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High resolution alpha-particle spectrometry for the determination of $^{240}Pu/^{239}Pu$ atom ratio in Pu samples from PHWR

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Abstract

High resolution alpha-particle spectrometry (HRAS), using electrodeposited sources and applying the WinALPHA program for spectral analysis, was evaluated for the determination of $^{240}Pu/^{239}Pu$ atom ratios in different Pu samples. The results obtained correspond well within 2–5% with the certified ratios determined by thermal ionization mass spectrometry and show the usefulness of HRAS for determining $^{240}Pu/^{239}Pu$ atom ratios in Pu samples. Using the alpha-particle energies of $^{239}Pu + ^{240}Pu$ for the energy calibration was found to be critical in achieving accurate results by HRAS.

Keywords: Alpha-particle spectrometry; Atom ratio; Mass spectrometry; Plutonium

1. Introduction

Alpha-particle spectrometry is a useful analytical technique for the determination of alpha-particle emitting radionuclides in environmental, biological and nuclear fuel samples. Using the commercially available Si detectors, a typical energy resolution that can be achieved is about 15 keV (FWHM) at 5.5 MeV using electrodeposited sources. But this resolution is not sufficient to perform quantitative analysis on material that contains some of the important actinides, e.g. ^{240}Pu (5.168 MeV), ^{239}Pu (5.156 MeV); ^{238}Pu (5.499 MeV), ^{241}Am (5.486 MeV); ^{233}U (4.824 MeV), ^{234}U (4.774 MeV); ^{243}Cm (5.785 MeV), ^{244}Cm (5.804 MeV); ^{232}U (5.320 MeV), ^{228}Th (5.340 MeV), etc. [1]. It is nevertheless possible to employ sophisticated computer algorithms to resolve these close lying alpha energies and obtain information on $^{240}Pu/^{239}Pu$ atom ratios, etc. However, most of the algorithms available in the past were highly complex and could not be adopted by all the interested laboratories worldwide. An intercomparison of commercially available PC-based softwares for alpha-particle spectrometry was conducted by the International Atomic Energy Agency (IAEA) during 1997, where it was concluded that there is ample scope for improvements in the software [2]. Recently, in the frame of a Coordinated Research Program (CRP) of the IAEA (Development and Application of Alpha-particle Spectrometry) [3], a more generalized and user-friendly software program to analyse alpha-particle spectra has been developed. This program, called WinALPHA [4] is available for different users. The analytical function used in this program is a combination of an asymmetrical gaussian for the main part of the peak and a low energy exponential tail function. Therefore, this program was considered to be interesting for evaluating the precision and accuracy in the determination of $^{240}Pu/^{239}Pu$ atom ratio in NIST reference material SRM-947-Pu as well as in Pu samples generated from Pressurized Heavy Water Reactors (PHWRs) using sources prepared and measured by alpha-particle spectrometry in our laboratory. The values obtained from HRAS were compared with those determined experimentally by thermal ionization mass spectrometry (TIMS).

2. Experimental

2.1. Source preparation

For the determination of $^{240}Pu/^{239}Pu$ atom ratio by HRAS, a few Pu samples obtained from PHWR reactors (burn-up about 10,000 MWD/TU) were taken up. These Pu samples were obtained after purifying the aliquots taken from irradiated fuel dissolver solutions, by using a suitable anion exchange procedure in HNO_3

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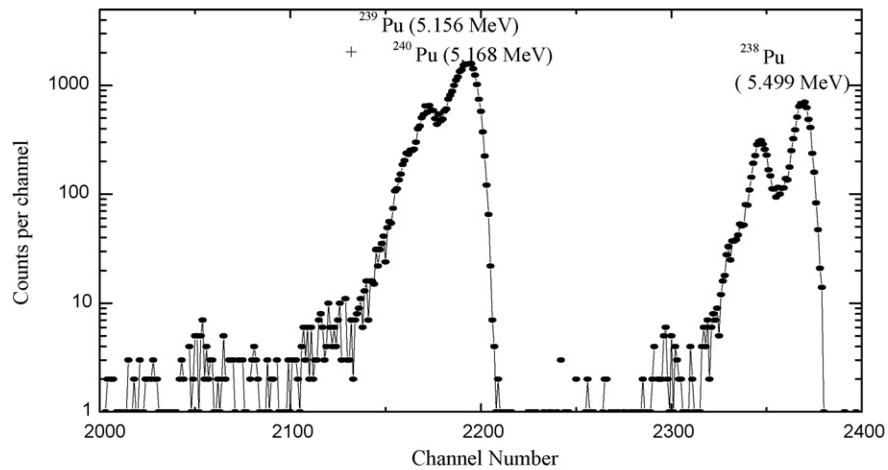

Fig. 1. A typical alpha-particle spectrum recorded from one of the sources showing ^{238}Pu and (^{239}Pu + ^{240}Pu) alpha-particle energies.

medium [5]. Electro-deposited sources were prepared using electro-polished stainless steel disks as the backing material and a Pt stirrer as the anode. The sources were used as such, without heating in a flame or furnace.

