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Self-consistent photothermal techniques: Application for measuring thermal diffusivity in vegetable oils

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The thermal wave resonator cavity (TWRC) was used to measure the thermal properties of vegetable oils. The thermal diffusivity of six commercial vegetable oils (olive, corn, soybean, canola, peanut, and sunflower) was measured by means of this device. A linear relation between both the amplitude and phase as functions of the cavity length for the TWRC was observed and used for the measurements. Three significant figure precisions were obtained. A clear distinction between extra virgin olive oil and other oils in terms of thermal diffusivity was shown. The high measurement precision of the TWRC highlights the potential of this relatively new technique for assessing the quality of this kind of fluids in terms of their thermophysical properties. *© 2003 American Institute of Physics.* [DOI: 10.1063/1.1517727]

I. INTRODUCTION

Vegetable oils have been used traditionally as ingredients in the preparation of food, both for domestic purposes and commercially in industry. In the latter they command an important economical role especially in the snack industry. They are also of increasing importance in other areas of applied science and technology, an example is their utility in the energy production sector. They have acquired exceptional importance because they can be used as fuel alternatives and lubricants.[1,2] Used extensively in the 19th century as base lubricants, vegetable oils were gradually replaced by mineral oils mainly for economic and practical reasons. Since then, their use in this area has been renewed because of the worldwide interest in environmental issues.[2]

A vegetable oil is a complex mixture of chemical substances[3] with fatty acids among chemical compounds present. However, even for a given type of vegetable oil, fatty acids profile often varies.[4] Besides a variety chemical composition of oils depends (at least for olive oil) on factors such as climatological conditions, time of ripening, duration, etc.[5] It is important to know such chemical composition because it allows food authentication and quality analysis.[6,7] Especially important is the measurement of the thermophysical properties of vegetable oils because of their widespread use as heat exchangers in the snack industry. Knowledge of these properties allows for the possibility to optimize of the processes in the food industry.

The utility of photothermal techniques for measuring thermal properties of liquids has been well documented in the literature.[8–10] The basic principle of these techniques relies on measuring the temperature fluctuations in a sample as a result of the nonradiative de-excitation process that takes place following the absorption of intensity-modulated radiation.

This article demonstrates the utility of a new liquid-state design of the thermal wave resonator cavity (TWRC)[10,11] for direct measurement of the thermal diffusivity of vegetable oils. The high sensitivity of this technique shows its potential to perform thermal characterization of vegetable oils and the possibility, in combination with other techniques (absorption spectroscopy for example), for quality control of these important substances.

II. THEORY

According to the mathematical theory of the TWRC[10–12] it has been shown that the pyroelectric signal from this device at a fixed thermal-wave oscillation frequency $f=\omega/2\pi$ can be reduced to

$$V(L,\alpha_\ell,\omega)=\mathrm{Const}(\omega)\times e^{-\sigma_\ell L}, \tag{1}$$

where V is the output voltage signal across the pyroelectric detector, L is the cavity length, and σ_ℓ is the complex thermal diffusion coefficient of the fluid, defined by

$$\sigma_\ell=(1+i)\sqrt{\omega/2\alpha_\ell}. \tag{2}$$

Here α_ℓ is the thermal diffusivity of the intracavity liquid medium.

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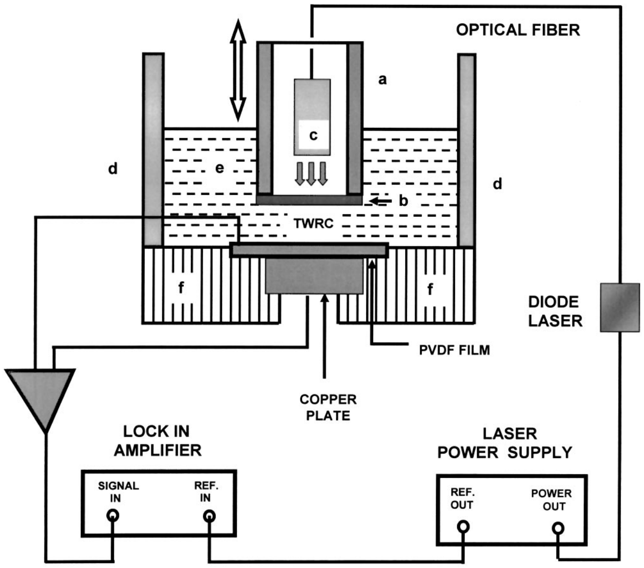

