



Arkansas Water Resources Center

LASER-PHOTOACOUSTIC DETECTION OF WATER POLLUTANTS PHASE I

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COMPLETION REPORT

LASER-PHOTOACOUSTIC DETECTION OF WATER POLLUTANTS
PHASE I

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TABLE OF CONTENTS

	<u>Page</u>
I. OBJECTIVES AND SIGNIFICANCE.	1
II. EXPERIMENTAL METHOD.	3
A. Background	
B. Phase I Study	
C. Planned Phase II Study	
III. RESULTS TO DATE.	11
IV. RELATED RESEARCH	16
V. FACULTY AND STUDENT INVOLVEMENT.	18
VI. PUBLICATIONS	18
VII. INFORMATION DISSEMINATION	18

COMPLETION REPORT

LASER-PHOTOACOUSTIC DETECTION OF WATER POLLUTANTS: PHASE I

October 1, 1977 to March 30, 1980

I. OBJECTIVES AND SIGNIFICANCE

Highly industrialized societies like our own tend to pollute their waters. Recognizing that water pollution can pose serious health hazards and unknown long term effects it is necessary to monitor the quantity and fate of these pollutants. The availability of information on the concentration and evolution of pollutants would then make it possible to theoretically model the behavior of pollutants in various types of natural water systems. These models would, in turn, allow water quality problems to be anticipated and hopefully avoided.

Despite this high degree of interest and apprehension about the role and fate of these pollutants there is presently little data available on the concentrations and therefore on the evolution of metal and toxic chemicals in our waters. This is a result of the fact that only in the last decade have reliable methods been developed to detect trace amounts of these water pollutants. Even now there is a need for further development of non-disturbing, easy-to-apply trace element detection instrumentation. That the detection technique should be non-disturbing was well noted by L. L. Ciaccio in a recently issued pollution handbook: "To obtain knowledge of the specific species present and of their current ratios, the effect of the analytical treatment should in no way change the system with its unique equilibrium and components. The analytical results should characterize the original system and not one that is a modification created by the analytical processing." The objective of this research is to

develop a non-disturbing laser based analytic technique for the detection of heavy metals and organic toxic chemicals. In particular, PHASE I of this study was to investigate the feasibility of a laser-photoacoustic technique to detect low concentrations of impurities in water. Results to date¹ indicate that the technique is both viable and competitive. That it is viable is indicated by the fact that we have utilized the laser-photoacoustic detection scheme to detect an organic toxic pollutant in water to about one part in 10^{11} . This sensitivity can be increased even further to about one part in 10^{13} . That it is competitive is indicated by the fact that other schemes such as flame atomization or fluorescence spectroscopy either disturb the sample or are difficult to use.

In the laser-photoacoustic method a resonant modulated laser beam is directed into the sample in its normal environment. The laser energy absorbed is converted into heat which produces pressure fluctuations. These pressure fluctuations or sound waves are then detected by a sensitive hydrophone. As a result, this method is not hampered with background scattered light as in the case of fluorescence monitoring techniques or the difficulty of measuring very small absorption from an intense laser beam as in conventional transmission monitoring techniques. In addition, the technique is totally non-destructive to the sample and, having little alignment difficulties, is simple to use. We have, however, encountered one difficulty. The technique is presently limited to pollutants which absorb light in the visible part of the spectrum. This is due to the fact that water absorbs light heavily in both the ultra-violet and infra-red regions. Since most heavy metals and toxic chemicals absorb in the ultra-violet region this limitation can be a serious one. Fortunately, this obstacle is not insurmountable. Based on results from our Phase I study, we propose to extend the laser photoacoustic technique down to the ultra-violet

region by using a novel frequency modulation scheme which allows the background signal, due to absorption of the laser light by water, to be discriminated against. Since the laser-photoacoustic technique is both non-disturbing and easy-to-apply, demonstrations of application in the ultra-violet region will make it an attractive candidate for the basis of future studies on the concentration and evolution of heavy metals and toxic chemicals.

