JP0350636

4.41 A method for the measurement of ^{99}Tc by Quadrupole ICP-MS in dry fallout and sea grass samples.

Jose Luis Mas[*1)], Manuel Garcia-Leon[2)] and Juan Pedro Bolivar[1)]

1) Dept. Fisica Aplicada. Universidad de Huelva. EPS La Rabida, Ctra. Palos de
la Frontera, s/n. 21819 Huelva (Spain)
2) Dept. Fisica Atomica, Molecular y Nuclear. Universidad de Sevilla. Facultad
de Fisica. Avda. Reina Mercedes, 41080 Sevilla (Spain)
• Corresponding author: pepemas@nirs.go.jp. Address while the stay at
NIRS: National Institute of Radiological Sciences. 4-9-1, Anagawa, Inage-ku,
263-8555 Chiba (Japan)

ABSTRACT

A method for the detection of ^{99}Tc by ICP-MS in environmental samples is proposed and explained in detail. This method combines the capabilities of anion exchange chromatographic TEVA·Spec^{TM} resin with prior isotope concentration using solvent extraction to Tributylphosphate. The problem that the excess of Mo in the solution analyzed by ICP-MS causes in the instrumental response at m/z ratio 99 is described in detail, and the proposed solution takes the form of the referred radiochemical method. The realistic limits of detection of this technique (bearing in mind the particular methodology here applied) are in the range of 20-70 mBq/kg when treating mass amounts in the range of 20-125 g dry weight. A few environmental samples proceeding from a region unaffected by any closer nuclear industry (the Southwest of Spain) are analyzed for checking ^{99}Tc concentration.

Keywords: Technetium, ICP-MS, sea grass, fallout.

1. INTRODUCTION.

^{99}Tc is a pure beta emitter with a long half-life, $T_{1/2} = 2.1 \times 10^5$ y, which appears during the fission of ^{239}Pu or ^{235}U at a relatively high fission rate of some 6%. Its environmental relevance is well established, though sub-ppt ^{99}Tc levels in non-perturbed sites pose serious limitations to traditional radiometric methods (1,2). In the last years, many authors have shown the use of inductively coupled plasma mass spectrometry (ICP-MS) as a powerful tool for the detection of ^{99}Tc in environmental samples (3-6), and even some of these methods have been successively improved, expanding thus the range of potential sample matrix that they are able to analyze (7). It is well know that the major counting interferences are due to the natural isotopes ^{99}Ru (12.6 % relative abundance), due to isobaric overlap, and ^{98}Mo (24%) and ^{100}Mo (9.6%), due the first to hydride generation and the second one to an excessive abundance to sensitivity. This could be really a major problem when quadrupole ICP-MS devices are involved in the measurements, as the typical concentrations of Mo could be as high as three orders of magnitude greater that those of Ruthenium or Technetium in natural soils. In our typical conditions, the abundance sensitivity could be estimated in the range of 100×10^{-6}, which means that when Mo is present in the final analyzed solution in a concentration in the order of 10 ppb or greater, concentrations of ^{99}Tc as high as 1 ppt could not be detected (8). The magnitude of hydride generation effect is well lower than for abundance sensitivity.

In this paper, a method for ^{99}Tc measurement by ICP-MS is developed and its abilities to decontaminate from Mo and Ru are analyzed. This method is applied to a few environmental samples

coming from a region out of the direct influence of any nuclear industry. Some conclusions on the obtained results could be arisen.

2. MATERIALS AND METHODS.

2.1. Samples and Materials.

The ICP-MS here involved is an Ar-feed commercial quadrupole spectrometer (Hewlett-Packard 4500) that works with a Babyngton-type nebulizer. For a counting time of 0.1 s, in the instrumental conditions found optimizing by the variable control method at mass 99, and when Tunning detection mode is used, the instrumental limit of detection is in the range of 0.2 pg/g, that is, two orders of magnitude lower than the found using the autotunning method. These operating conditions have been checked using the deformable five dimensions Spendley's Simplex algorithm as applied to five of the ion lenses.

