

^{99}Tc detection in water samples by ICP-MS

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Summary. In this work three radiochemical procedures are presented for the determination of ^{99}Tc in aqueous environmental samples by ICP-MS. Technetium is pre-concentrated from a dilute solution by a reduction-precipitation process using FeSO_4 as the reducing agent. The precipitate is treated to extract and isolate Tc by three alternative methods which combine ionic exchange, with conventional or TEVA resins, and solvent extraction techniques using TBP. Special emphasis is paid to isolating the technetium from Mo and Ru, which are the major interfering elements for the mass spectrometric determination of ^{99}Tc .

1. Introduction

^{99}Tc is a pure β -emitter with a long half-life, $t_{1/2} = 2.11 \times 10^5$ y, which appears during the fission of ^{235}U or ^{239}Pu at a relatively high rate of about 6%. The environmental relevance of ^{99}Tc is well recognised. The reason for that is its long half-life, which assures its presence in Nature for a long time. ^{99}Tc will probably be a significant contributor with respect future committed dose of radiation to the population. Furthermore, its high mobility makes its introduction into underground waters from nuclear waste disposal sites potentially troublesome [1].

On the other hand, ^{99}Tc is considered an excellent potential tracer of some environmental processes, such as marine water movements. From this viewpoint it is interesting to analyse to what extent this is also true for atmospheric processes.

All these facts support the need for methods, which allows its determination in water samples. However, the quantification of ^{99}Tc in environmental concentrations is very difficult. Indeed, sub-ppt ^{99}Tc levels in unperturbed sites pose serious limitations to traditional radiometric methods [2, 3] owing to the long half-life of the isotope.

ICP-MS has been used successfully in environmental analysis and recently has been applied to long-lived radionuclides determination [4–10]. As a consequence, reports in the scientific literature, on the determination of ^{99}Tc using ICP-MS are now abundant. The spectroscopic interferences associated with the determination of ^{99}Tc are well known. Samples containing naturally occurring Ru pose the

potential for interference owing to the presence of isobaric ^{99}Ru (12.6% natural abundance). There is also the potential for interference, owing to incomplete mass resolution from ^{100}Mo (15.4% natural abundance) and ^{98}Mo (24.1% natural abundance) in samples containing high concentrations of Mo. A systematic study of the possible counting interferences and their effect in the mass spectrum depending on their concentrations in the final sample can be found in [11].

To avoid such interferences, a number of radiochemical separation procedures have been reported for use with environmental samples. In the case of water samples, a number of methods have been reported [12, 13] but these are generally designed for dealing with low volume samples. In this paper three alternate methods are proposed and evaluated for the separation of ^{99}Tc from high volume water samples and its measurement by ICP-MS. In addition some results are given on the presence of ^{99}Tc in underground water and rainwater samples.

In Sect. 2 the experimental set up is described, as well as the key parameters of the problem used to evaluate the studied methods. The methods for ^{99}Tc isolation are deeply studied in Sect. 3. The results of such analysis serve us to propose three complete ^{99}Tc extraction methods from high volume water, what is carried out in Sect. 4. Then, they are applied to real samples in Sect. 5. Some conclusions close the paper in Sect. 6.

2. Materials and methods

$^{99\text{m}}\text{Tc}$ was used as yield monitor. The advantages and drawbacks of its use have been recently discussed [14]. $^{99\text{m}}\text{Tc}$ was eluted before each evaluation from one of several Amersham Amertec medical generators in the Nuclear Medicine Service of Hospital Juan Ramón Jiménez of Huelva (Spain). A solid scintillation $\text{NaI}(\text{Tl})$ EG&G Ortec counter was used for the chemical yield calculations. The quadrupole ICP-MS instrument used in the present work was a Hewlett–Packard 4500 that was equipped with a Babington type nebulizer. Typical instrumental conditions are summarized in Table 1. Solutions measured by ICP-MS were spiked with sufficient Rh to result in a 10 ppb concentration of ^{103}Rh , which was used to correct the instrumental signal drift.

In some cases the steps of the separation methods were checked by using soil samples previously analysed for other elements [15]. This way, the sample matrix effects in the results could be evaluated.

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Table 1. ICP-MS operating conditions.

