Available online at www.sciencedirect.com

Thermochimica Acta 405 (2003) 15–20

thermochimica acta

www.elsevier.com/locate/tca

A new general-purpose isothermal microcalorimeter for use at temperatures up to 200 °C

Ingemar Wadsö [a,*], Lars Wadsö [b]

[a] *Physical Chemistry 1, Chemical Center, Lund University, P.O. Box 124, Lund, S-221 00, Sweden*
[b] *Building Materials, Lund University, P.O. Box 118, Lund, S-221 00, Sweden*

Abstract

The design and some properties of a new general-purpose isothermal microcalorimeter are reported. The instrument is a twin thermopile heat conduction calorimeter, which is designed for use up to 200 °C. The calorimetric units and surrounding heat sink are suspended inside a hollow aluminium construction, which is thermostated. Above that unit a second thermostated block is positioned and the whole assembly is suspended inside a Dewar vessel. When the instrument is used at room temperature and below, the thermostated units are cooled by use of an insertion Peltier effect cooler. The instrument can be used with a wide range of different reaction vessels (diameter 14 mm). Baseline experiments have been conducted in the temperature range 15–200 °C. Typical values obtained during 10 h periods at 200 °C are ±3 and ±10 nW for the baseline drift and baseline fluctuations, respectively. The heat detection limit, determined by release of electrical energy, is about 2 μJ. Preliminary stability measurements have been conducted at 100 °C on samples of stabilised and non-stabilised polyamide film.

Keywords: Isothermal microcalorimeter; Nanowatt; 200 °C; Stability measurements

1. Introduction

The term ‘isothermal microcalorimeter’ is commonly used for calorimeters designed for measurements in the microwatt range, under essentially isothermal conditions. Calorimeters that are useful for measurements in the nanowatt range are sometimes referred to as ‘nanocalorimeters’, but that term is not used in the present paper.

We have earlier reported the on the design of several different isothermal microcalorimeters, see e.g. [1–4]. The useful temperature range for these calorimeters has been 5–90 °C. Throughout that development work the twin heat conduction principle was employed and semi-conduction thermocouple plates were used as heat flow sensors. In two cases air thermostats were used [5,6], but normally thermostatic water baths have been employed. Most of the microcalorimetric designs we have been concerned with during the past two decades have been parts of a modular system. Several of the different units have served as prototypes for units in thermometric’s system of microcalorimeters. The instrument described here is not part of the same system, but the vessels and working procedures developed earlier can to a large extent be used with the new instrument.

The aim with the development step reported here has primarily been to extend our earlier highest measurement temperature from 90 °C to about 200 °C, while retaining the high baseline stability and low

---

* Corresponding author. Tel.: +46-222-8180;
fax: +46-222-4413.
E-mail address: ingemar.wadso@fkem1.lu.se (I. Wadsö).

0040-6031/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00124-2

detection limits for heat and thermal power. Such properties are often required in, for example, the assessment of stability and compatibility of industrial compounds and products. Other examples of areas where there is a need for very stable base-lines in combination with measurement temperatures above 100 °C, are in the measurements of enthalpies of dissolution of slightly soluble compounds in non-aqueous media and enthalpies of vaporisation of compounds with low vapour pressure.

The present progress report describes the design and some properties of a general-purpose isothermal microcalorimeter for measurements up to 200 °C. The instrument is a twin calorimeter of the heat conduction type. Thermopiles are employed as heat flow sensors and a metal thermostat surrounds the calorimetric units.

2. Experimental

2.1. Instrument design

A section through the instrument is shown in Fig. 1. The main thermostat of the calorimeter consists of a cylindrical aluminium block (f) fitted with a heater made from manganine wire, which is insulated by glass fibres and lacquered (k). Four thermistors, resistance values at room temperature 2 kΩ–100 MΩ, are positioned in vertical bores (not shown in the figure) in the thermostat (f), which is in close thermal contact with a thick-walled aluminium tube (g) and its bottom plate (i). The three parts are firmly bolted together, with 'heat sink compound' applied on the contact surfaces. The heat sink, which surrounds the twin calorimetric units (h, shown in some detail in Fig. 2) is suspended in the cavity thus formed. A second thermostated cylinder (c) is positioned above the main thermostat (f).

