

TRACEABILITY OF THE NONDESTRUCTIVE ASSAY OF PLUTONIUM
USING CALORIMETRY FOR MEASUREMENT CONTROL

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ABSTRACT

Calorimetry provides a method to establish the traceability of the nondestructive assay (NDA) of plutonium utilizing the traceability of calorimetric assay and its relative insensitivity to sample matrix. Efforts at Mound Laboratory to establish the traceability of the calorimetric assay of plutonium are described. Results from the Plutonium Metal Exchange Program and a calibration alternatives experiment are the basis for determining the bias between calorimetric assay and chemical assay. The probable cause of the bias is identified. Current uses of calorimetric assay for NDA measurement control and extension of calorimetry to dynamic calibration of NDA are discussed.

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INTRODUCTION - The nondestructive assay (NDA) of special nuclear materials (SNM) has been under development for several years, primarily as part of the domestic and international safeguards efforts [1, 2]. For many scrap and waste materials, NDA provides the most accurate and cost beneficial measurement available and the demonstrated speed and precision of NDA has led to its increased use for product quality control. NDA is ideal for many inspection purposes since the instrumentation can be portable and sample integrity is maintained.

The major limitation of NDA is the difficulty in maintaining control of measurement accuracy. This limitation arises principally from the sensitivity of the NDA measurement to sample matrix materials and to sample geometry [3]. This has led to the requirement that assay standards used for NDA calibration represent as nearly as possible the samples being measured. Large errors in NDA measurements occur when the sample differs significantly from the standards [4]. Techniques for detecting these differences and for correcting the NDA instrument response for them are generally undeveloped; a notable exception is the transmission measurement for measuring absorption in gamma-ray assay [5].

The current dependence of NDA on assay standards has been reflected in considerations of the traceability* of NDA. Considerable emphasis has been placed on the traceability of NDA calibration standards [3, 6] with correction for differences between standards and samples discussed, but not in the framework of traceability. On the other hand, Glancy [7] has proposed comparative measurements to correct for these differences, and more recently Bingham [8] discussed traceability of NDA and brought into focus the practical realities of too much dependence on certified calibration standards and the necessity of developing methods to account for differences between standards and samples.

The calorimetric assay of plutonium is an NDA measurement with two important features:

- 1) Calorimetric assay can be, and is being, conducted with traceability established and maintained [9, 10, 11],
- 2) The calorimetric assay of plutonium-bearing solids is relatively insensitive to sample matrix and geometry [9, 10, 12].

These features of calorimetric assay have led to its use for plutonium NDA measurement control [12, 13, 14, 15]. This paper discusses the continuing efforts to establish and maintain the traceability of the calorimetric assay of plutonium and the current and proposed use of calorimetry in providing traceability for other plutonium NDA measurement methods, principally

*The use of the word traceability follows 10 CFR 70.57 (a)(4)- "Traceability means the ability to relate individual measurement results to national standards or nationally accepted measurement systems..." Operationally, the word is used to mean control of measurement bias so systematic and random error statements are valid.

by minimizing the NDA error due to differences between standards and samples. Conceptually, calorimetric assay is discussed as the control measurement in an NDA measurement system.

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 Pu) which is used to convert the sample power measurement to plutonium content [9, 10]. Mathematically, the plutonium content, M , of the sample is defined as:

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

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

Figure 1 diagrams the traceability of the calorimetric assay of plutonium with measurement standards and other traceability authorities included. The separate parts of the calorimetric assay measurement shown in Figure 1 are discussed in the following sections.

