LA-UR -79-2759

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AUTHOR(S): R. S. Marshall and B. H. Erkkila

SUBMITTED TO: Oak Ridge National Laboratory Conference
on
Analytical Chemistry in Energy Technology
October 9-11
Gatlinburg, TN

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

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THE MEASUREMENT OF PLUTONIUM OXALATE IN
THERMAL NEUTRON COINCIDENCE COUNTERS

R. S. Marshall and B. H. Erkkila
University of California, Los Alamos Scientific Laboratory,
Los Alamos, NM 87545

ABSTRACT

A coincidence neutron counting method has been developed for assaying batches of plutonium oxalate. Using counting data from two concentric rings of ^{3}He detectors, corrections are made for the effects that water has on the coincidence neutron count rate. Batches of plutonium oxalate varying from 750 to 1000 g of plutonium and from 34 to 54% water are assayed with an average accuracy of ±3%.

INTRODUCTION

Purification of plutonium by the selective precipitation of plutonium as plutonium oxalate is used extensively at the Los Alamos Scientific Laboratory (LASL) and Savannah River plutonium recovery facilities. Plutonium oxalate precipitation not only serves as a purification step, but also produces a product that is easily calcined to form low-fired PuO_2.

The plutonium oxalate precipitation process used at LASL precipitates plutonium as plutonium-III oxalate from a nitric acid solution. The slurry is filtered in a vacuum filter boat and air dried for several hours. Water content in the filter cake varies over a range of 34 to 54%, while the plutonium content varies from 30 to 42%. A typical batch size is about 800 g of plutonium and about 2200 g of total material.

Both the precipitation process and subsequent calcining steps are lengthy processes. To maintain real-time accountability of the plutonium moving through these processes, it is important that the plutonium oxalate be assayed by an

in-line nondestructive assay (NDA) method between the precipitation process and calcining steps. The highly variable water content of the plutonium oxalate makes accurate NDA measurements difficult to attain. Methods based on weighing or gamma counting provide only approximate information. Coincidence neutron counting provides accurate measurements only if corrections are made for water effects.

Coincidence neutron counting methods for plutonium analysis are based on counting coincidence neutrons coming from spontaneous fissioning of the isotopes ^{238}Pu, ^{240}Pu, and ^{242}Pu. The isotope ^{239}Pu can contribute to the coincident neutron signal if spontaneous fissioning neutrons or (α,n) neutrons interact with the ^{239}Pu nuclei that cause the fissions. Spontaneous fission neutrons and (α,n) neutrons typically are born with energies in the 1- to 2-MeV range; the ^{239}Pu fission cross section for neutrons in this energy range is about 1 barn. With this small neutron cross section, one would expect the coincidence neutron signal from ^{239}Pu fissions to be a trivial part of the overall coincident neutron signal in weapons-grade or reactor-grade plutonium. However, the ^{239}Pu fission cross section rises rapidly for neutrons of lower energy.

The water component in the plutonium oxalate studied effectively lowers the spontaneous-fission and (α,n) neutron energies by proton-neutron elastic scattering. Consequently, ^{239}Pu fissioning becomes a major contributor to the overall coincidence neutron signal and, more significantly, becomes a function of the amount of water in the plutonium oxalate.

This paper describes measurements made on a series of plutonium oxalate batches, and the measurement method and calculations we derived to successfully correct for the water effect on the plutonium oxalate.

INSTRUMENTATION

The neutron counter used for this study is a double-ring thermal neutron coincidence counter (TNC). The term "double-ring" refers to two concentric rings of ^3He detectors that surround a central counting well. The ^3He detectors are embedded in polyethylene, which serves as a moderator to decrease the energy of neutrons arriving at the detectors, thereby increasing the counting efficiency of the TNC. Figure 1 shows the location and number of ^3He detectors in the TNC; the mechanical components are described in detail elsewhere.[1]

The purpose of the double-ring design is to give a signal that is sensitive to the average energy of neutrons counted by

the ^{3}He detectors.[2] The thickness of the polyethylene be-
tween the inner ring of the ^{3}He detectors and the counting
well is insufficient to reduce 1- to 2-MeV neutrons to the
optimum energy range for detection. Conversely, the poly-
ethylene thickness between the outer ring of detectors and the
counting well is too thick for optimum moderation. Conse-
quently, if the average neutron energy from material being meas-
ured is in the 1- to 2-MeV range, the ratio of count rates
between the inner and outer rings of detectors will be rela-
tively low. If, on the other hand, the average neutron energy
from material being counted is low because of moderation of
neutrons within the material, then the ratio of inner- to
outer-ring count rates will be relatively high.

