ELSEVIER

Thermochimica Acta 251 (1995) 307–317

thermochimica
acta

Physical properties of a vacuum-deposited thermopile for heat measurements ☆

G.W.H. Höhne *, A.E. Bader, St. Hönle

University of Ulm, Sektion Kalorimetrie, P.F. 4066, D-89069 Ulm, Germany

Received 3 July 1994; accepted 6 July 1994

Abstract

The physical properties of a vacuum-deposited thermopile of antimony and bismuth with 69 hot junctions on 18 mm of a thin capton foil are presented. Using this, temperature changes down to a threshold of 0.15 mK with a rise time of 1.5 ms may be measured. The heat transfer properties have been both measured and simulated with the aid of the finite element method. This thermopile is suitable as a quasi-adiabatic calorimeter for fast heat measurements of small objects. In particular, it is possible to measure heats of single muscle fibres in quick-stretch experiments down to 1 μJ with a time resolution of 0.2 ms.

Keywords: EMF; Finite element method; Instrument; Model; Muscle; Thermopile; Vacuum deposition

1. Introduction

Thermopiles have been widely used for heat measurements in biological systems [1,2]. Nevertheless their physical properties and their influence on the measured signal have not been explored very intensively in this context. On the one hand, the interested biologist does not often have the necessary physics background, and on the other, the physicist seldom uses thermopiles for heat measurements in his workday and is thus not very motivated to investigate accurately this type of probe.

During a research project on the thermodynamics of the quick-stretch and quick-release behaviour of single muscle fibres, we were compelled to use sensitive

---

* Corresponding author.

☆ Presented at the Ninth Conference of the International Society for Biological Calorimetry, Berlin-Schmerwitz, 27–31 May 1994.

SSDI 0040-6031(94)02005-1

and speedy heat sensors. The task was to find an instrument able to measure precisely heats of some microjoules with a time resolution of better than one millisecond. As every heat transport is a rather slow process, the system in question can be considered as an adiabatically isolated one within the time frame of a quick-stretch experiment. The heat Q is then connected with a temperature change ΔT via the equation

$$Q = C_p \Delta T \tag{1}$$

where C_p is the heat capacity of the sample. Thus the problem alters to another one, namely to measure a temperature change of some millikelvin with a time resolution well below one millisecond, a task at the extreme of physical measurement techniques. This becomes even more difficult because any additional heat capacity from the sensor or other passive parts of the experimental equipment decreases the signal and causes a delay, because the temperature field needs time to spread. Thus, the experimental set-up should be carefully considered and the response behaviour be very reproducible and precisely known. In the linear case the true heat flow rate–time function $\Phi_{\mathrm{tr}}(t)$ within the sample can be calculated from the measured one $\Phi_{\mathrm{m}}(t)$ by solving the convolution integral

$$\Phi_{\mathrm{m}}(t) = \int \Phi_{\mathrm{tr}}(t - t')G(t')\,\mathrm{d}t' \tag{2}$$

where $G(t)$, the so-called Greens (or apparatus) function, is the response of the equipment on an impulse-like event inside the sample. The measured heat flow rate function can be calculated from the temperature change using Eq. (1)

$$\Phi_{\mathrm{m}}(t) = C_p \frac{\mathrm{d}}{\mathrm{d}t}\,\Delta T(t) \tag{3}$$

where C_p is the effective heat capacity of the total set-up including the sample, the temperature probe and other passive parts.

From the previous discussion it follows that a temperature sensor suitable for the experiments with single muscle fibres should have the lowest possible heat capacity at its highest possible sensitivity. From the shape of a muscle fibre, a thermopile (a number of thermoelements in series) is the sensor of choice, as it can be built in the required form (Fig. 1). Modern vacuum-deposition techniques allow, in principle, thermopiles with several hundred junctions per centimetre to be constructed on nearly every substrate material. But from the physics of such thermopiles, it follows that this is senseless from the sensitivity point of view. The thermopile which we shall present here seems to meet all requirements of the muscle fibre research project in an optimum manner.

