

Determination of environmental pollutants by thermal lens method

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Abstract--The thermal lens method to determine three environmental pollutants including carbon disulfide in carbon tetrachloride, anthracene in benzene and benzophenone in ethanol was introduced. The detection limits were 2.0×10^{-6} — 4.0×10^{-7} and 8.5×10^{-6} mol/L, respectively, equivalent to about 1.0×10^{-3} absorbance. Some work on the improvement of the thermal lens technique are also presented in this paper.

Keywords; thermal lens; carbon disulfide; anthracene; benzophenone.

1 Introduction

The thermal lens (TL) effect first described in detail by Gordon *et al.* (Gordon, 1965) has been developed into an extremely sensitive and relatively simple spectroscopic tool both in quantitative analysis and photochemistry study. As an analytic method, TL technique is widely used to determine trace - sample in aqueous and gaseous solution.

In our experiment, TL method was employed to determine three exemplary environmental pollutants. They were carbon disulfide, one of the most serious air pollutants in Shanghai, anthracene, the simplest one in the PAHs family, and benzophenone, a potential water pollutant that becomes important recently.

In the meantime, we made more efforts to improve TL technique and concluded that excitation laser energy, solvent and other experimental conditions all played important roles in the TL method.

2 Principle

As we know, when a laser passes through a weakly absorbing sample, if part of the absorbed energy is released as heat, it will produce a local change in temperature, density and refractive index. If the laser beam profile is approximately a Gaussian distribution and if the refractive index change is negative (in fact it is usually the case), the sample then acts as a diverging lens near the beam axis. A CW laser beam which overlaps the passed excitation beam through the sample cell will be defocussed, leading to an irradiance change on the far - field plate which is normally referred to as a thermal lens (TL) signal. The shape of the signal provides photophysical information while the intensity is proportional to the concentration of sample, which is the theoretical basis for the quantitative analysis by TL method.

The intensity of the thermal lens signal can be expressed by following equations (Zhu, 1989):

$$S = (I_0 - I_t)/I_0 = S_{p(t=0)}^{(1+2t/t_c)^{-2}}, \quad (1)$$

$$S_{p(t=0)} = 2.303E_p A, \quad (2)$$

$$E_p = -3^{\frac{1}{2}} E_t (dn/d\tau) / (\lambda_p \omega_{op}^2 \rho C_p). \quad (3)$$

where I_0 and I_t are the probe beam intensity at the beam center when time is 0 and t , respectively; t_c is time constant; E_t is the excitation laser power; λ_p is wavelength of the excitation laser; ω_{op}^2 is the radius of the excitation laser beam at beam waist; $(dn/d\tau)$ is the variation in refractive index with temperature; P and C_p are density and specific heat of the solvent respectively; E_p is the sensitivity enhancement factor.

3 Experimental

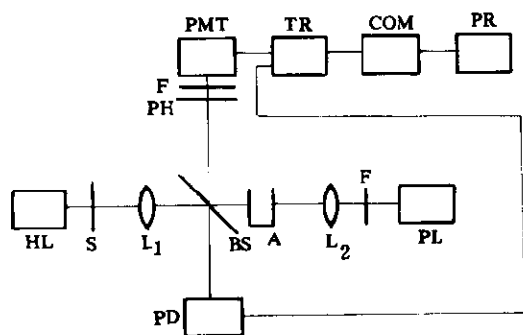


Fig. 1 Thermal lens apparatus

HL; heating laser; PL; probe laser; L; lens;
S; diaphragm; PD; photodiode; BS; beam splitter;
A; sample cell; PH; pinhole; PMT; photomultiplier
tube; F; filter; TR; transient recorder; COM; computer

The TL apparatus is shown in Fig. 1. A pulsed nitrogen laser of output energy about 20mJ/pulse was used to excite sample molecules ($\lambda = 337.1\text{nm}$). The laser beam was focused inside the sample cell. A He-Ne laser beam ($\lambda = 632.8\text{nm}$) was made collinear with the nitrogen laser beam to probe the change of the refractive index resulted from the non-radiative transition of the sample. The beam of He-Ne laser passing through a pinhole and a filter to remove scattered light was monitored by photomultiplier tube (PMT; Hamamatsu R955). After being amplified, the signal from the PMT was fed into a 20k - input of a transient recorder with a low-

est sampling time of 10ns. Data acquisition and signal averaging were performed by a personal computer. In each case, 100 signal traces were averaged. The repetition rate of the excitation laser was 1 Hz, which we considered as an appropriate value since typical thermal-recovery time constant was shorter than 0.1s.

All chemicals were analytical reagent grade or better. Carbon disulfide was washed with 0.5% KMnO_4 solution and with mercury and with 0.25% H_2SO_4 solution and dried over CaCl_2 free of H_2O prior to fractionation. Benzene was washed with concentrated H_2SO_4 and with H_2O and dried over Na_2SO_4 prior to fractionation over a column 1m long. Anthracene was recrystallized times from ethanol.

