CALORIMETRIC ASSAY OF REACTOR GRADE PuO₂

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ABSTRACT

This paper describes an experiment to estimate the random and systematic errors in determining the effective specific power of plutonium. Precisions and accuracies comparable to coulometric assay were demonstrated for a wide range of plutonium isotopic compositions. Thus, calorimetric assay can provide an effective method for plutonium assay of materials in the nuclear fuel cycle.

INTRODUCTION

Plutonium can be assayed in plutonium-bearing materials by calorimetric measurement of the rate of heat generation from radioactive decay, followed by conversion of this wattage to grams of total plutonium using a proper conversion factor. This conversion factor, known as the effective specific power (Peff), is analogous to the analytical factor (g Pu/g sample) used to convert weight measurements to grams of plutonium. The difference is that the Peff, expressed in watts/gram plutonium, applies equally well to all chemical compositions of plutonium provided there is no significant or uncorrectable change in the relative abundance of heat-producing isotopes. Thus, once Peff is determined for a batch of plutonium oxide, it is potentially valid for use in the plutonium assay of PuO₂, mixed oxide, scrap, waste and other indefinite chemical compositions. By contrast, the analytical factor for conversion of sample weight to grams of plutonium must be redetermined for each of the frequent changes in chemical composition which occur during processing.
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Calorimetry power measurements have been demonstrated to exhibit precisions and accuracies comparable to those achievable with an analytical balance. However, the technology of determining the effective specific power is not nearly so well advanced. This paper describes an experimental evaluation of several methods for experimentally determining the effective specific power using available "state-of-the-art" analytical procedures. These methods were tested using the range of plutonium isotopic compositions expected in the commercial nuclear fuel cycle.

METHODS EVALUATED

The effective specific power (\(P_{\text{eff}}\)) can be determined by two general methods. The first, known as the empirical method, is a direct comparison of the calorimetric measurement to a chemical assay of the total plutonium content of a small aliquot of material. \(P_{\text{eff}}\) is then calculated from:

\[
P_{\text{eff}} = \frac{W_i}{P_{\text{u}i}}
\]

where \(W_i\) = measured thermal power of the aliquot (watts)

\(P_{\text{u}i}\) = total plutonium content of the aliquot.

For the second general method, known as the computational method, the relative abundances of all heat-producing isotopes are measured and \(P_{\text{eff}}\) is calculated from:

\[
P_{\text{eff}} = \sum_{j=1}^{6} R_j P_j
\]

where \(R_j\) = mass abundance of the \(j^{\text{th}}\) isotope relative to total plutonium

\(P_j\) = specific power of the \(j^{\text{th}}\) isotope (watts/g)

\(j = 1, 2, 3, 4, 5\) and 6 for Pu-238, -239, -240, -241, -242 and Am-241, respectively.
Various methods are being used to make the necessary isotopic abundance determinations since no single technique available is adequate to provide all the relative isotopic abundances required. The following combinations were tested as the most likely methods for determining the isotopic abundances in the computational approach:

1. Alpha spectrometry for plutonium-238 and americium-241 plus mass spectrometry for the remaining isotopes;

2. Mass spectrometry for all plutonium isotopes and gamma ray spectrometry for americium-241;

3. Mass spectrometry for plutonium-242 and gamma ray spectrometry for the remaining isotopes.

EXPERIMENTAL APPROACH

These methods were tested on PuO₂ with three different isotopic compositions simulating the range of isotopic abundances expected in the commercial nuclear fuel cycle (see Table 1). Five sites, Mound Laboratory, New Brunswick Laboratory (NBL), Argonne National Laboratory (ANL), Savannah River Plant (SRP) and Lawrence Livermore Laboratory (LLL), took part in the experiment.

The basic experimental approach was to prepare three batches of PuO₂, each with a uniform isotopic composition. Fourteen samples were taken from each PuO₂ batch, weighed, and calorimetered. Six samples were supplied to Mound, six to NBL, and two were retained as historical samples. Isotopic analyses by gamma ray spectrometry were performed on the samples by Mound and ANL. The samples were then totally dissolved and the solution diluted by weight. Duplicate aliquots of this solution were analyzed for impurities, plutonium content (by coulometry), and relative isotopic abundances by both mass spectrometry and alpha spectrometry. Portions of the solutions were also supplied to SRP and LLL for isotopic analysis by gamma ray spectrometry.
From these data, Peff of each sample was determined for each method.