II. EXPERIMENTAL METHOD

A. Background

The photoacoustic or optoacoustic effect was discovered in 1880 by Alexander Graham Bell during his efforts to develop an optical communication system. Since then the effect has been used fairly extensively to analyze gases. Recently, photoacoustic studies have increased with the impetus coming from laser-based research carried out at Bell Laboratories.² Laser-photoacoustic measurement techniques are now widely applied to gases,³ solids,⁴ and liquids.⁵ For gaseous samples, the photoacoustic detection scheme has proven to be an excellent technique for the measurement of trace pollutants.⁶ Photoacoustic spectroscopy applied to liquids and solids has also found rather unique and valuable applications.⁷⁻¹⁰

In the photoacoustic effect¹¹ a modulated light beam is directed into a sample cell containing an absorber. The resulting intermittent absorption of light produces heat which in turn generates acoustic pressure oscillations in the cell. These pressure oscillations are then detected by a sensitive microphone. This method of detection is extremely sensitive as evidenced by reported detectivities in air of .12 parts in 10^9 SO_2 ¹²; 10 parts in 10^9 NO ¹³ and 10 parts 10^9 NO_2 .¹⁴ The fact that the photoacoustic signal is directly

proportional to the optical energy absorbed rather than the fractional change in transmitted optical intensity makes the sensitivity of the technique more promising than that of more conventional detection techniques. Moreover, in cases which the fluorescence yield is low, such as in flame studies where nonradiative decay processes dominate, the photoacoustic effect can be an extremely sensitive technique as demonstrated in recent experiments on combustion studies.¹⁵ These types of advantages have promoted researchers to say that "The photoacoustic effect offers higher sensitivity than conventional approach's advantage of nondestructive detection. Experiments performed by Kreuzer with a continuous wave carbon-dioxide laser indicate that detection limits for photoacoustic detection are lower than those for flame ionization and thermal conductivity, and in some cases approach the limits possible for mass spectrometry."¹⁶

A close examination of the photoacoustic effect reveals that two different types of signal-generation processes have for the most part distinguished condensed sample studies from noncondensed sample studies. For gaseous studies the optical energy is absorbed by the gas absorber and immediately changed into thermal energy via collisions. Studies on solids and liquids however have included an intermediate step whereby the optical energy absorbed heats the sample which is housed in a cell with an inert gas. The heat from the solid in turn heats the surrounding gas. The heated gas then acts as a piston and generates the acoustic signal. In some cases this intermediate step has been by-passed for solids by attaching a transducer to the sample¹⁷ and directly detecting the acoustic waves generated in the solid. Recently a similar idea has been demonstrated in our lab for liquids using a hydrophone which is directly in contact with the liquid.^{1,18}

B. Phase I Study

We have recently developed a non-disturbing technique¹ which can detect organic dye pollutants in water to the order of one part in 10^{11} . The high sensitivity associated with our technique is consistent with recent reports from experimenters at Bell Laboratories.¹⁸ Although the technique employed at Bell Laboratories is similar to ours in many respects, their application is primarily directed toward spectroscopy in pure liquids as opposed to trace element detection in water.

Our present detection scheme utilizes a laser-photoacoustic technique illustrated in Fig. 1.

