Quantitative Analysis of Formaldehyde by Use of the Thermal Lens Effect

Jan Alan Alfheim

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Abstract

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The possibility of using the sensitive thermal lens technique to measure gaseous formaldehyde in air has been investigated. The NIOSH chromotropic acid method of analysis for formaldehyde was modified to accomodate the thermal lens technique. The enhancement factor versus regular absorption techniques was determined to be 7.5 and 14 for the single and dual laser systems respectively. With these enhancement factors, the sensitivity of the chromotropic acid method has been increased to the point where it has been shown to be capable of detecting ppb concentrations of formaldehyde in air in sample volumes of approximately fifteen liters.

Acknowledgements

I wish to express my sincere gratitude to Dr. C.H. Langford for his guidance and undying patience throughout the course of this work. His dedication will always be appreciated.

I am also grateful to Mr. P. Cahill whose expertise and talented glass blowing was essential in the completion of this project, and to Mr. C. Arbour whose assistance in the programing of the fft data fitting was greatly valued.

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Part 1 INTRODUCTION

Part 1A: The Problem with Formaldehyde

Formaldehyde although omnipresent in the environment has been a controversial chemical, especially in the last few years, and emotionalism and controversy surround discussions of every aspect of this chemical. Unlike most carcinogens,or suspected carinogens, identified in animal cancer tests, formaldehyde is also a normal metabolite in human biochemistry. It can be found in ambient air even in remote areas, as well as in a large variety of consumer products such as permenant press fabrics, carpeting, and cosmetics. Cigerette smoke is known to contain up to forty ppm of formaldehyde.. The largest sources of formaldehyde to the nonsmoking general public are particle board, plywood, and urea formaldehyde foam insulation. When new, these materials emit large amounts of formaldehyde and can cause indoor air to have relatively high concentrations.

In the gaseous form, formaldehyde presents two major possible health hazards to humans. The first hazard which is known to exist is that it has an irritating and sensitizing effect. Sensory irritation of the eyes, nose and throat is the primary response. Irritation has been noted at levels as low as 0.25 ppm in chamber studies and at levels of 1 ppm in normal conditions. Accute symptoms such as coughing, diarrehea, nausea, vomiting, dizziness, and lethargy have been reported after prolonged exposure at

home or at work (1).

However these effects pale in comparison to the second hazard that is believed to exist in conjunction with exposure to formaldehyde. The question of formaldehyde's carcingenicity is quite disputed as can be observed by the numerous publications and rulings as to it's use (2,3).

Even large organizations such as EPA have shown their uncertainty over the potential danger by first deciding not to list formaldehyde as a priority chemical for regulatory assessment in February 1982 and then changing that decision in May of 1984.

It is agreed that formaldehyde induces nasal cancer in rats. Two independent studies showed that an exposure level of 14 ppm induced a fifty percent incedence of precancerous growths in the study groups. The dispute as to formaldehyde's carcingenicity lies in whether the human body is capable of metabolizing formaldehyde introduced externally. Further arguements exist as to the actual level at which formaldehyde becomes dangerous.

Some scientists believe that a human threshold for the chemical would have to be greater than the level of exposure provided naturally by the body itself. 3 to 12 nanograms per gram of tissue is the normal endogenous tissue level of formaldehyde produced by metabolism. About ten to forty percent of this exists as free formaldehyde. Others argue that our bodies are not necessarily capable of handling formaldehyde at levels above that manufactured by

the body. Nicholas A. Ashford and his collegues are among those in the latter group. In a letter to Science Magazine May 11, 1984, Ashford wrote explaining that some fraction of formaldehyde entering the body will reach the brain and react with the DNA. His arguements state that there is a finite concentration of enzyme molecules that can metabolize formaldehyde and a finite series of membranes providing barriers to diffusion. Subsequently the limited number of DNA repair enzymes may not be able to repair all the DNA lesions before the next cell replication. Even without exposure to external formaldehyde, that which is formed in the body could also effect the same damage, so that natural levels of formaldehyde do not necessarily constitute a harmless level and small increments above the natural level cause "additional biological cost and risk".

There are also those who believe that formaldehyde can react only at the site of contact. Mechanistic studies suggest that it may be nearly impossible for formaldehyde to reach the brain or the blood since it is metabolized quickly to formic acid which is broken down into carbon dioxide and water(4). Again there is a group that are of the opinion that even if a large proportion is metabolized a small fraction may escape metabolism and bind covalently to DNA in the brain as aforementioned.

With such arguements existing it is easy to understand why EPA although having prepared a quantitative risk assessment has not given a definite cutoff point above which

risk is always considered unacceptable. Since there is such uncertainty existing as to the danger of exposure to formaldehyde it is of paramount importance that methods exist to measure even minute levels of formaldehyde in the environment.

Part 1B: Formaldehyde Detection Methodology

Present methods for formaldehyde analysis are numerous and include titrimetric, spectrophotometric, fluorescence, polarographic, G.C., and H.P.L.C.. Titrimetric methods are useful in the case of high formaldehyde concentrations in solution. Sodium sulfite is used in three of the most common techniques employed. The sulfite method is based on the quantitative liberation of sodium hydroxide when formaldehyde reacts with sodium sulfite to form the formaldehyde bisulfite addition product.

$$HCHO_{(aq)} + Na_2SO_3 + H_2O \longrightarrow NaOH + HOCH_2SO_3Na$$

The sodium hydroxide is then titrated with standard sulfuric or hydrochloric acid with the end point being determined potentiometrically or by an indicator such as phenophthalien.

In the second technique as with the third an iodometric titration is exploited. It is dependent upon the oxidation of formaldehyde by hypoiodite, which is formed when potassium hydroxide is added to a solution of formal-

dehyde to which a known amount of a standard iodine solution has been added. Upon acidification the iodine is liberated and subsequently measured by back titration. The back titration is carried out using a standard thiosulfate solution.

1) $6KOH + 3I_2 \rightarrow 3KI + 3KIO + 3H_2O$

2) $HCHO + KIO + KOH \rightarrow HCOOK + KI + H_2O$

3) $3KIO \rightarrow 2KI + KIO_3$

4) $KIO_3 + 5KI + 6HCl \rightarrow 3I_2 + 6KCl + 3H_2O$

5) $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

The third titrimetric procedure was used by Goldman and Yogada (5) and applied to the determination of aldehydes in air. Formaldehyde first reacts with sodium bisulfite to form the formaldehyde-bisulfite addition complex. The analysis is performed by destroying the excess bisulfite at a neutral pH, after which the solution is made alkaline with a carbonate buffer liberating the sulfite complexed with formaldehyde. The liberated sulfite is then titrated with a standard iodine solution to give an indirect measure of formaldehyde. This method was employed in this study to standardize the stock solutions of formaldehyde used in the thermal lensing experiments.

In general, volumetric methods are not sensitive nor specific enough for detection of formaldehyde in air, especially at lower concentrations.

Electrochemical analysis of formaldehyde dates back to

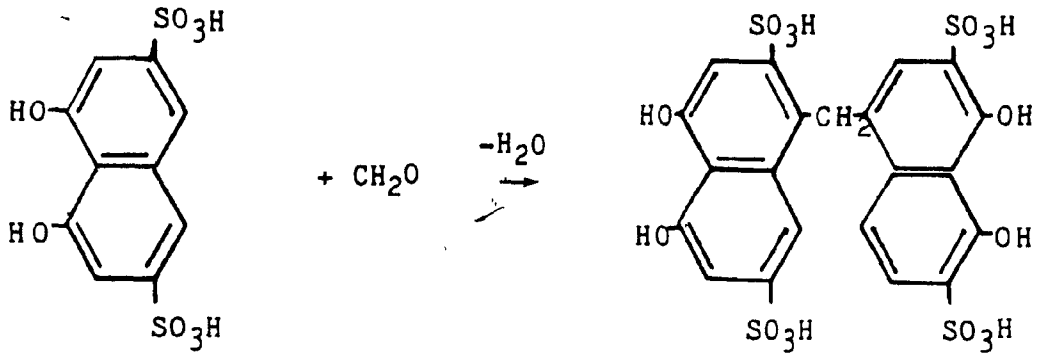
1935 when Jahoda first reported polargraphic measurements of formaldehyde (6). In the mid-seventies other electrochemical methods of analysis were reported; alternating current polarography (7), twin cell sweep voltammetry (8), argentimetric potentiometric titration using an iodide sensitive electrode (9), and short circuit argentiometric amperometric titration using a rotating platinum micro-electrode(10). However only the twin-cell method was used for trace determinations. A detection limit in the ppb region was reported. Electrochemical methods although shown to be sensitive in some cases, are really not acceptable for routine analysis due to their deficiencies. For the most part they tend to be extremely temperature dependent. Jahoda reported a 6.5% change in signal for each $1^{o}C$ change in temperature. They tend to be pH dependent to a fault as well, so that sample preparation tends to be long and complicated with addition of several reagents necessary (11).

In recent years emphasis has been placed on developing spectroscopic means for determining aldehydes in air. Either separately or in conjunction with GC or HPLC, fluorescent and spectrophotometric methods have proven reliable, sensitive, and efficient. Color developing reagents that have been used in spectrophotometric determinations of formaldehyde include; a) Schiff's reagent (pararosaniline and sulfite), b) modified Schiff's reagent (dichlorosulfitomercurate II), c) Chromotropic acid (1,8-

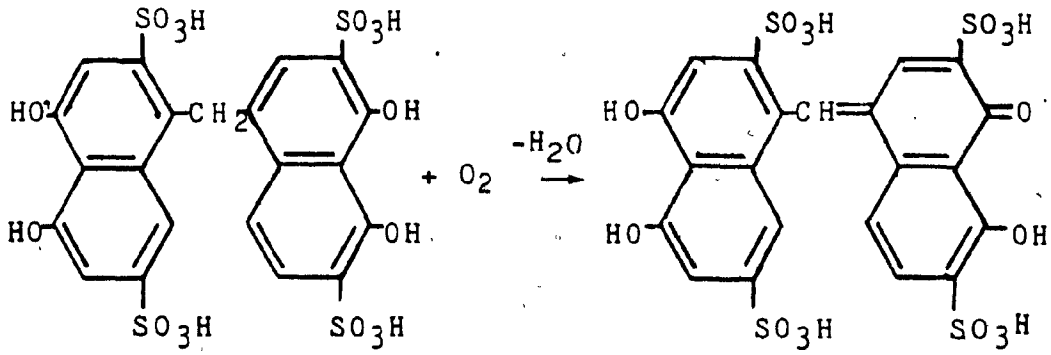
dihydroxy-3,6-disulfonic acid), d) MBTH (3-methyl-2-benzothiazolinehydrazone), e) J-acid (7-anilino-4-hydroxy-2-naphthalenesulfonic acid), and f) phenyl-J-acid (6-anilino-1-naphthol-3-sulfonic acid). Of these, Schiff's reagents, which have two modifications (12, 13), and the chromotropic acid methods are most commonly employed.

NIOSH (National Institute for Occupational Safety and Health) as well as other recognized organizations recommend the chromotropic acid method as the accepted methodology for formaldehyde in air analysis. Chromotropic acid was proposed as a specific reagent for fomaldehyde in 1937 by Eegrive (14). MacDonald further developed the method for air determination (15). Altshuleer, Miller, and Sleva (16) proposed a modification to the method which was propounded as a means of improving sensitivity, stability, and freedom from interferences. The proposed sampling method used chromotropic acid in sulfuric acid as the collection medium.

The NIOSH method which was first recommended by Care (17), uses a 1% aqueous solution of sodium bisulfite as the collection media. Feigl proposed the following mechanism for the reaction between chromotropic acid and formaldehyde(18).



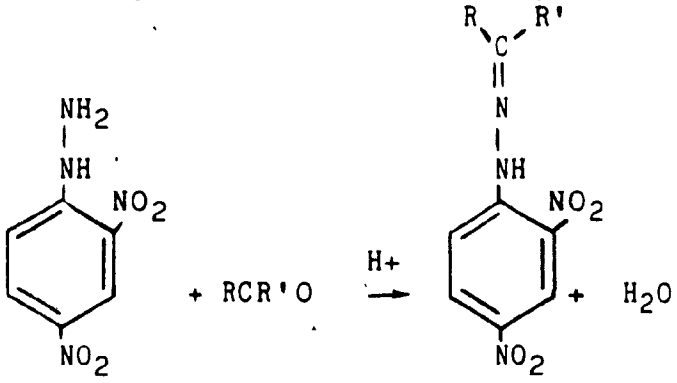
First the condensation of formaldehyde with chromotropic acid produces an hydroxydiphenylmethane which is soluble in sulfuric acid.



When the solution comes into contact with the air a colored oxidation product is formed. It is possible that the sulfuric acid acts to cause a phenol-aldehyde condensation to a quinoid compound.

Since 1980 several papers have been published on GC and HPLC analysis of formaldehyde (19, 20, 21, 22). Most have described techniques for aldehyde measurement in engine exhausts and use either MBTH, DNPH (2,4-dinitrophenylhydrazine),or similar compounds to form derivatives with the aldehydes. These derivatives are subsequently measured

with a UV lamp and detector assembly.



DNPH

The DNPH method is a non-selective method for aldehydes and ketones. The resultant product is a hydrazone derivative.

D. Grosjean reported measuring 11 - 39 ppb of formaldehyde in ambient air using DNPH and HPLC (23). 60 L samples were pulled through the samplers at 1 L min^{-1}. In a previous paper of his (19), the collection efficiency of the DNPH method was studied and found to be over 100 ± 20% for aqueous solutions of DNPH. Note that samples were tested at two humidity levels and actual deviations were 18% and 27% for the humid and dry samples respectively.

A detection limit of 20 ppb with a 10 minute collection time was reported by S.J.Swarin(22). His results showed DNPH solutions to have a 97.5 ± 1.0% collection efficiency. However his standard formaldehyde in air samples, which were generated using a Kin-Tek permeation tube to determine the efficiency of the DNPH solutions, ranged from 0.358 to 1.14 ppm. To determine the detection

limit of the method it was assumed that the efficiency remained constant in the ppb region. A value twice the noise level of a blank signal was therefore determined to be the detection limit (ie 20 ppb).

Several other authors have reported ppm and sub-ppm detection limits for formaldehyde using HPLC or GC (24,25).

T. Dumas compared three detectors for formaldehyde analysis; a FID (flame-ionization detector), a TCD (thermal conductivity detector) and a photoionization detector. All three were found to have ppm detection capabilities.

Several talks at the annual CIC conference in Montreal (1984), dealt with the subject of human exposure levels to toxic chemicals and the required calculation of said level. It is apparent from these discussions that there still doesn't exist one standard method for determining exposure to a substance. OSHA (Occupational Safety and Health Administration) however has set 3 ppm as their 8-h time-weighted average permissible exposure limit and at the American Conference of Government Industrial Hygenists in Cincinnati in 1980 a level of 2 ppm was proposed as the threshold limiting value for an 8-h exposure.

In light of the uncertainty as to what level of formaldehyde can be considered as safe, it would be a definite asset to have a technique capable of measuring sub-ppm levels in limited volumes of air. Rather than measuring overall formaldehyde levels in a household, individual areas could thus be "mapped" for their formal-

dehyde content. HPLC and GC methods, although presently the best alternatives for formaldehyde detection do not possess this capability.

The goal of this project is to improve upon the NIOSH chromotropic acid technique for formaldehyde analysis and increase it's sensitivity while decreasing the required sample size through the use of laser thermal lensing.

Part 2 **INTRODUCTION**

Laser Thermal Lensing (L.T.L.)

Thermal lensing works on the principle that absorption from of a laser beam passing through a material with a finite optical absorption generates thermal energy which heats the material. The temperature gradient causes a refractive index gradient. For a gaussian laser intensity distribution, a well defined transverse, gradient in the refractive index will be established. In most materials dn/dt (the change in refractive index with respect to temperature) is negative and thus this gradient has the same optical effect on a laser beam as a diverging lens. The change in refractive index with temperature may be caused by several phenomena. The most common is thermal expansion which leads to a decrease in density and a negative contribution to dn/dt. Molecular polarizability may also be a function of temperature and can lead to a net positive dn/dt.

It should be noted that thermal lensing is a function of true absorption in the same fashion as other absorbance techniques and not absorption plus scattering as in transmittance techniques. The intensity of the thermal lens effect is proportional to the absorbed light energy. For high average powers, the thermal lensing that occurs in passing through fluid cells may be significant even when these materials are relatively transparent.

Due to it's thermal origin, thermal lenses take a finite time to fully develop within a sample. A steady state is reached when the rate of laser heating equals the rate of heat loss. Heat loss is dependent on the thermal conductivity of the solvent and the temperature change produced. Hu and Whinnery reported (26) that the actual temperature variation in liquids is of the order of 10^{-5} °C using a 5 mw HeNe laser.

