History repeats itself: Progress in a.c. calorimetry

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Abstract

Periodic heating has been applied more than a century ago to study thermophysical properties of materials. The measurement of heat capacity using a.c. calorimetry was first performed by Corbino in 1910. In connection with the technological development and the progress in science and technology, new and sophisticated apparatus have been constructed in an a.c. calorimetric heat capacity measurements. In this measurement, the noise level of a.c. temperature can be reduced markedly as opposed to the other nonperiodic methods and, therefore, high precision determination can be attained. Furthermore, not only the amplitude but also the phase in a.c. temperature is a useful parameter in constructing much advanced apparatus. © 1997 Elsevier Science B.V.

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1. Prologue

I will use the terminology 'a.c. calorimetry' in this paper, since I began to study heat capacity measurements at the stage of rediscovery of such a calorimeter by Sullivan and Seidel [1–3] and by Handler et al. [4]. These authors had used the terms a.c. temperature calorimetry or a.c. measurement.

The first measurement of heat capacity by an a.c. calorimetric method was performed for metals in 1910 by Corbino [5]. In the measurement, an a.c. electric current was fed to a metal sample, the sample was heated with the double frequency and from the resistance oscillation the a.c. temperature of the sample was detected. Therefore, in the beginning the detec-

tion of the third harmonic signal had been developed [6]. In 1962, the similar measurement for tungsten was rediscovered but in a high temperature region of 1600 to 3000 K by Kraftmakher [7]. In the measurement, a characteristic of a.c. calorimetry was used efficiently, because the effects of the a.c. heat dissipation from a sample were excluded when the period of a.c. temperature was so chosen as to be far shorter than the relaxation time caused by the radiation heat loss.

An a.c. calorimeter which can be applied to electrical insulating materials in a low temperature region and in a medium temperature region was developed in 1966 by Sullivan and Seidel [1] and subsequently, in 1967 by Handler et al. [5]. In the former, a.c. heat is applied to a sample by Joule heating, where a.c. electric current is fed to a resistance attached to the sample. In the latter, a.c. heat is applied to a sample by chopped light-irradiation, where the sample is

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suspended, for instance, by a fine thermocouple. In both the measurements, a.c. signal is detected by a lock-in amplifier and therefore, the heat capacity can be measured with high precision. Therefore, they give a distinctly valuable evidence in comparison with the previous measurements. As a calorimeter, an a.c. calorimetric method has great advantage in comparison with the other nonperiodic methods, because the noise level can be reduced markedly by using a lock-in amplifier. It should be pointed out that the information of phase of a.c. temperature, detected by a lock-in amplifier, is useful for verifying the experimental conditions. Recently, using a computer-controlled system, both the amplitude and phase of a.c. temperature can be detected easily, since an a.c. calorimetric method usually works at a low frequency. The measurements of Sullivan and Seidel and Handler et al. have influenced the following a.c. calorimetric measurements. In particular, the a.c. calorimetric methods have been used extensively in the studies of phase transitions [8–10].

2. Monologue

2.1. Not only the amplitude but the phase in a.c. temperature also gives useful evidence

In a light-irradiation a.c. calorimetric method, chopped light with an angular frequency of ω is applied to the front surface of a sample, which is suspended in a vessel held at a constant temperature.

Then, the vessel works as a thermal bath. To analyze the behavior of a.c. temperature, let us consider the one-dimensional system shown in Fig. 1. This system has been discussed by Sullivan and Seidel [3]. Based upon their results, we modified the expression for the a.c. temperature $T_{a.c.}$ at the rear surface of the sample as [8]

$$T_{a.c.} = \frac{Q}{\omega C}\left[1 + \frac{1}{\omega^2\tau_e^2} + \omega^2\tau_i^2 + \sqrt{40}\frac{\tau_i}{\tau_e}\right]^{-1/2} e^{-i\theta}$$
(1)

and, in addition, we derived its phase as [8]

$$\theta = \arcsin\left[1 - \frac{1}{\omega^2\tau_e^2} - \frac{7\omega^2\tau_i^2}{3} - \sqrt{10}\frac{\tau_i}{\tau_e}\right]$$
(2)

where C is the heat capacity of a sample per unit area (=heat capacity per unit volume times sample thickness), Q the applied thermal energy per unit area, and τ_e and τ_i the external and internal relaxation times, respectively. τ_e is the relaxation time required for dissipation of thermal energy stored in the sample through thermal linkage between the sample and the vessel, which is given by CR (R being the thermal resistance per unit area between the sample and the vessel) and τ_i the internal relaxation time required for attaining a uniform temperature when thermal energy is applied to the sample, which is given by $\sqrt{90D}/2\pi L^2$ (D being the thermal diffusivity of the sample and L the sample thickness).

