

# Study on determination of environmental pollutants (nitrophenols)

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**Abstract**—The dual-beam pulsed thermal lens (TL) technique was employed to determine the environmental pollutants (nitrophenols). The detection limits of 4-nitrophenol in ethanol was  $5.0 \times 10^{-6}$  mol/L. The factors that influence the thermal lens effect, such as the characteristics of solvents, the excitation laser power, the loading resistance, the system response time, and the aqueous solution pH value, were also investigated in this paper.

**Keywords:** thermal lens; environmental pollutants; nitrophenols.

## 1 Introduction

The nitrophenols are potential environmental pollutants in the pollutants blacklist of P. R. C. and USA, which are usually used as chemical indicator and in organic synthesis. Some toxicological researches (Liu, 1995; Yuan, 1995) show that they can poison the organisms' cells. Being environmental pollutants, the ordinary analytical approach for nitrophenols are UV-visible photometry, HPLC and GC-MS methods.

The thermal lens (TL) effect was first described by Gordon (Gordon, 1965), and now TL technique is widely used in determination of trace-pollutants in aqueous and gaseous solution (Zhang, 1995; Power, 1988; Van der wal, 1985). In our experiment, we employ the dual-beam pulsed mode-mismatched TL technique which is the most superior TL technique up to now (Power, 1988) to detect the nitrophenols in the ethanol, and comparing with UV-photometry. Some factors influencing the TL effect are also investigated.

## 2 Experimental

The TL apparatus is also shown in reference (Zhang, 1995). 7520 spectrophotometer (The Analytical Instrument Factory, Shanghai) is used in 337.1 nm for UV-photometry. The length of quartz cell is 1.0 cm.

All chemicals are analytical reagent grade or better, and purified before use.

## 3 Results and discussion

### 3.1 Some factors influencing the TL effect

#### 3.1.1 Solvent and excitation laser power

The TL effect comes from nonradioactive transition of excited molecule. The TL signal

intensity ( $S_p$ ) is proportional directly to the output power of the excitation laser, and inverse to the density, specific heat, and other physical parameters of the solvent. The better sensitiveness and the lower detection limits will be obtained by selecting suitable solvents and excitation laser power. In this experiment, the 4-nitrophenol in different solvents was detected to select their best for the TL technique (Table 1).

**Table 1 Solvent background and TL signal intensity ( $S_p$ ) of 4-nitrophenol in different solvents**

Solvent	4-nitrophenol concentration, $10^{-3}$ mol/L	Solvent background	TL signal intensity, $S_p$
Ethanol	1.69	0.10	0.962
Diethyl ether	1.62	0.12	1.00
Acetone	1.62	0.62	1.00
Benzene	1.62	0.14	1.00
Water	1.64	0.00	0.166

The TL signal intensity ( $S_p$ ) of aqueous solution is too small and the solvent background of acetone solution is too big, so water (which has bigger density and specific heat) and acetone (which has bigger background) are not good solvents for our TL experiment. This explanation accords with the sensitivity enhancement factor ( $E_p$ ) in the TL effect principle:  $E_p$  is inversely to the density, and specific heat of solvent. Ethanol, diethyl ether and benzene are the better solvent for the experiment. In the experiment, we choose ethanol as solvent for nitrophenols.

In general, higher excitation laser power leads to lower detection limits, and also more obvious solvent background. The solvent background can be explained with different reasons for different solvent: benzene has two-photon TL signal (Ziegler, 1980) under higher excitation laser power; some solvents absorb the excitation laser; obvious convection and spherical aberration will exist in the solvent under higher excitation laser power. In principle, the TL effect has a hypothetical local change in refractive index, so it can be thought as ideal slight lens. But in the actual situation, the spherical aberration always exists in the solvent. If TL's maximal angle of deviation is smaller than initial angle of diffraction, the spherical aberration will be ignored. This can be expressed in the following formula (Luo, 1984).

