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Investigations on atomic and oxide ion formation of plutonium and uranium in thermal ionization mass spectrometry (TIMS) for determination of ^{238}Pu

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Abstract

Studies are reported on the atomic and oxide ion formation of Pu and U during thermal ionization mass spectrometry. Different synthetic mixtures with Pu/U amount ratios of 2–10 were used to study the vaporization and ionization characteristics under different heating currents of vaporization and ionization filaments using a double filament assembly. The different ions observed were U^+, Pu^+, UO^+, PuO^+ and two different sets of filament heating conditions were identified to maximize the production of UO^+ and Pu^+ ions. It is observed that by using interfering element correction methodology and employing suitable filament heating currents, there exists a potential of determining ^{238}Pu in Pu samples by TIMS with accurate accounting of isobaric interference from ^{238}U.

Keywords: Thermal ionization mass spectrometry; Isobaric interference; Pu/U ratio; Pu-238/Pu-239 atom ratio

1. Introduction

Thermal ionization mass spectrometry (TIMS) is a widely employed mass spectrometric technique for the determination of isotopic composition and concentration of different elements for nuclear, geo-chronological and clinical applications [1–3]. In particular, TIMS is well suited for obtaining data on the isotopic composition and concentration of uranium (U) and plutonium (Pu) required for various purposes in nuclear fuel cycle [4–7]. This is because of the high radioactivity associated with dissolver solution of irradiated fuel containing U and Pu as well as the requirement of providing the data with the best possible precision and accuracy. The former demands the handling of minimum possible amount of the sample thereby requiring an analytical technique like TIMS which has the potential of analyzing microgram to sub-microgram amounts of U and Pu. TIMS also holds the potential to provide the best possible data on isotopic composition and concentration for nuclear material accounting, etc.

The introduction of fully automated thermal ionization mass spectrometers with multi-detector system over the last two decades has enhanced the capabilities of TIMS in many aspects. These include the possibility of achieving high internal precisions (0.001% or better on isotope ratios), carrying out oligo-element analysis from the same filament loading, using internal normalization methodology to correct for the isotope fractionation during analysis, applying interfering element correction methodology to correct for the isobaric interference, etc. The availability of total evaporation and ion current integration software has nearly eliminated the ubiquitous problem of isotope fractionation which has been limiting the overall precision achievable on the isotope ratios of U and Pu. However, to exploit the full potential of the present generation thermal ionization mass spectrometers, it has become more important to understand the ion-source chemistry during thermal ionization of different elements.

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We have been using TIMS for the determination of isotopic composition and concentration of U and Pu for more than three decades [8–12]. For the first time, it was shown from our laboratory, that K-factors i.e., isotope fractionation factors for U and Pu are distinctly different for these two elements, contrary to the previous belief of using nearly same K-factors for U and Pu in view of nearly the same mass range [8]. Subsequently, studies were reported on the use of ^{239}Pu as a spike for determining the concentration of Pu using isotope dilution mass spectrometry [9,10]. Further, we reported studies on the evaporation and ionization characteristics of U and Pu in TIMS with an objective to carry out simultaneous mass spectrometric analysis of U and Pu from the same filament loading [11]. It was also shown that different methodologies can be adopted to correct for the isobaric interference of ^{238}Pu at ^{238}U during the simultaneous/sequential mass spectrometric analysis of U and Pu from the same filament loading [12]. It was also observed during these studies that using a double filament assembly and loading the sample from dilute nitric acid medium, the ion yield of Pu^+ was 5–10 times more than that of U^+. Furthermore, during these studies, the U/Pu amount ratio was maintained more than one to carry out the studies under the conditions of real dissolver solutions of U and Pu obtained after their separation and purification from Am and host of other fission products.

