Journal of Chromatography, 363 (1986) 207–215
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 745

NON-DESTRUCTIVE GAS CHROMATOGRAPHIC DETECTION USING LASER INTRACAVITY PHOTOTHERMAL SPECTROSCOPY

K. H. FUNG*
Environmental Chemistry Division, Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973 (U.S.A.)
and
J. S. GAFFNEY
Los Alamos National Laboratory, Group INC-7, MS-J514, Los Alamos, NM 87545 (U.S.A.)
(Received March 19th, 1986)

SUMMARY

A novel gas chromatographic detector is described which measures the infrared absorption of an eluting molecule by monitoring the photothermal perturbation in an intracavity laser. Laser intracavity photothermal spectroscopy is a non-destructive technique which can be highly selective by using specific infrared absorptions which are characteristic of the molecule or class of compounds of interest to the analyst. Gas chromatography–laser intracavity photothermal spectroscopy detection has comparable sensitivity and selectivity to the previously reported gas chromatographic use of phase-fluctuation optical heterodyne spectroscopy. Thus, absorption sensitivity of *ca.* 10^{-8} cm^{-1} and detection limits of *ca.* 1.0 pg s^{-1} (30 cc min^{-1}) are anticipated for species with absorption cross-sections of 10 cm^{-1} atm^{-1} (a typical absorption coefficient for the strongest infrared bands of most molecules). Analyses of sulfur hexafluoride and ethylene are presented which demonstrate the capabilities of this technique: the simplicity of the detector makes it attractive for non-destructive analyses, especially in the area of atmospheric trace gas analysis.

INTRODUCTION

The analysis of complex mixtures, particularly in trace gas monitoring, has led to the search for selective, sensitive, (and when possible) non-destructive detectors for chromatographic applications. The use of selective detector fingerprinting of these mixtures leads to increased reliability with regard to compound identification and quantification, since the detector response is directly related to a physical or chemical molecular characteristic (*e.g.*, IR absorption, mass, reaction with a specific reagent, etc.). Thus, gas chromatographic (GC) analysis based upon specific molecular property detection simplifies the work by increasing the instrumental response for the molecule(s) of concern while reducing the number of potential interferences. This approach to improving GC analyses will have applications in geochemistry, bio-

0021-9673/86/$03.50

chemistry, environmental chemistry, and any other discipline where specific molecules or classes of compounds need to be characterized in complex mixtures.

Although a number of highly sensitive detectors are available for GC analyses, few are selective, and fewer still are non-destructive[1]. Optical methods (IR, visible, ultraviolet) all have the potential for obtaining selectivity and sensitivity, while maintaining the sample integrity[1–4]. This is especially true with the advent of high-power tunable lasers, particularly in the IR region. GC–IR detection has been of interest due to the selective non-destructive nature of the technique[2]. A major drawback of many GC–IR detection schemes has been sensitivity (most IR band strengths of gases are very weak)[2–4]. Photoacoustic spectroscopy (PAS) has been used in conjunction with laser sources to improve detection sensitivities[3]. Recently, we described use of phase-fluctuation optical heterodyne spectroscopy (PFLOHS) as an alternative method of photothermal detection for GC analyses[4]. Presented here is the use of laser intracavity photothermal spectroscopy (LIPS)[5] as a simpler alternative to PFLOHS[6] detection in GC work. LIPS can be considered as a new detector for photothermal beam deflection spectroscopoy[7,8]. The angular deflection in LIPS is measured by modulating the probe laser cavity gain, *i.e.* laser power output, instead of a position detector as in the conventional beam deflection spectroscopy. Analyses of sulfur hexafluoride and ethylene were performed on gas samples using this method for direct comparison to the PFLOHS technique.

THEORY

In principle, both LIPS[5] and PFLOHS[6] are calorimetric detection methods and yield a signal proportional to the energy absorbed by the sample. This absorbed energy is related to the absorption coefficient, the detector path length and the laser intensity. Collisional quenching of the excited species results in heating of the carrier gas, subsequent gas expansion and change in density and index of refraction. This latter quantity can be measured by sensitive detection methods such as PFLOHS and LIPS.

