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# **The S1-calorimeter; eight student experiments with a simple isothermal calorimeter**

**Lars Wadsö**

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Lars Wadsö

February, 1998

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## 1 Introduction

In this paper ten experiments with an isothermal heat conduction calorimeter are reported. All experiments are simple enough to be used as student experiments. The experiments were done to test the design of the instrument and should therefore be seen as tests, not as scientific investigations.

The experiments reported here were done with the signal from the differentially coupled calorimeter recorded on a line recorder with a full range

of 1 mV at highest sensitivity. As the sensitivity of the calorimeter is 0.030 V/W, 1 mV corresponds to 33.3 mW. There was no short term noise seen at this amplification and only small long term drifts. The room that was thermostated to approx.  $24.5 \pm 0.5^\circ\text{C}$ . There was no problem to differentiate between output signals 1/200 of the full range of the recorder, i.e. the highest resolution was in the order of 0.1 mW. This can be further improved by using a pre-amplifier or a more sensitive data acquisition equipment. The design and properties of the isothermal calorimeter are further discussed by Wadsö (1998).

The results shown in this report have either been digitized by hand or copied by hand from the recorder papers by myself. A computerized data collecting system would have made the work easier and also the diagrams more accurate. However, when designing student experiments I believe that there is a contrasting relationship between understanding the basic principles (of calorimetry in this case) and making the experimental set-up nice looking and up-to-date (e.g. with a computer). Sometimes a computer is needed (e.g. when large amounts of data have to be collected), but in most of the experiments described in this report one can just as well do without a computer (one complication is of course that nowadays line recorders tend to be more expensive than computers). If a computer is used in a student experiment, the students should at least not spend more than 25% of the time trying to understand the computer and its programs.

## 2 Cement paste hydration

### 2.1 Materials and method

A Swedish ordinary Portland cement (Slite Std., Cementa, Danderyd, Sweden) was mixed by hand with water and a liquid melamine based water reducing agent (92M, Cementa, Danderyd, Sweden). Between 13 and 15 grams of this cement paste was charged into 10 ml glass ampoules and directly inserted down into the calorimeter. The ampoule was about half-filled with cement paste. An empty ampoule was used as a reference. For all experiments a water-cement ratio ( $w/c$ , the mass of water divided by the mass of the dry cement) of 0.35 was used. The aim of the experiment was to investigate the retarding effect of the water reducing agent. The following concentrations of 92M were used: 0, 1.5, 3 and 4.5% (of the dry cement

mass). The measurements were carried out at 25°C.

## 2.2 Result

Figure 1 (top) gives the primary result of the experiments and Fig. 1 (bottom) gives the evolved heat as a function of time. Figure 2 shows the results of three runs with the cement without any plasticizer..

## 2.3 Discussion

The cement hydration process is very complex. The different components of the dry cement powder will react with water at different rates to form minerals that make up the hydrated cement. When the water and the cement powder is mixed a lot of heat is produced from heat of wetting, dissolution and initial reactions. This is seen as an initial peak in Figs. 1-2 that lasts for approx. 10 minutes. Figure 2 shows that this type of measurement is quite reproducible even if only small amounts of cement (approx. 25 g) were mixed by hand.

To stop the cement paste from reacting too rapidly, gypsum has been added to the cement. The gypsum reacts with the most reactive cement components to form ettringite, a compound that covers the surface of the cement grains and delays further hydration for some time. The cement hydration therefore has an induction period before the start of the main reactions. The duration of this induction period may be changed by many different types of admixtures. It should be noted that the cement hydration cannot be looked at simply as an *n*:th order chemical reaction with *one* rate constant. The reaction rate is governed by the interplay of many processes; the diffusion of water into the cement grain is one such process.

The admixture 92M is added to plasticize the cement paste and therefore to reduce the amount of water needed to get a concrete that is easy to use, but still have a low water-cement ratio. Lower water-cement ratios give higher strength and better durability. The experiments performed show that it has the side-effect that it retards the cement hydration. It is clearly seen that the retardation increases with increasing concentrations of admixture. At 4.5% of admixture there is no setting of the cement paste during almost ten hours. From the results it is also seen that the main hydration peak is retarded and somewhat spread out, but not significantly changed, by the plasticizer. The

