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THE CALIBRATION OF PLUTONIUM NDA BY CALORIMETRIC ASSAY

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ABSTRACT

The calorimetric assay of plutonium is an established and documented technique used extensively in the U. S. Department of Energy facilities for accountability measurements. Multilaboratory studies have quantified an average bias of <0.2% for the calorimetric assay of a wide range of plutonium bearing materials and plutonium isotopic compositions. This average bias can be reduced to <0.1% using new half-life values provided in independent studies by the U. S. Half-Life Evaluation Committee.

An inspectors' verification program, utilizing calorimetric assay, has resulted in the increased use of calorimetric assay for calibration of plutonium nondestructive assay (NDA). The use of calorimetric assay as a standard reference methodology for improved plutonium NDA measurement control is recommended.

INTRODUCTION

Calorimetric assay has been demonstrated to be a practical method for providing traceable measurement control of plutonium NDA measurements. Most NDA systems are presently calibrated using physical standards as described in ANSI N15.20 "Guide to Calibrating Nondestructive Assay Systems." With these techniques, the

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DISCLAIMER

calibration is strictly valid only for the assay of samples which do not differ from the calibration standards with respect to any property to which the instrument is sensitive. D. Smith, in a definitive discussion of NDA calibration [1], wrote "It is the measurement biases, caused by differences between the material being assayed and the physical standards used for instrument calibration, which ultimately constitute the limit of our ability to control special nuclear material." He also observed that these biases may go completely unrecognized if the standard/sample differences are not identified and corrected.

In addressing the same problem from another view, Bingham, Yolken, and Reed [2] consider the chief impediment to the implementation of NDA to be a lack of demonstrable traceability of the measurements to a national or international measurement system. Traceability includes defining the limits of uncertainty of the measurement (random and systematic errors). They emphasize that having a series of traceable calibration standards is not, in itself, sufficient to meet traceability requirements; it is necessary to correct for differences between the samples and calibration standards or to include the effect of these differences in defining the limit of measurement uncertainty.

The traceability of calorimetric assay permits calorimetry to be used as a standard reference methodology for plutonium NDA calibration and measurement control [3]. When process material is calorimetrically assayed and used to calibrate the NDA measurement, sample/standard differences are minimized. This facilitates determination of NDA measurement uncertainties and demonstration of traceability.

This paper summarizes several multilaboratory experiments which have qualified calorimetric assay for plutonium bearing materials. The bias between calorimetric assay and chemical assay is quantified and the source of that bias discussed. Applications of calorimetric assay for NDA calibration and measurement control are presented.

TRACEABILITY OF THE CALORIMETRIC ASSAY OF PLUTONIUM

The calorimetric assay of plutonium consists of a measurement of sample power (watts) arising from radioactive decay and a determination of the plutonium effective specific power (watts/g of plutonium) which is used to convert the sample power measurement to plutonium content [4,5]. Mathematically, the plutonium content (in grams) of the sample is given by:

$$M = \frac{W}{P_{eff}} \qquad (1)$$

where W = sample power, and P_{eff} is the effective specific power of the sample.

The standard of the American National Standard Institute "Calibration Techniques for the Calorimetric Assay of Plutonium Bearing Solids" (ANSI N15.22-1975), describes the traceability of the component measurements of the calorimetric assay.

Calorimeter Power Measurement

The calorimeter power measurement uses standard four-terminal electrical power measuring techniques documented in ANSI N15.22-1975 [4]. Both the standard resistors and standard EMF cells are calibrated against standards certified by the National Bureau of Standards (NBS).

Calibrated ^{238}Pu heat standards are available from Mound. These heat standards have been calibrated in several calorimeters against electrical standards with direct traceability to NBS. In addition, two of these heat standards were measured independently by NBS in an entirely different type of calorimeter [6]. There were no significant differences between Mound certificate values and the NBS ice calorimeter measurements. A program is now in progress to certify and distribute heat standards under NBS auspices in a manner similar to plutonium assay and plutonium isotopic standards.

Effective Specific Power Determination

The effective specific power determination is traceable to the national measurement system by two alternate routes. The most direct is the empirical method of determining the effective specific power (P_{eff}). This method involves the calorimetric measurement of a small aliquot of plutonium and the dissolution and chemical analysis of the plutonium content of the aliquot. These measurements are combined to provide a direct measure of the P_{eff} value in watts/g of plutonium. The traceability of the empirical method is established through the use of NBS certified plutonium assay standards and the previously mentioned heat standards.

