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Article

Photoacoustic Spectroscopy as an Approach to Assess Chemical Modifications in Edible Oils

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Espectroscopia fotoacústica foi utilizada tanto para obter algumas propriedades ópticas de óleos de soja, canola e oliva quanto para avaliar as alterações ocorridas devido ao tratamento térmico dos óleos. A intensidade do sinal fotoacústico normalizado e a sua fase foram medidas, independentemente, como uma função do comprimento de onda da fonte de radiação. Amostras de óleo foram aquecidas por 30 min após atingido o ponto de fumaça visando sua degradação. Depois disso, as amostras de óleo foram resfriadas e medições fotoacústicas foram conduzidas de forma a obter os espectros de absorção de amostras em ambas as condições degradadas e não degradada. A comparação entre as duas condições indicou que as amostras de óleo degradado exibiram alargamento das bandas de absorção na região ultravioleta do espectro, em relação à respectiva amostra com óleo não-degradado. Os picos das referidas bandas de absorção apresentaram um desvio para a região do vermelho.

Photoacoustic spectroscopy was used to obtain optical properties of edible soybean, canola and olive oils as well to evaluate the oil modifications induced by thermal treatment. The normalized photoacoustic signal intensity and its phase were independently measured as a function of wavelength of the radiation source. The oil samples were heated up to the smoke point and then for additional 30 min in order to degrade them. After, the oil samples were cooled down and photoacoustic measurements were conducted in order to obtain the absorption spectra of samples at both degraded and non-degraded conditions. Comparisons between the two conditions indicate that the degraded oil samples exhibited widening of the absorption bands in ultraviolet region of the spectra, relative to the respective non-degraded sample. Also, the peaks of those absorption bands presented a red shift.

Keywords: thermal degradation, fatty acid, food process, physicochemical properties, vegetable oil

Introduction

The photoacoustic spectroscopy (PAS) is a useful photothermal technique to obtain thermal and optical parameters of materials based on heat transfer due to absorption of radiation by the matter.[1] Many applications of this technique is found in the scientific literature, such as adulteration studies in powdered coffee,[2] kinetic study of Maillard reactions in milk powder,[3] and measurements of thermophysical properties of poly(3HB) and poly(3HB-*co*-3HV) polymers.[4]

PAS is based on the photoacoustic effect discovered by Alexander Graham Bell in 1880.[5] This effect is obtained in a closed chamber which is filled with a gas (in general, air) and contains a transparent window which permits a modulated (chopped) radiation to reach the sample. If the sample absorbs this modulated radiation then heat is produced due to non-radiative de-excitation processes within it. Then the heat is transferred to the gas as according to the frequency of the radiation modulation. The gas acts as

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a piston in order to produce a sound wave which is detected by a microphone connected to the chamber.[6-10] As the microphone signal is proportional to radiation absorption by the sample, PAS gives results similar to absorbance spectra, i.e., conventional optical absorption spectroscopy. Also, as the signal depends on the modulation of the radiation source, PAS is able to perform a depth profile of the absorption in the sample, that is, at high modulation frequencies absorption information about the sample near the surface is obtained, while at low modulation frequencies the data come from deeper within the sample.[8,10]

Vegetable oil is a valuable and versatile compound used as stabilizer, additive or raw material in the foodstuffs production. Its composition includes triacylglycerol (95 to 98%) and mixtures of minor compounds (2 to 5%) such as glycerides, free fatty acids, phospholipids, carotenoids, chlorophylls, sterols, tocopherols, proteins, resinous and mucilaginous materials and oxidative products.[11-13]

