

Photoacoustic technique in the transmission configuration for quantitative analysis of liquids

J.A. Balderas-López

*Unidad Profesional Interdisciplinaria de Biotecnología del Instituto Politécnico Nacional,
Avenida Acueducto S/N, Col. Barrio la Laguna, Del. Gustavo A. Madero, México, D.F., 07340, México,
e-mail: abrahambalderas@hotmail.com*

J. Díaz-Reyes

*Centro de Investigación en Biotecnología Aplicada del Instituto Politécnico Nacional,
Ex-Hacienda de San Juan Molino Km. 1.5, Tepetitla de Lardizábal, Tlaxcala, 90700, México.*

Recibido el 26 de abril de 2011; aceptado el 10 de agosto de 2011

A photoacoustic methodology for the measurement of optical absorption coefficient for pigments in liquid solution is introduced. The mathematical model, involving the Beer-Lambert model for light absorption, is a generalization of a previously reported photoacoustic methodology, involving a surface absorption model, used for thermal diffusivity measurements of liquids. The optical absorption coefficient for aqueous solutions of copper sulfate and methylene blue at various concentrations were measured at a wave-length of 658 nm, to show the range of optical absorption coefficients where the Beer-Lambert model for light absorption applies. It was experimentally shown that at high pigment's concentrations the surface absorption limit is more adequate and, consequently, the sample's thermal diffusivity is obtained instead of the optical absorption coefficient. Optical and thermal properties obtained by means of this photoacoustic methodology resulted in close agreement with the corresponding ones obtained by means of conventional optical spectroscopy and the previously reported photoacoustic methodology for thermal diffusivity measurements, respectively. Results show that this technique has promise applications in the field of quantitative analysis.

Keywords: Photoacoustic; optical; absorption; thermal; diffusivity.

Se presenta un método fotoacústico para la medición del coeficiente de absorción óptico de pigmentos en solución líquida. El modelo matemático, el cual involucra el modelo de absorción luminosa de Beer-Lambert, es una generalización de un método fotoacústico previamente reportado que utiliza un modelo de absorción superficial que es adecuado para la medición de la difusividad térmica de líquidos. Se determinó el coeficiente de absorción óptico, a una longitud de onda de 658 nm, de soluciones acuosas de sulfato de cobre y azul de metileno a varias concentraciones para mostrar el rango de coeficientes de absorción ópticos a los cuales se aplica el modelo de absorción de Beer-Lambert. Experimentalmente se demostró que el límite de absorción superficial es más adecuado para soluciones de altas concentraciones de pigmento y, como consecuencia, se obtiene la difusividad térmica de las muestras en vez del coeficiente de absorción óptico. Las propiedades ópticas y térmicas medidas por medio de esta metodología fotoacústica resultaron en excelente concordancia con las correspondientes obtenidas por medio de la espectroscopía convencional y de la metodología fotoacústica previamente reportada para mediciones de difusividad térmica. Los resultados muestran que esta técnica puede ser de gran utilidad en el campo del análisis cuantitativo.

Descriptores: Fotoacústica; absorción óptica; difusividad térmica.

PACS: 65.20.-w; 78.20.Ci; 66.10.cd

1. Introduction

Optical properties are among the most important physical properties finding applications for analytical purposes. The optical absorption coefficient $\beta(\lambda)$, for example, characterizes the amount of light, of a given wavelength λ , been absorbed by a sample and is used for quantification of pigments in solution with the help of commercial spectrometers [1,2]. The usual manner of quantifying pigments in liquid solution involves comparison among monochromatic light passing through two fixed length cells which contain the solution and the corresponding solvent (usually called the blank), assuming the last one being transparent at the wavelength used for the analysis and applying the Beer-Lambert's law for the light absorbed. This law establishes an exponential decrease of the light's intensity passing through a given cell path length and, based on it, commercial spectrometers are designed to pro-

vide a non-dimensional magnitude called absorbance, A , which is defined as $A = -\log(I/I_0) = \beta(\lambda)l \log(e)$, where I_0 and I corresponds, respectively, to the light's intensity before and after passing through a length, l , of the absorbing sample. Since there is not a criterion for verification in advance on the validity of this absorption model a calibration curve is required, this curve establishes a linear relationship between the absorbance versus pigment's concentration. What is directly measured in conventional spectroscopy, at this manner, is the light transmitted through the sample, photoacoustic spectroscopy, on the opposite, points to the light which is absorbed [1,3-5]. Photoacoustic signal indeed, under the appropriate conditions, is proportional to this absorbed light [5,6] this fact makes that dispersed light, which is problematic in conventional spectroscopy, contributes very little to the photoacoustic signal. This signal is generated, on the first place, for the temperature fluctuations inside the sample as

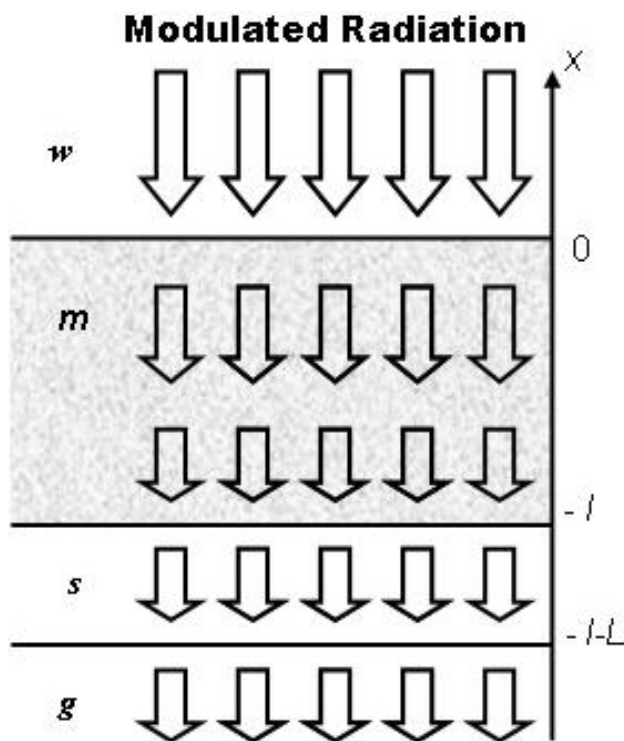


FIGURE 1. Schematic representation of the one-dimensional bilayered photoacoustic model. Medium m is assumed to absorb light by following the Beer-Lambert model, with optical absorption coefficient β .

