Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

International Journal of Mass Spectrometry 241 (2005) 83–88

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

A novel approach for the determination of ^{238}Pu by thermal ionization mass spectrometry (TIMS) using interfering element correction methodology

S.K. Aggarwal*, D. Alamelu

Mass Spectrometry Section, Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

Received 24 September 2004; accepted 20 October 2004
Available online 7 December 2004

Abstract

A novel approach using interfering element correction (IEC) methodology is presented for the determination of ^{238}Pu in Pu by thermal ionization mass spectrometry (TIMS). The IEC methodology is based on the use of ^{235}U as a monitor isotope to correct for the ubiquitous isobaric interference of ^{238}U at ^{238}Pu. The procedure involves the addition of enriched ^{235}U (>90 atom%) externally to the Pu sample. The ^{238}U/^{235}U atom ratio in the sample is determined experimentally by monitoring the intensities of ions with m/z 254 and 251, corresponding to ^{238}UO$^+$ and ^{235}UO$^+$, respectively. Subsequently, ^{238}Pu/^{239}Pu atom ratio is determined by using Pu$^+$ ion at different heating temperatures of vaporization and ionization filaments. The methodology is evaluated using NIST-SRM 947 isotopic reference material with ^{238}Pu abundance close to 0.25 atom% and a synthetically prepared sample containing about 2 atom% of ^{238}Pu. The approach is simple and holds promise for the characterization of new reference materials of ^{238}Pu using TIMS.

Keywords: Thermal ionization mass spectrometry; ^{238}Pu; Isobaric interference; Atomic and molecular ion

1. Introduction

Thermal ionisation mass spectrometry (TIMS) is a widely used mass spectrometric technique for the determination of isotopic composition of plutonium (Pu) [1,2]. However, ^{238}Pu is generally not determined by TIMS due to the ubiquitous isobaric interference of ^{238}U. Moreover, the main route of formation of ^{238}Pu in a reactor is by neutron induced reaction on ^{237}Np which is produced by β^- decay of ^{237}U, formed in situ, by two successive (n, γ) reactions on ^{235}U and (n, 2n) reaction on ^{238}U [3]. Prior to the determination of isotopic composition of Pu by TIMS, the Pu sample is separated and purified from ^{241}Am and bulk of uranium present in the dissolver solution of irradiated fuel. The U/Pu amount ratio in the dissolver solution of irradiated fuel can range from 1000 to 100, depending upon the burn-up of the fuel. However, inspite of chemical separation and purification of Pu from bulk of U, the purified Pu is always associated with small amounts (0.01–0.1%) of U which gives rise to isobaric interference from ^{238}U at ^{238}Pu. The two isobars ^{238}U and ^{238}Pu cannot be resolved in TIMS due to the limited mass resolution of about 500 in single focusing magnetic sector TIMS instruments. Therefore, the data obtained on ^{238}Pu determination by TIMS is always positively biased, unless suitable correction methodology is applied.

Accurate data on ^{238}Pu/^{239}Pu atom ratio is important for various applications in nuclear science and technology [4–7]. These include the development of isotope correlations, refinement of computer codes in reactor physics calculations to calculate the build-up of different Pu isotopes, the use of ^{238}Pu as a tracer (spike) in isotope dilution alpha spectrometry and the possibility of employing ^{238}Pu as a tracer (spike) in isotope dilution thermal ionization mass spectrometry

---

* Corresponding author. Tel.: +91 22 25593740; fax: +91 22 25505151.
E-mail address: skaggr@magnum.barc.ernet.in (S.K. Aggarwal).

