Simplified isoperibol calorimetry for thermal testing of dielectric and conducting materials

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Abstract: A simplified isoperibol calorimetry method for measuring specific heat in solids is described. Taking advantage of the classical Nernst dependency the specific heat is calculated from time-domain temperature curves registered for a sample forced heating and natural cooling phase. In order to improve accuracy of the measurements a correction factor, taking into account the heat transferred to the surrounding, is introduced along with a procedure of statistical elimination of unavoidable measurement deviations. The method is implemented in a simple and straightforward measuring system involving no vacuum calorimeter. The method is applicable for quick and routine specific heat measurements performed on small solid dielectric or metallic specimens at near-room temperature. Test results of various materials used commonly in electrical engineering are demonstrated and discussed as well as comparison to drop calorimetry and differential scanning calorimetry reference measurements is included. The overall repeatability of the test method and the simplified apparatus is estimated as not worse than 2.6%.

Key words: calorimeter, correction, cooling, heat transfer, specific heat

1. Introduction

Specific heat is one of the fundamental thermophysical properties of the solids. It directly enters into equations governing the steady-state heat transfer processes and indirectly – by means of the thermal diffusivity – in all unsteady transient cases. Efficient and effective heat transfer and evacuation, natural and forced cooling, thermal insulation and shielding are just a few design and manufacturing-related problems to be mentioned which become more and more significant in electrical engineering as the power of electrical machinery is still rising with regular reduction of the equipment size. Therefore, rapid and accurate estimation of the specific heat value is essential not only from a purely scientific point of view but also for engineering purposes.

Several methods have been developed so far to measure specific heat values of solids. Most of them could be described as calorimeter-based. In calorimetry the sample placed in a well-insulated calorimeter is heated by means of a given amount of heat flux and the corresponding rise in its temperature is measured. Classical Nernst vacuum calorimeter [1] or quasi-adiabatic calorimeters [2] are just to name a few well-known arrangements. Among the reference-based methods one should mention DSC (*Differential Scanning Calorimetry*) and DC (*Drop Calorimetry*). Last years have also brought pulse methods known also as AC calorimeters. The AC calorimetry measures specific heat in a different way – one side of a specimen is heated sequentially (by a chopped light beam or other periodic heat source) and the temperature amplitude of the other specimen side is measured using lock-in techniques [3-4]. Since the specific heat is bounded to the thermal conductivity and diffusivity by the density, methods applicable for determination of the latter two thermophysical properties are also applicable. The disadvantageous features possessed by the mentioned methods include complexity of the measuring apparatus, time-consuming measurement procedure as well as a laborious sample preparation phase. In case of many engineering-oriented applications (like selection of surrogates, post-production or quality testing), fully portable and automated measuring systems are required allowing for quick and routine specific heat determinations with limited accuracy.

Our simple approach to quickly measure the specific heat in small solid samples is based on a well-established calorimetric method of transient heating and relaxation cooling of a sample in a constant temperature environment, often called isoperibol calorimetry [5]. In classical Nernst approach a measured amount of energy is supplied electrically to the sample placed in perfectly insulated calorimeter and its temperature rise is observed. In our approach there is no real vacuum calorimeter involved. Instead, it is replaced by ordinary non-perfect thermal insulation, which is required just to reduce heat loses from the specimen during the heating phase and to slow down its natural cooling. Our simple apparatus is a minimal derivative of a classical Nernst vacuum calorimeter and a quasi-adiabatic calorimeter for measuring poor-conducting and highly moist solids described by Krischer [6]. Related techniques found in other papers [7-8] deal with very small specimens (mass of the order of tens milligrams) to fulfill condition on negligible temperature gradient within the specimen volume during transient experiment. This is a significant difference between the mentioned papers and our approach, using bulky samples. Although we can not neglect the temperature gradient within the specimen volume during the transient experiment when using bulky specimens of low thermal conductivity materials (like dielectric polytetrafluoroethylene PMMA or polymethylmethacrylate PTFE plastics) yet the applied mathematical model supplemented by statistical data processing allows for effective elimination of that effect. Solid thermal insulation used in the test set-up also disturbs the measuring process, however the introduced correction factor allows to account for this disturbance, too.

