

**SOME EXAMPLES OF THE ESTIMATION
OF ERROR FOR CALORIMETRIC ASSAY
OF PLUTONIUM-BEARING SOLIDS**

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Mound Laboratory
for
U. S. Nuclear Regulatory Commission

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**SOME EXAMPLES OF THE ESTIMATION
OF ERROR FOR CALORIMETRIC
ASSAY OF PLUTONIUM-BEARING SOLIDS**

W. W. Rodenburg

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Monsanto Research Corporation
Mound Laboratory
Miamisburg, OH 45342

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Some Examples of the Estimation of Error for Calorimetric Assay of Plutonium-Bearing Solids

by

W. W. Rodenburg

ABSTRACT

This report provides numerical examples of error estimation and related measurement assurance programs for the calorimetric assay of plutonium. It is primarily intended for users who do not consider themselves experts in the field of calorimetry. These examples will provide practical and useful information in establishing a calorimetric assay capability which fulfills regulatory requirements.

1. Introduction

The following examples are given as an aid in the use of calorimetric assay of plutonium for nuclear material accounting purposes. Although existing guides and standards are quite complete, it was felt that a few numerical examples of the error estimation process would speed understanding of the use of calorimetric assay for plutonium. The examples given are drawn from process experience at this Laboratory. For simplicity and ease of reference the terminology and methods used are consistent with ANSI N15.22-1975, "Calibration Techniques for the Calorimetric Assay of Plutonium-Bearing Solids Applied to Nuclear Materials Control" [1].

Calorimetric assay for plutonium content is essentially a two-step process. The first step is to determine the power in watts generated by nuclear decay in the bulk sample. The second step is to determine the conversion factor for watts to grams of plutonium defined in ANSI N15.22-1975 as the "effective specific power," P_{eff} . The following numerical examples cover error estimation for the power measurement as well as several methods for determining P_{eff} . Also included are tests for sampling errors and interferences caused by heat produced by chemical reactions.

2. Estimation of Error Associated with Power Measurement

2.1 INITIAL TESTING

Data from a Mound Laboratory Model 102 heat flow calorimeter as described in Reference 2 are used for this example. The calorimeter is a general purpose instrument with a sample chamber 12.1 cm (4.75 in.) in diameter and 27.9 cm (11.9 in.) high. The instrument, designated Calorimeter A,

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is designed to assay PuO₂ feed, mixed-oxide pellets, and process scrap and waste. Data were taken using calibration against electrical standards and the conventional mode of operation as defined in ANSI N15.22-1975 [1]. The method of data analysis, however, is completely general and can be applied to any of three operational modes described in ANSI N15.22-1975.

The data cover the range from 0.15 to 2.0 W. During a 60-day interval, 18 observations were made on various combinations of four plutonium-238-fueled heat standards with nominal values of 0.14, 0.29, 0.56, and 0.97 W. In addition, each sample was located randomly in one of three locations in a sample container filled with sand to simulate the heat transfer properties of PuO₂. Running the heat standards in this manner made it possible to determine the heat distribution error,* s(HDE); the calibration error, s(CALIB); and the error caused by calorimeter imprecision, s(W) [1]. The 60-day period was chosen so the data reflected the variations in such factors as room temperature, humidity, line voltage, etc. that normally occur during a monthly inventory period.

The difference ($X_i - \mu_0$) of each individual observation, X_i , from the standard value, μ_0 , is recorded in Table 1. Differences are used because this is the easiest way to account for the decay of the standards. Averages and standard deviations were calculated for each position and for all data (Table 1).

Next the data were fit to an equation of the form $Y = A + BX$, where Y = error in milliwatts and X = nominal wattage of the standard, to test for bias in the calibration. Since the intercept A was small, -0.03 mW, and the slope B nearly zero, -0.0068 mW/W, with a large uncertainty, ± 0.28 mW/W (one standard deviation), no bias corrections were applied.

As an aid in the analysis, the differences expressed both in milliwatts and as a percentage were plotted as a function of the nominal wattage of the heat standard. Since the absolute differences are of the same magnitude over the entire wattage range (Figure 1), the relative differences (Figure 2) increase at the low end of the range. This is a common occurrence indicating that the random noise of the instrument dominates the measurement error at the low end of the range. The relative standard deviation at any wattage in the operating range is thus obtained by dividing the absolute standard deviation s(mW) by the average wattage of the samples being analyzed.

*The heat distribution error is defined in ANSI N15.22-1975 to be the error arising from the spatial distribution of the heat source within the calorimeter chamber.

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TABLE 1

TEST DATA FOR CALORIMETER A

<u>Day</u>	<u>Position*</u>	<u>Nominal Wattage of Standard(s)</u>	<u>Difference ($X_i - \mu_0$) (mW)</u>	<u>Relative Difference** (%)</u>
3	T	1.26	-1.48	- 0.12
7	B	0.14	+0.11	+ 0.08
10	T	0.70	+1.10	+ 0.16
13	M	1.11	-0.11	- 0.01
17	B	0.14	-0.67	- 0.48
20	T	1.67	-0.25	- 0.02
23	M	1.26	-0.51	- 0.04
27	T	1.53	+0.28	+ 0.02
30	B	1.96	+0.40	+ 0.02
33	M	1.40	+0.78	+ 0.06
37	M	0.70	-0.71	- 0.10
40	T	1.82	+0.47	- 0.03
43	M	0.97	-0.85	- 0.09
47	M	0.85	-0.05	- 0.01
50	B	0.56	+0.56	+ 0.10
53	B	0.43	-0.13	- 0.03
57	T	1.96	+0.54	+ 0.03
60	B	0.29	+0.81	+ 0.28

	<u>Top</u>	<u>Middle</u>	<u>Bottom</u>	<u>All Data</u>
Average, $X_i - \mu_0$ (mW)	-0.05	-0.24	+0.18	-0.04
s(mW)	0.90	0.59	0.53	0.68
Average, $X_i - \mu_0$ (%)	+0.01	-0.03	-0.01	-0.01
s(%)	0.09	0.06	0.25	0.15