1387-3806/$ – see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.ijms.2004.10.016

(ID-TIMS), etc. The ^{238}Pu/^{239}Pu atom ratio is generally calculated using data on ^{238}Pu/(^{239}Pu + ^{240}Pu) alpha activity ratio determined using alpha spectrometry on purified Pu sample and ^{240}Pu/^{239}Pu atom ratio determined by TIMS. Alpha spectrometry has problems [8] of tail contribution at low energy peak of (^{239}Pu + ^{240}Pu) at 5.16 MeV, due to energy degradation of high energy peak of ^{238}Pu at 5.50 MeV. This tail contribution depends upon many parameters including the quality of alpha source and the activity ratio of high energy ^{238}Pu peak to that of low energy (^{239}Pu + ^{240}Pu) peak. The tail contribution can be accounted for by using suitable algorithms which are empirical as these are based on certain assumptions on the nature of tail contribution. Therefore, the uncertainty in tail contribution correction is one of the major sources of errors in ^{238}Pu determination by alpha spectrometry, in addition to the usual random error due to counting statistics. Thus, this technique has limitations for the charcterisation of reference materials for ^{238}Pu. Hence, it was of interest to develop a mass spectrometric method based on independent physico-chemical principle for the precise and accurate determination of ^{238}Pu/^{239}Pu atom ratio.

The availability of fully automated thermal ionization mass spectrometers with multi-detector system and sophisticated software procedures, over the last two decades, has enhanced the capabilities of TIMS from many aspects. These include the possibility of determining isobarically interfered isotopes by applying interfering element correction (IEC) methodology to account for the isobaric interference in each scan during data acquisition. This IEC methodology can only be used if the evaporation and ionization characteristics of the two elements are distinctly different. Previously, we have studied the ion source chemistry of U and Pu using synthetic mixtures with Pu/U amount ratios of 2, 5 and 10 using a double filament assembly in TIMS, with an objective to optimize the filament heating conditions for the production of UO$^+$ and Pu$^+$ ions at two different sets of filament heating conditions [9]. These studies prompted us to investigate the possibility of first determining ^{238}U/^{235}U atom ratio in the sample by monitoring the intensities of ions at m/z 254 and 251, corresponding to ^{238}UO$^+$and ^{235}UO$^+$, respectively, at filament temperatures where PuO$^+$ is not formed. This is followed by recording the intensity of ^{235}U as a monitor isotope in each scan during acquisition of data on Pu isotopes and giving the experimentally determined ^{238}U/^{235}U atom ratio as an input in IEC methodology, to correct for the contribution of ^{238}U at the intensity of peak at m/z 238, for the determination of ^{238}Pu/^{239}Pu atom ratio in the sample using Pu$^+$ ion.

The approach is based on the external addition of enriched ^{235}U (>90 atom%) to the unknown purified Pu sample. The studies were carried out using NIST-SRM-947 Pu isotopic reference material with ^{238}Pu abundance close to 0.25 atom% and a synthetically prepared sample containing about 2 atom% of ^{238}Pu. Efforts were also made to determine the isotope fractionation factor (i.e., K-factor) under the filament heating conditions used for ^{238}Pu determination by TIMS. The values obtained on ^{238}Pu/^{239}Pu atom ratios in the two Pu samples were compared with the data quoted by NIST in the certificate and those obtained using alpha spectrometry on electrodeposited sources. This paper gives a detailed discussion on this novel approach and presents the results obtained for validation of the IEC methodology for the determination of ^{238}Pu in Pu samples by TIMS.

2. Experimental

2.1. Sample preparation

Two different Pu samples viz. (i) NIST-SRM 947 and (ii) a synthetic mixture prepared by mixing solutions of enriched ^{238}Pu and ^{239}Pu, were used to demonstrate the applicability of the approach and for validation of the TIMS methodology. The NIST-SRM-947 Pu sample was purified from ^{241}Am using anion-exchange separation procedure in HNO$_3$ medium [6]. Approximately known amounts of the isotopic reference material of U, NIST SRM-930, containing about 93 atom% of ^{235}U were added to purified NIST-SRM-947 Pu sample and synthetic mixture prior to carrying out TIMS analysis. The amount of NIST-SRM-930 U added to the Pu samples was such as to obtain a Pu/U amount ratio of about 5 in the mixture.

