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The U. S. Defense Threat Reduction Agency

Pacific Northwest National Laboratory

Richland, Washington 99352

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Abstract: A series of measurements examining the gamma-ray emission from plutonium in various forms was performed by PNNL at the Plutonium Finishing Plant (Hanford Site, Richland, WA) in February 2001. These measurements are required to understand the gamma-ray signatures of plutonium items to be stored at the Fissile Material Storage Facility (located at the Mayak Production Association, Ozersk, Russia). Three different chemical forms of plutonium were analyzed: pure metallic plutonium, plutonium oxide, and a (nominally) partially oxidized sample. Four different high-resolution germanium detectors viewed each sample, with each detector optimized for a different energy range. The specific gamma rays of interest have energies of 871 keV, 2438 keV, and 2788 keV. Each of these lines should be specific to non-metallic plutonium, with the 871-keV line resulting from the interaction of alpha particles with nitrogen (^{14}N) and the 2438- and 2788-keV lines resulting from the interaction of alpha particles with oxygen (^{18}O, with a natural abundance of only 0.2%). Measurements included the samples of interest, room background with no sample present (required to subtract the fast neutron background from other material in the room), and calibration data with known sources. From these measurements, the emission rate of 2438 keV photons from PuO_2 is 1.7 photons per second per gram. All measurements were made with the material in an AT400-R container, nominally matching the assay conditions at the FMSF. These results show that gamma-ray spectroscopy, while potentially useful to identify plutonium oxide, is of limited utility for assessing partial oxidation of plutonium metal under high background conditions.

Prepared for the Defense Threat Reduction Agency.

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1. Summary

The Defense Threat Reduction Agency (DTRA) requires techniques to implement plutonium characterization at the Fissile Material Storage Facility, located at the Mayak Production Association site in Ozersk, Russia. One of the proposed attributes of the material is that it be metallic form, expressed in either a weak form as an "oxide" attribute or a strong form as a "presence of metal" attribute. The technical basis for an oxide attribute using gamma-ray spectroscopy is shown in Table 1. Since the storage lifetime may be decades, it is possible that metallic material may oxidize with time and no longer pass an oxide attribute test. While there are samples of plutonium metal and plutonium oxide available at many sites in the DOE complex, a partially oxidized metallic sample is not generally available. This type of item is usually the result of a non-normal event. A unique opportunity to measure this type of item was made available at the Plutonium Finishing Plant (located at the Hanford Site, Richland, WA). The current inventory of metallic plutonium at the PFP is being converted to the oxide form for final disposition. Radiographs made during routine non-destructive analysis (NDA) showed that some of the metal ingots were crumbling. After the cans were opened and inspected, it was clear that there is a correlation between crumbling and oxidation. By February 2001 only one apparently oxidized item remained in the inventory. Since this sample was uniquely appropriate to long-term storage at the FMSF, a measurement campaign was planned and executed before this sample was stabilized to oxide. This sample will be tracked throughout the stabilization process at PFP, furnishing an accurate weight for the oxide fraction.

The nominal signatures of storage form were characteristic gamma-ray lines resulting from (α,p) and (α,n) reactions with nitrogen and oxygen (summarized in Table 1).

Table 1: Characteristic gamma-rays sensitive to chemical composition of plutonium.

Gamma-Ray Line	Source	Comments	Reference
871 keV	$^{14}N(\alpha,p)^{17}O$	Strongly correlated with nitrogen, absent in metal	[Pe00] A. Peurrung et al., 2000; in press at *Nuclear Instruments and Methods*
2438 keV, 2788 keV	$^{18}O(\alpha,n)^{21}Ne$	Transitions from 2788 keV state; 2438/2788 intensity rate must be 5:1	[Na01] Nakae 2001, LLNL draft report UCRL-ID-142211
1634 keV	$^{17}O(\alpha,n)^{20}Ne$	First excited state; close to interfering ^{228}Ac decay line	[Na01]
1395 keV	$^{18}O(\alpha,n)^{21}Ne$	First excited state, large energy smearing (Doppler broadened)	[Na01]

The current leading candidate for an oxide-specific signature is the pair of lines emitted during the decay of the 2788-keV state in ^{21}Ne. This reaction is specific only to oxygen and a source of alpha particles. Combined with plutonium presence and mass measurement to verify that plutonium is the source of alpha particles, it could be the basis of a viable plutonium oxide attribute.

