Thermochimica Acta 593 (2014) 12–15

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Improvement of an optical fiber sensor for the detection of low concentrations of solutes using the photothermal effect

S. Alvarado [a], E. Marín [a,*], A. Calderón [a], A. Marcano [b]

[a] Instituto Politécnico Nacional, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada (CICATA-Legaria), Calzada Legaria 694 Col. Irrigación, Del. Miguel Hidalgo, Mexico D.F. 11500, Mexico
[b] Department of Physics and Engineering and Optical Science Center for Applied Research, Delaware State University, 1200 North Dupont Highway, Dover, DE 19901, USA

ARTICLE INFO

Article history:
Received 22 May 2014
Received in revised form 6 August 2014
Accepted 11 August 2014
Available online 13 August 2014

Keywords:
Photothermal
Thermal lens
Fiber optic sensor
Refractive index

ABSTRACT

We report on the use of an optical fiber sensor for the determination of concentration of contaminants in solutions below the micromolar level based on the photothermal lens effect. A pump laser beam has been added to a conventional configuration widely used as refractometer, so that the device is improved to detect tiny changes of the refractive index of a sample related to the amount of heat generated following optical absorption. In this way, concentrations as low as 0.1 μM of methylene blue in distilled water were measured. A simple experiment is also performed to demonstrate the photothermal effect.

1. Introduction

Optical fiber sensors have been developed for monitoring a large range of physical, chemical and biochemical properties of matter. Intrinsic properties of optical fiber sensors like low electromagnetic susceptibility, chemical inertness, light weight, compatibility with a variety of materials, among other properties, have made them a success history. Despite obvious advances, the need to develop even more sensitive, precise, reliable, practical, easy-to-use and low cost sensors remains an important area of research in modern photonics. Of particular interest are sensors for biomedical, food industry and environmental applications. Optical fiber sensors have been designed for measurement of distance, displacement and vibration [1], but similar devices have been also used as reflection refractometers [2] that are suitable also for concentration measurement in solutions [2,3]. In the present work, we propose a variation of the optical fiber refractometer where changes of the refractive index in the sample area that is trespassed by the probe beam sent and collected via the fiber tip are generated through the photothermal (PT) effect induced by a pump laser beam, in particular the so-called thermal lens (TL) effect. The absorption of light generates local gradients of temperature, which can substantially affect the propagation of the reflected light. The use of TL effects in analytical chemistry is becoming rapidly widespread, particularly for the determination of trace amounts of chemicals in solvents [4] and for light scattering free optical spectroscopy [5]. Other applications can be found in condensed matter physics, for example for thermal diffusivity determination [6]. We describe here a simple experiment for the demonstration and measurement of the PT effect in a liquid using a commercial fiberoptic sensor (Philtec, Inc., Model RC62 [1]), and its application for low concentrations measurements of a solute in a liquid solution. We show that the use of PT effects generated by a secondary laser beam improves the sensitivity of the optical fiber refractometer allowing the detection of absorbing species at concentration below micromolar level.

2. Experimental set-up and method

Fig. 1 shows a scheme of the proposed modified optical fiber refractometer. The basic design is similar to previously developed systems [1–3]. The Philtec, Inc., Model RC62 [1] optical fiber sensor is a transducer based upon detection of the intensity of reflected light. In this device 880 nm light from a LED (called here the probe beam) is transmitted using an optical fiber bundle to a mirror through the investigated sample contained in a 1 cm thick glass

---

[*] Corresponding author.
E-mail addresses: emarinm@ipn.mx, emarin63@yahoo.es (E. Marín).

http://dx.doi.org/10.1016/j.tca.2014.08.012
0040-6031/

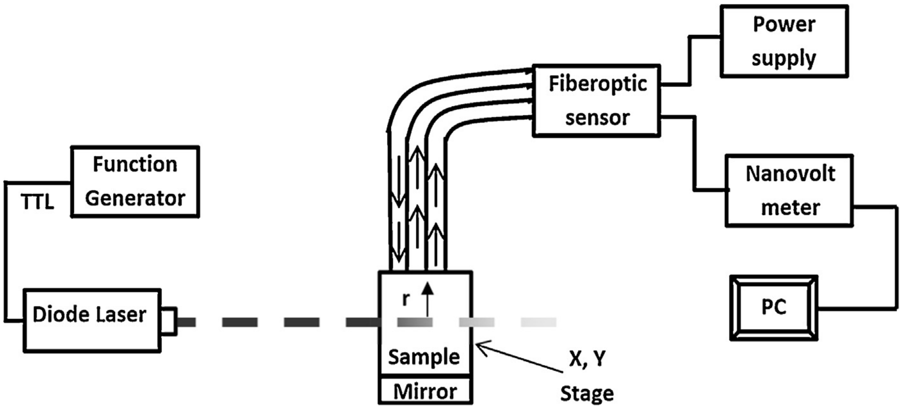

Fig. 1. Scheme of the experimental setup. The mirror covers one of the container walls, while the fiberoptic sensor tip is located in front of the other wall allowing the probe beam to impinge the sample following a path perpendicular to that of the pump beam. The fiberoptic sensor is switched on using a power supply (Matrix, MPS-3003 LK-3). The excitation beam and sample container are inside a black box (not shown in the figure) for removing parasitic contributions. Data acquisition is performed in an automatic way using a GPIB (NI GPIB-USB-HS) interface with a personal computer (PC) and a software developed on Lab-View.

