

A novel method for trace uranium determination in plutonium by thermal ionisation mass spectrometry

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Abstract

An isotope dilution-thermal ionisation mass spectrometric (ID-TIMS) methodology using enriched ^{235}U (>90 at.%) as a spike is described for the determination of trace uranium (U) in plutonium (Pu). The method is based on the monitoring of UO^+ instead of U^+ in order to overcome the isobaric interference of ^{238}Pu at ^{238}U . The present approach obviates the need for the chemical separation of microgram quantities of U from relatively large amounts of Pu. This method is useful for determining decontamination factors during U–Pu chemical separation, and also for determining trace U in a proposed Pu chemical assay reference material. In practice, the U isotopic concentration in the Pu sample must be known for highly accurate results.

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1. Introduction

Determination of trace amounts of uranium (U) in plutonium (Pu) is required for variety of purposes. These include chemical quality assurance of Pu bearing fuel materials, the characterisation of certified reference material for total Pu, and for determining the chemical purity of Pu obtained after reprocessed nuclear fuel. A longstanding problem in the quantitative analysis of trace U in Pu-rich matrices is the presence of U and Pu isobars at mass 238. Most analytical approaches involve prior separation of U from bulk Pu. Isotope dilution-thermal ionisation mass spectrometry (ID-TIMS) using U^+ also depends upon the separation efficiency of U from Pu prior to mass spectrometric determination.

Previous studies [1–3] from our laboratory demonstrate the formation of atomic and molecular ions (M^+ and MO^+) using synthetic mixtures of U and Pu in different ratios. These studies [2] showed that it was possible to produce UO^+ ions in the absence of PuO^+ by using a multiple filament assembly heated under specific conditions. These studies prompted us to further investigate the possibility of determining trace levels of U using

UO^+ ions in TIMS, without separating the trace U from the Pu sample matrix. In this work, this method has been adopted to determine trace U in a Pu chemical assay standard. This method may also be used to determine decontamination factors during U and Pu separation from actual samples, and may possibly obviate the need for radioactive tracers.

2. Experimental

Two synthetic samples having U/Pu ratios of 100 to 300 were prepared by mixing weighed aliquots of two purified standard reference materials (SRMs): NIST-SRM-947 Pu and NIST-SRM-U-950a. The resulting solutions represent Pressurized Heavy Water Reactor (PHWR) irradiated fuel dissolver solution samples. The synthetic mixtures were purified by anion exchange separation using DOWEX 1 \times 8 resin in 1:1 (v/v) HNO_3 . Uranium present on the column was washed with 1:5 HNO_3 , and Pu was eluted with 1:50 HNO_3 . The eluted Pu solutions contain traces of U, and were taken up in pre-weighed volumetric flasks. The concentration of Pu in these solutions was determined by liquid scintillation counting (LSC) using α -specific activity calculated from the isotopic composition data determined by TIMS.

Weighted aliquots containing 5–10 μg of Pu from each of these purified solutions, were taken and mixed with pre-calibrated NIST-SRM-930 U solution (^{235}U > 93 at.%) to obtain a Pu/U ratio of 5. The mixture solutions were evaporated to near dryness and 2 μL solution from this mixture was loaded on to the high purity rhenium filament in a double filament assembly [2]. The ionisation and vaporization filaments were heated to about 6 A and 2–2.4 A, respectively, to obtain sufficient UO^+ ion current without forming PuO^+ [2]. This is due to the difference in the ionisation energies of UO (5.6 eV) and PuO (5.8 eV) [4]. A

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Table 1

Determination of U in synthetic samples with U/Pu amount ratios as seen in PHWR irradiated fuel dissolver solution samples, after subjecting them to purification by anion exchange method

Initial U/Pu	Weight of solution (in g)		Measured $^{235}\text{UO}^+ / ^{238}\text{UO}^+$	Concentration (μg of element/g of solution)		% of U in Pu	Decontamination factor (DF) of Pu w.r.t. U
	Sample (purified Pu solution)	Spike (NIST-SRM-930-U) ^a		U	Pu		
100	5.97	0.1053	9.6318 (0.23%)	0.00894	0.87	1.028	9,730
300	5.96	0.0766	6.6549 (0.4%)	0.01307	0.89	1.469	20,422
300	13.46	0.0971	5.6959 (0.07%)	0.00934	0.42	2.225	13,483

^a Concentration of U in NIST-SRM-930-U used as a spike was 11.53 μg of U/g of solution.

thermal ionisation mass spectrometer (Finnigan MAT 261, Bremen) equipped with multi-Faraday cups was used to acquire the data in static multi-collector mode. The U isotope ratios in the samples were obtained using UO^+ ions at m/q values of 251 and 254, corresponding to $^{235}\text{UO}^+$ and $^{238}\text{UO}^+$, respectively. The concentration of U in the purified solution was then evaluated by ID-TIMS.

Independent experiments were also conducted to determine the amount of uranium in the proposed $\text{K}_4\text{Pu}(\text{SO}_4)_4$ chemical assay standard [5] without resorting to ion exchange separation, and using the same method as discussed above and in our previous work [2,3]. This compound was proposed as a chemical assay standard of Pu from our laboratory [5] in 1990 and has been used successfully since then.

