# CALORIMETER RESPONSE TIME

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The time constants of Calvet-type thermocouple microcalorimeters are compared with those with helical-type thermosensors.

Anatychuk et al. [1] have described a microcalorimeter with helical thermoelements and indicated several advantages over Calvet-type thermocouple microcalorimeters: lower sensitivity to external interference sources, significantly shorter settling time after lead application, etc. The superiority of the helical microcalorimeter in response time was especially stressed.

However, the formula presented in the study of Anatychuk et al. for calculation of the time constant of the helical thermoelement does not consider the heat capacity of the contents of the reaction chamber or the dimensions of the latter and, consequently, is only approximate. In the present study we will perform calculations of the thermosensor time constant for helical and thermocouple microcalorimeters with consideration of the effects of the reaction chamber.

As a model of the thermocouple microcalorimeter we will consider a thin-walled cylindrical chamber with infinite thermal conductivity and negligibly small wall heat capacity, on the surface of which thermocouples are mounted (Fig. 1a).

The helical thermoelectric sensor (Fig. 2a) consists of a rectangular monocrystalline spiral of anisotropic semiconductor material, the axis of which is perpendicular to the plane with maximum thermo-emf anisotropy [2, 3]. The reaction chamber is located within the cavity formed by the spiral. The temperature difference between the inner and outer (thermally stabilized) surfaces of the spiral produces a helical thermoelectric current (Fig. 2b) because of the thermo-emf anisotropy, which is then fed to an external circuit and carries information on the processes occurring within the reaction chamber (Fig. 2c). A section of the helical thermoelement is shown in Fig. 3a.

We will assume that the material studied and the specific power liberated in heat in the chamber q are homogenous and that the thermocouple ends (or external helix surface) are maintained at constant temperature, which, like the initial temperature of the entire system, we take as zero. Then, since the chamber height is large in comparison to its diameter [4] (or, correspondingly, the helix length is large compared to the width of the cavity), we can limit our examination to one-dimensional thermal-conductivity equations.

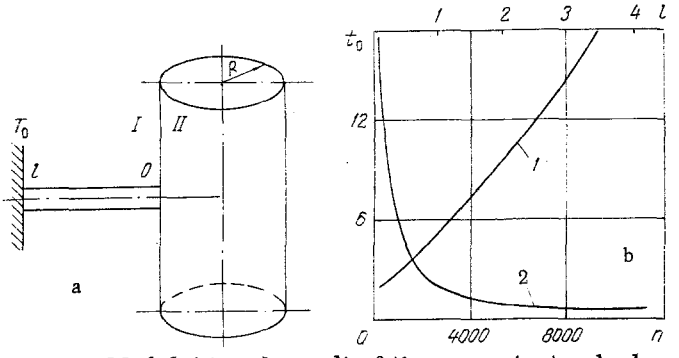


Fig. 1. Model (a) and result of time-constant calculation (b) for a Calvet microcalorimeter: 1) function of thermocouple length; 2) function of number of thermocouples. $l$, cm; $t_0$, min.

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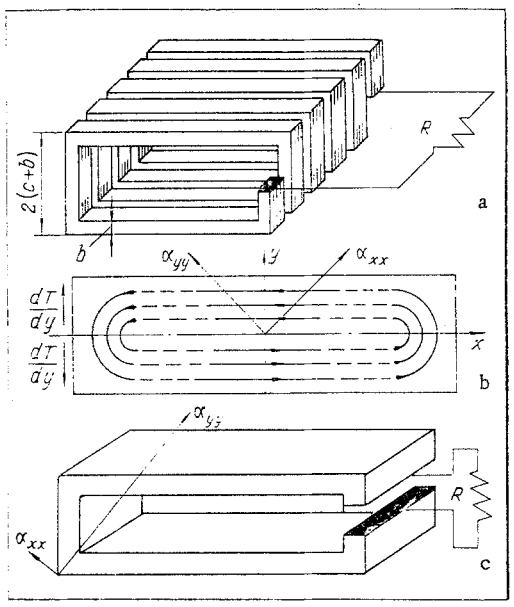


Fig. 2

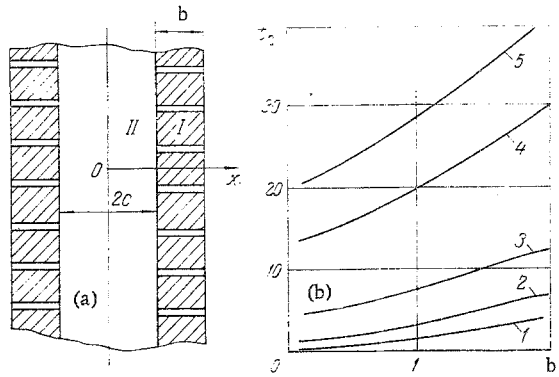


Fig. 3

Fig. 2. Helical thermoelectric sensor (a) and principle of operation (b, c).

