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Optimization of Various Factors for the Separation of Technetium Using Anion-Exchange Resins

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ABSTRACT

A radiotracer technique was used to optimize the separation of technetium using an ion-exchange resin through the selection of a resin, the elution conditions, and the nitric acid concentration. The average recovery was 91 ± 4% using Dowex 1-X8 resin, indicating that most of the Tc was eluted with 12 M HNO_3. Analyses of the tracers were carried out by ICP-MS and γ-ray spectrometry.

Key Words. Technetium; Anion exchange, ICP-MS, γ-Spectrometry

INTRODUCTION

The very low level of ^{99}Tc expected to be found in environmental water samples necessitated the use of large sample volumes. Many methods (e.g., evaporation, direct extraction, coprecipitation, and anion exchange) are used for the separation/concentration of Tc. Among these, anion exchange is a very efficient technique widely used for the separation and concentration of radionuclides. Examination of the literature shows that the pertechnetate ion (TcO_4^-) is very strongly adsorbed by strong base anion exchangers and can be eluted only by ions with a very high affinity for the resin (1, 2). The separation of Tc from fission products is based on the sorption of the TcO_4^- from weak acid, neutral, and alkaline media by anion exchangers; most of the fission products (^{137}Cs, ^{90}Sr, and others) are passed through anion exchangers (3). Several workers have compared a variety of anion-exchange resins and various eluants with different molarities (1, 3–7).

Gamma spectrometry and the new technique of inductively coupled plasma-mass spectrometry (ICP-MS), were applied. ICP-MS has significant advantages compared to other methods (8, 9). In addition to the concentration/separation of Tc, an anion-exchange column is used to meet the requirements of the ICP-MS instrument.

EXPERIMENTAL

Standard/Tracers

In order to determine the chemical yield of Tc in different steps, the following standards/tracers were used: (a) technetium-99, (b) rhodium-103 standard solution, and (c) technetium-95*m*. The necessity of using these standards/tracers was described earlier (10).

Column

The column dimensions were 20 cm long and 12 mm in diameter, and the support was a sintered glass plug instead of glass wool. The flow rate was controlled by a Teflon tap. The column head was closed with a glass wool plug and was loaded with a glass rod.

Instrumentations

The analyses were carried out using a VG PlasmaQuad PQ1 ICP-mass spectrometer and a NaI detector with a MCA (Canberra Series 35) for ^{99}Tc and ^{95m}Tc, respectively.

Procedures

Before use, the resins were soaked in deionized water for a few hours. A slurry of resin was placed in a column. The chloride form of the resin was converted to the nitrate form by washing the resin with 8 M HNO_3, followed by a rinse of distilled water to a near neutral pH.

A number of experiments were carried out to select various parameters of the column. The details of the procedures were given earlier (10). All samples were finally prepared in 5 or 10 cm^3 2% HNO_3 (depending on the ^{99}Tc concentrations). ^{103}Rh was added as an internal standard and measured at least in duplicate. Each analysis was based on three ICP-MS runs.

RESULTS AND DISCUSSIONS

In procedures involving high temperatures, Tc losses can occur due to volatilization. During precipitation, because of its tracer concentration, Tc tends to be coprecipitated, resulting in losses. When handling large volume samples, solvent extraction is often a difficult technique. Technetium losses, and the problems of handling large volumes, can be avoided by the use of anion-exchange methods; procedures can be made selective and efficient for the separation of Tc. Hence, keeping in mind the low concentration of the radionuclide and the high chemical recovery of Tc, the anion-exchange resin method was found much more attractive than other methods. Large volume water samples could be reduced by extracting the Tc onto an anion-exchange resin and then eluting the Tc from the resin in as small a volume of eluant as possible.

After initial pretreatment of biota/soil samples, a suitable form of solution was required for ICP-MS analysis. The final solution was clear, less than 2% in HNO_3, and had a salt concentration of less than 0.1%. To minimize corrosion and deposition in the spectrometer and to minimize a large "background" of electrolyte, ion exchange was used. The column was washed thoroughly with cold and then with hot distilled water to remove salts; Tc was stripped with 12 M HNO_3. The eluate was completely evaporated at <100°C because a high temperature led to high Tc losses. Finally, the residue was redissolved in 2% HNO_3 and filtered, if necessary.

