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Plutonium Isotopic Analysis of Highly Enriched Mixed Oxides

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PLUTONIUM ISOTOPIC ANALYSIS OF HIGHLY ENRICHED MIXED OXIDES

by

S. D. Clement and R. H. Augustson

ABSTRACT

We investigated the analysis method used by the International Atomic Energy Agency (IAEA) to determine the plutonium isotopic composition of highly enriched mixed oxides (MOX). The IAEA currently uses the Cicero multichannel analyzer and the IAEAPU algorithm for its analysis. In our investigation the plutonium isotopic measurements were found to be good for PuO_2 powder or low-enriched MOX, but unacceptable for highly enriched MOX in IAEA special nuclear material (SNM) accountability applications. The gamma-ray interferences from ^{235}U resulted in underestimation of the isotopic composition of ^{239}Pu and overestimation of all other plutonium isotopes. Samples with high ^{240}Pu content were found to have significantly higher error in plutonium isotopic analyses of highly enriched MOX. Code modifications or use of calibration curves are necessary for plutonium isotopic analyses of highly enriched MOX in IAEA SNM accountability applications.

I. INTRODUCTION

Concern about the spread of nuclear weapons has brought attention to the need for widespread nuclear materials accountability. The responsibility at the international level lies with the International Atomic Energy Agency (IAEA). The IAEA is responsible for nuclear materials accountability for those countries that have signed the Nuclear Non-Proliferation Treaty and therefore fall under the realm of IAEA safeguards. The primary goal of the IAEA is to detect the theft or diversion of special nuclear materials (SNM) for possible use in weapons programs or terrorist activities.

Nuclear materials accountability has been revolutionized by the use of nondestructive assay (NDA) techniques. These techniques allow the contents of an SNM package to be analyzed for material type, quantity, and isotopic abundance without breaching the container and disturbing the sample. Implementation of safeguards instrumentation therefore does not require modification to existing facility hardware but simple addition of equipment. SNM identification comes from analysis of radiation produced by the materials. Active and passive neutron coincidence counting provide us with the quantity of material, and high-resolution gamma-ray spectrometry provides us with the isotopic composition.

Different NDA techniques are used for different materials. In most situations, both neutron and gamma-ray assays must be combined to yield the required information for SNM accountability. For example, to quantitatively measure plutonium by nondestructive techniques requires high-level neutron coincidence counting or calorimetry and plutonium isotopic abundance measurements. This approach has been developed into a field-usable system for the IAEA^{1,2} [and implemented in the Cicero multichannel analyzer (MCA)] by Lawrence Livermore National Laboratory.

This investigation was conducted to examine the effects of highly enriched mixed oxides (MOX) on measured plutonium isotopic compositions. This report explains the calculational method for determining the isotopics, describes the experiment, discusses the results, and makes recommendations concerning the analysis.

II. THEORY

High-resolution gamma-ray spectrometry measurements are made on bulk plutonium samples to determine their isotopic abundances. The isotopic ratios are calculated from gamma-ray peaks in the 110- to 400-keV region. The general method for calculating these ratios is based on the following equation:

$$\frac{N_i}{N_j} = \frac{I_i B_i \epsilon_i t_i}{I_j B_j \epsilon_j t_j} \quad (1)$$

where N_i/N_j = atom ratios of isotopes i and j,

I = observed peak intensity,

B = gamma-ray branching intensity,

ϵ = detector efficiency, and

t = half-life.

The half-life and branching intensity are known values, whereas the detector efficiency is a function of energy. The influence of efficiency is minimized by using gamma-ray peaks that are nearly equal in energy. Neighboring peaks of known relative intensities are used to establish a calibration curve and correct for the small energy differences.

Accurate final results are dependent upon precise peak-intensity measurements. This requires proper delineation of peak shape, accurate background measurements, and methods for unfolding peak multiplets. The equation describing the peak shape consists of a Gaussian distribution function and a short-term tailing function:

$$y_i = y_0 e^{\frac{\alpha(X_i - X_0)^2}{2}} + A y_0 e^{\frac{B(X_i - X_0)}{C}} \left[1 - e^{\frac{C\alpha(X_i - X_0)^2}{2}} \right] \delta \quad (2)$$

where Y_1 = net data counts at i ,
 Y_0 = peak height,
 α = peak width parameter,
 X_1 = channel value at i ,
 X_0 = channel value at the peak centroid,
 A, B, C = shape parameters, and
 $\delta = 1$ for $X_1 - X_0 < 0$; 0 for $X_1 - X_0 > 0$.

