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AN NDA TECHNIQUE FOR THE ASSAY OF WET PLUTONIUM OXALATE

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ABSTRACT

A method has been developed to quantitatively measure batches of wet plutonium oxalate. The method is based on a count of coincidence neutrons to which a correction is applied for the effects of neutron moderation by water. A thermal-neutron coincidence counter (TNC) with two concentric rings of ^{3}He detectors provides the signal needed for the water correction. The signal is the ratio of neutron counts between the detector rings that changes with the percent of water in plutonium oxalate.

To evaluate the measurement technique, 26 batches of plutonium oxalate were measured in an in-line TNC. The evaluation showed th measurements to be essentially unbiased and precise to 2.2%.

INTRODUCTION

Plutonium is purified at the Los Alamos Scientific Laboratory (LASL) Plutonium Processing Facility by ion exchange and selective precipitation processes. The selective precipitation process most frequently used is plutonium oxalate precipitation. The processing is performed on a batch basis; each batch contains about a kilogram of plutonium.

Figure 1 shows how plutonium oxalate precipitation fits into a sequence of impure plutonium dioxide processing steps. To meet the requirements of the facility's near-real-time accountancy system, which is based on the DYnamic Materials ACcountability (DYMAC) System, the input and output of each process step must be measured quickly and accurately. The measurement points in the major product stream are indicated in the figure. For the plutonium oxalate precipitation step, samples of the incoming plutonium nitrate are assayed in an in-line solution assay instrument, using gamma-ray spectroscopy.[1]

Accurate measurement of the outgoing wet plutonium oxalate is difficult because the material is highly variable in water content (30-65 wt%), and inhomogeneous. Coincidence neutron counting is a promising technique for assaying large quantities of plutonium oxalate if corrections can be made for the effects of the varying water content. The presence of water in plutonium compounds increases the coincidence neutron count rate per gram of plutonium due to sample self-multiplication and increased counter detection efficiency. Neutrons generated by the spontaneous fissioning of the even-numbered plutonium isotopes, ^{238}Pu, ^{240}Pu, and ^{242}Pu are moderated from an initial average energy of about 1 MeV to thermal levels

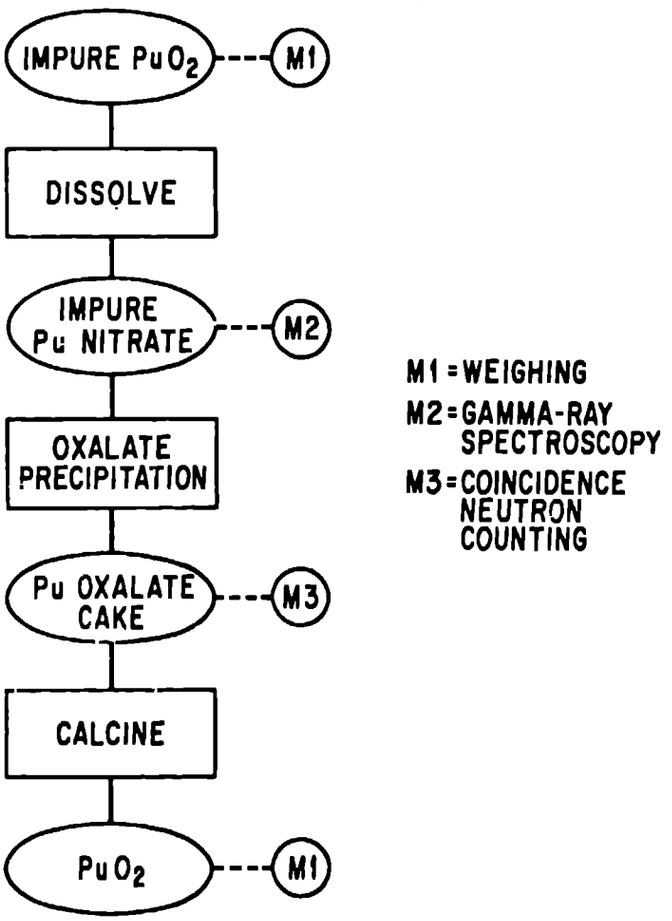

Figure 1.
Plutonium purification process steps and accountancy measurements.

