CHEMISTRY LETTERS, pp. 2061-2064, 1988.

Photothermal Spectrometry Using Pyroelectric Sensor

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Temperature change of a sample solution due to optical absorption was detected by a pyroelectric sensor. A calibration curve was linear at the low concentrations of dye and the detection limit was 0.0035 cm^{-1}. From a solvent dependence of the signal magnitude, the signal generation could be explained by thermal conduction.

Up to now a variety of photothermal spectrometries have been extensively studied and effectively applied to the determination of trace amount of light absorbing material.[1-5] However, direct detection of heat produced by the optical absorption has been scarcely tried in the field of light absorption spectrometric analysis. On the other hand, a ceramic pyroelectric temperature sensor, which is commercially available for an infrared sensor, is sensitive to a temperature change compared with other temperature sensors, such as thermistors and thermocouples, and easy to shape into various forms.[6] The pyroelectricity results from a spontaneous polarization change induced by temperature change in the pyroelectric material, and it is generally measured by a modulation technique. Therefore, the sensor is expected to be used as a suitable temperature sensor in the photothermal spectrometry. In the present work, a basic instrument with a simple sensor probe has been assembled, and the dependences of the signal magnitude on the concentrations of dye and on the solvents for samples have been examined.

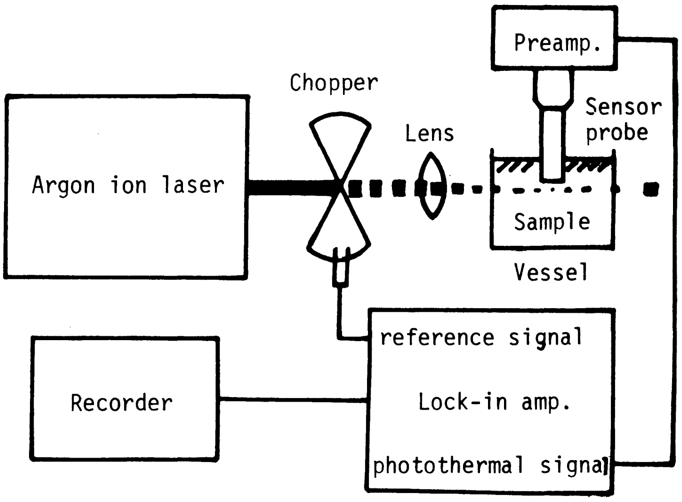

Fig. 1. Schematic diagram of photothermal spectrometer.

Figure 1 shows a schematic diagram of the photothermal spectrometer. The output beam of an argon ion laser (Spectra-Physics, 162D) was operated at 488.0 nm with the power of 15 mW and modulated at 6 Hz by an optical chopper. The modulated laser beam was introduced into an optical vessel (20×20×20 mm) filled with a sample solution through a convex lens (f=300 mm). A temperature change in the illuminated region of the sample solution due to the optical absorption was detected by a pyroelectric sensor just above the illuminated region and converted into an electric signal with a preamplifier connected to the sensor probe. The signal was amplified by a lock-in amplifier (Princeton Applied Research 5101) with the reference signal from the chopper and recorded on a Y-t recorder. Signal magnitudes were corrected with respect to that for the blank solution and the phase of the lock-in amplifier was adjusted so that the signal magnitude became the maximum. The design of the pyroelectric sensor probe is shown in Fig. 2. The pyroelectric material was attached onto a disc of stainless steel of 35 μm thick and was tightly enclosed in a Kovar pipe of 5 mm in diameter and 50 mm in length. Such design was effective in protecting the pyroelectric material from deterioration caused by the sample solution and in shielding it from scattered light of the laser beam. A position of the probe was carefully adjusted with an XYZ positioner so that the sensitive face of the probe was located closely just above the illuminated region of the sample solution. New coccine and methyl red, serving as a solute, were purchased from Tokyo Kasei Co., Ltd. and were used without further purification. The sample solutions were prepared with distilled water or organic solvents of reagent grade.

Figure 3 shows a plot of the signal magnitudes against the concentrations of new coccine in an aqueous solution in the concentration range up to 10^{-6} mol·dm^{-3}.

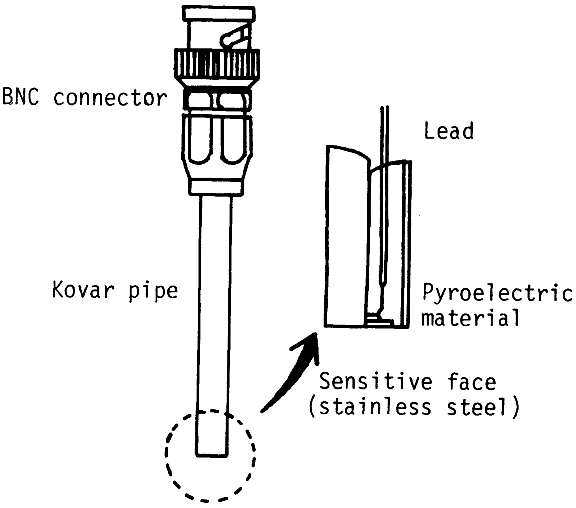

Fig. 2. Design of ceramic pyroelectric temperature sensor.