Both of them (c, f) and the heat sink (h) are linked together by use of 5-mm stainless steel rods (j) and distance tubes made from PEEK polymer (l). The lower parts of the steel rods are hollow in order to decrease their heat conductance. The entire assembly is suspended inside a glass Dewar vessel (e), which is positioned in a steel can (d). The lid (b) and the steel can are covered by a layer of 10 mm of mineral wool and an envelope of 1 mm sheet aluminium (not shown in the figure).

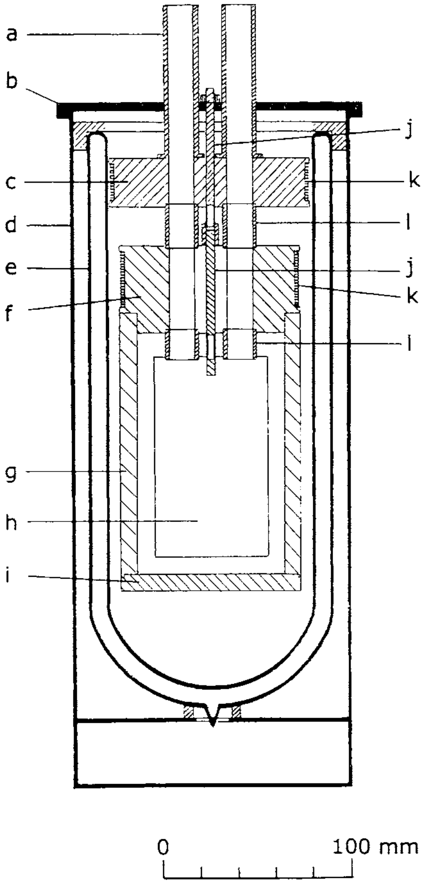

Fig. 1. Section through the twin microcalorimeter. (a) PEEK-tube for introduction of the reaction vessel; (b) steel lid; (c) thermostated aluminium cylinder (second thermostat); (d) steel can; (e) Dewar vessel; (f) thermostated aluminium cylinder (main thermostat); (g) aluminium tube; (h) heat sink, surrounding the calorimetric units (detailed picture in Fig. 2); (i) aluminium plate; (j) steel rod; (k) heater; and (l) PEEK tube.

Platinum resistance thermometers (not shown in the figure) are used for control of temperatures in the two thermostats (c, f), in the tube (g) and in the heat sink (t, Fig. 2).

For experiments conducted at room temperature, and at lower temperatures, the thermostats must be fitted with a cooling device. In the experiments at 15 and 25 °C reported here, a simple insertion Peltier effect cooler was used. An 8 mm copper rod, length 250 mm, was inserted into holes, positioned on top

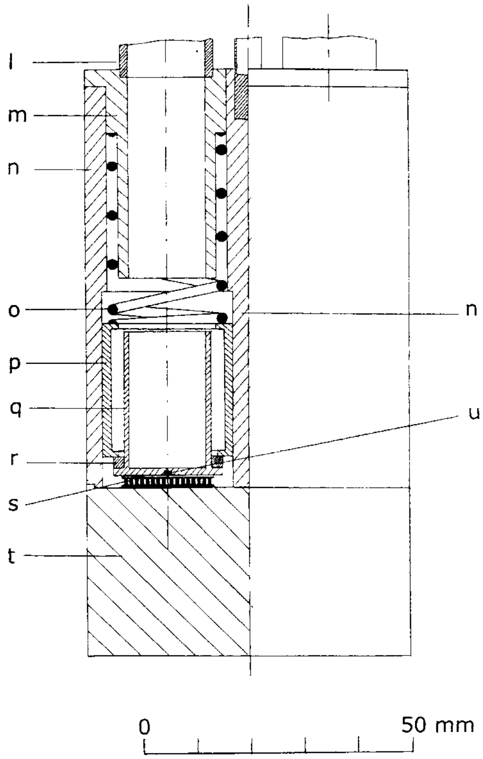

Fig. 2. (l) PEEK tube; (m) aluminium tube; (n) aluminium cylinder with bores for the calorimetric units; (o) steel spring; (p) aluminium tube; (r) PEEK ring; (s) thermopile; (t) solid aluminium cylinder; (u) calibration heater.