Radiofrequency power (W)	1240
Sampling depth (mm)	6.3
Carrier gas (l min ⁻¹)	1.17
Extraction lens 1 (V)	-150
Einzel lens N°2 (V)	5.5
Bias Omega lens (V)	-41
Omega minus lens (V)	-3
Quadrupole focus (V)	6

The chemical recovery R_Q , the concentration factor (CF) and the decontamination factor (DF) were used as figures of merit in evaluating each of the three radiochemical separation methods. If M_0 is the initial sample mass, M_f is the mass of the final 2%–5% HNO_3 acid solution which is aspirated into the ICP-MS, m_0 is the isotope mass in the initial sample and m_f is the remaining mass of this isotope after the chemical separation, the concentration factor (CF) can be defined as the ratio of concentrations of the isotope after and before the chemical separation. Therefore:

$$\begin{aligned} \text{CF} &= \frac{\text{Final isotope concentration}}{\text{Initial isotope concentration}} = \frac{\frac{m_f}{M_f}}{\frac{m_0}{M_0}} = \frac{m_f}{m_0} \frac{M_0}{M_f} \\ &= R_Q \frac{M_0}{M_f} . \end{aligned}$$

The interferences of Mo and Ru were checked respectively through the determination of ^{95}Mo (or ^{97}Mo) and ^{101}Ru by ICP-MS. On the contrary to the definition of CF, we define the $\text{DF}_{\text{Mo,Ru}}$ for each of the different interfering elements as the ratio of the concentrations of the interfering element before and after the chemical separation:

$$\begin{aligned} \text{DF}_{\text{Mo,Ru}} &= \frac{\text{Initial isotope concentration}}{\text{Final isotope concentration}} = \frac{\frac{m_0}{M_0}}{\frac{m_f}{M_f}} \\ &= \frac{1}{\frac{m_f}{m_0}} \frac{M_f}{M_0} = \frac{1}{P} \frac{M_f}{M_0} , \end{aligned}$$

being P the proportion of the interfering element retained in the final sample.

The Minimum Detectable Mass Concentration (MDMC) was also used to evaluate the proposed methods when they were applied to real samples. It is defined as:

$$\text{MDMC} = \frac{\text{LOD}}{b} ,$$

b (counts ppt⁻¹) being the slope of the calibration curve under typical operating conditions, while LOD is the Limit of Detection. A full discussion about the dependence of MDMC on the different variables of the experiment can be found in [14].

3. Chemical separation methods

Three radiochemical methods for ^{99}Tc determination are tested. Below we present a general review of each method.

This is followed by a discussion of the experiments that were carried out to optimise each method. Finally, each of the optimised methods is summarized.

3.1 Method A1

A summary of the analytical method is presented in Fig. 1. The preconcentration step and the removal of some inorganic impurities such as metallic cations using cation exchange are well described elsewhere [8, 16]. The analyte is loaded onto the anion exchange column using a solution of pH 9. After washing the column with 0.1 M HNO_3 (see details below) the Tc may be eluted with elevated concentrations of nitric acid. As described previously [17], ten 7 ml aliquots of 8 M HNO_3 could be sufficient to completely elute the Technetium from the anion exchange resin. However, according to a number of authors [18, 19], the temperature of the eluant has an influence on the recovery of the analyte. Therefore we have studied the influence of both acid concentration and temperature on Tc recovery.

The influence of acid concentration and temperature on the elution yield was studied using an apparatus that has been previously described [20]. In these tests, digested soil samples rather than standard solutions were used. This way, the matrix effects on the Technetium loading and elution efficiency could be evaluated.

Using this approach, about 2 kg of soil sample were reduced to ashes (1.5 h at 450 °C in a crucible, in subsequent processes), and the Tc was leached from the ashes using 2 ml of 8 M HNO_3 per gram of soil. Any residual particulate mat-

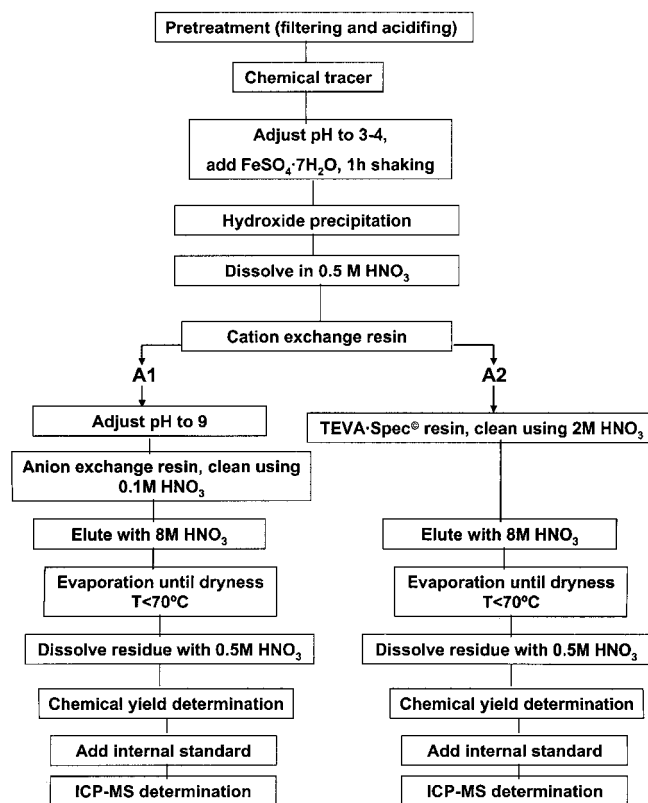


Fig. 1. Summary flow diagram for the preconcentration and separation of Tc using anion exchange and TEVA:Spec resins.

