Photopyroelectric Method for Determination of Thermophysical Parameters and Detection of Phase Transitions in Fatty Acids and Triglycerides. Part I: Principles, Theory, and Instrumentational Concepts

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ABSTRACT: The photopyroelectric (PPE) technique is proposed to detect solid-to-liquid phase transitions in fatty acids and triglycerides. Various PPE configurations and cell geometries were used to obtain thermal parameters in the vicinity of the melting points for these samples. In the standard (SPPE) configuration used to determine specific heat, the sample is thermally thin and optically opaque, while the sensor itself is thermally thick. The same configuration, but with a thermally thick sample instead, allows direct measurement of the sample's thermal diffusivity. The temperature dependence of the thermal effusivity was obtained for a thermally thick sample and a thermally thin sensor [inverse (IPPE) configuration], and for a semitransparent thermally thick sensor by making use of the front configuration.

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The ability to measure thermophysical properties of edible oils and fats in a quick, sensitive and reproducible fashion is an important aspect of their industrial manufacture (1). Another area where such data are useful is the development of new products. Among data of interest are those associated with phase transition, in particular with the process of melting. A great deal of information has become accessible on the thermal behavior of materials as they undergo physical (and chemical) changes during heat treatment through differential scanning calorimetry (DSC). DSC measures the amount of heat involved when the material undergoes an endothermic or exothermic transition (2). DSC, together with dilatometry and low-resolution pulsed (and continuous-wave) nuclear magnetic resonance (NMR) spectroscopies, is used to measure the solid-fat index (SFI) (a ratio of solid to liquid in partially crystallized lipid at a given temperature). However, these methods are tedious and costly; therefore, alternative and inexpensive techniques would be a welcome addition to thermal analysis practices.

In this paper, an instrument and a novel experimental methodology, based on the use of photopyroelectric (PPE) technique, have been proposed to determine values of thermophysical parameters (thermal conductivity, effusivity, diffusivity, and the volume specific heat) of some fatty acids and triglycerides within the range of temperatures that encompasses their melting points. During the last few years, the PPE technique has been applied to investigate the optical and thermal parameters of various materials. Basically, the PPE approach is concerned with the detection (pyroelectric sensor) of a voltage that is proportional to the temperature variation of a sample exposed to a modulated radiation (3,4). Various experimental configurations and PPE cell geometries have been proposed to increase the sensitivity of the method and the accuracy of measurements (5). In studies dealing with the determination of thermal parameters, much effort has been devoted to simplifying the general expression for the PPE signal (3) and to obtain experimental conditions for which the amplitude or phase of the PPE signal depends solely on a single sample's related thermal parameter, thereby allowing its direct evaluation. In principle, there are several PPE configurations that offer the possibility to measure one or two sample's related thermal parameters, provided some experimental conditions are well defined (6,7), i.e., the sample is optically opaque and thermally thin (or thick), the thick-

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ness of the sample is rigorously controlled, the sensor is opaque (or semitransparent) and thermally thin (or thick), etc. When, however, the sample is a partially transparent material (such as a fatty acid or triglyceride) that undergoes a solid to liquid phase transition, the requirements mentioned above are not easily met; consequently, filters or special PPE cell geometries must be used. For study, the simplest and most suitable among these configurations were selected and applied in practice to determine the temperature dependence (including the melting point) of thermophysical parameters for some lipids.

Theory. Figure 1 features major PPE configurations used successfully to investigate thermal parameters of various materials. In the so-called standard (SPPE) configuration, the front surface of the sample is exposed to a modulated light, while the pyroelectric sensor (glued to the rear side of the sample with a coupling fluid) measures the sample's temperature variation. In the inverse (IPPE) configuration (some authors call it "front configuration"), the light impinges directly on the front surface of the sensor, with the sample (in good thermal contact with the sensor's rear side) acting as a heat sink.

