Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Methods for the Separation of Technetium from Ruthenium for Inductively Coupled Plasma-Mass Spectrometry

Ihsanullah[a]
[a] HEALTH PHYSICS DIVISION, PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY, ISLAMABAD, PAKISTAN

To cite this Article Ihsanullah(1994) 'Methods for the Separation of Technetium from Ruthenium for Inductively Coupled Plasma-Mass Spectrometry', Separation Science and Technology, 29: 6, 781 — 797
To link to this Article: DOI: 10.1080/01496399408005608
URL: http://dx.doi.org/10.1080/01496399408005608

SEPARATION SCIENCE AND TECHNOLOGY, 29(6), pp. 781–797, 1994

Methods for the Separation of Technetium from Ruthenium for Inductively Coupled Plasma–Mass Spectrometry

IHSANULLAH
HEALTH PHYSICS DIVISION
PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY
P.O. NILORE, ISLAMABAD, PAKISTAN

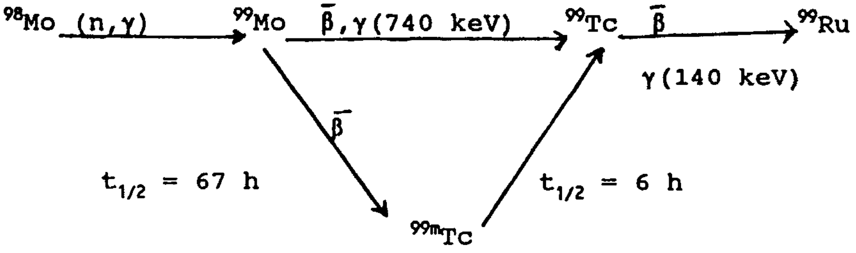
ABSTRACT

Because of its versatility, inductively coupled plasma–mass spectrometry (ICP-MS) is finding applications for trace multielement analysis in many fields. The technique has high sensitivity for the measurement of the long-lived technetium isotope ^{99}Tc. When using the ICP-MS technique, a key aspect of the development of a radiochemical separation procedure for technetium is that it should be optimized to achieve a maximum decontamination factor for the isobaric interfering ruthenium. Different methods, e.g., precipitation, anion/cation exchange, and solvent extraction, have been used. Comparison of the decontamination factors of Ru and the percent recoveries for various processes are reported. Complete decontamination, as required for environmental samples, was achieved.

Key Words. ICP-MS; ^{99}Tc; Ru; Decontamination; Separation

INTRODUCTION

Technetium (Tc) was the first of Mendeleev's missing element to be created artificially (1). To date, 21 isotopes and seven isomers are known (2), and none of these isotopes is stable. ^{99}Tc ($t_{1/2}$ = 2.1 × 10^5 years), the only important hazardous technetium isotope environmentally, is a pure β-emitter with a maximum energy of 0.292 MeV and a specific activity of 630 kBq·mg^{-1} (3). ^{99}Tc is produced either as a fission product, associated with the use of all types of reactor fuels including plutonium, uranium, and thorium, or by the thermal neutron bombardment of ^{98}Mo (3, 4). A high proportion (85%) of ^{99}Mo decays via the metastable nuclide ^{99m}Tc and then to the ground state ^{99}Tc (5):



The short-lived ^{99m}Tc also has become significant by serving as a body organ imaging agent in medical diagnoses (6). To date, thousands of kilograms of ^{99}Tc have been introduced into the biosphere from nuclear power plants, nuclear fuel reprocessing plants, nuclear weapons testing, and nuclear medicine (7). ^{99}Tc is produced naturally in very small quantities from the spontaneous fission of ^{238}U and the slow neutron-induced fission of ^{235}U (8). ^{99}Tc is of great concern because of its relatively high fission yield (6.1% from ^{235}U), its long half-life (2.1×10^5 years), and its high mobility in the environment (2, 3, 9).

As a result of worldwide nuclear programs, interest in future long-term collective dosing of the population and the behavior of ^{99}Tc in the environment is currently increasing exponentially. Jones and Davison (10) reviewed Tc chemistry and concluded that it is still poorly developed in comparison with that of its neighbors Mo, Mn, Ru, and Re and that the environmental behavior of Tc is at an immature stage. Data on the behavior of Tc is limited.

Keeping in view the low concentration levels found in the environment and the need to obtain more precise data for the assessment of the environmental impact of the nuclear fuel cycle, a comprehensive analytical separation procedure as well as a highly sensitive technique are desirable. In this regard, attention has been focused on a new powerful technique, i.e., inductively coupled plasma–mass spectrometry (ICP-MS). The ICP-MS takes less time for analysis and potentially offers very low limits of detection (L.O.D.). Moreover, the high sensitivity of ICP-MS compared to previous methods permits direct measurement of long-lived ^{99}Tc by this technique (11–13).

Since the ICP-MS technique is based on the measurement of the mass of an element rather than on its activity, any interference at mass 99 must be eliminated as far as possible. For ^{99}Tc, two isobaric nuclides are important. ^{99}Mo is a short half-life radionuclide which decays out completely after a few days. The other isobaric nuclide which will interfere is stable ^{99}Ru with a 12.7% abundance in natural ruthenium.

Various methods, i.e., coprecipitation (7, 14–17), solvent extraction (7, 14–28), anion/cation-exchange resins (14, 15, 17–19, 29, 30), and volatilization (7, 15–20), have been reported for the separation of Tc from the interfering Ru.

