

An absolute calibration method for microcalorimeters

P.F. Bunyan¹

Defence Evaluation and Research Agency, Fort Halstead, Building X48, Sevenoaks, Kent TN14 7BP, UK

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Abstract

An absolute method for calibrating isothermal microcalorimeters is described which uses a well-characterized, physico-thermal property of a stable, pure material of known mass. The technique exploits the loss or gain of heat from a sample of the specific-heat standard, alumina, following a small, but rapid change in the operating temperature of the calorimeter. The results obtained using this specific-heat calibration method are compared with calibrations made using electrically heated calibration devices. Crown copyright © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction and background

An isothermal microcalorimeter, the thermal activity monitor (TAM), has been used in this laboratory to study a variety of heat-generating reactions of energetic materials since 1986 [1,2]. The operating principles of this instrument are described in Ref. [3]. Until recently, the integral, internal, electric calibration heater supplied with a unit has been the sole means of calibrating the instrument for power. While the accuracy of the instrument specified by the suppliers was considered adequate for these investigations, there has, until recently, been no convenient, independent, absolute way of checking that the selected power is still a true description of the energy applied to the detectors. It would, therefore, be possible for the internal calibration to become invalid, as for instance due to a change in the resistance of the heater itself, its electrical connectors, or a malfunction

in the heater power supply, without the operator's knowledge. This would result in systematic errors in reported heat flow data when the calorimeter was used experimentally.

Internal calibration relies on generating heat from a resistance wire coil which is located in close proximity to the sample ampoule, although obviously not in precisely the same place. As the heater is not coincident with the sample and the heat flow detecting Peltier element cannot surround either heat source entirely, it is possible that the proportion of heat loss from each type of heat source (i.e. from the calibration heater, or due to a chemical reaction occurring inside an ampoule) which actually flows through the detector will differ and further errors could result. For this reason, the instrument operating manual suggests applying an approximate correction factor of ca. 4%, or, preferably, using an alternative method of calibration [4].

The problem of finding a suitable reaction that can be used for isothermal calorimeter calibration was discussed at a recent conference and the need for

¹Tel.: +1-959-51-4085.

more convenient, safe, universal and absolute calibration methods was highlighted [5]. The calibration requirements imposed by the need for laboratories to achieve ISO 9000 and NAMUS certification also make finding solutions to this requirement a priority.

An external method of chemical calibration which utilizes the heat generation during the hydrolysis of an imidazole/acetic acid buffer located inside a sample ampoule has been described by Wadsö and Chen [6]. In order to determine the true heat generated by such a reaction at a given time, it is essential to obtain a full description of the enthalpy changes, the temperature dependence of rate and the mechanism of the reaction. Even if these are known, the concentration and purity of all reactants must be carefully controlled and the method is a demanding task for the analyst.

A second external means of calibrating the calorimeter has been suggested, using a radioactive material of known activity [5]. An americium probe has been used for this purpose in Sweden for more than a decade. However, problems of licensing, toxicity, transport and availability make this procedure unattractive in most cases [5,7].

The manufacturers of the thermal activity monitor have recently introduced an external electric heater. With the aid of a good calibrated multimeter, the exact amount of heat formed in the stainless steel ampoule can be deduced [8].

This paper describes the development and assessment of an alternative method for calibrating isothermal microcalorimeters using a well-characterized, physico-thermal property of a stable, pure material of known mass, located in the same position that will be used for the experimental samples.

2. Theory

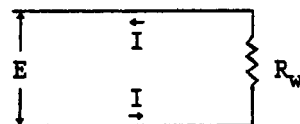
In order to deduce a valid calibration factor, it is essential to generate an accurately known amount of heat energy within an ampoule identical to those which will be used to study heat generating processes from thermally reactive samples. The energy produced must be capable of being determined using values of absolute quantities which can be measured accurately and independently.

2.1. Calibration using electric heaters

Both, the internal calibration device supplied with the TAM and the independent external calibration device rely on heating a resistance coil, located close to, or at, the intended site of the sample to be analyzed, electrically.

The manufactures supply a data acquisition and instrument control computer programme with their external electric heater. This will carry out a calibration experiment and, subsequently, process the data to check the accuracy of the internal calibration and, thereafter, calculate a correction factor. The programme requires that the voltage across the resistor and its resistance be measured manually prior to input by the operator through the keyboard. Alternatively, if an accurately measured voltage is applied across the resistor and its resistance is known, the resulting power dissipated within the ampoule may be calculated directly as follows.