$$\theta_{\max} = P_{\text{abs}} \cdot (dn/d\theta) / 1.6\pi Kr < \lambda / \pi r_0,$$

$$P_{\text{abs}} = Pbl.$$

where  $P_{\text{abs}}$  is the excitation laser power absorbing by sample;  $(dn/d\theta)$  is the variation in refractive index with temperature;  $k$  is the boltzmann constant;  $r$  and  $r_0$  are the excitation laser beam radius at someplace and beam waist;  $\lambda$  is the wavelength of the excitation laser;  $P$  is the excitation laser power;  $b$  is the sample absorption coefficient;  $l$  is the length of sample cell.

If thinking of  $r = r_0$ , we will get  $P < 1.6 \lambda k / (b l (dn/d\theta))$ .  $\lambda$ ,  $k$ ,  $b$ ,  $l$ ,  $(dn/d\theta)$  are constant, the excitation laser power must be limited to be smaller than a certain number. So we select the excitation laser power to eliminate the solvent background, as well as reduce the trace-samples' detection limits.

### 3.1.2 Loading resistance and system response time

The system response time influences the TL signals in time-resolved experiment. When system response time is not fitting, the TL signal will distort seriously. In the experiment, the pulse width of  $N_2$  laser is about 10ns, which can not influence the TL signals; the system response time depends on response time and loading resistance of photomultiplier tube (PMT). The response time of the PMT is constant, so PMT loading resistance plays an important role in the system response time. The TL signal amplitude increases and system response time slows when PMT loading resistance increases; the TL signal amplitude reduces and system response time quickens when PMT loading resistance reduces. Because the reading error of TL signal intensity is determined by TL signal amplitude and the infidelity of TL signal is determined by system response time, PMT loading resistance must be selected to satisfy the needs of system response time, as well as TL signal amplitude.

In this experiment, system response time with different PMT loading resistance are investigated. The detailed process is as follows (Pan, 1989): partial  $N_2$  laser beam passes through monochromater slit (monochromater wavelength is 337.1 nm). The signal is detected by PMT and the laser decay curve is recorded by transient recorder. The half-peak width of laser decay curve is defined as system response time.

Table 2 shows that system response time is shorter than 0.1  $\mu$ s when PMT loading resistance is smaller than 500 $\Omega$ . A typical TL signal slow risetime is about a few microseconds, so 500 $\Omega$  as PMT loading resistance will satisfy the needs of some time-resolved experiment, such as determination of substance's triplet lifetime and absolute quantum yield. When PMT loading resistance is 100 $\Omega$ , the TL signal amplitude is too small to determine accurately; Amp is an amplifier with 50 $\Omega$  as its loading resistance, amplifier response time is more important to system response time than loading resistance, so system response time with amplifier is 590 ns in the experiment.

Table 2 Relationship between system response time and loading resistance

Loading resistance, $\Omega$	100	300	500	1k	2k	5k	10k	Amp
System response time, ns	100	60	90	200	270	560	930	590

The TL signal intensity ( $S_p$ ) with changing PMT loading resistance is obtained in the experiment too.

The TL signal intensity ( $S_p$ ) is only concerned with sample concentration, so Table 3 shows that  $S_p$  is almost constant when PMT loading resistance increase.

Table 3 Relationship between TL signal intensity ( $S_p$ ) and loading resistance

Loading resistance, $\Omega$	400	500	600	800	900	1k	5k
TL signal intensity	0.237	0.220	0.223	0.240	0.230	0.236	0.238

### 3.1.3 pH value of aqueous solution

As we known, pH value of aqueous solution influences some analytical approaches experimental results. In this experiment, the TL signal intensity ( $S_p$ ) of 4-nitrophenol in different pH value aqueous solution is investigated, so that we will get useful information of solution pH value effect.

