Direct Determination of Thermophysical Parameter $\sqrt{K\rho c}$ in Mayonnaise, Shortening, and Edible Oil

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Inverse photopyroelectric (IPPE) spectroscopy, a novel variant among the photothermal spectroscopies, has been used for direct determination of $(K\rho c)^{1/2}$ in a variety of food samples. The method appears capable of thermal characterization, and when combined with more mature techniques may prove useful in food products industry and storage.

Index Headings: **Inverse photopyroelectric spectroscopy; Photothermal spectroscopy; Thermal effusivity; Thermal analysis of food.**

INTRODUCTION

Food samples are generally difficult to analyze thermally due to their complex composition and the intrinsic inhomogeneity. The methods most frequently used are differential scanning calorimetry (DSC), thermogravimetry (TG), and thermomechanical analysis (TMA). In addition, a variety of steady-state and transient methods to measure the transport parameters—such as, for example, thermal conductivity K and thermal diffusivity K/c' ($c' = c\rho$ is the volume-specific heat at the constant pressure, with ρ being density)—have also been developed and adopted. However, for heterogenous specimens such as food products, knowledge of the product Kc' is preferred because the square root of this quantity appears in the equation that governs the thermal response of the heated surface and, hence, plays a decisive role in the overall heat transfer coefficient. Since the physical parameters K, c, and ρ all change during the spatial and temporal structural chemical events in actual food samples, direct determination of $(K\rho c)^{1/2}$ is of interest in the establishment of thermal characterization criteria for quality assessment of samples.

Photothermal spectroscopic approaches are currently receiving rapidly growing attention within the broad scientific community, especially because of their relative simplicity and their potential for aiding optical and thermal analysis of transparent and optical samples in the condensed phase.[1–5] Various photothermal schemes deal essentially with either a direct measurement of the heat generated within the sample upon the absorption of the periodically modulated incident radiation or, alternatively, the effects of the very same heat on other physical properties (for example, the refractive index of the sample). One of the photothermal methods is the photopyroelectric (PPE) technique, which relies on direct measurement of the temperature increase in a sample by a pyroelectric temperature detector, which is brought into close contact with the nonirradiated side of the specimen, thereby sensing the thermal wave propagating through the sample. The first experimental reports on this method date back to 1984;[6–8] theoretical model studies followed.[9,10] In this paper we report for the first time on the application of the modified PPE method, the so-called inverse photopyroelectric technique (IPPE), to foodstuffs such as shortenings, edible fats, and oils.

Contrary to conventional PPE, in the IPPE approach it is the thin sensor (with one of its sides blackened) that faces the impinging radiation. The thermal wave propagating across the sensor eventually reaches the sample placed at the sensor's rear face, and the temperature amplitude efficiency depends (at the given modulation frequency) only on the thermal effusivity $(c'K)^{1/2}$ of the sample. Detailed analysis using the appropriate particularizations discussed in Refs. 10 and 11 shows that the magnitude V of the IPPE signal amplitude is proportional to:

$$V \approx 1/(c'K)^{1/2}. \qquad (1)$$

If conditions for IPPE measurement are met (i.e., the sensor is opaque and thermally thin, the sample is thermally thick, the black layer has a small thermal mass, and the heat losses from the front of the sensor to the air are negligible), the phase of the signal is constant and contains no information about the sample properties. The IPPE measurements yield only relative values, and it is customary to normalize the signals by relating them to those obtained with a known substance (e.g., distilled water). Since both c' and K are composition dependent, the IPPE scans provide means to discriminate between the various products.

EXPERIMENTAL

In the experimental arrangement shown in Fig. 1, the IPPE assembly is mounted horizontally in order to allow the accommodation of fluid and semi-solid samples. Such a configuration also enables the experimentalist to rinse the sensor surface with ethanol (for cleaning purposes) between successive measurements. The IPPE assembly basically consists of a heat-sensing element, the edges of which are attached to the backing perspex plate by means of flexible glue. The thin layer of air separating the central part of the sensor from the supporting perpex plate is needed to prevent heat losses to the perspex. Silicon rubber (Rhodorsil CAF4) glue was used to assemble the

