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CONTINUED STUDIES OF CALORIMETER PERFORMANCE AT THE LAWRENCE LIVERMORE LABORATORY

S. A. Steward and R. T. Tsugawa

November 17, 1975

MASTER

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CONTINUED STUDIES OF CALORIMETER PERFORMANCE AT THE LAWRENCE LIVERMORE LABORATORY

Abstract

Calibrations of two calorimeters used for tritium and plutonium assays were made. Data from three new standards of about 0.5, 1 and 5 W were added to the results of a previous report and analyzed together. The accuracies of both calorimeters appear to fall within the specified 0.5%, although the data now available for the large calorimeter is

insufficient to permit a more definite conclusion. An expression of the bias correction for each calorimeter with respect to the sample power cannot be determined. The bias of the medium thermopile-type calorimeter tends to be positive, however, and that of the large resistance-bridge design appears to be negative.

Introduction

This work is an extension of previously reported calibrations¹ of two calorimeters at the Lawrence Livermore Laboratory (LLL). New data, in combination with the earlier results, allow a detailed statistical analysis of the measurements obtained from the calorimeters, the larger one

designed and built by Mound Laboratory and the smaller of the two constructed at LLL. The calorimeter descriptions in this report are essentially identical to those in the earlier paper and are repeated here for the convenience of the reader.

Calorimeter Descriptions

MEDIUM CALORIMETER (No. 32)

The so-called medium calorimeter is the smaller of the two and was built at LLL. A report detailing its construction has been published

previously.² It is a twin-chamber, steady-state heat-flow type, using thermopiles as the sensing elements. The sample volume is 130 mm in diameter and 180 mm long. The specified accuracy of the calorimeter is

$\pm 0.5\%$ for power levels from 0.2-20 W.

The instrument basically consists of two cylindrical copper sample chambers mounted coaxially and immersed in a controlled-temperature water bath. Each chamber has a thermopile of 72 manganin-constantan thermocouples, each couple yielding an output voltage of 37.5 μ V per degree centigrade temperature change. The thermopiles of each chamber are connected in opposition, greatly reducing the effect of fluctuation in the bath temperature. The bath temperature is controlled to within ± 0.05 K. A removable heater is used to calibrate this medium calorimeter.

The thermopile-type calorimeter design has several advantages. These are:

- Independence from power variations, since no power supply is needed.
- Freedom from joule heating of the sample chamber, because there is no sensor current.
- Low zero drift compared to the resistance-bridge type, since the zero of the latter design depends on the time-variable relative resistance of the arms.
- A much smaller aging effect than that of the resistance bridge unit.

LARGE CALORIMETER (No. 143)

The largest calorimeter, designed and built at the Mound Laboratory, is a twin-resistance-bridge type. This particular instrument has an aluminum sample cavity 180 mm in diameter and 760 mm long. The accuracy specified by Mound Laboratory is 0.5% for sample powers between 2 and 30 W.

The sensor and the reference arms of the Wheatstone bridge were wound over the length of the calorimeter. The sample cavity extends approximately 40 mm beyond each end of the sample volume. The Lucite* end sections minimize heat losses.

The two reference arms of the bridge are wound on the plastic farthest from the metal sample area. Thus, the four bridge arms are wound on the same tube. This tube is mounted horizontally in a water bath that is controlled to ± 0.002 K. A heater that is wound along the aluminum sample cylinder is used for calibration. A smaller (180 mm) removable heater may be used for smaller samples.

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

Advantages of this large, resistance-bridge-type calorimeter are:

- Smaller heat distribution errors than those of the thermopile type, since the resistance sensor is

distributed more uniformly over the sample chamber.

- Relative insensitivity to short-term temperature fluctuations compared to the thermopile sensor.
- Less-expensive construction.

Radiometric Standards

In addition to the three ^{238}Pu standards used earlier,¹ of approximately 1.5, 9.3 and 20.4 W, calibrations using three new standards, 0.5, 1, and 5 W, have been made. The combined data are discussed here. The power values at the initial calibration date are given in Table 1 for each standard. These values, with daily decay rates, were furnished by Mound Laboratory, the supplier of the samples. The Laboratory indicates the reported power levels of each standard are accurate to $\pm 0.02\%$. As before, the standards are packed with copper shot in stainless steel cap-

sules 127 mm in diameter and 178 mm long.