**Table 4 Relationship between TL signal intensity ( $S_p$ ) and pH value of aqueous solution**

pH value	7	10	11	12	13
TL signal intensity, $S_p$	0.154	0.170	0.182	0.161	0.164

Table 4 shows that the TL signal intensity ( $S_p$ ) changes a little in the range from pH=7 to pH=13. The TL signal intensity is maximum when pH value of aqueous solution equal to 11, which corresponds to 4-nitrophenol converting into sodium 4-nitrophenoxide. We can conclude that pH value of 4-nitrophenol in water does not influence the TL signal intensity ( $S_p$ ) heavily. This conclusion is not fit for other systems, especially for such as metallic ion systems and so on.

### 3.1.4 Organic impurities

Even after pretest treatment, several compounds exist in multicomponent environmental sample. It is the same that organic impurities influence the determination of trace-samples by using TL technique and UV-photometry it's able to determine total content of compounds with similar character such as absorption band and coefficient and real difficult to determine them respectively. But if compounds which own the different photothermal character, energy transfer processes, and absorption band in UV, IR, visible regions, there are the differential TL effects (triplet lifetime and absolute quantum yield) and spectrums. So we can use TL spectrums in the differential absorption regions and substance's triplet lifetime and absolute quantum yield to determine compounds.

## 3.2 Comparison between TL technique and UV-photometry

In the experiment, the pulsed TL technique and UV-photometry are employed to determine nitrophenols including 3-nitrophenol, 4-nitrophenol, mixture (3-:4-nitrophenol=1:1) in ethanol. Their working curves by UV-photometry, plots of absorption versus concentration (mol/L) are shown in Fig. 1 and 2, and by pulsed TL technique, plots of TL signal intensity ( $S_p$ ) versus concentration (mol/L) are shown in Fig. 3, 4 and 5, respectively. The results from these curves are listed in Table 5 with their uncertain being 2%.

Table 5 shows that pulsed TL technique is superior to UV-photometry in detecting the trace-samples. The absorption coefficient of 4-nitrophenol and 3-nitrophenol in ethanol (got from slopes of working curves) are  $2.49 \times 10^3 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$  and  $1.92 \times 10^3 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ , respectively.  $S_p$  is concerned with absorption coefficient according to TL effect principle. In the same experimental condition, different sample's working curves, slopes of  $S_p$  versus concentration (mol/L) are obtained, the ratio of their slopes equal to the ratio of different sample's absorption coefficient. In the experiment, the slopes of 4-nitrophenol and 3-nitrophenol working curves are  $1.06 \times 10^4 \text{ mol}^{-1} \cdot \text{L}$  and  $8.27 \times 10^3 \text{ mol}^{-1} \cdot \text{L}$ , respectively. The ratio of slopes (4-:3-) equals to