Advanced theoretical models producing temperature functions characterizing isoperibol calorimeters can be found in the literature (e.g. [9, 10]). The theoretical model introduced to describe our approach is limited to only the most basic thermodynamic principles and does not consider (well established and applied in high-grade equipment) correction methods for

unavoidable deviations. Instead, a statistical (regression-based) approach of eliminating sus-pectted data points is implemented along with a correction factor, accounting for overall heat loses. As it is shown later, those measures are sufficient for achieving a good agreement with DS and DSC reference measurements.

2. Theoretical model

The infinitesimal heat amount dQ_1 transferred to a solid body having mass m results in its temperature rise by dT given by the following well-known relationship:

$$dQ_1 = m \cdot c \cdot dT, \tag{1}$$

where c is the specific heat of the solid material being considered.

The most convenient way to supply and measure the transferred heat quantity is the case of exchanging the work done by electric current into the heat energy. Thus in our further delibe-rations we will consider such way of heating up the body expressed by the following formula:

$$dQ_2 = P \cdot dt, \tag{2}$$

where dQ_2 is the energy supplied by an electric source of power P in infinitesimal time interval dt.

In a real case, when the body is enclosed in non-ideal thermal insulation, at the same time when it is heated up it is also loosing some amount of its thermal energy to the surrounding. The heat energy transferred to the neighboring environment in time interval dt may be expressed in the following terms:

$$dQ_3 = k \cdot \vartheta \cdot dt, \tag{3}$$

where: ϑ is the difference $T - T_{amb}$ between the body temperature T and the ambient tem-perature T_{amb}, $k = h \cdot s$, where h is the heat conductance coefficient and s is the area through which the heat flux penetrates.

Since the initial body temperature is T_{amb} we have a boundary condition $\vartheta_{(0)} = 0$. Writing a heat balance for the energy supplied to the system from the electric source, given by (2), consumed by the body according to (1) and employing the cooling correction given by (3) we obtain:

$$P \cdot dt = m \cdot c \cdot d\vartheta + k \cdot \vartheta \cdot dt. \tag{4}$$

Equation (4) may be rearranged to give the following form:

$$m \cdot c \frac{d\vartheta}{dt} + k \cdot \vartheta = P. \tag{5}$$

When P is set constant, differential equation (5) gives the following solution:

$$\vartheta_{(t)} = \frac{P}{k}\left(1 - e^{-t/\tau}\right) \tag{6}$$

and, when denoting $k = m\,c/\tau$, we may rewrite (6) as:

$$\vartheta_{(t)} = \frac{\tau \cdot P}{m \cdot c}\left(1 - e^{-t/\tau}\right). \tag{7}$$

Equation (7) applies to a body heated up. When it is cooled down, i.e. when $P = 0$, equation (7) needs to be written in the following form:

$$\vartheta_{(t)} = A \cdot e^{-t/\tau}, \tag{8}$$

where τ is a characteristic cooling time constant for the body in a given surrounding and A is a constant related to a cooling process. Value of τ is to be determined from the experimental record of the body temperature when cooled, as that shown in the right part of Fig. 1.
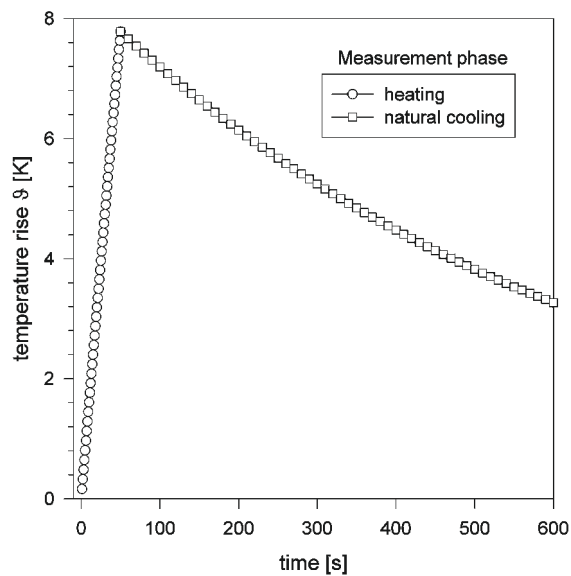

