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**Nuclear Safeguards Progress Report:
January-June 1976**

January 14, 1977

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MOUND LABORATORY

Miamisburg, Ohio

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MONSANTO RESEARCH CORPORATION

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for the

**UNITED STATES ENERGY RESEARCH
AND DEVELOPMENT ADMINISTRATION**

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R. P. Ratay, Editor

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Foreword

Under the sponsorship of the ERDA Division of Safeguards and Security and the Nuclear Regulatory Commission, Mound Laboratory is responsible for studies to advance nuclear safeguards technology in the public interest.

This report is submitted by W. T. Cave, Director, Nuclear Operations, and R. E. Vallee, Manager of Technology Applications and Development, from contributions prepared by members of the Applied Physics Section: W. H. Smith, Manager, and the Automation Development Section: C. F. Draut, Manager.

Summaries

DEVELOPMENT OF NONDESTRUCTIVE ASSAY TECHNIQUES

Plutonium Isotopic Measurements by Gamma-Ray Spectroscopy

A 1-cm³ planar Ge(Li) detector has been used to acquire spectra from 100-g ash samples of high-fissile, FBR, and LWR materials. Relative isotopic abundances for the plutonium isotopes have been calculated from peaks in the energy region from 148 to 208 keV. The results show that a precision of ~~3%~~ can be obtained for the $^{238}\text{Pu}/^{239}\text{Pu}$ ratio after 10000 sec for FBR and after 4000 sec for LWR material. The 3% precision level is obtained after 20000 sec for the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio and after 3000 sec for the $^{241}\text{Pu}/^{239}\text{Pu}$ ratio for these material types. (Page 5)

Prediction of Calorimeter Equilibrium

Calorimetry provides a highly accurate and precise method for the assay of plutonium in nuclear fuels, but is often limited by the time required to make a single measurement. Several hours may be required for temperature equilibration, depending on the physical size and heat capacity of the sample. A mathematical technique has been developed to predict the equilibrium value of a calorimeter output. When applied to an assay system, this predictive capability will reduce sample analysis time and, consequently, increase sample throughput. Reductions in analysis times ranging from 40 to 66% have been realized by applying this technique to resistance bridge calorimeters of three different sizes. (Page 5)

SYSTEMS DEVELOPMENT

Automated Plutonium Assay System

The X,Y,Z transporter system has been installed in the glovebox line. Handlers for operating the system under computer control have been completed and are presently in use.

Work is progressing on interfacing the calorimeters and the gamma spectroscopy system to the computer.

The gamma detector has been evaluated and data analysis programs for use with this system are being prepared.

The calorimeters have been completely installed and tested under manual operation. A set of plutonium-238 heat sources which simulate the expected wattage range from FFTF fuel samples is being used to evaluate calorimeter performance. (Page 13)

APPLICATIONS

Plutonium-239 Half-Life Study

The homogeneity of the plutonium-239 metal sample used by the half-life evaluation committee for half-life measurements was determined from calorimetric measurements of the effective specific power (in microwatts per gram) of several aliquots of the metal sample. Inhomogeneity was determined to be less than 0.02%, which is suitable for the 0.1% goal of the program for half-life measurements. (Page 16)

Plutonium Inventory Verification Program

Twenty ash and ten mixed-oxide samples have been assayed during this reporting period. Four aliquots were taken from one sample. The standard deviations from the means for the isotopic ratios for the aliquots are 0.6% for $^{238}\text{Pu}/^{239}\text{Pu}$, 0.1% for $^{240}\text{Pu}/^{239}\text{Pu}$, 0.3% for $^{241}\text{Pu}/^{239}\text{Pu}$, and 1.2% for $^{241}\text{Am}/^{239}\text{Pu}$. Two calorimeters were used to measure seven samples, and in all cases the agreement between the assay values is better than 1%. (Page 21)

Development of Nondestructive Assay Techniques

PLUTONIUM ISOTOPIC MEASUREMENTS BY GAMMA-RAY SPECTROSCOPY

F. X. Haas and
J. F. Lemming

INTRODUCTION

Efforts are being made to obtain the plutonium and americium isotopic data from the gamma-ray energy region of 148 keV to 208 keV.^{1,2} The emphasis has been toward reducing the acquisition times while still meeting the objective of 3% precision for each isotopic measurement. Previous work is described in a prior report.³

INSTRUMENTATION

A 1-cc Ge(Li) spectrometer having 600-eV resolution at 122 keV was used to acquire spectra of plutonium samples at energies up to 220 keV. A FORTRAN program (CANACQ) was written to automatically acquire up to 20 spectra at fixed acquisition times and to analyze the spectra using the programs GRPANL.

RESULTS

A series of spectra was acquired using 100-g ash samples of high-fissile, FBR, and LWR material. Ten spectra were acquired for acquisition times of 1,000, 2,000, 3,000, 4,000, 10,000, 20,000 and 40,000 sec for each sample.