4 Results

A typical TL signal obtained from our transient recorder is shown in Fig. 2.

We studied three aqueous solution systems including carbon disulfide in carbon tetrachloride, anthracene in benzene, and benzophenone in ethanol. Their working curves, plots of S_p versus

concentration (mol/L), are shown in Fig. 3-5, respectively and results from these curves are listed in Table 1 with their uncertainty being 2%.

Table 1 Detection limits and absorbances of carbon disulfide, anthracene and benzophenone in aqueous solution

System	Detection limit, mol/L	ppm	Absorbance
CS ₂ -CCl ₄	2.0×10^{-6}	0.53	7.0×10^{-3}
Anthracene - benzene	4.0×10^{-7}	0.25	3.1×10^{-3}
Benzophenone - ethanol	8.5×10^{-6}	5.42	5.0×10^{-3}

* Absorbance are estimated from the UV absorption spectrums obtained

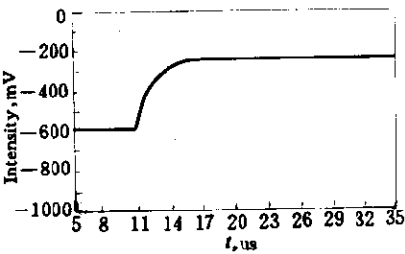


Fig. 2 Typical thermal lens signal

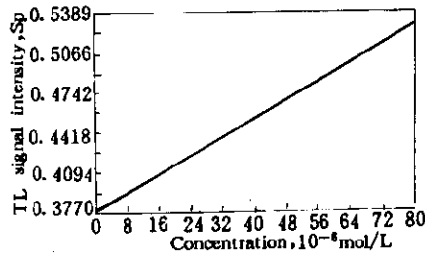


Fig. 3 Working curve of CS₂ in CCl₄ with large - sized diaphragm

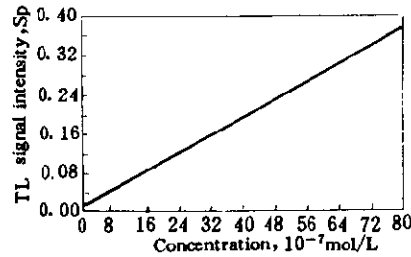


Fig. 4 Working curve of anthracene in benzene

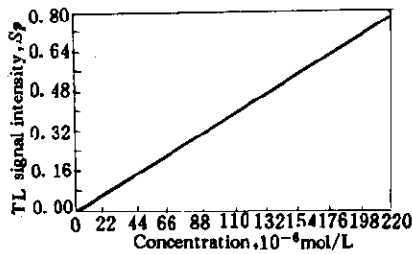


Fig. 5 Working curve of benzophenone in ethanol

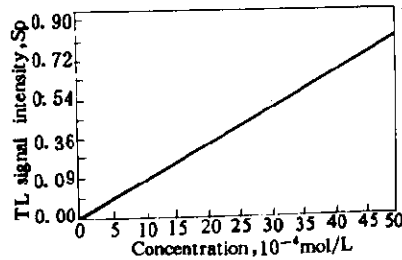


Fig. 6 Working curve of CS₂ in CCl₄ with small - sized diaphragm

5 Discussion

Equation (3) shows that the TL signal intensity is proportional directly to the output energy of the excitation laser (E_e), and inversely to the density (ρ), specific heat (C_p) and other physical parameters of the solvent. Solvent is an important factor that must be considered first in TL experiment. In general, non-polar solvent is superior to polar one. At the meantime, it is important in TL technique to lower the background absorption. In our experiment a diaphragm (S in experimental apparatus) to change excitation energy was employed and hence two working curves of different concentration ranges (Fig. 3, 6) were obtained. Of course, the higher the excitation energy, the lower the detection limit. However, an excessively high excitation energy to prevent the disorption of TL signals was avoided.

Some steps as following were taken in our experiment to improve the S/N ratio.

The experiment in a shielding cage to prevent high-frequency interference produced by the excitation laser was conducted.

A transient recorder was employed effectively to minimize the time-dependent noise, mainly resulted from the intensity fluctuation of the laser beams.

An interference filter in front of the probe laser was put to remove the excitation beam. Had part of the excitation beam entered the cavity of He-Ne laser, serious mode coupling would have influenced strongly the stability of the probe laser.

Both the excitation beam and the probe beam strictly collinear in the sample cell with their spot size matched were kept to avoid spatial noise.

6 Conclusions

Thermal lens method has been successfully used in the study of analytical chemistry with many advantages. TL method, with high sensitivity can be used to determine weak absorption sample, especially those with low fluorescence quantum yield. We introduce transient recorder in our experiment and data acquisition is never an arduous process. Because TL method utilizes heat measurement on which stray light has few effects, the experimental conditions and operation are relatively simple.

It can be foreseen that the simplicity and the high sensitivity of the thermal lens method will enable its rapid utilization, in laboratories already equipped with standard flash photolysis set up, for the determination of environmental pollutants.

References

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