The steady state focal length, $f_{(\infty)}$ of a thermal lens produced by a gaussian laser beam of spot size w can be calculated (27);

$$f_{(\infty)} = \frac{\pi k w^2}{2.303 P (dn/dt) A} \qquad (1)$$

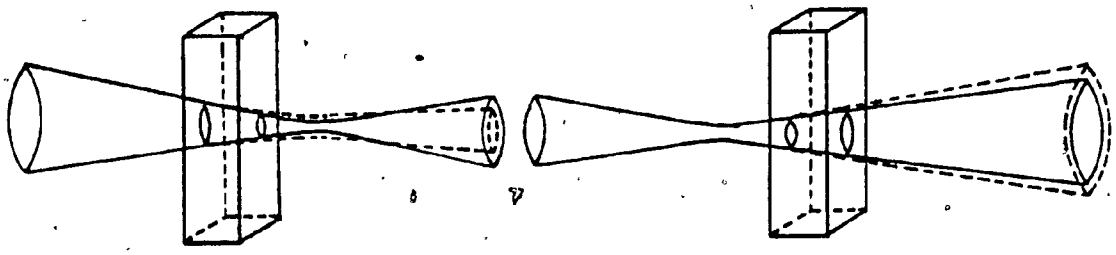
Of greater import to the analytical use of thermal lensing is the equation that relates the growth in the far field spot size of the laser beam with laser power and absorbance of an analyte.

$$\frac{\Delta w^2}{w^2} = \frac{-2.303\ P\ (dn/dt)\ A}{\lambda\ k} \cdot \frac{2\ Z_1\ Z_c}{Z_c^2 + Z_1^2} \qquad (2)$$

where; w = farfield spotsize of laser beam
Δw = change in spotsize
P = power of laser (in watts)
dn/dt = change in refractive index of the sample with temperature
A = absorbance of the sample
k = thermal conductivity of the sample
λ = wavelength of laser beam
Z_c = confocal distance of the focussing lens
Z_1 = distance of sample from lens

The dependence on sample cell position is expressed in the bracketed part of the equation. It is the product of a linear term, which demonstrates the effect of a lens of fixed focal length as the cell is moved through the beam waist of the laser, and a lorentzian term which accounts for the strength of the lens changing with the spotsize of the laser at the beamwaist. Normally the waist of a laser is found inside the laser cavity. However for LTL purposes a second waist is created artifically by placing a converging lens in the beam path. A second beam waist is thus created at the focal point of the converging lens. The product of the linear and lorentzian terms produces an antisymmetric curve about the focal point of the beam.

Note that the physical effect of placing a LTL cell before the focal point is to decrease the convergence of the beam before the beam waist which in turn decreases the divergence after the beam waist.



focussing effect defocussing effect

The thermal lens effect changes the rate at which the beam expands by changing the curvature of the phase fronts. By placing a detector at a long distance from the cell (ie. in the far field), one can measure the change in spotsize by measuring the change in intensity of the beam.

$$\frac{\Delta w^2}{w^2} = \frac{w^2(t=\infty) - w^2(t=0)}{w^2(t=0)} = \frac{\Delta I}{I_\infty} = \frac{I(t=0) - I(t=\infty)}{I(t=\infty)} \qquad (3)$$

For weak thermal lenses the linear equation can be used.

$$\frac{\Delta I}{I_\infty} = \frac{2.303\ P\ (dn/dt)\ A}{\lambda\ k} = 2.303\ E\ A \qquad (4)$$

where E is the enhancement factor

According to Dovichi and Harris(27) when the relative change in I is greater than ten percent a quadratic term

must be added.

$$\frac{\Delta I}{I_\infty} = 2.303\ E\ A + \frac{(2.303\ E\ A)^2}{2} \qquad (5)$$

Dovichi and Harris's work on a single laser system (28) using a HeNe laser demonstrated that the lens response is well behaved and analytically useful for $\Delta I/I_\infty \leq 1.5$ providing the quadratic term is included. Thermal convection becomes a problem for values greater than 1.5, which destroys the reproducibility of the results.

The above equations were first presented by Whinnery and his co-workers(26) and utilize a parabolic approximation for the temperature distribution. The attraction in this approximation is that it reduces a complicated theoretical description to a managible set of equations while introducing an error relative to the observed response of only a few percent.

Sheldon et al. have derived an aberrant model for the thermal lens effect (29). The aberrant lens model is derived using the temperature distribution equation in integral form. This means that the radial refractive index variation also contains the unevaluated temperature distribution integral. Rather than writing an expression for the focal length of the thermal lens, diffraction theory is used to find the intensity at the center of the beam after it has passed through the sample and propagated

to the far field.

Carter and Harris (30) have since published a paper in which they critically evaluate both Whinnery's parabolic lens model and Sheldon's aberrant lens model for accuracy in describing the effect of a thermal lens. Their conclusions are that with a slight modification, the parabolic lens model was determined to be more accurate. This is because of approximations required to evaluate the diffraction integral in deriving the aberrant model. Furthermore, the parabolic model has the advantage of being mathmatically simple thus lending itself to the task of fitting data. Also, since the concept of a lens is retained, it is possible to calculate the propagation of the laser beam through optical elements before and after the sample using ray transfer matrices. This simplifies the design and optimization of experiments.

In an effort to improve the capabilities and sensitivity of the thermal lensing technique, M.E. Long et al. have developed a dual laser system, in which an argon ion laser pumped dye laser is used to pump samples while a lower powered more stable HeNe laser is used as a probe (31). This system allows for study of substances over the wide range of wavelengths the dye laser is capable of. Ishibashi et al. have since used Long's dual laser system and have made further modifications (32,33). Among the modifications are a change in the detector system from a pinhole, single diode arrangement to a photodiode array

system, as well as a change in placement of the beam splitter which joins, and alligns the two laser beams. The change from a pinhole type detector to a photodiode array detector allows for more facile allignment of the beam on the detector and reduces the risk of missalignment and thus poor detection.

In a study on the LTL analysis of gaseous NO_2 Ishibashi et al introduced a design for a dual laser system in which the probe beam was not focussed before passing through the sample. It was reported that this modification increased sensitivity and allowed for a sample cell of greater length.

In keeping with the goal of minimizing apparatus complexity, both simple single and more complex dual laser systems were used in this study to evaluate their detection capabilities for quantitative formaldehyde determination.

Part 2 EXPERIMENTAL

Instrumentation

Figure 1A shows a block diagram for the simplified experimental set up. The optical train and lasers were fixed to a workbench which was isolated from building vibrations with a three-ply "sandwich" consisting of a sheet of cork, a piece of sheet metal, and a layer of sponge rubber. The Coherent CR-6 argon ion laser (A) was used to drive the Coherent CR-590 dye laser (B) which was used at a power of 150 mw at λ = 600 nm. The power was measured in front of the cell holder to account for power loss due to reflections off preceding optical components. The beam was elevated to the height of the optical train by means of a dual mirror system (C). The lens (D) which brought the light to a focus has a focal length of 23 cm. A manual shutter (E) blocked the pump beam for I_o readings. The cell holder (F) was placed one confocal distance (5 cm) beyond the focal point (34). The cell used was a Canlab blue label 1 cm square cell. A flat mirror in an adjustable mount was used to direct the beam towards the pinhole detector. The pinhole was 0.1 mm in diameter. the photodiode detector (I) behind the pinhole (H) was linked to a Tektronix oscilloscope which had a Type 2A63 differential amplifier, and a 2B67 time base with single sweep capabilities. The lens formation was recorded at various sweep rates to record the initial

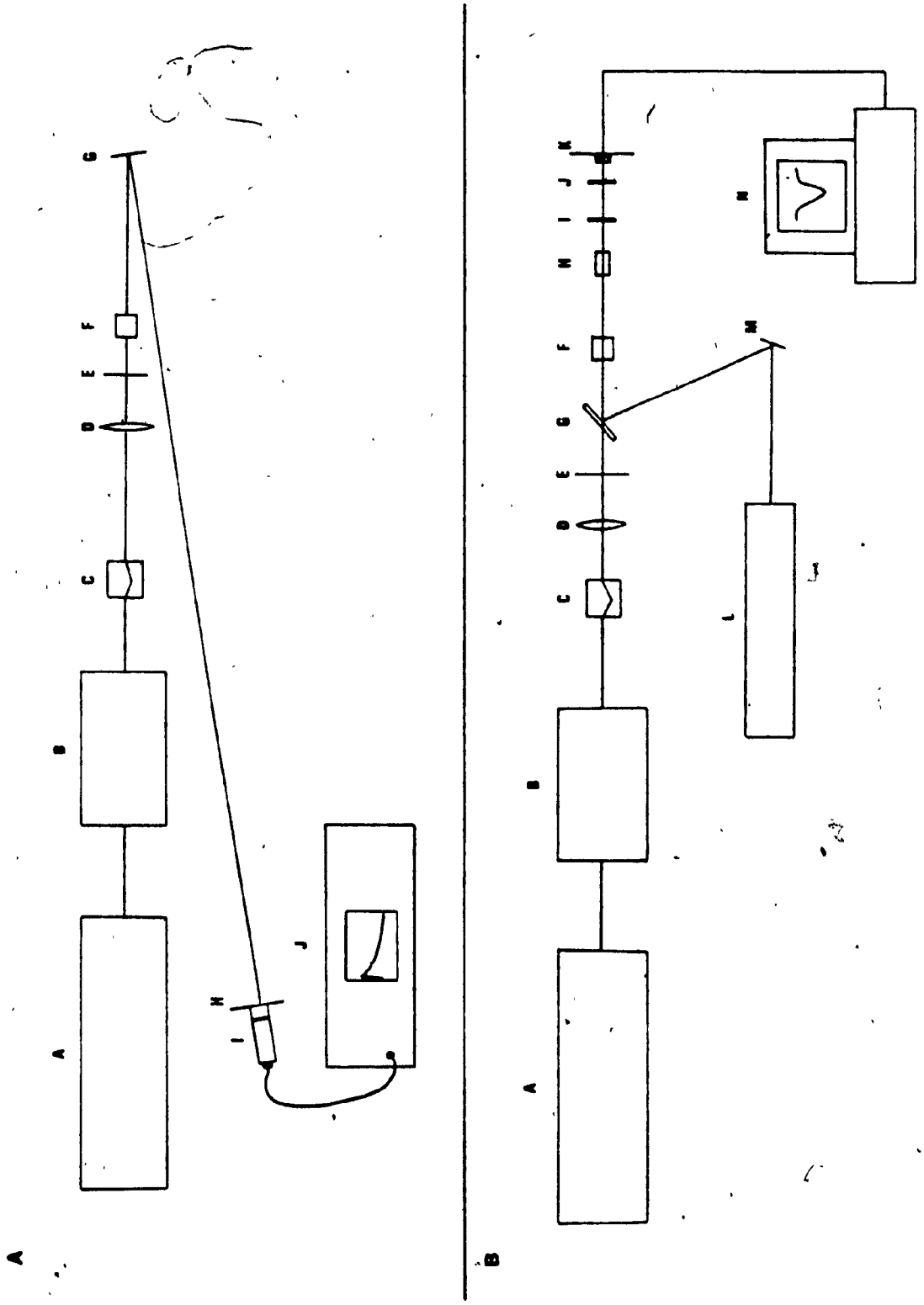


Figure 1. Block diagrams of the two laser systems used in this study

(I_o) and final steady state (I_∞) intensities following opening the laser beam shutter. The data was then read off the screen and recorded.

Figure 1B is a block diagram of the first dual laser thermal lensing system used in this study. It is comprised of the six first components of the simplified system plus eight new additions. A Siemens 10 milliwatt HeNe laser (L) was used as a probe beam which was directed to and alligned with the pump beam by means of a mirror (M) and an optical flat (G). A polarizing Nicol prism (H) was used to reduce the polarized pump beam intensity to prevent burning of the ensuing filter and polarizer. A 630 nm cut-off filter (I) separated the pump and probe beams and a rotating film polarizer (J) adjusted the probe beam intensity to maximize the signal from the diode array without saturating the Reticon RL128G self scanning linear photodiode array detector (K). The signal from the diode array was fed into a Processor Technology SOL computer via 8 bit ADC's for storage purposes. The SOL was interfaced with an IBM personal computer which handled all numerical manipulations. The IBM plotted the beam profile (see figure 2) and was programed to fit a best gaussian curve to the experimental data and to calculate the $\Delta I/I_\infty$ values. A further modification to the initial system was to switch from a square cell to a cylindrical cell to decrease interferences due to solution convection (35).

A revamped dual laser system was used for the final

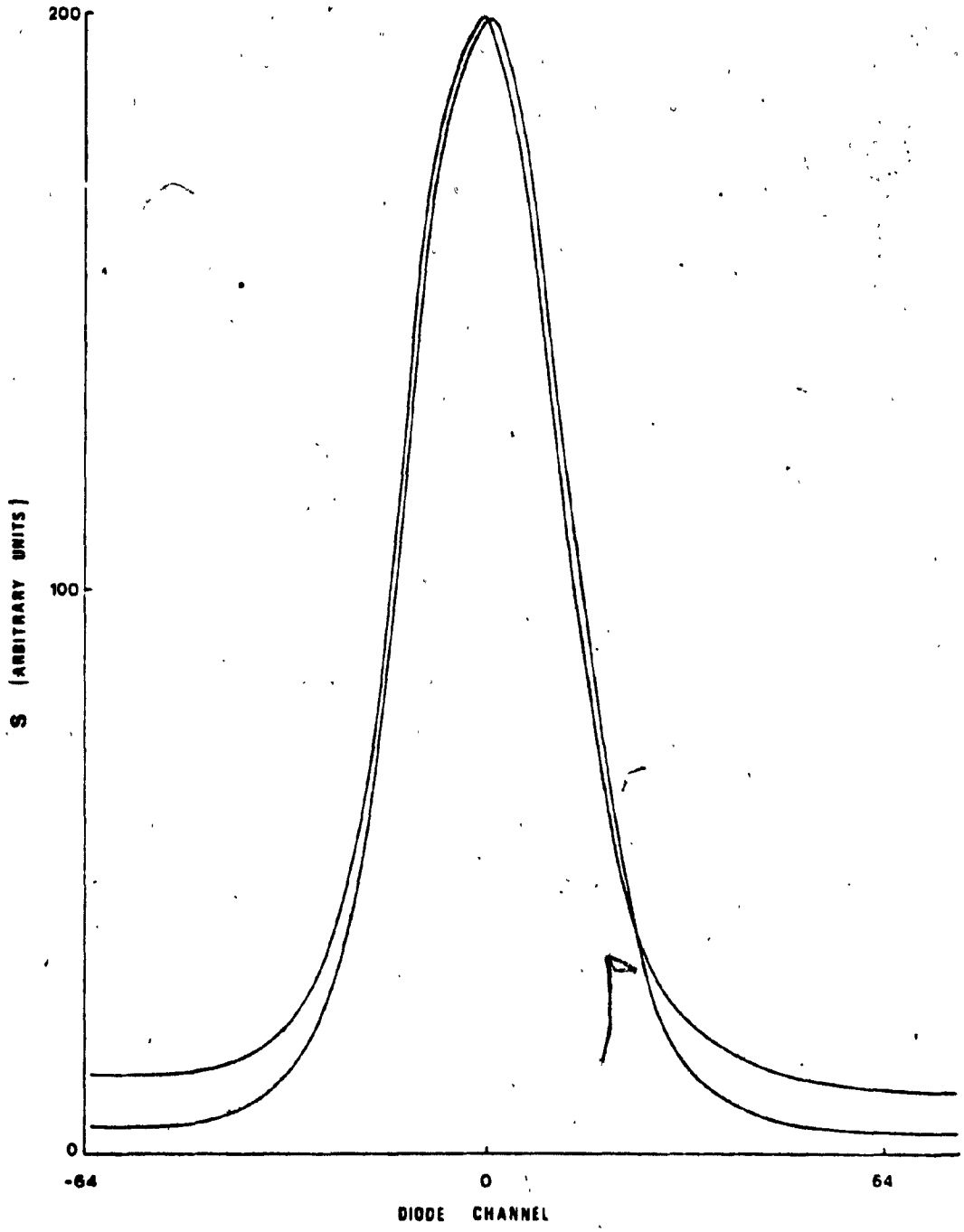


Figure 2. The beam profile and fitting as seen on the I-BM monitor

experiments. A pinhole was placed at the focal point of the lens (D) to reduce the size of the probe beam to contain it within the pump beam. An attempt was made to improve the efficiency of the system and increase the speed of data collection by replacing the photodiode board with a faster scanning board that contained a larger diode array (512 diodes), and removing the SOL computor while upgrading the IBM to accomodate the new board.

Reagents

The formaldehyde stock solution was prepared by dissolving 4.4703 g of sodium formaldehyde bisulfite (Eastman Chemicals) in one litre of deionized distilled water. This solution was standardized against iodine solutions using a starch indicator. Chromotropic acid (Fischer Chemicals) Formaldehyde solutions were prepared using doubly distilled H_2SO_4 (American Chemicals) following the NIOSH method (36).