Whether the sample (sensor) is thermally thin or thick depends on the ratio of actual thickness of the sample (sensor) and the corresponding thermal diffusion length at a given modulation frequency. The information collected in a PPE measurement is contained in the amplitude V and phase ϕ of the complex PPE signal. Figure 1 suggests that for the experimental conditions that are likely to be realized in practice, the amplitude (and/or phase) of the PPE signal depends on one (or two) sample's related thermal parameters, i.e., the volume-specific heat C_s, thermal effusivity e_s and the thermal diffusivity α_s, where subscript "s" refers to the sample. When analyzing the diagram, one can conclude that some configurations (a1.1, a2, b1.1, and b1.2, b2) eventually lead to the same results; in such cases, the most suitable option must be selected. For example, commercially available pyroelectric sensors are usually rather thick (400–1000 μm); and consequently, the standard configuration a1 appears more suitable than a2. On the other hand, the term "thermally thin" for a fatty acid implies a layer of 100 μm (or less) at a chopping frequency of 0.1–0.2 Hz. In the inverse configuration, this thickness must be precisely controlled while at the same time maintaining good thermal contact between the sample and a thin and flexible polyvinylidene difluoride (PVDF) foil is a necessity. Practical difficulties in performing an experiment of type b1.1 are self-evident.

Bearing in mind the characteristics of the sample, configurations a1, b1.2, and b2 appear most suitable to obtain the temperature dependence of the thermophysical parameters for fatty acids around their melting points.

Configuration a1.1. Mandelis *et al.* (8) showed that, for a thermally thick sensor and an optically opaque sample, the magnitude V of the PPE signal in the standard configuration is given by:

$$V = \frac{pH_0}{2\varepsilon} \bullet \frac{1}{\sigma_p k_s \, \sigma_s \sinh(\sigma_s L_s)} \qquad [1]$$

where p is the pyroelectric coefficient of the sensor, H_0 is the intensity of the incident radiation, ε represents the electrical permitivity of the detector, and L_s and k_s are the thickness and

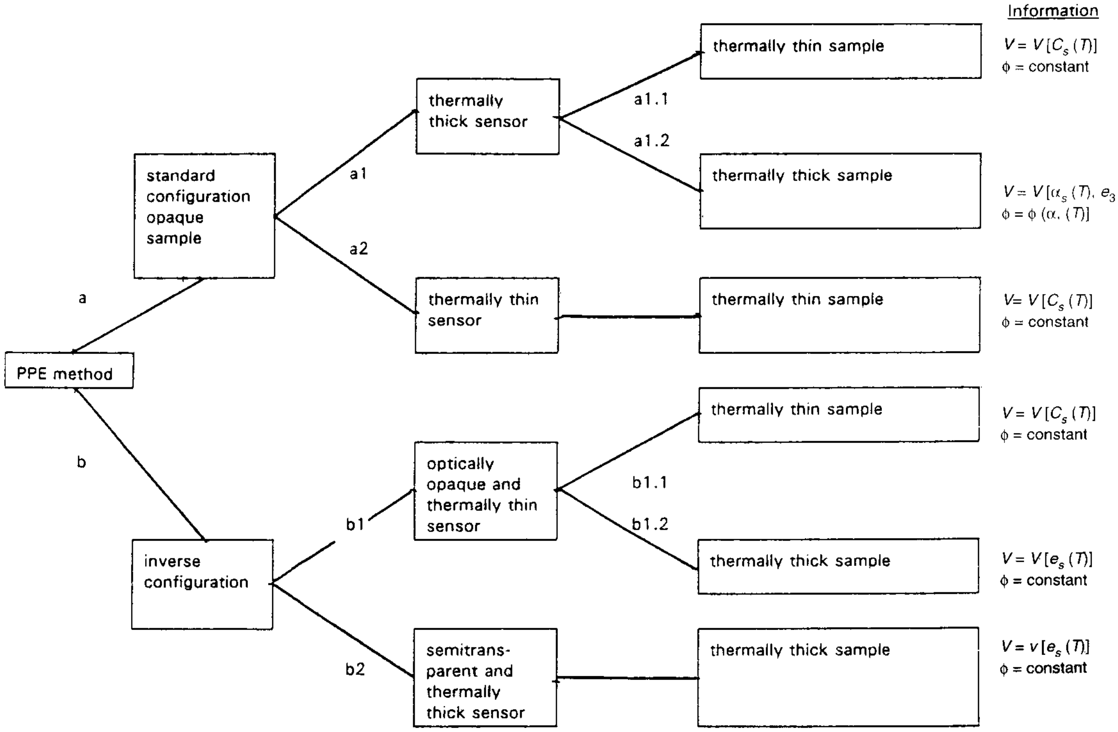

FIG. 1. Special photopyroelectric (PPE) configurations for investigation of thermal parameters.

