Overcoming ICP-QMS instrumental limitations for ^{99}Tc determination in environmental solid samples using radiochemistry

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Abstract

Besides its capabilities, quadrupole-based ICP-MS counting establishes several limitations on ^{99}Tc analysis in environmental samples. Overcoming these limitations requires the use of radiochemical methods. We have developed a new method for the detection of ^{99}Tc by ICP-QMS in solid environmental samples. In order to improve the limit of detection of the technique, high amounts of solid samples ($\geqslant 100$ g) are used. Hence, great amounts of the interfering elements are involved in the process, and therefore special emphasis is put on achieving a good commitment between adequate matrix elements removal and a minimization of the limit of detection. The performances of the method are analyzed in terms of conveniently defined figures of merit. The developed method is applied to several fallout level samples. In this way, the real performances and especially the real limitations of this method are shown.

1. Introduction

^{99}Tc ($T_{1/2} = 2.11 \times 10^5$ years) is a low energy β-emitter arising from the fission of ^{235}U or ^{239}Pu at a relatively high rate ($\sim 6\%$). Its environmental relevance is well established. However, its determination in non-perturbed sites is difficult due to the sub-ppt level concentrations in environmental samples (Ehrhardt and Attrep, 1978; García-León et al., 1984).

ICP-MS is becoming a powerful tool for the analysis of ^{99}Tc (Morita et al., 1991; Tagami and Uchida, 1993; Nicholson et al., 1993). No systematic differences were found in a recent interlaboratory study, when the results achieved by ICP-MS were compared to those others produced by radiometric counting (McCartney et al., 1999a). A wide variety of radiochemical methods have been developed for the measurements of ^{99}Tc in all sort of environment samples (Eroglu et al., 1998; Keith-Roach et al., 2002; Gómez et al., 2001; McCartney et al., 1999b).

Some of them are designed as routine methods: the limits of detection of the developed techniques are in agreement with the law regulations. The radiochemical work is minimized as much as possible dealing with small amount of samples (Nicholson et al., 1993; Eroglu et al., 1998; Gómez et al., 2001; Ramebäck et al., 1998).

However, we are interested in repeating our previous ^{99}Tc detection capabilities achieved using gas flow counting (García-León et al., 1984; Sánchez-Angulo and García-León, 1988; Garcia-Leon et al., 1993). To do that, the ICP-MS technique is proposed. That should imply a preconcentration of ^{99}Tc. Unfortunately, this technique is quite more sensitive to the sample matrix effects than gas flow detection (see below) or Liquid Scintillation Counting and, furthermore, dealing with a high amount of sample usually causes the lowering of chemical recoveries (e.g., Nicholson et al., 1993, limited the analyzed sample mass to 50 g when sediment samples were treated).

Special attention has been paid in the literature to the decontamination from Ru atoms due to the isobaric overlap from ^{99}Ru (12.6% natural abundance). However, to many authors it seems that the problem associated to the

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presence of Mo in the analyzed solution is not so serious. On the contrary, we found under our working conditions that aspirating solutions with Mo concentrations in the range of $10 \, \text{ng} \, \text{g}^{-1}$ (or higher) would introduce severe increases in the instrumental response of mass 99. This fact is due to the abundance sensitivity ($\sim 50 \times 10^{-6}$) calculated for the middle range of masses. On the contrary, the interferences from ^{98}Mo hydrides seem to be less important under our working conditions. The effect of other interferences has been previously studied (Eroglu et al., 1998; Mas et al., 2002). There, their negligible effect on the mass spectrum has been shown.

