

Notes

Design of Simple and Compact Thermal Lensing Spectroscopy System with Visible Diode Laser

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Since the thermal lensing spectroscopy (TLS) with laser beam was first described by Gordon *et al.* in 1965,¹ it has been an useful analytical technique due to its intrinsically high sensitivity. In TLS system, the various lasers such as Ar ion laser, N₂ pumped dye laser, He-Ne laser, and He-Cd laser have been used as light sources.²⁻¹⁰ There are several combinations of laser systems with pump-and-probe method²⁻⁵ or single source beam method.⁵⁻¹⁰ These laser systems with several hundred mW show the detection range upto ppt level.^{4,8} Even though the high power system is highly sensitive, it has a large dimension, complexities in operation, and difficulties in maintenance. So it still has a restriction as a detector in commercial instruments such as liquid chromatography.¹¹⁻¹³

Because of the reason, a relatively simple laser such as He-Ne of single beam system has been used in practical application.¹⁴⁻¹⁷ For the TLS with 4 mW He-Ne laser, the detection range of 10⁻⁴ M was reported.¹⁰ The He-Ne laser is, however, operated at high voltage (about 2 kV) with a separate power supply. For the modulation of the beam, the conventional mechanical chopper is further needed.

Due to the fast growing technology in recent electronics, the performance of a visible diode laser has been drastically improved.¹⁸ Especially the output power of the laser which is compact and easy to operate in red wavelength region, is comparable to that of He-Ne laser. The diode laser operated at 5-15V DC from dry cell is now commercially available at inexpensive price.¹⁹ For the application of diode laser in atomic spectroscopy, the wavelength was generally tuned by temperature and current control, in order to interact with the atomic resonance line.¹⁸ However, the diode laser is being used without tuning in molecular spectroscopy.²⁰⁻²² Therefore, in this study, the potential use of TLS system with diode laser for the development of an analytical detector has been focused.

A TLS detection system has been designed with the use of a visible diode laser as a light source. Because the laser can be operated at low voltage, the conventional mechanical chopper could be replaced with an electrically-controlled chopper for a simple, portable system. In order to evaluate the performance of the system, the analytical curve was ob-

tained at the wavelength of the diode laser. According to the theory of the TLS,^{2,10} thermal lensing intensity ratio, R_{TL} , is expressed by

$$R_{TL} = \frac{I_0 - I_\infty}{I_\infty} = -\theta + \frac{\theta^2}{2} \quad (1)$$

, where $\theta = P_{abs} \{ (dn/dT) / \lambda \kappa \} A$ and $P_{abs} = P(1 - 10^{-A})$, I_0 and I_∞ are the probe beam intensities at the beam center without and with radiational heating by the laser, P_{abs} is the power absorbed and P is the laser power in watts, dn/dT is the change in solvent refractive index with temperature (usually negative), λ is the laser wavelength, k is the thermal conductivity in W cm⁻¹ K⁻¹, and A is the absorbance of an analyte in Beer's law.

If θ is small, the equation (1) becomes

$$R_{TL} = -2.303 \frac{P}{\lambda k} \left(\frac{dn}{dT} \right) A \quad (2)$$

Since $A = \epsilon b C$, where ϵ is the absorption coefficient in M⁻¹ cm⁻¹, C is the concentration of an analyte, and b is the path length of the solvent medium, the equation (2) becomes

$$R_{TL} = -2.303 \frac{\epsilon b P (dn/dT)}{\lambda k} C \quad (3)$$

Consequently, the thermal lensing intensity ratio R_{TL} is proportional to the concentration of an analyte.

Design of the TLS detection system. Figure 1 shows the block diagram of the TLS detection system designed for this study. The laser diode used was a continuous-wave, InGaAlP semiconductor (MWK Industries, USA) at 670 nm with maximum power of 5 mW.²³ The laser beam was electrically chopped by a home-made current controller at the frequency of 14 Hz. The controller circuit of pulse generating type is also depicted in Figure 2. The modulated beam was focused by a convex lens ($F=6$ cm). The sample was contained in a 1 cm square quartz UV cell. The transmitted light was detected by a photodiode (Din-6DP, UDT Sensors Inc., USA). The decay signal was monitored by an oscilloscope (HP-model 54504A) equipped with HPIB data acquisition system. Acid Blue 25 (Aldrich Chemical Co.) was used as a model compound to evaluate this design because its

