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The Concentration of ^{236}Pu Daughters in Plutonium for Application to MOX Production from Plutonium from Dismantled US Nuclear Weapons

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THE CONCENTRATION OF ^{236}PU DAUGHTERS IN PLUTONIUM FOR APPLICATION TO MOX PRODUCTION FROM PLUTONIUM FROM DISMANTLED US NUCLEAR WEAPONS

by

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ABSTRACT

The isotope ^{236}Pu in the weapons-grade plutonium to be used in the US MOX (mixed-oxide) plant is of concern because the daughter products of ^{236}Pu are sources of high-energy gamma rays. The ^{208}Tl daughter of ^{236}Pu emits intense, high-energy gamma rays that are important for radiation exposure calculations for plant design. It is generally thought that the concentrations of ^{236}Pu and its daughters are well below 10^{-10}, but these concentrations are generally below the detection limits of most analytical techniques. One technique that can be used to determine the concentration ^{208}Tl is the direct measurement of the intensity of the ^{208}Tl gamma rays in the gamma-ray spectrum from plutonium. Thallium-208 will be in equilibrium with ^{228Th}, and may very well be in equilibrium with ^{232}U for most aged plutonium samples. We have used the FRAM isotopic analysis software to analyze dozens of archived high-resolution gamma ray spectra from various samples of US and foreign plutonium. We are able to quantify the ratio of minor isotopes with measurable gamma-ray emissions to the major isotope of plutonium and hence, through the measurement of the plutonium isotopic distribution of the sample, to elemental plutonium itself. Excluding items packaged in fluoropolymer vials, all samples analyzed with ^{240}Pu < 9% gave ^{228}Th/Pu ratios < 3.4 e-012 and all samples of US-produced plutonium, including ^{240}Pu values up to 16.4 %, gave ^{228}Th/Pu ratios < 9.4 e-012. None of these values is significant from a radiation dose standpoint.

Introduction

The isotope ^{236}Pu in weapons-grade plutonium to be used in the US MOX (mixed-oxide) plant is of concern to plant designers because the daughter products of ^{236}Pu are sources of high-energy gamma rays. The daughter ^{208}Tl decays emitting several intense high-energy gamma rays that have a maximum energy of 2614 keV. The intensity of these high-energy gamma rays is important for radiation exposure calculations for plant design. It is generally thought that the concentrations of ^{236}Pu and its daughters are well below 10^{-10}, but these concentrations are generally below the detection limits of most analytical techniques. One technique that can be used to determine the concentration ^{208}Tl is the direct measurement of the intensity of the ^{208}Tl gamma rays in the gamma-ray spectrum from plutonium. Thallium-208 gamma rays at 583, 860, and 2614 keV are visible in the gamma-ray spectrum from US weapons-grade plutonium.

Thallium-208 is at the end of the decay chain starting at ^{236}Pu and itself decays to stable ^{208}Pb. The characteristics of this decay chain are dominated by the first three elements in the chain. The longest half-life in the decay between ^{228}Th and ^{208}Tl is 3.6 days.

^{236}Pu--2.85y→ ^{232}U --72y→ ^{228}Th--1.91y→ ….. →^{208}Tl ---3m→ ^{208}Pb (stable)

Thallium-208 will be in equilibrium with ^{228}Th and may very well be in equilibrium with ^{232}U for most aged plutonium samples.

Measurement Approach

We have used the Los Alamos FRAM isotopic analysis [1-3] software to analyze dozens of archived high purity germanium (HPGe) detector gamma-ray spectra from various samples of US and foreign plutonium. With this software, we are able to quantify the ratio of minor isotopes with visible gamma-ray emissions to the major isotope of plutonium and, hence, through the measurement of the plutonium isotopic distribution of the sample, to elemental plutonium itself. These measurements are performed on arbitrary samples, in arbitrary measurement geometry. The measurements use fundamental nuclear constants in the analysis and do not require calibration.