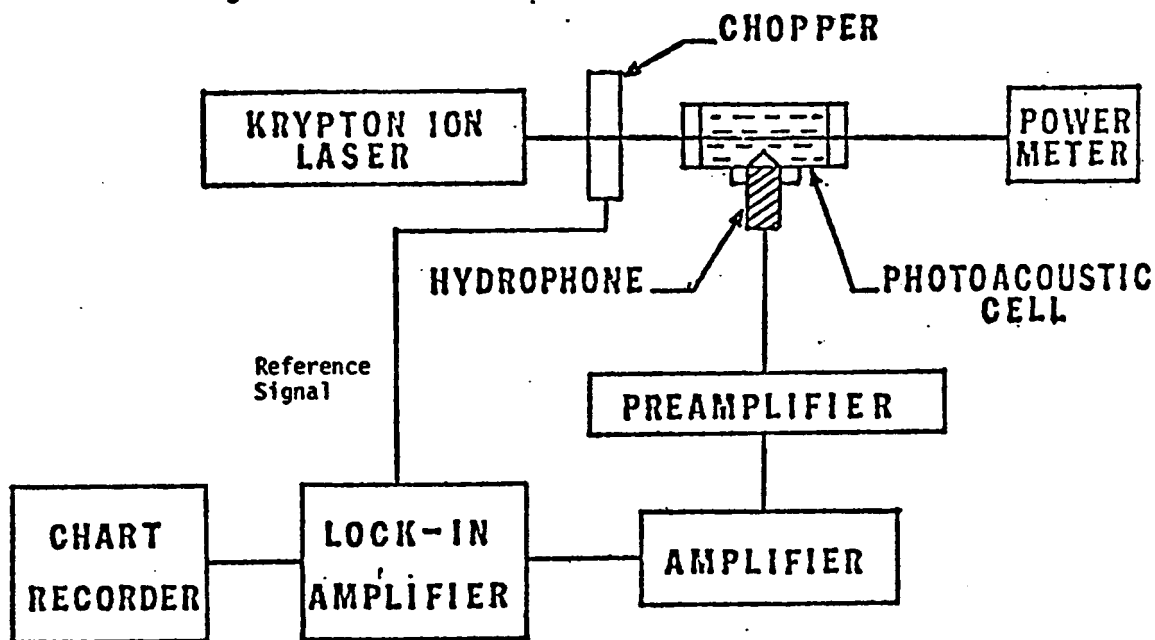


FIG.1 EXPERIMENTAL APPARATUS

The output of a continuous wave (cw) krypton ion laser is modulated at 100 Hz using a mechanical chopper. The modulated optical output is then directed into a cell which contains water, the pollutant dye molecules, and a hydrophone. The periodic optical absorption due to the interaction between

the incident optical pulse and the dissolved dye molecules results in a corresponding periodic pressure increase in the cell. The corresponding pressure modulation is detected by the hydrophone and results in a modulated electrical signal which is amplified and transmitted to a lock-in amplifier. The output of the lock-in is then monitored by a chart recorder.

In our experiment the optical pulse width is about 4 ms. The thermal diffusion length for $\tau_p = 4$ ms is given by:

$$S = (4\tau_p D)^{1/2} = 2 \times 10^{-2} \text{ cm}, \quad (1)$$

where D is the thermal diffusivity for water. Since this number is small compared to the laser beam diameter of 3×10^{-1} cm thermal diffusion can be neglected. During the time of the pulse, however, the generated acoustic wave moves rapidly. Since the velocity of sound in water is on the order of 10^5 cm s^{-1} and the cell diameter about 2 cm, the acoustic disturbance reaches the cell walls in about 20 μ s. In this case, therefore, the pressure in the entire cell increases due to the optical absorption. As a result, a shorter optical pulse is found to produce a lower acoustic signal as does leaving the cell open to air.

For a given concentration, the observed signal level is in agreement with the expected signal level based on a simple physical picture. In particular, for a concentration giving ten percent absorption, the energy absorbed per pulse is

$$E = I\tau_p = 4 \times 10^{-4} \text{ joules}. \quad (2)$$

Assuming that ten percent of this energy goes into heating the water sample of a volume of 77 cm^3 the temperature increase ΔT in the cell can be found using

$$\Delta T = \frac{H}{cV\rho} \approx 10^{-7} \text{ } ^\circ\text{K} , \quad (3)$$

where H is the heat absorbed, c the specific heat of water, V the volume of water in the cell, and ρ the density of water. This increase in temperature would result in a volume change of about $2 \times 10^{-9} \text{ ml}$ if the water sample were free to expand. However, since the cell is filled with water and closed to the atmosphere, the increased temperature results in an increased pressure ΔP which can be found using:

$$\Delta P = \frac{\Delta V/V}{\beta'} \approx -10^{-1} \text{ N/m}^2 , \quad (4)$$

where β' is the compressibility of water at room temperature. Using $100 \text{ } \mu\text{V/Pa}$ as the sensitivity of a commercial B&K Type 8101 hydrophone the observed signal is expected to be about $10 \text{ } \mu\text{V}$ and was observed to be $2 \text{ } \mu\text{V}$.

In addition to indicating the high sensitivity of the laser-photoacoustic technique to detect organic dye pollutants our research also indicates the basic factor preventing application of the technique to a broader class of pollutants. The limiting factor is the absorption of laser light by pure water which results in a photoacoustic background signal. Tam and Patel¹⁹ have studied the photoacoustic spectrum of pure water using a pulsed dye laser similar to that described in this proposal. As can be seen in Fig. 2 (from Tam and Patel) the absorption coefficient of pure water at a wavelength of 500 nm is about $\alpha = 2 \times 10^{-4} \text{ cm}^{-1}$. As a result, it is difficult to detect pollutants which absorb at this wavelength when their concentration is equal to or less than a value resulting in an absorption coefficient of $2 \times 10^{-4} \text{ cm}^{-1}$. This, in fact,

was the limiting factor in our experiments on detecting organic dye pollutants. More importantly, however, the absorption of light by water in the ultraviolet (UV) or infrared (IR) region rapidly grows to very large values. As a result, it becomes difficult to detect anything but very strong concentrations of pollutants absorbing light in the UV and IR regions. However, we propose to test a novel modification to our present laser-photoacoustic technique which may overcome this problem.