Analyses of the tracers were carried out by ICP-MS and γ-spectrometry. Calibration of the NaI detector was done with known sources of ^{137}Cs, ^{60}Co, and ^{22}Na. A typical ICP-MS spectrum of ^{99}Tc and ^{103}Rh peaks is shown in Fig. 1. The background, limit of detection (L.O.D.), and the

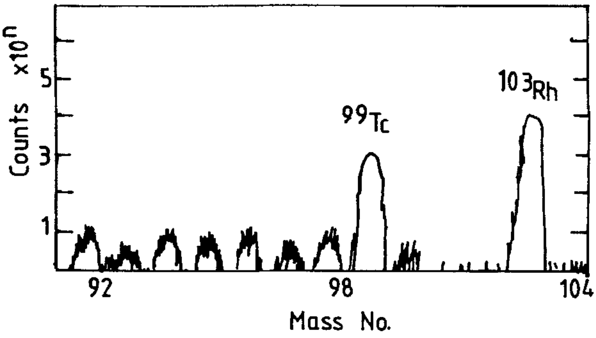

FIG. 1 ICP-MS spectrum for ^{99}Tc and ^{103}Rh.

stability of the instrument were checked each time analyses were carried out. Sample blanks were also run to check the background counts in the mass region of interest. Blank samples were presented in 2% v/v HNO_3, bracketing each sample.

The results of various experiments are discussed below.

Ion-Exchange Selection

The three Cl^- form resins available [Dowex 1-X8 (50–100 mesh), Duolite 113 (52–100 mesh), and Dowex 1-X4 (50–100 mesh)] were evaluated to check their efficiencies for Tc recoveries. The percent recoveries for Tc are given in Table 1. The maximum recovery was obtained for Dowex 1-X8 resin; therefore, this resin was adopted for further experiments.

Choice of the Quantity of Resin

A. The results of the analysis of filtrate, passed through various quantities of the resin, are plotted in Fig. 2. The results of ^{99}Tc analyses showed that the percent loss was very low (<0.4) when using 5 cm^3 or more resin.

The percents of Tc elution recoveries for different quantities of resin using ICP-MS are given in Table 2. Greater than 90% recovery was obtained with 2 cm^3 of resin, but the loss in the filtrate was large (>1.2%). Also, low quantities may not be feasible for large volumes/quantities of real samples. On the other hand, for resins of >5 cm^3, elution becomes difficult. Hence, on the basis of the results, it was concluded that a 5-cm^3 resin volume was the best to use.

B. Another experiment was designed to compare the yields of both the tracers (^{99}Tc and ^{95m}Tc). The results obtained are given in Table 3.

Effect of Eluant Concentration on Recovery

In this experiment, different concentrations of HNO_3 were used for elution of ^{99}Tc. Figure 3 shows the percent Tc recoveries for various

TABLE 1
Percent Chemical Recoveries of ^{99}Tc for Different Anion-Exchange Resins

Resin	Chemical recovery (%)
Dowex 1-X8 (50–100 mesh)	98 ± 2
Dowex 1-X4 (50–100 mesh)	96 ± 2
Duolite 113 (52–100 mesh)	93 ± 3