2. The thermopile

2.1. Production

In vacuum deposition technology, there are different methods to produce thin metal layers on substrates. The easiest and most successful method is the copper

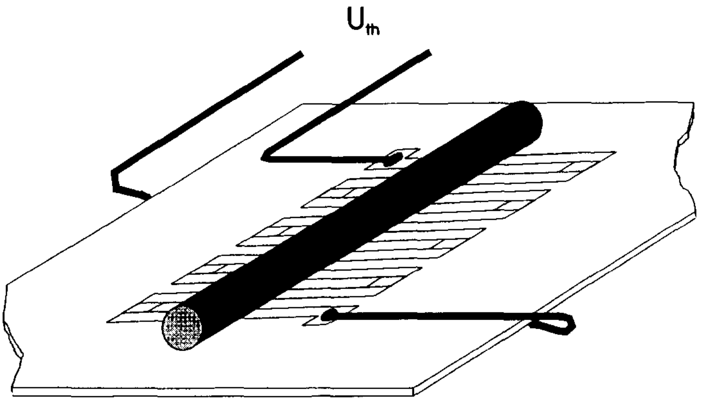


Fig. 1. Sketch of a muscle fibre on a thermopile.

mask technique, in which the structure in question is transferred photographically on a thin photosensitive copper sheet which is then developed and etched, in a way that is similar to the production of electronic circuits. The metal is evaporated in a high-vacuum chamber through this mask on to the substrate. The smallest structures producible with this method are about 100 μm, whereas the thickness of the deposition metal layers is selectable up to several micrometres (depending on the evaporation time).

Another method often used nowadays is the so-called lift-off technique. In this case the photosensitive varnish layer is attached directly on the substrate to be deposited. The exposed parts of this layer are etched away and after evaporation of a thin metal layer from this, the remaining varnish layer is detached together with the metal on it, whereas the metal deposited into the etched holes is left on the substrate. With this method structures down to a size of 15 μm can be built, but the maximum thickness of the evaporated metal layer should not exceed 0.2 μm to avoid destruction of the fine structures during the lift-off phase.

Following the arguments set out below, we chose a thermopile with 40 hot junctions per centimetre which was prepared by the copper mask technique, after Mulieri et al. [3]. But we used thin capton foils (7.5, 12.5, 25 μm thick) instead of mica foils as substrate and reduced the proportions of the thermocouples, especially the overlapping region of the hot junctions, from 254 μm to 140 μm to adjust it to the diameter of the muscle fibre (50–150 μm). A section of the copper mask showing the junctions is shown in Fig. 2, and the thermocouples in question can be seen in Fig. 3. The evaporation time was chosen so as to yield a metal layer thickness of 1.5 μm.

2.2. Physical design

The e.m.f. of the bismuth–antimony thermocouple depends on the evaporation rate, the pressure and the order of deposition of the two metals [4].

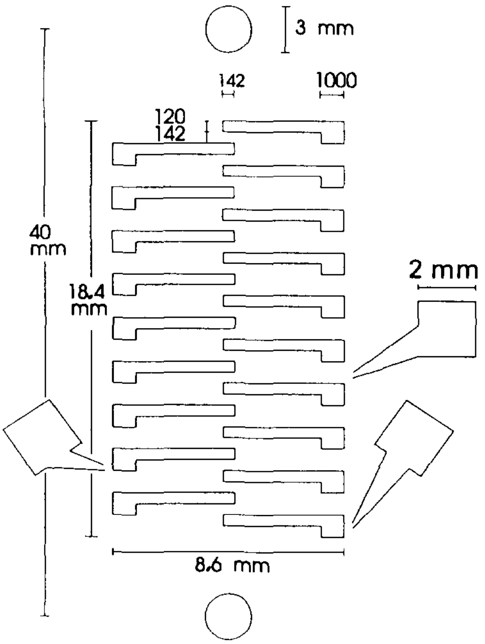


Fig. 2. Part of the copper mask for vacuum deposition of thermocouples. (The measures without units are μm.)

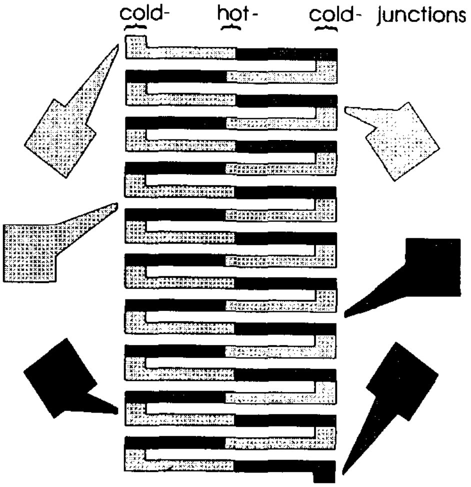


Fig. 3. Part of the deposited thermopile with different supply possibilities (grey: antimony; black: bismuth).

