Technetium

Environmental Measurements Laboratory
U.S. Department of Energy

Tc-01-RC

TECHNETIUM-99 IN WATER AND VEGETATION
(*see Volume II*)

Tc-02-RC

TECHNETIUM-99 IN WATER - TEVA Resin

Contact Person(s): Salvatore C. Scarpitta*

APPLICATION

This procedure has been applied to the analysis of water.

The sample containing ^{99}Tc is equilibrated with ^{95m}Tc, a gamma-emitting tracer. The technetium is separated from other elements by ferric and ferrous hydroxide precipitation from ammoniacal solutions. The sample is then passed through a commercially available column that selectively extracts Tc(VII) from a 0.1M HNO_3 solution. Technetium is purified, eluted from the column and counted directly in a suitable liquid scintillation cocktail. Typically, the sample is counted for 1 h to simultaneously determine ^{99}Tc activity and the ^{95m}Tc recovery.

Quench/efficiency calibration curves need to be established for the liquid scintillation spectrometer for both ^{95m}Tc and ^{99}Tc.

SPECIAL APPARATUS

1. Packard Tri-Carb 2250CA using Insta-Gel liquid scintillation cocktail - Packard Instrument Co., 1 State St., Meriden, CT 06540 or equivalent.

**Currently at Brookhaven National Laboratory, BSA, Upton, NY 11973.*

2. Column reservoir - 25 mL capacity (Part No. AC-120) - Eichrom Industries, Inc., 8205 Cass Ave., Suite 107, Darien, IL 60561 or equivalent.

SPECIAL REAGENTS

1. TEVA extraction chromatographic columns - (Part # TE-C50, 80-160 micron size) - Eichrom Industries, Inc. or equivalent.

2. ^{99}Tc standard solution - available from NIST.

3. ^{95m}Tc tracer solution (free from ^{97m}Tc) - prepare a solution containing about 8 Bq mL^{-1} in 0.1M NH_4OH - Brookhaven National Laboratory, BSA, Upton, NY 11973.

4. 6M sodium hydroxide solution - 240 g NaOH L^{-1} of water.

5. 2M sodium carbonate solution - 212 g Na_2CO_3 L^{-1} of water.

6. Calcium carrier solution, 200 mg of calcium mL^{-1} - dissolve 500 g of $CaCO_3$ in a minimum of 6M HCl and dilute to 1 L with 0.1M HCl.

7. Barium carrier solution, 20 mg of barium mL^{-1} - 30.4 g $BaCl_2$ L^{-1} in 1 L of 0.1M HCl.

8. Iron carrier solution, 5 mg of iron mL^{-1} - dissolve 36 g $Fe(NO_3)_3 \cdot 9\ H_2O$ in 1 L of 0.1M HNO_3.

9. $Fe(II)SO_4$ reductant solution, 0.14 mg mL^{-1} - dissolve 0.7 g of $Fe(II)SO_4 \cdot 7\ H_2O$ in 1 L of water.

10. 0.1M HNO_3 TEVA column wash solution - 6.5 mL HNO_3 L^{-1} of water.

11. Methyl red indicator solution - dissolve 100 mg of the dye in 65 mL of ethyl alcohol and dilute to 100 mL with water.

12. Nitromethane - Aldrich Chemical Co., Milwaukee, WI 53233.

SAMPLE PREPARATION

A. Water.

1. Evaporate a measured volume of sample containing ^{95m}Tc tracer (~8 Bq) to about 200 mL in an appropriate size beaker.

2. Prepare a reagent blank containing ^{95m}Tc tracer solution.

3. Add 10 mL of 30% H_2O_2, cover beaker and heat without boiling.

4. Cool and vacuum filter though a 15-cm glass fiber filter. Wash the filter and beaker with a minimum of water.

5. Transfer the supernate to a 400-mL beaker and discard filters.

SEPARATION

1. Place a magnetic stirring bar in the sample beaker.

2. Add 1 mL of 200 mg mL^{-1} calcium carrier solution, 5 mL of 20 mg mL^{-1} of barium carrier solution, and 10 mL of 5 mg mL^{-1} of iron carrier solution to the sample solution.

3. Without heating, add 6M NaOH with continuous mechanical stirring until the solution is alkaline (use pH paper). Then add 20 mL of 2M Na_2CO_3 and stir for 15 min.

