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RADIOMETRIC CALORIMETRY AT THE
LIVERMORE SITE OF THE UNIVERSITY
OF CALIFORNIA RADIATION LABORATORY

LIVERMORE SITE

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Stuart R. Gunn

July 1, 1955

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ABSTRACT

A macrocalorimeter and a microcalorimeter, both of the steady-state resistance-bridge type, are described. The theory of the method, operating procedures, and performance data are given.

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I. INTRODUCTION

The calorimetric method has been adopted at this laboratory for the assay of large amounts of radioactive nuclides. The purpose of this paper is to give a description of the equipment and the methods used and an estimate of their capabilities. It is to be understood that little of this work is of an original nature; the instruments and procedures duplicate in principle and in most details those developed at the Mound Laboratory over a period of years by J. F. Eichelberger, J. R. Parks, K. C. Jordan, and others.

Radiometric calorimetry differs from most chemical calorimetry in that the quantity to be measured is a power which is nearly constant over the period of the measurement rather than a quantity of energy which is liberated over a relatively short time. Several calorimetric methods have been used. In the adiabatic method, the rate of temperature rise of a system of known heat capacity containing the source is measured while the environment is maintained at the same temperature as the system in order to minimize thermal leakage. In fusion calorimetry, the rate of change of the volume of a system consisting of the solid and liquid phases of a substance, usually water, in equilibrium at the melting point is measured to determine the rate of melting due to absorption of heat from the source. Vaporization calorimetry is similar in principle, the rate of evolution of gas by boiling of a liquid, such as nitrogen or helium, being measured.

The method which we have adopted is that of the steady state, using twin resistance-bridge instruments. This method has the particular

advantages of simplicity and rapidity of operation and sturdiness and reliability of instrumentation.

II. PRINCIPLES OF THE METHOD

Consider a system of heat capacity C and temperature T_c separated by a barrier of thermal conductivity k from an environment of temperature T_b . Then, according to Newton's law of cooling, the rate of heat transfer from the system to the environment is

$$\frac{dH}{dt} = k(T_c - T_b) \quad (1)$$

and the rate of change of the temperature of the system is

$$\frac{dT_c}{dt} = \frac{-k(T_c - T_b)}{C} \quad (2)$$

With a source producing heat at a constant rate, P , added to the system, the equation becomes

$$\frac{dT_c}{dt} = \frac{P - k(T_c - T_b)}{C} \quad (3)$$

If T_b is a constant, we may write

$$\theta = T_c - T_b \quad (4)$$

And

$$d\theta = dT_c \quad (5)$$

Thus,

$$\frac{d\theta}{dt} = \frac{P - k\theta}{C} \quad (6)$$

or

$$\frac{d\theta}{(P - k\theta)} = \frac{dt}{C} \quad (7)$$

Integrating this expression,

$$\ln \frac{(P - k\theta)_2}{(P - k\theta)_1} = -\frac{k}{C} (t_2 - t_1) \quad (8)$$

As t_2 approaches infinity,

$$\frac{P - k\theta_\infty}{P - k\theta_1} = 0 \quad (9)$$

Hence,

$$\theta_\infty = \frac{P}{k} \quad (10)$$

Substituting this result in equation (6), it is seen that

$$\frac{d\theta_\infty}{dt} = 0 \quad (11)$$

Thus the system approaches a steady-state temperature at which the power of the source is equal to the rate of heat loss. We shall designate this steady-state temperature elevation of the system above the environment for a particular power as θ_p .

We may now derive an expression for the rate at which the system approaches the steady state. From equation (6),

$$\frac{d(\theta - \theta_p)}{dt} = \frac{P - k\theta}{C} \quad (12)$$

and substituting equation (10),

$$\frac{d(\theta - \theta_p)}{dt} = -\frac{k(\theta - \theta_p)}{C} \quad (13)$$

Integrating,

$$\ln \frac{(\theta - \theta_p)_2}{(\theta - \theta_p)_1} = -\frac{k}{C} (t_2 - t_1) \quad (14)$$