Different methods are compared in the present study to assess the degree of removal of Ru from environmental Tc samples. Comparison of decontamination factors (D.F.) with reported values are also ascertained. (See Table 1.)

TABLE 1
Percent Tc Recoveries and Decontamination Factors (D.F.) for Ru by Applying Various Processes

Process	Tc recovery (%)	D.F. (Ru)
NaOH washing of anion-exchange column	95	170
Precipitation of Ru with NaOH and methanol	85	350
Precipitation with NH_4OH and methanol	60	710
2 M H_2SO_4–5% TIOA–xylene extraction	95	700
NaOH washing of column and 5% TIOA–xylene	7	750
12 M HNO_3–tri-*n*-butyl phosphate (TBP) extraction and anion-exchange column	3	360
2 M H_2SO_4–TBP extraction and column	6–11	140
2 M H_2SO_4–50% TBP in xylene extraction and anion-exchange column	95	550
Cation-exchange column and chloroform extraction—water	95	40
NaOH washing of anion-exchange column, cation-exchange column, and cyclohexanone extraction	75	280
Water–cyclohexanone extraction—water	97	10
2 M H_2SO_4–cyclohexanone and anion-exchange column	95	1000
2 M H_2SO_4–1 M HCl–cyclohexanone and anion-exchange column	95	4000
Anion and then cation-exchange column	90	10
Water–chloroform extraction	99	1
Carbon tetrachloride extraction and anion-exchange column	75	700
NaOH washing of column and CCl_4 extraction	78	24

EXPERIMENTAL

Standards/Tracers

The following standards/tracers were used:

1. ^{99}Tc was utilized as a radiochemical yield monitor.
2. Atomic absorption (AA) grade standard ruthenium solution was chosen for calculating the Ru decontamination factor.
3. AA grade ^{103}Rh solution was used as an internal standard to check any drift in the response of the instrument.
4. ^{95m}Tc, a γ-emitting tracer ($t_{1/2}$ = 60 days), was used as an internal tracer.

Instrumentation

A VG PlasmaQuad PQ1 (ICP-MS) and a NaI detector with a 512 MCA (γ-spectrometry) were used for the measurement of ^{99}Tc and ^{95m}Tc, respectively. ICP-MS was also applied for the determination of Ru and ^{103}Rh.

Methods

The following methods were applied for the separation of interfering elements, in particular Ru.

Precipitation of Ruthenium

A sample of tap water (400 cm^3) was taken and spiked with 100 ppb of Ru(III) carrier solution. ^{99}Tc (13.6 ppb) was then added to this solution. After adding 10 cm^3 of 6 M NaOH and antibumping granules, the sample was brought to boiling. While boiling, a 10-cm^3 aliquot of methanol was carefully added to this solution. The reaction mixture was then allowed to cool slowly at room temperature, and the precipitate was filtered using GF/F glass fiber paper. The filtrate was passed through a 5-cm^3 Dowex 1-X8 anion-exchange resin which had been preconditioned with 8 M HNO_3. Following the elution, the column was washed with cold and hot deionized/distilled water. The eluate was evaporated and redissolved in 10 cm^3 of 2% HNO_3. The ^{99}Tc and Ru levels were measured by ICP-MS.

The precipitation procedure was repeated using a 20-cm^3 aliquot of NH_4OH (specific gravity of 0.88) in place of the 6 M NaOH.

NaOH Elution

Different experiments were carried out to monitor the use of NaOH as a "clean-up" eluent. A number of samples of 50 cm^3 deionized/distilled water were spiked with 13.6 ppb ^{99}Tc, 100 Bq ^{95m}Tc, 100 ppb Ru, and 50 ppb ^{103}Rh, and these were passed through a preconditioned (with 8 M HNO_3) 5 cm^3 Dowex 1-X8 anion-exchange resin. After elution of Ru with different volumes and concentrations of NaOH, the columns were washed with 50 cm^3 cold and hot deionized/distilled water. Tc was then stripped from the column with 40 cm^3 of 12 M HNO_3. The eluate was measured for ^{95m}Tc in 50 cm^3 counting geometry by γ-spectrometry. The solution was eventually evaporated to dryness, redissolved in 10 cm^3 of 2% HNO_3, and the concentrations of ^{99}Tc and Ru were measured using ICP-MS.

Solvent Extraction

Using different organic solvents, the following extraction methods for the separation of Tc from Mo and Ru were used.

Solvent Extraction into Cyclohexanone

1. A 20-cm^3 aliquot of organic solvent was added to 20 cm^3 of distilled water containing 100 ppb Ru and 13.6 ppb ^{99}Tc and stirred in a 100-cm^3 beaker. The mixture was transferred to a clean 100 cm^3 separating funnel and allowed to settle for 10 minutes. After separation, the aqueous layer was discarded while the organic layer was mixed with 20 cm^3 distilled water and 20 cm^3 cyclohexane, backextracted by shaking for 5 minutes in a 100-cm^3 beaker, and transferred to a 100-cm^3 separating funnel. Back-extraction was repeated by adding 20 cm^3 water to the organic phase. The aqueous phases were combined and analyzed for Ru and ^{99}Tc by ICP-MS.
2. A 30-cm^3 aliquot of cyclohexanone was taken and shaken with 50 cm^3 of 2 M H_2SO_4 (1–2 cm^3 H_2O_2) containing 100 Bq ^{95m}Tc and 100 ppb Ru. The organic layer was washed with 30 cm^3 of 4 M H_2SO_4 (containing few drops of H_2O_2), and the washings were discarded. Backextraction was carried out twice with 30 cm^3 of 0.5 M NaOH in the presence of 30 cm^3 cyclohexane. Cyclohexane was added to cyclohexanone in order to make backextraction easier. The aqueous phases were combined, neutralized to pH 7, and passed through preconditioned Dowex 1-X8 resin followed by elution with 40 cm^3 of 12 M HNO_3. ^{95m}Tc, ^{99}Tc, and Ru were measured as above.