Determination of ^{238}Pu by TIMS has always been plagued by the ubiquitous isobaric interference from ^{238}U. Though Pu is separated and purified from bulk of U using suitable ion-exchange procedure prior to the isotopic analysis of Pu by TIMS, the purified fraction of Pu would always contain trace amounts of U. Moreover, since the atomic percentage of ^{238}Pu is small (0.1–0.5%) depending upon the burn-up of the irradiated fuel and ^{238}U is the major isotope of uranium, the contribution due to isobaric interference remains appreciable and this always creates doubt on the ^{238}Pu data obtained by TIMS. Due to this, confidence in the data obtained on ^{238}Pu by TIMS is always poor and alpha spectrometry is employed for this purpose [13]. In alpha spectrometry, $^{238}\text{Pu}/(^{239}\text{Pu} + ^{240}\text{Pu})$ alpha activity ratio along with $^{240}\text{Pu}/^{239}\text{Pu}$ isotope ratio data obtained by TIMS is used to obtain $^{238}\text{Pu}/^{239}\text{Pu}$ atom ratio.

In our laboratory, we have been working on TIMS as well alpha spectrometry for the determination of ^{238}Pu in Pu samples. During the previous studies reported by us on the evaporation and ionization characteristics of U and Pu from the same filament loading [11], it was observed that UO^+ ion intensity was quite appreciable as well as stable and no PuO^+ signal was observed under the filament heating conditions employed. This observation motivated us to carry out the present studies on the ion source chemistry of U and Pu with a possibility to identify the optimum conditions for the sequential determination of U and Pu isotope ratios using UO^+ and Pu^+ ions from the same filament loading. During the present work, the studies on ion source chemistry of Pu and U were, therefore, undertaken by using synthetic mixtures of Pu and U with Pu/U amount ratios as 2, 5 and 10. These amount ratios were used keeping in mind the need to add externally a monitor isotope of U (say ^{233}U) which could possibly be used to account for the isobaric interference of ^{238}U at ^{238}Pu using interfering element correction methodology. The experiments were performed using a double filament assembly and the intensities of different ions of U and Pu were monitored at different heating currents of vaporization and ionization filaments.

It is worth mentioning that there are many other mass spectrometric techniques like resonance ionisation mass spectrometry (RIMS) [14], accelerator-based mass spectrometry (AMS) [15] and inductively coupled plasma mass spectrometry (ICPMS) [16] which can be employed for the determination of Pu isotopes. Among these, RIMS and AMS offer ultra-high sensitivity and have been used for the determination of Pu isotopes in environmental and biological samples containing 10^7 to 10^8 atoms of Pu. Recently, band-pass reaction cell has been employed in ICPMS for chemical resolution of Pu^+ and U^+ with an objective to determine rapidly Pu isotope ratios on a large number of environmental and biological samples following a nuclear event or accident [16]. However, TIMS still remains a gold standard for the determination of Pu isotopes in nuclear fuel cycle and is a well-established technique for characterisation of Pu and U reference materials, which demand high precision and accuracy.

2. Experimental

2.1. Sample preparation

Three different synthetic mixtures of U and Pu were prepared with Pu/U amount ratios as 2, 5 and 10. For preparing these synthetic mixtures, Pu sample containing 99 at.% of ^{239}Pu and U sample containing about 93 at.% of ^{235}U was used. Pu solution was purified from ^{241}Am and traces of U using Dowex 1X8, 200–400 mesh, anion exchange resin in HNO_3 medium. The concentrations of U and Pu in the two solutions were pre-determined by isotope dilution thermal ionization mass spectrometry (ID-TIMS).

2.2. Instrumentation

A Finnigan MAT-261 thermal ionization mass spectrometer equipped with nine Faraday cup detectors was used. A double filament assembly made out of high purity Re filaments was used. About 5–10 μL of the U/Pu synthetic mixture solution in 1 M HNO_3 containing about 5 μg of Pu was loaded on the sample filament. The solution was 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, and then immediately, the heating current was reduced to zero.

