International Journal of Mass Spectrometry 291 (2010) 140–144

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Studies on the formation of atomic and molecular ions of uranium and thorium in thermal ionization mass spectrometry

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ARTICLE INFO

Article history:
Received 26 October 2009
Received in revised form 21 January 2010
Accepted 25 January 2010
Available online 4 February 2010

Keywords:
Thermal ionization mass spectrometry (TIMS)
Thorium
Uranium
Atomic and molecular ion
Double filament
^{232}U

ABSTRACT

Studies are reported on the formation of atomic (M^+) and molecular (MO^+) ions of thorium and uranium in thermal ionization mass spectrometry. The studies were performed by using different synthetic mixtures with Th/U amount ratios as 10, 1 and 0.1. The results obtained on the formation of atomic and molecular ions from these synthetic mixtures employing high purity rhenium double filament assemblies are presented. It was observed that the presence of Th on the filament during TIMS analysis of U enhances the stability of UO^+ ion. Further, ThO^+ ion is ideal for the isotopic analysis of Th by TIMS whereas U^+ or UO^+ ion may be used for the isotopic analysis of U. These studies will be extremely useful to optimize the filament heating parameters for the simultaneous/sequential isotopic analysis of Th and U by TIMS. The optimized conditions of analysis were employed for the determination of ^{232}U in a synthetic U sample containing traces of ^{232}Th.

1. Introduction

Thermal Ionization Mass Spectrometry (TIMS) is an internationally recognized technique for the determination of concentration as well as isotopic composition of different elements in the Periodic Table [1,2]. Due to the high radiotoxicity associated with the actinide elements, it is necessary to use small amounts (ppm or sub-ppm) of elements and also obtain data with high precision and accuracy due to their strategic importance.

Conventionally, TIMS is a single element analysis technique and is based on the measurements using atomic ion (M^+) of the element. Sometimes, it becomes essential to monitor molecular ion e.g., $Cs_2BO_2^+$ using positive TIMS [3] or BO_2^- using negative TIMS [4] for the isotopic analysis of B. In addition, the information on the evaporation and ionization conditions leading to the formation of molecular (e.g., MO^+) and atomic ions is valuable for on-line correction of isobarically interfering isotope. For example, we have previously studied the formation of atomic and oxide ions of U and Pu in TIMS [5]. These studies led to the development of a novel methodology to account for the isobaric interference of ^{238}U in ^{238}Pu employing interfering element correction (IEC) based on the $^{235}U/^{238}U$ ratio determined from the same filament using UO^+ ion [6].

During TIMS analysis of an element, one can obtain atomic (M^+) or molecular ions (MO^+, MO_2^+) of different intensities, depending upon the sample loading procedure followed, filament assembly used and the heating temperatures of the filaments employed in the ion source of the mass spectrometer. Furthermore, studies on the formation of different ions are essential to perform the measurements with high sensitivity in cases when limited amount of the element (μg or lower) is available for the mass spectrometric analysis.

Actinide element pairs such as Pu and Am, U and Th, etc. are of great importance to the nuclear industry. The determination of U and Th is also of interest in geology where TIMS analyses of Th and U are required in geochronology for age determination of corals as well as for isotopic disequilibrium studies [7]. By understanding the ion source chemistry during TIMS analysis, precise, accurate and high sensitivity TIMS analyses of these actinide elements can be achieved.

Accurate determination of ^{232}U in irradiated thorium is of great importance in the thorium nuclear fuel cycle. Thorium is converted into the fissile material (^{233}U) by thermal neutron irradiation in the pressurized heavy water reactors (PHWRs). Irradiated thoria is then processed to recover the fissile material ^{233}U to be used in the future reactor systems such as Advanced Heavy Water Reactors (AHWRs) [8]. ^{233}U is generally associated with small amounts of ^{232}U (Half-life ~ 70 years) [9] and one of the radionuclides viz. ^{208}Tl produced in the decay chain of ^{232}U is a hard gamma emitter (2.8 MeV), and this necessitates additional shielding during

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doi:10.1016/j.ijms.2010.01.019

fabrication of nuclear fuels containing ^{233}U. Theoretical calculations using the reactor code calculations [10] showed that the ^{232}U content can be as high as 1500 ppm due to the recycling of ^{233}U in the further loadings of ^{233}U in AHWR. Accurate determination of ^{232}U/^{233}U ratio is thus of great importance as it decides shielding requirements during fuel fabrication for AHWR.