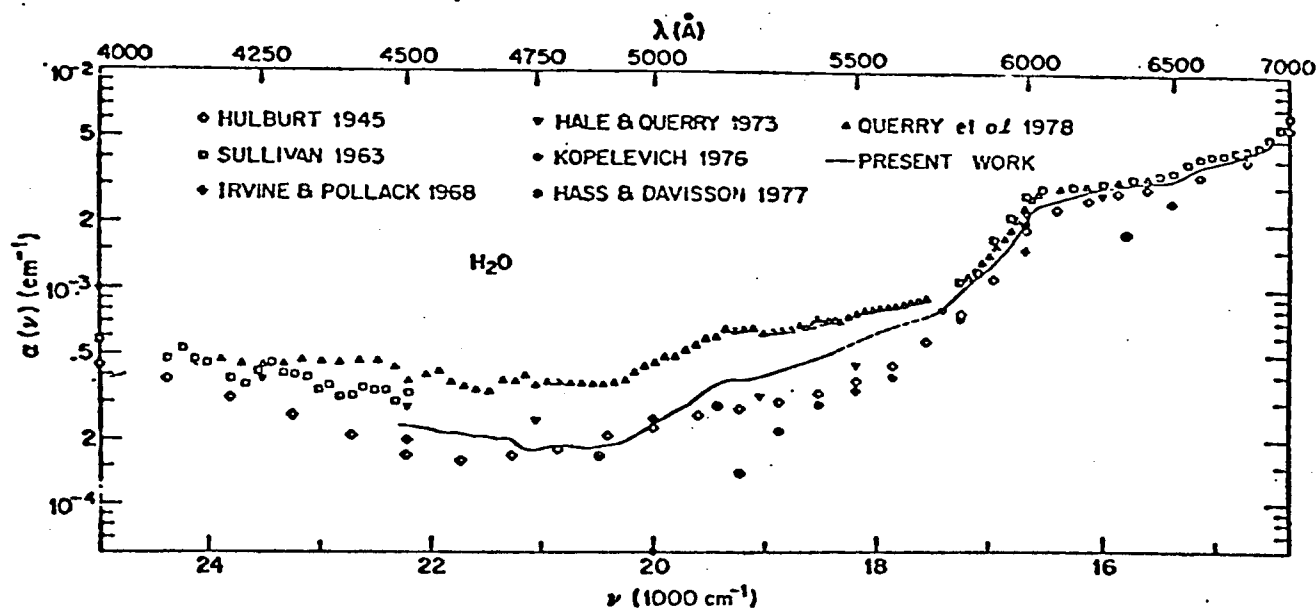


Fig.2 Absorption spectra of distilled light water by optoacoustic determinations (shown by solid line). The dashed part is interpolation not covered by the tuning range of the laser dyes used. Also shown are some experimental data from other authors for comparison.

C. Planned Phase II Study

Our newly proposed technique which will allow the photo-acoustic technique to extend to the UV and IR spectral regions is shown in Fig. 3. It involves the use of a flashlamp pulsed dye laser as opposed to the cw krypton ion laser shown in Fig. 1. The use of a pulsed dye laser is important for three reasons: (i) it is compact; (ii) it has high output powers; and (iii) it is tunable from the UV through to the IR spectral region. These attributes

make the flashlamp dye laser uniquely suited for multi-pollutant detection of trace metals and toxic chemicals.

In the proposed experiment, the output of the pulsed dye laser is modulated in frequency as opposed to the previous scheme in which a mechanical chopper was used to modulate the laser light (Fig. 1). In this new scheme the laser frequency is periodically tuned on and off the characteristic absorption frequency of the dissolved pollutant. If the periodicity of the frequency modulations is made one-half of the laser-pulse repetition rate then the background photoacoustic signal due to the unwanted water absorption occurs at frequency 2ω while the photoacoustic signal due to the pollutant absorption occurs at frequency ω . Using a lock-in detector the pollutant signal at ω can then be isolated and the pollutant concentration readily determined.