2.3. Measurement procedure

During the mass spectrometric analysis of synthetic mixtures, the temperature of the ionization filament was increased slowly by monitoring signal strength of $^{187}Re^+$ and was maintained constant in different mass spectrometric analyses. The temperature of the vaporization filament was increased in steps. Only a single Faraday cup detector was used in the present studies and the intensities of different ions of U and Pu (U^+, Pu^+, UO^+, PuO^+) were monitored at *m*/*z* values of 235, 239, 251 and 255, respectively. The intensities of different ions were monitored by varying the heating current of one of the filaments and maintaining the other filament at constant temperature.

For the determination of ^{238}Pu in NIST-SRM-947 and in an unknown Pu sample, ^{235}U (>90 at.%) was added as a monitor isotope to the purified Pu solution. The amount of U added was such as to obtain Pu/U amount ratio of about 5. The mass spectrometric analysis of the samples was carried out using double Re filament assembly. The atom ratio of $^{235}U/^{238}U$ was first obtained, in each sample, by using UO^+ ion and this ratio was given as an input for data reduction by interfering element correction (IEC) approach while determining atom ratios of Pu isotopes using Pu^+ ion.

3. Results and discussion

Fig. 1 shows the intensities of different ions observed during a typical mass spectrometric analysis of one of the synthetic mixtures with Pu/U amount ratio of 5, at the ionization filament heating current of 6 A, generally used during the TIMS analysis of U or Pu. Only the U^+, Pu^+, UO^+, PuO^+ ions were observed and are shown in the figure. The $UO_2{}^+$ ion was not observed at the ionization filament heating current of 6 A and vaporization filament heating current up to 2.4 A. It is seen that both UO^+ as well as U^+ ions start appearing at a lower vaporization filament heating current as compared to that for PuO^+ ion. This observation also supports the results reported previously [11] in synthetic mixtures with Pu/U ratios less than 1, where it was postulated that the presence of plutonium oxides on the filament enhances the formation of UO^+. Further, as expected, the intensities of all the ions increase with increase in temperature of the vaporization filament. The results presented in this figure indicate the possibility of obtaining atom ratio data on U isotopes using UO^+ ion with no contribution from PuO^+ ion at lower vaporization filament heating current (1.4–1.8 A). It may be noted that a similar behaviour was observed in the other two synthetic mixtures with Pu/U amount ratios of 2 and 10.

The effect of varying the heating temperature of the vaporization filament, at a constant temperature of the ionization filament, on the $^{235}UO^+/^{239}Pu^+$ intensity ratio in the two synthetic mixtures with Pu/U amount ratios of 5 and 10, is displayed in Fig. 2. The observed intensities of the ions have been plotted after normalization with respect to the Pu/U amount ratio in each of the mixtures and also taking into consideration the atomic percentage abundances of ^{239}Pu and ^{235}U. It is seen that $^{235}UO^+/^{239}Pu^+$ intensity ratio decreases with increase in the vaporization filament heating current in each mixture. Further, it is clear that there is significant difference in the $^{235}UO^+/^{239}Pu^+$ intensity ratio in the two synthetic mixtures with Pu/U amount ratios as 5 and 10. The $^{235}UO^+/^{239}Pu^+$ intensity ratio curve for Pu/U amount ratio of 2 also showed the similar shape, overlapping closely with that of synthetic mixture with Pu/U amount ratio of 5 and hence is not included in this figure for the sake of clarity. The $^{235}UO^+/^{239}Pu^+$ intensity ratio is quite low at different heating temperatures used (1–2.5 A) in the synthetic mixture with Pu/U amount ratio of 10 mainly due to the low intensity of UO^+ ion in view of the small amount of U present in the synthetic mixture.