The 16-cm-diam counting well shown in Fig. 1 is bolted to
the bottom of a glovebox and opens into the glovebox. Contain-
ers of plutonium oxalate to be measured are loaded into a sample
chamber in the glovebox and lowered into the counting well by a
motor-driven cable. The outer shielding, consisting of 10-cm-
thick polyethylene lined with a 0.4-mm-thick cadmium sheet,
shields the detector array from background neutrons.

The TNC electronics consists of a high-voltage power supply,
preamplifiers, amplifiers, and shift register counting cir-
cuits.[3] Using the shift registers, we are able to count
either single neutron events or coincidence neutron events.
Furthermore, by using two shift registers, we can count single
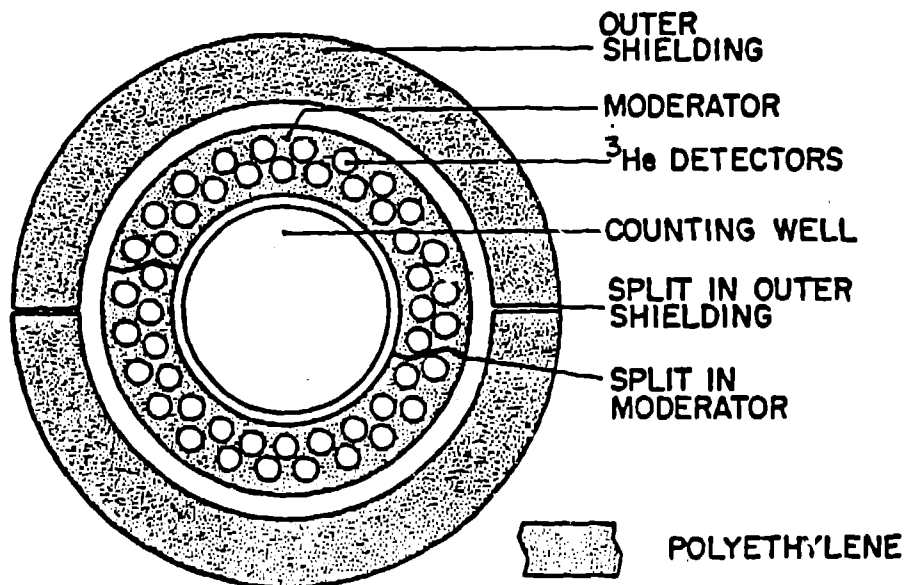

OUTER SHIELDING

MODERATOR

^{3}He DETECTORS

COUNTING WELL

SPLIT IN OUTER SHIELDING

SPLIT IN MODERATOR

POLYETHYLENE

Fig. 1
Cross section of the dual-ring TNC, showing the ^{3}He
detectors and the counting well.

and coincidence neutron events separately for the inner and outer concentric rings of ^{3}He detectors. The TNC has a single neutron counting efficiency of about 20%. We are able to count over 100 000 neutrons per second without large deadtime losses since the TNC electronics deadtime constant is only about 3.5 μs. A microprocessor, called the THENCS unit,[4] is built into the instrument to store calibration information, to make deadtime and background corrections, and to calculate grams plutonium for measured samples.

CALIBRATION

Five PuO$_2$ standards, ranging from 5 to 660 g of plutonium were used to calibrate the TNC. The THENCS microprocessor corrected the coincidence counting data for background and deadtime losses, and fitted the corrected count rates to a best-fit curve using regression analysis. The coincidence counting data used for calibration purposes was taken from the inner ring of ^{3}He detectors.

SAMPLING AND PREPARATION FOR COUNTING

Each batch of plutonium oxalate was sampled before counting. Because the plutonium oxalate was not likely to be uniformly dry across the filter boats, a number of core samples were taken from different locations across the filter boats and combined. These samples were weighed, dried, and low-temperature calcined to PuO$_2$. The dried samples were weighed and sent to the LASL Analytical Chemistry Laboratory for plutonium assay by coulometric titration and for isotopic determination by mass spectroscopy.

