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## The Application of Laser Intracavity Absorption Detector to Gas Chromatography of Trace Organic Pollutants in Water

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**THE APPLICATION OF A LASER INTRACAVITY  
ABSORPTION DETECTOR TO GAS CHROMATOGRAPHY  
OF TRACE ORGANIC POLLUTANTS IN WATER**

by  
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**Arkansas Water Resources Research Center**

**University of Arkansas  
Fayetteville**

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## ABSTRACT

### THE APPLICATION OF A LASER INTRACAVITY ABSORPTION DETECTOR TO GAS CHROMATOGRAPHY OF TRACE ORGANIC POLLUTANTS IN WATER

A helium-neon (HeNe) laser operating simultaneously at 3.39  $\mu\text{m}$  (infrared) and 0.63  $\mu\text{m}$  (visible) has been used as a selective detector for hydrocarbons in the effluent of a gas chromatograph. The infrared and visible laser transitions originate at the same energy level and are competitive. When a hydrocarbon enters the laser's resonant cavity, the 3.39  $\mu\text{m}$  energy is absorbed due to the C-H stretching vibration and the visible emission is enhanced. The visible laser emission is monitored with a photodiode as a quantitative measure of the concentration of the absorbing molecule. The minimum detectable concentration for propane using the double-beam configuration is 20  $\text{pg/mL}$ , which is 25 times lower than the best value reported for a thermal conductivity detector. In practice, the detector's selectivity for hydrocarbons is modified by various substituents. The detector responds to aliphatic and aromatic hydrocarbons with aliphatic side chains, except for those substituted with halogens. The HeNe laser intracavity absorption detector may be used without prior separation in some cases (e.g., methane in coal mines). This detector operates with nitrogen carrier gas without sacrifice of sensitivity and should be useful for monitoring organic pollutants since it does not respond to water or carbon dioxide. Also, it should be possible to manufacture this detector at competitive prices.

Green, Robert B.

THE APPLICATION OF A LASER INTRACAVITY ABSORPTION DETECTOR TO GAS CHROMATOGRAPHY OF TRACE ORGANIC POLLUTANTS IN WATER

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KEYWORDS-- laser\*/infrared spectroscopy\*/gas liquid chromatography detector\*/aliphatic hydrocarbons/air pollution/water pollution/instrumentation/research and development.



## OBJECTIVE

The objective of the proposed research was the evaluation of the potential of a laser intracavity absorption detector for gas chromatography of trace organic pollutants in water. The detector exploits the unique helium-neon (HeNe) laser energy level system and the sensitivity of intracavity absorption of laser emission. The coupling of this detector to a gas chromatograph provides a powerful tool for the analysis of organic pollutants in water.

The goals of the proposed research may be summarized as follows:

- (a) Determination and optimization of key parameters for detection of model molecules with the HeNe laser intracavity detector.
- (b) Coupling of the laser intracavity detector to a gas chromatograph.
- (c) Laboratory evaluation of gas chromatograph/laser intracavity detector system.
- (d) Application of the instrumentation to the analysis of trace organic pollutants in local natural water systems.

## BACKGROUND

The signs of water pollution are obvious to even the most casual observer. The diversity of these signs is indicative of the complexity of the problem. The origin of water problems may be attributed to many sources and types of pollutants.

The production of synthetic organic chemicals in the United States has increased by a factor of fourteen since the end of World War II. A commensurate burden on the environment and, in particular, natural water systems can be related to this increased production and use of organic chemicals. Compounds included in this group are used as fuels, plastics, plasticizers, fibers, elastomers, solvents, detergents, paints, pesticides, food additives, and pharmaceuticals.

Organic pollutants must be identified and quantitated in natural water systems for several reasons: (1) to monitor the level of pollution, (2) to follow and understand the fate of pollutants in the environment, (3) to test the effectiveness of control measures, and (4) to provide valid environmental quality "baseline" data where industrial development is anticipated. The U.S. Environmental Protection Agency estimates that almost one-third of the stream miles in the nation are polluted in excess of federal water quality standards so the problem is of immediate interest.