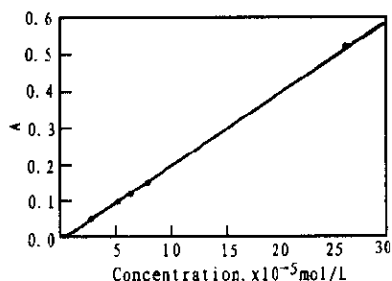


Fig. 1 Working curve of 3-nitrophenol in ethanol by UV-photometry

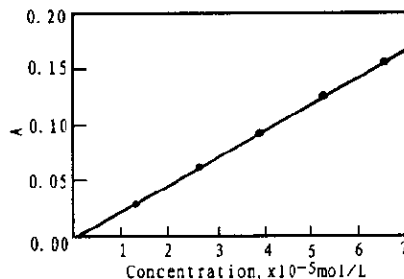


Fig. 2 Working curve of 4-nitrophenol in ethanol by UV-photometry

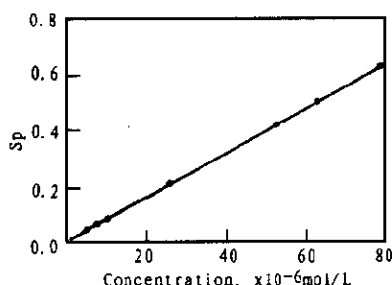


Fig. 3 Working curve of 3-nitrophenol in ethanol by pulsed TL technique

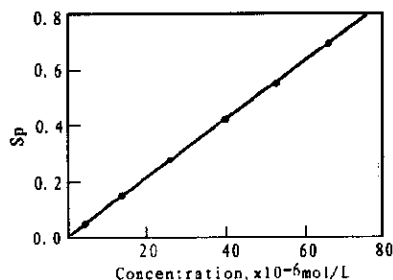


Fig. 4 Working curve of 4-nitrophenol in ethanol by pulsed TL technique

1.28, and the ratio of absorption coefficients equals to 1.29, which shows that our TL technique apparatus is reliable. The sensitivity enhancement coefficient ( $E_p$ ) equaling to 1.85 is also obtained (got from formula:  $S_p = 2.303 E_p A = 2.303 E_p \epsilon b c$ ). It is smaller than theoretical calculate value which equals to 3.24 (got from formula  $E_p = S_{p(t=0)}/S = -3^{3/2} E_t (dn/d\tau)/\lambda_p r_0^2 \rho C_p$ , where  $E_t$  is the excitation laser power which equals to 1 mJ;  $(dn/d\tau)$  is the variation in refractive index with temperature which equals to  $-4.0 \times 10^{-4}$ ;  $\lambda_p$  is the wavelength of the excitation laser which equals to 337.1 nm;  $r_0$  is the recitation laser beam radius at beam waist which equals to 1 mm;  $\rho$  is density of the solvent which equals to  $0.785 \text{ g/cm}^3$ ,  $C_p$  is specific heat of the solvent which equals to  $114.46 \text{ J/mol}$ . The main reasons are heterogeneity of probe laser beam and deviation of focus lens. Comparing Fig. 3, 4 and 5, we can find that slope of Fig. 3 is smaller than slope of Fig. 4 and Fig. 5, the main reason we think is intermolecular interaction (hydrogen bond effect).

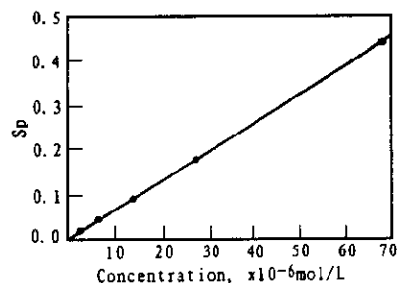


Fig. 5 Working curve of mixture (3:4-nitrophenol = 1:1) in ethanol by pulsed TL technique

**Table 5** Detection limits of 3-nitrophenol and 4-nitrophenol in ethanol

System	Detection limit by	Detection limit by pulsed TL
	UV-photometry, mol/L	technique, mol/L
3-nitrophenol	$2.7 \times 10^{-5}$	$6.0 \times 10^{-6}$
4-nitrophenol	$1.3 \times 10^{-5}$	$5.0 \times 10^{-6}$
mixture (3-:4- = 1:1)		$2.7 \times 10^{-6}$

Research about the determination of trace-pollutants in nature water by pulsed TL technique is studied now, and will be investigated in next time.

## 4 Conclusion

Comparing with UV-photometry, the TL technique is superior in detecting trace level samples. The suitable solvents, excitation laser power, PMT loading resistance, system response time, pH value of aqueous solution must be selected for the better thermal lens effect. The advantage of the TL technique is obvious, as well as its shortcoming. The thermal lens effect comes from nonradioactive transition of the excited molecular. So it is shortcoming that the TL effect is weaker when the ratio of nonradioactive transition of the excited molecular is lower. In a word, if we want to get better detection limits of samples, we must select the samples owning the higher ratio of nonradioactive transition in whole energy transition of the excited molecule.

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