In the present work, studies were performed on the formation of atomic and molecular ions of Th and U in TIMS by using conventional loading procedure from nitric acid medium with a double filament assembly. These studies were carried out with the objectives of arriving at the optimum filament heating conditions for the mass spectrometric analysis of Th and U from a dissolver solution of irradiated thoria sample. Conventionally, ^{232}U is not determined by TIMS due to the isobaric interference of ^{232}Th which is present in much larger amounts in the sample (e.g., $^{232}\mathrm{Th}/^{232}\mathrm{U} \sim 10^5$ in a typical irradiated Th sample with burn-up of 10,000 MW d/TU. Alpha spectrometry is preferred due to the low abundance of ^{232}U and its relatively high alpha specific activity. But alpha spectrometry has inherent problems due to the in-growth of ^{228}Th with overlapping α particle energies, tail contribution from the high energy α particles present due to the in-growth of various daughter products and random errors due to counting statistics as well as the possibility of contamination of the detector due to the implantation of the recoil daughter products of the ^{232}U decay chain leading to an increased background of the detector system. Moreover, when the amount of ^{232}U is high (1500 ppm) as predicted by theoretical calculations [10], it would be difficult to determine accurately ^{232}U by alpha spectrometry due to its large tail contribution at the low energy alpha peak of ^{233}U and ^{234}U. This limits the precision and accuracy achievable on the data for the amount of ^{232}U present in ^{233}U. Another promising approach for ^{232}U determination in ^{233}U is based on resonance ionization mass spectrometry (RIMS) [11,12]. However, limited spectroscopic data are available for these isotopes and detailed studies are needed prior to using RIMS for determination of ^{232}U on a routine basis.

Studies were, therefore, carried out on the formation of atomic and oxide ions of Th and U using synthetic mixtures of Th/U with amount ratios ranging from 0.1 to 10 to develop a suitable analytical protocol for analysis using TIMS. The Th/U amount ratio range was chosen so as to simulate the conditions of the uranium samples usually encountered from the irradiated thoria samples as well as the kind of samples encountered in geological samples. The formation of different ions was studied as a function of the vaporization filament heating temperature. Suitable filament heating conditions were identified to obtain the isotopic composition of uranium using U^+ ions in the presence of trace amounts of Th.

The optimized conditions of analyses were then employed for the determination of ^{232}U in a synthetically prepared U sample, with about 2000 ppm of ^{232}U. The results on ^{232}U/^{233}U atom ratio obtained for the pure U sample and the purified uranium fraction after separation of Th from the synthetic mixture agreed well. The methodology discussed here would be valuable for determining traces of ^{232}U in ^{233}U, employing the ion counting systems available in the present day TIMS instruments.

2. Experimental

2.1. Instrument

Thermal ionization mass spectrometer (Finnigan MAT 261 from Bremen, Germany) equipped with 9 Faraday cups, each cup connected to a resistor of 10^{11} Ω, was used for measurements. High purity rhenium was used as a filament material. Double filament assembly was employed for all the studies. Ion current data were obtained by static mode of multicollection using COL.5 software available with the instrument and isotopic ratio data were obtained using RED1.5 software.

2.2. Reagents

Analytical grade HNO_3 was used for preparing the solutions. Freshly prepared deionized water (18.2 MΩ cm^{-1}) from Milli Q system (Millipore) was used for dilutions. For separation of Th from U in the synthetic mixture of Th and U, U-TEVA resin 100–150 μ size (M/s. Eichrom, USA) was used.

2.3. Sample preparation

Standard solutions of Th and natural uranium with known concentrations were prepared for studying the formation of their atomic and molecular ions. The amount ratios of Th:U were in the region of 0.1–10. These mixtures were prepared keeping in view (i) Th/U amount ratios which will be encountered in the actual dissolver solution of irradiated thoria sample as well as in geological samples and (ii) the decontamination factors of Th and U during the anion exchange separation procedure in the HCl medium. The synthetic mixtures were evaporated to near dryness for homogenization and were then dissolved in 1 M HNO_3 such that 1 μL of the solution loaded onto the sample filament contained about 1 μg of U for each synthetic mixture.

