

CALORIMETRIC ASSAY OF PLUTONIUM

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U. S. Nuclear Regulatory Commission

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CALORIMETRIC ASSAY OF PLUTONIUM

W. W. Rodenburg

**Manuscript Completed: March 1977
Date Published: May 1977**

**Monsanto Research Corporation
Mound Laboratory
Miamisburg, Ohio 45342**

**Prepared for the U. S. Nuclear Regulatory Commission
Office of Standards Development
Under ERDA Contract No. EY-76-C-04-0053**

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by

W. W. Rodenburg

Abstract

THIS REPORT DESCRIBES PROCEDURES FOR APPLYING CALORIMETRY FOR THE CONTROL AND ACCOUNTING OF PLUTONIUM. THESE PROCEDURES WILL BE USEFUL IN ESTABLISHING A MEASUREMENT PROGRAM TO FULFILL THE REGULATORY REQUIREMENTS.

1. Introduction

Calorimetry can provide a precise nondestructive method for plutonium assay, especially for material of high plutonium concentration such as oxide powder, fuel pellets, and high density scrap and waste [1]. Since sealed containers can be calorimetered, this assay method can provide accurate and timely methods for verifying plutonium shipment and receipts [2,3]. In addition, calorimetry can be used as a comparative measurement [4] to improve the calibration of other nondestructive assay (NDA) techniques [5,6,7], thereby improving the control and accountability of plutonium.

2. Fundamentals of the Technique

A radiometric calorimeter is a device for measuring heat associated with the decay of radioactive materials. For plutonium, most of the decay energy is released as alpha or beta particles and converted to heat by absorption in the plutonium. A small portion of the decay energy is carried away from the calorimeter by neutrons and gamma rays but this energy is less than 0.01% of the total [8]. Thus calorimetric assay of plutonium consists of 1) a calorimeter measurement of the heat released due to the radioactive decay of plutonium and 2) the determination of the proper analytical factor for converting the calorimeter measurement to mass of plutonium. Calorimetric assay is described by the equation

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

*The formalism used here is the same as that used in ANSI N15.22-1975, "Calibration Techniques for the Calorimetric Assay of Plutonium-Bearing Solids Applied to Nuclear Materials Control" [8].

where $M(\text{Pu})$ is the mass of plutonium in grams, W is the calorimeter power measurement in watts, and P_{eff} is the effective specific power of the plutonium in watts/(g of Pu).

The effective specific power of plutonium is determined by the relative abundance of the plutonium isotopes present and by their individual modes and rates of decay. To account for changes in the relative abundances, the effective specific power must include a correction for radioactive decay for the time interval between its determination and the calorimeter power measurement. To make this correction, it is necessary to have an accurate knowledge of the half-lives, decay energies, and relative abundances of each of the isotopes present. For the nuclear fuel cycles considered in this guide, these isotopes are plutonium-238, -239, -240, -241 and -242 and americium-241 from the beta decay of plutonium-241.

Methods for determining the effective specific power of plutonium including the calculation of decay corrections as well as recommended half-lives and decay energies are given in ANSI N15.22-1975 [8].

Some of the features that distinguish calorimetric assay can be illustrated by a comparison with chemical assay. In this comparison, the calorimetric power measurement is analogous to the sample weight in grams, and the effective specific power is analogous to the analytical factor for weighing, which is the plutonium concentration in (g of Pu)/(g of sample).

For a process containing different material forms of plutonium, for example, PuO_2 , mixed oxide, and scrap, the plutonium concentration must be determined for each material form weighed. By contrast, for calorimetry, the effective specific power is the same for the different material forms and is redetermined only when relative isotopic abundances are changed. For example, a redetermination would be necessary if different batches of plutonium were mixed or if americium-241 were lost in the process.