ter was removed by filtration. The filtrate of the leaching stage was adjusted to pH 9 using 10 M NaOH. The resulting solution was then divided into 64 aliquots and spiked with a known activity of ^{99m}Tc . Solutions prepared in this manner are similar to those that might be obtained from an environmental water sample. The chief difference being those prepared from soil would be expected to have significantly higher concentrations of matrix elements.

After spiking each aliquot was loaded onto a column containing Dowex AG1-X8 anion exchange resin. At a pH of 9, Tc is strongly retained by the resin bed. Following [4], approximately 100 ml of 0.1 M HNO_3 are passed through the resin to remove impurities, such as minor amounts of Mo and Ru from the sample.

Nitric acid concentrations between 4.8 and 9.6 M and elution temperatures between 25 °C and 65 °C were studied as stripping solutions. In each case, five aliquots of 7 ml were used to elute the sample. The results are shown in Fig. 2. Each point in Fig. 2 represents the average of four determinations, while the errors bar represent the estimated standard deviation of these results. Counting relative uncertainties were always around 1%–2%.

Within the range of acid concentration studied, the elution yield is uniformly high from 25 to 45 °C. Consequently, 4.8 M HNO_3 would be sufficient to recover the technetium at high yield from the resin at room temperature. On the contrary, at temperatures greater than 45 °C, higher concentrations of HNO_3 are required to fully elute the Tc from the column.

With these results, the optimised method A1 for the analysis of water samples can be summarized as follows:

- 1) The water sample is filtered and acidified with 0.6 ml of concentrated HCl per litre of water sample. A ^{99m}Tc spike is added as a yield tracer.
- 2) Adjust pH to 3–4 with a suitable volume of 5% NH_4OH .
- 3) The technetium is reduced to the +4 oxidation state with 0.7 g $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ per litre of water followed by gentle shaking for 1 hour. Then, a precipitation carrier (such as 0.5 g FeCl_3 per litre of water) is added. After its complete dissolution, the pH is adjusted to 9 with a suitable volume

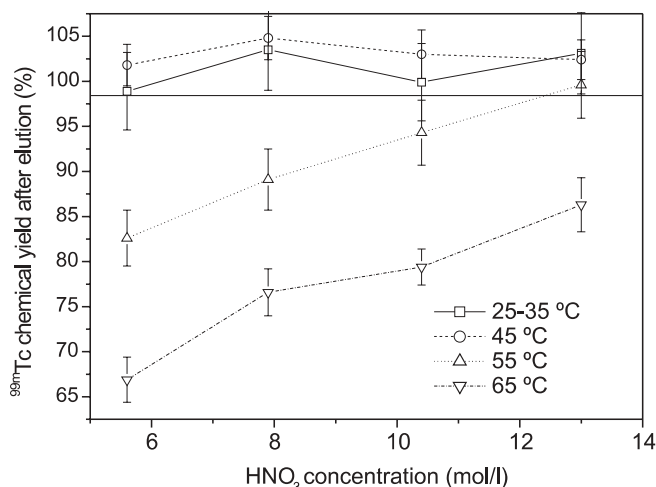


Fig. 2. Technetium elution yield from the AG1-X8 anionic exchange resin. Each of the points represents the average over four aliquots. The bar errors are the estimated standard deviations.

of 25% NH_4OH . Assuming the technetium reduction process was successful following hydroxide precipitation, this element would be concentrated in the precipitated.

- 4) The precipitate is dissolved with about 30 ml of 0.5 M HNO_3 per litre of water. Approximately 25 ml of 30% H_2O_2 are added to the solution which is heated under reflux to a temperature less than 75 °C. This assures an almost complete oxidation of the technetium to the pertechnetate state.
- 5) After cooling to room temperature the solution is added to a preconditioned Dowex AG50W cation exchange resin (0.5 ml of resin retained in a glass column with a glass-wool plug, washed with 20 ml of 0.5 M HNO_3), which removes inorganic trace elements that could interfere the process.
- 6) The pH is again adjusted to 9 using a suitable volume of 10 M NaOH, before loading the solution onto the Dowex AG1-X8 anion exchange column.
- 7) The anion resin is cleaned with 150 ml of 0.1 M HNO_3 to remove impurities such as minor quantities of Ru and Mo.
- 8) Technetium is stripped from the resin bed with 70 ml of 8 M HNO_3 at room temperature. The eluent solution is heated to near dryness at a temperature less than 90 °C.
- 9) Finally, the analyte is recovered with 10 ml of 0.5 M HNO_3 . The chemical yield is determined by gamma spectrometry and the internal standard is added before the ICP-MS analysis.

