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DEVELOPMENT OF CHEMICAL ISOLATION AND CONCENTRATION TECHNIQUES FOR Tc-99 ANALYSIS BY RESIN-BEAD MASS SPECTROMETRY

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MASTER

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DEVELOPMENT OF CHEMICAL ISOLATION AND CONCENTRATION TECHNIQUES FOR TECHNETIUM-99 ANALYSIS BY RESIN-BEAD MASS SPECTROMETRY

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ABSTRACT

A novel, highly sensitive, isotope-dilution analytical technique for the determination of technetium-99 has been developed around single ion-exchange bead mass spectrometry in collaboration with R. L. Walker of the Oak Ridge National Laboratory. Mass spectrometry is much more sensitive than direct counting for the low-energy, low-specific activity, Tc-99 isotope. Further, the point source provided by a single ion-exchange bead leads to a greater signal-to-noise ratio in the mass spectrometric measurement than does conventional application of a solution to the source filament. Recent results indicate a sensitivity greater than 0.1 picogram. Isolation of technetium from the samples occurs after addition of Tc-97 as a yield tracer. A combination of ion-exchange chromatography and ion-association solvent extraction provides decontamination from the potential interferences, Mo-97 and Ru-99. Subsequently, the technetium is loaded onto a pair of anion-exchange beads (diameter ∿0.3 mm). The noncritical isolation and bead-loading scheme typically concentrates the technetium in the sample by a factor of about a million with overall recoveries exceeding 50%. A variety of environmental samples from the Savannah River Plant (SRP) has been analyzed by this method.

INTRODUCTION

Technetium-99 is one of several long-lived fission products whose direct radiometric detection at environmental levels is not normally feasible because of low specific activity and low energy emissions. Its high mobility in aqueous systems, including water-saturated soils, and its several volatile forms provide transport opportunities from processes and disposal operations.[1,2] Furthermore, technetium-99 is produced in high yield from fission (6% from U-235).

Numerous studies have been conducted on the uptake of Tc-99 from various soil and plant systems at relatively high Tc-99 spike concentrations.[3,4,5] (Some controversy exists, however, in the transfer coefficients in such systems.)[6] Likewise, much is known about the acute behavior of large amounts of Tc-99m in the human body as a result of the widespread medical use of this isotope.[7,8,9,10] Unfortunately, few data exist describing the behavior of technetium in the body from chronic intake of environmental forms and levels.[1] In both areas, the lack of a sufficiently sensitive technetium analysis has hampered the definition of these systems under more realistic conditions.

Most recent analytical research aiming for a Tc-99 analysis with the highest possible sensitivity has centered around the use of mass spectrometry. Its principal attractions are high sensitivity and selectivity, as well as versatility for other applications. J. H. Kaye et al. of Pacific Northwest Laboratories have made notable contributions with this and other techniques.[12,13] The Chemistry Group of Savannah River Laboratory's Environmental Transport Division in collaboration with R. L. Walker of Oak Ridge National Laboratory's Mass Spectrometry Group has also concentrated on mass spectrometric techniques for Tc-99 analysis. This paper describes the resultant isolation chemistry of a novel technique which enhances mass spectrometry's already high sensitivity by concentrating the isolated technetium into a single anion exchange resin bead for filament loading. The resultant "point source" provides increased ion throughput for greater sensitivity than conventional solution loading of the filament. R. L. Walker will describe the mass spectrometry techniques in the following paper entitled "Development of Resin Bead Isotope Dilution Mass Spectrometric Techniques for Tc-99 Analysis."

ANALYSIS GOALS

Several goals were of primary importance in the design of this Tc-99 analysis: Foremost was the selection of mass spectrometry as the measurement system because of its ability to detect as little as 1 x 10^{-14} g of Tc-99. An isotope dilution technique using Tc-97 as a yield tracer was chosen to correct for isolation and detection inefficiencies. From these choices came the need for chemistry with high discrimination against the isobars of the measurement isotopes (Tc-97 and Tc-99), namely Mo-97 and Ru-99.

The decision to use ion-exchange resin bead mass spectrometry sample loading was based on the success of the technique for zirconium, uranium, and plutonium analysis at ORNL.[14,15] While it affords higher signal-to-noise mass spectrometric measurements than direct solution loading of mass spectrometer filaments, it dictates only the final phase of the chemical isolation scheme in a noncritical way.

Further goals included high recovery of technetium through the chemical isolation procedure, the elimination of technique-critical steps (e.g., distillation from concentrated H_2SO_4, electroplating, special reagent purification, etc.), elimination of reagents with potential for molybdenum and/or ruthenium contamination (e.g., CuS precipitation), and the use of a minimum volume of reagents, again to lessen contamination potential. Of lesser importance and suitable for later consideration are speed and cost of the analysis.