Calorimeter Power Measurement - The calorimeter power measurement uses standard four-terminal electrical power measuring techniques documented in ANSI N15.22-1975 [9]. Both the standard resistors and standard EMF cells are calibrated against standards certified by the National Bureau of Standards (NBS). Calibrated Pu-238 heat standards are available from Mound Laboratory. These heat standards have been calibrated in several calorimeters against electrical standards with direct traceability to NBS. In addition, two of these standards were measured independently by NBS in an entirely different type of calorimeter [16]. There were no significant differences between Mound certificate values and the NBS ice calorimeter measurements. These heat standards are now being used for calorimeter calibration for both weapon and nonweapon programs within ERDA. Moreover, discussions are in progress to certify and distribute these 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 also traceable to the national measurement system by two alternate routes. The most direct involves the empirical method [9, 10] 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. This provides 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 calorimeter standards.

The alternate method of determining P_{eff} is called the computational method [9, 10]. This method involves measuring the relative weight fractions, R_i , of all plutonium isotopes and Am-241 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:

$$P_{\text{eff}} = \sum_i R_i P_i \quad (2)$$

where i is summed over all plutonium isotopes and Am-241.

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 specific powers, as well as the half-lives used for making the calculation, are those recommended in ANSI N15.22-1975 and are thus open to scientific scrutiny.

Identification of Measurement Bias - An important part of establishing the traceability of calorimetric assay has been the determination of measurement bias relative to chemical assay and, where possible, the identification of the source(s) of that bias. Toward that end, Mound Laboratory participates in the ERDA Metals Exchange Program reporting both chemical assay and calorimetric assay measurements on nominal 8-g metal samples received quarterly. Plans are being made for similar participation in the SALE program. Further, Mound Laboratory is conducting a calibration alternatives experiment for the NRC to qualify calorimetric assay over the range of plutonium isotopic composition expected in commercial fuel cycles. The results of these efforts will now be discussed with emphasis on identifying bias.

The results of calorimetric assay and chemical assay measurements from these two programs are presented in Table 1. The chemical assay for the metals exchange samples (H and R) was a by-difference assay. The values shown are the effective exchange mean values calculated by Mound Laboratory. The calorimetric assay results are from Mound Laboratory measurements using the computational method for determining P_{eff} following ANSI N15.22-1975.

The assay values shown in Table 1 for oxide 1 and oxide 2 are initial results from the calibration alternatives experiment. The chemical assay values are from coulometric measurements; the average of coulometric measurements by Mound Laboratory and New Brunswick Laboratory (NBL) is shown for oxide 1 while the assay value for oxide 2 is a Mound measurement. The calorimetric assay results are from calorimetry measurements at Mound and isotopic measurements from Mound and NBL; the average of isotopic measurements from both laboratories* was used for oxide 1 while the Mound measurement was used for oxide 2. Again the computational method was used to determine P_{eff} .

The comparison (bias) of calorimetric assay and chemical assay in Table 1 and the subsequent discussion does not distinguish between the different chemical assay methods since they are considered the best methods for the types of samples on which they were used.

* Only the Mound alpha pulse height measurements of Pu-238 and Am-241 were used.

Table 1

Bias Between Chemical and Calorimetric Plutonium Assay

<u>Attribute</u>	<u>"H" Metal^a</u>	<u>"R" Metal^a</u>	<u>Oxide #1</u>	<u>Oxide #2</u>
Pu-238 (wt. %)	0.01	0.02	0.06	0.25
Pu-239 (wt. %)	93.67	93.65	86.56	73.21
Pu-240 (wt. %)	5.95	5.91	11.71	22.58
Pu-241 (wt. %)	0.35	0.40	1.48	2.97
Pu-242 (wt. %)	0.02	0.02	0.20	0.99
Am-241 (wt. %)	0.09	0.10	0.01	0.06
Sample weight (g)	8	8	4	2.5
Number of samples	11	21	6	6
Pu-Assay (calorimetry)	0.9963	0.9969	0.8797	0.8789
Pu-Assay (chemistry)	0.9980 ^b	0.9987 ^b	0.8806 ^c	0.8806 ^c
Bias ^d (%)	-0.17	-0.25	-0.09	-0.20

^aMound Laboratory metal exchange results from March 1973 to September 1975 for R-metal; December 1973 to September 1975 for H-metal. September 1974 results excluded.