Triacylglycerols are lipids whose molecules are formed by a glycerol of which each –OH group is acylated with a fatty acid. These compounds constitute the major part of the lipids present in both animals and plants. Physical-chemical characteristics of triacylglycerols, such as crystallization properties and melting point, are strongly influenced by the length of fatty acid chain and by the presence/absence of double bonds. Indeed, double bonds (unsaturations) generate more branched fatty acid chains, hindering the molecules packing. As a consequence, the melting points of unsaturated triacylglycerols are lower than those containing only saturated fatty acids. In addition to affecting the physical properties, unsaturation makes the fatty acid chains more susceptible to oxidation, which is often deleterious for the technological quality of the products. The oxidation of triacylglycerols is a complex set of reactions involving radical mechanisms, generating not only off-flavor compounds (aldehydes, ketones, hydrocarbons, among others), but also polymers, due to the formation of covalent bonds between chains of different molecules. The polymerization of fatty acids chains in triacylglycerols triggers an increase in the viscosity of the oils, being favored when it is exposed to high temperatures, e.g., during the fry processes.[11,13]

Different types of vegetable cooking oils are used in the food industry to prepare deep-fried foods. The evaluations of physical-chemical modifications due to the deep frying temperatures exposure are used in the quality control of oils and fats in the food industry.[14] It has been observed a growing number of research activities dealing with the development of new and rapid methods for quality assessment of oils and their derivatives that do not require separations steps such as gas and liquid chromatography. The chromatographic operations are expensive and time-consuming when compared with spectroscopic methods, which are cost-effective, rapid, and non-destructive. Spectroscopic methods could be also used for detecting oil adulteration and for using in oil routine analyses.[15] Sikorska *et al.*[15-16] reported the applicability of total luminescence spectroscopy for characterization of vegetable oils and monitoring their changes during photo and auto oxidation.

PAS is a suitable technique to obtain optical absorption spectra of vegetable oils because this class of compounds is known for their physical characteristics: highly ultraviolet (UV) absorbent due to unsaturated fatty acids,[14] and light-scattering samples (when degraded) due to arising of polymeric compounds. Then, they are unsuitable for conventional optical absorption spectroscopy, i.e., absorbance spectroscopy, since they give featureless spectra (UV saturation spectra) without dilution in organic solvents. On the other hand, those physical characteristics are not problems for PAS, which gives good optical absorption spectra of non-degraded and degraded oils without dilution in solvents. To our knowledge, there are scarce reports on the application of photoacoustic spectroscopy technique to the analysis of edible oil samples.

Photoacoustic spectroscopy theory

In PAS,[1,5-10,17] the heat propagation is considered in one dimension as shown in Figure 1, which depicts a closed cylindrical photoacoustic chamber. Chopped modulated radiation with frequency *f* reaches a transparent window of the chamber and illuminates the sample, which is placed against a non-absorbing backing material. The chamber is filled up with a non-absorbing gas, frequently ambient air. The radiation absorbed by the sample is converted in heat by non-radiative conversion mechanism. As the produced heat is periodically transferred to the gas according to the modulation frequency, only a thin adjacent layer of the gas acts as a piston in order to produce a sound wave which is detected by a microphone. This layer is shown in Figure 1. As the pressure fluctuation in the gas is proportional to the heat emanating from the sample, the photoacoustic signal intensity (absolute value) is proportional to the absorbed radiation by it in the wavelength λ:

$$|S| = K\, I_{abs}\, \eta_s \qquad (1)$$

where K = constant of proportionality which is given by thermal properties of the sample, geometry of the chamber and instrumentation of the photoacoustic system; I_{abs} = absorbed radiation intensity by the sample in the wavelength λ; and η_s = non-radiative conversion

efficiency of the radiation absorbed by the sample. Then the photoacoustic signal |S| depends on the absorbed radiation and the thermal properties of the sample.

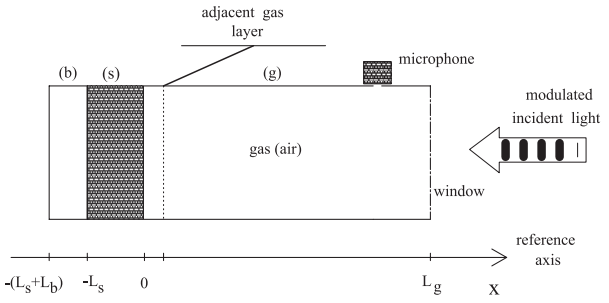

Figure 1. Sketch of the closed cylindrical photoacoustic chamber showing the adjacent gas layer which acts as an acoustic piston. The letters: b = backing, s = sample, g = gas, L_s = sample thickness, L_g = gas layer thickness, L_b = backing layer thickness and X = reference axis.