All peak parameters are determined from the 148.6-keV peak of ^{241}Pu and the 208.0-keV peak of ^{237}U . The only remaining parameter needed to describe the peak shape is the peak height. The equation then becomes linear in form and can be solved by a linear least-squares method.

The background beneath the peak must be removed before the net peak area can be determined. The following function is used to produce smoothed background steps at each peak position.

$$B_i = b_n + (b_m - b_n) \frac{\sum_{j=n}^{j=i} Y_j}{\sum_{k=n}^{k=m} Y_k}, \quad (3)$$

where B_i = computed background at i ,
 Y_i = spectrum count of channel i ,
 b_n = average low-energy background, and
 b_m = average high-energy background.

The background at channel i (B_i) can then be subtracted from the spectrum count of channel i (Y_i) to get the net counts.

III. EXPERIMENT

The algorithm IAEAPU is designed to return the isotopic analysis of pure plutonium samples that have no interferences from other radioactive materials. With the presence of other radioactive materials that emit gamma rays similar

in energy to those of plutonium, interferences can occur. Consequently, the results of the isotopic analysis will be changed because of the additional gamma rays. This situation is precisely what happens when an oxide containing both uranium and plutonium is analyzed by the Cicero. Uranium-235 gamma rays interfere with plutonium gamma rays and produce erroneous results. Figure 1 illustrates some of the interferences produced when a MOX sample is analyzed.

Fig. 1. Mixed-oxide and PuO_2 spectra.

The experiment consisted of studying the effect of ^{235}U interferences that occur in MOX samples. Because of the unavailability of highly enriched MOX for measurement, a scheme was developed to simulate MOX samples from pure PuO_2 powder and high-enriched uranium (HEU) foils.

A. Equipment

An intrinsic germanium detector was used for the high-resolution spectrometry. The output signal was fed to the Cicero 8-k MCA. The plutonium isotopic analysis unit built into the Cicero MCA examines the spectra and performs the calculations. The algorithm will best fit the peaks with the most channels. It is therefore desirable to have the highest gain possible. Table I lists the plutonium and uranium samples used to simulate the MOX; the Cicero data collection parameters are presented in the Appendix.

B. Procedure

The plutonium sample was first measured for 2000 s and a data analysis was performed. The HEU sample spectrum was then collected for 100 s, overlaying the plutonium spectrum, and the data analysis was repeated. The uranium samples were counted and analyzed in 100-s increments until a $^{235}\text{U}/^{239}\text{Pu}$ value of approximately 10 was reached.

TABLE I
PuO₂ AND URANIUM SAMPLES

Sample No.	Material	Mass (g)	Enrichment (%)	Isotopic Abundances				
				^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
118	PuO ₂	1.809	-	0.028	90.12	8.98	0.758	0.104
119	PuO ₂	1.722	-	0.04	86.87	11.74	1.17	0.167
116	PuO ₂	1.9002	-	0.384	78.33	15.18	5.08	1.03
120	PuO ₂	2.0307	-	0.384	78.33	15.18	5.08	1.03
121	PuO ₂	~3	-	0.0628	81.712	16.442	1.432	0.352
46	U	0.387	93.15	-	-	-	-	-
77	U	0.468	93.0	-	-	-	-	-
80	U	0.440	93.0	-	-	-	-	-

IV. RESULTS

The Cicero plutonium isotopic analysis unit utilizes 37 separate gamma rays grouped into nine regions. Table II lists the gamma rays by energy and gives the corresponding isotope and region. The peak areas are calculated once Eq. (2) has been fit to the peaks and the background has been removed. The peak areas are displayed in the analysis output along with the gain, channel-zero energy, resolution, and isotopic ratios. An example of the Cicero output is illustrated in Fig. 2. Note that the algorithm calculates the $^{235}\text{U}/^{239}\text{Pu}$ ratio.

TABLE II
ANALYZED GAMMA RAYS WITH CORRESPONDING ISOTOPES

<u>Gamma Energy</u> <u>(keV)</u>	<u>Isotope</u>	<u>Region</u>
122.92	^{241}Am	I
123.61	^{239}Pu	I
124.50	^{239}Pu	I
125.20	^{239}Pu	I
125.29	^{241}Am	I
129.29	^{239}Pu	I
141.56	^{239}Pu	II
144.21	^{239}Pu	II
146.07	^{239}Pu	II
146.55	^{241}Am	II
148.56	^{241}Pu	II
150.10	^{241}Am	II
152.67	^{238}Pu	III
154.19	Sum	III

TABLE II (cont)