This measurement campaign was necessarily limited in scope. As mentioned above, there is only the one remaining item exhibiting the characteristic features of partial oxidation. The measurement was also time limited to two evenings in the storage vaults at PFP, due to constraints imposed by the normal operation and mission of the PFP. As the PFP is being decommissioned, its role has changed from processing of plutonium into stabilization and disposal of the remaining material on site. The cooperation by Fluor-Hanford (FH), facility operations contractor, and Protection Technologies Hanford (PTH), security and safeguards contract, was superb. Throughout this campaign Bill Russell (FH), Larry McRae (PTH), and Rich Szempruch (FH) were committed to its successful conclusion, arranging timely completion of approval documents at PFP, assisting with scheduling, and furnishing background information regarding items of interest. Rich Wilbanks (FH) and the vaults operation staff were unfailingly helpful in assisting this measurement. Much of the success of this project is due to their efforts on its behalf.

2. Experimental Methodology

The relevant components of the experiment are described below in separate sections. In overall design, the methodology was designed to be multiply redundant. There were four separate HPGe detector systems, for example. These measurements were designed to be similar to those to be conducted at the FMSF, with all items placed in an AT400-R storage container.

2.1 Item Selection

Four items were selected for these measurements. Since the oxide measurement technique is still being developed, it was clear that there must be a good metal sample, a pure oxide sample, and the unique partially oxidized sample. A fourth oxide sample with a different process history was also added as a target of opportunity. The yield of the 871 keV line, for example, depends upon the nitrogen content of the sample. Table 2 below lists the characteristics of the particular items. The mass and isotopic composition of each sample is unclassified. Each sample is well characterized. For example, the production history of the oxide produced from the calcined oxalate precipitate is known back through its particular production run at the site. None of the samples have been through the current stabilization process at the PFP.

Table 2: Description of Measured Items

Item	Form	Elemental Mass	Isotopic Composition	Comments
1	Pu Metal	2151 grams	^{239}Pu: 80% ^{240}Pu: 17%	Good ingot
2	Pu Oxide	900 grams (from can label)	^{239}Pu: 85.0% ^{240}Pu: 13.6%	Oxide from calcined oxalate precipitate (typical Hanford product)
3	Pu Oxide	2245 grams	^{239}Pu: 81% ^{240}Pu: 17%	Oxide converted from metal with similar composition to 1 and 4
4	Pu Metal	2160 grams	^{239}Pu: 80% ^{240}Pu: 17%	Crumbing form, shown in Fig.1 below

A radiograph of Item 4 is shown below in Figure 1, along with a comparison of a nominally good ingot in Figure 2.[2] Note that Item 4 has crumbled; this pattern is indicative of oxidation in previous samples.

