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B-068-ARK

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ABSTRACT

LASER-PHOTOACOUSTIC DETECTION OF WATER POLLUTANTS

We have investigated the potential of amplitude-modulation laser-photoacoustic scheme for the detection of trace pollutants in water. The technique has been found to be non-disturbing and easy-to-apply. In particular, the technique could be used to detect pollutants with a concentration corresponding to an absorption coefficient of 10^{-6}cm^{-1}. The sensitivity was found to be limited by a background signal resulting from light absorption by water.

In addition to the amplitude-modulation scheme we also investigated the potential of a wavelength modulation scheme. Although this approach did reduce the background signal due to water absorption, we found the technique to be much more difficult to apply in practice.

Gregory J. Salamo and Richard J. Anderson

Completion Report to the Office of Water Policy, Department of the Interior, Washington, D.C., March, 1984.

KEYWORDS -- Trace Pollutant Detection

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INTRODUCTION

Over the last few years we have carried out an investigation at the University of Arkansas which was designed to investigate the development of a non-disturbing laser-based technique for the detection of trace elements in water. In particular, our effort was divided into two phases.

In Phase I of our study we utilized an argon ion laser and mechanical chopper to investigate the potential of a simple photoacoustic scheme to detect pollutants in water. Using a known dye as a pollutant we determined the sensitivity of the technique to be one dye molecule per 10^{11} water molecules corresponding to a dye absorption coefficient of $10^{-4}cm^{-1}$. Obvious improvements on the apparatus indicates that the sensitivity could easily be improved to one dye molecule per 10^{13} water molecules, or an absorption coefficient of 10^{-6} cm^{-1}. The limiting factor on our sensitivity was the absorption of light due to water which resulted in a background signal that could reach large values in the ultraviolet and infrared spectral regions.

In order to overcome this limitation we proposed and carried out Phase II of our work. In particular, we utilized a dye laser to investigate the potential of a wavelength scanning technique to remove the background water produced signal. Using a known pollutant we determined that the technique did in fact reduce the background signal by at least an order of magnitude. Unfortunately, we also learned that the laser intensity variations resulting from wavelength modulation reduced the pollutant signal level also by nearly one order of magnitude. In fact, the Phase II technique only resulted in a factor of two to three overall improvement over the Phase I technique and was substantially more complicated and not as easy to apply.

In the following sections we give details on each Phase of our study along with corresponding results. These are then followed by some concluding remarks.

I. OBJECTIVES AND SIGNIFICANCE OF THE PROJECT

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 rations, 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 was to investigate the development of a non-disturbing laser based analytic technique for the detection of heavy metals and organic toxic chemicals. In particular, Phase I of this study investigated the feasibility of a laser-photoacoustic technique to detect low concentrations of impurities in water. Our results indicate that the technique is both viable and competitive. That it is viable is indicated by the fact that we have utilized the laser-photoacousitc 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 our Phase I laser-photoacoustic method a intensity 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 did, however, encounter one difficulty. The Phase I technique is 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 has not proved insurmountable.
In particular, in Phase II of our project, we have designed, developed, and tested a modification of our Phase I technique which is based on a novel frequency modulation scheme. Our preliminary results indicate that this "modified" technique allows the troublesome background signal, due to absorption of laser light by water, to be discriminated against. As a result, the laser-photoacoustic technique is now non-disturbing, easy-to-apply, and applicable in all regions of the spectrum. The laser-photoacoustic technique should, therefore, prove to be an attractive candidate for the basis of future studies on the evolution of heavy metal and toxic chemical water pollutants.

II. METHODOLOGY OF THE PROJECT

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 effect[11] 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 when 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 and results in nondestructive detection. Experiments performed by Kreuzer with a continuous wave carbon-dioxide laser indicate that detection limits for optoacoustic 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 non-condensed 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 sample[17] 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.[1,18,19]

B. Phase I Study

We have recently developed a non-disturbing technique[1] 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.[18,19] 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 Phase I detection scheme utilizes a laser-photoacoustic technique illustrated in Figure 1.

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:

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

where D is the thermal diffusivity for water. Since this number is

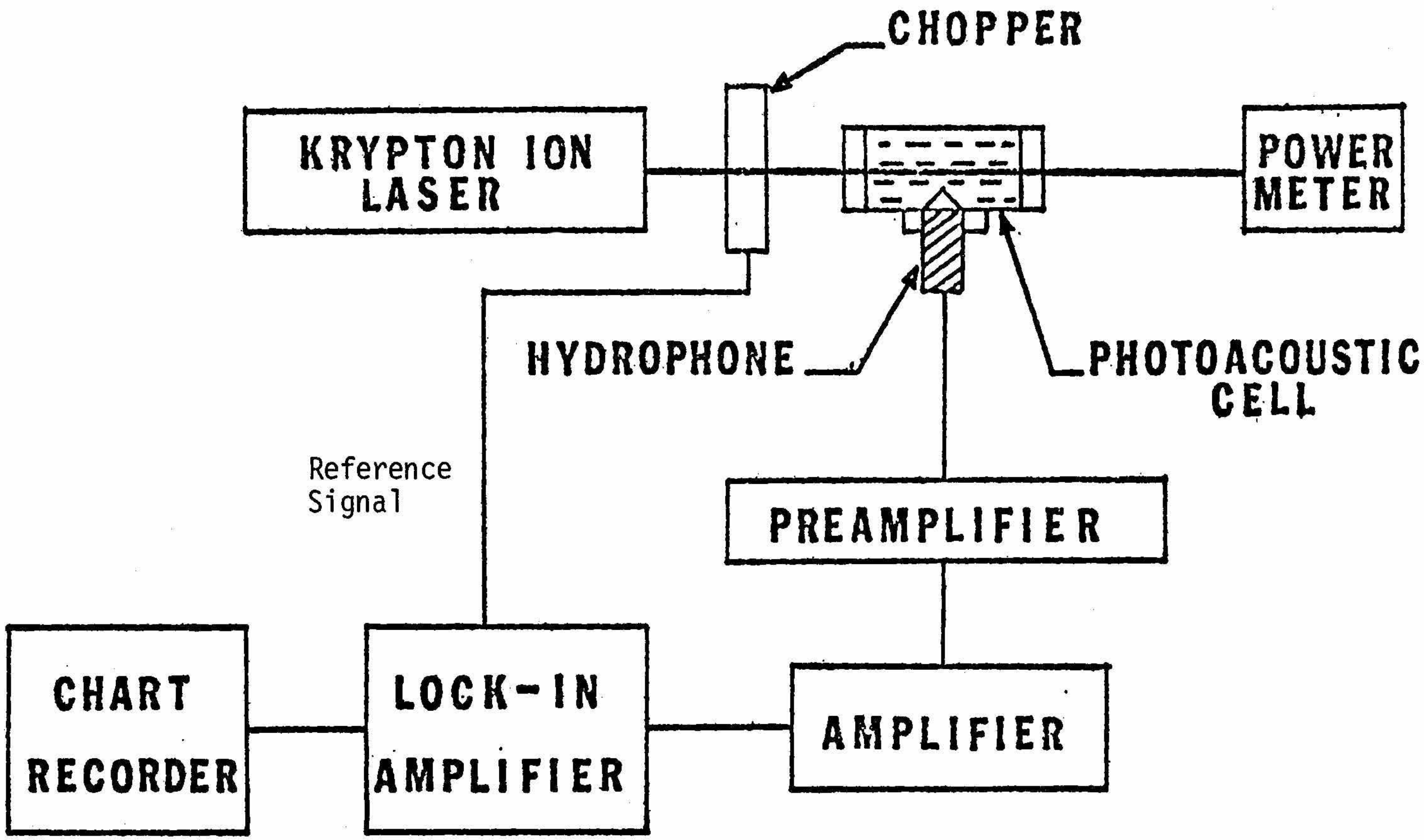

FIG.1 EXPERIMENTAL APPARATUS
PHASE I

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 μs. 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

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

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

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

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 2×10^{-9} 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:

$$\Delta P = \frac{\Delta V/V}{\beta'} \cong +10^{-1}\ \mathrm{N/m^2}\ , \qquad (4)$$

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

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. For example, Tam and Patel[19] have studied the photoacoustic spectrum of pure water using a pulsed dye laser. Their work indicates that the absorption coefficient of pure water at a wavelength of 500 nm is approximately the value of $\alpha = 2 \times 10^{-4}\ \mathrm{cm}^{-1}$. As a result, it is difficult to detect pollutants which absorb at this wavelength when their concentration is comparable to a value resulting in an absorption coefficient of $2 \times 10^{-4}\ \mathrm{cm}^{-1}$. This, in fact, has proved to be the limiting factor in our Phase I 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 using the

Phase I technique of Figure 1. For this reason, we have modified our laser-photoacoustic technique in Phase II of our work.

C. Phase II Study

Our modified technique which will allow the photoacoustic technique to extend to the UV and IR spectral regions is shown in Figure 2. It involves the use of a c.w. dye laser as opposed to the cw krypton ion laser shown in Figure 1. The use of the dye laser is important for three reasons: (i) it is compact; (ii) it has high output powers; and (iii) it is tunable in wavelength or color. These attributes make the dye laser uniquely suited to test our modified scheme for the detection of trace metals and toxic chemicals

In the Phase II work the output of the dye laser was modulated in frequency as opposed to the previous scheme in which a mechanical chopper was used to modulate the laser light (Figure 1). In this new scheme the laser frequency is periodically tuned on and off the characteristic absorption frequency of the dissolved pollutant. In this situation the water has a characteristically slowly changing absorption as a function of wavelength while the pollutant has a characteristically sharply changing absorption. As a result, the absorption of light by the water does not change significantly as the laser wavelength is scanned. Moreover, what little change does occur does so at the scanning frequency "ω". Meanwhile, the absorption of light by the pollutant changes substantially as the laser wavelength is scanned back-and-forth across its resonant