Our archival spectra have been acquired over an energy range from 0 to 1024 keV and do not contain the 2614 keV gamma ray from ^{208}Tl. However, the 583 and 860 keV gamma rays of ^{208}Tl are present and detectable in most of the archival spectra. We express the daughter product concentration in terms of the ratio of ^{228}Th/Pu because ^{208}Tl is in decay equilibrium with ^{228}Th. Table I displays the emission percentages per decay of the strongest gamma rays from the decay of ^{228}Th and its daughters. We analyzed the 583 keV ^{208}Tl gamma ray because it is the most easily detectable gamma ray in the energy range from 0 to 1024 keV. The ^{212}Pb gamma ray at 238.6 keV is slightly more intense, but is much harder to detect because the background continuum is much higher at 238 keV than at 583 keV.

Table I

The Principal Gamma Rays from the Decay of ^{228}Th and its Daughters

Isotope	**Energy (keV)**	**Emission % per ^{228}Th Decay**
^{212}Pb	238.63	43.5
^{208}Tl	583.187	30.6
^{208}Tl	860.56	4.50
^{208}Tl	2614.5	35.86

The low level of the ^{208}Tl gamma-ray emissions and interference from other gamma rays complicate the analysis of the spectra in the 583 keV region. Over all of the spectra examined, we find three contributions in this region. They are listed in Table II.

Table II

Gamma Rays in the 583 keV Region from Plutonium Samples

Energy (keV)	Source of Gamma Ray	Comment
582.89	^{239}Pu	Correct for ^{239}Pu contribution by the ratio of the intensity of this peak to known ^{239}Pu gamma ray at 646 keV.
583.03	^{22}Na resulting from ^{19}F(α,n)^{22}Na	Interfering peak arising from fluorine impurities or fluorine-containing packaging. From the fitting process used, the fluorine contribution, if present, gives an artificially high value to the ^{228}Th concentration. These cases are easily seen in the fits and will be noted in the results table.
583.187	^{208}Tl	Gamma ray in question.

Analysis of Gamma Rays in 583 keV Region

The three gamma rays listed in Table II form a single broad peak and cannot be resolved visually. We analyze this region in the following manner: the component from ^{239}Pu at 582.89 keV is easily determined using the measured intensity of the companion gamma ray from ^{239}Pu at 645.94 keV and the known intrinsic intensities (branching ratios) and relative detection efficiencies of the two gamma rays. The component from ^{208}Tl at 583.187 keV is fit with a response function placed at that energy.

The peak fitting method used in the FRAM code is not sensitive enough to give accurate results for both the ^{22}Na (fluorine) and ^{208}Tl contributions if they are considered as free peaks. The two peaks are separated by only 0.16 keV (1.3 channels at the 0.125 keV/ch gain of the archival data). Therefore, we choose to ignore the fluorine, leaving the 583.187 keV ^{208}Tl peak as the only free peak in the fitting. The presence of fluorine will give a ^{208}Tl contribution that is too large—a “fail-safe” result for these analyses. The extra contribution from fluorine is easily seen when examining the details of the peak fitting at 583 keV. The figures below demonstrate the fitting for different fluorine and ^{208}Tl contributions. The graphs in Figs. 1-3 have a Y axis scale of counts and an X axis scale of channel number. The values at the extremes of both axes are noted in the figures. The text at the bottom of each window denotes the channel number, energy in keV, and counts at the channel of the cross hair “cursor” in each picture.