*T = top; B = bottom; M = middle

** $100 \times \frac{(X_i - \mu_0)}{\text{nominal wattage}}$

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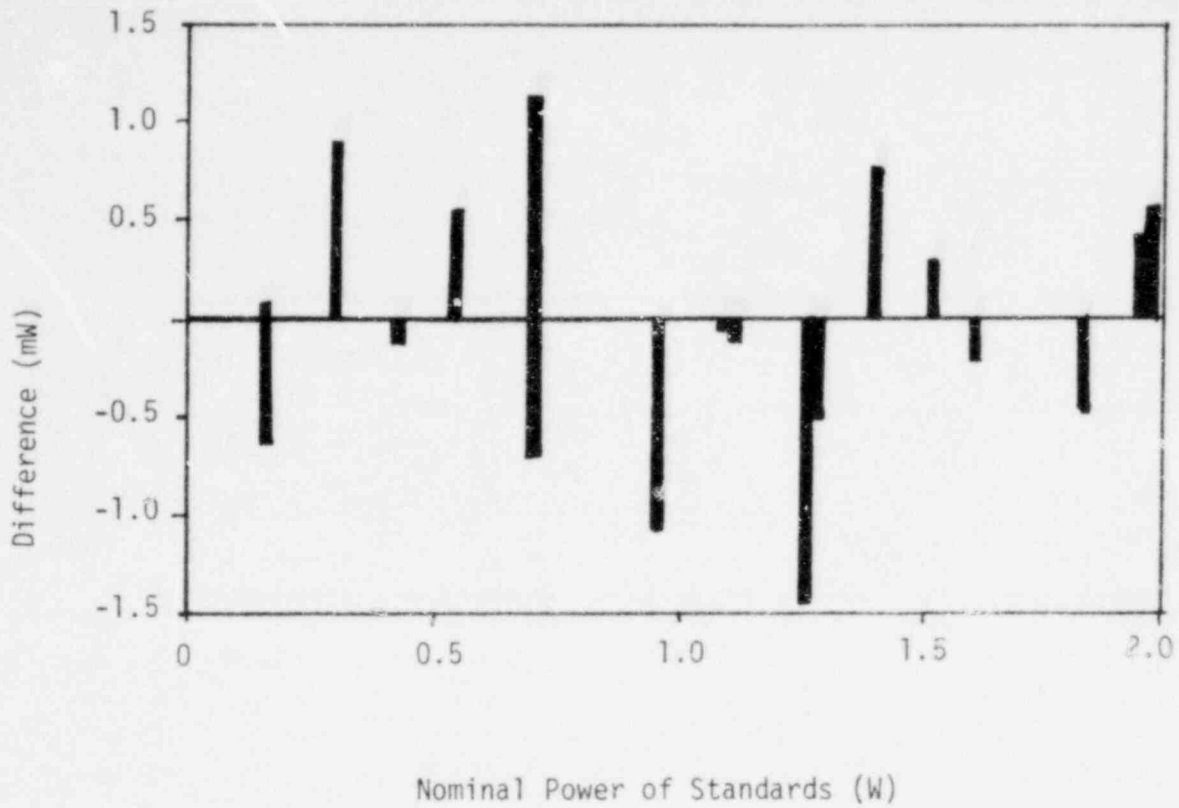


Figure 1: Calorimeter Error (mW) as a Function of Wattage

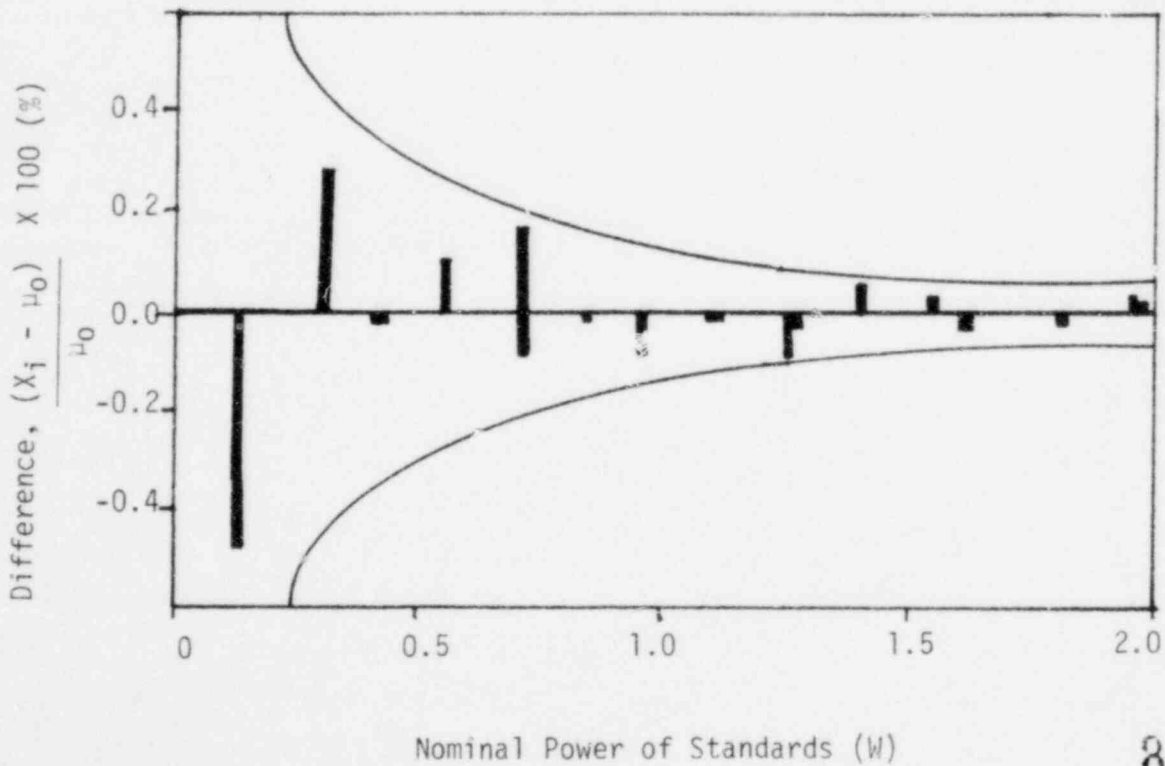


Figure 2: Calorimeter Error (%) as a Function of Wattage

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2.2 MEASUREMENT CONTROL PROGRAM

Once the initial testing was completed, a heat standard was measured after every six unknowns to provide a continuing assessment of system performance. The standards were alternated between the top, bottom, and middle positions in the sequence shown in Table 2. Thus all standards were measured in all positions once every 42 standard runs (14 wattages X 3 positions). This procedure randomizes the effects of the wattage and position. First, data are used to test for changes in instrument behavior since the previous period. Second, new calibration data are continually being generated to provide new calibration parameters. This provides an ongoing linkage to standards traceable to the national measurement system. The data are recorded and maintained on forms of the type shown in Figure 3.

The results were monitored by a control chart of the differences between the measured value and standard value as a function of time (Figure 4). The control limits were set at two and three sigma, 1.36 and 2.04 mW, respectively. If one value exceeds the three-sigma limit or two consecutive values exceed the two-sigma limit, another standard is immediately run. If the rerun also exceeds the two-sigma limit, measurements cease until the problem is resolved. A cumulative sum (CUSUM) of the last nine values is also maintained (Figure 5) to detect instrument drift.