resulted of the absorption of modulated radiation, this temperature fluctuations are converted in sound by a photoacoustic cell which consist in a close cavity coupled to a microphone [5-8]. The mathematical bases of photoacoustic techniques involve, at this way, differential heat diffusion equations. The analytical treatment, for the transmission configuration presented in this paper, provides moreover of an experimental criteria for deciding on the application of the Beer-Lambert model for light absorption assumed in the mathematical model [8]. This is a very important difference when this methodology is compared with other photoacoustic tech-

niques in the front configuration [9,10]. Water solutions of methylene blue and copper sulfate at different concentrations were used as to measure its optical absorption coefficients at 658 nm and, at the same time, to figure out on the range of optical absorption coefficients where Beer-Lambert's law applies and those to which a surface absorption model is more adequate. In particular it was experimentally shown, that this photoacoustic methodology simplifies to a one previously reported in the literature, for measuring thermal diffusivity for liquids and involving the surface absorption model [11]. The optical absorption coefficients and thermal diffusivities measured with this photoacoustic methodology are compared very well with the corresponding ones obtained by means of a commercial spectro- meter and also with the photoacoustic methodology previously reported for thermal diffusivity measurements.

2. Theory

The geometry of the one-dimensional model, depicted in Fig. 1, consists of two layers embedded between two semi-infinite optically non-absorbing media (w and g in this figure). When monochromatic radiation coming from media w , with intensity I_0 and modulation frequency f (angular modulation frequency $\omega=2\pi f$), strikes medium m and it is absorbed across it according to the Beer-Lambert model, with optical absorption coefficient β (assuming medium s transparent to the same radiation), it produces a heat source inside the sample. This heat, traveling across the different media, generates temperature fluctuations inside the different materials, named thermal waves. According to the Rosencwaig-Gersho model for gas-cell photoacoustic (PA) signal generation in the transmission configuration, this signal is proportional to the temperature fluctuations at the $s - g$ interlayer. Solving the corresponding heat diffusion equations with the proper boundary conditions (heat flux and temperature continuity at the interfaces $w - m$, $m - s$ and $s - g$) and the physical requirement of finite solutions as $x \rightarrow \pm\infty$, it is possible to shown that the photoacoustic signal is given by [12,13]

$$\delta P(l, L, f) = \frac{\gamma P_0 G(f)}{2\sqrt{2}T_0 l_g a_g} \frac{I_0}{k_m \sigma_m} \frac{r}{(1 - r^2)} e^{-\sigma_s L} \times \left[\frac{(1 - b_{wm})(r - 1)e^{-\beta l} e^{-\sigma_m l} + (1 + b_{wm})(r + 1)e^{-\beta l} e^{\sigma_m l} - 2(r + b_{wm})}{\Omega(1 + b_{wm})e^{\sigma_m l} - \Psi(1 - b_{wm})e^{-\sigma_m l}} \right] \quad (1)$$

where

$$\Omega = (1 + b_{gs})(1 + b_{sm}) + (1 - b_{gs})(1 - b_{sm})e^{-2\sigma_s L}$$

and

$$\Psi = (1 + b_{gs})(1 - b_{sm}) + (1 - b_{gs})(1 + b_{sm})e^{-2\sigma_s L}$$

In these equations k_m is the thermal conductivity of medium m , α_j , $j = g, s, m$, is the thermal diffusivity of medium j , $\sigma_j = (1+i)\alpha_j$, $j = s, m$, where $\alpha_j = (\pi f / \alpha_j)^{1/2}$, is the complex thermal diffusion coefficient of medium j ,

$r = \beta / \sigma_m$, and $b_{jh} = e_j / e_h$ is the ratio of thermal effusivities for media j and h , P_0 and T_0 are, respectively, the ambient pressure and temperature for the air inside the PA cham-

ber, $\gamma = c_p/c_v$, its ratio of specific heats and l_g its thickness. The experimental PA signal is multiplied by a modulation-frequency-dependent factor, $G(f)$, representing the instrumental transfer function. Eq. (1) is a very complicated complex expression, which depends, among others, on the thermal and optical properties of the involved media. It is then possible, in principle, to get information of these parameters by the analysis of this equation although this is in general a very complicated task unless the appropriate limiting conditions are considered.