Figure 1 shows graphically the ratio of the gamma-ray data to the chemical data supplied with the samples. The plutonium-

238 values are 25% below the chemical values for this sample and, based on our experience with high-fissile material, this large difference is assumed to arise from incorrect chemical values for the plutonium-238. This difference is being investigated further. For other samples the difference is -5% for FBR and +1% for LWR material. The differences for plutonium-240 values are -5% for high-fissile material and -10% for FBR and LWR material. Plutonium-241 values are within 2% for all categories.

Recognizing that these differences exist, one might correct for them by comparing data to a well-characterized standard of the same material category, or possibly by reexamination of the decay constants. These data show, however, the precision which can be obtained at the counting times chosen. Figure 2 shows the plot of precision at 1 σ , based on counting statistics alone, which can be obtained under the experimental arrangements described. The dashed line at 3% indicates the goal line we have set for our objective. This objective cannot be reached for plutonium-238 for high-fissile material even after 40,000 sec. It can be reached for plutonium-238 after 10,000 sec for FBR material and after 4,000 sec for LWR. The 3% objective for plutonium-240 can be reached after about 20,000 sec and for plutonium-241 after 3,000 sec for these material types.

PREDICTION OF CALORIMETER EQUILIBRIUM

C. L. Fellers and P. W. Seabaugh

INTRODUCTION

Prediction-of-equilibrium studies have continued using the same single-exponential model described in an earlier report.⁴ The technique has been applied to four calorimeters ranging in sample size from 1 in. in diameter by 3 in. long (2.5 cm X 7.6 cm) to 6-3/4 in. in diameter by 11 in. long (17.1 cm X 27.9 cm). Time savings ranging from 40 to 66% have been realized, depending on the size of the calorimeter. A technique has been devised for determining when to start the prediction process,

and criteria for selecting the time interval between observed data points have been established.

DATA COLLECTION AND ANALYSIS

To assure independence of raw data points and to reduce random fluctuations in the predicted values, some subjective criteria have been established. The criteria must be tested more thoroughly; however, they have been applied to tests discussed in this report and they are successful.

FIGURE 1 - Ratio of gamma-ray isotopic data to mass spectroscopic data as a function of acquisition time for three plutonium isotopes.

FIGURE 2 - Precision at 1 σ obtained for three plutonium isotopes as a function of acquisition time. The dashed line at 3% indicates precision set as the goal for the technique.

Successive raw data points must be separated by time intervals (ϵ) equal to or greater than 0.03 time constants ($1/\lambda$) of the calorimeter ($\lambda\epsilon \geq 0.03$). The three points used for the prediction must be separated by time intervals (Δt) equal to or greater than 0.3 time constants ($\lambda\Delta t \geq 0.3$). Consider the following example: The time constant of a calorimeter is 30 min and successive data points are collected at 1-min intervals ($1/30 \times 1 = 0.033$). For the prediction analysis, three evenly spaced points must be separated by at least 9-min intervals ($1/30 \times 9 = 0.3$). Therefore the first predicted value is determined using points 1, 10, and 19. The second value is determined using points 2, 11, and 20, etc.

The three-point prediction model is a viable technique only when the calorimeter is following a single exponential. In this case, successive predicted values repeat within the random noise of the system. However, in the early portion of the equilibrium process multiple exponentials are required to describe the equilibrium curve and the values predicted do not represent the actual equilibrium (Figure 3). A method has been devised for determining when the equilibrium curve is following a single exponential and, when, reliable estimates of the final equilibrium can be made.

The slope of the 10 latest predicted values is calculated and compared to a new 10-point slope calculated with the addition of a new predicted value. The first slope is calculated on points 1 through 10, the second on points 2 through 11, the third on points 3 through 12, etc. When the rate of change of the slopes with respect to time passes through four inflection points, a flag is set and all succeeding predicted values are properly weighted and accumulated. Four inflection points, identified in Figure 3, are used as the key since this number was needed to fit the worst observed case (sample loaded in a 6-3/4-in. by 11-in. or 17.1-cm by 27.9-cm calorimeter).

EVALUATION TESTS AND RESULTS

Four different resistance bridge calorimeters have been used to test the prediction model and are described in Table 1. The output from each calorimeter is monitored at preset time intervals by a common HP3490 multimeter, HP2740 scanner system interfaced to an HP9820 calculator. The data are reduced and predicted values are determined on the HP9820 calculator.

Table 1
CALORIMETERS USED FOR EVALUATION TESTS

Calorimeter	Sample Chamber (in.)	Time Constant with Empty Can (min)
1	1 x 3	8
2	4-3/4 x 8	30
3	4-3/4 x 8	32
4	6-3/4 x 11	44

Nine separate equilibration analyses have been conducted and are described as follows:

- Test 1 - Cal 1; empty sample can, 1 W from electric heater.
- Test 2 - Cal 1; 1-W plutonium-238 sample packed in lead shot; can heated before being loaded into calorimeter.
- Test 3 - Cal 1; 1-W plutonium-238 sample packed in lead shot; can loaded at room temperature.
- Test 4 - Cal 2; sample can half filled with lead shot; 1 W from electric heater.
- Test 5 - Cal 3; 0.2-W plutonium-239 sample packed in lead shot.
- Test 6 - Cal 2; sample can half filled with lead shot; 3 W from electric heater.
- Test 7 - Cal 4; empty sample can; 1 W from electric heater.
- Test 8 - Cal 4; 1-W plutonium-238 sample packed in lead shot.
- Test 9 - Cal 4; 1-W plutonium-238 sample packed in lead shot.