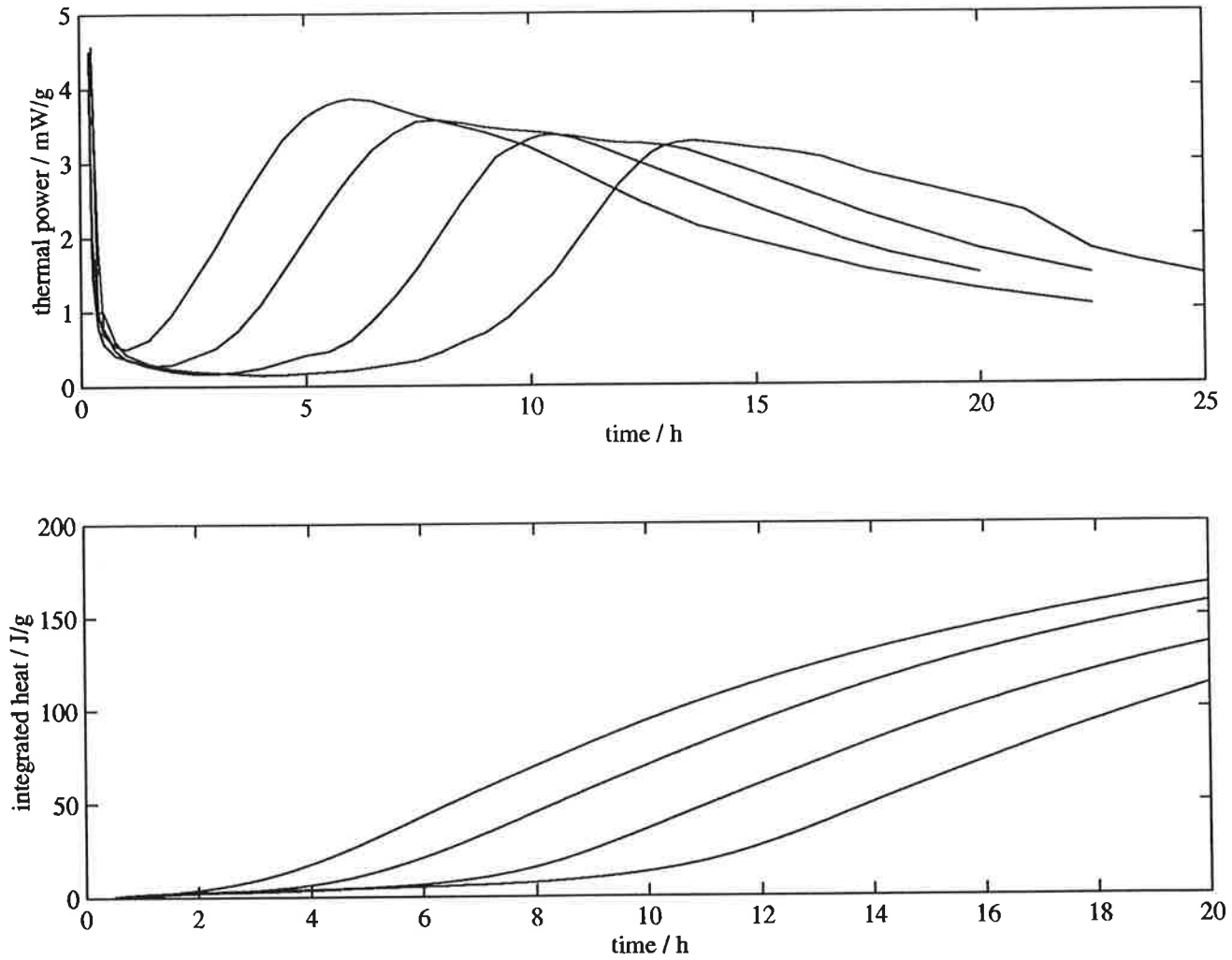


Figure 1: Results from experiments with cement hydration. **top:** The produced thermal power per gram of cement as a function of time. The plasticizer retarded the hydration and the curves are, from left to right, for 0%, 1.5%, 3.0% and 4.5% of the admixture. **bottom.** The integrals of the thermal powers in the top figure gives the heat produced as a function of time.

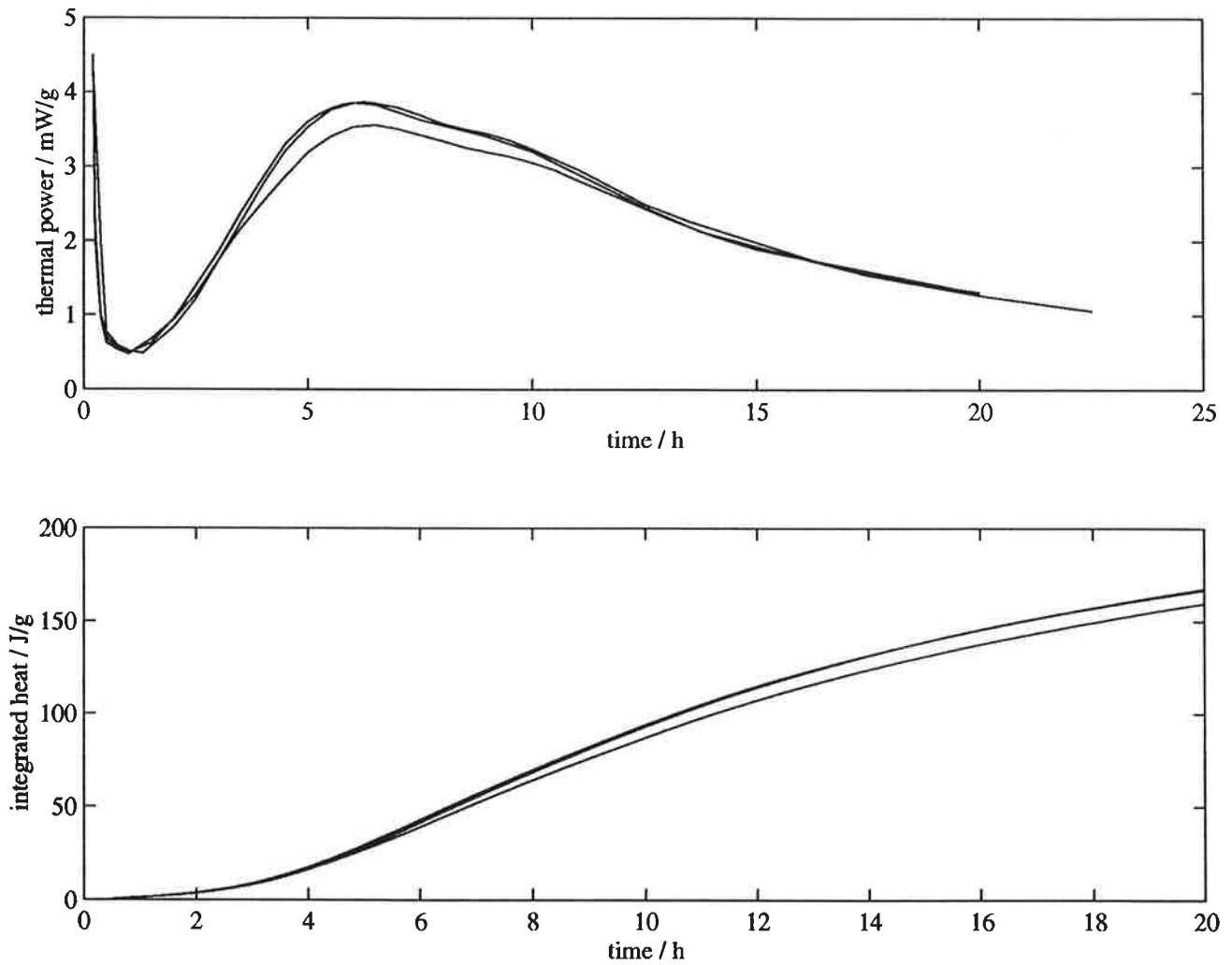


Figure 2: The results from three measurements of cement hardening with  $w/c=0.35$  (no plasticizer added). **top.** Thermal powers as function of time. **bottom.** Integrated thermal powers gives the heat produced as a function of time.



admixture influences the induction time, but does not significantly alter the main hydration once it has started.

Isothermal calorimetry has been used quite a lot to study cement hydration (see e.g. Bensted 1987), but it has never been standardized like semi-adiabatic calorimeters and adiabatic dissolution calorimeters. The result from experiments like the one performed here is, however, superior to the normal adiabatic type cement calorimeters in that one gets the heat production rate with as a function of time under isothermal conditions (Bronswijk et al. 1993). If such experiments are performed at different temperatures a total description of a hardening process as a function of time and temperature is obtained.

