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Determination of $^{241}Pu/^{239}Pu$ atom ratio in pressurised heavy water reactor (PHWR)-Pu samples using liquid scintillation counting

D. Alamelu, S.K. Aggarwal *

Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

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Abstract

The determination of ^{241}Pu is important in elucidating the isotopic composition of any Pu sample. The relatively short half-life (14.32 yr) of ^{241}Pu leads to inconsistency in the correlations involving this isotope unless the different Pu samples have either the same irradiation and cooling history or the exact cooling period is known to account for the decay of ^{241}Pu prior to using the data for developing isotope correlations. To overcome this limitation, a useful correlation based on the measurement of total β/total α activity of Pu sample using liquid scintillation counting method was developed. Total β/total α activity of the Pu sample is correlated to the $^{241}Pu/^{239}Pu$ atom ratio and thus does not depend upon the knowledge of the cooling period. For any unknown sample, the $^{241}Pu/^{239}Pu$ atom ratio can be determined by using the developed correlation and by measuring, using a liquid scintillation counter, the total β/total α activity of purified Pu sample.
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Keywords: $^{241}Pu/^{239}Pu$ atom ratio; Isotope correlation; Liquid scintillation counting; PHWR reactor

1. Introduction

Data on the isotopic composition of Pu produced in power reactors are required for knowing the fissile content of Pu when used as a fuel in fast reactors. Also, this information is useful to determine the α-specific activity of Pu, which is required to calculate the weight percentage of ^{241}Am in any Pu sample as well as for the determination of Pu concentration by radiometric methods. Usually, the atom ratios of different Pu isotopes in a Pu sample are obtained by thermal ionization mass spectrometry (TIMS), which requires a detailed chemical separation procedure. This increases the amount of analytical effort, in addition to the cost per analysis. There are many instances where such data, if available with a reasonable accuracy by an alternative fast and cost-effective method, suffice for the purpose, e.g. in assay of waste solutions by radiometric method. Isotope correlations can be used to generate the data, in such cases, without resorting to mass spectrometric analysis procedure.

We have developed and reported isotope correlations [1–3] for the determination of atom ratios of Pu isotopes, using the data obtained by alpha spectrometry and by thermal ionization mass spectrometry. With these correlations, the atom ratios of different Pu isotopes, except for the one involving ^{241}Pu, could be obtained with reasonable accuracy (2–5%). The uncertainty on the correlation involving ^{241}Pu was large due to its relatively short half-life (14.32 yr) which necessitates the availability of Pu samples with known irradiation and cooling history. Thus, an attempt was made to develop a simple and independent method for determining $^{241}Pu/^{239}Pu$ atom ratio. This method is based on the determination of total α and total β activity of Pu isotopes using a suitable liquid scintillation counter.

2. Principle

^{241}Pu being a soft β-emitter ($\beta_{max} = 20$ keV) with a half-life of about 14.32 yr, it was considered worthwhile to measure the β activity of ^{241}Pu in any Pu solution using liquid scintillation counting (LSC) [4]. To circumvent the problem of knowing the exact amount of Pu taken in the LSC vial for counting, ratio of the β activity due to ^{241}Pu with respect to total α-activity, also measured by LSC, due to other Pu isotopes was used. The ratio of the β activity to total α activity was correlated with the amount

* Corresponding author. Tel.: +91 22 2559 3740
E-mail addresses: alamelud@rediffmail.com (D. Alamelu), skaggr@barc.gov.in (S.K. Aggarwal).