In this paper, we present a robust radiochemical method designed for the detection of ^{99}Tc by ICP-MS. This method is tested with real soil samples in order to show their performances and limitations according to several figures of merit. First, the concentration factor (CF) for Tc is defined as

$$\text{CF} = \frac{M_0}{M_f} R_Q,$$

where M_0 is the sample mass submitted to chemical analysis, M_f the mass of the final 2–5% HNO_3 acid solution, which is aspirated by the ICP-MS, and R_Q is the chemical recovery for Tc. Hence, this coefficient represents the ratio of the Tc concentration in the solution aspirated by the ICP-MS to that concentration in the starting sample, before any chemical analysis. The desired method should have a CF as high as possible. The inverse of the CF, when referred to the interfering elements, has been used in this work as decontamination factor (DF); hence, it should be also as high as possible. Finally, the minimum detectable mass concentration (MDMC) for ICP-MS was also used to evaluate the proposed methods when they were applied to real samples. It is defined as

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

where b (counts ppt^{-1}) is the slope of the calibration curve of our system at the typical working conditions, while LOD is the Limit of Detection expressed in terms of the achieved counting rate. A complete discussion on the dependence of MDMC on the different variables of the experiment (including the presence of interfering isotopes) was published elsewhere (Mas et al., 2000).

2. Experimental

2.1. Instrumentation and samples

The quadrupole ICP-MS Agilent 4500 with a Babington type nebulizer was used for the presented experiments. The operating conditions are summarized in Table 1.

The yield tracer, ^{99m}Tc, was obtained from medical generators. Its contribution to MDMC arising from the ^{99m}Tc decay to ^{99}Tc is negligible, once provided that some

Table 1
Operating conditions for the ICP-MS instrument

Radiofrequency power (W)	1240
Sampling depth (mm)	6.3
Carrier gas (l min^{-1})	1.17
Extraction lens 1 (V)	−150
Einzel lens No 2 (V)	5.5
Bias Omega lens (V)	−41
Omega minus lens (V)	−3
Quadrupole focus (V)	6

given conditions are followed during the elution process (Mas et al., 2000). The tracer was determined by measuring the intensity of its 140.5 keV γ-emission using a NaI(Tl) scintillation counter. Mo and Ru concentrations were analyzed using the corresponding MERCK VI Certi-Prep$^{©}$ multi-element standard solution and an ALPHA APS-100046-2 Ru standard solution, respectively. ^{99}Tc calibrations were performed using successive dilutions of an ^{99}Tc DAMRI standard solution (Gif-sur-Yvette, Cedex, France).

Different tests were performed to optimise and develop the method here proposed by using unspiked real soil samples, which were previously analyzed for other radionuclides (Mas et al., 2001). We consider that this approach could be much more realistic than using standard solutions. The samples were taken in the Southwest of Spain. This area is only affected by atmospheric fallout, at a very low level bearing in mind the very low latitude. The samples have a very low organic matter content and the levels of ^{137}Cs are also very low ($< 0.7 \, \text{Bq} \, \text{kg}^{-1}$). Therefore, we can estimate ^{99}Tc concentrations in the range of $0.07 \, \text{mBq} \, \text{kg}^{-1}$. Our aim for limit of detection is not so ambitious. Therefore, this should be a good sample matrix for the realization of our experiments, once provided that their concentrations of Mo (in the range of 1–2 ppm) and Ru (up to 1 ppb) assure the possibility of using them to check the DF.

The method was validated analyzing the seaweed samples used in the previously mentioned intercomparison exercise for ^{99}Tc (McCartney et al., 1999a). Dr. Valerie Olive (Scottish Universities Research and Reactor Centre) kindly provided us with the samples.

Finally, several samples from the SW of Spain were analyzed in order to test the method. The so-called DFS sample corresponds to dry fallout. It was taken at the roof of the Faculty of Physics of the University of Seville and corresponds to a dry period from April to June 2001. Samples ZM1 and 2 correspond to marine sea-grass *Zostera Marina*, which were taken from the coast of Huelva (South–West of Spain) in March 2001. Finally, samples 1SD1 and 1SD4, and 2S1 and 2S2 correspond to forest soil samples collected from a Eucalyptus plantation also in the province of Huelva in 1997 (Vaca et al., 2001).

2.2. Radiochemical method

2.2.1. Pretreatment

To a porcelain beaker, 100–125 g per sample replicate are transferred and 150 ml of a 5% NH_4OH solution are poured inside. The tracer is added and mechanically homogenized while this mix is softly warmed until the evaporation of that solution. Thereafter the sample is reduced to ashes at 450 °C for 90 min. Technetium is dissolved from the ashes using 8 M HNO_3 in the presence of 30% H_2O_2 while warming on a hot plate at 90 °C under reflux. In this way, we expect that Tc appears in the TcO_4^- ion form. The solution is filtered through a Whatman CF/G glass fibre filter. The precipitate is leached again, and then the supernatants are mixed into a 1 l precipitate glass. Hence, Tc remains dissolved in a volume of approximately 100–250 ml 8 M HNO_3.

