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PHASE-FLUCTUATION OPTICAL HETERODYNE SPECTROMETER AS A NON-DESTRUCTIVE DETECTOR FOR GAS CHROMATOGRAPHY

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SUMMARY

A novel, selective, non-destructive gas chromatographic (GC) detector which measures the infrared (IR) absorption of the functional group of interest using a laser homodyne photothermal refractometer is described. This technique, called phase-fluctuation optical heterodyne spectroscopy (PFLOHS) has demonstrated an absorption sensitivity of 10^{-8} cm^{-1} . In the case of SF_6 , a measured detection limit of less than 1 pg of injected material was obtained. Sensitivities of *ca.* 0.75 pg sec^{-1} (corresponding to a flow-rate of 30 ml/min) are anticipated for materials possessing an absorption coefficient of $10 \text{ cm}^{-1} \text{ atm}^{-1}$, which is typical of the strongest IR bands exhibited by most species. We expect that the primary utilization of GC-PFLOHS will be in atmospheric trace-gas analysis.

INTRODUCTION

Sensitive, selective, non-destructive detectors for gas chromatographic (GC) applications offer the analyst the potential for "fingerprinting" complex mixtures with more than one detector, since the sample is not destroyed or altered. Selective property detectors, whose response is proportional to a characteristic molecular property [e.g. infrared (IR) spectrum, mass, etc.] simplify separation analysis by increasing detection sensitivity for the molecule or molecule of interest while reducing the detector response from potential interferences. GC detectors of this type are expected to find increasing usage in many areas of analytical chemistry ranging from process technology monitoring (e.g. coal liquefaction and gasification, enhanced oil recovery, etc.) to trace constituent analysis in environmental chemistry and medicine. Although a number of sensitive detection systems exist for GC analyses, few are non-destructive and fewer still are selective in their analyses. IR absorption detectors (GC-IR)^{1,2} constitute a major class of selective non-destructive detectors. In this scheme, the IR spectrum as well as the retention time can be used for compound identification. The major drawback of typical GC-IR systems is a lack of sensitivity (IR absorptions in gases are notoriously weak) and their use is therefore restricted to samples where a sufficient amount of material is available. An ultrasensitive form

of GC-IR detection employing an IR laser coupled to a photoacoustic spectroscopy (PAS) detector was described by Kreuzer³ and demonstrated an absorption coefficient sensitivity of approximately 10^{-8} cm^{-1} . PAS is one example of a general class of detectors called photothermal. Recently, another promising photothermal technique for trace-gas detection, called phase-fluctuation optical heterodyne spectroscopy (PFLOHS) has been demonstrated in pulsed^{4,5} and continuous wave (CW) form⁶⁻⁸. The anticipated absorption sensitivity of a realistic narrow bandwidth (CW) version of this device appears to be less than 10^{-10} cm^{-1} , superior to the best previously obtained (in the range 10^{-9} to 10^{-10} cm^{-1}) using PAS⁹. Preliminary experimental devices have achieved sensitivities of less than 10^{-8} cm^{-1} in a "windowless flowing gas mode"⁶ and less than 10^{-9} cm^{-1} in a "windowless static cell"⁸. The flowing gas configuration developed at our laboratory can be easily utilized as a GC detector using nitrogen as a carrier gas. This paper summarizes our initial investigations, which demonstrate the excellent potential of this device for atmospheric trace-gas analysis and compares use of PFLOHS detection to that of PAS. PFLOHS has demonstrated a sensitivity competitive to that previously exhibited by PAS in GC applications and does not suffer from complications associated with the presence of a microphone exposed to a heated environment or to possibly adhering column effluents.

