

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

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Received 21 September 2005; accepted 13 November 2005

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 (≥ 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.

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Keywords: Technetium; ICP-MS; Concentration factor; Decontamination factor

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 ng 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, $^{99\text{m}}\text{Tc}$, was obtained from medical generators. Its contribution to MDMC arising from the $^{99\text{m}}\text{Tc}$ 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 ($< 0.7 \text{ Bq kg}^{-1}$). Therefore, we can estimate ^{99}Tc concentrations in the range of 0.07 mBq 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).

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