Table 1. Initial dates and power values for each calibrated sample.

Sample No.	Power (W)	Calibration date
1	1.522	12-22-73
2	9.293	12-19-73
3	20.410	12-10-73
4	0.489 96	7-18-74
5	1.004 21	7-19-75
6	5.038 76	7-22-75

Experimental Procedure

MEDIUM CALORIMETER (No. 32)

Method of Operation

The medium calorimeter has a thermopile output for heat sensing. Therefore, no applied voltage is

needed. The thermopile voltage readings are sequentially V_0 , V_S , V_0 , where V_0 is the equilibrium voltage without the sample and V_S is the voltage with the sample in place.

The sample is inserted into one

arm of the calorimeter and the equilibrium thermopile output is recorded. Equilibration usually occurs within 24 hours. V_0 is used to adjust for the null point, and is about 2-3 μ V.

Heater calibrations over the range of interest are performed periodically to determine the calorimeter sensitivities needed for sample power calculations. This is necessary because the sensitivities vary with time.

Calculations

$$W_H = I_H \times P_H$$

$$W_S = \frac{V_S}{V_H} \times W_H$$

and

$$S = \frac{V_H}{W_H},$$

where

W_H = Heater power (W)

I_H = Heater current (A)

P_H = Heater potential (V)

V_H = Thermopile output from heater (mV)

V_S = Thermopile output from sample (mV)

S = Calorimeter sensitivity (mV/W)

Example:

Sample run - $V_S = 7.526$ mV

Heater run - $V_H = 7.523$ 85 mV

$P_H = 11.128$ V

$I_H = 0.124$ 10 A

$W_H = I_H \times P_H =$
1.380 9 W

$S = \frac{V_H}{W_H} =$
5.448 5 mV/W

$W_S = \frac{V_S}{V_H} \times W_H =$
1.381 3 W

LARGE CALORIMETER (No. 143)

Method of Operation

The sequence of bridge potential (BP) measurements for each determination is BP_0 , BP_S , BP_H , BP_0 , where BP_0 is the output for zero power input, BP_S is the equilibrium value with the sample and BP_H is the output using the heater. The bridge current for all runs is 15 mA.

The equilibrium bridge potential is measured with the sample in place. In order to determine the effect of the heater-lead resistance, the applied voltage is measured with the heater shorted out.

After the sample has been removed, the heater power is increased until approximately the same bridge potential output is attained as in the sample run. The following set of

heater currents and voltages are recorded:

BP_H = Heater bridge potential (mV)

I_H = Heater current (A)

P_H = Heater potential (V)

Calculations

$$W_H = I_H \times P_H$$

$$S_H = \frac{BP_H - BP_0}{W_H}$$

$$W_S = \frac{BP_S - BP_H}{S_H} + W_H$$

The term $(BP_S - BP_H)$ is the small difference between sample and heater potentials that arises because of the expected inability to match them exactly. Although this term must be taken into account it is always small, so that $W_S \approx W_H$.

Example:

$$\text{Sample run} - BP_0 = 6.963 \text{ 0 mV}$$

$$BP_S = 9.393 \text{ 5 mV}$$

$$\text{Heater run} - BP_H = 9.415 \text{ 3 mV}$$

$$P_H = 8.429 \text{ 45 V}$$

$$I_H = 0.115 \text{ 04 A}$$

$$W_H = P_H \times I_H = 0.969 \text{ 72 W}$$

$$S_H = \frac{BP_H - BP_0}{W_H} = 2 \text{ 528.9 } \mu\text{V/W}$$

$$W_S = \frac{BP_S - BP_H}{S_H} + W_H$$

$$= \frac{1.393 \text{ 5 mV} - 9.415 \text{ 3 mV}}{2.528 \text{ 9 } \mu\text{V/W}} + 0.969 \text{ 72 W}$$

$$= -0.008 \text{ 62 W} + 0.969 \text{ 72 W}$$

$$= 0.961 \text{ 10 W}$$

ERROR SOURCES

Since the discussion of the calibrations is mostly a statistical analysis, the sources of error should be addressed first. Errors may be customarily placed into two categories, random and systematic. Random errors occur in the collection of data and are, as the term indicates, independent of any bias in the collection process. As such they are unexplainable but predictable. The normal distribution of values about a mean results from these errors. Systematic errors occur as a result of some bias built into an instrument or collection procedure. A clock that "gains time" is such an example. The extent of this type of error can often be measured, but its cause and correction may not be so easy to determine.