Special limiting cases

1. Weakly absorbing sample in the thermally thick regime

If the sample behaves in the thermally thick regime, $|\sigma_m l| \gg 1$ ($|\exp(-\sigma_m l)| \approx 0$ and $|\exp(\sigma_m l)| \gg 1$), and its optical absorption coefficient is such that $|r| < 1$ then the expressions $(1 - b_{wm})(r - 1)e^{-\beta l}e^{-\sigma_m l}$ and $2(r + b_{wm})$, in the numerator, and $\Psi(1 - b_{wm})e^{-\sigma_m l}$, in the denominator of Eq. (3), can be neglected and this equation simplifies to:

$$\delta P(l, L, f) = \frac{\gamma P_0 G(f)}{2\sqrt{2}T_0 l_g a_g} \times \frac{I_0}{k_m \sigma_m} \frac{r e^{-\sigma_s L}}{(1 - r^2)} \frac{(1 + b_{wm})(r + 1)}{\Omega(1 + b_{wm})} e^{-\beta l}. \quad (2)$$

If, in addition, the sample's thickness, l , is considered as the only variable this last equation can be written in the very simple way

$$\delta P(f, l, L) = \frac{\gamma P_0 G(f)}{4\sqrt{2}T_0 l_g a_g} \frac{I_0}{k_m \sigma_m} (1 + \gamma_{wm})(1 + \gamma_{sm})(1 + \gamma_{gs}) \times \frac{e^{-\sigma_s L} e^{-\sigma_m l}}{[1 + \gamma_{gs} \gamma_{sm} e^{-2\sigma_s L} + \gamma_{wm} \gamma_{ms} e^{-2\sigma_m l} + \gamma_{wm} \gamma_{sg} e^{-2\sigma_m l} e^{-2\sigma_s L}]} \quad (4)$$

where γ_{jh} , $j, h = w, m, s, g$, are thermal coupling coefficients, defined as $\gamma_{jh} = (1 - b_{jh}) / (1 + b_{jh})$ [7,8,11]. This limit corresponds to the case of PA signal's "optical saturation"; under this condition the light's beam is absorbed along a short distance inside the sample and, in opposition to the previous limiting case, the sample's optical properties does not explicitly appear in the equation and only the sample's thermal properties are able to be measured. This approximation is equivalent to the surface absorption model, previously reported by Balderas-López and Mandelis [11], which have successfully used for the measurement of the thermal diffusivity of two layered systems in the frequency domain. If, in addition, the thermally thick regime for the sample is considered in Eq. (4), $|\exp(-\sigma_m l)| \approx 0$, and this equation simplifies furthermore to

$$\delta P(f, l, L) = \frac{\gamma P_0 G(f)}{4\sqrt{2}T_0 l_g a_g} \frac{I_0}{k_m \sigma_m} (1 + \gamma_{wm})(1 + \gamma_{sm})(1 + \gamma_{gs}) \frac{e^{-\sigma_s L}}{1 + \gamma_{gs} \gamma_{sm} e^{-2\sigma_s L}} e^{-\sigma_m l} \quad (5)$$

Considering again the sample's thickness l as the only variable, this equation can be written as

$$\delta P(l) = H e^{-\sigma_m l} \quad (6)$$

where H (as C in Eq. (3)), is a complex expression which is independent of the sample's thickness, l .

Equation (6) shows that both, PA amplitude (in semi-log scale) and phase have linear behavior as functions of the sam-

$$\delta P(l) = C e^{-\beta l} \quad (3)$$

here C is a complex expression which, although depending on the physical properties of the involved media, it is independent of the sample's thickness l . Eq. (3) predicts linear behavior for the PA amplitude (in semi-log scale) as a function of the sample's thickness while the PA phase remains constant. It is then possible to obtain the optical absorption coefficient, β , for the pigment in solution by means of Eq. (3), the experimental procedure consists in to carry out a PA signal scan as a function of the liquid sample's thickness (sample's thickness scan). The optical absorption coefficient can be obtained as the slope of the straight line which fits the experimental amplitude data (in semi-log scale) inside the sample's thickness range where the PA phase remains constant.

2. Strongly absorbing sample in the thermally thick regime

If, on the other extreme, the sample's optical absorption coefficient is assumed very large (theoretically $\beta \rightarrow \infty$ and $r \rightarrow \infty$) then $\exp(-\beta l) \approx 0$ and the following limits applies

$$\begin{aligned} \text{Lim}_{r \rightarrow \infty} \frac{r(r-1)}{1-r^2} &= -1, & \text{Lim}_{r \rightarrow \infty} \frac{r(1+r)}{1-r^2} &= -1, \\ \text{Lim}_{r \rightarrow \infty} \frac{r^2}{1-r^2} &= -1, & \text{Lim}_{r \rightarrow \infty} \frac{r}{1-r^2} &= 0 \end{aligned}$$

Eq. (1) simplifies, as a consequence, to

ple's thickness under these conditions. This phase behavior makes. the difference between this limiting case and the previously discussed one where the phase was shown to be a constant.

An adequate analytical treatment of Eq. (6) allows two independent thermal diffusivity values, one from the PA amplitude and the other one from the Phase, the procedure will

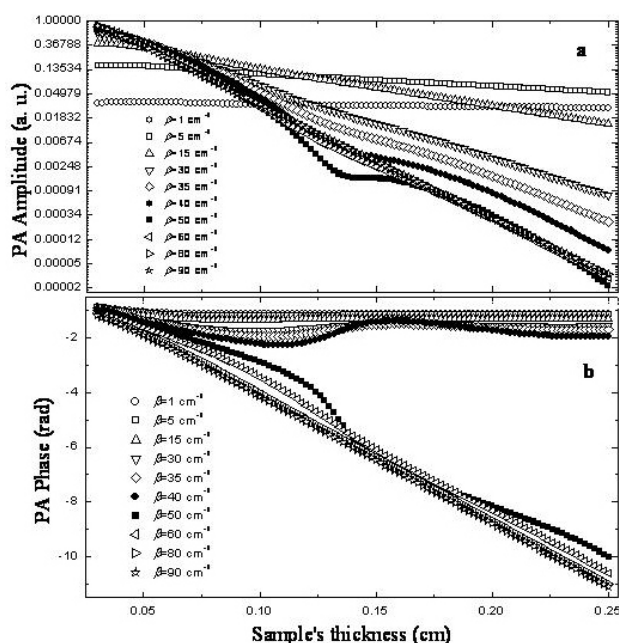


FIGURE 2. Computer simulations for Eq. (1). The fundamental parameters used for these simulations were $L=0.0140$ cm, $\alpha_m=0.001456$ m²/s, $\alpha_s=0.0058$ cm²/s, $e_m=0.16$ Ws^{1/2}/cm²K, $e_s=0.15$ Ws^{1/2}/cm²K and a modulation frequency of 1 Hz together with the optical absorption coefficients shown on the plots. **a.** Photoacoustic (PA) amplitudes and **b.** Photoacoustic (PA) phases.

render two very similar slopes, M , from which the thermal diffusivities can be obtained as $\alpha_m=(\pi/M)^2 f$.