the thermal conductivity of the sample, respectively. This latter parameter is related to the thermal effusivity e, thermal diffusivity α and the volume-specific heat C through the relationships:

$$C = \rho \bullet c = \frac{\mathrm{k}}{\alpha} \text{ and } e = (C \bullet \mathrm{k})^{1/2} \quad [2]$$

In Equation 1:

$$\sigma_j = (1 + i)a_j; j = (s,p) \quad [3]$$

where a_j^{-1} is the thermal diffusion length, defined as

$$\alpha_j^{-1} = \mu_j = (\frac{2\alpha_j}{\omega})^{1/2} \quad [4]$$

and $\omega = 2\pi f$ is the angular modulation frequency. Equation 1 implies maximal (100%) nonradiative quantum efficiency; the subscripts p and s refer to the pyroelectric sensor and sample, respectively. If the sample is thermally thin, Equation 1 can be written as:

$$V = \frac{V_o}{C_s} \bullet e^{-i\frac{3\pi}{4}} \quad [5]$$

where

$$V_o = \frac{p H_0}{2\sqrt{2}\,\varepsilon\omega\, a_p L_s} \quad [6]$$

Clearly, under such conditions, the amplitude V of the PPE signal is inversely proportional to the sample's volume-specific heat C_s, while the phase of the signal remains constant. With an appropriate calibration (using for example the value of C_s at room temperature), the amplitude of the PPE signal can be used to obtain the temperature dependence of volume-specific heat. Such an approach does not require precise knowledge of a sample's thickness because this latter parameter is included in the calibration factor V_o.

Configuration a1.2. Marinelli *et al.* (6) demonstrated that in a standard configuration when the sensor and sample are both thermally thick and the sample is optically opaque, the PPE voltage is given by:

$$V = V_o' \frac{e^{-L_s(\frac{\omega}{2\alpha_s})^{1/2}}}{e_s(\frac{e_m}{e_s} + 1)(\frac{e_p}{e_s} + 1)} e^{i\phi} \quad [7]$$

where

$$V_o' = \frac{H_0 p\, r\, e_p}{L_p C_p [1 + (\omega\tau_E)^2]^{1/2}} \quad [8]$$

and

$$\phi = -(\frac{\omega}{2\alpha_s})^{1/2} L_s \quad [9]$$

In Equations 7 and 8, symbol r represents the electrical resistance of the equivalent sensor-lock in amplifier circuit, and e_m is the thermal effusivity of the medium (above the sample). In this configuration, the measurement of phase ϕ of the complex PPE signal allows a direct and absolute (provided L_s is known) determination of the sample's thermal diffusivity. The amplitude of the signal is a function of two independent samples related thermal parameters (α_s and e_s); if α_s is determined from the phase (Eq. 9), then the second thermal parameter (e_s) can be calculated by solving Equation 7.

Configuration b1.2. When in the IPPE configuration, the sensor is thermally thin, the sample is thermally thick, and, in addition, the sensor operates in a current mode (7), the PPE signal is:

$$V = \frac{V_o''}{[(\frac{b_{sp}}{a_p L_p} + 1)^2 + 1]^{1/2}} \bullet e^{i\phi} \quad [10]$$

where

$$V_o'' = \frac{\tau_E p(1 - R)H_0}{\sqrt{2}\,\varepsilon C_p} \quad [11]$$

and

$$\phi = \frac{\pi}{4} - arctg \frac{a_p L_p}{a_p L_p + b_{sp}}; \; b_{sp} = \frac{e_s}{e_p}$$

R and τ_E represent the fraction of incident flux reflected by the sensor's electrode and the electrical time constant of the sensor-lock-in nanovoltmeter equivalent circuit, respectively. If in addition, the condition $b_{sp} \gg a_p L_p$ is satisfied, Equation 10 can be reduced to

$$V = \frac{V_o'''}{e_s} e^{i\frac{\pi}{4}} \quad [12]$$

with

$$V_o''' = e_p \alpha_p L_p V_o'' \quad [13]$$

For such a limiting case, a simple expression is obtained again. The amplitude of the IPPE signal is proportional to the reciprocal effusivity of the sample, while the phase of the signal remains constant.