of each other, in the two thermostats. The upper end of the rod was soldered to a copper plate that was cooled by thermocouple plates. Their hot sides were air-cooled using an aluminium heat exchanger and a fan. A layer of polyurethane foam prevented moisture condensation onto the cold parts of the device.

Fig. 2 shows a section through one of the calorimetric units and the surrounding heat sink. Each calorimetric unit of the twin instrument consists of a thermopile (s) and the vessel holder (q), made from aluminium. In its bottom is cut a grove where a miniature Pt thermometer (u), primarily used as calibration heater, is positioned.

The heat sink, made from aluminium, consists of several parts (m, n, p and t). The thermopile (s) (Melcor Corp., Trenton, NJ, USA) is in thermal contact with the solid aluminium cylinder (t), which forms one of the main parts of the heat sink. The other main part is an aluminium cylinder (n), with two bores housing the calorimetric units. Minor parts of the heat sink are the aluminium tubes (m) and (p).

The tube (m) and the cylinders (n) and (t) are firmly bolted together, with 'heat sink compound' on the contact surfaces. The steel spring (o) exerts a force against tube (p) and thus against the vessel holder (q) and the thermopile (s). A ring made from PEEK (r) serves as thermal insulation between tube (p) and the vessel holder (q).

Reaction vessels used in the experiments reported here were simple static ampoules; vol., 1 ml. They were made from Hastaloy and were obtained from Thermometric AB, (Järfälla, Sweden). The ampoules were sealed by use of a teflon ring. As in our earlier work 'ampoule lifters', which were fitted with radiation shields, were used to introduce and to take out the reaction vessels from the vessel holders. During measurements these devices were always positioned in the introductory channels.

Electronic units (amplifier for thermopile differential signal and units for thermostat regulation) were built by Sven Hägg, electronic engineer at Chemical Center) and are of the same kind as used in our earlier development work.

2.2. Test experiments

The calorimeter was calibrated electrically using the miniature Pt-resistance thermometer, (u) in Fig. 2, as calibration heater.

Temperature settings were controlled by use of an electronic thermometer (Labfacility 100, Feltham, UK), with its sensor positioned in an empty vessel holder or in a hole in the main thermostat.

The instrument has primarily been tested in long-term baseline experiments conducted in the temperature range 15–200 °C. Empty reaction vessels were positioned in the ampoule holders. The 'baseline drift' and 'baseline fluctuation' has been determined. These terms are defined as follows [7]. The 'baseline drift' is the change in the baseline value, over a specified period of time. A long-term drift can often be approximated to a straight line and evaluated by a least squares treatment. The 'baseline fluctuation' during a specified observation period is defined as the difference between the experimental baseline and the constructed straight line. The heat detection limit was evaluated in experiments where short (10–20 s) pulses of electrical energy were released in the in the calibration heater.

In a few measurements the stability of stabilised and non-stabilised polyamide 6 film was investigated at 100 °C. The phenolic antioxidant Irganox 1098 (Ciba Geigy) was used as stabiliser, concentration 200 ppm. Ampoules were charged with about 40 mg of the samples. The material was a gift from Dr D. Forsström, Thermometric, and was the same as was characterised by use of other methods, including isothermal microcalorimetry [8].