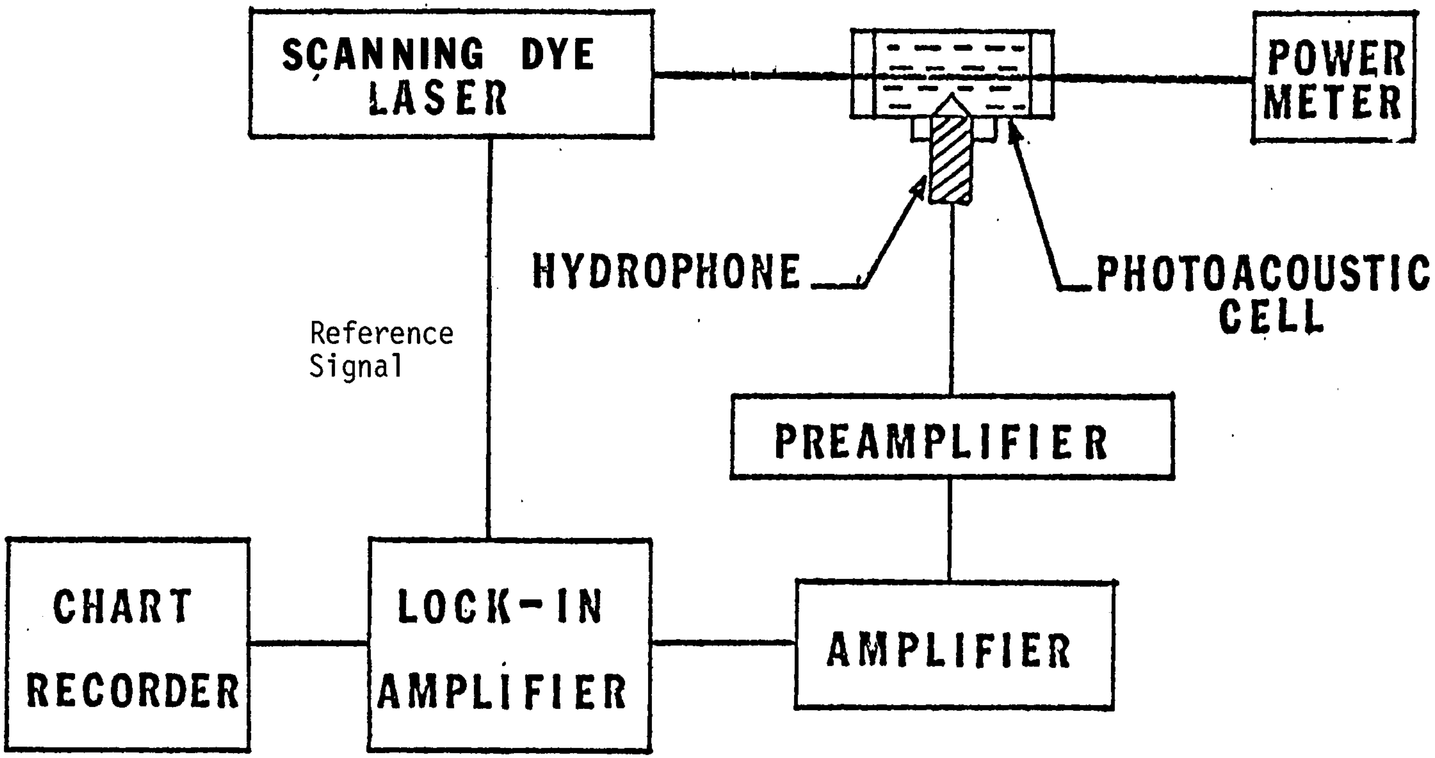

FIG.2 EXPERIMENTAL APPARATUS PHASE II

absorption line. In addition, this signal occurs at "2ω". As a result, the lock-in amplifier can lock in on the signal at "2ω" while it effectively discriminates against the reduced water background signal at "ω". This situation is depicted in Figure 3.

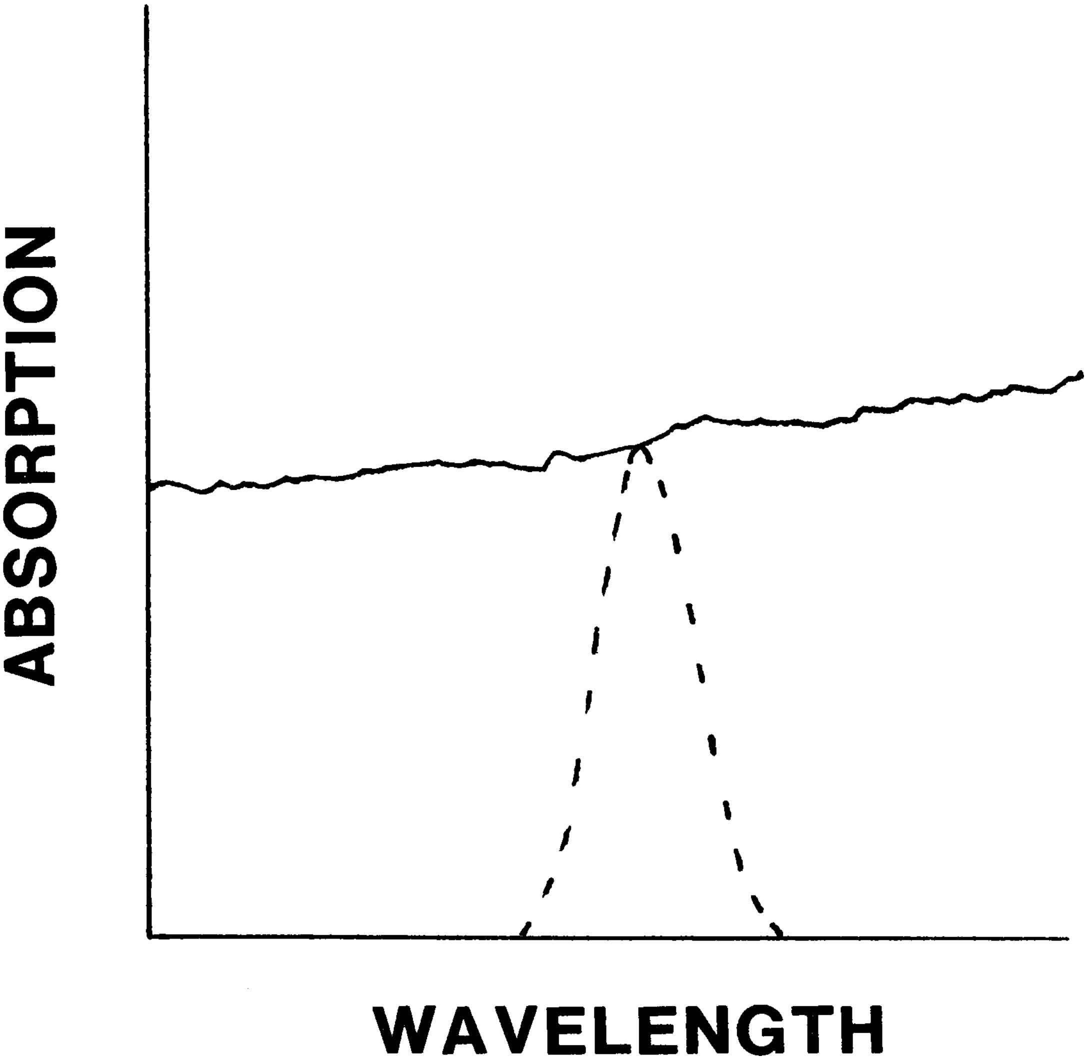

Fig. 3 Wavelength Modulation Technique

In our experiment the dye laser was modulated at about 800HZ. This was accomplished using an electro-optic tuning element in the laser cavity. Our laser typically operated at .5 watts power and was scanned several hundred Anstroms. The dye laser system is shown in Figure 4.

Using this technique we have demonstrated results as good as obtained in our Phase I study. However, the big difference is that this technique is *no longer limited by the spectral region under investigation*. Rather, the sensitivity of our Phase II technique was limited by the apparatus and could be improved in future work.

