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SPECIES-SELECTIVE DETECTION IN GAS CHROMATOGRAPHY BY PHOTOTHERMAL DEFLECTION SPECTROSCOPY

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SUMMARY

The use of photothermal deflection spectroscopy is demonstrated as a species-selective detection technique for gas chromatographic analyses. The technique is illustrated by selectively detecting Freons dissolved in dichloromethane. It was also used selectively to detect two of the three isomers of dichlorodifluoroethylene. The mass detection limits for the Freon mixture range from 0.7 to 4 ng, showing the good sensitivity of the technique. Several applications in atmospheric analysis and liquid chromatography are briefly discussed.

INTRODUCTION

Species-selective detection has been a topic of interest for chromatographic systems[1,2]. Selective detection can be accomplished either by species-specific separation as in affinity chromatography[1] or by species-selective detection as in some laser-based detection schemes[2]. The goal of selective detection is to remove much of the complexity and peak overlap of a chromatogram by obtaining a signal response only for those species of interest while all other components of the mixture pass by undetected.

In this report we demonstrate species-selective detection by the use of photothermal deflection spectroscopy (PDS). The PDS signal is generated by the absorption of light from a pulsed infrared laser by the analyte species and the subsequent non-radiative relaxation of the excited vibrational state. The energy transferred to the carrier gas by the relaxing species creates a spatial density gradient within the gas. A probe laser beam is passed through this density gradient and is deflected due to the change in refractive index of the carrier gas. The theory of PDS has been reported previously[3,4] and will only be summarized here. The spatial temperature distribution of the density gradient is given by

$$\delta T(r, t) = \frac{2\,\alpha E_p}{\pi \rho c_p \omega_p^2} (1 + 2t/t_c)^{-1} \cdot \exp\left[-\,2r^2/\omega_p^2\,(1 + 2t/t_c)\right] \qquad (1)$$

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where T is the temperature, E_p is the pump laser energy, ω_p is the pump beam-focus spot size, α is the absorption coefficient of the analyte species at the pump laser wavelength, ρ is the density of the gas phase, c_p is the heat capacity of the carrier gas and $t_c = \omega_p^2/4K$ is the characteristic time constant of the thermal gradient, where K is the thermal diffusitivity of the sample. The deflection angle of the probe beam is given by

$$\varphi = \frac{-l}{n_0}\left(\frac{dn}{dT}\right)_p \frac{\partial}{\partial r} \cdot \delta T(r, t) \tag{2}$$

where n_0 is the refractive index of the carrier gas and $(dn/dT)_p$ is the change in refractive index with temperature. Substitution of eqn. 1 into eqn. 2 followed by maximization of the deflection angle with respect to the pump-probe beam offset yields

$$\varphi = \frac{l}{n_0}\left(\frac{dn}{dT}\right)_p \frac{4\,\alpha E_p}{\pi \rho c_p \omega_p^3}(1 + 2t/t_c)^{-1} \cdot \exp\left[-1/2\,(1 + 2t/t_c)\right] \tag{3}$$

where l is the length of interaction between the pump and the probe laser beams. The important feature of eqn. 3 for our purpose is that the deflection angle from which the signal is derived is directly proportional to the absorption coefficient of the analyte species. It is this dependence that makes the technique useful for species-selective detection.

PDS is closely related to thermal lens spectrophotometry (TLS)[5–7]. Both of these photothermal techniques can utilize either a continuous wave (CW) laser or a pulsed laser excitation source. With CW laser excitation, the deposition of heat into the sample, and subsequently the signal risetime[7,10], is relatively slow. As a result, the signal magnitude will decrease as the sample flow-rate increases due to the removal of the heated material from the detection region before the signal can reach its maximum[8]. The signal will also be effected by turbulence within the cell because the heated material will be mixed more quickly with the surrounding cool material. On the other hand, deposition of heat into the sample is nearly instantaneous in pulsed laser TLS and PDS, so the bulk flow of the sample through the cell and turbulence within the cell will have very little effect on the signal magnitude[9,10].

The attractiveness of photothermal spectrophotometry can be understood by examining the theoretical enhancement factors using a pulsed laser[11,12]. The enhancement factor is the increase in the sensitivity of the photothermal technique compared with conventional spectrophotometry, both of which are assumed to be shot-noise limited[3]. The PDS enhancement factors can be within 1/e of those for TLS[4]. However, with the variety of detection schemes utilized in PDS, it is difficult to quantify the enhancement factors based on theoretical limits. Using typical experimental parameters, the enhancement factors for common carrier gases are 360 000 in helium, 1 700 000 in nitrogen and 2 800 000 in argon for pulsed laser TLS[13].