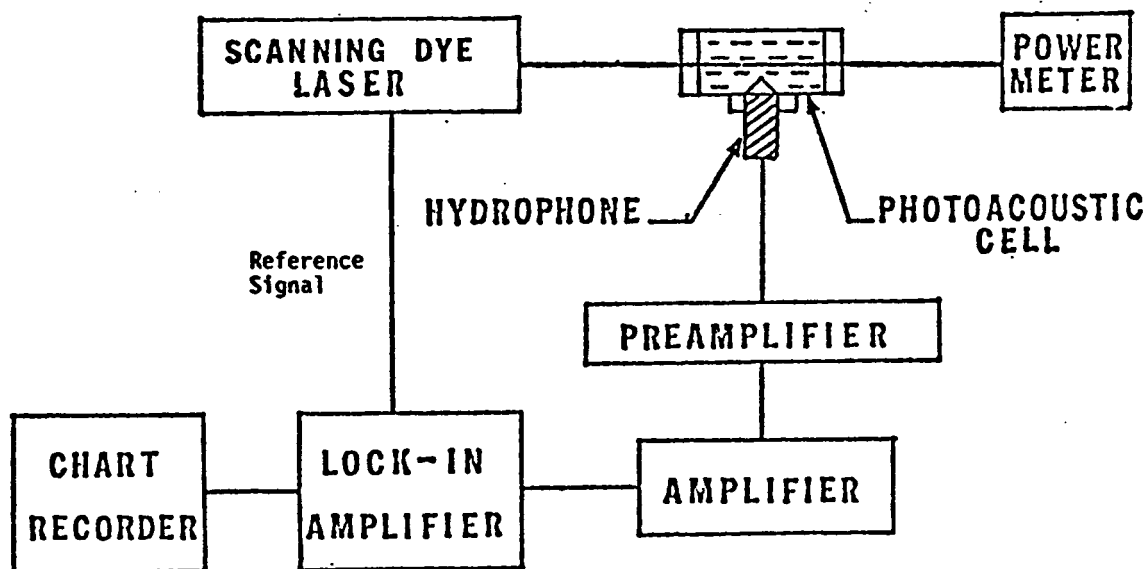


FIG.3 EXPERIMENTAL APPARATUS

Since the frequency of the flashlamp dye laser is tunable over a broad region (210 nm - 900 nm) the proposed technique will allow the detection of many different types of pollutants. For example, heavy metals absorb in the 200-300 nm range, acetone in the 220-330 nm range, benzene in the 250-270 nm range, and formaldehyde with six strong absorption bands in the 326-353 nm range. In addition UV absorption spectra for S^{2-} , $S_2O_3^{2-}$ in water have been reported.²⁰ In particular, absorptions have been studied in S^{2-} at 240 nm, SO_4^{2-} at 210 nm, SO_3^{2-} at 230 nm and $S_2O_3^{2-}$ at 220 nm.

Our experimental procedure to demonstrate the feasibility of the proposed technique to detect trace amounts of pollutants which absorb in the UV or IR spectral regions will be as follows:

- (i) Test the pulsed dye laser-photoacoustic detection technique in the visible spectral region at 530 nm using the pure water and toxic dye pollutant used in our previous studies.
- (ii) Tune the pulsed dye laser a few tens of nanometers in the UV or IR direction and test the technique on a known concentration of a different toxic dye pollutant which absorbs at the new wavelength.
- (iii) Continue to tune the pulsed dye laser in the UV or IR direction a few tens of nanometers at a time and test the technique using known concentrations of different toxic dye pollutants. Dyes are available to provide continuous absorption from 276 nm (p-Terphenyl) to 850 nm (IR-140).

This procedure will systematically demonstrate the ability of the dye laser-photoacoustic non-disturbing technique to detect trace amounts of heavy metals and toxic chemicals which absorb light in the UV and IR spectral regions.

III. RESULTS TO DATE

We have utilized the laser-photoacoustic technique to detect an organic toxic dye pollutant to about one part in 10^{11} or an absorption coefficient of 10^{-4} cm^{-1} . Results are shown in Fig. 4. Improvements on the detection limit can be made using a smaller photoacoustic cell, a resonant cell, or a multiple beam-pass scheme through the cell. Such improvements should lead to a detection limit of one part in 10^{13} or an absorption coefficient of 10^{-6} cm^{-1} .