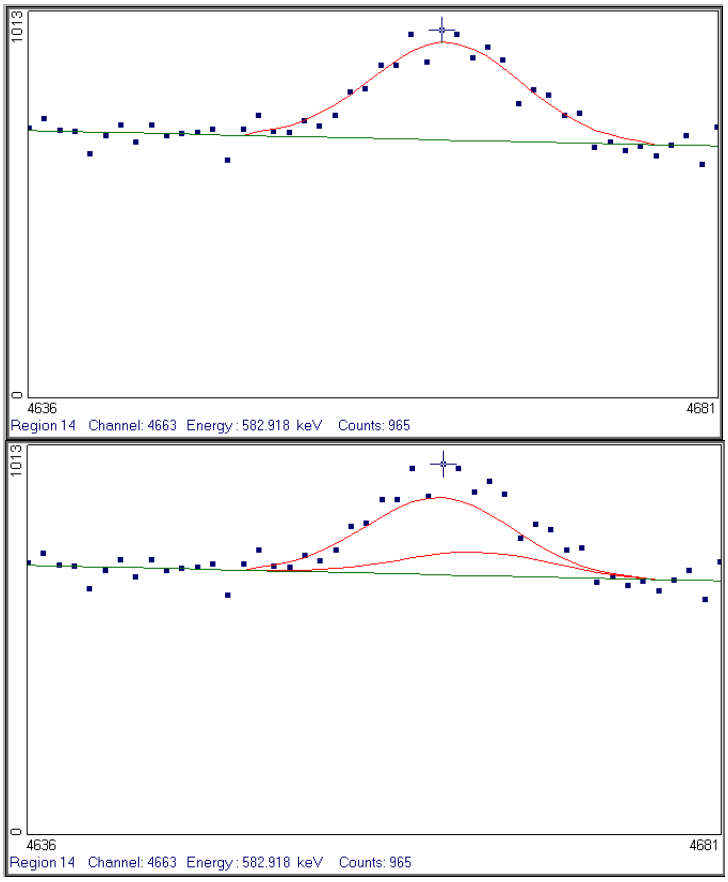

Fig. 1. These two figures show the 583 keV region from sample 4, a weapons-grade plutonium sample with 6% Pu-240 and a very small Tl-208 content. The top picture shows the envelope of the fit of the two peaks. The individual components are shown in the bottom picture. The smaller component is the 583.187 keV gamma ray from Tl-208, while the larger component is the 582.89 keV peak from Pu-239. The energy of the channel denoted by the cross hair is shown at the bottom of each frame.

No fluorine is seen in this spectrum. Fluorine, if present, would show up as excess counts on the low-energy side of the peak.

This spectrum yields a Th-228/Pu ratio of 4.3 e-013.

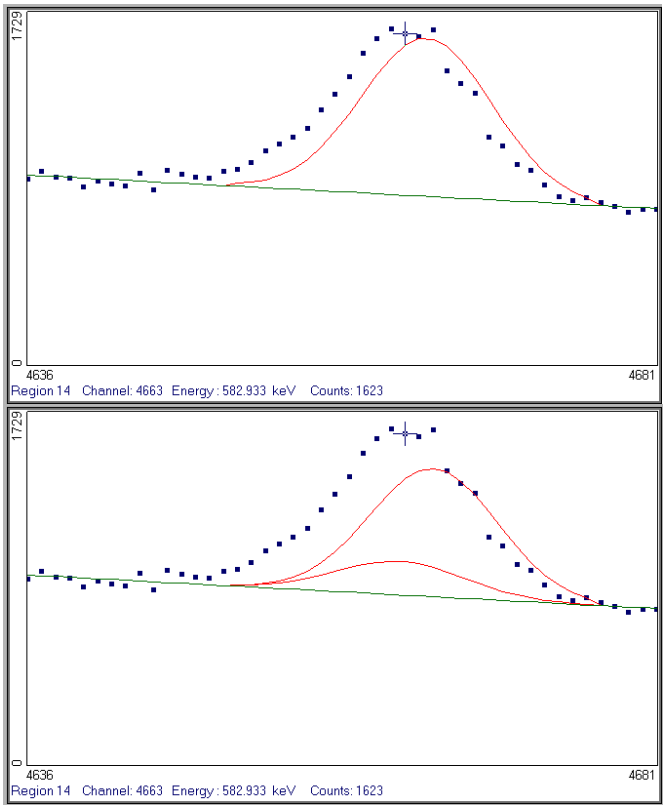

Fig. 2. These two figures show the 583 keV region from sample 21, a medium burnup sample (12% Pu-240) with a moderate Tl-208 content that is influenced by a fluorine contribution. The top picture shows the envelope of the fit of the two peaks. The excess counts to the left of the fitted response function are the contribution from fluorine. The individual components are shown in the bottom picture. The larger component is the 583.187 keV gamma ray from Tl-208, while the smaller component is the 582.89 keV peak from Pu-239. The Tl-208 component is influenced by the fluorine, as it is the only free peak in the fit. The energy of the channel denoted by the cross hair is shown at the bottom of each frame. In this spectrum the cross hair is at the approximate energy of the 583.03 keV from fluorine.

