Correctness of assessment of thermophysical properties of solvents by dual-beam thermal-lens spectrometry

Khabibullin VR[(1)*], Volkov DS[(1)], Proskurnin MA[(1)]

(1) Department of Analytical Chemistry, Chemistry Department, Lomonosov Moscow State University, Moscow, Russia

* Corresponding author's email: vladhab1995@gmail.com

The paper presents a dual-beam thermal-lens spectrometer with a mode-mismatch configuration. The most significant factors influencing the correctness of the measurement of thermophysical parameters are considered. Reference solvents (water, ethanol, acetonitrile, toluene, and chloroform) were studied, and thermophysical parameters (thermal diffusivity and heat capacity) were calculated. The experimental and theoretical values show a good concordance, indicating the correct operation.

Thermal lens spectrometry (TLS) is essential in photothermal spectroscopy due to its high sensitivity, rapidity, and simplicity of approach. From the viewpoint of chemical analysis, thermophysical parameters of complex samples are often more informative than optical ones. Studying the kinetics of processes, controlling chemical reactions, complex formation, and dimerization are solved with higher accuracy due to the registration of changes in sample thermal diffusivity (D) and specific heat (C_p). Currently, the primary attention is focused on the dual-beam version of the TLS with mode mismatch configurations, for which in 1992, Shen et al. [1] published a theoretical model describing the behavior of a thermal lens in a sample with high accuracy. On the other hand, the development of the instrumentation of the method (especially in the dual-beam version) cannot be called fast and straightforward. Therefore, all attention is paid to the accuracy of measurements, but not their correctness. This study presents the results of designing and implementing a setup for dual-beam TLS, studying reference solvents (water, ethanol, chloroform, acetonitrile, toluene), and finding D.

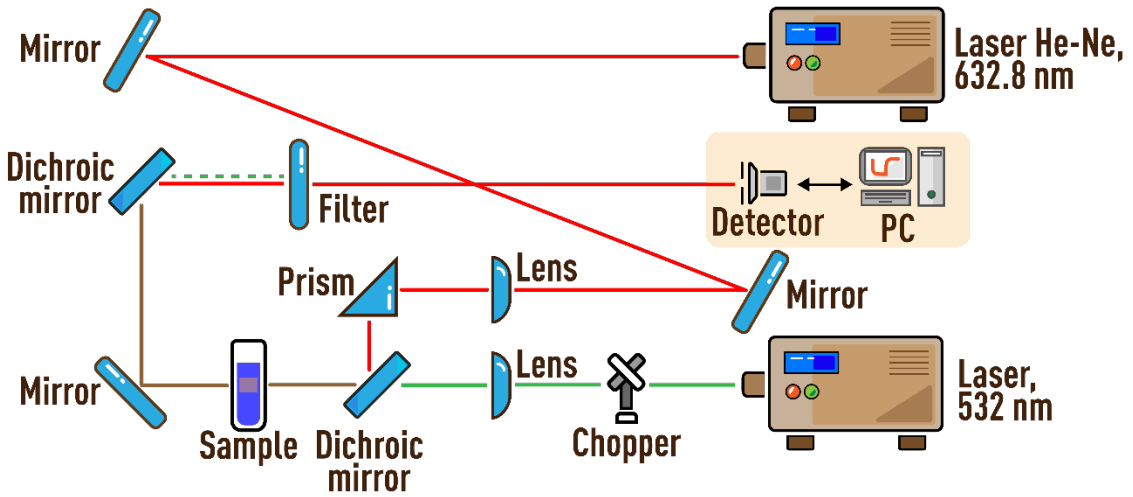

Fig. 1. Scheme of a two-beam thermal lens spectrometer

Figure 1 shows the scheme of the setup. A high-power solid-state laser (λ = 532 nm, P = 200.0 mV) was used as an excitation beam, and a He–Ne laser (λ=632.8 nm, P = 7.1 mV) was used as a probe. The waist size of the excitation beam is 42 ± 1 μm, while the probe-beam radius in the cell center is 60 ± 1 μm. Thus, the degree of mode-mismatch (m) is equal to 2. The chopper frequency was 0.01 Hz. The calculation of the characteristic time (t_c) and thermal diffusivity (D) was carried out according to the equation $t_c = \omega_{0e}^2/4D$.

The effects of fluctuations in the divergence of laser beams, incorrect measurement of the size of the beams in the sample, the frequency of the shutter operation, etc., on thermophysical parameters were studied. E.g., it was found that fluctuations in the divergence of the excitation laser beam of 5% lead to an error in determining D of 10% (Fig. 2).

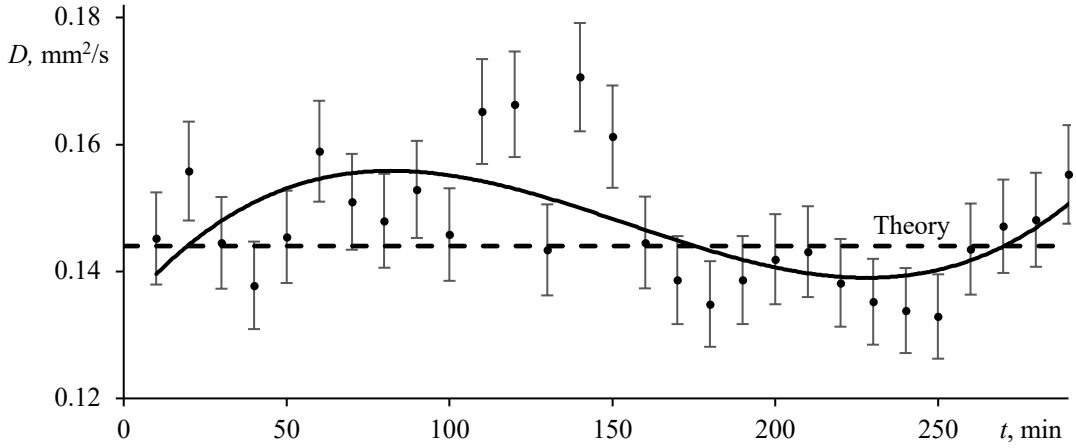

Fig. 2. Behavior of the thermal diffusivity of water with the course of measurements

As a result, considering all the factors, we got the correct results for thermal diffusivity on the instrument. Furthermore, the comparison of theoretical and experimental thermal diffusivity values showed a close-ratio, indicating the correct operation (Table 1).

Table 1. Thermal diffusivity of feference solvents, (mm²/s)

Solvent	Theory	Experiment
Water	0.144	0.149 ± 0.009
Ethanol	0.089	0.087 ± 0.004
Chloroform	0.083	0.086 ± 0.005
Toluene	0.091	0.090 ± 0.004
Acetonitrile	0.111	0.115 ± 0.008

Thus, a TLS setup in a dual-beam version was made. Many factors that affect the accuracy of measurements were considered. The results show the concordance of experimental and theoretical thermal conductivity values, which indicates the possibility of using the setup in further research work.

The study was funded by the Russian Foundation for Basic Research, project number 21-33-70143. This research was performed according to the Development program of the Interdisciplinary Scientific and Educational School of Lomonosov Moscow State University, “The future of the planet and global environmental change”.

The reported study was funded by RFBR, project number 21-33-70143.

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