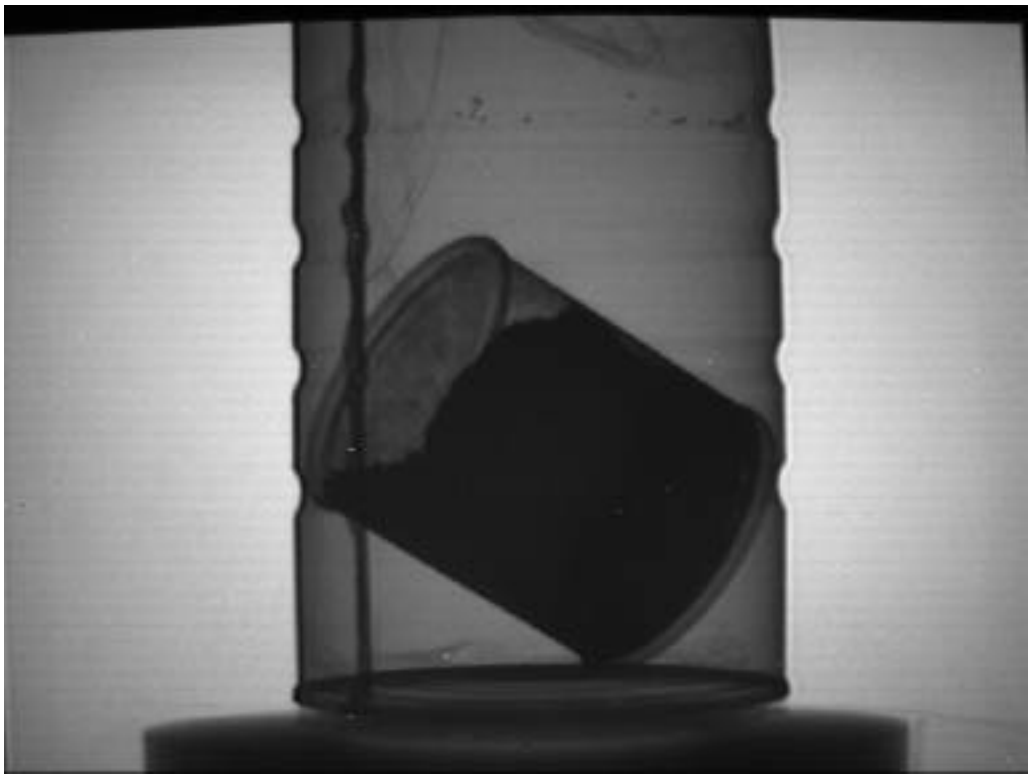

Figure 1: Item 4, showing the crumbling typical of partially oxidized Pu metal.

[2] Item 1 should be similar to the item shown in Figure 2 if it were not oxidized.

