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cw and pulsed photothermal deflection spectroscopy on textile dyes solutions

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Abstract: Textile dyes solutions have been investigated in a flow through cuvette by comparing transverse pulsed and continuous wave photothermal deflection spectroscopy (PDS). The results show that PDS is not only suitable for ultra trace determinations in the environment, but also for process control with very high analyte concentrations.

1. Introduction

Photothermal deflection spectroscopy has recently emerged as a very sensitive method for the detection of traces of environmental pollutants in water. PDS experiments are generally categorised as being either transverse or collinear [1, 2]. The geometry of the collinear arrangement is advantageous in that the beams can interact over a long distance, thereby yielding a greater signal magnitude [2], however, with the disadvantages of light scattering and absorption of the excitation beam by higher analyte concentrations on its long way across the samples. For these reasons, we investigated the partially very highly concentrated textile dyes samples in the transverse PDS beam arrangement. In the context of a future commercial exploitation of the PDS in e.g. process control, in-line measurements on flowing media are mandatory. Hence it follows, that we investigated the influence of the flow velocity of the sample and laser pulse duration on the PDS signal, either with a 5 Hertz modulated cw laser or a 10 ns pulse width dye laser.

2. Experimental

All PDS experiments have been performed in a transverse 90° crossed beam set up, built to measure liquid samples as described earlier [3]. Briefly, in the cw excitation (a), a continuous UV argon ion cw laser beam (363.8 nm) modulated at a rate of 5 Hz by a mechanical chopper, impinges into a quartz fluorescence cell. In case of pulsed excitation (b) we use an excimer pumped dye laser with a repetition rate of 2 Hz, a pulse width of 10 ns and a power of 10 mJ at 365 nm. The He-Ne probe laser (632.8 nm) is focused perpendicularly at the focus of the actual excitation laser beam inside the flow through sample cell. Behind the sample cell the He-Ne probe laser hits the two dimensional lateral-position-sensitive detector. With cw-excitation applied, the pre-amplified PDS-signal is transferred into a lock-in amplifier, whilst the pulsed PDS signal is evaluated with a digital storage oscilloscope. As analytes we investigated various aqueous dye solutions, such as reactive yellow 27 and reactive red 123 used in the textile industry and the pesticide 2-methyl-4,6-dinitrophenol (DNOC).

3. Results and discussion

3.1. Comparison of pulsed and cw- excitation

The calibration curve for pulsed photothermal spectroscopy with a repetition rate of 2 Hz, is taken for a standard dye solution, that is reactive yellow 27. It shows a nearly linear correlation ($r^2=0,98$) due to the amplitude of the PDS signal versus absorbance a in the range of 6 orders of magnitude, between $a=1,3 \cdot 10^{-4} \text{ cm}^{-1}$ and $a=1 \cdot 10^{+2} \text{ cm}^{-1}$ of the analytes (fig. 1). The only limitation is that, at a high analyte concentration, a decrease of the signal occurs because of the decrease of the absorbed excitation laser in front of the deflection area inside the sample cell. Similar results were obtained with the cw excitation laser (364 nm), modulated by a mechanical chopper at 5 Hz and a power of 150 mW.

Fig 1 Calibrationcurve of the photothermal deflection signal with pulsed excitation as a function of absorbance. The concentration (abscissa) is calculated into absorbance units (cm^{-1}) by the Lambert Beer law.

In the in-line experiments, the PDS signals have been investigated due to the influence of the velocity of a flow medium with a cw-laser excitation time of $\tau=0,2 \text{ s}$ and pulse excitation time of $\tau=10 \text{ ns}$. In figures 2a, b the profiles of the thermal lenses caused by absorption of the excitation beam are plotted for both, the cw- and pulsed excitation. The arbitrary PDS signals which originate in the lock-in-device and the digital oscilloscope are plotted as a function of the distance of the exciting laser beam and the probe HeNe-laser beam. Whereas the pulsed PDS signal profile is only slightly changed by the velocity of the medium, a shift of the signal-profile is seen in the cw- case. Also the shape of the profile changes: the PDS signal at maximum deflection in the negative direction decreases whereas the signal at the maximum deflection in positive direction increases with increasing velocity of the medium. The increase of the positive PDS signal maximum can be explained by the growing density in flow-direction and by the deformation of the time dependant PDS signal. The flowing medium is slowed down and the thermal-gradient of the travelling lens is pushed together. Due to the negative maximum of the profile it is the other way around: the density goes down, the speed increases and the thermal gradient itself will be stretched.