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IPPE cell but also to avoid shortcircuiting between two sides of the foil via the fluid sample. Sample quantities of typically 0.1 mL were poured, without any preparation, directly on the pyroelectric sensor, which has an effective area of 8 mm × 8 mm. The actual sensor is an oriented and metalized (Al) polyvinylidenedifluoride (PVDF) foil of thickness $L_{\text{foil}} = 25$ μm (the bottom side of which was painted black), manufactured by Solvay; its properties are documented in Ref. 12. The modulated radiation reaches (through the transparent perspex plate) the black-painted side of the PVDF foil where it is being absorbed, causing a periodic increase in the temperature of this surface. In general, damping of the thermal wave at the given angular modulation frequency $\omega = 2\pi f$ is determined by a thermal diffusion length μ (the inverse of the thermal diffusion coefficient) defined as $\mu = \sqrt{(2\ \alpha/\omega)}$ with $\alpha = K/c'$. At a distance equal to one diffusion length, the amplitude of thermal wave in the sample S is reduced by a factor exp(2π) compared to its initial value. At an operating modulation frequency $\omega = 2\pi f$ of 0.64 Hz, pyroelectric foil is thermally thin ($L_{\text{foil}}/\mu_{\text{foil}} = 0.15 \ll 1$), and hence it does not attenuate the thermal wave. With no actual food sample present atop the foil, little heat will flow away from the foil into the surrounding air (low c' and K), and the voltage measured across the sensor reaches its maximal value. However, the majority of samples to be investigated (typical physical thickness L_{sample} about 1 mm) are thermally thick ($L_{\text{sample}}/\mu_{\text{sample}} \gg 1$) since the corresponding thermal diffusion length at 0.64 Hz is about 0.1 mm. The thermal wave will therefore be almost completely attenuated within this short range, making the amount of the bulk sample used in this measurement irrelevant. In such case the sample acts as a sink; consequently some fraction of deposited thermal energy will "leak" into the sample, causing a corresponding drop in the voltage measured across the foil. The thin layer of air separating the PVDF foil from the supporting perspex plate (Fig. 1) is required in order to prevent heat losses to the perspex.

Very good stability of the rotating chopper at very low modulation frequencies (<1 Hz) was achieved with a stabilized Hall sensor motor from a conventional direct-drive turntable. The radiation source was a Spectra-Physics (Model 156) He-Ne laser providing 0.5 mW power at 632.8 nm. Its beam was expanded (with a lens) to form a diameter of 6 mm at the sensor surface (this is large enough in comparison to the thermal diffusion lengths involved), and one-dimensional analysis can be applied. Local inhomogeneities of the radiation absorbing layer are also smoothed out. The periodic temperature increase in the IPPE cell is of the order of 10^{-2} K, resulting in a pyroelectric voltage signal of about 1 mV. The stability of the laser was monitored by the photodiode PD that sampled the fraction of incident power reflected at the partially transmitting beamsplitter (BS). The signal across the foil was processed with a two-phase vector lock-in voltmeter, Model PAR 129 (bandwidth 0.5–100 Hz). The input impedance was 100 MΩ, and the total capacity of the sensor and cable was 430 pF. The filtered (20-s time constant) dc output signal, measured on a chart recorder, had a signal-to-noise ratio better than 100.