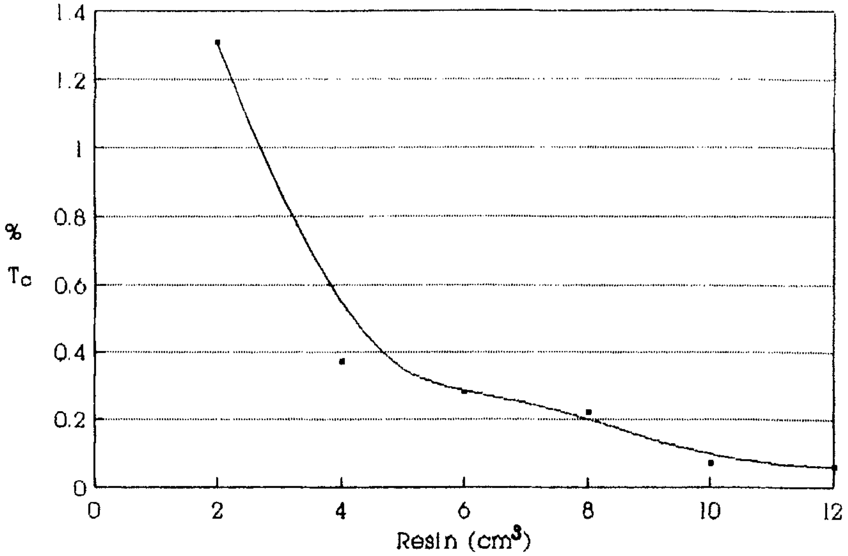

FIG. 2 Percent Tc loss in the filtrate.

molarities. The elution was incomplete with 100 cm^3 of 4 M solution. Almost 100% yield was achieved in a 40 cm^3 solution of higher acid concentrations (12 and 16 M). However, to minimize acid consumption, 12 M HNO_3 was selected for future work.

Effect of Various Reagents on Tc Retention

The aim of this experiment was to select a medium to retain maximum Tc on the resin when passed through the column. The results of experi-

TABLE 2
Percent Recoveries of ^{99}Tc by ICP-MS in the Eluates Using Different Quantities of Dowex 1-X8 Slurries

12 M HNO_3 (eluate)	Resin quantities (in cm^3)					
	2	4	5	6	8	10
1st 20 cm^3	92.4	94.4	89.0	83.6	55.3	38.2
2nd 20 cm^3	2.4	3.0	9.6	13.8	42.1	57.7
3rd 20 cm^3	0.2	0.0	0.1	0.1	0.3	0.9
4th 20 cm^3	0.0	0.1	0.1	0.1	0.0	0.2
5th 20 cm^3	0.0	0.0	0.0	0.1	0.0	0.0

TABLE 3
Comparison of Percent ^{99}Tc and ^{95m}Tc Recoveries

Resin Dowex 1-X8 (cm^3)	12 M HNO$_3$ (eluate)	Percent ^{99}Tc recovery (ICP-MS)	Percent ^{95m}Tc recovery (γ-spectrometry)
2	1st 20 cm^3	91.9	86.5
	2nd 20 cm^3	3.6	6.4
	3rd 20 cm^3	0.4	0.1
4	1st 20 cm^3	84.6	83.0
	2nd 20 cm^3	13.6	16.3
	3rd 20 cm^3	0.4	0.0
6	1st 20 cm^3	81.0	85.4
	2nd 20 cm^3	13.5	12.7
	3rd 20 cm^3	0.1	0.0
8	1st 20 cm^3	38.1	37.1
	2nd 20 cm^3	53.6	51.6
	3rd 20 cm^3	6.6	6.3
10	1st 20 cm^3	21.3	21.4
	2nd 20 cm^3	20.9	19.2
	3rd 20 cm^3	14.1	17.6

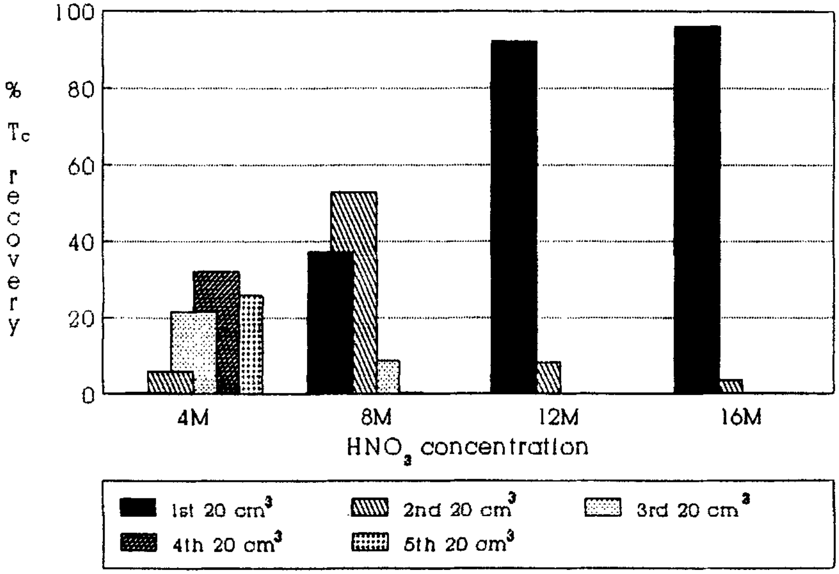

FIG. 3 Elution of ^{99}Tc from Dowex 1-X8 at various HNO$_3$ concentrations.

