Thermal Wave Resonator Cavity Applied to the Study of the Thermal Diffusivity of Coffee Infusions

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Abstract Among the photothermal methods, the photopyroelectric technique, in its several experimental configurations, has been extensively used to measure the thermal properties of liquids, mainly the thermal effusivity and diffusivity. In this paper, the use of the so-called thermal wave resonator cavity method, in the cavity-length-scan mode, to measure the thermal diffusivity of commercial coffee infusions with samples at different concentrations and degrees of degradation induced by heating cycles is reported. A linear relationship between the logarithm of the pyroelectric signal amplitude and the sample thickness was observed, in agreement with the basic theory for the experimental configuration used here, from which the thermal diffusivity values of the samples were obtained. The thermal diffusivity was found to be almost independent of the coffee concentration in water but that this parameter is sensitive to sample modifications induced by degradation. This work represents another step to demonstrate the capability of the used method for characterization of the thermal properties of liquids.

Keywords Coffee infusions · Photopyroelectric technique · Thermal diffusivity · Thermal wave

1 Introduction

Monitoring the quality of coffee is an important area of research due to the fact that coffee is one of the most popular beverages worldwide. An in-depth search into the

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scientific literature published on this subject (see, for example, the compilation presented by Flament [1]) shows that the majority of studies are related to the investigation of the chemical composition of coffee and how properties such as its aroma and flavor depend on it. It seems paradoxical that although coffee is mainly consumed in the form of beverages, the majority of the published work deals with the characterization of grains and powders of roasted and soluble coffee by means of spectroscopic and chemical analysis methods, whose limitations have been discussed recently by Fontes et al. [2]. These authors proposed the use of a photothermal (PT) technique, the so-called thermal lens (TL) method, to investigate the adulteration of coffee using brew samples. Although the technique does not show significant variation of the thermal diffusivity of solutions of soluble powdered coffee in water in a range of concentrations from 0% to 20% w/w, the authors show that the rate of change of the sample refractive index temperature coefficient can be used to discriminate between pure and adulterated samples.

Besides adulteration, degradation of coffee samples is another aspect of interest. For example, it is well known that coffee infusions are often exposed to cyclic periods of heating that can affect their quality (this can be observed in our daily life by noting the changes in the flavor and aroma for longer times); this paper addresses this later aspect. To avoid the direct illumination of the sample by electromagnetic radiation, as takes place in spectroscopic methods as well as in the TL technique, and the disadvantages of light scattering due to the solid particles suspended in the analyzed liquid solutions, we resorted to the use of an indirect sample heating PT method based on photopyroelectric (PPE) detection of thermal waves. The PPE method [3,4] has been recognized as a reliable tool for the measurement of thermal properties of condensed matter samples and, in particular, of liquids. One of the most widely used PPE experimental setups is the direct (or back) [5] detection configuration for thermal diffusivity, α, determination. In the case of liquids the sample is enclosed in a cavity formed between a metal light absorber and a pyroelectric (PE) sensor. Thermal waves generated in the metal, by the absorption of a modulated laser beam, are detected with a sensor, whose signal will be proportional to the temperature variation and will depend on the value of α in a straightforward way. As the proportionality factor is modulation frequency dependent, it is advantageous to perform cavity length measurements instead of frequency scanning. Because the signal results from the interference of the thermal wave trains propagating through the cavity encountering multiple successive reflections at the interfaces between liquid and sensor and also between liquid and metal, the resulting experimental configuration has been first denoted as a thermal wave resonator cavity (TWRC) [6]. The possibilities of this method to perform the thermal characterization of liquids have been demonstrated for the first time by Balderas et al. [7] and Lima et al. [8] (the latter denoted the method as thermal wave interferometry), and it has been used successfully in this field by several authors [9–12]. It is our objective in this work to show the potential of a TWRC method to follow the degradation process of coffee infusions through the monitoring of their thermal diffusivity changes. Complementary measurements of pH, ultraviolet-visible, and infrared (UV-vis and IR) spectroscopy, and differential scanning calorimetry (DSC) were carried out in order to aid in the interpretation of our results.

2 Experimental Details

2.1 Experimental Setup

Figure 1 shows schematically our experimental setup. It consists of a cavity of variable length containing a liquid sample (*l*) formed between a 95 μm thick circular Cu foil (*m*), with a diameter of 5 mm, and a LiTaO$_3$ pyroelectric (*P*) temperature sensor. A diode laser (another light source should be used as well, including a non-monochromatic one) light beam, modulated at a frequency $f = 5$ Hz impinges on the black-painted outer surface of the metallic foil, which acts as a light absorber. Following the absorption of the intensity-modulated light beam, the foil temperature fluctuates periodically at the modulation frequency of the incident beam, thereby launching a thermal wave into the liquid-filled cell. The temperature oscillations at $x = L$ can be measured with the sensor as a function of the liquid layer thickness. The complex signal is then sent to a lock-in amplifier synchronized at the modulation frequency, where its amplitude is measured as a function of L. For a thermally thin Cu foil, the output voltage can be expressed as

$$V(L) = V_0 \frac{\exp(-qL)}{1 - \gamma \exp(-2qL)} \tag{1}$$

where V_0 is a modulation frequency dependent factor $q = (2\pi f i/\alpha)^{1/2}$ and γ is the product of the thermal wave reflection coefficients at the metal–liquid and liquid–pyroelectric interfaces [6], i.e., $\gamma = R_{lm}R_{lp}$, where $R_{ij} = (1 - b_{ij})/(1 + b_{ij})$, with $b_{ij} = e_i/e_j$ as the quotient of the thermal effusivities, e.

