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Rapid determination of Technetium-99 by automatic solid phase extraction and inductively coupled plasma mass spectrometry

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Abstract

Technetium-99 (^{99}Tc) is a key nuclide, produced by the fission of Uranium-235 (^{235}U) and Plutonium-239 (^{239}Pu), through a cascade decay process, and is one kind of target element in environmental analysis due to its long half-life ($t_{1/2}$ = 2.1 x 10^5 years). This study developed a ^{99}Tc analytical technique using automatic solid phase extraction (SPE) with TEVA resin and inductively coupled plasma mass spectrometry (ICP-MS). The chemical recovery of ^{99}Tc was 94.15 ± 3.14 % and the minimum detectable activity (MDA) for cement solidified samples spiked with ^{99}Tc was 1.5 mBq/g (2.4 pg/mL). In this study, standard reference material (SRM), an environmental sample was measured by this analytical method. The proposed method is more convenient than traditional radiochemical methods in terms of reducing the time required for analysis, the consumption of reagents, and radiation exposure of operators.

Keywords: Technetium-99, automatic solid phase extraction, inductively coupled plasma mass spectrometry, TEVA resin

Introduction

Technetium-99 (^{99}Tc) is an artificial element derived from the Greek word "technetos", meaning "artificial". ^{99}Tc is a high yield (6%) fission product of ^{235}U and ^{239}Pu [1], widely distributed in the environment as a result of fallout from nuclear weapons testing and discharge from nuclear facilities [2]. The measurement of ^{99}Tc is of particular interest due to its high mobility in the environment, and the fact that it is a beta-emitter with a long half-life ($t_{1/2} = 2.1 \times 10^5$ years) with long-term radiological effects. One important aspect in assessing the safety of potential sites for the disposal of radioactive waste is the geochemical behavior of key radionuclides (e.g., ^{99}Tc, ^{129}I or ^{90}Sr) that could lead to their release from the site [3]. During reprocessing, pertechnetic acid ($HTcO_4$) and technetium heptoxide (Tc_2O_7) can be volatilized. Volatilization is a concern in radiology, which has prompted the monitoring of effluent streams in reprocessing operations. Once technetium heptoxide is volatilized, pertechnetate (TcO_4^-) can form in the environment in the presence of water. Under oxidizing conditions, TcO_4^- can spread throughout aqueous and soil phases in the environment [4].

Determining ^{99}Tc in the environment samples or in the low level radioactive waste was very difficult due to various forms of interference. A liquid scintillation counter (LSC) has traditionally been used for measurement, however, matrix interference and shifts in the energy window can lead to high uncertainty in these measurements. The major hindrance of the matrix effect is high concentrations of isotopes found in natural uranium such as ^{234}Th. It is a challenge to the deal with beta emissions from interfering isotopes measured within the ^{99}Tc window of LSC. This may cause biases against the accurate measurement of 99Tc [5]. In addition, the detection limit of LSC depends on counting efficiency, background levels, and counting time. Prior to 2005, ^{99}Tc in gaseous and liquid effluents from nuclear plants were always assessed by using LSC [6].

Inductively coupled plasma mass spectrometry (ICP-MS) is a good alternative for the determination of ^{99}Tc in low level radwaste samples. This technique offers several advantages over traditional radiometric methods, including high sensitivity and relatively short measurement times

[7,8]. Due to the very low concentrations of ^{99}Tc in the environment and the need to reduce interference with the matrix, sample separation and purification techniques must be applied to lower the ratio of total dissolved solids, such that the analytic method is concentrated prior to measurement. As previously report, the electrothermal vaporisation (ETV) as a sample introduction has been used to remove ruthenium due to its lower boiling point. The contribution from ^{98}Mo to mass 99 is mainly due to the abundance sensitivity and in a less extent due to the formation of ^{98}MoH. However, isobaric interference from ruthenium (^{99}Ru) is the major difficulty in the measurement of ^{99}Tc using ICP-MS [9,10]. ^{99}Ru is a natural stable isotope with a far higher concentration in the environment than ^{99}Tc [11].

