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ABSTRACT

A novel isotope dilution mass spectrometric technique has been developed for the analysis of Tc-99 in environmental samples. After spiking with Tc-97, technecium is isolated from the sample by a combined ion-exchange chromatography and ion-association solvent extraction technique. The isolated technecium is finally concentrated onto a pair of anion exchange beads (diameter ~0.3 mm). The beads are individually analyzed on rhenium "V" filaments of a surface-ionization mass spectrometer. Sensitivities at least as great as 1 pg (0.017 pCi) have been achieved through the enhanced ionization efficiency afforded by the resin bead source. Tc-99 has been quantified in several environmental samples taken at the Savannah River Plant (SRP) site (a nuclear materials production complex) and its aqueous Tc-99 emission has been estimated.

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INTRODUCTION

Tc-99 is produced in high yields from the fission of U-235 and Pu-239 (6.3% and 6.1%, respectively). Coupled with its 2.1×10^5 year half-life, these high yields will result in the accumulation of large amounts of Tc-99 concurrent with energy production by atomic fission. Other sources of Tc-99 include weapons testing, incidental neutron activation of molybdenum in reactor cooling water, and disposal of Tc-99m from medical diagnostic procedures (1).

Technetium has the potential to escape to the environment due to volatility ($HTcO_4$, and Tc_2O_7) and aqueous mobility in soil systems (TcO_4^-). Instances of the latter have been reported (2,3). Although uptake of technetium by a variety of plants has been studied (1,4,5), pathways to man have not been well-defined. One recent paper suggests that commonly used concentration factors for uptake of technetium by plants from soil may be underestimated by a factor of 100 to 1000 (6).

Studies of acute medical administration of Tc-99m to humans as TcO_4^- found localization in the thyroid and/or salivary glands, gastrointestinal tract, stomach, liver, and bladder, followed by quick elimination (7-10). However, little is known about the behavior of technetium in man when uptake of environmental forms occurs over long periods (6).

Direct counting of Tc-99 at environmental concentrations is difficult because of its low specific activity (1.7 x 10^{-2} Ci/g) and its emission of only low energy beta(-) particles (E_{max} = 0.29 meV). The most sensitive analytical technique yet reported is isotope dilution mass spectrometry with Tc-97 as the yield tracer. A detection limit of 1 pg has been achieved (11,12). However, the isolation scheme is quite lengthy and includes an electrodeposition step whose timing and technique are critical for acceptable recovery of technetium.

In this paper, an improved isotope-dilution mass-spectrometric procedure is described. Important improvements are a highly selective (yet non-critical) isolation scheme devised primarily from the work of Maeck et al. (13), and a significant increase in the mass spectrometric ionization efficiency for technetium obtained by analyzing the technetium absorbed on individual anion exchange resin beads.

Major improvements in thermal emission mass spectrometric measurement sensitivity for small samples have been made in recent years at the Oak Ridge National Laboratory (ORNL) using a resin-bead sample preparation and filament loading technique (14,15). Application of this technique requires the use of mass spectrometers equipped with pulse-counting capability for increased ion detection sensitivity and preferably two magnetic stages for increased spectrum cleanliness.

The use of reducing agents (benzene, sucrose, etc.) to improve metal ion production and to increase ionization efficiency from samples loaded as solutions is an accepted practice in many mass spectrometry laboratories (16-18). The mechanism for the increased ion emission (for technetium, about a factor of 50) obtained from a single resin bead compared to solution loading is speculative, but probably results from the point-source loading combined with carburization of the filament at the point where the organic resin bead is decomposed at about 1000 to 1200°C during the initial filament heating. This reducing condition prevents loss of sample as volatile oxide and produces mostly metal ion emission.

Initial measurements performed by this technique (described below) project a limit of detection at least as small as 1 pg. Also described are the Tc-99 concentrations found in samples taken from the environment of SRP.