In the interlude there will be a range of pigment's concentration where none of these limiting cases will apply, being the experimental photoacoustic phase the criteria to decide on each case as it will be shown later.

3. Computer simulations

Some computer simulations, using matlabTM, were done to show on the theoretically predicted behavior of Eq. (1) and, at the same time, to illustrate on the different limiting cases described above. These computer simulations were done assuming β -values ranging from 1 to 90 cm⁻¹, for $L=0.0140$ cm and the following thermal parameters: $\alpha_m=0.001456$ cm²/s, $\alpha_s=0.0058$ cm²/s, $e_m=0.16$ Ws^{1/2}/cm²K and $e_s=0.15$ Ws^{1/2}/cm²K, and a modulation frequency of 1 Hz.

Figure 2 shows the collection of theoretical amplitudes (Fig. 2a) and phases (Fig. 2b) as functions of the sample's thickness, for the different values of β . As theoretically predicted there are two limiting cases in which the PA amplitude has linear behavior in a semi-log scale (empty symbols in Figs. 2a and 2b); this happens from a certain sample's thickness (in the sample's thermally thick regime) which depends on the value of optical absorption coefficient. For β -values ranging from 1 to 35 cm⁻¹ in Fig. 2a this linear behavior in the PA amplitude is followed by an approximately constant PA phase (see Fig. 2b), this range of optical absorption coef-

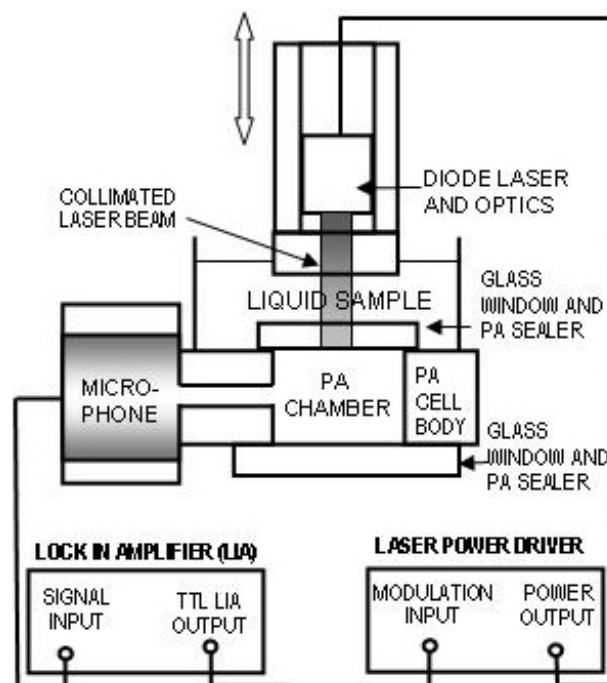


FIGURE 3. Schematic cross section of the photoacoustic (PA) experimental set-up.

icients corresponds to the first limiting case in which Eq. (3) applies; meanwhile that for optical absorption coefficients in the range of 60 to 90 cm⁻¹ in Fig. 2a, the linear behavior of the PA amplitude is followed by a similar linear behavior of the PA phase (Fig. 2b), these two linear behaviors share approximately the same slopes for which this range of optical absorption coefficient corresponds to the second limiting case for which Eq. (6) applies this time. These theoretical predictions means that for this PA technique in the transmission configuration $\beta=35$ cm⁻¹ is approximately the limit for weak optical absorption fluids for which the optical absorption coefficient can be obtained and $\beta=60$ cm⁻¹ is approximately the onset of optical absorption coefficients from which the sample can be considered as strong absorber and then only its thermal diffusivity can be obtained. It is clear that the PA phase can be used as a criterion for to decide which one of these two limiting cases is fulfilled. For intermediate β -values (between 40 and 60 cm⁻¹) neither the PA amplitude nor the PA phase show such a simple behaviors as the ones previously described meaning that Eq. (1) strictly applies inside this range, then it is very difficult to obtain sample's optical and thermal properties in this intermediate β -range. The general conclusions obtained here are independent on the involved thermal properties since they just determine the range of sample's thickness in which the sample's thermally thick behavior applies.

4. Experimental setup

Photoacoustic experiments were carried out using a Locking amplifier (Stanford Reaserch Systems, model SR830) and a