Previously study was reported that rhenium can be used as a ^{99}Tc yield monitor, following experiments showing that, despite the complex behavior of ruthenium and with good decontamination of technetium, a high recovery could be achieved at each stage of the procedure [12]. Moreover, the ion peak of ^{99}Tc obtained by ICP-MS can be impaired by the peak tailing of ^{98}Mo and ^{100}Mo. ^{99}Tc concentrations in environmental and biological samples are below the detection limit of ICP-MS; therefore, pre-concentration is required. Hollenbach et al. developed a rapid method based on flow injection pre-concentration using TEVA Spec. extraction resin followed by ICP-MS measurements [13]. As a result, the detection limit for ^{99}Tc in soil was lowered to 0.02 ng/g (13 mBq/g). In this process, ^{99}Tc is extracted from the sample using TEVA Spec. extraction chromatography and it is strongly retained due to the neutral pH of the solution, while the isobaric interference caused by elemental Mo is weakly retained and Ru is not retained at all [14].

The aim of this study was to develop a reliable technique for the separation and determination of ^{99}Tc by using TEVA extraction chromatography and ICP-MS from samples of solidified cement of low-level radwaste. This automatic method of analyzing ^{99}Tc can be used to deal with a wide range of environmental samples, such as particularly radwaste and soil. This study developed a convenient and rapid chemical separation system for solid phase extraction (SPE) for the concentration of ^{99}Tc to facilitate analysis by ICP-MS at a ^{99}Tc detection limit of 1.5 mBq/mL.

Materials and Methods

Chemical reagents

This study used the ultrapure analytical nitric acid, extra pure grade hydrochloric acid, as well as analytical grade ammonium nitrate were all from Merck, Germany. The water used to prepare the reagents was 18.2 MΩ deionized water obtained from a Milli-Q water system (Millipore). Columns were packed with 0.35 g of Tc-selective chromatographic resin (TEVA resin, Eichrom Industries) before use. Packed columns were then used for the cleanup and separation of ^{99}Tc in each sample. ^{99m}Tc solution was obtained from Global Medical Solutions (USA) for use in the monitoring of chemical yield throughout the process. ^{99}Tc solution was purchased from the National Institute of Standards and Technology, USA (NIST SRM 4288A) for spiking samples of solidified cement. This standard reference material (NIST SRM 4359, USA) is a blend of seaweed collected off the coast of Ireland and the White Sea. The SRM has been developed in cooperation with member laboratories of the International Committee for Radionuclide Metrology (ICRM) and experienced metrology laboratories. It is the intended for use in tests of measurements of radioactivity contained in matrices similar to the sample; the evaluation of analytical methods and as a generally available calibrated "real" sample matrix for laboratory inter-comparison. The SRM sample was stored in a dry location at room temperature. In this study, SRM was used to demonstrate the accuracy and precision of the ^{99}Tc concentrations obtained by the proposed SPE system. Ru and Mo were obtained from ICP standard solution (CertiPUR™, Merck, Germany).

Apparatus

The samples were digested using a microwave device (Model MARS-5, CEM, USA) to eliminate cross contamination and loss of volatiles. The mixture of sample materials and digestive reagents was digested in a double-walled vessel (HP-500 Plus) under standard control mode. The maximum pressure was set at 300 psi (2070 kPa). An automatic solid phase extraction (SPE) System (RapidTrace$^+$, Biotage, Switzerland) was used for sample preparation with the TEVA resin system, which made it more convenient and faster to purify ^{99}Tc from the samples. The system was comprised of a pump, Teflon pipelines (id. 1.58 mm), and 12-port valves controlled by commercial software (Zymark Rapid Trace SPE workspace version 2.0). The gamma rays emitted by ^{99m}Tc were measured using a well counter (Caprac-R, Capintec, USA). The quantitative analysis of ^{99}Tc and chemical yields were calculated from the spiked samples of solidified cement and the removal of Ru was performed using an ICP-MS (X SeriesII, Thermo, Germany). The measurement of Mo was performed using inductively coupled plasma atomic emission (ICP-AES, JY 38S, Jobin Yvon, France).