The chemical recovery is calculated using the internal standard method. The chemical tracer is the 140.5 keV gamma emitter ^{99m}Tc, obtained from ^{99}Mo generators from a Nuclear Medicine Service. Even not being the better option (9), this one is easily achievable, and besides its very low half-life (6.02 h) and its decay to ^{99}Tc, it has been shown (10) that this tracer could be added to the sample in amounts as high as 0.5-1 MBq without very hard effect on the limit of detection, if several simple cares are taken account regarding the tracer elution from the clinical generator. In this case, the classical IUPAC definition of Limit of Detection (understood as the equivalent concentration to 3σ of the blank counting) must be adapted to achieve a more realistic Minimum Detectable Mass Concentration. The gross counting rates due to interferences and due to the own tracer are given account. Therefore, is assumed that theoretically every sample could have a slightly different MDMC value according to the chemical recovery there obtained. The gamma counting was performed using a NaI(Tl) solid scintillation detector EG&G Ortec.

The method performances were characterized using the chemical recovery (R_Q) for tracer, the concentration factor (CF) for Tc and the decontamination factor (DF) for Ruthenium and Molybdenum, being these two numerical quantities depending on the initial sample mass involved in the analysis.

For checking the suitability of the method, two soil samples, previously analyzed for other elements (11), were used. Their negligible Tc contents could be justified on base of their origin from layers below the surface of a metal extraction quarry. That hypothesis is supported on their very low organic matter contents and the activities of some other man-made radionuclides such as ^{137}Cs under the limit of detection of the semiconductor Ge(HP) used. Once checked the method, it was applied to the analysis of two samples of sea grass (Zostera Marina) collected in the Southwest of the Atlantic Spanish coast, at Huelva. The other sample here analyzed is a dry fallout sample collected in the rooftops of the Faculty of Physics Sciences of the University of Seville (Spain). This one corresponds to a very dry period in this region, from April to July of 2001, and could serve us to support some other works that uses rainwater as environmental monitor for ^{99}Tc.

2.2. The chemical method.

A detailed scheme of the proposed method appears in Fig. 1. About 30 g of dry weight sea grass or 125 g of atmospheric deposition are used for the analysis. After sample tracing and pretreatment, Tc remains dissolved in ca 250 ml of 8M HNO$_3$, too concentrated to be load directly onto a TEVA·Spec resin. Thus, a matrix adaptation to H$_2$SO$_4$ is carried out through a reduction-precipitation step, and then the Tc is concentrated using a solvent extraction process to TBP. Some Ru decontamination is performed in the washing step. After back extraction, Tc is concentrated in a volume almost ten times lower than for the previous leaching, in a matrix easily adaptable to the TEVA·Spec resin management.

As not 0.1M HNO_3 but 0.5M HNO_3 is used to load the Technetium onto the column, some differences could appear against previously published results of other authors (7,12). Anyway, if great amounts of Mo are involved, this process of sample concentration and purification using this chromatographic extraction could be repeated until three times with the same microcolumn. In these conditions, and if little sample volumes are involved in the chemical separations (13), the resin performances are not affected. This way, the DF for Mo could be increased in more than three orders of magnitude.

The results for these two samples appear in Table 1. The chemical recoveries are qualitative, in the range of 30 %. This means that optimizing this technique in the future is necessary. However, the achieved CFs for technetium are relatively high, and high enough DF for Mo and Ru are achieved. The different values of DF for Mo are not yet explained. Anyway, these values assures than even when so high abundance sensitivity appears at the spectrometer, counting overlaps from the adjacent mass will be avoid.