Procedure

All glassware was soaked in an H_2SO_4-HNO_3 acid bath or a Decon (BDH Chemicals) cleaning solution bath overnight and then rinsed with deionized-distilled water before use. The stock formaldehyde solutions were diluted successively to obtain the desired concentrations. Samples prepared following the NIOSH methodology were allowed to stand

overnight to insure full color development although it was noted that 1 h would have been sufficient (37). Before analysing the samples and blanks using thermal lensing a further tenfold dilution was required to reduce the sulfuric acid concentration. The reason for the dilution is explained in the discussion section.

All alignments and cell positions were optimized using a concentrated solution of formaldehyde (10^{-5}M). For the simple system the flat mirror (G) was adjusted until a maximum intensity was observed on the oscilloscope screen. Then the cell was moved along the rail until the thermal lens effect was maximized. The results are shown in table I. The two laser system required alignment of the probe and pump beams which was performed before each day's run to accomodate any shift in the beams that might have occurred. This was accomplished by using the lens (D) which was on a horizontal and vertical adjustable mount to shift the pump beam in the appropriate direction to maximize the thermal lens signal observed on the monitor.

Table I

Dependence of cell position on the thermal lens signal

CELL POSITION (cm)	$\Delta I/I_\infty$
75.6	.239
75.4	.235
75.2	.297
75.0	.286
74.8	.236
74.6	.228
74.4	.247

Part 2 DISCUSSION

The first step in developing a new technique of analysis or modifying an existing one, is to ensure that no changes or interferences are created by the modifications that will invalidate the technique. The main difference between LTL and normal absorption techniques is the light source.

As part of an undergraduate project (38), a study was done on the stability of the chromotropic acid/formaldehyde chromogen under varying conditions. An experiment was performed in which the absorbance spectra of various concentrations of the chromogen was taken before and after the chromogen had been irradiated by a laser beam (λ =600 nm), for extended periods of time. After fifteen minutes of irradiation at a power of 320 mw the spectra showed large increases in absorbance below 400 nm. At 600 nm however, the absorbance showed only a five percent increase. Considering that under normal LTL experimental conditions each sample would be exposed for less than one minute at lower powers than 320 mw, the chromogen was deemed sufficiently stable for use in the ensuing experiments. In addition to the above experiment, an experiment was done to measure the stability of the chromogen with respect to time. It was determined that it was stable for at least a period of a week. This concurred with previous literature (37).

Dovichi and Harris (27) noted that the sensitivity enhancement that can be realized for a particular laser power is dependent on the thermooptical properties of the solvent in which the sample is dissolved. Solvents that exhibit high dn/dt and low thermal conductivity are desirable for the thermal lens effect. In our experiments it was discovered early that the blank (a mixture of chromotropic acid, sulfuric acid, and water) created such a large lens that the pinhole detector was unable to differentiate between a dark signal and the I_∞ value at low powers of 150 mw. Since the blank solution was clear in color it was assumed that the effect was due in part to absorption by the chromotropic acid and sulfuric acid, and to a great deal to the solvent properties of the sulfuric acid which led to large thermal convection effects.

Preliminary experimentation showed that a tenfold dilution of the blank was necessary to obtain a signal that wasn't seriously affected by thermal convection (35). Thus a tenfold dilution of the color developed solutions of formaldehyde was added to the procedure.

To achieve the maximum sensitivity our system was capable of, the dye laser's most stable wavelength which closely matched the absorption maximum of the formaldehyde/chromotropic acid chromogen (λ_{max} = 580 nm) was chosen. The absoptivity of the chromogen at 600 nm was found to be 4.6×10^3 $M^{-1}cm^{-1}$. See figure 3. A moderate power of 150 mw chosen and found to be sufficient to pump

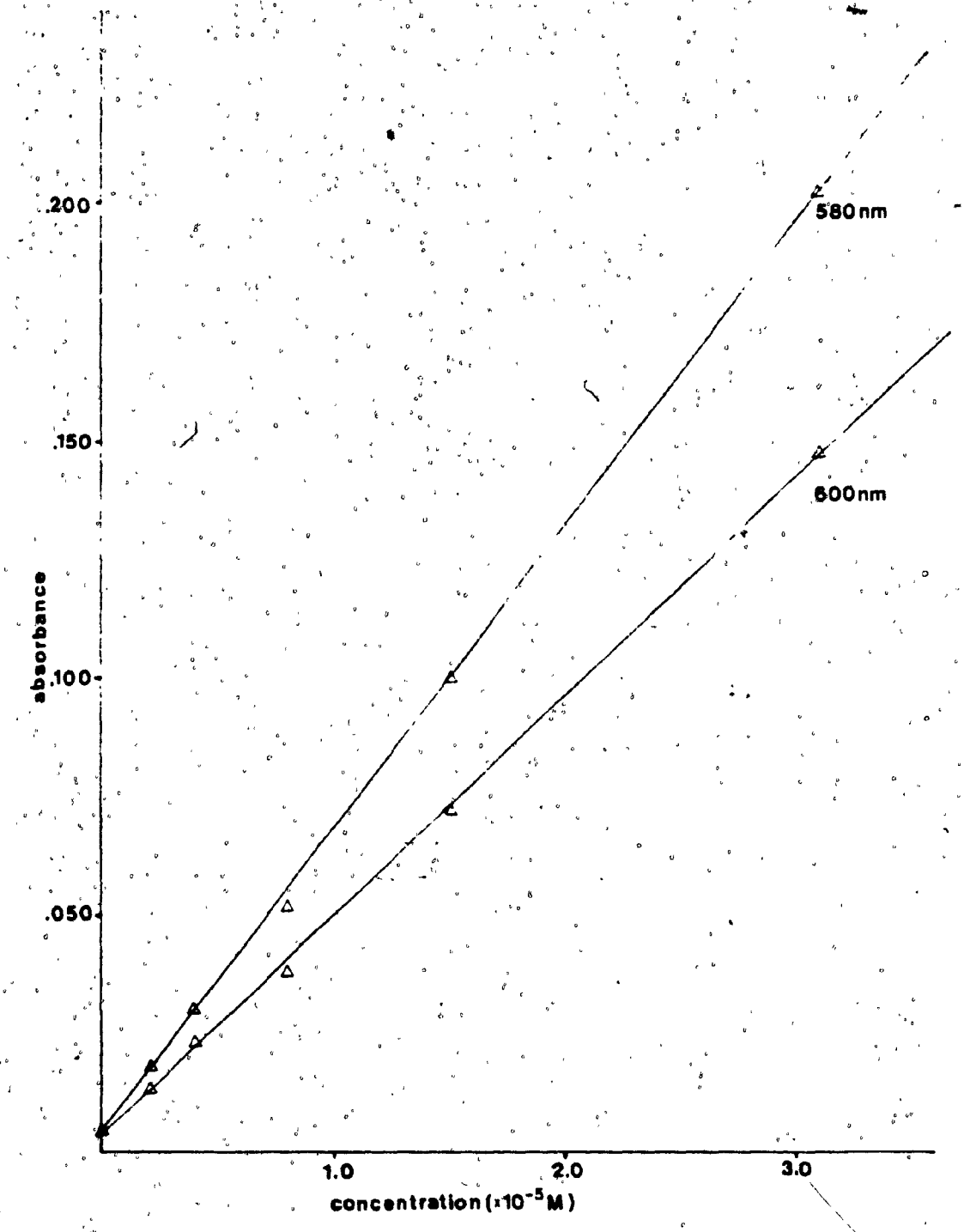


Figure 3. Plot of concentration of formaldehyde versus absorption

the samples.

After completion of the original thermal lens experiments on formaldehyde using the pinhole detector the possibility of using another color developing agent (other than chromotropic acid) was investigated. The modified pararosaniline method was considered as a potential candidate since it was reported that the formaldehyde/pararosaniline chromogen had an absorption coefficient at 600 nm approximately double that of the chromotropic acid chromogen. An attempt was made to run samples of varied formaldehyde concentrations to construct an absoption vs. concentration curve. Bizarre results were continuously obtained day after day with negative absorbance, relative to the blank, values being the norm. It was first thought that inexperience with the methodology was the culprit for the unexplained results. However after consultation with the analysts at Technitrol(39), it was concluded that the methodology reported by Mirch et al. (40) was incomplete. Papers published since, have shown the pararosaniline method to be pH and temperature dependent (41), as well as being vunerable to interference from SO_2 (42).

Since no other existing colorimetric methodologies had the sensitivity of chromotropic acid nor absorption bands suitable to the wavelengths accessible to our lasers, chromotropic acid was used for the remaining experiments.

The results from the single laser experiments are shown in table II and figure 4 while the results from the first dual laser experiments are presented in table III and figure 5. Each point in figure 4 represents the average of three scans of eight samples. Each point in figure 5 represents the average of three scans of five samples. A detection limit of twice the standard deviation of the blank, where the blank is averaged over all runs with all sample concentrations, for each system was calculated to be 22 x 10^{-7} M and 5.6 x 10^{-7} M respectively.

Although the standard deviation of the blank value as determined over all runs was quite large, the deviation of the triplicate readings of each day's blank was much smaller and it was felt that the detection limit reported was not representative of the best performance achieveable. As seen in figure 4 there are several values that lie below the above detection limit that appear to be significant. To determine whether these points could be considered to reflect real signals, they were compared to blanks prepared concurrently. At the lowest concentration of 1.5 x 10^{-8}M a t test indicated signal significance at the 99.9% level. Thus, it was apparent that higher sensitivity than quoted for the collection of data in the tables can be achieved with careful control of blanks and the extra effort implied.

Further experimentation was performed to test the variation in the blank. This was done to ascertain whether one could justifiably use the variation in the daily blank

Table II

Results from the single laser thermal lens experiment.

CONCENTRATION OF FORMALDEHYDE SOLUTION (M)	AVERAGE * $\Delta I/I_\infty$	THEORETICAL ABSORBANCE (A)	ENHANCEMENT FACTOR (E)	CALCULATED ** $\Delta I/I_\infty$
blank	.000	.000	--	.000
2.0×10^{-7}	.014	9.2×10^{-4}	6.6	.018
2.8×10^{-7}	.021	13×10^{-4}	7.0	.025
3.6×10^{-7}	.038	16×10^{-4}	10.3	.033
4.0×10^{-7}	.045	18×10^{-4}	10.8	.036
$12. \times 10^{-7}$	.091	55×10^{-4}	7.2	.084
$20. \times 10^{-7}$	.128	93×10^{-4}	6.0	.133
$28. \times 10^{-7}$	.185	.013	6.2	.181
$36. \times 10^{-7}$	.228	.017	5.8	.230

Parameters

Blank mean value - $.177 \pm .072_{(s)}$

Correlation coefficient - .996

Intercept - $.0113 \pm .0027_{(s)}$

Slope - $2012 \pm 72_{(s)}$

Average Enhancement Factor - $7.5 \pm 2.0_{(s)}$

Power - 150 mw

* All ΔI values were subtracted from their corresponding blank values before averaging.

** Calculated ΔI values were obtained from concentration values which were transformed into absorbance values, which were applied to the equation;

$$\Delta I/I_\infty = 2.303 \; E \; A$$

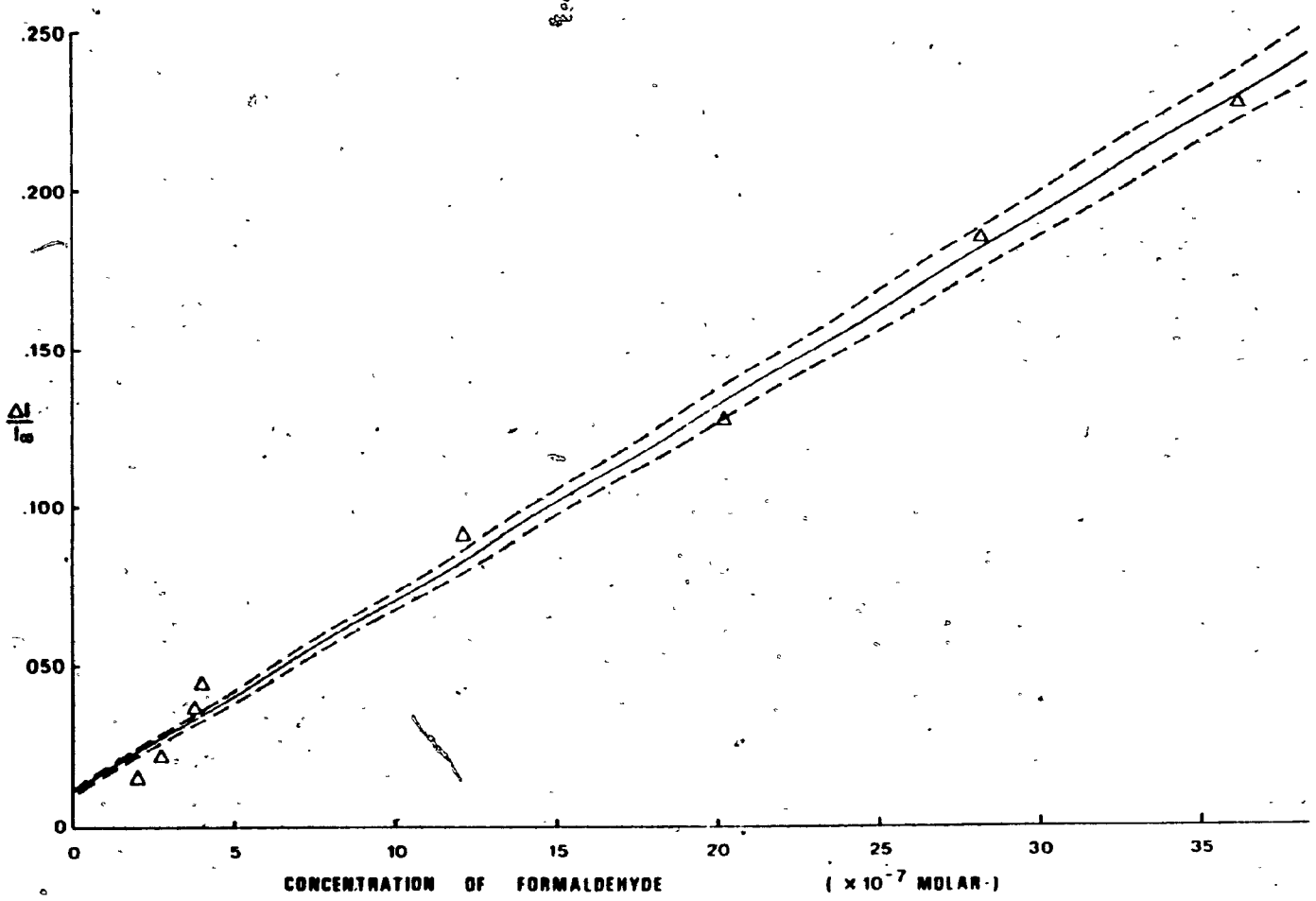


Figure 4. Plot of concentration of formaldehyde versus $^{\Delta I}/_{I_\infty}$ for the single laser experiment. The dotted lines represent the slope deviation.

Table III

Results from the first dual laser thermal lens experiment.

CONCENTRATION OF FORMALDEHYDE SOLUTION (M)	AVERAGE * $\Delta I/I_\infty$	THEORETICAL ABSORBANCE (A)	ENHANCEMENT FACTOR (E)	CALCULATED ** $\Delta I/I_\infty$
blank	.000	.000	---	.000
1.5×10^{-8}	.023	6.9×10^{-5}	145	$.002^2$
2.3×10^{-8}	.024	1.1×10^{-4}	95	$.003^5$
3.1×10^{-8}	.025	1.4×10^{-4}	78	$.004^5$
7.7×10^{-8}	.030	3.6×10^{-4}	36	.012
1.5×10^{-7}	.038	6.9×10^{-4}	24	.022
3.1×10^{-7}	.055	1.4×10^{-3}	17	.045
5.4×10^{-7}	.079	2.5×10^{-3}	14	.080
7.7×10^{-7}	.104	3.6×10^{-3}	12	.116
$15. \times 10^{-7}$	.184	6.9×10^{-3}	12	.222
$23. \times 10^{-7}$	.262	.011	10	.350
$31. \times 10^{-7}$	.350	.014	11	.451

Parameters

Blank mean value - $.175 \pm .051_{(s)}$

Correlation coefficient - .983

Intercept - .0223

Slope - 1.06×10^5

Average Enhancement Factor - $14 \pm 4_{(s)}$

Power - 150 mw

* All ΔI values were subtracted from their corresponding blank values before averaging.