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where: R_w is the resistance of wire in ampoule (Ω), E the applied voltage (V), and I the current (A). From Ohm's law

$$I = E/R_w \quad (1)$$

and from the power law

$$q = I^2 R_w \quad (2)$$

where q is the power generated within the ampoule (W).

Substituting Eq. (1) in Eq. (2)

$$q = (E/R_w)^2 R_w$$

2.2. Calibration using specific-heat standard material

A method to determine the specific heat of reactive materials, which relied on measuring the area under the recorded signal imbalance curve as the temperature of the TAM thermostat bath was altered, was described earlier [9]. If the total area under the imbalance

ance curve given by an accurately weighed sample of *known* specific heat is recorded during a temperature step, it is possible to calibrate the TAM for power by following the inverse procedure:

For a temperature step experiment in a calorimeter which has previously been calibrated using the internal electric heater:

$$C_{P(\text{app})} = \frac{Q}{M_{\text{CAL}} \times T_{\text{STEP}}}$$

where $C_{P(\text{app})}$ is the apparent specific heat of the calibration material, Q the total heat generation/consumption following temperature change indicated by internally calibrated calorimeter, M_{CAL} the mass of the calibration sample employed, and T_{STEP} the temperature change experienced by the system. Then the correction factor to be applied to heat generation data is given by $C_{P(\text{true})}/C_{P(\text{app})}$, where $C_{P(\text{true})}$ is the correct C_P of calibrant at the test temperature as reported in the literature [11].

3. Experimentation and results

Two microcalorimeter cylinders, A and B, were investigated. These were installed in the thermostated water bath of the same calorimeter unit. All experiments were conducted between 76° and 77°C.

3.1. Equipment and materials

A Thermometric 2277 microcalorimeter ‘thermal activity monitor’ (TAM) was used for this purpose. This calorimeter was purchased in 1986 and has been in continuous use since then. It is still using its original amplifiers, detectors and electronics. The specifications of the calorimeter, with regard to signal-to-noise ratio and long-term drift, quoted at the time [4] are slightly inferior to those reported now for a new 2277 calorimeter [10].

Temperature-step calibration experiments used an alumina specific-heat calibration sample ($\alpha\text{-Al}_2\text{O}_3$, Mettler–Toledo accessory 29801) contained in 5-cm³ stainless steel ampoules. The temperature in the sample detection region of each TAM cylinder was measured using a calibrated Hewlett–Packard 2804A digital quartz thermometer (Serial No. 02296/Calibration Certificate No. 35756T), which is

accurate to better than 1/1000°C. Samples were weighed on a Mettler AE163 analytical balance (Serial No. D48019/Calibration Certificate No. E002148).

External electric calibration was performed using a Thermometric 4 ml external calibration heater (Thermometric accessory 2611). Resistance and applied voltage were both measured using the Keithley 196 system DVM (Serial No. 381016/Calibration Certificate No. 23717), which meets the accuracy, precision and four-wire resistor reading requirements of the external calibration heater [8].

3.2. Electric calibration

3.2.1. Internal

The instrument was calibrated, at the sensitivity range under investigation, internally using the thermal activity monitor’s integral electric heater, as recommended by the manufacturers, prior to each type of external calibration [10].

3.2.2. External

Following internal calibration, the external calibration ampoule and matched blank ampoule were lowered into the detection regions of the calorimeter’s sample and reference wells, respectively. The system was allowed to equilibrate until a constant, zero signal was observed. After measuring the resistance of the heater, a voltage was applied by using the TAM’s own power supply. When the resulting positive heat flow signal had settled to a constant rate, this apparent rate was recorded. The applied voltage was measured and used to calculate the true rate of heat generation within the calibration ampoule. Results are summarized in Table 1.

3.3. Specific-heat calibration method

In order to utilize the dynamic range of the detector more efficiently and improve the signal-to-noise ratio, the reference ampoule was ballasted at all times with approximately half the mass of alumina which would eventually be used for the calibration temperature-step experiment – that is to say, the ampoules were intentionally not of equal thermal capacities.

