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Accuracy of Calorimetric Plutonium Determinations

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Abstract

As calorimetry is one of the few methods for an absolute determination of plutonium, it is devoid of problems associated with the calibration procedure by means of so-called standards. So the main sources of error in the nondestructive assay of plutonium by calorimetric methods are

- errors in the measurement of the power output of the sample,
- errors in the isotopic composition, and
- uncertainties of the specific power of the isotopes involved.

An estimate of the effect of the different error sources upon the overall accuracy shows that, depending upon the composition of the sample material, each of the three can account for the largest error contribution.

Zusammenfassung

Kalorimetrie ist eine der wenigen Methoden für eine absolute Plutoniumbestimmung, weil keine Eichungen anhand sogenannter Standards erforderlich sind. Die hauptsächlichen Fehlerquellen bei der zerstörungsfreien Bestimmung von Plutonium nach kalorimetrischen Verfahren sind daher

- Fehler in der Messung der Wärmeleistung der Probe,
- Fehler in der Isotopenzusammensetzung und
- Unsicherheiten der spezifischen Leistung der beteiligten Isotope.

Eine Abschätzung über die Auswirkung der verschiedenen Fehlerquellen auf die Gesamtgenauigkeit zeigt, daß, je nach Zusammensetzung des Probenmaterials, jede der drei den Hauptbeitrag liefern kann.

1. Introduction

Calorimetry is a slow, but simple and accurate method for the nondestructive determination of plutonium in nuclear fuel. Unlike most other methods for nondestructive fuel assay, which depend upon the availability of a set of accurately known standards resembling the unknown samples as closely as possible, no standards are needed in calorimetry because the alpha decay heat, after conversion into electrical power, can be measured absolutely and to high precision. On the other hand, this procedure requires the exact knowledge of the isotopic composition and of the specific power (say, in watts/gram) of each of the isotopes involved. Because the composition cannot, to date, be measured nondestructively to the required accuracy but must be determined by alpha or mass spectrometry, calorimetry may be called a semi-nondestructive, though absolute, plutonium assay method. The error associated with the result of a calorimetric plutonium determination will thus depend upon uncertainties in

- the measurement of the power output from the sample,
- the determination of the isotopic composition,
- the knowledge of the specific power constants, and
- the time elapsed between the separation of the ^{241}Pu decay product ^{241}Am and isotopic analysis, and the calorimetric measurement.

It is the purpose of this paper to investigate the influence of the different sources of error upon the accuracy of the final result of a calorimetric plutonium determination.

2. The Model

We assume that the separation of americium and analysis of the isotopic composition are performed about simultaneously[+] at time t_a, and that the calorimetric measurement occurs at some later time $t_m = t_a + t$. Then, using H for the heat output in the measurement, the plutonium quantity M is computed from the relation

$$M = H \Big/ \sum_{i=8}^{a} p_{mi}\, s_i \quad \text{, with} \tag{1}$$

$$\sum_{i=8}^{2} p_{mi} = 1 \quad , \tag{2}$$

where p_{mi} is the fraction of isotope i in the material at time t_m, and s_i its specific power. For plutonium only the last digit of the mass number, for ^{241}Am an "a" is used as index. Note that the sum in eq.(2) extends only over the plutonium isotopes.

Now the p_{mi} must be computed from the fractional abundances p_{ai} ($\equiv p_i$, dropping the index a) at time t_a from

$$p_{mi} = p_i\, e^{-t/\tau_i} \Big/ \sum_{i=8}^{2} p_i\, e^{-t/\tau_i} \quad (i=8...2) \text{ and} \tag{3}$$

$$p_{ma} = p_1\, (1-e^{-t/\tau_1}) \Big/ \sum_{i=8}^{2} p_i\, e^{-t/\tau_i} \quad . \tag{4}$$

[+] If the ^{238}Pu content is determined by α spectrometry, this assumption is certainly reasonable because ^{238}Pu α peaks at 5452 and 5495 keV are perturbed by ^{241}Am α peaks at 5443 and 5486 keV, and no decent ^{238}Pu determination is possible in the presence of americium.

Here $\tau_i = T_{hi}/\ln 2$ is the decay constant and T_{hi} the half-life of isotope i. We assume that

$$T_{hi} \ll t \qquad (i=8,1) \text{ and} \tag{5}$$

$$T_{hi} = \infty \qquad (i=9,0,2,a). \tag{6}$$

This latter assumption for T_{ha} is necessary for the validity of eq.(4). Eq.(1) then becomes

$$M = H \frac{1 - \sum_{i=8,1} t \ln 2/T_{hi}}{p_1 s_a t \ln 2/T_{h1} + \sum_{i=8,1} p_i s_i (1 - t \ln 2/T_{hi}) + \sum_{i=9,0,2} p_i s_i} . \tag{7}$$