THEORY

PFLOHS detection is calorimetric and yields a signal proportional to the energy absorbed by the sample. For GC detection a laser line is chosen which is strongly absorbed by the solute. In the absence of absorption saturation and thermal diffusion effects, the energy absorbed is related to the absorption coefficient (and consequently the solute concentration), the sample length and the laser intensity. Collisional quenching of the excited species results in heating of the carrier gas (nitrogen), subsequent gas expansion and a change in density and index of refraction. This latter quantity, although small, can be measured by placing the laser-heated sample in a sensitive laser heterodyne interferometer⁴⁻⁸.

It is instructive to estimate the magnitude of the various quantities involved. If the exciting laser is modulated at frequency, ω_m , it can be shown that the corresponding Fourier component of induced index of refraction $\Delta n(t)$ is given by

$$\Delta n(t) = \frac{(n - 1)I_0 \alpha \sin(\omega_m t)}{2 \omega_m C_p T \rho} \quad (1)$$

Here, I_0 is the CW intensity of the laser, n is the index of refraction, α the absorption coefficient of the trace species, ρ is the density of the sample, C_p is the specific heat at constant pressure, and T is the temperature. Eqn. 1 is derived by assuming that I_0 is non-saturating and that the thermal conduction time is greater than ω_m^{-1} and that the sample cell is wall-less. For samples in nitrogen, typical values are $\omega_m = 2\pi \cdot 27 \text{ Hz}$, $T = 293^\circ\text{K}$, $(n - 1) = 2.92 \cdot 10^{-4}$, $\rho = 1.165 \cdot 10^{-3} \text{ g/cm}^3$, $C_p = 1.006 \text{ J}^\circ\text{K}^{-1}\text{g}^{-1}$ and $I = 250 \text{ W/cm}^2$. An amount of 1 ppb* ethylene in 1 atm nitrogen excited by the P(14)

* Throughout this article, the American billion (10^9) and trillion (10^{12}) are meant.

line of a 10- μm band CO_2 laser [$\alpha = 32.14 \text{ (cm atm)}^{-1}$] (ref. 10), will result in an induced index-change amplitude of $\Delta n = 2 \cdot 10^{-11}$.

Indices of this magnitude can in fact be measured using a laser heterodyne interferometer⁴⁻⁸. In this scheme a stable single frequency probe beam, usually from a helium-neon laser source, is utilized in a Mach-Zehnder interferometer¹¹ containing the sample in one of its arms. This probe beam is split into a reference component and a component to be passed through the sample. The sample probe is consequently phase modulated by the time varying index of refraction and later recombined with the reference beam and heterodyned in a photodiode. The photodiode acts as a non-linear device (square law detection) and yields a low frequency signal at the difference frequency, corresponding to ω_m . The voltage amplitude, V_m of this component is related to the magnitude of the index of refraction by

$$V_m = V_s \sin \frac{[2\pi L \Delta n(t)]}{\lambda} \quad (2)$$

Here V_s is an experimentally determined electrical calibration constant, L is the sample length and λ the wavelength of the probe laser. In practice the minimum measurable Δn is limited by interferometer vibrations, sample turbulence or window absorption. In a previously described windowless flowing-gas cell⁶, an absorption coefficient sensitivity of 10^{-8} cm^{-1} was obtained in a 20-cm long sample cell. Since the strongest IR absorption features of many species are typically $10 \text{ cm}^{-1} \text{ atm}^{-1}$, this implies that concentrations of typically 1 ppb can be detected, although much better results can be obtained for unusually strong absorbers (e.g. SF_6 , $\alpha \approx 500 \text{ cm}^{-1} \text{ atm}^{-1}$). In terms of its utility for chromatography, the minimum detectable amount of material using this approach is approximately

$$W_{\min} \approx \frac{M}{(24.2 \text{ l})} \cdot \frac{\alpha_{\min}}{\alpha_{\text{gas}}} \cdot \pi a^2 L \quad (3)$$