2.2.2. Concentration

After that, Tc is reduced and precipitated following a process widely used for water samples (García-León et al., 1984, 1993; Sánchez-Angulo and García-León, 1988). In this case, we propose this technique for solid samples. The solution pH is turned to 3–4 by using 5% NH_4OH. A suitable mass of $FeSO_4 \cdot 7H_2O$ (see Section 3 for details) is added in order to reduce the Tc to the $+IV$ valence state. A certain mass of $FeCl_3$ is also added as a precipitation carrier. Thereafter, the solution is adjusted to pH ~ 9 using NH_4OH, and the coprecipitation of Tc occurs.

This precipitate is dissolved with 3 M H_2SO_4 (Nicholson et al., 1993; Sánchez-Angulo and García-León, 1988; Garcia-Leon et al., 1993). Then Tc is extracted into 40–70 ml of TBP, which was previously conditioned with the same volume of 3 M H_2SO_4. Finally, the technetium is back-extracted into 25–30 ml of 25% NH_4OH, in the presence of Xylene. In this way, the Tc is concentrated as the final volume decreases, and a certain fraction of Ru is removed from the sample.

This solution is not suitable to be directly analyzed by ICP-MS. Thus, that basic solution is gently evaporated to almost dryness. We have not found losses of Tc during the evaporation from such a basic solution. Then the residue is dissolved with 0.5 M HNO_3 and the solution is adjusted to 2–5% HNO_3. This solution would be ready for our ICP-MS system. However, many Mo atoms would be present in this solution according to our experiments. Hence, further sample purification is peremptory.

2.2.3. Purification

An Eichrom's TEVA·Spec^{TM} chromatographic resin micro-column is used following the solvent extraction step. Very high capacity factors for Tc and Re have been already reported (Tagami and Uchida, 2000). As we will show below, their performances are also quite helpful for removing the Mo atoms.

The 0.5 M HNO_3 previously produced is directly loaded onto such a micro-column, which was previously conditioned using first 5 ml of 8 M HNO_3 and then 5 ml of a 0.5 M HNO_3 blank solution. The micro-column is washed using about 40 ml of 2 M HNO_3 to remove a fraction of the interfering elements (Mo and Ru). Finally, the Tc is stripped using a small volume (approximately 10 ml) of 8 M HNO_3. Ru is almost totally removed from the solution with a single process of loading, washing and stripping with this micro-column (Mas et al., 2004). However, the process must to be repeated in order to improve the Mo decontamination. This can be done using the same micro-column, without remarkable losses on Tc retention. This approach has the advantage of reducing treatment costs without affecting the radiochemical quality of the analysis. The re-loading process has to be carried out as follows: once the stripping is done, the drain is evaporated at low temperature and the residue is recovered with 0.5 M HNO_3. This approach is less time-consuming than diluting the first stripping solution, as the flow rate through the column is small. This scheme could be repeated two or three times depending on the initial sample mass. Then the last eluted solution is evaporated again to near dryness and recovered with 2% HNO_3. Finally, recovery calculation and atom counting are carried out.

3. Results and discussion

3.1. Pretreatment performances

In order to check the losses of Tc after the reduction to ashes, we developed a first test. A 150 g aliquot of every sample (test soils A, B,..., G) was spiked with the tracer and reduced to ashes as described above. As we show in Fig. 1, this pre-treatment does not produce any loss of Tc, since the retention is always around 100%, being the mass loss into the same range already determined in previous works (Mas et al., 2001).

An experiment was carried out to find the adequate mass of the reducing agent. Several aliquots of soil ashes, unspiked with the tracer, were filtered as described above, following the pretreatment. Each filtrate was spiked with the tracer in the $^{99m}TcO_4^-$ form. Different amounts of reducing agent were used and the precipitation step was carried out. The supernatant was recovered by centrifugation, and the precipitation degree was measured in each solution (Fig. 2).

