

## Thermal constants measurement techniques applied to thermal analysis<sup>1</sup>

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### Abstract

Recent development and applications of many new materials have resulted in them being made available only in small amounts or in special configurations such as thin films. In order to characterize their thermal transport and related properties in these forms, it has been necessary to develop new and improved quantitative measurement techniques having high measurement precision and operating more rapidly than conventional methods. In use, these can be valuable thermal analysis tools because they provide precise quantitative information that can also be used qualitatively.

Instrumentation based on several new techniques for rapid measurement of thermal and related properties of small specimens over broad ranges of temperatures is described. Their potential in thermal analysis, quality control and other applications is discussed. Such methods include thermal conductivity, thermal diffusivity and heat capacity of a.c. calorimetry, pulse and other transient techniques, and thermal expansion using laser interferometry.

### INTRODUCTION

Historically, materials scientists have utilized thermal analysis and thermal parameters determination as two distinct and separate tools in the overall development and characterization of their materials. The former has been considered primarily as the means to obtain essential qualitative information on structure, behavior, etc. during development, whereas the latter provides the necessary quantitative performance values for the material and its applications once it has been developed.

Classical thermal analysis techniques involve the use of “small” test specimens of a material in various configurations and forms to provide results. However, special measurement techniques involving “large” specimens of different configurations, depending upon the form of the material, are required for thermal parameters determination. Furthermore, thermal analysis techniques using heating rates of from 2 to 50°C min<sup>-1</sup> and now

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even higher ( $> 20^{\circ}\text{C s}^{-1}$ ) with IR gold imaging furnaces are rapid in operation, whereas many of the methods for thermal parameters determination, especially those using steady state techniques, are often time consuming.

More recently, the explosion in materials development for all of the many emerging technologies, especially electronics, has produced very substantial quantities of new and improved but often expensive materials in different forms, especially thin films. This has stimulated a corresponding need for a more rapid evaluation of their thermal properties using configurations not suitable for current classical methods.

Excluding cost considerations, the overall change in measurement needs may be summarized as being the combined result of five specific but interrelated changes: the availability of materials in only limited quantities and forms; properties and performance in materials applications replacing intrinsic properties as the major driving force; small “non-ideal” rather than large “ideal” specimens; the attraction of transient over steady state measurements; and apparatus automated rather than manually operated.

A critical issue is the numbers and types of materials that require investigation and characterization. Results for even a limited temperature and/or environmental range are required quickly. This has been the major stimulus towards the applicability of transient techniques for transport properties appropriate to the application, especially where a material exhibits anisotropy in a property. The past ten years can well be summarized as the “thin” decade. Materials development became one that involved sheets, wafers and films provided by various processes. This further reduction in the most critical specimen dimension provided new and greater problems for the experimentalist, especially with materials of high thermal conductivity and of low thermal expansivity. Whereas successful techniques had been developed to measure specimens of up to a few millimeters thick, we were now faced with maximum dimensions of microns and ångströms.

As a result of such stimuli as small specimens, more rapid measurement, and a higher precision of measurement, some of these newer quantitative techniques can also be used for qualitative purposes. The present paper describes the essential principles of several of these newer methods that provide the materials scientist with additional more flexible tools. Some examples of their use as thermal analytical tools are described elsewhere [1].

## PROPERTIES

### *Specific heat*

For the past two decades or more, the predominant method used, especially for a moderate temperature range up to 500–600°C, has been

the differential scanning calorimeter. Its attraction is that it uses only a very limited amount of material (milligram quantities) and is based on the principles of differential thermal analysis, a tool available in many laboratories.

Although it is in very wide use for quantitative measurement, there are some drawbacks to its general use particularly for composites and other heterogeneous materials where small quantities of specimen are not representative of the bulk material. Furthermore, the results obtained on different forms (powder, granules, solids etc.) of the same material are often variable and dependent on heating rate and are often not sensitive enough to quantify second- and third-order transitions. These factors also prevent it being suitable for thermal conductivity determination. Other techniques are necessary to supplement DSC for measurements of heat capacity on small specimens.

