Spectral analysis of the photoacoustic spectroscopy measurements

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Abstract

It is shown that by calculating and analyzing the projection of the photoacoustic signal in each phase or direction, the particular phase angles in which the contributions to the optical absorption spectrum are isolated can be determined. The method for obtaining the projection of the photoacoustic signal as a function of the phase angle and the corresponding spectrum analysis is discussed. This methodology is applied in measurements of mango fruit (Mangifera indica L.) skin obtaining the isolated contributions corresponding to their photoprotective pigments in the epidermis and the hypodermis.

Keywords: Photoacoustic spectroscopy, optical absorption spectrum, thermal waves.

Resumen

Se muestra que mediante el cálculo y el análisis de la proyección de la señal fotoacústica en cada fase o dirección pueden ser determinados los ángulos de fase particulares en los que aparecen aisladas las contribuciones al espectro de absorción óptico obtenido mediante la técnica de espectroscopía fotoacústica. Se discute el método para obtener la proyección de la señal fotoacústica en función del ángulo de fase y el análisis del espectro correspondiente. Se aplica esta metodología en mediciones de piel de mango (Mangifera indica L.) obteniendo las contribuciones aisladas correspondientes a los pigmentos fotoprotectores en la epidermis y la hipodermis.

Palabras clave: Espectroscopía fotoacústica, espectro de absorción óptico, ondas térmicas.

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I. INTRODUCTION

Photothermal phenomena form a very general class of physical phenomena in which light energy, when absorbed by a material, is transformed into heat, via non-radiative de-excitation processes. The basic design of a photothermal experiment consists of a radiation source whose light beam impinge on the sample under study, generating a thermal response inside it. This response is detected and transformed in an electric signal, which is subsequently amplified and captured to carry out a subsequent analysis of the information obtained. Depending on the type of detector used to transform the thermal response of the material into an electrical signal, it is the name assigned to the measurement technique. In this way, when an acoustic detector is used, the technique is called photoacoustic (PA), if the detector is a pyroelectric, the technique is called photo-pyroelectric, when an optical detector is used, the technique is called photothermal radiometry [1].

In the PA technique it is possible to have, in general, three types of measurement schemes that depend on the physical parameter that is varied to determine the FA signal as a function of this parameter. The first is the one in which the modulation frequency of the light source is varied. Then, by analyzing the amplitude and phase of the measured PA signal, the parameters of heat transport can be determined, as well as relaxation times and carrier recombination speeds, among other properties of the sample under study. [2, 3, 4]. The second case is that in which both the frequency of modulation and the characteristics of the radiation source (wavelength and intensity) are kept constant and the parameter that varies is the exposure time, it is said that we deal with the PA technique solved in time. This technique allows us to study, among other things, the evolution of photosynthetic oxygen and the storage of energy in plants [8]. The third configuration, which is the one that interests us in this work, is that in which keeping the modulation frequency of the source constant, the wavelength of the light source incident on the sample is varied. This is the photoacoustic technique solved in wavelength, called photoacoustic spectroscopy (PAS), which allows to study the optical absorption spectrum of the sample under study [5, 6, 7].

This work shows the fundamentals of the data analysis methodology of the PA signal obtained by means of the PAS technique. It shows how to perform the separation of the independent contributions that make up the PA signal by generating the isolated spectra of the optical absorption spectrum and the phase difference between these contributions. This methodology is applied to the isolation of the contributions to the optical absorption spectrum in mango fruit (Mangifera indica L.) skin.

II. METHODOLOGY

For a sample given, the signal obtained by means of the photoacoustic spectroscopy measurement (S,ϕ) can be decompose in its phase-component S_0 and in its quadrature-component S_{90},

$$S_0 = S \cdot cos\emptyset$$
$$S_{90} = S \cdot sin\emptyset \qquad (1)$$

where S and ϕ are the amplitude and phase of the PA signal, respectively, see figure 1.

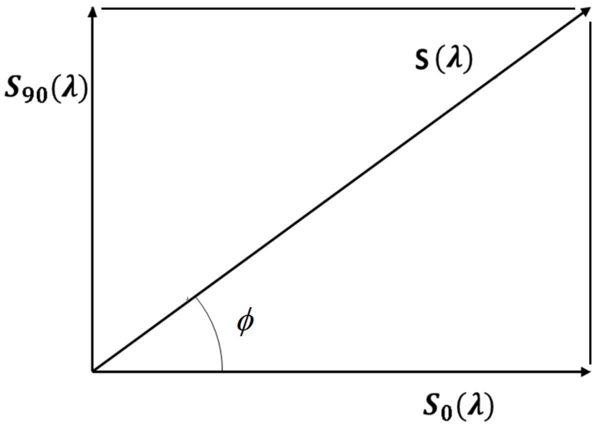

FIGURE 1. Components in-phase S_0 and in-quadrature S_{90} of the photoacoustic signal with amplitude S and phase ϕ.