As a measure of the operating time of an instrument, we may use the half-time, $t_{1/2}$, the time necessary for $\theta - \theta_p$ to be reduced to one-half its initial value. From equation (14),

$$t_{1/2} = -\frac{C}{K} \ln \frac{1}{2} \quad (15)$$

$$t_{1/2} = 0.693 \frac{C}{K} \quad (16)$$

Similarly,

$$t_{1\%} = 4.606 \frac{C}{K} = 6.65 t_{1/2} \quad (17)$$

$$t_{0.01\%} = 9.212 \frac{C}{K} = 13.29 t_{1/2} \quad (18)$$

In order to integrate equation (3), it was necessary to assume that the T_b was constant. If during a measurement T_c has reached a steady temperature, $T_c = T_b + \theta_p$, and T_b then changes, T_c will approach a new value, $(T_c)_2 = (T_b)_2 + \theta_p$. If T_b is fluctuating continually, T_c will not reach a steady value but will attempt to follow T_b and θ will vary since there is a lag in the following. However, if a calorimetric system identical to the first, except for absence of the source of power, is established, we may measure the temperature difference, T_c° , between the two:

$$T_c^\circ = T_c' - T_c'' \quad (19)$$

If $C' = C''$ and $k' = k''$, T_c' and T_c'' will be affected identically by changes in T_b , and T_c° and θ_p° will be independent of T_b . In practice it is possible to match the thermal characteristics of the two components of a twin calorimeter within a few percent, thus reducing the effect of fluctuations in the thermostat by this factor.

From equation (10) it is seen that θ_p is directly proportional to P insofar as k is a constant. We may define the sensitivity of the calorimeter as

$$S = \frac{\theta_p^\circ}{P} = \frac{1}{K} \quad (20)$$

Calibration of the instrument consists of determination of the factor S . In the calorimeters under discussion, the thermal barrier is an air-filled gap. This gap is sufficiently narrow to minimize convection currents at the thermal gradients involved; hence, the main mechanism of heat transfer is by conduction and k is nearly constant. The temperature difference, θ_p° , is measured with a resistance bridge, the output of which is essentially proportional to temperature insofar as dR/dT for the nickel thermometers is a constant. The over-all characteristics of the instruments are such that the sensitivity expressed in microvolts per watt is nearly constant over the useful power range.

It may be seen from equations (16) and (20) that the half-time is directly proportional to C and inversely proportional to k and that S is independent of C and inversely proportional to k . Thus to obtain the desirable characteristics of high sensitivity and short half-time, C should be made as small as possible but k must be a compromise.

III. INSTRUMENTATION

Two of the calorimeters, designated as Calorimeters III and IV, have been built in this laboratory. The former is a microcalorimeter and the latter is a macrocalorimeter. A third instrument, identical with IV, is under construction.

A. The Macrocalorimeter

Fig. 1 shows some details of the construction of Calorimeter IV. Table I gives the dimensions of the more important parts.

The sample can is fitted with a twist-locking cap which on its upper side has slots to engage a crossbar on the end of a rod which is used to remove the cans from the instrument. The space available for samples has a diameter of 1.124 in. for a length of 2.475 in. and a diameter of 1.095 in. for an additional length of 0.375 in. The heater form is turned down 0.036 in. on the outside for a length of 2.50 in. to provide space for the heater; two slots of the same depth and 0.050 in. wide lead through the bottom flange to provide passage for the leads. The heater form is held in place in the thermel form by a 0.125 in. dural pin (I) 1.350 in. long, which also serves as a stop for the sample can.

Table I

Dimensions of Calorimeter IV

Part	Material	I. D. (in.)	O. D. (in.)	Length (in.)
A Sample can	Brass	1.124	1.154	2.750
B Heater form	Dural	1.154	1.245	4.000
C Thermel form	Dural	1.245	1.350	5.500
D Upper support tube	Polystyrene	1.165	1.350	3.375
E Lower support tube	Polystyrene	1.165	1.350	3.375
F Spacing sleeve	Dural	1.532	2.010	11.125
G Submarine tube	Brass	2.010	2.250	15.750
H Upper tube plug	Polystyrene	1.165	1.995	4.565

The polystyrene support tubes are turned down for a length of 1/2 in. for a medium force fit into the thermel form. This assembled unit is then held centered in the spacing sleeve by flanged polystyrene rings (J, K) at either end. Two six-point electrical terminal strips (L), are attached to the lower rings. The whole working calorimetric unit, consisting of the two spacing sleeves and their contents, can be removed from the submarine by removing the lower cover plate (M), disconnecting from the terminal strips the leads which are brought down through a third smaller tube and removing two screws which hold the lower flanged rings. Calorimeters III and IV are interchangeable in the same nickel-plated brass submarine. The central hole above and below the sample can is filled by styrofoam plugs, the upper of which is removable.