ANALYSIS METHODOLOGY

In its current state, the core of the Tc-99 analysis is designed to accept aqueous technetium solutions of low to moderate ionic strength (Figure 1). It is based on two

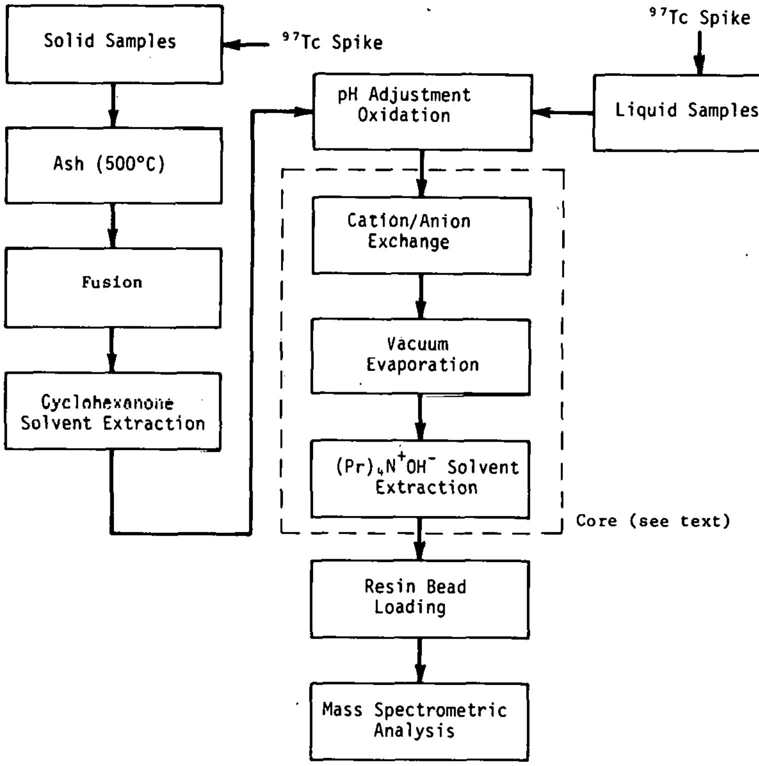

Figure 1. Procedural Diagram

chemical isolation techniques: tandem column ion-exchange and ion-association solvent extraction. The former is a modification of the work of Huffman et al.[16] and the latter is adapted from Maeck et al.[17]

Spiking of samples with Tc-97 precedes any chemical treatment. Aqueous samples are then oxidized with H_2O_2 and adjusted to a pH <5 with HCl, as necessary, to ready them for ion-exchange. With solid samples, the spike is applied in multiple portions to the finely divided sample with as wide a distribution as possible. Uniformity is enhanced by slurrying with a small excess of concentrated NH_4OH. Following drying at 100-120°C, samples with significant organic content are charred and ashed. Ashing temperatures must be kept low (∿500°C) to prevent loss of technetium by volatilization.

The ash or soil is then fused with either a Na_2O_2 flux or a mixed flux of (5.08) K_2CO_3: (3.92) Na_2CO_3: (1.00) $NaNO_3$ (w:w:w). The latter flux requires a somewhat higher temperature than Na_2O_2, but the fusion can be performed in inexpensive Ni crucibles without significant dissolution of the crucible. This avoids the need to use zirconium or platinum crucibles or to deal with large quantities of hydrated nickel oxide when dissolving the fuse. The mixed flux leaves very little residue when applied to the sand and clay soils and pine straw common to the SRP site. About 4 g of flux are used for each gram of soil.

The dissolved fuse is subjected to a single extraction/back-extraction cycle with cyclohexanone and cyclohexane[18] to transfer the technetium to an aqueous medium of low ionic strength suitable for ion-exchange. Freshly distilled cyclohexanone greatly speeds phase separations. Typical technetium recoveries for the procedure through back-extraction are 87%.

The apparatus for the tandem column ion-exchange is shown in Figure 2. Its purpose is a gross cationic cleanup and some initial discrimination against molybdenum and ruthenium. Tandem operation, as opposed to two discrete column steps, significantly shortens the time needed for ion-exchange. Elution of much of the molybdenum and ruthenium from the anion exchange column by 1M HCl is followed by elution of technetium with 4M HNO_3. Typically, 99% of the input technetium is recovered from the tandem ion-exchange step.