EXPERIMENTAL

Apparatus. Ion-exchange chromatography was conducted with tandem ion-exchange columns (Figure 1). Multiple reservoirs were stacked for handling large samples. Alternatively, a siphon feed could be set up with the sample bottle acting as a reservoir.

The vacuum evaporation apparatus is diagrammed in Figure 2. Two vacuum stills were run simultaneously from a single vacuum pump manifold.

Solvent extractions were carried out in 15-mL graduated screw-cap centrifuge tubes. Disposable Pasteur pipets were used for phase transfers.

Resin bead and attendant solution manipulation were observed with a stereo microscope equipped with 10X eyepieces (magnification range: 8 to 40X). Bead diameters were measured at 40X with a reticule previously calibrated with a 1-mm stage micrometer. Beads and solutions were transferred with Pasteur pipets drawn to long fine tips. When necessary to transfer solution only, a pipet whose tip was smaller than a resin bead was used. A resin bead without solution was transferred by a tungsten needle tipped with a small globule of adhesive teased from cellophane tape.

Loading of resin beads with technetium was accomplished in 400-μL polypropylene micro test tubes (Brinkman 22 36 390-5) agitated either by a vortex mixer or a pipet shaker (Technilab Instruments, Inc., Model No. 31). The latter was able to accommodate at least four tubes at a time.

The mass spectrometer used in this investigation is a single focusing ("C" configuration), tandem magnet type (19), based on a design developed by White and Collins (20). The instrument has a 30-cm radius and 90° deflection in each magnet which gives a very clean spectrum because of the reduction of scattered ions. A typical abundance sensitivity for the ORNL two-stage instrument under routine operating conditions is 10^6; to attain higher abundance sensitivity requires narrowing the slits, causing a loss of sensitivity with respect to sample size. Ions are detected by a secondary electron multiplier behind the receiver slit. The detector is a 14-stage multiplier with a gain exceeding 10^6 (pulse-counting mode). Data are stored either in a 400-channel analyzer or a PDP-11 computer for later processing.

Reagents. The water used for all solution and resin preparation was obtained from a commercial 3-module purification system (Millipore Corp., "Milli-Q"). The water was stored in a 20-L polyethylene container.

A stock solution of Tc-99 (5.8×10^{-8} g/mL) in 0.1M ammonium hydroxide was prepared from a commercial solution. Development and evaluation samples were prepared by dilution of the stock solution with various solvents (e.g., water, nitric acid, ammonium hydroxide, etc.) depending on the application.

Twenty mL of a 0.15M ammonium hydroxide solution containing 2.30×10^{-8} g/mL of Tc-97 was prepared by neutron irradiation of ruthenium enriched in Ru-96 and subsequent isolation by a modification of the procedure of Kaye et al (12).

Stock quantities of AG 50W-X8 (100 to 200 mesh, hydrogen ion) and AG 1-4X (100 to 200 mesh, chloride ion) ion-exchange resins were each washed 5 to 6 times in double their volumes of high-purity water from the "Milli-Q" unit. After a brief settling time, the supernates and suspended fines were decanted to waste. The resultant resins were stored under small excesses of water and slurried for column preparation when needed.

Tetrapropylammonium hydroxide (10% in water; Eastman 6189), 4-methyl-2-pentanone (Eastman 416), cyclohexanone (Aldrich C10,218-0) flexible collodion (MCB #CX1885) diluted 1:1 (vol) with absolute ethanol, and cyclohexane (Eastman 13045) were used as received. All other reagents were ACS grade and were used without further purification.

About 0.5 mL of AG 1-X10 (50 to 100 mesh, chloride ion) anion exchange resin was placed in a 48-mm ID, covered, plastic Petri dish with a few mL of water. Beads were selected from this supply for loading with technetium.