The expression for the normalized photoacoustic signal, that is, the ratio of the photoacoustic signal produced by the sample to that produced by a black absorber is a hard mathematical challenge obtained firstly by Rosencwaig and Gersho.[5] The heat propagation across the whole chamber is governed by heat diffusion equations of each medium coupled via boundary conditions at the interfaces ($T_a = T_b$ and $k_a dT_a/dx = k_b dT_b/dx$, a and b are adjacent media, T is temperature and k is thermal conductivity). After all mathematical treatment, the normalized photoacoustic signal (S_n) produced by the microphone is:[5-10,17]

$$S_n = \frac{\eta_s r_s b_{bs}}{r_s^2 - 1}\left[(r_s - 1)(b_{bs} + 1)e^{\sigma_s L_s} - (r_s + 1)(b_{bs} - 1)e^{-\sigma_s L_s} + 2(b_{bs} - r_s)e^{-\beta_s L_s}\right] \div \left[(b_{gs} + 1)(b_{bs} + 1)e^{\sigma_s L_s} - (b_{gs} - 1)(b_{bs} - 1)e^{-\sigma_s L_s}\right] \quad (2)$$

where $r_s = \beta_s/\sigma_s$, β_s is the sample optical absorption coefficient, $\sigma_s = (1 + i)a_s$ with $i = (-1)^{1/2}$ and $a_s = (\pi f/\alpha_s)^{1/2}$, α_s is the sample thermal diffusivity, $b_{nm} = k_n a_n / k_m a_m$ (n = g, s, b, that is, g = gas, s = sample, b = backing), and L_S is the sample thickness. This equation is a complex mathematical function of the optical, thermal and geometrical parameters of the system, and it governs our results for all the chopper frequencies.

Experimental

The photothermal spectrometer

The photothermal spectrometer depicted in Figure 2, is composed of a Sciencetech monochromator (model 9055F), a Stanford Research System SR (540) mechanical slotted wheel chopper and a 450 W Xenon lamp (Thermo Oriel) used as excitation source. The homemade photoacoustic chamber can be placed in a horizontal table in order to work with liquid samples at controlled temperature by a thermostatic bath. The measuring system was composed by a lock-in amplifier (Stanford Research System SR 830) locked at the chopper frequency. Data were acquired automatically and the system was controlled by a computer via a GPIB interface.

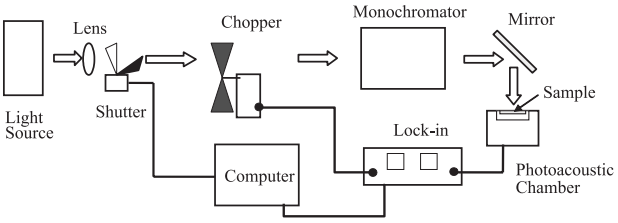

Figure 2. Experimental setup of the photothermal spectrometer.

The photoacoustic chamber

The homemade photoacoustic chamber is depicted in Figure 1. It is consisted by an aluminum body and possesses a fused silica window. The sample is placed on an acrylic backing material. The microphone is a Brüel & Kjaer model 4192 using a conditioning amplifier model Nexus, which is connected to the lock-in amplifier.

Sample preparation

The edible soybean, canola and olive oils were obtained commercially from a reliable source. Volumes of 10 mL of oil samples were heated up from temperature of 22 °C to the smoke point of each one: 234 °C for soybean oil, 248 °C for canola oil and 217 °C for olive oil. The oils were continuously heated up for 30 min to reach the respective temperatures: 345 °C for soybean oil, 353 °C for canola oil and 318 °C for olive oil to assure that oil samples were completely decomposed. The oils were cooled to 22 °C in order to obtain the photoacoustic spectra measurements. The volume of sample inserted in the chamber was in the range of 0.2 to 0.3 mL (three drops approximately). Each sample was placed on the acrylic backing material of the photoacoustic chamber for each spectrum scanning in the 220 to 1200 nm wavelength range. Each experiment was carried out in duplicate.