The weights in grams of the essential components of the two sides are given in Table II. It is desirable that these be as similar as possible in order to equalize the time constants.

The heater is a bifilarly-wound coil of No. 30 enamelled constantan wire having a resistance of about 165 ohms. The leads are No. 34 copper;

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Fig. 1. Sectional view of Calorimeter IV.

a potential lead is soldered to each current lead a short distance below the heater form and these four leads are then brought to the outside of the lower support tube through small holes below the thermometer coils.

Table II

Weights of Components of Calorimeter IV

Part	Left (g)	Right (g)
Sample can and cap (Brass)	33.71	34.47
Heater form and pin (Dural)	18.66	18.50
Thermel form (Dural)	54.00	54.37
Upper and lower support tubes (Polystyrene)	43.98	43.93

There are two thermometer coils on each side, each 9.50 in. long and hence extending two inches beyond the thermel form onto the support tubes at each end. The coils consist of 1400 ohms of No. 38 double-nylon-covered nickel wire wound bifilarly with the aid of a lathe at a spacing of 112 turns per inch. The outer coil is laid directly over the inner.

The heater and thermometer leads are brought into the lower chamber of the submarine through holes in the lower flanged polystyrene rings. The thermometer leads are soldered to form a bridge with the two coils on the same side of the calorimeter forming opposite arms of the bridge. The coils are adjusted to nearly balance the bridge at zero power.

B. The Microcalorimeter

Calorimeter III is similar in general design. The sample can and hence all parts of the core assembly are smaller to decrease the heat capacity, and the air gap is wider to increase the sensitivity. Dimensions are given in Table III.

Table III

Dimensions of Calorimeter III

Part	Material	I. D. (in.)	O. D. (in.)	Length (in.)
Sample can	Dural	0.410	0.450	1.000
Heater form	Dural	0.450	0.490	1.150
Thermel form	Dural	0.490	0.509	2.000
Upper support tube	Polystyrene	0.480	0.509	2.625
Lower support tube	Polystyrene	0.480	0.509	2.625
Spacing sleeve	Dural	1.500	2.010	6.750
Submarine tube	Brass	2.010	2.250	15.750
Upper tube plug	Polystyrene	0.490	2.010	9.125

The support tubes extend $1/4$ in. into the thermel form, and their outside diameter is increased to 0.530 beyond one inch from the thermel form. The heater form is turned down to a diameter of 0.475 in. for a length of 0.940 in. to accommodate a 150-ohm heater of No. 35 enamelled constantan. The thermometer coils consist of 350 ohms of No. 40 double nylon covered nickel. The inside diameter of the sample can is 0.410 in. for a length of 0.812 in. and 0.390 in. for a length of 0.158 in.

C. Associated Equipment

The electrical circuits are shown in simplified form in Fig. 2. Power is provided by a Kaylab 100 v, 500 ma regulated dc supply which is stable to about 0.01 percent. The current through the thermometer bridge is adjusted by means of R_1 and monitored by observation of the potential E_B across the 100-ohm standard resistor, R_3 . A bridge current of 5 ma has been adopted as standard and all subsequent data will pertain to this value.

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Fig. 2. Electrical circuits for steady-state calorimeters.