In these calorimeter experiments the systematic errors consist of:

- Heat distribution effects and heat leakage out of the tube ends.

- The bias of the heater power determination including that associated with changes in sensitivity at different power levels.

- The bias of the standards.

Mound Laboratory indicates that the reported power levels of the radiometric standards are within

0.02% of the true values. Therefore, this error source has been ignored. One of the purposes of the calibrations was to determine the systematic bias versus power level for each calorimeter. Then actual assays at any power level could be corrected to yield the true value. The results of such attempts are given in the following section.

Results and Analysis

The data from the earlier report¹ are included here, in order to augment the new figures. The format was changed to make the presentation more informative. The raw and calculated data are given in Table 2 for the medium calorimeter and in Table 3 for the large unit. The "corrected observed" value was calculated by adding to the actual measured value (column 2) the difference between the reported value of the decayed standard on the day of the measurement (column 4) and the initial standard value (Table 1). This method produced the same results as with a proportional adjustment. This correction was necessary so that an average of the measured power levels could be determined.

The last two columns of each table contain the biases, or differences, between the observed and standard values. These are reported as both absolute and percentage differ-

ences. The means and 95% confidence limits are listed in Table 4. The confidence limit was determined with the t-test, where $\sigma/\sqrt{N} \approx t_{\alpha} s/\sqrt{N}$. Here σ is the true population standard deviation, s the sample standard deviation, N the number of observations and t_{α} is the uncertainty factor from the t-distribution for $N-1$ degrees of freedom at the 2α confidence limits. The term t_{α} must be greater than 1.96, its limit at $N = \infty$. These confidence limits and the biases are smaller for the medium calorimeter than for the larger one. This point is discussed in detail later.

The biases and associated errors are graphically illustrated in Fig. 1, where they are plotted with respect to the power level of the standard. A confidence level of 95% is chosen somewhat arbitrarily, but should be acceptable since the true bias would have only a 5% chance of being outside these limits. Also the range at the 95% confidence level is 1.96σ , very

Table 2. Raw and calculated data for the medium calorimeter, No. 32.

Date	Observed value (W)	Corrected value (W)	Standard value (W)	Bias	
				Observed (mW)	Standard (%)
Sample No. 1					
12/22/73			1.522		
1/04/74	1.525	1.526	1.521	4	0.263
1/08/	1.525	1.526	1.521	4	0.263
Sample No. 2					
12/19/73			9.293		
1/10/74	9.307	9.311	9.289	18	0.194
1/14	9.304	9.308	9.389	15	0.161
1/16	9.306	9.311	9.288	18	0.194
1/18	9.305	9.310	9.288	17	0.183
1/22	9.309	9.315	9.287	22	0.237
1/24	9.311	9.317	9.287	24	0.258
1/28	9.311	9.318	9.286	25	0.269
1/30	9.309	9.317	9.285	24	0.258
2/04	9.310	9.318	9.285	25	0.269
2/05	9.308	9.317	9.284	24	0.258
2/11	9.315	9.325	9.283	32	0.344
2/13	9.314	9.324	9.283	31	0.334
2/25	9.312	9.325	9.280	32	0.344
2/26	9.312	9.325	9.280	32	0.344
2/27	9.310	9.323	9.280	30	0.323
2/28	9.310	9.323	9.280	30	0.323
3/01	9.310	9.324	9.279	31	0.334
Sample No. 3					
12/10/73			20.410		
12/15	20.451	20.480	20.381	70	0.343
Sample No. 4					
7/18/74	0.489 56	0.489 56	0.489 96	-0.40	-0.082
8/8	0.489 37	0.489 59	0.489 74	-0.37	-0.076
8/14	0.489 32	0.489 60	0.489 68	-0.36	-0.074
8/16	0.489 26	0.489 56	0.489 66	-0.40	-0.082
8/26	0.488 78	0.489 18	0.489 56	-0.78	-0.159
9/3	0.488 69	0.489 18	0.489 47	-0.78	-0.159