Spectrophotometric measurement of the oils

The results obtained by PAS were compared with a conventional method utilizing a spectrophotometer (Cary 50, Varian, Mulgrave, Australia) in the 190 to 1100 nm wavelength range. Absorbances of samples were measured

using a cuvette with a path length of 1 cm. The baseline was obtained using as reference ambient air inside the cuvette.

Results and Discussion

Figures 3 and 4 show the photoacoustic spectra of non-degraded olive, canola and soybean oils at 40 Hz of chopper frequency in the 220 to 1200 nm wavelength range, in ambient temperature.

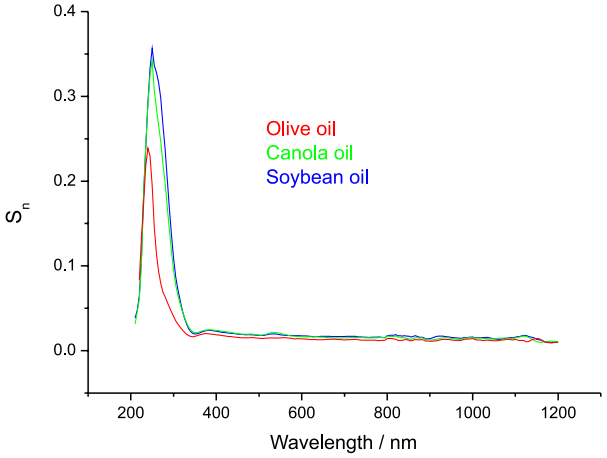

Figure 3. Photoacoustic S_n spectra of olive, canola and soybean oils.

Figure 3 is the normalized signal intensity ($S_n = |S_n|$) and Figure 4 is the respective normalized phase (F_n). As according to the figures, the phase spectra are inverted to signal intensity showing a transmission-like behavior. F_n represents a phase lag between the moment of radiation illumination and the signal amplification by the lock-in, and so it strongly depends on the chopper frequency.

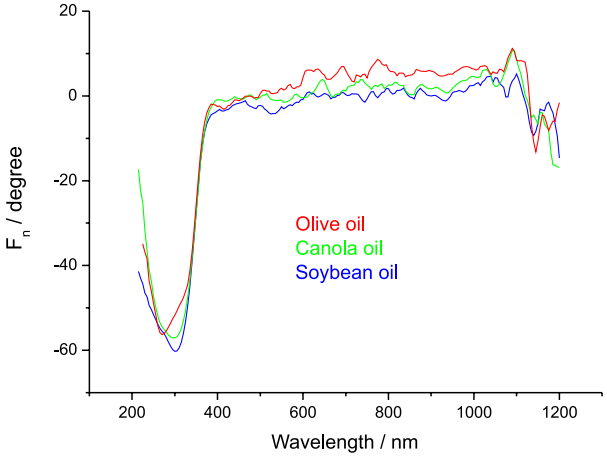

Figure 4. Photoacoustic F_n spectra of olive, canola and soybean oils.

Figure 4 shows that in the region of radiation reflection by the samples, i.e., above at about 390 nm, the phase lag is null, and below that point, where the samples absorb radiation, the phase lag is strong. According to equation 2, S_n is a complex function which gives intensity and phase signals, shown in Figures 3 and 4, respectively. The peaks are at about 240 nm for olive oil and 250 nm for canola and soybean oils in the S_n spectra. In the phase spectra, the peaks are at about 270 nm for olive oil and 300 nm for canola and soybean oils. The difference among those peaks in S_n and F_n spectra is related to chopper frequency and instrumental phase shifts, then in order to compare to absorbance spectrum peaks, we have to consider only the S_n spectrum. The peaks in ultraviolet region (UV) of the absorption spectra of vegetable oils are related to π-π* and the forbidden n-π* electronic transitions due to C=C (non-conjugated double bond) and C=O (carbonyl groups) of unsaturated fatty acids, respectively.[18-19] The thinner band of olive oil and its blue shifted peak in that region is related to higher concentration of unsaturated fatty acids compared to the other two oils.[20] All spectra measured are in the correct range of absorption of fatty acids presents in vegetable oils.[21-22]

