Optimization of PTD system for characterization of transparent and semi transparent samples

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Photothermal beam deflection (PTD) spectroscopy belongs to a group of high sensitivity methods that are used to measure the optical absorption and determine the thermal characteristics of samples. [1] The basic principle behind the PTD technique is that the excitation and associated nonradiative de-excitation of the molecules of the material due to photon absorption result in the temperature oscillations (TOs) of the sample and the surrounding medium that further changes its refractive index, which is probed by a laser beam passing through it. [2, 3]

In this study, the PTD system setup is upgraded by the introduction of a resonant cavity (RC) for both the excitation (EB) and pump beam (PB) (Fig. 1) to provide better spatial resolution and higher sensitivity of the analysis. In case of EB, it enables to use low power lasers. The aim of applying RC for PB is to enhance its intensity change by increasing the length of its interaction with TOs, thus, further increasing the sensitivity of the technique.

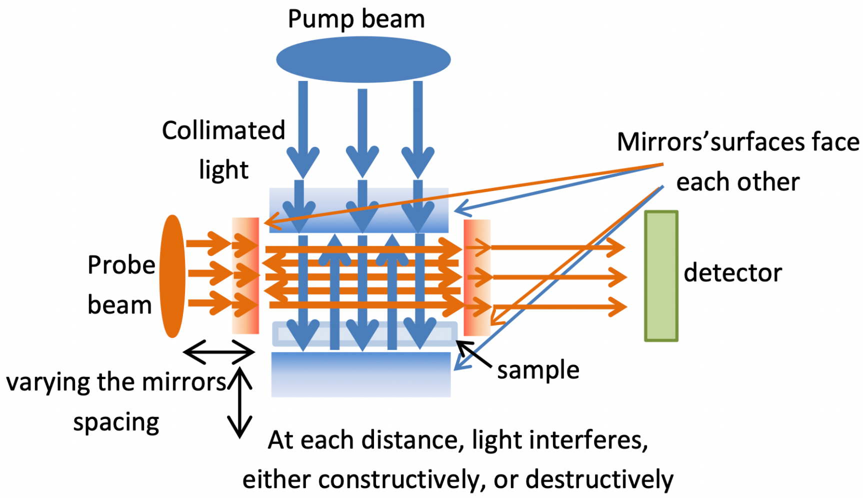

Fig. 1. Geometry of the upgraded PTD system with a resonant cavity

The effect of the PTD system optimisation on the value of its signal was examined by the use of transparent polyacrylamide gel (APA) and semi-transparent Chelex-100 resin. The gels are used in a passive sampling method of transition metals from the aquatic environments [4] and therefore are of great interest for research. The coloured complex of iron (Ferroin) with the maximum absorption at 510 nm was chosen to be uploaded into the gels. Firstly, the gels were immersed in a solution containing different concentrations of Fe^{2+} (0 – 1000 nM) for 5 days. Then they were transferred into the o-phenanthroline solution (c = 3000 nM) for 1 day in order to produce the Ferroin complex inside the gels. After that, the samples were dried on the glass slides and finally, the PTD measurements were performed.

In order to enhance the PTD signal, the number of EB passes through the sample was increased using the additional mirror under the sample. As an excitation beam, a solid-state laser of 532 nm output wavelength and 30 mW output power (BWI-532-10-E/66966) was used, which corresponds to the absorption of the chosen sample. The measurements with two additional mirrors directing the PB passages twice through the TOs were performed as well. He-Ne laser (Uniphase, Model 1103P) was used as a probe beam source of 633 nm output wavelength and 3 mW output power.

The calculated values of the experiment are presented in Table 1.

Table 1. Results of the gels analysis

Type of the gel	**Linear regression equation and correlation coefficient**			**Limit of detection** / [nM]		
	Standard setup	**Multiplied EB**	**Multiplied PB**	**Standard setup**	**Multiplied EB**	**Multiplied PB**
APA	y = 0.001x - 0.026 r^2 = 0.998	y = 0.002x + 0.011 r^2 = 0.995	y = 0.004x + 0.093 r^2 = 0.994	110	70	50
Chelex-100	y = 0.003x - 0.050 r^2 = 0.996	y = 0.003x - 0.042 r^2 = 0.997	y = 0.008x + 0.049 r^2 = 0.996	60	50	20

Limits of detection (LODs) for APA gel are higher in case of multiplied EB compared to measurements on the standard setup of the system. This is due to the fact that the EB is reflected by the mirror and passes through the sample more than once, thereby increasing the value of PTD signal. In the case of Chelex-100 gel, LODs are hardly changed. This is due to the fact that the Chelex-100 resin is semi-transparent and strongly scatters EB, thus, the signal is not enhanced. Opposite to that the increasing PB passes through TOs has an effect on the LODs values for both gels.

It was found that the optimization of the PTD technique by the addition of a reflecting mirror under the sample in order to increase the number of passages of the EB through the sample is useable only when working with a transparent sample. The optimization of the PTD technique by adding mirrors increasing the PB passers through the TOs is useful in case of both, transparent and semi-transparent samples.

References

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