Furthermore, the e.m.f. depends on the thickness of the layer of the metals at the junction; it reaches a maximum at about 1 μm and drops down quickly to one third at a layer of 0.1 μm [5,6]. As the lift-off technique allows only a 0.2 μm maximum layer thickness, the sensitivity of the thermopiles produced in this way is reduced by about a half.

The thermal noise of any resistor is proportional to the square root of the resistance. Thus the noise of the thermopile increases with decreasing cross section of the metals. As a result the signal–noise ratio of a thermopile with five times more thermocouples per length unit but five times smaller proportions should not change in principle, whereas the e.m.f. of the Bi–Sb couple drops due to the thinner layer produced by the lift-off technique.

From a physical point of view, a thermopile produced by the copper mask technique is less sensitive but more suitable, because of the lower internal resistance and a better signal–noise ratio, than a more sensitive thermopile produced by the lift-off technique.

Another relevant condition is the dimension of the overlapping region of the two metals (the hot junction). From the physics of the thermoelectric effect, it follows that the e.m.f. of a thermocouple depends on its temperature. Usually the thermocouple is small relative to the object of temperature measurement. In the case of muscle fibres with a diameter of 0.1 mm, this is not true and the rise time and maximum e.m.f. depend on the temperature field in the overlapping region of the thermocouple. The maximum voltage is only achieved if the total overlapping region has the same temperature; it is not sufficient to heat only a certain part of the couple which will not give a substantial signal.

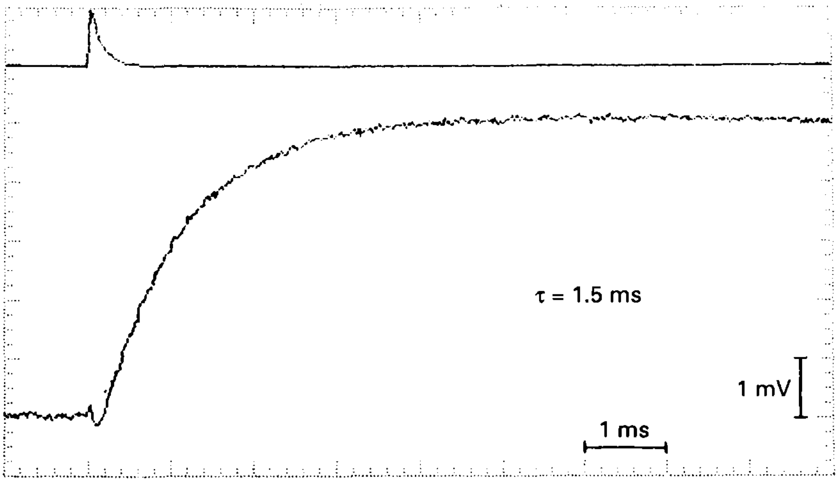
2.3. *Properties*

The optimum thermopile consists of 69 hot junctions on 18.4 mm on the bottom side of a 7.5-μm-thick capton foil. The resistance was about 50 Ω per hot junction (total 3.5 kΩ). From this value the mean amplitude of the thermal noise can be calculated to be 8 nV $\mathrm{Hz}^{-1/2}$ or 0.8 μV for a band width of 10 kHz. The e.m.f. was evaluated as 93 μV K^{-1} for every hot junction (total 6.4 mV K^{-1}). From this noise and sensitivity we arrive at a temperature threshold (signal–noise ratio 1:1) of about 0.13 mK for a time resolution of 0.1 ms.