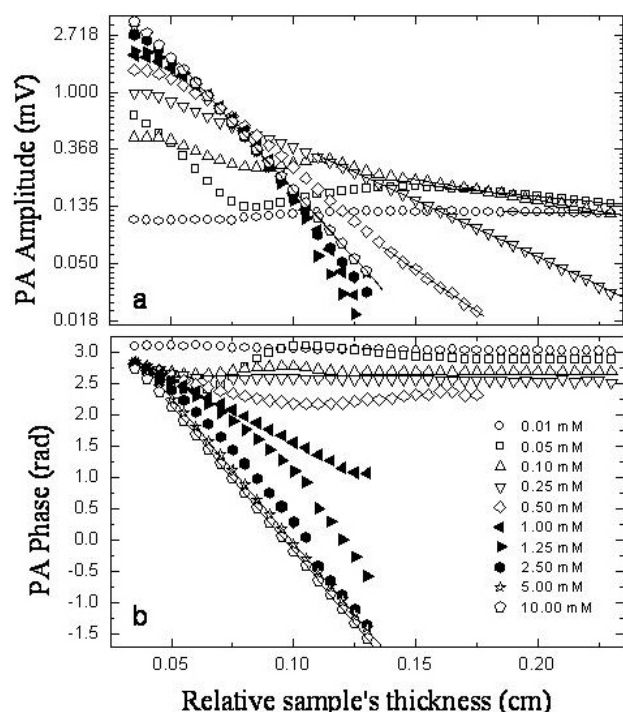


FIGURE 4. Photoacoustic signals at 1 Hz (a. Photoacoustic amplitude and b. Photoacoustic phase), as functions of the sample's thickness, for the methylene blue samples used in this work. Open symbols stand for the sample's concentrations for which optical or thermal properties were obtained, meanwhile full black symbols stand for the ones which nor of these physical properties were able to be obtained. The photoacoustic phase (b) was used as an experimental criterion to decide on each case. Continuous lines represent the best fits to the linear models used for the analysis by means of Eq. 5 and Eq. 8.

current source (Thorlabs model LDC202C) meanwhile the spectrometric measurements were carried out by means of a commercial spectrometer (VELAB, 722-2000). Samples for the analysis were prepared using methylene blue and copper sulfate from the company Reactivos analíticos REASOL.

The experimental photoacoustic set-up, shown schematically in Fig. 3, consisted of a red diode laser (Single mode Hitachi HL6512MG, $\lambda=658$ nm, 50 mW CW power) whose light-intensity was modulated by means of the current source driven by the TTL (Transistor-Transistor-Logic) lockin's output. The PA chamber consisted of a cylindrical tunnel (3 mm diameter and 3 mm height), made of a brass body, communicating with an electret microphone and its built-in pre-amplifier through a hollow channel. The PA signal was monitored as a function of the sample's thickness l (a sample's thickness scan). Several solutions of methylene blue and copper sulfate in distilled water (see Tables I and II, respectively) were used to test on the methodologies presented in this work. For to do this, 10 mL of each aqueous copper sulfate solution at 0.1, 0.25 and 0.5 M were obtained diluting 1, 2.5 and 5 mL of a 1 M aqueous solution of copper sulfate in 9, 7.5 and 5 mL of distilled water, respectively. This 1 M solution of copper sulfate was prepared diluting 62.42 g of

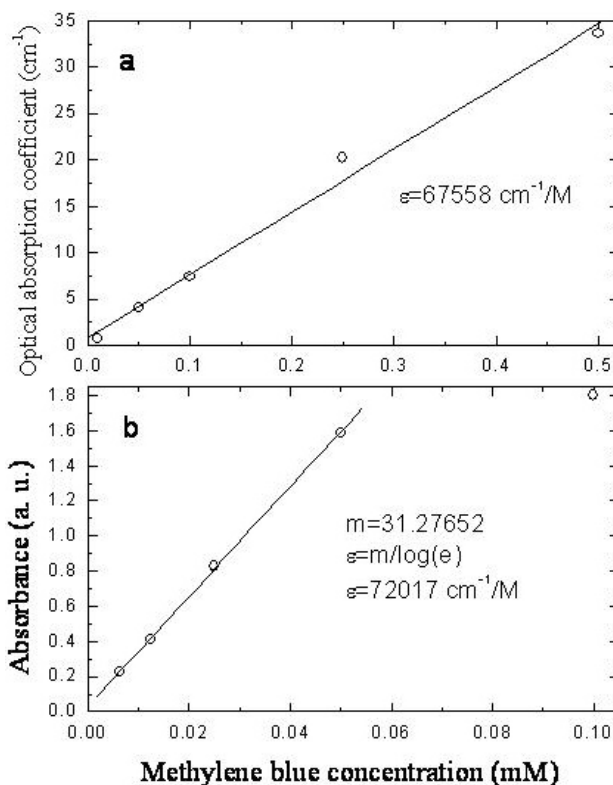


FIGURE 5. Optical absorption coefficients, as measured by means of the photoacoustic methodology described in this paper, as function of the dye concentrations for the methylene blue samples used in this work. b. Absorbance as functions of dye concentrations for some methylene blue samples in the range of 0.00625 to 0.01 mM. The continuous lines represent the best fits to linear models for measuring the molar absorption coefficients for each case. The corresponding values are shown on the same plots.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (M.W. 249.68 g/mol) in 250 mL of distilled water using a 250 mL volumetric glass flask. 10 mL of each methylene blue solution was obtained in similar way starting with a 10 mM aqueous solution of this substance in distilled water which was prepared by diluting 0.935 g of methylene blue (standard, M. W. 373.9 g/mol) in 250 mL of distilled water using a 250 mL volumetric glass flask. Sample's thickness scans at 1 Hz were made three times for each of the pigment's solution, setting the lockin's time constant at 3 s. These sample's thickness scans were made from an initial sample's thickness l_0 (which was unknown) taking steps of 0.0050 cm by using a micrometer stage of 5 microns of step. For matter of comparison conventional measurements of optical absorption coefficients for each sample were done by means of a commercial spectrophotometer. As to compare with the results obtained for the strong absorbing solutions independent measurements of thermal diffusivities for some representative methylene blue samples (see Table III) were also done by triplicate by means of a previously reported photoacoustic technique using the surface absorption model [11].