A synthetic ^{233}U mixture with ^{232}U/^{233}U isotope ratio of about 2000 ppm was prepared by mixing the ^{233}U and ^{232}U solutions obtained by irradiation of ^{232}Th and ^{231}Pa, respectively. One portion of this mixture was directly taken up for TIMS analysis. The other portion of this synthetic mixture was divided into two parts and each was mixed with natural thorium nitrate solution. Thorium was added to achieve Th/U amount ratio of around 100 to simulate the irradiated thoria samples with a burn-up of 10,000 MW d/TU. The separation of U from Th was carried out using U-TEVA resin in an acid leached glass column of 5 mm inner diameter and resin column bed of 4 cm. The column was conditioned by washing with 12 mL of 4 M HNO_3.

Loading of U and Th onto the resin was done using 4 M HNO_3. Thorium was eluted using 3 mL of 9 M HCl followed by 15 mL of 5 M HCl. U was then eluted using 10 mL of 0.1 M HNO_3. The separated uranium fraction was converted into 1 M HNO_3 medium and was taken up for TIMS analysis. Chemical yield was more than 95% for both U and Th.

2.4. Sample loading for TIMS analysis

About 10 μL of the sample solutions containing 2–3 μg of actinides was loaded on the sample filament. The solution was then dried by passing a current of about 1.5 A in air and then heated in steps to 1.8 A. Subsequently, the filament was heated to red hot momentarily and the heating current was reduced to zero.

2.5. Analysis by TIMS

2.5.1. Synthetic mixtures of U and Th

During the analyses of synthetic mixtures of U and Th, the ionization filament was heated upto 5 A at 200 mA/min. Subsequently, the vaporization filament was heated upto 1 A at a heating rate of 100 mA/min. The temperature of the ionization filament was further increased slowly by monitoring the signal strength of $^{187}\mathrm{Re}^+$ and was maintained constant (170 mV) in the different mass spectrometric analyses. The temperature of the vaporization filament was then increased in steps of 100 mA. The intensities of atomic and oxide ions of U and Th were monitored as a function of the vaporization filament heating current, maintaining the temperature of the ionization filament constant. A cold finger was always

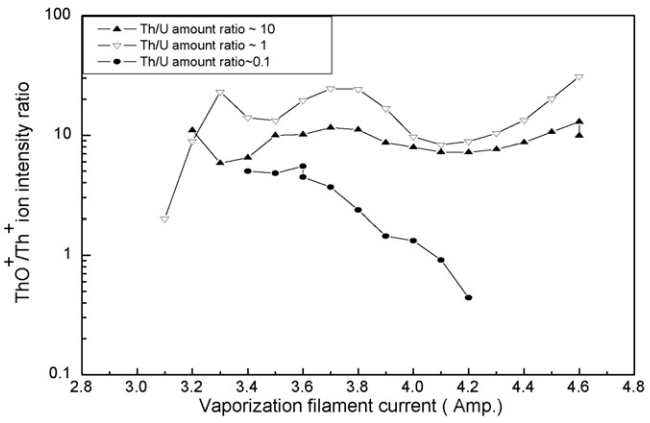

Fig. 1. Variation in ThO^+/Th^+ ion intensity ratio as a function of vaporization filament heating current (at constant ionization filament current of 6 A).

employed at the sample chamber during the TIMS analysis. Vacuum in the sample chamber was around 10^{-7} torr while that in the analyzer was around 10^{-8} torr during analysis.

2.5.2. Determination of ^{232}U

About 5–10 μL from the virgin synthetic mixture as well as the purified fraction of U after separation from thorium were loaded onto the high purity rhenium double filament assembly. The isotope ratio data were obtained by employing static mode of multicollection. Three blocks, each block consisting of 12 scans, with an integration time of 4 s for each scan, were taken. To confirm the absence of isobaric interference due to $^{232}Th^+$ at $^{232}U^+$, the ion intensity of ThO^+ at $m/q = 248$ was monitored simultaneously during the mass spectrometric analysis.

3. Results and discussion

3.1. Variation of ion intensity as a function of vaporization filament temperature

The ionization filament current was maintained at around 6 A, which is used generally for U isotopic analysis using U^+ ions. The intensities of U^+, UO^+, Th^+ and ThO^+ were monitored at m/q 238, 254, 232 and 248, respectively. The $UO_2{}^+$ ions were not observed under the presently used filament loading procedure and heating conditions.