** ΔI values were obtained as per table II.

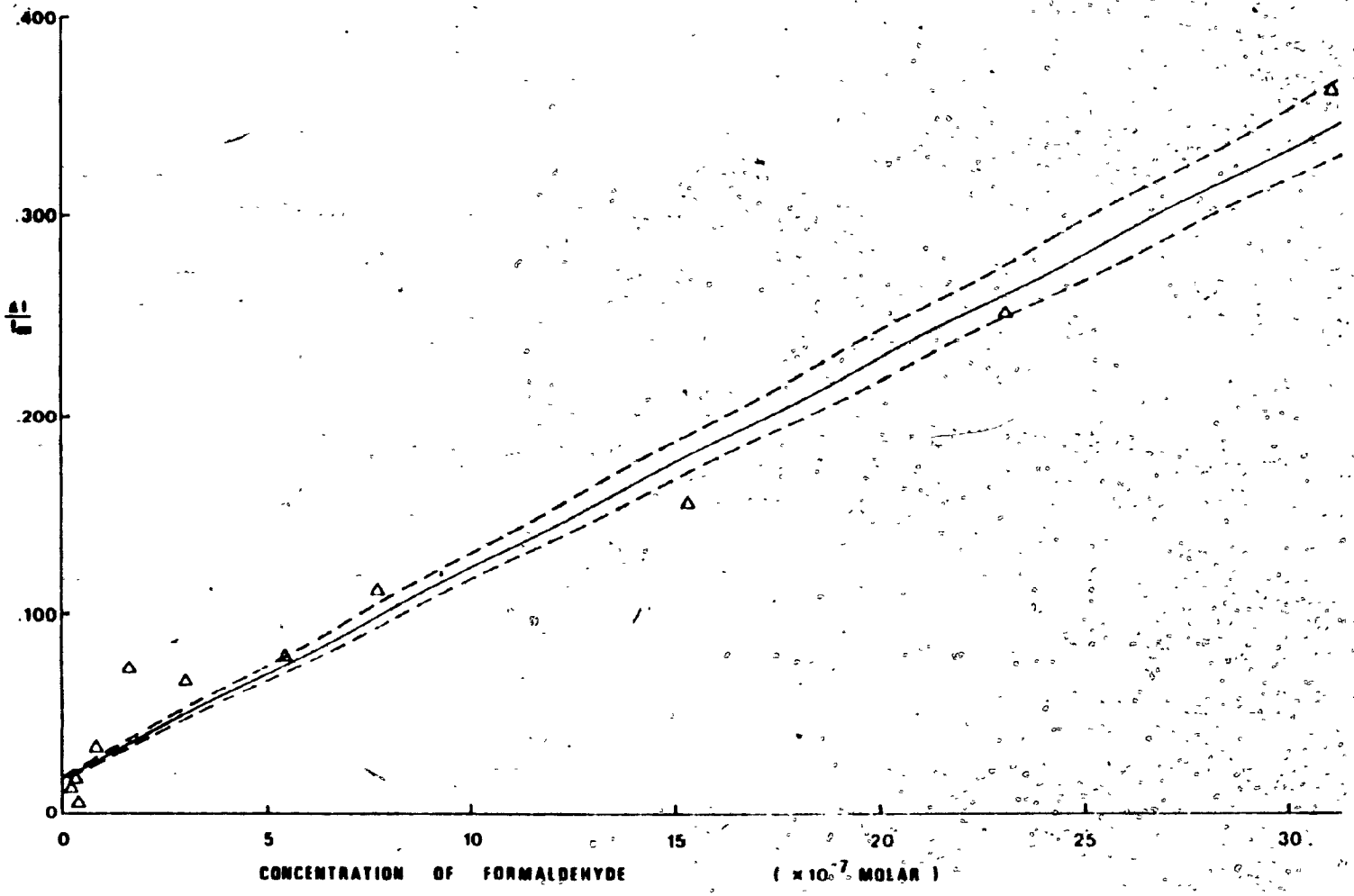


Figure 5. Plot of concentration of formaldehyde versus $\Delta I/I_\infty$ for the dual laser experiment. The dotted lines represent the slope deviation.

to determine the detection limit rather than use the standard deviation of all the blanks from all the runs covering a period of over a week. The experiment consisted of preparing five separate blanks per day for five days and using LTL to measure their absorbance. All blanks were made using the same batch of chromotropic acid solution. The results are shown in Table IV and V. A comparison of the standard deviation of each day's average versus the standard deviation of all samples of all days shows quite clearly that indeed the variation in blank from day to day is larger than the daily variation. It has been suggested* that the day to day variation is due to a change in ambient formaldehyde in the laboratory contaminating the samples. Although the samples were tightly stoppered this is a plausible explaination.

Whatever the reason for the large deviation in the day to day blanks, it is important that the experiment demonstrates, that providing one runs a sufficient number of blanks one can use the daily deviation to determine the detection limit.

Note that the addition of the second laser into the system proved to be beneficial. The reduction in noise in the probe beam which occurred when the probe was changed from the dye laser to the HeNe laser, allowed a large improvement in sensitivity. The dual laser system is modeled after Ishibashi et al's system (33) in that the HeNe probe laser is not focussed before passing through the sample.

* Suggested by a referee in his comments on a paper to be published(43)

Table IV

Results from the blank variation experiment.

DAY	BLANK ($^{\Delta I}/_{I_\infty}$)				
	#1	#2	#3	#4	#5
1	.1058	.0998	.1124	.0681	.0359
2	.1152	.0544	.0489	.0450	.0599
3	.0901	.0933	.0768	.0793	.0485
4	.1079	.1180	.0728	--	--
5	-.0187	.0935	.0935	--	--

* all BLANK $^{\Delta I}/_{I_\infty}$ values are the average of 3 trials of scans

** the last four values were lost due to computer programing errors

Table V

DAY	AVERAGE $^{\Delta I}/_{I_\infty}$
1	$.0965 \pm .0196_{(s)}$
2	$.0520 \pm .0065_{(s)}$
3	$.0849 \pm .0080_{(s)}$
4	$.0996 \pm .0237_{(s)}$
5	$.0935 \pm .0000_{(s)}$
overall average (from 20 values)	$.0809 \pm .0257_{(s)}$

Ishibashi et al discuss Sheldon's abherent thermal lens model and calculate enhancement factors using his equations. They point out that both the parabolic and abherent models predict linear dependence at lower concentrations. The similarity of the two model's predictions for weak thermal lenses is further discussed by Harris and Carter . The analytical curve for formaldehyde from our data based on parabolic lens equations gave the better straight line.

In one of his early papers, Harris reported that he was able to increase the sensitivity and precision of his LTL system by two orders of magnitude ($10^{-6}cm^{-1} - 10^{-8}cm^{-1}$) by increasing the speed of his data collection (44). In an effort to do the same, the detector system for our dual laser system was upgraded. No attempt will be made to explain the technical changes other than to state that the modifications include; the replacement of the photodiode board with a faster scanning board, the removal of the SOL computer, and an upgrading of the IBM to accomodate the new board. The actual upgrading was accomplished by a colleague and will be discussed in detail in her doctoral thesis*. Suffice it to say that the improvement has allowed for triplicate collection and averaging of 96 scans of each sample.

It was felt that the gaussian fitting of the experimental beam profiles was an inadequate representation of the data. The upgrading of the system along with the aquisition

* Ph.D. Thesis of Joan Power, Concordia University

of a superior software package (ASYST Macmillan Corp.) allowed a change from a gaussian fitting of the data to a fast fourier transform fitting. Data from the dual laser system runs were fitted with fourier transforms using a range of harmonics from 2 through 10. The "fitted" data were then used in a straight line equation and the correlation coefficients calculated. The results are shown in table VI. Using ten harmonics in the fft gave a fitting that closely resembled the original data and the best correlation. For this reason all dual laser LTL data were fitted with tenth harmonic ffts.

Improving the data collection efficiency has improved the precision of our data as Harris noted, however unlike Harris the sensitivity of our analysis has not been improved upon. As seen in table VII and figure 6 the range of detection is essentially the same as in the first dual laser system results.

This makes sense in light of the original single laser experiments. As well as running solutions of varying concentrations, an experiment was performed in which a solution of high known concentration of formaldehyde was reacted with chromotropic and sulfuric acids as per the NIOSH method. The resulting solution was then successively diluted to various concentrations and analysed with LTL. The results are shown in table VIII and figure 7 . Each point in figure 7 represents the average of three scans of ten samples. When comparing the values in tables II and

Table VI

Determination of the best fitting.

HARMONIC	FITTED $\Delta I/I_\infty$							
	0	7.6	15.2	30.3	76.0	152	228	303
	(x 10^{-8} M)							
2nd	.2428	.2882	.2689	.2804	.2861	.3191	.3835	.4640
3rd	.2643	.3103	.2934	.3117	.3200	.3595	.4349	.5343
4th	.2659	.3147	.2969	.3175	.3270	.3684	.4464	.5462
5th	.2641	.3158	.2956	.3170	.3270	.3677	.4480	.5470
6th	.2617	.3162	.2928	.3155	.3244	.3633	.4471	.5450
7th	.2579	.3142	.2896	.3120	.3203	.3582	.4401	.5431
8th	.2522	.3091	.2851	.3065	.3153	.3531	.4434	.5392
9th	.2451	.3017	.2784	.2980	.3100	.3477	.4387	.5358
10th	.2369	.2939	.2772	.2887	.3063	.3458	.4342	.5304

HARMONIC	CORRELATION COEFFICIENT (ΔI VS. concentration)
2nd	.9615
3rd	.9693
4th	.9719
5th	.9712
6th	.9683
7th	.9667
8th	.9670
9th	.9685
10th	.9719

Table VII

Results from second dual laser thermal lens experiment.

CONCENTRATION OF FORMALDEHYDE SOLUTION (M)	AVERAGE * $\Delta I/I_\infty$	THEORETICAL ABSORBANCE (A)	ENHANCEMENT FACTOR (E)	CALCULATED ** $\Delta I/I_\infty$
blank	.000	.000	--	.000
7.6×10^{-8}	.042	3.5×10^{-4}	52	.008
1.5×10^{-7}	.026	6.9×10^{-4}	16	.016
3.0×10^{-7}	.036	1.4×10^{-3}	11	.032
7.6×10^{-7}	.079	3.5×10^{-3}	10	.081
1.5×10^{-6}	.099	6.9×10^{-3}	6	.159
2.3×10^{-6}	.219	$.010^5$	9	.242
3.0×10^{-6}	.267	$.014^0$	8	.322

Parameters

Blank mean value - $.203 \pm .009_{(s)}$

Correlation coefficient - .981

Intercept - .0118

Slope - 8.32×10^4

Average Enhancement Factor - $10 \pm 3_{(s)}$

Power - 200 mw

* Unlike the previous experiments, values were averaged before being subtracted from the average blank value.

** Calculated as per table II.

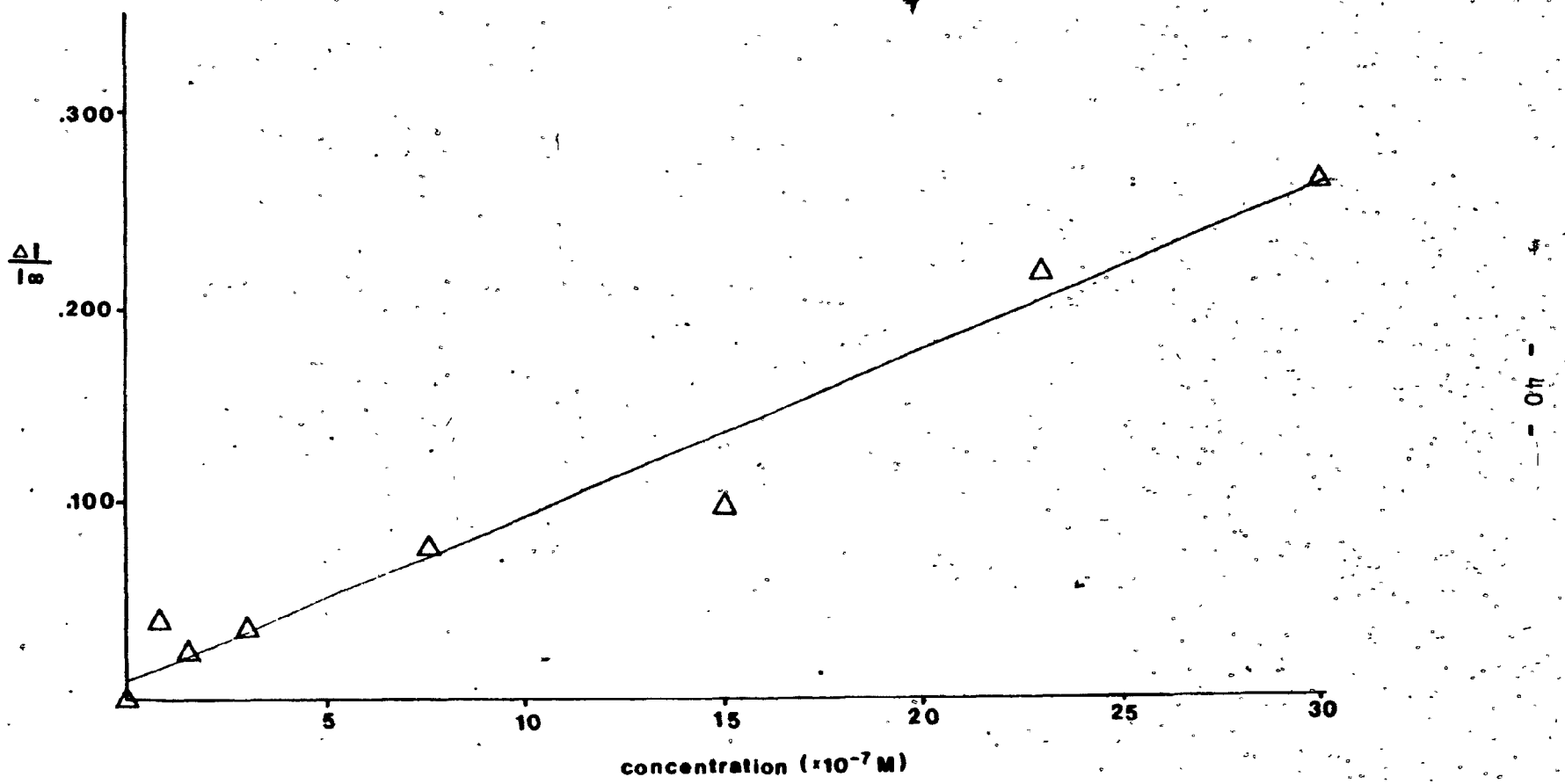


Figure 6. Plot of concentration of formaldehyde versus $^{\Delta I}/_{I_\infty}$ for the second dual laser experiment.

VIII what becomes immediately evident is that the enhancement factor is higher when the formaldehyde solutions were reacted with chromotropic acid and then diluted versus when the formaldehyde solutions were first diluted amd then reacted with the acid. This would appear to indicate that there is a certain concentration level of formaldehyde at which competing reactions take precedence over the formaldehyde-chromotropic acid reaction and no color is developed.

The results of the single laser experiments along with the lack of improved sensitivity with improved data collection efficiency would lead one to believe that the LTL analysis is "chemically" limited and not equipment limited.

Even so, it is clear from the results in tables II, III and VII that thermal lensing is capable of analysing low concentrations of formaldehyde <u>in solution</u>. To ensure that the LTL analysis of formaldehyde can compete with GC and HPLC methods it still remained to be demonstrated that these low concentrations can translate into even lower concentrations in air.

To calibrate the system against gas samples of formaldehyde, standard samples with known concentrations of formaldehyde were required. This neccessitates the development of a system for producing said samples.

Table VIII

Results from preliminary single laser thermal lens experiment.

CONCENTRATION OF FORMALDEHYDE SOLUTION ($\times 10^{-8}$ M)	AVERAGE * $\Delta I/I_\infty$	THEORETICAL ABSORBANCE ($A \times 10^{-4}$)	ENHANCEMENT FACTOR (E)	CALCULATED ** $\Delta I/I_\infty$
4.0	.018	1.8	43	.009
8.0	.004	3.7	5	.020
12.	.034	5.5	27	.028
16.	.016	7.4	9	.038
20.	.042	9.2	20	.048
24.	.048	11.	19	.057
28.	.048	13.	16	.067
32.	.085	15.	25	.078
36.	.081	17.	21	.088
40.	.149	18.	36	.093
44.	.091	20.	20	.104
52.	.170	24.	21	.124
62.	.137	29.	20	.150
96.	.211	44.	21	.228
160.	.327	74.	19	.383
223.	.662	103.	28	.534

Parameters

Correlation coefficient - .973

Intercept - .011

Slope - 2.69×10^5

Average Enhancement Factor - $22 \pm 9_{(s)}$

Power - 100 mw

* All ΔI values were subtracted from their corresponding blank values before averaging.