3.2 Method A2

It is easy to see, from Fig. 1 that the only differences between the methods A1 and A2 are the different chromatographic columns used to concentrate technetium and isolate the analyte from Ru and Mo. For Ru decontamination, the use of the TEVA-SpecTM resins (Eichrom Industries, Inc.) has been proposed [1]. The DF for Ru and Mo are high [21] and since the eluant volumes involved are very low, its use is clearly advantageous when compared to conventional exchange resins.

The conditions for loading, cleaning and the Tc elution for this microcolumn have been well described elsewhere [1, 10, 21], thus our efforts are to investigate the column performance when high volume solutions are loaded. Or, when the same microcolumn is reused multiple times using modest sample volumes. There appears to be little information of the performance of such columns after repeated use in the literature.

A TEVA microcolumn was conditioned with 20 ml of 0.5 M HNO_3 . Then approximately 50 ml of a test solution containing 102 ± 2 ppb of natural Mo, 1.07 ± 0.02 ppm of natural Ru and 50 ± 6 Bq/ml of ^{99m}Tc in 0.5 M HNO_3 were loaded on the microcolumn. Impurities such as Mo and Ru were then removed from the column using 20×2 ml aliquots of 2 M HNO_3 . Finally, the Tc was eluted with five 2 ml aliquots of 8 M HNO_3 . The elution yields as well as the Tc contents in the initial 0.5 M HNO_3 solutions and the 2 M HNO_3 cleaning solutions were determined by gamma spectrometry. The contents of the Ru and Mo interferents were also determined in each of the three solutions using ICP-MS.

The results of these separation experiments for four replicate determinations are shown in Tables 2 for Mo, 3 for

Table 2. Mo efficiency recoveries after repeated use of a TEVA-Spec column. (See the text for details).

Mo: $5.1 \pm 0.1 \mu\text{g}$ Experiment number	Recovery after loading (%) as 0.5 M HNO_3	Recovery after clean up process using 2 M HNO_3 (%)	Recovery after elution using 8 M HNO_3 (%)
1	81.1 ± 1.3	4.5 ± 0.5	4.7 ± 0.2
2	82.6 ± 1.6	5.8 ± 0.5	4.7 ± 1.6
3	74.6 ± 0.6	6.0 ± 1.5	5.3 ± 0.8
4	74.3 ± 0.8	12.5 ± 0.8	5.0 ± 0.1

Table 3. Ru efficiency recovery after repeated use of a TEVA-Spec column. See the text for an easier comprehension.

Ru: $53.6 \pm 0.9 \mu\text{g}$ Experiment number	Recovery after loading (%) as 0.5 M HNO_3	Recovery after clean up process using 2 M HNO_3 (%)	Recovery after elution using 8 M HNO_3 (%)
1	98.1 ± 2.1	1.5 ± 0.4	0 ± 3
2	98.2 ± 1.8	1.2 ± 0.3	0 ± 2
3	99.1 ± 1.4	1.1 ± 0.4	0 ± 4
4	99.6 ± 1.7	0.8 ± 0.1	1 ± 2

Table 4. Tc efficiency recoveries after repeated use of TEVA-Spec column. See text for an easier comprehension.

$^{99\text{m}}\text{Tc}$: $2.5 \pm 0.3 \text{ kBq}$ Experiment number	Recovery after loading (%) as 0.5 M HNO_3	Recovery after clean up process using 2 M HNO_3 (%)	Recovery after elution using 8 M HNO_3 (%)
1	0 ± 2	0 ± 3	99.4 ± 0.7
2	0 ± 2	0 ± 3	100.2 ± 1.8
3	4.1 ± 3.6	6.0 ± 4.3	94.1 ± 2.1
4	8.2 ± 5.4	6.1 ± 4.4	85.9 ± 4.2

Ru and 4 for Tc. It is apparent that Tc remains on the resin while the major proportions of Mo and, particularly, Ru pass through the microcolumn when the Tc is initially loaded onto the column. The clean up process is effective, and it is very easy to see that the percentage of Ru that co elutes with the Tc is negligible. A DF of about 10^5 for Ru can be estimated. However, some Mo is eluted together with the Tc. Thus, the Mo DF would be only of about 10. These results are in agreement with previous reports [21].

