

Photothermal Spectrometry in Small Liquid Channels

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Abstract: A novel apparatus for performing photothermal lens spectroscopy is described. The apparatus uses a low-volume cylindrical sample cell, a chopped or pulsed excitation laser, and a continuous probe laser. The full volume of the sample is irradiated with constant, e.g., non-Gaussian, irradiance beam produced by the excitation laser. Constant irradiance excitation source does not directly produce the photothermal lens element in the sample. The lens element is formed by thermal diffusion from the irradiated sample volume, through the sample cell walls. Under continuous irradiation, thermal diffusion results in a parabolic temperature change profile. The apparatus has been found to work with cells designed to contain sample volumes from 6 μL down to 24 nL. Larger and smaller volume cells are practical but signals produced in the smallest sample cells exhibit deviation from that expected based on the theory. This is attributed to probe laser diffraction by the circular aperture of the sample cell.

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Introduction

Photothermal lens spectrometry is a novel means to measure optical absorption.¹ It is one of several ultra-sensitive photothermal spectroscopy methods applicable to trace analysis. The applicability to trace analysis is due to the high sensitivity and small sample volumes needed for an analysis.

There are several physical effects that limit sensitivity and influence the accuracy of measurements obtained using photothermal lens spectrometry.² First, the photothermal lens signal is related to the lens formed the sample as a consequence of light absorption and subsequent energy transfer to the matrix. The optical element produced when laser beams are focussed into a homogeneous sample is not a simple lens. The aberrant nature of the photothermal lens results in signal magnitudes that are somewhat smaller than expected and also more difficult relate to sample absorbance.³ Second, sample irradiation can produce large temperature changes. In theory, the on-axis temperature change approaches infinity at long times for any excitation power when using continuous laser excitation sources. In practice, large temperature changes distort the thermal lens perturbation due to density differences and convection heat transfer or even boiling may occur.⁴ The later distorts the signal and ruins the analytical utility.

Other factors resulting in inaccurate absorbance determination are related to the photophysics of sample excitation and solvent (matrix) relaxation. Nonlinear optical absorption and bleaching, transient volume changes, and excited state analyte absorbance can occur when using high irradiance laser excitation sources.⁵⁻⁷ These effects may generally be avoided only by using low irradiance. This is often accomplished by choosing continuous over pulsed lasers for sample excitation.

An apparatus utilizing a two-laser photothermal lens apparatus that is immune to many problems associated with photothermal lens spectrometry and capable measuring optical absorbance in very small samples is described in this work. The apparatus uses a nanoliter-volume sample cell with a visible laser used as the excitation source. The sample cell is constructed from high thermal conductivity metal and has a large surface area and

relatively large heat capacity. A simplified version of the theory for describing the photothermal lens developed in a cylindrical sample cell is given.⁸ A model for relating signals to sample absorbance is given and experimental evidence is presented. Time-dependent photothermal signals are detected. The technique exhibits high sensitivity and can be used for ultra-sensitive detection. Analyte excitation is often performed using laser light sources. The resulting photothermal lens is measured using a probe laser. Excitation and probe lasers may be the same. Laser light sources produce a small spot size at a focus. The small spot size allows one to probe extremely small sample volumes.

Theory

Theoretical time-dependent temperature changes and inverse photothermal lens focal lengths for both standard and cylindrical sample cells are described in the literature.^{1,8} The cylindrical sample cell used here has a large thermal conductivity compared to the solvent. Little temperature change occurs at the sample cell wall because of the high thermal conductivity ratio. The solution to the thermal diffusion equation for a zero temperature change at the cell wall temperature change is⁹

$$\delta T_{\text{cyl}}(r,t) = \frac{\alpha E Y_H}{\kappa} \left[\frac{a^2 - r^2}{4} - 2a^2 \sum_{n=1}^{\infty} \frac{J_0(\chi_n r/a)}{\chi_n^3 J_1(\chi_n)} e^{-\chi_n^2 t/4t_c} \right] \quad (1)$$

α (m^{-1}) is the exponential absorption, E (W m^{-2}) is the excitation irradiance, Y_H is the heat yield, κ ($\text{W m}^{-1} \text{K}^{-1}$) is sample thermal conductivity, J_n are Bessel's functions, and χ_n are the n 'th root of the equation; $J_0(\chi_n)=0$. The characteristic thermal time constant is defined as $t_c = a^2/4D_T$, where a (m) is the cylindrical sample cell radius and D_T ($\text{m}^2 \text{s}^{-1}$) is the thermal diffusion coefficient. It is easy to see that the temperature profile is parabolic for long irradiation times.

$$\delta T_{\text{cyl}}(r,\infty) = \frac{\alpha E Y_H}{4\kappa} (a^2 - r^2) \quad (2)$$

The time-dependent inverse focal length for the cylindrical sample cell is found by integration of the second radius

derivative over pathlength, then multiplying by the thermal-optical coefficient (dn/dt).