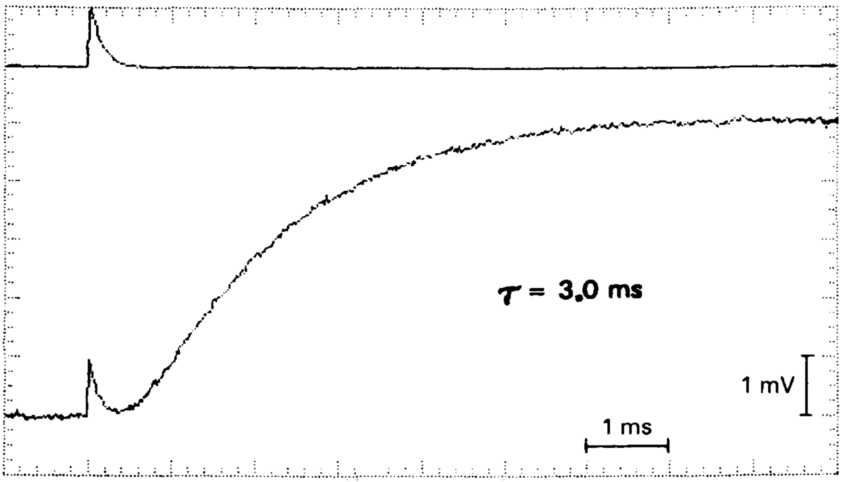
The temperature relaxation behaviour was tested with a copper wire as dummy, which was heated electrically by a capacitor discharging impulse. The wire (diameter, 52 μm) was bifilar, positioned on the hot junctions of the thermopile as in Fig. 1. The thermal coupling to the foil was achieved by water films of different thickness to simulate Ringer solution which is used with muscle fibres.

Fig. 4 shows the experimental results of the rise time measurements. The upper curve gives the heat impulse, the lower curve the temperature change for different thick foils. As can be seen the current impulse from the capacity discharging impulse is inductively coupled to the output signal, but this has no influence on the rise time measurements. The thermocouples were in every case deposited on the bottom side of the capton foils.

Fig. 5 shows the influence of the amount of water (to couple the wire to the foil) on the signal. The dry wire yields the highest signal but the response time is much larger, because of the bad heat transfer conditions. With 1 μl of water the signal drops by about 50% because of the additional heat capacity (see Eq. (1)), but the rise time is much shorter.



(a)



(b)

Fig. 4. E.m.f. signal of a short heat impulse inside a thin copper wire coupled with 1 μl of water to the foil of the thermopile: curve a, 7.5 μm capton foil: curve b, 25 μm capton foil. τ gives the rise time of the signal in question.

Fig. 6 shows the temperature relaxation behaviour after one heat impulse. Again the influence of the amount of water on the sensitivity is visible, whereas the time constant of the temperature relaxation is not influenced by the water film: it is caused by the heat transport inside the capton foil away from the heat source.

The effect of the dimension of the overlapping region of the hot junctions in the thermopile on the sensitivity and rise time is shown in Fig. 7. In one case (upper curve) the dimension of the hot junctions is in the same order of magnitude as the

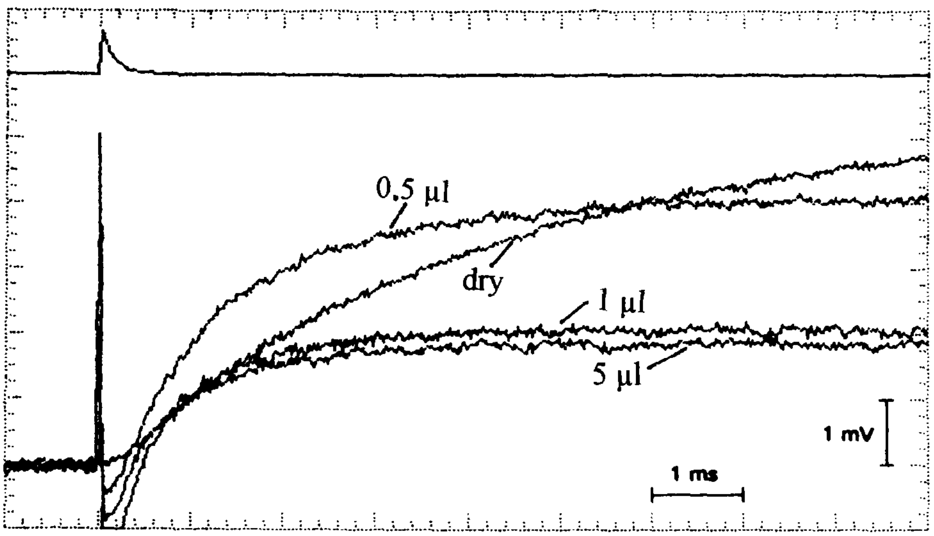


Fig. 5. Influence of the amount of coupling water on the rise time and sensitivity of a thermopile with 12.5-μm-thick capton foil. The upper curve shows the heat impulse inside the copper wire as a dummy heat source.