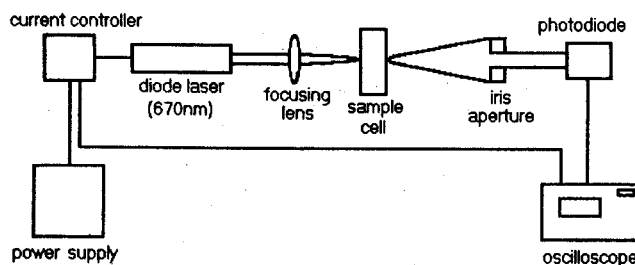
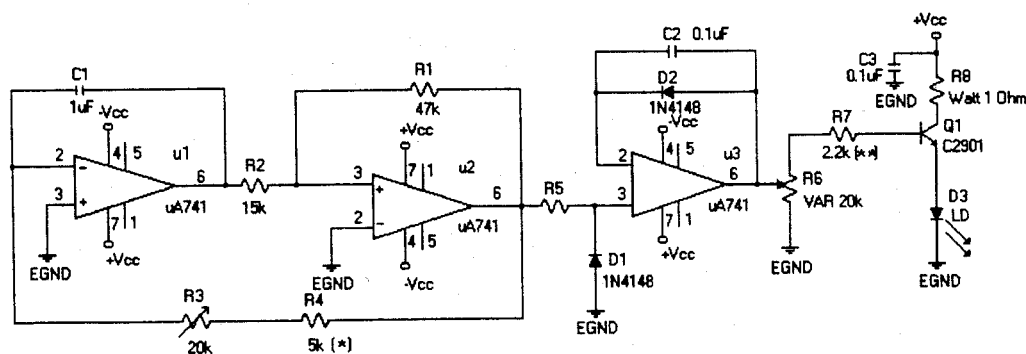


Figure 1. Experimental setup for the measurement of thermal lensing signal using visible diode laser.



Specification : duty Cycle = about 37%
+Vcc=+5V, -Vcc=-5V

Note : (*) - This resistor determines the frequency range.
Especially, the Maximum Frequency value.

(*) - This resistor determines the Maximum Current which goes through the LD.

Figure 2. The circuit diagram of home-made current controller for electrical chopping system.

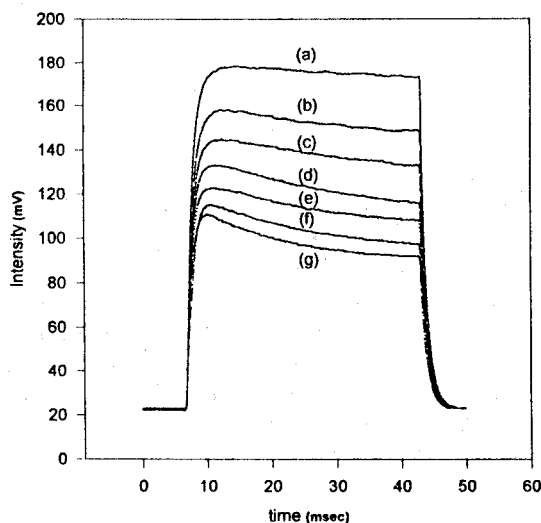
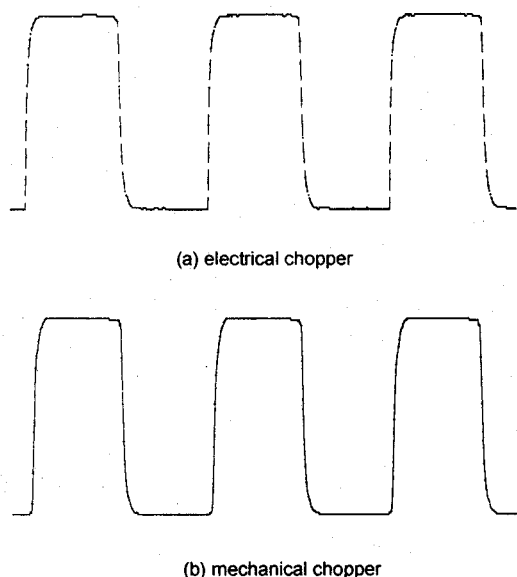


Figure 4. Transient thermal lensing signal of Acid Blue 25 by a visible diode laser at the concentration of (a) 1.13×10^{-5} M, (b) 1.68×10^{-5} M, (c) 2.25×10^{-5} M, (d) 2.81×10^{-5} M, (e) 3.38×10^{-5} M, (f) 3.94×10^{-5} M, and (g) 4.50×10^{-5} M.

Figure 3. The photovoltaic signal of modulated light by (a) electrical chopping and (b) mechanical chopping system.

UV maximum is at 635 nm. The concentration of Acid Blue 25 dissolved in butanol was determined by measuring the thermal lensing signal ratio between the concentration of 1.13×10^{-6} M and 6.50×10^{-5} M. C_{70} was also used in the application of the TLS system for the selective determination of fullerene mixture in spite of its small extinction coefficient at the given laser wavelength. C_{70} was dissolved in toluene and determined at the concentration of 2×10^{-4} M.