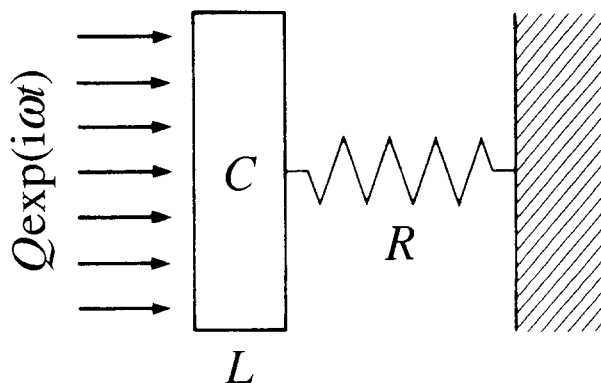In Eqs. (1) and (2), the frequency dependencies of the bracketed terms are similar to one another. When

Fig. 1. One-dimensional model for an a.c. calorimetric heat capacity measurement. Periodic heat flux $Q\exp(i\omega t)$ is applied to a sample with heat capacity C and thickness L. A part of the periodic heat flux dissipates to the thermal bath held at a constant temperature through a thermal resistance R.

$1/\tau_e < \omega < 1/\tau_i$, Eq. (1) becomes

$$T_{\text{a.c.}} = \frac{Q}{i\omega C} \qquad (3)$$

since $\theta = \pi/2$. In the above-mentioned inequality for the frequency conditions, the low-frequency limit is due to the external relaxation time. For instance, in a medium temperature region, it is usually several seconds. On the other hand, the high-frequency limit is due to the internal relaxation time. The internal relaxation time depends markedly on materials, i.e., in a metal it is quite short, but in a polymer it is long. Further details will be discussed later.

In the measurements at low temperatures, a Joule-heating a.c. calorimetric method is useful. In this case, equations similar to Eqs. (1) and (2) hold except for the terms of τ_i/τ_e. The meaning of τ_i and τ_e should be slightly modified, that is, the main component in τ_i is due to the internal relaxation times between a sample and a temperature sensor and between a sample and a heater attached to the sample, since the thermal diffusivity of a sample becomes markedly large in a low temperature region and, furthermore, τ_e is largely due to the thermal conductance between a sample and a thermal bath through the lead wires for the temperature sensor and the heater.

As discussed above, the frequency region in which an a.c. calorimetric heat capacity measurement is performed should be chosen rightly. As seen in Eq. (1), from the frequency dependence of the amplitude of a.c. temperature we can set the measuring frequency, i.e. in a proper frequency region the amplitude of a.c. temperature is proportional to the inverse of the frequency. The frequency dependence of the phase of a.c. temperature is very sensitive as seen in Eq. (2), i.e. the derivation from $\pi/2$ is comparatively large. It should be pointed out that, when we measure the temperature dependence of heat capacity, the phase gives another useful parameter for verifying the experimental conditions. Because both τ_i and τ_e generally depend on temperature and therefore, the proper frequency condition can be examined during the heat capacity measurement by detecting the phase deviation with temperature.

Sometimes, however, it happens that the proper frequency range is too narrow. For such a case, it was considered to extend the measuring frequency range to a low-frequency range, where the contribu-

tion of heat loss was remarkable. If the external relaxation is expressed by a single exponential decay which was the case in [11,12], the a.c. temperature in a low-frequency range is given strictly by [13,14]

$$T_{\text{a.c.}} = \frac{Q}{\omega C}\left[1 + \frac{1}{\omega^2\tau_e^2}\right]^{-1/2} e^{-i\theta} \qquad (4)$$

$$\theta = \arcsin\left[1 + \frac{1}{\omega^2\tau_e^2}\right]^{-1/2} \qquad (5)$$

This corresponds exactly to the situation for Fig. 1. Therefore, the thermal diffusivity of a sample is large enough, i.e. $\omega\tau_i \ll 1$. However, the term related to the relaxation time τ_e remains. On measuring both the amplitude and the phase in a.c. temperature, we can obtain the heat capacity without the correction for heat loss as seen from Eqs. (4) and (5). In the measurement using this method, attention should be paid to the fact that the external relaxation time depends on temperature, and that the phase should be measured at each temperature.