With respect to the DF, the behaviour of the resin is the same after reuse. However, the Tc retention appears to slightly decrease after three or four repetitions of Tc loading, cleaning and elution. This means that possibly after loading volumes in excess of 250–300 ml onto the column, some performances losses are observed.

Bearing in mind such results, the method A2 could be resumed as follows:

- 1) Repeat the preconcentration and dissolution processes as in the steps 1–4 of the Method A1.
- 2) The solution is directly poured onto the TEVA-Spec™ microcolumn.
- 3) The resin is cleaned with 40 ml of 2 M HNO_3 .
- 4) Tc is eluted with 10 ml of 8 M HNO_3 at room temperature.
- 5) The eluent solution is heated to near dryness at a temperature less than 90°C .
- 6) Finally, the analyte is scavenged with 10 ml of 0.5 M HNO_3 . The chemical recovery is determined by gamma spectrometry and the internal standard is added before the ICP-MS analysis.

3.3 Method A3

It may be necessary to add a preconcentration step prior to the purification on the TEVA-Spec resin in order to reduce the loading solution volume (see Sects. 4 and 5). Therefore, as shown in Fig. 3 a new scheme is proposed that combines the performance of this resin with a Technetium concentration step using a solvent extraction with Tributylphosphate (TBP). Therefore, the performances of such a preconcentration and separation scheme are described below.

TBP is known to efficiently extract Tc from a H_2SO_4 medium [2, 16, 22, 23]. To evaluate the solvent extraction, several soil aliquots were reduced to ashes and leached as described above. The pH of the solution was adjusted to 3–4 by addition of 5 ml aliquots of 5% NH_4OH . The technetium was subsequently reduced to the +4 oxidation state by adding 15 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ per litre of solution and gently shaking. Finally, 25% NH_4OH was added until the pH was 9. The resulting precipitate was then redissolved using 200 ml of different concentrations of H_2SO_4 , and spiked with a known activity of $^{99\text{m}}\text{Tc}$. The effects of H_2SO_4 concentration and volume ratio of the aqueous to organic phases were evaluated.

Acid concentrations between 1 and 4 M were tested in the present experiments. For each acid concentration four aqueous to organic volume ratios were studied. Prior to each extraction procedure the TBP was equilibrated with H_2SO_4 at the same concentrations used in this study.

In Fig. 4, we present the percentage of $^{99\text{m}}\text{Tc}$ retained in the aqueous phase as a function of acid concentration and aqueous to organic phase volume ratio. As shown in Fig. 4,

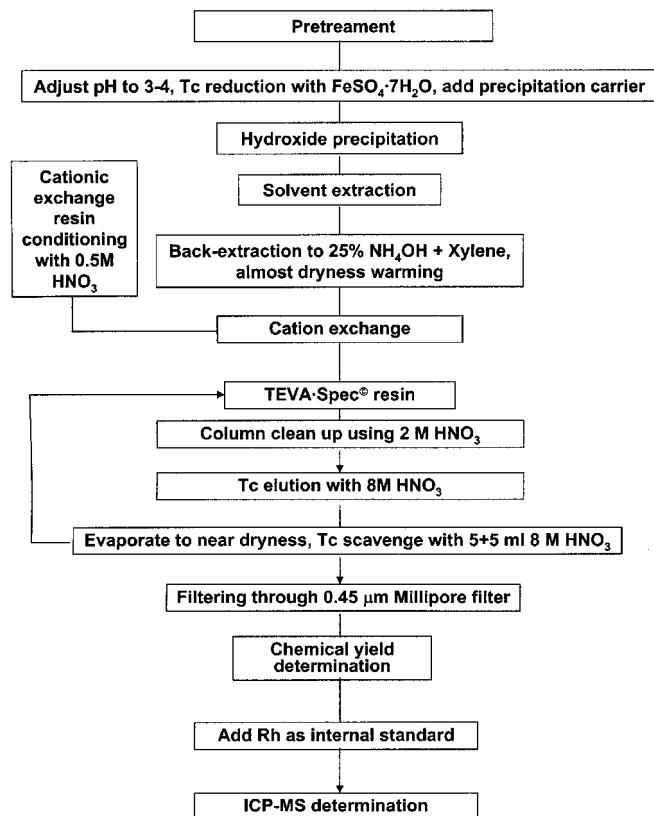


Fig. 3. Summary flow diagram for the preconcentration and separation of Tc using TBP and TEVA:Spec resins.