Fig. 1 shows the variation in ThO^+/Th^+ intensity ratio observed as a function of the heating current of vaporization filament, at constant heating current (5.5–6 A) of ionization filament for different synthetic mixtures. It was observed that both Th^+ and ThO^+ start appearing at vaporization filament heating current of about 3.0 A. There is no significant change in the ThO^+/Th^+ intensity ratio with increase in the vaporization filament current. The ion current of ThO^+ was found to be 10 times more than that of Th^+ at vaporization filament heating current of about 3.5 A, inspite of low ionization energy of Th (6.307 eV) as compared to that of ThO (6.602 eV) [13–15]. This may be attributed to the combined effect of vaporization characteristics of thorium oxide from the rhenium filament and relative stabilities of the species in the vapor phase. Therefore, for TIMS analysis of Th, molecular ion ThO^+ should be preferred in comparison to Th^+. During the present analysis conditions, $ThO_2{}^+$ ions were not observed for any of the samples. This is due to the high ionization energy of ThO_2 (8.7 ± 0.2) eV [13,16]. The mixture with Th/U amount ratio of 0.1 showed a different behavior for ThO^+/Th^+ intensity ratio and this needs further investigations.

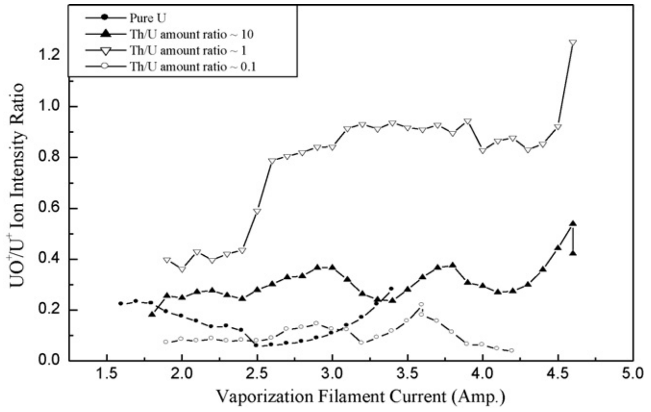

Fig. 2. Variation in UO^+/U^+ ion intensity ratio as a function of vaporization filament heating current (at constant ionization filament current of 6 A).

Fig. 2 shows the observed variation in the UO^+/U^+ intensity ratio as a function of the vaporization filament heating current, at a constant heating current (6.0 A) of ionization filament for different synthetic mixtures and for pure U. In contrast to data shown for Th in Fig. 1, the UO^+/U^+ intensity ratio is less than 1 at all the heating temperatures of vaporization filament inspite of lower ionization energy of UO (6.031 eV) as compared to that of U (6.194 eV) [17]. This may be attributed, as in case of thorium, to the combined effect of vaporization characteristics of uranium oxide from the rhenium filament and relative stabilities of the species in the vapor phase. The presence of Th on the filament leads to the stabilization of UO^+ ion as is seen in the mixtures containing Th to a significant extent. However, the intensity of U^+ remains higher than that of UO^+ at all the heating temperatures of the vaporization filament in all these mixtures, suggesting that for the TIMS analysis of U, the atomic ion U^+ should be preferred in comparison to UO^+ in samples containing U and Th. Simultaneous analysis of U and Th from the same filament using a multi-cup collector assembly with present day instruments having sufficiently large dispersion is a definite possibility in the samples containing U and Th in the amount ratio of 0.1–10, which are similar to those encountered in geological samples. It may be mentioned that $UO_2{}^+$ ions were observed during these studies, but the intensities were not significant for analytical applications.

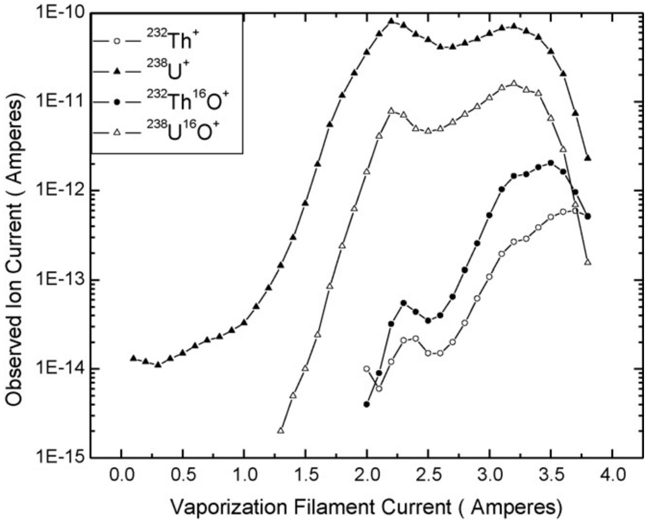

Fig. 3. Variation in ion intensities of M^+ and MO^+ as a function of vaporization filament heating current for the mixture with Th/U amount ratio of 0.1 (at constant ionization filament current of 6 A).