where M is the molecular weight, α_{\min} is the minimum detectable absorption coefficient ($\alpha_{\min} \approx 10^{-8} \text{ cm}^{-1}$ in our experiment), α_{gas} the absorption coefficient of the species of interest, a is the radius of the sample cell and L is the sample length. Eqn. 3 was derived assuming a cylindrical sample geometry and assuming that all of the material was in the sample cell at one time (i.e. zone volume equal to the cell volume). For realistic experimental conditions (e.g., $a = 1.5 \text{ mm}$, $L = 20 \text{ cm}$, $\alpha_{\min} \approx 10^{-8} \text{ cm}^{-1}$), W_{\min} is typically in the picogram range and approaches femtogram sensitivity for favorable species. Assuming an absorption coefficient of 10 cm^{-1} and a flow-rate of 30 ml/min , the sensitivity would typically correspond to 0.75 pg sec^{-1} . In practice, some of the solute will be lost to the walls, etc., and consequently eqn. 3 will predict an optimistic detection limit.

A favorable feature of this approach is the potentially large dynamic range available. For high concentration measurements the intensity of the excitation laser can be decreased to insure that the optical path length change of the sample remains in the linear regime. Thus, in principle a dynamic range spanning ppt quantities to pure samples is possible.

EXPERIMENTAL

A schematic of our experimental apparatus is shown in Fig. 1. The excitation laser is a grating tuned axial flow $^{12}\text{C}^{16}\text{O}_2$ gas laser (Molelectron Model IR250). Multi-watt single line operation can be obtained on *ca.* 100 lines in the 9–11 μm range. The beam from this laser is amplitude modulated using a commercial beam chopper (P.A.R. Model 25) and enters and leaves the interferometer via two germanium (Ge) Brewster windows. Although transparent at 10.6 μm , the Ge windows form two of the high reflectivity visible mirrors of the interferometer. The interferometer portion of the detector utilizes a relatively inexpensive commercial stable single frequency helium–neon laser (Tropel Model 100; $\lambda = 633 \text{ nm}$). This particular model laser has been shown to provide a laser source very close to photon noise limited over a wide frequency range¹². Both CO_2 beam and helium–neon beam overlap in the sample region; the CO_2 beam inducing the index of refraction change and the helium–neon laser beam probing it. The sample cell is a 20 cm \times 3 mm I.D. quartz tube, with a central gas inlet, through which the column effluent is introduced. After traversing the cell, the gas is allowed to escape through the windowless ends. A silicon diffused PIN photodiode (EG & G Model HAD 1000) is used to process the heterodyned beams and the signal component at the chopping frequency is synchronously detected in a lock-in amplifier (P.A.R. Model 128A). The interferometer consists of six reflectors, two of which are 50/50 beam splitters at 633 nm. As the interferometer yields an optimum (linear) response midway between destructive and constructive interference, this phase condition is maintained using a servo control system which drives a transducer displacing one of the interferometer mirrors. The PFLOHS device was vibrationally and acoustically isolated by means of an air suspension table (NRC Model RS-510-8) and an aluminum box enclosure.

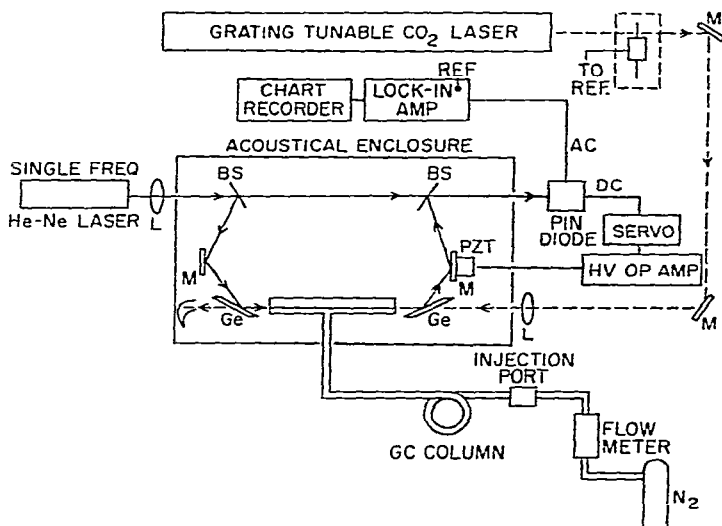


Fig. 1. Schematic of experimental GC-IR-PFLOHS apparatus.

