Effect of radioactive decay of Pu isotopes on the determination of Pu concentration with high accuracy by isotope dilution mass spectrometry (IDMS) and isotope dilution alpha spectrometry (IDAS)

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Abstract

Isotope dilution techniques, using a suitable tracer or spike isotope, are commonly used for determining Pu concentration in complex matrices like dissolver solution of irradiated fuel. One of the main reasons for this is the high accuracy achievable due to the elimination of matrix effects present in other analytical techniques. However, the radioactive decay of Pu isotopes in the tracer, if not accounted for, would lead to systematic uncertainty in the results. Taking examples of ^{240}Pu and ^{238}Pu tracers used in our laboratory for isotope dilution mass spectrometry (IDMS) and isotope dilution alpha spectrometry (IDAS), respectively, it is shown that depending upon the isotopic composition of the tracer and the time elapsed after tracer calibration, the radioactive decay could lead to an overall correction factor ranging from 0.1 to about 4% over a period of 5 years. The calculations shown in this work demonstrate the importance of considering radioactive decay, especially when high accuracies are desirable, e.g. in nuclear material accounting.
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1. Introduction

Determination of total amount of Pu at the input point of a fuel reprocessing plant is one of the very important requirements of nuclear material accounting. This determination usually involves two measurements: (i) the total volume or weight of the solution in the tank and (ii) the concentration of Pu in the solution. The latter is generally achieved by following isotope dilution methodology due to complex nature of the irradiated fuel dissolver solution and also due to high radiation dose associated with the solution. The use of isotope dilution involves the addition of a known amount of tracer solution to an accurately known amount of the sample solution followed by the determination of change in the atom ratio by thermal ionisation mass spectrometry (TIMS) or change in the alpha activity ratio by alpha spectrometry (AS). The two methodologies are popularly known as isotope dilution mass spectrometry (IDMS) and iso-

tope dilution alpha spectrometry (IDAS). In our laboratory, we have developed and demonstrated the use of ^{240}Pu and ^{238}Pu as spikes (tracers), respectively, for IDMS [1,2] and IDAS [3] experiments on Pu. In the IDMS experiments, we have used Pu containing about 29 atom% of ^{240}Pu as a spike for Pu from low burnt fuels with ^{239}Pu abundance of 90 atom% or higher.

The uncertainty in Pu concentration measurements by IDMS or IDAS depends upon many components including the uncertainty in the determination of atom ratio or the alpha activity ratio in the spiked mixture. It is well recognised by the scientific community that any uncertainty in the data of Pu spike will contribute to a systematic uncertainty in the concentration value of Pu in the sample. Thus it is essential that the isotopic composition of Pu in the spike, average atomic weight of Pu in the spike and the amount of Pu in the spike aliquot used must be known with the smallest possible uncertainty. These measurements again involve the use of thermal ionisation mass spectrometry and calibration of the spike by IDMS or IDAS by using a primary reference material of Pu. It is generally assumed that once the spike calibration is done, the aliquots of the spike distributed in different vials and stored properly

may be employed for several years in future. However, due to the radioactive decay of Pu isotopes present in the spike, there would be changes in these parameters (i.e. isotopic composition, total amount of Pu in the aliquot, etc.) which could contribute additional uncertainties in the Pu concentration measurements. This paper presents our experience in using two such spikes viz. ^{240}Pu about 29 atom% and ^{238}Pu about 93 atom% for IDMS and IDAS experiments, respectively. It is shown that the radioactive decay of Pu isotopes, if not considered properly, can contribute appreciable uncertainty in the Pu concentration values, particularly, when using ^{238}Pu as a spike in IDAS or in IDMS. This assumes great importance in the present global scenario when tonnes of Pu are available and the concentration measurements are expected to have overall uncertainties of less than 0.1%.

2. Principle of isotope dilution

Isotope dilution is based on the addition of a known amount of suitable tracer to the solution of unknown sample, followed by the determination of change in the atom ratio by mass spectrometry or change in the alpha activity ratio by alpha spectrometry. The choice of tracer to be used in isotope dilution mass spectrometry (IDMS) or in isotope dilution alpha spectrometry (IDAS) depends upon several criteria. For example, for IDMS of Pu, ^{242}Pu, ^{244}Pu, ^{239}Pu, ^{240}Pu have been used as tracers whereas for IDAS, ^{236}Pu and ^{238}Pu are commonly used as tracers. Based on the first principles, it can be shown that the concentration of Pu (C_s) in the sample can be calculated from the equations given below, when using ^{240}Pu and ^{238}Pu as tracers, respectively, in IDMS and IDAS:

$$C_s = C_{sp} \times \frac{W_{sp}}{W_s} \times \left[\frac{1 - R_m/R_{sp}}{R_m - R_s} \right] \times \frac{(at.wt.)_s}{(at.wt.)_{sp}} \times \frac{(AF\ of\ 240)_{sp}}{(AF\ of\ 239)_s},$$

$$C_s = C_{sp} \times \frac{W_{sp}}{W_s} \times \left[\frac{1 - A_m/A_{sp}}{A_m - A_s} \right] \times \frac{(at.wt.)_s}{(at.wt.)_{sp}} \times$$

$$\times \left[\frac{(AF\ of\ 238)_{sp} \times \lambda_{238}}{(AF\ of\ 239)_s \times \lambda_{239} + (AF\ of\ 240)_s \times \lambda_{240}} \right]$$