Heat production rate from cement hydration has several uses:

1. To find the strength development of cements as function of time, as it has been shown that the strength of a cement or a concrete is proportional to the heat produced, i.e. to the extent of the cement hydration.
2. To assess the influence of admixtures on the rate of hydration. Many admixtures are primarily used to modify the rate at which a cement hydrates (e.g. retarders), but some other admixtures primarily used for other purposes (e.g.g super plasticizers) have the secondary affect of changing the hydration rate.
3. To predict the temperature increases in thick concrete constructions during hardening. In constructions like dams, that may be several meters thick, most of the heat produced by the hydration in the central parts of the construction will cause a temperature rise there as the heat conduction paths out to the surface of the construction are so long. If special measured are not taken (e.g. cooling the fresh concrete or the use of slow hardening cement) heavy concrete constructions may be damaged by cracks. Measurements with an isothermal calorimeter at several temperatures makes it possible to calculate the temperature distribution in any type of construction during the concrete hardening. The only assumption that has to be made is that it is only the rate of hydration, not the reaction processes, that is changed by temperature changes. When a measurement is made in an adiabatic calorimeter one will get the temperature rise in the adiabatic case. To calculate the temperature increase in a non-adiabatic hardening concrete structure one has to make an assumption about how the hydration rate changes with

temperature (activation energy). Even if adiabatic calorimeters are the most common in the cement industry today isothermal calorimeters would be a more rational choice..

## 2.4 Student experiments

The influence of a large number of parameters in the cement hydration can be investigated:

- Different types of cement (e.g. Ordinary Portland Cement (OPC) and Slow Hardening Portland Cement (SHPC)).
- Many admixtures change the duration of the induction period or the rate of hydration; the one used in the described measurement in one example.
- The water-cement ratio influences the rate of hydration.
- The influence of all types of unwanted substances (oil, grass, tar, salt...)

## 3 Enthalpy of vaporization of water (and the saturation vapor pressure)

### 3.1 Materials and method

For each experiment a small amount of Millipore water was injected into an empty ampoule that was in the measurement position in the calorimeter. The mass of the injected water was found by weighing the syringe used before and after the injection. Air that had been dried over  $P_2O_5$  was perfused (flowed) through the ampoule at a rate of approx. 9 ml/min. When the dry air stream passed through the ampoule an endothermic signal was measured until all water had evaporated. Table 1 gives data on the three experiments made with water.

Table 1: Results from three experiments to find the vaporization enthalpy and saturation vapor pressure of water. The nomenclature is described in the text.

exp.	$F$ / ml/s	$m$ / mg	$Q$ / J	$\Delta_v h$ / J/g	$P_{\max}$ / mW	$v_{\text{sat}}$ / g/m <sup>3</sup>
1	0.150	16.03	40.2	2510	6.44	17.1
2	0.153	19.64	48.5	2471	7.10	18.8
3	0.161	53.54	138.7	2591	7.43	17.8
			mean:	2524	mean:	17.9
			correct:	2444	correct:	23.0
			error:	+3%	error:	-22%

When water is injected a quite constant endothermic thermal power is measured. The total heat produced during an experiment ( $Q$ ) is proportional to the mass of the water evaporated ( $m$ ) and the vaporization enthalpy ( $\Delta_v h$ ):

$$Q = m \cdot \Delta_v h \quad (1)$$

From this it is possible to calculate  $\Delta_v h$ , the enthalpy of vaporization as both  $Q$  and  $m$  are measured.

If it is assumed that the air that leaves the ampoule is saturated with water vapor at least when the maximum thermal power ( $P_{\max}$ ) of a measurement is measured, the following relation holds true:

$$P_{\max} = F(v_{\text{eq}} - v_{\text{in}})\Delta_v h \quad (2)$$

Here  $F$  (m<sup>3</sup>/s) is the gas flow rate,  $v_{\text{eq}}$  (g/m<sup>3</sup>) is the vapor content in equilibrium with the water ( $v$  is the mass of vapor found in a unit volume of air), and  $v_{\text{in}}$  (g/m<sup>3</sup>) is the vapor content of the gas entering the ampoule. In the evaluation of the present results it was assumed that  $v_{\text{eq}}=v_{\text{sat}}$  and  $v_{\text{in}}=0$ . The vapor pressure  $p$  (Pa) corresponding to a vapor content  $v$  may be found with the ideal gas law:

$$p = \frac{vRT}{M_m} \quad (3)$$

Here  $M_m$  (g/mol) is the molar mass of the vapor,  $R$  (4.18 J/mol/K) is the gas constant, and  $T$  (K) is the temperature.

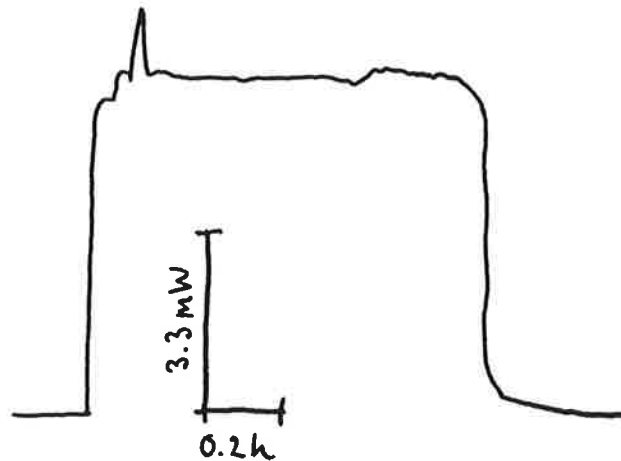


Figure 3: A typical output from a measurement in which a small amount of water was injected into the ampoule and left to evaporate into a stream of dry gas.

### 3.2 Results

Figure 3 shows the primary result from one experiment and Table 1 gives the calculated results from the three experiments.

### 3.3 Discussion

From the results in Table 1 it is seen that the measured values for the enthalpy of vaporization of water are only a few percent from the correct values, but the saturation vapor contents are not at all as close to the true values. The main reason for this is probably that the outgoing gas was not saturated with water. As is seen in Eqs. 1 and 2 the enthalpy of vaporization is calculated from the integral  $Q$ , whereas the saturation vapor pressure is found from  $P_{\max}$ .

The measurement of saturation vapor pressure may be improved by bubbling dry gas through the liquid in the calorimetric ampoule as the vapor pressure of the outgoing gas will then be much closer to equilibrium with the liquid (saturation). In such an experiment corresponding values of  $Q$  and  $m$  cannot be evaluated if the ampoule is not weighed before and after an experiment (or the outgoing vapor collected in a drying agent so that its mass

may be found). If the enthalpy of vaporization is known the vapor pressure can be evaluated in such a measurement.