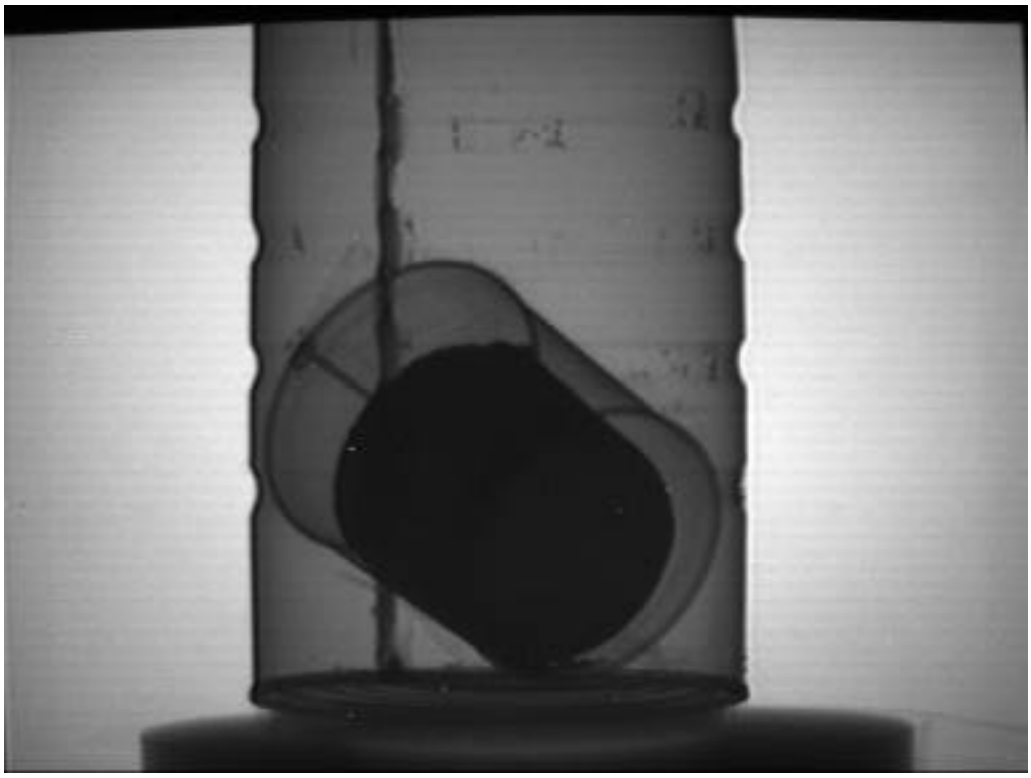

Figure 2: Nominally unoxidized Pu ingot. Note sharp edges and no evidence of crumbled material.

2.2 Detector Systems

Since this measurement campaign had a narrow and unique window of opportunity, it was important to eliminate catastrophic single point failures. For example, there were four separate HPGe detectors, with one detector having two data acquisition systems. This approach also allowed each detector to be optimized for separate regions. Table 3 below lists the detectors and relevant parameters.

Table 3: Detector and data acquisition arrangement.

System ID	Detector ID	Nominal Efficiency	ADC system	Energy Range
1	1	35%	8K ADCAM (analog)	0-3 MeV
2	2	110%	8K ADCAM	0-3 MeV
3	3	35%	8K ADCAM	0-1.5 MeV
4	4	140%	8K ADCAM	0-12 MeV
5	2	110%	16K DSA-2000 (digital)	0-12 MeV

The heart of the measurement was to acquire good spectra through 0-3 MeV, spanning the range of the non-metallic lines. Two data acquisition systems were devoted to this task. A third system was devoted to high-resolution measurements over the range 0-1.5 MeV. Two other systems were attached to the large, high efficiency detectors for measurements over the energy range 0-12 MeV.

2.3 Arrangement of AT400-R Container, Detectors, and Shielding

Each item was placed on a turntable placed inside an AT400-R container. The container included both the outer can and inner enclosure; neither the inner nor outer lid was used. In addition, there was no inner packaging corresponding to the foam enclosure to be used at the FMSF. The sample was rotated at about 5 rpm.

Figure 3: Top view of AT400-R and turntable during PFP measurements. The two detectors are placed inside the lead cave, with the 110% detector (#2) on the left and one of the 35% detectors (#1) on the right.

A particular concern during the measurement was background from other material in the room. On both nights additional nuclear material was stored in the room after the day's material transfers. There was a significant flux of both gamma-rays and neutrons from this material. The detectors were shielded with lead boxes built around the detectors, with an extra thick wall (8" or 20 cm) between the crystals and the background sources. There was 2" (5 cm) of lead on the top, bottom, and other side. Lead was also placed between the detector and the item to reduce system deadtime to less than 20% in all cases. Several photographs are included to show the detectors and AT400-R geometry.

Figure 4: View of 140% detector (#4) and second 35% detector (#3, in the back) during PFP measurements.

Table 4: Details of Detector Geometry and Shielding.

System ID	Detector ID and Efficiency	Distance to Source	Lead Absorber Thickness
1	1, 35%	58 cm	1.27 cm
2,5	2, 110%	58 cm	3.18 cm
3	3, 35%	103 cm	0.64 cm
4	4, 140%	98 cm	1.27 cm

Figure 5: Side view of AT400-R, 110% detector (#2, large white dewar), and 35% detector (small dewar) during PFP measurements.

2.4 Calibration and Background Data

With much of the background due to fast neutron interactions in the crystal, background measurements without the source item are critical. On the first night, the items were stored in a different vault between measurements. During the second night's program, the items were stored in the room. While the background will change due to the item being kept in the room, the net change in stored material mass was sufficiently small that an accurate background subtraction can be made.