2.2. Instrument

A Finnigan MAT-261 thermal ionization mass spectrometer equipped with 9 Faraday cup detectors, each of them coupled to a 10^{11} Ω resistor, was used for TIMS analysis. A double rhenium filament assembly made out of high purity Re was used. Five to ten microlitres of the Pu solution in 1 M HNO$_3$ containing about 3 μg of Pu was loaded on the sample filament and was dried by passing a current of about 1.5 A in air. After drying the solution, the filament was further heated slowly to 1.8 A and was then taken momentarily to red hot and then immediately, the heating current was reduced to zero.

2.3. Mass spectrometric analysis procedure

The mass spectrometric analysis for determination of ^{238}U/^{235}U atom ratio using UO$^+$ ion was carried out first (Experiment I) at ionization filament heating current of about 6 A and vaporization filament heating current of 1.6–2.0 A. The heating current of ionization filament was maintained constant, in different mass spectrometric analyses, by observing nearly the same signal strength of ^{187}Re$^+$ ion. The ions with m/z values of 251 and 254 were collected on FAR 5 and FAR 3, respectively with the baseline taken at m/z value of 246.5. Data were acquired in static mode of multicollection using COL.5 available in the software. Run summary of data on (m/z 254)/(m/z 251) intensity ratio determined in two blocks, each block consisting of 10 scans, was given as an input during the analysis of Pu from the same filament loading. During the analysis of Pu as Pu^+ ion (Experiment II), the $^{235}U^+$ ion intensity was monitored to account for the isobaric interference of ^{238}U at *m*/*z* 238 signal. For this experiment, the heating temperatures of the ionization and vaporization filaments were about 5A (∼2000 °C) and 2.8–3 A (∼1300 °C), respectively. Data were again acquired in static mode of multi-collection using FAR 8, FAR 6, FAR 5 and FAR 4 for *m*/*z* values of 235, 238, 239 and 240, respectively and the background was measured at *m*/*z* value of 230.5. It may be mentioned that no change in the Faraday cup positions was required for data acquisition using either UO^+ ion (Experiment I) or Pu^+ ion (Experiment II). Two different experiments were defined and only change in the experiment number in the software was sufficient to perform the TIMS analysis. All the mass spectrometric analyses were completed within a priod of 2 weeks.

3. Results and discussion

It is worthwhile discussing the choice of a suitable isotope of U to be used as a monitor isotope in the interfering element correction methodology and also the optimum amount of this U isotope to be added to the purified Pu sample.

3.1. Selection of monitor isotope of uranium

The selection of U isotope added externally to purified Pu fraction is one of the important parameters of the present approach. In principle, one could use any enriched isotope of U different from ^{238}U which causes isobaric interference at ^{238}Pu. These include the two easily available isotopes viz. ^{233}U and ^{235}U to most of the laboratories. However, a number of other criteria were also kept in mind before selecting the monitor isotope of U. For example, the monitor isotope of U should be available in enriched form (>90 atom%) and it should not increase the handling problem because of radioactivity associated with it as well as with other isotopes present in minor amounts. From these considerations, the selection of ^{233}U was ruled out since it has a half-life of 1.6×10^5 years and also has 50–1000 ppm of ^{232}U associated with it. The latter has alpha decay half-life of about 70 years and its decay products also increase the radioactivity associated with it. It is not desirable to increase the level of radioactivity in the ion source of TIMS from the point of view of any maintenance and cleaning of the ion source at a later date. Another important consideration was that, if possible, there should not be any change in the Faraday cup position while switching over from the acquisition experiment of uranium isotopes to that for plutonium isotopes. This would facilitate the fast acquisition of data without unnecessarily increasing the time required to adjust the Faraday cup positions. Based on these considerations, ^{235}U was found to be a suitable isotope to be used as a monitor isotope and was employed in the present work.