Figures 5 and 6 show the photoacoustic spectra of degraded olive, canola and soybean oils at 40 Hz of chopper frequency in the 220 to 1200 nm wavelength range, in ambient temperature. Figure 5 is the normalized signal intensity (S_n) and Figure 6 is the respective normalized phase (F_n). As in the former case, the phase spectra show transmission-like behavior. All the peaks in the S_n spectra for the degraded oils are red shifted: at about 270 nm for olive oil, i.e., 30 nm of shifting, and 257 nm for canola and soybean oils, which is 7 nm of shifting. Also, all the peaks are red shifted in the phase spectra: at about 373 nm for olive oil, this is more than 100 nm of shifting, and 324 nm for canola and soybean oils, i.e., 24 nm of shifting. As well known, peak shifts

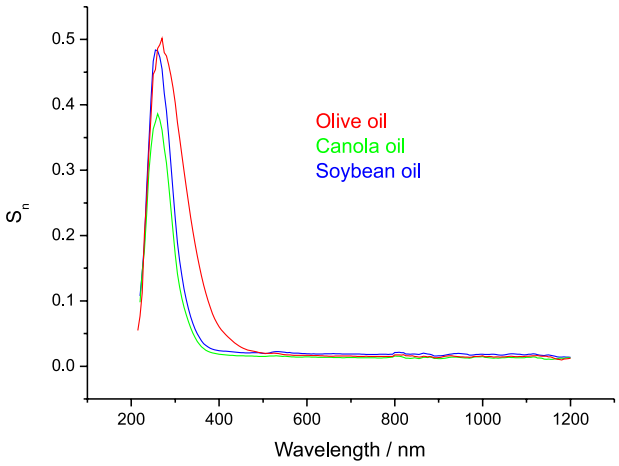

Figure 5. Photoacoustic S_n spectra of degraded olive, canola and soybean oils.

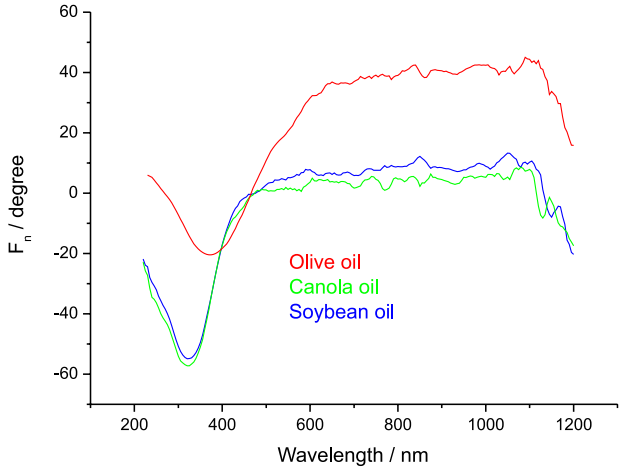

Figure 6. Photoacoustic F_n spectra of degraded olive, canola and soybean oils.

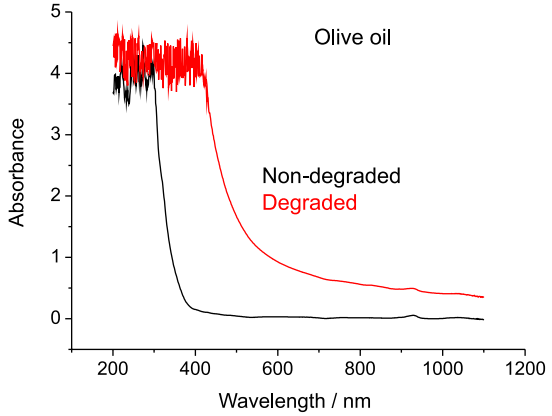

Figure 7. Conventional absorbance spectra of non-degraded and degraded olive oil.

in absorption spectra represent molecular compounds alterations in the samples.