It may be mentioned that though UO^+ signal starts appearing at lower temperature of the vaporization filament as compared to the appearance of Pu^+ signal (as seen from Fig. 1), the increase in the Pu^+ intensity is much larger than that of UO^+ intensity with increasing vaporization filament heating current. This increased vaporization of Pu species leading to

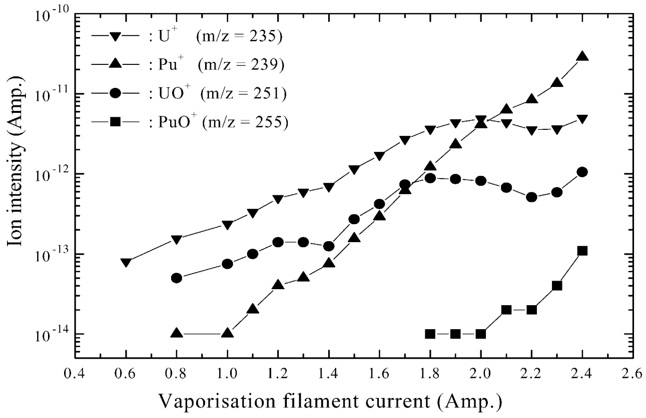

Fig. 1. Variation of U^+, Pu^+, UO^+ and PuO^+ ion intensities as a function of vaporization filament current (at constant ionization filament current).

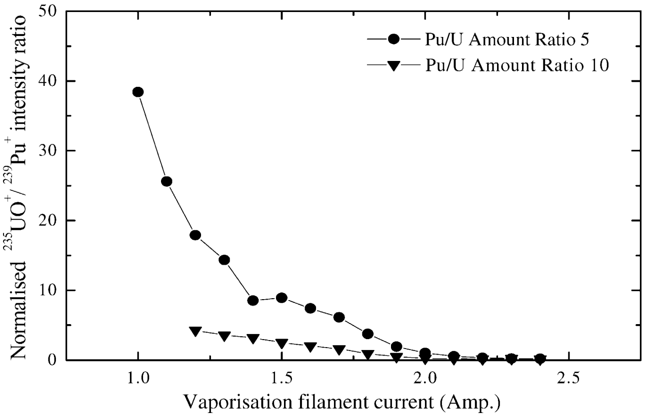

Fig. 2. Normalized $^{235}UO^+/^{239}Pu^+$ ion intensity ratio as a function of vaporization filament current (at constant ionization filament current).

an increase in the intensity of Pu^+ ions is responsible for a decrease in $^{235}UO^+/^{239}Pu^+$ intensity ratio with increase in the vaporization filament heating current, shown in Fig. 2. These data suggest that to obtain good intensity of UO^+, without losing much of Pu from the sample (vaporization) filament during this stage of data acquisition for U isotope ratios using UO^+ ion, the sample with Pu/U amount ratio of 2–5 is preferable. Since the ion current due to UO^+ is quite small in the synthetic mixture with Pu/U amount ratio of 10, this will lead to large errors in the U atom ratio data to be used for isobaric interference correction in the interfering element correction methodology. This in turn will introduce errors in the corrected $^{238}Pu/^{239}Pu$ atom ratios. As shown in Fig. 1, PuO^+ ion formation starts at vaporization filament heating current of 2 A or more and, therefore, synthetic mixture with high value of Pu/U amount ratio (say 10) is not desirable since PuO^+, if present, would lead to erroneous data for $^{235}U/^{238}U$ atom ratio using UO^+ ion due to isobaric interference from $^{238}PuO^+$. These data suggest that mixtures with Pu/U amount ratios of 2–5 would be preferable to maximize the intensity of UO^+, at vaporization filament heating current of 1.4–1.8 A.