Fig. 3. Model (a) and result of time-constant calculation (b) for helical microcalorimeter with following reaction chamber thicknesses: 1) 0.5 mm; 2) 1; 3) 2; 4) 4; 5) 5 mm. $t_0$, sec; b, mm.

The equations for the model of the thermocouple microcalorimeter

$$\frac{1}{a_1}\cdot\frac{\partial T_1}{\partial t}=\frac{\partial^2 T_1}{\partial x^2};\quad \frac{1}{a_2}\cdot\frac{\partial T_2}{\partial t}=\frac{\partial^2 T_2}{\partial r^2}+\frac{1}{r}\cdot\frac{\partial T_2}{\partial r}+\frac{q}{k_2},$$

$$T_1(x=0)=T_2(r=R),\quad T_1(x=l)=0,$$

$$S_2k_2\frac{\partial T_2}{\partial r}\Big|_{r=R}=S_1k_1\frac{\partial T_1}{\partial x}\Big|_{x=0}$$

are supplemented by the requirement of finite $T_2$ at the origin.

The thermal-conductivity equation for region I [Fig. 3(a)] and the boundary conditions for the case of the helical microcalorimeter are written in an analogous manner. Only the equation for region II differs:

$$\frac{1}{a_2}\cdot\frac{\partial T_2}{\partial t}=\frac{\partial^2 T_2}{\partial x^2}+\frac{q}{k_2}$$

and the boundary condition at the origin

$$\frac{\partial T_2}{\partial x}\Big|_{x=0}=0.$$

In these equations $a_i$ is thermal diffusivity; $k_i$ is the thermal conductivity of the material in the i-th region; $S_i$ and $T_i$ are the surface area and temperature.

The solutions of these problems, obtained by the Laplace transform method, may be written in the form

$$T_i(x,\ t)=T_i(x,\ \infty)+\sum_{n=1}^{\infty}f_i(n)\exp(-a_2z_n^2t), \tag{1}$$

where $T_i(x, t)$ is the stationary temperature distribution in the i-th region; $f_i(n)$ are some functions independent of time t; $z_n$ are roots of the following transcendental equations:

for the thermocouple model

$$d\,\mathrm{tg}(mlz_n)=\frac{J_0(Rz_n)}{J_1(Rz_n)}, \tag{2}$$

where $J_0$ and $J_1$ are Bessel functions of the first kind;

$$d = \frac{k_2 S_2}{k_1 S_1} m, \quad m = \left(\frac{a_1}{a_2}\right)^{1/2};$$

for the helical model

$$d \operatorname{tg}(cz_n) \operatorname{tg}(mbz_n) = 1. \tag{3}$$

From Eqs. (1)-(3) it follows that the microcalorimeter time constant in both cases will be determined by the expression

$$t_0 = \frac{1}{a_2 z_1^2}, \tag{4}$$

where $z_1$ is the nonzero root of smallest absolute value of Eq. (2) for the thermocouple model and of Eq. (3) for the helical calorimeter.

Equations (2)-(4) were used for calculation of the time constant of a microcalorimeter using copper–Constantan thermocouples and a helical model using a bismuth monospiral, where the reaction chamber was filled with water. Results of the calculations are shown in Figs. 1b and 3(b).

As is evident from the figures, the time constant of the thermocouple device is significantly larger than that of the helical model. With given reaction chamber dimensions it may be reduced by either decreasing the length of the thermocouples (Fig. 1b, curve 1) or increasing their number (Fig. 1b, curve 2). However, even under ideal conditions the response time of thermocouple microcalorimeters is slower than that of helical devices. In fact, for unlimited reduction in thermocouple length, the first root of Eq. (2) coincides with the first null $j_{01}$ of the function $J_0(Rz_n)$ and Eq. (4) takes on the form

$$t_0 = R^2 a_2^{-1} j_{01}^{-2},$$

from which it follows that the time constant of thermocouple microcalorimeters with no inverse feedback is not less than 1 min for the reaction chamber dimensions chosen here and exceeds the time constants of helical devices by a factor of tens, as is evident from Fig. 3(b).

Thus, the monocrystalline semiconductor spiral, whose small thickness is combined with maximum contact area with the reaction chamber, is the optimum sensor for creation of rapidly responding microcalorimeters.

## LITERATURE CITED


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