Gas chromatography is one of the most powerful and widely-used techniques for the study of trace levels of organic contaminants in environmental samples. In a gas chromatograph (GC), molecules are separated in a column by partitioning the sample between the gas mobile phase and the liquid stationary phase. Next to the column itself, the detector which senses the separated compounds as they elute from the column is the most important component of the gas chromatograph. The measurement of infrared absorption is potentially a useful detection technique for GC because most molecules have fundamental absorption transitions in this region of the spectrum. Interference from molecules other than the analyte is a possibility but the judicious choice of a single absorption line for measurement can eliminate most spectral overlaps if sufficient resolution (i.e., selectivity) is available. Unfortunately, at typical trace concentrations, infrared absorption is too small to be determined by standard transmission measurements through any reasonable pathlength. In addition, conventional thermal sources of infrared radiation are

limited in the amount of infrared flux that can be obtained because of Planck's law restrictions. An optoacoustic detector coupled with a CO<sub>2</sub> laser has been successfully used for monitoring the infrared absorption of molecules in the effluent of a gas chromatograph (1).

This report describes the use of a helium-neon (HeNe) laser as an intracavity absorption detector for hydrocarbons in the effluent from a gas chromatograph. The first application of intracavity absorption in a HeNe laser was reported in 1965. C. Bradley Moore recognized the coincidental overlap of the 3.39  $\mu\text{m}$  emission and the carbon-hydrogen stretching frequency and used the absorption of methane to discriminate between two neon emission lines in the infrared (2). Since then, methane absorption within the resonant cavity has been used extensively to frequency stabilize HeNe lasers (3-5).

Intracavity absorption of laser emission can significantly improve the sensitivity of absorption measurements. It has been demonstrated that the measurement of small optical losses (or gains) can be enhanced by insertion of the absorbing sample within the resonant cavity of a laser. Depending on the cavity's length and the gain medium, one or more longitudinal modes oscillate within the laser. Two types of interaction between the absorber and the laser modes have been described (6). In type 1, the laser mode falls within the absorption linewidth of the sample. This case applies to an inhomogeneously broadened laser with one of its modes overlapped by the absorption line. Insertion of an absorber into the cavity results in a reduction in laser power due to increased cavity loss. Enhancement over extracavity absorption measurements is primarily due to the

extended effective pathlength. When several of the modes of a homogeneously broadened laser fall outside the absorption linewidth, type 2 intracavity absorption prevails. In type 2, the absorption interacts with a relatively few modes and the laser power is shifted into the remaining modes. Enhancement factors of 10 to 1000 have been observed and attributed to this mode competition.

The coincidence of the C-H stretching vibration with the HeNe laser line at 3.39  $\mu\text{m}$  presented a potential detection scheme for GC. Although many intracavity absorption experiments have been reported for atomic, ionic and molecular species in the gas phase, flames, and solutions (7-11), only limited results have been reported with the HeNe laser because of its fixed frequency. HeNe laser intra-cavity absorption analysis has been reported for a cobalt chelate with an absorption maximum at 0.63  $\mu\text{m}$  (12). The intracavity method was approximately 100 times more sensitive than classical colorimetry and competitive with the most sensitive methods for trace analysis. A two-wavelength HeNe laser was used recently to detect methane in the atmosphere (13). The methane absorption was coincident with one HeNe line (3.3922  $\mu\text{m}$ ) and essentially non-coincident with the other (3.3912  $\mu\text{m}$ ). Therefore the absorption ratio of the two lines was sensitive to methane concentration.

Although it was possible to detect intracavity absorption at 3.39  $\mu\text{m}$ , this report demonstrates the superiority of an approach which involves the indirect measurement of infrared absorption. The 3.39  $\mu\text{m}$  HeNe laser line is competitive with the 0.63  $\mu\text{m}$  visible line since both transitions originate at the same excited state. Since the discovery

of the HeNe laser in 1961 (14), this competition has been the subject of many theoretical and experimental studies (15-18). This report describes the sensitive, selective detection of molecules by exploiting this competition. When a molecule which absorbs at 3.39  $\mu\text{m}$  was placed within the cavity of a HeNe laser operating simultaneously at both the visible and infrared wavelengths, the 0.63  $\mu\text{m}$  radiation was enhanced at the expense of the 3.39  $\mu\text{m}$  transition. Since many hydrocarbons absorb at 3.39  $\mu\text{m}$ , a gas chromatographic separation prior to detection is necessary for further discrimination.