Configuration b.2. The information provided by this configuration is rather similar to that obtained for b1.2. However, it is sometimes preferred because of the sensor's rigidity. With a special cell design, the thickness of the sample can be rigorously controlled. If the sample and the sensor are both thermally thick, the PPE signal is (9):

$$V = V_o'''' \frac{e_p}{e_s + e_p} e^{-i\frac{\pi}{2}} \qquad [14]$$

where

$$V_o'''' = \frac{\tau_E p H_o \omega^{1/2}}{8 \varepsilon a_p L_p} \qquad [15]$$

Equations 14 and 15 suggest that, for a given configuration, the amplitude of the PPE signal depends in a simple way on the sample's effusivity while the phase remains constant.

EXPERIMENTAL PROCEDURES

The experimental set-up used in this study is shown in Figure 2. The radiation emitted by a 50-mW He-Ne (model 125A Spectra-Physics; San Jose, CA) laser, serving as excitation source, was chopped by a 1205-603 F acousto-optical modulator (Isomet Corp., Springfield, VA). The signal from the detector was processed by an Ithaco Dynatrac model 399 two-phase lock-in amplifier (Ithaco, Inc., Ithaca, NY) and recorded on a 7090 A Hewlet-Packard x-y plotter (Palo Alto, CA). Typical values for signal-to-noise ratios were 20 (for b1.2) and 100 (for other configurations). For high-resolution measurements in the critical region, the experimental set-up was improved with a computer loop to control the temperature rate (Fig. 3). The reference input was supplied from the internal circuitry of EG&G 5302 lock-in amplifier (EG&G Princeton Applied Research, Princeton, NJ).

Two types of PPE cells were designed. One of them (Fig. 4), used at temperatures above 293°K, is actually a stainless-steel cylinder with a bottom plate and a cover lid; each of them carries a transparent perspex window to allow the laser radiation to enter the cell (either from above or from below, depending on a desired mode of operation). The copper block Cu with a central hole supports the sensor-sample assembly and, at the same time, reduces thermal gradients in the cell. A polytetrafluorethylene (PTFE) Teflon block (with dimensions slightly larger than those of the copper block), also provided with a central hole and bolted to the copper block, prevents direct thermal contact between the copper block and the cell walls (the external walls are heated electrically by a resistive coil). The sensor-sample assembly is thus heated indirectly *via* the air in the cell. The thermal inertia of the cell is rather high, but temperature control is good. The temperature was measured with a thermocouple (diode or termistor), situated in air close to the sensor.

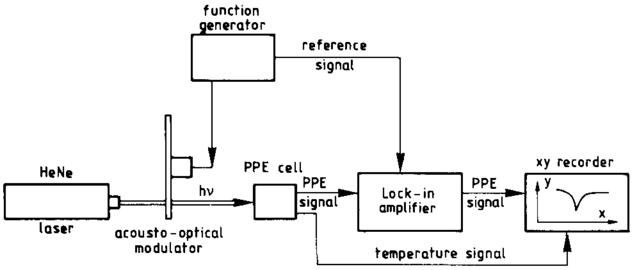

FIG. 2. Schematic diagram of the experimental set-up used in this study; see abbreviation in Figure 1.

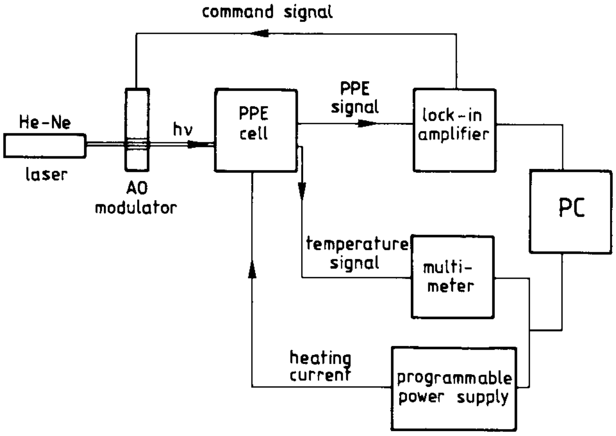

FIG. 3. Schematic diagram of computer-controlled set-up used for high-resolution measurements in the critical region of the phase transition; incident energy (hν), acousto-optical modulator (AO), photopyroelectric (PPE), personal computer (PC).