cell, being reflected off the target back to other two separate bundles which follow independent paths back to light detectors. The detectors provide an electrical voltage dependent on the distance, *d*, between target and fiber tip. By measuring the ratio of both outputs, effects of light source intensity variations, sample reflectivity, the opacity of the transmitting medium and loss of light due to diffraction can be eliminated [2]. In this way, the dependence of the sensor signal magnitude (measured with a Keithley 2182 A voltmeter) on the distance *d* has features that depend on the refractive index of the medium. A simple geometrical optics model has been developed elsewhere [2] to estimate the amount of collected light. The amount of reflected light power captured by the secondary fibers depends on the refraction index. The maximum value of the signal shows a nearly linear dependence on the changes of refraction index. We modify the original design by using a secondary excitation beam, namely a pump beam from a 650 nm diode laser (LSR650NL Lasever Inc.) propagating in the direction perpendicular to the probe light beam and intersecting it at the center of the measurement cell. The pump beam intensity is modulated at a 50% duty cycle using the TTL signal provided by a function generator (Matrix, MFG-8216A), although a continuous laser can be used as well, because the same results are obtained without modulation. We notice that in this work we do not measure the photothermal lens directly, which is in general a modulation dependent signal [6]. Instead, we measure the effect of the thermal lensing on the optical fiber signal. Experiments show independence from frequency of the value of the signal for the range of frequencies used. The explanation is that the sensor signal is not synchronized with the laser modulation frequency, i.e., the signal is actually due to an average of the heat injected during a cycle of radiation. Therefore, the signal should not have a frequency dependence because on average it is injected the same amount of heat even if the modulation frequency change. Due to local light absorption, local temperature gradients are formed that affect the refractive index due to its temperature dependence. The result is the formation of a cylindrical lens of thermal origin that affects the amount of reflected light reaching the detectors and improve the sensitivity of the device as will be seen later.

If the light beam is Gaussian and the laser operates in the TEM_{∞} mode the beam intensity in the radial direction obeys the equation

$$I(r) = I_0 \exp\left[-\frac{2r^2}{r_0^2}\right] \qquad (1)$$

where r is the distance in the radial direction, r_0 is the beam waist spot size, or beam radius, defined as the radial distance at which the intensity is down by a factor e^{-2} from its value I_0 at $r = 0$. If the amount of heat generated in the sample is proportional to the absorbed light energy, and if this energy is proportional to I, then it can be assumed that both the temperature distribution and the refractive index generated by the thermal lens effect have a similar Gaussian dependence on r as $I(r)$ has.

The dependence of the amount of collected reflected light on the position d has been previously reported [2]. The value of the signal amplitude can be maximized by scanning along d.

3. Results and discussion

The normalized sensor signal as a function of d is shown for distilled water sample in Fig. 2. The pump beam is turned off. The curve shape is similar as that reported elsewhere [2]. The sensor tip is initially in contact with the sample container wall and it is moved away from this zero point. During this experiment the pump beam is turned off. The curve amplitudes become different

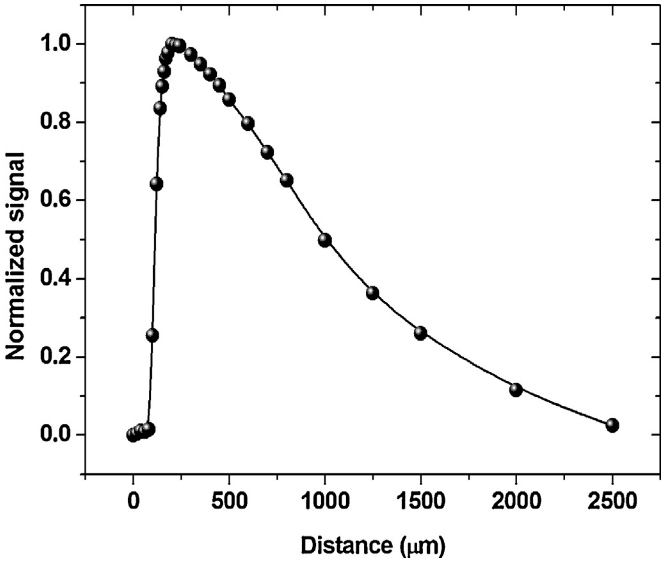

Fig. 2. Plot of the fiber optic sensor normalized signal as a function of the distance between sample's container and sensor tip for distilled water. The solid curve is shown only for visualization purposes.