of 0.0[illegible] eV by proton collision. Thermal neutrons have a high probability of inducing fissions in the fissile plutonium isotopes, ^{239}Pu and ^{241}Pu. Plutonium-239 is the principal isotope in most of the plutonium processed at the plutonium facility. For large batches of plutonium oxalate, the contribution of coincidence neutrons from induced fissions is quite large compared to the baseline coincidence signal from spontaneous fissioning isotopes.

Coincidence neutrons from spontaneous fission or induced fission events are indistinguishable to thermal-neutron coincidence counters (TNCs). However, if the mass and geometry of plutonium oxalate batches are controlled within limits, the induced fission contribution varies directly with the percent water, or more correctly, with the average energy of the neutrons emitted by the batch. This paper describes

(a) a special TNC that provides a signal proportional to the average neutron energy,

(b) a mathematical model that uses this signal and the coincidence neutron count rate to calculate mass of plutonium, and

(c) the results of an in-plant evaluation of this technique when applied to the assay of plutonium oxalate.

EXPERIMENTAL

Figure 2 shows the major components of a special in-line TNC used for assaying the plutonium oxalate. The important feature of this instrument is the two rings of ^{3}He detectors arranged concentrically around the cylindrical counting well. The inner ring of detectors is separated from the counting well by 11 mm of polyethylene; the outer ring is separated by an additional 33 mm of polyethylene. The different thickness of moderating polyethylene between the detector rings and the central counting well makes the inner ring more efficient than the outer ring for detecting the low energy neutrons emitted from the sample. As the plutonium material matrix becomes more moderating (as, for example, plutonium oxalate with increasing percentages of water) the inner ring detection efficiency

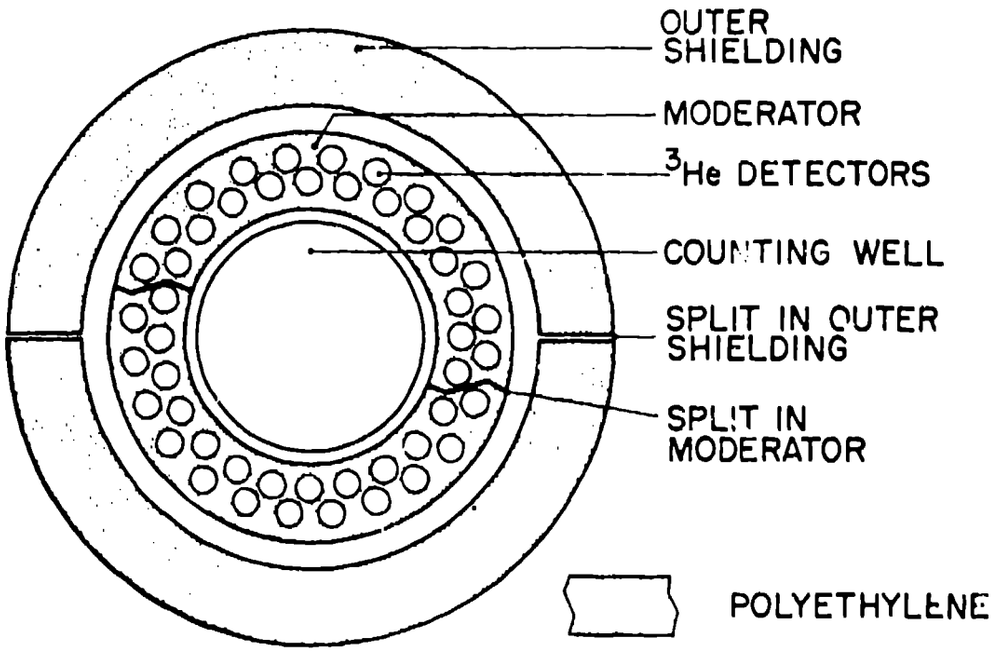

Figure 2.
Cross section of the dual-ring TNC, showing the ^{3}He detectors and the counting well.

increases relative to that of the outer ring. The ratio of counts between the inner ring and outer ring, the ring ratio, is then proportional to the sample moderation.