Extraction was also carried out for Tc and Ru in a 2 M H_2SO_4–1 M HCl system instead of 4 M H_2SO_4–H_2O_2.

Solvent Extraction into Chloroform

A 25-cm^3 aliquot of distilled water containing 13.6 ppb ^{99}Tc and 100 ppb Ru was shaken for 4 minutes in the presence of 25 cm^3 chloroform. The organic phase was discarded. The chloroform wash step was repeated twice, and the aqueous phase was analyzed by ICP-MS.

Solvent Extraction into 5% TIOA–Xylene

50 cm^3 of a 2 M H_2SO_4 (1 cm^3 H_2O_2) solution containing ^{95m}Tc, ^{99}Tc, and Ru was placed in a 250-cm^3 beaker, 40 cm^3 of 5% TIOA–xylene was added, and the mixture was stirred for 5 minutes. The mixture was transferred to a 250-cm^3 separating funnel and settled for 10 minutes. A second aliquot of 35 cm^3 of 5% TIOA–xylene was added to the aqueous phase and mixed. After separation, the organic phase was washed with 50 cm^3 of 2 M H_2SO_4 by shaking for 5 minutes. The organic phase was backextracted twice with 20 cm^3 of 1 M NaOH and shaken for 2 minutes. The aqueous phases were passed through the resin for Tc elution. Tc and Ru were analyzed as above.

Solvent Extraction into Carbon Tetrachloride

An aliquot of 50 cm^3 of water containing 100 Bq ^{95m}Tc and 100 ppb Ru was adjusted to pH 4 (by using NaOH and H_2SO_4 solutions) and extracted with 50 cm^3 CCl_4 by shaking for 1 minute. The organic layer was discarded.

The extraction was repeated with a second aliquot of 50 cm^3 CCl_4. The aqueous phase (pH 7) was passed through Dowex 1-X8 resin. ^{95m}Tc was analyzed by γ-spectrometry. The eluate was finally adjusted to 2% HNO_3 for ICP-MS.

Solvent Extraction into Tri-n-butyl Phosphate

In the initial investigations of this work, 5 cm^3 TBP was added to a 20-cm^3 aliquot of 12 M HNO_3 containing 1 cm^3 H_2O_2, 13.6 ppb ^{99}Tc, and 100 ppb Ru and shaken for 5 minutes. After separation, the aqueous phase was again extracted with a further 5 cm^3 of TBP and discarded. The organic phase was backextracted twice by shaking for 2 minutes with 7 cm^3 of 2 M NaOH. The aqueous phase was processed and analyzed as above.

The procedure was repeated by taking 2 M H_2SO_4 in place of 12 M HNO_3 and using ^{95m}Tc instead of ^{99}Tc.

Cation-Exchange Separation of Tc

1. An aliquot of 50 cm^3 of 1.7 M HNO_3 containing ^{99}Tc was passed through a 5-cm^3 cation-exchange AG-50WX resin, preconditioned with 1.5 M HNO_3, followed by 2 × 20 cm^3 rinses with water. The filtrate and washings were evaporated to 10 cm^3 for analysis by ICP-MS.
2. 50 cm^3 distilled water containing ^{99}Tc and Ru was passed through a 5-cm^3 slurry of Dowex 1-X8(NO_3^-) followed by a 12 M HNO_3 elution. The eluate was evaporated and redissolved in 1.7 M HNO_3 and passed through a cation exchange AG-50WX resin(NO_3^-). The eluate was analyzed by ICP-MS.

RESULTS AND DISCUSSION

Because of its potential accumulation in the environment, ^{99}Tc is considered to be radiotoxic as well as highly chemical toxic. Hence, it is necessary to establish knowledge of the behavior of long-lived Tc radioisotopes in the environment. The use of ICP-MS was investigated for the analysis of ^{99}Tc present in low level environmental samples. When using ICP-MS, the main problem is elimination of the isobaric contaminant ^{99}Ru which is likely to be present in environmental samples.

Percent Recoveries of Tc and Ru Decontamination of Ru

Radiochemical separations often involve carrier (Ru) or spiked (^{95m}Tc or ^{99}Tc) procedures in which trace amounts of the elements or radionuclides of interest are added at the beginning of the procedure. Since the amount of inactive Ru carrier or tracer (^{95m}Tc or ^{99}Tc) added is known, determination of the amount present at the end of the separation will allow the chemical yield or D.F. to be calculated.

The percent recovery of each step and the final recovery were determined by using ^{95m}Tc or ^{99}Tc:

$$\%\text{ Tc recovery at each step} = \frac{\text{activity at each step}}{\text{activity added}} \times 100$$

Similarly, the percent Ru was determined from the quantity added and retained.