Often it is of interest to measure the equilibrium vapor pressure or activity coefficient of aqueous solutions. It is possible to arrange the experiment in another way so that the equilibrium vapor pressure can be evaluated without any knowledge of the enthalpy of vaporization of a liquid (Berling et al. 1997): equilibrate the gas stream with the sample solution and then bubble it through pure water in the calorimeter. Then in Eq. 2  $v_{in}$  is the unknown vapor content,  $v_{out}=v_{sat}$ , and  $\Delta_v h$  is that of pure water.

### 3.4 Student experiments

The measurement of enthalpy of vaporization may be used in a student experiment to:

- measure  $\Delta_v h$  of a number of vapor forming liquids with different types of molecular interactions.

## 4 Heat from a compost

### 4.1 Materials and method

Fresh cut grass from an ordinary grass lawn was further divided with scissors and 2.9 grams of this was charged into a 10 ml glass vessel. The rubber stopper was equipped with two 0.7 mm (inner diameter) stainless steel tubes. Air with an approximate relative humidity of 20% was intermittently perfused through the vessel.

### 4.2 Result

Figure 4 shows the measured result thermal power. Until the time marked A the air flow rate was zero. At the times marked A-E the following occurred:

A An air volume of 30 ml was perfused through the ampoule at a high flow rate. After that the flow was stopped.

B Same as A.

C Perfusion with a continuous flow rate of 45 ml/h was started.

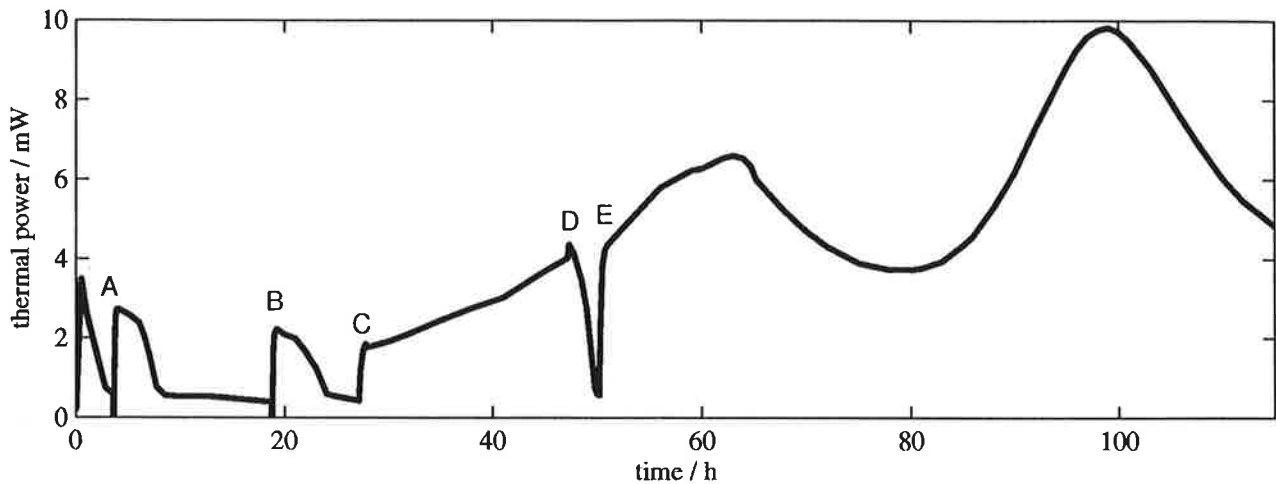


Figure 4: The heat production rate from a 2.9 g sample of grass. The labeling is described in the text.

D The air flow was stopped.

E Same as C.

### 4.3 Discussion

The processes in a compost are very complicated and include both micro-biological (fungal and bacterial) decomposition, chemical processes and the activity of worms, insects etc. The processes in a compost should be aerobic, i.e. oxygen should be supplied at high enough rates (mainly through diffusion) so that the processes do not become anaerobic (fermentation).

In the present example it is seen that the thermal powers go down a few hours after the air perfusion was stopped. This indicates a lowered activity (degradation rate) or lowered enthalpies from the compost processes; or a combination of both. When a carbohydrate is metabolized aerobically a heat ( $\Delta h$ ) of approx. 460 kJ/mol  $O_2$  is produced. As the air contains 21% oxygen with a molecular mass ( $M_m$ ) of 32 g/mol, the air flow rate ( $F$ ) was 45 ml/h =  $1.2 \cdot 10^{-8}$  m<sup>3</sup>/s, and the density of air ( $\rho$ ) is approx. 1200 g/m<sup>3</sup>, the maximal thermal power produced may be calculated as:

$$P_{\max} = \frac{0.21F\Delta h\rho}{M_m} = 50 \text{ mW} \quad (4)$$

The maximal thermal power measured (10 mW) is less than this, so all the oxygen introduced is not used in aerobic metabolism.

The shape of the curve in Fig. 4 implies that we have a succession of organisms or processes. Firstly, we may have a microorganism that rapidly establishes itself, but can only consume easily assessable sugars in the grass. When it runs out of this another type of microorganism that can degrade less easily metabolized compounds may take over etc.

The heat produced in a compost raises the temperature of the compost. This is easily tested by putting your hand into the center of a one day old large pile of newly cut grass. If the compost heap is large and oxygen can still diffuse in to all its parts, the temperature may raise so much that most organisms in the compost are killed. At high temperatures thermophilic bacteria and fungi may still be active, but it is questionable whether one should desire this type of composting.

From the calorimetric measurement of thermal power per unit volume it is possible to estimate the rate of temperature rise in composts of different sizes if one knows the thermal properties (heat capacity and thermal conductivity) of the compost material. If measurement are made at only one temperature one can, however, only assess the rise in temperature from that temperature as the rate of the degradation processes increase rapidly with temperature. There are two limiting cases:

- The outside of the compost that is exposed to the ambient temperature will not rise in temperature at all.
- The center of a large compost that will be almost adiabatic (i.e. with no heat losses, acting as it was totally insulated). With 1 mW/ml from the experiment, a heat capacity of 3 J/g/K and a density of 0.29 g/ml the adiabatic temperature rise will be approx. 4 K/h; a significant rate of temperature increase.