The TNC was calibrated with six PuO_2 standards varying from 5 to 460 g of plutonium. Since the isotopic composition of plutonium varies, the quantity of plutonium is best expressed as g ^{240}Pu effective, where mass ^{240}Pu effective is defined as that mass of ^{240}Pu that would yield the same spontaneous fission neutron flux as the mass of ^{238}Pu, ^{240}Pu, and ^{242}Pu actually measured. Figure 3 shows the PuO_2 calibration data. The solid line is the least squares fit to the data points of the function

$$M = aR^b \quad , \tag{1}$$

where M is the ^{240}Pu effective mass, R is the coincidence neutron count rate, and a and b are constants that describe the counter efficiency and the sample multiplication, respectively.

For small masses of plutonium, the coincidence neutron count rate R increases linearly with mass and the mass equation M = aR applies. As mass increases, induced fissioning contributes increasingly to R, and the exponential term b in Eq. 1 accommodates this induced fission component. The upper curve in Fig. 3 illustrates the R observed from plutonium oxalate containing 40% water. Had the plutonium oxalate contained a higher percentage of water, a curve with an even steeper slope would be observed.

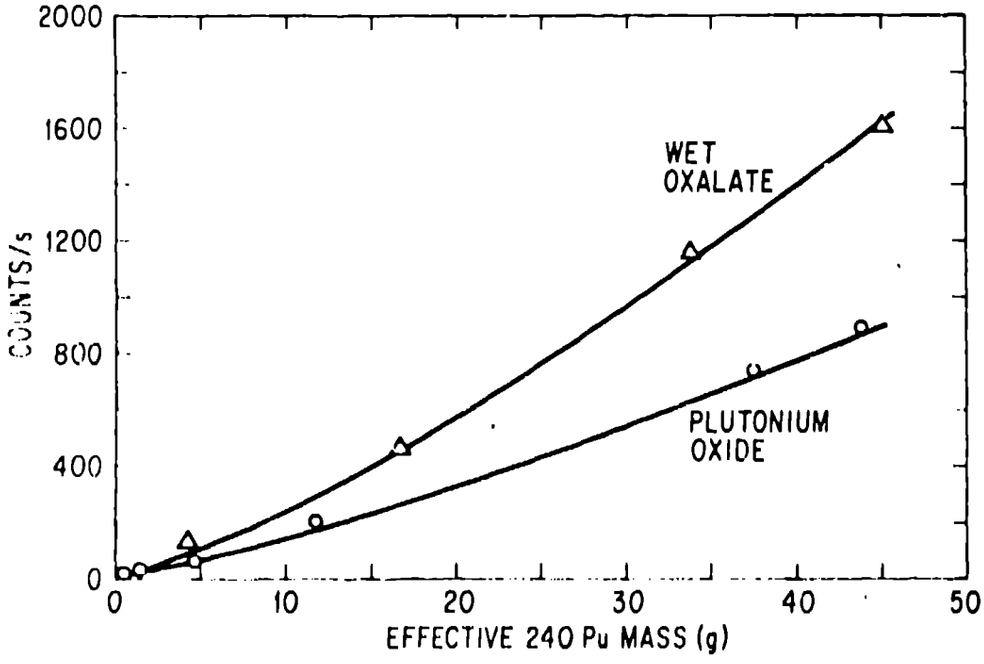

Figure 3.
Calibration curves for dry plutonium dioxide and 40 wt% plutonium oxalate.