Figures 4, 5, and 6 present plots of the equilibrium curves and the predicted equilibrium values versus time for tests 2, 5, and 8, respectively. The vertical line crossing the predicted value plot indicates the time when the accumulation of predicted values is started. Reliable equilibrium values can be predicted whether the calorimeter temperature is approaching equilibrium from above or below the final temperature. A portion of the same data is presented numerically in Table 2. The percentage deviations at the corresponding time intervals of the predicted values and actual data are given as well as the standard deviation of the mean of the predicted value. Note that in test 2 the predicted value is within 0.25% before the accumulation and weighting process is started.

FIGURE 3 - The early portion of the predicted value curve is nonlinear and should not be averaged with later data. Following the fourth inflection point the data accumulation is started.

FIGURE 4 - Equilibrium curve and predicted values for Test 2. Time constant 11 min; data collection interval (ϵ) 0.5 min; data analysis interval (Δt) 3.5 min.

FIGURE 5 - Equilibrium curve and predicted values for Test 5. Time constant 68 min; data collection interval (ϵ) 3 min; data analysis interval (Δt) 21 min.

FIGURE 6 - Equilibrium curve and prediction curve for Test 8. Time constant 45 min; data collection interval (ϵ) 1.5 min; data analysis interval (Δt) 15 min.

Table 2

PERCENTAGE DEVIATION FROM TRUE EQUILIBRIUM OF PREDICTED
VALUES AND RAW DATA AT CORRESPONDING TIME INTERVALS

Time (min)	No. of Points	Prediction Data		Raw Data
		% Deviation from Equilibrium	Standard Deviation of Mean (%)	% Deviation from Equilibrium
Test 2				
28	2	0.22	± 0.01	4.47
30	6	0.18	± 0.00	3.77
32	10	0.09	± 0.01	3.17
34	14	0.08	± 0.02	2.68
36	18	0.11	± 0.01	2.26
38	22	0.10	± 0.01	1.91
40	26	0.06	± 0.01	1.61
42	30	0.04	± 0.01	1.36
Test 5				
168	2	0.57	± 0.01	-18.93
180	6	0.25	± 0.05	-15.91
192	10	-0.09	± 0.08	-13.26
204	14	-0.10	± 0.07	-11.22
216	18	0.09	± 0.06	-9.39
228	22	0.04	± 0.05	-7.94
240	26	-0.18	± 0.04	-6.65
252	30	-0.10	± 0.04	-5.59
Test 8				
121.5	2	0.41	± 0.04	-10.70
129	7	0.71	± 0.04	-8.88
136.5	12	0.73	± 0.05	-7.42
144	17	-0.04	± 0.06	-6.29
151.5	22	-0.60	± 0.10	-5.27
159	27	-0.56	± 0.11	-4.44
166.5	32	-0.26	± 0.10	-3.71
174	37	-0.01	± 0.08	-3.11

The extent of success of this prediction model is not constant for all calorimeters or even for the same calorimeter from one analysis to the next, but a reduction in equilibrium time has been realized in every test case examined. The time required for the actual and predicted data to be within 1%, 0.5%, 0.25%, and 0.1%, along with the ratios of these times for the three different size calorimeters, is shown in Tables 3, 4, and 5. Time savings of 66% have been realized by applying this technique to calorimeters 1, 2, and 3, and at least a 40% savings can be achieved on the relatively large calorimeter 4. These time benefits are essentially the same for any level of accuracy requirement. The four calorimeters used for the tests cover the range of physical sizes of resistance bridge calorimeters used for approximately 90% of radiometric calorimetric analyses at Mound Laboratory. Therefore, the results obtained are representative of the time savings that can be expected in routine assay by applying the prediction model.

CONCLUSIONS

The prediction model is applicable to calorimeters ranging in sample size from 1 in. X 3 in. to 6-3/4 in. X 11 in. (2.5 cm X 7.6 cm to 17.1 cm X 27.9 cm), and significant reductions in assay time are realized without degrading the accuracy of the results. A summary of the average ratios of the actual to predicted times at various percent deviations from actual equilibrium for all tests is shown in Table 6.

Time savings from 40 to 66% have been achieved with a single-exponential prediction model. Additional tests will be conducted to confirm the data collection and analysis criteria and to evaluate the potential of a multiple exponential model for further reduction in calorimeter assay time.