Before proceeding to the solvent extraction step, it is necessary to reduce the volume of the column effluent and its content of NO_3^-. The latter suppresses recovery of technetium in the subsequent solvent extraction step. Both objectives

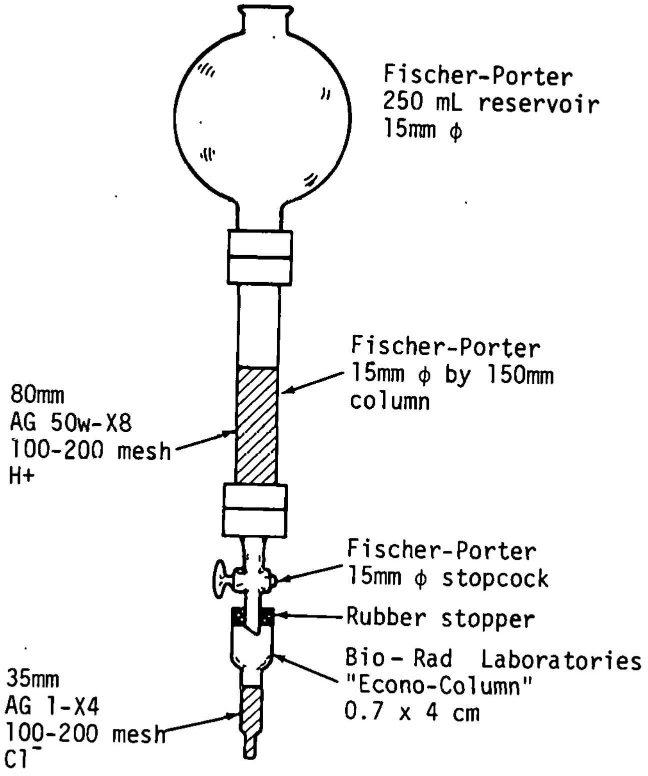

Figure 2. Tandem Ion-Exchange Column

are accomplished by a room temperature vacuum evaporation of the column effluent to a final volume of about 0.2 mL. The apparatus is shown in Figure 3. Recovery of input technetium is normally 91%. This technique conforms to an early suggestion of Anders[19] and solves the problem of low and inconsistent recoveries of technetium experienced by evaporations at higher temperatures.

Solvent extraction of the tetrapropylammonium ion-association compound of technetium into 4 methyl-2-pentanone follows the vacuum evaporation. Back extraction into an aqueous phase is accomplished by diluting the 4 methyl-2-pentanone with cyclohexane after the work of Boyd et al.[18] A double extraction cycle is used to reduce the contamination potential from incomplete phase separation. Early experiments with Mo-99 tracer indicated that the distribution ratio for molybdenum in the forward extraction was less than $\sim 1.3 \times 10^{-5}$. Recovery of technetium through the solvent extraction procedure has been about 95%.

Technetium is then loaded onto pairs of anion exchange beads following another room temperature evaporation of the aqueous back-extract to a volume of 0.2 mL. Beads of 2.7 to 3.3×10^{-4}m diameter are microscopically selected from a