** Calculated as per table II

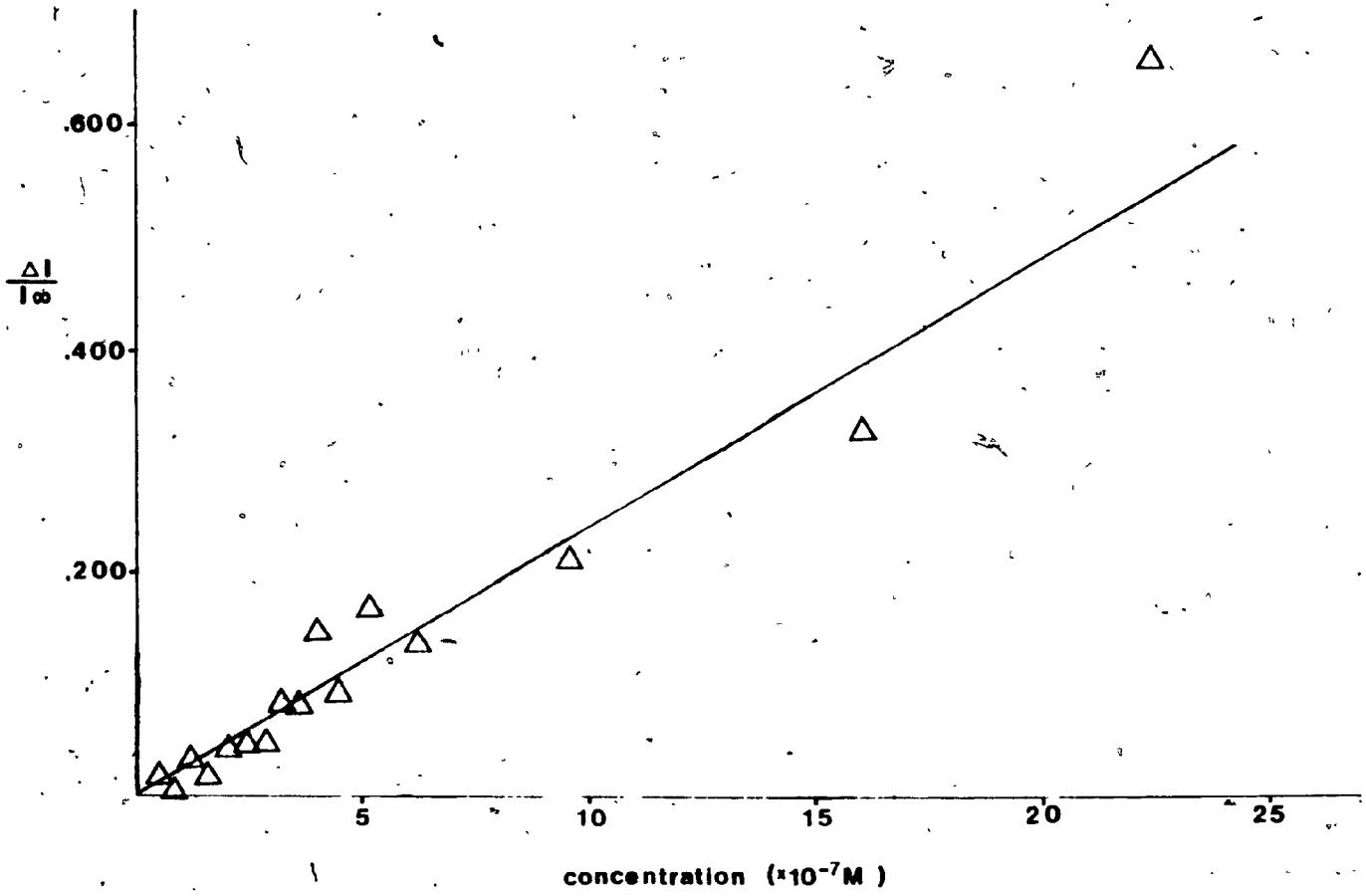


Figure 7. Plot of concentration of formaldehyde versus $\Delta I/I_{\infty}$ for the preliminary single laser experiment.

Part 3 INTRODUCTION

Primary standards of known low concentrations of air pollutants serve a dual function of testing the variety of methods of analyses as well as calibrating current analytical instruments. To calibrate our LTL spectrometer, an independent means of analysis was required. The concentration of the standard gas samples, which were used for the calibration purposes, was determined gravimetrically. The gravimetric analysis was further cross referenced against absorbance measurements. Currently a few techniques exist for the production of standard formaldehyde in air samples. Most of these methods have some serious drawback or possess a potential danger to the operator (45;46,47). Our work on the laser themal lens analysis of formaldehyde required large volumes of standard formaldehyde gas samples which led to the development of a simple flow system. The system has several advantages over previous systems in that it is much more compact and doesn't contain any large cost intensive collection vessels (45), does not neccessitate undue heating of the formaldehyde (46), nor elaborate cooling and vacuum atmospheres (47). Thus it is a much more efficient system for day to day production of formaldehyde in air samples of varied concentrations.

The concentration of the gas samples produced by the new method is essentially determined by the weight loss of

pellets of paraformaldehyde. A microbalance, the main expense, is used to accurately determine the weight loss of these pellets.

A dynamic flow design was chosen for the system as opposed to a static design for four reasons. The first reason is that static methods are limited as to the amount of gas mixture produced, so testing is limited unless a large chamber is used. For example, considering that 60 litre samples are commonly employed for formaldehyde analysis, a chamber capable of producing several standard samples must have a total volume in the order of hundreds of litres. The second difficulty with static systems is that losses of a test gas due to adsorption of the surface of static apparatus is quite high whereas adsorption losses are less serious in flow dilution systems since a steady state equilibrium is reached after relatively short flushing periods after which no further adsorption occurs. Finally, the flow through regime allows for the actual size of the apparatus to be much more compact while providing the large volumes of gas mixture required in a very short time. Furthermore it permits rapid changes in concentration levels and provides unlimited volumes simply by changing the parameters (i.e. flow rate, temperature, or flow rate of the dilutant gas).

In the last two years permeation tubes filled with paraformaldehyde have become available for the production of standard formaldehyde gas samples (48). When used in

conjunction with a flow system, they are reported to give precise and accurate samples. In many ways the system that will be discussed in this thesis parallels the permeation tube system. Comparisons will be drawn and the two systems compared, in the discussion.

Part 3 EXPERIMENTAL

Instrumentation

The final version of the sampling train is shown in figure 8 . The design is essentially all glass with O-ring joints and spring clips, with exceptions indicated, to minimize the possibility of leakage. Air enters the system through two drying tubes (A), passes through a flow meter (B), and a cold trap (C). The cold trap is used to ensure that no glycerol and/or water vapours interfere. After being thus dried the air passes through an open ended manometer (D), and finally over the sampling tube (E). The formaldehyde pellet is placed in a small ground glass flask (F) which in turn is placed in the sampling tube. Assembly (G) consists of a train of two 20 ml. bubblers (H) followed by a ball flow meter (I) which is connected to a pump via copper G.C. tubing. The flow of air to the pump is regulated by a cutoff valve and a metering valve (Nuclear Products Company). This assembly is used to calibrate the system.

The first drying tube contains colored dryrite which removes most of the water from the air entering the system. The second drying tube contains P_2O_5 on glass wool plugs. The cold trap contains a mixture of ice and $CaCl_2$ and is maintained at a temperature of minus ten to twenty degrees Celcius. The small flask (F), is fitted with a ground

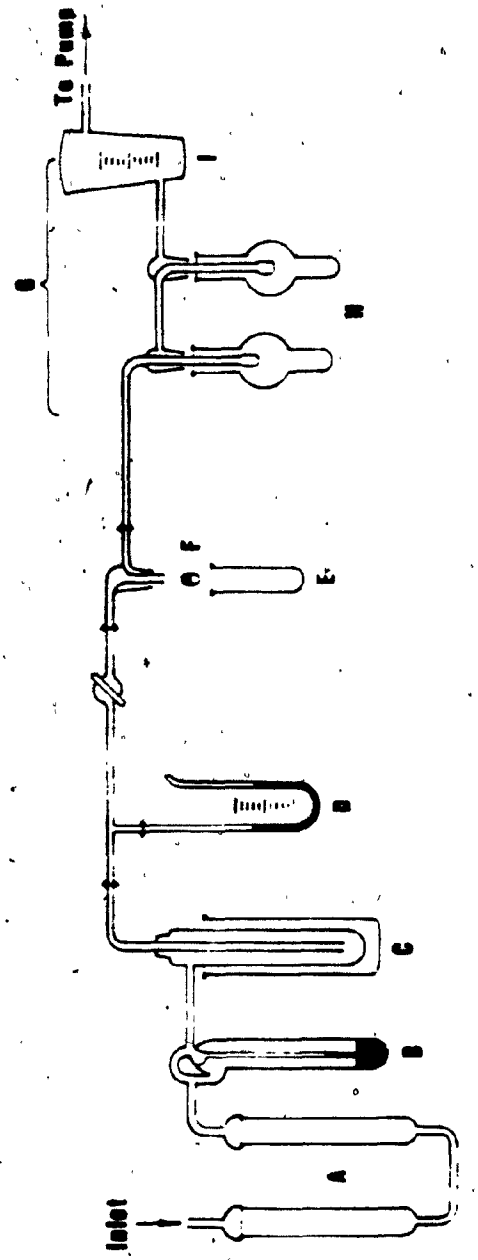


Figure 8. Schematic diagram of the flow system sampling train.

glass stopper which is removed immediately prior to exposing the formaldehyde pellet to the flow of dry air and placed back on again immediately afterwards for weighing purposes. A tool was devised to aid in the removal and placement of the lid, which consists of the casing of a 3 ml plastic syringe minus the bottom and a wooden rod with a metal hook. While the syringe casing holds the flask in place, the hook is lowered though the middle of the casing and engages the stopper.

Preliminary experimentation with various sized bubblers and sampling tubes was performed until a system was found in which the sublimation rate of the formaldehyde was sufficiently low for dilution purposes. Reagent grade paraformaldehyde polymer was used without any further purification as the source of formaldehyde. Preliminary experiments used the paraformaldehyde in powder form. The final design required paraformaldehyde in pellet form. The pellets were pressed into shape using a KBr IR die set (Barnes Analytical) and a calibrated hydrolic press (Fred S Carver Ltd.). For the final experiments the formaldehyde was dried in a vacuum oven at 120°C to drive off the water and methanol impurities for two hours before use.

The source of air for calibration of the flow system was laboratory air pulled through the system by an pressure-vacuum pump (Eberboch Corporation). For sample preparation where dilution of the prepared gas was required, a cylinder of medical grade air (Union Carbide)

was used to prepare the gas sample while the pump was used to provide the lab air used to dilute the sample.

Both flow meters listed in figure 8 were calibrated by a 25 ml. bubble meter. Formaldehyde sublimation was measured by weight difference with a microbalance (Mettler Corp. model M5).

Once the performance of the paraformaldehyde pellets had been characterized, the dilution apparatus was mounted onto the sampling train. Figure 9 is a diagram of the system readied for the dilution experiments. Air is pulled through sampling train by the action of the venturi mixer (A). The dilution venturi mixer with metering screw-valves on it's output and exhaust ports allows for collection of all or part of the sample gas. For the preparation of the formaldehyde samples using the dilution apparatus, the venturi mixer is situated in between the sampling tube (B) and the bubblers (C).

To aid in pushing air through the bubblers, a second pump is used to create a slight negative pressure drop on the outlet end of the bubblers. The pressure and flow rate of the diluted sample is measured by an open ended mercury manometer (D) and a 1 l bubble meter (E). The 1 l bubble meter was calibrated volumetrically. A series of ground glass three-way stopcocks (F) direct the flow of air through the dilution apparatus.

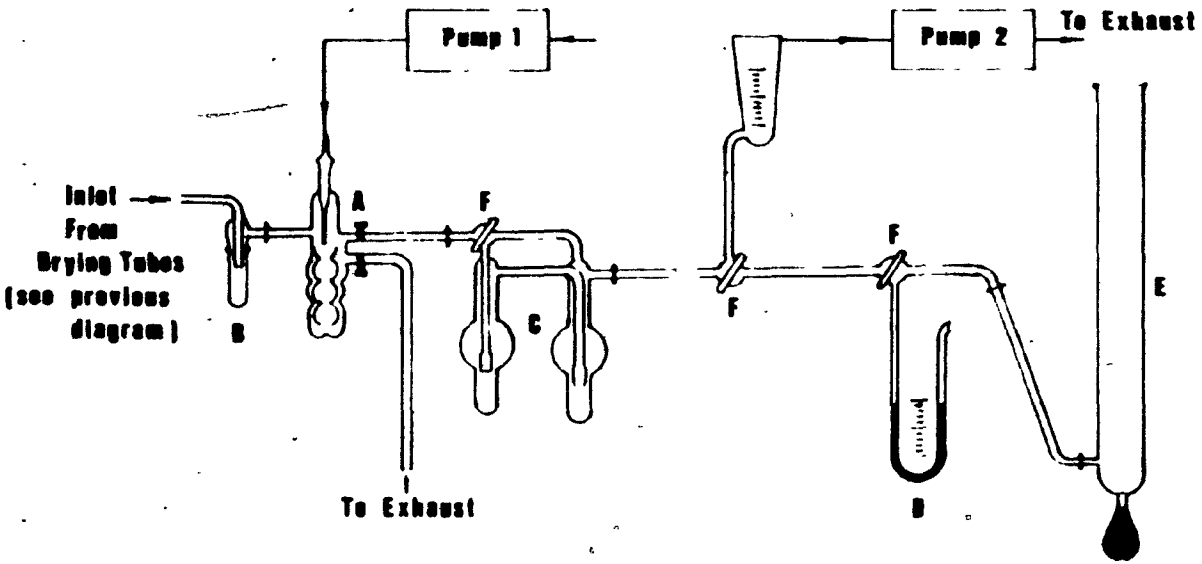


Figure 9. Schematic diagram of the sampling train readied for the dilution experiment.

Procedure

Standardization of the final version of the apparatus included several tests. Weight loss with respect to time tests were preformed to observe whether weight loss was linear with time. The variation in weight loss with respect to the flow rate of air was also studied and reported. The effect of pressure on the sublimation rate of the pellet was measured to study the effect of varying the air pressure above the pellet. The final standardization test involved measuring weight loss as a function of temperature.

After the apparatus had been quantified, the collection efficiency of the trapping solution (1% aqueous sodium bisulfite) for formaldehyde in air at low concentrations was studied via LTL. This was also done as a verification for the weight loss experiments at higher concentrations where the collection efficiency has already been established (36,37). The collection solutions were developed colorimetrically and their absorbances measured on a Perkin Elmer 552 spectrophotometer.

Part 3 DISCUSSION

Part 3A: Development of the Sampling System

At the outset of the experiments concerning the development of a formaldehyde sampling system, there was very little available in the way of literature concerning actual development of such a system. What was gathered from the literature (49) was the concept of producing a gas which could be evaluated by an accepted technique, and then diluted to a usuable concentration for standardization purposes.

The initial step in developing the system was to choose a source of formaldehyde. Formaldehyde can be found in various materials. Formalin solutions, used in storage of animal tissues, contain 37% by weight formaldehyde in an aqueous medium. Urea-formaldehyde contains free formaldehyde as well as formaldehyde links in the urea polymer chain. However having decided to use gravimetric techniques to verify the formaldehyde concentrations in air, these sources were deemed unacceptable for use as there were too many impurities present that could affect the results. The purest form of formaldehyde was chosen for the ensuing experiments.

Poly(oxymethylene); poly(formaldehyde)with the monomeric unit $+ CH_2O +$ can be produced from formaldehyde. This polymer can have a variety of end groups such as H and OH, H and OCH_3 ,and CH_3 and OCH_3.

The formaldehyde oligomer with 6 - 10 monomeric units which has the end groups H and OH is known as paraformaldehyde. Amorphous paraformaldehyde $H(OCH_2)_nOH$ which is produced spontaneously in aqueous formaldehyde solutions, depolymerises to formaldehyde at 180 -200°C (50,51).

Without previous knowledge of the behavior of paraformaldehyde (ie. sublimation rate below it's depolymerization temperature), experimentally it was difficult to determine what type and size of flasks were necessary for producing ppm and lower formaldehyde concentrations in air. Furthermore since it was unknown as to the relationship between formaldehyde sublimed and paraformaldehyde present, the amount of paraformaldehyde to be used per experiment was at first chosen arbitrarily. The original experiments consisted of placing approximately one and a half grams of paraformaldehyde in a fifty milliliter round bottom flask (A) and connecting this flask to a system of tygon tubing (B), a compressed air cylinder (C), and a one liter bubbler flask (D), and a bubble meter (E).

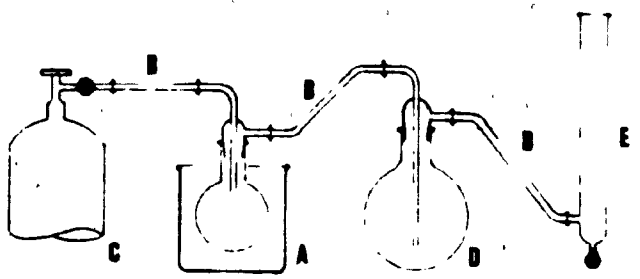


Figure 10. Original sampling device.