^bBy-difference assay

^cCoulometry

^dPu-Assay (calorimetry-chemistry)

In an attempt to resolve such measurement biases, the ERDA Half-life Evaluation Committee* has been established to resolve existing discrepancies in plutonium half-life values. While this work is still in progress, several experiments have been completed and there are strong indications that the half-life values of Pu-239 and Pu-240 are somewhat low. To test the effect of potential revisions in the half-lives and thus the specific powers, the observed biases between chemical assay and calorimetric assay were recalculated using tentative values of 24,119 years** and 6570 years [17] for the Pu-239 and Pu-240 half-lives respectively. Table 2 summarizes the effect of these half-life values on the bias between the calorimetric and chemical assay measurements presented in Table 1.

The biases for calorimetric assay using ANSI N15.22-1975 half-lives and also substituting both tentative, new half-lives are shown diagrammatically in Figure 2. The error bars shown are primarily due to uncertainties in the specific powers used to calculate P_{eff} . Incorporation of these new half-life values does reduce the biases. Further work is planned on the Pu-240 half-life and it is expected that this effort will reduce the biases and decrease the associated uncertainties.

APPLICATIONS OF CALORIMETRIC ASSAY FOR PLUTONIUM NDA MEASUREMENT CONTROL - For over five years, the ERDA Albuquerque Operations Office (ALO) has used calorimetric assay to verify contractors' accuracy statements for plutonium NDA measurements [13, 14]. Table 3 shows the categories of scrap and feed materials from which samples have been selected. The variety of materials illustrates the independence of calorimetric assay from sample matrix, an attribute which makes it ideal for the ALO verification program.

ALO inspectors select assayed samples from a contractor's inventory and send them to Mound Laboratory for calorimetric assay. The results are used by ALO to verify the contractor's accuracy statement or to identify the measurement bias. An important result has been increased emphasis by the contractors on their measurement control programs and, significantly, an increased use of calorimetric assay.

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

- 1) The standards provide traceability of the NDA calibration,
- 2) The standards minimize standard-sample differences.

* Current member laboratories are Los Alamos Scientific Laboratory, Lawrence Livermore Laboratory, Argonne National Laboratory, Rockwell-Rocky Flats Plant, the National Bureau of Standards and Mound Laboratory (W. W. Strohm, Mound Laboratory, chairman).

**Preliminary values: The Pu-239 half-life measurements of the Half-life Evaluation Committee are completed and are to be published.

Table 2

Effect of Half-life Values
on Calorimetric Assay Bias

	<u>"R" Metal</u>	<u>"H" Metal</u>	<u>Oxide #1</u>	<u>Oxide #2</u>
% Bias Using:				
ANSI Half-lives	-0.25	-0.17	-0.09	-0.20
ANSI except Pu-239 = 24119 yr.	-0.13	-0.05	0.00	-0.15
ANSI except Pu-239 = 24119 yr. and Pu-240 = 6570 yr.	-0.04	+0.04	+0.15	+0.03

Table 3

Verification Program has Included a
Wide Variety of Pu-Bearing Material

Oxides

Metals

Mixed Oxides

Incinerator Ash

Ash Heel

Fluorides

Sand, Slag, and Crucibles

Graphite Scarfings

Greencake

Pu-238 Scrap

Mixed Nitrides

Because of day-to-day variabilities in the process and inter- and intra-batch variabilities, the facility measurement control program must accept the responsibility of maintaining traceability once it is established.

ALO laboratories using samples from the verification program are Los Alamos Scientific Laboratory and Rockwell-Rocky Flats Plant. The ERDA Chicago Office sent several scrap samples to Mound Laboratory to be calibrated specifically as NDA assay standards. These have been distributed to Battelle-Columbus and Argonne National Laboratory.

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.

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 variations; it provides a linkage between measurement systems to reduce net systematic error; and it reduces the need for storage of calibration standards.