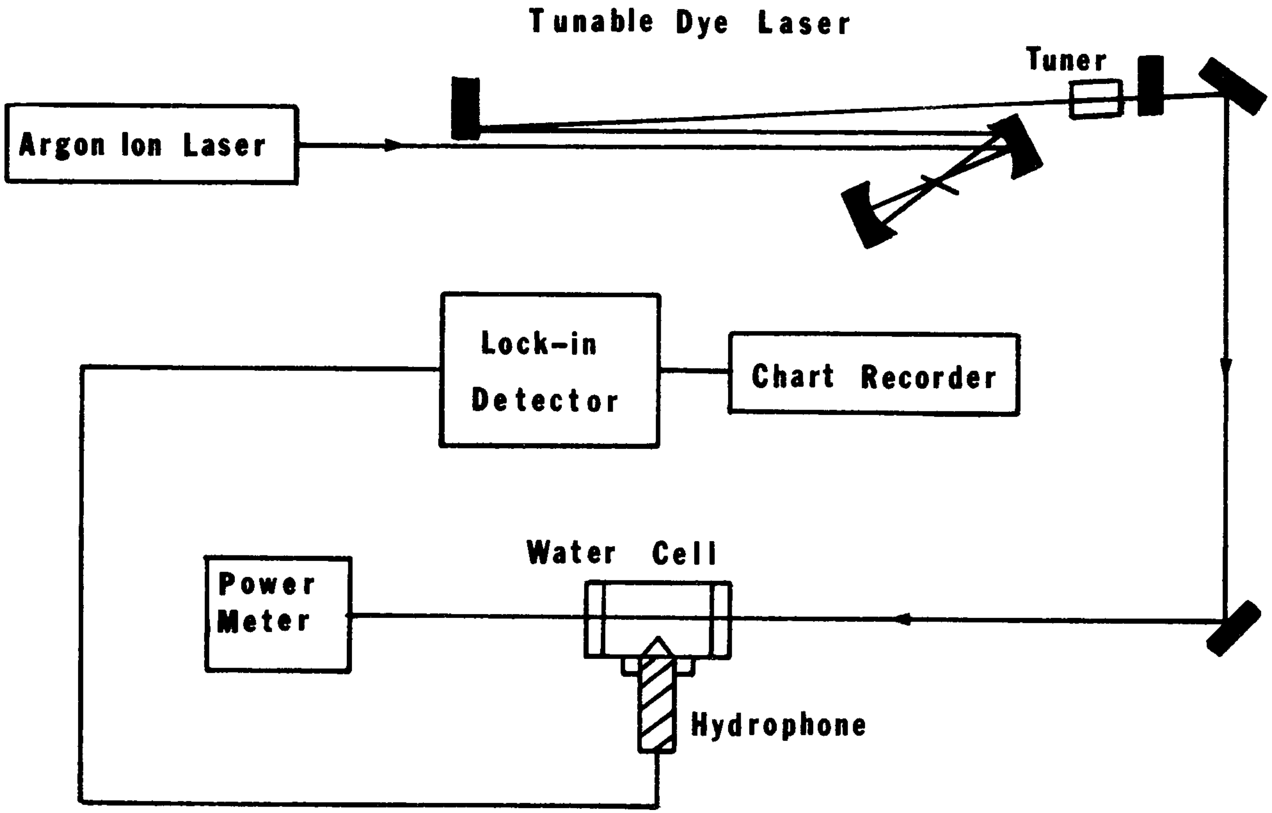

Fig. 4 Krypton-ion pumped dye laser for testing modulating frequency detection concept

III. RESULTS FROM THE PROJECT

A. Phase I Study

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 Figure 5. 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}.

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.

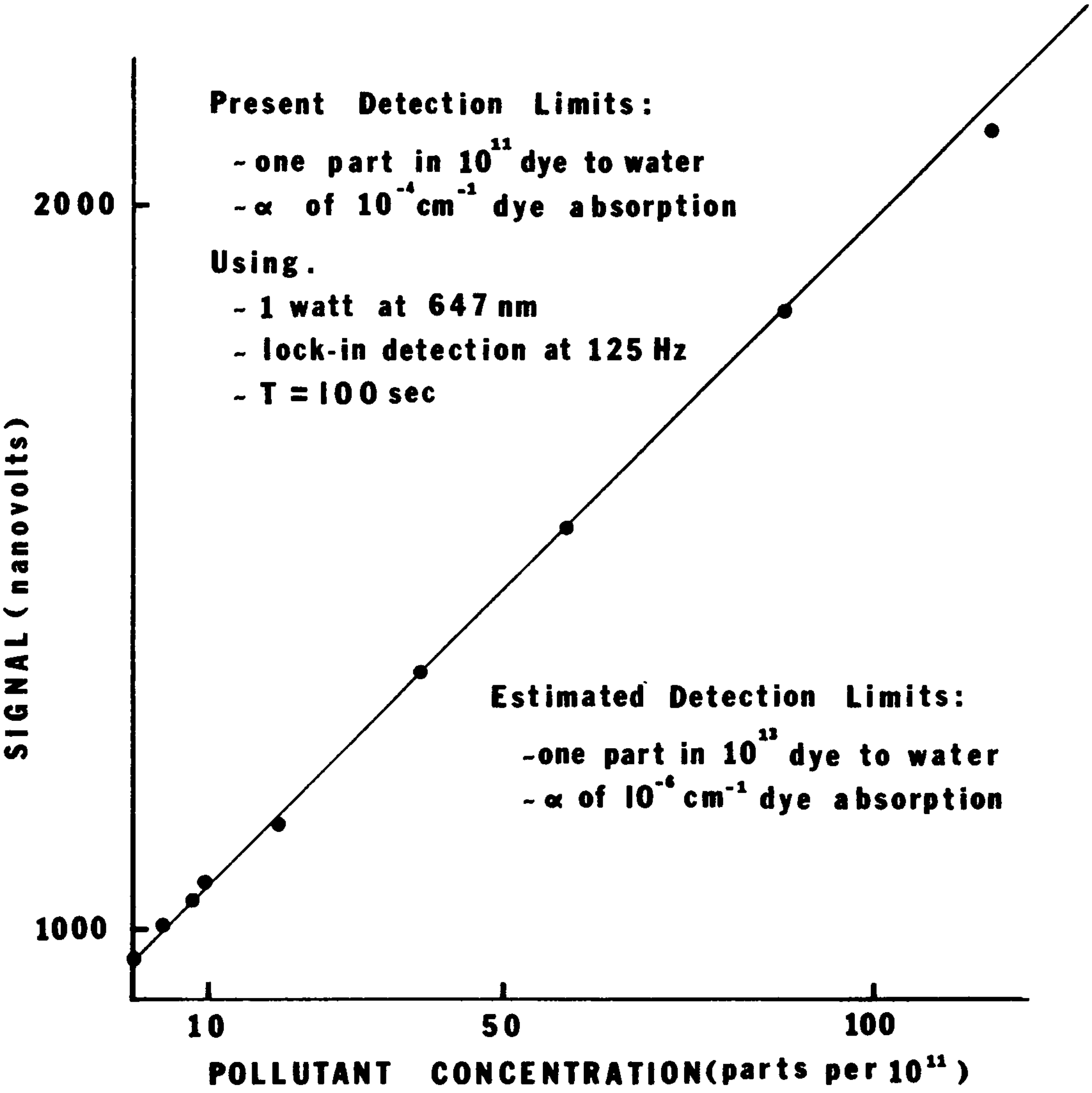

Fig. 5 Results for Phase I

(3) independent of the laser beam diameter. Since the optical energy deposited per pulse is independent of the laser beam diameter so is the phtoacoustic signal. For this reason, focusing the laser beam into the cell resulted in no charge in the photoacoustic signal.

