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MICROCALORIMETRIC DETERMINATION OF THE HEAT CAPACITY OF ILL-DEFINED MATERIAL

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ABSTRACT

A method is described to determine the heat capacity of several grams of biological material by means of an isoperibolic calorimeter. The procedure is easy and quick and gives good reproducibility of a few per cent.

In biology it is often necessary or desirable to determine the heat capacity and specific heat of inhomogeneous or ill-defined material like wood, insulating substances or even small animals. Usually applied physicochemical methods for evaluating heat capacity require solutions of organic material or homogeneous samples of some tens of milligrams or several microlitres [1—4]. Therefore, we were interested in developing and testing a simple and quick procedure to measure the heat capacity of larger specimens of several grams weight or millilitres volume. This assay has been used for the evaluation of the specific heats of various biological materials, including isopods, adult and pupa ants, and substances forming ant hills.

To this end an isoperibolic differential calorimeter (type BCP; Thermanalyse, Grenoble) with two 15-ml vessels was used, always set to an initial temperature of 25°C. This calorimeter is equipped with a digital temperature controller so that temperature jumps are easily adjusted. The sensitivity of the instrument is 43 μV mW^{-1}. Dissimilarities in the heat capacity between the experimental and the reference system of up to 60 J °C^{-1} lead to a maximum heat flow of about 20 mW. The specimen under examination was enclosed in a stainless steel vessel of known weight and heat capacity, while the reference cavity of the calorimeter remained uncharged.

The heat capacity was determined in three different ways from the curves of heat flow versus time (thermograms) which occurred when a temperature jump from 25°C to 26°C was induced in the calorimeter. Such a graph is shown in Fig. 1. After a zero line has been established, the temperature jump is induced. Owing to the thermal inequality of the two heat flow meters, at first there is a small exothermic effect, followed by a strong endothermic reaction which represents the heat consumed in raising the temperature of the specimen by one degree. After a few minutes the heat flow reaches a maximum and then decreases slowly, showing that the thermal balance is re-established. Finally the initial zero line is reached again.

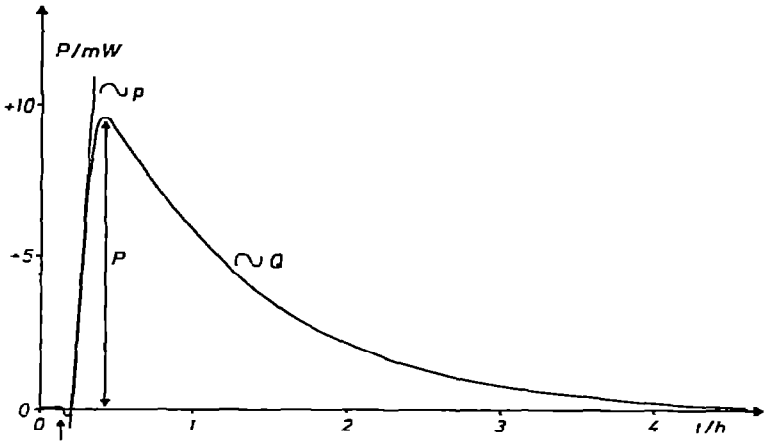


Fig. 1. Endothermic heat effect during a temperature jump from 25°C to 26°C. For calibration purposes the maximum heat flow P, the area Q between the graph and the zero line, and the initial slope p are used. At ↑ the temperature jump is induced.

The area between the thermogram and the zero line represents the integral over the total heat flow and therefore the total heat exchanged between the sample and the thermostat during the temperature jump. The procedure is thus an independent and absolute way to determine heat capacities. However, because of slight deviations in the two heat flow meters, calculated and measured heats are not identical (see Table 1), so that it is more convenient to use a relative method and to calibrate unknown samples against known standards. In these experiments, standards in the shape of the cylindrical

TABLE 1

Maximum heat flow P and energy consumed Q as function of heat capacity C of different probes

Sample	Slope [mW $(J\,°C^{-1})^{-1}$]	Intersect (mW)	Standard deviation (mW)	Correlation coefficient
Maximum heat flow				
Aluminium	0.320	−0.84	0.13	0.9996
Water	0.313	+2.11	0.52	0.9945
Various materials	0.315	−0.49	0.32	0.9990
Mean	0.316			
	[J $(J\,°C^{-1})^{-1}$]	(J)	(J)	
Energy consumed				
Aluminium	0.78	−0.33	1.49	0.993
Water	1.04	+10.8	2.58	0.988
Various materials	0.92	−2.41	2.72	0.992
Mean	0.91			