#### EXPERIMENTAL SECTION

APPARATUS. Typically, commercial HeNe lasers operate at a single wavelength, most commonly in the visible. Unwanted emission lines are suppressed by using optical materials and coatings appropriate for the line of interest. Permanent magnets are also used to broaden the Zeeman splitting and reduce the higher gain 3.39  $\mu\text{m}$  infrared emission if a visible laser is desired. The HeNe laser used in this research operated at 3.39  $\mu\text{m}$  and 0.63  $\mu\text{m}$  simultaneously. A standard HN 517 HeNe laser was modified (S/N 824) to the author's specifications by Jodon Engineering Associates, Inc. (Ann Arbor, Michigan). The plasma tube was shortened to provide a 5-cm space for intracavity experiments and the mirrors were coated to reflect both the 0.63  $\mu\text{m}$  and 3.39  $\mu\text{m}$  laser lines. These modifications required that the output mirror reflectivity be reduced from approximately 99% to 55.2%. The laser output was approximately 1.5 mW in each line, rather than the normal 7 mW. In experiments where the laser mirror separation was varied, the

totally reflecting back mirror was mounted on a piezoelectric transducer (Model No. PZ-40, Burleigh Instruments, Fishers, NY) which was inserted in a precision mirror mount (Daedel, Inc., Pittsburgh, PA). The mirror mount was attached to an XY translation stage (Newport Research Corporation, Fountain Valley, CA). A precision flat mirror (Oriental Corporation, Stamford, CT) with approximately 90% reflectivity for the visible and infrared laser lines was used for double-beam experiments.

A Model J-12A InAs photodiode (Judson Infrared, Inc., Ft. Washington, PA) was the detector for infrared radiation in some experiments. A silicon photodiode (PIN-0408, United Detector Technology, Inc., Santa Monica, CA) was used for visible measurements and monitored the 0.63  $\mu\text{m}$  HeNe laser line in the final instrumental configuration. A signal processor was constructed with Datel-Intersil sample-and-hold chips (Mansfield, MA). All other electronic components were purchased from Jameco Electronics (Belmont, CA).

A Carle AGC-311 gas chromatograph equipped with a thermal conductivity (TCD) detector was used for all separations (Carle Instruments, Anaheim, CA). A miniature personal air sampling pump with charcoal filters (Environmental Compliance Corp., Venetia, PA) was used to collect laboratory air samples. A Model 125A mechanical chopper (EG&G Princeton Applied Research, Princeton, NJ) and a strip chart recorder, model SRG-2 (Sargent Welch Scientific Co., Dallas, TX) were also used.

REAGENTS. All gas samples were Scotty II calibration gases purchased from Alltech Associates (Houston, TX). These gases were supplied in