EXPERIMENTAL

The PDS optical arrangement used in these experiments has been described elsewhere[3]. The typical energy per pulse of the carbon dioxide laser was less than 20 mJ. The sample cell was constructed of stainless steel in this laboratory and had dimensions of 2.5 cm × 0.4 cm I.D. The cell was mounted with sodium chloride windows and was connected to the output port of a Hewlett-Packard Model 5890A gas chromatograph by a stainless-steel transfer line (18 in. × 1/16 in. O.D.). Data acquisition was accomplished through the use of a least-squares digital filter routine[14] in which each signal waveform was fitted by an optimum filter function. The latter was determined prior to the gas chromatographic (GC) experiments by time averaging the PDS signal 500 times at high concentration to produce a very high signal-to-noise ratio (SNR) waveform. The fitting was performed using least-squares analysis in which the magnitude of the filter function present in the signal waveform was calculated. This value was considered to be the signal value for that laser pulse and was divided by the measured energy of the carbon dioxide laser pulse to account for variations in the pump laser energy. For a 512-point filter-function waveform, this resulted in a ten-fold improvement in SNR compared with gated integration. This acquisition routine resulted in a real-time improvement in the SNR of the chromatographic experiment. Upon completion of the GC, the chromatograms were smoothed using a 15-point quadratic Savitzky-Golay filter[15]. With this basic experimental set-up, two different procedures were employed to show the utility of the PDS technique for species-selective detection.

Freon mixture

An analyte mixture of Freons was made by sealing 40 ml of liquid dichloromethane in a 125-ml flask with a rubber septum. Into this sealed flask were injected 10 ml of each of the following gases: trichlorofluoromethane (Freon-11; PCR Research Chemicals, Lot No. 10233), dichlorodifluoromethane (Freon-12, PCR Research Chemicals, Lot No. 10231), chlorodifluoromethane (Freon-22, Matheson) and chlorotrifluoroethylene (PCR Research Chemicals, Lot No. 9523). This mixture was allowed to stand overnight to help in the dissolution of the gases into the solvent. GC was performed on a Porapak Q (80–100 mesh) packed column (6 ft. × 1/8 in.) held at a constant temperature of 120°C and at a flow-rate of 24 ml/min. Helium was used as the carrier gas. A 2-μl volume of the liquid sample was injected into the column. The carbon dioxide pump laser was tuned to wavelengths of 9.282, 9.473 and 10.719 μm.

The concentrations of each analyte in solution were determined through the use of a Perkin-Elmer Model 599 IR spectrophotometer to measure the relative absorbance of each gas under identical conditions. From these relative absorbances and the peak areas in the chromatograms, the concentration (mole fraction) of each analyte in dichloromethane was found to be $5 \cdot 10^{-5}$ Freon-11, $5 \cdot 10^{-4}$ Freon-12, $3 \cdot 10^{-4}$ Freon-22 and $2 \cdot 10^{-4}$ chlorotrifluoroethylene.

Dichlorodifluoroethylene

A 0.5-ml volume of a mixture of the three isomers of dichlorodifluoroethylene (PCR Research Chemicals, Lot No. 1475) was injected into a column (6 ft. × 1/8

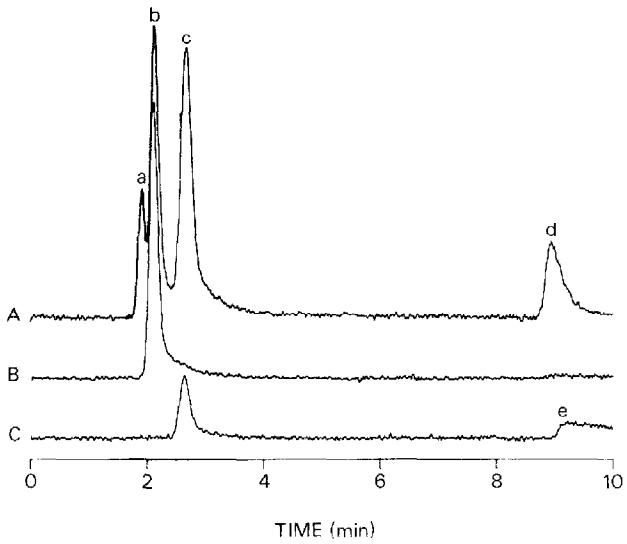

Fig. 1. Chromatograms of 2 μl of the Freon solution injected at carbon dioxide laser wavelengths of (A) 9.282 μm, (B) 9.473 μm and (C) 10.719 μm. The peaks are (a) Freon-22, (b) Freon-12, (c) chlorotrifluoroethylene, (d) Freon-11 and (e) dichloromethane.

in.) packed with 1% SP-1000 coated on Carbopak B (60–80 mesh). Helium was used as the carrier gas at a flow-rate of 40 ml/min. The temperature was initially held at 40°C for 10 min and then increased at 4°C/min to 80°C. With this temperature program it was possible to separate the 1,1-dichlorodifluoroethylene isomer from the *cis* and *trans* isomers of 1,2-dichlorodifluoroethylene. GC was performed at carbon dioxide laser wavelengths of 9.676 and 10.171 μm.