A new method that has been developed as a very sensitive calorimetric tool, particularly useful for materials in the form of thin films and sheets, is a.c. calorimetry [2]. Figure 1 illustrates schematically the principle on which the calorimeter is based. The front surface of a specimen is irradiated with light from a halogen lamp chopped at frequency  $f$ , usually between 0.01 and 30 Hz. By using a specially designed lock-in amplifier, the temperature amplitude  $T_{ac}$  is measured with high sensitivity on the rear surface of the specimen.

The heat capacity  $C$  is given by

$$C = \frac{Q}{\omega |T_{ac}|} \quad (1)$$

where  $Q$  is the heat flow during one cycle,  $\omega$  the frequency, and  $T_{ac}$  is an amplitude of temperature variation.

In this measurement and that of thermal diffusivity, as discussed later, the thickness of the specimen has to be less than the thermal diffusion length which is given by  $(2D/\omega)^{1/2}$ . For the measurement a small specimen of the order of a maximum of 4 mm  $\times$  4 mm  $\times$  (0.1–0.3) mm for absolute values and 2 mm  $\times$  2 mm by 0.01 mm for relative values is supported inside the furnace by two 25  $\mu$ m thermocouple wires welded together and attached with a silver paste. Helium gas is introduced in the specimen cell to maximize heat transfer between the specimen and surroundings.

Absolute values can be obtained provided that  $T_{ac}$  values are also measured for a reference specimen(s) of known specific heat, e.g. sapphire, and the slopes of the plots of  $1/T_{ac}$  vs. frequency are compared. However, the technique is most valuable for determining changes in heat capacity, e.g. changes due to phase transitions, over a very small temperature range. Because the actual rise in temperature during a measurement is only millikelvins, the conditions may be described as stationary or quasi-adia-