We used NIST-SRM-930 isotopic reference material of U containing about 93 atom% of ^{235}U. This was mainly due to the fact that this material was available with us and also has the additional feature of certified $^{235}U/^{238}U$ atom ratio. It may be added that it is neither necessary to use the isotopic reference material nor it is mandatory in the present methodology to have a prior information on $^{235}U/^{238}U$ atom ratio of the enriched ^{235}U used as a monitor isotope. Since the $^{235}U/^{238}U$ atom ratio is determined during each filament loading, a prior information of $^{235}U/^{238}U$ atom ratio in the enriched ^{235}U facilitates the analyst to get an idea about the extent of U present in the sample loaded on the filament. The use of 93 atom% enriched ^{235}U was also considered optimum from the point of view of getting reasonable intensity of the two uranium isotopes which would reduce the error on the experimentally obtained $^{235}U/^{238}U$ atom ratio, to be given as an input in IEC methodology for data reduction during Pu isotope ratio.

3.2. Optimization of Pu/U amount ratio in Pu sample

The amount of U to be added to the purified Pu sample was also optimized. This is because the addition of large amount of uranium would not only increase the contribution of ^{238}U at ^{238}Pu peak but would also affect the yield of ion production of Pu^+ ions during TIMS analysis. On the contrary, the additional of small amounts of uranium would not give sufficient signal intensity of UO^+ to obtain precise $^{235}U/^{238}U$ atom ratio. In fact, during the initial stages of this work, it was thought that the addition of large amounts of U (about 10 times that of Pu present in the sample) followed by ion exchange removal of most of the uranium may appear promising to account for small amounts of U originally present in the Pu sample. But it was not pursued further considering the fact that the purified Pu would contain relatively small amounts of U and this would not give precise data on $^{235}U/^{238}U$ atom ratio. In addition, it was considered worthwhile not to increase the experimental effort of separation and purification since this can also lead to loss of Pu during the ion exchange separation procedure, due to well known tailing effects observed during elution of Pu in anion exchange separation procedure [10].

Based on the experiments carried out for studying the ion source chemistry of U and Pu, using synthetic mixtures of U and Pu, it was observed that Pu/U amount ratio of about 5 is optimum [9]. This amount ratio does not affect the yield of Pu^+ ions and at the same time, one gets sufficient signal intensity of both the isotopes of U using UO^+ ion. It may be noted that the amount of U present in the purified Pu fraction need not be known, since the decontamination factors of U and Pu in the anion-exchange separation and purification procedure used in the present work are well established. Considering an initial U/Pu amount ratio of 100–200 in the dissolver solution of irradiated fuel, and decontamination factor of 10^4 for Pu w.r.t. U, the U/Pu amount ratio in the purified Pu will be 0.01–0.02 [10]. Thus the presence of 1–2% of uranium in

Table 1a
Data on the $^{238}UO^+/^{235}UO^+$ ratio during mass spectrometric analysis of NIST-SRM 947 using Experiment I

Block no.	$^{235}UO^+$ intensity (mV)	$^{238}UO^+/^{235}UO^+$ ratio[b]
1	216	0.057785 (0.16%)[a]
2	143	0.057924 (0.16%)
Run summary		0.057855 (0.17%)

[a] Denotes standard deviation obtained on the mean value from a block consisting of 10 scans.

[b] Certified value of $^{238}U/^{235}U$ atom ratio in NIST-SRM-930 = 0.057641 ± (0.1%).

the purified Pu fraction will not significantly alter the amount of enriched U to be added for determination of ^{238}Pu by the present methodology using TIMS.

3.3. Results of TIMS analysis of NIST-SRM 947

Tables 1a and 1b present typical data obtained during TIMS analysis of one of the filament loadings of NIST-SRM-947 Pu mixed with NIST-SRM-930 U with Pu/U amount ratio of about 5. Table 1a gives the data obtained in Experiment I for the determination of $^{235}U/^{238}U$ atom ratio using UO^+ ion. This Table also includes the signal intensity of major isotope, i.e., of $^{235}UO^+$. The $^{238}U/^{235}U$ atom ratio determined is higher compared to the certified $^{238}U/^{235}U$ atom ratio in NIST-SRM 930 due to small amounts of U present in SRM-947 Pu sample [11]. Table 1b gives the signal intensities of $^{235}U^+$ and $^{239}Pu^+$ isotopes (in mV) in different blocks and the data on $^{238}Pu/^{239}Pu$ atom ratios obtained during Experiment II. The intensities given in Tables 1a and 1b correspond to the signals of the various peaks observed during first scan in each block. It is seen that intensities of $^{235}U^+$ and $^{239}Pu^+$ signals are fairly constant over the acquisition period of 10 blocks. For data reduction in Experiment 2, $^{238}U/^{235}U$ atom ratio from Experiment 1 was given as an input for IEC methodology to obtain the corrected intensity of ^{238}Pu, in each scan, after accounting for the isobaric interference of ^{238}U. It is seen that mean $^{238}Pu/^{239}Pu$ atom ratios obtained during each of the 10 blocks are in good agreement with one another and the run summary of 10 blocks agrees well with the value of 0.003022 ± (2%) quoted by NIST, after decay correction.