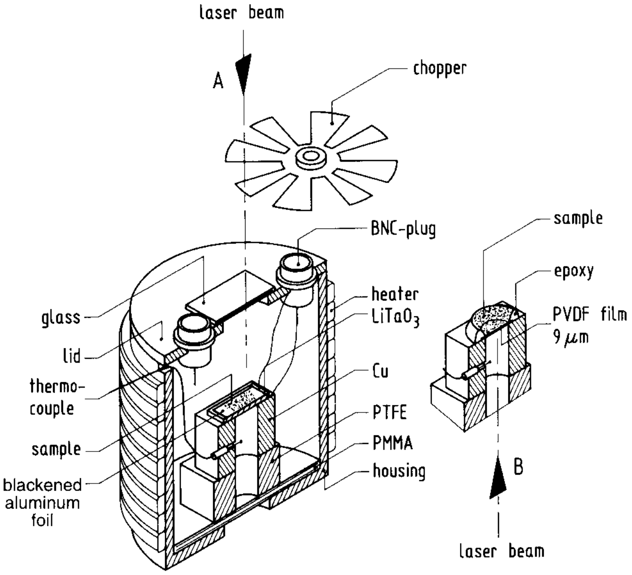

FIG. 4. The PPE cell used in standard (A) and inverse (B) configurations at temperatures exceeding that of the ambient BNC; PMMA, polymethyl methacrylate; PVDF, polyvinylidene difluoride; PTFE, polytetrafluorethylene.

The second PPE cell (Fig. 5) makes use of a cold-finger concept and permits working at temperatures both above and below that of the ambient. This cell, also provided with two windows, can be used in either SPPE or IPPE configurations. In the inverse configuration, a good thermal conductor and