Table 2. Raw and calculated data for the medium calorimeter, No. 32.
(continued)

Date	Observed value (W)	Corrected value (W)	Standard value (W)	Bias	
				Observed (mW)	Standard (%)
Sample No. 5					
7/19/74	1.006 76	1.006 76	1.004 21	2.55	0.254
8/6	2.005 4	1.005 8	1.003 82	1.58	0.157
8/9	1.005 7	1.005 8	1.003 76	1.94	0.193
8/13	1.005 43	1.005 97	1.003 67	1.76	0.175
8/19	1.005 15	1.005 82	1.003 54	1.61	0.160
8/20	1.005 32	1.006 01	1.003 52	1.80	0.179
8/30	1.004 93	1.005 83	1.003 31	1.62	0.161
Sample No. 6					
7/22/74	5.038 11	5.038 11	5.038 76	-0.65	-0.013
8/7	5.035 7	5.035 30	5.037 03	-1.3	-0.03
8/12	5.056 3	5.037 90	5.036 49	-0.2	-0.000
8/15	5.035 9	5.036 18	5.036 17	-0.3	-0.01
8/28	5.033 3	5.038 10	5.034 77	-1.5	-0.03
8/29	5.031 8	5.037 28	5.034 66	-2.9	-0.06

close to the 2 σ level used in Ref. 1. The selection of a percentage confidence level gives a more intuitive feel for the precision of the measurements than does a simple integral multiple of the standard deviation.

The sensitivities were experimentally determined for each run. They decrease slightly as the power increases. The medium calorimeter has a sensitivity of about 5.4 mV/W and the large one about 2.5 mV/W. The values are fit by a polynomial equation quite well (within 0.1%) and

these expressions are used to determine sensitivities for routine assays. This approach reduces the analysis time considerably. Periodic sensitivity measurements are made to check the accuracy of the polynomial fit. Environmental factors such as humidity and temperature affect the sensitivity but their influence is reflected in the 0.1% error.

The percentage biases and 95% confidence limits are plotted against power in Fig. 1. No confidence limits are shown when there was only

Table 3. Raw and calculated data for the large calorimeter, No. 143.

Date	Observed value (W)	Corrected value (W)	Standard value (W)	Bias	
				Observed (mW)	Standard (%)
Sample No. 1					
12/22/73	1.529	1.529	1.522	7	0.460
12/26	1.526	1.516	1.522	-6	-0.394
1/07/74	1.522	1.523	1.522	1	0.066
1/09	1.526	1.527	1.521	5	0.328
Sample No. 2					
12/19/73	9.257	9.257	9.293	-36	-0.387
12/20/73	9.275	9.275	9.293	-18	-0.194
1/11/74	9.297	9.301	9.289	8	0.086
1/15	9.263	9.268	9.288	-25	-0.269
1/17	9.249	9.254	9.288	-39	-0.420
1/21	9.334	9.340	9.287	47	0.506
1/23	9.284	9.290	9.287	-3	-0.032
1/25	9.250	9.257	9.286	-36	-0.387
2/01	9.263	9.271	9.285	-22	-0.237
2/07	9.268	9.277	9.284	-16	-0.172
2/14	9.267	9.278	9.282	-15	-0.161
Sample No. 3					
12/10/73	20.328	20.328	20.410	-82	-0.402
12/13	20.352	20.353	20.409	-57	-0.279
2/20/74	20.247	20.278	20.379	-132	-0.647
Sample No. 4					
8/8/74	0.480 9	0.481 i	0.489 74	-8.8	-1.8
8/9	0.484 2	0.484 4	0.489 73	-5.5	-1.1
10/14	0.489 0	0.489 9	0.489 04	-0.04	-0.0
Sample No. 5					
8/6/74	1.014 0	1.104 4	1.003 82	+0.18	+1.0
8/13	0.999 2	0.999 7	1.003 67	-4.5	-0.4
8/19	0.990 3	0.991 0	1.003 54	-13.2	-1.3
9/3	0.990 3	0.991 3	1.003 22	-12.9	-1.3
Sample No. 6					
7/24/74	5.024 2	5.024 4	5.038 54	-14.3	-0.29
8/15	5.013 4	5.016 0	5.036 17	-22.8	-0.45
8/27	5.033 4	5.037 3	5.034 87	- 1.5	-0.03
9/18	5.072 4	5.018 7	5.032 50	-20.1	-0.40
9/20	5.014 1	5.020 6	5.032 28	-18.2	-0.36
9/23	5.016 5	5.023 3	5.031 96	-15.8	-0.31