After sampling, the plutonium oxalate was removed from the filter boats with a spatula and dumped into a tared 12-cm-diam, 30-cm-high stainless steel can. The dark blue-green plutonium oxalate, in the form of large lumps, filled the cans to within 10 cm from the top. A close-fitting lid was put on the can, and the can was weighed and lowered into the TNC counting well for measurement.

CALCULATIONS FROM ANALYTICAL RESULTS

Using the analytical lab data and weight data, we calculated the percent water and percent plutonium for each plutonium oxalate batch. The plutonium weight fraction for each batch was calculated as follows:

$$(1) \qquad \frac{\text{g Pu}}{\text{g Pu oxalate}} = \frac{\text{g Pu}}{\text{g dried sample}} \times \frac{\text{g dried sample}}{\text{g Pu oxalate}} \quad .$$

Grams of plutonium for each batch were then calculated:

$$(2) \qquad g\ Pu = \frac{g\ Pu}{g\ Pu\ oxalate} \times batch\ weight\ .$$

The assay and weighing errors are quite small; more signifi-
cant errors are associated with cross-contamination and other
sampling problems. We estimate that the mass plutonium values
listed in Table I have associated uncertainties of about ±1%.

TABLE I

MEASUREMENT DATA FOR PLUTONIUM OXALATE BATCHES

Batch Number	Actual Mass Pu (g)	Measured Mass Pu (g)	Ratio of Measured Mass to Actual Mass	Water (wt%)	Ring Ratio
1	887	1291	1.46	44.3	1.070
2	797	1025	1.29	42.7	1.053
3	756	1088	1.44	43.0	1.068
4	781	1260	1.61	48.4	1.095
5	851	1318	1.55	46.5	1.075
6	855	1332	1.56	47.1	1.091
7	917	1164	1.27	37.4	1.054
8	880	1564	1.78	52.7	1.097
9	799	1238	1.54	47.5	1.073
10	925	1450	1.57	47.7	1.083
11	861	1631	1.90	53.9	1.110
12	864	1560	1.81	53.7	1.101
13	912	1019	1.12	34.4	1.036
14	803	991	1.24	36.2	1.029
15	770	1037	1.35	41.9	1.045
16	787	960	1.22	40.5	1.036

The weight fraction of water for each batch was calculated
as follows:

$$(3) \quad \frac{g\ H_2O}{g\ Pu\ oxalate} = 1 - \left[\frac{g\ Pu}{g\ Pu\ oxalate} \left(1 + 0.552\ \frac{g\ oxalate}{g\ Pu} \right) \right],$$

where the constant 0.552 is based on the assumption that plutonium oxalate is $Pu_2(C_2O_4)_3 \cdot x\ H_2O$. This assumption is not entirely valid, because surface oxidation to $Pu(C_2O_4)_2 \cdot x\ H_2O$ was observed.

Combining the plutonium oxidation state uncertainty and sampling uncertainties, the percent water values shown in Table I are probably accurate to only ±1% absolute.

MEASUREMENT RESULTS AND CALCULATIONS

Each can of plutonium oxalate was counted in the TNC for 500 s. The count rates were very high (singles, approximately 40 000 counts/s; coincidence, approximately 3 300 counts/s). Hence the precision of the counting data is good. The THENCS microprocessor used the inner ring coincidence count rate for each plutonium oxalate batch to calculate plutonium mass versus the PuO_2 calibration curve.

Table I lists the actual mass plutonium, the measured mass plutonium, the measured-mass to actual-mass ratio, and the weight percent water for each batch. Notice that the measured mass was always biased high and that there is a correlation between the amount of bias and the percent water characteristic of each batch. A correction to the measured mass based on percent water would reduce the measured mass bias, but percent water is not measured directly by the TNC.

As discussed earlier, the ratio of neutron counts between the inner ring of detectors and the outer ring should be sensitive to the average neutron energy and, therefore, to the water content of the plutonium oxalate. The ring ratios and measured-mass to actual-mass ratios from Table I are plotted in Fig. 2; a good correlation is apparent. To evaluate the correlation, we fitted the data to an exponential curve of the following form:

$$(4) \quad y = ae^{bx} ,$$

where y = measured mass divided by actual mass,
  a = 0.0015372,
  b = 6.38986, and
  x = ring ratio.