Solid sample pretreatment

Solidified cement blank samples (0.25 g) were produced by the Institute of Nuclear Energy Research. A known concentration of ^{99}Tc (35.5 pg/ml) was added to the blank solidified cement sample in order to monitor chemical yield throughout the separation process. The percentages of the solidified cement samples were as follows: 71.54 %, NaCl: 12.61 %, $Ba(OH)_2$: 6.00 %, Na_2SO_4: 4.50 %, NaOH: 3.15 %, $NaNO_3$: 1.18 %, Na_2CO_3: 0.62 %, Na_3PO_4: 0.26 %, $NaHCO_3$: 0.14 %. The samples and digestive reagents (HNO_3: 9 ml and HCl: 4 ml) were mixed and digested in the microwave device at 180°C for 11.5 minutes with a ramp up time of 25 min and a cooling time of 30 min. Following microwave digestion, the sample solution was evaporated under a heating temperature of 90°C to near dryness. The sample was then dissolved in 10 mL of 0.05 mol/L HNO_3 for sample injection into the SPE separation system.

SPE separation method

The automatic SPE system used in this study is illustrated in Figure 1. Samples were placed in a cannula and the empty port of a 12-port valve to store the extraction solution of the nuclides. The flow rate of solution through the column in the above stage was 5 mL/min. Eichrom TEVA resin was used in the automatic SPE system for the following step involving the extraction of solvent. In this system, 10 mL of 0.05 mol/L HNO_3 was injected directly into a TEVA resin column to facilitate conditioning in the first stage, where upon a sample solution with 0.05 mol/L HNO_3 was loaded into TEVA resin column. The TEVA resin column was then cleaned using 10 ml of 1 mol/L HNO_3 via two or three successive cleaning procedures to remove a fraction of the interfering elements (Mo and Ru) of high concentration. In this manner, Ru and Mo were almost entirely removed from the sample solution using the TEVA resin column. Finally, the Tc was stripped using a small volume (10 mL) of 5 mol/L HNO_3. After heating dry, the eluted product was dissolved using 2 % HNO_3, as the recovery rate was determined by ICP-MS. The analytical procedures are outlined in Figure 2.

Results and Discussion

TEVA resin columns optimized conditions

Various concentrations of nitric acid (0.1, 0.05, 0.01, 0.005 and 0.001 mol/L) were used to determine the optimal ^{99}Tc adsorption (uptake) efficiency in TEVA resin, to provide a more convenient counting method using a well counter. As shown in Figure 3, 0.05 mol/L HNO_3 provided the highest ^{99}Tc adsorption efficiency. According to paired t-test analysis, 0.05 mol/L HNO_3 differed significantly from the other concentrations ($p < 0.05$). When using 10 mol/L HNO_3, an elution efficiency of 100 % was achieved using the TEVA resin. For 8 mol/L HNO_3, the elution efficiency was 97 %. This suggests that at lower concentrations of HNO_3, the uptake of Tc (VII) using TEVA resin (represented as R_3N, an aliphatic quaternary amine, where R denoting C_8H_7 or $C_{10}H_{21}$) is governed by the solvent extraction ability of pertechnetic acid with resin (Eq. 1). In contrast, the uptake (%) of Tc (VII) tends to gradually decrease above concentrations of 0.1 mol/L HNO_3. This may be due to the effects of related reactions including solvent extraction (Eq. 2) and ion exchange (Eq. 3), indicating that nitric acid extraction using TEVA is the dominant process and that the forward reaction of Eq. (3) is restricted at higher concentrations of HNO_3.

$$R_3N_{(o)} + H^+ + TcO_4^-{}_{(aq)} \rightleftharpoons R_3NH^+TcO_4^-{}_{(o)} \qquad \text{(Eq. 1)}$$

$$R_3N_{(o)} + H^+ + NO_3^-{}_{(aq)} \rightleftharpoons R_3NH^+NO_3^-{}_{(o)} \qquad \text{(Eq. 2)}$$

$$R_3NH^+NO_3^-{}_{(o)} + 2TcO_4^- \rightarrow R_3NH^+TcO_4^-{}_{(o)} + NO_3^-{}_{(aq)} \qquad \text{(Eq. 3)}$$

Typical concentration of HNO3 injected into the ICP-MS should be between 0.3-0.6 mol/L, otherwise, the sampling cone of the ICP-MS could be damaged. High concentration of HNO3 as eluent requires a high dilution before ICP-MS measurement, resulting in a higher detection limit. Thus, the use of 10 or 8 mol/L HNO_3 requires dilution with water prior to ICP-MS measurement, which would result in poor detection limits. We therefore determined that the optimal concentration of HNO_3 would be 5 mol/L for ^{99}Tc elution, in which the average elution efficiency could reach 94 %, as shown in Figure 4. After ^{99}Tc eluted by 5 mol/L HNO_3, the sample solution was evaporated under a heating temperature of 90°C to dry down. The sample was added with 10 mL of 2% (0.24 mol/L) HNO_3 and injected into the SPE separation system following ICP-MS analysis.