Table 1b
Data on the determination of $^{238}Pu^+/^{239}Pu^+$ ratio in NIST-SRM 947 using Experiment II

Block no.	$^{235}U^+$ intensity (mV)	$^{239}Pu^+$ intensity (mV)	$^{238}Pu^+/^{239}Pu^+$ ratio
1	2.77	1545	0.0030389 (0.17%)[a]
2	3.05	1653	0.0030427 (0.31%)
3	3.31	1737	0.0030501 (0.33%)
4	3.61	1787	0.0030435 (0.22%)
5	4.25	1785	0.0030426 (0.22%)
6	4.18	1784	0.0030395 (0.24%)
7	4.34	1780	0.0030362 (0.32%)
8	4.14	1830	0.0030356 (0.40%)
9	3.69	1687	0.0030364 (0.25%)
10	2.89	1601	0.0030444 (0.42%)
Run summary			0.0030410 (0.32%)[b]

[a] Denotes standard deviation obtained on the mean value from a block consisting of 10 scans.

[b] Stands for external standard deviation calculated from the mean value obtained in each of the 10 blocks.

It was of interest to study the isotope fractionation behaviour of Pu during Experiment 2, which uses different filament heating conditions than those employed normally [12], i.e., comparatively lower ionization filament heating current of 5 A and higher evaporation filament current of 2.5–3 A in the former versus 6 and 2 A, respectively, in the latter [12]. The isotope fractionation factor per mass unit, also known as *K*-factor, was calculated by comparing the experimentally obtained $^{239}Pu/^{240}Pu$ atom ratios with the certified ratio in NIST-SRM 947 Pu. Fig. 1 depicts the *K*-factor calculated from one of the typical mass spectrometric analyses. As expected, the *K*-factor is initially positive due to preferential evaporation of the lighter isotope. The data plotted from different blocks shows that as expected, *K*-factor decreases with time and also becomes negative during the data acquisition. The two run summary points included in the figure are from mean of means of data after 3 and 10 blocks.

The values obtained for *K*-factors during eight independent filament loadings of NIST-SRM-947 Pu and analysed using filament heating conditions of Experiment 2 are shown in Table 2. During each filament loading, the *K*-factor was calculated from the run summary of three blocks. A mean value of 0.99994 ± 0.00055 is obtained for *K*-factor per amu. This *K*-factor, if not applied, would contribute a small systematic error in the determination of $^{238}Pu/^{239}Pu$ atom ratio. This *K*-factor is clearly different from a value of 0.9982 of *K*-factor per amu observed previously in our laboratory [12] for Pu isotope ratios using the filament heating conditions of about 6 A and about 2 A for ionization and vaporization filaments, respectively. It may be mentioned that variations in the *K*-factor, from one mass spectrometric analysis to the other, under the nearly same heating conditions are a source of variable systematic error which cannot be eliminated in unknown samples. However, during the preparation and characterization of reference materials for $^{238}Pu/^{239}Pu$ atom ratios, one can use internal normalization methodology based