Since the process of thermal ionization is governed by Saha–Langmuir equation which gives an exponential dependence of the ion yield on ionization potential of the element, it was, therefore, of interest to monitor the changes in the intensities of U^+ and Pu^+ ions as a function of heating temperature of the ionization filament, at a constant temperature of the vaporization filament. Fig. 3 depicts the intensity ratios of $^{239}Pu^+/^{235}U^+$, in the three different synthetic mixtures, normalized with respect to $^{239}Pu/^{235}U$ amount ratio, as a function of decrease in the heating current of the ionization filament from 6.0 to 4.6 A while maintaining the vaporization filament at a heating current of 2.4 A. It is seen that in each synthetic mixture, the $^{239}Pu^+/^{235}U^+$ intensity ratio increases with decrease in heating current of the ionization filament. This is consistent with the fact that the ionization potential of Pu is lower than that of U and thus lowering the temperature of the ionization filament has more pronounced effect (decrease in the ion yield) on U^+ which gives rise to an increase in the $^{239}Pu^+/^{235}U^+$ intensity ratio. Further, it is observed that mixtures with Pu/U amount ratios of 2 and 5 show nearly identical behaviour in the $^{239}Pu^+/^{235}U^+$ intensity ratios variations. Further lowering of the ionization filament heating current though indicates further increase in the $^{239}Pu^+/^{235}U^+$ intensity ratios, however, the ion intensity of Pu^+ also decreases appreciably which would increase the random error in $(^{238}Pu + ^{238}U)/^{239}Pu$ atom ratio data and hence lower the accuracy of ^{238}Pu determination by TIMS. These data suggest that sufficient ion yield of Pu^+ can be obtained by lowering the heating current of the ionization filament from 6 A to about 5 A, with minimum contribution from isobarically interfering ^{238}U isotope at ^{238}Pu.

It was of interest to study the effect on the $^{239}Pu^+/^{235}U^+$ ion intensity ratio by increasing the heating current of the vaporization filament, by maintaining a low and constant heating current (5 A) of the ionization filament. It was considered worthwhile to see if further increase in the heating current of vaporization filament from 2.4 A onwards would lead to an increase in the intensity of Pu^+ ion, with an objective to reduce the random error in data for Pu atom ratios. Fig. 4 gives the $^{239}Pu^+/^{235}U^+$ ion intensity ratio, normalized with respect to $^{239}Pu/^{235}U$ amount ratio, as a function of increase in the heating current of vaporization filament, in the three synthetic mixtures, at a constant heating temperature of the ionization filament. It is noted that in all the mixtures, the $^{239}Pu^+/^{235}U^+$ intensity ratio increases with increase in heating current of the vaporization filament which was attributed to an increase in the ion intensity of Pu^+. Further, the normalized $^{239}Pu^+/^{235}U^+$ intensity ratio decreases with increase in the Pu/U amount ratio, under the identical heating currents of the two filaments. Here again, the synthetic mixture with Pu/U amount ratio of 10 gives most unfavourable $^{239}Pu^+/^{235}U^+$ intensity ratio. These data along with those of Fig. 3 show that synthetic mixtures with Pu/U amount ratio of 2–5 can be employed for determining the atom ratios of Pu isotopes using Pu^+ ion, with minimum isobaric interference of $^{238}U^+$ ion at $^{238}Pu^+$ ion. The data on absolute intensities showed that it is possible to get sufficient and reasonably stable signal intensity

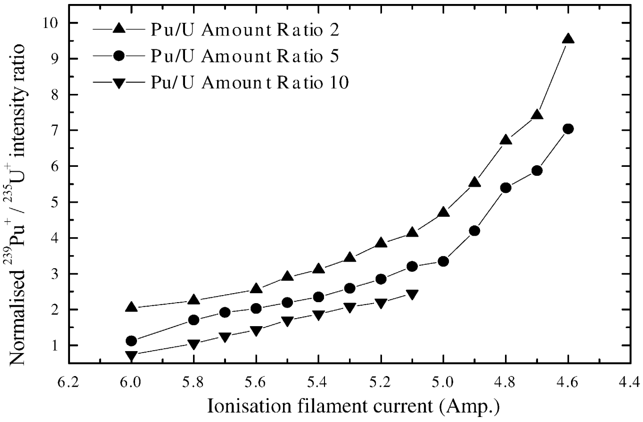

Fig. 3. Normalized $^{239}Pu^+/^{235}U^+$ ion intensity ratio as a function of ionization filament current (at constant vaporization filament current).