The perfusion of relatively dry air (20% RH) into the ampoule with humid material (approx. 100% RH) may pose a problem as the gas stream will be saturated with moisture and the corresponding evaporation of water will cool the sample. The thermal power of such cooling may be calculated from:

$$P = F\Delta_v h v_{\text{sat}} \Delta\phi$$

Here  $F$  ( $\text{m}^3/\text{s}$ ) is the flow rate,  $\Delta_v h$  ( $\text{J/g}$ ) is the enthalpy of vaporization of water,  $v_{\text{sat}}$  ( $\text{g/m}^3$ ) is the saturation vapor content of air, and  $\Delta\phi$  is the difference in relative humidity (expressed as a fraction). With figures from the present experiment ( $F=1.2 \cdot 10^{-8}$   $\text{m}^3/\text{s}$ ;  $\Delta_v h=2440$   $\text{J/g}$ ;  $v_{\text{sat}}=23$   $\text{g/m}^3$ ;  $\Delta\phi=0.8$ ) we get a cooling effect of 0.6 mW. This can be seen in the measurements, e.g. at D where the thermal power rises 0.5 mW when the perfusion is stopped (the evaporation stoppes, but the biological processes continue as there is still enough oxygen in the ampoule).

#### 4.4 Student experiments

It is not possible to draw conclusions about the type of organisms active in the compost from the calorimetric measurement. One may therefore combine the calorimetric measurement with visual or microscopical examination of parallel samples. Other possibilities include:

- Compare the heat production rates from composts based on different types of organic materials, e.g. grass, leaves etc., or mixes of several materials.
- Test the effect of adding "foreign" substances in a compost, e.g. paint particles, coffee powder, orange peel (usually contains fungicides) etc. Substances that are added to food stuffs to delay spoilage (e.g. sodium benzoate), household chemicals, and anti-mildew agents used on plants are other examples of substances that could influence the activity of the microorganisms in a compost.

## 5 Metabolic activity of yeast cells

### 5.1 Materials and method

Approximately 1 g of bakers yeast and 4 g of water were mixed in a 10 ml ampoule. The ampoule was then closed with a rubber stopper with two 0.7 mm tubes (inner diameter) and lowered into measuring position in the calorimeter. The reference was a similar arrangement without any yeast cells. During the measurement air was bubbled through the water in the measurement cell.



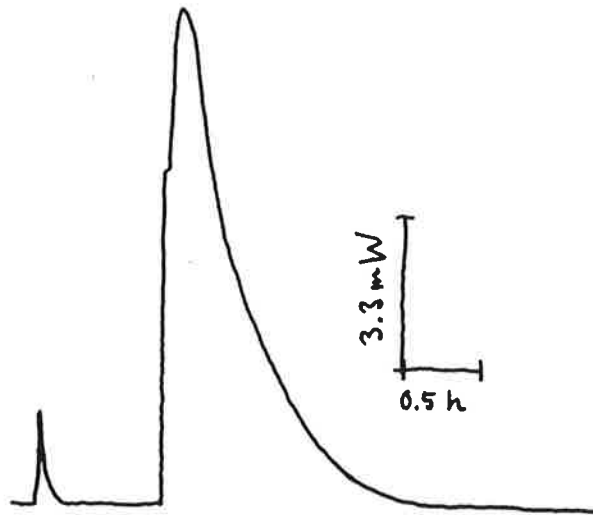


Figure 5: Two peaks from the injection of beverages into an aqueous solution of yeast cells. The first small peak is from injection of mineral water, the second larger peak is from injection of soft drink.

At regular intervals small amounts (0.5-0.9 g) of different beverages were injected into the ampoule with the yeast cells. A glucose solution was also used as a reference. The injected amount was calculated by weighing the syringe before and after the injection. Different beverages were used. In the example shown here a mineral water and an ordinary soft drink were used. The solid contents of the beverages were also found by weighing before and after the water was evaporated in an oven at 60°C.

## 5.2 Result

Figure 5 shows the recorder output when first 0.432 g of a mineral water (small peak) and then 0.694 g of a soft drink (large peak) were injected. The solid contents of the beverages were 0.15% and 11% for the mineral water and the soft drink, respectively. The reference glucose solution contained 0.12 g glucose and gave a peak of 110 J.

### 5.3 Discussion

The heat released from the glucose solution may be compared to the calculated value of the heat from the (aerobic) reaction of glucose with oxygen to form water and carbon dioxide. The  $\Delta h$ -value for this process is approx. 16 kJ/g glucose and the resulting heat is approx. 1900 J for 0.12 g glucose. As much less heat was produced in the experiment it is probable that the yeast cells were under at anaerobic conditions (fermentation).

### 5.4 Student experiments

In the present experiments the aeration was not enough to get aerobic metabolism. This could, however, certainly be achieved with better aeration and stirring. The following are examples of studies that could be made with bakers yeast as a model microorganism:

- Test the effect of different toxic or potentially harmful substances on the heat production from the cells.
- Test different ways of aerating the aqueous cell suspension and the effect of stirring.
- Make measurements on different types of doughs.

## 6 Curing of epoxy adhesives

### 6.1 Materials and method

Two epoxies adhesives were used. One was a slow hardening Araldite Std. (Ciba-Geigy) and the other was the more rapidly hardening Loctite 5 min. epoxy (Loctite). The epoxies were mixed outside the ampoules. The samples were then transferred to the ampoules, weighed and charged into the calorimeter. Table 2 describes the four measurements made.

### 6.2 Result

Figure 6 shows the result from the experiments with Araldite Std. and Loctite 5 min. adhesives.