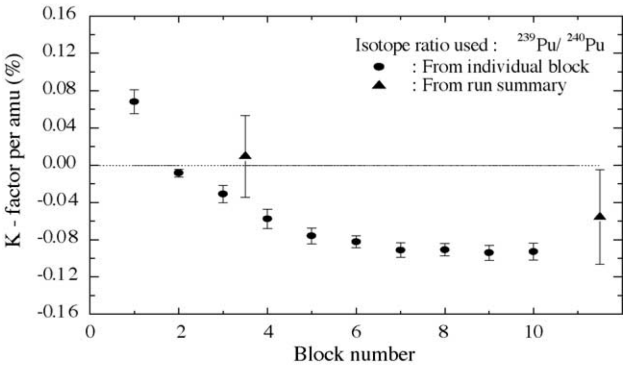

Fig. 1. *K*-factor amu^{-1} from $^{239}Pu/^{240}Pu$ ratio in NIST-SRM 947 calculated from different blocks data.

Table 2
K-factor per atomic mass unit for Pu from the TIMS analysis of NIST-SRM 947 for ^{238}Pu determination

Sample no.	MSA no.	Observed ^{240}Pu/^{239}Pu atom ratio	*K*-factor amu^{-1} from ^{240}Pu/^{239}Pu
1	16872	0.241073 (0.016%) [4][a]	1.00034
2	16873	0.241073 (0.024%) [3]	1.00020
3	16877	0.240867 (0.022%) [4]	0.99949
4	16881	0.240970 (0.031%) [3]	0.99992
5	16882	0.241070 (0.029%) [3]	1.00033
6	16885	0.241160 (0.016%) [2]	1.00071
7	16912	0.240796 (0.029%) [10]	0.99920
8	16914	0.240817 (0.023%) [10]	0.99929
Mean value			0.99994 ± 0.00055

[a] Denotes the number of blocks in each mass spectrometric analysis; *K*-factor amu^{-1}calculated as $(^{239}\text{Pu}/^{240}\text{Pu})_{\text{Certified}}/(^{239}\text{Pu}/^{240}\text{Pu})_{\text{Observed}}$; Certified ^{240}Pu/^{239}Pu atom ratio in NIST-SRM 947 = 0.240989 ± (0.1%) (decay corrected as on 14 July 2004).

Table 3
Results obtained for ^{238}Pu/^{239}Pu isotope ratio determination in NIST-SRM 947 using different amount ratios of Pu/U

Sl no.	MSA no.	Pu/U amount ratio	Observed ^{240}Pu/^{239}Pu atom ratio	Observed ^{238}Pu/^{239}Pu atom ratio	*K*-factor per amu	Corrected ^{238}Pu/^{239}Pu atom ratio
1	16878	2	0.240890 (0.014%)	0.003050 (0.39%) [3]	0.99959	0.003049
2	16882	5	0.241070 (0.029%)	0.003049 (0.61%) [4]	0.99966	0.003048
3	16875	10	0.240827 (0.013%)	0.003041 (0.32%) [5]	0.99933	0.003049
Mean value						0.0030486 (0.02%)

^{238}Pu/^{239}Pu atom ratio quoted in NIST certificate for SRM 947 = 0.003022 ± (2%) (decay corrected as on 14 July 2004).

on ^{240}Pu/^{239}Pu atom ratios and thus eliminate the variable systematic error.

Table 3 gives the results obtained for the determination of ^{238}Pu/^{239}Pu atom ratios in NIST-SRM-947 Pu using its three different mixtures with NIST-SRM-U-930 with Pu/U amount ratios 2, 5 and 10. These experiments were conducted with a view to observe, differences if any, in the extent of isobaric interference correction using IEC methodology. However, no significant difference in the isobaric interference correction was observed and the ^{238}Pu/^{239}Pu atom ratios obtained from the three mixtures are in good agreement with one another as well as with the value expected in the sample. This was attributed to the fact that NIST-SRM 947 originally contains only traces of uranium (about 600 ppm) [11]. The study shows that Pu/U amount ratio need not be known exactly. For the unknown sample, Pu/U amount ratio of 2–5 would be preferable with a view to getting sufficient intensities of both ^{235}UO$^+$ and ^{238}UO$^+$.