Fig. 1. Temperature curves for model body during heating and cooling phase

The experimental record of the body temperature obtained for heating period is used to read off the co-ordinates of any two points on the curve given by (7): $(t_1,\ \vartheta_1)$ and $(t_2,\ \vartheta_2)$. We may therefore write:

$$\begin{aligned}
\vartheta_1 &= \frac{\tau P}{m\,c}\left(1 - e^{\frac{-t_1}{\tau}}\right) \\
\vartheta_2 &= \frac{\tau P}{mc}\left(1 - e^{\frac{-t_2}{\tau}}\right).
\end{aligned} \tag{9}$$

System of equations (9) can be solved for *c* giving:

$$c = \frac{P(t_2 - t_1)}{m(\vartheta_2 - \vartheta_1)} \left(\frac{e^{\frac{-t_1}{\tau}} - e^{\frac{-t_2}{\tau}}}{t_2 - t_1} \right) \tau, \tag{10}$$

where the term:

$$\frac{P(t_2 - t_1)}{m(\vartheta_2 - \vartheta_1)} \tag{11}$$

is the specific heat according to a classical equation derived by Nernst and the term:

$$\frac{e^{\frac{-t_1}{\tau}} - e^{\frac{-t_2}{\tau}}}{t_2 - t_1} \tau \tag{12}$$

is a correction factor introduced by our approach, taking into consideration the heat losses given off from the body to its surrounding.

In the above theoretical approach we assume that each infinitesimal delivery of energy instantly shifts the thermal state of the body to another quasi-stationary state, in which its temperature is constant and uniform across the whole bulk of the body – in other words effects of thermal diffusivity are not taken into account.

The heat conduction coefficient *h* is not the same in the heating and cooling period, however all the above deductions are based on constant *h* as in practical realization, covering a relatively small range of temperature variations, the change of *h* is diminutive and it does not bring about serious inaccuracies to the measurement results.

Presented method is an absolute one as the calculated results of the specific heat measurement are not dependant on or relative to any selected standard required in the experimental run. Since the specific heat depends on the temperature the measurements must be carried out for small temperature variation range; otherwise a mean value of the specific heat is determined over the temperature range used to heat up the specimen. The measurement is done under constant pressure therefore the really measured value is the specific heat at constant pressure c_p. It may be recalculated to yield the specific heat at constant volume c_v when the volumetric expansion coefficient, density and compressibility of the evaluated body are taken into account.

3. Experimental

3.1. Sample preparation

Samples used in test measurements were cut into thin (2-5 mm) rectangular (20×30 mm) prisms from blocks of native material. Copper (99.9% purity), brass (Cu/Zn = 70/30), PMMA (technical grade), PTFE (technical grade) and proprietary composite dielectric material mar-