A simple gas chromatograph consisting of a 3 to 4.5 ft. \times 1/8 in. I.D. stainless-steel column packed with either Porapak N (50–80 mesh) at -15°C or Durapak *n*-octane–Porasil C (100–120 mesh) at room temperature was used. Ultrapure nitrogen (99.999%) carrier gas flowed through the system at a rate of typically 10 ml min^{-1} during analysis. Gas samples were prepared by volumetric dilution and calibrated using flame ionisation detection (FID) and electron capture detection (ECD) analysis. Gastight syringes were used to deliver the samples to an injector port. In our preliminary experiment, with the exception of the column, the injector and detection system was kept at ambient temperature.

RESULTS AND DISCUSSION

Fig. 2 illustrates the excellent demonstrated sensitivity of our GC-PFLOHS apparatus. The dual signal corresponds to replicate 2.5-ml injections of a 3-ppb SF_6 in nitrogen sample (*ca.* 45 pg of SF_6 per injection) excited by the P(16) line of a 001–100 (10 μm) band CO_2 laser [*i.e.* P₁₀(16)]. Here a flow-rate of 2 ml/min and a detector time constant of 10 sec were employed. The peak of the signal in Fig. 2 corresponds to 0.28 pg sec^{-1} . Since the signal-to-noise ratio is greater than 50:1, this implies a detection limit of less than 6 fg sec^{-1} at this flow-rate and the capability of detecting less than 1 pg total weight of SF_6 . The initial injection volume of 2.5 ml apparently expands to a zone *ca.* 5.33 ml (full width at half maximum) in volume. The lowest detectable concentration is therefore 28 ppt SF_6 (signal-to-noise ratio = 1) and corresponds to a sensitivity of about 10^{-8} cm^{-1} . The major noise source appears to be fluctuations due to vibrations of the interferometer mirrors. Our interferometer was breadboarded using commercially available optical mounts and the level of spurious vibrations can be greatly reduced by using a more stable structure as demonstrated in refs. 7 and 8. It appears that at least a factor of ten reduction should be realizable.

The absorption sensitivity of our system could be alternatively calibrated by flowing a 10-ppb ethylene in nitrogen sample directly through our detection cell,

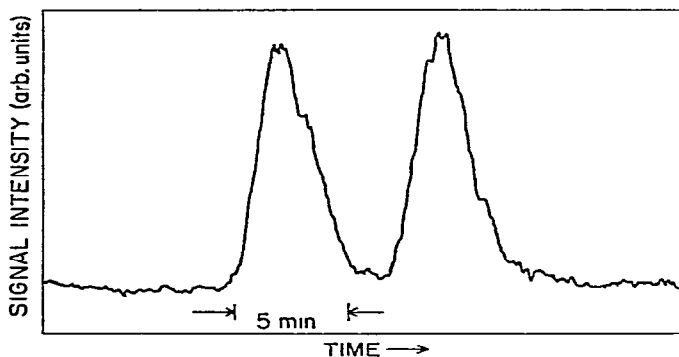


Fig. 2. PFLOHS signal (arbitrary units) versus time for replicate 2.5-ml injections of 3 ppb SF_6 in N_2 samples (*ca.* 45 pg of SF_6 per injection) excited by a CO_2 laser operating at 250 W/cm^2 on the P₁₀(16) line. The column (3 ft. \times 1/8 in. I.D.) was packed with Porapak N (50–80 mesh) at -15°C . The carrier gas was nitrogen. A detection limit (signal-to-noise ratio = 1) of *ca.* 28 ppt or 1 pg was obtained.