ICP-MS was used for the analyses of stable isotopes of Ru. However, the limitations of ICP-MS (salt concentration < 0.1%, in 2% HNO_3, no organic traces, and clear solutions are required), did not allow the measurement of Ru after each step. Therefore, in many cases an anion-exchange step was also carried out.

The D.F. for Ru was determined from the percent yield of Ru by ICP-MS. Percent yield was selected because the response of the instrument was not always the same. Standard Ru and Tc solutions were used for the determination of percent yields.

The D.F. for Ru was calculated by applying the following equation:

$$\text{D.F.} = \frac{100\%\ \text{Ru added}}{\%\ \text{Ru remaining}}$$

The average amount of Ru reported in crustal rocks (31) was at the 10 ppb level whereas the lower limit of detection (L.O.D.) for ^{99}Tc was 0.004 ppb. The concentration of ^{99}Tc in most environmental samples is just above the L.O.D. Hence, the potential interference from Ru is highly significant, and samples have to be decontaminated from Ru before analysis. Therefore, the ease with which this element could be removed was investigated.

A D.F. > 4000 (for blank samples) was required to reduce Ru levels to the background levels at mass 99, i.e., <10 counts. As ^{99}Ru/^{101}Ru is not constant at low concentrations, monitoring the ^{101}Ru could not be used for eliminating the ^{99}Ru contribution to the ^{99}Tc peak. By using step-by-step decontamination procedures, a D.F. of >4000, as required, for Ru was achieved.

To preserve the great sensitivity of the technique, the possible ways (i.e., precipitation, elution with NaOH, and solvent extraction) for separating Tc from Ru are shown in Fig. 1. The results obtained from the present work are discussed below.

Precipitation of Ruthenium

The results obtained by the precipitation method are given in Table 2. A D.F. of Ru of 345 and 715 and percent chemical recoveries of 82.9 and 58.0 of Tc were obtained using NaOH and NH_4OH, respectively. Less than 1% of Ru was present in the solution in both cases after removing the precipitate.

Although the D.F. with NH_4OH was almost double that with NaOH, the chemical recovery of Tc was very low. This might be explained by the severe bumping produced by the addition of alcohol which led to spillage. In addition, alcohol tended to evaporate when it was slowly added to the sample, so it was not possible to add exactly the same amount of alcohol to each sample.

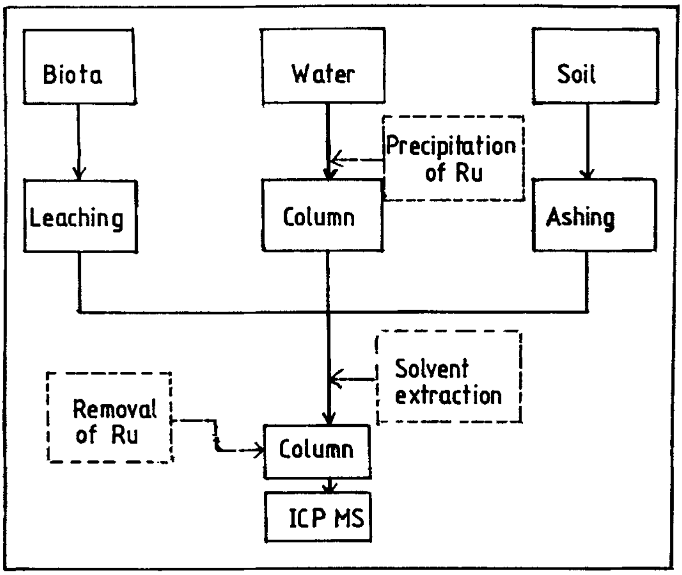


FIG. 1 Possible methods for the decontamination from Ru.

Precipitation and coprecipitation are widely applied for the separation of Cu, Fe, Ag, etc. NH_4OH and NaOH were used in a study (14) for separate precipitation. When using NH_4OH, Tc was not detected in the precipitate and 30 ± 3% Ru was found in the precipitate, but when NaOH was used, 92 ± 2% Ru was found in the precipitate.

A wide range of Tc losses (0–10%) have been reported (15–20) due to evaporation, sorption on walls, or by systematic error. Decontamination in the 98.69–99.64% range (D.F. 76–281) is also quoted (7).

NaOH Washing

The ease with which a number of nuclides, particularly Ru, could be removed from the anion-exchange resin prior to the elution of Tc by using

TABLE 2
Percent Recoveries of ^{99}Tc and D.F. of Ru by Precipitation

Process	^{99}Tc recovery (%)	D.F. (mean)
NaOH, methanol, precipitation, anion-exchange column	83 ± 12	345
NH_4OH, methanol, precipitation, column	58 ± 8	715

NaOH was investigated. The results obtained for various volumes and concentrations of NaOH are given in Table 3 and are plotted in Figs. 2 and 3.

This finding clearly showed that most of the sorbed Ru was removed from the resin by using NaOH. The maximum decontamination from Ru was achieved by 200 cm^3 of 3 M, 50 cm^3 of 2 M, 100 cm^3 of 1 M, and 150 cm^3 of 1 M NaOH. To avoid high concentrations of salts, 100 cm^3 of 1 M NaOH was preferred for the present work. The D.F. and percent recovery for 2 M and 1 M NaOH were found to be almost the same, but the loss of Tc was high when 3 M NaOH was used.