For inhomogeneous materials, for example, scrap and waste, the accuracy of chemical assay [9,10] is limited by the difficulty in obtaining representative samples rather than by the ability to accurately characterize samples submitted for analysis. When the plutonium is of a uniform isotopic composition, such sampling problems can be circumvented by the use of calorimetric assay since calorimetry relies on obtaining a sample representative of the isotopic composition of the plutonium, not of the elemental concentration.

Another feature of the calorimetric assay is illustrated by comparison with other nondestructive assay techniques which are based on direct measurements of nuclear radiation. Since almost all (>99.99%) [8] the radioactive decay energy of plutonium is absorbed by the sample, the resultant heat measurement by calorimetry is highly insensitive to the composition and distribution of the plutonium-bearing matrix. This is in sharp contrast to other nondestructive assay measurements which are susceptible to matrix composition and uniformity, e.g., spontaneous fission assay [6] and quantitative gamma-ray assay [7]. Hence, they require highly representative assay standards. As a consequence, calorimetric assay not only provides

a useful routine assay of plutonium, but can also be used to accurately calibrate other nondestructive assay measurements [5] by providing assay standards or by providing accurate comparative plutonium assay values.

Heat absorbing or producing processes, for example, fission-product radioactivity in reprocessor solutions and chemical reactions such as oxidation, can interfere with the calorimeter measurement. The error due to such interferences can be determined by:

- (1) observation of the time dependence of the calorimeter measurement to detect chemical reactions;
- (2) gamma-ray spectrometry to detect fission-product contamination;
- (3) comparison of the plutonium assay with an assay by an independent technique; and
- (4) process control information.

Calorimeters have been used extensively in and out of process lines in ERDA contractor and licensee facilities [1,2,11]. In addition, developmental programs are under way to:

- (1) decrease the time to perform a calorimeter measurement by improved systems designs [12,13];
- (2) develop a method to predict thermal equilibrium of the calorimeter in a real-time mode to further speed up the calorimeter measurement [14]; and
- (3) develop a nondestructive method for determining the isotopic composition of process materials by high-resolution gamma-ray spectroscopy [4,15,17].

3. Operational Controls

Under the sponsorship of the Institute of Nuclear Materials Management (INMM), Subcommittee N15.8 of the American National Standards Institute (ANSI) Standards Committee N15, "Methods of Nuclear Materials Control", has developed American National Standard N15.22, "Calibration Techniques for the Calorimetric Assay of Plutonium-Bearing Solids Applied to Nuclear Materials Control"*. This standard identifies procedures for the calibration and operation of calorimeters. Methods for determining the effective specific power of plutonium and applying the necessary corrections for radionuclidic decay are also discussed. In addition, procedures are described for determining a valid estimate of the total error in the plutonium assay to be used in calculating the limit of error in the material unaccounted for (See also Reference 16 for numerical examples of such error estimates.)

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*Copies available through the American National Standards Institute, Inc., 1430 Broadway, New York, New York 10018.

4. Thermal Power Calibration

The calorimeter thermal power calibration is established and periodically verified by comparison with electrical or heat source standards which are traceable to the National Bureau of Standards. Heat source standards are preferred since they provide a direct indication of total system performance. Procedures for this calibration of the calorimeter are outlined in ANSI N15.22.

5. Effective Specific Power Determination

The thermal power can be measured quite accurately (for example, total error less than 0.1%) on a wide range of plutonium-bearing materials; however, the ability to accurately determine the effective specific power generally limits the accuracy of calorimetric plutonium assay. Thus, the selection of the procedure used to determine the effective specific power is important. ANSI N15.22 describes two approaches, the empirical method and the computational method.

5.1 EMPIRICAL METHOD

The most direct method of determining the effective specific power of a batch of isotopically blended plutonium is to compare the calorimeter power measurement with chemical assay on the same sample. An aliquot of the batch is measured in a microcalorimeter and its plutonium content is determined by chemical analysis [9]. The effective specific power of the plutonium is calculated from these measurements. The traceability of this method is established by the use of heat standards for the calorimeter and elemental standards for the chemical analysis whose values are traceable to the national measurements system.