2.5 Details of Measurement Sequence

2.5.1 Planned and Actual Sequence

Only two nights (February 20 and 22, 2001) were available for these measurements. The planned order of samples was that the first night's measurements would include both the crumbling metal sample (4) and a large (2.5 kg) stabilized oxide sample (3) and the second night's samples would be a large clean metal sample (1) and an oxide sample (2) typical of output from a US plutonium reprocessing facility. With the lower priority

measurements on the second night it would be possible to recover from problems during the first night's measurement. Unfortunately there was a miscommunication to the operations staff and the order of samples was reversed. Fortunately, PFP operations allowed overnight counting on the second night, ensuring long data collection times for the metal item of interest.

2.5.2 Measurements on February 20, 2001

The first measurement was of item 1, a 2 kg plutonium metal sample to establish baseline rates. After the sample was placed in the AT400-R, lead was placed in front of each detector to reduce the deadtime to reasonable levels (10-15%). Item 2 was 900 grams of PuO_2 produced by calcining plutonium nitrate, the typical product from the US production complex at Hanford. After removing the items and before securing the vault a short calibration run (10 minutes) with ^{60}Co and ^{137}Cs showed that detector checks with sources in the AT400-R were viable. A long background run was made overnight with both items removed from the room. Throughout this measurement there were many additional items staged in the vault, contributing a significant neutron background.

2.5.3 Measurements on February 22, 2001

Before the items were available, both the ^{60}Co and ^{137}Cs sources were placed in the AT400-R container and counted for approximately 2 hours. After coverage was available, the large (2.5 kg) stabilized oxide sample was counted first, followed by a background run. Both items were present in the room during the background run. There was sufficient additional material, however, that the presence of these two additional sources had little effect. With PFP approval, the crumbling, nominally oxidized metal sample was counted overnight.

3. Relevant Information for Analysis

3.1 Data Release

The data (spectra) from this measurement campaign are being released for use in the Mayak FMSF project, together with additional information required for comprehensive analysis. All data have been posted to the Electronic File Cabinet at Sandia National Laboratory. This set includes data from the PFP measurements, background spectra with no source, calibration data at PFP, and calibration data at PNNL.

3.2 Energy and Efficiency Calibrations

With kilograms of material in the sources, a good energy calibration is simple. In addition to the characteristic photon emission from plutonium and americium, photons from neutron capture and reactions in the germanium crystal and iron excitation lines in

the AT400-R were present. An additional calibration was made with ^{137}Cs and ^{60}Co sources in the AT400-R during the measurement. After the detectors were taken back to PNNL, supplementary measurements of the efficiency were made with multiple sources. These secondary measurements were made using the same detector/source spacing, lead absorbers, and location in the AT400-R can as during the PFP measurements.

Figure 6: Efficiency measurements at PNNL after measurement campaign at PFP.

The tables included below list relevant detector efficiencies from the measurements at PNNL for the three cases of bare source, source in the AT400-R can, and source in the AT400-R can plus lead absorbers identical to those used during the measurement.

Table 5: Efficiency data for detector 1, from measurements at PNNL.

Detector 1

Energy	Efficiency		
	Bare	in AT 400R	in AT 400R w 0.5" Pb (as per measurements at PFP)
122.07	3.36E-04	7.91E-05	
661.62	1.13E-04	6.34E-05	1.91E-05
834.81	8.96E-05	5.38E-05	2.23E-05
1173.23	7.21E-05	4.62E-05	2.61E-05
1274.54	6.80E-05	4.43E-05	2.64E-05
1332.5	6.53E-05	4.25E-05	2.62E-05
2614.4		2.67E-05	1.42E-05

Table 6: Efficiency data for detector 2, from measurements at PNNL.