It was found that only 3 ± 1% ^{95m}Tc was eluted with 100 cm^3 of 1 M NaOH. After Ru elution, the column was washed with cold and hot water in order to remove the salt concentration of NaOH from the column. This was followed by Tc elution with 12 M HNO_3 for analysis of ^{99}Tc and Ru (if any remained) by ICP-MS.

Robb (14) applied 1 M NaOH for Ru washing prior to the elution of Tc with NaSCN, and reported that 58 ± 1% of the applied ^{106}Ru was sorbed onto the resin. Sodium hydroxide removed 15% of the sorbed Ru, while only 0.6 ± 0.2% Tc was found in the premature elution. During the anion-exchange step, various percent Tc losses have been reported: 14% (27), 5% (17), 6% (19), and 2.4% (15). A D.F. of 5 for Ru was obtained in the anion-exchange step without using NaOH solution (17).

TABLE 3
Ruthenium Decontamination with NaOH

Molarity (M)	Quantity (cm^3)	^{99}Tc recovered (%)	^{101}Ru left (%)	D.F. (Ru)
1	10	—	37.5	3
	20	95.0	20.1	5
	40	89.7	8.8	10
	50	82.8	2.1	50
	60	93.4	0.9	110
	100	90.4	0.8	120
	150	88.8	0.6	160
2	50	90.6	0.6	160
	100	92.5	1.9	55
3	50	60.4	0.9	110
	100	72.5	0.6	160
	200	74.7	0.6	170
4	100	89.5	1.9	55
6	100	94.7	2.1	50

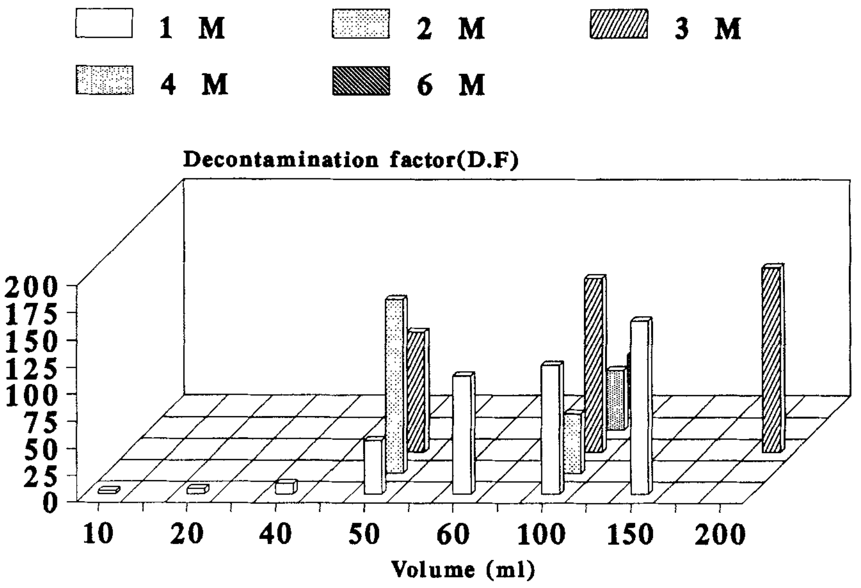


FIG. 2 Percent technetium recoveries for various quantities and concentrations of NaOH.

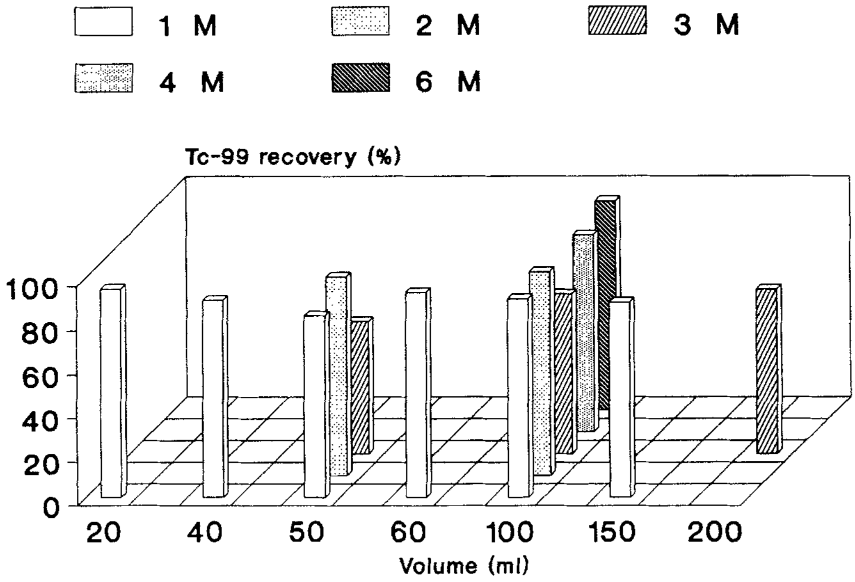


FIG. 3 Decontamination factor for ruthenium using different quantities and concentrations of NaOH.

Solvent Extraction

Because of its general advantages over other methods, solvent extraction is widely used (32, 33) for the separation of Tc. Boyd and Larson (28) and Gerlit (34) studied the extraction of Tc with 75 and 21 solvents from acid, alkaline, and neutral media, respectively. In the present study, different organic solvents were used for the decontamination of Ru from Tc solution. The distribution coefficients and percent Tc extraction for various solvents are summarized in Table 4. Table 5 reports the percent Tc recoveries and D.F. (Ru) during solvent extraction.

