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Technetium-99 in Water

1. Scope

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

2. Summary of Method

- 2.1 Technetium-99 is separated from water samples using TEVA Resin prior to liquid scintillation counting. After removal of the pertechnetate ion, TcO_4^- , with TEVA Resin, Tc-99 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 Tc-99 to the cocktail for counting. Each sample is analyzed with and without a Tc-99 spike to determine chemical recovery. Alternately, the short-lived gamma emitter, Tc-99m, can be used as a tracer. The detection limit for this method is 1 pCi / L.

3. Significance of Use

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

4. Interferences

- 4.1 All radionuclides that undergo beta emission or quench the liquid scintillation counting are effectively removed (including C-14, P-32, S-35, and Sr-90) using TEVA Resin. Tritium may sometimes follow the technetium due to the absorption of tritium-labeled compounds by the resin. Possible interference by tritium is eliminated by setting the Tc-99 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 L of solution may be passed through a 2 mL prepacked TEVA Resin column without breakthrough of Tc-99.

5. Apparatus

- 5.1 *Column rack, single or double decker if prefilter column required*
- 5.2 *Glass beakers*
- 5.3 *Liquid scintillation counter*
- 5.4 *Liquid scintillation vials, glass (column strip option with evaporation)*
- 5.5 *Liquid scintillation vials, polyethylene*
- 5.6 *Watch glasses*

6. Reagents

- 6.1 Unless otherwise indicated, all references to water should be understood to mean deionized distilled water.
- 6.2 *Hydrogen peroxide (30 wt %)*
- 6.3 *Liquid scintillation cocktail - Ultima Gold-XR™ or Ultima Gold-AB™*
- 6.4 *Nitric acid solution (0.1M)* - Add 6.4 mL of concentrated nitric acid (sp gr 1.42) to 950 mL of water and dilute to 1 L with water.
- 6.5 *Nitric acid solution (12M)* - Add 764 mL of concentrated nitric acid (sp gr 1.42) to 150 mL of water and dilute to 1 L with water.
- 6.6 *Nitric acid solution (0.01M)* - Add 100 mL of 0.1M nitric acid to 800 mL of water and dilute to 1 L with water.
- 6.7 *Prefilter column (Eichrom)*
- 6.8 *TEVA Resin* - prepacked columns, medium particle size, with top frit replaced with glass wool (so resin can be extruded later) or small particle size (50-100 µm) in appropriate plastic column.

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.

Note: An alternative is to use Tc-99m as a tracer, measuring the short-lived gamma activity of Tc-99m (6.02 hour half-life) using gamma counting, allowing the Tc-99m to decay for approximately 1 week and then measure the Tc-99 beta cpm using liquid scintillation counting.
- 7.1.3 Pipet 10 mL of 30 wt % H₂O₂ (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 TcO₄⁻, oxidize some of the organics present, and destroy excess H₂O₂.
- 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 column preparation:*

- 7.2.1 For each sample aliquot analyzed, place a TEVA Resin column in a column rack.
- 7.2.2 If organics that cause quenching are known to be present or may be present, place a prefilter column directly above each TEVA Resin column.
- 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 Pipet 5 mL of 0.1M HNO₃ into each column to condition the resin and allow to drain.

7.3. *TEVA Resin column separation:*

7.3.1 Transfer each water sample from step 7.1.7 into the appropriate prefilter (if required) and TEVA Resin columns.

Note: One option of loading a large sample volume is as follows: transfer the sample to a 1 L polyethylene bottle, which is attached to an empty 50 mL disposable column, followed in line by the prefilter and TEVA Resin columns. Invert the assembly to begin sample flow and, if needed, punch pinholes in the top of the bottle to improve flow rate.

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

7.3.3 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.

7.3.4 Allow the rinse solution to drain through each column.

7.3.5 Pipet 50 mL of 0.01M HNO₃ directly into each column.

Note: As a time-saving step, this volume may be reduced, for example, to 25 mL if tests confirm that adequate clean-up is achieved for certain routine sample types.

7.3.6 Allow the 0.01M HNO₃ rinse solution to drain through each column. Discard the rinses.

7.4. *Counting preparation options:*

7.4.1 *Resin counting option (most rapid):*

7.4.1.1 Transfer the TEVA Resin into a liquid scintillation vial by removing the glass wool, attaching a syringe to the column tip and washing the resin from each column with 3 mL of 0.01M 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 0.01M HNO₃.

7.4.1.2 Add 10 mL of the scintillation cocktail into each vial containing the resin. Cap the vial and shake well. GOTO 7.6.1.

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 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 glass beaker or vial below each TEVA Resin column.

7.4.2.2 Pipet 20 mL of 12M HNO₃ into each column to elute the Tc-99. Allow to drain. 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 Pipet 0.5 mL of the 12M HNO₃ from step 7.4.2.2 into a liquid scintillation vial.

7.4.2.3.2 Add 2 mL 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 HNO₃ per 10 mL of cocktail.

7.4.2.3.2 Cap each vial, mix well and GOTO step 7.6.2.

7.4.2.4 Evaporation of strip solution option:

7.4.2.4.1 To minimize dilution, heat the beakers from step 7.4.2.2 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 2 mL 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 0.5 mL ± 0.1 mL. Allow to cool, add 2 mL 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 Pipet 10 mL of liquid scintillation cocktail (or more volume, if desired) into each vial. Cap each vial, mix well and GOTO step 7.6.2.

7.6 *Liquid scintillation counting:*

7.6.1 *Resin counting option:*

7.6.1.1 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.

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

7.6.2 *Tc-99 column stripping option:*

7.6.2.1 Prepare a blank by preparing a vial containing the same amount of 12M HNO₃ and scintillation cocktail as used in the column stripping method to determine background counts.

7.6.2.2 Prepare a Tc-99 matrix standard by adding a known amount of Tc-99 to a vial containing the same amount of 12M HNO₃ and scintillation cocktail used in the Tc-99 column stripping option to determine counting efficiency.

Note: If the evaporation option was used, evaporate the 12M HNO₃ used to prepare the blank and standard just as the samples were prepared.

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

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

7.6.5 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.

7.6.6 Analyze a blank with each set of samples analyzed.

8. Calculations

8.1 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
- E = counting efficiency = measured cpm/dpm of Tc-99 matrix standard, steps 7.6.1.2 (resin option) or 7.6.2.2 (strip option)
- V = sample volume, L

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

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

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

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

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 (12M HNO₃) pipetted into cocktail, mL

Conversion of dpm/L to pCi/L:

$$\text{pCi/L} = (\text{dpm/L}) / 2.22$$

9. Precision and Bias

- 9.1 *Precision* - A relative standard deviation of 3.4% at the 10,000 dpm level has been reported.
- 9.2 *Bias* - A mean recovery of 92.5% has been reported. Since results are corrected based on spike recovery, no significant bias exists for the method.

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