For a given direction θ the component of the PA signal can be written as

$$S_\theta = S_0 \cdot cos\theta + S_{90} \cdot sin\theta \qquad (2)$$

In figure 2 it is shown S_θ as the sum of the components of S_0 and S_{90} along the direction θ.

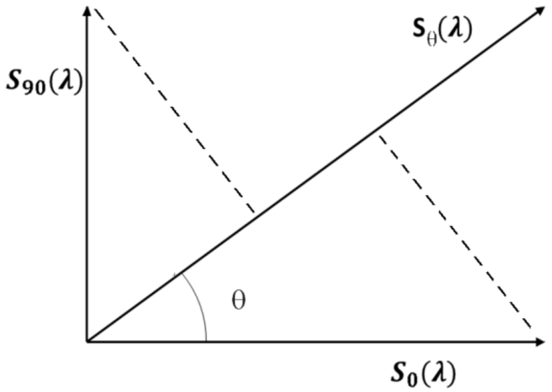

FIGURE 2. Projection S_θ of the photoacoustic signal S in the direction θ.

Thus, by varying the phase θ, it is searched the phase θ' at which only one component of $\mathbf{S}$ is present in the graph of $S_{\theta'}$ vs λ. Once found θ', the phase θ_B of the contribution S_B is obtained adding or subtracting π/2 radians from θ', since $\mathbf{S}_B$ and $\mathbf{S}_{\theta'}$ are perpendicular. In the same way, varying the phase θ, it is searched the phase θ' at which the other component of $\mathbf{S}$ appears in the graph of $S_{\theta''}$ *vs* λ. Once found θ', the phase θ_A of the contribution S_A is obtained adding or subtracting π/2 radians from θ', since $\mathbf{S}_A$ and $\mathbf{S}_{\theta''}$ are perpendicular.

III. EXPERIMENTAL RESULTS AND DISSCUSION

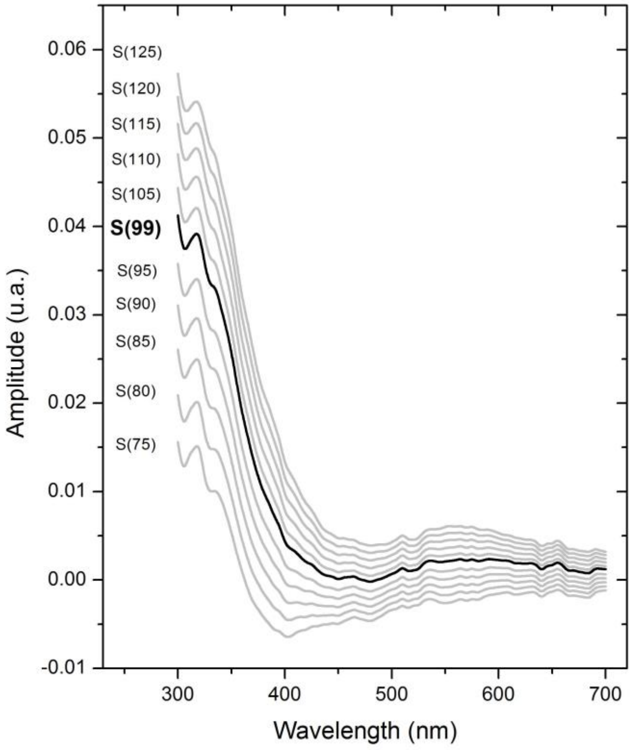

FIGURE 3. Graphs of S_θ vs λ for a variety of values of θ. The black curve represents the curve sought $S_{\theta'}$.

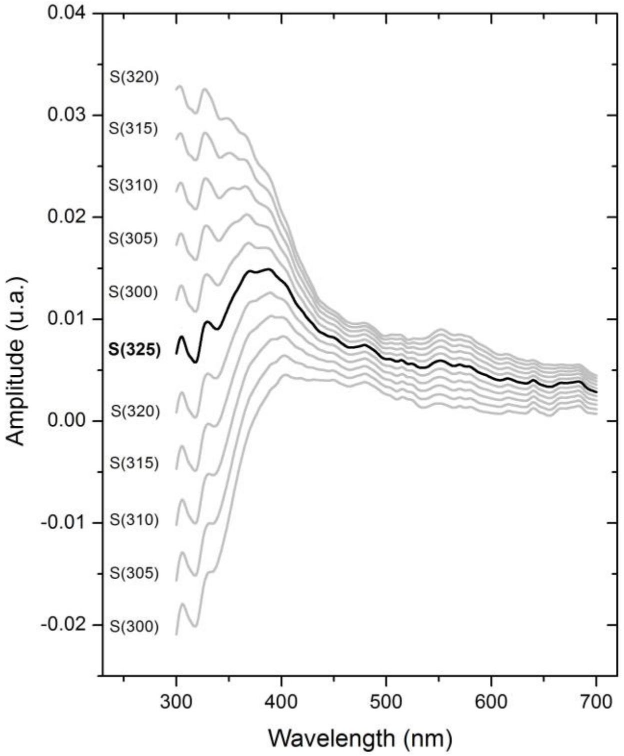

FIGURE 4. Graphs of S_θ vs λ for a variety of values of θ. The black curve represents the curve sought $S_{\theta''}$.