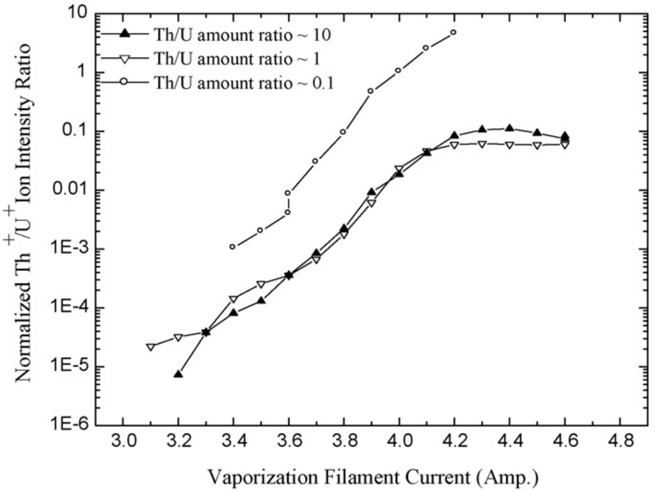

Fig. 4. Normalized Th$^+$/U$^+$ ion intensity ratio as a function of vaporization filament heating current (at constant ionization filament current of 6 A) [Normalized ion intensity ratio = Observed ion intensity ratio/(Th/U) amount ratio].

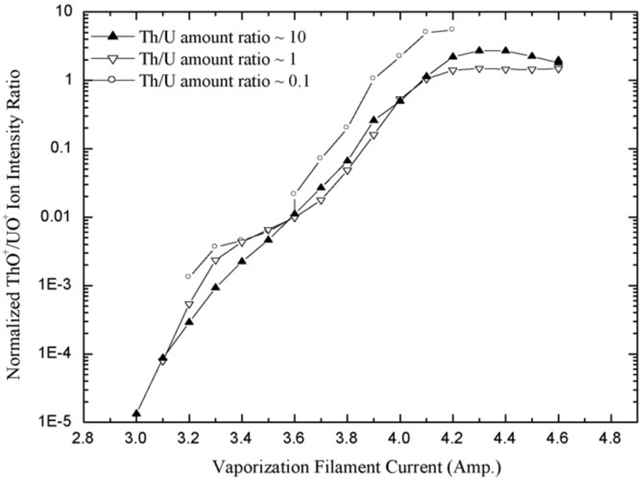

Fig. 5. Normalized ThO$^+$/UO$^+$ ion intensity ratio as a function of vaporization filament heating current (at constant ionization filament current at constant ionization filament current of 6 A) [Normalized ion intensity ratio = Observed ion intensity ratio/(Th/U) amount ratio].

Fig. 3 shows the absolute intensities of M$^+$ and MO$^+$ ions for the synthetic mixture with Th/U amount ratio of 0.1 during a typical mass spectrometric analysis. This mixture is of interest especially for nuclear technology, since Th/U amount ratio is close to that expected in the U fraction after separation from thorium, for the irradiated thorium sample with a burn-up of 10,000 MW d/TU. It is seen that the intensities of U$^+$ and ThO$^+$ are significantly higher than those of UO$^+$ and Th$^+$, respectively. Further, U$^+$ and UO$^+$ start appearing at much lower vaporization filament heating current compared to that for Th$^+$ and ThO$^+$ in the mixture. These observations suggest that the isotope ratio data of U can be obtained using U$^+$ ion at a lower vaporization filament current, without significant contribution from the Th$^+$ ion. These results are interesting to arrive at suitable filament heating conditions for the TIMS analysis of low abundant ^{232}U isotope using U$^+$ ions in the presence of isobarically interfering ^{232}Th in the irradiated thoria samples.