Five days before the end of the accounting period, the control data are evaluated to test for changes in instrument performance during the period. The format used, shown in Figure 6, is a simple one, so that all calculations can be made on a pocket calculator capable of computing standard deviations. First, the averages and standard deviations computed in the previous period are entered in lines one through five. Next, the averages and standard deviations for the present period are computed and entered in lines six through ten. Note the sum of the deviations and the deviations squared are also recorded for ease in combining the data later.

The first test is computation of the F ratio of the standard deviations of the present period with the previous period (line 7 divided by line 2, the quantity squared). The operator then looks up the F ratio from a table* for $n_1 - 1$ and $n_2 - 1$ degrees of freedom (from lines 5 and 10) and the chosen confidence level (95% in this case) and enters it on line 12. If the computed F ratio exceeds the limits (line 11 greater than line 12), the supervisor is notified and remedial action is taken.

*See for example Appendices C and D of Reference 3.

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TABLE 2

CALORIMETER MEASUREMENT CONTROL SCHEDULE

Order	Heat Standard(s) to be Used				Nominal Wattage	Position in Calorimeter*
	0.14	0.29	0.56	0.97		
1		X		X	1.26	
2	X				0.14	
3	X		X		0.70	
4	X			X	1.11	
5	X		X	X	1.67	
6	X	X			0.43	
7	X	X	X	X	1.96	
8	X	X		X	1.40	
9		X	X	X	1.82	
10				X	0.97	
11		X	X		0.85	
12			X		0.56	
13			X	X	1.53	
14		X			0.29	

*Enter T (top), B (bottom) or M (middle) to indicate position as standard is loaded.

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Figure 4: Control Chart of Random Error

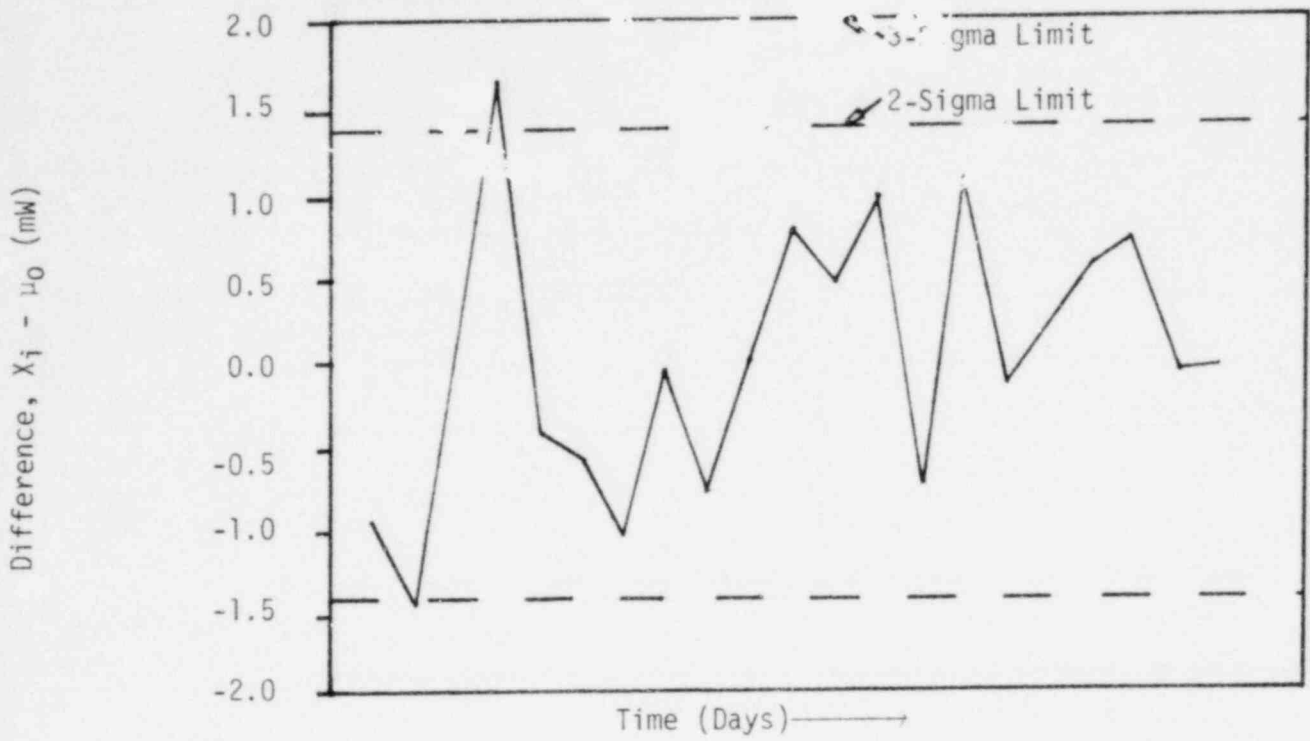
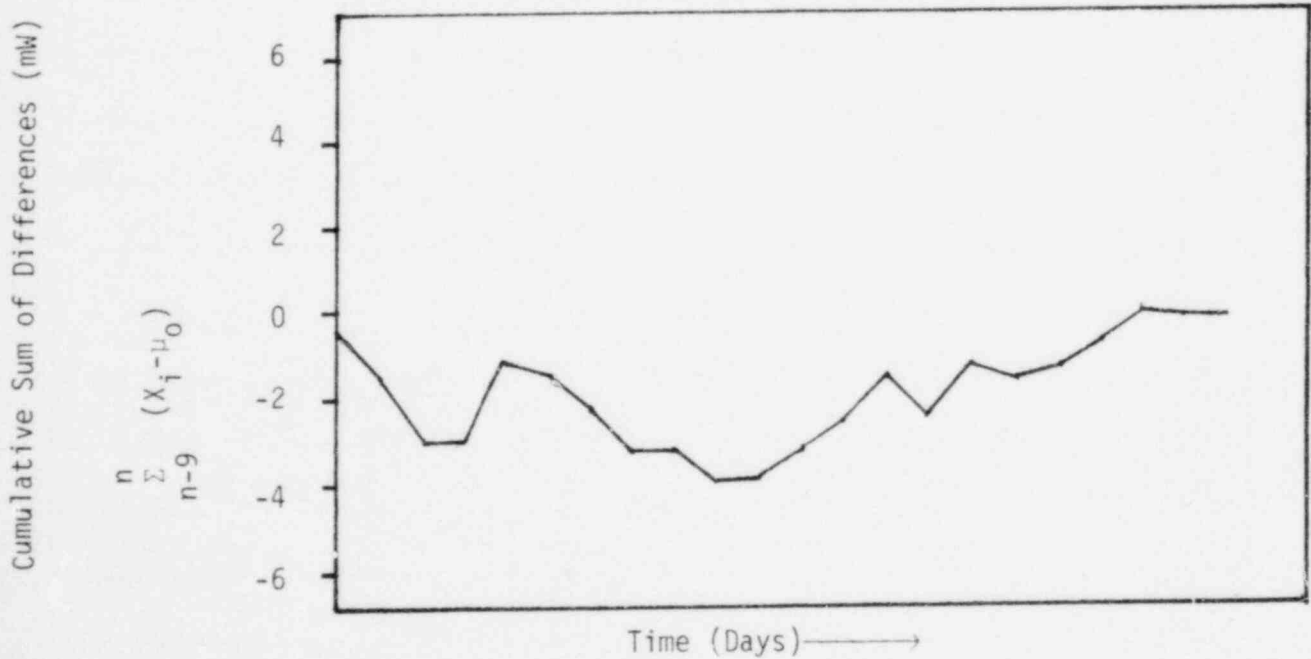