The random error in the effective specific power is determined from replicate measurements. Some factors which can contribute to this error are 1) the sampling error due to isotopic variations in the material, particularly of the low-concentration, high-specific-activity isotopes plutonium-238 and americium-241; 2) interferences from chemical reactions; and 3) random errors in the analysis.

At present, the precision of microcalorimeters is $\pm 15 \mu\text{W}$ (Relative Standard Deviation of a single measurement). Thus to achieve a precision of $\pm 0.1\%$ on the wattage measurement, the aliquot must generate at least 15 mW

of thermal power. This is equivalent to an aliquot of 5 g of FFTF-type plutonium* or one gram of high burnup plutonium**.

Considering the size of the aliquot required to determine the specific power for calorimetry, it is desirable to make the effective specific power determination at a point in the process where the plutonium content is high, for example, PuO₂ feed in a mixed oxide process. Once the specific power determination is achieved, it is applicable for the life of the material in the process (with corrections for radioactive decay and assuming no alteration of the americium-to-plutonium ratio). Gamma-ray techniques may be used to nondestructively monitor the consistency of the radionuclidic composition [4,15,17-21].

The correction of the effective specific power for radioactive decay, principally the ingrowth of americium-241 from the decay of plutonium-241, can be determined directly by repeated power measurements at one week intervals on a control sample. Alternatively, the relative abundances of the plutonium isotopes and americium-241 may be measured, and the expected decay may be calculated according to procedures outlined in ANSI N15.22. Once the decay factor is established, it is necessary to correct the effective specific power to the nearest day to maintain the correction error at less than 0.01%. The error in the correction due to uncertainties in the half-lives of the various isotopes is less than 0.01%/yr based on error estimates in ANSI N15.22-1975, page 21. Should the plutonium-to-americium ratio be disrupted by the process, radiocounting or gamma-ray techniques can be used to redetermine the relative americium-241 abundance to correct the previously determined effective specific power. Alternatively, the effective specific power must be remeasured.

5.2 COMPUTATIONAL METHOD

The effective specific power of plutonium can be computed from the relative abundance of each of the individual isotopes. ANSI N15.22 defines the effective specific power as:

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

*Typical composition 0.06 wt % Pu-238, 86.3 wt % Pu-239, 11.7 wt % Pu-240, 1.7 wt % Pu-241, 0.2 wt % Pu-242, and 0.10 wt % Am-241 relative to Pu.

**Typical composition 2 wt % Pu-238, 45 wt % Pu-239, 27 wt % Pu-240, 15 wt % Pu-241, 11 wt % Pu-242, and 0.7 wt % Am-241 relative to Pu.

where R_i = mass abundance of the i^{th} isotope relative to total Pu, and P_i = specific power of the i^{th} isotope (recommended specific powers and uncertainties are given in ANSI N15.22).

Equation 2 is simply the summation of the heat contributions of the individual plutonium isotopes and americium-241 per gram of plutonium.

Several techniques can be considered for the determination of the relative isotopic abundances including mass spectrometry [9], alpha counting [9], and gamma-ray spectroscopy [4,15,17-21]. The gamma-ray measurements can be used on solids nondestructively [4,15,17,19-21] or on dissolved aliquots [18].

The random error in the determination of the effective specific power using the computational method is primarily determined by the precision of the isotopic abundance measurements. In particular, the errors in the determination of the relative abundances of plutonium-238 and americium-241 are critical since their specific powers are much greater than the specific powers of the remaining plutonium isotopes. A mass spectrometric determination of plutonium-238 can suffer an interference from uranium-238; therefore, radiocounting or gamma-ray techniques are usually preferred for these measurements. Preferential dissolution of americium over plutonium can lead to large errors in the americium-241 determination. Where this potential exists, a nondestructive gamma-ray measurement of the relative abundance of americium-241 is used.