Table 3

TEST RESULTS FROM 1-IN. X 3-IN. CALORIMETER

Test No.	% Deviation from Equilibrium	Actual Time (min)	Predicted Time (min)	Ratio of Actual/Predicted Time
1	1	38	12	3.16
1	0.5	44	15	2.93
1	0.25	50	19	2.63
1	0.1	59	23	2.56
2	1	50	21	2.38
2	0.5	59	26	2.27
2	0.25	67	29	2.31
2	0.1	77	34	2.26
3	1	57	15	3.80
3	0.5	65	18	3.61
3	0.25	74	20	3.70
3	0.1	85	22	3.86

Table 4

TEST RESULTS FROM 4-3/4-IN. X 8-IN. CALORIMETER

Test No.	% Deviation from Equilibrium	Actual Time (min)	Predicted Time (min)	Ratio of Actual/Predicted Time
4	1	270	84	3.21
4	0.5	320	98	3.26
4	0.25	360	116	3.10
4	0.1	408	131	3.11
5	1	242	78	3.10
5	0.5	284	90	3.16
5	0.25	330	112	2.95
5	0.1	396	128	3.09
6	1	366	120	3.05
6	0.5	414	183	2.26
6	0.25	456	192	2.38
6	0.1	484	216	2.24

Table 5

TEST RESULTS FROM 6-3/4 IN. X 11-IN. CALORIMETER

Test No.	% Deviation from Equilibrium	Actual Time (min)	Predicted Time (min)	Ratio of Actual/Predicted Time
7	1	227	121	1.87
7	0.5	257	138	1.86
7	0.25	282	190	1.48
7	0.1	312	-	-
8	1	217	116	1.87
8	0.5	251	147	1.70
8	0.25	275	172	1.60
8	0.1	311	178	1.75
9	1	179	98	1.82
9	0.5	213	101	2.11
9	0.25	234	129	1.81
9	0.1	282	147	1.92

Table 6

AVERAGE RATIO OF ACTUAL TIME TO PREDICTED TIME
FOR GIVEN DEVIATION LIMITS

Percent Deviation	Calorimeter Sample Size (in.)		
	<u>1 x 3</u>	<u>4-3/4 x 8</u>	<u>6-3/4 x 11</u>
1	3.11	3.12	1.85
0.5	2.94	2.89	1.89
0.25	2.88	2.81	1.63
0.1	2.89	2.81	1.84 ^a

^aThis average is comprised of only two points since Test 7 did not predict within 0.1%.

Systems Development

AUTOMATED PLUTONIUM ASSAY SYSTEM

R. A. Neff, J. F. Lemming, J. H. Birden,
T. K. Ferguson, D. O. Page and M. F. Duff

INTRODUCTION

The Automated Plutonium Assay System (APAS) is being developed to demonstrate automated, in-line, nondestructive plutonium assay for mixed oxide fuels utilizing calorimetry and isotopic ratios determined by gamma-ray spectroscopy. A process control computer will direct and control the movement of the samples from the storage area to the measurement stations. The data will be acquired and analyzed by the computer and the generated reports will assist in providing material control and safeguards accountability.

AUTOMATION

Transport System

The three-dimensional (X,Y,Z) transport system was installed in the APAS glovebox line (Figure 7) and in-situ tested using a PDP-8/F computer and the software package which was previously used for the test frame shakedown testing.⁵ The PDP-8/F computer was used for the initial tests because the software, which would have permitted the dedicated APAS PDP-11/40 computer to control the transporter, was not yet completed. These final operational tests of the transport system revealed no major deficiencies in the control unit or in the X,Y,Z mechanism. The transport system is now operating reliably on a daily basis under PDP-11/40 control to support calorimeter studies (Figure 8).

All revisions performed during initial development testing were recorded by proper documentation on the design drawings. A complete operations manual and a spare parts listing are being written for use with the transport and position system.

Computer

The drivers and handlers necessary to operate the X,Y,Z transport system using the PDP-11/40 computer have been written. These programs are callable from both MACRO and FORTRAN IV programs. A set of subprograms has been written to initialize the transporter, to load and unload samples

from the calorimeters, and to allow an operator to transfer samples to any location in the assay system. A first draft of a manual describing these programs has been prepared.

The hardware interfacing of the calorimeter readout system to the computer has been completed and tested. The handlers which will allow reading of water bath temperatures as well as the heater current and heater potential are being written.

A new multichannel analyzer interface with the capability of interrupting the computer has been acquired. This interface should allow for more efficient real-time usage of the computer.

Gamma-Ray Spectroscopy System

A 2-in. (5-cm)-thick lead collimator with a 0.25-in. (0.63-cm) slit has been fabricated to fit around the sample well under the glovebox. This collimator will reduce the background and improve the resolution of the spectrometer.

The intrinsic germanium detector for the system has been received. The resolution for this detector has been measured to be 655 eV at 122 keV and 1.83 keV at 1332 keV.

Several ash samples with typical FFTF isotopic ratios have been measured with this detector. Data analysis programs for use with this detector are being investigated with a PDP-8 spectroscopy system.

Calorimeters

After testing of the servo-control electronics for the calorimeters and the temperature controls for the calorimeter and preequilibration baths, the entire calorimeter package was installed. Manual checks on these systems after installation in the glovebox line have been performed.

A set of plutonium-238 heat sources has been packed in UO₂ in order to simulate the expected wattages of the FFTF fuel samples. These samples range from 3.0 W in 1 kg of UO₂ to 0.1 W in 100 g of UO₂.