$$\frac{1}{f_{cyl}(t)} = \left(\frac{dn}{dT} \right) \frac{\alpha I E Y_H}{2\pi a^2 \kappa} \left[1 - 2 \sum_{n=1}^{\infty} \frac{e^{-\chi_n^2 t / 4t_c}}{\chi_n J_1(\chi_n)} \right] \quad (3)$$

The photothermal lens signal for the cylindrical sample cell is defined in the same fashion as in the large-volume sample cell.¹ Approximations are not needed. The time-dependent signal is found from; $S(t) = [\Phi_p(0) - \Phi_p(t)] / \Phi_p(t)$, where $\Phi_p(t)$ is the probe laser power. For a pinhole aperture placed far from the sample cell, the signal is $S(t) 2 z'/f(t)$, where z' (m) is the distance from the probe laser beam focus position to the sample cell.

Model calculations exhibit an exponential response after a relatively short induction period. The model behavior indicates that a single Bessel's root dominates the time-dependent behavior. Examination of the model data shows that the first root, $\chi_1 = 2.405$, dominates after an initial induction period. The inverse focal length is approximated by

$$\frac{1}{f_{cyl}(t)} \approx \left(\frac{dn}{dT} \right) \frac{\alpha I E Y_H}{2\pi a^2 \kappa} \left[1 - 2 \frac{e^{-\chi_1^2 t / 4t_c}}{\chi_1 J_1(\chi_1)} \right] \quad (4)$$

The characteristic time constant may be obtained from $t_c = 2.632 \Delta t_{10\%-90\%}$, where $\Delta t_{10\%-90\%}$ is the time required for the signal to change from 10% to 90% of the maximum.

Experimental

The apparatus used in this study is essentially the same as that used in our previous reports.⁸ An apparatus schematic is shown in Fig. 1. A Coherent model Innova 90 Ar⁺ laser operating at 514.5 nm is used for sample excitation. Laser output is filtered and collimated to produce a cm diameter beam. The collimated beam passes through a neutral density filter, a beamsplitter that directs a fraction of the light to a reference photodiode detector, and a Prontor magnetic shutter. The beam then reflects off a dichroic mirror and is combined with the probe laser.

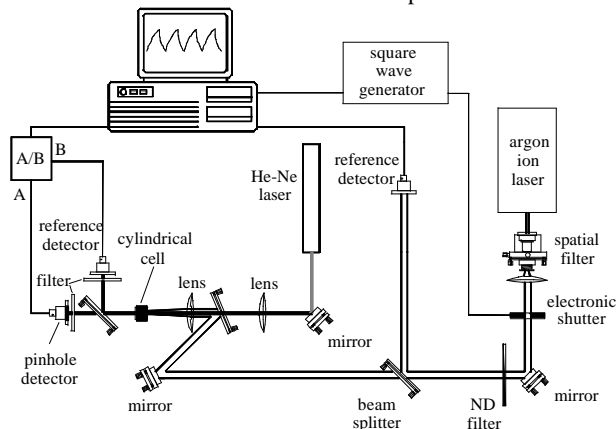


Figure 1. Diagram of the experimental apparatus

A 2 mW, 632.8 nm He-Ne laser is used to probe the photothermal lens. The beam passes through a lens prior to combination with the Ar⁺ laser. The collinear beams both are focused into the sample. The positions of all three lenses are adjusted to image the Ar⁺ laser into the sample cell while focusing the He-Ne laser to a point about one confocal distance in front of the sample cell.

The probe laser beam is split into two parts. Part of the beam passes through a 632.8 nm laser line filter and onto a large area detector. The other part passes through the pinhole aperture, then through a second line He-Ne laser filter onto a similar detector. Silicon photovoltaic detectors are used. Photothermal signal and

He-Ne reference signals are processed with an operational divider to eliminate apparent signals produced from absorption and reflection losses, and sample luminescence.

The photothermal lens signal is digitized with a 16 bit analog-to-digital converter in a PC data collection computer. Data processing is performed using a spreadsheet program. All photothermal lens data is processed to produce signals proportional to inverse focal length.

Several sample cells are used. A commercial HPLC spectrophotometer cell (ISA 0.25 μ L, 2 mm pathlength) is used as purchased. This cell has an estimated inside radius of 200 μ m. A standard 1 cm pathlength spectrophotometry cell is used for comparison studies.

Two "custom" cells were made out of 25 mm by 75 mm Stainless steel sheets of 1.25 mm thickness. These are the same dimensions as a standard microscope slide. Round holes were made using commercial electrolysis. The holes were accurately positioned in the center of these slides for kinematics mounting in the microscope and the photothermal apparatus. The hole diameters were measured with the aid of a Nikon Photomat microscope calibrated with side imprinted with a ruler accurate to 1 μ m (Edmund Industrial Optics). The diameters were 154 μ m and 170 μ m.