Following internal calibration, the pair of stainless steel ampoules were lowered into the detection region

Table 1
Calibration using external electric heater

Cylinder identity	Amplifier sensitivity – as set with internal electric calibration heater/ μW (full scale)	Nominal power selected through Digitam Software/ μW	Resistance of external calibration heater/ Ω	Voltage across external calibration heater/mV	Calculated heat generation rate/ μW	Indicated heat generation rate/ μW	Required correction factor to be applied to an experiment, calibrated internally
A	300	300	49.2559	121.08	297.6	301.5	0.987
B	3000	3000	49.2579	381.8	2959	3010	0.983
A	3000	3000	49.2536	382.2	2966	3015	0.984
B	300	300	49.2706	120.89	296.6	300.2	0.988

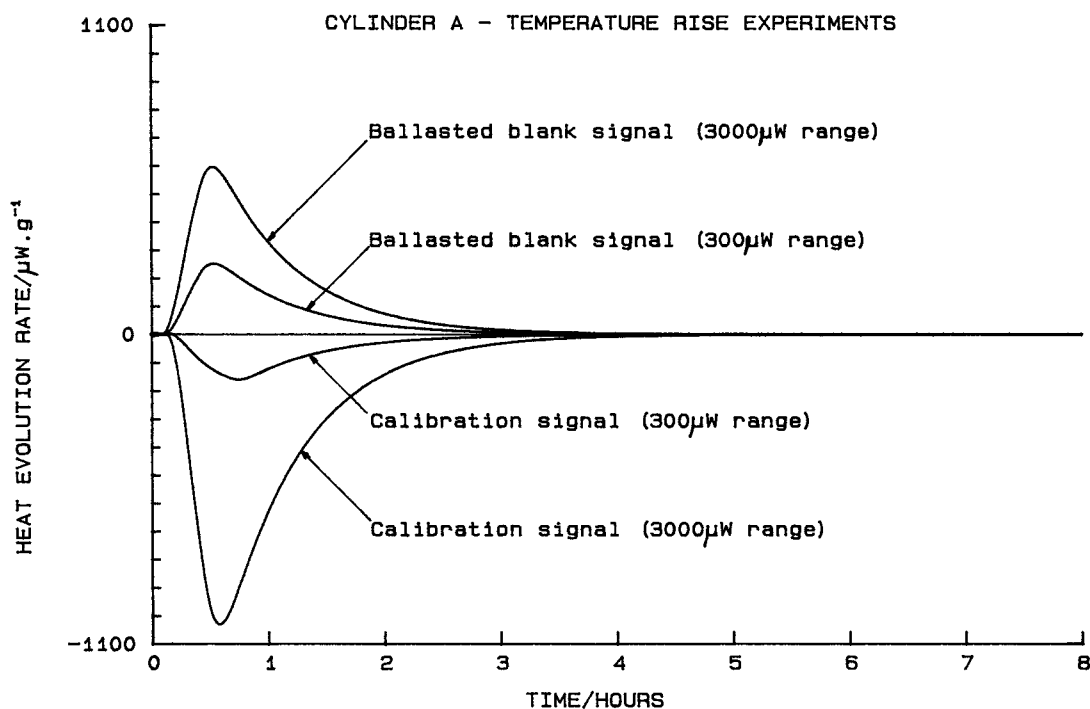


Fig. 1. Thermal activity curves resulting from temperature rise calibration experiments performed in cylinder A.

of the calorimeter and the system was allowed to equilibrate until a constant, zero signal was observed. The temperature of the calorimeter thermostat was recorded by a digital quartz thermometer probe located in an adjacent analytical cylinder. The operating temperature of the calorimeter was then either raised or lowered by approximately 1°C by altering the TAM's thermostat decade resistor settings manually. The resulting blank imbalance peak was recorded until the signal returned to zero. The final temperature of the system was then recorded using the quartz thermometer probe. This indicated that the true temperature variation experienced by the ampoules was actually 0.997°C in each case. The sample ampoule was removed from the calorimeter and an accurately weighed alumina calibration sample placed in it. The ampoule was returned to the calorimeter and a calibration temperature-step experiment was performed using identical conditions to those employed for the earlier blank experiment. The total thermal activity due to the calibration sample could then be found by adding the areas under each imbalance peak together.

The appearance of the resulting thermal activity curves obtained from cylinder A at ranges of 300 and $3000\ \mu\text{W}$ are illustrated in Figs. 1 and 2. The curves obtained from cylinder B resembled these and are not shown. Results are summarized in Table 2.

