TECHNETIUM-99 IN WATER

(TEVA DISC METHOD)

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 Eichrom's TEVA Disc prior to liquid scintillation counting. After concentration of the pertechnetate ion (TcO_4^-) on the disc, ^{99}Tc is measured by liquid scintillation counting by adding the disc directly to the scintillation cocktail. The sample can be 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 (37 mBq/L).

3. SIGNIFICANCE OF USE

3.1. This is a rapid, reliable method for measurement of ^{99}Tc in environmental samples that combines the selectivity of Eichrom's TEVA Resin with the fast flow rates achievable with a disc format.

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.

4.3. Up to six (6) liters of solution may be passed through an Eichrom TEVA Disc without breakthrough of ^{99}Tc. Larger volumes have not been tested.

4.4. In samples high in natural uranium, it has been observed that trace amounts of ^{234}Th remain on the TEVA Disc. This causes a positive bias in the ^{99}Tc window during LSC. A rinse with HF or NaF is used in column methods to elute all residual Th. These solutions are not compatible with Eichrom's TEVA Disc. In this method, 0.5M HCl is used in place of the HF/NaF rinse.

5. APPARATUS

- Beakers, glass
- Filter apparatus: suitable to hold 47mm TEVA Disc: Nalgene reusable filter holder recommended (Nalgene part: 300-4000 or 300-4050 or 300-4100)
- Forceps
- Liquid scintillation counter
- Liquid scintillation vials, glass
- Watch glass

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
Hydrochloric acid (37%), concentrated HCl
Hydrogen peroxide (30%), concentrated H_2O_2
Liquid Scintillation Cocktail
TEVA® Disc, 47 mm, Eichrom Part TE-D50-F (50 discs)

6.1. *Hydrochloric acid (0.5M)* - Add 41.7mL of nitric acid 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. Adjust the pH of the sample to pH 2, if required.

7.1.3. Analyze the 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 gamma activity of ^{99m}Tc. If ^{99m}Tc is used, allow the ^{99m}Tc to decay for approximately 1 week after measuring the gamma activity and before measuring ^{99}Tc using liquid scintillation counting.

7.1.4. Add 10mL of 30wt% H_2O_2 (per liter of sample) to the beaker, stir and cover with a watch glass. Remove cover once the sample begins to boil.

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

7.1.6. 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 stirring rod.

7.1.7. Allow the beaker to cool to room temperature.

7.1.8. If the sample contains insoluble matter, filter the sample to remove solids prior to using the TEVA Disc.

7.2. Eichrom TEVA Disc separation

7.2.1. Using forceps, carefully place a TEVA Disc on the filtering apparatus.

7.2.2. Place the funnel over the disc and transfer the water sample from step 7.1.7 into the filtering funnel.

7.2.3. Allow the sample solution to filter through the disc by gravity or vacuum. (No vacuum is necessary.) Depending on which filtering apparatus is used, it is possible to achieve a flow rate as high as 33 mL/min with gravity. An average of 98%

Tc-99 recovery achieved using 200 mL/min with vacuum on 1 L simulated ground water sample type.

7.2.4. After filtering the sample, rinse the original beaker or container with the minimal volume of water required (depending on beaker size) and transfer this rinse into the filtering funnel.

7.2.5. Allow the rinse solution to drain through the disc completely.

7.2.6. Rinse disc with 25mL 0.5M HCl.

7.2.7. Rinse disc with 100mL of water.

7.2.8. Rinse the sides of the funnel with 5mL of water. This will remove any residual material of the disc which may have suspended during filtration.

7.2.9. Connect the filtering apparatus to a vacuum pump (if gravity flow used to this point) and apply vacuum for a few seconds to remove any residual liquid from the disc. Alternately, if the filtration apparatus has a Luer fitting, attach a 50cc syringe and draw residual liquid from the disc.

7.3. Counting preparation:

7.3.1. With forceps, remove the TEVA Disc from the filtering apparatus and transfer it into a liquid scintillation vial.

Note: The disc can be rolled gently while it is still on the filter apparatus so that it can be easily inserted into the LSC vial.

7.3.2. Add 15mL of Ultima Gold LLT into the LSC vial containing the disc. Cap the vial and vortex until the disc disintegrates and forms a colorless translucent gel.

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

8. CALCULATIONS

Calculate chemical yield

Measurement of spiked and unspiked samples

$$Y = \frac{(C_S - C_U)}{E \times A_S}$$

where:

Y = chemical yield
C_s = count rate spiked sample, cpm
C_U = count rate unspiked sample, cpm
E_s = counting efficiency for Tc-99
A_s = Tc-99 tracer activity, dpm, corrected for decay from reference date

Tc-99m (or Tc-95m) Tracer Method

$$Y = \frac{(C_s - B_s)}{E_s * A_s}$$

where:

C_s = measured Tc-99m (or Tc-95m) tracer, gamma cpm
B_S = background, gamma cpm
E_s = gamma counting efficiency for Tc-99m (or Tc-95m)
A_s = Tc-99m (or Tc-95m) tracer activity, dpm, corrected for decay from reference date

Calculate the Tc-99 activity as follows:

$$A = \frac{(S-B)}{E \times V \times Y \times 60}$$

where:

A = Tc-99 activity in the sample (Bq/L)
S = sample counts/time in minutes, cpm
B = blank counts/time in minutes, cpm
E = counting efficiency for Tc-99 determined from a direct spike of Tc-99 in LSC vial containing a TEVA Disc dissolved in 15 mL Ultima Gold LLT.
V = sample volume, L
Y = chemical yield (determined in section 8.1)
60 = conversion from cpm to cps

9. REFERENCE

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 ^{99}Tc in Water by Solid Phase Extraction Disk.”