These samples are being used to determine a calibration curve for the calorimeters

and also to determine the long-term reproducibility of the calorimeters. They will also be used to determine time to equilibrium for both preequilibrated and non-preequilibrated samples. These data are necessary for designing optional sample flow.

Engineering

The X,Y,Z transporter has been installed on the transporter rails in the

gloveboxes. The environmental baths and control module with related plumbing have also been installed.

The final drawings of the X,Y,Z transporter, environmental bath control module, pickup mechanism, process calorimeter, and environmental baths are complete.

The final drawings of the system are 50% completed.

FIGURE 7 - The three-dimensional automated transport system which moves a plutonium sample container between the storage and measurement stations of the Automated Plutonium Assay System.

760265

760256

FIGURE 8 - The transport system removing and replacing an insulation baffle into the mouth of the calorimeter.

Applications

PLUTONIUM-239 HALF-LIFE STUDY

P. W. Seabaugh and W. W. Strohm

INTRODUCTION

The half-life evaluation committee consisting of representatives from Mound Laboratory, LLL, LASL, ANL, and Rockwell (Rocky Flats) is administering a half-life measurement program to resolve discrepancies in published values of plutonium half-lives.

The program calls for half-life measurements of plutonium isotopes to be made on aliquots from a single metal sample of high isotopic and chemical purity. Three different half-life measurement techniques (calorimetry, alpha counting, and mass spectrometry) are being used.

This report describes the homogeneity determination of the plutonium-239 metal sample using calorimetry measurements on several aliquots.

STATISTICAL MODEL

Whether explicitly stated or implicitly assumed, some model always provides the basis for statistical analysis. For this current analysis on plutonium-239 and subsequent subsamples an analysis-of-variance (ANOVA) model is utilized. A two-factor (subsamples and calorimeters) fixed-effect model is considered since these subsamples and calorimeters constitute the total population under consideration here. The inferences then, to that extent, are limited to these subsamples and to these calorimeters.

Historically, normality and homogeneity of variance assumptions have been considered critical for ANOVA. Nevertheless, Box⁷ has shown that relatively large departures from homogeneity do not affect ANOVA F tests in any practical sense and Cochran⁸ has discussed the relationship between homogeneity of variance and normality. Thus, the assumption of normality utilized for this fixed-effect analysis will not detract from the inferences drawn.

All subsamples represent a subdivision of the original 55.5126-g sample of plutonium metal, designated as Pul(239). For convenience and clarity the subsamples, hereafter likewise referred to as samples, will carry the labels utilized when the samples were shipped to the participating laboratories. Table 7 lists the individual samples with their respective weights. For the calorimetric stacking experiments any combination of individual samples also is considered as a sample and is so labeled.

Table 7

SAMPLE IDENTIFICATION AND WEIGHTS FOR
SEVEN SAMPLES USED IN Pul(239)
HALF-LIFE STUDY

Samples	Weight (g)
Pul(239)	55.5126
Pul(#3)	5.02155
Pul(#2)	5.15934
Pul(#2 + #3)	10.18089
Pul(#4)	5.04893
Pul(#1)	5.07088
Pul(#1 + #2 + #3)	15.25177

Although up to seven samples including combinations were run on one calorimeter (116), only five were common to the three calorimeters used in this experiment. Consequently, to simplify this preliminary analysis of the data, 15 treatment combinations (5 samples X 3 calorimeters) are considered. In this way the data can be analyzed as a fixed two-way ANOVA with only one observation per cell where that observation represents the average of all the observations on a given sample with a given calorimeter. The model equation is

$$Y_{ij} = \mu + S_i + C_j + SC_{ij} + e_{ij}$$

$$i = 1, \dots, 5$$

$$j = 1, 2, 3$$

where: Y_{ij} = power in $\mu\text{W/g}$ of the i th sample measured on the j th calorimeter

μ = overall mean

S_i = the effect of the i th sample (fixed)

C_j = the effect of the j th calorimeter (fixed)

SC_{ij} = the interaction effect of the i th sample with the j th calorimeter

e_{ij} = the experimental random error, $N(0, \sigma_e^2)$

The appropriate ANOVA table is given in Table 8.

Table 8

ANALYSIS OF VARIANCE TABLE

Source	Degrees of Freedom (df)	Expected Mean Squares (EMS)
Sample (S)	$i - 1 = 4$	$\sigma_e^2 + 3S^2$
Calorimeter (C)	$j - 1 = 2$	$\sigma_e^2 + 5C^2$
SC and/or Error	$(i-1)(j-1) = 8$	$\sigma_e^2 + \sigma_{SC}^2$

Since only one observation per cell is considered, the experimental error variance (σ_e^2) is confounded with the interaction effect (σ_{SC}^2). But, in practice, the testing of samples and calorimeters can be accomplished by assuming the interaction is zero or by using one degree of freedom (df) for nonadditivity or interaction.⁹ Both assumptions will be used in the analysis.