Figure 5: Control Chart of Cumulative Error



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Figure 6: Sample Calculation of Measurements Control Data

CALORIMETER MEASUREMENT CONTROL DATA EVALUATION
 SHEET FOR THE PERIOD 3-1, 1976 THROUGH 5-1, 1976

CALORIMETER NUMBER A
 ANALYST WWR

Previous Period

1. Means, \bar{X}_1 (mW)
2. Standard Deviations, S_1 (mW)
3. ΣX_i
4. ΣX_i^2
5. Number of Observations, N_1

This Period

6. Means, \bar{X}_2 (mW)
7. Standard Deviations, S_2 (mW)
8. ΣX_i
9. ΣX_i^2
10. Number of Observations, N_2

Comparison

11. F Ratio (line 7 \div line 2)²
12. F Ratio from Table*, 95% confidence with N_1-1 and N_2-1 degrees of freedom
13. Check if 12 > 11 (if 11 > 12 circle and notify supervisor)

	Positions			
	Top	Middle	Bottom	All
1. Means, \bar{X}_1 (mW)	-0.05	-0.24	+0.18	-0.04
2. Standard Deviations, S_1 (mW)	0.90	0.59	0.53	0.68
3. ΣX_i	-0.28	-1.45	1.08	-0.65
4. ΣX_i^2	4.05	2.11	1.61	7.71
5. Number of Observations, N_1	6	6	6	18
6. Means, \bar{X}_2 (mW)	+0.18	+0.11	-0.23	+0.02
7. Standard Deviations, S_2 (mW)	1.00	0.61	0.70	0.78
8. ΣX_i	1.24	0.74	-1.62	+0.36
9. ΣX_i^2	6.29	2.53	3.31	12.13
10. Number of Observations, N_2	7	7	7	21
11. F Ratio (line 7 \div line 2) ²	1.23	1.07	1.74	1.32
12. F Ratio from Table*, 95% confidence with N_1-1 and N_2-1 degrees of freedom	4.95	4.95	4.95	2.23
13. Check if 12 > 11 (if 11 > 12 circle and notify supervisor)	✓	✓	✓	✓

*J. Jaech, Statistical Methods in Nuclear Material Control, TID-26298, USAEC, Dec., 1973, p. 386-387.

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$$14. \quad t = \frac{\bar{X}_1 - \bar{X}_2}{\frac{S_1^2}{n_1-1} + \frac{S_2^2}{n_2-1}} =$$

15. t factor from tables*

16. Check if 15 > 14 (circle if 15 < 14, and notify supervisor)

Combined Data

17. $\Sigma \bar{X}_i$

18. Σx_i^2

19. Number of Observations n_T

20. Mean \bar{X}_T

21. Standard Deviation, S_T

Positions			
Top	Middle	Bottom	All
0.40	0.96	1.10	0.26
2.20	2.20	2.20	2.20
✓	✓	✓	✓
0.96	-0.71	-0.54	-0.29
10.34	4.64	4.92	19.90
13	13	13	39
0.07	-0.03	-0.04	-0.01
0.93	0.58	0.60	0.72

*Ibid., p. 383.

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The second test is a student t-test of the means. First, t is calculated (line 14), and then t for 95% confidence levels and $n_2 + n_1 - 2$ degrees of freedom is obtained from statistical tables*. If no significant biases are detected (line 14 less than line 15) no changes are made. If a bias is judged to be significant, new calibration parameters are computed as before (Section 2.1) and/or bias corrections are made.

2.3 ASSIGNMENT OF RANDOM AND SYSTEMATIC ERRORS

After the tests outlined in previous sections are made, the data from the present month are combined with data from the previous five months to provide a larger data base for the analysis. It is these combined data that are used to make estimates of the random and systematic errors in the calorimetric power measurement. The random error is the standard deviation of the calorimeter in milliwatts divided by the average wattage of the unknowns. For example, samples from a scrap category containing an average of 100 g of FFT-type plutonium would have an average wattage of 300 mW; thus the random error of the calorimeter for this category is $0.72/300$ or 0.0024 (0.24%) relative standard deviation.

The systematic error variance, S_s^2 , is determined from an equation of the form [3] which is applicable when no bias corrections are made.

$$S_s^2 = (\bar{X}_i - \mu_0)^2 + S_0^2 + S^2/n$$

where S_s = systematic error

$\bar{X}_i - \mu_0$ = bias (delete this term when bias corrections are made)

S_0 = systematic error assigned to standards

S = random error.

The heat standards have an assigned uncertainty of 0.02%. Thus the systematic error estimate $S_s(W)$ for power measurements of the scrap category is:

$$S_s^2(W) = (-0.0001)^2 + (0.0002)^2 + (0.0024)^2/39$$

$$S_s^2(W) = 20 \times 10^{-8}$$

$$S_s(W) = 0.044\%$$

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*See for example Appendices C and D of Reference 3.

2.4 TEST FOR CHEMICAL INTERFERENCES

Interferences to the power measurement may also occur when heat emitting (or absorbing) impurities or processes occur in the plutonium-bearing matrix. The errors introduced by such interferences are in addition to the random and systematic error estimates made in the previous section. ANSI N15.22-197F suggests that the error caused by such interferences may be estimated by:

1. A comparison of the calorimetric assay with an assay by an independent technique;
2. Analytical techniques such as gamma-ray spectroscopy to detect fission product contamination;
3. Process control information;
4. Observation of the time dependence of the power emission to detect chemical reactions.

An example of the fourth method follows. The amount of chemical interference possible is limited by the amount of reactants present, the heat of reaction, and the rate of reaction. If a reaction is fast, all the heat will be released in a short period of time and the interference will go to zero since the reactants are depleted. Thus a second calorimetry measurement at a later time is used to detect interferences from chemical reactions. On the other hand, if the reaction is very slow, the amount of heat generated per unit time in watts will be small. As a rule of thumb, two calorimetry measurements a week apart will detect any significant interferences from chemical reactions. For example, when visible traces of moisture were found in a particular scrap category, repeat wattage measurements at least one week apart were made on the suspect samples. The measured wattage of the first run was corrected for decay to the date of the second run, and differences were calculated (Table 3).