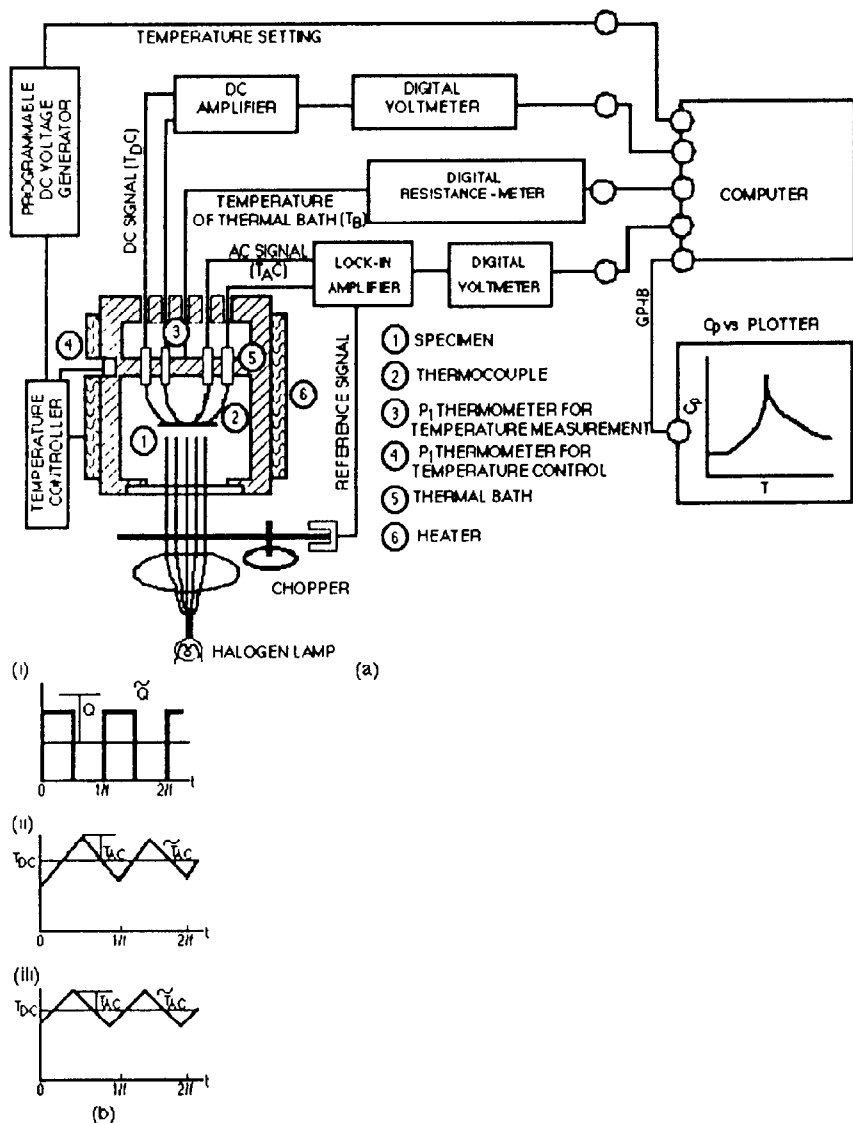


Fig. 1. (a) Schematic diagram of the principle of a.c. calorimetry. (b) (i) Square periodic wave of the a.c. heat produced by chopping light. (ii) A.c. temperature response to the square of the periodic heat wave for the case with small heat capacity. (iii) A.c. temperature response for the case with large heat capacity.

batic. The sensitivity is some  $10^2$ – $10^3$  greater than that obtained by DSC measurements [3].

This precise high sensitivity apparatus has been used over a broad temperature range from 20 to 800 K for a variety of applications particularly in studying minute phase transitions in materials that include polymers, liquid crystals, and dielectric and superconductive ceramics.

### *Thermal diffusivity and thermal conductivity*

There are two widely used transient techniques for measurements of the thermal diffusivity of small specimens and the derived thermal conductivity. In both cases it is possible to measure specific heat directly by modifying the basic technique to include measurements on specimen(s) of known heat capacity.

#### *Transitory temperature (“flash”) method*

This method was originally developed around 1960 by Parker et al. [4] for measuring the thermal diffusivity, and specific heat under certain conditions, of small, flat, uniform, homogeneous discs using a flash lamp source of energy. Since that time the basic method, now using a laser energy source, and its many variations and modifications based on a variety of models for different applications, has evolved into the one that has been used for the broadest range of materials over a very wide temperature range.

The principle and application are well documented and need not be discussed in detail [5]. The front face of a specimen is subjected to a short burst of radiant energy for 1 ms or less. The temperature history of the rear surface is measured and the thermal diffusivity  $D$  is computed from values of the half-time (time to reach 50% of maximum) and the square of the thickness. Other percentage times can be used depending on the analytical model used.

The prime advantages are utilization of small disc-shaped specimens of the order of 10 mm in diameter and 1–4 mm thick, depending on the thermal properties of the material, and short measurement times of much less than 1 s. More recently we have evaluated specimens less than 1 mm thick by attenuating the laser beam by a factor of 10 or more to ensure that the temperature rise is kept below 5 K.

While this technique may be considered revolutionary it is by no means a panacea for all materials and applications. There are instances where the method has been misapplied to an inhomogeneous or a highly anisotropic material. A more common occurrence has been in a mistaken application of the common relationship relating  $D$  to the thermal conductivity  $\lambda$ , the volume specific heat  $C_p$  and density  $\rho$

$$D = \lambda / \rho C_p \quad (2)$$

in order to derive thermal conductivity for all materials from the results. It must always be remembered that use of the term  $D$  applies only for the case where predominant heat transmission is by the solid conduction mode. It is not truly applicable to inhomogeneous materials, where other heat transmission modes, particularly radiation, occur.

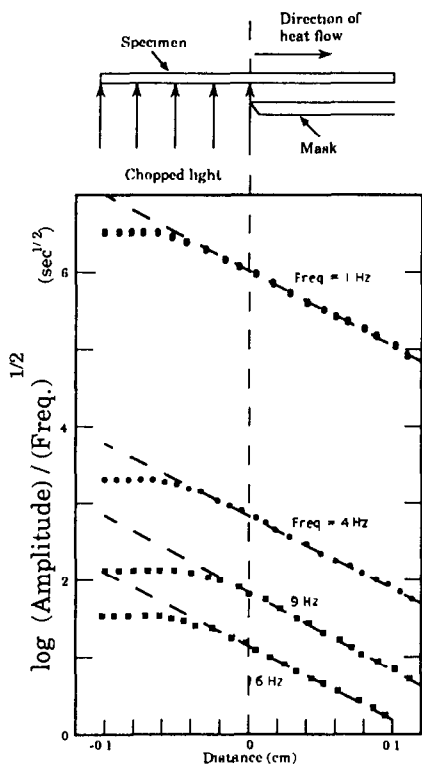


Fig. 2. Cross-section view of modified a.c. calorimeter technique and relation of output in distance for a specimen measured at different frequencies.