If the relative errors $\delta x_j/x_j$ of the variables x_j (standing for the p_i, s_i, T_{hi}, t and H) are independent+ the relative error $\delta M/M$ of the quantity of plutonium can be expressed as

$$\sigma M = \sqrt{\sum_j (w_j \sigma_j)^2} \tag{8}$$

where the abbreviations $\delta M/M = \sigma M$ and $\delta x_j/x_j = \sigma x_j$ for the relative errors and $(x_j/M)(\partial M/\partial x_j) = wx_j$ for the relative weights have been used. If the denominator of eq.(7) is denoted by D, the wx_j are readily computed as

$$wH = 1, \tag{9}$$

$$wp_i = ws_i = \left| s_i p_i / D \right| \qquad (i=9,0,2), \tag{10}$$

$$wp_8 = \left| \left[(H/M - s_8)(t \ln 2/T_{h8}) + s_8 \right] p_8 / D \right|, \tag{11}$$

$$wp_1 = \left| \left[(H/M - s_1 + s_a)(t \ln 2/T_{h1}) + s_1 \right] p_1 / D \right|, \tag{12}$$

$$ws_i = \left| \left[1 - t \ln 2/T_{hi} \right] p_i s_i / D \right|, \ (i=8,1) \tag{13}$$

$$ws_a = \left| \left[t \ln 2/T_{h1} \right] p_1 s_a / D \right|, \tag{14}$$

$$wT_{h8} = \left| \left[H/M - s_8 \right] \left[p_8 t \ln 2 / T_{h8} \right] / D \right|, \tag{15}$$

$$wT_{h1} = \left| \left[H/M + s_a - s_1 \right] \left[p_1 t \ln 2/T_{h1} \right] / D \right|, \tag{16}$$

$$wt = \left| \left[\frac{p_8 s_8}{T_{h8}} - \frac{p_1 (s_a - s_1)}{T_{h1}} - \frac{H}{M} \left(\frac{p_8}{T_{h8}} + \frac{p_1}{T_{h1}} \right) \right] \frac{t \ln 2}{D} \right| . \tag{17}$$

3. Accuracy of Parameters

3.1. Power Output

Present-day calorimeters achieve, under routine conditions$^{2,3)}$, accuracies σM between 0.25 and 0.5 %. There is little doubt that this error will be reduced further so the lower of the two values (0.25 %) is certainly a realistic estimate.

+ In a rigourous treatment it would have to be considered that there are indeed correlations between the $\delta x_j/x_j$ not only because $\sum p_i = 1$ but also because some, but not all of the s_i are computed from the T_{hi} into the evalutation of which enter, in turn, all T_{hk} $(k \neq i)$. An investigation of this question is presently under way$^{1)}$.

3.2. Isotopic Composition

The determination of the abundance of ^{238}Pu is most delicate. Mass spectrometry requires that

i) samples be absolutely free ($\lesssim 10^{-5}$) from uranium and organic impurities, and that

ii) memory effects in the mass spectrometer be under careful control.

Alpha spectrometry is limited by

i) the high-energy tail of the very intense α group of ^{239}Pu and ^{240}Pu around 5150 keV, and

ii) the presence of small quantities of americium (cf. first footnote in paragraph 2).

Alpha spectrometry is certainly the more accurate method, at least for abundances $\lesssim$ 0.1 %, and an error σp_8 of 2.5 % appears reasonable[4].

Isotopic ratios of the other plutonium isotopes are always determined by mass spectrometry. It seems to be generally accepted[5] that, under normal laboratory conditions, accuracies are achieved that amount to

0.1 % - 0.3 %	for ratios of	1 -	10
0.3 % - 1.0 %	" " "	10 -	100
1.0 % - 5.0 %	" " "	100 -	1000.

If the ratios are denoted by α the error $\delta\alpha/\alpha$ follows roughly the law

$$\delta\alpha/\alpha = 10^{-3}\sqrt{\alpha} \qquad (18)$$

from which the errors in the abundances, $\delta p_i/p_i$, are computed as

$$\delta p_9/p_9 = 10^{-3}\sqrt{\sum_{i\neq 9}\alpha_i}\; p_9, \text{ and} \qquad (19)$$

$$\delta p_i/p_i = 10^{-3}\, p_9 \sqrt{\left[(1+\sum_{j\neq i}\alpha_j)^2/\alpha_i\right] + \sum_{j=i}\alpha_j} \quad (i=8,0,1,2) \qquad (20)$$

with $\alpha_i = p_i/p_9$.

3.3. Specific Power

The best values available to date for the specific powers of the isotopes involved are listed in Table I. A critical evaluation of these data is highly desirable.

3.4. Time

It occurs that the americium separation and isotopic analysis are not performed simultaneously and only one of the dates is available at the time of calorimetry, or that only the month is given in which the separation or analysis took place. Although this error could be made zero, a figure of t = 0,5 % was assumed to show the effect upon the total error.

Table I.

Specific powers of the plutonium isotopes and of ^{241}Am, and associated estimated standard deviations. If data are calculated from α decay energy and half-life, these values are also given, with errors as quoted by the authors.