In the absence of saturated absorption and thermal diffusion effects, the induced change of index of refraction Δn in the PFLOHS method is given by[4]:

$$\Delta n = \frac{(n - 1)I_0\alpha}{2\omega C_p \mathrm{T} \rho} \tag{1}$$

where n is the index of refraction, I_0 is the laser intensity, α is the absorption coefficient of the trace species, ω is the modulation frequency, C_p is the specific heat at constant pressure, T is the temperature and ρ is the density of the sample. Boccara *et al.*[9] have derived general expressions for the deflection of a laser beam by an absorbing medium. The corresponding expression for the deflection angle φ is:

$$\varphi = \left(\frac{\mathrm{d}n}{\mathrm{d}T}\right) \frac{P}{\omega\rho C_p \pi^2 a^2} [1 - \exp(-\alpha l)] [-2(x_0/a^2) \exp(-x_0^2/a^2)] \tag{2}$$

where P is the incident laser power, a is the radius of the pump beam at $1/e$ intensity,

x_0 is the separation between the intensity maxima of the pump and probe beams, and l is the optical path length in the absorbing medium. It is found that φ exhibits a maximum near $x_0/a \approx 1$. For weak absorbing samples, *i.e.* $\alpha l \ll 1$, the expression can be simplified to the following:

$$\varphi = \frac{dn}{dT}\frac{P}{(\omega\rho C_p\pi^2a^2)}[\alpha l]\left[-\frac{2}{ex_0}\right] \tag{3}$$

Using the Clausius–Mossotti equation, which states

$$\Delta n = -(n-1)\frac{\Delta T}{T} \tag{4}$$

and $I_0 = P/\pi a^2$, the expression for the deflection angle becomes

$$\varphi = \frac{(n-1)}{T}\frac{2I_0\alpha}{\pi\omega\rho C_p}\frac{l}{ex_0} \tag{5}$$

One can now compare expressions for deflection angle φ and the induced change of index of refraction. The distinction between the two quantities lies in the additional deflection angle parameters, namely l and x_0. It is instructive to compare and estimate the magnitude of the various quantities involved in LIPS and PFLOHS. For samples in nitrogen, typical values are $\omega = 2\pi \cdot 27$ Hz, $T = 293$K, $(n-1) = 2.92 \cdot 10^{-4}$, $\rho = 1.165 \cdot 10^{-3}$ g cm^{-3}, $V_p = 1.006$ J K^{-1} g^{-1} and $I_0 = 250$ W cm^{-2}. An amount of 5 ppb* ethylene in 1 atm nitrogen, which represents the present LIPS detection limit, excited by the $P(14)$ line of a 10-μm band CO$_2$ laser [$\alpha = 32.14$ (cm atm)$^{-1}$] will yield a value of 10^{-10} for Δn. With $l = 3$ cm and $x_0 = 10$ μm, a deflection angle of *ca.* 0.4 μrad can be obtained, which is in good agreement with the experimental results.

In terms of its utility for chromatography, the minimum detectable amount of material is approximately[3,4]:

$$W_{\min} = \frac{M}{24.21}\frac{\alpha_{\min}}{\alpha_{\text{gas}}}\pi a_0^2 L \tag{6}$$

where M is the molecular weight, $\alpha_{\min}$ is the minimum detectable absorption coefficient, α_{gas} is the absorption coefficient of the species of interest, a_0 is the radius of the sample cell and L is the sample length. For realistic experimental conditions (*e.g.* $a_0 = 1.5$ mm, $L = 5$ cm, $\alpha_{\min} = 5 \cdot 10^{-7}$ cm^{-1}) $W_{\min}$ is typically in the picogram range. Assuming an absorption coefficient of 10 cm^{-1} and a flow-rate of 30 ml min^{-1}, the LIPS sensitivity would typically correspond to 1 pg s^{-1}, which is quite competitive with the detection limit of the PFLOHS method.

---

* Throughout this article, the American billion (10^9) is meant.