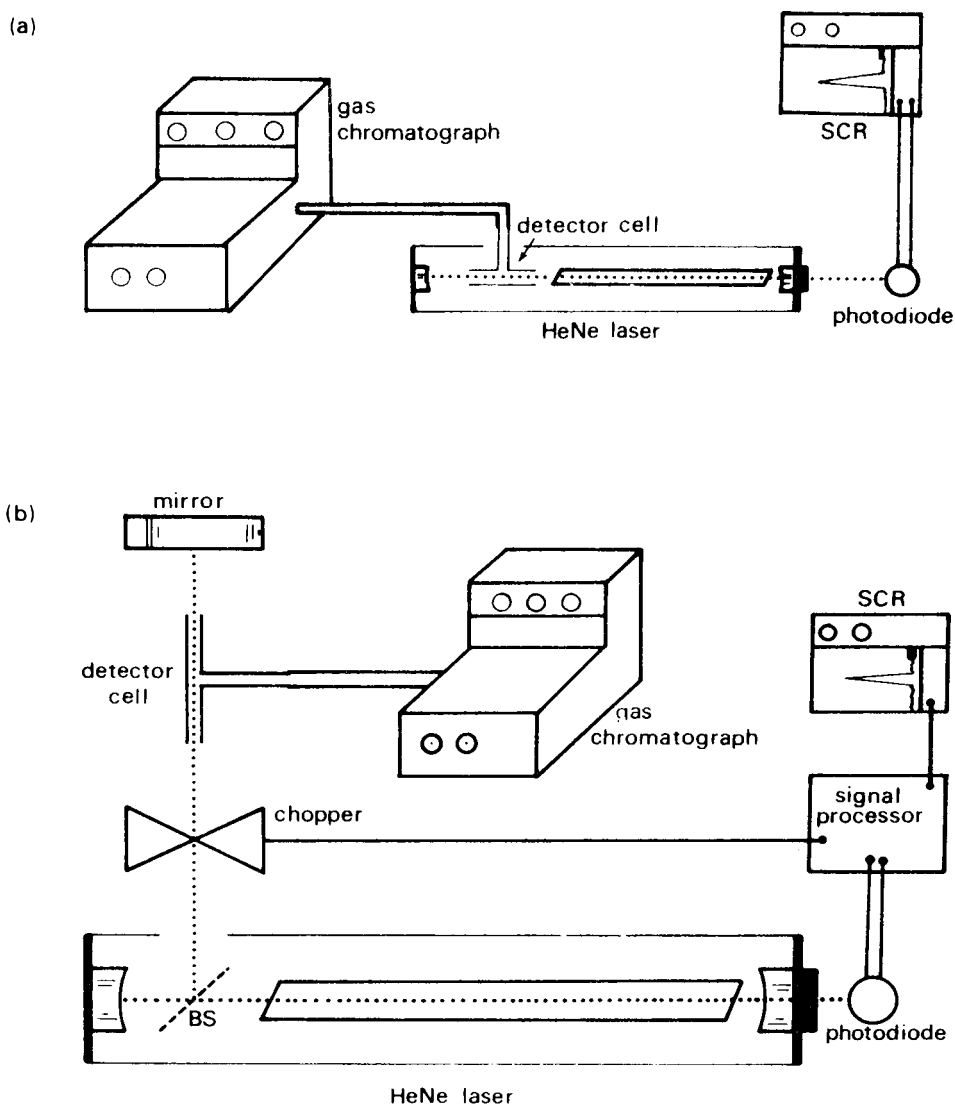
14 L throwaway containers. Maximum pressure was 240 psig. A valved outlet on each container accepted a 1/8" male NPT connection. A syringe adaptor (Cat. no. 8810) containing a septum was used to facilitate sample withdrawal by syringe. A 10  $\mu$ L Unimetrics gas-tight syringe (Cat. no. 11010) was also purchased from Alltech and used for sample introduction into the GC.

PROCEDURE. A 1/8" x 6' Porapak Q 80/100 mesh column was used for all separations. A 40 psig, 40 mL  $\text{min}^{-1}$  helium flow was used with the TCD bridge set at 1. All runs were made with the oven at ambient temperature (25°C). The "minimum detectable level" was calculated using the method described by Sullivan and O'Brien with a signal-to-noise ratio equal to two (19).

## RESULTS AND DISCUSSION

SENSITIVITY. The single-beam experimental configuration is shown in Figure 1a. The sample was injected into the GC. The column effluent passed through the standard TCD and then was conducted to the 5-cm pathlength "Tee" cell with capillary tubing. Both the capillary tubing and detector cell were heated to prevent condensation of the sample. The laser emission was monitored with a photodiode whose output voltage was used to drive the strip chart recorder pen. Comparative extracavity absorption measurements were made initially to confirm the best location for the detector Tee cell. The detector cell was positioned adjacent to the laser output mirror for extracavity experiments and standard transmission measurements were made. The bias on the infrared and visible photodiodes was adjusted so that

Figure 1. Schematic diagrams for HeNe laser intracavity absorption detectors: (a) single beam, (b) double beam.





both gave the same voltage output when illuminated with the same laser power. Table I shows the results of these experiments using methane as the model absorber. Since both enhancements and reductions in beam power were measured, the absolute signal resulting from methane absorption is indicated in Table I without regard for whether it was detected as an increase or decrease. The signal produced when extracavity measurements were made at  $3.39 \mu\text{m}$  was assigned a value of one. When the sample was moved inside the laser cavity, only a small enhancement was noted. Intracavity enhancement of this absorption measurement was minimal for two reasons: (1) the multipass advantage was reduced because of the relatively low reflectivity of the output mirror, and (2) a single longitudinal mode oscillates at  $3.39 \mu\text{m}$  because of the long wavelength and relatively short resonant cavity. When the detector cell was positioned outside the laser and measurements were made at the visible line, no signal was detected because methane does not absorb at  $0.63 \mu\text{m}$ . Since the sample was outside the laser cavity, it did not interfere with the visible-infrared line competition. A large signal enhancement due to methane absorption was observed when the detector cell was placed within the resonant cavity of the laser and the visible output was monitored. Since both laser transitions compete for the same excited atoms, it is not surprising that a small change in the upper state population induced by loss at the high gain infrared line can make a large difference in the output at the low gain visible transition. Subsequent measurements were made at the visible line with the sample in the laser cavity.