Again based on an F test of variances and a t test of the difference, it was concluded that there was no significant interference from chemical reactions and no bias corrections were made.

3. Estimation of Error in Effective Specific Power Determination

3.1 EMPIRICAL METHOD (RANDOM ERROR)

This example is based on analysis of metal exchange samples [4]. In the empirical method, the aliquots are weighed and calorimetered before being dissolved and assayed for plutonium content.

The effective specific power, P_{eff} , of a sample is defined as follows:

$$P_{eff} = \frac{W}{Mx[Pu]}$$

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where W = wattage of the aliquot
M = mass of the aliquot
[Pu] = Pu concentration (g/g)

TABLE 3
TEST FOR CHEMICAL INTERFERENCES

Sample I.D.	Date of 1st Run	Days between Runs	Run #1 Measured Value (W)	Run #1 Decayed to Date of 2nd Run (W)	Run #2(W)	Difference (#1-#2)	
						mW	
A	6/5/75	13	1.9786	1.9792	1.9793	-0.1	-0.005
B	6/12/75	13	1.6434	1.6439	1.6438	+0.1	+0.006
C	6/24/75	21	1.9672	1.9680	1.9675	+0.5	+0.026
D	7/1/75	41	2.0355	2.0371	2.0380	-0.9	-0.044
E	7/11/75	37	1.9692	1.9706	1.9712	-0.6	-0.030
F	7/15/75	56	2.0334	2.0356	2.0350	+0.6	+0.030
G	7/17/75	8	1.8834	1.8835	1.8834	+0.1	+0.005

$$\bar{D} = -0.04 \text{ mW} - 0.002\%$$

$$S = 0.55 \text{ mW}, 0.027\%$$

$$F = \frac{(0.55)^2}{(0.72)^2} = 0.61$$

$$t = \frac{0.04}{0.55 \sqrt{7}} = 0.192$$

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TABLE 4

EFFECTIVE SPECIFIC POWER DETERMINATION BY THE EMPIRICAL METHOD

<u>Sample I.D.</u>	<u>Date</u>	<u>Observed Value (mW/g)</u>	<u>All Values Decayed to 4/10/73 (mW/g)</u>
M0373-3	4/10/73	2.3818	2.3818
M0373-4	4/11/73	2.3797	2.3796
M0673-2	7/10/73	2.3922	2.3862
M0673-3	7/11/73	2.3901	2.3840
M0973-2	10/10/73	2.3946	2.3826
M0973-3	10/11/73	2.3934	2.3813
M01273-1	1/9/74	2.4010	2.3833
M01273-4	1/6/74	2.4005	2.3828

Avg. 2.3827

s = 0.00195 mW/g

$s(P_{\text{eff}})$ = 0.082%

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The relative standard deviation of the effective specific power measurements, $s(P_{\text{eff}})$, is calculated from multiple determinations of P_{eff} presented in Table 4.

3.2 EMPIRICAL METHOD (SYSTEMATIC ERROR)

The systematic error in the effective specific power determination, $S_S(P_{\text{eff}})$, is made up of two components: the systematic error in the power measurement, $S_S(W)$, and the error in determining the mass of plutonium, $S_S(M)$. Using the methods outlined in sections 2.1, 2.2, and 2.3, the bias and standard deviation of the microcalorimeter, based on 12 measurements, was found to be $+0.7 \mu\text{W}$ and $10 \mu\text{W}$, respectively. The average wattage of the aliquot was $20,000 \mu\text{W}$. The systematic error assigned to the heat standards was 0.02%. $S_S(W)$ of the observed values is calculated to be:

$$S_S^2(W) = [(0.7/20,000)^2 + (10/20000)^2/12 + (0.0002)^2]$$

$$S_S^2(W) = 6.20 \times 10^{-8}$$

$$S_S(W) = 0.025\%$$

The estimate of the systematic error in the plutonium determination, $S_S(M)$, is based on the measured precision (eight replicates) of the assay on a NBS standard of 0.08% and a bias of less than 0.02%.

$$S_S^2(M) = \frac{(0.0008)^2}{8} + (0.0002)^2$$

$$S_S^2(M) = 12 \times 10^{-8}$$

$$S_S(M) = 0.035\% \text{ and}$$

$$\begin{aligned} S_S(P_{\text{eff}}) &= [S_S^2(M) + S_S^2(W)]^{1/2} \\ &= (18.0 \times 10^{-8})^{1/2} \\ &= 0.042\%. \end{aligned}$$

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3.3 COMPUTATIONAL METHOD

The effective specific power can also be computed from the relative abundances of each of the individual isotopes using the equation:

$$P_{\text{eff}} = \sum R_i P_i$$

where R_i = mass abundance of the i^{th} isotope relative to total Pu,
 P_i = specific power of the i^{th} isotope,
 i = 8, 9, 0, 1, 2, and A for the plutonium-238, 239, 240, 241, 242, and americium-241 isotopes, respectively.

The random error associated with this method of specific power determination is defined in ANSI N15.22-1975 as:

$$s(P_{\text{eff}}) = \sum_i (R_i P_i / P_{\text{eff}})^2 s^2 (R_i)^{1/2}$$

where $(R_i P_i / P_{\text{eff}})$ = heat fraction due to the i^{th} isotope, and

$s(R_i)$ = relative standard deviation in the R_i measurement.

In the following examples, two methods of determining the relative isotopic abundances were used. In the first example, the isotopic abundances were determined by mass spectroscopy and radiocounting. In the second example, stream average values were combined with high resolution gamma-ray spectroscopy measurements.

3.3.1 COMPUTATIONAL METHOD I (RANDOM ERROR)

Table 5 shows the calculation of $s(P_{\text{eff}})$ from isotopic data on the same eight samples used in the example in section 3.2 [4]. Note that only the R_i for americium-241 was corrected for decay. The random errors for R_8 and R_1 would be slightly lower if they had been corrected for decay. However, the effect on the final calculation of $s(P_{\text{eff}})$ is negligible.

3.3.2 COMPUTATIONAL METHOD I (SYSTEMATIC ERROR)

3.3.2.1 USING NUCLEAR DECAY CONSTANTS

ANSI N15.22-1975 defines the systematic error, $S_s(P_{\text{eff}})$, associated with the computational method as:

$$S_s(P_{\text{eff}}) = \sum (R_i P_i / P_{\text{eff}})^2 s^2 (P_i)^{1/2}$$

where $s(P_i)$ is the systematic error associated with specific power of the i^{th} isotope.

