Tc-01-RC

TECHNETIUM-99 IN WATER AND VEGETATION

APPLICATION

This procedure has been applied to the analysis of water and vegetation.

Technetium-99 is equilibrated with ^{95m}Tc tracer. The technetium is separated from other elements by anion exchange and electrodeposition. The ^{99}Tc is β counted. Gamma spectrometry measurement of ^{95m}Tc provides the chemical yield.

SPECIAL APPARATUS

1. Virgin platinum discs - 17.6 mm diameter x 0.127 mm mirror finish on one side.

2. Plating cells - see Specifications 7.15 and 7.16, Vol. I.

3. Electrodeposition power supply - constant, capacity 0-1.5 A, 0-20 V; transistorized variable speed stirring motor.

4. Ion exchange columns - see Specification 7.5, Vol. I.

5. Mylar film - see Specification 7.3, Vol. I.

6. Beta phosphor - see Specification 7.9, Vol. I.

7. Rings and discs - see Specification 7.2, Vol. I.

8. Germanium lithium, Ge(Li), γ-ray spectrometer.

SPECIAL REAGENTS

1. ^{99}Tc standard solution - available from NIST.

2. Technetium-95m tracer solution (free from ^{97m}Tc) - prepared by helium nuclei bombardment of pure ^{93}Nb foil in a cyclotron. (Special production on request at Brookhaven National Laboratory, Upton, NY).

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

4. Bio-Rad AG 1-X4 (100-200 mesh, Cl^- form) anion exchange resin or equivalent - see Specification 7.4, Vol. I.

5. 6M sodium hydroxide solution - 240 g NaOH L^{-1} of water.

6. 2M sodium carbonate solution - 212 g Na_2CO_3 L^{-1} of water.

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

8. Barium solution - 20 mg Ba mL^{-1} - 30.4 $BaCl_2$ L^{-1} of 0.1M HCl.

9. Iron solution - 5 mg Fe mL^{-1} - dissolve 36 g $Fe(NO_3)_3 \cdot 9 H_2O$ in 1 L of 0.2M HNO_3.

10. 5M HNO_3 eluting solution - dilute 310 mL of HNO_3 to 1 L.

11. 0.1M HNO_3 wash solution - dilute 6.5 mL of HNO_3 to 1 L.

SAMPLE PREPARATION

A. General.

Technetium is volatile at elevated temperatures. The samples are prepared by wet ashing with nitric acid.

To a measured quantity of sample in a glass beaker, add a known amount of ^{95m}Tc tracer which gives 60 counts sec^{-1} at 204 keV as of count date on a Ge(Li) γ-ray spectrometer.

B. Water.

Evaporate the sample to a small volume. Cool and transfer the sample solution to a 1 L beaker. Dilute the sample solution to 800 mL with H_2O. Stir the sample solution and filter with suction through a 15 cm glass fiber filter. Wash the filter with H_2O. Discard the filter which contains the silica and insoluble material.

C. Vegetation.

Wet ash the sample with HNO_3. After wet ashing is completed, evaporate the to the smallest volume possible with no salting out. Cool and transfer the sample solution to a 1 L beaker. Dilute the sample solution to 800 mL with H_2O. Stir the sample solution and filter with suction through a 15 cm glass fiber filter. Wash the filter with H_2O. Discard the filter which contains the silica and insoluble material.

SEPARATION

1. Transfer the filtrate into the original 1 L beaker and evaporate to about 200 mL.

2. Add 1 mL of 200 mg Ca mL^{-1}, 5 mL of 20 mg Ba mL^{-1}, and 10 mL of 5 mg Fe mL^{-1} to the sample solution. Place a magnetic stirring bar in the beaker and stir to mix.

3. With continuous mechanical stirring, add 6M NaOH until the solution is alkaline to pH paper. Then add about 60 mL of 2M Na_2CO_3.

4. Filter the sample with suction through a double 15-cm glass fiber filter. Discard the precipitate, which should contain any alkaline earth metals, transition metals, rare earths, Sr, actinides, Ra, Pb, CrO_4^{-2}, PO_4^{-3}, and SO_4^{-2}.