This type of arrangement was found to be totally inadequate for producing any concentrations lower than in the parts per thousand region.

The first modification to the experiment was thus to reduce the amount of surface area of paraformaldehyde available to the air stream. A smaller flask of approxiamately 5 ml in volume replaced the 50 ml round bottom flask. The decrease in surface area did indeed decrease the rate of formaldehyde sublimation however only by one order of magnitude.

It was at this stage of development that some of the first experimental characterizations of paraformaldehyde sublimation were made. An experiment was run to determine the sublimation rate versus temperature. The results are shown in table IX and figure 11. A second experiment was done to determine whether the collection efficiency of aqueous sodium bisulfite was as high as reported (50). The temperature dependence experiment showed that paraformaldehyde started to break down quite readily at temperatures above 45° C. To determine the efficiency of the bisulfite solution, the solutions from both bubblers were mixed together and aliquots taken from the combined mixture. The results are shown below in table X. Within experimental error the results are consistant with what has been reported.

As mentioned in Part 2 of the thesis the reason for developing the formaldehyde sampling system was to produce

Table IX

Variation in weight loss with respect to temperature.

TEMPERATURE (°C)	AVERAGE WEIGHT LOSS* (grams)	CONCENTRATION OF FORMALDEHYDE IN AIR (ppm_m)
84	.0310	4260
74	.0135	1860
64	.0092	1260
54	.0063	866
44	.0026	358
34	.0020	275
24	.0013	179

Parameters

Air flow rate - 187.5 ml min^{-1}

Aeration time - 30 minutes

Air pressure ≈ 790 torr

* average values calculated from an average of 3 runs

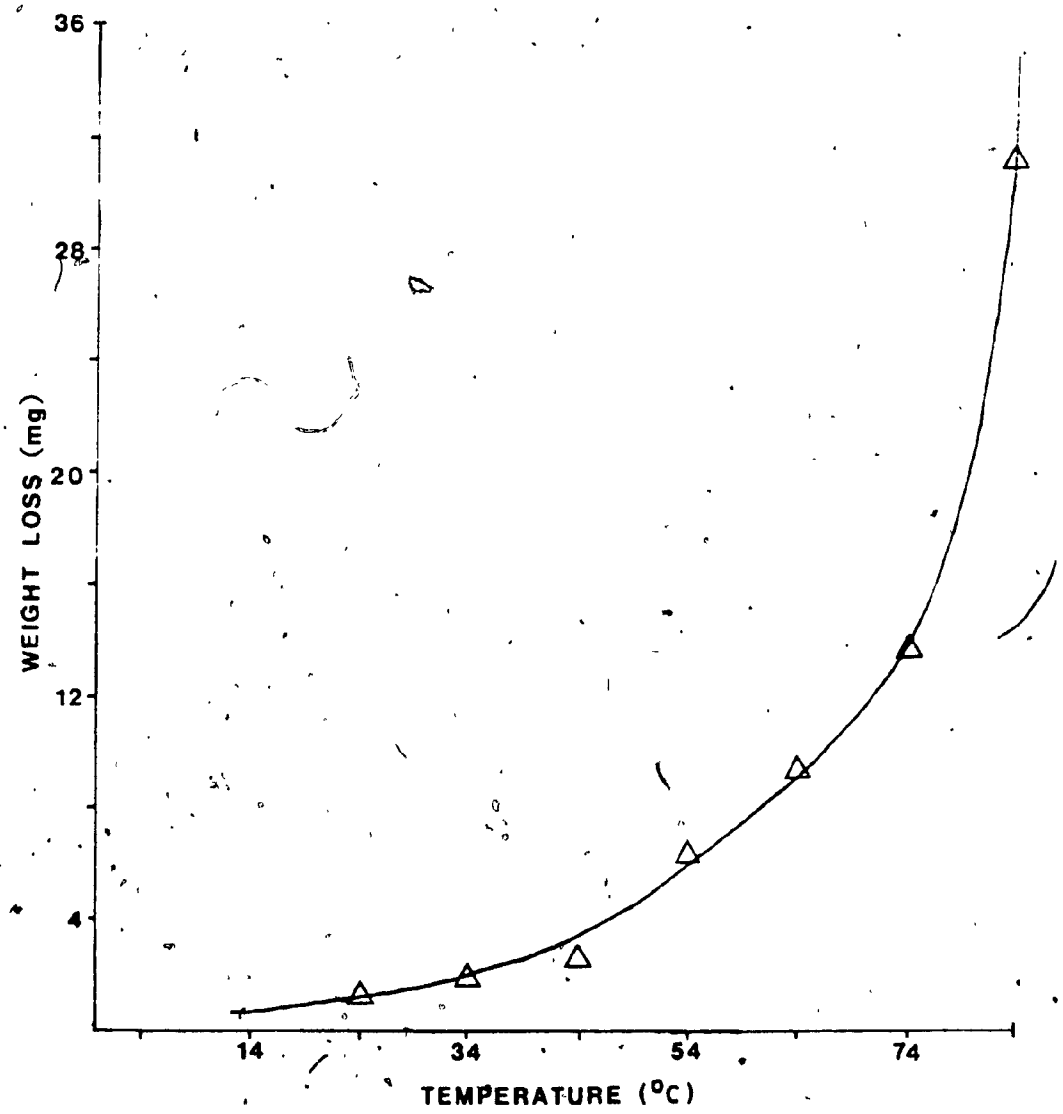


Figure 11. Plot of temperature versus weight loss using paraformaldehyde powder. The aeration time was 30 minutes.

Table X

Collection efficiency of the trapping solution experiment.

RUN	WEIGHT LOSS (gms)	CALCULATED CONCENTRATION OF CH_2O ($\times 10^{-3}$ M)	ABSORBANCE	ACTUAL CONCENTRATION ($\times 10^{-3}$ M)	COLLECTION EFFICIENCY (%)
1	.0359	1.19	.824	1.30	108
2	.0336	1.11	.817	1.29	115
3	.0361	1.20	.693	1.09	91
4	.0420	1.39	.830	1.31	93
5	.0369	1.22	.667	1.05	86
6	.0244	0.81	.471	0.74	92
7	.0219	0.73	.495	0.78	107
8	.0204	0.68	.459	0.74	106
9	.0258	0.86	.593	0.94	109
10	.0302	1.00	.496	0.78	78
11	.0321	1.06	.647	1.02	95

average: 98 ± 11%

Parameters

temperature of sampling flask - 92° C

aeration time - 30 minutes

air flow rate - 187.5 ml min^{-1}

air pressure = 790 torr

(absorbance measurement) - 600 nm

standard formaldehyde in air samples for analysis with the LTL spectrometer. To do so, a further decrease of two orders in magnitude in formaldehyde concentration in the samples was necessary before dilution to the ppb region could be realized. Not only would dilution of samples, with concentrations in the range of 100 ppm, down to the ppb region introduce large errors, the actual dilution would require vast amounts of air to dilute the prepared sample.

To effect a decrease in formaldehyde concentration, major changes were required in the procedure and system. Up until this point an analytical balance (Sartorius Corp.) with detection of 0.1 mg capabilities had been used for the gravimetric measurements. Decreasing the weight loss of paraformaldehyde required an increase in gravimetric sensitivity. Thus a microbalance (Mettler Corp. #M5) was incorporated into the experiments. The change in balances created a problem. The weighing of the sampling flask had been a relatively simple operation with the large pan available in the analytical balance. The microbalance had a much finer and delicate pan assembly and a total weight capacity of 20 grams. The sampling flask was found to be much too cumbersome and awkward for use in the microbalance. Various sized vials were experimented with, unfortunately with little success. Eventually the idea of using a basket arrangement which could fit inside the flask and could also be weighed quite easily, came to mind. To insure that no formaldehyde would be lost in between weighings, thus

affecting the results, the powder was compressed into pellets.

The compressing of the paraformaldehyde into pellets served a dual purpose. As well as preventing random loss during transfer of the pellet to and from the microbalance, it was thought that the tighter packing would inhibit formaldehyde sublimation thus decreasing the formaldehyde concentration in air.

To form the pellets, it was found experimentally that a minimum pressure of 1000 psi was required to produce pellets that would not crumble through useage.

With all the above experiments, it had been incorrectly assumed that the paraformaldehyde was sufficiently pure, with methanol and water impurities being minimal, for use in the system. Since the collection efficiency had already been shown to be approximately 98 percent, it was believed that the loss in weight of paraformaldehyde was due to formaldehyde sublimation. On this premise, the system was upgraded with tygon tubing etc. being replaced with an all glass component system. O-ring joints were placed in between various components (i.e. sampling tube, bubblers, manometer, etc...) to allow for facile adjustments to meet the various experimental requirements.

Using the all-glass system, standardization experiments were run on the formaldehyde pellets in an attempt to monitor their behavior. Experiments were run to measure weight loss with respect to temperature, time, flow rate,

and air pressure. The results are shown in tables XI, XII, XIII, XIV, and figures 12, 13,and 14. Once all the experiments had been run, a second collection experiment was run to ensure that the collection efficiency of the 20 ml bubblers was as high as the 100 ml bubblers previously used. Disappointingly the collection efficiency dropped to approximately thirty percent (see table XV). During the efficiency experiments the solutions in the twin bubblers were analysed separately and it was observed that the concentration of formaldehyde in the second bubbler was consistantly very much lower than in the first. This ruled out the the possibility of formaldehyde managing to pass through the two solutions without being solvated.

Four possible causes for the drop in collection efficiency were considered. The first possible cause was thought to be that the the formaldehyde could be being released as particulate matter rather than as a gas. An experiment was performed in which a "heat tube" was placed in between the sampling tube and the bubblers. The heating tube, which consisted of a glass tube twenty five centimeters long with O-ring connections at either end, surrounded in a heating tape, was regulated to have a temperature gradient with a maximum temperature of approximately 160^{o} C at the middle of the tube. It was thought that if the paraformaldehyde particles were released, they would be vapourized as they passed through the tube.

Table XI

Variation in weight loss with respect to temperature.

TEMPERATURE (°C)	AVERAGE WEIGHT LOSS* (% of total pellet weight)	APPROXIMATE CONCENTRATION OF FORMALDEHYDE IN AIR (ppm_m)
21.5	$.036 \pm .004_{(s)}$	9
31.5	$.044 \pm .002_{(s)}$	10
41.5	$.038 \pm .014_{(s)}$	9
51.5	$.063 \pm .024_{(s)}$	20
61.5	$.192 \pm .033_{(s)}$	50
71.5	$.319 \pm .033_{(s)}$	80
81.5	$.811 \pm .075_{(s)}$	200

Parameters

Average pellet weight - .15 grams

Aeration time - 15 minutes

Air flow rate - 300 ml min^{-1}

Air pressure = ambient

* average values calculated from an average of 5 runs

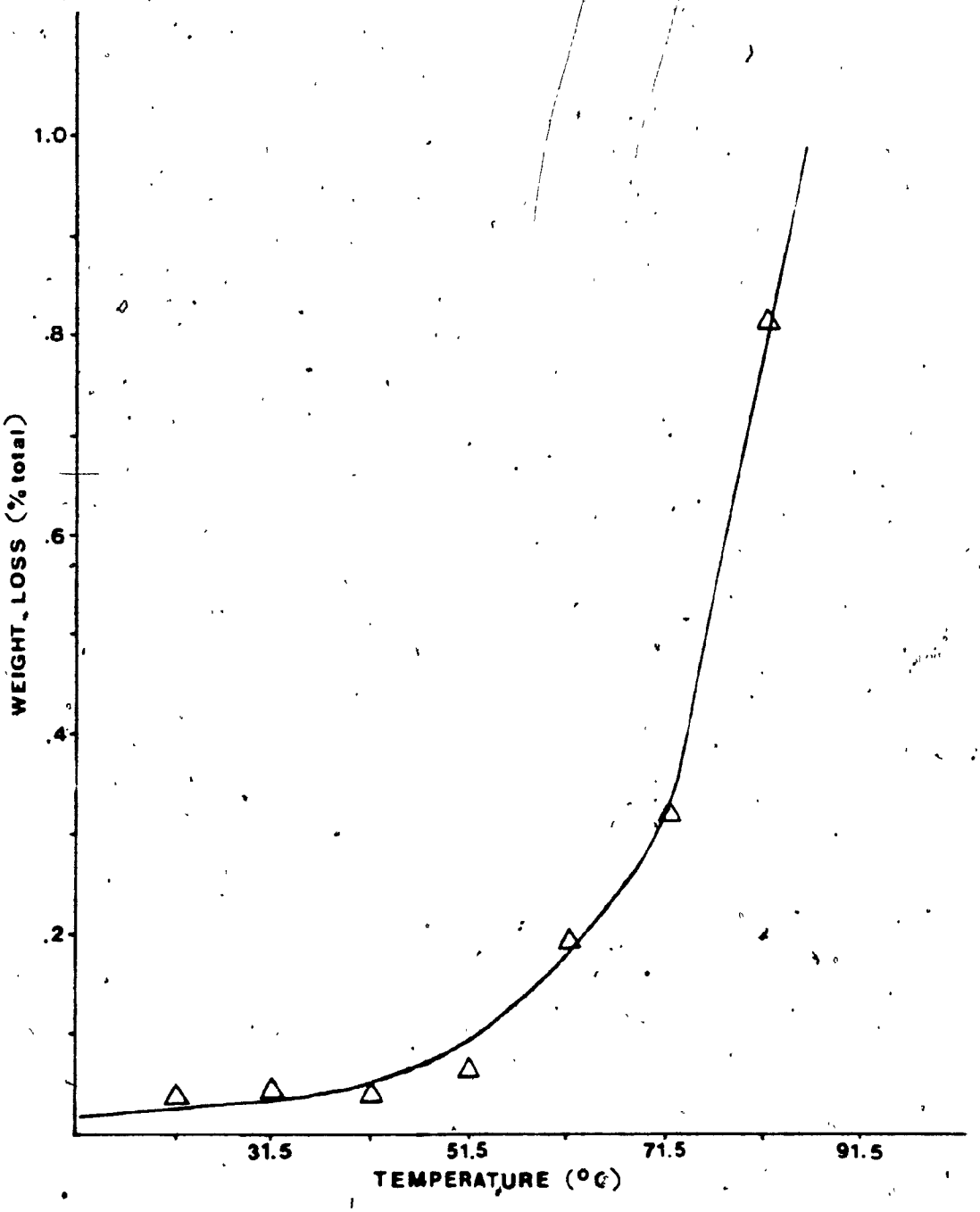


Figure 12. Plot of temperature versus weight loss using paraformaldehyde pellets. The aeration time was 15 minutes.

Table XII

Variation in weight loss with respect to time.