Results and Discussion

The circuit diagram of the home-made electrical chopper is shown in Figure 2. Using the resistor of R_4 and R_7 , current and frequency of a diode laser are controlled. When the resistance of R_4 is 5 k Ω , the frequency could be controlled up to 200 Hz. With 2.2 k Ω resistance of R_7 , the maximum current is 120 mA. By controlling variable resistors, R_3 and R_6 , lasing power of 5 mW with 14 Hz frequency was obtained.

The photovoltaic signal of a diode laser itself modulated by electrical and mechanical chopper was compared in Figure 3. The rectangular peak shape from electrical chopper was the same as that from the commercial mechanical chopper. In the case of conventional laser with mechanical system, it needs an expensive power supply and complicated appliance. Otherwise, in the visible diode laser system, the combination of the light source and electrical modulation system can be easily achieved by the use of dry cell with ± 5 V DC. The system in this study, therefore, showed a compact and portable design compared to conventional TLS system.

To evaluate the performance of the system, the thermal lensing signal intensity by a modulated diode laser was measured according to the concentration of Acid Blue 25 in butanol from 2.25×10^{-6} M to 6.50×10^{-5} M. The absorption maximum of Acid Blue 25 is at 635 nm, which nearly coincides with the emitting wavelength of the diode laser. As shown in Figure 4, when thermal lensing phenomena occur, the

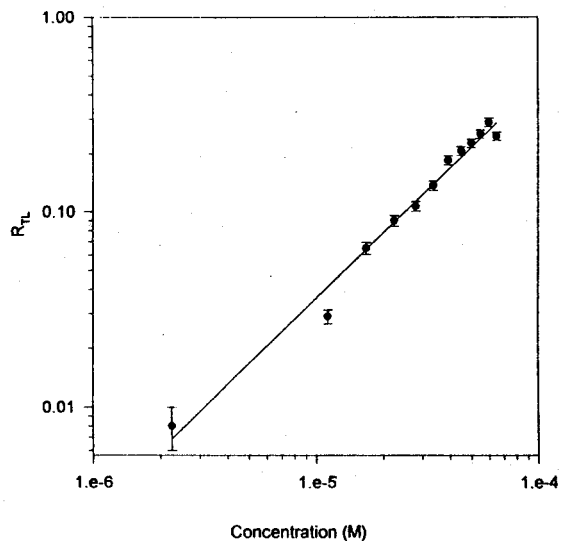


Figure 5. Calibration curve of Acid Blue 25 dissolved in butanol.

photovoltaic signal changes from I_0 , which is the height change of the signal intensity at left-hand side of the rectangular peak, to I_∞ , which is steady at the right-hand side of the peak. By calculating of $(I_0 - I_\infty)/I_\infty$, the thermal lensing intensity ratio, R_{TL} , can be obtained. As the concentration of Acid Blue 25 increases from 2.25×10^{-6} M to 6.00×10^{-5} M, R_{TL} also increases from 0.008 ± 0.002 to 0.290 ± 0.016 .

To determine the analytical curve, the linear dependence of R_{TL} on the concentration of Acid Blue 25 was investigated. As shown in Figure 5, it represents a linearity with regression coefficient of 0.983 at the given concentration range, which is in good agreement with the theoretical consideration described in equation (3). The minimum detectable amount of Acid Blue 25 is 2.25×10^{-6} M with the signal to noise ratio of 3.

In order to examine the possibility of further applications of the diode laser TLS system especially for the detection system in liquid chromatography, the measurement of thermal lensing signal of fullerene, mainly consisting of C_{60} and C_{70} , was investigated. In the process of fullerene production, C_{70} can be separated from C_{60} by means of column chromatography.²⁴ C_{60} and C_{70} have broad absorption bands ranging from 211 nm to 800 nm. At the wavelength of 670 nm of the visible diode laser, the absorption of C_{70} is large enough, while that of C_{60} is too small to be detected as thermal lensing signal. Therefore the concentration of C_{70} could be determined selectively in the fullerene mixture. With the given experimental setup, the thermal lensing signal intensity of C_{70} could be measured at the concentration of 2×10^{-4} M in 1 mL volume of the solution. So it shows the possibility of application for such type of column chromatography. The thermal lensing system used in this study has no monochromator nor complicate photomultiplier tube. It consists of a cheap and simple diode laser and a photodiode. Recently the performance of a diode laser has been improved rapidly. The diode laser with an output power of 30 mW is commercially available at low price.²⁵ Since the intensity of TLS sig-

nal is proportional to the laser output power, the use of higher power lasers will improve its performance. In conclusion, a strong possibility for the application of TLS with a visible diode laser in the development of a simple and cheap detection system in analytical instruments such as liquid chromatography is suggested in this study.

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