Detector 2

Energy	Efficiency		
	Bare	in AT 400R	in AT 400R w 1.25" Pb (as per measurements at PFP)
122.07	2.92E-04	1.40E-04	
661.62	3.96E-04	2.16E-04	5.20E-06
834.81	3.45E-04	2.04E-04	1.09E-05
1173.23	3.11E-04	1.98E-04	2.27E-05
1274.54	3.02E-04	1.92E-04	2.38E-05
1332.5	2.97E-04	1.93E-04	2.65E-05
2614.4		1.68E-04	4.40E-05

Table 7: Efficiency data for detector 3, from measurements at PNNL.

Detector 3

Energy	Efficiency		
	Bare	in AT 400R	in AT 400R w 0.25" Pb (as per measurements at PFP)
122.07	1.12E-04	5.86E-06	
661.62	3.78E-05	2.13E-05	9.93E-06
834.81	2.98E-05	1.81E-05	9.72E-06
1173.23	2.42E-05	1.56E-05	9.97E-06
1274.54	2.26E-05	1.49E-05	9.69E-06
1332.5	2.17E-05	1.45E-05	9.48E-06

Table 8: Efficiency data for detector 4, from measurements at PNNL.

Detector 4

Energy	Efficiency		
	Bare	in AT 400R	in AT 400R w 0.5" Pb (as per measurements at PFP)
122.07			
661.62	1.82E-04	1.06E-04	2.20E-05
834.81	1.65E-04	1.12E-04	2.78E-05
1173.23	1.39E-04	9.40E-05	3.82E-05
1274.54	1.33E-04	9.15E-05	3.72E-05
1332.5	1.30E-04	8.96E-05	3.96E-05
2614.4		7.72E-05	4.31E-05

Table 9: Efficiency data for detector 2, with the DSA 2000 data acquisition system (from measurements at PNNL).

Detector 2 - DSA2000
Multichannel analyzer

Energy	Efficiency Bare	in AT 400R	in AT 400R w 1.25" Pb (as per measurements at PFP)
122.07	2.71E-04	1.76E-04	
661.62	3.74E-04	2.04E-04	4.87E-06
834.81	3.24E-04	1.87E-04	1.29E-05
1173.23	2.99E-04	1.88E-04	2.31E-05
1274.54	2.96E-04	1.86E-04	2.35E-05
1332.5	2.83E-04	1.83E-04	2.70E-05
2614.4		1.64E-04	4.37E-05

3.3 Neutron Background

Since the vault was being used as a staging area for material transfers, the additional material furnished a large background flux of fast neutrons. Extended measurements were made on both nights. The spectra and recorded data from this campaign are likely one of the few data sets available with a wide variety of HPGe detectors and items in a typical production and storage environment. These results may be useful to evaluate the analysis techniques for data from the Passport systems, where there will be several containers of nuclear material in the receiving room.

3.4 Preliminary Analysis of Pu Metal and Oxide Items

Items 1 and 3 represent the limiting cases of item 4. The background-subtracted spectra for Item 3 (2245 grams PuO_2) are shown in Figure 7 below for detector systems 4 (140%, 8K channels, 7800 seconds live time) and 5 (110%, 16K channels, 8700 seconds live time). Note that there is clear evidence of the 2438-keV line from the $^{18}O(\alpha,n)^{21}Ne$ reaction, with some indication of a slight enhancement in the region of the 2788-keV line. The measured rates are low, with the net peak area for the 2438-keV region in spectrum D4 below being only 1250 counts in 7800 seconds live time. Using the measured detector efficiency, the corresponding emission rate is approximately 1.7 photons per gram per second from the 2438 keV transition in ^{21}Ne. Without background subtraction, the search algorithm does not find this peak. In general, these data and the other spectra are “noisy” at the 2438 keV peak due to the fast neutron background. These plots have been produced to show the features and spectra, using the online energy calibrations.