2.2. Precise heat capacity determination of liquid and the importance of phase measurement

The determination of absolute value of heat capacity is important when analyzing the results for further thermodynamic analysis, theoretical consideration, etc. However, it is not so easy to obtain this value with a high accuracy using a.c. calorimetric method. Because the thermal energy applied by light-irradiation is not determined directly, the addenda, e.g. a temperature sensor, a heater, etc. also contribute and therefore it is difficult to quantitatively estimate the heat loss.

For a small amount of a liquid sample, we have developed a method to measure the absolute value of the heat capacity [15]. A stainless steel cell was used, shown in Fig. 2, as a sample cell . The size of the cell: 130 μm i.d ; 170 μm o.d; and 39 mm in length. The cell was filled with 0.52 μl of a liquid sample. Polyethylene tubes with low thermal conductivity were connected to both ends of the tube-like stainless steel cell, and through the polyethylene tubes a liquid sample was injected into the sample cell by a microsyringe. Here, it should be pointed out that it is quite easy to handle the sample. The a.c. heat flux was applied to the cell by chopped light from a halogen
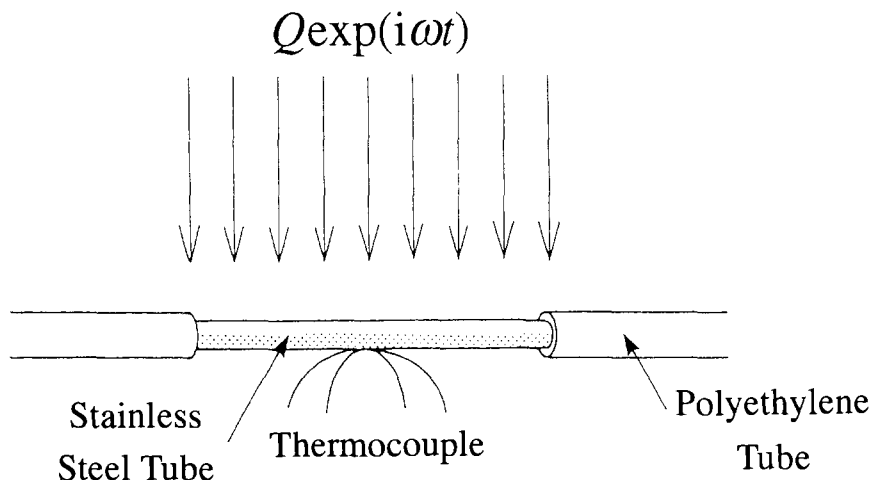
$$Q\exp(i\omega t)$$

Fig. 2. A cell for precise heat capacity determination of a liquid sample. The cell is composed of a fine stainless steel tube with thin wall, to whose inlet and outlet polyethylene tubes are connected. Periodic heat flux $Q\exp(i\omega t)$ is applied to the upper side of the tube. The a.c. temperature of the tube is detected by a thermocouple.

lamp. The a.c. temperature was detected by a thermocouple of 12.5 μm diameter, which was welded to the stainless steel tube. The measuring frequency was chosen to be 1 Hz so as to satisfy the condition of $1/\tau_e < \omega < 1/\tau_i$.

To obtain the absolute value of the heat capacity, the a.c. temperatures of the empty cell, the cell filled with a standard sample and the cell filled with a liquid sample were measured and are denoted by T_c and T_{cr} and T_{cs}, respectively. The a.c. temperature T_c is given by

$$T_c = \frac{Q_0}{i\omega C_c} \tag{6}$$

where Q_0 is the applied a.c. thermal energy per unit length and C_c is the heat capacity of the empty cell per unit length. The a.c. temperature T_{cr} is given by

$$T_{cr} = \frac{Q_0}{i\omega(C_c + C_r)} \tag{7}$$

where C_r is the heat capacity of the standard sample per unit length filed in the inner cell. On the other hand, the a.c. temperature T_{cs} is given by