3. Results

Table 1 shows the results of ID-TIMS determinations of uranium at ppm levels in synthetic samples with U/Pu ratios as seen in PHWR irradiated fuel dissolver solution. The table includes the data on the amount of purified Pu solution taken, the weight of NIST-SRM-930U spike solution added and the $^{235}\text{UO}^+ (m/q\ 251) / ^{238}\text{UO}^+ (m/q\ 254)$ ratio determined experimentally. The U concentration was calculated by using the measured $^{235}\text{UO}^+ (m/q\ 251) / ^{238}\text{UO}^+ (m/q\ 254)$ ratio in the spiked samples and then applying the standard isotope dilution

equations. The PHWR irradiated fuel simulants (Table 1) also provide data on the decontamination factor achieved for U w.r.t. Pu by the anion exchange separation procedure employed here for the purification of Pu.

Table 2 gives the results of U determination in a Pu-rich matrix. The results given in Tables 1 and 2 clearly demonstrate the applicability of the present ID-TIMS approach using enriched ^{235}U (>93 at.%) for the determination of trace amounts of U in Pu samples without resorting to any separation and purification procedure.

We assumed a natural $^{238}\text{U} / ^{235}\text{U}$ ratio for U concentration calculation in the aliquot. In actual practice, for high accuracy results, one must separate the trace uranium from the Pu matrix in order to determine its true isotopic composition [6]. This is essential since U in Pu can originate from two different sources; one as a trace impurity after column separation, and the other due to the radioactive decay of Pu isotopes. Contributions of the latter will depend upon both the isotopic composition of the Pu matrix and the time elapsed after Pu purification. In actual practice, the isotopic composition of U in the Pu sample will not be natural. An experimental determination of the U isotopic composition would then require the separation of microgram

Table 2

Determination of U in $\text{K}_4\text{Pu}(\text{SO}_4)_4$ chemical assay standard of Pu

Weights of the solution (g)		Measured $^{235}\text{UO}^+ / ^{238}\text{UO}^+$	Concentration (μg of element/g of solution)		Measured U/Pu amount ratio ($\times 10^{-6}$)
Pu standard sample	NIST-U-930 spike		U	Pu	
1.06225	1.00905	17.1849 (0.14%)	0.0057	71.171	80.23
1.3127	1.0123	17.1483 (0.12%)	0.0071	87.951	80.82

Table 3

Effect of radioactive decay of Pu isotopes on the calculation for U concentration

Number of years	Number of atoms of U isotopes formed due to radioactive decay of 1 g of Pu ^a ($\times 10^{17}$)			Total number of U atoms of the isotope present in 1 g of Pu ($\times 10^{17}$)		$^{235}\text{U} / ^{238}\text{U}$ ratio (R_S)	^{238}U atom fraction in the sample	U amount calculated ^b (ppmw)
	^{234}U	^{235}U	^{236}U	^{235}U	^{238}U			
	0	–	–	–	0.018 ^c			
1	0.033	0.70	0.17	0.69	2.51	0.276	0.74	137.0
2	0.065	1.35	0.33	1.37	2.51	0.545	0.59	175.4
5	0.16	3.38	0.83	3.40	2.51	1.353	0.36	299.6

^a Isotopic composition of Pu (at.%) used for calculation: $^{238}\text{Pu} = 0.0165$, $^{239}\text{Pu} = 93.39$, $^{240}\text{Pu} = 6.24$, $^{241}\text{Pu} = 0.32$, $^{242}\text{Pu} = 0.024$.

^b Assuming: measured $R_M = 15$; $R_{SP} = 17.3$ in the isotope dilution mass spectrometry equation.

^c Considering 100 ppmw of natural U present in Pu matrix.

quantities of U from a few grams of Pu. This was not done in the present work, since the aim was to demonstrate the mass spectrometric method of trace U quantification as UO^+ ion in a Pu matrix without involving any chemical separation.

Table 3 gives a typical calculation of the total effect of U isotopic composition (100% natural versus natural + radiogenic) for Pu initially containing 100 ppmw of natural uranium at zero time. The table includes the calculated data on the growth of different U isotopes (^{234}U , ^{235}U and ^{236}U) due to alpha decay of Pu isotopes for durations of 1, 2 and 5 years. The radiogenic growth of ^{235}U and other isotopes would affect the $^{235}\text{U}/^{238}\text{U}$ ratio (R_S) in the sample as well as the atom fraction of ^{238}U in the sample. Assuming U to be of 100% natural isotopic composition and using the measured R_M (assumed as 15) would result in under-estimation of U concentration in the sample. For example, the calculated concentration will be 100 ppmw versus 137, 175.4, 299.6 ppmw after a decay period of 1, 2 and 5 years, respectively, of the Pu isotopes. This uncertainty is more pronounced in case the purified Pu originally contains less amount of U. However, in any reprocessing plant, the data on the U isotopic composition can be easily obtained independently and can directly be used for determining the U traces in purified Pu product using the present method.

4. Conclusions

The applicability of a new method using UO^+ is demonstrated for determining trace U in Pu-rich matrices. The method is based

on the addition of enriched ^{235}U (>90 at.%) as a spike and use of multiple filament assembly to produce UO^+ in the source without concomitant PuO^+ production. The method is also useful to determine decontamination factors during U–Pu chemical separations.

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