The coefficient of determination value for this fit is 0.9625, indicating that the exponential form fits the data quite well.
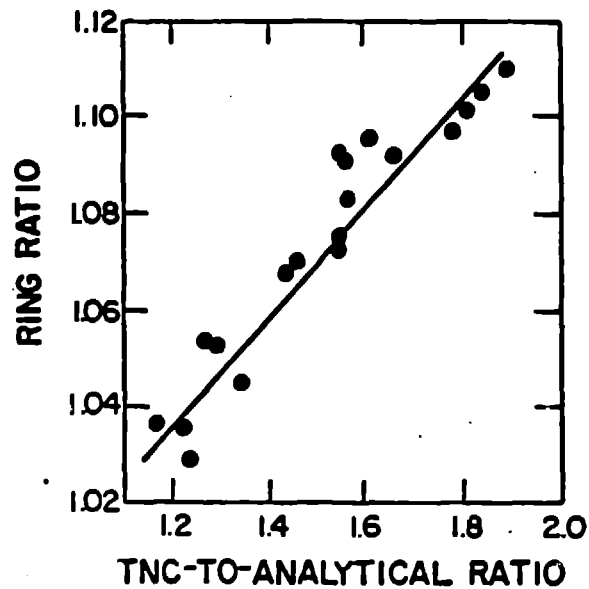
Fig. 2.
Correlation of the ring ratios and the
measured-mass to actual-mass ratios.

Using Eq. 4 and the ring ratios, we then calculated the y
values for each plutonium oxalate batch. We next corrected the
measured plutonium mass values in Table I with their corre-
sponding y values as follows:

$$(5) \qquad \text{corrected mass} = \frac{1}{y} \text{ (measured mass)} \qquad .$$

Table II shows the results of applying this correction to
the 16 batches of plutonium oxalate. Notice that the average
difference between the corrected mass and actual mass is 2.7%,
and the three worst cases had errors of 5.4%, 4.9%, and 4.5%.

DISCUSSION

The ring ratio correction worked well for the 16 batches of
plutonium oxalate investigated. It is important to note that
the batches ranged over a limited mass range of 756 to 925 g of
plutonium. We have done some preliminary measurements of smal-
ler masses of plutonium oxalate; the ring ratio correction
generated a significant bias for plutonium masses below 500 g.
The 16 batches investigated represented a wide spectrum of water
content. We suspect that the correction equation constants are

incorrect for the very dry plutonium oxalate that might be generated by vacuum drying.

The ring ratios were calculated from inner- and outer-ring single neutron counts. Using ring ratios of coincidence counts yields similar, but less precise results. The presence of high cross-section (α,n) nuclei such as beryllium, lithium, or fluorine could shift the average neutron energy spectrum and bias the ring ratio correction. Generally, the oxalate precipitation process provides good purification of these

TABLE II

RING RATIO CORRECTED MASS PLUTONIUM

Batch ID	Actual Mass Pu (g)	Measured Mass[a] Pu (g)	Error[b] (%)
FOX 1177	887	886	-0.2
FOX 1180	797	787	-1.3
FOX 1178	756	756	0.0
FOX 1181	781	739	-5.4
FOX 1185	851	877	3.1
FOX 1183	855	803	-6.1
FOX 1182	917	886	-3.4
FOX 115C3	880	907	3.1
FOX 115C6	799	835	4.5
FOX 115C7	925	918	-0.8
FOX 116C3	861	871	1.2
FOX 116C4	864	883	2.1
FOX 116C5	912	872	4.5
FOX 116C6	803	816	1.7
FOX 11CC	770	771	0.1
FOX JRC-1	787	826	4.9

[a] Ring ratio corrected.

[b] Average error = 2.7%.

elements, but should these el ments be present in 0.1% or greater concentrations, the correction may be biased. None of these limitations pose problems for the particular oxalate precipitation process investigated at LASL because the process is operated within the limiting parameters.

CONCLUSION

Using a double-ring TNC, we have developed a ring ratio correction method that successfully compensates for the effect that water has on the coincidence count rate of plutonium oxalate. Batches of plutonium oxalate can now be assayed with an average measurement error of about 3%. The method provides the rapid in-line measurement capability required to maintain real-time SNM accountability around a plutonium oxalate purification process. At LASL, plutonium oxalate measurements are performed by production technicians, and require a 500-s counting time and approximately 10 min for calculating and recording the data.

ACKNOWLEDGEMENTS

The authors wish to thank Eldon Christensen and Milton Haas for providing the batches of plutonium oxalate used in this study.

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