The flat surfaces were polished to a mirror-like finish. This resulted in a high degree of reflection of light not passing through the cylindrical hole thereby reducing heating by optical absorption by the cell itself. The samples were introduced using a micropipetter. The slide cells were mounted on a microscope to observe sample loading. After loading, the cell was sealed using microscope slide cover plates. The cover plates were held in place by capillary forces on the smooth surfaces.

Ethanol was used as the solvent for all these experiments. Absorbing reagents used in the present study is dicyclopentadienyl iron, FeCp₂ (Eastman). Samples were deoxygenated with solvent-saturated argon. Concentrations resulting in about used result in absorbances of about 0.005 cm⁻¹, or about 99 %T through the cylindrical sample cells.

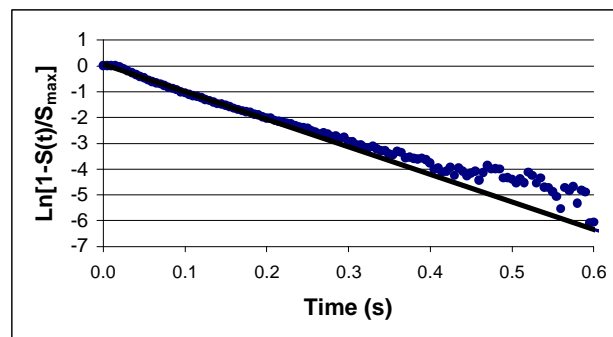


Figure 2. Natural logarithm plot of cylindrical sample cell photothermal lens data.

Results and Discussion

The results for the larger sample cell were presented earlier and will not be described here. Fig. 2 shows a plot of the signal versus time for the 250 nL (0.25 μ L) commercial sample cell plotted on a log scale. This figure illustrates that the sum over Bessel's functions can be approximated by the first root, especially after the small induction time. The smooth line is the theory from Eq. 4 while the points are data measured with the 250 nL sample cell. The simpler model allows for easy data fitting and relatively easy determination of the characteristic time constant.

Results typical of the 25 nL sample cell are shown in Fig. 3. The data is for 0.005 AU sample of FeCp₂ in ethanol and excited with 10 mW of argon ion laser power. The signal shows a

characteristic rise time of 45 ms. However, the expected characteristic time constant was 20 ms for this cell which had 80 μm cylinder radius. The experimental fall time is much shorter, about 20 ms. We do not have an explanation for the apparent time constant discrepancy at this time. The characteristic decay time should be equal to the rise time.⁸

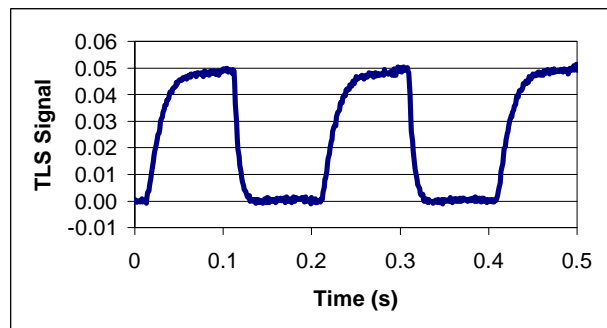


Figure 3. Typical cylindrical sample cell photothermal lens data obtained for the 25 nL cell with 10 mW irradiance.

The data in Fig. 3 show a signal strength of 0.05 for a sample with an absorbance of 0.005. This corresponds to a signal enhancement⁴ of 5. The theoretical enhancement for the 10 mW power used is 23. This discrepancy is not surprising. The maximum theoretical enhancement is rarely realized due to the dependence on optical design parameters such as the probe laser focus position and distance to the pinhole detector.

Conclusions

The apparatus has advantages over the conventional photothermal lens using a relatively large volume sample cell. First the small volume of the sample cell, 250 nL, 30 nL, or 25 nL, in experiments to be presented here, requires little sample. Second, photothermal lens signals produced by thermal diffusion through the sample cell walls are less susceptible to the bulk heat transfer effects due to convection. Third, although the refractive index change may depend on the partial refractive index and partial molar volume of transient species, these changes do not result in a photothermal lens element. By monitoring both the central portion and the full probe laser beam, the apparatus can compensate for transmission changes due to bulk density, refractive index, or absorbance changes. Fourth, the maximum temperature change is finite. The maximum on-axis temperature change produced by continuous laser excitation of a homogeneous sample using the normal photothermal apparatus is, in theory, infinite. This temperature change can be high enough to boil solvents and produce signal instabilities due to turbulent convection heat transfer. In any event, the sample's thermal and physical properties are likely to be significantly different than those prior to irradiation. The cylindrical sample cell circumvents the large temperature changes by heat transport to the surrounding. Fifth, the parabolic-form photothermal lens produced by thermal diffusion is aberration free. Subsequently, the beam propagation theory that only approximately describes the effect of the photothermal lens produced from laser excitation exactly describes the effect of the cylindrical cell lens.

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