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Thermal effusivity measurement of conventional and organic coffee oils via photopyroelectric technique

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ABSTRACT

In this work, oil samples extracted from organic and conventional coffee beans were studied. A fatty acids profile analysis was done using gas chromatography and physicochemical analysis of density and acidity index to verify the oil purity. Additionally, Mid-Infrared Fourier Transform Photoacoustic Spectroscopy (FTIR-PAS) aided by Principal Component Analysis (PCA) was used to identify differences between the intensities of the absorption bands related to functional groups. Thermal effusivity values between 592 ± 3 and 610 ± 4 $Ws^{1/2} m^{-2} K^{-1}$ were measured using the photopyroelectric technique in a front detection configuration. The acidity index was between 1.11 and 1.27% and the density changed between 0.921 and 0.94 g/mL. These variables, as well as the extraction yield between 12,6 and 14,4%, showed a similar behavior than that observed for the thermal effusivity, demonstrating that this parameter can be used as a criterion for discrimination between oil samples extracted from organic and conventional coffee beans.

1. Introduction

Nowadays, the organic agriculture has a high demand due to the benefits that it offers for food safety and sustainability, due to the absence of pesticides and synthetic fertilizers (Gabriel, Sait, Kunin, & Benton, 2013; Gomiero, Pimentel, & Paoletti, 2011). The certification process that provides a guarantee of traceability and quality has facilitated the success of organic food in specialized markets (Kleemann, Abdulai, & Buss, 2014). There are companies that offer this kind of legitimization, such as Biotropico S.A., CERTIMEX S.C., SCS global services, CERES and BCS Oko-Garantie. Particularly in Colombia, the organic coffee certification improves the socioeconomic condition on the different actors in the productive chain, life quality and product sustainability (Sunarharum, Williams, & Smyth, 2014). Although the remunerations of organic agricultural practices are superior compared with those of conventional methods, normally the certification processes can be quite lengthy, complex and expensive, so that the potential economic profit of the small and medium producers is reduced and delayed. Due to this reason, there is a great interest for finding new certification methods (Guedes Pinto, Gardner, McDermott, & Lara Ayub, 2014). In this context, the analysis of the thermophysical parameters are an alternative, since they are directly related to structure and chemical composition of the material, which in the case of coffee beans depend on the environmental conditions, plant variety, soil types, etc. (Gordillo-Delgado, Marín, Cortes-Hernández, Mejía-Morales, & García-Salcedo, 2012; Rasool, Kukal, & Hira, 2008; Saldaña y Hernandez et al., 2014; Telci, Toncer, & Sahbaz, 2011).

The thermal effusivity, e, is defined as $e = (kC)^{1/2}$, where k is the thermal conductivity and $C = \rho c$ is the specific volume heat capacity, given by the product of the density, ρ, and the specific heat, c (Marín, 2006). The effusivity plays a very important role in the thermal phenomena determining the behavior of thermal waves at surfaces and interfaces (Marín, 2007a, 2007b) and the sample's thermal impedance value (Martínez et al., 2015). This thermo-physical parameter has been used before to characterize the quality of foods (Dadarlat, Gibkes, Bicanic, & Pasca, 1996; Dadarlat & Neamtu, 2009a; Szafner, Bicanic, Kulcsar, & Doka, 2013), among other applications.

The photopyroelectric (PPE) technique has been emerged as one of the most useful methods for thermal characterization of materials (Chirtoc & Mihailescu, 1989). Two main configurations exist. In the back detection (BPPE) configuration (Chirtoc, Chirtoc, Bicanic, & Pelzl, 1995) an intensity modulated light beam impinges on the front surface of a sample and a pyroelectric sensor is attached to the rear side. This is a heat transmission configuration widely used for thermal diffusivity

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measurements. In the front (FPPE) configuration (Dadarlat, Chirtoc, Nematu, Candea, & Bicanic, 1990), the sample is attached to the rear side of the sensor and the light beam impinges on the sensor front face, so that the sensor acts as both a source of thermal waves propagating through the sensor-sample system, and as the detector of them. The FPPE configuration (Guimaraes, Machado, da Silva, & Mansanares, 2012; Ivanov, Marin, Moreno, & Araujo, 2010; Szafner, Bianic, Gaal, & Doka, 2012) is one of the most used techniques for measuring the thermal effusivity of liquid substances due to several factors, among them the small quantity of sample required and the excellent thermal contact achieved between sample and pyroelectric detector. This photothermal method has been used to characterize oils, in particular, to differentiate between corn, soy and avocado vegetable oils (Cervantes-Espinosa et al., 2014; Longuemart et al., 2002; Machado, Zanelato, Guimares, da Silva, & Mansanares, 2012). This fact inspired the present work that explores the potential of the PPE technique for discriminating between organic and conventional coffee oils by measuring their thermal effusivity. This study is aided with measurements of the acidity index and density of the oil. The gas chromatography technique was used to identify the purity level of the extracted coffee oil and the fatty acids. Mid-Infrared Fourier Transform Photoacoustic Spectroscopy (FTIR-PAS) aided by Principal Component Analysis (PCA) (Dunteman, 1989; Wojcicki, Khmelinskii, Sikorski, & Sikorska, 2015) was used to find possible changes in functional groups due to the type of coffee farming.