<u>Gamma Energy</u> <u>(keV)</u>	<u>Isotope</u>	<u>Region</u>
159.95	^{241}Pu	IV
160.18	^{239}Pu	IV
160.30	^{240}Pu	IV
161.48	^{239}Pu	IV
164.59	^{237}U	IV
165.93	^{241}Am	IV
185.72	^{235}U	V
203.53	^{239}Pu	VI
207.99	$^{237}\text{U}-^{241}\text{Am}$	VII
322.38	$^{237}\text{U}-^{241}\text{Am}$	VIII
332.84	^{239}Pu	VIII
335.42	$^{237}\text{U}-^{241}\text{Am}$	VIII
336.10	^{239}Pu	VIII
341.51	^{239}Pu	VIII
345.01	^{239}Pu	VIII
367.04	^{239}Pu	IX
368.54	^{239}Pu	IX
368.60	^{241}Am	IX
370.93	^{241}Am	IX
375.04	^{239}Pu	IX
376.59	^{241}Am	IX
380.16	^{239}Pu	IX
382.74	^{239}Pu	IX

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Spec # 3; LT = 2000 S

Gain = 0.1145 keV/CH

CHNL zero E = 113.955

FWHM (208 keV) = 0.907

Peak en	Counts	%ER
185.72	0.	60.1

Peak en	Counts	%ER
203.54	6927.	1.5

Peak en	Counts	%ER
208.00	439530.	0.2

Peak en	Counts	%ER
122.92	20323.	0.9
123.61	298.	FIXD
124.50	910.	FIXD
125.21	848.	FIXD
125.29	78873.	0.4
129.29	92923.	0.4

Peak en	Counts	%ER
141.57	204.	46.3
141.21	4428.	2.5
146.08	1869.	FIXD
146.56	9738.	1.5
148.56	191185.	0.2
150.11	1577.	FIXD

Peak en	Counts	%ER
152.68	14428.	1.4
154.20	0.	52.0

Peak en.	Counts	%ER
159.96	6037.	FIXD
160.20	86.	FIXD
160.29	5965.	2.3
161.45	1672.	5.7
164.58	46304.	0.5
165.93	347.	25.5

238PU/239PU = 0.003577
+ - 0.000075

240PU/239PU = 0.263086
+ - 0.007487

241PU/239PU = 0.038897
+ - 0.000576

241AM/241PU = 0.619975
+ - 0.010919

235U/239PU = 0.000000
+ - 0.000000

Time since Sep =
3671.+ - 52. days

%238 = 0.272 + - 0.006

%239 = 75.933 + - 0.442

%240 = 19.977 + - 0.580

%241 = 2.954 + - 0.47

%242 = 0.864 CALC

%AM/PU = 1.831 + - 0.43

Fig. 2. Sample Cicero output.

HEU foils were counted on top of each PuO_2 spectra in 100-s increments with the isotopic analyses being repeated after each increment. As the uranium count time increased, the enrichment of the simulated MOX increased. For each additional 100-s uranium count, a linear increase in the $^{235}\text{U}/^{239}\text{Pu}$ ratio was observed. With the the increase in enrichment, the calculated isotopic error relative to the declared isotopics (see Table I) increased.

The ^{238}Pu , ^{240}Pu , and ^{241}Pu concentrations in each sample were well calculated at low $^{235}\text{U}/^{239}\text{Pu}$ values. However, with increased values of $^{235}\text{U}/^{239}\text{Pu}$, the calculated fractional content of each isotope became increasingly over-predicted. The relative error vs $^{235}\text{U}/^{239}\text{Pu}$ ratio for ^{238}Pu , ^{240}Pu , and ^{241}Pu is illustrated in Figs. 3 to 5, respectively. In each case, the magnitude of the error is highest for the samples with the highest ^{240}Pu content.

Figure 6 illustrates the relative error vs $^{235}\text{U}/^{239}\text{Pu}$ ratio for ^{239}Pu . This fissile isotope is especially significant in IAEA SNM accountability

Fig. 3. Relative error for ^{238}Pu .

Fig. 4. Relative error for ^{240}Pu .

Fig. 5. Relative error for ^{241}Pu .

Fig. 6. Relative error for ^{239}Pu .

applications. The figure shows that the ^{239}Pu content is increasingly underpredicted as the $^{235}\text{U}/^{239}\text{Pu}$ ratio increases. Again, as with the previous isotopes, the magnitude of the error is largest in those samples with the largest ^{240}Pu content.