### *A.c. calorimeter method*

This recent modification [6] of the previously discussed a.c. calorimeter technique was developed specifically for very thin specimens of a variety of materials, including composite layered structures.

The basic technique and apparatus are somewhat similar to those for the a.c. calorimeter. The principle is illustrated schematically in Fig. 2. The optimum specimen is a rectangle  $10 \text{ mm} \times 4 \text{ mm}$ , less than  $0.3 \text{ mm}$  thick. Instead of illuminating the complete surface of the specimen, only part of it is subjected to the periodic thermal energy from a light source such as a halogen light or laser. The remainder is masked from the chopped-light irradiation. The a.c. temperature at a position on the specimen under the mask is measured using a very fine thermocouple ( $25 \mu\text{m}$  wires) attached by means of a silver paste to and supporting the specimen.

The thermal diffusivity  $D$  in the direction parallel to the surface of the specimen is obtained by measuring the a.c. temperature  $T$  as a function of distance  $x$  between the position of the sensor and the edge of the mask. In the instrument, the mask is moved with respect to a fixed specimen.

The relation  $|T|$  vs.  $x$  is given by

$$|T| = \frac{Q \exp(-kx)}{2\omega cl} \quad (3)$$

where  $Q$  is the amplitude of the applied energy flux for unit area,  $\omega$  is the angular frequency of the periodic heating,  $c$  the heat capacity of the specimen,  $l$  the specimen thickness and  $k$  the thermal decay constant  $(\omega/2D)^{1/2}$  or  $(\pi f/D)^{1/2}$  where  $f$  is  $\omega/2\pi$ , the a.c. frequency. The value of  $D$  can thus be obtained very accurately from the decay constant. Because the temperature rise is very small, the measurement can be considered as quasi-steady state and the method is particularly useful for detailed quantitative studies, for example in transition regions.

Frequently,  $k$  is called the thermal wavenumber and  $1/k$  the thermal diffusion length. In order to satisfy the one-dimensional system condition, the relationship  $kl < 0.1$  must be satisfied. Some examples of maximum thickness at 1 Hz for materials commonly used as thin films range from 0.02 mm for polymers to 0.6 mm for copper and 2 mm for diamond. Thus it is seen that measurements are possible for most kinds of materials in the form of thin films and for a broad range of thermal diffusivity values.

More recent work indicates that  $D$  for the direction perpendicular to the surface can also be determined but with lower accuracy than for the parallel direction [7]. Measurements can also be made on specimens consisting of single wires and fibers. It should also be pointed out that thermal diffusivity and thermal conductivity are very sensitive to structure differences. Thus the evaluation can be used for studying the existence of local variations of quality over larger areas of a specimen [8].

### *Thermal expansion*

Accurate measurements of the expansivity of specimens of limited length can be considered analogous to those on materials of very low coefficient of thermal expansion. The change in the measured dimension is very small and thus the technique used has to be one where such small changes can be measured accurately. Push rod dilatometry and thermomechanical analysis techniques are unsuitable for such measurements because the most accurate detection of change in thickness is at best in the order of  $\pm 1 \mu\text{m}$ . For small specimens and low expansion materials a detection precision of better than  $0.1 \mu\text{m}$  is necessary.