As shown in Figures 5 and 6, all the absorption bands presented wide broadening for the degraded oils, but for olive oil this behavior was wider. This band broadening explains the color darkening of the degraded oils, mainly for olive oil which passed from light yellow to dark brown color. Also olive oil, which is higher in viscosity than the other two oils in ambient temperature, presented the highest viscosity after the temperature degradation. Furthermore, the F_n spectrum of olive oil is phase shifted throughout the spectrum as shown in Figure 6, which could be related to more light-scattering after the degradation. As olive oil is composed by 83.6% of unsaturated fatty acids,[20] it suffers great alterations when heated,[23] presenting more intense degradation by temperature rise showing more viscosity increasing than that for canola and soybean oils. Then, more viscosity increasing represents more radiation absorption, causing band broadening in the absorption spectra. Canola oil presented the smallest band broadening as shown in Figure 5. This behavior is probably associated to small viscosity increasing as compared with the other two oils after the temperature degradation.

In order to compare PAS with conventional optical absorption spectra, Figure 7 shows the absorbance spectra of olive oil, both non-degraded and degraded, obtained with a Varian spectrometer in the 200 to 1100 nm wavelength range.

Both spectra were saturated below 420 nm for the degraded oil and below 300 nm for the non-degraded one. In order to resolve the UV absorption bands of the oils in this conventional absorption spectroscopy, we would have to dissolve them in appropriate non-polar organic solvents, such as petroleum ether, diethyl ether[14] and n-hexane. This shows the power of PAS over absorbance spectroscopy, since PAS gives good UV absorption spectra without the necessity of oil dilution. Also, Figure 7 shows the broadening of the UV absorption band for the degraded olive oil and the whole spectrum is shifted to higher absorbance, even for the infrared region where the oil is non-absorbing. This behavior is consistent to the increasing of viscosity of the degraded oil due to polymerization of degradation products.[14] Thus, the arising of polymerized products increases the absorbance over the whole wavelength range, and this is characteristic of light scattering samples. Also, this is consistent to Figure 6, which shows photoacoustic phase shifting throughout the spectrum for the degraded olive oil. As we can see, absorbance spectra of undiluted oils are UV-saturated (optical saturation) and are featureless, i.e., without the entire absorption band (a Gaussian curve format). Then, we do not show the absorbance spectra for the other two oils because they presented the same behavior (UV-absorption saturation).

The physical and chemical properties of the non-volatile compounds of the studied oils change when they are heated to the smoke point. These changes involve fatty acid decreasing, increasing of viscosity and density, color alterations, and changes of concentrations of free fatty acids, polar substances and polymeric compounds.[24-25] All these changes result in peak shifts and absorption band broadening as shown in Figures 5 and 6. The peak shifts and absorption band broadening is due to high temperatures heating after the smoke point of the oils, which starts the oil degradation. In the beginning of heating, the oils present a viscosity decreasing due to higher freedom degree of their molecules, following by volatile and substance losses, such as peroxides, epoxides, hydroxides and ketones, which provoke viscosity increasing and color darkening due to non-polar compounds arising, and dimerization and polymerization.[14]

Conclusions

This paper presented an application of a particular photothermal technique, PAS, to study optical properties of edible oils. From the experimental point of view, this technique provides a powerful investigation of such properties since it produces non-saturated spectra for strongly UV-absorbing and highly light-scattering oil samples, without the necessity of dilution in hazardous organic solvents. Nevertheless, dilution causes solvent-solute interaction which shifts the absorption band peaks, and so it is undesirable for obtaining optical absorption spectra of pure samples. Then, despite the complexity of the PAS theory, it was obtained good optical absorption spectra of the studied oils, which gave saturated UV-absorbance conventional spectra (without dilution). The peak shifts and band broadening of the PA spectra, after the heat degradation, are related to molecular compounds alterations of the studied degraded oils. We believe the data will assist in the ongoing efforts being made to understand the temperature degradation of these important commercially edible oils, and also show the power of PAS over absorbance spectroscopy for studying this type of compounds.

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