2. Experimental and details

2.1. Materials

2.1.1. Coffee oil samples

Fruits from organic and conventional *Coffea arabica* plants (Caturra variety) were collected in farms, which are located in Risaralda-Colombia between 1500 and 1700 m above the sea level. The samples were identified as shown in Table 1. All samples were subjected to the same wet pulping process (Montilla-Pérez et al., 2008) for reducing possible differences in the beans due to the post-harvest treatments. After drying process, the moisture content of the coffee beans was 12%.

Oil extraction was made by the Soxhlet Method (Al-Hamamre, Foerster, Hartmann, Kroger, & Kaltschmitt, 2012) using a SCHOTT DURAN apparatus. The coffee in parchment was dried in an air-circulating oven for 6 h at 378 K to achieve a moisture content of 5%. The coffee beans were grinded and then the particles with diameters between 500 and 710 μm were mechanically separated using Test Sieves ASTME11 SERIES 6083992 and 6093828, respectively; 150 g of the coffee powder and hexane (EMSURE ACS – 96%) were used in the solvent extraction method. The hexane was subsequently removed using a rotary evaporator (N-1110 EYELA). The density and acidity index were determined using the Colombia's standards NTC 336 (2016) and NTC 218 (2011), respectively.

2.2. Methods

2.2.1. Gas chromatography

The lipid compounds analysis of coffee oil was done using gas chromatography coupled to mass spectrometry (GC–MS - QP2010 ULTRA, SHIMADZU) with a C18 column (length: 60 mm, inner diameter: 0.32 mm) and hydrogen carry gas with flow of 40 mL min^{-1}. An initial temperature of 373 K was programmed for 4 min, after which it was elevated to 513 K at a rate of 3 K min^{-1} and kept constant for 10 min. The sample quantity was 1 μL and the volatile compounds were determined using the library present in the device. According to the Colombian Technical Standards NTC 4967 (2014), a transmethylation process of acid-catalyzed glycerides was applied to the sample before the measurement.

Table 1
Characteristics of the coffee samples.

Sample	Type of crop	Altitude (m)
C1	Conventional	1682
C2		1591
O1	Organic	1639
O2		1591

2.2.2. Fourier Transform Infrared Photoacoustic Spectroscopy (FTIR-PAS)

A spectrophotometer (IR Prestige-21 – SHIMADZU) was used to obtain the optical absorption spectra in the mid-infrared range of the electromagnetic spectrum between 400 and 4000 cm^{-1}, and a photoacoustic (PA) cell (MTEC300) with a KBr window was used as the signal detector. The PA cell internal chamber was purged with Helium for reducing the water vapor and CO_2 presence (McClelland, Jones, & Seaverson, 1992). This enhances the signal/noise ratio and avoids spectral interferences, which ensures the reproducibility of the measurement. The oil amount deposited in the sample holder was 100 μL and 100 scans per sample were done to guarantee the data reliability.

2.2.3. Photopyroelectric measurements

The PPE technique consists in measuring the temperature variations that take place in a liquid sample exposed to modulated light using a pyroelectric (PE) detector in direct contact with the sample (Dadarlat & Neamtu, 2009a). In the FPPE configuration showed schematically in the Fig. 1, a modulated light beam pass through a transparent window (*wi*) and impinges the PE sensor (*p*), which is heated by the absorption of this radiation. The generated heat diffuses to the sample (*s*) that is located in direct contact with the opposite side of the sensor. Because of the induced temperature oscillations, a voltage (*V*) is generated between the metallic electrodes of the sensor, which is called the PE signal.

If the window and the sample are thermally thick and the illuminated sensor surface is optically opaque, the PE signal is described as follows (Dadarlat & Neamtu, 2009b):

$$V = \frac{V_0}{(b_{wip}+1)}\frac{1 - e^{-\sigma_p l_p} + R_{sp}(e^{-2\sigma_p l_p} - e^{-\sigma_p l_p})}{1 - R_{wip}R_{sp}e^{-2\sigma_p l_p}} \quad (1)$$

where R_{sp} and R_{wip} are the thermal wave reflection coefficients at the sample-pyroelectric and window-pyroelectric boundaries, respectively; σ_p and l_p are the complex thermal diffusion coefficient and sensor

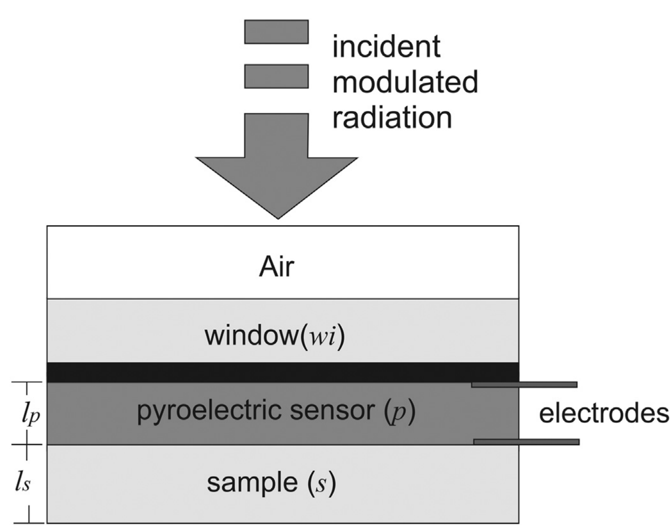

Fig. 1. Representation of material layers in the front configuration.