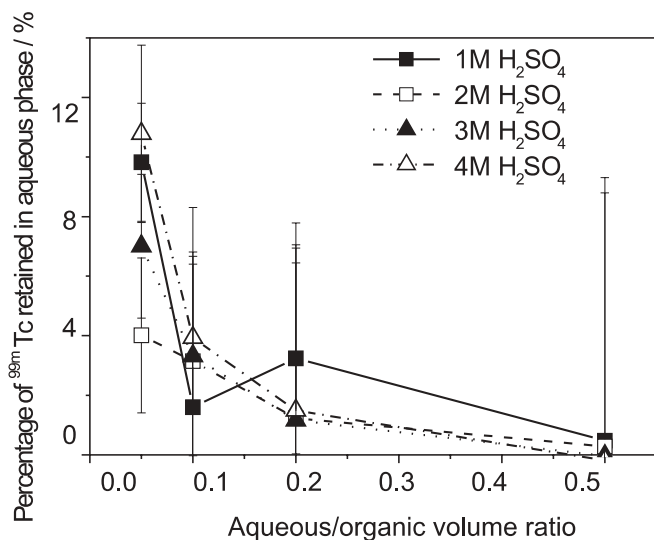


Fig. 4. Percentage of $^{99\text{m}}\text{Tc}$ retained in the aqueous phase following solvent extraction into TBP as a function of acid concentration and aqueous/organic volume ratios.

the fraction of Tc retained in the aqueous phase appears to be independent of the sulphuric acid concentration.

Tc is typically recovered from an organic phase, such as xylene, by back-extracting with a basic solution [20]. We have found that NH_4OH typically adds less background to the samples than does NaOH . For the present work 25% NH_4OH was used as the back extracting. Four test aliquots were prepared, spiked with the tracer and the technetium extracted with TBP. The volume of Xylene was used as vari-

able of control. The back-extraction was performed with a TBP/Xylene ratio of 1 : 1 and with an aqueous/organic ratio of 1/8. Using this method, an average chemical yield of $68 \pm 8\%$ was achieved.

The same experiment was carried out with a TBP/Xylene volumes ratio of 1/3 and an aqueous/organic phase volumes ratio of 1/17. The chemical yield reaches a value of $89 \pm 3\%$. Finally, we repeated this experience doubling the volume of NH_4OH in the back-extraction. No differences were observed since the obtained average chemical yield was $95 \pm 6\%$, the same than in the previous test within the considered uncertainties.

These data show that solvent extraction using TBP can be used to achieve a high CF. Furthermore CF does not depend strongly on acid concentration or the phase ratio. In addition CF can be improved by carrying out the back-extraction into a small concentrated NH_4OH volume. This sample matrix is easily converted, as described below, to a dilute HNO_3 matrix typical of those used in ICP-MS.

Therefore, the method A3 can be summarized as follows:

- 1) Repeat the pre-treatment steps 1 to 3 as in the method A1.
- 2) The precipitate is dissolved with 1–2 ml of 3 M H_2SO_4 per gram of precipitate.
- 3) Approximately 25 ml of 30% H_2O_2 are added to the solution which is heated at a temperature less than 75°C under reflux to assure the re-oxidation of the Tc.
- 4) After cooling to room temperature, the Tc is extracted into the TBP at an aqueous/organic phase volumes ratio of 1 : 5. Prior to extraction the TBP aliquot should be previously equilibrated with the same volume of 3 M H_2SO_4 .
- 5) The Tc is then back-extracted from the TBP volume V in the presence of a three times excess of xylene using a 1/17 volume ratio of 25% NH_4OH to organic. This back-extraction is repeated twice.
- 6) The organic phase is discarded and the aqueous phase heated to near dryness and dissolved with 15 to 20 ml of 0.5 M HNO_3 .
- 7) The solution is directly loaded onto a TEVA resin. The remainder of the procedure is similar to that of the method A2.

4. Results and discussion

The different methods were tested compared to one another using 5 litre aliquots of tap-water and the results appear in Table 5. The chemical recoveries and, consequently, the CF, increase sequentially from the method A1 to A3. The MDMC, is expressed in mBq/l and is higher in the method A1 due to the lower recovery obtained. Possibly, this fact is a consequence of the incomplete oxidation of Tc to the +7 state. TcO_4^- ion is strongly retained in the resin, and therefore a complete oxidation prior to the use of the resin is peremptory. From this point of view, method A3 is apparently superior to the other methods, although it requires more chemical manipulations.

The method performances must be also evaluated in terms of its ability to remove Ru and Mo from the final solution. In the case of Mo, it was checked by directly measuring the Mo contents of an aliquot of the samples. This could not be done for Ru, since its concentration was below the limit

Table 5. ^{99}Tc and Mo results from three water aliquots using the radiochemical methods described in the paper.