4. Filter the sample using suction through two 15-cm glass fiber filters. Wash the precipitate with 2M Na_2CO_3 solution. Discard the precipitate that contains any alkaline earth metals, transition metals, rare earths, strontium, lead, CrO_4^{-2}, PO_4^{-3}, and SO_4^{-2}. Transfer the sample solution to the original beaker.

5. Slowly add concentrated HCl to the filtrate until the solution is acidic to pH paper. Add 2 mL of 0.14 mg mL^{-1} Fe(II) reductant solution and heat to 75°C for 1 h. This reduces Tc(VII) to Tc(IV).

6. Coprecipitate Tc(IV) with iron hydroxide by the addition of 50% ammonia solution to pH 9 and allow to stand, covered, for 1 h.

7. Centrifuge the solution in a conical 250-mL tube for 10 min at 2,000 rpm and discard the supernate.

8. Dissolve the precipitate in 1 mL of 16M HNO_3, which oxidizes Tc(IV) to Tc(VII).

9. Add a sufficient amount of NH_4OH to precipitate $Fe(OH)_3$, about pH 8.

10. Adjust the alkaline supernate solution (10 - 15 mL) for **Sample Purification** by adding one drop of 0.1% methyl red indicator.

11. Add 8M HNO_3 dropwise until the solution is yellow (pH 6.2).

12. Add 7.5M NH_4OH until the solution is red (pH 4.2). Then add two drops of 1.6M HNO_3.

SAMPLE PURIFICATION

1. Condition the TEVA extraction columns by passing 8 mL of 0.1M HNO_3 wash solution at full flow (about 20 mL h^{-1}).

2. Apply the entire sample to the 25-mL capacity reservoir. Collect the column effluent in a 100 mL beaker.

3. Wash the column with 8 mL of 0.1M HNO_3. Discard the column effluent and wash solutions.

4. Cut the column body with a sharp blade and carefully extrude the resin into a 20-mL low potassium borosilicate glass liquid scintillation counting (LSC) vial, using a rubber pipetting bulb applied to the exit port of the column.

5. Wash the column body with exactly 2.0 mL of deionized water and add to the LSC vial.

6. Pipette 15 mL of Insta-Gel cocktail into the vial, cap, and shake vigorously for several minutes.

7. Wipe the external surface clean with ethyl alcohol.

8. Count the sample along with the reagent blank for 1 h with a window setting of 1-500 keV.

9. Record the gross counts per minute (gcpm), quench index parameter (QIP), and spectral index of sample (SIS) on attached **Technetium Worksheet**, Section 1.

SAMPLE MEASUREMENT

A. Technetium-99 quench/efficiency calibration curve.

1. Prepare six labeled LSC vials, each containing 1.0 g of NIST ^{99}Tc standard (about 8 Bq g^{-1}).

2. Evaporate the ^{99}Tc standard solution in the LSC vials to dryness under a heat lamp.

3. Add 15 mL of Insta-Gel to each vial.

4. Into each of the six labeled LSC vials, add successively increasing amounts of nitromethane in 10 µL increments.

5. Prepare a separate vial containing 15 mL of Insta-Gel, plus 2 mL of deionized water **without** ^{99}Tc or nitromethane.

6. Shake capped vials for 1 min and count in the LSC for 1 h with a window setting of 1-500 keV.

7. Record the gcpm, QIP, and SIS on the **Technetium Worksheet**, Section 2.

B. Technetium-95m quench efficiency calibration curve.

1. Repeat Steps 1-6 above in Section A above with ^{95m}Tc tracer in separate vials.

2. Record the gcpm, QIP, and SIS on **Technetium Worksheet**, Section 3.

3. Also record the SIS value of the "zero" ^{95m}Tc vial in the **Technetium Worksheet**, Section 1, LSA Ref. Std.

SAMPLE CALCULATION

1. Calculate the efficiency for ^{99}Tc and ^{95m}Tc using the **Technetium Worksheet**, Sections 2 and 3, Step 6.

2. Plot % efficiency vs. QIP, which should be linear over a wide range of QIP values (see Figure 1).

3. Calculate the ^{99}Tc activity (Bq kg^{-1}) in a sample containing a mixture of ^{95m}Tc and ^{99}Tc using the following equation (see **Technetium Worksheet**, Section 1, Steps 1-10).