FIG. 1. Schematic representation of the experimental setup. (a) Cylindrical thermal-wave emitter head containing the absorbing aluminum foil, and (b) the photothermal chamber with the optical fiber (c). (d) Container walls. (e) Liquid sample filling the TWRC. (f) Dielectric substrate. The bottom surface of the PVDF was attached to a copper plate acting as electrical contact and mechanical support.

The magnitude and phase of the complex expression given in Eq. (1) can be written, respectively, as

$$|V(L,\alpha_\ell,\omega)|=C(\omega)\times e^{-A_\ell L}, \tag{3}$$

$$\Theta=B-A_\ell L, \tag{4}$$

where $A_\ell=(\pi f/\alpha_\ell)^{1/2}$ and B is a frequency-dependent constant. Equations (3) and (4) show that it is possible to carry out simple TWRC measurements of the thermal diffusivity of liquids. The process consists in measuring the polyvinylidene fluoride (PVDF) complex signal as a function of the cavity length, and fitting the experimental phase and amplitude to a linear equation (in a semilog scale for the amplitude). The thermal diffusivity can be obtained from the slope fitting parameter A_ℓ.

III. EXPERIMENT

The experimental setup used in this work, shown in Fig. 1, consisted of an infrared (806 μm) semiconductor laser (Opto Power Corporation) operating at powers up to 200 mW. The intensity-modulated laser light was incident on an aluminum foil (80 μm thick and 1 cm in diameter) mounted on a micrometer stage. This stage allowed the cavity length, L to vary with a 10 μm step resolution. The cross-sectional design of the signal generation head (a cylinder) is also shown in Fig. 1. The bottom was sealed hermetically with the highly conducting thin aluminum foil acting as an optical-to-thermal power converter, as a thermal-wave generator, and as a sealant to prevent liquids from seeping into the photothermal signal-generation chamber. The cylindrical module was dipped in the various vegetable oils as shown in Fig. 1. Thermal waves conducted across the liquid interface (“intracavity region”) reached the pyroelectric sensor consisting of a PVDF pyroelectric film (25 μm thickness and 1.5 cm diameter) with metal electrodes (Ni–Al) on both sides. The pyroelectric voltage signal generated in the sensor was preamplified (ITHACO model 1201) and then processed by a lock-in amplifier (EG&G model 5210).

TABLE I. Thermal diffusivities obtained by the TWRC technique for vegetable oils.

Vegetable oil	$\alpha_{\mathrm{Amp}}(\times 10^{-2}\ \mathrm{cm^2/s})$	$\alpha_{\mathrm{Phase}}(\times 10^{-2}\ \mathrm{cm^2/s})$
Extra virgin olive oil	0.0880 ± 0.0004	0.0892 ± 0.0007
Canola oil	0.0890 ± 0.0001	0.0903 ± 0.0002
Corn oil	0.0892 ± 0.0003	0.0904 ± 0.0003
Peanut oil	0.0893 ± 0.0002	0.0906 ± 0.0001
Sunflower oil	0.0893 ± 0.0002	0.0904 ± 0.0001
Soybean oil	0.0894 ± 0.0002	0.0904 ± 0.0002

For this work six different commercial vegetable oils were acquired from food markets in the urban area of Toronto (Table I) and their thermal diffusivities measured by cavity-length scan in the TWRC device. For this purpose the TWRC container was filled with the corresponding sample (Fig. 1). The cavity-length scan was carried out in 10 μm steps and at a modulation frequency of 4.40 Hz, all measurements were performed at 26 °C.