In an actual process, the cost of using chemical techniques to prepare dynamic calibration standards might be prohibitive. The product must be destroyed, extra waste and scrap streams are generated, and extended analytical capabilities are required. For these reasons calorimetric assay is being developed as an alternate method for the preparation of dynamic calibration standards.

Calorimetric assay should be effective 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. Figure 3 is a flow diagram which shows how dynamic calibration might be used in a process.

CONCLUSION - The calorimetric assay of plutonium has been demonstrated to provide effective measurement control for plutonium NDA and should be used more for that purpose. With an appropriate measurement control program, calorimetric assay can provide traceability of plutonium NDA now.

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Figure 1

Traceability of the Calorimetric Assay of Plutonium

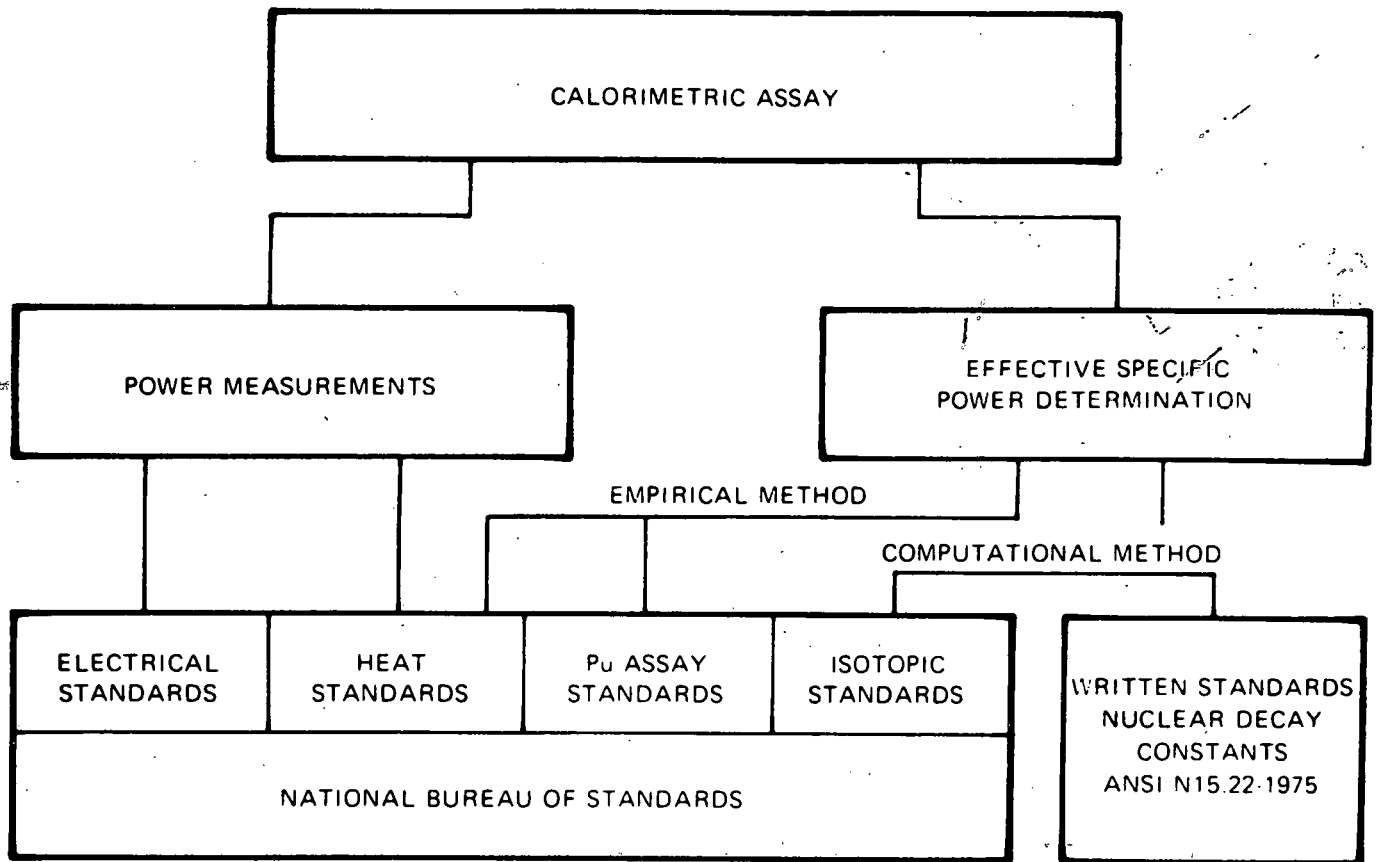


Figure 2

Bias of Calorimetric Assay Compared to Chemical Assay

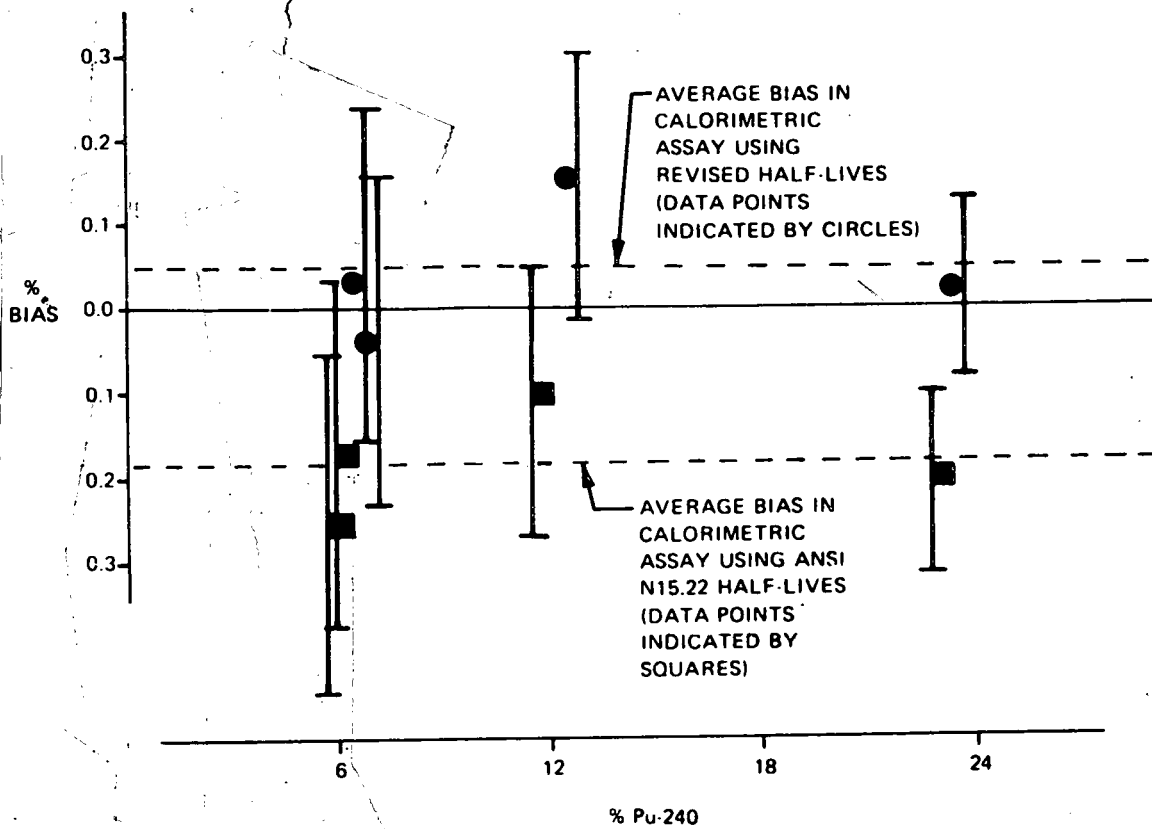


Figure 3

Dynamic Calibration is Being Developed Using Calorimetry for Measurement Control