ked 2721 (epoxy resin filled with silica flour, 50% w/w) were used for testing. The rough surfaces of the samples were finished by mechanical surface milling (with no lubricant). When the samples were cut out of flat sheets no additional surface treatment was applied. To perform the measurement two identical specimens were required. A surface foil heater was then sandwiched between the specimens. The heater used in the experiments had a negligible thickness (0.2 mm) and very small heat capacity (smaller than 50 mJ/K). The heater dimensions were the same as those of the test specimens. A miniature surface-type K thermocouple of a negligible thermal capacity was fixed right in the middle of the outer wall of one of the specimens to register its temperature variations. Thin insulating clips of low thermal conductivity kept the heater, the sandwiched specimens and the temperature probe together. The assembly is shown schematically in Fig. 2a. Specimen-heater assemblies mounted this way were then stabilized for 30 min in standard temperature and humidity conditions (approx. 25°C and 55% RH).
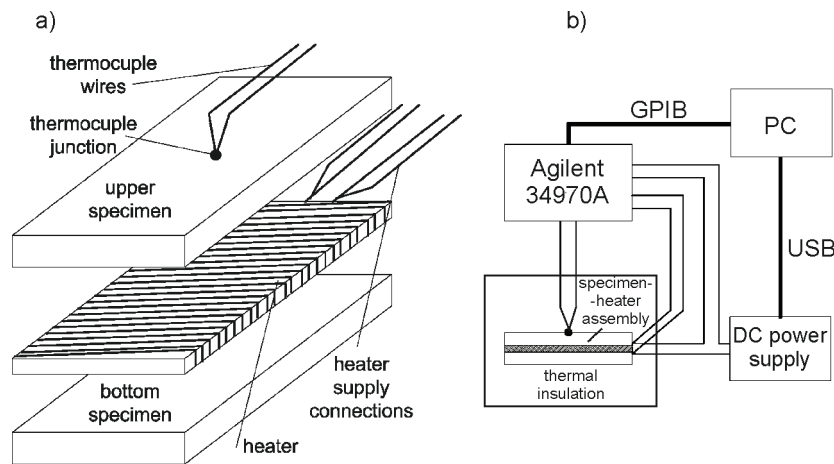

Fig. 2. Schematic view: (a) specimen-heater assembly; (b) sketch of the test set-up

3.2. Test set-up

The specimen-heater assembly was wrapped into a 5 cm thick layer of mineral wool and confined in additional metal enclosure. The heater was supplied from a stabilized direct current power supply. By recording a current and a voltage drop directly on the heater input terminals the actual heating power delivered to the samples was calculated. The temperature of the specimen was recorded using a data acquisition unit (DAQ Agilent 34970A), which was also used to meter the heater supply current and voltage. All devices (DAQ and the power supply) were controlled remotely by a PC running a control application program prepared in Agilent VEE software. A schematic sketch of the test set-up is shown in Fig. 2b.

3.3. Measurement procedure

Every single measurement run was performed by supplying the heater with a chosen constant power to obtain moderate temperature ramp rise of the specimen and registering the

specimen temperature at constant time intervals. 60 s heating period and 0.25 s measurement intervals were used. After that time the heating power was remotely measured, the power supply was disconnected and the specimen temperature was further monitored and registered for next 420 s every 5 s, when the sample-heater assembly was slowly cooling down. The temperature record was then automatically processed by the software control application to calculate the specific heat value.

3.4. Reference measurements

Reference specific heat measurements were performed using either DSC (Mettler Toledo STARe System) or DC (own construction, tested and verified against DSC). The results, together with test measurement uncertainty, are collected in Table 1.

Table 1. Specific heat reference measurement results

Specimen material (temperature)	c_p (kJ · kg^{-1} · K^{-1})	Std. deviation (%)	Test method
PTFE (308 K)	1.03	3.5	DSC
composite 2721 (308 K)	0.97	4.0	DSC
PMMA (308 K)	1.31	3.7	DSC
copper; 99.9% purity	0.38	8.0	DC
brass; Cu/Zn = 70/30	0.39	8.4	DC

4. Results and discussion

Figure 3a presents superimposed temperature curves recorded for specimens made of four different engineering materials (PTFE, brass, composite 2721, and copper). The selected constant 60 s heating period resulted in increasing the specimen temperature by 7-10 K above the ambient, depending on the particular specimen dimension, mass (thus its heat capacity) and heating power. The last parameter was varied from 1.6 to 2.3 W for 2721 composite, from 2.6 to 2.8 W for PMMA, from 1.8 to 2.3 W for brass, from 2.3 to 2.8 W for copper, and from 2.7 to 2.8 W for PTFE. Since the temperature rise was small it could be assumed, that the calculated c_p value is characteristic for heating mid temperature (30-35°C). Although the difference between PTFE and Cu thermal conductivity is nearly 3 orders of magnitude similar heating regime used for PTFE and Cu specimens of comparable thickness gave similar slope of temperature rise as the thermal capacitance of the samples was also similar.