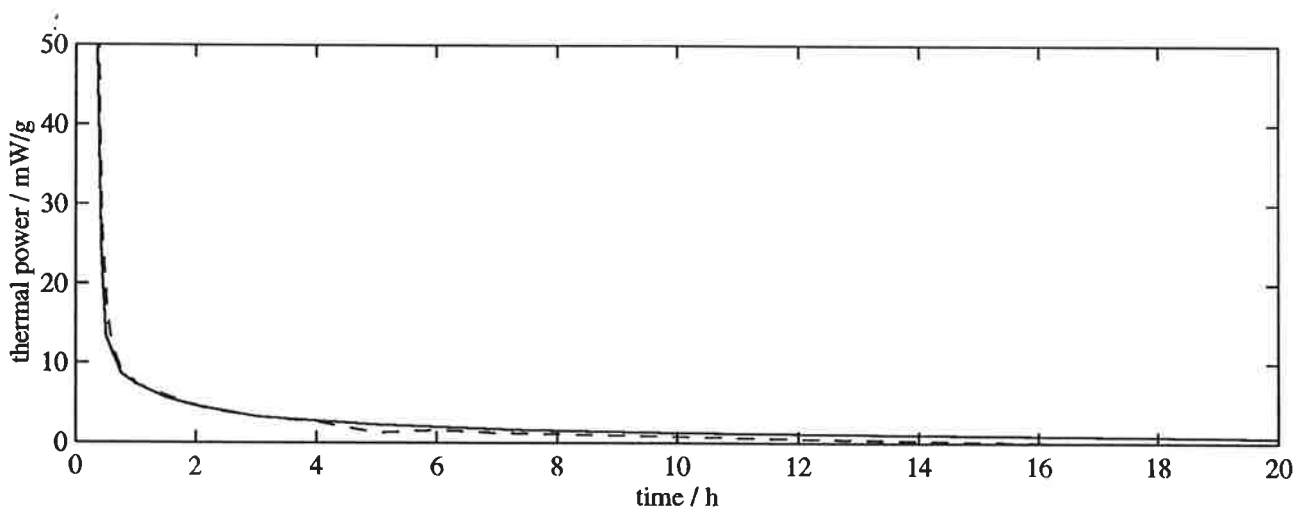
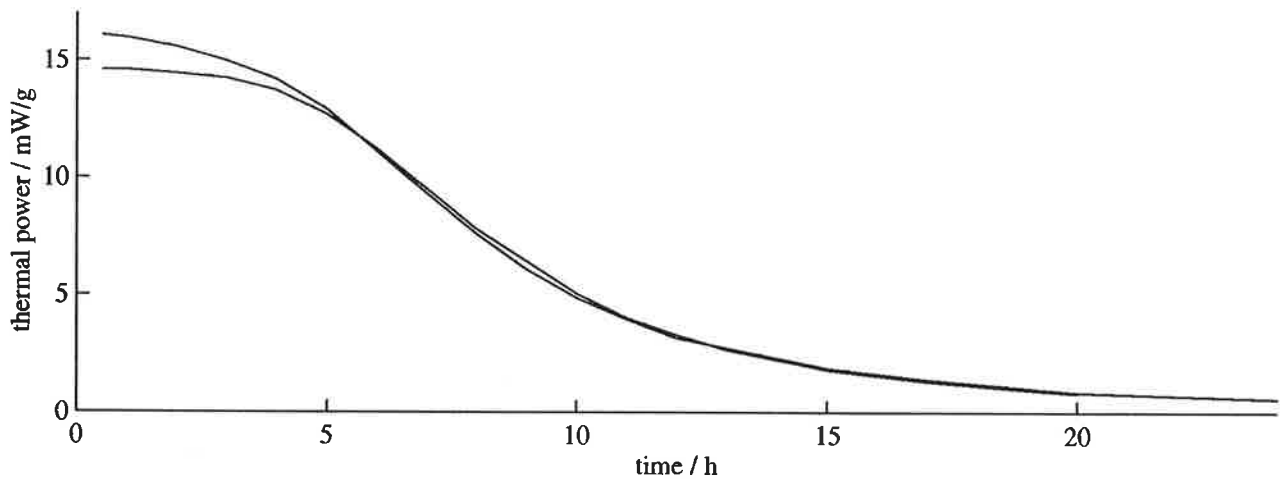


Figure 6: The measurement with Araldite Std. epoxy adhesive (top) and Loctite 5 min adhesive (bottom).

Table 2: The four experiments made with epoxy. The integrated heats for the Araldite were taken from 0 to 20 hours. For the rapidly hardening Loctite adhesive part of the curing may have taken place before the ampoule was changed into the calorimeter.

#	adhesive	mass / g	total heat / J/g
1	Araldite Std.	3.88	476
2	Araldite Std.	3.07	489
3	Loctite 5 min.	3.32	-
4	Loctite 5 min.	5.08	-

### 6.3 Discussion

Calorimetric measurements is a way of assessing the course of hardening processes, e.g. to determine how much of an epoxy that has not reacted at a certain time. In the case of the Araldite Std. adhesive the process is rather slow and the measured curve represents the isothermal process. For the rapidly hardening Loctite the heat production rate is so high in the beginning of the experiment (not seen in the figure) that the temperature goes well over the temperature of the calorimeter. In fact, if one holds an ampoule filled with a newly mixed rapidly hardening epoxy it becomes so hot so one has to put it down. The calorimeter does not work under isothermal conditions for such a process, and the process will be accelerated by the increased temperature. One solution to this is of course to run smaller samples than was done here.

### 6.4 Student experiments

Slow hardening epoxies are interesting to work with in the present type of instrument, but one must be careful with the un-hardened epoxy because it can cause allergies. Possible experiments are the following:

- Study the effect on the hardening process by different additives. Do they change the rate of hardening?
- Epoxies should usually be mixed with a hardener in the proportions 1:1. How will the reaction proceed if the mixture deviates from this ideal proportion.

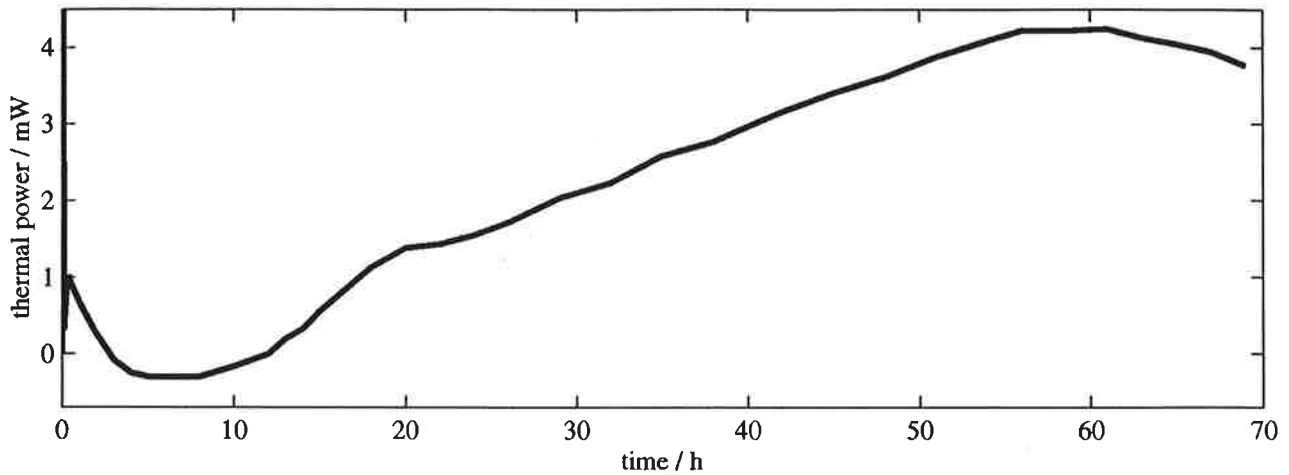


Figure 7: The result from the experiment with germination of 20 wheat grains.