Method	R_Q (%)	CF	MDMC (mBq/l)	Mo DF	Ru counting rate/ Background counting rate
A1	47.9 ± 1.4	248 ± 7	0.6	0.06	4.0 ± 0.1
A2	60.4 ± 0.5	299 ± 2	0.2	5	1.8 ± 0.2
A3	79 ± 1	409 ± 41	0.3	44	1.1 ± 0.1

of detection, *i.e.*, the ruthenium contents of the tap water was some three orders of magnitude lower than the Molybdenum contents. Therefore, the ability to decontaminate the sample from ruthenium was checked in terms of the counting rate obtained for the sample against the corresponding background.

As we can see, method A1 results in a DF for molybdenum of less than 0.1. This means that the Mo is concentrated in the solution introduced into the ICP-MS. Although some separation between Mo and Tc could be achieved by using an anion exchange resin, insufficient separation was achieved under our experimental conditions. Better results with respect to the separation of Mo and Tc are achieved using methods A2 and A3. However, better results are achieved again with the method A3. This difference could be attributed to a different performance of the TEVA resin in method A2, when it has to deal with greater solution volumes (see Sect. 5).

With respect to Ru, it is easy to see that the smaller contributions to the counting rate in the mass to charge ratio 101 occurs in the method A3, where the background counting rates are recovered for a test sample. And then, this is the method that results in superior means of separating this element.

With this information, the volume dependence of the figures of merit for method A3 was studied. Results are shown in Table 6. As expected the chemical yield decreases as

the volume of the sample increases. Nevertheless, the product of the chemical yield and volume ratio increases faster than chemical yield decreases. The consequence is a rapid decrease of the MDMC with the volume as observed in Fig. 5. Therefore, when environmental waters are sampled for Tc determinations, the present results seems to justify the practise of previously concentrate the technetium from a high water volume, rather than dealing with low volume water sampling, even although the Mo is not completely removed.

5. Applications

Methods A2 and A3 have been applied to real environmental water samples, as a demonstration of the abilities and performances of the different techniques outlined above.

5.1 Water from El Cabril

As stated in the introduction, ^{99}Tc is of special concern because its long half-life and the concurrent problems associated with its storage and disposal. For that reason, we wanted to determine how applicable our methods are for measuring ^{99}Tc concentrations in naturally occurring water samples. Samples were taken from the surroundings of El Cabril, the Low to Medium Radioactivity Waste Storage Centre in Spain located in Cordoba in the south of Spain which opened in 1992.

Eight water samples were analysed for ^{99}Tc . seven of them were prepared using the A2 method and one with the A3 method. Approximately 20 litres were processed from each location. The results are shown in Table 7. As expected the concentrations found are below the MDMC. This is expected given the nature of the stored wastes.

The chemical recoveries are very low. We measured the ^{99m}Tc losses after washing the resins, and these were in a range of 15% to 38%, with an average value of 26%. The losses are quite high which decreases the chemical yield. It is possible that a large amount of solution in a 0.5 M HNO_3 matrix could cause a weaker adsorption of the Tc to the resin. This way, the losses after washing the resins become evident.

As shown in Table 5, method A3 produced higher recovery. Consequently the MDMC obtained were significantly lower than for the other cases. On the other hand, the method A2 is more time consuming than A3 when applied to high water volumes. Everything points towards method A3 as the

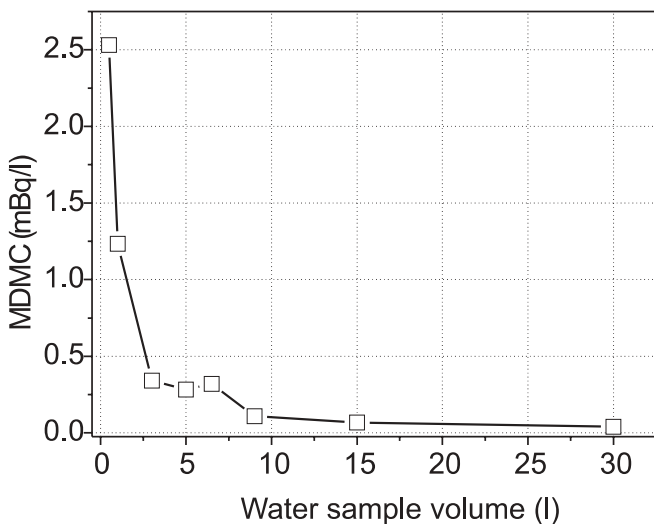


Fig. 5. Dependence of the MDMC on the analysed water volume (Method A3).

Table 6. Recovery efficiency of ^{99}Tc (including CF) from El Cabril water samples (see Sect. 4).