Tc fraction remaining in the solution rapidly falls down when the reducing agent mass is greater than 0.05 g *per* gram of solid sample. As a result it was found that some 15 g of reducing agent per litre of acid solution was sufficient to get a quantitative reduction and an effective precipitation of Tc. That is quite different from the amount of $7 g l^{-1}$ found for rainwater samples (Sánchez-Angulo and García-León, 1988). But this is not strange, however, due to the differences of the studied matrix: the leaching solution contains many more matrix elements in competi-
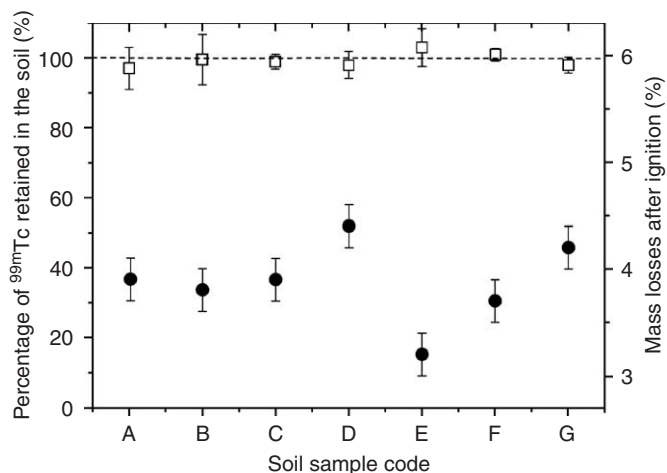
Fig. 1. ^{99m}Tc retention (%) and mass losses (%) after reducing to ashes the soil samples used to check the pretreatment step of the method. Please, note the double scaling. □: Percentage of tracer retained in the soil. ●: Mass losses after reduction to ashes.
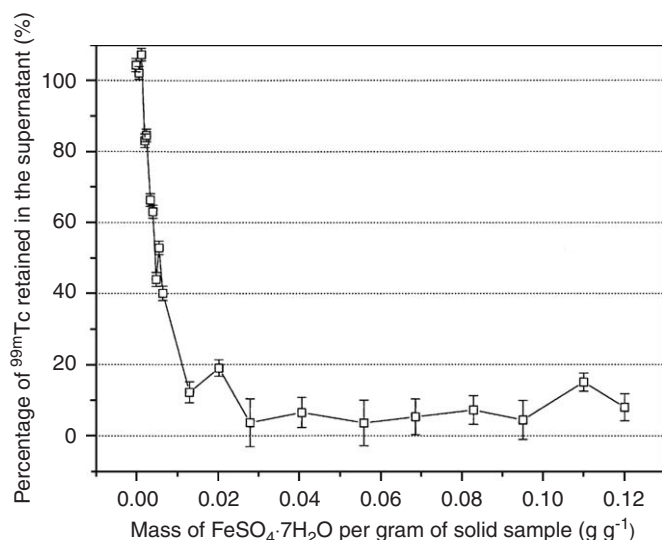

Fig. 2. ^{99m}Tc retention (%) in the supernatant as a function of the reducing compound ($FeSO_4 \cdot 7H_2O$) mass added to each test soil sample prior to the Technetium precipitation step (See the text for details).

tion with Tc for the reducing compound than a rainwater sample.

3.2. Performances of the method

Two test soils samples (125 g each) were analyzed using this method, whose performances are summarized in Table 2. Mo concentration in the solutions are far below our upper limit of 5–10 ppb; using this information, it is possible to assure that ^{99}Tc counting could be done in several environmental samples without spectral interferences associated to concomitant Mo isotopes. It is quite interesting to see that DF for Molybdenum increases almost an order of magnitude after repeating the TEVA

Table 2
Results obtained for the different aliquots of the test soil samples after applying the different methods explained in the text

Chemical yield (%)	CF	DF for Mo	DF for Ru	MDMC (Bq kg^{-1})
32.0±1.4	4.6±0.2	487	⩾9500	0.02
29.0±1.4	4.0±0.2	3500	⩾9500	0.01

resin separation procedure three times (aliquot S32) instead of two times (aliquot S31). This fact is in agreement with our previous studies (Mas et al., 2004).