(4) inversely proportional to cell volume: This result will be explained later. Physically, the energy deposited into a smaller volume results in a greater pressure increase.

(5) 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 phtoacoustic signal follow suit.

(6) 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

$$\beta_W = \frac{-P_e}{\frac{\Delta V_W}{V_W}} ; \beta_R = \frac{-P_e}{\frac{\Delta V_R}{V_R}} \qquad (5)$$

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

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

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 volume.

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

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

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:

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

or

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

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

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

in our experiment $\beta_R \propto \beta_W$ so that

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

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

$$\Delta V_{air} \simeq \frac{P_e'}{P_o} \frac{V_a}{\alpha} \simeq \frac{P_e'}{P_o} \frac{\gamma V_T}{\alpha} \qquad (12)$$

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

$$\Delta V' = P_e' \left[\frac{V_T}{\beta} + \frac{\gamma V_T}{\alpha P_o} \right] = \frac{\alpha H}{C_p} = P_e \frac{V_T}{\beta} \tag{13}$$

or

$$\frac{P_e}{P_e'} = \frac{\frac{V_T}{\beta} + \frac{\gamma V_T}{\alpha P_o}}{\frac{V_T}{\beta}} = 1 + \frac{\gamma\beta}{\alpha P_o} \tag{14}$$

and

$$\frac{P_e}{P_e'} = \beta_{eff}\, \gamma + 1 \tag{15}$$

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

$$\frac{P_e}{P_e'} = \beta_{eff}\, \gamma + 1$$

indicates that the photoacoustic signal should decrease linearly with the volume of air bubble. This was observed in our experiments and is shown in Figure 6. It is interesting to note that the slope of the curve in Figure 6 can be used to determine the effective Bulk modulus of a photoacoustic cell.

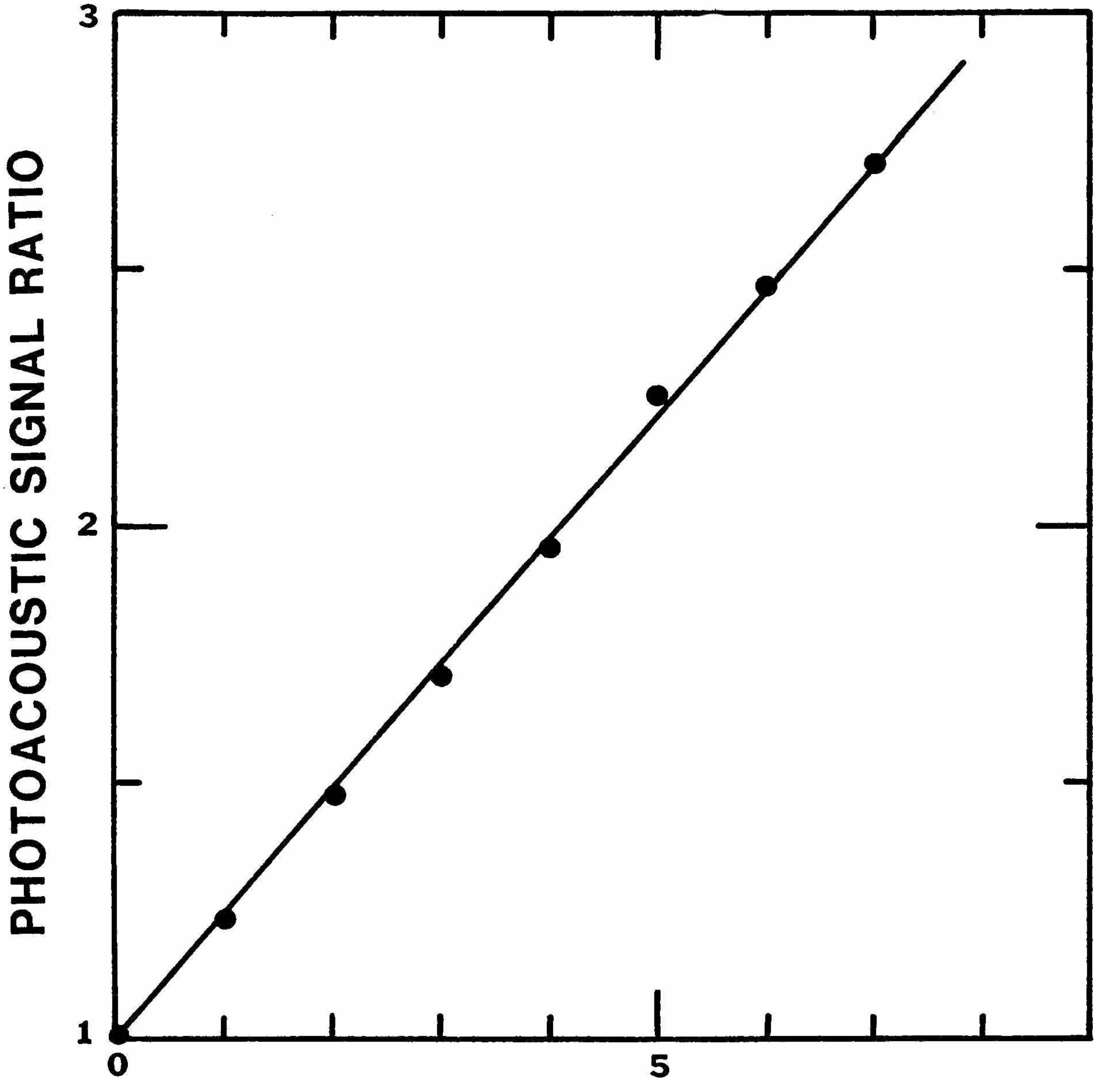

FIG. 6 EFFECT OF BUBBLES ON SIGNAL

B. PHASE II STUDY

In our wavelength modulation technique, the laser wavelength can be modulated on either side of the pollutant absorption resonance or back-and-forth across the absorption peak. If the modulation is on the side of the line then the effective intensity change as seen by the absorber was typically about 10% in our experiments. This small change was a result of allowing only a small ($\sim 50 A^{o}$) change in wavelength. Any larger change produced too large a variation in output power of the laser. As a result of this limitation we were unable to improve upon our results from Phase I. In particular, we found that we were able to reduce the background water signal by a factor of ten but also found that our restriction on the wavelength scan also resulted in a factor of ten lower pollutant signal.