The alternate method of determining P_{eff} is called the computational method. This method involves measuring the relative weight fractions, R_i, of all plutonium isotopes and ^{241}Am relative to total plutonium. These weight fractions are then multiplied by the specific power, P_i, of each isotope to give the effective specific power of the particular plutonium isotopic composition, and summed over all plutonium isotopes and ^{241}Am.

$$P_{eff} = \sum_i R_i P_i$$

The traceability of this method relies on the use of NBS certified plutonium isotopic standards to calibrate the isotopic measurements (i.e., mass spectroscopy, gamma-ray spectroscopy, and/or alpha pulse height analysis) The techniques and nuclear constants are those recommended in ANSI N15.22 and are thus open to scientific scrutiny.

THE QUALIFICATION OF THE CALORIMETRIC ASSAY OF PLUTONIUM

For a measurement system to be considered as a standard reference methodology, it is necessary to demonstrate measurement performance following standard procedures and using available standard reference materials for the material types which it is to measure. Several experimental studies have been performed and are under way which qualify calorimetric assay for a wide variety of material types and plutonium isotopic composition. All the experiments described are multilaboratory studies. In each case, the bias between calorimetric assay and chemical assay was determined.

Plutonium Metal

The U. S. Department of Energy (DOE) laboratories participate in the plutonium metal exchange as part of their measurement quality control program. Eight gram plutonium metal samples, nominally 6 wt % ^{240}Pu, are distributed quarterly for chemical assay, impurity analysis, and isotopic analysis. In addition to chemical assay, Mound performed calorimetric assay on these samples for several years. The effective specific power has been determined by the computational method using isotopic compositions measured by mass spectrometry for plutonium isotopes and alpha pulse height analysis for ^{238}Pu and ^{241}Am.

The results, labeled A and B in Table I and Figure 1, are for calorimetric assay compared to by-difference assay (sample weight minus weight of impurities) for the two different metal samples distributed simultaneously in the exchange.

Reactor grade PuO_2

This experiment was part of a program conducted by Mound for the U. S. Nuclear Regulatory Commission (NRC) to evaluate the performance of different methods of determining effective specific power (P_{eff}) for the range of plutonium isotopic compositions expected in the commercial nuclear fuel cycle. Mound, Argonne National Laboratory (ANL), New Brunswick Laboratory (NBL), Savannah River Plant (SRP), and Lawrence Livermore Laboratory (LLL) participated in this program. The results, labeled D, E, and F in Table I and Figure 1, are based on the comparison of P_{eff} by the empirical method to the computational method, using mass spectrometry for plutonium isotopes and alpha pulse height analysis for ^{238}Pu and ^{241}Am. The design of this experiment allowed a direct comparison to chemistry (coulometry) without the sampling problems often encountered with oxides. Results of this experiment are reported in reference No. 7.

Process Materials and Scrap

Sixty-five containers of process materials were selected for an NDA sample exchange in 1972. The material types included: metal buttons, dirty oxide, greencake, fluoride, and incinerator ash. The container size varied from 1 pint to 1 gallon cans with a plutonium content ranging from 22 to 2200 g.

Passive and active NDA measurements were performed by Los Alamos Scientific Laboratory (LASL) and Gulf General Atomic (GGA), and calorimetric assay was performed at Mound. The effective specific power was determined by the computational method using a combination of nondestructive gamma-ray isotopic measurements and stream average isotopic information. Sixteen of the samples were then sent to LASL for chemical assay. The result of the comparison of calorimetric assay and chemical assay is labeled C in Table I and Figure 1. A more complete discussion of the results of this NDA sample exchange has been given by Reilly and Evans [8].

Summary of the Qualification Studies

These multilaboratory experiments have qualified calorimetric assay as a standard reference methodology for a wide range of plutonium bearing materials and isotopic compositions. These results reflect the insensitivity of calorimetric assay to matrix material and geometry, which affect most other NDA measurements.

Based on these studies, calorimetric assay exhibits a small negative bias which may be attributed to errors in the half-life values in ANSI N15.22. While the committee writing ANSI N15.22 considered the half-lives used to be the best available, it was recognized that large discrepancies appeared in the literature and that other compilations of nuclear data contained different values. As a result, the U. S. Half-Life Evaluation Committee (HLEC)[1] was organized under the auspices of the Department of Energy to evaluate these discrepancies.