2.2. Measurements

The alpha spectra were recorded using a 25 mm^2 PIPS detector, mounted in a vacuum chamber. The system has a resolution of 15 keV (FWHM) at 5.50 MeV. The minimum detectable activity of the system was around 1 Bq for a counting period of 1000 s, with a geometrical efficiency of 1%.

2.3. Spectral analysis

The multiplets of ^{240}Pu + ^{239}Pu were resolved into individual components using the WinALPHA program. The WinALPHA program performs a non-linear fit of the alpha particle spectra, determines the positions of the selected peaks and computes the peak areas. The program was run in the library driven mode which is based on the analysis of multiplets using the internal data base of intensities of different energies of ^{239}Pu and ^{240}Pu alpha peaks. The energy calibration, using the energies of the main peaks of ^{239}Pu and ^{240}Pu separately or using the average energy of the two main peaks, was found to be critical for the final result of the ^{240}Pu/^{239}Pu ratios w.r.t. the mass spectrometry values.

All spectra were fitted in an energy region from 4.93 to 5.20 MeV to exclude the alpha-particle energies of ^{241}Pu and ^{242}Pu and to include the main alpha particle peaks of ^{239}Pu and ^{240}Pu with intensities >0.5% (Table 1) [1].

Table 1
Energies and relative intensities of the major alpha peaks of ^{239}Pu and ^{240}Pu radionuclides [1]

Nuclide	Energy (keV)	Intensity (%)
^{239}Pu	5156.59 ± 0.14	70.77 ± 0.14
	5144.3 ± 0.8	17.11 ± 0.14
	5105.5 ± 0.8	11.94 ± 0.07
^{240}Pu	5168.17 ± 0.15	72.80 ± 0.10
	5123.68 ± 0.23	27.10 ± 0.10

The ^{240}Pu/^{239}Pu atom ratios in these samples were also determined by thermal ionization mass spectrometry using a double filament assembly of high purity rhenium and a static mode of multicollection using a multi Faraday cup Collector system [6]. An uncertainty of about 0.01% (relative standard deviation) was obtained for ^{240}Pu/^{239}Pu atom ratios using an amount of about 5 μg of Pu loaded on the filament.

3. Results and discussion

The ^{240}Pu/^{239}Pu atom ratios have been measured in different Pu samples. Fig. 1 shows a typical alpha spectrum recorded from

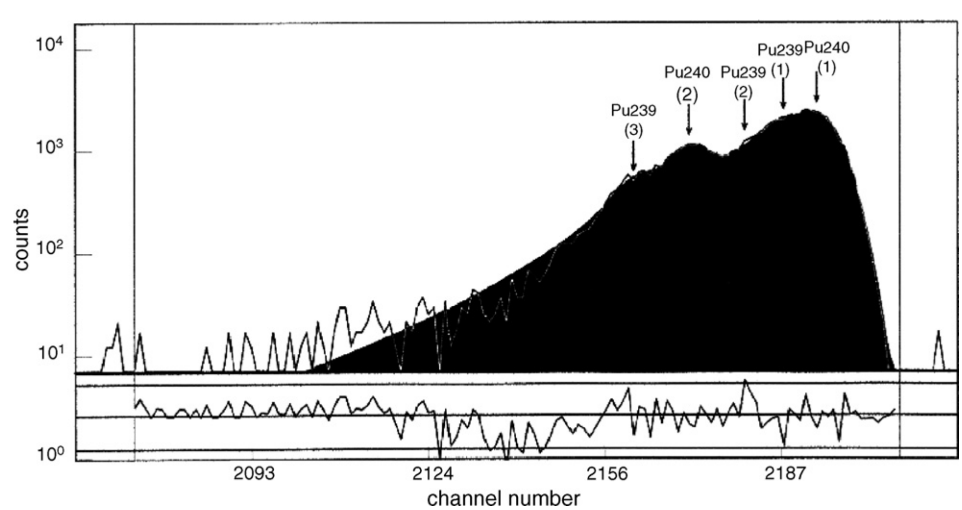

Fig. 2. A typical alpha-particle spectrum displaying different alpha-particle energies from ^{239}Pu and ^{240}Pu and residuals after spectral fitting.