4. Discussion

Results obtained with both, the external electric heater and temperature-step method are broadly in agreement with regard to the magnitude of the systematic calibration error introduced by employing internal calibration. Since the two approaches rely on determining entirely different, absolute quantities, this is consistent with the view that both the methods can be considered valid calibration procedures.

At a low sensitivity ($3000\ \mu\text{W}$), both approaches indicate that a correction factor of 0.983 ± 0.003 should be applied to experimental results obtained after internal calibration. At a higher sensitivity ($300\ \mu\text{W}$), the electric-heater method indicates a very similar correction factor to that obtained at low sen-

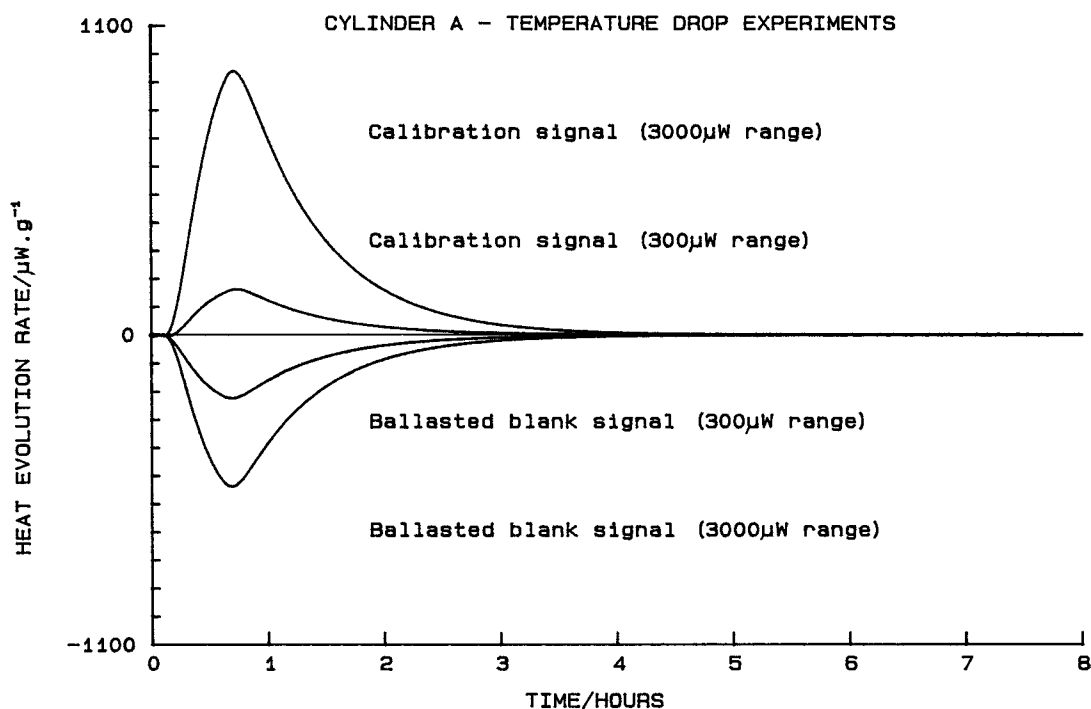


Fig. 2. Thermal activity curves resulting from temperature drop calibration experiments performed in cylinder A.

sitivity (0.987), while the temperature-step method suggests that a gain of 0.965 is required.

The necessary corrections required to correct the internal calibration are, therefore, quite small; still less than the estimated error of 4% recommended when the calorimeter was purchased [4]. Considering that this calorimeter is over a decade old and is in continuous use at elevated temperature, it would appear that the longevity, stability and robustness of the original calibration system has been good. An annual external calibration check would, therefore, appear adequate for most quality assurance purposes.

The age of the instrument used for this study, the fact that it is used at elevated temperature and is not located in a constant-temperature environment may account for the slight discrepancy in factors indicated by the two external methods at the more sensitive range. As the temperature-step approach requires sample and reference ampoules to be poorly thermally balanced, this would exacerbate the effects of these environmental factors on the signal noise, whereas drift characteristics and variability might be reduced if the calorimeter was relocated in a constant-

temperature room, or if a new calorimeter was employed.

In general, the temperature-step approach utilizes materials and equipment that a thermal analysis laboratory would normally be equipped with anyway for unrelated, general experimental tasks; the calibration material used for this work is chemically inert, readily available as an inexpensive pure substance and is re-useable. All laboratories should have an analytical balance with a valid traceable calibration. However, an accurate, high precision, calibrated thermometer is essential.