TABLE 4
Percent ^{99}Tc Retained/Not Retained on Resin (Dowex 1-X8)

Reagent (medium)	Percent Tc	
	In filtrate	Retained on resin
2 M HNO_3 (acidic)	23	77
2 M NaOH (basic)	—	93
Distilled H_2O (neutral)	<1	>99

ments in which ^{99}Tc in different media were passed through Dowex 1-X8 resin are given in Table 4. From an analysis of the results, it is clear that neutral solutions can give high chemical yields. The filtrate of the basic media was not analyzed by ICP-MS because of its large salt concentration.

Effect of Flow Rate on the Elution

In addition to such factors as the medium of solution and the molarity of eluate, the most important parameter for large losses of Tc is the flow rate.

An experiment was performed to check flow rate effects for elution recoveries using ^{95m}Tc as a tracer. The results are given in Table 5. Slow flow rates were preferred because they gave comparatively high yields. Columns were never allowed to run dry. If the flow rates were slow enough to allow dryness, then the method became useless. On the basis of this experiment, a flow rate of 0.2–0.3 $cm^3 \cdot min^{-1}$ was selected.

Loss of Tc in the Resin

After the elution of Tc, the discarded resins were checked for Tc losses. The analysis of ^{95m}Tc of the anion-exchange resin after elution with 12 M

TABLE 5
Effect of Flow Rate on Elution

Time in minutes for 40 cm^3 eluate	Percent ^{99}Tc recoveries
15	82
22	88
89	89
>360	83

HNO_3 gives the following values:

$$^{95m}\text{Tc retained in the resin} = 7.5 \pm 3.2\% \qquad (n = 41)$$

where n = number of observations.

Reproducibility of the Anion-Exchange Elution Step

The following two experiments were carried out to determine the reproducibility of the anion-exchange step.

In the first experiment, four columns of 5 cm^3 resin were taken. After passing ^{99}Tc solution through them, Tc was eluted with four 20 cm^3 fractions of 12 M HNO_3, and the eluate was evaporated at 84–95°C. The results are given in Table 6. The small variation found may be explained by various factors mentioned above.

In the second experiment, ^{95m}Tc and ^{99}Tc were eluted with two 40 cm^3 12 M HNO_3 fractions using a 5-cm^3 slurry of Dowex 1-X8. The final recoveries after the evaporation were found to be:

$$^{99}\text{Tc} = 91 \pm 4\% \qquad (n = 4)$$

$$^{95m}\text{Tc} = 93 \pm 4\% \qquad (n = 3)$$

Tc and Ru Resin Blanks

A 5-cm^3 slurry of Dowex 1-X8 resin was taken in a column, and 2 × 50 cm^3 12 M HNO_3 was passed through the resin as eluant. The eluate was evaporated and redissolved in 2% HNO_3 for analysis. The results showed that there was no ruthenium, but only in one case was trace contamination (0.07 pg/g) of Tc present. This might be due to a high instrument response, a statistical error in the background counts, or contamination,

TABLE 6
Experiment Carried Out for Checking the Reproducibility of Eluates/Filtrates of the Anion-Exchange Step

12 M HNO_3 (eluate)	Column I	II	III	IV
1st 20 cm^3	85.7	80.3	79.6	89.6
2nd 20 cm^3	13.3	16.1	16.4	7.4
3rd 20 cm^3	0.2	0.5	0.9	0.1
4th 20 cm^3	0.2	0.1	0.1	0.1
Filtrate	0.3	0.3	0.3	0.6

although precaution was taken to avoid contamination. Overall, it was assumed that there was no ^{99}Tc blank in the resin.

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