Optical interferometry offers one of the best means of measuring length changes to such higher orders of accuracy. In the past, single-beam interferometry has been used [9]. However, we have recently developed a dual-beam automated system based on a modified Michelson interferometer which now provides twice the sensitivity [10]. In addition, owing to the

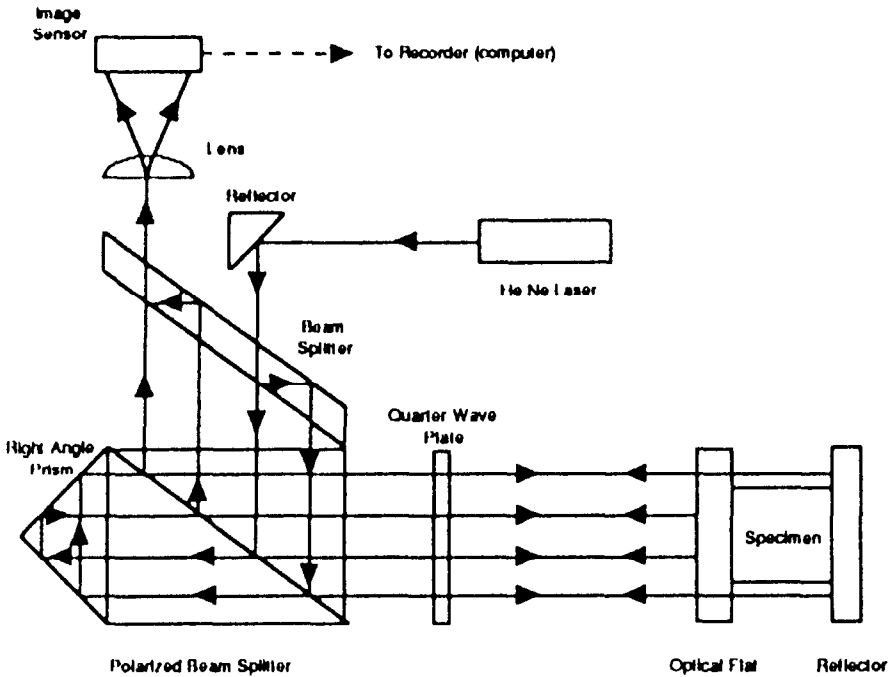


Fig. 3. Optical arrangement of the dual beam interferometer for linear expansion measurement.

design, the specimens require less critical attention in fabrication or machining.

The method, illustrated schematically in Fig. 3, employs a highly stabilized He–Ne gas laser and optical system. The test specimen is sandwiched between two mirrors which are maintained parallel to each other by a specially designed parallel springs movement mechanism with zero friction. The mirrors are made of fused silica with the surfaces partially coated with gold. The linearly polarized laser beam is split into two by the beam splitter; these go through the quarter waveplate, are reflected at the inner and outer mirrors and return, thus creating interference fringes as the specimen changes in length. As the specimen is heated and cooled, the fringe pattern is expanded by the negative cylindrical lens and falls on the linear image sensor which detects movement of the multipeak pattern.

A microcomputer analyzes this every 0.5 s to obtain the position of the peaks  $A_0, A_1, A_2, \dots$ , and calculates the absolute positive or negative length change  $l$  (nm) using

$$l = \frac{A_1}{A_1 - A_0} \frac{632.8}{4} \quad (4)$$



with the wavelength of the HeNe laser (632.8 nm) as the reference for calibration. Dimensional changes can be resolved with an absolute accuracy of  $0.02 \mu\text{m}$  ( $200 \text{ \AA}$ ) which is equivalent to  $1/32$  of the wavelength of the gas laser.

For any measurement of thermal expansion, the specimen should have as large a length dimension as practically possible for the particular measurement device. While the present system is designed for specimens up to 15 mm long and 6 mm in diameter, it can also be used for thin sheets, certainly for those less than 1 mm in thickness. For this, the specimen is sandwiched between glass distance pieces of known thermal expansion, flat on the inner faces and rounded on the opposite ends and placed between the mirrors.

The necessary high performance required to demonstrate the potential of this system has been shown by measurements on reference materials and more recently on two low-thermal-expansion glasses (Zerodur and ULE) over the approximate range 120–420 K [11]. In this study, the reproducibility of measurement by the dual-beam technique was  $\pm 3 \times 10^{-8}$  and  $\pm 3.8 \times 10^{-8} \text{ K}^{-1}$  for the linear coefficient of the two glasses and the overall uncertainty was  $\pm 4 \times 10^{-8} \text{ K}^{-1}$ .

## SUMMARY

Several new or improved techniques developed specifically for accurately measuring thermal parameters but which can also be used for qualitative measurements are described. These provide the materials scientist with more flexible, higher precision tools for materials characterization purposes.

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