The chemical yields for Tc are very low. This is a consequence of a combination of circumstances: (1) the used sample masses are greater than 100 g, and in this way, possibly, the extraction efficiency during the acid leaching diminishes in a very important proportion. (2) Using 0.5 M HNO_3 during the separation with the TEVA·Spec resin instead of 0.1 M HNO_3 decreased the resin's selectivity for Tc along the washing process (Tagami and Uchida, 2000).

It is easy to see that these MDMC values are smaller than those achieved in some of the previously mentioned routine methods. However, our MDMC values are higher than the ^{99}Tc concentrations reported at fallout level (e.g., Tagami and Uchida, 2002). They previously proposed the Tc volatilization from soil samples (Tagami and Uchida, 1993), followed by trapping in aqueous solutions. Using this approach, the effective concentration of up to 500–1000 g of soil has been done. Furthermore, effective removal of many matrix elements was achieved. Unfortunately we do not have that kind of fusion devices at our laboratory. However, our limits of detection are in a range of 50–700 times less than those Tc concentrations arising from heavily contaminated places, such as forest soil samples near to Chernobyl nuclear plant (Uchida et al., 1999). This fact marks the limit capabilities of our method: although we are not yet able to detect fallout level technetium, we could easily detect severe contamination events, which could be difficult to detect using the routine methods already mentioned.

It is necessary to bear in mind that the capabilities of this method for a greater sample mass amount are limited by the fact that the only way of effectively removing Mo atoms is related to the capabilities of the TEVA·Spec resin (according to our previous results, it seems that the combination of precipitation + LLX does not introduce a very effective decontamination from Mo). Thus, if necessary, an alternative scheme would consider a batch separation of Tc from Mo mixing the loading solution with a larger amount of resin into a barrel, and then repeating the previously explained method using a home-made column, instead of the commercially available microcolumns.

It can be concluded that this method offers a good commitment between limit of detection and interfering element DF, after less than 20 h real time analysis.

3.3. Validation of the technique

Due to the lack of reference materials for Tc with certified concentrations, validation of the method was carried out using five brown algae samples (McCartney et al., 1999a). Two replicates were analyzed for every sample (A–E in order of increasing radioactive concentration). Masses ranging from 0.5 to 20 g were used in each analysis, depending on the expected concentration. The average and uncertainty values are presented in Table 3. Our results are in good agreement with the consensus values of the inter-comparison exercise. Under these conditions, we can assume this method as validated for a wide range of technetium concentrations.

3.4. Environmental samples from the South–West of Spain

Different kinds of samples taken from the South of Spain were analyzed using this method. Our hypothesis is that undetectable ^{99}Tc concentrations are expected, as this isotope would proceed mainly from global fallout. In this way, we expect to show the real capabilities (and, specially, the real limitations) of this method. Results are given in Table 4.

It is easy to see that almost all the radioactivity concentrations for soils are under the MDMC, although the CFs are usually high. The mass activity corresponding to the DFS is actually equal to the MDMC, into the

uncertainty intervals. This fact shows the extraordinarily low amounts of ^{99}Tc present in samples from regions not directly affected by nuclear industries. The origin of Tc in these kinds of samples would be related to the military atmospheric nuclear tests during the second middle of 20th century. Assuming a mean residence time of about 18 months (Garcia-Leon et al., 1993), the working hypothesis would be an almost complete return of Tc to the earth surface. Our result seems to support such a hypothesis. Our previous analysis of rainwater samples taken at the same location seems to support this conclusion (Mas et al., 2004). Furthermore, Tagami and Uchida (1996) recently published some of these data calculated from samples taken at Hitachinata (Japan). They estimated Tc concentrations in dry fallout as less than 0.4–$0.9\,\mathrm{mBq\,m^{-2}\,month^{-1}}$. Our results show an activity deposition equal to (or lower than) $0.06\,\mathrm{mBq\,m^{-2}\,month^{-1}}$. And then, very high agreement between the referred conclusions is observed.