The relative error for ^{242}Pu (Fig. 7) is slightly different than that exhibited by the other isotopes. For the other isotopes, as Figs. 3 to 6 show, the magnitude of the relative errors begins to saturate with increased values of $^{235}\text{U}/^{239}\text{Pu}$. The error for ^{242}Pu is better represented as linear. The lack of this saturation effect is due to the uncertainty of the ^{241}Pu isotopic concentration. Therefore, the ^{241}Pu isotopic concentration must be corrected for decay since the time of removal of the isotope from the reactor. However, in many cases the removal date is unknown. The ^{242}Pu isotopic concentration is calculated from the following correlation:

$$(242) = \frac{k(240)(241)}{(239)^2} \quad (4)$$

The magnitude of the error for the isotope ^{242}Pu at a given $^{235}\text{U}/^{239}\text{Pu}$ value is greater than that of any of the other isotopes.

V. ANALYSIS OF RESULTS

The plutonium isotopic composition measurements made by the Cicero MCA and analyzed by the algorithm IAEAPU produced good results for pure PuO_2 powder samples. The results are, in fact, excellent for ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{241}Pu , being within a few per cent; the results for ^{242}Pu are moderate, being

Fig. 7. Relative error for ^{242}Pu .

off by up to 15%. The results indicate that the IAEA would benefit by using this analysis method for SNM accountability of pure PuO_2 samples.

Uranium peaks can interfere directly with plutonium peaks or with background regions of one of the nine peak groups. Direct interference with a peak will make the peak contain a larger number of counts so that the results of the computer analysis will exhibit a higher concentration in the isotope corresponding to the peak interfered with. This effect in turn will cause the remaining isotopes to be underpredicted because the sum of the isotopic fractions must equal 1.0. Interference peaks that occur in the background regions will produce lower isotopic compositions for each isotope having a peak in the region. Background interferences increase the background counts, which are subtracted from the peak areas in the group. The additional reduction in peak areas makes the affected isotopes appear to have smaller abundances, and the remaining isotopes appear to have larger abundances than they really have. The larger the interference peak, the larger the error in the isotopic measurement.

The isotopic analysis uses peaks that range from 110 to 400 keV. Any uranium gamma rays that have energies out of this range can immediately be ignored. Uranium-238 has only four gamma rays between these energies; none of the four directly interfere with the plutonium peaks or any of the background regions. We can therefore conclude that ^{238}U does not interfere with plutonium isotopic measurements. Figures 3 to 7 illustrate that at low $^{235}\text{U}/^{239}\text{Pu}$ ratios where virtually all of the uranium in the MOX is ^{238}U , the error is very small. We can conclude from Figs. 3 to 7 that all interferences must be from ^{235}U because as the $^{235}\text{U}/^{239}\text{Pu}$ ratio increases, the error increases.

Sixteen ^{235}U gamma rays are present in the 110- to 400-keV region. The most prominent gamma ray is at 185.7 keV (see the MOX spectra of Fig. 1). Of the sixteen ^{235}U gamma rays, five significantly interfere with the plutonium spectra; Table III lists these gamma rays and their interferences. The first interference is at 140.75 keV; this gamma-ray lies in the low-energy background region of group 2. The branching ratio is small, therefore the impact of the interference is small. The next interference occurs at 143.77 keV; this gamma ray directly interferes with the 144.21-keV ^{239}Pu peak of group 2. The effect of this interference on plutonium isotopic measurements would be to increase the calculated isotopic composition of ^{239}Pu , whereas the 140.75-keV low-energy background interference would tend to decrease the isotopic composition of any isotopes having peaks in group 2. The next interference is the

TABLE III
URANIUM-235 INTERFERENCES

^{235}U Gamma-Ray Energy (keV)	Branching Intensity	Plutonium Gamma-Ray Interference ^a (keV)	Isotope Peak	Group
140.75	0.00208	LEB	-	2
143.77	0.107	144.21	^{239}Pu	2
163.37	0.0485	164.59	^{237}U - ^{241}Am	4
202.1	0.0107	LEB	-	6
205.33	0.0487	HEB	-	6
205.33	0.0487	LEB	-	7

^aLEB stands for low-energy background; HEB, for high-energy background.

164.59-keV peak of ^{237}U - ^{241}Am in group 4. Both ^{237}U and ^{241}Am are decay products of ^{241}Pu . The ^{237}U - ^{241}Am peaks are sometimes used to determine the ^{241}Pu isotopic composition. Again, with the direct interference, the isotopic composition of ^{241}Pu increases. Group 6 consists of one peak, a ^{239}Pu gamma ray at 203.53 keV. This single peak has both low- and high-energy background interferences at 202.1 keV and 205.33 keV, respectively. Both background interferences cause the ^{239}Pu peak to be dramatically reduced in size. This interference is the most significant in that it produces the largest percentage of error (see Figs. 3 to 7). The ^{239}Pu fraction is the only isotope to be underpredicted with increasing $^{235}\text{U}/^{239}\text{Pu}$. All other isotopes are overpredicted to balance the isotopic fractions. The final interference is at 205.33 keV, a low-energy background interference with group 7.