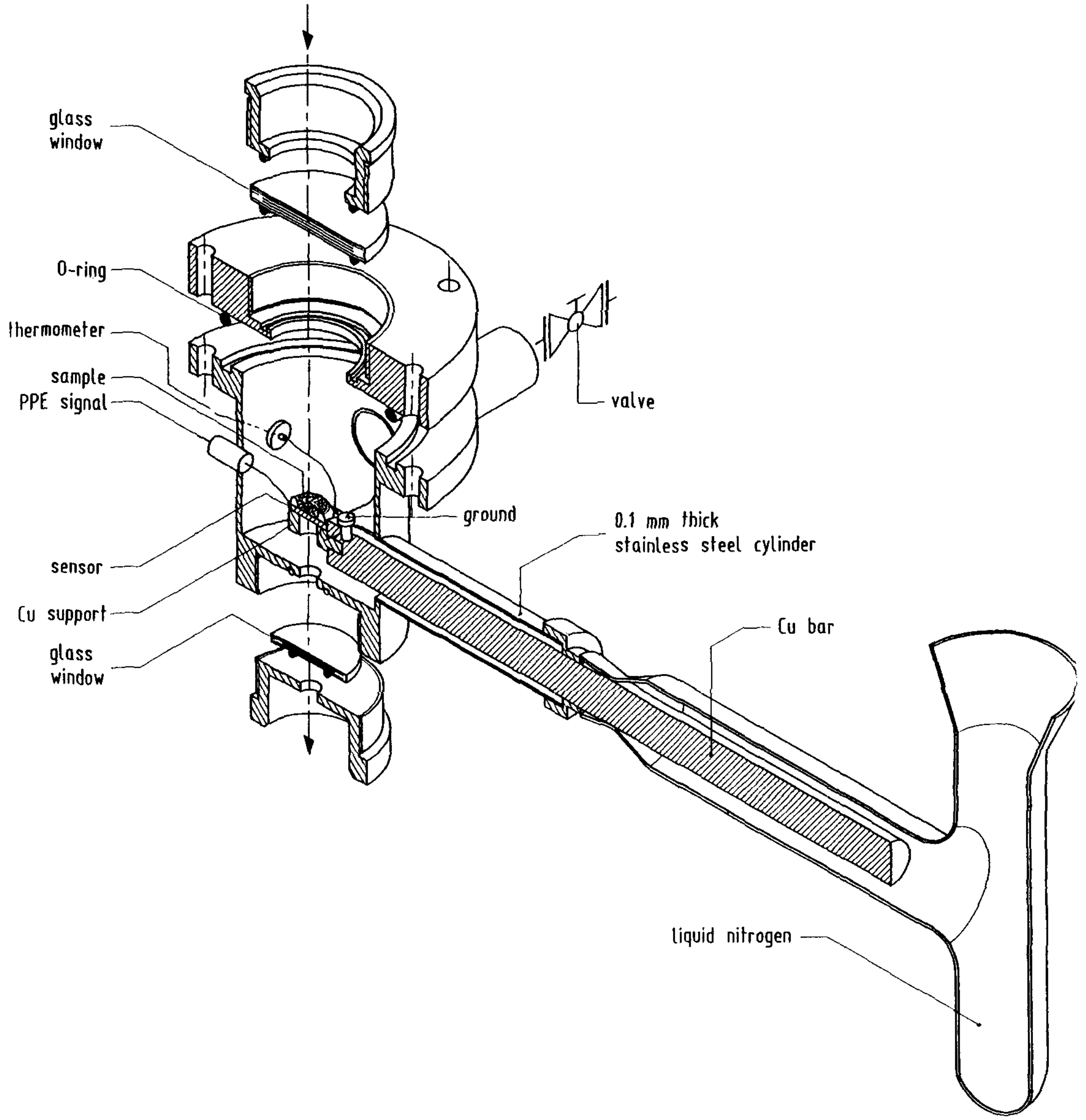

FIG. 5. The PPE "cold finger" cell. See Figure 1 for abbreviation.

electrical isolator (such as a sheet of mica) ought to be placed between the sensor and the cold finger (copper block). Admission of dry nitrogen (at atmospheric pressure) into the cell prevents condensation when operating at reduced temperatures. The temperature of the sample was measured with a diode glued (by means of a silicon grease) to the cold finger (in the vicinity of the sensor). The cell can be used in a broad temperature range, but due to the presently used way of heating/cooling (through the cold finger), minor differences between the actual sample's temperature and that measured by the thermometer are inevitable. In the a1.1 configuration, the sample (present in a powdered or liquid form at room temperature) fills the space between the sensor and a thin (15-μm thick) blackened aluminum foil (that acts as absorbing layer), thus ensuring optical opacity for the sample (Fig. 4). It is assumed that aluminum foil does not affect the measured data because, at low chopping frequencies, its thermal diffusion length is large (12 mm at 0.2 Hz, for example). For samples that are solid at room temperature, the cell was (prior to the measurement) heated to a temperature well above the melting point and then gradually reduced again to obtain a thin layer of sample with a uniform thickness and good thermal contact between the sensor, sample, and aluminum foil. A diaphragm, placed in front of the foil, prevents direct illumination of the sensor. In this configuration, knowing the exact thickness (100 μm is a reasonable estimate) of sample is not a necessity because it is included in the calibration factor (Eq. 6).

A more sophisticated geometry of the sample-sensor assembly is presented in Figure 6. A 30-μm thick layer of sample accommodates the space between a piece of quartz and the sensor. The radiation is absorbed by a thin layer of gold (or chromium) deposited on a quartz cell. Due to the capillar-

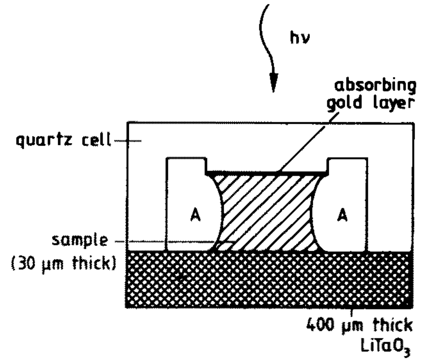

FIG. 6. Calibrated sample-sensor assembly used in the standard configuration.

ity, a uniform layer of sample (admitted into the cell as liquid) is formed. The function of channels A is to assure a constant sample thickness when its expansion during measurements is large. This calibrated cell, which can also be used for configuration a1.1, ought to be utilized as well for a1.2 where the sample's thickness must be controlled (see Eq. 9). In the inverse b1.2 configuration, the sample (typically 3 mm thick) is confined within a rectangular "cup," formed by (Rhone-Poulenc, Saint Fons, France) on the sensor surface (as shown in Fig. 4B). To assure good thermal contact between the sample and the sensor, heating and cooling cycles (as described above) of the cell were performed. The precise knowledge of the thickness of the sample is not needed here (Eqs. 12 and 13), but the requirement for the sample's thermally thick regime must be fulfilled.