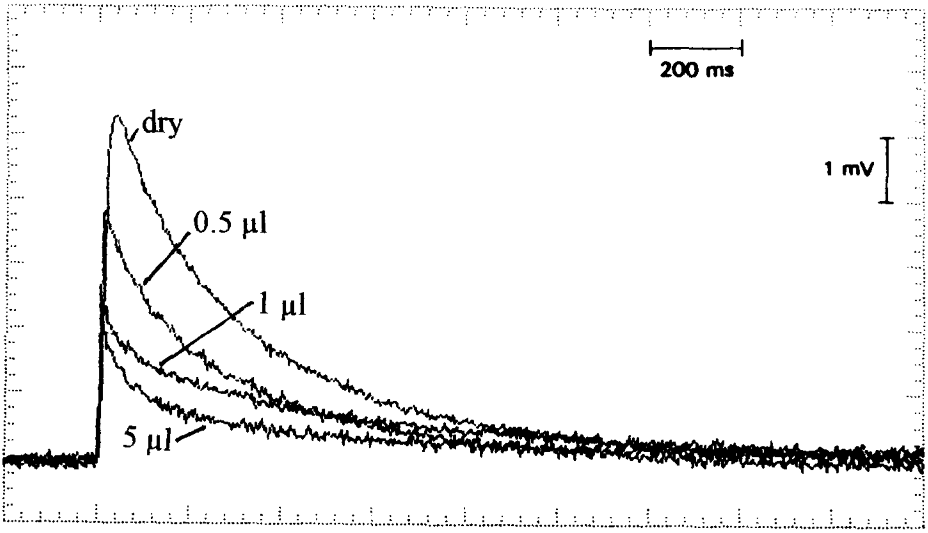


Fig. 6. Influence of the amount of coupling water on the relaxation behaviour of the e.m.f. signal of a thermopile with 12.5 μm capton foil.

heat source and the thermocouples are heated homogeneously. In the other case (lower curve), the heat source is much smaller and the temperature field must spread first along the junction to yield the proper e.m.f. In both cases the end signal, i.e. the end temperature after the heat relaxation, is the same, because of the unchanged overall heat capacity of the arrangement.

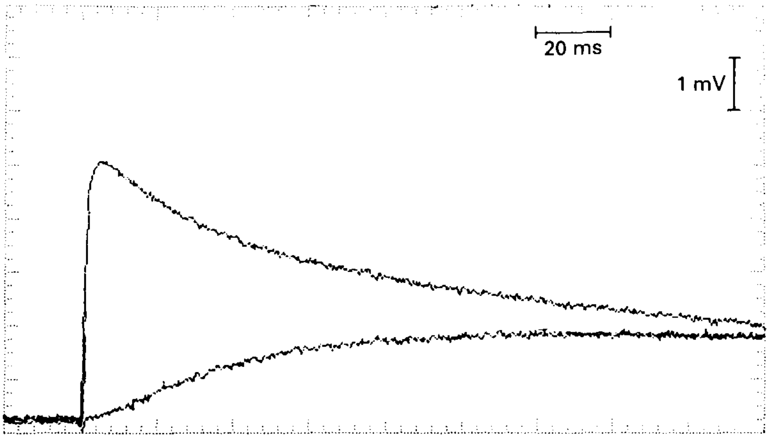


Fig. 7. Influence of the width of the overlapping region of the thermocouples on the e.m.f. signal of a thermopile with 12.5 μm capton foil: upper curve, overlapping of 142 μm; lower curve, overlapping of 1150 μm; 1 μl coupling water.

3. Model calculations

To investigate the heat transport and the development of the temperature field of the muscle fibre and the thermopile in detail, we used the finite element method (FEM) for a simulation of the experimental set-up. Fig. 8 shows the model in question; the material properties were chosen as in reality. The model includes convection heat loss and evaporation heat loss from the surface of the water layer to the surroundings.