For real samples in process control and in the environment, in-situ and real time measurements are required. Therefore, the influence of flowing media on the stability of the thermal lens formed by laser excitation was investigated. The results of these experiments are shown in figure 3a, b. The cw- and pulsed PDS signals are plotted for both, the positive deflection signal at maximum and negative deflection signal at minimum versus the flow velocity of the liquid samples, respectively. In flowing media cw excitation is disadvantageous compared with pulsed laser excitation, because of large changes by a factor of two in the cw-PDS signal in dependence on the flow velocity.

Fig. 2a: cw PDS signal of reactive red 123 vs. flow velocity

Fig. 2b: pulsed PDS signal of reactive yellow 27 vs. flow velocity

Fig. 3a: cw PDS signal at maximum deflection vs. flow velocity (see text; reactive red 123)

Fig. 3b: pulsed-PDS signal at maximum deflection vs. flow velocity (reactive yellow 27)

3.2. Temperature dependence

The theoretical evaluation of the temperature dependence due to the thermal deflection signal $S(T)$ refers to the temperature function of the refractive index $n(T)$. The calculation of the first derivative of refractive index dn/dT can be explained by following expression:

$$\frac{dn}{dT} = \left. \frac{dn}{dT} \right|_p + \left. \frac{dn}{d\rho} \cdot \frac{d\rho}{dT} \right|_p \quad (\text{eq. 1})$$

A way to take into account the temperature dependence of the first derivative of refractive index $dn/dT = F(T)$ comes from the Lorentz local field treatment. It can be written as:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \cdot \pi \cdot N \cdot \alpha \quad (\text{eq. 2})$$

Here n is the refractive index of an isotopic medium made up of N molecules per unit volume, α is the scalar polarizability of a free molecule. For the PTDS the first derivation of dn/dT [5] is of interest:

$$\frac{dn}{dT} = \frac{1}{V} \frac{dV}{dT} \frac{1}{6n} \cdot (n^2 - 1) \cdot (n^2 + 2), \quad (\text{eq. 3})$$

If the sample is free of thermal stresses one can use the fact that $A = -(1/V)(dV/dT)$ is the coefficient of thermal expansion.

The experimental information of refractive index measurements reveals an unexplained discrepancy. [4,5]. The reported refractive index is less by up to 10% than that calculated from the Lorentz-Lorenz formula. The reason may be the strong interactions due to the hydrogen bonding of the water molecules. Abbate et. al. [5] uses therefore for calculation of dn/dT the function as best fit of their experimental data:

$$-\frac{dn}{dT} = B \cdot \left(1 - \exp\left(-\frac{T - T_0}{T_k}\right)\right) \quad (\text{eq. 4})$$

The reported parameters are: $B=26.2 \cdot 10^{-5} \text{ K}^{-1}$, $T_0=2.0^\circ\text{C}$, and $T_k=48.5^\circ\text{C}$, with a standard deviation of $\sigma=0.2 \cdot 10^{-5} \text{ K}^{-1}$ to the experimental points. They used an interferometric technique to get their results.

Since our previous interest was the measurement of pesticides [2,3], we choose the wavelength of 365 nm in UV. In this region the deflection signal of pure water is too low to be detected. Our measurements with PTDS and an analyte depicts a nearly linear growth with increasing temperature. The measurements of figure 4 were taken with the pesticide DNOC, 47.5 $\mu\text{g/l}$ and continuous excitation. The value of dn/dT is calibrated at 25 $^\circ\text{C}$. Due to regression formula mentioned above (eq. 4), the standard deviation of our measurements is $\sigma=0.27 \cdot 10^{-5} \text{ K}^{-1}$ whereas the standard deviation due to the Lorentz-Lorenz formula is $\sigma=0.6 \cdot 10^{-5} \text{ K}^{-1}$.

Fig. 4: Refractive index gradient dn/dT from the thermal deflection signal, dependent on the temperature of the liquid sample with 47.5 $\mu\text{g/l}$ of DNOC (experimental points). The solid curve shows calculations using (eq. 4), the dotted line shows calculations using the Lorentz-Lorenz equation (eq. 3)

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