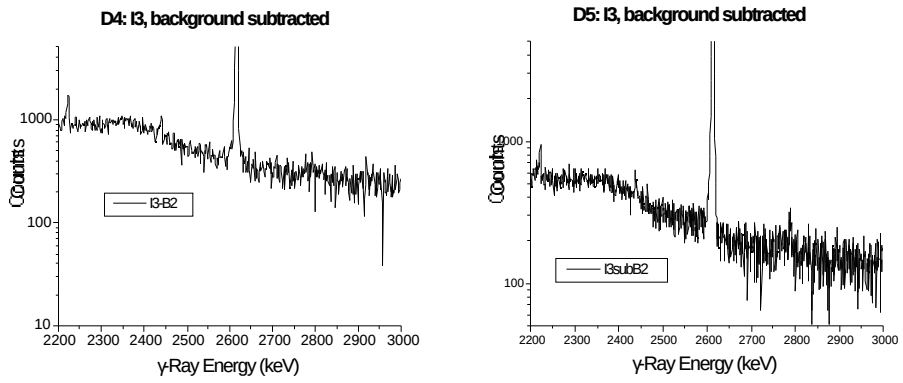

Figure 7: Background subtracted spectra for 2.5 kg of PuO2. The 2438-keV peak is seen in both.

Similar spectra are shown in Figure 8 for item 2, a 900-gram sample of PuO_2 produced by calcining oxalate-precipitated plutonium nitrate. There is again clear evidence for the 2438 line from neon (D4, 5300 seconds live time and D5, 6000 seconds live time).

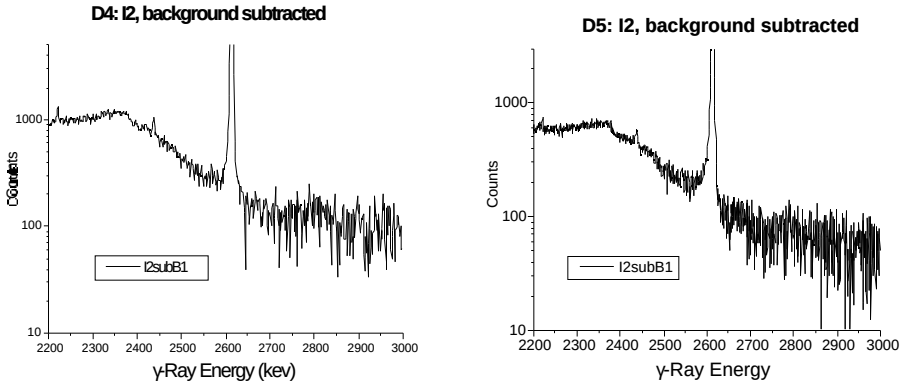

Figure 8: Background subtracted spectra for 900 grams of PuO2. The 2438-keV peak is seen in both.

A pure metal sample (2151 grams) does not show these lines in runs lasting 4700 seconds (D4 live time) and 5100 seconds (D5 live time) (Figure 9). In particular, the 2438-keV line is not evident.

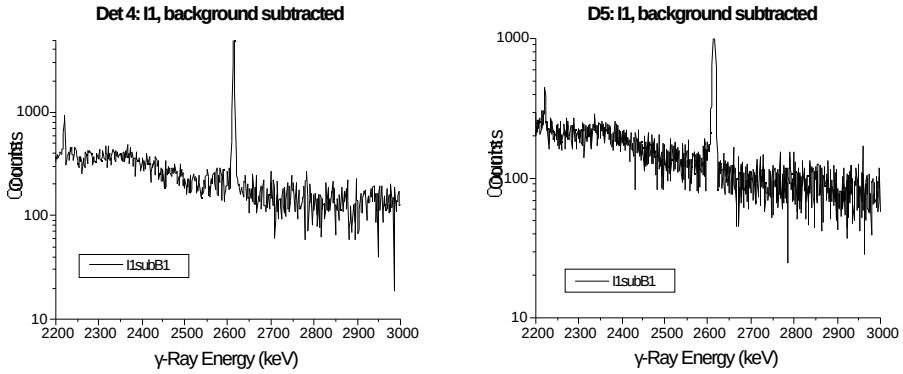

Figure 9: Background subtracted spectra for a 2151 gram metal sample. The 2438-keV peak is not seen.