EXPERIMENTAL

The basic experimental system has been described previously for the GC–PFLOHS method[4]. The GC–LIPS detection system indicating the essential modifications is schematically represented in Fig. 1. The excitation source is a cw CO_2 laser (Molectron IR-250), which is line tunable (9.2–10.8 μm). The beam from this laser is amplitude modulated using a mechanical beam chopper (PAR Model 25). The He–Ne laser plasma tube (rated 1 mW, 6328A) equipped with a Brewster window and a high reflector (M2) is obtained from Melles Griot (Model 05-LHB-270). The probe laser resonator consists of a flat high reflector (M2: transmittance less than 0.03% at 6328A) and a partial transmitting concave reflector (M1: transmittance = 30% at 6328A, 60-cm radius of curvature). The laser cavity length is typically 50 cm, which in effect provides a space for the sample cell of *ca.* 25–28 cm in length between the Brewster window and the output coupler M1. The sample cell is a windowless pyrex tube (20 cm × 5 mm I.D.). Both the probe laser and the excitation are aligned to be centered within this tube and overlap spatially over a length of *ca.* 3 cm. The crossing angle of the laser beams is no greater than 8 mrad. Carrier gas flow-rates were varied from 20 ml min^{-1} to *ca.* 40 ml min^{-1}. The intensity modulation of the probe He–Ne laser due to changes in the refractive index is monitored through the leakage in the flat output coupler, M2 (see Fig. 1). Its typical leakage power is *ca.* 10 μW, which is *ca.* 2% of the curved coupler (M1) outpout power level. The modulated probe laser intensity is detected by a photomultiplier (Hamamatsu R-508) and is demodulated by a phase-sensitive lock-in amplifier (PAR-124A). The present LIPS experimental setup is isolated from mechanical vibrations by means of an air sus-

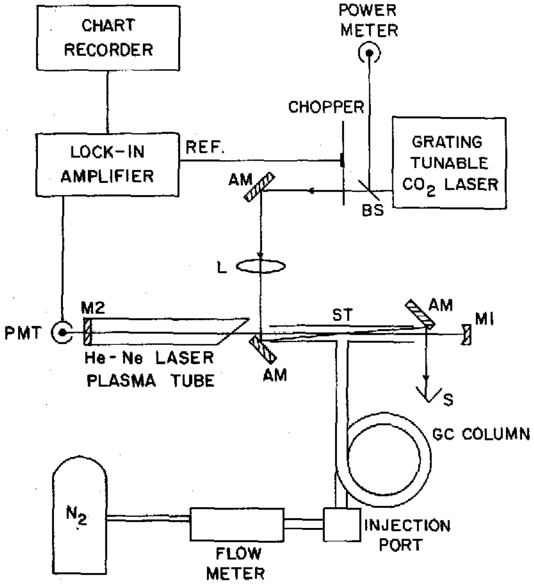

Fig. 1. Schematic diagram for GC–LIPS experiment: AM = aluminum mirror; BS = beam splitter; L = focusing lens; M1 and M2 = laser resonator mirrors; PMT = photomultiplier; S = beam stop; ST = tubular sample cell.

pension table (NRC Model RS-510-8). A simple enclosure made out of 2.5-cm thick styrofoam is employed to cut down the air turbulence in the immediate vicinity of the LIPS detector.

The gas chromatograph used in this experiment consists of a 6 ft. × 1/8 in. I.D. stainless-steel column packed with either Porapak Q (at 24°C) or Porapak PS (at 0°C). Ultrapure nitrogen (99.999%) was employed as the carrier gas. Test gas samples were prepared by volumetric dilution and subsequently calibrated using flame ionization detection (FID) and electron-capture detection (ECD) analysis. Samples were delivered into the gas chromatograph through an injection port by means of gastight syringes. With the exception of the gas chromatograph column, both the injector and the detection (LIPS) system were kept at ambient temperature.

RESULTS AND DISCUSSION

Dilute samples of sulfurhexafluoride (SF_6) and ethylene (C_2H_4) in nitrogen were employed to demonstrate the sensitivity of the present GC–LIPS apparatus.