The geometry of the sample-sensor assembly used in the b2 configuration is displayed in Figure 7. The radiation impinging onto the front surface of a transparent pyroelectric sensor [the front surface is a transparent indium tin oxide (ITO) deposited layer] is absorbed by a second electrode, which is in thermal contact with the 200-μm thick sample. The advantages of this cell are similar to those of the other calibrated cell presented above. Additionally, due to its transparency, the sensor does not act as a low pass filter (as is usually the case for the IPPE configuration). The pyroelectric sensors used in the studies were 300/400-μm thick $LiTaO_3$ crystals (a1 and b2) and a 9-μm thick PVDF foil (Pennwalt Corp., Edinburgh, Scotland) (b1.2), respectively. In all measurements, the temperature range included the critical region of the solid-to-liquid phase transition. A typical temperature variation rate was 1°C/min, but for high-resolution measurements, rates between 0.005°C/min and 0.03°C/min were used. For sharp anomalies around the melting point, the acquisition rate was 0.003°C. The chopping frequency was 0.2 Hz for a1.1, 0.1 Hz for b1.2, and 78 Hz for a1.2 and b.2 configurations.

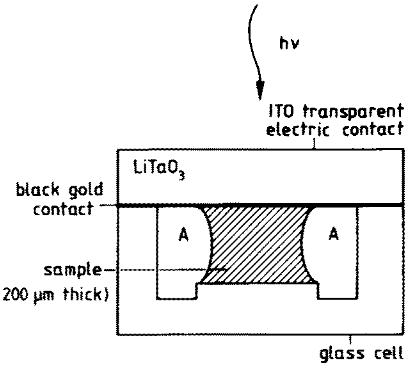

FIG. 7. Calibrated sample-sensor assembly used for inverse configuration.

RESULTS

With the experimental set-up from Figure 2 and the PPE cell presented in Figure 4, measurements on lauric acid (C12:0) in a1.1 and b1.2 configurations were performed; the results are displayed in Figure 8. The experimental set-up of Figure 3 and calibrated cells (Figs. 6 and 7) were then used to detect the phase transition in capric acid (C10:0) (configurations a1.2 and b2); results of these studies are shown in Figures 9 and 10. In all plots, large anomalies in the amplitude of the PPE signal are observed near the melting point. As expected from the theory, they are associated with critical anomalies of

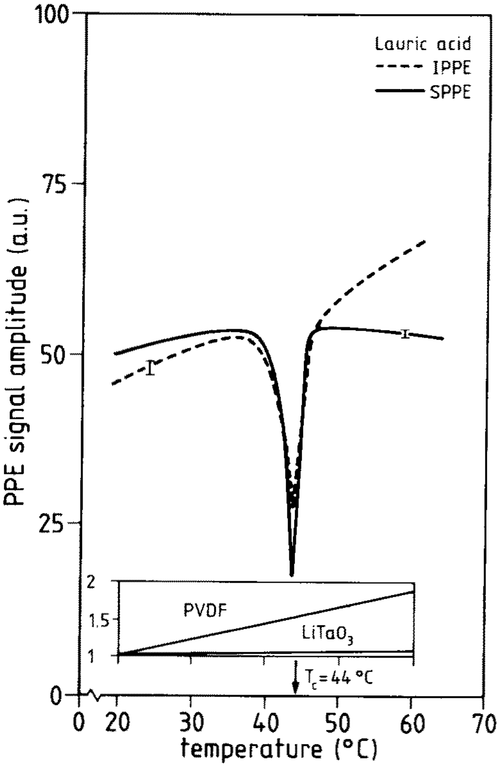

FIG. 8. The amplitude of PPE signal (a1.1 and b1.2) plotted vs. temperature. Insert: the magnitude of signals obtained with unloaded sensors (used for normalization); SPPE, standard configuration for the photopyroelectric technique; IPPE, inverse configuration for the photopyroelectric technique. See Figures 1 and 4 for other abbreviations.