In these equations, C's denote the concentrations of Pu; W's stand for aliquot or solution weights; the subscripts s, sp

and m stand for sample, spike (tracer) and mixture respectively; R's and A's denote the ^{240}Pu/^{239}Pu atom ratios and ^{238}Pu/(^{239}Pu + ^{240}Pu) alpha activity ratios, respectively; (at.wt.) is the average atomic weight of Pu and (AF) denotes the atom fraction. As is obvious, the atom fraction of an isotope in the tracer would change with time depending upon the isotopic composition of Pu, half-lives of the Pu isotopes and the time elapsed after calibration of the tracer solution by using appropriate chemical assay standard. Further, this would also lead to changes in the concentration of Pu in the tracer solution as well as in the average atomic weight of Pu. The overall effect in C_s would, therefore, be a combined effect of all these changes. It is thus extremely important to understand the effect of these changes in the final concentration value of unknown sample to realize the full potential of these isotope dilution techniques for achieving high accuracy in the results. It may also be added that the tracer (spike) solution is also calibrated using a chemical assay standard of Pu and the radioactive decay of Pu isotopes in the aged Pu chemical assay standard would also need to be considered.

3. Results and discussion

Table 1 gives the isotopic composition data of ^{240}Pu and ^{238}Pu spikes used in our laboratory for IDMS and IDAS work on Pu. In the ^{240}Pu spike, the amount of ^{238}Pu was determined by alpha spectrometry whereas the amounts of all other isotopes in the two spikes were obtained by thermal ionization mass spectrometry. Table 2 shows the changes in the atom% abundance, average atomic weight of Pu and the amount of Pu in the spike aliquot

Table 1
Data on the amounts of different Pu isotopes in ^{240}Pu and ^{238}Pu spikes

Sl. no.	Amounts (atom%) of different isotopes in spike		
	Nuclide (half-life in year) [4]	^{240}Pu spike	^{238}Pu spike
1	238 (87.74)	0.225	92.254
2	239 (24110)	65.14	7.3017
3	240 (6564)	28.62	0.4143
4	241(14.4)	3.604	0.0277
5	242 (3.76 × 10^5)	2.406	0.00212

Table 2
Change in atom% abundance, average atomic weight of Pu and the amount of Pu in the spike due to radioactive decay of Pu isotopes

| Methodology	Decay period (years)	Spike isotope	Correction factor due to radioactive decay			
			Atom fraction (*a*)	Average atomic weight (*b*)	Pu amount (*c*)	Combined effect (*a*) × (*c*)/(*b*)
IDMS	0	^{240}Pu	1.00	1.00	1.00	1.00
	1		1.0017	0.999989	0.998	0.9999
	2		1.0032	0.999978	0.996	0.9998
	5		1.0076	0.999949	0.992	0.9995
	10		1.0136	0.999909	0.985	0.9990
IDAS	0	^{238}Pu	1.00	1.00	1.00	1.00
	1		0.9994	1.000003	0.993	0.992
	2		0.9988	1.000005	0.985	0.984
	5		0.9970	1.000012	0.964	0.961
	10		0.9938	1.000025	0.930	0.924
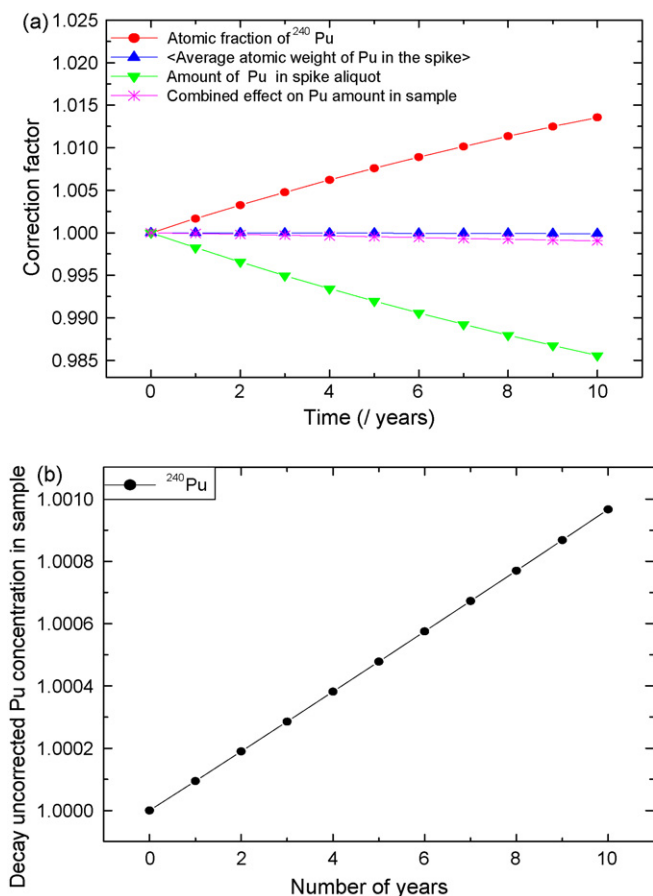
Fig. 1. (a) Fractional changes in different parameters with time due to radioactive decay of Pu isotopes in ^{240}Pu spike. (b) Pu concentration determined in Pu sample without accounting for the of decay of the Pu isotopes in the ^{240}Pu spike.