5. Transfer the filtrate with water back into the 1 L beaker.

6. Add five drops of methyl red indictor to the filtrate.

7. Adjust the pH to the red end point of the indicator (pH 4.2) with 8M HNO_3.

8. Prepare an ion exchange column containing 10 mL of settled Bio-Rad AG 1-X4 (100-200 mesh, Cl^- form). Place a 1 L beaker under the column and condition the resin with 100 mL of 0.1M HNO_3.

9. Pass the sample solution from Step 5 through the resin bed at a full flow.

10. Wash the column with 500 mL of 0.1M HNO_3. Discard the column effluent and washes.

11. Place a 250 mL beaker under the column. Elute the technetium with 100 mL of 5M HNO_3. (Note: This anion exchange procedure separates the technetium from most other elements, but not from chromate. However, the chromate should have precipitated as a barium chromate during the earlier alkaline precipitation.)

12. Evaporate the eluate to dryness or near dryness, avoiding excessive heat.

ELECTRODEPOSITION

1. Add 1 mL of HCl to dissolve the sample residue in the beaker. Transfer the sample solution to an electroplating cell which contains a platinum disc, using three successive 1 mL water washes to complete the transfer.

2. Add one drop of 0.1% methyl red indicator. Add NH_4OH dropwise until the solution is yellow. Add the minimum amount of 2.5M dropwise until the solution is red, then add two drops of 2.5M in excess.

3. Dilute the sample solution in the electrodeposition cell to 5 mL with water and connect to the electrodeposition apparatus. Electroplate onto the platinum disc cathode while stirring at a current of 1.2 A. The plating cell is supported on a lucite pedestal which is immersed in an ice water bath throughout the electrodeposition.

4. Observe the voltage versus time. (A strip chart recorder recorder may be used.). When the curve breaks (after about 1 h), quench the electrolyte with 1 mL of

NH_4OH. Immediately turn off the current, dismantle the cell, and rinse the electroplated disc with water and ethanol. Dry the disc on a hot plate with gentle heat.

5. Mount the plated platinum disc on a nylon disc. Centering is facilitated if the plastic discs are machined with an appropriate sized, shallow depression. Place a β scintillation phosphor directly over the platinum disc, cover with Mylar, and fasten with a nylon ring.

MEASUREMENTS

Measure the platinum sample disc with a Ge(Li) γ-ray spectrometer, integrate the 204 keV line and record the date and time. Determine the spectrometer response at this energy for a 100% chemical yield with platinum discs onto which known quantities of ^{95m}Tc from the stock tracer solution have been electroplated. The ratio of these two activities, corrected to the same date, provides the chemical yield of the sample.

Measure the platinum sample disc in a low-level β scintillation counter and record the date and time. Determine the counting efficiency of this system for ^{99}Tc with platinum discs containing known quantities of ^{99}Tc. Also measure the platinum discs electroplated with known quantities of ^{95m}Tc and record the date and time. The ^{99}Tc activity in the sample is determined by correcting for counter background and for the β contribution from the ^{95m}Tc tracer, and by adjusting for chemical yield and counting efficiency:

$$^{99}\text{Tc (Bq sample}^{-1}) = \frac{(A - C)}{Y \times E}$$

where

A = net β cps of sample

C = β cps from ^{95m}Tc tracer

Y = chemical yield

E = counting efficiency

and

$$C = \gamma \bullet R$$

where

γ = net γ cps of sample from the Ge(Li) γ-ray spectrometer at 204 keV, decay corrected to the time of the sample β count.

R = mean ratio of the net β cps of the ^{95m}Tc standard discs to the net γ cps of these same discs from the Ge(Li) γ-ray spectrometer at 204 keV; both activities are decay corrected to the same time. For the EML systems, this ratio (R) is about 0.5.

LOWER LIMIT OF DETECTION (LLD)

Counter Efficiency	(%)	40
Counter Background	(cps)	0.005
Yield	(%)	80
^{95m}Tc Interference*	(cps)	0.007
LLD (1000 sec)	(mBq)	6.7
LLD (3000 sec)	(mBq)	3.3
LLD (10,000 sec)	(mBq)	1.7

* The ^{95m}Tc tracer interacts with the phosphor in the EML low-level β scintillation counters producing about 0.5 counts sec^{-1} for each counts sec^{-1} registered in the 204 keV photopeak of our Ge counts (Li) γ-ray spectrometer. The ^{95m}Tc interference can be reduced by a factor of two if the sample is held 61 days, one half-life of ^{95m}Tc, before β counting.