TABLE I. Relative signals for extra-cavity and intra-cavity measurements with a 10  $\mu\text{L}$  methane sample.

<u>SAMPLE LOCATION</u>	<u>RELATIVE SIGNAL</u>	
	<u>3.39 <math>\mu\text{m}</math></u>	<u>0.63 <math>\mu\text{m}</math></u>
Extra-Cavity	1.0	-
Intra-Cavity	1.2	46.7

Figure 2 compares chromatograms for the same samples using the standard TCD and the laser intracavity absorption detector (LICAD) connected in series. Although direct comparison of the sensitivities using this data is not possible, the inset for the 1  $\mu$ L methane sample gives an indication of the noise on the respective signals. The limits of detection determined for the single-beam LICAD are shown in Table II. Figure 2 also shows that the LICAD peak shapes are symmetrical and similar to those produced by the TCD. The analytical calibration curve for the single-beam HeNe LICAD was linear over a wide range. Unfortunately, the uncertainty in individual measurements was relatively large and a non-zero x-intercept was present. A closer study of the HeNe output revealed a low voltage, low frequency (0.013 Hz) oscillation. When the laser output was measured simultaneously at 3.39  $\mu$ m and 0.63  $\mu$ m, these fluctuations were observed to be 90° out of phase, apparently resulting from competition between the lines. Observations of these fluctuations using several different detectors confirmed that this was not an artifact. Similar oscillations were also observed from a 0.5 mW HeNe laboratory alignment laser.

The experimental arrangement used to discriminate against this background is shown in Figure 1b. A quartz plate was used to split a small fraction of the beam from the resonant cavity to a second totally reflecting mirror. This created a laser oscillating in two legs at 3.39  $\mu$ m and 0.63  $\mu$ m. The detector cell was positioned in the external leg and the beam mechanically chopped to produce a "double beam in time" absorption detector. The visible photodiode monitored the HeNe laser output. The photodiode output voltage was fed to a

Figure 2. Comparison of chromatograms for the thermal conductivity detector (TCD) and the HeNe laser intracavity absorption detector (LICAD) in series. The inset shows a scale expansion of ten for the 1- $\mu$ L methane sample.