Fig. 9 presents the propagation of the resulting temperature field during the first six milliseconds after the simulated quick-stretch temperature change of 3 mK inside the muscle fibre (a value near to reality). The influence of the heat losses on

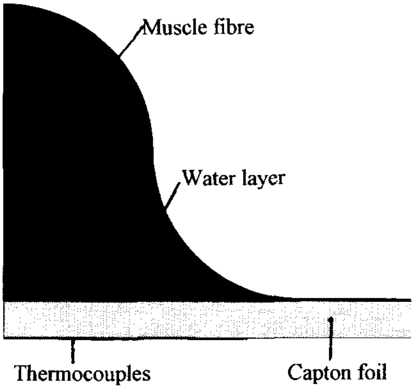


Fig. 8. Model of the set-up of Fig. 1 for FEM simulation calculations.

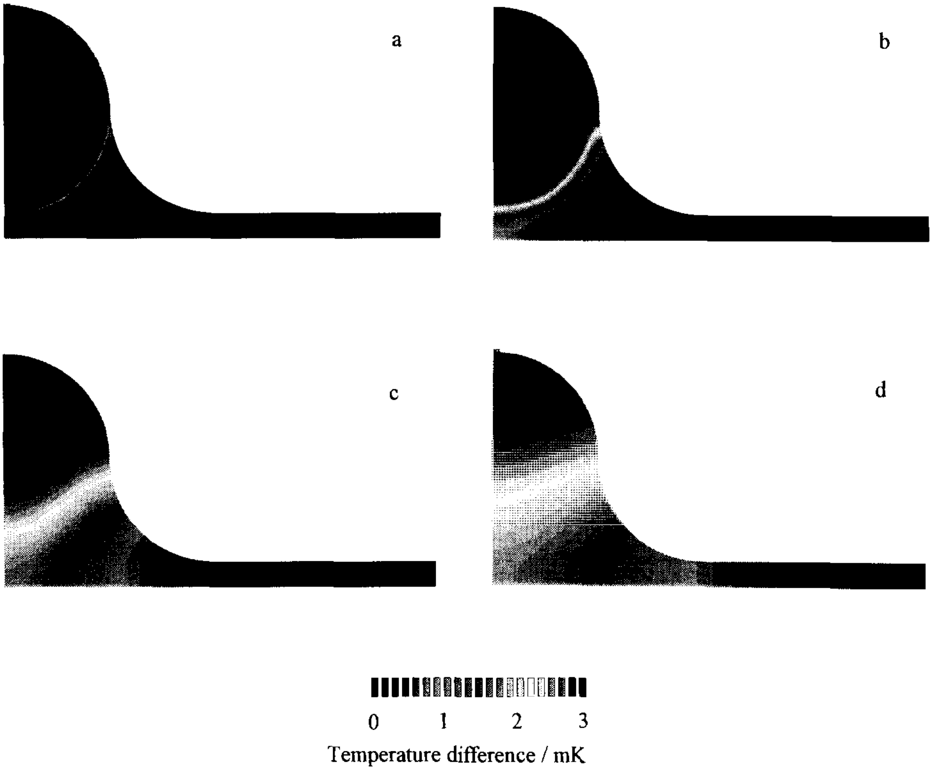


Fig. 9. Propagation of the temperature field after a sudden heating (3 mK) of the muscle fibre: a, after 0.1 μs; b, after 0.1 ms; c, after 2.4 ms; d, after 6.4 ms.

the water surface has been found to be very low within this time period, as can be seen from the shape of the temperature field on the muscle fibre which otherwise should show a larger decrease toward the fibre and water layer surface.

In Fig. 10 the calculated temperature–time functions at different points of the overlapping region of the hot junctions on the bottom of the foil are represented. The distance measure starts from the point exactly below the fibre and proceeds transverse to the direction of the fibre. If we compare these curves with the measured ones, we find that the e.m.f. rise time is mainly caused by the heat transfer through the foil. Taking into account the fact that the e.m.f. of the thermocouple depends on the average temperature of the overlapping region, we have to draw the conclusion that the latter should be as small as possible. In every case it should not be larger than the diameter of the fibre, otherwise the rise time of the e.m.f. signal would be distinctly larger.