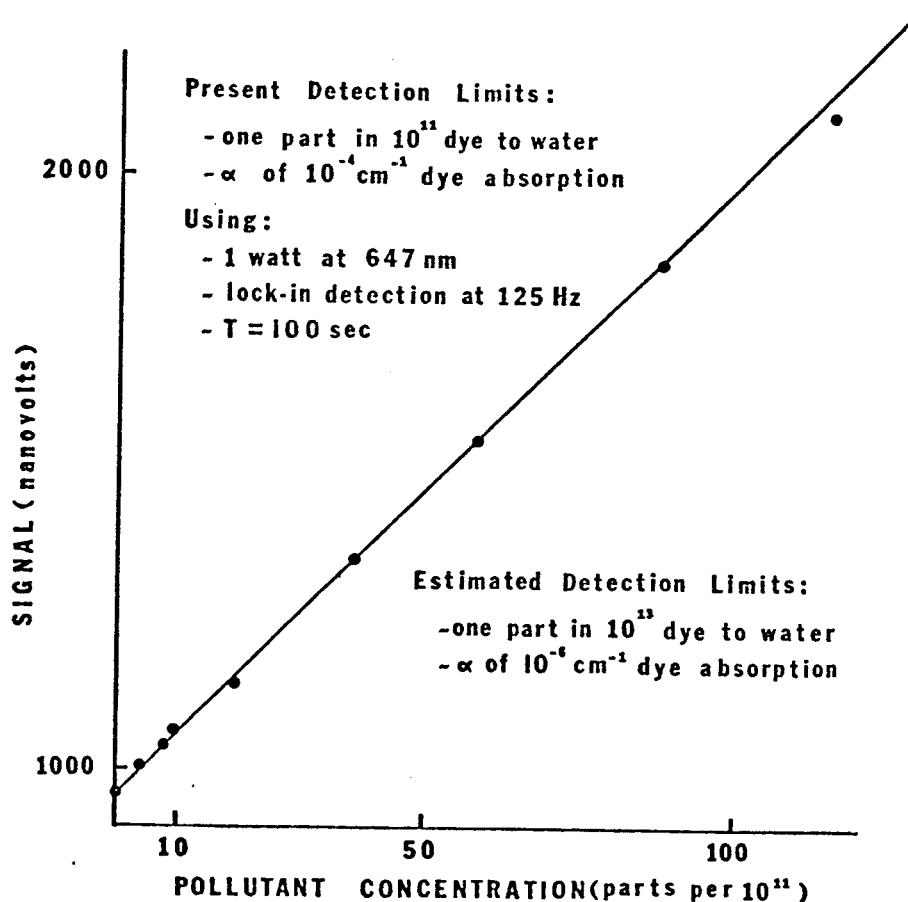


FIG. 4. PHOTOACOUSTIC SIGNAL
VERSUS
DYE CONCENTRATION

In addition to demonstrating the feasibility of the technique to detect low pollutant concentrations we have also investigated in detail the behavior of the photoacoustic signal. In particular, we have determined that the photoacoustic signal is:

1. linear with laser intensity and dye concentration: Since the photoacoustic signal is dependent on the absorbed energy, it is not surprising to find a linear dependence on input laser power or pollutant concentration as long as saturation is not taking place.
2. zero when stopper is removed: In our experiments, the increased pressure in the cell results from the fact that the liquid is not permitted to expand as the liquid temperature increases. Opening the cell to the atmosphere does permit the liquid to expand with increased temperature and therefore keeps the cell pressure at atmospheric pressure.
3. more easily detectable with higher chopping frequency: The noise varies inversely as the square of the chopping frequency while the laser energy per pulse varies as the pulse width or inversely with the chopping frequency. As a result the signal to noise varies linearly with the chopping frequency.
4. independent of the laser beam diameter. Since the optical energy deposited per pulse is independent of the laser beam diameter so is the photoacoustic signal. For this reason, focusing the laser beam into the cell resulted in no change in the photoacoustic signal.
5. inversely proportional to cell volume: This result will be explained later (eq. 11). Physically, the energy deposited into a smaller volume results in a greater pressure increase.

6. proportional to laser pulse width; Since the optical energy deposited varies as the pulse width increases, the increase in pressure in the cell and hence the photoacoustic signal follow suit.
7. linear with coefficient of expansion of the liquid. The greater the expansion per unit energy deposited, the greater the pressure and photoacoustic signal.
8. proportional to the number of laser beam passes. The more passes an optical pulse makes through the sample, the greater the amount of energy deposited per pulse and therefore, the greater the increase in pressure and resulting hydrophone signal.
9. linear with the volume of air bubbles relative to the total volume of the cell. This last point is interesting but requires a long explanation which now follows.