This spectrum yields a Th-228/Pu ratio of 5.0 e-012 that clearly overestimates the ratio because of the presence of fluorine.

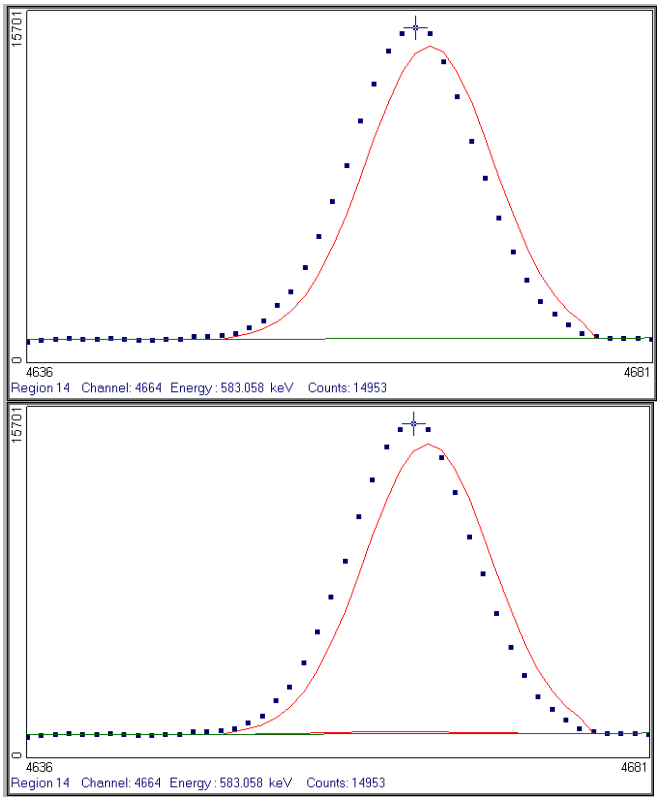

Fig. 3. These two figures show the 583 keV region from sample 14, a low burnup sample (9% Pu-240) with a very strong fluorine contribution arising from its Kel-F vial. The top picture shows the envelope of the fit of the two peaks. The excess counts to the left of the fitted response function are the contribution from fluorine. The individual components are shown in the bottom picture. The larger component is at the energy of the 583.187 keV gamma ray from Tl-208, while the smaller component is the 582.89 keV peak from Pu-239, and is barely seen. The Tl-208 component is dominated by the fluorine as Tl-208 is the only free peak in the fit. The energy of the channel denoted by the cross hair is shown at the bottom of each frame. In this spectrum the cross hair is at the approximate energy of the 583.03 keV gamma ray from fluorine.

This spectrum yields a Th-228/Pu ratio of 1.7 e-010 that clearly overestimates the ratio because of the presence of fluorine. The actual Th-228/Pu ratio cannot be determined in this spectrum.