As its first task, HLEC initiated half-life measurements of ^{239}Pu to resolve an approximate 1% discrepancy between reported measurements by alpha particle counting techniques, calorimetry, and mass spectrometry. Based on this multilaboratory half-life determination [9], the HLEC recommends a half-life of 24,119 ±26 years for the half-life of ^{239}Pu (compared to ANSI N15.22 24,082 ±46 years). Using this new half-life for ^{239}Pu for the data shown in Table I, the average bias is reduced from -0.17% to -0.08%. This effect is shown graphically in Figure 2.

The half-lives of ^{238}Pu, ^{240}Pu, and ^{241}Pu are being investigated by the HLEC. New values for the half-lives of these isotopes may further reduce the bias in the calorimetric assay of plutonium.

The Half-Life Evaluation Committee is reporting the results of its efforts to the writing group responsible for a required 1980 revision of ANSI N15.22. This is an important step in the continuing effort to improve this written standard.

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[1] Member laboratories are Los Alamos Scientific Laboratory, Argonne National Laboratory, Lawrence Livermore Laboratory, National Bureau of Standards, Rockwell Rocky Flats, and Mound.

APPLICATIONS OF CALORIMETRIC ASSAY FOR PLUTONIUM NDA MEASUREMENT CONTROL

Inspectors' Verification Program

For six years, the DOE/Albuquerque Operations Office (ALO) has used calorimetric assay to verify contractors' accuracy statements for plutonium NDA measurements [10,11]. Because of its insensitivity to matrix effects, calorimetric assay has been used by the inspectors to measure plutonium content in a variety of feed materials and scrap categories:

- Oxides
- Metals
- Mixed Oxides
- Mixed Nitrides
- Incinerator Ash
- Ash Heel
- Fluorides
- Sand, Slag, and Crucibles
- Graphite Scarfings
- Greencake
- ^{238}Pu Scrap

ALO inspectors select assayed samples from a contractor's inventory and send them to Mound for calorimetric assay. The results are then used by ALO to identify measurement biases. One important result has been increased emphasis by the contractors on their measurement control programs and, increased use of calorimetric assay. Also, the material unaccounted for, MUF, has been significantly reduced at these facilities.

An important spin-off has been the retention of some of the samples by the contractors, after calorimetric assay at Mound, as NDA assay standards. Using standards which originated in the inventory is an effective way of minimizing standard/sample differences and the resulting measurement biases. The use of these samples as assay standards thus satisfies the two important requirements for establishing traceability of plutonium NDA measurements:

1) The standards provide traceability of the NDA calibration;

2) The standards minimize standard/sample differences.

The inspectors' verification program has proved to be a practical demonstration of the use of calorimetric assay for plutonium NDA measurement control by providing: 1) verification of prior measurements, 2) quantification of measurement biases, and 3) calibration of plutonium NDA.

Dynamic Calibration of NDA

Measurement control programs for NDA instruments are designed to ensure the quality of the measurements. These programs are extensive and include, for example, preparation of standards, calibration procedures, and operator training programs. For high-throughput plants, a dynamic calibration procedure using calorimetry as a measurement control technique is being developed at Mound for NRC.

The dynamic calibration technique selects current samples from the inventory of items being assayed to become calibration samples. The samples selected for calibration are standardized using reliable methods traceable to the national measurement system. Dynamic calibration offers several advantages: it provides continuous recalibration of the measurement system; it automatically accounts for intra- and inter-batch process process variations; it provides a linkage between measurement systems to reduce net systematic error; and it reduces the need for storage of calibration standards.

An example of dynamic calibration for the plutonium fuel cycle is shown in Figure 3. Calorimetry has been introduced as the control measurement for the NDA device.

In this example, the entire process flow is measured by NDA; a portion of the flow is measured by using calorimetric assay and returned to the process. In this measurement system, calorimetric assay is used to monitor the process and to provide calibration data. Chemistry is used in this system as a part of the measurement control program for the calorimetric assay. The amount of chemical analysis required in this plan is much less than that required using chemistry for controlling measurement because calorimetry assumes the burden of monitoring the NDA measurement and providing recalibration.

Calorimetric assay is an effective control measurement because it can be traced to a national measurement system, it can give absolute assay from first principles since isotopic composition is known as a part of process control information, and it is nondestructive.