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of ^{241}Pu with respect to the other Pu isotopes in the sample as given below:

$$\frac{A_\beta(^{241}\mathrm{Pu})}{[A_\alpha(^{238}\mathrm{Pu}) + A_\alpha(^{239}\mathrm{Pu}) + A_\alpha(^{240}\mathrm{Pu}) + A_\alpha(^{242}\mathrm{Pu})]} = \frac{N(^{241}\mathrm{Pu})\lambda_{241}}{[N(^{238}\mathrm{Pu})\lambda_{238} + N(^{239}\mathrm{Pu})\lambda_{239} + N(^{240}\mathrm{Pu})\lambda_{240} + N(^{242}\mathrm{Pu})\lambda_{242}]}$$

Here, N denotes the number of atoms and A denotes the activity. Denoting α and β count rate by T_α and T_β, respectively; the atom ratio of two isotopes as R, the above equation may be written as

$$\frac{T_\beta}{T_\alpha} = \frac{(R_{1/9}\lambda_1)}{[(R_{8/9}\lambda_8) + \lambda_9 + (R_{0/9}\lambda_0) + (R_{2/9}\lambda_2)]}$$

where the subscripts 8, 9, 0, 1 and 2 stand for ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu, respectively.

$$R_{1/9} = \left[\frac{T_\beta}{T_\alpha}\right] \frac{[(R_{8/9}\lambda_8) + \lambda_9 + (R_{0/9}\lambda_0) + (R_{2/9}\lambda_2)]}{\lambda_1}$$

Considering the efficiency values of α and β counting by LSC as η_α and η_β, respectively, and the observed α and β count rates by t_α and t_β, respectively; the above equation can be re-written as

$$R_{1/9} = \left[\frac{t_\beta \eta_\alpha}{t_\alpha \eta_\beta}\right] \frac{[(R_{8/9}\lambda_8) + \lambda_9 + (R_{0/9}\lambda_0) + (R_{2/9}\lambda_2)]}{\lambda_1}$$

$$R_{1/9} = \left[\frac{\eta_\alpha}{\eta_\beta}\right] \left[\frac{t_\beta}{t_\alpha}\right] \frac{[(R_{8/9}\lambda_8) + \lambda_9 + (R_{0/9}\lambda_0) + (R_{2/9}\lambda_2)]}{\lambda_1}$$

$$R_{1/9} = \left[\frac{\eta_\alpha}{\eta_\beta}\right] X\text{-value} \quad (1)$$

$$R_{1/9} \propto X\text{-value}$$

Thus, a correlation between $R_{1/9}$ obtained by thermal ionization mass spectrometry and X-value calculated from $[t_\beta/t_\alpha]$ determined by LSC and using the atom ratios of other Pu isotopes was established for determining ^{241}Pu/^{239}Pu atom ratio. It may be mentioned that atom ratios of other Pu isotopes can be obtained from the previously developed correlations [3]. It is essential to confirm that the efficiency values of α as well as β counting by LSC have not changed after establishing the correlation. Otherwise, suitable correction must be incorporated into the LSC data by using a Pu standard sample of known isotopic composition.

3. Experimental

Five PHWR Pu samples, with varying amounts of different Pu isotopes, were used for the present study. The Pu samples were purified from ^{241}Am by anion exchange resin in 1:1 (v/v) HNO_3 using anion exchange separation and purification procedures [5]. From each of the purified Pu samples, about 50 μL of the solution containing about 100 ng of Pu, was taken in a glass scintillation vial. The solution was dried under an infrared lamp. Five millilitres of Ultima Gold AB scintillator (DIN based) was then added to the vial which was subjected to ultra-sonication for re-dissolving the Pu in the scintillation cocktail. The vials were then counted in a low background Liquid Scintillation Spectrometer (Packard Tri-Carb 2900 TR) for sufficient time in order to reduce the uncertainties due to counting. The total counts in the alpha region (100–400 keV) from ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{242}Pu and in beta region (0–20 keV) from ^{241}Pu were recorded. The overall counts in the beta channel were much higher due to the high β specific activity of ^{241}Pu (half-life = 14.32 yr). In order to improve the statistics of measurements in the alpha region, the counts in the alpha region were recorded for 5 min. It may be mentioned that we used Ultima Gold AB (particularly useful to discriminate α and β) since this was readily available to us without any specific advantage of α and β discrimination in the present work. Pulse shape discrimination was not necessary in view of the two distinct energy regions for pulses from alpha and beta particles. The overlap of beta particles in the energy region used for alpha particles was also obtained using ^{3}H standard and was found to be less than 0.01%.