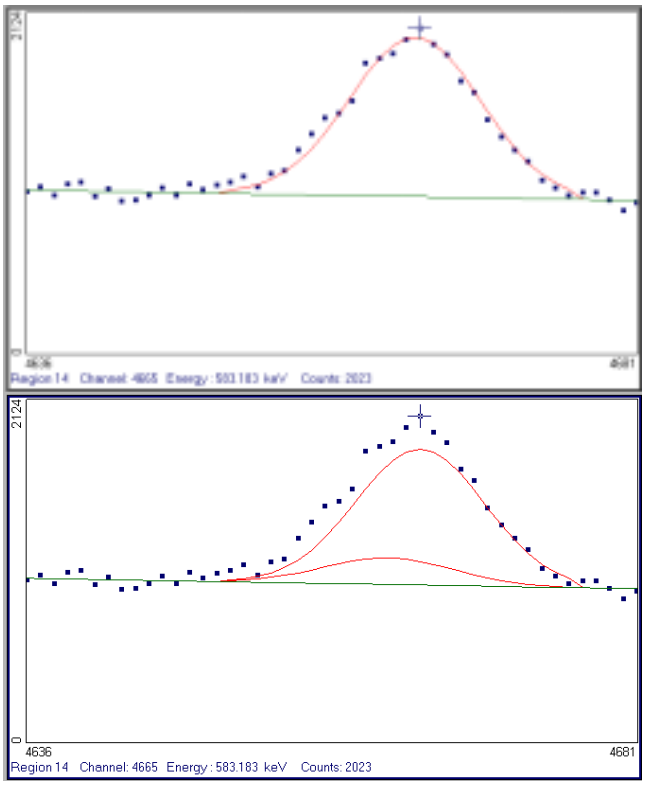

Fig. 4. These two figures show the 583 keV region from sample 11, a medium burnup sample (12% Pu-240) with a moderate Tl-208 content. The top picture shows the envelope of the fit of the two peaks. There is no fluorine contribution seen here. The individual components are shown in the bottom picture. The larger component is the 583.187 keV gamma ray from Tl-208, while the smaller component is the 582.89 keV peak from Pu-239. The energy of the channel denoted by the cross hair is shown at the bottom of each frame. In this spectrum the cross hair is at the approximate energy of the 583.19 keV gamma ray from Tl-208.

This spectrum yields a Th-228/Pu ratio of 6.7 e-012 that is believed to be accurate because of the absence of fluorine.

Pu-236 Concentration—A Meaningless Specification

The US government's contract with the builders of the MOX plant specifies that the ^{236}Pu concentration in the plutonium input should be less than 10^{-9} relative to plutonium. However, the ^{236}Pu concentration is meaningless because it is the ^{208}Tl daughter product concentration that is of importance. For most US weapons-grade plutonium, the ^{236}Pu concentration itself will have decayed by 2 to 4 orders of magnitude since its production because of its 2.85-year half-life. Weapons plutonium production stopped in 1988 in the US. By the planned 2007 startup date of the MOX plant, even this most recently produced plutonium will have a ^{236}Pu concentration 2 orders of magnitude less than when it was produced. A more pertinent specification would be the ^{232}U concentration, because its 72-year half-life is the rate-determining step for the ^{236}Pu decay. Note, however, that plutonium that has been reprocessed will have its ^{232}U removed, likely eliminating the major source for the ^{208}Tl isotope and its concomitant high-energy gamma rays. In general, the complex recycling process and lengthy time since production leaves only a small contribution from ^{208}Tl gamma emissions in most US weapons-grade plutonium.

Results

The results from the analysis of archival spectra are shown in Table III. The samples are grouped according to similar characteristics such as container, burnup of the plutonium, or impurity levels. We have analyzed all burnups available to us, although the weapons-grade plutonium is of primary interest. We expect to see a higher $^{228}Th/Pu$ ratio as burnup increases. The ratios seen in the higher burnup plutonium provide a proof of principle for this study. The rather colloquial comments in the "Any Fluorine?" column can be viewed in the context of Figs. 1-4.