bypassing the column. Based on the observed detection limit (≈ 300 ppt C_2H_4 at a signal-to-noise ratio of 1), the limiting sensitivity was again determined to be 10^{-8} cm^{-1} , consistent with the above estimate and with a previously published result⁶. The observed signal, $20 \mu V$, was in reasonable agreement with the value of $28 \mu V$ calculated using eqns. 1 and 2 and the values $I = 250$ W/cm^2 and $V_s = 70$ mV. The value of V_s was experimentally determined by impressing a ramp voltage upon the interferometer mirror transducer (PZT) and observing the PIN photodiode voltage change due to the resulting optical path length change; the amplitude of the resulting sinusoidal voltage yielded V_s . When the column was reattached the background absorption due to column bleed did not appreciably affect the sensitivity limit although a small background was observed. We found it convenient to operate the columns at room temperature or lower. However, columns operated at higher temperatures will have significant bleed and may produce a background that will limit useful sensitivity.

As calculated in the theory section, an absorption coefficient sensitivity of 10^{-8} cm^{-1} leads to a "typical" sensitivity of 0.75 $pg\ sec^{-1}$ which compares favorably to existing techniques such as thermal conductivity (TC), FID and PAS. PFLOHS is more sensitive than TC and is typically at least one order of magnitude more sensitive than FID. However, it is difficult to generalize in such comparisons since absorption coefficients vary by many orders of magnitude between species. In the most favorable cases, PFLOHS sensitivity approaches that of ECD. Previously Kreuzer³ has discussed in detail the respective merits of the PAS detection scheme and that of the other more familiar schemes. Because the PFLOHS technique has strong similarities to PAS, we will confine comparisons in this paper to these two.

The absorption sensitivity observed here (10^{-8} cm^{-1}) is approximately the same as that reported³ using PAS. The PAS scheme utilizes a microphone¹³ to measure the pressure change induced upon collisional heating of the buffer gas following absorption of IR laser photons by the solute. Both PAS and PFLOHS are photothermal detection schemes. Thus, the PAS signal is also proportional to the absorption coefficient and excitation laser intensity. Because of their similarities, they share many advantages and disadvantages^{4,5,7,8}. A previous study^{7,8} indicates however that the ultimate anticipated sensitivity of PFLOHS is superior to that of PAS. Although PFLOHS appears at first glance to be more complex due to the requirement of an additional laser and vibration isolation, it is in other ways simpler; in particular, in sample handling. The presence of the PAS microphone would necessarily complicate the design of the detection cell since it is not compatible with a heated environment or with certain gases. It should be noted that the sensitivity reported in this device was obtained directly. An equivalent sensitivity was obtained in ref. 3 by utilizing a well-engineered acoustically resonant PAS cell. Even so, in that work it was necessary to carefully monitor the CO_2 laser power to estimate and compensate for a significant background signal ($\approx 10^{-7}$ cm^{-1}). The background exhibited by our windowless PFLOHS cell was an order of magnitude less and in future versions of this device a sensitivity improvement can be anticipated by employing background compensation, improved vibration isolation and acoustic resonances. Overall, it appears to the authors, that PFLOHS has a greater potential for future development in this particular application than has PAS.

In the apparatus described here, we utilized a windowless cell to bypass a background signal equivalent to 10^{-7} cm^{-1} due to IR window absorption which

would complicate signal extraction. However, a disadvantage of our present geometry is that the sample escapes the windowless cell and is not easily recovered. Fortunately, a practical flow cell which is sealed to the gas except for inlet and outlet tubes and is "windowless" in a "PFLOHS physics" sense is easily visualized. Such a cell was described in a non-flowing version in refs. 7 and 8. The key feature is that the beam geometry be arranged so that the helium-neon laser probe beam and the CO₂ laser beam overlap only in the sample gas and not in any window, thereby avoiding a window signal. One possible geometry to achieve this can be visualized by referring to Fig. 1. Here imagine the quartz sample tube extended so that its ends are now bounded by the Ge Brewster windows. By providing visibly transmitting side windows for the entering and exiting helium-neon beam, the beam geometries shown can be maintained. A gas inlet and outlet and associated tubing can be arranged at either end to maintain a turbulent-free plugged flow.

