AP5

DETERMINATION OF TECHNETIUM-99

PART A

PRINCIPLE

Solid samples are leached with dilute nitric acid. The leachates are passed through an extraction chromatographic column containing a resin (TEVA resin) which is highly specific for technetium in the pertechnatate form. The technetium is absorbed onto the extraction resin. The resin is added to a scintillation vial containing an appropriate cocktail and counted using a liquid scintillation analyzer. Water samples are treated as leachates and carried through the same procedure. All interfering beta emitting radionuclides are effectively removed (including C-14, P-32, S-35, Sr-90, Y-90, and Th-234) using TEVA resin under the conditions in this procedure. Tritium may follow technetium due to the absorption of some tritium-labeled compounds by the resin. Possible tritium interferences are eliminated by setting the technetium counting window above the maximum energy for tritium beta particles.

REFERENCES

1. Eichrom Industries, Inc., Analytical Procedures, "Technetium-99 in Soil", April 29, 2002.

2. F.O. Hoffman et al. <u>Sampling of Technetium-99 in Vegetation and Soils in the Vicinity of Operating Gaseous Diffusion Plants.</u> ORNL/TM-7386.

3. DOE Methods Compendium RP550. "Technetium-99 Analysis Using Extraction Chromatography".

4. 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.

5. Wyse, E.J. and Fadeff, S.K., "Alternative Techniques for the Determination of Technetium-99 in Groundwater: ICP/MS and Extraction Resin", To be submitted for publication.

6. Eichrom Industries, Inc., Analytical Procedures, "Technetium-99 in Water", April 2, 2002.

Certification Record for

PROCEDURE AP5

DETERMINATION OF TECHNETIUM-99

CHECKPOINTS

1. JOB HAZARD ANALYSIS(JHA) _____ ___________
2. MSDS/HAZARDS DISCUSSED _____ ___________
3. SAMPLE PREPARATION _____ ___________
4. Tc LEACHING _____ ___________
5. COLUMN PREPARATION _____ ___________
6. EXTRUSION OF RESIN _____ ___________
7. COUNTING PREPARATION _____ ___________
8. FINAL CALCULATIONS

ANALYST SIGNATURE: ____

CERTIFIED BY: ____

DATE: ____

ANALYSIS VALUE: ____

KNOWN VALUE: ____

MEASURED/KNOWN RATIO: ____

COMMENTS:____
____
____
____

PART B

1.0 PURPOSE AND SCOPE

This is a procedure for the determination of technetium-99 in sediment, soil, smears, and water at environmental levels.

2.0 REAGENTS

All chemicals are hazardous. See MSDS for specific precautions. **See step 2.0 of AP5 JHA.** Unless otherwise indicated, all references to water should be understood to mean reagent grade water.

Ammonium hydroxide, NH_4OH, 14.8 M, concentrated, reagent grade.

Ammonium hydroxide, NH_4OH, 4 M, slowly add 135 mL 14.8 M NH_4OH to 300 mL reagent water. Dilute to 500 mL with reagent water. Mix well.

Hydrofluoric acid, HF, 28 M, concentrated, reagent grade.

Hydrofluoric acid, HF, 1 M, slowly add 18 mL 28 M HF to 400 mL water. Dilute to 500 mL with water and mix.

Hydrogen peroxide, H_2O_2, 30-35% (w/v).

Nitric acid, HNO_3, 0.01 M, slowly add 10 mL 1 M HNO_3 to 900 mL water. Dilute to 1 L with reagent water and mix.

Nitric acid, HNO_3, 1 M, slowly add 64 mL 16 M HNO_3 to 900 mL water. Dilute to 1 L with reagent water and mix.

Nitric acid, HNO_3, 16 M, concentrated, reagent grade.

Nitric acid (0.02 M) - Hydrofluoric acid (0.05 M) solution: Add 10 mL 1 M HNO_3 to 25 mL 1 M HF. Dilute solution to 500 mL with water and mix well.

Liquid Scintillation Cocktail, Ultima Gold-XR or equivalent

TEVA Resin, prepacked 2 mL columns, 100-150 µm size or prepacked cartridges.