If one compares Fig. 1 and 3a it becomes obvious that the empirical temperature curves shown in Fig. 3 overlap with that predicted by the deduced relationship for the model body. However, some departures from the relationships (7) and (8) are experienced in the initial period of the sample heating (delayed thermal reaction of the specimen) and also just after isolation of the heater circuit (temperature overshoot). Those discrepancies arise from the finite thermal diffusivity, which was not taken into account by the simple model and the assumption on a spatial thermal homogeneity across the heated body. There are detailed studies of this

problem to be found in literature (e.g. [11]). However, as it will be shown, an appropriate processing of the measurement data and application of some basic statistical procedures allow for calculating correct and reliable specific heat values without a need to extend and complicate the assumed model, alter the test set-up or miniaturize samples.

First, to calculate τ from the cooling record we reject those temperature data that were registered right after disconnecting the heating power. Tests performed on various engineering materials show that in our set-up 60 s period is long enough to remove "overshoot" temperature data. Then, for the remaining points we apply a numerical regressive procedure of finding the most exponential part in the data set when fitting to equation (8). The algorithm of finding the most exponential dataset has been adopted after [12]. Having τ calculated we apply a similar procedure of finding the most linear part in the heating period data set. The coordinates of initial and terminal points of the best-fitting line are used as (t_1, ϑ_1) and (t_2, ϑ_2) values in formula (10) to finally calculate the specific heat, as illustrated in Fig. 3b. Such procedure has an additional advantage of rejecting most of the measurement noise introduced by the measurement environment and the test apparatus itself.
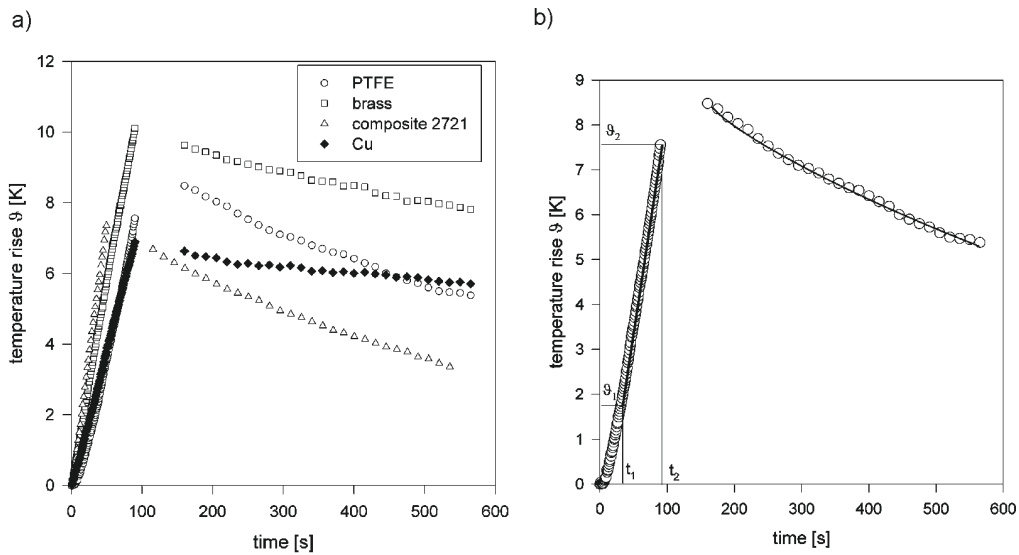

Fig. 3. Temperature curves registered for: (a) selected sample materials (every 3rd point plotted for figure clarity); (b) temperature curve recorded for PTFE approximated numerically

The measured corrected (according to (10)) and uncorrected (according to (11)) c_p values are listed in Table 2 as mean values calculated for 20 successive measurements. It should be stated that the correction factor, accounting for the cooling effects greatly improves the accuracy of the presented method as a good agreement between the corrected values and the reference c_p measurements (Table 1) is found.