Aliquots containing about 10 μg of Pu from the purified solutions were taken for mass spectrometric analysis. The solutions were concentrated under an IR lamp and were loaded on to the vaporization filament of a double filament assembly of high purity rhenium. The TIMS used was equipped with a multi-Faraday cup detector system. ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu atom ratios were obtained by acquiring the data in static mode of multi-collection. ^{238}Pu/^{239}Pu atom ratios were determined by using electrodeposited sources of Pu samples and recording the alpha spectra using a 100 mm^2 PIPS semiconductor detector. TIMS was not used due to ubiquitous isobaric interference at m/q of 238 from $^{238}U^+$. The alpha spectra were acquired using a PC based multi-channel analyser. The ^{238}Pu/^{239}Pu atom ratios in the samples were calculated by using the ^{238}Pu/(^{239}Pu + ^{240}Pu) alpha activity ratios determined by alpha spectrometry and ^{240}Pu/^{239}Pu atom ratio determined by TIMS. The half-life values of 87.74 ± 0.03 yr for ^{238}Pu, 24110 ± 30 yr for ^{239}Pu, 6561 ± 7 yr for ^{240}Pu, 14.32 ± 0.03 yr for ^{241}Pu, (3.73 ± 0.03) × 10^5 yr for ^{242}Pu isotopes were used in the present work.

Table 1
Data showing the effect of scintillator volume and drying on quenching

Sample no.	tSIE values using undried samples			tSIE values using dried sample
	5 mL[a]	10 mL[a]	15 mL[a]	5 mL[a]
1	501.4	596.2	607.1	643.6
2	564.7	633.0	624.7	644.6
3	567.8	628.6	630.2	644.1
4	562.2	631.8	623.9	639.7
5	566.9	629.9	630.1	645.0
6	570.9	629.9	631.6	653.7
Blank (only scintillator)	629.0	666.0	645.5	639.5

[a] Scintillator volume.

Table 2
Experimental LSC and TIMS data on Pu samples used for correlation

Sample no.	t_β (obs. counts)	t_α (obs. counts)	t_β/t_α	Atom ratios of Pu isotopes in the samples				X-value
				$^{238}Pu/^{239}Pu$	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$	
1	152,245	16,972	8.97	0.00297	0.4160	0.04905	0.0332	0.0179
2	152,379	17,096	8.91	0.00283	0.4060	0.04677	0.0312	0.0174
3	138,532	15,649	8.85	0.00261	0.3902	0.04348	0.0285	0.0166
4	90,138	8,787	10.26	0.00165	0.3354	0.04545	0.0179	0.0164
5	84,655	8,521	9.93	0.00151	0.3173	0.04191	0.0155	0.0153
6	106,992	20,414	5.24	0.00092	0.2626	0.01822	0.0100	0.0069

Table 3
A comparison on $^{241}Pu/^{239}Pu$ atom ratio determination by LSC and by TIMS

Sample no.	Atom ratios by TIMS				t_β/t_α by LSC	$^{241}Pu/^{239}Pu$ by correlation	LSC/TIMS
	$^{238}Pu/^{239}Pu$	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$			
S-1 (P-68)	0.00142 ± 0.00000	0.3194 ± 0.0001	0.04387 ± 0.00004	0.0154 ± 0.0001	10.69	0.0443	1.01
S-2 (P-69)	0.00132 ± 0.00000	0.3198 ± 0.0001	0.04446 ± 0.00004	0.0152 ± 0.0001	11.01	0.0451	1.02