In addition, the $\mu\text{W/g}$ values particular to each individual calorimeter will be analyzed and compared. Here the model equation is

$$y_k = \mu + \tau_k + \bar{e}_k$$

$$k = 1, 2, \dots, 7$$

where: y_k = average $\mu\text{W/g}$ of the k th sample

μ = mean value for a given calorimeter

τ_k = effect of the k th combination of the i th level of time with the j th sample

$\bar{e}_k$ = error averaged over days for the k th sample

Throughout the report $\mu\text{W/g}$ refers to micro-watts per gram of sample and not to micro-watts per gram of plutonium.

Data Analysis

All data have been decayed to a common date, the day of the first calorimetric measurement. The decay rate is based on a single best estimate of the isotopic composition and might change with the accumulation of additional isotopic data. However, only a small, if any, change is expected.

Some of the tables utilize a four-digit code which represents the number of days from January 1, 1966 to signify the measurement date or the range in measurement dates for a given sample. By this code 3097 is the day of the first calorimetric measurement and is the common decay date for all subsequent measurements.

A listing of the average $\mu\text{W/g}$ for the 15 sample/calorimeter combinations is given in Table 9. Here the sum of two or more sample numbers indicates the samples were stacked in a calorimeter and the total wattage was measured simultaneously.

The corresponding ANOVA and the critical F values are given in Table 10. Here df denotes the degrees of freedom, SS is the sum of squares, MS is the mean sum of squares, F is the computed F ratio and $F_{df, 0.05}$ is the critical F ratio at the 0.05 significance level.

None of the effects are significant at the 0.05 level. But the F tests are based on using the SC/error mean square for the denominator. This is equivalent to setting the interaction (samples X calorimeters) to zero. However, the sum of squares for SC/error can be split⁹ into an SC part with one degree of freedom and an error part with five degrees of freedom by utilizing the sample mean, the calorimeter mean, and the overall mean. The appropriate equation for the SC sum of squares with one degree of freedom is

$$SS_{SC} = [\sum Y_{ij} (\bar{y}_i - \bar{y})^2 (\bar{y}_j - \bar{y})]^2 /$$

$$[\sum (\bar{y}_i - \bar{y})^2] [\sum (\bar{y}_j - \bar{y})^2]$$

where: y_{ij} = $\mu\text{W/g}$ of the i th sample measured on the j th calorimeter

$\bar{y}_i$ = mean of the i th sample

$\bar{y}_j$ = mean of the j th calorimeter

$\bar{y}$ = overall mean

With these additional computations the appropriate ANOVA is given in Table 11. Again, all of the F tests are not significant at the 0.05 significance level. Thus it can be concluded that all samples

Table 9
AVERAGE VALUES FOR FIVE SAMPLES AND THREE CALORIMETERS^a

Samples	Calorimeter Numbers			Total
	116	91	90	
Pul(#3)	1970.3959	1970.0717	1970.1433	5910.6109
Pul(#2)	1970.6025	1970.0434	1970.3041	5910.9500
Pul(#2 + #3)	1970.3936	1970.6256	1970.1715	5911.1907
Pul(#1)	1970.6676	1969.7518	1969.3099	5909.7293
Pul(#1 + #2 + #3)	1969.9533	1970.5630	1969.8183	5910.3346
Total	9852.0129	9851.0555	9849.7471	

^aValues are in microwatts per gram.

Table 10
ANOVA OF DATA IN TABLE 9

Source	df	SS	MS	F	F _{df, 0.05}
Sample (S)	4	0.44	0.11	0.78	4.12
Calorimeter (C)	2	0.50	0.25	1.79	4.74
SC/Error	8	1.09	0.14		
Total	14	2.03			

Table 11
ANOVA WITH NONADDITIVE (INTERACTIVE) SOURCE

Source	df	SS	MS	EMS	F	F _{df, 0.05}
Sample (S)	4	0.44	0.11	$\sigma_e^2 + 3\sigma_S^2$	0.98	4.12
Calorimeter (C)	2	0.50	0.25	$\sigma_e^2 + 5\sigma_C^2$	2.22	4.74
SC (Interaction)	1	0.30	0.30	$\sigma_e^2 + \sigma_{SC}^2$	2.68	5.59
Error	7	0.79	0.11	σ_e^2		
Total		2.03				

are homogeneous at least to the extent of the mean sum of squares for samples. From Table 11 this is estimated to be very close to zero.

Although samples Pul and Pul(#4) were not included in this analysis, their $\mu W/g$ values are consistent with the five analyzed samples. Consequently, inhomogeneity is not considered to be a relevant factor in this half-life study.

No corrections of any type have been applied for this analysis. Nevertheless, concurrent measurements made on heat standards of similar wattages suggest that some correction is in order. An estimate of the magnitude of that correction is indicated by the mean sum of squares for the interaction of samples times calorimeters (SC).