Chemical yield

The chemical recoveries (%) of ^{99}Tc used to spike the solidified cement samples are listed in Table 1. In this study, the recovery from 0.25 g of solidified cement samples were 92.5 %, 92.2 %, and 97.7 % respectively (average recovery of 94.12 ± 3.11 %). Each concentration was measured there times, such that the correlation coefficients of the calibration curves could exceed 0.999, indicating the reliability of the analytical system.

Detection limit

The ^{99}Tc detection limit in this study, calculated as 3 σ, was 1.5 mBq/g for the soil sample and was obtained from the measurements of blank solidified cement samples throughout the experimental process (Figure 2). The instrument detection limit (IDL) was 0.0182 mBq/ml according to the results using blanks (2 % HNO_3).

Efficiency in the removal of Mo and Ru from the proposed system

For the ICP-MS analysis, the major hindrance was the potential interference having the same m/z. In this study, there are several isotopes having the same m/z of 99, such as Mo and Ru. To prevent the interference of Mo and Ru, the known quantities of Ru (100 pg/ml) and Mo (10 μg/ml) standard solution dissolved in 10 mL of 0.05 mol/L HNO_3 were independently added to the proposed SPE system throughout the separation process. Removal efficiencies of approximately 100 % were obtained for Mo and Ru, as shown in Table 2. The correlation coefficients of the Mo and Ru calibration curve exceeded 0.995, demonstrating the applicability of the proposed automatic SPE system for the efficient removal of Mo and Ru. Thus, the Mo and Ru can be removed in the chemical separation procedure by using TEVA resin. However, the solidified cement samples were still contained within the complex chemical compositions and they should be mentioned and studied in the future.

SRM sample analysis

A previous study has reported the development of an automatic SPE with 8-port valve for urine samples. The minimum detectable activity (MDA) of this method was 0.1 Bq or 1 Bq/L when preconcentrating 100 mL of urine. In comparison, the elution containing ^{99}Tc was detected using a LSC which achieves a lower MDA thanks to its integration with ICP-MS. The main techniques for ^{99}Tc measurement were using β-counting using gas flow Geiger-Muller (GM) counter and LSC. The detection limit for ICP-MS and β-counting is similar, if quadrupole ICP-MS and low background GM counters are used [16]. The detection limits in radiometric method depended on the LSC counting time [17]. Another report indicated that ^{99}Tc was determined by isotope dilution mass spectrometry with ^{97}Tc as spike. The detection limit of Wang's method by using TIMS for ^{99}Tc was determined at the concentration below 1 ng/g (63 mBq/g), which was much higher than that of this study (1.5 mBq/g in 0.25 g sample) [18]. Compared to previous works involving the manual pretreatment of samples, the proposed automatic SPE method is easier to adjust, faster, and requires lower quantities of reagent.

Prior to 2005 [19-21], detection limits could be reduced by increasing the sample size, which required additional time for the concentration of ^{99}Tc prior to detection. This study required samples of only 0.25 g, which could help to reduce the operators' exposure to radiation and reduce sample preparation time. Our study used SRM to demonstrate the analytical system. Approximately 0.25 g of sample material (NIST SRM 4359) was processed using the above experimental procedures. As shown in Table 3, the mean value was 41.58 ± 4.07 (mBq/g) and the analytical values were within the reference range of 14-48 mBq/g. These results demonstrate the suitability of the proposed method for the environmental samples with complex matrices.

Conclusions

In this study, the seaweed was used as a standard reference material for the method validation. The matrix compositions of seaweed and solidified cement are very different. However, using the proposed automatic SPE system with TEVA resin followed by ICP-MS measurement was successfully applied to the determination of ^{99}Tc in different environmental samples, making it applicable to the analysis of low level radwaste near nuclear facilities. The improved analytical method for the determination of ^{99}Tc provides a more convenient approach compared to traditional radiochemical techniques in terms of reducing the analysis time and reagent consumption. Most importantly, the radiation exposure to the operators can be significantly minimized.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Figure legends

Figure 1. Schematic drawing of the automatic SPE system setup used in this report.