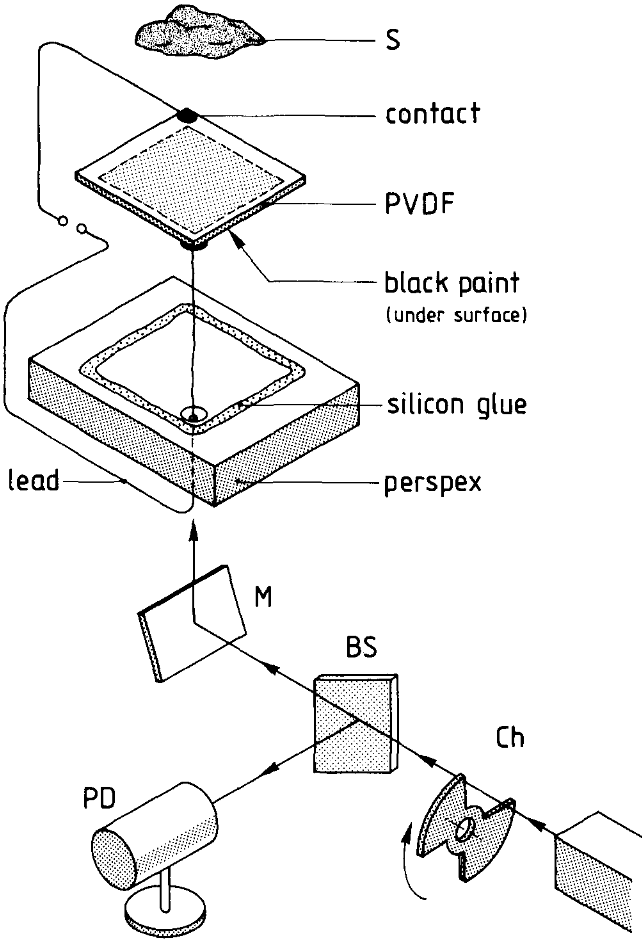

FIG. 1. An exploded view of the experimental setup including the cell assembly for studies of food samples by the IPPE method. L, laser; **Ch**, chopper; **BS**, beamsplitter; **M**, mirror; **PD**, photodiode; **S**, sample. The lens used to expand the laser beam is not shown. The signal generated across the foil is processed at the modulation frequency by a lock-in amplifier.

Three different sorts of products have been investigated: mayonnaise, edible vegetable oil, and shortening. As far as the mayonnaise is concerned, three types produced by the same manufacturer and varying only in the percentage of fat have been selected. Olive oil (75% monounsaturated oleic acid, 8% polyunsaturated linoleic acid, and a remaining fraction of saturated acids such as palmitic, stearic, and others) and sunflower oil (22% oleic acid, 63% linoleic acid, and a remaining fraction of palmitic and oleic acids) were chosen among the edible oils. Finally, two commercially available brands of shortening have been tested. One of these consisted of hardened marine and vegetable oils, while nonhardened vegetable oil rich in linoleic content dominated the composition of the other shortening. Each of the products was measured several times, and the results averaged. The signals normalized to the values observed with the pure water showed reproducibility of better than one percent. Due to a satisfactory degree of short-term stability in the laser, there was no need for additional corrections.

RESULTS AND CONCLUSIONS

In order to interpret the experimental results obtained with the selected samples, one needs to generate the calibration curve for the instrument. For data consisten-

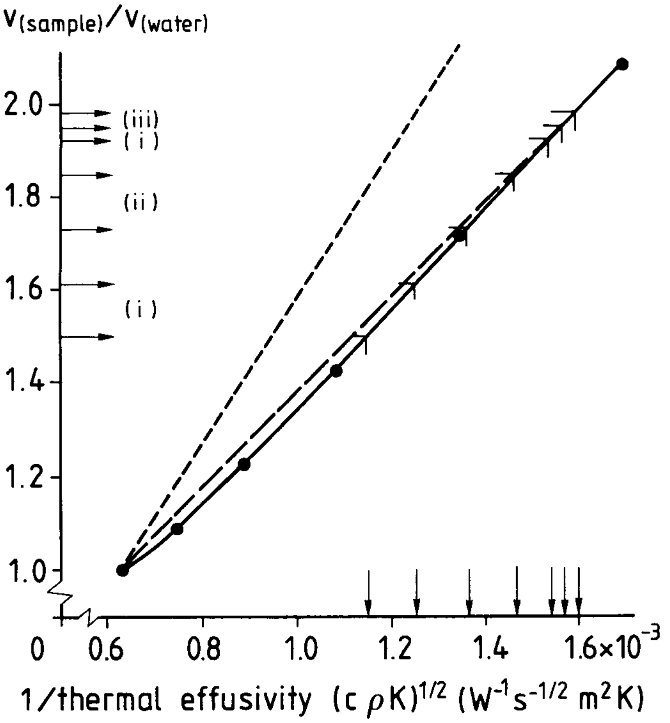

FIG. 2. Magnitude of the normalized IPPE signal vs. the inverse of thermal effusivity according to: Eq. 1 (dotted line); theoretical model[10] (dashed line); experimental calibration (solid line). Also shown is the procedure for determining the thermal effusivity for samples from Table I.