The bias in the determination of the effective specific power using the computational method arises primarily from the uncertainties in the specific powers of the individual isotopes and biases in the measurement of individual isotopic abundances. A direct comparison of the computational and empirical methods can be used to estimate the bias between the two methods and, hence, to reduce the bias in the computational method to nearly that of the empirical method [16].

6. Applications

Calorimetric assay procedures performed under appropriate controls may provide a means to strengthen material control and accounting of plutonium [1,22]. It is important that licensees processing plutonium evaluate the applicability of calorimetry to their assay needs for direct assay of feed, process and product materials, and process scrap and the use of calorimetry to characterize nondestructive assay plutonium calibration standards.

The procedures for operation, calibration, and error estimation for heat-flow calorimeters for plutonium assay, as specified in the American National Standard N15.22-1975, "Calibration Techniques for Calorimetric Assay of Plutonium-Bearing Solids Applied to Nuclear Material Control", and further specified in this report may be used for meeting the accountability requirements specified in 10 CFR 70.51 and 70.57.

6.1 CALORIMETER PERFORMANCE SPECIFICATIONS

It is important that the calorimeter manufacturer supply information relevant to the sensitivity of his instrument's response to variations in line voltage, temperature, and humidity over the ranges expected in the licensee's plant as well as estimates of potential heat distribution errors (ANSI N15.22 defines heat distribution error to be the error arising from the spatial distribution of the heat source within the calorimeter chamber). The licensee can then evaluate this information in light of the normal operating conditions in his plant to determine acceptability of the instrumentation.

6.2 CALORIMETER INITIAL TESTING

During the initial testing, the operator first determines the magnitude of any heat distribution errors according to the procedures in ANSI N15.22. The heat distribution error is reevaluated any time changes or modifications are made to the calorimeter which affect heat flow patterns, for example, installation of new thermal insulating baffles. Rechecking the heat distribution error at least once a year to ensure no changes have occurred is important.

6.3 CALORIMETER CALIBRATION

It is important that the following stipulations be considered when the calibration procedures outlined in ANSI N15.22 are used:

- (1) The standards used, whether electrical or (preferably) heat source standards, are traceable to a national measurement standard to meet requirements of 10 CFR 70.57, "Measurement Control Program for Special Nuclear Materials Control and Accounting".
- (2) If heat source standards are used, a minimum of four such standards are needed whose total power spans the expected range of operation.
- (3) Since the random error in the calorimeter measurement will be used as one criterion for testing the stability of the calorimeter in the measurement control program, it is important that the calibration measurements cover a sufficient period of time to indicate instrument stability under normal variations of temperature, humidity, and line voltage.

6.4 MEASUREMENT CONTROL

Once the initial calibration parameters are determined, the standards are run periodically to ensure the continued validity of the calibration parameters. The thermal power of the standards used are varied over the normal operating range. The frequency of such tests will depend on the number of items assayed between calibration measurements, quantity of material in each item, stability of the instrument, and contribution of the calorimeter calibration error to the plant LE-MUF*. At least one calibration measurement per week is needed.

The error in the response is tested against previous calibration data using control chart techniques. When the error exceeds three times the standard deviation of the instrument or when two consecutive errors exceed two times the standard deviation, the test is repeated. If the repeated test also fails this control criterion, calorimetry operations is stopped and the problem is investigated and remedied. Those items assayed between the previous acceptable test and the unacceptable test is reassayed whenever possible. Alternatively, a bias correction can be determined, if a fixed shift occurred. If the time of the onset of instability is unknown, one solution is to apply the bias correction to only half the items assayed during the between test interval.

In addition, either a rolling average or a cumulative sum of the error in the response is maintained to detect instrumental drift.