Having run into this difficulty we tried our modulation scheme by varying the laser wavelength back-and-forth across the absorption peak. This technique resulted in a pollutant acoustic signal at twice the modulation frequency. Once again, however, the frequency or wavelength variation which was allowed was limited by the laser power variations which were also produced. In particular, the laser output power peaks at some wavelength much like the absorption line. As a result, too great a variation in wavelength produced output power variations also at twice the scanning frequency. This difficulty limited our preliminary results to an improvement in detection sensitivity to a factor of 2 to 3 with our apparatus. However, in principle we have demonstrated that the background signal can be greatly reduced using the wavelength scanning scheme. It would appear that the technique holds promise for detecting specific pollutants while it would take a very complicated laser system to handle more than one at a time.

In summary, we have learned several important aspects to the Phase II technique

(1) Off-resonance frequency modulation is limited by the fact that the true laser intensity becomes modulated and results in a background water signal. It would be possible, however, to design improvements into this approach, such as, (i) using a specially designed filter which would hold the laser intensity constant as the frequency is scanned, or by (ii) using a normalizing system which divides the lock-in signal by a signal which follows the laser output intensity.

(2) On-resonance frequency modulation is also limited by the laser light true intensity variations as a function of wavelength scanned. In particular, if the laser gain curve overlaps too closely to the pollutant absorption curve then there will result a background water signal at 2ω, twice the modulation frequency.

(3) In attempting to look for a signal at 2ω we were constantly plagued with pick-up noise at "2ω". In many ways this pick-up noise causes difficulties which are similar to acoustic pick-up problems associated with the mechanical

chopper used in Phase I. However, this difficulty should be possible to eliminate with reasonable effort.

APPENDIX I. Improved Cell Model - Phase I

When the laser beam passes through the water sample, part of the energy absorbed by the water is converted into heat. We can write, therefore,

$$dT = \frac{dH}{C_1 V_l \rho_1}$$

$$dV = V_l \, \beta_1 \, dT = \frac{\beta_1 \, dH}{C_1 \, \rho_1} \qquad (1)$$

$$dp = \frac{1}{K} \, \frac{dV}{V} = \frac{\beta_1 \, dH}{C_1 \rho_1 K V}$$

where β_1, C_1, ρ_1, are the thermal expansion, heat capacity, and density coefficients for water while K is the Bulk Modulus and V the sample volume of water. In these expressions V_l is the laser irradiated volume.

If we assume no energy loss through the interface of the aluminum cell and the water sample, we can write

$$dH = \left[P(t)dt \right] \alpha \, \ell \, \gamma$$

$$\equiv cP\,(t)\,dt \qquad (2)$$

where P(t) is the laser power, α the water absorption coefficient, ℓ the cell length and γ the fraction of absorbed energy which goes into heat.

At the end of the first half period of the chopped laser beam the pressure increment in the cell will be

$$\Delta p = \int_0^{T/2} dp$$

$$= \frac{\beta_1}{C_1 \rho_1 K V} \int_0^{T/2} dH$$

$$= \frac{\beta_1 C}{C_1 \rho_1 KV} \int_0^{T/2} P(t)dt$$

$$= \frac{\beta_1 C}{C_1 \rho_1 KV} \quad \frac{PT}{2}$$

If we relax our approximation of zero energy loss through the water-Aℓ-air interfaces we would write

$$dH_1 \;=\; cPdt - A_1H_1dt + A_2\,H_2dt - B_1H_1dt \qquad (4)$$

where the first term is the gain from the incoming light beam; the second term the loss due to transfer of energy from water to Aℓ, the third term is gain due to energy returned from the Aℓ to water while the last term is added to represent attenuation losses.

In a similar way we can write for the energy in the Aℓ

$$dH_2 = A_1H_1dt - A_2H_2dt - B_2H_2dt - A_3H_2dt \qquad (5)$$

where B_2 represents the attenuation in Aℓ while A_3 represents the energy loss to air. In fact, the attenuation losses are much smaller than the other terms in (4) and (5) so that we can write:

$$d(H_1 + H_2) \cong cP\,(t)dt - A_3H_2dt \qquad (6)$$

From a comparison between (2) and (6) we see that we now have a second order equation. To simplify further we solve equation (6) neglecting the A_3 term and get

$$H_1 + H_2 = CPt \qquad (7)$$

or

$$H_2 = CPt - H_1 \qquad (8)$$

If we now substitute back into (4) we get,

$$dH_1 \;=\; CPdt - A_1\,H_1\,dt + A_2(CPt - H_1)\;dt$$

This expression can be integrated to give:

$$H_1 = \int_0^t dH_1 = \frac{A_1CP}{(A_1+A_2)^2} \left(1 - e^{-(A_1+A_2)+} \right) + \frac{A_2\ CPt}{A_1+A_2} \tag{9}$$

while

$$H_2 = \int_0^t dH_2 = \frac{A_1CP}{(A_1+A_2)^2} \left(1 - e^{-(A_1+A_2)t}\right) + \frac{A_1CPt}{A_1+A_2} \tag{10}$$

using this expression

$$H_1\ ({}^{T}/2) \simeq \frac{A_2}{A_1+A_2} \quad CPT/2 \tag{11}$$

and using equation (3)

$$\Delta P = \frac{\beta C}{C_1\rho_1\ KV} \left[\frac{A_2}{A_1 + A_2} \right] \frac{CPT}{2} \tag{12}$$

As a result we can compare

$$\frac{(\Delta P)_{1\text{st order}}}{(\Delta P)_{\text{no losses}}} = \frac{A_2}{A_1+A_2} \simeq .588 \tag{13}$$