RESULTS AND DISCUSSION

The purpose of the present work is to illustrate the use of PDS in species-selective detection. The resulting chromatograms of the Freon mixture under the conditions described are shown in Fig. 1. Three of the components, namely Freon-12, Freon-22 and chlorotrifluoroethylene, have similar retention times as can be seen in Fig. 1A. By varying the pump laser wavelength it is possible to detect only Freon-12 or chlorotrifluoroethylene, while the other two components of this "cluster" are unobserved as in Fig. 1B and C. The other interesting aspect of this mixture is that Freon-11 and the dichloromethane solvent overlap to a large extent. However, the solvent is nearly transparent at all wavelengths of the carbon dioxide laser so that Freon-11 can be detected without interference from the solvent peak. This can be seen by comparing Fig. 1A and C.

Fig. 2 shows the results obtained for the dichlorodifluoroethylene mixture. This is an interesting problem in that the separation of the three possible isomers is not trivial; the 1,1-dichloro isomer has a boiling point of 20.4°C while the 1,2-dichloro isomers both have boiling points of 21.1°C. The approach taken here was to separate the 1,1-dichloro isomer from the 1,2-dichloro isomers and use the wavelength-de-

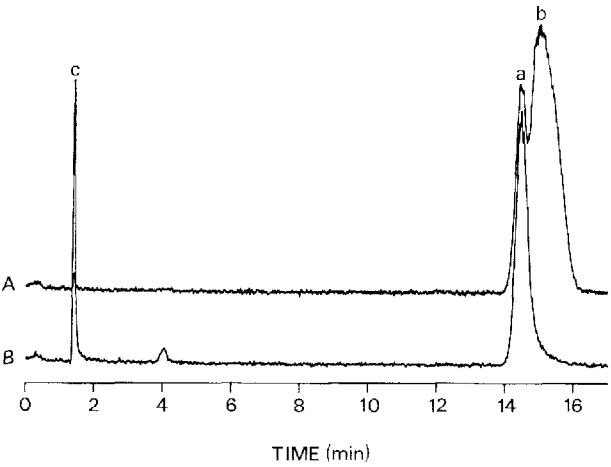

Fig. 2. Chromatograms of 0.5 ml of the dichlorodifluoroethylene mixture injected at carbon dioxide laser wavelengths of (A) 10.171 μm and (B) 9.676 μm. The peaks are (a) 1,1-dichlorodifluoroethylene, (b) *trans*-1,2-dichlorodifluoroethylene and (c) an impurity which is most likely a Freon.

pendent absorption of each isomer to detect the species. This is simplified by the fact that the *cis*-1,2-dichloro isomer has no significant absorbance in the wavelength range accessible to the carbon dioxide laser, while the *trans*-1,2-dichloro isomer absorbs strongly at 10.173 μm and the 1,1-dichloro isomer absorbs strongly at 9.690 and 10.101 μm[16,17]. In Fig. 2A the two large peaks correspond to the 1,1-dichloro and the *trans*-1,2-dichloro isomers respectively, with the small peaks up to 4 min corresponding to impurities in the reagent gases. The first peak in Fig. 2B is also due to an impurity, most likely a Freon, and the second peak corresponds to the 1,1-dichloro isomer. Thus it is possible to differentiate between the 1,1-dichloro isomer and the *trans*-1,2-dichloro isomer, while the *cis*-1,2-dichloro isomer remains transparent to the analysis. By using some other pump laser with a different wavelength range it would also be possible to detect the *cis*-1,2-dichloro isomer.

These two examples demonstrate the effectiveness of this technique in species-selective detection. The pump laser wavelengths at which the above analyses were performed were chosen by examining IR spectra and absorption data for the species in each mixture and then selecting those wavelengths at which only one or two of the components had a significant absorption coefficient.

The application of this technique is not limited to the gas-phase analysis of small molecules, although it is potentially very useful for atmospheric analysis such as in the extraction of Freons using activated charcoal and dichloromethane[18]. It has also been shown that the general technique can be applied to liquid-phase analyses by using ultraviolet or visible laser sources[10]. This could be useful for high-performance liquid chromatography (HPLC) or in special techniques such as that reported by French and Novotny[19] in which xenon is used as the mobile phase in supercritical fluid chromatography because of its optical transparency. However one limitation not apparent in eqn. 3 is the temperature dependence of the PDS signal. The term $(dn/dT)_p$ has a $1/T^2$ dependence[20] while p has a $1/T$ dependence. This gives an overall

signal dependence of $1/T$, so the signal magnitude will decrease at elevated temperatures. This limits its use in the gas phase to temperatures below approximately 100°C at which point the signal decrease becomes quite significant. The species used as mixture components in these experiments were all gases at room temperatures so the PDS cell could be left unheated, but for other compounds it would be necessary to heat both the transfer line and the PDS cell.