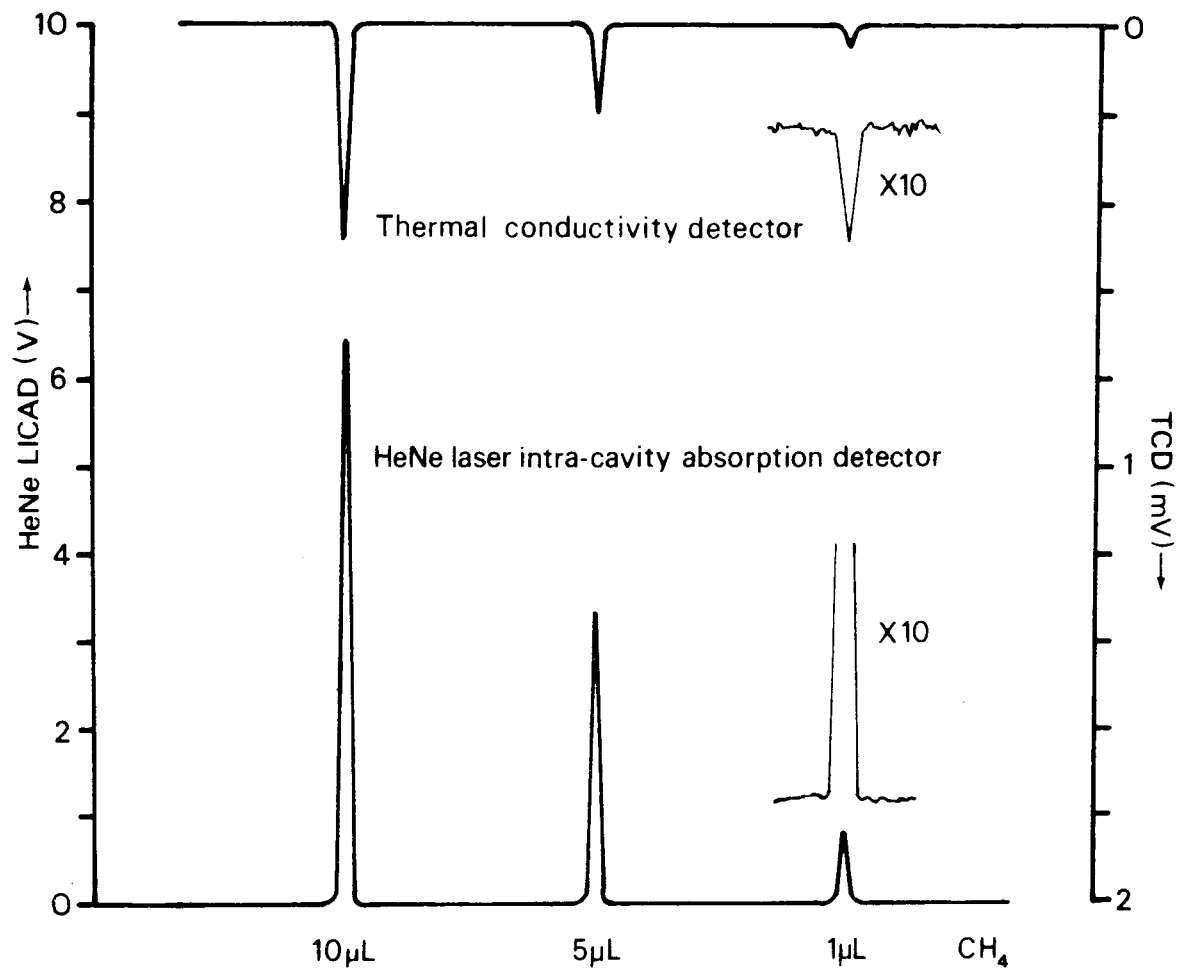


TABLE II. Comparison of minimum detectable concentration levels.

<u>DETECTOR</u>	<u>MINIMUM DETECTABLE LEVEL</u>		<u>SAMPLE</u>
	This Work	Literature (19)	
TCD	$1 \times 10^{-9} \text{ g/cm}^3$	$5 \times 10^{-10} \text{ g/cm}^3$	C <sub>3</sub> H <sub>8</sub> , C <sub>3</sub> H <sub>8</sub>
HeNe LICAD	$5 \times 10^{-7} \text{ g/cm}^3$ *	-----	CH <sub>4</sub> , -----
	$9 \times 10^{-11} \text{ g/cm}^3$ †	-----	C <sub>3</sub> H <sub>8</sub> , -----
	$2 \times 10^{-11} \text{ g/cm}^3$ #	-----	C <sub>3</sub> H <sub>8</sub> , -----