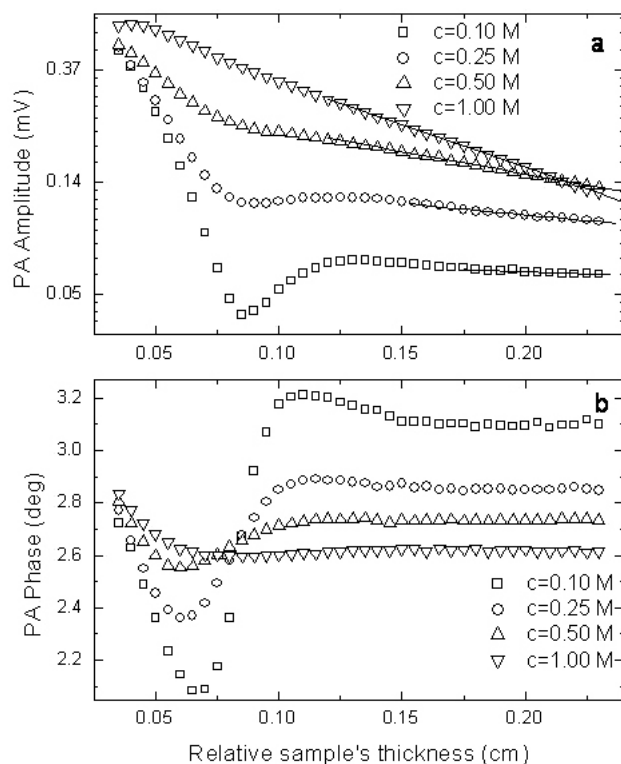


FIGURE 6. Photoacoustic signals at 1 Hz (a. Photoacoustic amplitude and b. Photoacoustic phase), as functions of the sample's thickness, for the copper sulfate samples used in this work. Continuous lines represent the best fits to the linear models for measuring the sample's optical absorption coefficient by means of Eq. 5. Photoacoustic phase (b) was used as a criterion for validation in the sample's thickness range used for the analysis.

5. Results and discussion

Representative PA signals as functions of the sample's thickness for the case of the methylene blue solutions are shown in Figs. 4a and 4b. The similitude with the theoretical data, shown in Figs. 2a and 2b, is evident. From Fig. 4a, which shows the PA amplitudes (in semi-log scale), is clear a sample's thickness range in which the first limiting case experimentally applies, this happens for a pigment's concentration ranging from 0.01 to 0.5 mM. This conclusion is also obtained from the PA phase, shown in Fig. 4b, which is approximately constant inside the sample's thickness ranges used for the analysis. The second limiting case is clearly obtained for pigment's concentrations of 5 and 10 mM since both PA amplitude (Fig. 4a) and PA phase (Fig. 4b) show similar linear behavior, with approximately the same slope, inside the sample's thickness ranges used for the analysis. These two limiting cases are shown in Figs. 4a and 4b with open symbols. It is also evident that none of these two cases are experimentally obtained for pigment's concentration in the range of 1 to 2.5 mM. This conclusion can be obtained from Fig. 4 since although some linear behaviors for the PA amplitude (Fig. 4a) and the PA phase (Fig. 4b) can be figure out inside

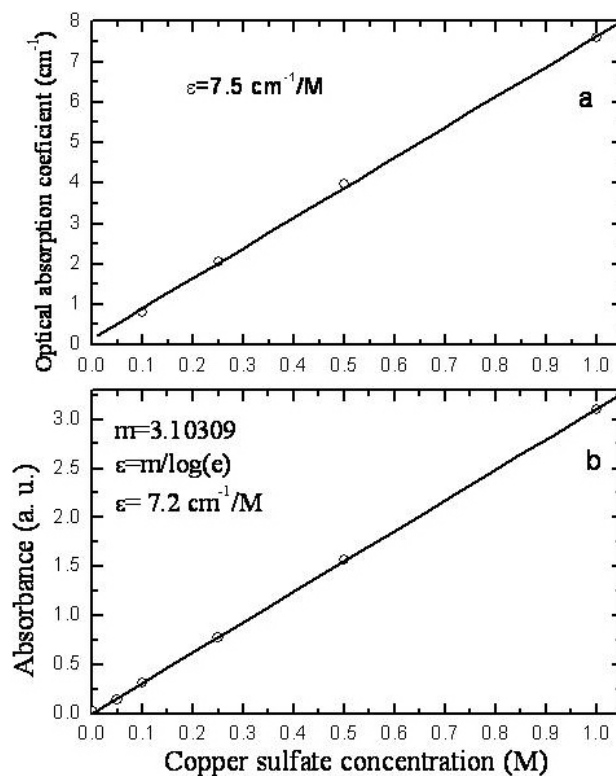


FIGURE 7. Optical absorption coefficients, as measured by means of the photoacoustic methodology described in this paper, as function of the dye concentrations for the copper sulfate samples used in this work. b. Absorbance as functions of dye concentrations for some copper sulfate samples in the range of 0.05 mM to 1 mM. The continuous lines represent the best fits to linear models for measuring the molar absorption coefficients for each case. The corresponding values are shown on the same plots.

some thicknesses ranges, the respective slopes are very different to each other.

As described in the theory section the optical absorption coefficient for the methylene blue samples in the range of 0.01 to 0.5 mM and the thermal diffusivities for the ones at 5 and 10 mM were obtained by linear fits of the PA amplitude (Eq. (5)) and from the PA amplitude and the PA phase (Eq. (8)), respectively. These linear fits are shown as continuous lines in Fig. 4a, for the amplitude, and Fig. 4b, for the phase. The corresponding average values for optical absorption coefficients and thermal diffusivities are summarized in Table I, columns 2 and 3 (from the amplitude) and 4 (from the phase), respectively, taking the standard deviation as a measure of uncertainty.