TIME (minutes)	AVERAGE WEIGHT LOSS* (% of total pellet weight)	APPROXIMATE CONCENTRATION OF FORMALDEHYDE IN AIR (ppm_m)
10	$.013 \pm .003_{(s)}$	5
20	$.022 \pm .001_{(s)}$	4
30	$.038 \pm .006_{(s)}$	5
40	$.045 \pm .007_{(s)}$	4
50	$.059 \pm .011_{(s)}$	5
60	$.068 \pm .019_{(s)}$	4

Parameters

Average pellet weight - .15 grams

Air flow rate - 300 ml min^{-1}

Temperature - 21.5° C

Air pressure = ambient

* average values calculated from an average of 5 runs

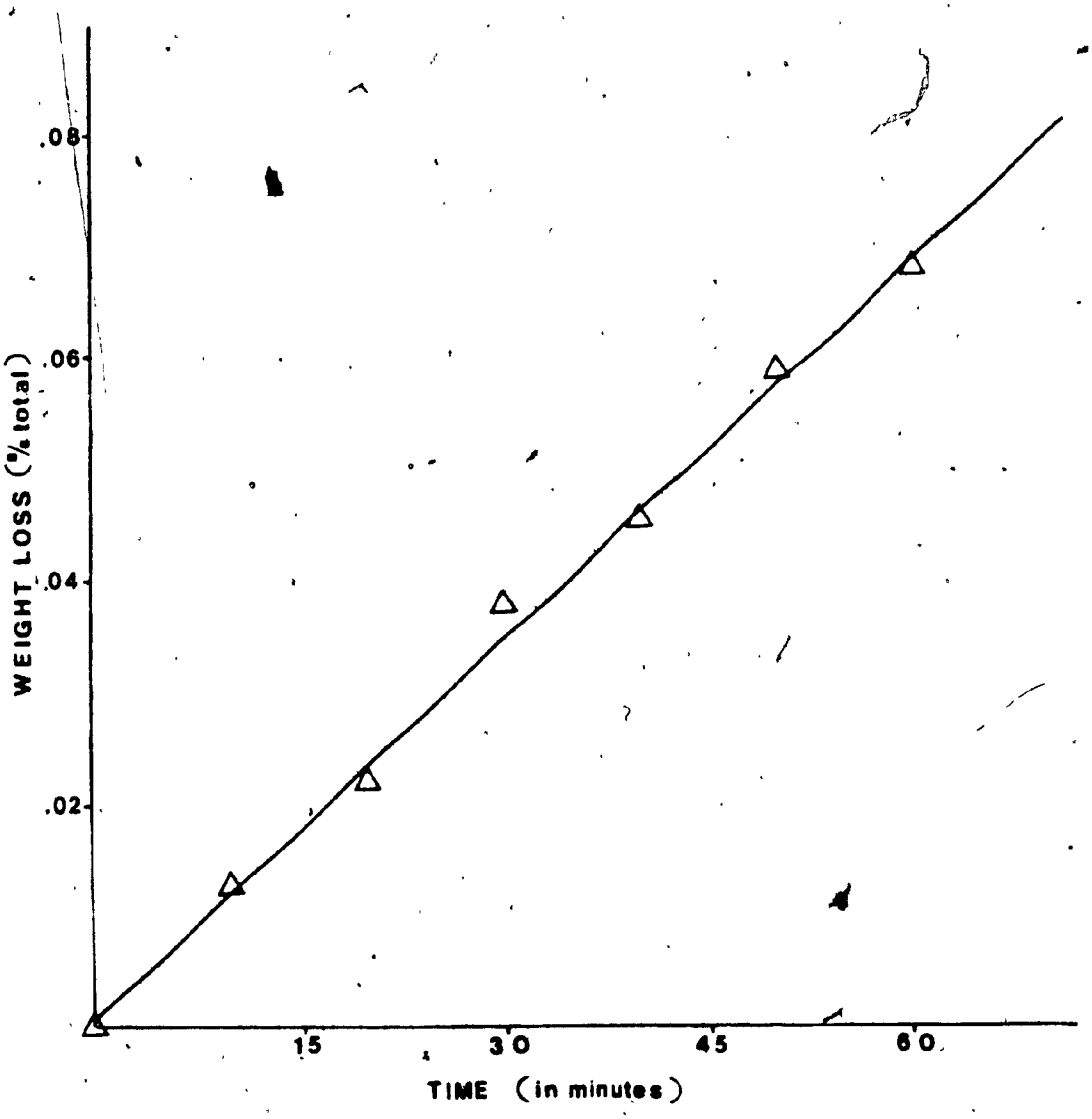


Figure 13. Plot of time versus weight loss using paraformaldehyde pellets.

Table XIII

Variation in weight loss with respect to flow rate.

FLOW RATE (ml/min.)	AVERAGE WEIGHT LOSS* (% of total pellet weight)	APPROXIMATE CONCENTRATION OF FORMALDEHYDE IN AIR (ppm_m)
0	$.010 \pm .004_{(s)}$	-
100	$.039 \pm .005_{(s)}$	15
200	$.039 \pm .006_{(s)}$	8
300	$.032 \pm .005_{(s)}$	4
400	$.044 \pm .005_{(s)}$	4
500	$.044 \pm .004_{(s)}$	3

Parameters

Average pellet weight - .15 grams

Aeration time - 30 minutes

Temperature - 21.5° C

Air pressure = ambient

* average values calculated from an average of 5 runs

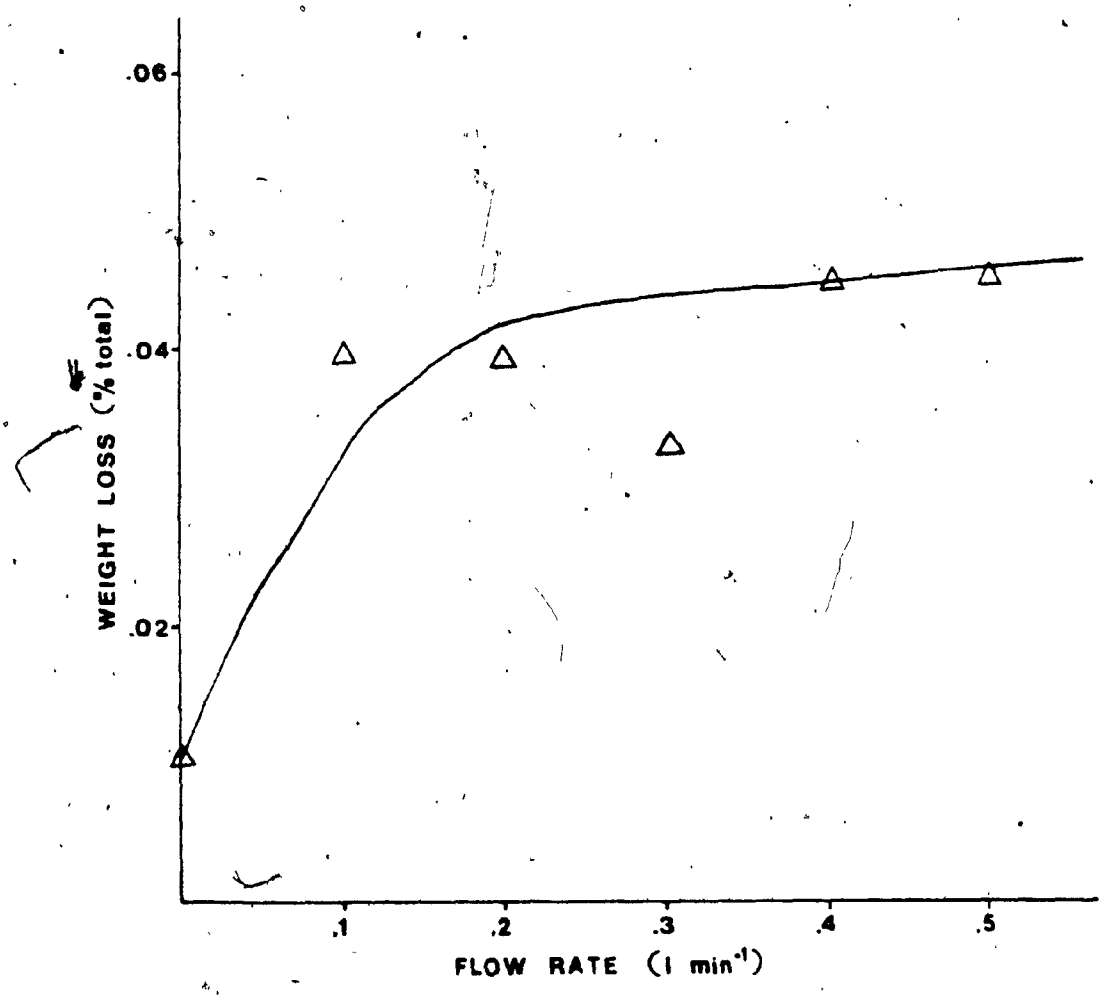


Figure 14. Plot of flow rate versus weight loss using paraformaldehyde pellets.

Table XIV

Variation in weight loss with respect to pressure.

RUN	WEIGHT LOSS ($x10^{-6}$ gm)			
	740 torr	760 torr	740 torr*	770 torr*
1	43	60	34	140
2	79	60	51	65
3	41	29	36	12
4	16	37	42	38
5	0	26	90	102
6	76	49	124	33
7	70	56	--	--
8	70	14	--	--
9	36	20	--	--
10	77	58	--	--
11	65	--	--	--
average	$62 \pm 17_{(s)}$	$41 \pm 18_{(s)}$	$63 \pm 36_{(s)}$	$65 \pm 48_{(s)}$

Parameters

Air flow rate - 300ml min^{-1}

Aeration time - 15 minutes, *30 minutes

Temperature - 21.5° C

* Pellets were dried as specified, before use to remove any impurities.

Table XV

Collection efficiency of the trapping solution.

RUN	WEIGHT LOSS (grams)	ABSORBANCE 1	ABSORBANCE 2	% EFFICIENCY 1	% EFFICIENCY 2	TOTAL % EFFICIENCY
flow rate 500 ml/min.						
1	.000066	---	.006	---	1	---
2	.000035	.058	.004	27	2	29
3	.000043	.064	.027	24	10	34
4	.000100	.070	.007	11	1	12
5	.000086	.088	.016	17	4	21
flow rate 400 ml/min.						
1	.000043	.094	.045	24	15	39
2	.000063	.077	.021	15	5	20
3	.000078	.064	.018	13	5	18
4	.000028	.069	---	40	---	---
5	.000066	.100	.006	25	2	27
flow rate 300 ml/min.						
1	.000061	.096	---	26	---	---
2	.000057	.085	.015	24	6	30
3	.000094	.105	.016	18	4	22
4	.000040	.084	.012	34	6	40
5	.000095	.088	.004	15	1	16
flow rate 200 ml/min.*						
1	.000058	.086	.011	24	3	27
2	.000036	.076	.004	34	2	36
3	.000077	.070	.004	15	1	16
4	.000033	.063	.007	31	3	34
5	.000060	.049	.004	13	1	14
flow rate 200 ml/min.						
1	.000054	.092	.020	28	6	34
2	.000033	.080	.029	39	14	53
3	.000047	.080	.010	28	3	31
4	.000062	.079	.016	21	4	25
5	.000062	.077	---	18	---	---

average: 27 ± 10

Parameters

Temperature - 21.5° C Aeration time - 15 minutes

* samples prepared for analysis day of collection

This experiment yielded no better efficiencies than before so the particulate matter explanation was discarded.

A second possibility contemplated was that initially in each run an amount of formaldehyde once released as a gas was being adsorbed on the glass walls of the system. After fitting the bubblers with a bypass and wrapping heating tape around the glassware, an experiment was performed in which the system was run for thirty minutes with the air bypassing the bubblers. This was done in an attempt to reach a steady state equilibrium between the formaldehyde in air and that adsorbed on the glass wall. After the 30 minute equilibrating period the air flow was directed through the bubblers. The results again indicated no improvement.

The third possible cause considered, was leakage of formaldehyde and air through the ground glass and O-ring joints. This was ruled out however since the system was operated at a relatively high flow rate and a slightly negative pressure relative to atmospheric pressure.

The final possibility was not immediately obvious. As previously mentioned, since the first collection efficiency experiment had shown a 98 % efficiency, the paraformaldehyde had been considered fairly pure. However there were two very important differences between the first efficiency experiment and the second. The first experiment was done at an elevated temperature of 92° C while the second was done at room temperature (21° C). The second difference was that the weight losses in the first experiment were approximately two percent of the total

weight of paraformaldehyde present, whereas the value was only approximately 2×10^{-2} percent in the second, due to the nature of the pellet. Even if methanol and water impurities existed in minute concentrations, since their heats of vapourization are lower than the depolymerization heat of paraformaldehyde, they would be expected to be emitted before the formaldehyde. When dealing with a limited weight loss with respect to the total weight it would therefore be expected that these impurities would be a major portion of the material weight loss. Furthermore the temperature experiments had already shown that the rate of formaldehyde sublimation increased greatly at temperatures above 45° C. Thus while in the first efficiency experiment, formaldehyde was the majority of the material sublimed, in the second due to the conditions set, the impurities were concluded to be responsible for the majority of the weight loss.

To prove this explanation the system was once more modified. The basket used for carrying the paraformaldehyde pellets to and from the microbalance was replaced with the ground glass minature flask which was discussed in the experimental section. The flask was used to reduce the risk of water being absorbed by the pellet, before the pellet could be weighed, to a minimum. Para formaldehyde was dried for two hours at 120° C under vacuum in a vacuum-oven, to remove the water and methanol. The dried paraformaldehyde was then made into pellets which

were dried for an additional fifteen minutes under the same conditions. After drying the pellets, the collection efficiency experiment was once again run. The results are shown in table XVI.

The collection efficiency was found to be once more as high as the accepted value. There was however, a difference between the experimental deviation and the expected deviation of ± 5% (36). This increase from 5 to 22 % is readily explained by a 5 to 10 % increase due to deviations in the gravimetric analysis as well as another 10 to 12 % due to the composition of the pellet. Although the paraformaldehyde was dried for over two hours before use, there was no method to verify the purity (or lack of) of the powder. An attempt was made to dry the paraformaldehyde for a longer period of time. Unfortunately doing so caused a change in the paraformaldehyde as well as removing the impurities. All that remained was a residue of paraformaldehyde which did not exhibit any noticeable weight loss during subsequent experiments.

It is believed that drying the paraformaldehyde for an extended period of time at 120° C caused the shorter length polymer molecules to depolymerize into free formaldehyde thus leaving a residue of the longer length chains behind. This residue was then not susceptible to further depolymerization at room temperature, or it depolymerized at a much slower rate which was not detected.

To elaborate on the increase due to gravimetric errors, the average total weight loss for all the runs during the last collection efficiency experiment was approximately 40 micrograms. Since each weight loss determination contained an inherent ± 4 microgram error, the average error introduced would be roughly ten percent.

The lack of precision on the part of the sampling system in the production of formaldehyde gas amply demonstrates the usefulness of permeation tubes.

Table XVI

Collection efficiency of the trapping solution.

RUN	WEIGHT LOSS (grams)	ABSORBANCE 1	ABSORBANCE 2	COLLECTION EFFICIENCY (%)
1	.000018	.148	.003	136
2	.000027	.137	.001	82
3	.000028	.133	.003	78
4	.000046	.174	.006	63
5	.000053	.340	.001	105
6	.000060	.225	.042	72
7	.000042	.222	.025	96
8	.000008	.050	.003	106
9	.000033	.105	.023	63
10	.000027	.135	.023	95
11	.000043	.256	.037	111
12	.000125	.633	.027	86
13	.000091	.691	.036	130
14	.000109	.425	.016	66
15	.000070	.372	.024	92

average: 92 ± 22

Parameters

Air flow rate - 500 ml $min.^{-1}$

Aeration time - 30 minutes

Temperature - 30,40,& 50° C

Air pressure = ambient

Part 3B: Permeation Tubes

Permeation tubes have come into popular use as sources for production of standard gas samples for trace analysis in recent years. When used in conjunction with a temperature regulated flow system they are reported to produce accurately known samples with deviations as small as 3 % (47). The construction of the permeation tubes is quite simple in design. The tube is made of teflon and is cut to length depending on the desired permeation rate of sample. Once a quantity of standard sample has been placed in the tube the ends are sealed with teflon plugs.

Commercially sold tubes are normally pre-conditioned and calibrated for permeation rate before being sold. AID (Analytical Instrument Development Inc.) has very recently introduced a permeation tube to the market which is filled with paraformaldehyde. The literature available on the permeation tubes specifies that "proprietary" selected and treated paraformaldehyde is used in the construction. Once the tube is constructed it is allowed to stabilize for a period of a week before the permeation rate at 70° C and 100° C is measured gravimetrically. Providing that during use the temperature around the tube is controlled to within 0.1° C, the permeation rate of formaldehyde will remain constant to within a 3 % standard deviation.

AID also offers temperature controlled flow systems that are designed to accomodate the permeation tubes.

Sample preparation flow rates normally range in between 50 to 150 $ml\ min.^{-1}$ for most models. This corresponds to production of samples of 470 ppb to 150 ppb. The prepared gas can be further diluted by a flow of .1 to 1.5 $l\ min^{-1}$ of dilutant air. This would create samples in the low ppb region.

It was initially hoped that a system could be built that could produce samples in the ppb region that would not require further dilution. This aspiration was soon replaced simply by the desire to build a system which could compete with permeation tubes and at the same time be less restricted (i.e. require less exacting temperature and tube specifications).

Part 3C: Permeation Tubes VS. Paraformaldehyde Pellets

Using the results obtained in this study, one can understand the workings of the permeation tube. The reason for the necessity of setting and controlling the temperature around the permeation tube at exactly 70° C or 100° C becomes clear when observing the temperature versus sublimation rate in figure 12. The slope of the curve at 70° C is such that any deviation in either direction can cause a substantial drop or increase in formaldehyde sublimed. Since the permeation rate is the limiting value for formaldehyde evolution, it is also obviously sensitivly temperature dependent.

The need for purification of the paraformaldehyde to

remove impurities was noted in this study. The required one week stabilization period for the tubes is also obviously implimented as a means of allowing the more volatile impurities to escape from the tube.

In the final weight loss versus time, temperature, and flow rate experiments the paraformaldehyde exhibited a rather large variation in weight loss. The results are to be found in tables XVII, XVIII, and XIX and figures 15-17. The high variance in weight loss is to be expected when dealing with non-uniform substances such as polymer mixtures. The true value of the permeation tube comes to light in this context. By using as high a temperature as 70°, an abundance of free formaldehyde in the gaseous state is produced, however the rate of emission of formaldehyde from the tube is limited by it's permeation rate through the teflon. Thus a non-uniform situation is carefully controlled which allows for the low deviations as reported by AID. Note however, the very rigid conditions that must be observed.

In the final analysis it is obvious that using the elaborate temperature controlled flow system, the permeation tube is the superior method for formaldehyde in air production. However providing that all that is required by the operator is a sample range, i.e. ppm versus 100ppb, 100ppb versus 10 ppb, the simple system described in this thesis is an adequate replacement for the more costly and elaborate permeation tube system.