Filaments for this work were made from zone-refined rhenium. They were of the single V-shaped design and were prebaked in an auxiliary vacuum system for at least 30 minutes at 2000°C to remove impurities and reduce the molybdenum background. Measurements were made to determine the best filament material for the technetium analyses. Of the three metals tested (Re, W, and Ta), the order of sensitivity for technetium was Re>W>Ta. The sample changer, a "Ferris" wheel, upon which six sample filaments were mounted, has been described by Christie and Cameron (21). The sample was driven from outside the vacuum system by a rotary-motion feedthrough.

SAMPLE HANDLING

Technetium Isolation Procedure. The procedure for both aqueous and solid samples is outlined in Figure 3. With either type of sample, 917 pg of Tc-97 spike are added before processing begins. For solid samples (up to 25 g), the Tc-97 spike is distributed over the sample as uniformly as possible and is followed by addition of 10 mL of concentrated ammonium hydroxide solution.

Solid samples are then slowly dried and charred over a burner and subsequently ashed for 24 hours at 500°C in a furnace. A low ashing temperature minimizes technetium loss. The ash is fused for 4 minutes at red heat with 10 g of Na_2O_2 in a nickel crucible. The cooled melt is reacted cautiously with 40 mL of water and the solution and residue transferred to a 250-mL beaker with 30 mL of water and small portions of concentrated HCl totaling 40 to 45 mL. The mixture is heated on a hot plate to dissolve any soluble residue. The residue remaining after heating is discarded. The solution is extracted twice with 25-mL portions of cyclohexanone. The combined extracts are diluted with 40 mL of cyclohexane and back-extracted three times with 15-mL portions of water. The back-extracts are combined, oxidized with 100 μL of 30% hydrogen peroxide, and acidified with two drops of concentrated HCl. The solution is ready for ion-exchange.

Aqueous samples (up to 2 L) are, after Tc-97 addition, oxidized with 1 mL of 30% hydrogen peroxide and acidified as necessary to a pH <5 with concentrated HCl. If the sample contains much suspended matter, a preliminary filtration will enhance passage through the ion-exchange columns.

The aqueous solution from the previous steps and then 50 mL of water are passed through the tandem ion-exchange column at a rate of 3 to 5 mL/min. The effluent is discarded. The stopcock is closed, the reservoir removed, and the cation resin thoroughly aspirated from the top column. A clean reservoir is fitted and 250 mL of 1M HCl are passed through the anion exchange column at 3 to 5 mL/min. The effluent is discarded. The anion-exchange column is removed from the stopper. Three 1.0-mL portions of 4M nitric acid are added to the "Econo Column" reservoir (Figure 1) without disturbing the resin bed. Each portion is allowed to drain to the top of the bed before the next is added. The effluent is discarded. Finally, the technetium is eluted with 25 mL of 4M nitric acid into a 250-mL round-bottom flask. To the effluent is added 0.5 mL of 0.1M ammonium hydroxide solution.

The 250-mL round-bottom flask containing the column effluent is manually rotated in liquid nitrogen to freeze the effluent in a thin film over a large portion of the flask interior. The flask is attached to the vacuum evaporation apparatus and vacuum is applied. Momentary use of a blower thaws the solution to begin the evaporation process (Figure 2). (The initial phase is taken slowly to minimize out-gassing.) When ice begins to reform on the outside of the flask, the blower is turned back on (no heater) to keep the exterior of the flask near room temperature. The evaporation is stopped when about 0.2 mL of solution remains. The interior portion of the flask is then thoroughly rinsed with several portions of water totaling 5.0 mL. The residual solution and rinses are combined in a 15-mL graduated centrifuge tube for solvent extraction.