Table 4. Means and 95% confidence limits for the "zero-corrected" observed values and the biases.

Sample No.	Mean corrected observations (W)	Mean bias		Error (%)
		Observed (mW)	Standard (%)	
<u>Medium calorimeter (No. 32)</u>				
1	1.526	4	0.263	-
2	9.318	25.3	0.272	±0.032
3	20.480	70	0.343	-
4	0.489 45	-0.51	-0.105	±0.044
5	1.005 00	1.8	0.183	±0.032
6	5.037 15	-1.2	-0.024	±0.022
<u>Large calorimeter (No. 143)</u>				
1	1.524	2	0.115	±0.598
2	9.279	-14	-0.152	±0.178
3	20.320	-90	-0.443	±0.464
4	0.485 1	-4.7	-0.970	±2.6
5	1.021 6	-5.1	-0.500	±1.7
6	5.023 4	-18	-0.360	±0.15

one measurement of a standard. If the biases are less than 0.5% as specified and the bias ranges are greater than 0.5%, there is no way of determining whether the 0.5% precision specification is statistically valid. In other words, a probable value inside the bias range may lie outside the 0.5% limit even if the mean bias is zero.

The bias ranges for four sets of measurements with the large calorimeter were greater than 0.5%, the specified accuracy of both calorimeters. Only one of these points, however, is within the stated range (2-20 W) of the large calorimeter. Such a large variation is, therefore, of little concern to this analysis. The bias ranges of

Fig. 1. Variation of bias with power level for two calorimeters.

the medium calorimeter are all less than 0.1% and present no problem in this regard. All other average biases and their ranges lay inside the specified 0.5% precision.

In order to obtain the true magnitude of unknown sample power levels, we attempted to derive a smooth relationship between the bias and power level for each calorimeter. A bias correction could then be applied to each measurement to yield a more accurate value. A cursory examination of Fig. 1 shows that this was not possible. The average biases of the measurements of each calorimeter show wide scatter. However, certain conclusions may be drawn.

Within the power range of the medium calorimeter all average biases are less than 0.3%, well within the specified accuracy, and they tend to be positive. The scatter of these biases for this calorimeter is less than 0.1%, much smaller than the

larger unit. As pointed out earlier, the 0.5% accuracy is statistically valid at the 95% confidence limit, since the sum of the average and scatter is less than 0.5%.

The average biases of the larger calorimeter are greater than with the medium-sized unit and their scatter is greater. However, the average biases are still within the specified accuracy of 0.5% over the stated range of 2-30 W. Unfortunately, only three of the power standards were within this range and the scatter of the 20 W bias extends outside the 0.5% limits. Therefore, the present data is inadequate to decide whether or not the 0.5% specified accuracy is valid. Qualitatively this limit seems reasonable, however, since all of the average biases fall within this range. In contrast to the medium calorimeter, these biases tend to be negative.

Conclusions

The following points summarize our findings:

- The accuracies of both calorimeters fall within the specified 0.5%, although such a statement is not yet statistically valid for the large calorimeter.

- The calculated accuracy ($\sim \pm 0.3\%$) of the medium unit is greater than specified ($\pm 0.5\%$) and the bias ranges are smaller compared to the large calorimeter. This indicates that this instrument is inherently more accurate.

- No expression of the bias for each calorimeter with respect to sample power can be determined. Therefore, no correction for bias can be made and the specification of a $\pm 0.5\%$ accuracy is the best error

statement that we may now make.

- The bias of the medium calorimeter is positive; that of the large resistance-bridge type unit is negative.

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