$$T_{cs} = \frac{Q_0}{i\omega(C_c + C_s)} \tag{8}$$

where C_s is the heat capacity of the liquid sample per unit length filled in the inner cell. From Eqs. (6)–(8), we obtain the simple relation:

$$C_s = \frac{T_{cs}^{-1} - T_c^{-1}}{T_{cr}^{-1} - T_c^{-1}} C_r \tag{9}$$

In this measurement, it is of importance to keep the stability of the intensity of a halogen lamp. To test the accuracy of the calorimeter, the heat capacity of n-heptane was measured at 30°C. As a standard sample, we used pure water. From this test, it was established that the heat capacity of a liquid sample can be obtained within an accuracy of 1%.

It should be pointed out that this method can be extended to the case when heat loss takes place. In such a case, in Eqs. (6)–(8) the thermal conductance K between the cell and the vessel is added to the denominators. Nevertheless, the same relation as Eq. (9) holds. Then, the measuring frequency can be easily extended to a low-frequency range. Thus, when there is no heat loss in the measurement, we can observe the a.c. temperatures with the phase of $\pi/2$ as expected from Eqs. (6)–(8) and, on the other hand, when heat loss becomes significant, the phases of the a.c. temperatures are no longer the same and, therefore, the complex a.c. temperatures should be taken into account. Even in the latter situation, if we use the complex a.c. temperatures instead of the a.c. temperatures with the same phase, $\pi/2$, in Eq. (9), we can obtain the heat capacity C_s from Eq. (9) with the complex a.c. temperatures. The foregoing fact indicates that the measurements of both the amplitude and

the phase in a.c. temperature hold significance in an a.c. calorimetric heat capacity measurement.

Recently, a dynamic differential scanning calorimeter has been developed by Reading et al. [16]. From the viewpoint of a.c. calorimetry, it offers the possibility to measure the absolute value of heat capacity and, furthermore, it is easy to handle since a sample pan for a usual differential scanning calorimeter can be used. However, insofar as we are interested in the modulated temperature mode operation, it is not necessary to scan the temperature. In the a.c. calorimetric measurement at a stationary temperature, the a.c. heat flux is supplied to a cell on the base plate through a heat conducting material. In usual differential scanning calorimetry, two cells, one sample and the other reference, are placed symmetrically on the base plate and the temperature difference between the two cells is measured. In the a.c. calorimetric operation, there are mainly two important parameters. One is related to the effective heat capacity around the cell [17,18], and the other is the thermal conductance between the cell and the base plate [19]. We considered a thermal system by taking into account two parameters. A model system is shown in Fig. 3, in which we do not place a reference cell at the reference side, because, if we do so, another uncontrollable thermal conductance between the cell and the base plate is added.

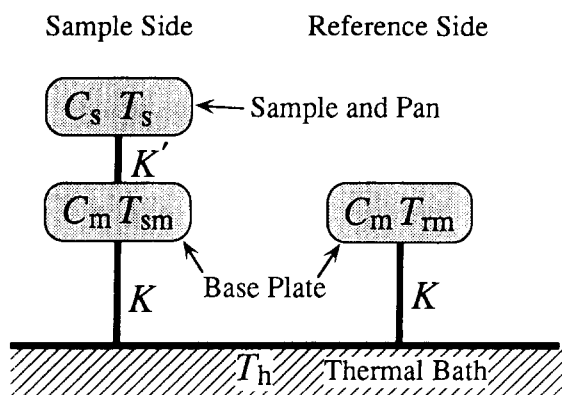Sample Side   Reference Side

Fig. 3. A model system for high precision heat capacity measurement by means of dynamic differential scanning calorimetry. A pan containing a sample is placed on the sample side with no pan on the reference side. C_s is the total heat capacity of the pan and the sample, K' is the thermal transfer coefficient between sample pan and the base plate.