To the centrifuge tube are also added 3.0 mL of 10M NaOH, 0.5 mL of 30% hydrogen peroxide, and 100 μL of 10% TPA-OH, with mixing after each addition. The aqueous phase is extracted twice with 1.0-mL portions of 4-methyl-2-pentanone. The extracts are combined and washed with 1.0 mL of 3M NaOH, diluted with 8.0 mL of cyclohexane, and back-extracted twice with 1.0-mL portions of water. The back-extracts are combined and diluted with 3.0 mL of water. The extraction/back-extraction cycle is repeated on the combined, diluted, aqueous back-extract. After the second cycle, the final 2.0 mL of aqueous back-extract are evaporated at room temperature (under a nitrogen stream) to a volume of 0.2 mL.

Two anion exchange resin beads of about 0.3-mm diameter are placed in a 400-μL test tube. The concentrated back-extract is added with a drawn Pasteur pipet and the micro-test tube is stoppered. The assembly is vigorously agitated for 2 hours with a vortex mixer or pipet shaker. To minimize leakage while maintaining good mixing, a vigorous solution vortex pattern avoiding the integral micro-test tube stopper is sought.

The solution is then removed from the micro-test tube and discarded. The beads are transferred to a microscope slide and mounted with flexible collodion for shipment or storage, or mounted directly on filaments.

Filament Loading Procedure. Resin beads secured on glass slides by collodion are removed by cutting out a small section of the collodion containing a single resin bead and transferring the chip to a stainless steel needle. This operation is performed under a stereo microscope using ~60X magnification. After the collodion chip is removed, it is put into a rhenium V-shaped filament using a second low-powered (30X) microscope which has the stage removed to allow the placement of the sample filaments at the focal point. The chip of collodion containing the bead is placed on the filament and a few μL of amyl acetate are added to dissolve the collodion. The bead is then centered. Although the collodion would probably hold the bead in place during its insertion into the source region, the filament is crimped around the bead to ensure its presence during the loading operation. A more detailed description of the filament loading operation has been reported (22).

MASS SPECTROMETRY PROCEDURE

Calibration. Mass scanning is accomplished by sweeping the accelerating voltage. A correction for bias is necessary. Since no primary standard is available for instrument calibration, molybdenum (which covers the technetium mass range) is used for this purpose. Possible errors introduced as a result of different efficiencies for the elements are expected to be minimal. Calibrations have been done using known quantities of Tc-97 and Tc-99, but the uncertainties of the quantities of the technetium isotopes are not known to better than a few percent, thus the molybdenum calibration is used for voltage-sweeping bias-correction.

Sample Filament and Resin Bead Pretreatment. The decomposition of the resin bead in the mass spectrometer before mass analysis requires considerable operator care and should be done holding all procedural conditions as rigidly as possible to minimize interferences and fractionation effects. After a source pressure of $<5 \times 10^{-7}$ torr is achieved, the temperature of the filament is increased very slowly until a pressure increase is noted. After waiting a few seconds for the vac-ion pump to recover to the original pressure, the operation is repeated until a second large increase in pressure (usually from 10^{-7} to 10^{-6} torr) occurs. Usually when a temperature of about 1000°C is achieved, the bead will have been decomposed and a slow increase of current can be applied to the filament without further pressure fluctuations. This method allows the bead to decompose on the filament without undue fragmentation, thus retaining most of the sample. The time required for bead decomposition is about five minutes from the start until a dull red heat is achieved at about 1000°C. Experience has shown better than 99% sample retention for this procedure. If pressure increases are not noted, the bead has probably been lost during filament loading and the expected ion signals will not be observed.

Isotopic Analysis. The masses of interest (97, 98, 99, 100, 100.5) are scanned as the filament temperature is slowly increased until technetium ions are observed. Focus conditions are optimized on the metal ion peak using the heavier of the two technetium isotopes. Analysis is made at the lowest possible filament temperature to minimize molybdenum interference in the 97 mass position. Reliable data are usually obtained at about 50,000 counts sec^{-1} at a temperature of 1900°C from 1 ng of technetium loaded on a resin bead. Both molybdenum peaks are scanned and the average of the two ratios is taken for the molybdenum-97 correction. Electronic noise is monitored at mass 100.5 and subtracted from the mass peaks. The correction for Mo-97 interference can be reliably made if the Tc-97 ion signal equals or exceeds the Mo-97 signal. Data are taken by peak hopping to improve statistics and sensitivity.