3.4. Results of TIMS analysis of synthetic mixture of Pu isotopes

Since isotopic reference materials with certified values higher than ∼0.3 atom% of ^{238}Pu content are not available, it was of interest to apply the methodology discussed in the present paper to a synthetic mixture having ^{238}Pu content of about 2 atom%. The synthetic mixture was prepared by mixing solutions of ^{238}Pu and ^{239}Pu isotopes. ^{238}Pu/^{239}Pu atom ratio in this mixture was determined by the usual method of alpha spectrometry on electrodeposited sources [4]. Tables 4a and 4b show the data obtained on ^{238}U/^{235}U atom ratio using UO$^+$ ion and ^{238}Pu/^{239}Pu atom ratio using Pu$^+$ ion determined in this synthetic mixture during a typical mass spectrometric analysis by TIMS. The values of ^{238}U/^{235}U atom ratio obtained using UO$^+$ ion in this synthetic sample is higher (Table 4a) than that obtained during the analysis of SRM 947 given in Table 1a. This was attributed to the presence of comparatively large amounts of U in solutions of ^{238}Pu and ^{239}Pu isotopes used to prepare the synthetic mixture. It is possible to quantify the amount of U present in the synthetic mixture based on changes in the ^{238}U/^{235}U atom ratio, however, it was not done since this is of no consequence to the present work. The run summary value of 0.019376 (Table 4b) obtained by TIMS for ^{238}Pu/^{239}Pu atom ratio was found to be in good agreement with the value of 0.019341 determined using alpha spectrometry. The alpha spectrometry value of ^{238}Pu/^{239}Pu atom ratio was calculated from the ^{238}Pu/(^{239}Pu + ^{240}Pu) alpha activity ratio obtained from triplicate spectra recording from each of the four alpha sources, using a value of 0.011207 ± (0.1%) for ^{240}Pu/^{239}Pu atom ratio determined by TIMS and half-life values of 24 110, 6553 and 87.74 year, respectively for ^{239}Pu, ^{240}Pu and ^{238}Pu.

Table 4a
Data on the ^{238}UO$^+$/^{235}UO$^+$ atom ratio during mass spectrometric analysis of synthetic mixture using Experiment I

Block no.	^{235}UO$^+$ intensity (mV)	^{238}UO$^+$/^{235}UO$^+$ ratio
1	550	0.059698 (0.05%)
2	356	0.059791 (0.05%)
3	234	0.059885 (0.18%)
4	156	0.060011 (0.20%)
Run summary		0.059846 (0.24%)

Table 4b
Data on the determination of $^{238}Pu^+/^{239}Pu^+$ ratio in synthetic mixture using Experiment II

Block no.	^{235}U intensity (mV)	^{239}Pu intensity (mV)	$^{238}Pu^+/^{239}Pu^+$ ratio
1	4.08	1729	0.0193784 (0.055%)
2	3.77	1794	0.0193852 (0.042%)
3	3.24	1851	0.0193662 (0.080%)
4	2.91	1888	0.0193737 (0.068%)
5	2.70	1911	0.0193739(0.031%)
6	2.49	1948	0.0193759 (0.050%)
7	2.41	1983	0.0193741 (0.048%)
8	2.38	2023	0.0193766 (0.040%)
9	2.28	2061	0.0193754 (0.031%)
10	2.23	2096	0.0193768 (0.025%)
Run summary			0.0193756 (0.053%)

Expected atom ratio as per alpha spectrometric data on = 0.019341 ± (0.5%) ^{238}Pu/(^{239}Pu + ^{240}Pu) α activity ratio of 5.10437 ± (0.37%) determined from triplicate spectra recording from each of the four alpha sources.

However, as is known in alpha spectrometry, the tail contribution at low energy peak (5.16 MeV) of (^{239}Pu + ^{240}Pu) due to energy degradation of high energy peak (5.50 MeV) of ^{238}Pu increases with increase in ^{238}Pu content and this increases the uncertainty in the data obtained by alpha spectrometry, particularly, in cases where the quality of the alpha sources is not good. These types of Pu samples can be generated during IDAS [5] on Pu as well as ID-TIMS of Pu using ^{238}Pu as a spike and in such cases, the present methodology can be easily used for Pu analysis by TIMS.