When calibrating an analytical cylinder electrically, it would be possible to carry out isothermal microcalorimetry experiments in adjacent analytical cylinders. In contrast, most experiments would be interrupted during a temperature step calibration, except in the case of experiments to determine unknown thermal capacities, which can apply similar temperature step methodology [9].

A variety of different ampoules may be used in this type of calorimeter, such as glass ampoules, which are sealed with a crimped rubber-lined lid. More sophis-

Table 2
Calibration by temperature-step method

Cylinder identity	Amplifier sensitivity – as set using internal electric calibration heater/ μW full scale	Mass of alumina calibration standard/g	Temperature Rise or Fall/ $^{\circ}\text{C}$	Integral of ballasted blank experiment/mJ	Integral of calibration experiment/mJ	Total heat evolved or consumed by alumina calibration sample/mJ	Apparent C_p indicated for alumina/($\text{J g}^{-1} \text{K}^{-1}$)	Required correction factor needed, (given true C_p of alumina is $0.8717 \text{ J g}^{-1} \text{K}^{-1}$ [11])
A	300	1.6667	R (0.997)	882	628	1510	0.9087	0.959
B	3000	6.4926	R (0.997)	1695	4053	5748	0.8879	0.982
A	300	1.6667	F (0.997)	881	631	1512	0.9099	0.958
B	3000	6.4926	F (0.997)	1701	4044	5745	0.8875	0.982
A	3000	6.4926	R (0.997)	2076	3673	5749	0.8881	0.982
B	300	1.6667	R (0.997)	529	967	1496	0.9002	0.968
A	3000	6.4926	F (0.997)	2081	3674	5755	0.8891	0.980
B	300	1.6667	F (0.997)	529	968	1497	0.9009	0.968

ticated sample containers, with gas or liquid flow through tubing connections, titration, mechanical stirring and relative-humidity control facilities, are also employed for specific experimental situations. It is not clear to what extent the different geometries, sample positions, construction materials and connecting tubing would alter the proportion of the total heat evolved during an experiment which passes across the heat-flow detecting Peltier element compared to heat produced by a calibration device located in a dissimilar ampoule. It would be possible to investigate this possibility by manufacturing a version of each type of sample container with an electric heater located in the same position normally occupied by the sample. The development and construction of these ampoules would be a demanding engineering task, which would result in additional expense. Alternatively, it should be possible to achieve a similar result by doing a temperature-step calibration within the same sample containers as will be used for experiments, without the need to construct or purchase any additional equipment.

5. Conclusions

An external calibration method suitable for use with isothermal microcalorimeters has been described which requires knowing only the mass of a pure, well-characterized, chemically stable material and the initial and final experimental temperatures. These absolute quantities can be determined accurately using

calibrated instruments commonly available in an analytical laboratory.

Results obtained in stainless steel ampoules using the method show good agreement with those obtained using an external electrically heated calibration device, which relies on the measurement of entirely different, absolute quantities. This suggests that both these methods are valid, absolute calibration procedures.

References

- [1] P.F. Bunyan, *Thermochim. Acta* 207 (1992) 147.
- [2] P.F. Bunyan, A.V. Cunliffe, *Thermochim. Acta* 276 (1996) 131.
- [3] J. Suurkuusk, I. Wadsö, *Chemica Scripta* 20 (1982) 155.
- [4] LKB 2277 Bioactivity Monitor Instruction Manual – No. 90 01 2963, LKB-Produkter AB, February 1985.
- [5] Proc. of TTCP Open Workshop on the Microcalorimetry of Energetic Materials – Final Discussion Section Lead by Dr. P. Laye, Leeds, UK, 7–9th April, 1997.
- [6] I. Wadsö, A.T. Chen, *J. Biochem. Biophys. Methods* 6(4) (1982) 297.
- [7] J. Suurkuusk, Proc of TTCP Open Workshop on the Microcalorimetry of Energetic Materials, Leeds, UK, 7–9th April, 1997, Paper Z1-1.
- [8] Thermometric Technical Instruction Manual, Validation and Performance Service for TAM V1.0, Thermometric AB, November 1996.
- [9] P.F. Bunyan, *Thermochim. Acta* 130 (1988) 335.
- [10] Thermometric 2277 Thermal Activity Monitor instruction manual, Thermometric AB, 1995.
- [11] D.C. Ginnings, G.T. Furukawa, *J. Am. Chem. Soc.* 75 (1953) 522.