Table 2
Typical data after spectral fitting using WinALPHA on replicate sources for NIST-SRM-947 Pu

Source number	Area under the peak		Parameters after spectral fitting			$^{240}Pu/^{239}Pu$ atom ratio[a]
	^{240}Pu	^{239}Pu	χ^2	Tail parameter	FWHM (keV)	
1	105761	120493	15.4	0.94	16.7	0.23856
2	212640	238013	39.2	1.06	17.8	0.24282
3	145356	157580	16.2	1.05	17.9	0.25071
4	106330	123130	11.9	1.03	17.1	0.23471

[a] Certified $^{240}Pu/^{239}Pu$ atom ratio (corrected for decay): 0.24099 ± (0.1%).

one of the sources and Fig. 2 presents the details of the different alpha-particle energies from ^{239}Pu and ^{240}Pu and the residuals after spectral fitting. Tables 2 and 3 give the typical results of independent sources prepared from NIST material SRM-947-Pu and Pu samples from PHWR, respectively. The samples were measured by HRAS and the alpha-particle energy spectra were analyzed with the program WinALPHA. The resultant $^{240}Pu/^{239}Pu$ activity ratios were used to calculate the $^{240}Pu/^{239}Pu$ atom ratios using the half-life values for ^{239}Pu and ^{240}Pu, being 24110 ± 30 year [1] and 6564 ± 11 year [1], respectively. For spectral fitting, the initial value of tail parameter was given as 1.2 (default value in the program) and FWHM value was based on that calculated from the ^{238}Pu peak. The FWHM value ranged from 15 to 17 keV. The values given in Tables 2 and 3 for these parameters are the final values obtained after iterative analysis of the observed alpha-particle spectra using WinALPHA. The tailing of ^{238}Pu alpha particles at ($^{239}Pu + ^{240}Pu$) peak was very small (less than 0.1%) and was, therefore, not considered. The mean value given in Table 3 for HRAS was calculated as unweighted mean in view of the fact that the two values were determined independently and uncertainties associated were only random in nature arising from counting.

The results obtained by HRAS for $^{240}Pu/^{239}Pu$ atom ratios in PHWR Pu samples as well as those in NIST material SRM-947-Pu [7] agree within 2–5% with TIMS values and the certified value, respectively.

The influence of the energies that were used for the energy calibration, was investigated by calculating the $^{240}Pu/^{239}Pu$ atom ratios using the energies of the main peaks of ^{239}Pu and ^{240}Pu separately and using the average energy of the two main peaks. Since the alpha-particle spectrum of the samples used in this work contained nearly an equal proportion of the alpha-particle activities of ^{239}Pu and ^{240}Pu, a mean value of the main alpha-particle energies of these two isotopes was observed to give the correct $^{240}Pu/^{239}Pu$ atom ratio. The use of the energies of the main peaks of ^{239}Pu and ^{240}Pu separately was found to lead to erroneous results, negatively or positively biased, as shown in Table 4.

Table 4
Typical example showing effect of peak energy used for calibration during evaluation of alpha spectrum for $^{240}Pu/^{239}Pu$ atom ratio

Energy used for calibration	Area under the peak		$^{240}Pu/^{239}Pu$ amount ratio by HRAS	HRAS/TIMS[a]
	^{240}Pu	^{239}Pu		
5.156 MeV (^{239}Pu)	83172	90354	0.2502	0.64
5.168 MeV (^{240}Pu)	118123	59986	0.5352	1.37
5.162 MeV	103041	72063	0.3886	1.00

[a] $^{240}Pu/^{239}Pu$ atom ratio by TIMS = 0.3902 ± (0.01%).

This work demonstrates the applicability of HRAS and the analysis program WinALPHA for the determination of $^{240}Pu/^{239}Pu$ atom ratios. Rigorous evaluation of the analysis program varying different parameters, e.g. source quality, counting statistics, etc. is necessary for enhancing the confidence in using the software on a routine basis.

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Table 3
Typical data after spectral fitting using WinALPHA on replicate sources for PHWR Pu samples

Sample no.	Source no.	Time of counting (s)	Area under the peak		Parameters after spectral fitting			$^{240}Pu/^{239}Pu$ atom ratio by HRAS	Mean value from HRAS/TIMS value
			^{240}Pu	^{239}Pu	χ^2	Tail parameter	FWHM (keV)		
1	A	850	9479	5643	3.0	1.02	17.7	0.4566 ± (1.6%)[a]	1.029
	B	2400	18843	11957	2.7	1.01	16.2	0.4283 ± (1.2%)	
2	A	2300	20783	13031	3.5	1.02	16.9	0.4335 ± (1.1%)	1.036
	B	1150	18828	12553	2.6	0.96	15.8	0.4077 ± (1.1%)	
3	A	10220	103041	72063	11.9	1.00	16.2	0.3886 ± (0.5%)	0.986
	B	18110	136125	97132	16.7	1.01	16.9	0.3809 ± (0.4%)	
4	A	13180	141488	109582	11.9	1.05	17.6	0.3509 ± (0.4%)	1.008
	B	6420	150385	125655	15.9	1.04	17.7	0.3253 ± (0.4%)	

[a] The uncertainty is calculated by combining, in quadrature, the uncertainties on counting data and the half-life values.

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