Solid sample (20-125 g)

Bath in 5% NH_4OH, add tracer

Evaporate to almost dryness + incineration at 450° C for 1.5 h

Leaching with 150 ml 8M HNO_3 + 30 ml 30% H_2O_2 under reflux (T<80° C)

Whatman CF/G glass fiber filtering

Adjust pH to 3-4 using 5-25% NH_4OH, reduce Tc using $FeSO_4·7H_2O$

Add $FeCl_3·7H_2O$ carrier, adjust pH to 9 with conc. NH_4OH

Dissolve precipitate using 3M H_2SO_4, oxidize with $(NH4)_2S_2O_8$

Solvent extraction to previously equilibrated TBP

Wash organic phase with the same volume of 3M H_2SO_4 + HF

Back extracion to 25% NH_4OH in the presence of Xylene (twice)

Evaporate to dryness, scavenge residue with 20 ml 0.5M HNO_3

Filter through 3 ml of Dowex 50W-X8 cation exchange resin

Load solution onto TEVA ·Spec resin

Wash the columns using 40 ml 2M HNO_3

Elute Tc with 8M HNO_3

Evaporate to almost dryness, recover with 0.5M HNO_3
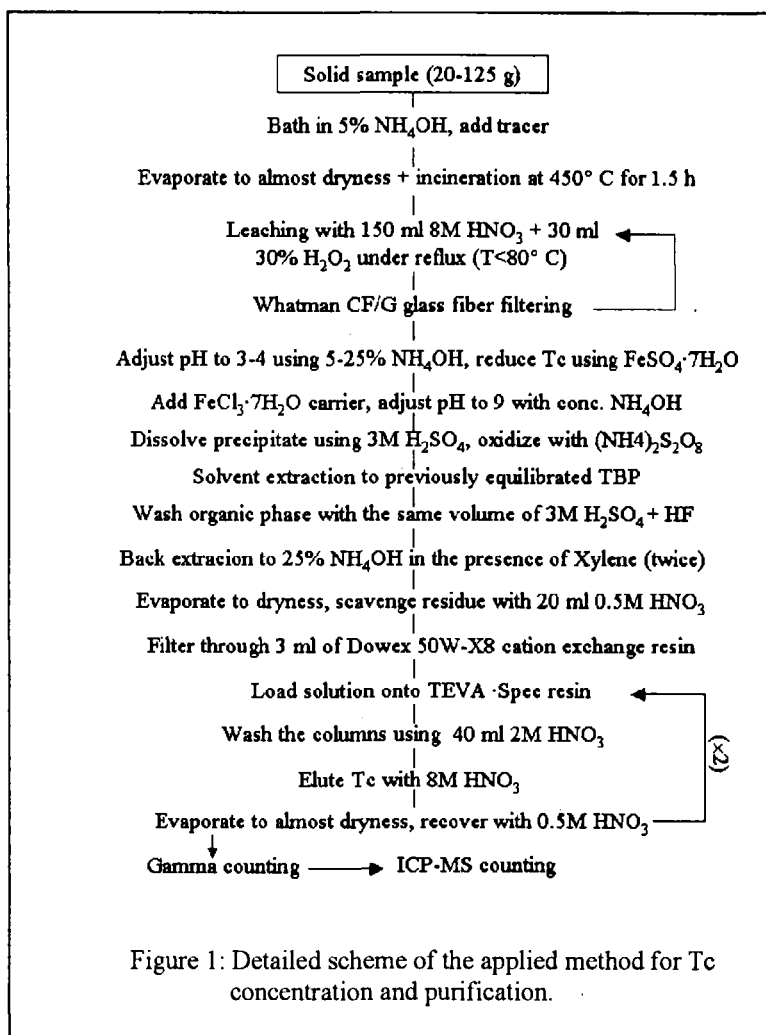
(x2)

Gamma counting ——→ ICP-MS counting

Figure 1: Detailed scheme of the applied method for Tc concentration and purification.

Table 1. The obtained results for two test soil samples used to check the method performances.

Sample	Recovery (%)	CF for Tc	MDMC (Bq/kg)	DF for Ruthenium	DF for Molybdenum
S63	32.0±1.4	4.55±0.20	0.013	≥9500	500
S64	29.0±1.4	3.98±0.19	0.024	≥9500	3500

The method could be easily adapted to the analysis of other environmental samples as borehole water or rainwater. The only differences appear, of course, in pretreatment and the aqueous and organic phase volumes involved in the solvent extraction process. An experimental evaluation of the MDMC dependence on the water volume analyzed is shown in Figure 2.