CONCLUSION

Since the calorimetric assay of plutonium has been demonstrated to provide effective measurement control for plutonium NDA, it should be used more for that purpose. With an appropriate measurement control program, calorimetric assay can provide traceability of plutonium NDA.

Table I

MEASURED BIAS BETWEEN CALORIMETRIC ASSAY OF PLUTONIUM AND CHEMICAL ASSAY FROM THREE MULTILABORATORY STUDIES

	Plutonium Metal		Process Materials and Scrap	PuO$_2$		
Attribute	A "H" Metal	B "R" Metal	C	D	E	F
Pu-240 (wt %)	5.95	5.91	∿6%	11.71	22.58	24.06
Number of Samples	11	21	16	6	6	6
Pu Content (g)	8	8	24 to 2200	4	2.5	1.2
Relative Bias[a] (%)	-0.17	-0.25	-0.17	-0.11	-0.22	-0.07
Standard Error of the Bias	±0.03	±0.02	±0.41	±0.02	±0.02	±0.02

Average Bias = -0.17%

Standard Deviation of the Biases = ±0.07%

[a] Calorimetric Assay - Chemical Assay

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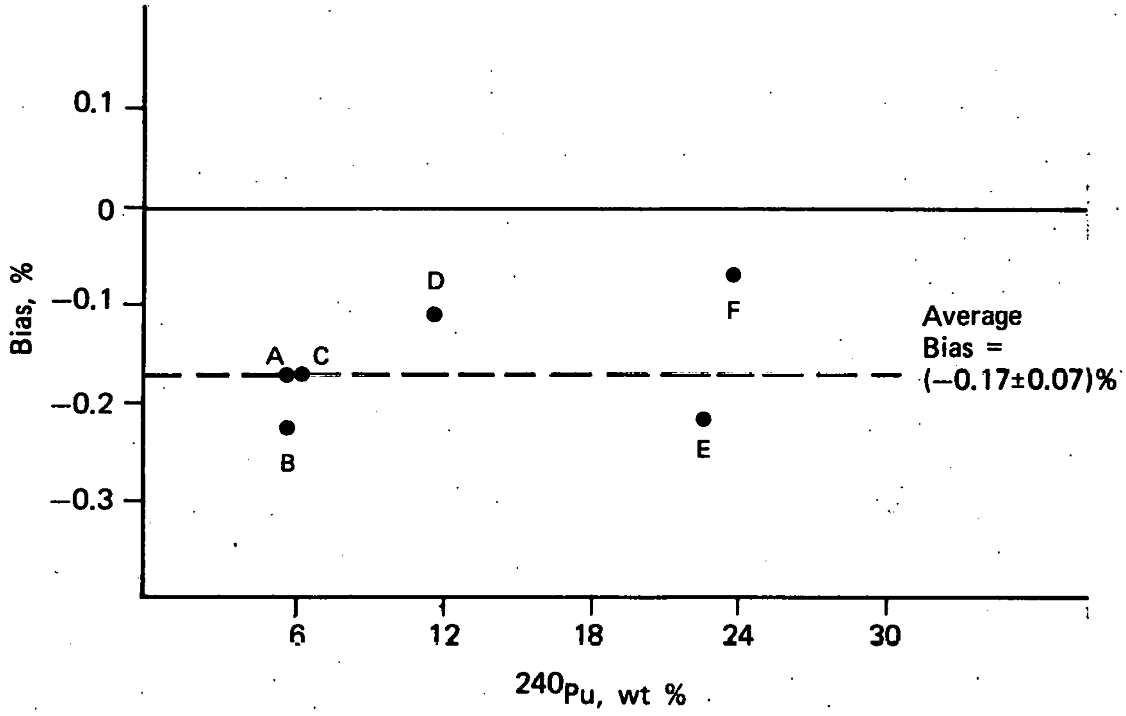

FIGURE 1 - Bias of calorimetric assay compared to chemical assay from three multilaboratory studies.