To accommodate the varying percent water effect for large plutonium masses, the exponential term b is made a function of the ring ratio, r:

$$M = aR^{b(r)} \quad . \tag{2}$$

To determine the form of the term b(r), Eq. 2 was solved as follows:

$$b(r) = \frac{\ln M - \ln a}{\ln R} \quad . \tag{3}$$

Data for M and R were obtained by counting 19 batches of plutonium oxalate. Each batch of plutonium oxalate was sampled and the samples were destructively analyzed for weight percent plutonium and isotopic composition. The plutonium mass per batch varied from 747 to 926 g. The water content in the 19 batches varied from 34 to 54 wt%, causing the mass ^{240}Pu effective (calculated using Eq. 1) to be biased 11 to 87%, respectively. A b(r) value was then calculated for each batch and the values plotted versus the corresponding ring ratio values. The results are shown in Fig. 4. The one-sigma error bar shown is typical for all the data points and includes uncertainties associated with M, a, and R. These data were fitted to a straight line using a least-squares-fitting technique; the

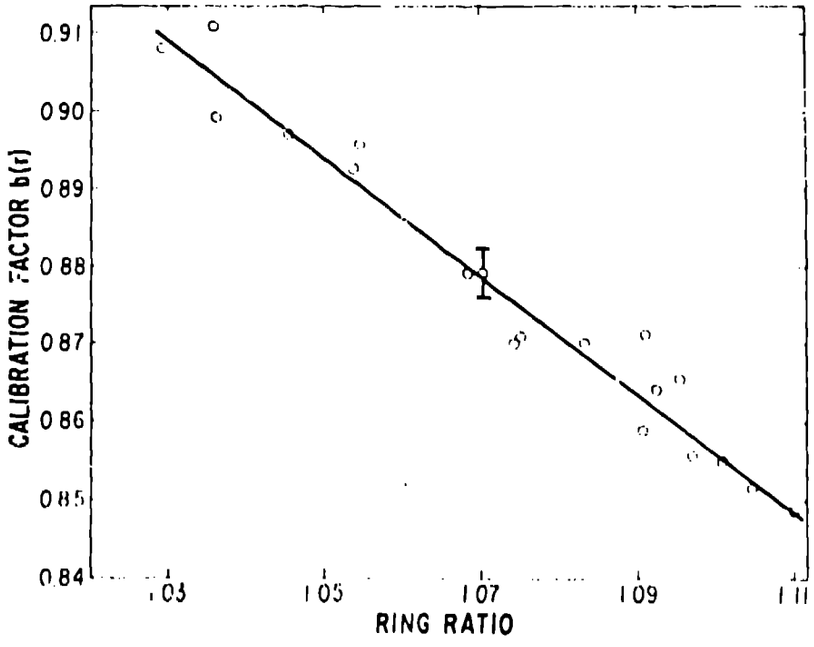

Figure 4.
Measured TNC calibration factor b(r) versus measured ring ratio.

result is illustrated by the solid line in Fig. 4. This linear relationship has subsequently been shown to be valid over a water range of 30 to 60 wt%. At more than 60 wt% water, the plutonium oxalate changes from a wet, lumpy solid to a slurry and b(r) ceases to be linear. Substituting the straight-line equation form for the exponential constant b of Eq. 1 gives the following mass equation for plutonium oxalate:

$$M = aR^{(\alpha+\beta \cdot r)} \quad . \tag{4}$$

EVALUATION

To determine the overall accuracy of this technique as employed by process personnel in the plutonium facility, an evaluation was performed using 26 batches of plutonium oxalate. Measurement information was used from the calcination process step that follows the plutonium oxalate measurement (see Fig. 1).

In the calcination process step, pairs of plutonium oxalate batches are combined and calcined to PuO_2. The PuO_2 is weighed and the weight is multiplied by a plutonium assay factor to obtain mass of plutonium. The combined uncertainties (including spillage, dusting, weighing, and assay factor uncertainties) associated with this method of determining plutonium mass in paired batches of plutonium oxalate is only 0.33%. Because of the inhomogeneous nature of the batches of plutonium oxalate, using the calculated PuO_2 weight times an assay factor to calculate plutonium mass is as accurate as the destructive analysis of plutonium oxalate samples.