It is worth mentioning that in the present methodology, since ^{238}U/^{235}U atom ratio to be used in IEC approach, is determined from the same filament loading, pick-up or contamination of Pu sample with small amounts of U during sample processing will not affect the data obtained for ^{238}Pu isotope in the sample. This is quite attractive since at times, there could be contamination from natural/depleted/enriched U, when a large number of samples are handled in any facility. Further, U contamination from reagents, apparatus and the environment will also not affect the results.

4. Conclusions

A novel approach based on the use of interfering element correction methodology is demonstrated for the determination of ^{238}Pu/^{239}Pu atom ratio in Pu samples by thermal ionization mass spectrometry. The methodology involves the external addition of enriched ^{235}U (>90 atom%) to the Pu sample, use of UO$^+$ ion for determination of ^{238}U/^{235}U ratio, followed by the IEC approach using Pu$^+$ ion for ^{238}Pu/^{239}Pu atom ratio determination. The studies show the methodology discussed in this work is promising and has the potential to give a precision and accuracy of better than 0.5% on ^{238}Pu determination for characterisation of ^{238}Pu isotopic reference materials, in future. The methodology is also attractive for obtaining high accuracy data on ^{238}Pu/^{239}Pu atom ratios in various Pu samples with different burn-up values.

Acknowledgments

The authors are thankful to Dr. V.N. Vaidya, Head, Fuel Chemistry Division and Dr. V. Venugopal, Director, Radio-Chemistry and Isotope Group of BARC for their interest in the activities of Mass Spectrometry Section. The authors are thankful to the Instrumentation Group in Radiochemistry Division of RC&I Group for their constant support in maintaining the MAT-261 thermal ionization mass spectrometer.

References

[1] S. Richter, S.A. Goldberg, Int. J. Mass Spectrom. 229 (2003) 181.

[2] P. DeBievre, in: N.R. Daly (Ed.), Advances in Mass Spectrometry, vol. 7A, The Institute of Petroleum, London, 1978, p. 395.

[3] M. Taube, Plutonium—A General Survey, vol. 4, Verlag Chemie, 1974.

[4] S.K. Aggarwal, S.A. Chitambar, V.D. Kavimandan, A.I. Alamula, P.M. Shah, A.R. Parab, V.L. Sant, H.C. Jain, M.V. Ramaniah, Radiochim. Acta 27 (1980) 1.

[5] M.V. Ramaniah, H.C. Jain, S.K. Aggarwal, S.A. Chitambar, V.D. Kavimandan, A.I. Alamula, P.M. Shah, A.R. Parab, V.L. Sant, Nucl. Technol. 49 (1980) 121.

[6] S.K. Aggarwal, D. Alamelu, P.M. Shah, Radiochim. Acta 81 (1998) 129.

[7] D. Alamelu, S.K. Aggarwal, Radiochim. Acta 89 (2001) 131.

[8] H.C. Jain, S.K. Aggarwal, in: K.N. Rao, H.J. Arnikar (Eds.), Artificial Radioactivity, Tata McGraw-Hill, 1985, p. 263.

[9] D. Alamelu, P.S. Khodade, P.M. Shah, S.K. Aggarwal, Int. J. Mass Spectrom. 239 (2000) 51.

[10] O.J. Wick, Plutonium Handbook—A Guide to the Technology, vol. I, Gordon and Breach, Science Publishers Inc., New York, 1967.

[11] S.K. Aggarwal, S. Kumar, M.K. Saxena, P.M. Shah, H.C. Jain, Int. J. Mass Spectrom. Ion Processes 151 (1995) 127.

[12] S.K. Aggarwal, A.I. Almaula, P.S. Khodade, A.R. Parab, R.K. Duggal, C.P. Singh, A.S. Rawat, G. Chourasiya, S.A. Chitambar, H.C. Jain, J. Radioanal. Nucl. Chem. Lett. 87 (1984) 169.