3. RESULTS AND DISCUSSION.

The obtained results for the dry fallout sample (DFS) and the two samples of sea grass (ZM1 and ZM2) are shown in Table 2. The CF values for technetium are quite different depending on the type of sample, as the initial masses involved are too. The DFS sample presents a mass activity that really is, into the uncertainty intervals, equal than the MDMC. This shows the extraordinarily scarce contents in ^{99}Tc of samples from regions not directly affected by nuclear industries, and supports the hypothesis of an almost complete back to the earth surface of the Tc injected into the stratosphere due to military atmospheric nuclear tests after a mean residence time of about 18 months (14). Some other data dealing with the analysis of Technetium in rainwater, which support this result, are to be published. There are not too much other data concerning the Tc contents in atmospheric deposition. Tagami and Uchida (15) recently published some of these data calculated from samples taken at Hitachinata (Japan), estimating them as lower than 0.4-0.9 mBq m^{-2} month^{-1}. Our result shows an activity deposition equal to or lower than 0.06 mBq m^{-2} month^{-1}. And then, very high agreement between the referred conclusions is observed.
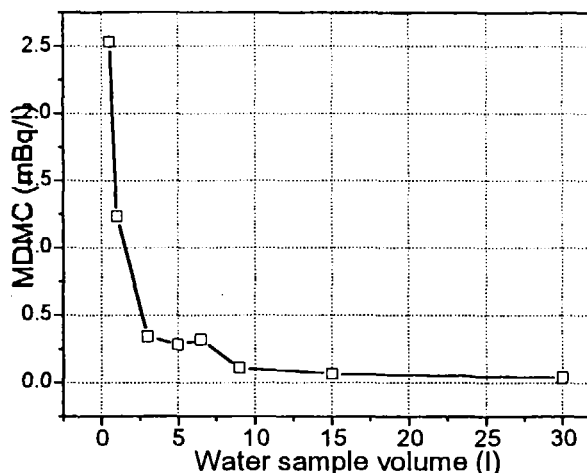

Figure 2. Experimental dependence of Minimum Detectable Mass Concentration with the water volume analysed using the method described in the text. Line is depicted to guide the eye.

Table 2. Obtained results for two sea grass samples (ZM1 and ZM2), and a dry fallout sample (DFS).

Sample	Chemical Yield (%)	CF	MDMC (mBq/kg)	[99]Tc (mBq/kg)
DFS	35.6±0.9	4.4±0.1	16	19±5
ZM1	32.0±0.8	1.04±0.03	70	66±19
ZM2	26.3±0.7	0.84±0.03	77	60±28

Regarding the sea grass samples, no detection of Tc was possible, as expected. Their concentrations in samples of biological concentrators such as seaweed, coming from the same region, were in the range of 0.1-0.4 Bq/kg dry weight (16). With the results shown in Table 2, it results clear that the concentrations in sea grass are below 0.07 Bq/kg d.w. This is according to the CF values given in the literature (17) for these two marine species, being for sea grass more than three orders of magnitude lower than for seaweed. Different results to those previously explained would have suggested some other local sources for ^{99}Tc not yet identified.

4. CONCLUSIONS.

A method for the detection of ^{99}Tc by ICP-MS in environmental samples is proposed. The method combines the capabilities of anion exchange chromatographic TEVA•Spec^{TM} resin with prior isotope concentration using solvent extraction to Tributylphosphate. The interferences in the mass counting are analyzed and the combination of the radiochemical method and the optimization of counting conditions allow minimizing them. ^{99m}Tc is used as a tracer of the method. This causes the need of re-defining the limit of detection so as to take into account the contribution to the counting at the mass of interest. The values are in the range of 20-70 mBq/kg when treating mass amounts in the range of 20-125 g dry weight. Some previsions on the possible range of ^{99}Tc concentrations in environmental samples proceeding from a region unaffected by any closer nuclear industry (the Southwest of Spain) are made, and subsequently checked by applying this method.