$$^{99}\mathrm{Tc}\left(\mathrm{Bq\ kg^{-1}}\right) = \frac{\left(\text{Net Total cpm}\right) \times \left(\mathrm{SIS_{Mix}} - \mathrm{SIS_{95m_{Tc}}}\right)}{\left(\mathrm{E_{99}}\right) \times \left(\mathrm{R}\right) \times \left(60\ \text{sec min}^{-1}\right) \times \left(\mathrm{SIS_{99_{TC}}} - \mathrm{SIS_{95m_{TC}}}\right)} \times \mathrm{W} \qquad (1)$$

where

E_{99} = ^{99}Tc counting efficiency (cps Bq^{-1}) at the QIP value of the sample
R = fractional ^{95m}Tc yield recovery (see Eqn 3 below)
W = weight of sample (kg)
$SIS_{^{99}Tc}$ = SIS component of dual labeled sample due to ^{99}Tc, calculated using Eqn 2, unitless
SIS_{Mix} = spectral index of dual-labeled sample, unitless
$SIS_{^{95m}Tc}$ = spectral index of the sample containing ONLY ^{95m}Tc (an LSA reference vial), unitless

The ^{99}Tc contribution to the SIS of a dual-labeled sample, $SIS_{^{99}Tc}$, is calculated from the following relationship by taking the anti-log (i.e., the exp(ln SIS):

$$\ln SIS_{99_{Tc}} = \frac{\left(\ln SIS_{95m_{TC}}\right) \times \left(\ln SIS_{Bl}\right)}{\ln SIS_{MIX}} \quad (2)$$

where

SIS_{Bl} = spectral index of water blank sample (see **Sample Measurement**, Section 1, Step 5, Column-A), unitless.

The results of these calculations are recorded on the **Technetium Worksheet**, Section 1. A computer program can be used for data reduction using the full spectrum analysis.

The fractional yield recovery, R, is determined directly from the LSA data using

$$R = \frac{\text{Net cpm of sample}}{\text{Net cpm } ^{95m}\text{Tc Ref. vial}} \times \frac{\left(SIS_{99_{Tc}} - SIS_{MIX}\right)}{\left(SIS_{99_{Tc}} - SIS_{95m_{Tc}}\right)} \times \frac{1}{E_{95}} \quad (3)$$

where

E_{95} = ^{95m}Tc efficiency as a function of the QIP, determined from the **Technetium Worksheet**, Section 3, Step 6.