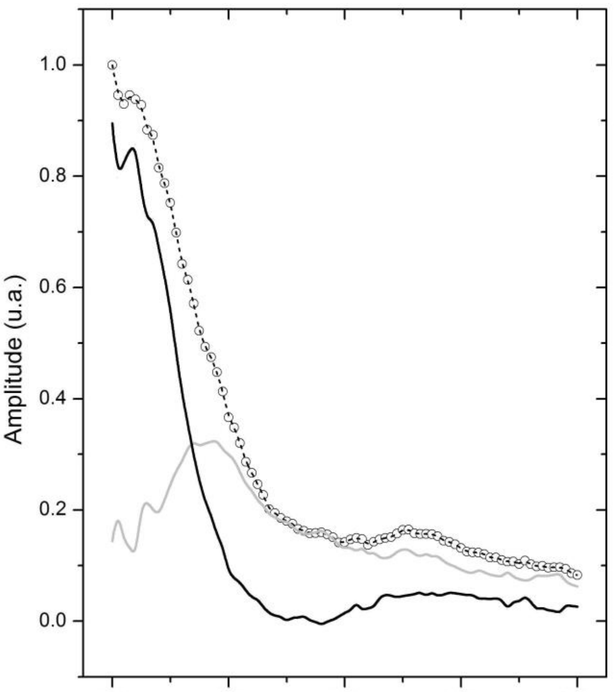

FIGURE 5. PA signal amplitude (u. a.) vs wavelength (nm) for mango fruit (Mangifera indica L.) skin. The open circles show the experimental data, black and gray solid curves show the separated spectra of the epidermis and the hypodermis, respectively, and dashed curve represent the reconstruction of the PA signal from the isolated spectra.

Spectral analysis of the photoacoustic spectroscopy measurements

To show the result of the application of the methodology described, PAS spectrum of mango fruit (Mangifera indica L.) skin was obtained. Then, by calculating and analyzing the projection of the photoacoustic signal in each phase or direction, the phase angles in which the contributions to the optical absorption spectrum are isolated were determined. Figure 3 and 4 show the family of curves $S_\theta(\lambda)$ obtained from application of Eq. (1-2) and PA experimental data for various values of θ. The black curves in figures 3 and 4 represents the curves sought $S_{\theta'}$ and $S_{\theta''}$, respectively. The gray curves represents the family of curves obtained in the search for $S_{\theta'}$ and $S_{\theta''}$.

In figure 5 are shown with open circles the experimental data, black and gray solid curves show the separated spectra of the epidermis and the hypodermis, respectively, and dashed curve represent the reconstruction of the PA signal from the separate spectra.

From de results $\theta' = 99^{o}$ and $\theta'' = 325^{o}$, it follows $\theta_A = \theta' - 90^{o} = 9^{o}$ and $\theta_B = \theta'' + 90^{o} = 55^{o}$, respectively. Hence, $\Delta\theta = 46^{o}$ or 0.80 rad is the difference in phase between the thermal response of each contribution. The modulation frequency used in the measurement was $f = 17$ Hz and the typical value of the thermal diffusivity of the fruits is $\alpha = 0.14\ mm^2/s$ [8], hence, the thermal diffusion length of the thermal response

$$\mu = (\alpha/\pi f)^{1/2}, \tag{3}$$

is $\mu = 51\ \mu m$. Then, considering the expression to calculate the spatial separation between the absorption centers [6]

$$d = \mu \cdot \Delta\theta, \tag{4}$$

it is obtained $d = 40.8\ \mu m$. This result is congruent with the thickness of the epidermis and its average distance to the hypodermis in the skin of fruits.

IV. CONCLUSIONS

The methodology to carry out the separation of independent contributions of a given optical absorption spectrum obtained from photoacoustic spectroscopy was described. It was also shown that this methodology provides the phase difference between the isolated contributions from which can be obtained the spatial separation between contributions in the sample. As an example, this methodology was applied to measurements of mango fruit (Mangifera indica L.) skin obtaining in a remarkable way the isolated contributions corresponding to their photoprotective pigments in the epidermis and the hypodermis. Also, it was obtained the spatial separation of these absorption centers.

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