Technetium-99, standardized solution

3.0 APPARATUS

Balance
Beakers, appropriate for sample matrix
Centrifuge
Centrifuge tubes
Column rack
Column snips
Extension funnels, 25 mL
Filters, Supor-450, 25mm, or equivalent
Hotplate
Liquid Scintillation Analyzer
pH paper
Scintillation Vials
Vacuum Box Assembly
Watch glasses

4.0 PROCEDURE

4.1 General Requirements

Before proceeding, you must be certified as indicated in QCP1 of this manual and Section 3 of the QA Manual. See page two for a copy of the certification record.

A batch yield sample must be run with each batch to determine chemical recovery for the batch (see section 6.0 for calculation). This is not a QC sample; two QC samples must be run with each batch.

4.2 Water Samples

Measure the water sample using a volumetric flask and pour into an appropriate size beaker. Use reagent water for a method blank. Adjust samples, blank, batch yield sample, and Laboratory Control Sample (LCS) to pH of 2 using either 1 M HNO_3 or 4 M NH_4OH. Go to step 4.3.8. **See step 4.2 of AP5 JHA**.

4.3 Soil, sediment, and smear samples

4.3.1 Weigh up to 10 g of soil, sediment, or solid material in an appropriate size beaker. Use clean sand for a method blank. Place smear in a beaker. Use a clean smear for method blank. **See step 4.3.1 of AP5 JHA**.

4.3.2 Add 50 mL of 1 M HNO_3 to each beaker. Add 1 mL 30% H_2O_2 to each beaker. **See step 4.3.2 of AP5 JHA**.

4.3.3 Place a watch glass on each beaker on a hot plate and heat to 80°C for 4 hours, while stirring. Add 1 M HNO_3 as needed to keep volume at 50 mL. **See step 4.3.3 of AP5 JHA**.

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

4.3.5 Transfer the solution and solids to a centrifuge tube using water and centrifuge for approximately 10 minutes at 2000 rpm. **See step 4.3.5 of AP5 JHA**.

4.3.6 Decant supernatant into a 150 mL beaker.

4.3.7 Add 10 mL of 1 M HNO_3 to the centrifuge tube. Vortex, and centrifuge for 5 minutes at 2000 rpm. Add supernate to the 150 mL beaker. Discard solids to the appropriate waste stream. **See step 4.3.7 of AP5 JHA** .

4.3.8 Add 1-5 mL of 30% H_2O_2 (use 1 mL per 50 mL of solution). Heat to 80°C with stirring until the effervescence disappears. **See step 4.3.8 of AP5 JHA.**

Note: It is imperative that all the H_2O_2 is decomposed. If any H_2O_2 remains, the flow rate may decrease or even stop.

4.3.9 Allow beakers to cool to room temperature.

4.3.10 Filter samples with visible solids using Supor-450 filter paper. **See step 4.3.10 of AP5 JHA**.

4.3.11 For solid samples, adjust pH to 2 slowly and with stirring using 4 M NH_4OH. If the addition of the NH_4OH is too rapid, iron (III) hydroxide may form and will be difficult to re-dissolve. **See step 4.3.11 of AP5 JHA.**

4.4 Column Preparation

NOTE: Either a TEVA resin column or a TEVA resin cartridge may be used. The steps that follow are the same for both the column and cartridge except for two items. First, the flow rate for the column is forced by gravity and the flow rate for the cartridge is forced by a vacuum pump. **Using the vacuum pump, do not exceed a flow rate of 1 mL per minute**. Second, the way the resin is extruded prior to counting is different. For the column, the tip is cut off and the resin is placed in a scintillation vial. For the cartridge, air is passed through the cartridge until the resin is dried and then the resin is poured into a scintillation vial.

4.4.1 Place either the TEVA Resin column in a column rack or a TEVA cartridge in the vacuum box assembly.

4.4.2 If using the cartridge method, go to step 4.4.3. If using the column method place a beaker below each column, remove the bottom plug from each column, allowing each column to drain. **See step 4.4.2 of AP5 JHA**.