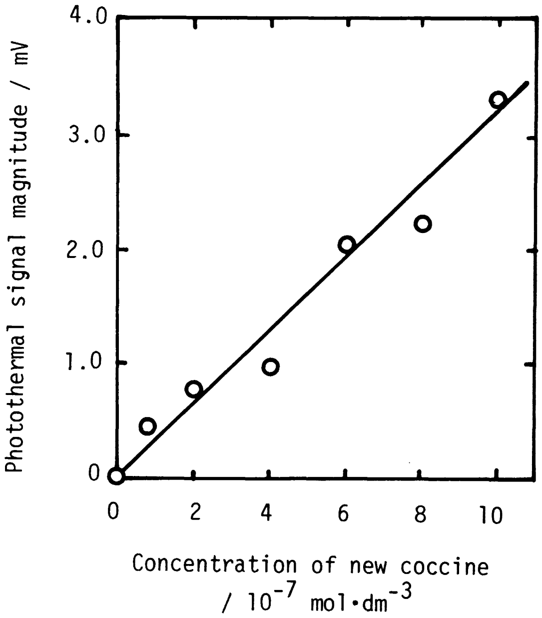

Fig. 3. Plots of photothermal signal magnitude against concentration of new coccine.

Table 1. Detection limits of various photothermal spectrometries

Spectrometry[a)]	Sample	Solvent	Power[b)] mV	Detection limit[c)] cm^{-1}	Reference
PAS	β-carotene	chloroform	700	2.2×10^{-5}	2
PAS	MnO_4^-	water	400	2.1×10^{-4}	3
PAS	Cd complex	chloroform	500	1.3×10^{-5}	4
TLS	Fe complex	water	600	2.3×10^{-5}	5
TLS	Fe complex	chloroform	600	1.4×10^{-6}	5
PTS	New coccine	water	15	3.5×10^{-3}	this work

a) PAS, TLS, and PTS represent photoacoustic, thermal lens, and the proposed photothermal spectrometries, respectively. b) Power of an argon ion laser. c) Expressed in the Napierian absorption coefficient.

As can be seen in this figure, the plot gives a straight line. Such linear relationships were always found for the sample solutions of different dyes dissolved in organic solvents, as long as the dye concentration was low enough so that the laser beam was little attenuated by the sample solution. The slope of the straight line, i. e. the sensitivity, was appreciably affected by the position of the sensor probe and the kind of solvent, as will be discussed later. The lowest detection limit was calculated from Fig. 3, because water was the most suitable solvent among tested solvents, and the value was 0.0035 cm^{-1} when expressed in the Napierian absorption coefficient at the signal-to-noise ratio of ca. 2. Table 1 lists the detection limits of three different kinds of photothermal spectrometries. The detection limit in this work is two or three orders of magnitude higher than those of other spectrometries. This is mainly due to the power of excitation light, and the detection limit per unit power is no poorer than those of other spectrometries. The signal-to-noise ratio may be improved by using two pyroelectric materials in series with the same polarity connected, so as to eliminate a signal coming from surrounding mechanical vibration, because the pyroelectric material also exhibits an undesired piezoelectric effect owing to the mechanical vibration. Consequently both of the detection limit and the sensitivity may be possibly more improved.

Table 2 lists the sensitivities for the sample solutions prepared with different solvents.

Table 2. Sensitivities for various solvents

Solvent	Dye[a)]	Sensitivity mV·cm
water	NC	320.3
methanol	NC	194.6
benzene	MR	122.0
chloroform	MR	69.2
carbon tetrachloride	MR	58.4

a) NC and MR represent new coccine and methyl red, respectively.

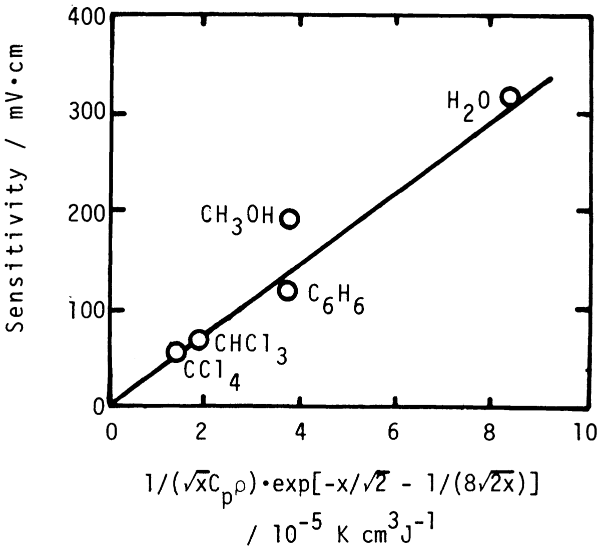

Fig. 4. Dependence of sensitivity on solvent
The distance from the laser beam is assumed to be 0.6 mm.

The solvent dependence of the sensitivity was analyzed by using a simple model assuming a periodic line source.[7)] In the present case, the region of the sample solution illuminated by the modulated laser beam can be regarded as the periodic line source. According to the mathematical expression for the model,[7)] the sensitivity in a stationary state, S, is expressed as follows:

$$S \propto 1/(\sqrt{x}\cdot C_p\cdot \rho)\cdot \exp[-x/\sqrt{2} - 1/(8\sqrt{2\cdot x})]. \quad (1)$$

Here C_p and ρ denote the specific heat and the density, respectively, and x is $r\cdot\sqrt{\omega/\alpha}$, where r, ω, and α are the distance from the heat source, the chopping angular frequency, and the thermal diffusivity, respectively. Figure 4 shows a plot of the sensitivities against the term on the right hand side of Eq. 1 under the condition of r=0.6 mm. The plot is nearly a straight line through the origin. From this result, it is confirmed that the signal generation mechanism of the proposed photothermal spectrometry can be explained by a thermal conduction from the illuminated region of the sample solution to the sensitive face of the sensor probe. Further Eq. 1 will be a convenient basis for analytical applications of the proposed spectrometry.

The present work has been supported partially by a Grant-in-Aid for Special Project Research No. 63108003 from the Ministry of Education, Science and Culture.

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(Received August 13, 1988)