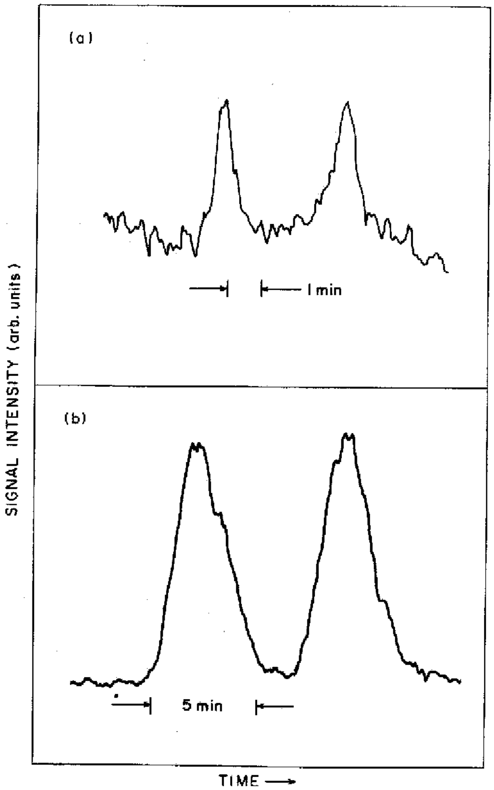

Fig. 2. (a) GC–LIPS signal *versus* time for replicate 5-ml injections of 3 ppb SF_6 in nitrogen samples excited by a CO_2 laser [250 W cm^{-2} $P_{10}(16)$ line]. The GC column was Porapak Q at 24°C. The carrier gas was nitrogen and the detection time constant is 3 s. (b) GC–PFLOHS signal *versus* time for replicate 2.5-ml injections of 3 ppb SF_6 in nitrogen sample. The GC column was packed with Porapak N at −15°C and the detection time constant is 10 s. Other conditions were the same as in (a).

The signal corresponding to replicate 5-ml injections of a 3 ppb SF_6 in nitrogen sample excited by the $P(16)$ line of a 001–100 (10 μm) band CO_2 laser [*i.e.*, $P_{10}(16)$] is shown in Fig. 2a. A carrier gas flow-rate of 42 ml min^{-1} and a time constant of 3 s were used. Each injection contains *ca.* 90 pg of SF_6. The peak of the signal in Fig. 2a represents a flow-rate of 3.0 pg s^{-1} of SF_6. This implies a detection limit (signal-to-noise ratio = 1) of 0.3 pg s^{-1} can be obtained at this flow-rate. With the present experimental configuration the lowest detectable concentration of SF_6 in nitrogen is *ca.* 60 ppt (which is equivalent to a change in index of refraction of $5 \cdot 10^{-8}$ cm^{-1}). In Fig. 2b, the previoiusly reported PFLOHS analysis of the SF_6 (3 ppb) in nitrogen sample is given for direct comparison[4]. The lowest detectable concentration for PFLOHS was 28 ppt SF_6 and the ultimate sensitivity is *ca.* 10^{-8} cm^{-1}. The laser power was maintained at approximately the same level for the two measurements. The present result indicates that the GC–LIPS has comparable sensitivity with the previously developed GC–PFLOHS technique[4]. It is important to note here that the LIPS method is much simpler and requires less hardware than the PFLOHS interferometer apparatus. Thus, LIPS method can yield comparable detection limits with a simpler and less expensive configuration.

As described in the Experimental section, a windowless cell was employed in the GC–LIPS apparatus. The main reason is to offset background signal due to infrared window absorption. In principle, a closed cell can be used in place of the windowless system. However, this should be done with careful consideration. First of all, any overlap of the probe (He–Ne laser) and pump (IR laser) beams should be minimized on the window. Secondly, since GC–LIPS is an intracavity experiment, these cell windows must be at the appropriate Brewster angle in order to maximize the cavity gain. One can expect some trade-off of the ultimate sensitivity with installed windows, *e.g.* increasing noise due to the windows, etc.

LIPS linearity has been found to be good to excellent. A plot of injection volume versus instrumental response (peak height) for a 700 ppb SF_6 in nitrogen