Independent verification of the Beer-Lambert's law was done by plotting the optical absorption coefficients, obtained by means of the photoacoustic technique, versus the pigment's concentration; the result is shown in Fig. 5a. The linear fit, shown as the continuous line on the same figure, directly yields in this case the molar absorption coefficient for methylene blue in distilled water, which resulted in $\varepsilon=67558 \text{ cm}^{-1}/\text{M}$, at a wave-length of 658 nm. As a matter of comparison this optical property for methylene blue in dis-

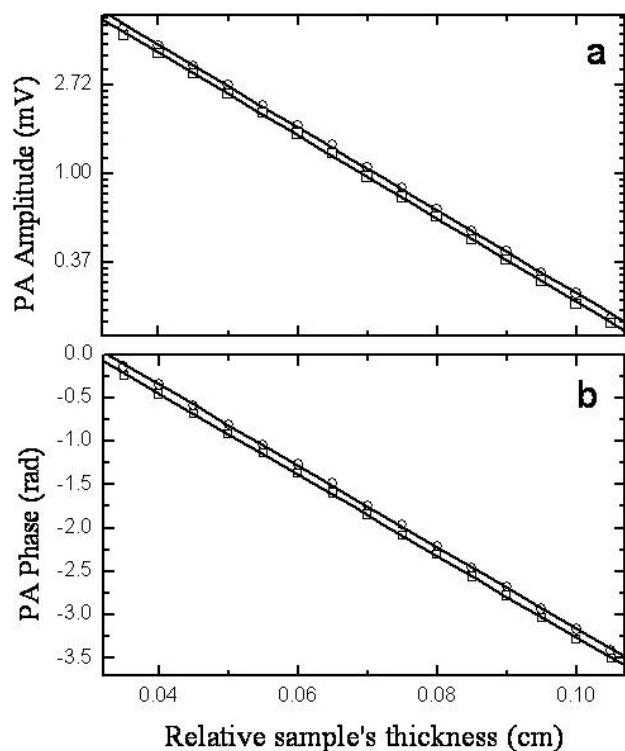


FIGURE 8. Photoacoustic phase (a) and photoacoustic amplitude (b), as functions of the sample's thickness, at a modulation frequency of 1 Hz, using a photoacoustic methodology in the surface absorption model, for methylene blue solution at two different dye concentrations. Circles (O) correspond to a dye concentration of 0.01 mM, and squares (◻) to a dye concentration of 10 mM. The continuous lines on each plot represent the best fits to the linear models used for to obtain the thermal diffusivity for each sample by mean of the PA amplitude (a) and the PA phase (b).

tilled water was also measured by means of a standard procedure using the commercial spectrophotometer, the absorbances for a set of methylene blue solutions, with concentrations in the range of 0.00625 to 0.1 mM, were obtained and plotted as function of the pigment's concentration. The fitting procedure in the linear range of pigment's concentrations render in this case the pigment's absorptivity by means of $\varepsilon = m/\log(e)$, where m is the slope of the best straight line, this linear range was obtained from 0.00625 to 0.05 mM as shown in Fig. 5b, the corresponding molar absorption coefficient obtained was $\varepsilon = 72017 \text{ cm}^{-1}/\text{M}$, as shown on the same figure. These two values of absorptivity are in good agreement with the reported one of $70273 \text{ cm}^{-1}/\text{M}$ [14], photoacoustic methodology, at a difference of conventional spectroscopy, allows however a wider range of concentrations for measuring this optical property (0.01 to 0.5 mM versus 0.00625 to 0.05 mM, respectively) for this pigment, which experiment strong absorption at 658 nm. This is because photoacoustic signal is directly generated by the absorbed radiation in opposition to conventional spectroscopy in which the signal is obtained through the transmitted radiation. That's why dispersed light it is a minor problem when using photoacoustic spectroscopy but it is strong limitation

TABLE I. Optical absorption coefficient (β) and Thermal diffusivities (α) for aqueous solutions of methylene blue, as measured by means of the PA methodology described in this paper. α_{Amp} (α_{Ph}) refers to the thermal diffusivity obtained by means of the analysis of the PA amplitude (PA Phase).

| Dye's concentration (mM) | β (cm^{-1}) | α_{Amp} ($\text{cm}^2/\text{s} \times 10^{-2}$) | α_{Ph} ($\text{cm}^2/\text{s} \times 10^{-2}$) |
|--------------------------|------------------------------|---|--|
| 0.01 | 0.8 ± 0.2 | — | — |
| 0.05 | 4.1 ± 0.3 | — | — |
| 0.10 | 7.2 ± 0.2 | — | — |
| 0.25 | 19.7 ± 0.2 | — | — |
| 0.50 | 32.2 ± 0.3 | — | — |
| 1.00 | — | — | — |
| 1.25 | — | — | — |
| 2.50 | — | — | — |
| 5.00 | — | 0.00140 ± 0.00002 | 0.00148 ± 0.00001 |
| 10.00 | — | 0.00141 ± 0.00001 | 0.00146 ± 0.00001 |

TABLE II. Optical absorption coefficient (β) for the aqueous solutions of copper sulfate, as measured by means of the PA methodology described in this paper.

| Dye concentration (M) | β (cm^{-1}) |
|-----------------------|------------------------------|
| 0.1 | 0.8 ± 0.1 |
| 0.25 | 2.1 ± 0.3 |
| 0.5 | 4.0 ± 0.2 |
| 1.0 | 7.6 ± 0.1 |

TABLE III. Thermal diffusivities for some of the methylene blue solutions studied in this work, as measured by using the PA methodology in the surface absorption limit, described by Balderas-López and Mandelis [6]. α_{Amp} (α_{Ph}) refers, to the thermal diffusivity measured by means of the analysis of the PA amplitude (PA phase).

| Methylene Blue concentration (mM) | α_{Amp} ($\text{cm}^2/\text{s} \times 10^{-2}$) | α_{Ph} ($\text{cm}^2/\text{s} \times 10^{-2}$) |
|-----------------------------------|---|--|
| 0.01 | 0.00145 ± 0.00001 | 0.00144 ± 0.00001 |
| 0.10 | 0.00143 ± 0.00001 | 0.00144 ± 0.00001 |
| 1.00 | 0.00144 ± 0.00001 | 0.00145 ± 0.00001 |
| 10.00 | 0.00143 ± 0.00001 | 0.00143 ± 0.00001 |

for conventional spectroscopy for which a reference sample is also needed (the blank).