Table III
Th-228/Pu Ratios in Plutonium Measured by Gamma Spectrometry

No.	Sample ID	% Pu-240	Ratio: Th-228/Pu	Any Fluorine?	Comment
1	sgcoax8k.001	3.56	1.35 e-012	Very little	
2	92coax8k.001	5.07	1.71 e-012	Very little	Pu dates from 1968 or before
3	86coax8k.001	5.19	3.41 e-012	Very little	Pu dates from 1970 or before
4	calex30pb.101	5.86	4.3 e-013	None seen	Pu dates from 1979 or before
5	j1325pb1.101	5.82	Too low to analyze	None seen	Metal dating from 1979
6	pueu730.101	5.98	2.2 e-012	Very little	Oxide from Los Alamos
7	pueu7pb.101	5.98	1.7 e-012	None seen	Same sample through Pb shielding, different date
8	std830.101	6.43	1.04 e-012	Very, very little	Pu dates from at least 1976
9	std8pb.101	6.43	8.1 e-013	Very, very little	Same sample through Pb shielding, different date
10	sd4030.101	11.76	7.8 e-012	Very little	FFTF oxide, higher concentration probably real, sample dates from 1980
11	sd4030pb.101	11.76	6.7 e-012	None seen	Same sample through Pb shielding
12	lao225pb.101	16.44	2.1 e-012	Very little	FFTF oxide, through lead shielding, sample dates from 1982
13	lao22530.101	16.44	3.16 e-012	Very little	Same sample without lead, different date
14	2g118cx8.001	8.90	1.71 e-010	Large F peak seen	Sample in KelF vial, ratio not valid
15	2g119cx8.001	11.81	2.28 e-010	Large F peak seen	Sample in KelF vial, ratio not valid
16	2g120cx8.001	14.51	1.60 e-009	Large F peak seen	Sample in KelF vial, ratio not valid
17	2g121cx8.001	16.86	4.06 e-010	Large F peak seen	Sample in KelF vial ratio not valid. Same Pu as lao225 above
18	iso3cx8k.001	3.56	4.19 e-013	None seen	
19	iso6cx8k.001	5.97	1.38 e-012	Very little	
20	iso9cx8k.001	6.81	1.38 e-012	Very little	
21	iso12c8k.001	12.03	5.01 e-012	Somewhat more	
22	iso15c8k.001	15.86	9.42 e-012	Somewhat more	Higher Th-228 probably real

No.	Sample ID	% Pu-240	Ratio: Th-228/Pu	Any Fluorine?	Comment
23	93coax8k.001	6.31	8.62 e-013	Very little	International reference standard from Europe
24	84coax8k.001	14.36	4.41 e-012	Some F contribution	International reference standard from Europe
25	70coax8k.001	19.18	1.21 e-010	None seen	International reference standard from Europe. Large ratio is likely real.
26	61coax8k.001	25.69	2.30 e-010	None seen	International reference standard from Europe. Large ratio is likely real.
27	lao250pb.001	16.36	9.88 e-013	None seen	Pure PuO_2
28	252c10pb.001	16.18	1.26 e-012	None seen	Pure PuO_2
29	253c10pb.001	16.40	1.40 e-012	None seen	Pure PuO_2
30	261c10pb.001	16.44	1.12 e-012	None seen	Pure PuO_2
31	peo381pb.001	10.40	4.37 e-012	None seen	Impure PuO_2
32	382dpb.001	9.49	4.90 e-012	None seen	Impure PuO_2
33	peo447pb.001	9.93	4.67 e-012	None seen	Impure PuO_2
34	srp121pb.001	11.72	3.65 e-012	Very little	

Discussion

The first 13 samples consist of Los Alamos plutonium of various ^{240}Pu isotopic fractions, mostly weapons grade. These samples do not show any significant contribution from the fluorine (α,n) reaction, therefore, we believe that all of the ^{228}Th/Pu ratios are valid. The values of the ratio for weapons-grade plutonium range from none detectable to 3.4 e-12. At these levels, the ^{208}Tl daughter peaks are very, very weak and of no consequence whatsoever for dose considerations as seen in Fig. 5. As seen in Table I, the accompanying 2614 keV ^{208}Tl gamma ray of concern for dose calculations has an intrinsic intensity that is 36/30 times that of the 583 keV line marked in Fig. 5.

Samples 14-17 consist of PuO_2 packaged in Kel-F (polychlorotrifluoroethylene) vials. This plastic contains fluorine and the gamma-ray spectra from these four items shows a 583 keV peak contribution that is 2 to 3 orders of magnitude greater than most other samples. The FRAM analysis has not been configured to differentiate between the fluorine and the ^{208}Tl contributions, so the ratios for these four samples may not be used to characterize ^{228}Th/Pu. Note that sample 17 in this set contains the same plutonium as samples 12 and 13. Sample 17, influenced by the Kel-F vial, yields a ^{228}Th/Pu ratio that is more than 2 orders of magnitude greater than those measured for samples 12-13.