Isotope	Specific Power mW / g	Relative Error	Data Used, and References Q / keV	T$_h$ / years
^{238}Pu	567.2	0.027 %	5.592.8 ± 0.8 [6]	87.80 ± 0.02 [7]
^{239}Pu	1.923	0.1 %	calorimetry [8]	
^{240}Pu	7.008	0.76 %	5.255.3 ± 0.7 [6,9]	6620 ±50 [10]
^{241}Pu	3.62	4.9 %	calorimetry [11]	
^{242}Pu	0.1137	0.45 %	4.980.3 ± 7.0 [9,12]	(3.834 ± 0.016)×10^5 [13]
^{241}Am	114.5	0.15 %	calorimetry [14]	

3.5. Half-life of ^{238}Pu and ^{241}Pu

It follows from Table I that σT_{h8} = 0.02 % and σT_{h1} = 1.85 %.

4. Total Error

In Table II the most important contributions, in terms of weights wx_j and errors σx_j of the individual parameters, have been listed for different kinds of reactor grade plutonium[4,15]. Times after separation of americium of 0, 90, and 180 days have been considered realistic. The largest effect is clearly the uncertainty in p_8, the percentage of ^{238}Pu in the mixture. Only for very low contents in ^{238}Pu ($\lesssim$ 0.05 %) the error in the heat output H becomes dominant. Next come the uncertainties in s_o and s_1, the specific powers of ^{240}Pu and ^{241}Pu, with the relative importance depending upon the composition. All other contributions remain unsignificant until accuracies of p_8 and H can be improved by factors of at least 10 and about 3, respectively.

Table II

Contributions to the overall relative standard deviation σM of a calorimetric plutonium determination, in terms of weights wx_j and relative errors σx_j of the different parameters according to the formula $\sigma M = \sqrt{\sum_i (wx_j \; \sigma x_j)^2}$, for different reactor-grade plutonium. For clarity wx_j and σx_j are put in heavy boxes.

Fuel Batch	ALKEM, 1968		Yankee V + VI, 1		Yankee V + VI, 16	
Composition	p_i in %	σp_i in %	p_i in %	σp_i in %	p_i in %	σp_i in %
Pu-238	0.041	2.50	0.289	2.50	1.228	2.50
Pu-239	90.517	0.03	85.050	0.04	69.309	0.04
Pu-240	8.265	0.30	10.294	0.26	16.337	0.18
Pu-241	1.113	0.89	4.011	0.44	10.853	0.23
Pu-242	0.064	3.40	0.356	1.52	2.274	0.42

Time after separation, days		0	90	180	0	90	180	0	90	180
Quantity x_j	Relative error σx_j in %	Weight wx_j								
Power output H	0.25	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Composition p_8	see above	0.0897	0.0890	0.0883	0.3958	0.3902	0.3848	0.7079	0.6971	0.6866
p_9		0.6713	0.6676	0.6639	0.3949	0.3901	0.3854	0.1355	0.1337	0.1319
p_o		0.2234	0.2221	0.2209	0.1742	0.1721	0.1700	0.1164	0.1148	0.1133
p_1		0.0155	0.0214	0.0271	0.0351	0.0481	0.0608	0.0399	0.0555	0.0706
p_2		0.0000	0.0000	0.0000	0.0001	0.0001	0.0001	0.0003	0.0003	0.0003
Specific Power s_8	0.03	0.0897	0.0890	0.0883	0.3958	0.3902	0.3848	0.7079	0.6971	0.6866
s_9	0.10	0.6713	0.6676	0.6639	0.3949	0.3901	0.3854	0.1355	0.1337	0.1319
s_o	0.76	0.2234	0.2221	0.2201	0.1742	0.1721	0.1700	0.1164	0.1148	0.1133
s_1	4.90	0.0155	0.0153	0.0150	0.0351	0.0342	0.0334	0.0399	0.0389	0.0379
s_2	0.45	0.0000	0.0000	0.0000	0.0001	0.0001	0.0001	0.0003	0.0003	0.0003
s_a	0.15	0	0.0060	0.0119	0	0.0134	0.0264	0	0.0152	0.0300
Half-life T_{h8}	0.02	0	0.0002	0.0003	0	0.0008	0.0015	0	0.0013	0.0026
T_{h1}	1.85	0	0.0059	0.0118	0	0.0134	0.0265	0	0.0161	0.0317
Time t	0.50	0	0.0057	0.0114	0	0.0127	0.0251	0	0.0147	0.0291
Total error in percent		0.40	0.40	0.40	1.05	1.03	1.02	1.80	1.77	1.75
Main contributions from x_j =		H p_8 s_o s_1, s_9, p_o			p_8 H s_1 s_o			p_8 H s_1 s_o		
Approximate value of $wx_j \sigma x_j$ in %		0.25 0.22 0.17 0.07 each			0.98 0.25 0.17 0.13			1.74 0.25 0.19 0.09		

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