Table 2. Specific heat measured according to modified Nernst approach

Specimen material	c_p $(kJ \cdot kg^{-1} \cdot K^{-1})$ uncorrected	c_p $(kJ \cdot kg^{-1} \cdot K^{-1})$ corrected	Repeatability expressed as std. deviation for corrected c_p [%]
PTFE	1.10	1.04	0.9
Composite 2721	1.01	0.97	1.0
PMMA	1.45	1.38	1.1
Copper 99.9% purity	0.40	0.39	1.7
Brass (Cu/Zn = 70/30)	0.42	0.41	2.6

In order to estimate a repeatability of the discussed method 20 successive measurements of c_p were made for each specimen with reassembling of the specimen-heater assembly. The results are given in Table 2 as standard deviation values for corrected c_p values (the spread of the results was determined for 95% confidence level). The overall repeatability may be specified as fine; generally it is enhanced for materials with higher c_p value due to higher temperature rise and therefore, smaller effects of temperature reading errors. The results also agree well with the reference measurements, the differences are within 5%.

To make a few further remarks we should point to the fact that the specimens may also be manufactured by casting, pressing, injection molding or punching from sheet metal plates, laminates or finished goods. The overall specimen dimensions are not critical but it is important that the inner surfaces of the specimen – those facing the heater – must be flat, smooth and adhere entirely to the heater. The thermal contact between the heater and the sample should be improved by applying a thin layer of thermo-conducting paste based on Al_2O_3 or other agent. The thickness of the specimens should also be balanced. Too thick samples result in augmented departures from the modeled temperature curve shapes and therefore in lowering the overall accuracy. Too thin samples are also not exploitable as it becomes difficult to balance the heating power to obtain a suitable temperature ramp and the thermophysical properties of the heater are no longer negligible in this case. Measurement runs should be performed for sample-heater assemblies stabilized at ambient temperature i.e. after necessary "calming" period mentioned in sample preparation procedure.

Thermal insulation applied for shielding of the specimens should provide very slow natural cooling of the sample-heater assembly; in practice time constant τ for 5 cm thick layer of fine mineral wool was much over 1000 s. The time constants determined from the measurements contain physical information (e.g. information on the heat conductance coefficient). However they are neither analyzed in details nor discussed in this paper as the heat coefficient is not representative for the specimen itself but rather for the whole test set-up.

We suppose the power P supplied to the specimens to be constant and therefore it is enough to measure P at any time during the heating period. Since we use well-stabilized power supply with constant voltage, the delivered power depends solely on the resistance of the heater coil. It was verified experimentally that the resistance is independent on voltage and the temperature up to several tens of degrees Centigrade. The transients related to energizing and isolating the heating circuit are automatically removed by the numerical procedure discussed above. However, it could be meaningful to repeatedly register the momentary power

supplied to the heater along with the temperature record and calculate the true value of energy used to heat up the specimens from this record (but such approach seems not to be justified on the basis of any likely accuracy augmentation).

5. Conclusion

Easy-to-handle, simple and reliable quasi-calorimetric method for use in modern electrical engineering practice has been evaluated. The numeric fitting procedure, applied for post-heating curve, avoids complicated calorimeters with multiple thermal shields, multi-section heating or thermal stabilization. A good agreement between reference (DC and DSC) measurements and correction-calculated c_p values was found for a set of engineering materials (metals and plastics) common to electrical engineering applications. Although instruments of similar type are commercially available but they are offered as immobile laboratory units. The presented approach makes it possible to build a miniature, fully portable (battery-supplied) and automatic (turnkey operation supervised by a microprocessor-based controller) device for quick on-site engineering-oriented (i.e. with moderate level of precision) or occasional thermo-physical testing of solids.

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