In the model system, C_s is the sum of the heat capacities of the sample and the pan, C_m the effective heat capacity of the base plate, K' the heat transfer coefficient between the pan and the base plate, and K the heat transfer coefficient between the base plate and the heater. T_s is the a.c. temperature of the sample with the pan, T_{sm} and T_{rm} the a.c. temperatures of the base plate on the sample and the reference sides, respectively, and T_h the a.c. temperature of the heater. Let us define T_{sm} and $\Delta T (= T_{rm} - T_{sm})$ as

$$T_{sm} = A_{sm}\exp[i(\omega t + \varepsilon)] \tag{10}$$

$$\Delta T = A_\Delta \exp[i(\omega t + \delta)] \tag{11}$$

where A_{sm} and A_Δ are the amplitudes of the a.c. temperature, and ε and δ the phases with respect to the a.c. temperature of the heater. From the measurement, A_{sm} and A_Δ are observable and $\Phi(= \delta - \varepsilon)$ can be obtained. Furthermore, K is determined separately. By analyzing the thermal system, the following relations are finally obtained [19]:

$$R = \frac{\frac{KA_\Delta}{\omega A_{sm}}}{C_s} = \frac{1}{\sqrt{\left[1 + \omega^2 \left(\frac{C_s}{K'}\right)^2\right]\left[1 + \omega^2 \left(\frac{C_m}{K}\right)^2\right]}} \tag{12}$$

$$\sin\Phi = \frac{1 - \omega^2 \frac{C_s C_m}{K' K}}{\sqrt{\left[1 + \omega^2 \left(\frac{C_s}{K'}\right)^2\right]\left[1 + \omega^2 \left(\frac{C_m}{K}\right)^2\right]}} \tag{13}$$

where the ratio R is defined by Eq. (12). For an angular frequency at a given temperature, as seen in Eqs. (12) and (13), R and $\sin\Phi$ are given as functions of C_s/K' and C_m/K. C_s/K' depends on a sample and the setting condition of the sample pan and, on the other hand, C_m/K is constant when the system is given. If the sample is altered, both R and $\sin\Phi$ vary as a single-valued function and, as a result, the relation of R vs. $\sin\Phi$ gives a single curve. In Fig. 4(a), the curves for the periods $P(= 2\pi/\omega) = 100$ and 20 s are shown. They represent a calibration curve for each period, i.e. when we observe Φ, we can determine the value of R and, finally, obtain C_s from the relation, $R = (KA_\Delta/\omega A_{sm})/C_s$. It should be pointed out that, even if K' is changed by setting the pan, the point moves along the single curve, i.e. the calibration can be performed notwithstanding the existence of an uncontrollable parameter K'.
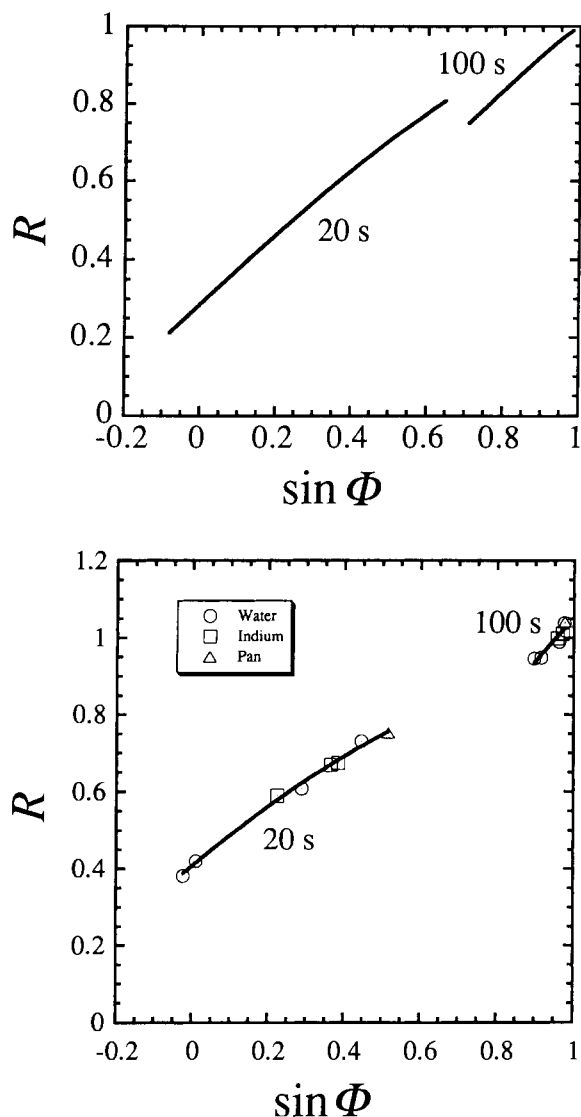
Fig. 4. (a) Calibration curves theoretically obtained at $P = 100$ and 20 s. R is defined in Eq. (12). C_m/K is 1 s. As seen in Eqs. (12) and (13), under the above conditions which are fixed during the experiment, the only variable is C_s/K'. Thus, according to this magnitude the calibration point moves along each curve. (b) Calibration plots obtained from the experimental test for $P = 100$ and 20 s. On both the curves for $P = 100$s and $P = 20$s, the empty triangle indicates the plot for a vacant aluminum pan, the empty squares for the pan with indium whose weight in both curves is 65, 90 and 173 mg moving downward, and the empty circles for the pan with water whose weight in both curves is 6, 11, 14 and 17 mg moving downward. The thick curves are drawn for guiding the eye. It is clear that the experimental results for $P = 100$ and 20 s lie on a single curve. Furthermore, it should be pointed out that the behavior of these curves is quite similar to that of the theoretical curve.