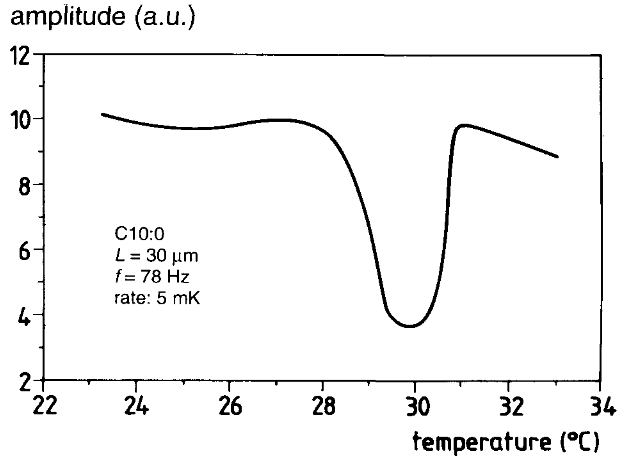

FIG. 9. The amplitude of PPE signal (a1.2). See Figure 1 for abbreviation.

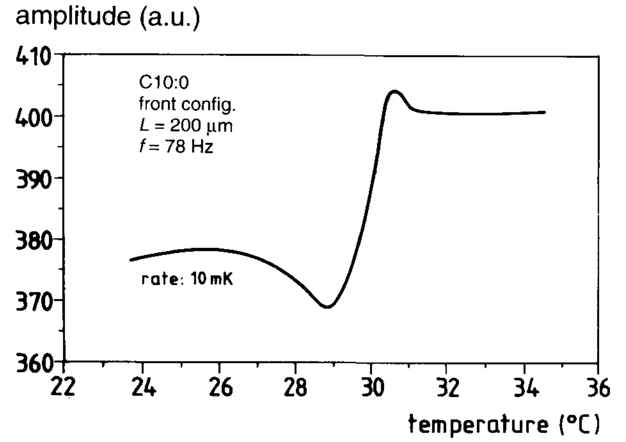

FIG. 10. The amplitude of PPE signal (for b2). See Figure 1 for abbreviation.

thermophysical parameters. In the second part of this study (9), results obtained with various fatty acids and triglycerides will be discussed. After a proper calibration procedure, the temperature dependence of thermophysical parameters in the critical region will be studied.

This paper has shown the feasibility of the PPE method to detect phase transitions in lipids. Four PPE configurations were selected to evaluate critical behavior of the thermophysical parameters near the melting point. Proper choice of PPE cell components (sensor material, forward and backing medium) and of experimental conditions (chopping frequency, sample's and sensor's thickness) leads to simple analytical expressions in which the amplitude (or phase) of the complex PPE signal depends on one (case a1.1, b1.2, and b2) or two (case a1.2) sample-related thermal parameters. Three (volume-specific heat, thermal diffusivity, and thermal effusivity) of the four thermophysical parameters can be measured directly by this technique. The remaining thermal conductivity can then be calculated from Equation 2 and the information contained in the amplitude and phase (case a1.2), or by combining data obtained with other two configurations. The PPE technique is a simple, relatively inexpensive, reproducible and sensitive method for this kind of measurements. Sample temperature variations of less than 1 μ°C are detectable with this technique. Due to selective processing of the signal, changes in ambient temperature do not affect the results. Signal-to-noise ratios were typically larger than 100, except for the b1.2 configuration (for which noise in the critical region is slightly larger, probably due to imperfect thermal contact between the sample and the flexible PVDF sensor during the melting process). Unfortunately, when investigating lipids, no coupling fluid (such as silicon grease) could be used because of potential reaction with the sample. To satisfy the requirements imposed by each specific case is a condition *sine qua non* to obtain correct results. Experimental arrangements for rapid measurements across a large temperature range (Fig. 2) and for accurate studies in the vicinity of the melting point (Fig. 3) have been proposed. With some minor modifications, specially designed PPE cells and sensor-sample geometries can be used in both SPPE-IPPE configurations. The temperature range of a current cell design extends from –50°C (due to difficulties experienced with condensation below this temperature, and sample properties prohibit operation under reduced pressure) to the Curie temperature of the sensors (100°C for PVDF and 600°C for $LiTaO_3$) used in this study.

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