For the experimental situation in which the sample in the TWRC may be considered as thermally thick, i.e., $qL \gg 1$, the pyroelectric sensor output voltage, as given by Eq. 1, reduces to

$$V(L) = V_0 \exp(-qL) \tag{2}$$

In this case the thermal diffusivity can be obtained in a simple manner from the slope of the logarithm of the signal amplitude as a function of L. This situation is
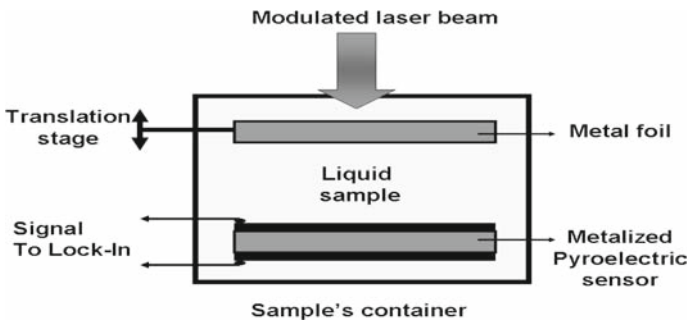

Fig. 1 Experimental setup for TWRC measurements

often encountered, when liquid samples of low thermal diffusivity are studied at the modulation frequency and TWRC length used here. Note that Eq. 2 is similar to that describing a back detection PPE configuration mentioned in Sect. 1.

2.2 Samples

The analyzed sample was prepared by mixing 500 ml of bi-distilled water with 50 g of commercial Legar^{MR} soluble coffee powder from Sabormex, México. The mixture was appropriately stirred to obtain a homogeneous suspension, after this the obtained solution has been introduced in a homemade reflux system, where it could be heated at a controlled temperature of 86 °C during 5 min while avoiding liquid losses and then cooled to ambient temperature. After that, 15 ml of sample was collected for thermal-diffusivity measurements. The above described procedure was repeated cyclically 10 times.

3 Experimental Results and Discussion

Figure 2 shows the results of a typical measurement of the signal amplitude as a function of the cavity length for a sample after the first heating–cooling cycle. The solid line is the best linear fit using Eq. 2. We obtained a value for the thermal diffusivity of $(14.4 \pm 0.2) \times 10^{-4} \mathrm{cm}^2 \cdot \mathrm{s}^{-1}$. Similar measurements were carried out to determine the thermal diffusivity as a function of the number of heating–cooling cycles in a series of samples. Figure 3 shows the mean obtained α values for these cycles.

The solid line in Fig. 3 is the result of the fit to a logistic function, which is only shown for visualization purposes. Until the fourth heating cycle is achieved, the
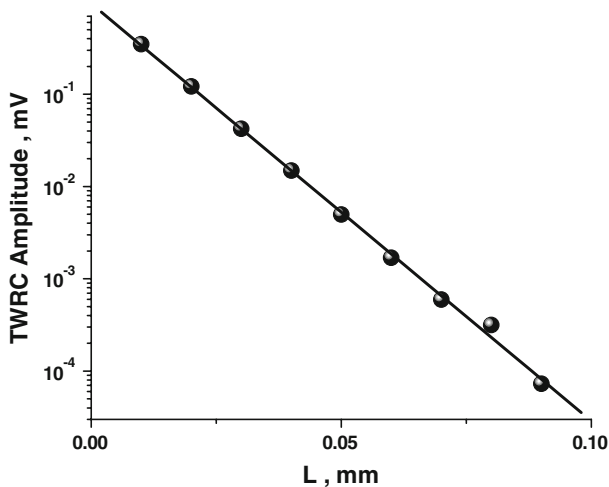