5. ACKNOWLEDGEMENTS.

6. REFERENCES.

1. Ehrhardt, K.C., Attrep Jr., M. Technetium-99 in the Atmosphere, *Envir. Sci. Technol.* **12**, 55 (1978).

2. Holm, E., Rioseco, J., and Garcia-Leon, M. Determination of ^{99}Tc in Environmental Samples, *Nucl. Instr. Meth. Phys. Res.* **223**, 204 (1984).

3. Tagami, K., and Uchida, S, Separation procedure for the determination of Technetium-99 in soil by ICP-MS, *Radiochim. Acta* **63**, 69 (1993).

4. Nicholson, S., Sanders, T.W., and Blaine, L.M. The Determination of Low Levels of ^{99}Tc in Environmental Samples by Inductively Coupled Plasma-Mass Spectrometry, *Sci. Total Environ.* **130-131**, 275 (1993).

5. Ihsanullah, and East, B.W., Method for the determination of Technetium-99 using Inductively Coupled Plasma-Mass Spectrometry, *Radioactivity and Radiochemistry* **2**, 20, (1994).

6. McCartney, M., Rajendran, K., Olive, V., Busby, R., and McDonald, P., Development of a novel method for the determination of ^{99}Tc in Environmental Samples by ICP-MS, *J. Anal. Atom. Spectrom.* **14**, 1849, (1999).

7. Uchida, S., and Tagami, K., Separation and concentration of Technetium using a Tc-selective extraction chromatographic resin., *J. Radional. Nucl. Chem.* **221**, 35, (1997).

8. Mas, J.L., Garcia-Leon, M., and Bolivar, J.P., ^{99}Tc atom counting by quadrupole ICP-MS. Optimisation of the instrumental response, *Nucl. Instr. and Meth. in Phys. Res. A*, **484**, 660, (2002).

9. Sekine, T., Konishi, M., Kudo, H., Tagami, K., and Uchida, S., Separation of Carrier Free ^{95m}Tc form Niobium Targets Irradiated with Alpha-Particles, *J. Radioanal. Nucl. Chem.*, **239**, 48 (1999).

10. Mas, J.L., Garcia-Leon, M., Bolivar, J.P., and Sanchez-Angulo, C.I., The Use of ^{99m}Tc as a tracer in the Determination of ^{99}Tc by ICP-Mass Spectrometry, *J. Anal. Atom. Spectrom.*, **15**, 1369, (2000).

11. Mas, J.L., Bolivar, J.P., Garcia-Tenorio, R,. Aguado, J.L., San Miguel, E.G., and Gonzalez, J., A dosimetric model for determining the effectiveness of soil covers for phosphogypsum waste piles, *Health Physics*, **80**, 34, (2001).

12. Tagami, K., and Uchida, S., Comparison of the TEVA·Spec resin and liquid-liquid extraction methods for the separation of Technetium in soil samples, *J. Radioanal. Nucl. Chem.*, **239**, 643 (1999).

13. Mas, J.L., Detection of Technetium-99 by ICP-MS, PhD. Thesis, University of Seville (2002), Seville, Spain.

14. Garcia-Leon, M., Manjon, G., and Sanchez-Angulo, C.I., $^{99}Tc/^{137}Cs$ activity ratios in rainwter samples collected in the South of Spain., *J. Environ. Radioactivity*, **20**, 49 (1993).

15. Tagami, K., and Uchida, S., Analysis of technetium-99 in soil and deposition samples by inductively coupled plasma mass spectrometry., *Appl. Radiat. Isot.*, **47**, 1057, (1996).

16. Manjon, G., Garcia-Leon, M., Ballestra, S., and Lopez, J.J., The Presence of Man-Made Radionuclides in the Marine Environment in the South of Spain, *J. Environ. Radioactivity* **28**, 171, (1995).

17. Coughtrey, P.J., Jackson, D., and Thorne, M.C., Radionuclide Distribution and Transport in Terrestrial and Aquatic Ecosystems., A.A. Balkema Publishers, Rotterdam, The Netherlands, Vol. 3, p210 (1983).