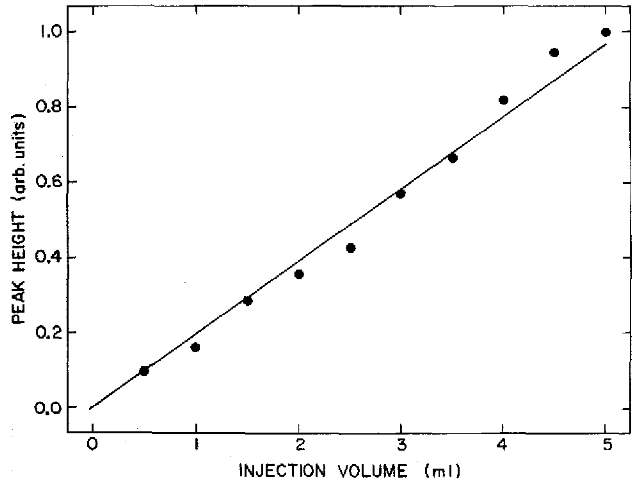

Fig. 3. GC–LIPS signal (peak height) *versus* injection volume for 700 ppb SF_6 in nitrogen sample using $P_{10}(16)$ CO_2 laser line for excitation. [Porapak Q at 24°C, carrier gas (nitrogen) flow 42 ml min^{-1}.]

sample and $P_{10}(16)$ CO_2 laser excitation is given in Fig. 3. For the range that was investigated, the result illustrates typical linearity of LIPS response. In both Figs. 2 and 3, *ca.* 2 W of CO_2 laser power was focused into the sample to yield power density of *ca.* 250 W cm^{-2}. The variation and slight deviation of the experimental data from linearity are most certainly due to uncertainties in the syringe injection volume. Under similar conditions, no absorption saturation effects were observed for the instrumental response *versus* CO_2 laser power, which is in agreement with our LIPS results.

Chromatographic runs for triplicate 5-ml injections of a mixture of 1 ppm SF_6 and 1 ppm C_2H_4 in nitrogen using the $P_{10}(14)$ CO_2 laser line for excitation are shown in Fig. 4a. The excellent reproducibility is typical of this scheme. For analysis of compounds with similar retention times, it is possible to use selective excitation in discriminating one from another as demonstrated in previous work using PFLOHS[4].

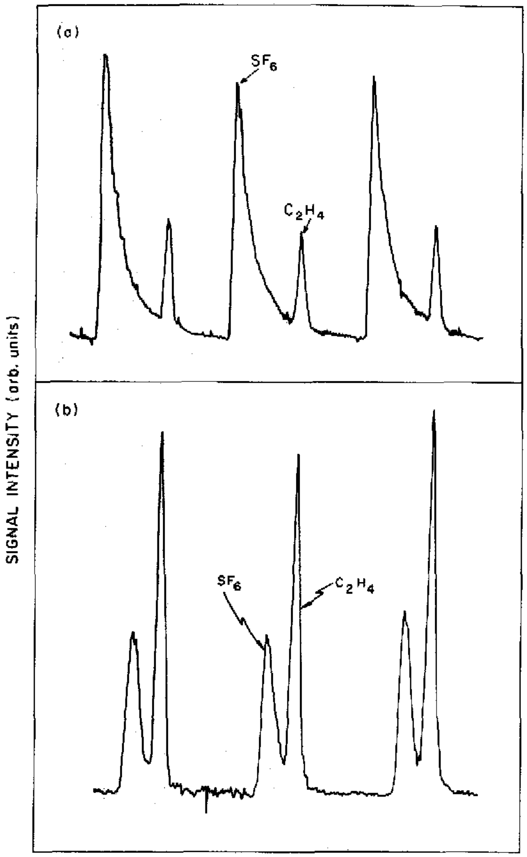

Fig. 4. (a) GC–LIPS run for triplicate 5-ml injections of a mixture of 1 ppm SF_6 and 1 ppm C_2H_4 in nitrogen using $P_{10}(14)$ CO_2 laser line for excitation. The GC column was Porapak PS at 0°C and the detection time constant is 1 s. (b) GC–PFLOHS triplicate 0.1-ml injections of a mixture of 10 ppm SF_6 and 76 ppm ethylene in nitrogen using $P_{10}(14)$ CO_2 laser excitation. The column was Porapak N at −15°C.

In Fig. 4b, a plot for triplicate 0.1-ml injections of a mixture of 10 ppm SF_6 and 76 ppm C_2H_4 in nitrogen using PFLOHS detection is shown for comparison[4].