3. Results and discussion

Typical results of some of the baseline experiments conducted in the temperature range 15–200 °C are summarised in Fig. 3. Values for the 'baseline drift' and random 'baseline fluctuations' are shown for each curve. In all cases the observed baseline drifts are hardly significant. The relatively large fluctuations found at 15 and 25 °C are possibly linked to the properties of the insertion cooler. However, we cannot explain why fluctuations are larger at 100 °C then at 200 °C. Similar results were found in other experiments at the two temperatures. In Fig. 4 is shown the baseline observed for a very long observation period, i.e. 22 day. The baseline drift was not significant and the baseline fluctuation was calculated to ±22 nW.

In experiments with a different microcalorimeter, with a design very similar to the present instrument, much smaller baseline fluctuations were observed at 100 °C. In that instrument a different type semi-conducting thermocouple plates was used and the Dewar vessel was made from steel.

Fig. 5 shows results from experiments where short electrical heat pulses were released. These measurements were conducted at 50 °C. Measured heat quantities are plotted against the heat quantities released in the heater. No significant deviation from a straight line

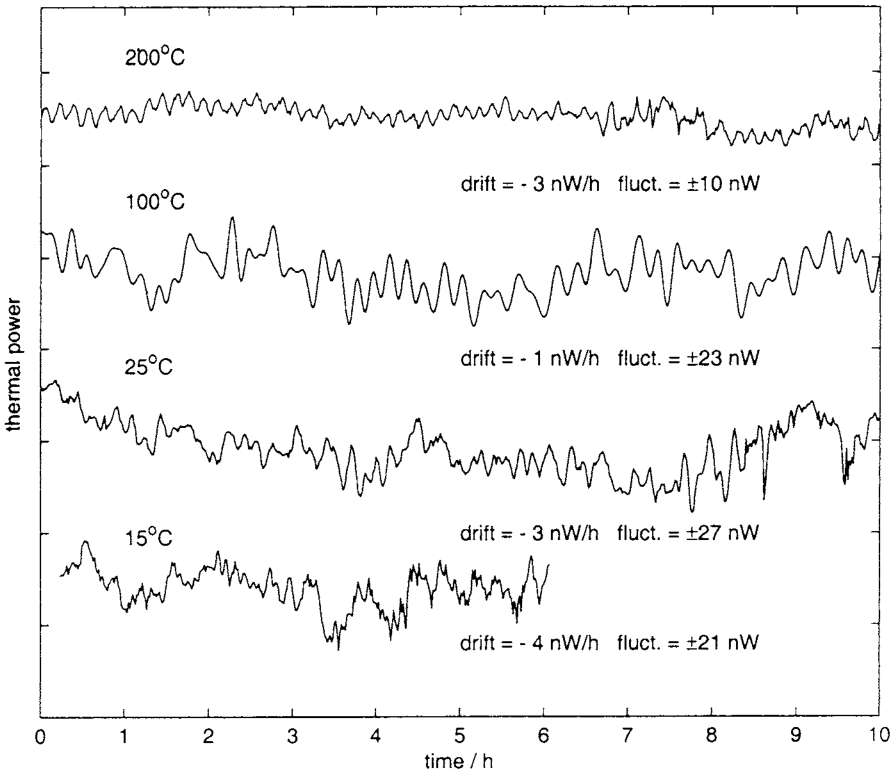

Fig. 3. Typical results of baseline experiments conducted at 15, 25, 100, and 200 °C. Derived values for 'baseline drift' and 'baseline fluctuation' are indicated for each curve (±S.D.).