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TABLE 5

Calculation of $s(P_{\text{eff}})$ for the Computational Method

Sample I.D.	Isotope Composition (wt %) ^a						Analysis Date
	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	Am-241	
M0373-3	0.0165	93.609	5.894	0.458	0.023	0.0461	4/17/73
-4	0.0166	93.626	5.877	0.458	0.023	0.0462	4/18/73
M0673-2	0.0169	93.640	5.871	0.450	0.024	0.0531	7/24/73
-3	0.0170	93.640	5.872	0.450	0.023	0.0518	7/24/73
M0973-2	0.0170	93.643	5.873	0.447	0.023	0.0592	10/5/73
-3	0.0167	93.620	5.894	0.449	0.023	0.0594	10/5/73
M01273-1	0.0164	93.539	5.923	0.448	0.024	0.0637	1/29/74
-4	0.0162	93.584	5.926	0.449	0.023	0.0644	1/29/74
Average	0.01666	93.6126	5.8912	0.4511	0.0232	0.0461 ^b	
s	0.00029	0.0357	0.0225	0.0044	0.0005	0.0006	
$s(R_i)$	0.0174	0.0004	0.0038	0.0098	0.0216	0.0130	
$(R_i P_i / P_{\text{eff}})$.040	.757	.175	0.006	-	0.022	
Var^c	48×10^{-8}	9×10^{-8}	44×10^{-8}	-	-	8×10^{-8}	
$s^2(P_{\text{eff}}) = \Sigma \text{var} = 1.09 \times 10^{-8}$							
$s(P_{\text{eff}}) = 0.10\%$							

^aDetermined by mass spectrometer except for plutonium-238 and americium-241 which were determined by radiocounting.

^bAll values corrected to 4/17/73.

^c $(R_i P_i / P_{\text{eff}})^2 s^2(R_i)$

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Using the values for $s(P_i)$ recommended in ANSI N15.22-1975 and the heat fractions calculated in Table 5, the systematic error $S_S(P_{eff})$ is calculated to be 0.21% in Table 6.

3.3.2.2 REDUCTION OF SYSTEMATIC ERROR BY COMPARISON WITH THE EMPIRICAL METHOD

The data used in the two previous examples were from measurements on the same samples. Thus it is possible to establish a bias correction for the computational method. A comparison of the two methods is given in Table 7. In this case, the bias is 0.18% with a relative standard deviation, $s(\text{bias})$, of 0.066% based on eight determinations. By using the systematic error, 0.042%, computed for the empirical method and applying a bias correction, a lower systematic error for the effective specific power determined by the computational method can be calculated.

$$S_S^2(P_{eff}) = s(\text{bias})^2/n + S_0^2$$

$$S_S(P_{eff}) = [(0.00066)^2/8 + (0.00042)^2]^{1/2}$$

$$S_S^2(P_{eff}) = 2.31 \times 10^{-7}$$

$$S_S(P_{eff}) = 0.048\%$$

Therefore, by comparing the two methods of determining the specific power, the systematic error associated with the computational method can be reduced from 0.21% to 0.048%.

3.3.3 COMPUTATIONAL METHOD II (RANDOM ERROR)

Stream average isotopic abundances are calculated in Table 8 based on the isotopic compositions of nine batches of FFTF material. When the effective specific power of FFTF material is computed using these stream averages, the uncertainties in the plutonium-238 and americium-241 mass abundances represent 50% and 49% of the total random error of the effective specific power. In addition, the americium-241 grows into this material at a rate of 0.08%/yr, further increasing the uncertainty of the assay.

High-resolution gamma-ray spectroscopy with a standard deviation of 5% may be used to reduce the uncertainty in the plutonium-238 and americium-241 isotopics. The random component of the effective specific power was calculated by summing the errors from the plutonium-238 and americium-241 measurements and the errors due to variations in the stream average values, $\text{Var}(R_1)$, for plutonium-239, -240, and -241.

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TABLE 6

Calculation of $S_s(P_{\text{eff}})$ for the Computational Method

	Isotope				
	<u>Pu-238</u>	<u>Pu-239</u>	<u>Pu-240</u>	<u>Pu-241</u>	<u>Am-241</u>
$s(P_i)$	0.0010	0.0027	0.002	0.0006	0.0014
Var*	-	418×10^{-8}	12×10^{-8}	-	-

$$\sum \text{Var} = 430 \times 10^{-3}$$

$$S_s(P_{\text{eff}}) = 0.0021$$

$$= 0.21\%$$

$$*\text{Var} = (R_i P_i / P_{\text{eff}})^2 s^2(P_i)$$

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TABLE 7

COMPARISON OF METHODS OF SPECIFIC POWER DETERMINATIONS

Sample I.D.	Date	Empirical Method (mW/g)	Computational Method (mW/g)	Difference	
				(mW/g)	(%)
M0373-3	4/10/73	2.3818	2.3850	0.0032	0.13
M0373-4	4/11/73	2.3797	2.3848	0.0051	0.21
M0673-2	7/10/73	2.3922	2.3937	0.0015	0.06
M0673-3	7/11/73	2.3901	2.3929	0.0028	0.12
M0973-2	10/10/73	2.3946	2.3999	0.0053	0.22
M0973-3	10/11/73	2.3934	2.3995	0.0061	0.25
M01273-1	1/9/74	2.4010	2.4061	0.0051	0.21
M01273-4	1/6/74	2.4005	2.4057	0.0052	0.22
			Average	0.0043	0.18
			s(bias)	0.0016	0.066

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TABLE 8

SOME TYPICAL ISOTOPIC COMPOSITIONS OF FFTF-TYPE PLUTONIUM [5]

Batch No.	Isotopic Composition (wt %)					Am-241
	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242	
1	0.049	86.229	11.673	1.890	0.159	0.148
2	0.044	86.266	11.672	1.863	0.155	0.175
3	0.051	86.655	11.469	1.585	0.240	0.091
4	0.065	86.328	11.695	1.701	0.211	0.075
5	0.054	86.390	11.794	1.586	0.176	0.057
6	0.049	86.368	11.818	1.586	0.179	0.048
7	0.061	86.447	11.644	1.635	0.213	0.120
8	0.066	86.199	11.788	1.721	0.226	0.120
9	0.068	85.993	11.816	1.911	0.212	NA
Average	0.0563	86.3194	11.7077	1.7198	0.1968	0.1042
Std Dev	0.0088	0.1832	0.1126	0.1358	0.0303	0.0445
$s(R_i)$	0.1563	0.0021	0.0096	0.0790	0.1540	0.4271
$(R_i P_i / P_{\text{eff}})$	0.1063	0.5576	0.2783	0.0195	-	0.0382
$\text{Var}(R_i)^*$	273.4×10^{-6}	1.4×10^{-6}	7.1×10^{-6}	2.4×10^{-6}	-	266.2×10^{-6}
$\text{Var}(P_i)^{**}$	-	2.3×10^{-6}	0.3×10^{-6}	-	-	-
$S(P_{\text{eff}}) = [\sum \text{Var}(R_i)]^{1/2} = 2.35\%$						

$$* \text{Var}(R_i) = (R_i P_i / P_{\text{eff}})^2 s^2(R_i)$$

$$** \text{Var}(P_i) = (R_i P_i / P_{\text{eff}})^2 s^2(P_i)$$

$$\begin{aligned}
s^2(P_{\text{eff}}) &= (0.1063)^2(0.05)^2 + 1.4 \times 10^{-6} + 7.1 \times 10^{-6} \\
&\quad + 2.4 \times 10^{-6} + (0.0382)^2 (0.05)^2 \\
&= 42.80 \times 10^{-6} \\
&= 0.65\%
\end{aligned}$$

Therefore, by using high-resolution gamma-ray spectroscopy, the random error of the specific power could be reduced from 2.35% to 0.65%.