Figure 2. Scheme of the overall experiment to analyze ^{99m}Tc.

Figure 3. The absorption efficiency of ^{99m}Tc via TEVA at various concentrations of HNO_3(aq) (mean ± standard deviation (SD), n=5, *p < 0.05, paired t-test)

Figure 4. The elute efficiency of ^{99m}Tc via TEVA at various concentrations of HNO_3(aq) (mean ± standard deviation (SD), n=5)

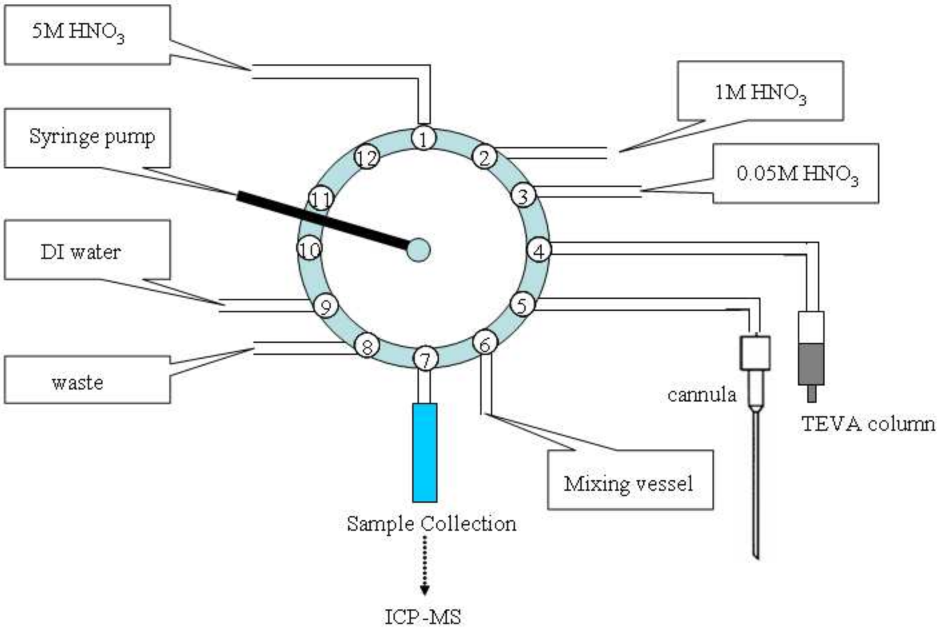
5M HNO_3
Syringe pump
DI water
waste
1M HNO_3
0.05M HNO_3
1
2
3
4
5
6
7
8
9
10
11
12
cannula
TEVA column
Mixing vessel
Sample Collection
ICP-MS