The same procedure described for the methylene blue samples were made for water solutions of copper sulfate at different concentrations (Table II). The set of PA signals for these solutions are shown in Fig. 6a, for the amplitude, and 6b for the phase.

Copper sulfate in distilled water has very weak absorption at 658 nm, in contrast to methylene blue in water, for which, even for copper sulfate solutions near of the saturation limit (1.0 M) the thermal approximation (limiting case 2) was not reached this time. The continuous lines in Fig. 6a show best linear fits for to obtain the optical absorption coefficients for each sample in the sample's thickness range where the optical limit was fulfilled, as it was indicated by the phase (Fig. 6b). These values are summarized in Table II, column 2. The plots of optical absorption coefficients and absorbances as function of the dye concentration are shown in Figs. 7a and 7b, respectively. The corresponding molar absorptivities obtained with these two procedures were 7.5 and 7.2 cm^{-1}/M , respectively, in very good agreement to each other.

To test on the reliability of the thermal diffusivity values obtained by means of the PA methodology described in this paper for the methylene blue solutions at high concentrations, this thermal property was independently measured for some of these methylene blue solutions, by using other reported photoacoustic methodology, based on the surface absorption limit [11]. The experimental setup used in this case was essentially the same one shown schematically in Fig. 3 with the exception that a very thin slab (about 0.0200 cm) of silicon was attached between the laser light beam and the liquid sample. Figs. 8a and 8b, respectively, show the corresponding amplitudes (in semi-log scale) and phases for two of these pigment's solutions (0.01 and 10 mM). The thermal diffusivity values resulting from this last procedure, for some of the dye solutions studied in this work, are summarized in Table III, columns 2 (for the amplitude) and column 3 (for the phase). The thermal diffusivity values obtained by using these two methodologies (columns 3 and 4 in Table I and columns 2 and 3 in Table III) show excellent agreement to each other.

6. Conclusions

A photoacoustic methodology for the measurement of the thermal and optical properties for pigments in liquid solution

has been described. For pigments at low concentration this PA methodology provides the optical absorption coefficient while for concentrate solutions it provides the thermal diffusivity, instead. Simple criteria for to decide on which one of these two physical properties are been measured are also given. This characteristic allows the measurement of molar absorptivity (or molar absorption coefficient) for a pigment in liquid solution by measuring the optical absorption coefficient for just one sample of known dye concentration. This fact represents a great advantage over the traditional methodology, carried out with commercial spectrometers, for the measurement of this optical property which involves the construction of a calibration curve of absorbance vs. concentration for the verification of the Beer-Lambert model.

Conventional spectroscopy and this PA methodology could be considered as complementary techniques, being the first one adequate for dilute solutions and the second one for the concentrate ones, as suggested by Fig. 5, indeed PA signal is stronger and provides better results for high dye concentrations, however, on a difference of conventional spectroscopy, PA signal can be improved by increasing the intensity of the light's source and it could also provide good results even for dilute solutions.

Finally the range of sample's concentrations where this photoacoustic technique provided measurements of optical absorption coefficients was experimentally established between 0.01 and 0.5 mM for the methylene blue samples, as shown in Fig. 4. This means that, independently of the dye sample, this photoacoustic technique provides optical properties if the sample's optical absorption coefficient is in the range of 0.8 and 33 cm^{-1} (see Tables I and II), this contrast with conventional spectrometry for which the upper limit of optical absorption coefficients where applies was established about 7 cm^{-1} , in agreement with Figs. 5 and 7.

Acknowledgments

The authors thank the financial support of COFAA-IPN and CONACyT (projects 40079F and 61062).

1. D.A. Skoog and J.J. Leary, *Principles of Instrumental analysis* Fourth edition (Saunders College Publishing, Toronto, 1997).
2. D.J. Pietrzyk and C.W. Frank, *Analytical Chemistry* 2nd Ed. (Academic Press, London, 1979).
3. W. Demtröder, *Laser spectroscopy* Vol. 2 (Springer, Berlin, 2008).
4. Deepak V. Bageshwar, Avinash S. Pawar, Vineeta V. Khanvilkar, and Vilasrao J. Kadam, *Eurasian J. Anal. Chem.* **5** (2010) 187.
5. Rosencwaig Allan, *Photoacoustics and photoacoustic spectroscopy* (John Wiley & Sons, New York, 1980).
6. Allan Rosencwaig and Allen Gersho, *J. Appl. Phys.* **47** (1976) 64.
7. J.A. Balderas-López and A. Mandelis, *J. Appl. Phys.* **90** (2001) 2273.
8. J.A. Balderas-López, *Rev. Sci. Instrum.* **77** (2006) 086104.
9. O. Delgado-Vasallo *et al.*, *Meas. Sci. Technol.* **11** (2000) 412.
10. J.A.P. Lima *et al.*, *Analytical Sciences* **17** (2001) 530.
11. J. A. Balderas-López and A. Mandelis, *Int. J. of Thermophys.* **23** (2002) 605.
12. Andreas Mandelis and Martin M Zver, *J. Appl. Phys.* **57** (1985) 4421.
13. M. Chirtoc and G. Mihăilescu, *Phys. Rev. B.* **40** (1989) 9606.
14. See the web page: <http://omlc.ogi.edu/spectra/mb/mb-water.html>, for a list of optical absorption coefficients of aqueous solution of methylene blue.