Table 1 - ISOTOPIC COMPOSITION OF PuO₂ ISOTOPIC BATCHES

<table>
<thead>
<tr>
<th>Attribute*</th>
<th>Batch 1</th>
<th>Batch 2</th>
<th>Batch 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu-238</td>
<td>0.057</td>
<td>0.25</td>
<td>1.14</td>
</tr>
<tr>
<td>Pu-239</td>
<td>86.56</td>
<td>73.21</td>
<td>70.31</td>
</tr>
<tr>
<td>Pu-240</td>
<td>11.71</td>
<td>22.58</td>
<td>24.06</td>
</tr>
<tr>
<td>Pu-241</td>
<td>1.48</td>
<td>2.97</td>
<td>3.23</td>
</tr>
<tr>
<td>Pu-242</td>
<td>0.20</td>
<td>0.99</td>
<td>1.25</td>
</tr>
<tr>
<td>Am-241</td>
<td>0.005</td>
<td>0.056</td>
<td>0.025</td>
</tr>
<tr>
<td>Peff</td>
<td>2.883</td>
<td>4.595</td>
<td>9.671</td>
</tr>
<tr>
<td>(mW/g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample Size</td>
<td>4.0</td>
<td>2.5</td>
<td>1.2</td>
</tr>
<tr>
<td>(g)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Weight percent relative to plutonium content

The experiments were designed not only to test for sampling, dissolution and other errors, but also to estimate the random and systematic error inherent in each Peff method.

RESULTS

A summary of the results to date is given in Tables 2 and 3. For the better methods the precisions approach that of coulometry, which ranged from 0.05 to 0.12% with an average of 0.07%. For example, the precision of the empirical method varied from 0.033 to 0.13% with an average of 0.08%. The contributions of the calorimetric and coulometric errors to the Peff were approximately equal.

Likewise, the precision of the best computational method (Comp. No. 1) ranged from 0.031% to 0.10% with an average of 0.07%. This is very encouraging since it was previously thought that for high (>1%) Pu-238 concentrations, the error in the computational method would become very large because of errors in determining Pu-238 abundance.
### Table 2 - Comparison of Methods for Determining the Effective Specific Power

<table>
<thead>
<tr>
<th>Method</th>
<th>Batch</th>
<th>Precision (％ rel. std. dev.)</th>
<th>Bias from Reference Value (％)</th>
<th>Standard Error of the Bias (％)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical</td>
<td>1</td>
<td>0.069 0.065</td>
<td>+0.012 -0.020</td>
<td>0.028 0.026</td>
</tr>
<tr>
<td>Comp No. 1b</td>
<td>1</td>
<td>0.059 0.10</td>
<td>+0.11 -0.01</td>
<td>0.03 0.05</td>
</tr>
<tr>
<td>Comp No. 2c</td>
<td>1</td>
<td>0.11 0.32</td>
<td>+0.08 -0.49</td>
<td>0.05 0.16</td>
</tr>
<tr>
<td>Empirical</td>
<td>2</td>
<td>0.033 0.13</td>
<td>+0.007 -0.007</td>
<td>0.013 0.05</td>
</tr>
<tr>
<td>Comp No. 1b</td>
<td>2</td>
<td>0.031 NA</td>
<td>+0.21 NA</td>
<td>0.03 NA</td>
</tr>
<tr>
<td>Comp No. 2c</td>
<td>2</td>
<td>0.085 NA</td>
<td>-0.048 NA</td>
<td>0.04 NA</td>
</tr>
<tr>
<td>Empirical</td>
<td>3</td>
<td>0.062 NA</td>
<td>- NA</td>
<td>- NA</td>
</tr>
<tr>
<td>Comp No. 1b</td>
<td>3</td>
<td>0.058 NA</td>
<td>+0.10 NA</td>
<td>0.03 NA</td>
</tr>
<tr>
<td>Comp No. 2c</td>
<td>3</td>
<td>0.20 NA</td>
<td>+0.67 NA</td>
<td>0.12 NA</td>
</tr>
</tbody>
</table>

*Reference Value = Average of NBL and empirical values.

b Using alpha spectrometry for Pu-238 and Am-241 and mass spectrometry for remaining isotopes.

c Using mass spectrometry for all plutonium isotopes and gamma ray spectrometry for Am-241.

NA = Not available.