Fig. 3 shows a plot of injection volume *versus* instrumental response (peak height) for a 500-ppb SF₆ in N₂ sample and P₁₀(16) CO₂ laser excitation. For injection volumes of 1.5 ml (the volume of our sample cell) or less, the response is linear. In both Figs. 2 and 3, *ca.* 2 W of CO₂ laser power was focused into the sample to yield an intensity of about 250 W/cm². The instrument response *versus* CO₂ laser intensity was also found to be linear for intensities at this value and lower indicating that no absorption saturation effects occurred.

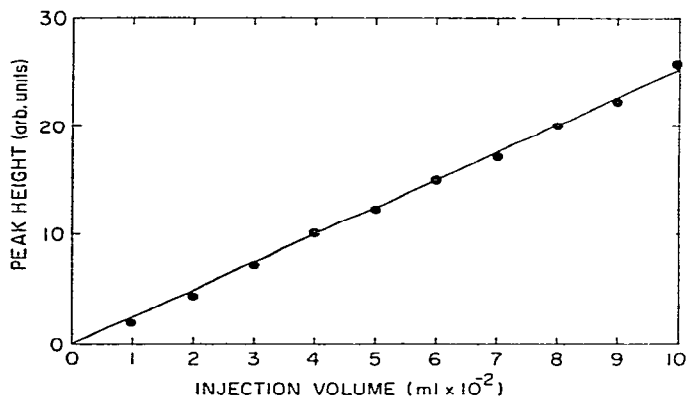


Fig. 3. Plot of PFLOHS signal (peak height) *versus* injection volume for 500 ppb SF₆ in N₂ sample using P₁₀(16) CO₂ laser excitation. The column (3 ft. × 1/8 in. I.D.) was packed with Porapak N (50–80 mesh) at -15°C.

Fig. 4 shows chromatographic runs for triplicate 0.1-ml injections of a mixture of 10 ppm SF₆ and 76 ppm ethylene in nitrogen using P₁₀(14) and P₁₀(16) CO₂ laser excitation (Figs. 4a and 4b, respectively). The excellent reproducibility is typical of this scheme. By choosing a CO₂ laser line to favor absorption by one species over another, the inherent IR selectivity of this device can be demonstrated as in the case of the strong SF₆ absorption at P₁₀(16) in Fig. 4b. This feature of GC-PFLOHS is potentially useful in distinguishing compounds with similar retention times.