The heating circuit is shown connected to pass current through the heater in the right side, H_R . In order to eliminate the effect of the small amount of heat generated in the current leads below the point where the potential leads are attached, the current is passed through L_3 and L_4 on the left side. The four pairs of leads are of similar length and position, and hence the net power delivered by H_R to the right side is that measured between its potential terminals. R_4 , R_5 , and R_6 are standard resistors of 10 ohms, 10,000 ohms, and 1,000 ohms, respectively; the last two have a low-resistance link between them. The current through the heater is controlled at the desired value by adjusting R_2 and monitored by measuring the potential E_I across R_4 . Measurement of the potentials E_D , E_{L+} , and E_{L-} then permits calculation of the potential across the heater and hence its power, the equations being,

$$I_H = \frac{E_I}{R_4} = \frac{E_I}{10} \quad (21)$$

$$E_H = E_D \left(\frac{R_5 + R_6}{R_0} \right) - E_{L+} - E_{L-} = 11E_D - E_{L+} - E_{L-} \quad (22)$$

$$P_H = E_H I_H \quad (23)$$

Switching arrangements are also provided whereby current can be passed through the opposite heater in the same manner, through both heaters in series, through both heaters simultaneously from different resistance banks, or through two sets of dummy leads in series.

All standard resistors are by Leeds and Northrup, certified to 0.01 percent. All potential measurements except E_T are performed with a Rubicon Type B precision potentiometer and a Leeds and Northrup Type E enclosed lamp-and-scale galvanometer. The same combination has been adequate for measurement of E_T in all work with Calorimeter IV. However, to secure sensitivity of less than a microvolt with Calorimeter III, a White 10,000-microvolt double potentiometer, a Liston-Becker Model 14 breaker amplifier, and a Bristol recording potentiometer have been used. This permits observation of the noise and recording of the small error signal from the potentiometer. However, it is necessary to use storage batteries rather than the regulated power supply as a source of current for the bridge in order to avoid ground currents through the amplifier.

In much of the work with Calorimeter IV, a circuit was used in which R_1 and R_2 each consisted of three or four Ohmite rheostats connected in series and immersed in an unstirred oil bath. This was reasonably satisfactory, but the contact noise is somewhat objectionable when making fine adjustments of the current. More recently six-dial decade resistance boxes with manganin resistors and low contact-resistance switches have been built. Those for the heaters are variable from 0 - 10,000 ohms in steps of 0.01 ohm and for the thermometer bridge from 0 - 100,000 in steps of 0.1. Resistors in the highest two decades of the former and highest three of the latter are immersed in oil. These banks are much more satisfactory.

The thermostat used with Calorimeter IV is mounted with its top flush with the bottom of a wooden glove box. This permits handling of samples above the calorimeter with diminished danger should a container leak. The stainless steel tank is 22 in. deep and 10 in. in diameter and communicates at top and bottom with a 5-in. stirring well located immediately behind it. The latter contains a 3-in. propellor driven by a 1/30 hp motor, a control heater, a cooling coil, and a thermoregulator. The tank is set into a rectangular wooden box insulated with a 2-in. layer of styrofoam, and the free spaces are filled with shredded styrofoam. The thermostat is usually operated at about 30°C. Tap water is passed through the cooling coil to compensate the heat of stirring. A small mercury thermoregulator operating a knife-blade heater through a thyatron relay controls the temperature within $\pm 0.005^\circ\text{C}$.

The experiments with Calorimeter III were performed using a conventional open-tank thermostat controlled to about the same precision.

IV. OPERATION

The most complete procedure for measuring the power of a sample may be outlined as follows, where the designations Can 1, Can 2, and Can 3 refer to three sample cans indicated as Part A in Figure 1:

1. In Can 1, place the source with a clip to hold it firmly in position.
2. In Cans 2 and 3, load inert slugs corresponding approximately to the source in thermal capacity, thermal conductivity, and geometry.

3. Insert Can 2 in the "Dummy side" and Can 3 in the "Sample side." Determine the bridge zero E_T° by measuring E_T until it reaches a constant value.

4. Replace Can 3 with Can 1 and measure the bridge potential E_T^S at the steady state.

5. Replace Can 1 with Can 3 and again measure the bridge zero.

6. Heat the sample side electrically at a constant power approximately equal to that of the sample and measure the bridge potential E_T^H at the steady state. Measure E_I , E_D , E_{L+} , and E_{L-} and calculate P_H .