Fig. 4 shows the normalized ion intensity ratios of Th$^+$/U$^+$ in the different synthetic mixtures as a function of the vaporization filament heating current. It can be seen that the normalized U$^+$/Th$^+$ intensity ratios in all the mixtures are close to 100 or even higher upto vaporization filament heating current of about 3 A. This may reflect lower vapor pressure of Th as compared to that of U. Based on this observation, it can be stated that except for samples which require ^{232}U determination, the isotopic analysis of U in the presence of Th can be performed using U$^+$ as well as UO$^+$ ions at lower vaporization filament heating current. Subsequently, Th can be analyzed using ThO$^+$ ion from the same filament loading, at higher vaporization filament heating current. However, for ^{232}U determination, anion exchange separation followed by TIMS analysis of purified U fraction using U$^+$ ion is essential.

Fig. 5 shows the variation of the normalized ThO$^+$/UO$^+$ ion intensity ratio as a function of vaporization filament current. It can be seen that this ratio is less than unity till vaporization filament heating current of about 4 A. This may reflect lower ionization energy of UO (6.031 eV) as compared to that of ThO (6.602 eV). From the data displayed in Figs. 1 and 5, it can be concluded that for TIMS analysis of thorium, ThO$^+$ ions are the most preferred ions to achieve high sensitivity. Further, TIMS analysis of thorium can be performed in a mixture containing U, at a higher vaporization filament current, without any interference from U. These results are interesting for geological samples, where U as well as Th can be determined sequentially from the same filament loading.

Since in these studies, it was observed that there is a possibility for the determination of ^{232}U even in the presence of traces of Th, it was considered worthwhile to demonstrate the applicability of the present method for determining ^{232}U in presence of traces of ^{232}Th.

The virgin U synthetic mixture as well as the purified U fractions obtained after separation of thorium were analyzed by TIMS. The optimized analyses conditions of vaporization and ionization filament currents used were those obtained in this study. U isotopic ratio was obtained using U$^+$ ions at low vaporization filament current (upto 2.5 A). The results of this analysis are shown in Table 1. The data on the ^{233}U ion intensity as well as the ion intensity ratio of $m/q = 232/248$, due to ^{232}U$^+$ and (^{232}UO$^+$ + ^{232}ThO$^+$) are also included in the table. It can be seen that the ^{232}U/^{233}U isotope ratio data obtained in the virgin sample and the purified U fractions obtained from two completely independent experiments agree well with each other within 0.5%. An accuracy of 0.5% was observed in the present studies. It may be noted that though U-TEVA resin can provide nearly 100% yield for both U and Th, a decontamination factor of 10^5 for chemical separation of a mixture with an initial amount ratio of Th/U as 100 with ^{232}U as 1000 ppm, will still yield an amount of ratio of $\sim$1 for ^{232}U/^{232}Th, which can lead to isobaric interference at ^{232}U.

Table 1
Data on the determination of ^{232}U/^{233}U isotope ratio in presence of trace amounts of ^{232}Th.

Sample details	^{233}U$^+$ intensity (mV)	248/232 ion intensity ratio	^{232}U/^{233}U atom ratio	Accuracy[b]
Virgin U mixture	682.8	–	0.002175 (±0.7%)[a]	–
Purified sample—I	2284.0	1.663	0.002170 (±0.4%)	0.9977
Purified sample—II	737.8	1.169	0.002166 (±0.7%)	0.9959

[a] Specifies one standard deviation based on data obtained in three blocks.
[b] Calculated with respect to the virgin mixture.

4. Conclusions

The studies carried out on the formation of atomic and molecular ions (M^+ and MO^+) for Th and U using pure fractions of Th and U as well as their synthetic mixtures by using TIMS are the first of its kind and will be extremely useful in optimizing the vaporization filament heating currents for the TIMS analyses of Th and U in samples from nuclear technology. Since ^{229}Th and ^{230}Th used as spikes for isotope dilution-TIMS of Th are quite expensive and are available in limited amounts to a few of the international laboratories, these studies would help in optimizing the amount of spike to be added while monitoring M^+ or MO^+ ion. The results shown here would also be useful for simultaneous/sequential mass spectrometric analysis of U and Th using MO^+ or M^+ ions depending upon the Th/U amount in the unknown sample. As demonstrated, the studies are valuable to determine trace amounts of ^{232}U in ^{233}U sample by TIMS in the purified U sample obtained from irradiated Th which is useful for the effective utilization of thorium in nuclear technology.

Acknowledgement

The authors are thankful to Dr. V. Venugopal, Director, Radiochemistry and Isotope Group at BARC for his interest in these studies.

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