Figure 1

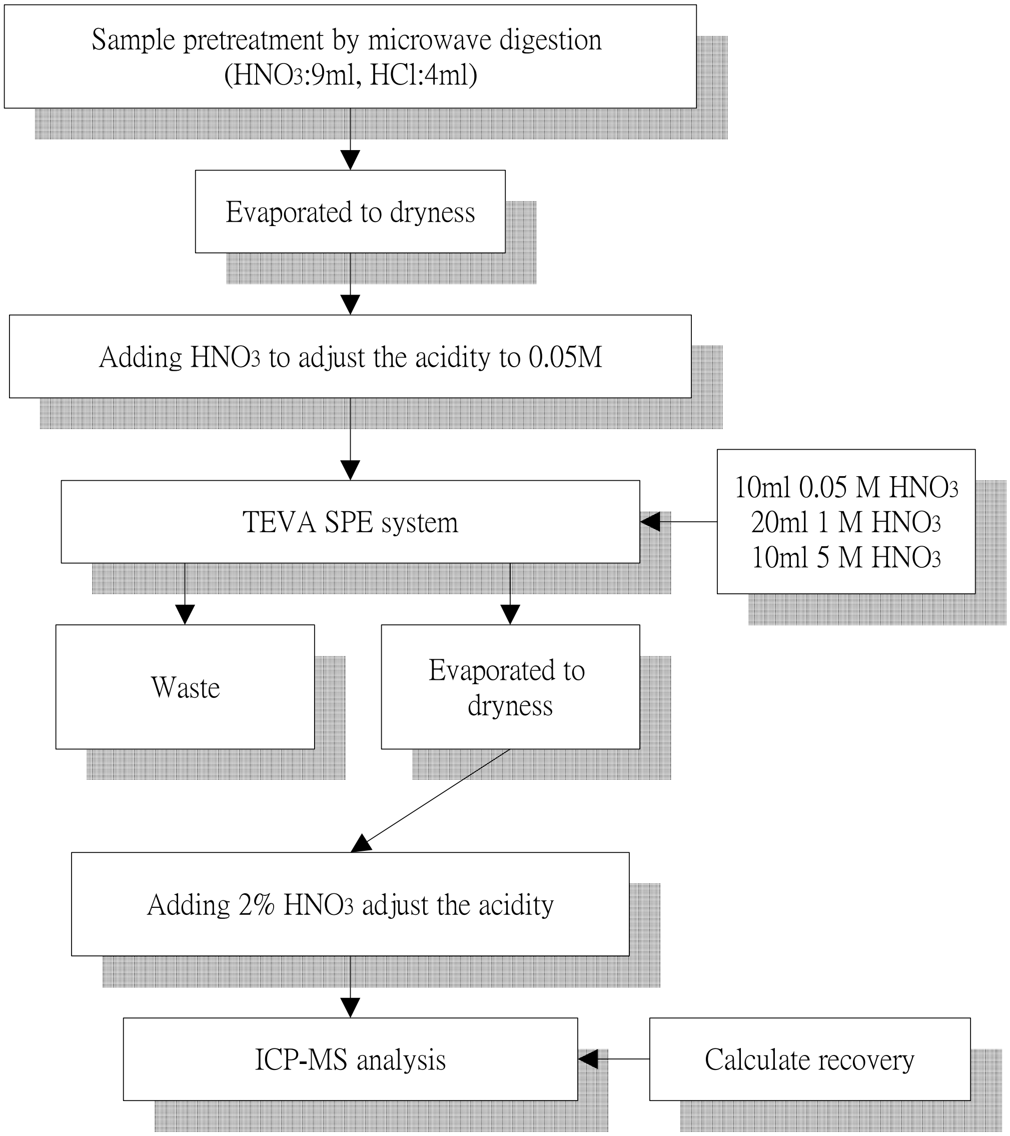
Sample pretreatment by microwave digestion
(HNO_3:9ml, HCl:4ml)
Evaporated to dryness
Adding HNO_3 to adjust the acidity to 0.05M
TEVA SPE system
10ml 0.05 M HNO_3
20ml 1 M HNO_3
10ml 5 M HNO_3
Waste
Evaporated to dryness
Adding 2% HNO_3 adjust the acidity
ICP-MS analysis
Calculate recovery

Figure 2

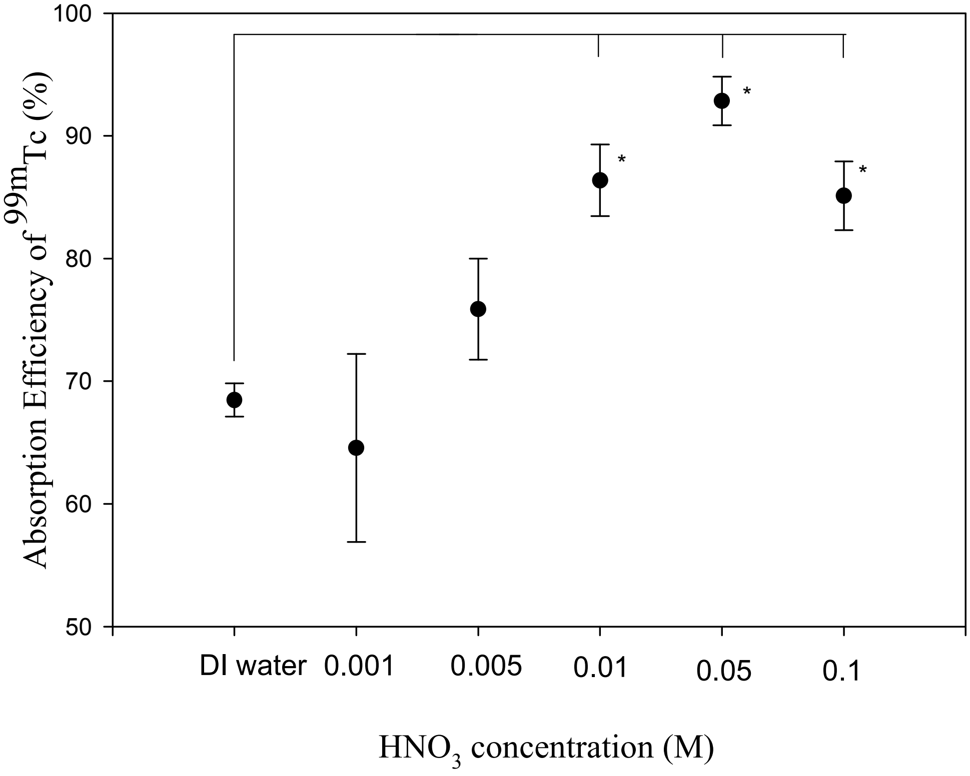
100
90
80
70
60
50
Absorption Efficiency of ^{99m}Tc (%)
*
*
*
DI water
0.001
0.005
0.01
0.05
0.1
HNO$_3$ concentration (M)

