cocktail used in the Tc-99 column stripping option to determine counting efficiency.

Note: If the evaporation option was used, evaporate the 8M HNO_3 used to prepare the blank and standard just as the samples were prepared.

7.5.3. Set up the scintillation counting window to measure from 20 Kev to 300 keV or alternate window optimized for the measurement of the ^{99}Tc beta emission.

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:

$$\text{Sample dpm/L} = \frac{(S - B) * D}{E * V * Y}$$

Where:

S = sample counts/time in minutes, cpm
B = blank counts/time in minutes, cpm, steps 7.5.1.1 (resin counting option) or 7.5.2.1 (stripping option).
E = counting efficiency = measured cpm/dpm of Tc-99 matrix standard, steps 7.5.1.2 (resin option) or 7.5.2.2 (strip option)
V = sample volume, L
Y = yield = $\frac{\text{(spiked sample cpm - unspiked sample cpm)}}{\text{E x Tc-99 spike activity, dpm}}$

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

$$\text{Yield} = \frac{(Cs - Bs)}{Es * As}$$

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

D = dilution factor = V_s / V_p, included in calculation only if column strip method with direct addition to cocktail is used, step 7.4.2.3

Where:

V_s = strip volume, 20mL
V_p = volume of strip solution (8M HNO_3) pipetted into cocktail, mL

Conversion of dpm/L to pCi/L: pCi/L=(dpm/L)/2.22

9. PRECISION AND BIAS

9.1. *Precision* - A relative standard deviation of 3.4% at the 10,000 dpm level has been reported for procedure option #1 (7.3.1.)

9.2. *Bias* - A mean recovery of 92.5% has been reported for procedure option #1 (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).
5) ASTM Method D7168-11, "Standard Test Method for 99Tc in Water by Solid Phase Extraction Disk."

1) Aliquot up to 1000mL of sample into glass beaker.
2) Add appropriate tracer and 10mL of 30% H_2O_2.
3) Place a watch glass on beaker and heat at 90°C for 1 hour.
4) Cool sample.
5) If necessary, filter sample to remove solids.
6) If necessary, user prefilter column to remove colored material.
Water Sample in glass beaker.
Heat with 10mL of 30% H_2O_2
If necessary, filter to remove solids
or use prefilter to remove color.
7) Precondition TEVA cartridge with 5mL 0.1M HNO_3.
8) Load sample on to TEVA. Allow liquid to drain to waste. Tc is retained.
9) Rinse sample beaker with 5mL water.
Add beaker rinse to TEVA.
10) If sample contains Th-234/natural U, rinse TEVA with 25mL 0.5M HF-0.02M HNO_3.
11) Rinse TEVA with 50mL 0.01M HNO_3.
Allow liquid to drain to waste.
12) Extrude resin into LSC vial or strip Tc with 20mL 8M HNO_3.
2mL
TEVA
Cartridge
(7) (8) (9) (10) (11)
Waste
(12)
Tc sample to preparation for
measurement technique