### Table 3 - \textit{P}_{eff} Computed from Isotopic Abundance Determined by Gamma Ray Spectrometry Measurements

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Batch</th>
<th>Precision (％ rel. std. dev.)</th>
<th>Bias from Reference Value (％)</th>
<th>Material Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLL</td>
<td>1</td>
<td>0.06</td>
<td>-0.23</td>
<td>Liquid</td>
</tr>
<tr>
<td>LLL</td>
<td>2</td>
<td>0.15</td>
<td>-0.84</td>
<td>Liquid</td>
</tr>
<tr>
<td>SRP</td>
<td>1</td>
<td>0.52</td>
<td>-1.01</td>
<td>Liquid</td>
</tr>
<tr>
<td>SRP</td>
<td>2</td>
<td>1.05</td>
<td>-1.25</td>
<td>Liquid</td>
</tr>
<tr>
<td>ANL</td>
<td>2</td>
<td>1.1</td>
<td>-1.5</td>
<td>Solid</td>
</tr>
</tbody>
</table>

*Americium Analysis Not Available.
The sensitivity of the $P_{eff}$ to errors in the Pu-238 determination results from the fact that the specific power constant of Pu-238 is much higher than that of the other isotopes (i.e., 293 times that of Pu-239). For composition 3 (1.15% Pu-238), nearly 70% of the heat is due to Pu-238.

The biases observed arise from several sources, the most significant one being an error in the Pu-238 determination. For example, a 1% error will result in errors of 0.1, 0.3 and 0.7% in the $P_{eff}$ of isotopic compositions 1, 2, and 3, respectively.

Errors attributed to americium analysis were not significant in this experiment, since americium had been recently separated out and was present only at low levels. In older materials this is potentially a source of error since the specific power of Am-241 is approximately one-fifth that of Pu-238.

Biases between the empirical and the computational methods can also arise from errors in the specific power constants of the heat-producing isotopes. The constants used and their associated uncertainties were those recommended by ANSI N15.22-1975 "Calibration Techniques for Calorimetric Assay of Plutonium-Bearing Solids Applied to Nuclear Materials Control". Based on the uncertainties assigned by this standard, the computational $P_{eff}$ has estimated uncertainties (95% confidence limits) of 0.34, 0.22, and 0.16% for isotopic compositions 1, 2, and 3, respectively.

Recent half-life measurements indicate the specific powers of Pu-239 and Pu-240 are too high and should be revised. These revisions would cause the biases in the computational methods to be slightly more negative than the present estimates. This is consistent with the positive biases observed in what is believed to be the most accurate computational method (Comp. No. 1).

Other potential sources of bias are errors in the standards used. The stated uncertainties
(95% confidence level) of the plutonium assay and
heat standards used are 0.10% and 0.02%, respec-

The effect of the error in the Pu-238 deter-
mination is also quite pronounced in the preci-
sions and biases observed when the relative iso-
topic abundances were determined by gamma ray
spectrometry. In addition, the accuracy and pre-
cision of the technique varied widely from labora-
tory to laboratory. The precision of the LLL
solution measurements is very encouraging, ranging
from 0.06% to 0.15% on batches 1 and 2. On the
other hand, the precision of the SRP measurements
was much larger, 0.52 and 1.0%, respectively, on
batches 1 and 2 using basically the same tech-
nique and equipment. No cause for this labora-
tory-to-laboratory difference was identified. Pre-
suming that the LLL precision can be achieved con-
sistently by other laboratories, the method
appears to be competitive with mass spectrometry
for many applications.

The higher uncertainties of the ANL solid
measurements are not so surprising since the
solids cause much more scattering than the liquids
and thus the observed peaks are not nearly so
sharp. Even so, 1% measurements on solids have
many applications in the nuclear fuel cycle, for
example, scrap and other materials which are
either chemically inhomogeneous or extremely dif-
cult to dissolve. The 1.5% bias in the solids
is primarily due to bias in the Pu-238 measure-
ments. This bias can be eliminated by applying
a bias correction unless the bias is found to be
a function of the material.

SUMMARY

Calorimetric assay provides an effective
method for plutonium assay of materials in the
nuclear fuel cycle.

- Precisions and accuracies comparable to those
  of coulometry are achievable for a wide range
  of plutonium isotopic compositions.
The method is applicable to a wide variety of materials since representative sampling for determination of \( P_{\text{eff}} \) is dependent upon isotopic homogeneity rather than chemical homogeneity.

The method can be used to assay entire sample streams or to provide a calibration method traceable to NBS for other nondestructive assay measurement systems.

ACKNOWLEDGEMENTS

Mound Laboratory is operated by Monsanto Research Corporation for the U. S. Energy Research and Development Administration under Contract No. EY-76-C-04-0053.

This work was supported by the U. S. Nuclear Regulatory Commission, Office of Standards Development and Office of Nuclear Regulatory Research.

We gratefully acknowledge the assistance of C. E. Pietri, NBL; F. O. Ballenger, ANL; A. Gibbs, SRP; R. Gunnink, LLL; and R. L. Goss, R. J. Seiler, W. E. Sheehan, and H. S. Carden of Mound Laboratory.