7. Discontinue heating and again measure the bridge zero.

8. Using the average of the values of E_T° , determined in steps 5 and 7, calculate the sensitivity,

$$S = \frac{E_T^H - E_T^\circ}{P_H} = \frac{\Delta E_T^H}{P_H} \quad (24)$$

Then, using the average of the values of E_T° determined in steps 3 and 5, calculate the power of the source,

$$P_S = \frac{E_T^S - E_T^\circ}{S} = \frac{\Delta E_T^S}{S} \quad (25)$$

In practice it is usually possible to shorten this procedure considerably. The zero is generally taken less frequently, step 5 being most often omitted, and of course when many samples are being run consecutively, step 7 for one becomes step 2 for the next. Except where it is important to minimize the noise level, Cans 2 and 3 can be left empty, thus decreasing the half-time.

The usual procedure in measuring E_T is to take readings at intervals of one half-time. Thus, the difference between successive readings decreases by a factor of two for each reading. There is a "stretching" effect, due to the patterns of heat flow, which results in some apparent increase of the half-time as the steady-state is approached, but it is possible to make a sufficiently accurate extrapolation of E_T by taking readings until its change in the last half-time is one or two times the desired precision of the measurement and then adding the magnitude of the change to the last reading. If the approximate power of the sample is known, the measurement can be speeded by using the heater to bring the instrument close to the steady-state; the

same can be done during the calibration by heating at a higher power for a short period. When determining the bridge zero following a calibration, the sample can may be removed, quickly cooled, and replaced in the instrument.

The sensitivity of Calorimeter IV is constant within a few tenths of a percent over the entire useful power range and is also quite stable with time. Where a precision of 0.5 percent is adequate, a standard calibration factor may be applied for an indefinitely large number of samples; where 0.1 percent or better is required, it should be determined for each run, and in the intermediate region it should be determined occasionally.

V. PERFORMANCE

A. The Macrocalorimeter

Calorimeter IV has been used with sources ranging from 0.015 to 1.3 watts. The sensitivity is 40,100 microvolts per watt. For sources above 0.4 watt, duplicate runs agree within 0.1 percent and could undoubtedly be improved to 0.05 percent or better. For sources from 0.015 to 0.06 watt, agreement averages within 0.0001 to 0.0002 watt.

The most probable systematic error in the instruments would result if the resistance of the thermometers were changed to a different extent by a given amount of power generated in the heater than by the same power generated at an arbitrary point within the sample can. This heat distribution error has been studied extensively by workers at the Mound Laboratory and found to be negligible in models similar to Calorimeter IV. In this instrument, the heater most closely approximates a power source uniformly distributed over the walls of the sample can in the central 2.50 in. of height. In a series of experiments, the distributional error was checked by placing an alpha radioactive source in the form of a 3/8 in. diameter sphere in contact with the wall of the sample can at a point midway between the top and bottom and measuring ΔE_T^S four times with the can being rotated 90° between measurements and also by placing the source in the center of the bottom of the can. The five readings agreed within 0.03 percent.

As a further check, a one-watt alpha-radioactive source which had been measured in Calorimeter-50 was also measured in Calorimeter IV

and found to agree within 0.03 percent. Calorimeter-50 had been built at the Mound Laboratory and was used here prior to the construction of Calorimeter IV. Several samples of radioactive materials previously measured at the Mound Laboratory have also been measured here; agreement is within the precision of the earlier determinations.

The half-time of Calorimeter IV is five or six minutes with empty cans; the samples in the 0.015 to 0.06 watt range mentioned previously were in massive containers which doubled the time. In general, an operator measuring sources of several tenths of a watt and relatively low thermal capacity to 0.1 percent precision can measure the sample in fifty to sixty minutes and the zero and calibration somewhat more rapidly.

B. The Microcalorimeter

Calorimeter III was built to study the useful sensitivity of small instruments for sources of low power. It has a sensitivity of 112,000 microvolts per watt. The half-time is about three minutes but shows considerable stretching near the steady state. Table IV shows the results of a series of measurements of a small alpha-radioactive source.

It seems that there is a probable error of about ± 0.2 microvolt or ± 2 microwatts in the average of a number of measurements of a single source.

TABLE IV

Performance of Calorimeter III

Time	E_T°	E_T^S	$E_T^{\circ} - E_T^S$
8:43		40.64	
9:20	54.74		13.73
10:20		41.39	13.49
11:40	55.02		13.94
13:06		40.77	14.14
13:36	54.81		13.90
14:30		41.05	13.80
15:00	54.90		

/wld