IV. RESULTS AND DISCUSSION

Figures 2 and 3 display a typical behavior of the amplitude and phase of the pyroelectric signal from extra virgin olive oil on the cavity length. The continuous line in Fig. 2 is the best fit to Eq. (3) and the corresponding phase line is shown in Fig. 3 along with the best fit to Eq. (4). Resulting thermal diffusivity values of vegetable oils, summarized in Table I, are averages over at least five measurements, and reported uncertainties therefore constitute the standard deviation.

When comparing the thermal diffusivities obtained for a given vegetable oil using two different criteria (columns 2 and 3 of Table I) one finds a remarkable similarity among the corresponding magnitudes. A relative percent deviation below 1.5% is found for all cases. In both data channels a clear difference between the thermal diffusivity of extra virgin ol-

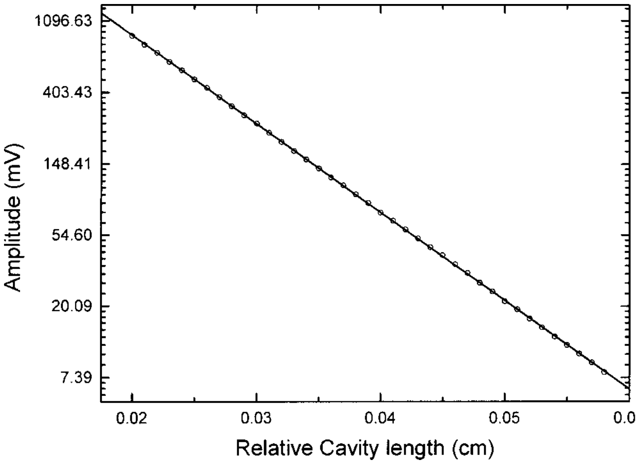

FIG. 2. Typical dependence of the amplitude of the pyroelectric signal on the relative cavity length in case of extra virgin olive oil. The continuous line is the best fit to Eq. (3).

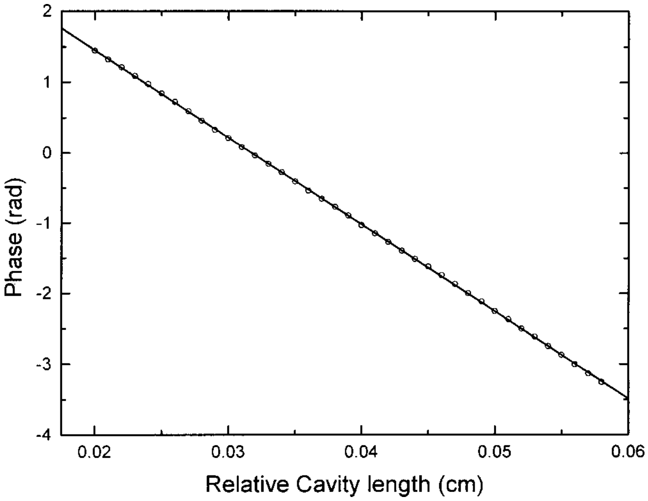

FIG. 3. Typical dependence of the phase of the pyroelectric signal on the relative cavity length in case of extra virgin olive oil. The continuous line is the best fit to Eq. (4).

ive oil and the other vegetable oils was found. This could be ascribed to the different composition of olive oil (rich in oleic acid, a monounsaturated fatty acid) as compared to the others, containing other unsaturated fatty acids in their composition.[3,4] This fact is also evident from the different tonality (color) of these substances. The extra virgin olive oil studied in this work exhibited a green tonality as compared with the yellow tonality of the other vegetable oils. In fact, the hue of yellow tonality varied among them: that of the canola oil was stronger than those of the others. We wish to hypothesize that these optical property differences are reflected in the different thermal diffusivities measured for these oils. However the suggested connection cannot be deduced from the thermophysical measurements alone, because the various thermal diffusivities measured with the TWRC overlap within the uncertainty range. To establish this fact other more sensitive thermophysical and optical measurements (for example, spectroscopic studies) are necessary.[13,14]

The thermal diffusivity values of extra virgin olive oil determined with the TWRC showed significant differences (~50%) when compared to a reported literature value. This reported value,[15] 0.00145 cm^2/s, is far from the ones obtained in this work (0.000 880 cm^2/s for the amplitude and 0.000 892 cm^2/s for the phase). By opposite, taking the thermal properties reported for olive oil[16] and a density[17] of 0.918 $\mathrm{g/cm}^3$, a thermal diffusivity value of 0.000 799 cm^2/s is estimated, in close agreement with the one reported by using the TWRC technique.