## 7 Wheat grain germination

### 7.1 Materials and method

Twenty wheat grains (1.1 g) were mixed with 0.15 mm dry sand (2.8 g) and water (1.1 g) and charged into the calorimeter. Room air was perfused through the ampoule at a rate of 45 ml/h during the whole measurement.

### 7.2 Result

Figure 7 shows the result of the measurement.

### 7.3 Discussion

As seen in Fig. 7 there is an initial decrease in thermal power from an initial value of about 1 mW. This is the heat of wetting and absorption when the water is taken up by the dry seeds (imbibition as it is called by seed scientists). After that it takes a few hours before the germination processes starts in the seeds, and during this time we see a negative thermal power caused by the evaporation of water into the perfused gas stream. This will result in a cooling of 0.6 mW (same as for the compost measurement).

The phase with increasing thermal power is the germination of the grains. When the experiment was stopped after nearly 70 hours the grains had 10-20 mm roots, but looked quite dry. The decreasing thermal power at the end of the measurement is probably caused by lack of water for the germinating seeds.

#### **7.4 Student experiments**

The following experiments may be interesting to make on various kind of seeds and grains:

- Measure the calorimetric response for seeds that have been aged artificially (e.g. at high temperature for short periods of time) and compare with the results from measurements on untreated seeds.
- Study the effect of the composition of the water on the germination, e.g. salinity, pH, toxic substances.

### **8 Absorption of water on an absorbent**

#### **8.1 Materials and method**

A mass of 3.19 g of room dry clay particles (sold as cat sand) was charged into a 10 ml glass ampoule and put down into the calorimeter. An empty glass ampoule was used as a reference. Injections of 0.1 ml of water were then made into the measurement cell and the reference cell.

#### **8.2 Result**

Figure 8 shows the result from the experiment. The peaks marked M were caused by injections on the measurement side and peaks marked R were from injections on the reference side. The heats in the five peaks marked M are approx. 20, 10, 5, 3 and 1 J, respectively.

#### **8.3 Discussion**

It is seen that the peaks from the injections into the reference side are small compared to the peaks originating from the interaction between the dried

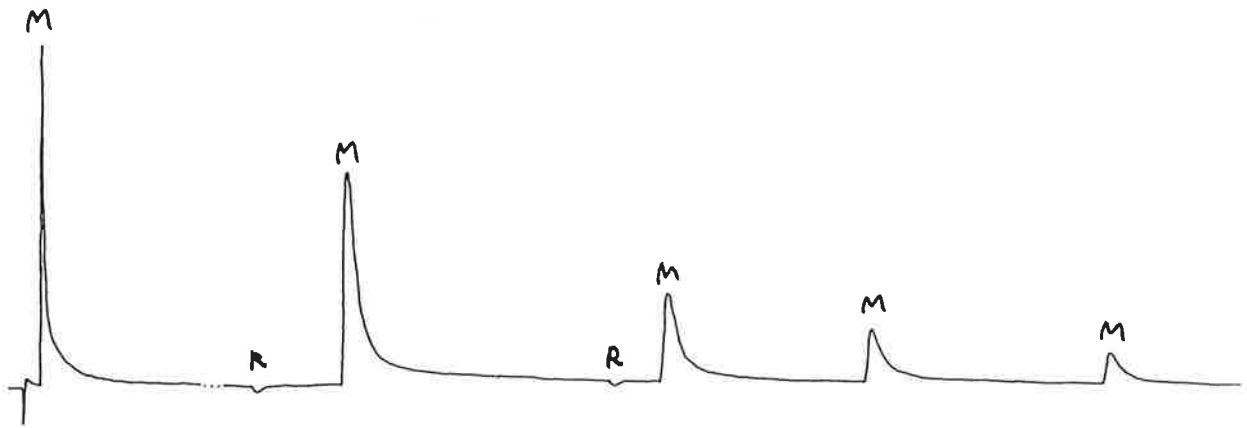


Figure 8: The result of an experiment with water injections onto a dried clay material. The peaks marked M are injections on the measurement side (onto the clay) and the peaks marked R are injections into the empty reference ampoule.

clay and the water. The 20 J exothermic heat released when 0.1 ml of water meets the clay may be compared to the 240 J exothermic heat from condensation of 0.1 g of water and the 33 J exothermic heat from 0.1 g of liquid water that freezes. The absorption of liquid water may be seen as a parallel process to freezing as the freedom of the water molecules becomes restricted in both these processes. In the clay the water molecules will be absorbed to different sorption sites and maybe also as capillary condensed water in very small pores.

## 8.4 Student experiments

This experiment may be made in a number of different ways:

- Measure heats of wetting by water on different materials (wood, clay, wool, polymers, hardened cement, molecular sieves...)
- Use different liquids (water, ethanol, acetone etc.) and different materials

## 9 The use of the calorimeter for temperature scanning; transitions in a butter

### 9.1 Introduction

The present instrument is an isothermal heat conduction calorimeter, but it can also be used for low rate temperature scanning measurements by putting the whole calorimeter in an air thermostat. In the present experiment an incubator cabinet was used. To scan up the calorimeter with a sample in the measurement position is exposed to a high temperature in the thermostat. The calorimetric block will then slowly heat up and the heat flux to the sample is measured by the calorimeter. If the sample undergoes a transition which consumes heat (e.g. a melting) this will be seen as an extra influx of heat to the sample. To scan down in temperature the same procedure may be used but with the calorimeter initially at a high temperature and the thermostat at a low temperature.

The temperature scanning rate is quite low and depending on the temperature difference between the calorimeter and the thermostat. If the thermostat is held at a constant temperature the temperature of the calorimeter will go asymptotically towards that temperature, i.e. the absolute rate of temperature change will decrease during the whole measurement. The time constant of the whole calorimeter is normally approx. 17 h (Wadsö 1998). In the present experiment this would have resulted in a too slow scanning rate so the top insulation on the calorimeter was removed. This resulted in a time constant for the whole calorimeter of approx. 6 h (Wadsö 1998).