\* single beam

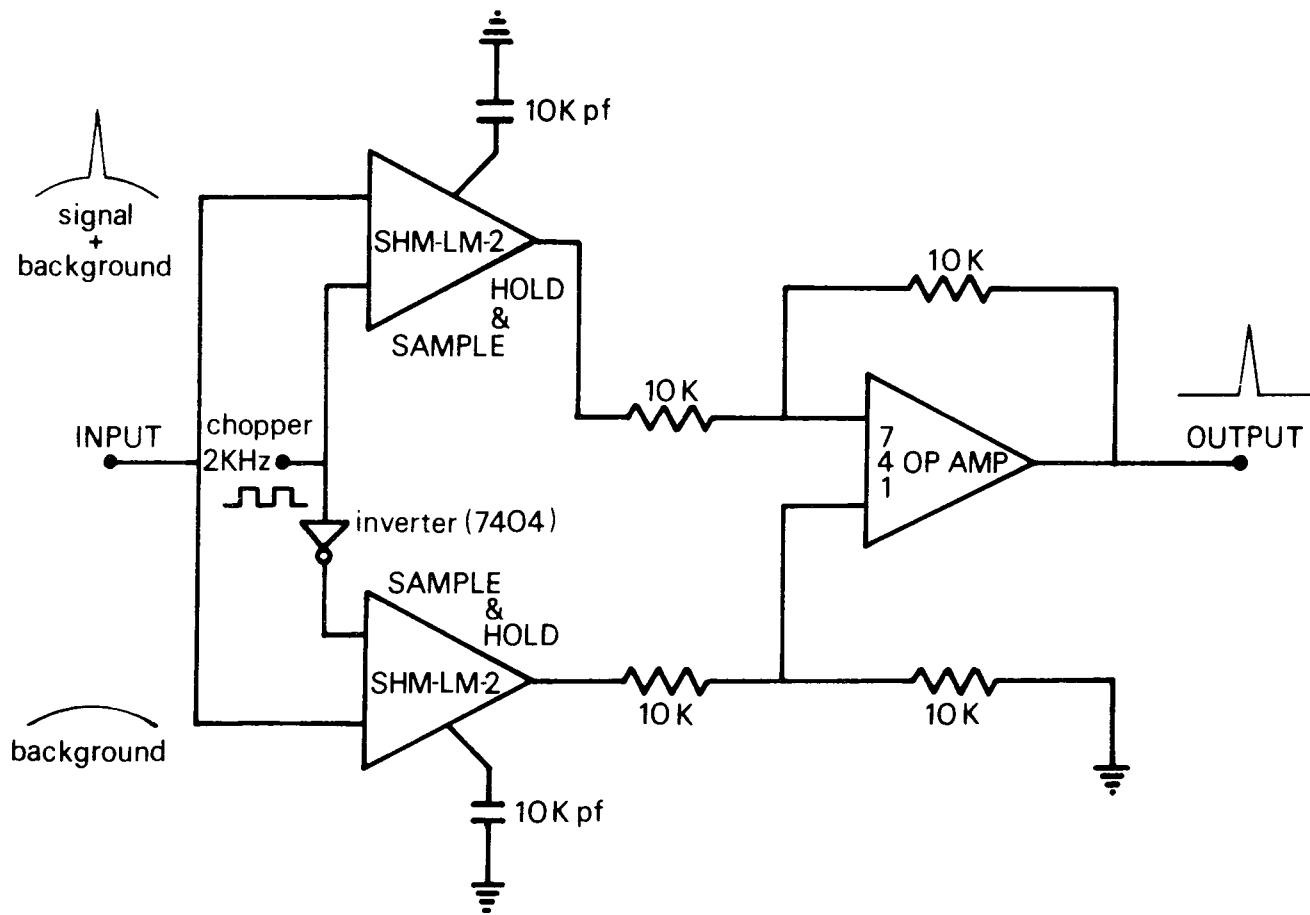
† double beam

# optimized double beam

signal processor which was synchronized with the chopper frequency (2 KHz). A functional schematic of the differential sample-and-hold signal processor is shown in Figure 3. The output of the photodiode was directed to two sample-and-hold (SH) circuits. The reference signal from the chopper controlled which SH was sampling and which was holding. One SH sampled the signal plus background (i.e., the external laser beam) while the other was holding the previous background value. On the second half of the chopper cycle, the order was reversed and the background (i.e., the internal laser beam) was sampled. The outputs from the SH's were subtracted in a difference circuit and the analytical signal was recovered from the background. This type of signal processing was successful because the signal was modulated at a much higher frequency than the background oscillation. The output of the signal processor was read out on a strip chart recorder. Signal processing eliminated the zero offset and low frequency noise resulting in the improved results reported in Table II for the double-beam LICAD. Using the signal processor lowered the detection limits for the double-beam HeNe LICAD three orders-of-magnitude. The precision for the injection of five consecutive samples of the same concentration was now better than 1%. The linear dynamic range for double-beam LICAD was approximately eight orders-of-magnitude.

A further improvement was made in the LICAD's sensitivity by optimizing the laser mirror separation. Sample absorption was measured at each mirror position. Coarse adjustments were made with the XY translation stage and fine adjustments were accomplished with

Figure 3. Functional schematic of differential sample-and-hold signal processor.



the piezoelectric transducer. The greatest signal (i.e., enhancement of the visible emission) occurred at the mirror separation where the gain on the 632 nm visible transition was maximized. The limits of detection for propane for the single-beam, double-beam, and optimized double-beam HeNe LICAD configurations are compared with the best published results for the TCD in Table II. The best LICAD detection limits are 25 times lower than the TCD.