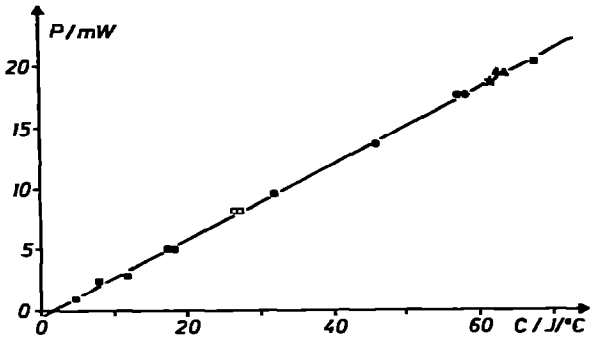


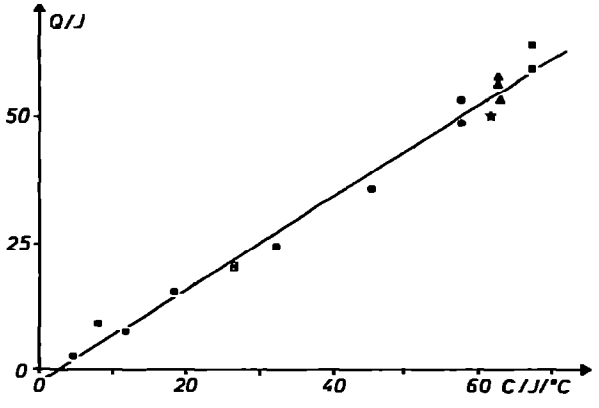
Fig. 2. Maximum heat flow P as function of heat capacity C for different samples: (●) aluminium, (▲) iron, (■) stainless steel, (∗) brass, (★) copper, (□) lead.

calorimeter vessels were used, fabricated from iron, stainless steel, copper, lead, aluminium and brass, with heat capacities ranging from 4 to 60 J $°C^{-1}$.

In two further experiments aluminium cylinders with central holes of varying diameter as well as increasing amounts of water in a calorimeter vessel were used to obtain samples with different heat capacities but similar conductivity.

Three methods of establishing a calibration graph can be deduced from Fig. 1.

(1) The most exact, simple and efficient way is to calculate the maximum heat flow P as a function of heat capacity (Fig. 2). This gives straight lines for aluminium, water and mixed samples with a mean slope of 0.316 mW J^{-1} $°C^{-1}$, a mean standard deviation of 0.32 mW and a correlation coefficient better than 0.997 (see Table 1). Such a determination takes about 10 min and afterwards half an hour to bring the calorimeter back to its initial temperature.



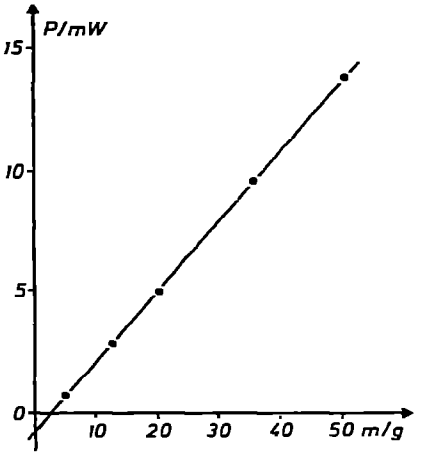


Fig. 3. Endothermic heat uptake Q at a temperature jump of 1° as function of heat capacity C. The symbols are as in Fig. 2.

Fig. 4. Maximum heat flow P as function of the mass m of various aluminium cylinders. The deviation of the intersect from zero is due to an inbalance of the two empty calorimeter holes.

TABLE 2

Some heat capacities of fresh and dry biological material at 25°C

Sample	Heat capacity (fresh) ($J\,g^{-1}\,°C^{-1}$)	Heat capacity (dry) ($J\,g^{-1}\,°C^{-1}$)
Ants (adults)	3.71	2.10
Ants (pupae)	3.74	1.94
Hill material	2.44	1.92
Pine wood	—	1.57
Isopod	—	2.59

(2) It is less convenient and takes several hours longer to determine the total heat Q exchanged during heating up as a function of heat capacity (Fig. 3). The data obtained are compiled in Table 1. The deviations between the different slopes are rather large and show that not all heat is recovered in these experiments. As pointed out by Funck and Hoffmann [5] earlier, the linearity between the heat capacity (mass) and the area between the graph and the zero line holds only for small masses. At larger masses, a saturation effect appears which demonstrates that an effective volume of the calorimeter exists. In our experiments such a limit was not achieved and all the samples used for calibration were in the linear range, but the deviation from 1 for the slope of the measured versus the calculated heat capacity shows that such an effective volume of the calorimeter does exist.

(3) The least accurate method is to establish the initial slope p of the heat flow as a function of the heat capacity. The deviations are significant and lead to correlation coefficients smaller than 0.94. Therefore, all the biological materials were investigated using the first method of maximum heat flow P. Some of the specific heats obtained in this way are compiled in Table 2.

The method described here is easy and quick and gives results which are reproducible within a few per cent. This is sufficient for biological samples which are ill defined and differ from sample to sample in their constitution.

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