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Determination of ^{99}Tc in fresh water using TRU resin by ICP-MS

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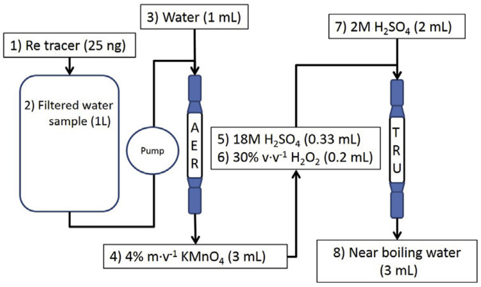
HIGHLIGHTS

- Tc(VII) can be extracted and purified from potential interferents with a TRU resin.
- Re(VII) can be used as a recovery tracer.
- No vaporisation step is needed for this method.
- Potassium permanganate can be used to elute Tc(VII) and Re(VII) from an anion exchange resin.
- A low detection limit of 4.01×10^{-13} Bq·L^{-1} was obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Technetium-99 (^{99}Tc) determination at trace level by inductively coupled plasma mass spectrometry (ICP-MS) is challenging because there is no readily available appropriate Tc isotopic tracer. A new method using Re as a recovery tracer to determine ^{99}Tc in fresh water samples, which does not require any evaporation step, was developed. Tc(VII) and Re(VII) were pre-concentrated on a small anion exchange resin (AER) cartridge from one litre of water sample. They were then efficiently eluted from the AER using a potassium permanganate ($KMnO_4$) solution. After the reduction of $KMnO_4$ in 2 M sulfuric acid solution, the sample was passed through a small TRU resin cartridge. Tc(VII) and Re(VII) retained on the TRU resin were eluted using near boiling water, which can be directly used for the ICP-MS measurement. The results for method optimisation, validation and application were reported.

1. Introduction

Technetium-99 (^{99}Tc) is a high yield fission product of ^{235}U and ^{239}Pu (6%) [1,2], is very mobile in the environment as Tc(VII) (TcO_4^-) [3,4], and has a long radiological half-life of 2.13×10^5 years [5]. Significant amounts of ^{99}Tc have been released to the environment since the beginning of the nuclear era, mainly from the Sellafield and La Hague reprocessing plants, but also from nuclear weapons testing [6]. Technetium-99 is of environmental concern since it was largely dispersed to the environment by human activities and that bio-accumulation has been observed in some species of lobsters and seaweeds [7]. Despite that ^{99}Tc is of environmental concern, its emission by the Canadian nuclear installations has not yet been studied due to the lack of appropriate analytical method for its routine monitoring. Therefore, rapid, sensitive and robust radio-analytical methods are needed to monitor ^{99}Tc in environmental

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samples released from nuclear facilities.

Although ^{99}Tc has often been measured using radiometric methods such as liquid scintillation counting (LSC) and gas ionisation detectors, mass spectrometry techniques such as ICP-MS and AMS (accelerator mass spectrometry) would be more sensitive for the measurement of this long-lived nuclide [6]. Due to its rapidness, good sensitivity and easy accessibility, ICP-MS is one of the preferred method used to measure ^{99}Tc at trace levels. However, one of the limitations for the analysis of ^{99}Tc by ICP-MS is the lack of ideal isotopic tracer [6]. Other two long-lived technetium isotopes ^{97}Tc (radiological half-life ($t_{1/2}$) of 4.2×10^6 y) and ^{98}Tc ($t_{1/2}$ of 6.6×10^6 y) are not commercially available and are generally not pure enough for ICP-MS measurements [6]. The short-lived ^{95m}Tc ($t_{1/2}$ of 62.2 d) and ^{99m}Tc ($t_{1/2}$ of 6.01 h) are usually measured by gamma spectrometry, which does not correct for the instrument signal variations during the ICP-MS analysis [8–12]. As Re(VII) has a similar electronic configuration and chemical properties to Tc(VII), it can be used as a tracer for the determination of ^{99}Tc [13–16]. The use of stable Re tracer has the advantages of being easily available, time stable, and exempt of ^{99}Tc impurities. However, it is crucial to be able to demonstrate that Re tracer will behave exactly as Tc through all of the method steps [17].

Several techniques such as co-precipitation, solvent extraction, filtration, and resin extraction have been employed for the pre-concentration and purification of ^{99}Tc [6]. A commonly employed technique for the selective extraction of Tc(VII) and Re(VII) consists of passing the solution sample through a column containing a quaternary amine adsorbed or fixed on a solid support. The strong basic anion exchange resins (AER) [8] and the Eichrom TEVA [12,17] resin have been commonly used for this purpose. Tc (VII) is usually extracted on the resin at low acid molarity (e.g. 0.01 M HNO_3) [3,8,12,18]. Most elements are not retained under these conditions [6]. The main isobaric and molecular interferents for the measurement of ^{99}Tc are $^{99}Ru^+$ and $^{98}MoH^+$, which can be partially removed from the resin after an appropriate rinsing step [1,6]. Note that sometimes the decontamination factor is not satisfactory and an additional purification step is required [6]. After extraction, Tc(VII) and Re(VII) are eluted from the resin using a high acid molarity solution (e.g. 4–16 M HNO_3) [12,17,19]. The acidity of the eluate is usually too high to be directly injected into an ICP-MS without causing significant corrosion of its metallic components. Thus, the eluate is frequently evaporated to reduce the sample acidity [6,11]. Because $HTcO_4$ and $HReO_4$ have very different vapor pressures in acidic solutions ($HTcO_4$ is more volatile than $HReO_4$ [20,21]), this could lead to an underestimation of the method recovery [17]. Also, the evaporation step is very time consuming and could cause corrosion of laboratory equipment with time.