Regarding the sea grass samples, no detection of Tc was possible. This is the expected result, as according to Bohn et al. (1984), the technetium CFs for these species are at least three orders of magnitude less than for brown seaweed. Bearing in mind previous results for brown seaweed collected from the same region, (Manjón et al., 1995), the technetium concentration in sea grass would be $<0.1\,\mathrm{mBq\,kg^{-1}}$. Hence, once again, our results below MDMC are in agreement with our hypothesis, supporting the lack of any strong Tc entrance to this area.

4. Summary and conclusions

Measurement of ^{99}Tc by ICP-MS in environmental samples requires decontamination from Mo and Ru to avoid isobaric overlap and interferences due to instrumental abundance sensitivity. A radiochemical method has been proposed for the treatment of different kinds of solid samples, which satisfactorily decontaminates the sample from Mo and Ru. It couples high sample concentration using a coprecipitation-LLX step with further solution purification achieved by anion exchange chromatography. A very interesting point has been found, as repeating the separation with a TEVA·Spec$^{\mathrm{TM}}$ resin greatly improves the separation from Mo atoms present in the sample; thus, the sensitivity of the method is improved. This effect is achieved in a less time consuming way than diluting (or even evaporating to dryness) the leaching solution.

The greater part of Tc concentrations found seems to lie under the limits of detection (which is in the range of several tenths of $\mathrm{mBq\,kg^{-1}}$), as expected bearing in mind that all the samples were taken from a region far from any nuclear industry.

Table 3
Consensus values obtained for five brown algae samples in an intercomparison exercise, and the results we found when applying the S3 method

Sample	Consensus value (Bq kg^{-1})	This work (Bq kg^{-1})
A	5.9 ± 1.1	4.6 ± 0.3
B	58.3 ± 4.6	48.8 ± 1.0
C	$(3.91 \pm 0.13) \times 10^3$	$(3.29 \pm 0.14) \times 10^3$
D	$(1.791 \pm 0.078) \times 10^4$	$(1.614 \pm 0.055) \times 10^4$
E	$(1.33 \pm 0.12) \times 10^5$	$(1.18 \pm 0.03) \times 10^5$

Table 4
Obtained results for ^{99}Tc in a dry fallout sample (DFS), two Seagrass (Zostera Marina) samples (ZM1 and ZM2) and four Mediterranean forest soil samples (1SD1, 1SD4, 2S1 and 2S2) collected in the South–West of Spain

Sample	Mass amount (g)	CF	MDMC (mBq kg^{-1})	^{99}Tc (mBq kg^{-1})
DFS	125	4.4 ± 0.1	16	19 ± 5
ZM1	35	1.04 ± 0.03	70	66 ± 19
ZM2	35	0.84 ± 0.03	77	60 ± 28
1SD1	125	3.65 ± 0.06	21	—
1SD4	125	4.35 ± 0.04	36	—
2S1	75	3.37 ± 0.06	32	7 ± 9
2S2	90	3.76 ± 0.16	30	15 ± 26

References

Bohn, B., Luxenburger, H.J., Schüttelkopf, H., 1984. Radiochemical determination of ^{99}Tc and release of ^{99}Tc from nuclear facilities. In: Desmet, G., y Myttenaire, C. (Eds.), Technetium in the Environment. Elsevier, Essex, pp. 29–36.

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

Eroglu, A.E., McLeod, C.W., Leonard, K.S., McCubbin, D., 1998. Determination of technetium in sea-water using ion-exchange and inductively coupled plasma mass spectrometry with ultrasonic nebulisation. J. Anal. Atom. Spectrom. 13, 875.

García-León, M., Piazza, C., Madurga, G., 1984. ^{99}Tc in Surface air samples during the years 1965–1967. Int. J. Appl. Radiat. Isot. 35, 961–963.

Garcia-Leon, M., Manjon, G., Sanchez-Angulo, C.I., 1993. ^{99}Tc/^{137}Cs activity ratios in rainwater samples collected in the South of Spain. J. Environ. Radioactivity 20, 49–61.