Figure 3

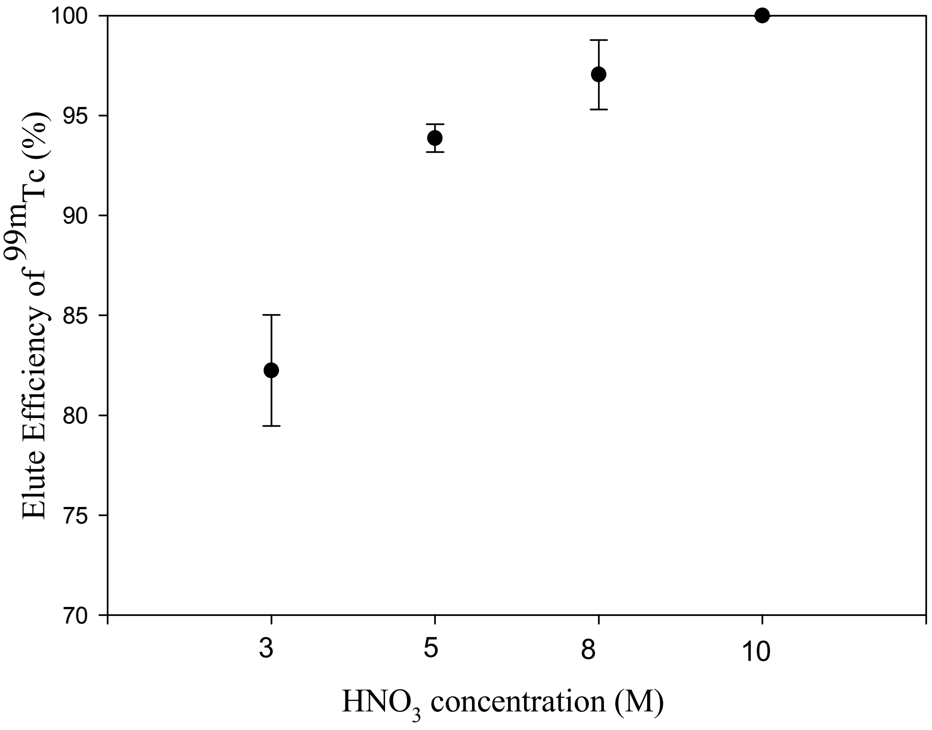
100
95
90
85
80
75
70
Elute Efficiency of ^{99m}Tc (%)
3
5
8
10
HNO$_3$ concentration (M)

Figure 4

Table 1. Chemical recoveries (%) of ^{99}Tc spikes from solidified cement samples

Solidified cement ID	^{99}Tc recovery (%)
Standard Spike-1	92.5
Standard Spike-2	92.16
Standard Spike-3	97.7
Average (mean ± standard deviation)	94.12 ± 3.11

Table 2. Removal efficiency (%) of Mo and Ru

	Added amount	Detector	R-squared	Removal efficiency
Mo	10 μg/ml	ICP-AES	0.9983	100
Ru	100 pg/ml	ICP-MS	0.9988	99.76

Table 3. Analytical results of SRM samples

SRM sample ID	^{99}Tc, mBq/g
SRM sample-1	44.3
SRM sample-2	45.4
SRM sample-3	45.3
SRM sample-4	36.4
SRM sample-5	41.0
SRM sample-6	37.1
Average (mean ±standard deviation)	41.58 ± 4.07