Solvent Extraction into Cyclohexanone. Based on Tables 4 and 5, it was found that a high decontamination factor was achieved with the 2 M H_2SO_4–1 M HCl–H_2O_2 medium. The water medium was comparatively better than the rest of the media, but this medium was not feasible for dissolving the residue after evaporation. The water–cyclohexanone system gave a distribution coefficient of 0.35. Cyclohexane was added in order to make the backextraction easy and efficient. The first backextraction with 30–50 cm^3 H_2O gave almost the same degree of extraction (94%) as was obtained with 0.5 M NaOH. In the second backextraction, 3–4% Tc was recovered.

Cyclohexanone was considered to be the best extracting agent for the separation of technetium(VII) among a large number of organic solvents (28). The distribution coefficients of Tc for cyclohexanone for 1 M HCl and 0.5 M H_2SO_4 are between 50 and 100, respectively. More than 98% of the Tc(VII) could be rapidly and efficiently separated by cyclohexanone extraction from a long-lived fission product mixture of ^{141}Ce, ^{144}(Ce-Pr), ^{140}(Ba-La), ^{95}(Zr-Nb), ^{103}(Ru-Rh), ^{106}(Ru-Rh), and ^{137}Cs with a D.F. of

TABLE 4

Distribution Coefficient and Percent Tc Extraction for Different Solvents and Media

Medium	Solvent	Distribution coefficient	Percent Tc extraction (maximum)
H_2O	Cyclohexanone	1200	97
2 M H_2SO_4	Cyclohexanone	100	98
2 M H_2SO_4–1 M HCl	Cyclohexanone	2000	98
H_2O	Chloroform	0.003	1
pH 4 + NaOCl	CCl_4	—	90
2 M H_2SO_4–H_2O_2	5% TIOA–xylene	100	98
12 M HNO_3–H_2O_2	TBP	0.25	3
2 M H_2SO_4–H_2O_2	TBP	40	11
2 M H_2SO_4–H_2O_2	50% TBP in xylene	40	80

TABLE 5

Losses and Recoveries of ^{99}Tc (or ^{95m}Tc) and Ru in Different Solvent Extraction Processes

		After extraction		Backextraction				
				First backextraction			Second backextraction	
Aqueous media	Organic solvent	% Tc in aqueous	% Ru in aqueous	Media	% Tc backextracted	% Ru backextracted	% Tc backextracted	D.F.
H_2O	Cyclohexanone	0.02 ± 0.04	74 ± 17	H_2O	92 ± 9	17 ± 2	3.0 ± 1.3	10
2 M H_2SO_4	Cyclohexanone	1.1 ± 1.5	[a]	0.5 M NaOH	94 ± 6	[a]	4.0 ± 1.2	1000
2 M H_2SO_4–1 M HCl	Cyclohexanone	4.0 ± 1.6	[a]	[a]	[a]	[a]	[a]	4000
H_2O	Chloroform	99	91 ± 10	[a]	[a]	[a]	[a]	1
2–3 M H_2SO_4	5% TIOA–xylene	6 ± 6	[a]	1 M NaOH	93 ± 9	[a]	4 ± 4	700
NaOH–H_2SO_4 (pH 4)	CCl_4	80 ± 0.1	[a]	[a]	[a]	[a]	[a]	700
12 M HNO_3	TBP	80 ± 9	96 ± 10	[a]	[a]	[a]	[a]	2600
2 M H_2SO_4	TBP	1.7 ± 0.7	[a]	2 M NaOH	2.5 ± 0.1	[a]	3.0 ± 0.8	1000
2 M H_2SO_4	50% TBP in xylene	[a]	[a]	2 M NaOH	79 ± 1.4	[a]	20 ± 0.4	4000

[a] Analysis not performed.

10^5–10^6 (27). The percent Tc recovery was found to be 95 ± 2 (7, 18), and a D.F. of 230 for Ru was obtained (7). Ruthenium is reduced to a low valence state and Tc is kept in the TcO_4^- state at a controlled valence with H_2O_2, hence Ru cannot be extracted but Tc can be by using cyclohexanone (7).

Solvent Extraction into Chloroform. Foti et al. (19) suggested the use of chloroform to minimize cyclohexanone and cyclohexane content in the strip solution and also to obtain a high Tc yield. The purpose of using chloroform in the present work was to clarify the level of decontamination from Ru. The distribution coefficients for ^{99}Tc and ^{99}Ru were 0.0033 and 0.1, respectively. More than 99% of Tc and about 91% of Ru were found in the aqueous phase after the chloroform wash.

Solvent Extraction into 5% TIOA–Xylene. Tri-isooctylamine (TIOA) in xylene was used to assess its suitability as an extractant. In the present case, extraction with 5% TIOA–xylene was extremely variable, especially for biota/soil samples. The loss of ^{95m}Tc for these samples was up to 15–20% but provided a high D.F. of 700 for Ru. A distribution coefficient up to 100 was obtained.