TABLE I. The magnitude of the IPPE signal (relative to water) for three classes of foodstuffs and the corresponding thermal effusivities determined from Fig. 2. The same data for ethanol/water mixtures for calibration purposes with thermal effusivities calculated according to Ref. 15 are also given.

Sample	Composition	$\frac{V_{(sample)}}{V_{(water)}}$	Effusivity (W s$^{1/2}$/m^{2}K)
(i) Mayonnaise			
(a) Low fat content	25% Fat	1.50	869
(b) Medium fat content	50% Fat	1.61	796
(c) High fat content	80% Fat	1.92	648
(ii) Edible vegetable oils			
(a) Olive oil	75% Oleic acid 8% Linoleic acid	1.73	733
(b) Sunflower oil	22% Oleic acid 63% Linoleic acid	1.85	676
(iii) Shortenings			
(a) Brand 1	Hardened marine and vegetable oils	1.95	636
(b) Brand 2	Only vegetable oils rich in linoleic acids	1.98	623
(iv) Calibration			
Ethanol-water mixture in % mass ethanol	0%	1.00	1580
	20%	1.08	1344
	40%	1.22	1119
	60%	1.42	919
	80%	1.71	741
	100%	2.08	588

cy it is preferable to use not more than two well-characterized substances for extreme points and mixtures of substances for intermediate points. Convenient substances that cover the range of effusivities of investigated samples are water and ethanol. The effusivity values given in Table I (class iv) were calculated according to available data[13,14] for thermal conductivity (K), and the volume-specific heat values (c') were derived by linear interpolation of volume concentrations corrected for the volume contraction effect upon mixing. The volume concentrations were expressed as functions of the respective mass concentrations. Details of the procedure are given in Ref. 15. Equation 1 suggests a natural representation of the calibration curve as a plot of the IPPE signal magnitude vs. the inverse of thermal effusivity. Figure 2 displays the experimental curve based on the measurement of ethanol/water mixtures (solid line) as well as the ideal curve (dotted line) described by Eq. 1. The experimental sensitivity to effusivity variations in the sample is obviously lower; this is mainly due to heat losses from the radiation-absorbing side of the sensor across the air layer (or gap) to the perspex support. The general theory for a six-layer PPE cell[10] is able to account for this effect, and by fitting two extreme points of the experimental curve with the gap thickness as a parameter we obtain $L_{gap} = 53\ \mu$m. For intermediate concentrations the model predicts a very good linearity (dashed line), with deviations less than 1.5% from the solid curve for the signal values of interest. The experimental nonlinearity is larger with respect to proximity to pure water (i.e., for the substances with larger effusivity). The likely explanation of this situation is associated with the reflection phenomena of the thermal wave at the interface between two media caused by the effusivity mismatch[16] (the effusivity ratio is 2.77 for a water/PVDF system), when the condition for a thermally thin pyroelectric is more critical. Also the theory does not account for the additional thermal capacity of a black layer having a thickness of some μm and for thermal contact resistance between the latter and the pyroelectric.

The results for three classes of investigated samples are given in Table I. Their thermal effusivities were determined as illustrated in Fig. 2, with a relative uncertainty of 2%, by using the experimental calibration curve. The absolute uncertainty is determined by the inherent errors contained in the calibration curve itself (preparation of the mixtures, temperature dependence of the pyroelectric coefficient, etc.) and is on the order of 5% for the present experimental setup. With respect to the accuracy of the effusivity values for the calibrants, a better choice would be to directly measure their thermal properties by other methods, instead of using the indirect approach used in the present work. As expected, the effusivity is influenced by the class of product (ii and iii) and, to an even larger extent, is sensitive to the fat/water ratio (class i). The results of this study demonstrate that the IPPE method is a technique that is simple, inexpensive, and very easy to apply, yet capable of quantitative and qualitative characterization of foodstuffs by means of their thermal effusivities. Unlike the photoacoustic methods,[17] when appropriately calibrated it possesses the unique advantage of being able to provide thermal information for specimens having very different optical properties (such as transparent, translucent, diffusely scattering, and opaque samples, respectively). As such, the IPPE method, a versatile complement to more mature techniques,[18] might prove useful in obtaining missing data on the thermal properties of food products at various stages of processing and storage.

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