6.5 CALORIMETER RECALIBRATION

Every month the calibration data from the measurement control program is tested against previous calibration data and a new set of calibration parameters determined based on all relevant data collected in the previous six months. In addition, the calorimeter is recalibrated when a shift is indicated or following a repair or adjustment to the calorimeter system. If the time of an onset of a shift can be established, the calibration data taken since the onset may be used to establish new calibration parameters. If repairs or adjustments are not significant, only one standard need be run to ensure the continued validity of the previous calibration before resuming operation.

6.6 EFFECTIVE SPECIFIC POWER DETERMINATION

The conversion of the power measurement to plutonium mass is made according to one of the methods discussed in ANSI N15.22 and in Section 5 of this report, i.e., either by the empirical method of direct calibration of calorimeter measurements against chemical assay

*A Regulatory Guide entitled, "Measurement Control Program for Special Nuclear Material Control and Accounting" is in progress.

or by the computational method using the measured abundances of the plutonium isotopes and americium-241 and the nuclear decay constants of the radionuclides given in N15.22. In either case, it is important that the licensee calibrates his instruments against chemical or heat standards whose values are traceable to national measurement standards.

When material is processed in identifiable batches characterized by a single blend of plutonium isotopes, the effective specific power should be the same for all material in the batch. If calorimetry is applied for plutonium assay using a batch calibration or batch radionuclidic composition, the following procedures are used to ensure that calorimetric assay is accurate and reliable:

- (1) Samples are taken at a point in the process where each lot of material with a unique plutonium isotopic composition is introduced. Measurement of the effective specific power of the plutonium is made on a sufficient number of samples to generate a reliable estimate of the sampling error.
- (2) Corrections are made for the increase of the effective specific power due to ingrowth of americium-241. Guidelines are given for these corrections in ANSI N15.22.
- (3) The process is studied to determine whether separation of americium from plutonium could occur in process steps between the point of sampling for measuring the effective specific power and the point of measurement of the thermal power. If separation behavior is unpredictable, the americium-to-plutonium ratio can be monitored by gamma-ray or radiocounting techniques. Alternatively, a redetermination of the effective specific power at later steps of the process is made.
- (4) When mixing of plutonium isotopic blends is suspected, either the effective specific power is redetermined or the radionuclidic abundances are monitored to detect such mixing and to allow the average effective specific power to be computed.

7. Conclusions

Minimal matrix interference, direct traceability to NBS standards, and insensitivity to elemental homogeneity make calorimetry a unique nondestructive method for the assay of plutonium. With the proper controls, calorimetry can provide valuable assistance to the licensee in meeting regulatory requirements. At present there are several

other programs under way at this laboratory to further ease the implementation of calorimetric assay in licensee facilities.

1. *A NUREG report is now in preparation for publication in mid-1977 entitled, "Numerical Examples of the Estimation of Error for the Calorimetric Assay of Plutonium-Bearing Solids". This will give numerical examples of typical calibration, measurement assurance, and overall error estimation calculations.
2. *An evaluation of the present "state of the art" of calorimetry combined with gamma-ray isotopics for shipper-receiver verification is being performed during FY-1977.
3. **A direct comparison of the precision, accuracy, cost, and general merit of the empirical and the computational methods for determining the effective specific power is in progress for completion in FY-77.
4. ***A method of reducing the time required to perform a calorimetry measurement is being developed using prediction of equilibrium [14] techniques.

*With support from the U. S. Nuclear Regulatory Commission/Office of Standards Development.

**With support from the U. S. Nuclear Regulatory Commission/Office of Nuclear Regulatory Research.

***With support from the U. S. Energy Research and Development Administration/Division of Safeguards and Security.

Acknowledgments

The author wishes to extend his appreciation to the following individuals for their valuable comments and suggestions: Mr. Philip Ting of U. S. Nuclear Regulatory Commission/Office of Standards Development, Mr. C. P. Sutter of Atlantic Richfield Hanford Company, Mr. Roy Tsugawa of Lawrence Livermore Laboratory, and Mr. F. M. Smith of Westinghouse Hanford Operations, and Dr. W. W. Strohm of Mound Laboratory.

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