Extraction of pertechnetate into 5% TIOA–xylene is considered to be rapid and effective. About 90% of the Tc is backextracted with an equal volume of NaOH solution, and 99% with two backextractions (16). Losses of 1% (16) and 5% (7, 17) for Tc were reported. The addition of H_2O_2 leaves Tc as TcO_4^- whereas Ru is reduced, hence, Tc is extracted into 5% TIOA–xylene but Ru is not (17). The extraction efficiencies of ^{99}Tc from an anion-exchange eluent into hexane, tri-*n*-octylamine (TOA), and TOA in xylene are given in Table 6 (14).

Solvent Extraction into Carbon Tetrachloride. Tc and Ru are oxidized to RuO_4^- by NaClO. RuO_4^- can be extracted with CCl_4, leaving TcO_4^- in solution (7). By using CCl_4, Chen et al. (7) obtained distribution coefficients in the 7.9×10^{-4} to 3.4×10^{-3} and 73.3–110.4 ranges and percent extraction rates between 0.08–0.34 and 98.5–99.1 for ^{99m}Tc and ^{103}Ru, respectively. A high extraction of ruthenium tetroxide into CCl_4 from acid solutions was reported (35). About 5% of Tc is lost in the CCl_4 extraction (7).

TABLE 6

Percent Extraction Efficiencies of ^{99}Tc in Different Organic Solvents

Solvent	Extraction efficiency (%)
TOA	73.9 ± 1.6
60% TOA–xylene	94.9 ± 3.6
30% TOA–xylene	99.9 ± 4.0
10% TOA–xylene	67.9 ± 1.4
Hexane	1.1 ± 0.8

When using CCl_4 in the present work, the percent extraction for Tc was about 90%. In order to minimize the acidity/basicity of the solution, an anion-exchange column is essential. After the extraction and column steps, about 80% ^{99}Tc and a D.F. of 700 from Ru were achieved.

Solvent Extraction into Tri-n-butyl Phosphate. Tri-*n*-butyl phosphate is widely used in the nuclear industry for the extraction of nuclides into an organic phase. Tables 4 and 5 show that the distribution coefficient for 2 M H_2SO_4-TBP is 160 times higher than for 12 M HNO_3-TBP extraction, and that 98% of Tc was extracted by TBP from 2 M H_2SO_4. The measured extraction was only 11%. It was found that Tc was not efficiently backextracted from TBP. An alternative procedure was investigated in which TBP was diluted with an equal volume of xylene (50% in xylene); then 95–98% ^{95m}Tc was backextracted with 2 M NaOH. More than 5 and 99% of ^{95m}Tc were backextracted from TBP and 50% TBP-xylene, respectively. To run the sample by ICP-MS, the solution was passed through an anion-exchange column and a final yield of 75–85% (^{99}Tc) was obtained. A D.F. of 4000 from Ru was achieved.

Nearly 5% Tc is not extracted by TBP from the aqueous phase while 1–2% is lost in washing and 2–4% is lost in backextraction with 1–4 M NaOH (20). 83 ± 1% of the Tc used was extracted into TBP from an aqueous pertechnetate solution, while the extraction efficiency of ^{106}Ru was 5 ± 1% and 2 ± 1% when no carrier and when "$RuCl_3 \cdot H_2O$" was used, respectively. However, satisfactory phase separation occurs when the aqueous phase has been acidified (14). A D.F. (Ru) of >4000 (20) and 1×10^4 (36) were obtained by TBP.

Cation-Exchange Separation of Tc

In the first experiment, 92.6 ± 1.3% ^{99}Tc was found in the filtrate of the cation-exchange resin and 3.4 ± 0.3% ^{99}Tc was passed with the first 20 cm^3 distilled water wash. In further water washings, no additional ^{99}Tc was detected.

In the second experiment, the eluate of the anion-exchange resin was dried, redissolved in 1.7 M HNO_3, and passed through Dowex 50 WX resin. The ^{99}Tc recovered was 83–90%, and a D.F. (Ru) of 10 was achieved.

Technetium was separated from many cation contaminants on a cation-exchange resin. Tc has a very low K_d and thus will pass through the resin quantitatively (19, 32). Roberts et al. (37) used an anion followed by a cation-exchange column for Tc purification of neutralized Purex waste supernatants. Some workers used cation resins for the separation of Cu(II) ions (26). Matsuoka et al. (30) obtained a D.F.s (Ru) of 1.04 and 1.52 for anion-exchange and cation-exchange columns, respectively. A D.F. of 5 was obtained in another study (17). About 6% Tc was lost in an anion-exchange step, but no loss was reported when a cation-exchange column was used (19).

The use of cation-type exchangers for the separation of Ru does not appear promising, perhaps because of the ease of formation of anionic-type complexes. For this reason, cation exchange is not considered useful based on the present work.

CONCLUSION

The significance of ^{99}Tc isotopes warrants reliable procedures for their analysis. Due to various analytical difficulties, however, there is still a serious shortage of the information required to assess properly its body burden and the impact of the nuclear industry on man and his environment. The main requirement when using highly sensitive ICP-MS is the elimination of isobaric interference. Therefore, possible methods to achieve this were studied.

Precipitation was not feasible for soil/biota samples, large environmental water samples, and due to losses by spillage when using methanol. An efficient decontamination of Ru was obtained by washing a column with NaOH solution prior to elution of Tc with HNO_3 and liquid–liquid extraction.

Adequate decontamination from Ru could be achieved by a single or a combination of simultaneous procedures.