Although we have attempted to demonstrate only the selectivity of this technique, the sensitivity of PDS is also quite good. In other studies conducted in this laboratory using both pulsed laser TLS and PDS with a static cell, the detection limits obtained compare very favorably with those of other techniques such as electron-capture detection (ECD)[3,21,22]. These previous studies reported mass detection limits of 0.3 pg Freon-12 for PDS and 1.4 pg Freon-12 for ECD. The mass detection limits of the components in the Freon mixture used in these experiments range from 0.7 ng Freon-11 to 4 ng Freon-22. They were calculated using using a SNR of 4 where the latter is defined as the peak height divided by the standard deviation of the chromatogram baseline. These detection limits are not as low as those reported previously because first, signal averaging on a flowing sample is not possible in contrast to the static measurements, and secondly, the purpose of this report was to illustrate selective detection, so the experimental conditions and cell design were not optimized for low detection limits. However, as mentioned above, the sensitivity of PDS compares favorably with that of ECD based on our earlier measurements, and moreover, the selectivity of this technique is clearly superior to that of ECD.

In this report we have demonstrated the use of PDS as a very selective detection technique for chromatographic analyses. This, coupled with the high sensitivity, makes PDS a useful tool for low concentration analysis. Because it is a dual laser technique, the pump laser can be chosen to suit the best region of the spectrum for the given problem without a affecting the response of the probe laser detector. Thus PDS is quite general in the scope of problems to which it can be applied both in gas and liquid chromatography.

REFERENCES

1 R. R. Walters, *Anal. Chem.*, 57 (1985) 1099A–1114A.
2 E. S. Yeung, *Adv. Chromatogr. (N.Y.)*, 23 (1984) 1–63.
3 G. R. Long and S. E. Bialkowski, *Anal. Chem.*, 57 (1985) 1079–1083; 58 (1986) 80–86.
4 W. B. Jackson, N. M. Amer, A. C. Boccara and D. Fournier, *Appl. Opt.*, 20 (1981) 1333–1344.
5 H. L. Fang and R. L. Swofford, in D. S. Kliger (Editor), *Ultrasensitive Laser Spectroscopy*, Academic Press, New York, 1983, pp. 176–223.
6 A. J. Twarowski and D. S. Kliger, *Chem. Phys.*, 20 (1977) 253–258.
7 J. R. Barker and T. Rothem, *Chem. Phys.*, 68 (1982) 331–339.
8 N. J. Dovichi and J. M. Harris, *Anal. Chem.*, 53 (1981) 689–692.
9 S. L. Nickolaisen and S. E. Bialkowski, *Anal. Chem.*, 57 (1985) 758–762.
10 S. L. Nickolaisen and S. E. Bialkowski, *Anal. Chem.*, 58 (1986) 215–219.
11 N. J. Dovichi and J. M. Harris, *Anal. Chem.*, 51 (1979) 728–731.
12 K. Mori, T. Imasaka and N. Ishibashi, *Anal. Chem.*, 54 (1982) 2034–2038.
13 S. L. Nickolaisen, *Thesis*, Utah State University, 1986.
14 S. L. Nickolaisen and S. E. Bialkowski, *J. Chem. Inf. Comput. Sci.*, 27 (1986).
15 A. Savitzky and M. J. E. Golay, *Anal. Chem.*, 36 (1964) 1627–1639.
16 J. R. Nielsen and H. H. Claasen, *J. Chem. Phys.*, 18 (1950) 485–494.
17 D. E. Mann and E. K. Plyler, *J. Chem. Phys.*, 26 (1957) 773–779.

18 *Manual of Analytical Methods*, Method S108, National Institute for Occupational Safety and Health, Atlanta, GA, 2nd ed., 1976, p. S108.
19 S. B. French and M. Novotny, *Anal. Chem.*, 58 (1986) 164–166.
20 R. T. Bailey, F. R. Cruikshank, D. Pugh and W. Johnstone, *J. Chem. Soc., Faraday Trans. 2*, 76 (1980) 633–647.
21 G. R. Long and S. E. Bialkowski, *Anal. Chem.*, 56 (1984) 2806–2811.
22 S. J. Sheldon, L. V. Knight and J. M. Thorne, *Appl. Opt.*, 9 (1982) 1663–1669.