Furthermore it can be seen from Fig. 10 (and Fig. 9 as well) that the end temperature of the thermocouples approaches a steady state value of about 1.7 mK, a value well below the temperature of the fibre after a quick-stretch of 3 mK. This is caused by the additional heat capacities of the water film and the foil which need

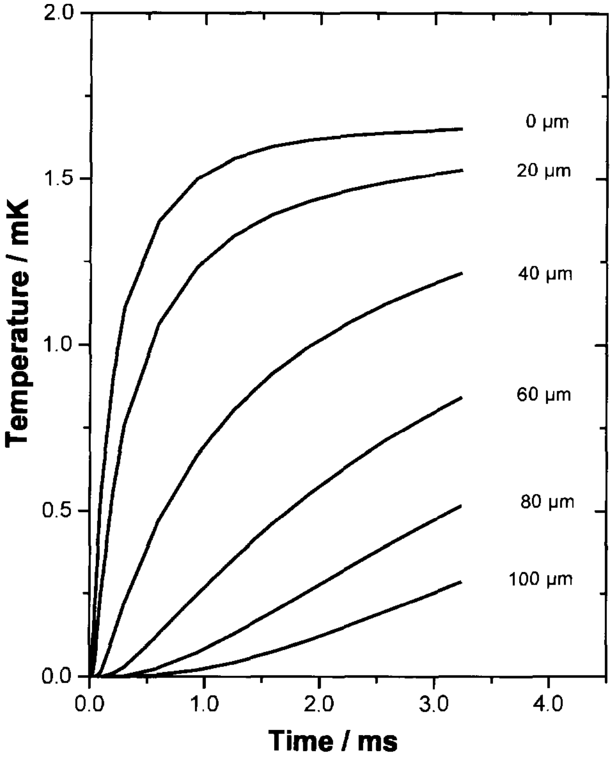


Fig. 10. Temperature change at different parts of the thermocouple. The measure counts from the very left corner of the model (Fig. 8) below the centre of the muscle fibre.

nearly half of the heat produced in the fibre to warm up to the measuring temperature. Consequently the sensitivity, i.e. the e.m.f. signal for a certain heat, of the total set-up is reduced to about half that of the dry thermopile. In every case this calibration factor (see Eq. (3)) is highly dependent on the amount of water around the fibre, which must be known precisely for quantitative heat measurements. Every change during the experiment (for instance by evaporation) will also change the calibration factor.

4. Conclusions

The measurement of temperature changes is a common method to determine heats. In the case of very fast processes, every arrangement of a thermometer and a heat source is also an adiabatic calorimeter, because the heat loss through each heat-conducting pathway needs a lot of time. The rather massless probe of a vacuum-deposited thermopile on a thin capton foil has a fast heat exchange from the surface to the thermocouples on the bottom, which is orders of magnitude faster than the heat loss to the surroundings. The low heat capacity, combined with a high sensitivity and a fast rise time, enables the heats of small objects to be measured within milliseconds. The thermopile described allows the measurement of heats causing a temperature rise as low as 0.2 mK with a time resolution of 1.5 ms. For such small signals, a 10 kHz electronic chopper and a lock-in amplifier must be used. To calculate the heat from the temperature change, the total heat capacity must be well known (see Eq. (1)). In the case described of a muscle fibre coupled with 1 μl of water to the thermopile the detection limit would be 0.1 μJ, a value far below that expected in quick-stretch experiments. The experimental rise time of about 1.5 ms can be improved to a resolution below one millisecond by mathematical deconvolution techniques (see Eq. (2)), as the Greens function of the set-up is known both from experiments and from model calculations. Unfortunately the noise increases unavoidably on application of these methods. Nevertheless it is possible to determine heats of 1 μJ with a time resolution of 0.2 ms with the aid of the thermopile described.

Acknowledgements

The authors dedicate this, presumably the smallest and fastest calorimeter in the world, to Ingolf Lamprecht on the occasion of his 60th birthday. Calorimetrists have to thank him for several rather uncommon ideas in the construction of unusual calorimeters, and we should be honoured if he would add our apparatus to this collection.

References

[1] A.C. Downing and A.V. Hill, J. Sci. Instrum., 12 (1935) 91.
[2] N.A. Curtin. J.V. Howarth, J.A. Rall. M.G.A. Wilson and C.R. Woledge, J. Muscle Res. and Cell Mortility, 7 (1986) 327.
[3] L.A. Mulieri, G. Luhr. J. Tretry and N.R. Alpert, Am. J. Physiol., 233 (1977) C146.
[4] P.A. Walters, Thermocouple Improvement, NASA-CR-80768, 1966.
[5] E.A. Johnson and L. Harris. Phys. Rev., 44 (1933) 944.
[6] R. Koike, H. Kurokawa and Y. Tijima. Jpn. J. Appl. Phys., 7 (1968) 293.