In this estimate we have neglected A_3H_2 in equation (6) and have, therefore, overestimated H_1 and ΔP. We can, therefore, think of equation (13) as an <u>upper limit</u> answer. If we now use the second term in equation (10) for H_2 and substitute back into (6) we get

$$d\ (H_1+H_2) = CPdt - A_3 \left[\frac{A_1CPt}{A_1+A_2}\right] dt$$

or

$$H_2 = CPt - \frac{A_1A_3CPt^2}{2\ (A_1+A_2)} - H_1 \tag{14}$$

substituting (14) into (4) as before, we now get

$$H_1 = \frac{A_1 CP}{(A_1+A_2)^2}\left[1 - \frac{A_2A_3}{(A_1+A_2)^2}\right]\left[1 - e^{-(A_1+A_2)t}\right]$$

$$+ \frac{A_2 CPt}{A_1+A_2}\left[1 + \frac{A_1A_3}{(A_1+A_2)^2} - \frac{A_1A_3t}{2(A_1+A_2)}\right] \qquad (15)$$

which therefore gives when $t = T/_2$,

$$H_1(T/_2) \approx \frac{A_2}{A_1+A_2}\left[CP^T/_2\right]\left[1 - \frac{A_1A_3}{2(A_1+A_2)}\ \frac{T}{2}\right]$$

$$\approx .4045 \quad CP\ \frac{T}{2} \qquad (16)$$

this therefore gives us a ratio

$$\frac{\Delta p \text{ 2nd}}{\Delta p \text{ no loss}} \approx .4045 \qquad (17)$$

However, neglecting the first term in (10) makes this result an underestimate. Perhaps the best value to choose without very much more mathematics is

$$\frac{(\Delta p) \text{ ave}}{(\Delta p) \text{ no loss}} \approx \frac{.4045 + .5880}{2} = .496 \qquad (18)$$

$$\approx .5$$

This result indicates that we should expect only 50% of our earlier estimated signal value! In fact, this answer proves to be relatively insensitive to the physical parameters of our cell. Using the same analysis one can also show that the change in energy H_1 during the second half of the laser pulse is also about $\frac{1}{2}\ \frac{CPT}{2}$ giving a total change in cell energy of $\frac{CPT}{2}$ as expected. That is, the physical picture is that the pressure in the cell increases to a value where to net energy loss from the cell is equal to the energy added to it. Some of the energy loss is due to "heating" of the cell material while the remainder is lost to the air surrounding the cell.

APPENDIX II. Frequency Modulation Model - Phase II

For our sample we can write the change in temperature as

$$dT = \frac{dH}{CV_L\rho}$$

the change in volume as

$$dV = V_L \beta \, dT$$

and the change in pressure as

$$dP_{gain} = \frac{1}{K} \frac{dV}{dV}$$

$$= \frac{\beta dH}{C\rho KV} = C_H dH \qquad (1)$$

Meanwhile, the pressure loss is given as

$$dP_{loss} = L(t)\,dt$$

so that the total pressure change is

$$dP = C_H dH - L(t)\,dt \qquad (2)$$

Since,

$$\gamma P_A(t) = P_o(t)\,\ell\,[\gamma_d\alpha_d + \gamma_w\alpha_w] \qquad (3)$$

and

$$dH = \gamma P_A(t)\,dt \qquad (4)$$

where P_O is the incident power, P_A the absorbed power, and γ the fraction of energy absorbed which is converted into heat.

Therefore,

$$dP = C_H \gamma P_A(t)\,dt - L(t)\,dt$$

and the pressure variation in the sample is

$$\Delta P\ (t) = C_H \int \gamma\ P_A\ (t)\ dt - \int L\ (t)\ dt \tag{5}$$

The first term on the right can be expanded in a Fourier Series with the constant term cancelling the second term on the right assuming L (t) to be nearly constant. As a result ΔP (t), or the change in sample pressure as a function of time consists of the Fourier components of

$$C_H \int \gamma P_A\ (t)\ \ dt$$

Case 1 : Mechanical Chopper

In this case we have:

$$\begin{aligned} P_o\ (t) &= P_o \qquad \text{for} \quad o < \omega t < \Pi \\ &= o \qquad \text{otherwise} \end{aligned}$$

A Fourier expansion of P_o (t) gives:

$$P_o\ (t) = P_o \quad \left[\frac{1}{2} + \sum_{n=\text{odd}} \frac{2}{n\Pi} \ \sin nwt \right]$$

Therefore,

$$\Delta P\ (t) = C_H \int (\gamma_d\alpha_d + \gamma_w\alpha_w)\ \ell P_o\ \left[\frac{1}{2} + \sum_n \frac{2}{n\Pi}\ \sin wt\right] dt - \int L dt$$

letting the constant terms cancel

$$\Delta P(t) = C_H\ (\gamma_d\alpha_d + \gamma_w\alpha_w)\ \ell P_o \int \sum_n \frac{2}{n\Pi} \quad \sin nwt$$

$$= -C_H\ (\gamma_d\alpha_d + \gamma_w\alpha_w)\ \ell P_o\ \sum_n \frac{2}{n^2\Pi w} \qquad \cos nwt$$

From this expansion we see that the amplitude

at ω is $\dfrac{2\ C_H\ (\gamma_d\alpha_d + \gamma_w\alpha_w)\ \ell P_o}{\Pi\,\omega}$

at 2ω is $\quad 0$

at 3ω is

$$\frac{2\, C_H\, (\gamma_d\alpha_d + \gamma_w\alpha_w)\ \ell P_o}{4\,\pi\,\omega}$$

at 4ω is

$$0$$

Case 2 Using Electronic Turning Fork Chopper

in this case

$$P_o\,(t) = P_o\ \left|\sin \frac{\omega t}{2}\right|$$

$$= \frac{2}{\pi} - \frac{4}{\pi}\sum_n \frac{\cos \frac{n\omega t}{2}}{n^2-1}$$

with n even.