RESULTS AND DISCUSSION

The two primary constraints on the isolation/concentration scheme are that species capable of interfering with measurements at masses 97 and 99 (i.e., Mo-97 and Ru-99) be reduced to a correctable or negligible level; and that overall recovery of technetium to the filament be high enough (>50%) to assure good sensitivity.

In this work, ruthenium has not been an interference. Ruthenium ions have not been observed in the analysis of blank filaments, chemical blanks, and technetium standards, thus indicating clean chemical separation and the absence of ruthenium in rhenium filaments. As indicated by Kaye (12), Mo-97 is the most troublesome interference at mass 97.

The potential for the removal of molybdenum from the sample afforded by the solvent extraction procedure was evaluated by attempting to extract ^{99}Mo at tracer levels from a 0.15M ammonium hydroxide matrix. Observation of the 740 keV gamma-ray of Mo-99 by Ge(Li) detection in both the organic and aqueous phases indicated that the distribution ratio of molydbenum was $<1.3 \times 10^{-5}$. Molybdenum from the rhenium filament is the main source of interfering ions at the 97 mass position. A correction can be estimated by scanning either Mo-98 or Mo-100 and ratioing to the natural abundance of Mo-97.

A hydrocarbon background problem has been observed in the technetium mass region. The background is variable and a background correction cannot be made accurately. In Tc-99 analyses with one nanogram of Tc-97 tracer, the hydrocarbon interference causes insignificant errors in samples containing nanogram quantities of Tc-99 because the amount of hydrocarbon background is usually equivalent to a few tenths of a picogram of Tc-99. The source of hydrocarbon is unknown, but may result from oil pumps used to rough down the source region. The hydrocarbon interference does not result from the resin bead, since it also occurs when observing clean baked-out filaments with no beads. Attempts to reduce the hydrocarbon background using liquid nitrogen pumping in the source region has failed. Modifications to the mass spectrometer (i.e., eliminating oil pumps) should reduce this problem.

Typical recoveries for the various portions of the isolation scheme are indicated in Table I. All steps preceding the ion-exchange bead uptake have high and reproducible recoveries. Of special interest is the need to perform the evaporation step between the ion-exchange column and solvent extraction steps (Figure 3) at low (room) temperature to avoid major volatility losses. This practice conforms to an early suggestion by Anders (23). The evaporation is performed in a vacuum to attain useful rates. The evaporation not only reduces the volume of the solution to the scale of the subsequent solvent extraction; but it simultaneously reduces the amount of nitrate ion transferred to the solvent extraction, and thus eliminates loss of technetium caused by high nitrate ion concentrations in the extraction.

Bead uptake has demonstrated the lowest and most variable recoveries of any of the steps. While uptake from 0.1M ammonium hydroxide solutions of Tc-99 tracer has generally been greater than 90%, recoveries from solutions prepared by applying the isolation scheme to Tc-99 tracer solutions have ranged from 37 to 85%. Recent investigation of the uptake behavior with simulated evaporates containing 3.2 moles of nitrate ion indicated that high and reproducible uptakes can be obtained. Pairs of beads in seven trials averaged 86.0% uptake with a standard deviation of only 1.7%. Critical parameters are thought to be adequate bead size (>270 μm) and vigorous agitation. The bead size probably mainly affects the solution-bead contact during agitation.