In order to understand the effect of air bubbles on the photoacoustic signal we first examine the case without an air bubble. In this case, the only material which can affect the photoacoustic signal is the water and rubber (o-rings, etc.) parts of the cell. The Bulk Modulus of interest then is

$$\beta_w = \frac{-P_e}{\frac{\Delta V_w}{V_w}} \quad \beta_R = \frac{-P_e}{\frac{\Delta V_R}{V_R}} \quad (5)$$

where P_e is the equilibrium pressure in the cell and ΔV represents the change in volume of the water and rubber that would occur if they were free to expand. The change in temperature in the cell is given by

$$\Delta T = \frac{H}{CV'\rho} \quad (6)$$

where H is the energy absorbed by the water from the laser pulse, C the specific heat of water, ρ the density of water, and V' the laser heated water.

The change in volume of the water that would occur if allowed to expand is given by

$$\frac{\Delta V'}{V'} = \alpha \Delta T \quad (7)$$

where $\Delta V'$ and V' are the change in volume and the total volume of water heated by the laser pulse. Combining these two expressions gives for the expected change in volume:

$$\frac{\Delta V'}{V'} = \alpha \frac{H}{CV'\rho} \quad (8)$$

or

$$\Delta V' = \frac{\alpha H}{C\rho} \quad (9)$$

Since this change in volume must be shared between the water and rubber in the cell we have

$$\Delta V' = P_e \left\{ \frac{V_W}{\beta_W} + \frac{V_R}{\beta_R} \right\} = \frac{\alpha H}{C\rho} = \text{constant} \quad (10)$$

In our experiment $\beta_R \sim \beta_W$ so that

$$P_e \frac{V_T}{\beta} = \frac{\alpha H}{C\rho} = \text{constant} \quad (11)$$

For the case where bubbles are present $\Delta V'$ is shared between the water, rubber, and air. For an adiabatic process $PV^\alpha = \text{constant}$ so that

$$\Delta V_{\text{air}} = \frac{P_e'}{P_e' + P_0} \frac{V_a}{\alpha} = \frac{P_e'}{P_0} \frac{\gamma V_T}{\alpha} \quad (12)$$

where P_0 is atmospheric pressure.

where $\gamma \equiv \frac{V_a}{V_T}$ and α is the ratio of specific heat at constant pressure and constant volume. Using this result we can write

$$\Delta V' = p_{e'} \left\{ \frac{V_T}{\beta} + \frac{\gamma V_T}{\alpha P_0} \right\} = \frac{\alpha H}{C_p} = p_e \frac{V_T}{\beta} \quad (13)$$

or

$$\frac{p_{e'}}{p_e} = \frac{\frac{V_T}{\beta} + \frac{\gamma V_T}{\alpha P_0}}{\frac{V_T}{\beta}} = 1 + \frac{\gamma \beta}{\alpha P_0} \quad (14)$$

and

$$\frac{p_{e'}}{p_e} = \beta_{\text{eff}} \gamma + 1 \quad (15)$$

where β_{eff} is a constant $\beta_{\text{eff}} \equiv \frac{\beta}{\alpha P_0}$ and is the effective Bulk modulus of the cell. The resulting relationship

$$\frac{p_{e'}}{p_e} = \beta_{\text{eff}} \gamma + 1$$

indicates that the photoacoustic signal should decrease linearly with the volume of air bubble. This was observed in our experiments and is shown in Fig. 5. It is interesting to note that the slope of the curve in Fig. 5 can be used to determine the effective Bulk modulus of a photoacoustic cell.