Figure 5 shows the difference between the plutonium oxalate measurements in the TNC and the calcined PuO_2 values. The predicted measurement uncertainty (which includes the uncertainties associated with the PuO_2 calibration, the constants in Eq. 4, and the counting statistics) is 2.0% and is illustrated as an error bar on the data point 93. The data for the paired 26 batches of plutonium oxalate show a standard deviation of 2.2%, which is in good agreement with the predicted uncertainty. The observed bias, -0.8%, is shown as a solid line in Fig. 5. The accuracy of these measurements is particularly impressive when one considers that: (a) all of the measurement data used for the evaluation were generated by process personnel during routine processing, (b) each plutonium oxalate measurement required less than 10 minutes, and (c) the TNC was in operation for 9 months without any repairs or adjustments.

CONCLUSION

Plutonium oxalate can be measured quickly and accurately with an in-line, double-ring TNC. Corrections for the effects of neutron moderation by water can be made by using the ratio of neutron counts between the inner and outer rings of ^3He detectors. The method has been shown to be accurate over a water range of 30 to 60 wt% and a total plutonium mass

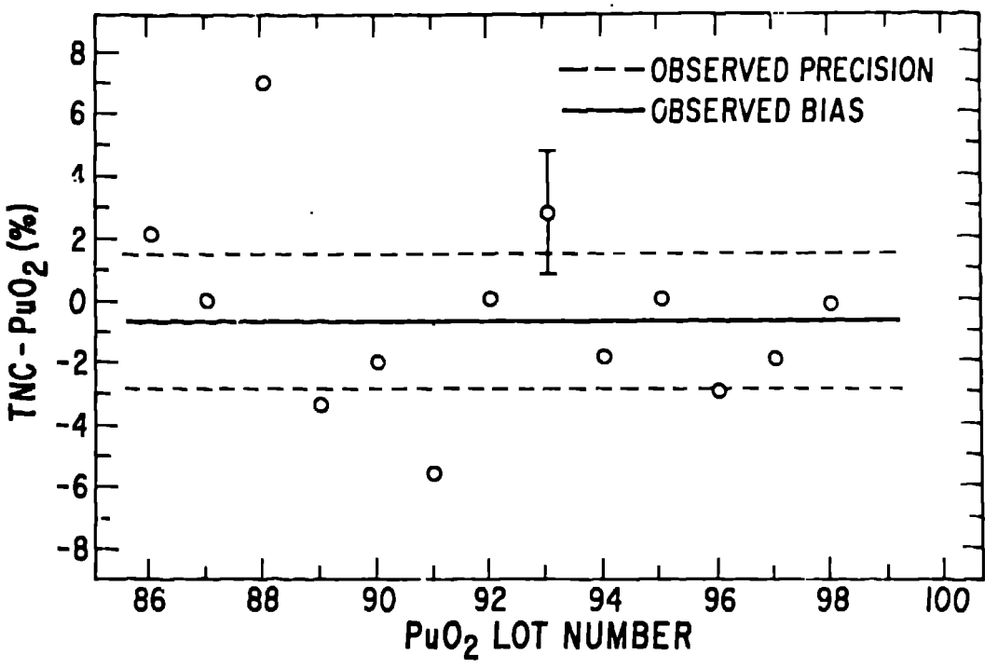

Figure 5.
Difference, in percent, between plutonium oxalate measured as wet plutonium oxalate and as calcined plutonium dioxide.

range of 750 to 1100 g. It is quite likely that the method can be applied with equal success to the assay of other plutonium materials that have moderating matrices.

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REFERENCE

1. T. K. Li and F. Rose, "Automated In-Line Measurements of Plutonium Solutions," presented at the 1980 Annual Meeting of the American Nuclear Society, Las Vegas, Nevada, June 8-13, 1980.