The next set of samples, 18-22, form a set of PuO_2 samples used for NDA analyses in NIS-5. The two highest burnup samples, 21-22, exhibit a somewhat higher ratio than the three lower burnup samples that closely bracket weapons-grade plutonium specifications. The two highest burnup samples have ^{228}Th/Pu ratios consistent with those for samples 10-11.

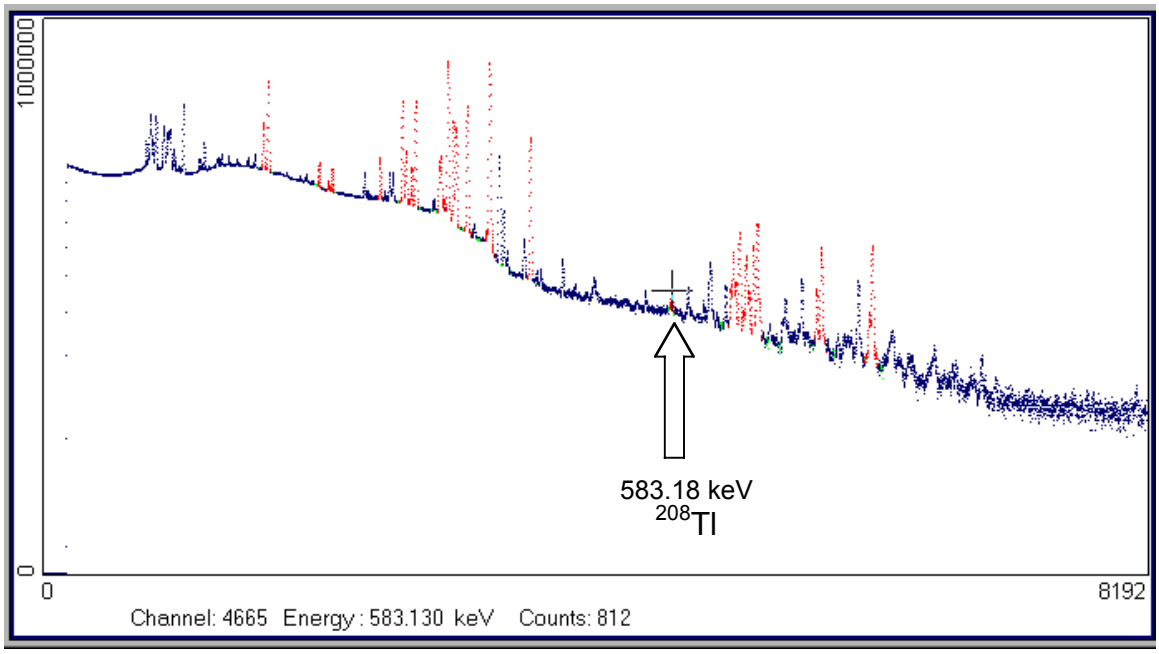

Fig. 5. Gamma-ray spectrum from sample 6 with ^{228}Th/Pu = 2.2 e-012, a typical number for weapons-grade plutonium found in this analysis. The 583 keV ^{208}Tl peak is marked with the cross hair and arrow. The intensity of this peak is insignificant.

Samples 23-26 form a set of internationally certified reference materials used for characterizing nondestructive plutonium isotopic measurements. Samples 23-24 are consistent with other low burnup plutonium. Samples 25-26 have significantly higher ^{228}Th/Pu ratios than any other valid data shown here. These ratios are believed to be real, i.e., no fluorine is present. These samples were produced in Europe, not in US production reactors, and have higher burnup than any other samples in the table. The spectrum of the highest burnup sample, 26, is shown in Fig. 6.

Samples 27-30 are part of a set of pure PuO_2 standards used in the NIS-5 training program. Although these have higher burnup than most of the other samples, they exhibit ^{228}Th/Pu ratios consistent with those from weapons-grade plutonium. Samples 31-34 have lower burnup than 27-30 but higher ^{228}Th/Pu values. These values are still only slightly higher than those from weapons-grade plutonium.