For the experimental test, we used a commercial modulated differential scanning calorimeter, Type 2920 of TA Instruments. We measured R and Φ at modulated periods P of 20 and 100 s. Indium and pure water were chosen as samples with known heat capacities. The samples were sealed in an aluminum pan. The measurements were carried out at 60°C. Fig. 4(b) shows the experimentally obtained relationships between R and $\sin\Phi$. The tendency of the curves is well expressed in terms of Eqs. (12) and (13). Therefore, this result indicates that the two parameters, C_m/K and K', play an important role. Practically, it is important to clarify the fact that the relation of R vs. $\sin\Phi$ gives a single curve in the experimental test. If this is the case, the curve can be used strictly as a calibration curve. From these experiments, it was found that the heat capacity can be determined within an accuracy of 1% at the period of 100 s.

I should say again that measurement of both the amplitude and the phase in a.c. temperature is generally important in the a.c. calorimetric method. Furthermore, in the precise heat capacity measurement, using a dynamic differential scanning calorimeter, it is noteworthy to point out that we can exclude the uncertainty caused by thermal conductance between a sample cell and the base plate.

3. Epilogue

A temperature modulation method has a variety of applications not only in heat capacity measurements but also in measurements of other thermophysical properties. As early as 1861, Ångström [20] had developed a method, in which a rod is heated at one end periodically and the temperature wave is detected at two points along the rod. At that time the importance of the measurement of both the amplitude and the phase in a.c. temperature had already been revealed in determining thermal diffusivity of the rod. Later, the same method of the measurements was proposed once again. For instance, I have found that our paper [21] concerned with the a.c. calorimetric thermal diffusivity measurement of *thin films* under a heat-loss condition was essentially the same.

Methods of measurements, developed subsequently, using thermal wave or periodic heating are more or less related to the treatment of Ångström [20].

A very useful and elegant expression has been offered by Carslaw and Jalger [22]. When periodic heating takes place inside a material, it results in a temperature wave, giving rise to the a.c. temperature which is expressed as [22],

$$T(x) = T_0 \exp[-(1 + i)kx] \tag{14}$$

$$k = \sqrt{\frac{\omega}{2D}} \tag{15}$$

where T_0 is a constant, x the distance and D the thermal diffusivity of the material. As can be seen from Eq. (14), and k implies not only the thermal decay constant but also the thermal wave number. We can find these quantities in many fields, for instance, a photoacoustic method [23], heat capacity spectroscopy [24], etc. Besides, $1/k$ is sometimes called thermal diffusion length or thermal wavelength, according to the field.

In a.c. calorimetry, it is also useful to consider the quantity k as an experimental condition. The condition for the high-frequency limit $\omega \tau_i < 1$, is replaced by $kL < 1$. Since, $1/k$ is 6 mm in aluminum, 0.5 mm in glass, and 0.2 mm in polyethylene at room temperature and at 1 Hz, the condition depends on the sample. In this way, according to the sample, the sample thickness L should be chosen in a proper length.

It is noteworthy that a.c. calorimetry originated more than a hundred years ago. With the passage of time, it has been reconsidered according to the development of technology and, therefore, much sophisticated apparatus have been constructed. Although the progress appears to be slow, the methodology of a.c. calorimetry advances steadily.

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