4.4.3 Pipette 5 mL of 0.01 M HNO_3 into each TEVA Resin column or cartridge to condition the resin and allow to drain. If using the cartridge method, do not exceed a flow rate of 1 mL per minute. **See step 4.4.2 of AP5 JHA.**

4.5 Tc-99 column separation

4.5.1 Transfer each sample leachate from step 4.3.9 (water samples) or 4.3.11 (solid samples) to a labeled column or cartridge, allow the leachate to flow through and discard to the appropriate waste stream. **See step 4.5.1 of AP5 JHA**.

4.5.2 Rinse beaker with 5 mL 0.01 M HNO_3. Transfer rinse to column or cartridge and allow to drain. **See step 4.5.1 of AP5 JHA**.

4.5.3 Pipette 25 mL 0.02 M HNO_3 - 0.05 M HF solution directly into each column or cartridge, allow to drain and discard to the appropriate waste stream. **See step 4.5.3 of AP5 JHA.**

Note: If greater sample cleanup is needed (i.e. samples which may contain high levels of natural uranium or Th-234), add up to 25 mL of 0.02 M HNO_3 - 0.05 M HF solution to enhance the Tc-99 purification.

4.5.4 Pipette 5 mL 0.01 M HNO_3 into each column or cartridge and allow to drain. **See step 4.5.4 of AP5 JHA**

4.5.5 If using columns, transfer the resin to a liquid scintillation vial by carefully cutting the plastic column with the column snips near the bottom and pushing the resin into the vial using a glass stir bar. If using cartridges, pull air through the cartridge with a strong vacuum for 10 minutes. Pry open the top of the cartridge with pliers and pour the dry resin into a scintillation vial (you may need to squeeze the cartridge with pliers). **See step 4.5.5 of AP5 JHA**.

4.5.6 Add 10 mL of the desired scintillation cocktail to each vial, cap, shake well, and allow the resin to settle for at least one hour before submitting for counting. **See step 4.5.6 of AP5 JHA**.

Note: It is important to shake the vial well to completely strip all the Tc from the resin.

5.0 CALIBRATION

5.1 Create an efficiency standard by transferring the resin from a new TEVA column or cartridge to a liquid scintillation vial by using the procedure described in step 4.5.5. **See step 5.1 of AP5 JHA**.

5.2 Add 10 mL of the desired scintillation cocktail to each vial, cap, and shake well. **See step 5.2 of AP5 JHA**. .

5.3 Using a NIST traceable Tc-99 standard add approximately 2000 pCi to the scintillation vial containing the resin from the previous step. Cap the vial and shake well. **See step 5.3 of AP5 JHA**.

Note: It is important to shake the vial well to completely strip all the Tc from the resin.

5.4 This efficiency standard is counted with each sample batch. The calculated efficiency and the quench indicating parameter (tSIE) are monitored to ensure that the efficiency standard does not deteriorate. If the calculated efficiency does not agree with the established value, a new efficiency standard is prepared. If the tSIE value does not agree within 20 percent of the established value, a new efficiency standard is prepared.

6.0 CALCULATIONS

Critical data values will be documented on standard forms maintained as critical records. The following equations define the critical data values. All data will be recorded and reduced according to these calculations.

NOTE: The analyst and reviewer must ensure that the tSIE values for all samples in a batch agree within ± 20% of the tSIE values for the detector background and the efficiency standard.

$$Concentration = \frac{G - B}{Q \cdot E \cdot Y} = pCi / unit$$

$$2\sigma\ Error = \frac{1.96\sqrt{(G + B) \cdot T}}{Q \cdot T \cdot E \cdot Y} = pCi / unit$$

$$2\sigma\ TPU = C \cdot 1.96\sqrt{\frac{(G+B)\cdot T}{((G-B)\cdot T)^2} + RY^2 + RE^2 + RQ^2} = pCi/unit$$

$$MDC = \frac{3 + 4.65\sqrt{B \cdot T}}{Q \cdot T \cdot E \cdot Y} = pCi/unit$$

Efficiency: $$E = \frac{G_E - B}{E_{ACT}} = cpm/pCi$$

Yield: $$Y = \frac{G_{BY} - B}{E \cdot By_{ACT}}$$

where:

B	=	background cpm beta
By_{ACT}	=	pCi of Tc-99 added to batch yield sample
C	=	concentration in pCi/unit
E	=	counting efficiency (cpm/pCi)
E_{ACT}	=	pCi of Tc-99 added to efficiency standard
G	=	sample gross cpm beta
G_E	=	efficiency standard gross cpm beta
G_{By}	=	batch yield gross cpm beta
MDC	=	minimum detectable concentration
Q	=	quantity
RE	=	1σ relative uncertainty of the efficiency
RY	=	1σ relative uncertainty of the yield
RQ	=	1σ relative uncertainty of the quantity
T	=	time minutes
TPU	=	total propagated uncertainty
Y	=	chemical yield

7.0 RECORDS

7.1 Reference QA Manual for general record requirements.

7.2 The raw count data is saved during the weekly backup of the Liquid Scintillation Analyzer to the ORISE network disks.

7.3 Hard copies of assignment and calculation sheets are maintained in the archived site file. Electronic copies of assignment and calculation sheets are saved during the daily incremental backup of the network system. The following data sheets should be completed and retained:

- Tc-99 Analysis Assignment Form
- Tc-99 Lab Data Sheet
- Tc-99 Concentration and Uncertainty Report

AP5(Rev 16) - Tc-99 ANALYSIS ASSIGNMENT FORM

Assigned To: ______________ **Date:** ______________ **Batch:** ______________

Task #: ______________ **LWR #:** ______________ **Activity Level*:** ______________

Sample #s: ____

____

____

Analysis Required:

Batch Yield ☐ **Sample#** ______________________
Initial below sample

Tc-99 STD # ______________________ **Quantity:** ______________
Units: ______________

Eff. Spike ☐ **Tc-99 STD #** ______________________ **Quantity:** ______________
(see Special Instructions, if any) **Units:** ______________

QC Required:

Blank ☐

LCS ☐ **Tc-99 STD #** ______________________ **Quantity:** ______________ **Initials** ☐
Units: ______________
Pipette # ______________ Volume (mL) ______________ Weight (g) ______________

Replicate ☐ **Sample #** ______________________ **# Replicates** ______________

Matrix Spike ☐ **Sample #** ______________________

Tc-99 STD # ______________________ **Quantity:** ______________ **Initials** ☐
Units: ______________

SPECIAL INSTRUCTIONS: ____

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* If Activity Level is indicated as Moderate or High, perform area survey.

COMMENTS: ____

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AP5(Rev 16) - Tc-99 LAB DATA SHEET

BATCH YIELD SAMPLE

Sample #							
Quantity							
Units							

Sample #							
Quantity							
Units							

Sample #							
Quantity							
Units							

Sample #			
Quantity			
Units			

AP5(Rev 16) - Technetium-99 (by batch yield) Concentration and Uncertainty Report

INPUT BY:

DATE:

TASK#

BATCH#

Batch Yield (BY) Calculation	
BY sample ID	
BY sample cpm	
BY Sample Quantity (SQ)	
BY SQ error	
Sample cpm	
SQ	
SQ error	
BY pCi added	
By pCi added error	
BY	
BY Error	
BY Relative Error	

Efficiency (Eff) Calculation	
Eff spike cpm	
Background cpm	
pCi added	
pCi added error	
Eff (cpm/pCi)	
Eff Error (cpm/pCi)	
Eff Relative Error	

Counting time for Eff and BYcalculations (min)	

Position #	SAMPLE ID	GROSS cpm	SQ	SQ ERROR	UNITS	TIME (min)	CONC.	TPU	4.65 sigma MDC
1									
2									
3									
4									
BY									
BY Sample									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

Tc-99 Known Activity	**Unc.**	**Meas./ Known**	**Unc.**

BLANK CORRECT? YES[ ] NO[ ] INIT________

LCS CORRECT? YES[ ] NO[ ] INIT________

BATCH YIELD CORRECT? YES[ ] NO[ ] INIT________

IF NO, SPECIFY REASON:

ANALYST REVIEW:______________________ DATE:______________

REVIEWED BY:______________________ DATE:______________

GIVEN TO:______________________ DATE:______________

QC ENTERED BY:______________________ DATE:______________