### 9.2 Method and material

The calorimetric ampoule was charged with refrigerated Swedish household butter ("Bregott") made from 75% butter and 25% vegetable oil. The whole calorimeter was then put in an air thermostat (Seiko) set to 0°C and left for some time. The temperature of the thermostat was then set to 50°C and the temperature increased towards this value for 8.5 h when the thermostat was once more set to 0°C to scan down in temperature. Figure 9 (top) shows the temperature of the calorimetric block during the measurement. The temperature of the sample was not measured.



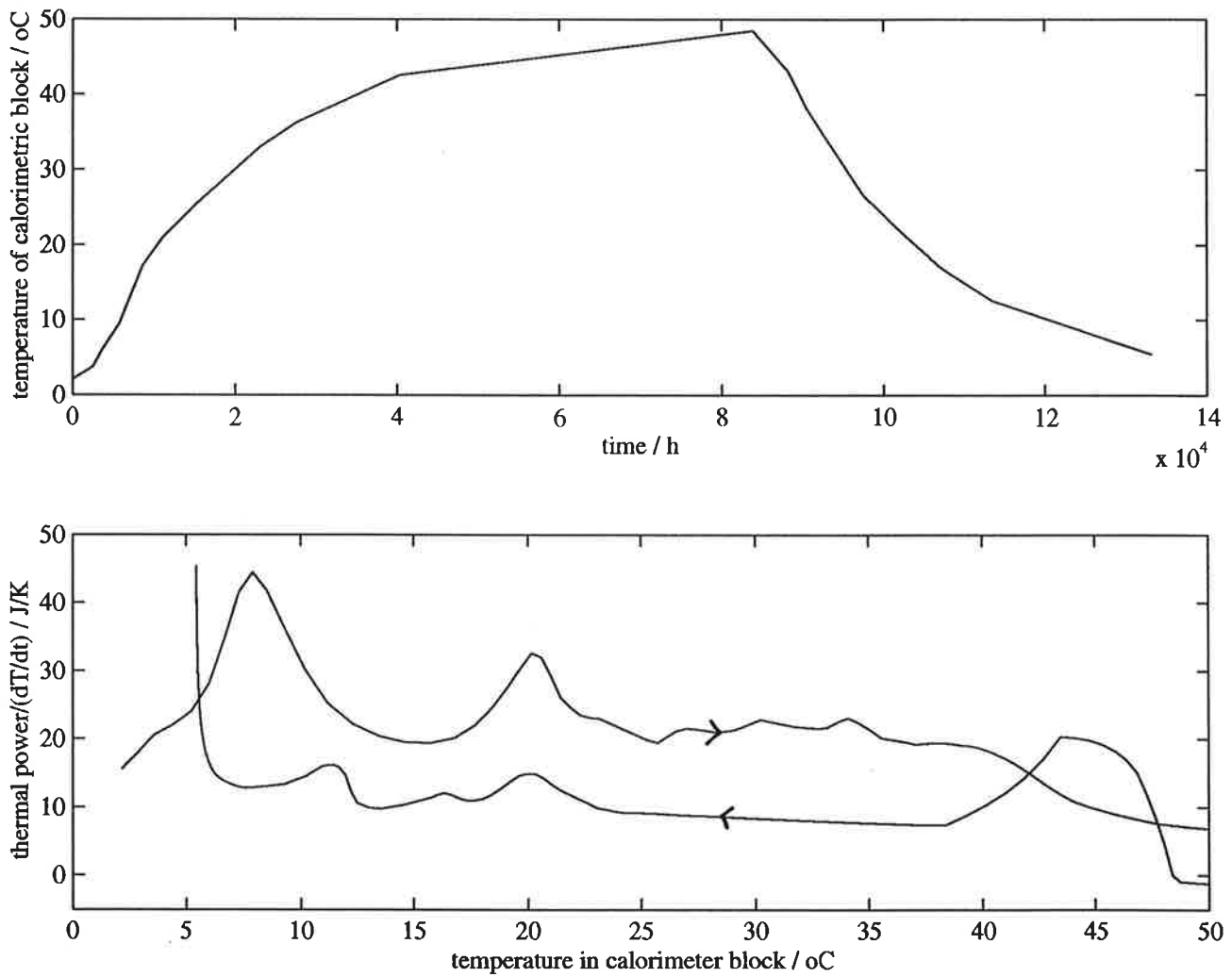


Figure 9: The results of an experiment with the calorimeter used as a temperature scanning calorimeter. **top:** The temperature of the calorimetric block during the experiment. **bottom:** The apparent heat capacity (J/g) as a function of the temperature in the calorimetric block.

### 9.3 Results and discussion

Figure 9 (bottom) shows the heat capacity ( $C$ ) of the sample (including ampoule and ampoule holder) as a function of the temperature of the calorimetric block. It has been evaluated by the following equation:

$$C = \frac{P}{\frac{dT}{dt}} \quad (5)$$

Here,  $P$  is the measured thermal power (heat flux),  $T$  is the temperature, and  $t$  is time. This gives the total heat capacity of the sample, the ampoule, the stopper, the ampoule holder and half the thermopile. If a measurement with no sample had been made this could have been subtracted from the present result to give the heat capacity of only the sample; however, no such measurement was done in the present case.

As only one measurement was made the result does not deserve too much interpretation. It is, however, seen that there are two large peaks at approx. 8 and 20°C during the up-scan. These probably represents the melting of some major components of the sample (e.g. the oil and the butter). On the down-scan there is a corresponding, but much smaller, peak at 20°C, but no peak at 8°C. This is explained by the fact that the melting-solidification of a sample such as this is not reversible; once it has been heated it will not form the same structure when it is cooled.

### 9.4 Student experiments

The present example of a measurement was not too well done, and would require improvements and would require further testing before being used as a student experiment. One such improvement is to refer the measured heat flux to the temperature of the sample (not the temperature of the calorimeter). By measuring the temperature of both the sample and the calorimetric block we may make an evaluation of transitions like one does with a DTA (differential temperature analysis). As the instrument is calibrated as a thermal power meter (and it can be assumed that the calibration coefficient does not change much with temperature) it can also be used like a DSC (differential scanning calorimeter), like in the above example. As the present instrument can be used up to 70°C the following experiments may be performed:

- study the melting of solid compounds (stearin, paraffin, beeswax etc.)

- measure the coagulation of egg white and other foodstuffs

## 10 References

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