Sample volume (l)	0.5	1.0	3.0	5.0	6.5	9	15	30
Chemical recovery (%)	93 ± 1	94 ± 2	82 ± 2	79 ± 1	76 ± 2	71 ± 2	65 ± 1	53 ± 1
CF	47 ± 9	98 ± 10	243 ± 41	409 ± 41	400 ± 32	690 ± 43	974 ± 36	1552 ± 39

Table 7. ⁹⁹Tc results from El Cabril (Sect. 4).

Sample code	Method	Chemical yield (%)	Concentration Factor	MDMC (mBq/l)	⁹⁹ Tc (mBq/l)
35(II)	A2	12.4 ± 0.2	328 ± 14	0.25	N.D.
35(III)	A2	14.0 ± 0.6	364 ± 15	0.23	N.D.
35(IV)	A2	16.8 ± 0.8	326 ± 58	0.26	0.02 ± 0.15
36(I)	A2	14.7 ± 0.2	347 ± 25	0.24	N.D.
36(III)	A2	21.2 ± 0.6	458 ± 36	0.19	N.D.
Burrero 1	A2	22.2 ± 0.5	517 ± 27	0.14	0.11 ± 0.14
Burrero 3	A2	21.0 ± 0.6	507 ± 29	0.12	0.012 ± 0.037
Burrero 4	A3	37.5 ± 0.9	873 ± 48	0.06	0.022 ± 0.021

Table 8. ⁹⁹Tc results from rainwater samples. The dates are supplied as day/month/year. Samples RH1 and RH2 were collected through a complete month.

Sample code	Date of collection	Method	Chemical recovery (%)	CF	MDMC (mBq/l)	⁹⁹ Tc (mBq/l)
RH1	June–November 2000	A3	56.0 ± 1.4	896 ± 60	0.10	0.12 ± 0.05
RH2	December 2000	A2	27.5 ± 0.9	687 ± 53	0.11	0.052 ± 0.039
RS1	19/12/2000	A2	18.3 ± 0.8	439 ± 32	0.12	0.007 ± 0.110
RS2–3	20–21/12/2000	A3	31.3 ± 0.2	1502 ± 69	0.034	0.036 ± 0.027
RS4–5	23/12/00–3/1/01	A3	29.8 ± 0.7	1458 ± 63	0.041	0.016 ± 0.035
RS6–7	4–5/01/2001	A3	39.6 ± 1.1	1817 ± 77	0.024	0.009 ± 0.098
RS8–9	9–10/03/2001	A3	45.9 ± 1.3	2065 ± 83	0.021	0.17 ± 0.05

more advisable to extract Tc from a high volume of environmental water.

5.2 Rainwater samples

Rainwater has been used in the past as a marker of anthropogenic radionuclide releases to the environment. Following a research line that started in the Eighties of the past century, seven rainwater samples were analysed as radioecological indicators of the fallout magnitude in the southern regions of Europe [16]. Five of them (samples RS1 to RS8-9) were collected between December 2000 and March 2001 from the rooftops of the faculty of Physics of the University of Seville (Spain). Two samples were collected in La Rábida (Huelva, Spain) for comparison (samples RH1 and RH2). The processed water volumes ranged from 15 to 30 litres. Five samples were analysed with the A3 method while two of them were analysed with the A2 method. The results are given in Table 8.

As previously observed, the chemical recoveries were higher in the samples analysed with the A3 method than for those analysed with the A2 method. In the majority of cases the ⁹⁹Tc concentration was below MDMC with the exception of sample RS8-9, which was collected in Seville during the last part of the winter. Tc appears in the atmosphere as a consequence of the atmospheric nuclear military tests in 1950s and 1960s. After almost 40 years following the last atmospheric nuclear test, one would expect such material would have completely returned to the earth as “fall-out”. And our results (all the concentrations in the range of MDMC) would support such a hypothesis. The case of sample RS8-9 requires a more detailed analysis, which is under progress.

6. Conclusions

In this paper three radiochemical procedures for the extraction of ⁹⁹Tc from high water volumes and its subse-

quent determination by ICP-MS are presented. Tc is pre-concentrated from the water by a reduction-precipitation process. After, it is extracted and isolated from the precipitate by using alternatively three methods: ion exchange, with conventional or TEVA resins, and solvent extraction coupled to TEVA resins.

A detailed study of the different steps of the extraction-isolation process for the three methods has also been performed.

In general terms it seems that the combination of solvent extraction and ion exchange with TEVA resins for the extraction and isolation of ⁹⁹Tc, is the preferred method since it provides the best average chemical recovery and Decontamination Factor from Mo and Ru.

Some results for high volume environmental water samples are presented which show the capacity of the methods.

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