Tables 12, 13 and 14 give a summary of the data for calorimeters 116, 91, and 90, respectively. These tables essentially reflect a one-way classification with five to seven levels of combinations of time of measurement and samples. The analysis of differences among the sample means includes both interaction and main effects. If the expected value for the interaction (days X samples) and main effects is zero $[E(\bar{\tau})=0]$, then the unweighted means of the sample means represent a best estimate of the $\mu W/g$ value for a given calorimeter. Three sigma confidence limits are given for the overall mean but, due to the small degrees of freedom, the associative probability is somewhat less than 0.99.

Examination of results from the stacking experiments is consistent with the prior analysis that some interaction exists.

Within the context of this analysis a best estimate of the $\mu W/g$ value for Pul is 1970.1739 which is the unweighted mean of the overall means from the three calorimeters. The 3 σ confidence limits are

$$1969.8065 < 1970.1739 < 1970.5413$$

The number of retained digits presented above is for computation purposes and, of course, not all are significant.

FUTURE WORK

Further partitioning of the SC/error sum of squares will be determined through the analysis of days sum of squares, through analysis of days X samples interaction, and through analysis of other main and interaction effects. A similar analysis will be made on the concurrently measured heat standard data and an appropriate correction factor will be documented and applied if warranted. Also, an analysis of the correlation between weights and wattage will be made.

When all the refined computations have been made a best estimate for the micro-watts per gram of plutonium and subsequently the half-life and the associative uncertainty for Pul(239) will be calculated.

Table 12

CALORIMETER 116^a DATES, ID, WEIGHT, μW AND $\mu W/g$ FOR SEVEN SAMPLES

Dates	ID	Weight (g)	Power (μW)	$\mu W/g$
3220-3489	Pul(#3)	5.02155	9894.4415	1970.3959
3223-3492	Pul(#2)	5.15934	10167.0081	1970.6025
3226-3229	Pul(#2 + #3)	10.18089	20060.3603	1970.3936
3206-3209	Pul(#4)	5.04893	9949.2290	1970.5619
3437-3472	Pul(#1)	5.07088	9993.0187	1970.6676
3461-3575	Pul(#1 + #2 + #3)	15.25177	30045.274	1969.9533
3106-3131	Pul	55.5126	109355.377	1969.9199
	Mean			1970.3564

^aThree sigma confidence limits: $1970.0100 < \mu < 1970.7028$

Table 13

CALORIMETER 91^a DATES, ID, WEIGHT, μ W AND μ W/g FOR SIX SAMPLES

Dates	ID	Weight (g)	Power (μ W)	μ W/g
3220-3489	Pul(#3)	5.02155	9892.8134	1970.0717
3223-3492	Pul(#2)	5.15934	10164.1239	1970.0434
3226-3229	Pul(#2 + #3)	10.18089	20062.723	1970.6256
3475-3480	Pul(#1)	5.07088	9988.375	1969.7518
3500-3516	Pul(#1 + #2 + #3)	15.25177	30049.648	1970.2400
3097-3127	Pul	55.5126	109391.070	1970.5630
	Mean			1970.2159

^aThree sigma confidence limits: $1969.8060 < \mu < 1970.6258$

Table 14

CALORIMETER 90^a DATES, ID, WEIGHT, μ W AND μ W/g FOR FIVE SAMPLES

Dates	ID	Weight (g)	Power (μ W)	μ W/g
3223-3225	Pul(#3)	5.02155	9893.1730	1970.1433
3230-3232	Pul(#2)	5.15934	10165.4685	1970.3041
3233-3236	Pul(#2 + #3)	10.18089	20058.099	1970.1715
3447-3450	Pul(#1)	5.07088	9986.134	1969.3099
3454-3457	Pul(#1 + #2 + #3)	15.25177	30043.216	1969.8183
	Mean			1969.9494

^aThree sigma confidence limits: $1969.4128 < \mu < 1970.4861$

PLUTONIUM INVENTORY VERIFICATION PROGRAM

J. F. Lemming, J. Y. Jarvis
and F. X. Haas

Twenty ash and ten mixed-oxide samples were assayed during this period. The data are presented in Tables 15 and 16.

One mixed-oxide sample (EIO-13) did not have a corresponding aliquot. Isotopic ratios have been determined by gamma-ray spectroscopy for this sample. However, due to the inability of gamma-ray spectroscopy to determine the plutonium-242/plutonium-239 ratio and the large range of this ratio in the mixed-oxide category (290-4132 ppm), the power measurement for this sample has not been converted to grams of plutonium.

The aliquot samples have been measured by mass spectroscopy, radiocounting, and two gamma-ray spectrometers. Within the experimental uncertainties, all the measurements agree except for the americium-241/plutonium-239 ratio. For this reason the gamma-ray and radiocounting values were averaged to obtain the americium-241 results on the aliquots.

The ratios used in the power conversion calculation were as follows: plutonium-238/plutonium-239 (radiocounting); plutonium-240/plutonium-239 (mass spectrometry); plutonium-241/plutonium-239 mixed oxide (mass spectrometry); plutonium-241/plutonium-239 and americium-241/plutonium-239 (gamma-ray spectroscopic measurement on the bulk sample).