In conclusion the application of a new TWRC experimental device for measurements of the thermal properties in liquids has been presented. In particular the TWRC was used to measure thermal diffusivity for vegetable oils with a third-significant-figure precision. This was achieved using the linear behavior of both amplitude and phase of the photothermal signal as a function of the cavity length for this device. Major advantages of using cavity length scan, instead of scanning the modulation frequency, is the fixed noise bandwidth of the system, which improves the signal-to noise ratio, as well as disposing with the requirement of instrumental transfer function normalization.

There was a clear difference between the thermal diffusivity of extra virgin olive oil and that of other vegetable oils. This difference measurable at the third significant figure level could be attached to the different fatty acid composition of these oils. The high sensitivity in TWRC measurement of thermal diffusivity suggests additional applications in thermal studies of vegetable oils, or even in mixtures of them (examples are the effect of temperature, oxidation, etc.). Therefore, the TWRC device may develop an easy-to-use tool in determining the quality of vegetable oils. It is a well-known economic fraud fact that in some regions extra virgin olive oil is adulterated by adding other inferior vegetable oils but sold as a genuine product. The earlier mentioned approach of thermophysical quality control may be used to rapidly detect adulteration in such mixtures, this in contrast to conventional chemical inspection that involves time consuming and costly analytical procedures (HPLC, etc.).[7]

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[1] F. Karaosmanoglu, G. Kurt, and T. Ozaktas, Renewable Energy **19**, 219 (2000).

[2] U. S. Choi, B. G. Ahn, O. K. Kwon, and Y. J. Chun, Tribol. Int. **30**, 677 (1997).

[3] *Lipids Analysis in Oils and Fats*, edited by R. J. Hamilton (Chapman and Hall, London, 1998).

[4] L. Dong-Sun, N. Bong-Soo, B. Sun-Young, and K. Kun, Anal. Chim. Acta **358**, 163 (1998).

[5] C. Nergiz and Y. Engez, Food Chemistry **69**, 55 (2000).

[6] M. J. Dennis, Analyst (Cambridge, U.K.) **123**, 151R (1998).

[7] H. El-Hamdy Ali and K. El-Fizga Naima, J. Chromatogr., A **708**, 351 (1995).

[8] J. A. Balderas-López, G. Gutiérrez-Juárez, M. R. Jaime-Fonseca, and F. Sánchez-Sinencio, Rev. Sci. Instrum. **70**, 2069 (1999).

[9] D. Dadarlat, H. Visser, and D. Bicanic, Meas. Sci. Technol. **6**, 1215 (1995).

[10] J. A. Balderas-López, A. Mandelis, and J. A. García, Rev. Sci. Instrum. **71**, 2069 (2000).

[11] J. Shen and A. Mandelis, Rev. Sci. Instrum. **66**, 4999 (1995).

[12] J. Shen, A. Mandelis, and B. D. Aloysius, Int. J. Thermophys. **17**, 1241 (1996).

[13] A. Mandelis, S. Paoloni, and L. Nicolaides, Rev. Sci. Instrum. **71**, 2440 (2000).

[14] S. Paoloni, L. Nicolaides, and A. Mandelis, Rev. Sci. Instrum. **71**, 2445 (2000).

[15] D. Dalarlat, J. Gibkes, D. Bicanic, and A. Pasca, J. Food. Eng. **30**, 155 (1996).

[16] J. Caerels, C. Glorieux, and J. Thoen, Rev. Sci. Instrum. **69**, 2452 (1998).

[17] *Handbook of Chemistry and Physics*, 56th ed. (CRC Press, Cleveland, 1975–1976).