3.3.4 COMPUTATIONAL METHOD II (SYSTEMATIC ERROR)

In addition to calculating the systematic error in the assay due to uncertainties in the specific power, it is necessary to estimate a systematic error in the stream averages. This is not covered in ANSI N15.22-1975, but the following method is based on the general approach used there.

The systematic error in the stream average $S_s(R_i)$ of the i^{th} isotope is defined to be

$$S_s(R_i) = [s^2(R_i)/n + s_0(R_i)^2]^{1/2}$$

where $s^2(R_i)$ is computed in Table 8, $S_0(R_i)$ is the assigned systematic error of the R_i ratio of the isotopic standard, and n is the number of isotopic determinations to determine the stream average. For plutonium-239,

$$\begin{aligned}
S_s(R_9) &= (0.0021)^2/9 + (0.0002)^2 \\
&= 5.3 \times 10^{-7}
\end{aligned}$$

$$S_s(R_9) = \pm 0.07\%$$

Similarly for plutonium-240 and plutonium-241, respectively,

$$\begin{aligned}
S_s^2(R_0) &= (0.0096)^2/9 + (0.001)^2 \\
&= 1.1 \times 10^{-5}
\end{aligned}$$

$$S_s(R_0) = \pm 0.33\%$$

$$\begin{aligned}
S_s^2(R_1) &= (0.079)^2/9 + (0.005)^2 \\
&= 7.2 \times 10^{-4}
\end{aligned}$$

$$S_s(R_1) = \pm 2.7\%$$

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$S_s(R_i)$ times the heat fraction of R_i gives a systematic error due to using a stream-average value of R_i . The total systematic error is then estimated to be:

$$S_s^2(P_{\text{eff}}) = \sum_i (R_i P_i / P_{\text{eff}})^2 S^2(P_i) + \sum_j (R_j P_j / P_{\text{eff}})^2 S_s^2(R_j)$$

where j = index of those isotopes for which a stream-average value is used.

$$\begin{aligned} S_s^2(P_{\text{eff}}) &= (0.1063)^2(0.001)^2 + (0.5576)^2(0.0027)^2 + (0.2783)^2(0.002)^2 \\ &\quad + (0.0195)^2(0.0006)^2 + (0.0382)^2(0.0014)^2 \\ &\quad + (0.5575)^2(53 \times 10^{-8}) + (0.2783)^2(1.1 \times 10^{-5}) \\ &\quad + (0.0195)^2(7.2 \times 10^{-4}) \\ &= 3.88 \times 10^{-6} \end{aligned}$$

$$S_s(P_{\text{eff}}) = 0.20\%$$

4. Estimation of Sampling Errors

To estimate sampling errors, two samples were taken from each of six batches. The effective specific power of each sample was measured by the empirical method, and a duplicate analysis was performed on one of the two samples. The data are presented in Table 9. The random error of the within sample duplicates provides an estimate of the variability of the specific power determination. The random error of the between sample determinations, $S(B)$, provides an estimate of both the sampling and analytical variability. The sampling error, $s(S)$, was estimated using a simple additive model.

$$S^2(B) = S^2(P_{\text{eff}}) + s^2(S)$$

Therefore,

$$s^2(S) = 3302 \times 10^{-8} - 855 \times 10^{-8}$$

$$s^2(S) = 2448 \times 10^{-8}$$

$$s(S) = 0.0049 \text{ mW/g } (\pm 0.16\%)$$

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5. Estimation of Error Due to Decay Corrections

ANSI N15.22-1975 describes a graphical method of estimating the error in the correction of the effective specific power for radionuclide decay. A simpler and more general method is to estimate the error in the plutonium-241 composition since the rate of increase of the effective specific power is directly related to the amount of americium-241 which grows into the sample by the beta decay of plutonium-241. The corrections for all other isotopes are insignificant. For example, the effective specific power of the FFTF-type plutonium shown in Table 3 increases by about 3.3%/yr. When stream average isotopics are used, the random error and systematic error in the plutonium-241 mass ratios are 7.9 and 2.7%,

TABLE 9
SAMPLING ERROR DETERMINATION

Batch I.D.	Differences in Effective Specific Power (mW/g)	
	Within Samples	Between Samples
A	0.0021	-0.0015 0.0006
B	-0.0032	0.0100 0.0068
C	0.0029	-0.0014 0.0015
D	-0.0027	-0.0128 -0.0155
E	0.0054	-0.0038 0.0016
F	-0.0051	0.0109 0.0058
Std Dev*	0.0029	0.0057
Rel Std Dev**	0.10%	0.19%

*For duplicate analysis $\text{Std Dev} = \sqrt{(\text{Differences})^2 / 2(n-1)}$

**Using a nominal specific power of 3 mW/g.

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respectively (determined in Section 3.3.4).

These errors in the mass ratios caused by decay result in proportionate errors in the specific power. Thus, the random error in the specific power from decay is $0.079 \times 0.033 = 0.26\%/yr$ or $0.00071\%/day$, and the systematic error is $0.089\%/yr$ or $0.00024\%/day$. These errors are to be considered when the effective specific power measurement and the thermal power measurement are on different dates.

Consider the example of a batch of mixed oxide produced from an identifiable PuO_2 feed stock. If the operator has reasonable assurance no mixing of batches has occurred during the process, he may use the P_{eff} determination from the PuO_2 feed with appropriate corrections for decay. For example, if the calorimetry measurement is made 60-days after the P_{eff} determination, the estimated errors from the decay corrections are 0.043% random and 0.014% systematic. One method of ensuring that the plutonium in the product was correctly identified with the right feed stock is to monitor the plutonium-241 and its daughter americium-241 with high-resolution gamma-ray spectroscopy. These two isotopes provide a rather unique identifier of a given batch since they are a function of both the original plutonium-241 and americium-241 content and the time since analyses. In addition, these two isotopes can be measured quite precisely because they have characteristic gamma rays that are easily resolved.

When more reliable methods are used to determine the plutonium-241 mass ratio, R_1 , the error from decay correction is negligible. For example, see ASTM C759-73, "Standard Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear and Radiochemical Assay of Nuclear Grade Plutonium Nitrate Solutions"*.