Fig. 2. (a) Fractional changes in different parameters with time due to radioactive decay of Pu isotopes in ^{238}Pu spike. (b) Pu concentration determined in Pu sample without accounting for the of decay of the Pu isotopes in the ^{238}Pu spike.

due to radioactive decay of Pu isotopes over a period of 1, 2, 5 and 10 years after fresh calibration of the spike (assumed as zero time). Figs. 1(a) and 2(a) present the effects of these changes in ^{240}Pu and ^{238}Pu spikes respectively. Figs. 1(b) and 2(b) clearly show that the results for Pu concentration in the sample would be positively biased in both ^{240}Pu and ^{238}Pu spikes, if decay corrections for Pu isotopes in the spikes are not considered. It is evident that there is a combined effect to the extent of 0.10% and nearly 4%, respectively, when using pre-calibrated ^{240}Pu and ^{238}Pu spikes with amount % of different isotopes given in Table 1. These changes must be included in the isotope dilution equation used for calculation of concentration after measuring the atom ratio or alpha activity ratio in the spiked mixtures. When these measurements are carried out on a routine basis by an operator and all the calculations are made by using an excel sheet, there is a possibility of overlooking the changes in the parameters given here and the concentration values will, therefore, have uncertainties due to the radioactive decay of Pu isotopes in the spikes used. The investigations presented in this paper are extremely important when aiming at an overall uncertainty of better than 0.1% in the Pu concentration or in the total amount of Pu at a reprocessing plant. As a matter of fact, the uncertainties in the half-life values should also be included
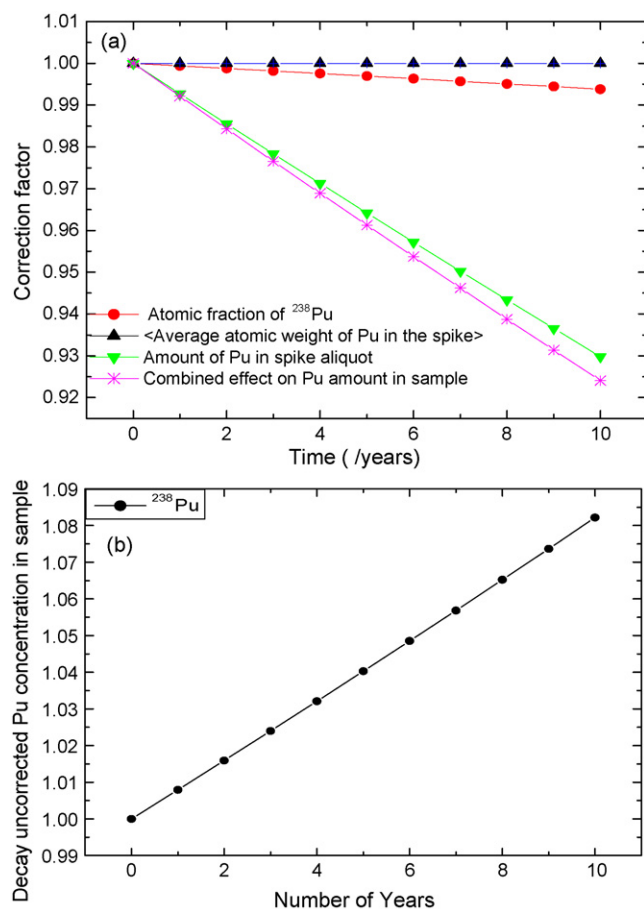
while calculating the overall uncertainties of IDMS and IDAS results.

It may be added that these effects would become much pronounced when ^{236}Pu with a half-life of about 2.5 years is used as a tracer in IDAS. An additional uncertainty can also be introduced when an aged chemical assay standard of Pu, prepared from reactor grade Pu, is used [5] for calibrating the Pu tracers. Changes in the isotopic composition of Pu, due to radioactive decay of Pu isotopes, e.g. ^{238}Pu, ^{240}Pu and ^{241}Pu, would lower the amount of Pu present per unit weight in the chemical assay standard and this would be a source of systematic uncertainty, if not taken into account.

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