One mixed sample (IEO-13) had four aliquots. The mean and standard deviation for each ratio for these are: plutonium-238/plutonium-239 - 318 ± 2 ppm; plutonium-240/plutonium-239 - 104973 ± 113 ; plutonium-241/plutonium-239 - 8840 ± 30 ; and americium-241/plutonium-239 - 4116 ± 48 .

Seven samples were measured three times each with the gamma-ray spectrometer. The average standard deviation for the plutonium-241/plutonium-239 ratio was 1%, and for americium-241/plutonium-239 it was 2%.

In following a policy of being conservative in the error estimates, the following uncertainties have been used: plutonium-238/plutonium-239 $\pm 3\%$; plutonium-240/plutonium-239 $\pm 0.85\%$; plutonium-241/plutonium-239 $\pm 3\%$; and americium-241/plutonium-239 $\pm 7\%$.

Calorimeters S/N's 111 and 133 were used for this inventory. Standard heat sources were measured before and after inventory samples. No bias correction is needed. Seven samples were measured more than once. These data are summarized in Table 17.

The calculation of the quantity of plutonium in the samples for the calorimetric power measurements and the relative isotopic abundances was obtained using the equations in ANSI Standard N15.22.¹⁰

Table 15

SPRING 1976 PLUTONIUM INVENTORY SERIES (ASH)

<u>Sample I.D.</u>	<u>Date Assayed</u>	<u>Total Plutonium (g)</u>
AA-24-6-53	3/31/76	59.1 $\pm$ 0.5 ^a
AB-24-6-53	3/31/76	44.3 $\pm$ 0.4
AA-24-4-80	4/1/76	82.5 $\pm$ 0.7
AB-24-4-80	4/1/76	66.2 $\pm$ 0.5
AA-24-4-77	4/2/76	81.1 $\pm$ 0.7
AB-24-4-77	4/2/76	74.3 $\pm$ 0.6
AA-24-4-81	4/5/76	69.4 $\pm$ 0.6
AB-24-4-81	4/5/76	59.6 $\pm$ 0.5
AA-25-1-92	4/6/76	22.0 $\pm$ 0.2
AB-25-1-92	4/6/76	27.1 $\pm$ 0.3
AA-24-6-2	4/7/76	32.7 $\pm$ 0.3
AB-24-6-2	4/7/76	41.5 $\pm$ 0.4
AA-24-6-47	4/9/76	53.2 $\pm$ 0.5
AB-24-6-47	4/12/76	55.7 $\pm$ 0.5
AA-24-6-24	4/12/76	72.2 $\pm$ 0.6
AB-24-6-24	4/13/76	118.6 $\pm$ 1.0
AA-24-6-23	4/13/76	75.5 $\pm$ 0.7
AB-24-6-23	4/14/76	93.4 $\pm$ 0.8
AA-24-6-56	4/14/76	49.4 $\pm$ 0.4
AB-24-6-56	4/15/76	41.6 $\pm$ 0.4

^aUncertainties are at 1 σ .

Table 16

SPRING 1976 PLUTONIUM INVENTORY SERIES (MIXED OXIDE)

<u>Sample I.D.</u>	<u>Date Assayed</u>	<u>Total Plutonium (g)</u>
EIO-24	4/15/76	152.4 $\pm$ 1.5
IEO-7	4/19/76	117.5 $\pm$ 1.2
IEO-24	4/20/76	54.3 $\pm$ 0.6
IEO-20	4/21/76	108.3 $\pm$ 1.2
IEO-1	4/20/76	91.3 $\pm$ 0.8
EIO-29	4/21/76	60.5 $\pm$ 0.6
EIO-31	4/22/76	63.2 $\pm$ 0.6
IEO-13	4/22/76	143.0 $\pm$ 1.6
EIO-11	4/23/76	66.4 $\pm$ 0.6
EIO-13 ^a	4/19/76	(0.20517 W)

^aAliquot was not available on this sample.

Table 17
REPRODUCIBILITY MEASUREMENTS

<u>Sample I.D.</u>	<u>Date Assayed</u>	<u>Total Plutonium (g)</u>
AA-24-4-77	4/2/76	81.1 ± 0.7 ^a
	5/17/76	81.0 ± 0.7
AB-24-4-77	4/2/76	74.3 ± 0.6
	5/17/76	74.3 ± 0.6
AA-25-1-92	4/6/76	22.0 ± 0.2
	5/13/76	22.1 ± 0.2
	5/18/76	22.2 ± 0.2
AB-25-1-92	4/6/76	27.1 ± 0.3
	5/13/76	27.2 ± 0.2
	5/18/76	27.2 ± 0.3
AA-24-6-2	4/7/76	32.7 ± 0.3
	5/12/76	32.6 ± 0.3
AB-24-6-2	4/7/76	41.5 ± 0.4
	5/12/76	41.6 ± 0.4
	5/19/76	41.5 ± 0.4
AA-24-6-24	4/12/76	72.2 ± 0.6
	5/14/76	72.1 ± 0.6
AB-24-6-24	4/13/76	118.6 ± 1.0
	5/14/76	118.5 ± 1.0

^aUncertainties are at 1σ.

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