SELECTIVITY. According to a chart of vibrational frequencies, the HeNe laser detector should respond selectively to hydrocarbons. As would be expected, certain atoms and functional groups modified this primary selectivity by shifting the C-H vibrational frequency away from 3.39  $\mu\text{m}$ . In some cases, hydrocarbons were not detected as a result of the influence of a substituent. In other cases, the sensitivity for a particular molecule was lower than expected based on the number of C-H bonds. For example, the LICAD responded linearly to equimolar concentrations of a homologous series of alkanes. On the other hand, ethanol and pentanol produced lower signals than would be predicted based on the results for a series of alcohols. Substitution of a functional group on a molecule with more than six C-H bonds did not alter the sensitivity. The following rule-of-thumb was developed based on an experimental survey of potentially-detectable molecules: the LICAD is sensitive to aliphatic hydrocarbons and aromatic hydrocarbons with aliphatic side chains except those with substituted halogens. In general, the LICAD's sensitivity and specificity for molecules could be predicted based on the rule-of-thumb and published infrared spectra, but it is prudent to experimentally determine



individual response factors for quantification. The LICAD did not respond to water, even as the major constituent.

APPLICATION. The practical application of the HeNe LICAD was demonstrated by determining the concentration of ether in air samples taken in an undergraduate organic chemistry laboratory at the University of Arkansas. In this laboratory, ether was used to separate two compounds by liquid-liquid extraction and constituted a potential inhalation hazard. Air samples were collected and analyzed according to Method No. P&CAM 127 in the NIOSH Manual of Analytical Methods (20). This method involves collection of the air sample on a charcoal adsorbent, desorption, and subsequent analysis by gas chromatography. The glass tube containing the adsorbent is subdivided into two sections containing 100 mg and 50 mg of activated charcoal, respectively. The 50 mg backup portion was used to determine if the capacity of the initial 100 mg section had been exceeded by the sample. During the 3-hr sampling time, laboratory air was drawn through the sampling tube by a battery-operated pump at a controlled flow rate (20 mL/min). Then the charcoal sections were removed, placed in separate vials with 1 mL of the solvent, carbon disulfide, and sealed. To assure complete desorption, the vials were agitated a minimum of 30 minutes. After agitation, five  $\mu\text{L}$  aliquots were withdrawn from each vial and injected into the GC. If the concentration of the ether analyte in the 50 mg charcoal section was greater than 10% of the concentration determined for the 100 mg section, the run was voided because an unacceptable quantity of the analyte was lost. Quantitation of ether was based on a calibration curve generated by

plotting the concentration of a series of standards (i.e., ether in carbon disulfide) versus the chromatographic peak area. The level of ether in the laboratory atmosphere was 50 ppm. This concentration is well under the OSHA 400 ppm "ceiling" level. The unique characteristics of the LICAD for environmental analysis are illustrated by the chromatogram. The solvent peak for carbon disulfide is absent because of the LICAD's selectivity. This is a definite advantage because solvent peaks may partially overlap or totally obscure analyte peaks. In this case, the use of the LICAD will permit a significant reduction in analysis time since the ether and the carbon disulfide peaks no longer must be resolved by the chromatographic separation. Benzene, carbon tetrachloride, and water are other common solvents which are invisible to the LICAD. It is anticipated that the results of this research will be of interest to the following: (1) agencies whose mission is to monitor environmental quality, (2) agencies and industries who must comply with water regulations, and (3) the scientific community who may apply this information to other problems.

#### CONCLUSIONS

The potential of the HeNe LICAD as a detector for GC has been demonstrated. The prototype model has produced limits of detection which are 25 times better than the TCD, a detector which has found wide acceptance for gas chromatography. The HeNe LICAD is selective, responding to species which absorb at  $3.39 \mu\text{m}$  (mainly hydrocarbons). This selectivity has an advantage for the detection of organic pollutants since the LICAD does not respond to water or carbon dioxide. Also many common solvents, such as benzene, are invisible to the

LICAD. In some cases, the LICAD could be used without prior separation (e.g., methane in coal mines). Many analytical techniques also produce methane as an indication of other components (e.g., digestion of sewage). The HeNe LICAD is non-destructive and less expensive; non-flammable carrier gases such as nitrogen may be used without sacrifice of sensitivity. Once development has been completed, a mass-produced HeNe LICAD would be potentially inexpensive.

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