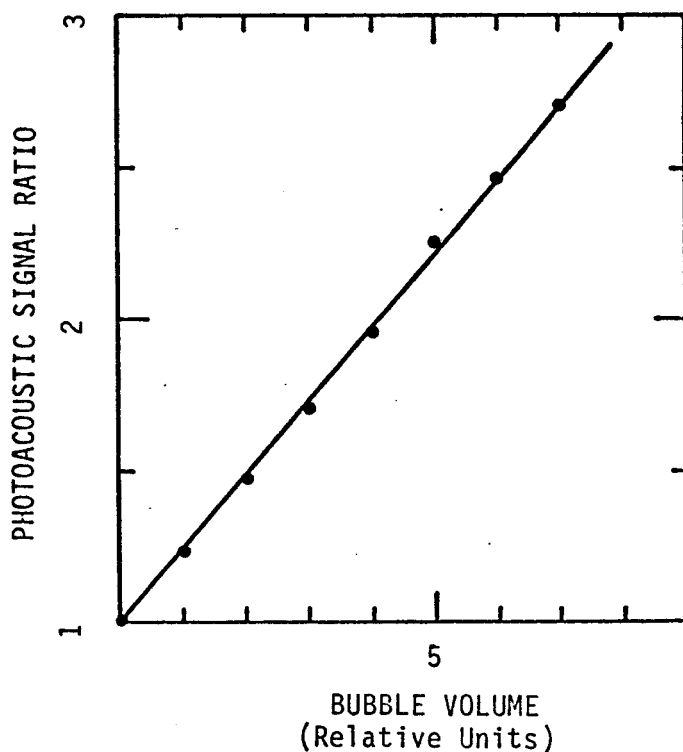


FIG. 5. Ratio of Photoacoustic Signal without Bubbles to Signal with Bubbles

IV. RELATED RESEARCH

The combination of lasers and the photoacoustic effect has been successfully applied to the detection of many types of air pollutants¹²⁻¹⁴. However, to our knowledge, a dye laser-photoacoustic technique for the detection of water pollutants, such as that described in this report, has not been and is not now under study by other researchers.

Recently, laser-photoacoustic schemes, similar to that described in Section III-B, have been applied to the study of liquids.¹⁸ For example, the work by Patel and Tam on optoacoustic Raman-gain spectroscopy of liquids has provided interesting spectra for benzene, acetone, 1, 1, 1-trichloroethane, toluene, and n-hexane.²¹ In all of these studies, however, the emphasis has been on spectroscopic data of pure liquids as opposed to a study of detection of trace amounts of liquid impurities.

While there appear to be no other laser-photoacoustic water pollution detection studies, there do exist other types of laser-based water quality studies. Non-disturbing techniques which monitor sample fluorescence, transmittance, or reflectance are under study at many laboratories.²²⁻²⁷ In addition, new versions of conventional techniques,^{28,29} such as laser enhanced ionization, in which the sample is highly disturbed, are presently under development. While many of these laser-based techniques now under study may one day result in useful detection instrumentation the proposed study does not in any way duplicate these efforts. Rather, the dye laser-photoacoustic technique under study here will compliment these efforts for the following reasons:

- (i) Since the photoacoustic technique is non-disturbing it can be used to characterize the original water system and in this way compliments disturbing techniques.
- (ii) Since the photoacoustic scheme is most sensitive when fluorescence emission is minimal, it can be used to study pollutants whose principal decay mechanisms are non-radiative and in this way compliments fluorescence monitoring detection schemes.
- (iii) Since the photoacoustic scheme is directly proportional to the optical energy absorbed rather than the fractional change in transmitted optical intensity it can be used to detect weak absorbers and in this way compliments transmission monitoring detection schemes.

V. FACULTY AND STUDENT INVOLVEMENT

a. Students

Two graduate students have contributed to the project:

B. Chuang- will receive a Masters Degree for his research on Phase I of the project.

J. Tung - will work on Phase II of the project for his Ph.D. dissertation.

b. Faculty

In addition to Dr. Gregory J. Salamo, who was principal investigator on the Phase I study, an additional faculty member, Dr. Richard J. Anderson, has joined the effort for both the Phase I and Phase II study.

VI. PUBLICATIONS

1. B. Chuang and G. J. Salamo, Refereed paper on "Photoacoustic Detection of Water Pollutants" presented at the Conference on Laser and Electro-Optical Systems (CLEOS), San Diego, California, February 1980.
2. Chuang, Tung, Salamo, and Anderson, "Laser-Photoacoustic Detection of Water Pollutants," to be submitted to the Journal of Applied Physics.

VII. INFORMATION DISSEMINATION

1. Presented a paper on "Photoacoustic Detection of Water Pollutants" at the Conference on Laser and Electro-Optical Systems (CLEOS), San Diego, California (February, 1980).
2. Dr. Salamo visited Dr. Patel at Bell Laboratories to discuss similarities and differences between the work carried out at University of Arkansas and the recent work at Bell Laboratories (June, 1980).

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