Therefore, we have

$$\Delta P\,(t) = -C_H(\gamma_w\alpha_w + \gamma_d\alpha_d)\ \ell P_o \int \frac{4}{\pi}\sum_n \frac{\cos \frac{n\omega t}{2}}{n^2-1}\ dt$$

$$= \frac{4}{\pi}\, C_H\ (\gamma_w\alpha_w + \gamma_d\alpha_d)\ \ell P_o \sum_n \frac{\sin \frac{n\omega t}{2}}{n\,(n^2-1)\ \frac{\omega}{2}}$$

from this expression we see that the amplitude

at ω is $\dfrac{4\, C_H\, (\gamma_w\alpha_w + \gamma_d\alpha_d)\ \ell P_o}{3\pi\,\omega}\ \sin \omega t$

at 2ω is $\dfrac{2\, C_H\, (\gamma_w\alpha_w + \gamma_d\alpha_d)\ P_o\ell}{15\,\pi\,\omega}\ \sin 2\omega t$

Case 3 Wavelength Modulation

In this case we treat P_o as a constant but

$$\alpha_d = \alpha_{do} - \alpha_{dm}\ |\sin \omega t|$$

$$\alpha_w = \alpha_{wo} - \alpha_{wm}\ \sin \omega t$$

Therefore,

$$\gamma P_A = P_o \ (\gamma_d \alpha_d + \gamma_w \alpha_w) \ \ell$$

$$= \ell P_o \ [\ (\gamma_d \alpha_{do} + \gamma_w \alpha_{wo}) - \gamma_d \alpha_{dm} \ |\sin \omega t| + \gamma_w \alpha_{wm} \ \sin \omega t]$$

$$= \ell P_o \ [\ (\gamma_d \alpha_{do} + \gamma_w \alpha_{wo}) - \gamma_d \alpha_{dm} \ \left(\frac{2}{\pi} - \frac{4}{\pi} \sum_n \frac{\cos n\omega t}{n^2 \quad 1}\right)$$

$$+ \ (\gamma_w \alpha_{wm} \ \sin \omega t) \ ]$$

with n even.

$$\gamma P_A = \ell P_o \ [\ (\gamma_d \alpha_{do} + \gamma_w \alpha_{wo} - \frac{2\gamma_d \alpha_{dm})}{\pi} + \frac{4\gamma_d \alpha_{dm}}{\pi} \sum_n \frac{\cos n\omega t}{n^2 - 1}$$

$$+ \ \gamma_w \alpha_{wm} \ \sin \omega t \ ]$$

therefore,

$$\Delta P \ (t) = C_H \ \ell P_o \ [\ \frac{4\gamma_d \alpha_{dm}}{\pi} \sum_n \frac{\cos n\omega t}{n^2 - 1} \ dt + \gamma_w \alpha_{wm} \ \sin \omega t \ dt]$$

$$= C_H \ \ell P_o \ [\ \frac{4\gamma_d \alpha_{dm}}{\pi \ \omega} \sum_n \frac{\sin n\omega t}{n(n^2-1)} - \frac{\gamma_w \alpha_{wm}}{\omega} \ \cos \omega t \ ]$$

As a result the detected signal at

ω is $\dfrac{C_H \ell P_o \ \gamma_m \alpha_{wm}}{\omega}$ $\cos \omega t$ (due to water)

while at

2ω is $\dfrac{2\gamma_d \alpha_{dm}}{3 \ \pi} \dfrac{C_H \ell P_o}{\omega}$ $\sin 2 \ \omega t$ (due to dye)

Unfortunately, this result does not hold in practice if the laser power goes as

$$P_o \ (\lambda) = P_o - P_m \ |\sin \omega t|$$

In this case a signal at 2ω due to variation in the water absorption is also produced. In particular,

$$\gamma P_A \ (t) = \ell P_o \ [\ 1 - \gamma_m \ |\sin \omega t|\ ] \ (*)$$

$$(*) \ [\gamma_d \alpha_{do} \ + \ \gamma_w \alpha_{wo}) \ - \ \gamma_d \alpha_{dm} \ |\sin \omega t| \ + \ \gamma_w \alpha_{wm} \ \ \sin \omega t \ ]$$

$$= \ \ell P_o \ [\ (\gamma_d \alpha_{do} + \gamma_w \alpha_{wo}) \ - \ \gamma_d \alpha_{dm} \ |\sin \omega t| \ + \ \gamma_w \alpha_{wm} \ \sin \omega t \ ]$$

$$- \ \ell P_o \ \gamma_m \ |\sin \omega t| \ \ [\ (\gamma_d \alpha_{do} + \gamma_w \alpha_{wo}) \ - \ \gamma_d \alpha_{dm} \ |\sin \omega t| \ + \ \alpha_w \gamma_w \ \ \sin \omega t]$$

As a result we have the following correction terms:

	Original Term at	Correction Term
ω	$\dfrac{-C_H \ \ell P_o \ \gamma_w \alpha_{wm} \ \cos \ \omega t}{\omega}$	$\dfrac{8C_H \ \ell P_o \gamma_m \ \gamma_w \alpha_{wm}}{3\pi \ \ \omega} \ \cos \omega t$
2ω	$\dfrac{2}{3\pi\omega} \ C_H \ \ell P_o \ \gamma_d \alpha_{dm} \ \sin 2\omega t$	$\dfrac{2}{3\pi\omega} \ C_H \ell P_o \gamma_m \ (\gamma_d \alpha_{do} + \gamma_w \alpha_{wo}) \ \sin 2\omega t$ $- \ \dfrac{1}{4\omega} \ C_H \ell P_o \gamma_m \gamma_d \alpha_{dm} \ \ \sin 2\omega t$

CONCLUSIONS:

We have investigated the potential of a laser-photoacoustic technique for the detection of trace pollutants in water. In particular our efforts have been divided into two phases.

In Phase I of our study we have utilized an intensity modulated laser-photoacoustic scheme to detect a known molecular dye pollutant in a water sample. This technique has resulted in the detection of one dye molecule per 10^{11} water molecules corresponding to a dye concentration of $10^{-4}cm^{-1}$. Simple improvements on the apparatus indicates that the sensitivity could easily be improved to one dye molecule per 10^{13} water molecules, or a dye absorption coefficient of $10^{-6}cm^{-1}$. In addition, we have found the technique easy to apply and non-disturbing. Moreover, the sensitivity which we report is totally consistent with the work of other researchers and with similar investigations carried out by our own group on combustion studies[22].

In Phase II of our study we utilized a scanning wavelength technique to remove what has proved to be an annoying and limiting water produced background signal. Although this technique has proved to be considerably more difficult to apply than our Phase I approach, we were able to reduce, by at least one order of magnitude, the water produced background signal. Because of the difficulties in application, however, we believe that this wavelength modulation scheme is more suitable to detection of specific pollutants as opposed to the more general detection of composite pollutants in water.

In conclusion, therefore, we believe that both techniques which we have investigated show significant potential for development into instrumentation for the detection of trace pollutants in water and further studies along this direction are highly recommended.

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