3.5 Analysis of the Partially Oxidized Metal Sample

The "partially oxidized" metal sample had spectra similar to that from the pure metal sample, with no evidence of the 2438- and 2788-keV lines (Figure 10). These spectra are shown below (D4, 18000 seconds; D5, 20000 seconds).

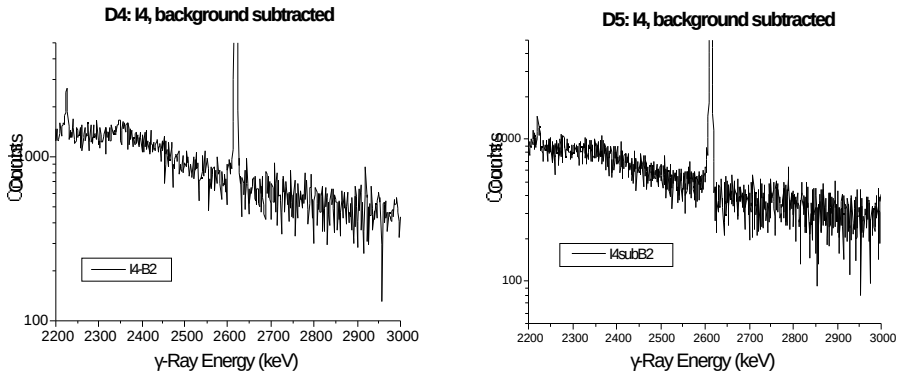

Figure 10: Spectra for the 2160 gram "partially oxidized" sample. The 2438-keV peak is not seen.

4. Preliminary Analysis and Conclusions

There is no gamma-ray evidence for partial oxidation of Item 4 (the purported "partially oxidized" item). Characteristic lines of PuO_2 were present in all examined cases for both

of the oxide samples, with the 2438-keV line being present in all cases. There are three possible explanations for these results:

1. there is no oxidation of item 4
2. the lines are weak for item 4
3. the lines are absorbed by item 4

Certainly there is good evidence for the more intense neon line in plutonium oxide, including data from LLNL [Na01], previous data from PNNL [unpublished, distributed in October 2000], and these new results. The most likely explanations are the simplest, with a combination of weak emission, small sample size, self-shielding in the ingot (the oxidized volume would be shadowed by the metal during a large part of the rotation), and minimal oxidation. Note that Item 4 is not known to be partially oxidized; but, it has the characteristic radiograph of other items known to be oxidized. Until such time as another partially oxidized sample can be procured for a further test, the conclusion from this study is that the proposed oxide signature is not sufficiently sensitive to identify partial oxidation of stored material.

5. Further Analysis and Work in Progress

These preliminary results are presented as a semi-quantitative guide to the results from the measurement campaign at PFP. Additional data (e.g. detector efficiency measurements) have also been acquired to further evaluate the validity of the proposed oxide attribute itself. Most of these data have been posted to the electronic filing cabinet at SNL for independent analysis. An extensive catalog of lines and peak listings has been produced for data runs without background subtraction. This catalog is available by request; it is not in a form suitable for e-mail.

Since the initial circulation of this report additional measurements have been made on a wide variety of plutonium sources at LANL. Participants from LANL, LLNL, and PNNL participated in this measurement campaign at TA-18. These measurements are currently being analyzed for inclusion in a final report.[Me01]

6. References

[Pe00] Anthony Peurrung et al., "The 871 keV Gamma Ray from Oxygen –17 and the Misidentification of Plutonium Oxide", PNNL-SA-33134 (also in press, *Nuclear Instruments and Methods in Physics Research*)

[Na01] "Gamma-Ray Signatures in PU Oxide", Les Nakae, UCRL-ID-142211 (January 2001)

[Me01] David Mercer et al., in preparation [LANL]