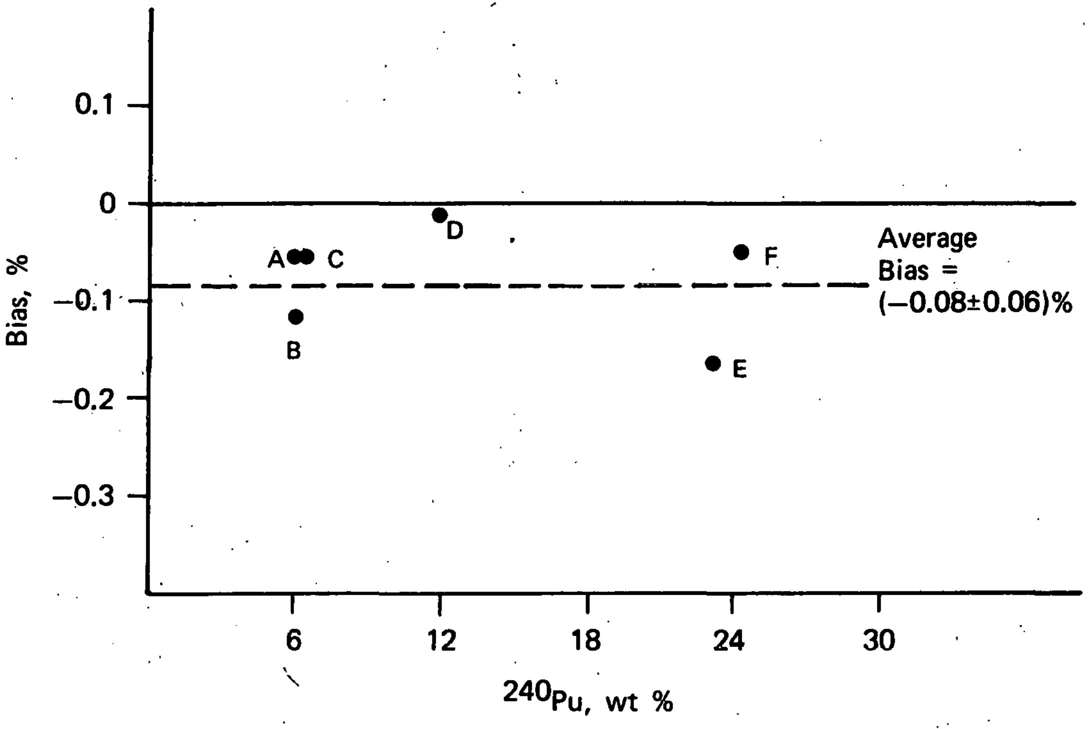

FIGURE 2 - Bias of calorimetric assay compared to chemical assay using $T_{\frac{1}{2}}$ = 24,119 yr for ^{239}Pu.

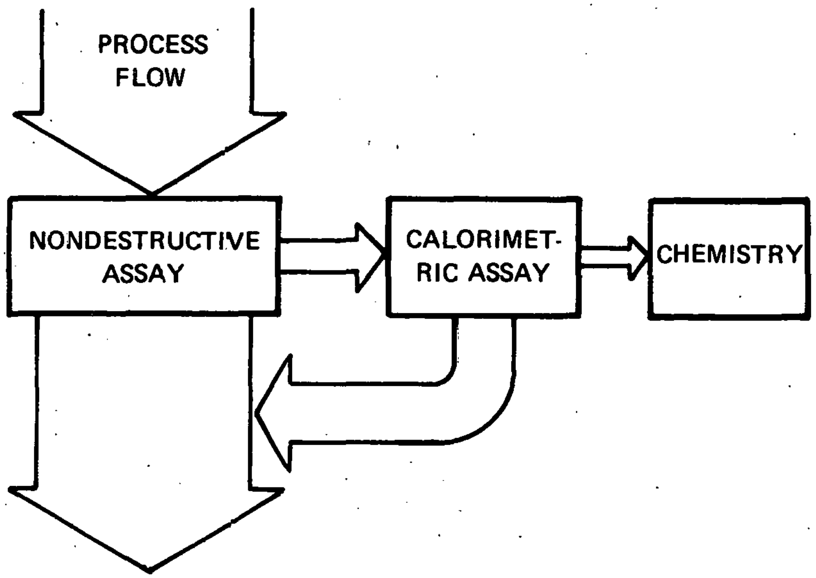

FIGURE 3 - Dynamic calibration of plutonium NDA is being developed using calorimetric assay for measurement control.

FIGURE CAPTIONS

Figure 1. Bias of calorimetric assay compared to chemical assay from three multilaboratory studies.

Figure 2. Bias of calorimetric assay compared to chemical assay using $T_{1/2} = 24.119$ yr for ^{239}Pu.

Figure 3. Dynamic calibration of plutonium NDA is being developed using calorimetric assay for measurement control.