6. Summary

In Table 10, the effects of the various sources of error are combined to provide estimates of the random and systematic errors associated with the calorimetric assay of various forms of plutonium. Note that, in the last example, the same P_{eff} determination is used for the feed and product assay. Thus when LEMUF is computed, the error in P_{eff} is canceled if it is common to both the input and output measurement. In this case, the only error contributions are those caused by the power measurement and the decay corrections. This is only possible where the input and output measurements are on the same material.

In addition to these examples, there is also work now under way at Mound Laboratory to evaluate the errors in various methods of determining P_{eff} for high burnup fuels containing up to 2% plutonium-238 (60% fissile content).

*Copies may be obtained from the American Society for Testing Materials, 1916 Race St., Philadelphia, Pa. 19103.

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TABLE 10

SUMMARY OF ERROR VARIANCES FOR CALORIMETRIC ASSAY

Material Type	Approximate Quantity	Method of Specific Power Determination	Source of Error	Variances		Relative Error (%)	
				Random	Systematic	Random	Systematic
1) PuO ₂ Feed	>670 g	Empirical	Power Measurement	12X10 ⁻⁸	19X10 ⁻⁸	0.19	0.06
			P _{eff} Determination Including Sampling	361X10 ⁻⁸	18X10 ⁻⁸		
			Decay Correction	<1X10 ⁻⁸	<1X10 ⁻⁸		
			Totals	374X10 ⁻⁸	38X10 ⁻⁸		
2) PuO ₂ Feed	>670 g	Computational I (using error in nuclear decay constants, see Sections 3.3.1 and 3.3.2.1)	Power Measurement	12X10 ⁻⁸	19X10 ⁻⁸	0.20	0.21
			P _{eff} Determination	109X10 ⁻⁸	430X10 ⁻⁸		
			Sampling	272X10 ⁻⁸			
			Decay Corrections	<1X10 ⁻⁸	<1X10 ⁻⁸		
			Totals	394X10 ⁻⁸	450X10 ⁻⁸		
3) PuO ₂ Feed	>670 g	Computational I (calibrated against Empirical method, see Section 3.3.2.2)	Power Measurement	12X10 ⁻⁸	19X10 ⁻⁸	0.20	0.07
			P _{eff} Determination	109X10 ⁻⁸	23X10 ⁻⁸		
			Sampling	272X10 ⁻⁸			
			Decay Corrections	<1X10 ⁻⁸	<1X10 ⁻⁸		
			Totals	394X10 ⁻⁸	43X10 ⁻⁸		
4) Scrap	>100 g 6.3 W	Computational III (see Sections 3.3.3 and 3.3.4)	Power Measurement	576X10 ⁻⁸	19X10 ⁻⁸	0.70	0.20
			P _{eff} Determination	4280X10 ⁻⁸	388X10 ⁻⁸		
			Decay Corrections	<1X10 ⁻⁸	<1X10 ⁻⁸		
			Totals	485X10 ⁻⁸	408X10 ⁻⁸		
5) Mixed Oxide ~3% PuO ₂	5 kg mixed oxide	Empirical*	Power Measurement	12X10 ⁻⁸	19X10 ⁻⁸	0.20	0.06
			P _{eff} Determination	361X10 ⁻⁸	18X10 ⁻⁸		
			Decay Corrections**	18X10 ⁻⁸	2X10 ⁻⁸		
			Totals	391X10 ⁻⁸	39X10 ⁻⁸		

*Using P_{eff} determination on PuO₂ in Item 1

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7. Definition of Terms

P_{eff} = effective specific power, (W/g of Pu).

s or S = relative standard deviation (RSD). The standard deviation of an individual measurement divided by the mean of the distribution, sometimes expressed in percent. This term is also referred to as "coefficient of variation" [6].

s_s or S_s = relative systematic standard deviation (RSSD) or "systematic variance" [3].

$S(W)$ = total RSD in the power measurement
 $= [s^2(W) + s^2(\text{CALIB}) + s^2(\text{HDE}) + s^2(Q)]^{1/2}$

$s(W)$ = RSD due to imprecision of power measurement

$s(\text{CALIB})$ = RSD due to calibration

$s(\text{HDE})$ = RSD due to heat distribution error

$s(Q)$ = RSD due to presence of heat emitting impurities or processes

$S_s(W)$ = RSSD of the power measurement

$s(P_{\text{eff}})$ = RSD of the P_{eff} determination due to imprecision of the measurements

For the Computational Method:

$$s(P_{\text{eff}}) = \left[\sum_i (R_i P_i / P_{\text{eff}})^2 s^2(R_i) \right]^{1/2}$$

where i = index indicating sum over the radionuclides plutonium-238, -239, -240, -241, and americium-241.

$s(R_i)$ = RSD in measurement of the radionuclide abundance, R_i , or if NDA is used on each item, it is the established standard deviation due to imprecision of the NDA.

$R_i P_i / P_{\text{eff}}$ = the fraction of the total power emitted by radionuclide, R_i

$S_s(P_{\text{eff}})$ = RSSD of the P_{eff} determination due to uncertainties in the specific powers of the individual isotopes. May also include a term due to uncertainties in stream average isotopic values.

$$= \left[\sum_i (R_i P_i / P_{\text{eff}})^2 s^2(P_i) \right]^{1/2} + \sum_j [R_j P_j / P_{\text{eff}} + S_s^2(R_j)]$$

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where $s(P_i)$ = RSD in the specific power, P_i , as estimated in ANSI N15.22-1975.

(R_j) = RSSD of "stream average" isotopic values

S(bias) = RSD of the determination of the bias between the empirical and computational methods

$S_s(R_i)$ = RSSD of the R_i value

S(B) = RSD of the P_{eff} determination estimated from duplicate analyses

s(S) = RSD of P_{eff} due to sampling error

FFTF = Fast Flux Test Facility

LEMUF = Limit of Error - Material Unaccounted For

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8. References

1. American National Standard Calibration Techniques for the Calorimetric Assay of Plutonium-Bearing Solids Applied to Nuclear Materials Control, N15.22-1975.
2. F. A. O'Hara, J. D. Nutter, W. W. Rodenburg and M. L. Dinsmore, Calorimetry for Safeguards Purposes, MLM-1798, Mound Laboratory (January 5, 1972), 44 pp.
3. J. Jaech, Statistical Methods in Nuclear Material Control, TID-26298, USAEC, December, 1973.
4. Mound Laboratory Activities for the Division of Safeguards and Security: January-June, 1974, MLM-2186, Mound Laboratory (December 27, 1974), pp. 13-17.
5. Letter, V. Panesko and R. Carpenter, ARHCO, to W. W. Rodenburg, May, 1975.
6. American National Standard Statistical Terminology and Notation for Nuclear Materials Management, N15.5-1972.

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