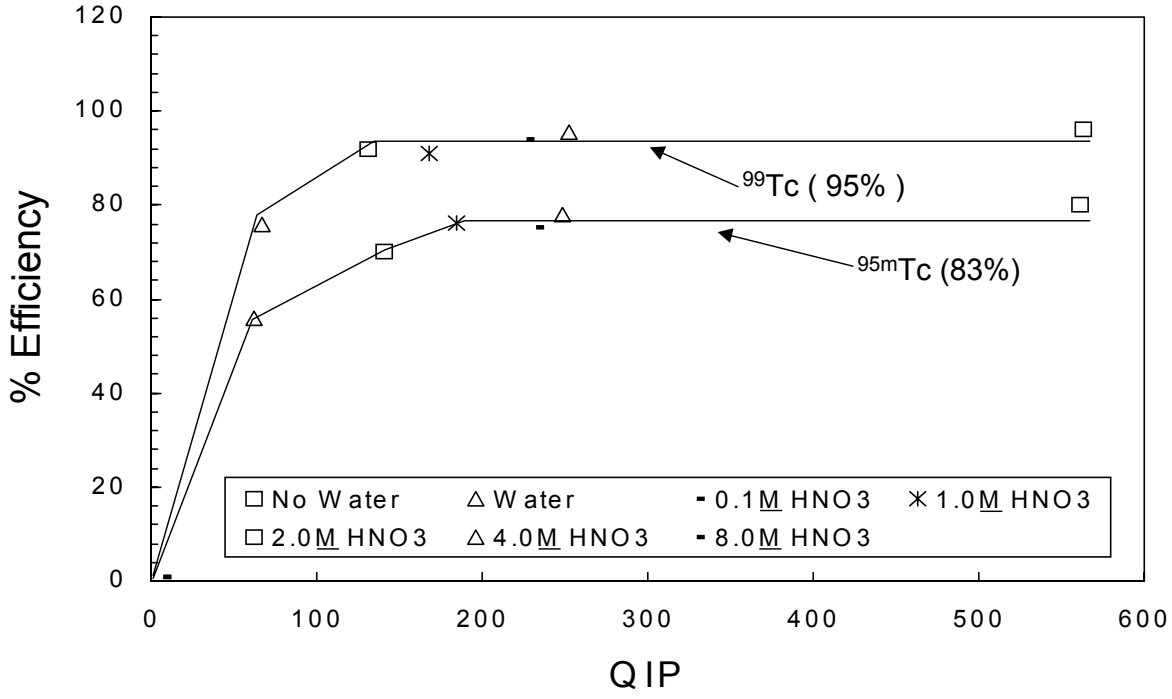

Figure 1. Counting efficiency for ^{99}Tc and ^{95m}Tc in Insta-Gel cocktail [Insta-Gel (50/50 mix); ROI = 1-500 keV].

TECHNETIUM WORKSHEET

1. UNKNOWN SAMPLE DATA

Matrix _____ Lab. I.D. _____
Date _____ ^{95m}Tc Added _____ Bq g^{-1} _____
Net cpm ^{95m}Tc: LSA Ref. Std. (1) _____ (2) _____
SIS ^{95m}Tc (1) _____ (2) _____
Net gamma counts of Ref. Std. _____ in _____ min

	(A)	(B)	(C)	(D)
1. Sample ID No.	H_2O Blank	Reagent Blank	Sample	Sample
2. Sample Mass (kg)	xxxxx	1.0	_____	_____
3a. Total Gross cpm	_____	_____	_____	_____
3b. Total Net cpm (Bkg)	_____	_____	_____	_____
4. 2 sigma uncertainty	_____	_____	_____	_____
5. SIS	_____	_____	_____	_____
6. QIP	_____	_____	_____	_____

Calculated Values:

7. SIS-^{99}Tc (use Eqn. 2 and Section 1.5 data)	xxxxx	_____	_____	_____
8. LSA Yield Rec (R) (use Eqn. 3 and Ref. Std. Data)	xxxxx	_____	_____	_____
9a. E_{99} @ QIP of Sample (use Calibration Curve-I)	xxxxx	_____	_____	_____
9b. E_{95} @ QIP of Sample (use Calibration Curve-II)	xxxxx	_____	_____	_____
10. ^{99}Tc (Bq kg^{-1}) (use Eqn. 1)	xxxxx	_____	_____	_____

TECHNETIUM WORKSHEET (Cont'd)

Results:

Net Average ^{99}Tc (Bq kg^{-1}) = _____ ± _____

Average Yield Recovery = _____%

Instrument Calibration Date _____ Code _____

Count Time (h) _____ : Region of Interest (keV) _____ to _____

---

2. ^{99}Tc QUENCH/EFFICIENCY DATA ^{99}Tc (Bq) Added _____

	Quencher is Nitromethane in 10 µL Amounts						
	A	B	C	D	E	F	G
1. Sample (µL)	0	10	20	30	40	50	60
2a. Gross cpm	____	____	____	____	____	____	____
2b. Net ^{99}Tc cpm	____	____	____	____	____	____	____
3. 2 sigma uncertainty	____	____	____	____	____	____	____
4. SIS	____	____	____	____	____	____	____
5. QIP	____	____	____	____	____	____	____
6. E_{99} (Step 2b ÷ Bq ^{99}Tc Added)	____	____	____	____	____	____	____

Plot E_{99} vs. QIP for ^{99}Tc Efficiency Calibration Curve

3. ^{95m}Tc QUENCH/EFFICIENCY DATA ^{95m}Tc (Bq) Added _____

	Quencher is Nitromethane in 10 µL Amounts						
	A	B	C	D	E	F	G
1. Sample (µL)	0	10	20	30	40	50	60
2a. Gross cpm	____	____	____	____	____	____	____
2b. Net ^{99}Tc cpm	____	____	____	____	____	____	____
3. 2 sigma uncertainty	____	____	____	____	____	____	____
4. SIS	____	____	____	____	____	____	____
5. QIP	____	____	____	____	____	____	____
6. E_{95} (Step 2b ÷ Bq ^{95m}Tc Added)	____	____	____	____	____	____	____

Plot E_{95} vs. QIP for ^{95m}Tc Efficiency Calibration Curve