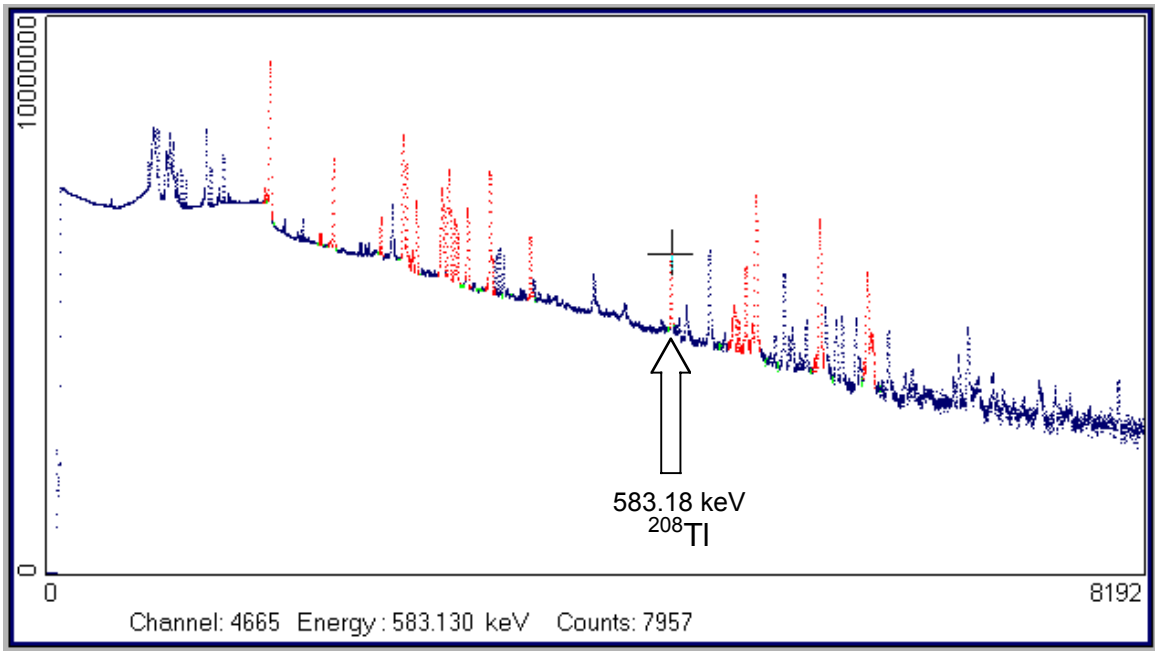

Fig. 6. Gamma ray spectrum from sample 26 with ^{228}Th/Pu ratio = 2.3 e-010, the highest ratio found in this analysis. The 583 keV ^{208}Tl peak is marked with the cross hair and arrow. Its intensity is not significant compared with the multitude of plutonium gamma rays. This sample is of European origin and is of a burnup far in excess of weapons grade specifications.

Future Work

More spectra will be obtained from actual Advanced Recovery and Integrated Extraction System (ARIES)* product oxide. There is no reason to believe that the results will be any different, but the analysis of actual ARIES oxide will give us further confidence in these results.

Summary

We have analyzed gamma-ray spectra from 30 different plutonium-bearing items with the Los Alamos FRAM isotopic analysis software. The purpose of the analysis was to determine the fraction, relative to plutonium, of thorium daughters in the plutonium for application to radiation dose calculations. Excluding samples with fluorine in the sample vial, all samples (regardless of origin) analyzed with ^{240}Pu < 9% gave ^{228}Th/Pu ratios < 3.4 e-012 and all samples of US-produced plutonium including ^{240}Pu values up to 16.4% gave ^{228}Th/Pu ratios < 9.4 e-012. None of these values is significant from a radiation dose standpoint.

* ARIES – Advanced Recovery and Integrated Extraction System. This is the Los Alamos demonstration process to be used to produce the PuO_2.

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