ACKNOWLEDGMENTS

I express my sincere thanks to my supervisor, Dr. B. W. East (Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow, UK), for his guidance and constant help toward completion of this work. I am also grateful to Dr. M. A. Atta and Dr. S. M. Hasany at PINSTECH for their valuable suggestions during the preparation of this manuscript.

REFERENCES

1. C. Perrier and E. Segre, *J. Chem. Phys.*, *5*, 712 (1937).
2. J. Rioseco, Doctoral Dissertation, Lund University, Sweden, 1987.
3. S. E. Long and S. T. Sparkes, *AERE-R 12742*, 1988.
4. J. E. Till, in *Technetium in the Environment* (G. Desmet and C. Myttenaere, Eds.), Elsevier Applied Science, London, 1986, pp. 1–20.
5. C. Keller, *Radiochemistry*, Ellis Horwood, England, 1988.
6. F. Luykx, in *Technetium in the Environment* (G. Desmet and C. Myttenaere, Eds.), Elsevier Applied Science, London, 1986, pp. 21–27.

7. Q. Chen, A. Aarkrog, H. Dahlgaard, S. P. Neilsen, E. Holm, H. Dick, and Mandrup, *Radioanal. Nucl. Chem.*, *131*, 171 (1989).
8. B. T. Kenna and P. K. Kuroda, *J. Inorg. Nucl. Chem.*, *26*, 493 (1964).
9. J. H. Kaye, J. A. Merrill, R. R. Kinneson, M. S. Rapids, and N. E. Ballou, *Anal. Chem.*, *54*, 1158 (1982).
10. A. G. Jones and A. Davison, *J. Appl. Radiat. Isot.*, *33*, 867 (1982).
11. A. R. Date and A. L. Gray, *Applications of Inductively Coupled Plasma Mass Spectrometry*, Blackie, Glasgow, 1989.
12. Ihsanullah, Ph.D. Thesis, Glasgow University, Glasgow, 1991.
13. A. S. Hursthhouse, Ph.D. Thesis, Glasgow University, Glasgow, 1990.
14. P. Robb, Ph.D. Thesis, Loughborough University, Loughborough, UK, 1983.
15. H. J. Luxenburger and H. Schuttelkopf, in *Proceedings of the 5th International Conference on "Nuclear Methods in Environmental and Energy Research"* (J. R. Vogt, Ed.), CONF-840408-DE84 017348, 1984.
16. N. W. Golchert and J. Sedlet, *Anal. Chem.*, *41*, 669 (1969).
17. Q. Chen, H. Dahlgaard, H. J. M. Hansen, and A. Aarkrog, *Anal. Chim. Acta*, *228*, 163 (1990).
18. T. J. Anderson and R. L. Walker, *Anal. Chem.*, *52*, 709 (1980).
19. S. Foti, E. Delucchi, and V. Akamian, *Anal. Chim. Acta*, *60*, 269 (1972).
20. E. Holm, J. Rioseco, and M. Garcia-Leon, *Nucl. Instrum. Methods Phys. Res.*, *223*, 204 (1984).
21. A. Martinez-Lobo, M. Garcia-Leon, and G. Madurga, *Int. J. Appl. Radiat. Isot.*, *37*, 438 (1986).
22. M. Garcia-Leon, C. Piazza, and G. Madurga, *Ibid.*, *35*, 961 (1984).
23. P. Sattelberger, M. Mang, G. Herrman, J. Riegel, H. Rimke, and N. Trautmann, *Radiochem. Acta*, *48*, 165 (1989).
24. J. W. T. Meadows and G. M. Matlack, *Anal. Chem.*, *34*, 89 (1962).
25. W. W. Schulz, *Trans. Am. Nucl. Soc.*, *34*, 395 (1980).
26. M. Koide and E. D. Goldberg, *J. Environ. Radioact.*, *2*, 261 (1985).
27. G. Goldstein, ORNL-3750, 1964.
28. G. E. Boyd and Q. V. Larson, *J. Phy. Chem.*, *64*, 988 (1960).
29. J. P. Riley and S. A. Siddiqui, *Anal. Chim. Acta*, *139*, 167 (1982).
30. N. Matsuoka, T. Umata, M. Okamura, N. Shiraishi, N. Momoshima, and Y. Takashima, *J. Radioanal. Nucl. Chem.*, *140*, 57 (1990).
31. B. Mason and C. B. Moore, *Principles of Geochemistry*, 4th ed., Wiley, New York, 1982.
32. E. Anders, *The Radiochemistry of Technetium*, National Academy of Sciences (NAS-NS 3021), 1960.
33. A. K. Lavrukhina and A. A. Pozdnyakov, *Analytical Chemistry of Technetium, Astatine and Francium* (R. Konders, trans.), Ann Arbor-Humphrey Science, London, 1956.
34. J. B. Gerlit, *Proceedings of the International Conference on "Peaceful Uses of Atomic Energy,"* Vol. 7, United Nations, New York, 1956.
35. E. I. Wyatt and R. R. Rickard, *The Radiochemistry of Ruthenium*, National Academy of Sciences (NAS-NS 3029), 1961.
36. M. H. Campbell, *Anal. Chem.*, *35*, 2052 (1963).
37. F. P. Roberts, F. M. Smith, and E. J. Wheelwright, *Nucl. Sci. Abstr.*, *31*, 345 (1962).

Received by editor October 14, 1992
Revised July 7, 1993