Fig. 2 TWRC signal amplitude as a function of the cavity length for the coffee sample after the first heating–cooling cycle. *Solid line* is the best linear fit using Eq. 2
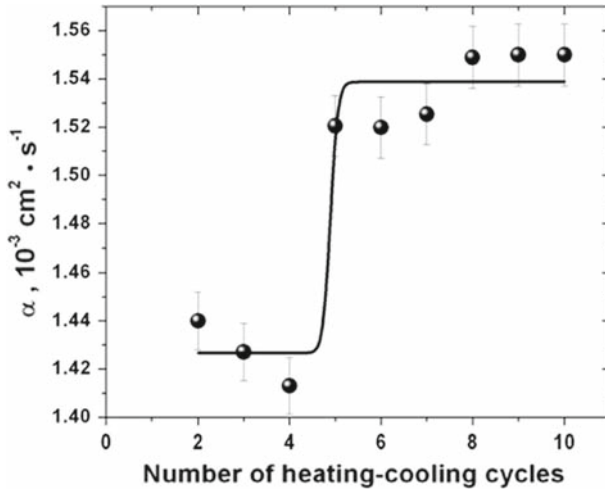
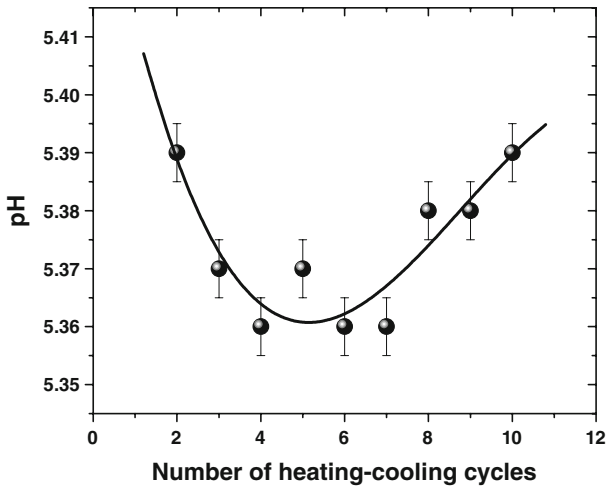**Fig. 3** Thermal diffusivity as a function of the number of heating cycles

Fig. 4 pH as a function of the number of heating cycles

thermal diffusivity has approximately the same value, as for water, while the value of α increases about 7 % for higher cycle numbers.

We have accompanied our measurements with pH monitoring of our coffee solutions which were performed using a WG BenchScan 4 Wag-WE30340 pH/ ion meter. Figure 4 shows the measured pH values as a function of the cycle number. The obtained values are of the same order of magnitude as those found by Fontes et al. [2] for low concentrations of coffee in distilled water.

Coincidently the pH curve exhibits a minimum at about the same number of heating cycles at which the thermal diffusivity changes. Thus, contrary to previous studies of adulteration in brewed coffee [2], which showed that the thermal diffusivity was
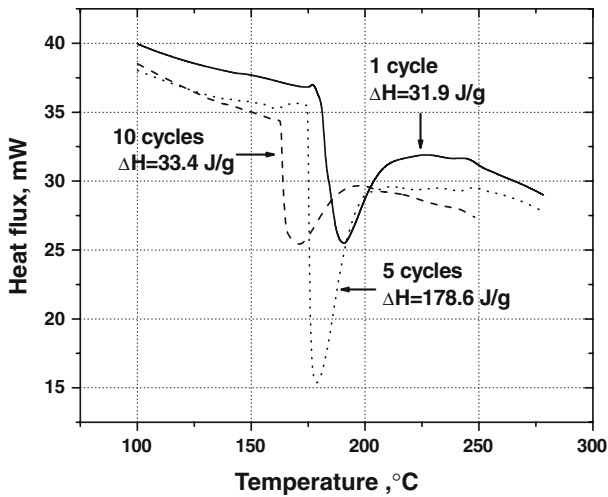
Fig. 5 Typical DSC curve showing the regions where melting takes place

almost independent of concentration while the pH showed a strong dependence on it; in the case of coffee infusions degradation in this study, the pH changes are reflected somewhat in the behavior of the thermal diffusivity. Due to the presence of several components in the powder of instant coffee, the observed behavior cannot be attributed to a single component. It is probable that the carbohydrates present in the sample can experience oxidation due to the cycles of heating–cooling, promoting the formation of gluconic acids, and consequently the diminution of pH, while the thermal diffusivity remains at approximately the same value as water. After several cycles, the excessive amount of these acids can promote their neutralization with the other components of the extract, which would explain the further increase of the pH. These structural changes could also be the cause of the observed increase of thermal diffusivity after the fifth cycle. This behavior is also corroborated in the results obtained for the enthalpy (ΔH) by means of differential scanning calorimetry (DSC). Typical DSC thermograms are shown in Fig. 5 (only representative graphs are shown due to visualization purposes). Measurements were made in a Pyris 1 (Perkin Elmer) equipment. The liquid samples were dried in vacuum in a rotary evaporator apparatus (Yamato RE 500) before approximately 4 mg of the resulting powders were weighed into aluminum pans and heated from 30 °C to 300 °C at a rate of 10 °C · min^{-1}. In all measurements an empty pan was used as reference. The graphs show a peak corresponding to a fusion temperature (T_m) of some molecular component, which diminishes with the heating–cooling cycles, revealing that a structural change could be the cause of the observed behavior of the thermal diffusivity. The enthalpy was calculated from the area under the curve. One can see that while T_m diminishes with the degradation cycles, the enthalpy initially grows before it diminishes to approximately its initial value after passing the fourth cycle. It is worth to note that UV-vis and IR spectroscopic measurements performed by us do not reveal clearly any compositional modification in the analyzed samples.

4 Conclusions

From the preliminary results presented in this paper we propose that the thermal wave resonator cavity technique with pyroelectric detection and a cavity length scan may be eventually used for routine investigation of the degradation of coffee infusions. Further work to explain the observed behavior of the thermal diffusivity received immediate attention and is still in progress.

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