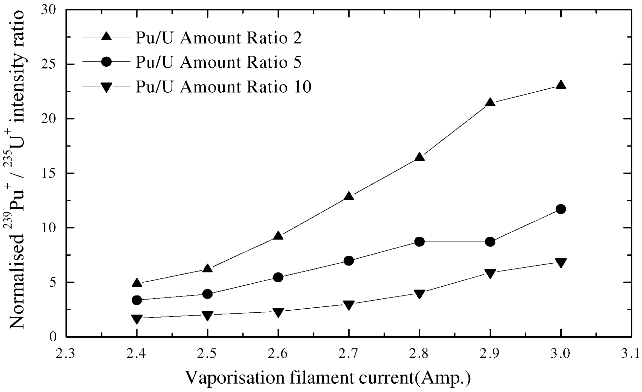

Fig. 4. Normalized $^{239}Pu^+/^{235}U^+$ ion intensity ratio as a function of vaporization filament current (at constant ionization filament current).

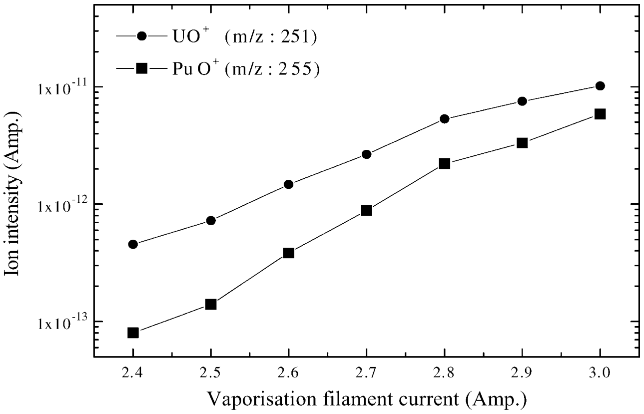

Fig. 5. Variation of UO^+ and PuO^+ ion intensities as a function of vaporization filament current (at constant ionization filament current).

of Pu^+ at ionization filament heating current of about 5 A and vaporization filament heating current of 2.6–3 A. Under these heating conditions, the intensity of U^+ ion is quite small and the interfering element correction methodology would be able to correct for small isobaric interference at these heating temperatures of ionization and vaporization filaments.

The data obtained and shown above on different synthetic mixtures of Pu and U and under different heating temperatures of ionization and vaporization filaments indicated the possibility of determining U atom ratios by monitoring UO^+ ion at filament heating conditions of 6 A for ionization filament and 1.6–2.2 A for vaporization filament (Experiment I). Subsequently, Pu atom ratios can be determined by monitoring Pu^+ ion at filament heating currents of about 5 A for ionization filament and 2.8–3 A for vaporization filament (Experiment II). It was considered worthwhile investigating the possibility of determining U atom ratios using UO^+ ion at heating temperatures used in Experiment II, corresponding to that used for determining Pu atom ratios, with a view to eliminating the data acquisition for Experiment I. Under these heating conditions, as shown in Fig. 5, the intensity of UO^+ was low but significant enough to obtain U atom ratios. However, it was noted that PuO^+ ion starts appearing under these conditions of filament heating and its intensity was observed to increase with increase in temperature of the vaporization filament. These observations ruled out the possibility of obtaining U atom ratios using UO^+ ion under heating conditions used for obtaining Pu atom ratios using Pu^+ ion (Experiment II) on a routine basis, since the interference from $^{238}PuO^+$ at m/z 254 corresponding to $^{238}UO^+$ would depend upon the amount of Pu loaded on the filament as well as the atomic percentage of ^{238}Pu in the unknown sample. This observation of showing the formation of PuO^+ is also important in total evaporation and ion current integration methodology used for determining atom ratios of different Pu isotopes using Pu^+ ion. This is because of the fact that the methodology of total evaporation and ion current integration assumes that the ions of only one type are produced during thermal evaporation and ionization. Additional investigations are needed to study the extent of formation of PuO^+ ions, under different loading conditions, as these would provide a valuable insight into the ion source chemistry of Pu in thermal ionization mass spectrometry.