To estimate the method's sensitivity and to reveal significant operating problems, sets of beads were prepared from known Tc-99 solutions whose Tc-99/Tc-97 weight ratio varied from about 13 (total Tc-99 = 11.6 ng) to 1.15×10^{-4} (total Tc-99 = 1.05×10^{-4} ng). Procedural blanks were also prepared with no added Tc-99. The entire isolation procedure for aqueous samples was employed in the preparation to give meaningful blanks. Table II presents the results of that analysis. The inflation of the normalized ratio of the 0.0106 ng standard is thought to be due to the hydrocarbon background. Based on these and other data and a spike level of 917 pg, a sample containing 1×10^{-12} g of Tc-99 can be quantified with a relative standard deviation of 10%.

Various environmental samples from the vicinity of SRP were analyzed by this method (Table III). The seepage basins, which receive low-level radioactive waste from the fuel reprocessing area, depend on the cation exchange capacity of the clay soil to remove cationic radioactive materials (e.g., Sr-90, Cs-137) from the seepage, and on the underground transit time to the external aqueous environment to lessen the quantities of others released through decay (e.g., tritium). However, a comparison of the Tc-99 concentrations in an adjacent flowing spring with the Tc-99 concentrations in Basin F3 (its prime source of radioactivity), indicates that Tc-99 has high mobility in water-saturated soil

(Table III). The groundwater transit time from basin to spring has been estimated to be nine years from tritium migration studies (25), and the Tc-99 concentration of the basin can be expected to vary substantially with reprocessing parameters. The contribution of Tc-99 by the basin system to the Savannah River is seen by comparing the upstream and downstream Tc-99 concentrations. Based on flows at the time the samples were taken, an annualized instantaneous release rate of 0.05 Ci/yr to the aqueous environment was calculated. A herb and litter sample taken less than a mile from the reprocessing release stacks gave a value (Table III) of 8 to 16 pg/m^2 (0.14 to 0.28 pCi/m^2).

The range of Tc-99/Tc-97 values seen for two beads from the same sample has occasionally been much larger than the expected imprecision based on pulse-counting statistics. The effect is especially large in the herb-litter sample (Table III) which had counting relative standard deviations for the two beads of only 8.6 and 4.9%. The most probable cause is the variable hydrocarbon background of the mass spectrometer described above. An instrument devoid of this spurious signal is needed to test the theory.

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TABLE I. Typical Technetium Recoveries for the Isolation Procedure

step	recovery of step
Ion-Exchange	99 ± 4%
Evaporation	91 ± 2%
Two-Cycle Solvent Extraction	95 ± 2%
Resin Bead Uptake	37-85% (86 ± 1.7%)[a]
Overall	32-73% (73%)[a]

[a] Based on results with simulated evaporates and beads >270 μm diameter. See text.

TABLE II. Analysis of Standard Bead Sets

^{99}Tc added, ng	$\left(\dfrac{\text{counts } ^{99}\text{Tc}}{\text{counts } ^{97}\text{Tc}}\right)$ / ^{99}Tc added, ng
11.6	1.08 ±0.03[a]
1.16	1.05 ±0.03
0.116	1.10 ±0.04
0.0106	1.65 ±0.02
0.0116	1.09, 1.13[b]
0.00105	1.1, 1.1
0.000105	1.8, 1.1

a. Counting standard deviation shown.

b. Results from both beads of a pair shown.

TABLE III. Technetium Recovered from SRP Environmental Samples

sample	Tc-99 concentration, pg/L[a,b]
H-Area Seepage Basin	$(1.4, 1.5) \times 10^5$
F-Area Seepage Basin	$(3.8, 3.9) \times 10^3$
F-Area Spring	$(7.3, 10) \times 10^3$
4-Mile Creek	10.4, 11.0
Savannah River (Upstream SRP)	$<8 \times 10^{-2}$
Savannah River (Downstream SRP)	0.4, 0.5
Herb-Litter from F-Area	$(8.1, 16) \times 10^2$ (pg/m^2)

a. Results calculated for each resin bead of a sample pair.

b. Federal regulations limit the concentration of soluble Tc-99 in water released to unrestricted areas to 3×10^{-4} Ci/mL; i.e., 1.7×10^7 pg/L (24).