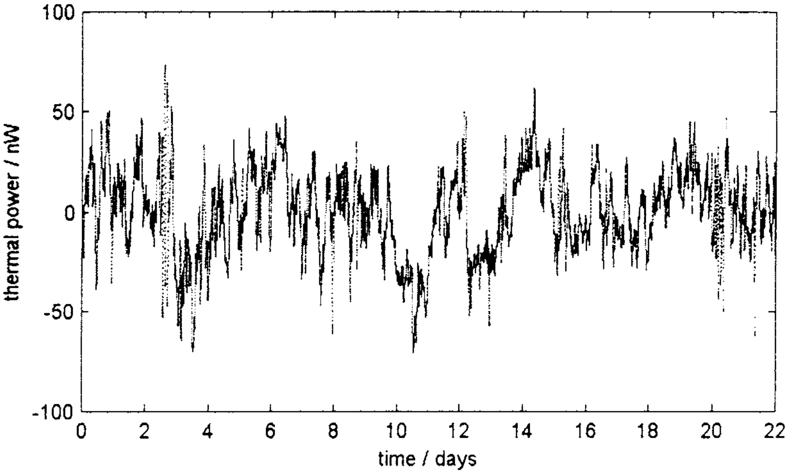

Fig. 4. Results from a baseline experiment conducted at 100 °C. 'Baseline drift' during the 22 day experiment was not significant. 'Baseline fluctuation' was 22 nW per day (±S.D.).

is observed. From the results we estimate the heat detection limit to be about 2 μJ. It should be noted, that values for the detection limit derived from chemical test experiments are more realistic, and will normally result in significantly higher values [7].

Significant baseline shifts were sometimes observed following the release of small heat pulses in the calibration heater. The cause of that effect is not understood.

In the stability measurements with polyamide film broad maxima were observed after 1–2 days, with significantly higher thermal power values for the non-stabilised samples. Mean values were 21.0 ± 2.4 and 35.1 ± 1.0 μW/g, for stabilised and non-stabilised samples, respectively. (±S.D., four samples of each type was measured). Our experiments were conducted in closed vessels filled with air. In the calorimetric measurements reported in [8] air was perfused through the reaction vessel and larger samples were used. The present results can thus not be closely compared with those from the earlier measurements.

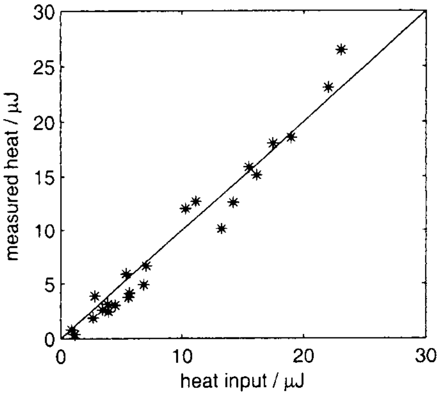

Fig. 5. Results of experiments conducted at 50 °C, where short heat pulses were released in the calibration heater.

4. Conclusions

It is concluded that basic properties of the present comparatively simple isothermal microcalorimeter are very satisfactory. A few properties that are not well understood will be further investigated.

Acknowledgements

This work was made possible by the financial support (to I.W.) from Carl Tryggers Stiftelse and Kungl. Fysiografiska Sällskapet.

References

[1] I. Wadsö, in: K.N. March, P.A.G. O'Hare (Eds.), Solution Calorimetry (IUPAC Experimental Thermodynamics), vol. 4, Blackwell Scientific Publishers, Oxford, 1994, p. 267.

[2] P. Bäckman, M. Bastos, L.-E. Briggner, D. Hallén, P. Lönnbro, S.-O. Nilsson, G. Olofsson, A. Schön, J. Suurkuusk, C. Teixeira, I. Wadsö, Pure Appl. Chem. 66 (1994) 375.
[3] P. Johansson, I. Wadsö, Thermochim. Acta 342 (1999) 19.
[4] L. Wadsö, N. Markova, Thermochim. Acta 360 (2000) 101.
[5] I. Wadsö, Acta Chem. Scand. 22 (1968) 927.
[6] L. Wadsö, in: Proceedings of the International Congress on the Chemistry of Cement , Durban, South Africa, 15 May 2003, in press.
[7] I. Wadsö, R.N. Goldberg, IUPAC Technical Report, Pure Appl. Chem. 73 (2001) 1625.
[8] D. Forsström, L.-G. Svensson, B. Terselius, Polym. Deg. Stab. 67 (2000) 263.