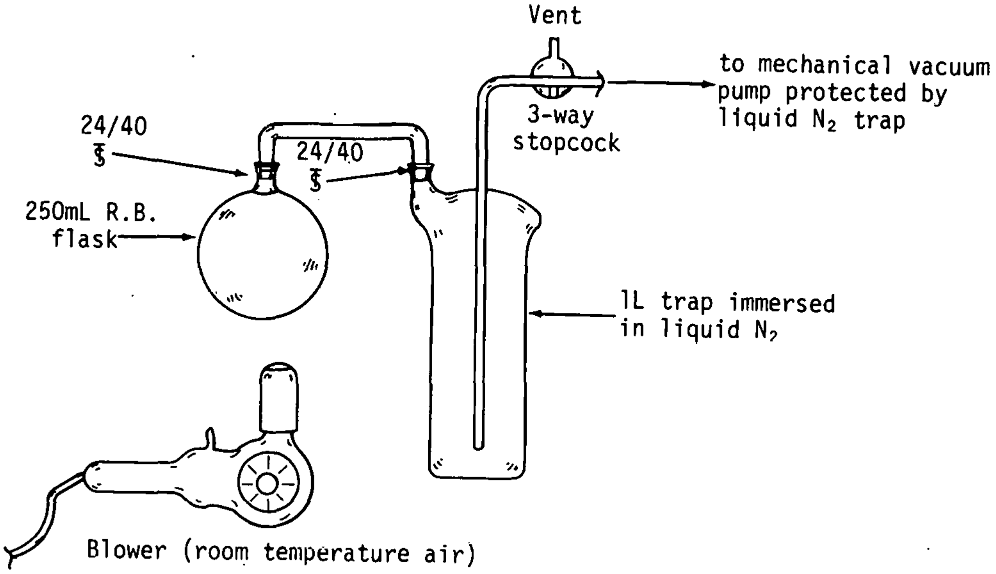

Figure 3. Vacuum Evaporation Apparatus

supply of AG-1X10, Cl$^-$, 100-200 mesh beads. A pair of such beads is combined with the 0.2 mL of evaporated back-extract in a 400 µL micro test tube (Brinkman 22-36-390-5) and agitated vigorously for two hours. The second bead is a backup in case the first is lost during handling. Both a vortex mixer and a pipet shaker (TechniLab model 31) have been used. The latter allows facile agitation of at least four micro test tubes at once. In a series of trials with simulated evaporated back-extract under the above conditions, the uptake of technetium for seven pairs of beads averaged 86% with a standard deviation of only 1.7%. Earlier experience with small beads ($<2.5 \times 10^{-4}$m diameter) and 4% cross-linkage gave inconsistent uptakes, some as low as 32%.

Following uptake, the beads are isolated from the solution and mounted on glass microscope slides with 1:8 (vol:vol) flexible collodion:ethanol for storage or shipment. The handling of the beads is conducted with the aid of an 8X to 40X stereoscopic zoom microscope. Transfer tools consist of drawn Pasteur pipets and a tungsten needle probe. The pipets are drawn to tips larger than the bead diameters for transferring beads plus solution; and to tips smaller than the bead diameters for transferring solution alone. After the solution is removed, beads can be transferred by the tungsten needle when tipped with a globule of adhesive teased from cellophane tape. Experience with this handling system has been excellent; most novices can be trained to handle beads without loss in a matter of hours. Overall recoveries from aqueous sample through bead uptake are typically 73%.

In addition to purification, another necessary function of the isolation scheme is concentration. Considering an aqueous sample of 100 mL and a 0.3-mm diameter pair of anion-exchange beads, an overall concentration of $\sim 1 \times 10^6$ is effected by the procedure, $\sim$3500 being attributable to the bead uptake step. The important aspect of this is that the spatial distribution of the technitium on the mass spectrometer filament remains confined by the bead to a "point source" during filament loading.

The procedure for mass spectrometric measurement will be discussed by R. L. Walker in a following paper.

RESULTS

Standards

A number of standards has been prepared spanning the values from 0.1 pg to 12 ng of Tc-99. All contained 917 pg of Tc-97. The standards were subjected to the entire analysis procedure for aqueous samples (Table I). Good consistency in the normalized Tc-99/Tc-97 corrected count ratios is evident throughout the 6-decade range. The method clearly has potential sensitivity beyond 0.1 pg.

Samples

Various environmental samples, both aqueous and solid, from the vicinity of SRP have been analyzed for Tc-99 by this method (Table II). It should be noted that these data were generated with less than normal bead uptake and some results, namely F-Area Spring and the herb-litter sample, show poor internal precision for the bead pair. Nonetheless, one concludes that Tc-99 in the F-Area seepage basin easily migrates with the groundwater to the F-Area Spring ($\sim$9 years travel time based on H-3 studies).[20] From there it is transported to the spring's receiving stream, 4-Mile Creek, and finally the Savannah River. These data, when combined with Savannah River flow rates, generate an annualized instantaneous Tc-99 release rate from SRP of 0.05 Ci/yr to the river. In all cases, the measured Tc-99 aqueous concentrations have been well below the Federal concentration guides for releases to uncontrolled areas.[21]

Table I

Table I. Analysis of Standard Bead Sets

^{99}Tc Added, ng	$\dfrac{\dfrac{\text{Counts } ^{99}\text{Tc}}{\text{Counts } ^{97}\text{Tc}}}{^{99}\text{Tc Added, ng}}$
11.6	1.08 ± 0.03[a]
1.16	1.05 ± 0.03
0.116	1.10 ± 0.04
0.0106	1.65 ± 0.2
0.0116	1.09, 1.13[b]
0.00105	1.1, 1.1
0.000105	1.8, 1.1

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a. Counting standard deviation shown.
b. Results from both beads of a pair shown.

Table II

^{99}Tc Results from Environmental Samples

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

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

In summary, the current Tc-99 analysis can determine as little as 0.1 pg of Tc-99. It has been applied successfully to a variety of environmental samples and thus provides a powerful tool for realistic determination of the environmental behavior of Tc-99. Through further development, increased sensitivity can be expected. Productivity gains might be possible through elimination of the second ion-association solvent extraction cycle and a shorter, less tedious solubilization procedure for solid samples.

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