Fig. 5 shows chromatographic runs at six laser wavelengths for five hydro-

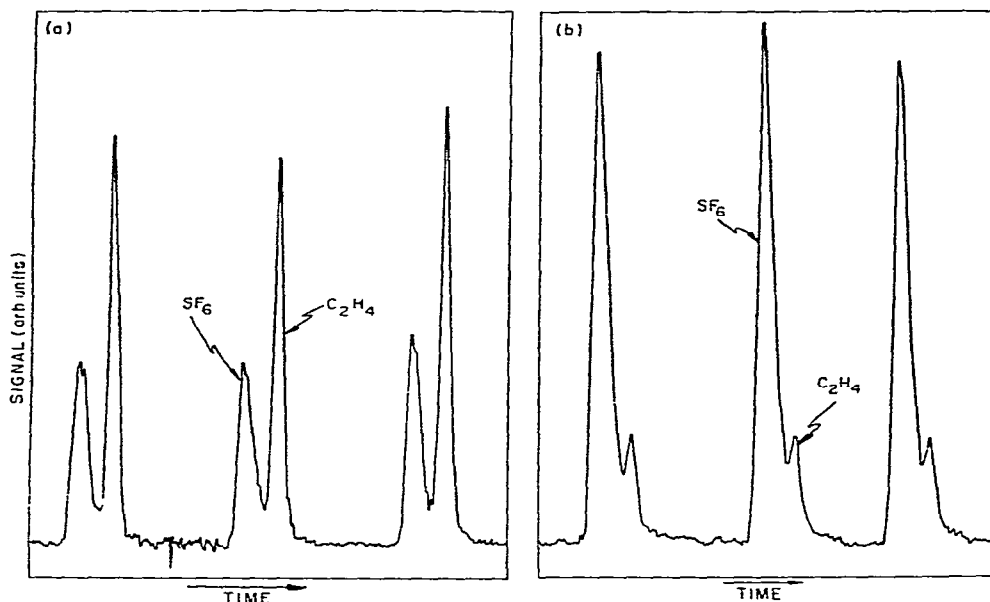


Fig. 4. Chromatographic runs for triplicate 0.1-ml injections of a mixture of 10 ppm SF_6 and 76 ppm ethylene in nitrogen using (a) P_{10} (14) and (b) P_{10} (16) CO_2 laser excitation. The column (3 ft. \times $\frac{1}{8}$ in. I.D.) was packed with Porapak N (50–80 mesh) at -15°C . The excellent reproducibility of the PFLOHS detector signal is typical of this scheme.

carbons: ethylene, 1-butene, isobutylene, *trans*-2-butene and *cis*-2-butene. The selectivity of IR-PFLOH detection is readily apparent, and can be an aid in accurate identification of the compounds as each has a unique infrared absorption fingerprint besides their GC retention time.

Other lasers in addition to the CO_2 laser employed in this study can be utilized. These include CO, HF, DF, spin-flip Raman lasers, etc. We chose the CO_2 laser because of its simplicity and reliability and because many molecular species have absorptions within the 9–11- μm range. Other isotopes of CO_2 can be used to extend operation to 12 μm . If sufficient material is available during analysis then a conventional light source-monochromator combination can be employed to improve versatility. However, because this technique is inherently "noisy" (*i.e.* possesses a large noise equivalent power) it is optimally utilized in conjunction with laser excitation.

The arrangement depicted in Fig. 1 is well suited for atmospheric trace-gas analysis. It possesses the requisite sensitivity, selectivity and is applicable to a wide range of species likely to be encountered in the environment. A persistent problem in trace-gas studies using IR absorption techniques has been the presence of a background absorption signal from interfering constituents¹³; for example, hot band CO_2 absorption and water vapor absorption. These can be quite significant even in the atmospheric spectral windows, the latter for example exhibiting absorptions as high as 10^{-6} cm^{-1} on most CO_2 laser lines. Such a background signal would correspond to *ca.* 30 ppb ethylene, for example. However, in the configuration shown in Fig. 1, the additional discrimination provided by varying retention times makes it possible