All these interferences contribute to error in either the positive or negative direction, but only the effect of the group 6 background interferences can be seen. Not only do the interferences displace the plutonium isotopic measurements, but also the $^{235}\text{U}/^{239}\text{Pu}$ ratio. This ratio is determined from the 185.7-keV ^{235}U peak and the 203.6-keV ^{239}Pu peak. The background interferences on the ^{239}Pu peak cause it to look much smaller, increasing the value of $^{235}\text{U}/^{239}\text{Pu}$. This effect can be observed by studying MOX samples of known

enrichments. Several samples from the Hanford Engineering and Development Laboratory (HEDL) were analyzed with the Cicero MCA. From the known uranium enrichment and isotopics, the actual $^{235}\text{U}/^{239}\text{Pu}$ ratio can be calculated and compared with the Cicero value. These data are presented in Table IV. Table IV shows that the ratio of the Cicero $^{235}\text{U}/^{239}\text{Pu}$ value to the actual value increases with uranium enrichment. For a standard MOX sample of 80% uranium enrichment, the Cicero MCA will calculate a $^{235}\text{U}/^{239}\text{Pu}$ value approximately two times the actual value.

The ^{240}Pu content plays a significant role in the isotopic measurement of both MOX and pure PuO_2 samples. Only one ^{240}Pu peak (160.3 keV) is available for measurement. For samples having low ^{240}Pu content, short count times may not provide the required statistics for the ^{240}Pu analysis. For pure PuO_2 samples, large ^{240}Pu fractions have no effect on the isotopic analysis. In MOX samples however, the ^{240}Pu content is related to the magnitude of the relative error; the higher the ^{240}Pu content, the larger the error. Sample 120 has a ^{240}Pu content of 15% as compared to 11% for sample 119. Comparison of the two samples in Fig. 3 shows that the relative error for sample 120 is 20% higher at a $^{235}\text{U}/^{239}\text{Pu}$ ratio of ~ 5 . At lower $^{235}\text{U}/^{239}\text{Pu}$ values, the error is about the same for both samples.

The Cicero MCA with the IAEAPU algorithm would not be acceptable for plutonium isotopic measurement of highly enriched MOX for IAEA SNM accountability applications. The fissile isotope ^{239}Pu would be underestimated in measurements of highly enriched MOX samples. Two courses of action might solve the

TABLE IV
HEDL MIXED-OXIDE SAMPLES

Sample No.	Enrichment (%)	$^{235}\text{U}/^{239}\text{Pu}$		Ratio
		Cicero	Actual	
1939	80.2	5.8	2.77	2.1
1940	80.2	6.45	2.76	2.3
1987	30	1.34	1.04	1.3
2006	93	8.83	3.22	2.7

problem. First, the algorithm could be modified to correct for ^{235}U interferences. The code could identify the interferences of significance, determine the peak intensities, and subtract the ^{235}U counts from the plutonium spectrum. The second course of action would be to use well-established calibration curves to correct the results distorted by the ^{235}U interferences. Curves such as those shown in Figs. 3 to 7 could be used, but caution must be observed. These curves were generated using the $^{235}\text{U}/^{239}\text{Pu}$ values calculated by the Cicero and therefore incorporate the uncertainty in the $^{235}\text{U}/^{239}\text{Pu}$ ratio. These curves apply only if the Cicero-calculated ^{240}Pu content and $^{235}\text{U}/^{239}\text{Pu}$ ratio are used.

REFERENCES

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2. W. D. Ruhter, "A Portable Microcomputer for the Analysis of Plutonium Gamma-Ray Spectra," Vol. II, Lawrence Livermore National Laboratory report UCRL-53506 (1984).

APPENDIX

DATA COLLECTION PARAMETERS

High voltage = -2500 V

Course gain = 50

Fine gain = 0.674

Back bias = 927

PUR: On

Rate: Auto

BLR: Auto and Sym

ADC: Var DT and DC Input

Amp polarity: positive (PGT detector with negative bias)

Shaping time = 2 μs

RTP = 8 μs

Cadmium absorber = 2.286 mm

Maximum count rate = 20 000 counts/s