TRU resin (from Eichrom) contains tributyl phosphate (TBP) [22], which can simultaneously extract Tc(VII) and Re(VII) in 2 M H_2SO_4 [23]. Ru(IV) and Mo(VII) interferents are poorly retained by the resin under this condition [23]. Tc(VII) and Re(VII) can be eluted from the resin using near boiling water [23]. This eluant, after being cooled to room temperature, can be directly injected into an ICP-MS with no need of any evaporation steps [23]. This is extremely advantageous compared to the quaternary amine extraction technique. However, a pre-concentration factor of 10 obtained with the TRU resin can be a major limiting factor for measuring low levels of ^{99}Tc in environmental water samples. Without an appropriate pre-concentration technique, it will not be possible to measure ^{99}Tc at trace level using the TRU resin. There are only a limited number of the known pre-concentration techniques that would allow Tc and Re to be simultaneously extracted or precipitated. In these pre-concentration techniques, the AER or TEVA resins are often used, and Tc and Re are usually eluted with a concentrated acid solution followed by a slow evaporation as explained above. The other eluent sometimes used to for the elution of Tc(VII) and Re(VII) from an AER is a perchlorate salt or perchloric acid solution [24,25]. The perchlorate anion competes with the exchange sites and strips off Tc(VII)/Re(VII) from the resin. Because ClO_4^- has a similar chemical behavior to Tc(VII)/Re(VII), it could compete with their extraction on the TRU resin. The removal of ClO_4^- is usually achieved by the selective precipitation of Tc and Re in the form of sulfide.

Since potassium permanganate ($KMnO_4$) also has a structure similar to $HTcO_4$ and is strongly bonded to the AER, we propose to use a solution of $KMnO_4$ as a new eluent for stripping Tc(VII) and Re(VII) from the AER. After elution, $KMnO_4$ could then be reduced to Mn(II) in 2 M H_2SO_4, which would no longer compete with the extraction of Tc(VII)/Re(VII) on the TRU resin. Moreover, to shorten the sample preparation time for routine monitoring, a reasonable size of the water sample (around 1–10 L) should be processed. Therefore, a great focus should be given to quickly concentrate ^{99}Tc as much as possible before introducing to the ICP-MS.

In this work, a new method to determine ^{99}Tc in fresh waters at trace level by ICP-MS using Re as a recovery tracer is described. Tc(VII) and Re(VII) are pre-concentrated using an AER. Both elements are eluted from the AER using a solution of $KMnO_4$ and then passed through a TRU resin without a need for evaporation. After the elution from the TRU resin with a small volume of near boiling water, Tc and Re are measured by ICP-MS. First, the optimal extraction and elution conditions for Tc(VII) and Re(VII) were determined. For each step, the similar behavior between Tc(VII) and Re(VII) was demonstrated. Then, the method performances (figures of merit, decontamination factor) were evaluated. Finally, the method was validated using spiked river water samples and environmental samples.

2. Experimental

2.1. Reagents and standards

All solutions were prepared using ultra-pure water (UPW) produced from a water purification system (Millipore Direct-Q5, Bellerica, MA, USA). Sulfuric acid (H_2SO_4) trace metal grade, nitric acid (HNO_3) trace metal grade, potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2) trace metal grade 30% $v \cdot v^{-1}$, and sodium hydroxide (NaOH) were bought from Fisher Scientific (Fair Lawn, NJ, USA). The TRU® resin (50–100 μm) and AG®MP-1M resin (100–200 mesh) were obtained from Eichrom Technologies (Lisle, IL, USA) and Bio Rad Laboratories Inc. (Hercules, CA, USA), respectively. Standard solutions of ICP-MS grade Re, Ru, and Mo (1000 $\mu g\ mL^{-1}$) were obtained from SCP Science (Baie d'Urfé, QC, Canada). A certified solution of ^{99}Tc was bought from the National Institute of Standards and Technology (NIST) (Gaithersburg, Maryland, MD, USA).

2.2. Procedure

The method includes 3 major steps: 1) The sample preparation, 2) Tc(VII)/Re(VII) pre-concentration on AER, and 3) Tc(VII)/Re(VII) purification on TRU resin.

2.2.1. Sample preparation

A 1 L water sample was filtered through a 0.45 μm pore filter (Millipore, Etobicoke, ON, Canada) to remove suspended particles and the filtrate was transferred into a 1 L polyethylene bottle. A weighed amount of the Re tracer (1.34×10^{-10} mol) and 2 mL of H_2O_2 were added into the sample. The water bottle was vigorously shaken once. The sample was put aside for 1 h to enable H_2O_2 to oxidize Tc(IV) to Tc(VII) and decompose part of the organic matter.