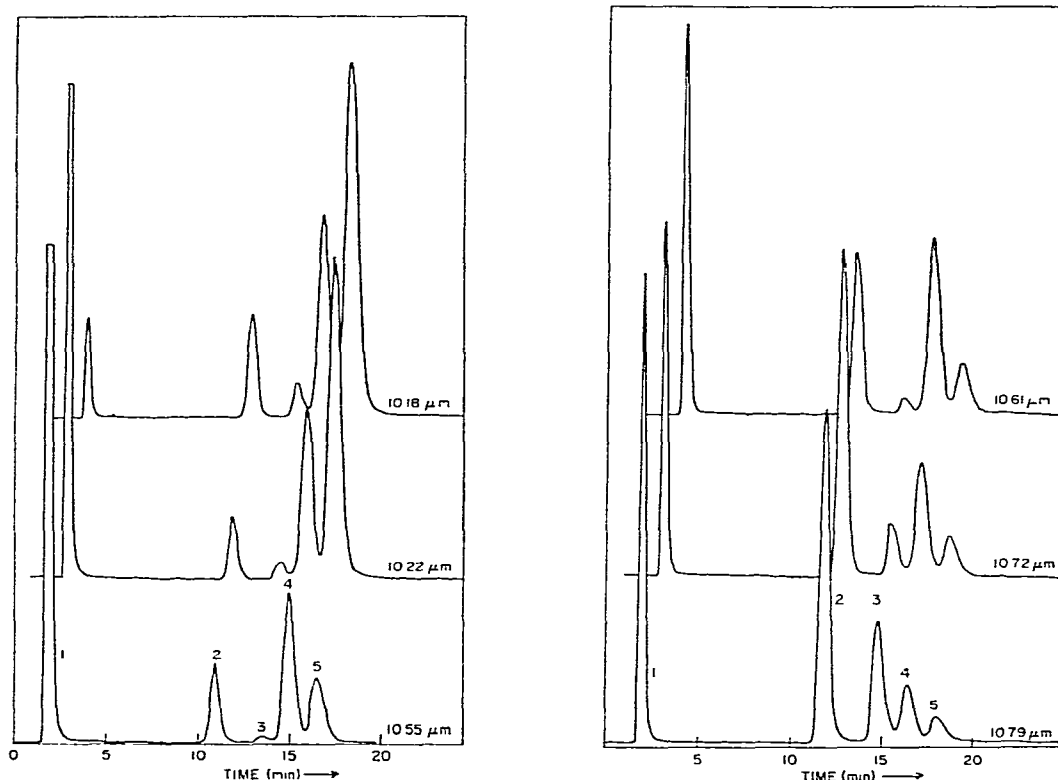


Fig. 5. Chromatographic runs at six laser wavelengths for five hydrocarbons in nitrogen: 1 = ethylene; 2 = 1-butene; 3 = isobutylene; 4 = *trans*-2-butene; 5 = *cis*-2-butene. The column (4.5 ft. \times $\frac{1}{8}$ in. I.D.) was packed with Durapak *n*-Octane-Porasil C (100-120 mesh) at room temperature. The relative amounts chosen for the various species varied somewhat to favor those possessing weak absorptions but all were in the 10 to 50 ppm range in concentration. By choosing a CO₂ laser line to favor absorption by one species over another, the inherent IR selectivity of PFLOHS detection is demonstrated. This feature of GC-IR-PFLOHS is potentially useful in distinguishing compounds with similar retention times (*e.g.* isomers).

to extend the measurement to 10^{-8} cm⁻¹ (corresponding to 300 ppt in the case of ethylene). Thus in practice, a syringe can be employed to gather and inject air or sample into the GC-PFLOHS system and the analysis performed in nearly real time.

CONCLUSIONS

From these results, PFLOHS detection has demonstrated that it is rapid, sensitive, selective and easily adapted for use in GC analysis. PFLOHS has demonstrated at least an equivalence in sensitivity with PAS in this application and at least a 10^4 sensitivity advantage over other IR absorption schemes. The demonstrated background reduction (factor of 10) over that previously reported³ using PAS is primarily due to our use of a windowless cell. At the present time we have not exploited the inherent sensitivity advantage of this scheme and further sensitivity improvement through additional vibration isolation and scaling is anticipated. Furthermore, the

windowless and microphone-free features of PFLOHS are advantages that lend themselves to greater sensitivity and fewer material handling problems. In comparison to other more familiar detection schemes, PFLOHS is generally an order of magnitude more sensitive than FID, for example. However, IR-PFLOHS is a non-destructive selective technique and can be applied to most species. Because of its complexity, it is anticipated that this detector's usage will be limited to specialized applications such as atmospheric pollutant analysis. In this application, in particular, the superior sensitivity and selectivity of GC-PFLOHS permit accurate and meaningful analyses to be performed on most environmentally important species.

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