Gómez, M.B., Gutiérrez, A.M., Cámara, C., Gómez, V., 2001. Determination of ^{99}Tc in drinking waters by radiochemical techniques and inductively coupled plasma mass spectrometry. Radioact. Radiochem. 12 (1), 27.

Keith-Roach, M.J., Stürup, S., Oughton, D.H., Dahlgaard, H., 2002. Comparison of two ICP-MS set-ups for measuring ^{99}Tc in large volume water samples. The Analyst 127, 70–75.

McCartney, M., Olive, V., Scott, E.M., 1999a. The measurement of ^{99}Tc in seaweed: results from an international intercomparison exercise. J. Radional. Nucl. Chem. 242, 413–418.

McCartney, M., Rajendran, K., Olive, V., Busby, R.G., McDonald, P., 1999b. Development of a novel method for the determination of

^{99}Tc in environmental samples by ICP-MS. J. Anal. Atom. Spectrom. 14, 1849–1852.

Manjón, G., García-Leon, M., Ballestra, S., López, J.J., 1995. The presence of man-made radionuclides in the marine environment in the south of Spain. J. Environ. Radioactivity 28, 171–189.

Mas, J.L., García-León, M., Bolívar, J.P., Sánchez-Angulo, C.I., 2000. The use of ^{99m}Tc as a tracer in the determination of ^{99}Tc by ICP-mass spectrometry. J. Anal. Atom. Spectrom. 15, 1369–1373.

Mas, J.L., Bolívar, J.P., García-Tenorio, R., Aguado, J.L., San Miguel, E.G., González-Labajo, J., 2001. A dosimetric model for determining the effectiveness of soil covers for phosphogypsum waste piles. Health Phys. 80, 34–40.

Mas, J.L., García-León, M., Bolívar, J.P., 2002. ^{99}Tc atom counting by quadrupole ICP-MS. Optimisation of the instrumental response. Nucl. Instr. Methods Phys. Res. A 484, 660–667.

Mas, J.L., Garcia-León, M., Bolivar, JP., 2004. ^{99}Tc detection in water samples by ICP-MS. Radiochim. Acta 92, 39–46.

Morita, S., Kim, C.K., Takaku, Y., Seki, R., Ikeda, N., 1991. Determination of technetium-99 in environmental samples by inductively coupled plasma-mass spectrometry. Appl. Radiat. Isot. 42, 531–534.

Nicholson, S., Sanders, T.W., Blaine, L.M., 1993. The determination of ^{99}Tc in environmental samples by inductively coupled plasma mass spectrometry. Sci. Tot. Environ. 130–131, 275–284.

Ramebäck, H., Albinsson, Y., Skålberg, M., Eklund, U.B., 1998. Determination of ^{99}Tc in bentonite clay samples using inductively coupled plasma mass spectrometry. Fresenius J. Anal. Chem. 362, 391.

Sánchez-Angulo, C.I., García-León, M., 1988. A method for the measurement of ^{137}Cs and ^{99}Tc from the same rainwater sample. Nucl. Geophys. 2, 69–73.

Tagami, K., Uchida, S., 1993. Separation procedure for the determination of technetium-99 in soil by ICP-MS. Radiochim. Acta 63, 69–72.

Tagami, K., Uchida, S., 1996. Analysis of technetium-99 in soil and deposition samples by inductively coupled plasma mass spectrometry. Appl. Radiat. Isot. 47, 1057–1060.

Tagami, K., Uchida, S., 2000. Separation of rhenium by an extraction chromatographic resin for determination by inductively coupled plasma—mass spectrometry. Anal. Chim. Acta 405, 227–229.

Tagami, K., Uchida, S., 2002. Global fallout technetium-99 Distribution and behaviour in Japanese soils. J. Nucl. Radiochem. Sci. 3, 1–5.

Uchida, S., Tagami, K., Wirth, E., Rhüm, W., 1999. Concentration levels of technetium-99 in forest soils collected within the 30-km zone around the Chernobyl reactor. Environ. Pollution 105, 75–77.

Vaca, F., Manjon, G., Garcia-León, M., 2001. The presence of some artificial and natural radionuclides in a eucalyptus forest in the south of Spain. J. Environ. Radioactivity 56, 309–325.