The inferences drawn from the above studies show that using a suitable monitor isotope for U (say ^{233}U or ^{235}U), it may be possible to account for the isobaric interference of ^{238}U at ^{238}Pu by employing interfering element correction (IEC) methodology. This IEC methodology is available these days as a standard software provided by commercial manufacturers and suppliers of TIMS instruments. The methodology would involve the addition of a monitor isotope externally to the purified fraction of Pu being taken for isotopic analysis for obtaining data on ^{238}Pu during the same mass spectrometric analysis. The results obtained from studies reported in the present work suggest that amount of monitor isotope should be such that Pu/U amount ratio of 2–5 is obtained in the sample. The atom ratio of U ($^{233}U/^{238}U$ or $^{235}U/^{238}U$) can be obtained first by using UO^+ (Experiment I). The data of U atom ratio obtained can be given as an input for data reduction by IEC approach, while determining atom ratios of different isotopes of Pu including that of ^{238}Pu using Pu^+ (Experiment II), monitoring the signal of monitor isotope of U during data acquisition.

The above methodology was tested for the determination of $^{238}Pu/^{239}Pu$ atom ratio in NIST SRM-947 Pu isotopic reference material, containing about 0.25 at.% of ^{238}Pu and about 600 ppm of uranium [12] as well as in an unknown Pu sample. The $^{238}Pu/^{239}Pu$ atom ratio was also determined by conventionally used approach of alpha spectrometry in these samples. Table 1 gives the results of these determinations. The values obtained on $^{238}Pu/^{239}Pu$ atom ratio by

Table 1
Results on ^{238}Pu determination by TIMS

Sample	Filament loading	$^{238}Pu/^{239}Pu$ atom ratio by	
		TIMS	Alpha spectrometry[a]
NIST-SRM-947	1	0.003044 (0.32%) [3][b]	0.003043 (0.14%)
	2	0.003039 (0.43%) [3]	
EN-3-Pu	1	0.003026 (0.21%) [4]	0.003032 (0.15%)
	2	0.003029 (0.33%) [3]	

[a] Value obtained from triplicate alpha spectra recording from each of the five electrodeposited sources, using $^{240}Pu/^{239}Pu$ atom ratio determined by TIMS and half-life values of 87.74, 24110 and 6553 years, respectively, for ^{238}Pu, ^{239}Pu and ^{240}Pu.

[b] Denotes the number of blocks in the mass spectrometric analysis.

TIMS are in good agreement with those obtained by alpha spectrometry [13]. The value in NIST-SRM-947 obtained by TIMS is well within the statistical uncertainty quoted in the certificate. This work highlights the need to study the ion source chemistry of different actinides using TIMS to exploit the full potential of present generation fully automated thermal ionization mass spectrometers. Studies are in progress to determine ^{238}Pu/^{239}Pu atom ratios in different Pu samples by TIMS to evaluate the day today applications of filament heating conditions optimized in the present work. It is also planned to carry out experiments to evaluate the precision and accuracy in determining ^{238}Pu/^{239}Pu atom ratios at different atomic percentage abundances of ^{238}Pu by accounting quantitatively the isobaric interference of ^{238}U at ^{238}Pu using interfering element correction methodology.

4. Conclusions

Investigations carried out on atomic and oxide ion formation of U and Pu with synthetic mixtures containing Pu/U amount ratios of 2–10 show that it is possible to identify the optimum heating conditions of vaporization and ionization filaments of a double filament assembly in TIMS for the determination of ^{238}Pu/^{239}Pu atom ratio. Results reported on NIST-SRM-947 Pu and an unknown Pu sample demonstrate the applicability of the methodology presented in this paper for determination of ^{238}Pu by TIMS.

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