The absorption sensitivity measured using LIPS is comparable to that measured using PFLOHS. Both LIPS and PFLOHS are photothermal detection schemes. The former uses a "mirage" beam deflection, while the latter takes a Mach-Zehnder interferometer to measure the heat-induced change of index of refraction in the medium. The detection limit of a conventional beam deflection technique is very often controlled by the probe beam (He–Ne Laser) diameter and the angular resolving power of the detector, such as in the case of position detector. In LIPS, this deflection is measured as modulation in the probe laser cavity gain. Based on experimental data, it indicates that LIPS has improved detection capability over the convention beam deflection by a factor of *ca.* 10. As a result, LIPS becomes very competitive with PFLOHS.

In terms of instrumentation, LIPS is extremely easy to set up in comparison with PFLOHS[4]. LIPS has eliminated all the interferometric stabilization devices such as the mirror transducer (PZT), PIN photodiode and high voltage op-amp. The single frequency He–Ne laser used in PFLOHS is now replaced by a multi-mode He–Ne laser in LIPS. However, the excellent sensitivity of PFLOHS is nearly maintained in our new GC–LIPS detector, as illustrated by our sensitivity measurement on the 3 ppb SF_6 in nitrogen sample (see Fig. 2).

Unlike PAS, both LIPS and PFLOHS suffer interference from mechanical vibrations and air turbulence. This type of noise can be easily corrected by employing an air suspension table and some simple box enclosures. In PAS, the problem of improving sensitivity is centered around the design of the acoustic sample cell. The interference from the windows, which are almost permanent features of a resonant PAS cell, can be quite high ($\approx 10^{-7}$ cm^{-1})[3]. Previous studies indicate that the ultimate anticipated sensitivity of PFLOHS can be superior to that of PAS[10,11]. With the present results, one can visualize that LIPS would be yet more attractive to use in view of operational costs, simplicity and sensitivity than PFLOHS.

The GC–LIPS experiment here is to demonstrate its capabilities in its relation to our previous developed technique GC–PFLOHS[4]. The major noise source appears to be fluctuations in the probe laser intensity which can be cause by vibrations and air turbulence. Improvement can be made towards suppression of low frequency noises by stabilizing the probe He–Ne laser. One can also reduce the dead volume in the GC–LIPS detector for better instrumental response. With the above considerations, ppt sensitivity can be expected in the near future.

CONCLUSION

LIPS detection has demonstrated that it has comparable sensitivity and species selectivity as the previously developed technique PFLOHS in GC[4]. Absorption sensitivity of *ca.* 10^{-8} cm^{-1} has been obtained for SF_6. The simplicity and low operational cost make this new technique attractive for non-destructive analyses.

ACKNOWLEDGEMENTS

We thank Drs. Gunnar Senum and Horn-Bond Lin for technical assistance and helpful discussions and acknowledge Dr. Leonard Newman for his interest in this project. This work was supported under the auspices of the United States Department of Energy under Contract No. DE-AC02-76CH00016 and was carried out at Brookhaven National Laboratory.

REFERENCES

1 S. Freeman, in L. S. Ettre and W. H. M. Fadden (Editors), *Ancillary of Gas Chromatography*, Wiley-Interscience, New York, 1969.
2 D. Welti, *Infrared Vapor Spectra: Group Frequency Correlations, Sample Handling and Examination of Gas Chromatographic Fractions*, Heyden and Son, London, 1970.
3 L. B. Kreuzer, *Anal. Chem.*, 50 (1978) 597A, and references therein.
4 H. B. Lin, J. S. Gaffney and A. J. Campillo, *J. Chromatogr.*, 206 (1981) 205.
5 K. H. Fung and H.-B. Lin, *Appl. Optics*, 25 (1986) 749.
6 C. C. Davis and S. J. Petuchowski, *Appl. Optics*, 20 (1981) 2539.
7 A. C. Boccara, D. Fournier and J. Badoz, *Appl. Phys. Lett.*, 36 (1980) 130.
8 F. R. Grabiner, D. R. Stebert and G. W. Flynn, *Chem. Phys. Lett.*, 17 (1972) 189.
9 A. C. Boccara, D. Fournier, W. Jackson and N. M. Amer, *Optics Lett.*, 5 (1980) 377.
10 C. C. Davis, *Appl. Phys. Lett.*, 36 (1980) 515.
11 A. J. Campillo, H.-B. Lin, C. J. Dodge and C. C. Davis, *Optics Lett.*, 5 (1980) 424.