4. Results and discussion

Quenching of the activity during measurements by LSC is well known [6] and is particularly important when dealing with β-emitting radionuclides. Studies were, therefore, carried out to find out the quench levels measured as tSIE, i.e. transformed spectral index of the sample for external standard (^{133}Ba) by taking the aqueous solution of Pu in 5 mL, 10 mL as well as in 15 mL of the scintillator. Also the Pu solution was subjected to dryness and re-dissolved in 5 mL of scintillator to compare the tSIE levels with those obtained without drying. Table 1 gives a comparison of the data obtained for tSIE values. It is clearly seen that increasing the volume of the scintillator as well as adding the scintillator solution after drying are useful to obtain consistent quenching in all the samples in view of decrease in the nitrate content. Since the present experiments involved only the measurement of relative activity ratio, drying of the sample was preferred which also helps in reducing the volume of the radioactive waste generated.

Table 2 gives the experimental data on observed α and β activities as well as the atom ratios of Pu isotopes in different Pu samples used for developing the correlation. The table also includes the X-value (see Eq. (1) above) calculated using the observed α and β activities, the atom ratios and the half-lives of the nuclides involved. An uncertainty of about 3% (95% confidence level) was obtained on the X-value considering uncertainties of different terms involved.

Fig. 1 shows the correlation developed for the determination of the $^{241}Pu/^{239}Pu$ atom ratio using the X-value calculated from ratio of total beta counts to the total alpha counts obtained by LSC in dried samples and the atom ratios obtained from TIMS as discussed above. It can be seen that this relation is linear over the entire region of $^{241}Pu/^{239}Pu$ atom ratios for Pu. A slope value of 2.72 ± 0.02 was obtained which represents the ratio $[\eta_\alpha/\eta_\beta]$. The slope was calculated by linear regression through origin using Origin software. This gives a value of 36.7% for η_β, assuming a value of 100% for η_α. The value of η_β can also be obtained

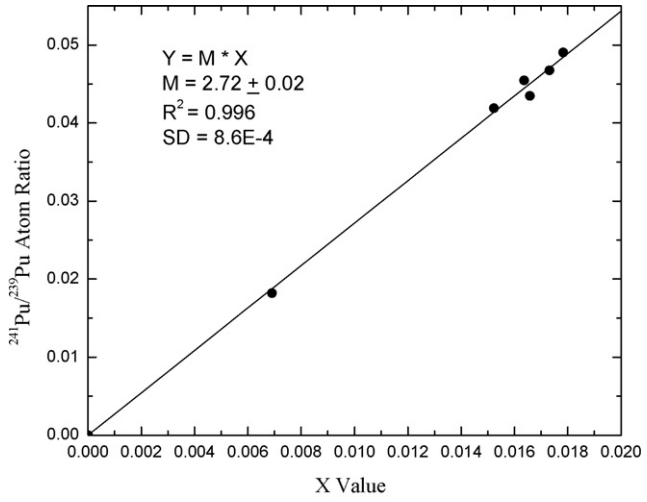

Fig. 1. Correlation between X-value and $^{241}Pu/^{239}Pu$ atom ratio.

using ^3H standards with quench levels similar to those obtained for the samples. Table 3 gives a comparison of $^{241}Pu/^{239}Pu$ atom ratio obtained by TIMS as well as that calculated using the developed correlation for two unknown Pu samples. As can be seen, there is good agreement in the $^{241}Pu/^{239}Pu$ isotope ratios obtained by correlation and those determined by TIMS.

5. Conclusions

The present work reports an independent approach for obtaining $^{241}Pu/^{239}Pu$ atom ratio using liquid scintillation counting. The limitations of the isotope correlations reported previously by us [1–3] for obtaining this atom ratio are circumvented since the ratio of count rates of beta and total alpha does not demand a knowledge of the irradiation and cooling history of Pu sample. Thus, it provides a method to characterise all the isotopes of Pu using isotope correlations, employing the present approach

for obtaining $^{241}Pu/^{239}Pu$ atom ratio. This would provide a simple and cost-effective approach for verification of Pu isotopic composition without resorting to TIMS.

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