Table XVII

Variation in weight loss with respect to temperature.

TEMPERATURE (°C)	AVERAGE WEIGHT LOSS* (% of total pellet weight)	APPROXIMATE CONCENTRATION OF FORMALDEHYDE IN AIR (ppm_m)
22	$.052 \pm .015_{(s)}$	1
30	$.061 \pm .028_{(s)}$	2
40	$.096 \pm .035_{(s)}$	2
50	$.188 \pm .040_{(s)}$	5
60	$.223 \pm .031_{(s)}$	6
70	$.585 \pm .089_{(s)}$	15
80	$1.162 \pm .250_{(s)}$	30

Parameters

Average pellet weight - .05 grams

Aeration time - 30 minutes

Air flow rate - 500 ml min^{-1}

Air pressure ≈ ambient

* average values calculated from an average of 4 runs.

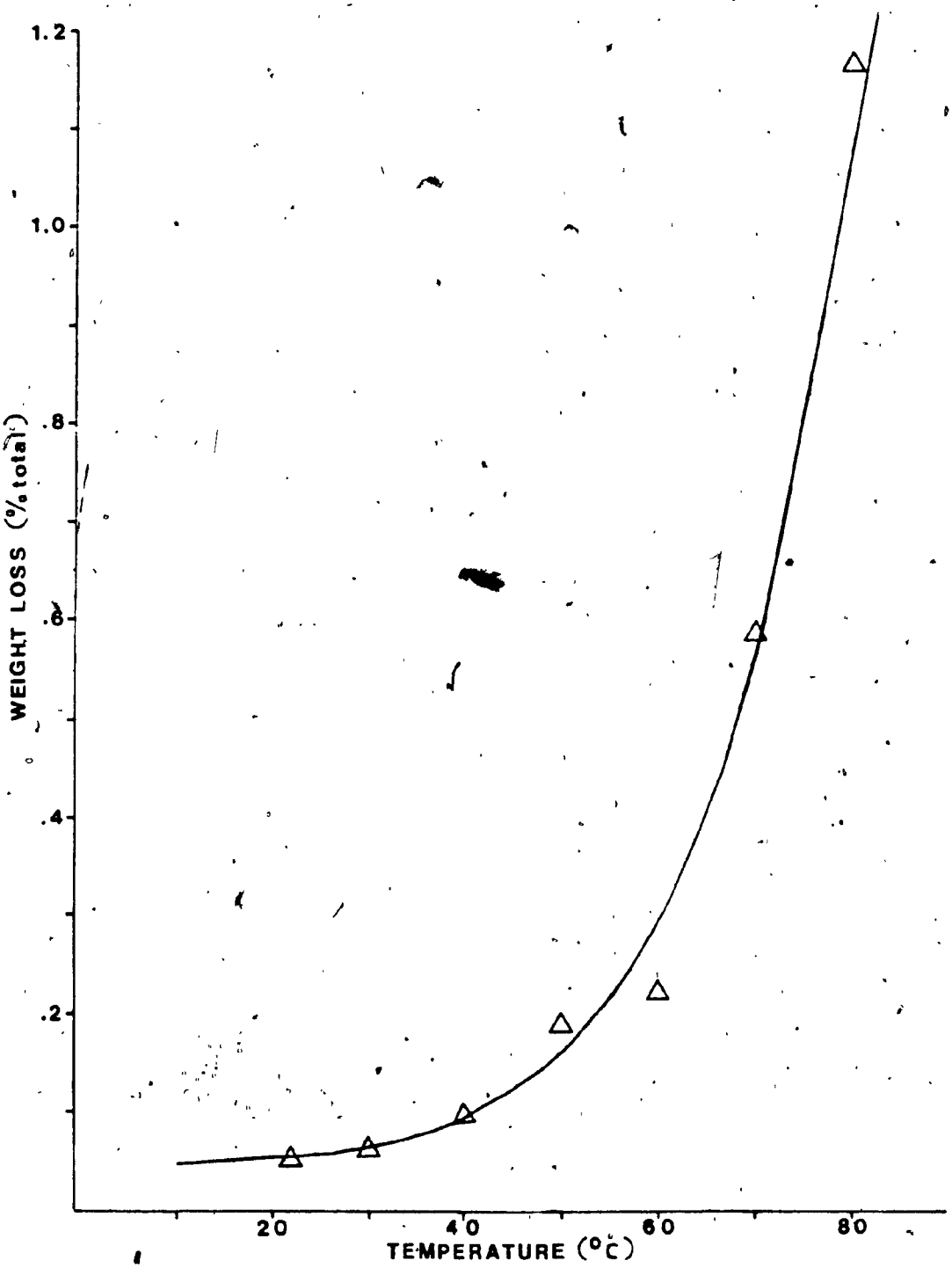


Figure 15. Plot of temperature versus weight loss using purified paraformaldehyde pellets. The aeration time was 30 minutes.

Table XVIII

Variation in weight loss with respect to time.

TIME (minutes)	AVERAGE WEIGHT LOSS* (% of total pellet weight)	APPROXIMATE CONCENTRATION OF FORMALDEHYDE IN AIR (ppm_m)
30	$.052 \pm .015_{(s)}$	1
40	$.083 \pm .017_{(s)}$	2
50	$.099 \pm .015_{(s)}$	2
60	$.114 \pm .049_{(s)}$	1
70	$.127 \pm .068_{(s)}$	1

Parameters

Average pellet weight - .05 grams

Air flow rate - 500 ml min^{-1}

Temperature - 22° C

Air pressure = ambient

* average values calculated from an average of 4 runs

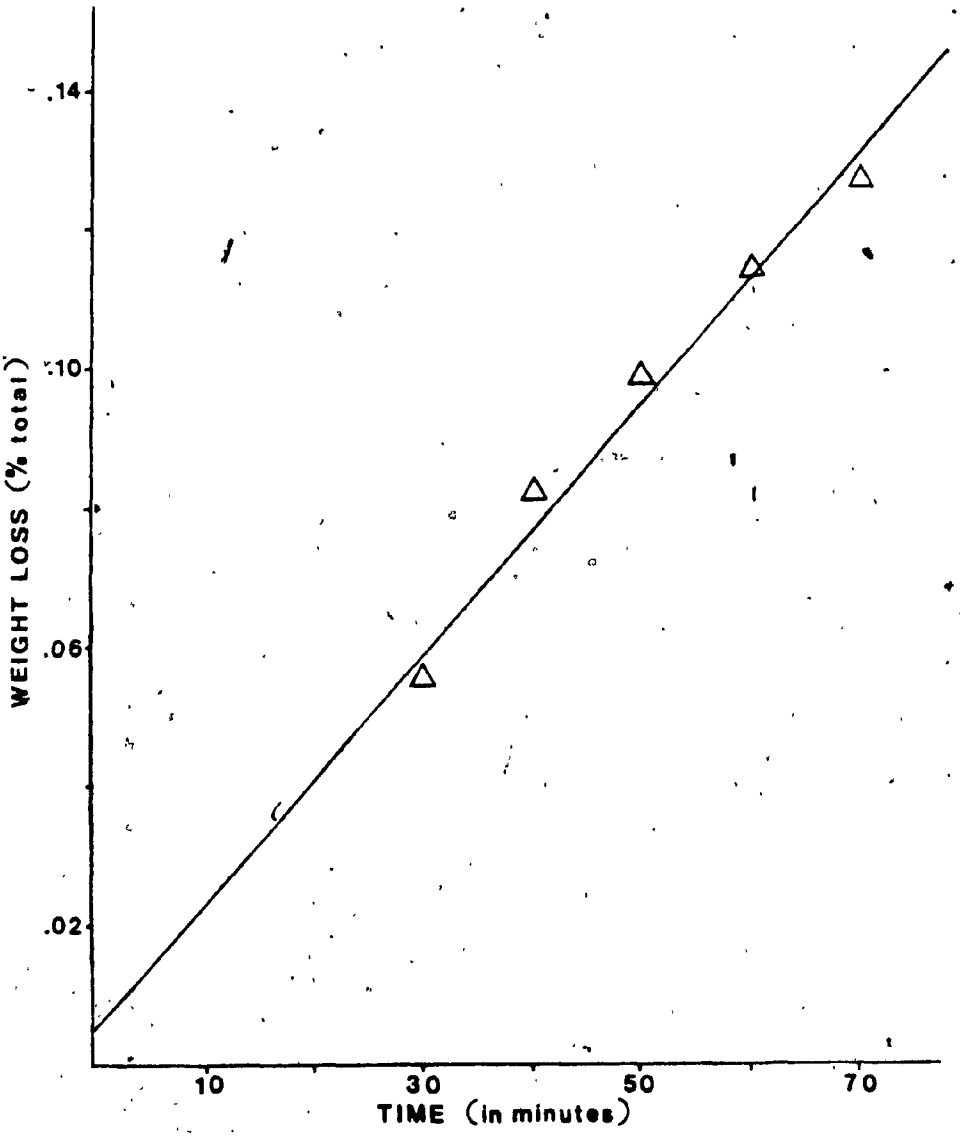


Figure 16. Plot of time versus weight loss using purified paraformaldehyde pellets.

Table XIX

Variation in weight loss with respect to flow rate.

FLOW RATE (ml/min.)	AVERAGE WEIGHT LOSS* (% of total pellet weight)	APPROXIMATE CONCENTRATION OF FORMALDEHYDE IN AIR (ppm_m)
100	$.022 \pm .011_{(s)}$	3
200	$.038 \pm .013_{(s)}$	2
300	$.057 \pm .018_{(s)}$	2
400	$.047 \pm .022_{(s)}$	2
500	$.090 \pm .016_{(s)}$	2

Parameters

Average pellet weight - .066 grams

Aeration time - 30 minutes

Temperature - 22° C

Air pressure = ambient

* average values calculated from an average of 3 runs

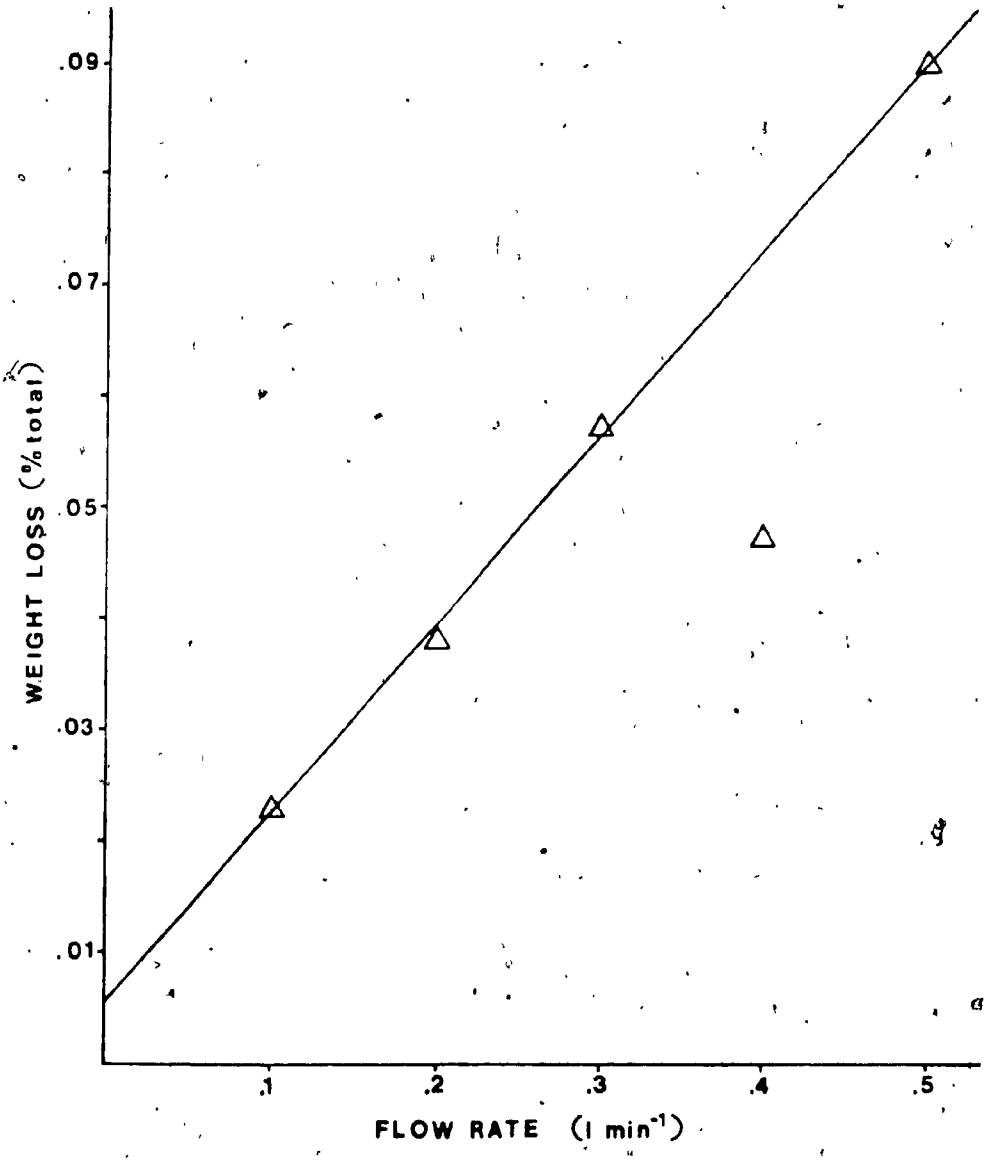


Figure 17. Plot of flow rate versus weight loss using purified paraformaldehyde pellets.

Part 3D: Sample Production for LTL Analysis

Although the results from the system and pellet characteristization experiments were somewhat dissapointing, they do show that the system is functional and capable of fulfilling it's ultimate purpose. That is, to demonstrate that the LTL analysis of formaldehyde in air can detect ppb concentrations of formaldehyde in small sample volumes.

Due to the lack of definite pellet composition, it is not feasible to calibrate the LTL analysis using gas samples produced by the pellet system at the same level of precision as the measurement can be made . This is not essential however. Since the collection efficiency of aqueous sodium bisulfite has been established for concentrations in the low and sub ppm region, there is no reason to believe that the collection efficiency would decrease if the concentration of formaldehyde is lowered. In fact one would expect it to increase if not remaining the same.

Using the paraformaldehyde pellet system, gas samples were produced and analysed by LTL. The results can be seen in table XX.

Zero concentration samples were made by running the system without a pellet present. Along with the air samples, triplicate blanks were also run. The blanks, as before, consisted of water, chromotropic acid, and sulfuric

acid.

A comparison of the zero concentration samples "air blanks" against the triplicate blanks clearly indicates that interfering species were present in the laboratory air which was used to dilute the gas samples. This caused a negative interference. Among those chemical substances that can cause such decreases, which are common to the laboratory environment, are phenols, ethanol, and other higher molecular weight alcohols, olefins as well as other aromatic hydrocarbons (36). Purifying the dilution air before use would perhaps have reduced the negative interference and thus the difference between the two types of blanks. During an analysis however, one should always attempt to compare samples against references under similar conditions. This would dictate the use of the air blank as the reference in any case.

With the zero concentration samples as reference, an increase in signal proportional to the increase in formaldehyde concentration was observed. As is to be expected the deviation was quite large as is evident in figure 18. It should be noted that some difficulties were encountered with the dye laser as well as the photodiode detector during experimentation, which could have compounded the observed error. Since it was not possible to predict when the situation could be rectified, it was thought best that the thesis be written without the benefit of repeating the experiment under ideal conditions.

Table XX

L T L analysis of prepared formaldehyde gas samples.

RUN	PELLET WEIGHT LOSS (grams)	TOTAL AIR MASS (grams)	FORMALDEHYDE CONCENTRATION ($p.p.m_m$)	TRAPPING* SOLUTION CONCENTRATION (molar)	$\Delta I/I_\infty$
1	0	210	0	---	.174
2	0	210	0	---	.163
3	0	207	0	---	.173
4	4×10^{-6}	259	16	1.4×10^{-7}	.194
5	4×10^{-6}	219	18	1.7×10^{-7}	.200
6	8×10^{-6}	199	40	3.7×10^{-7}	.274
7	30×10^{-6}	220	138	1.3×10^{-6}	.258
8	34×10^{-6}	219	155	1.4×10^{-6}	.219
9	43×10^{-6}	205	210	1.9×10^{-6}	.224
10	50×10^{-6}	203	246	2.3×10^{-6}	.432
blank#1	---	---	---	---	.249
blank#2	---	---	---	---	.301
blank#3	---	---	---	---	.301

Parameters

Volume of sample analysed	= 15 l
Sampling flow rate	- .5 l
Dilution flow rate	- 5 - 10 l min^{-1}
Sample preperation flow rate	- .1 - .5 l min^{-1}
Temperature of system	- 21.5 ^oC
Air pressure in system	= ambient

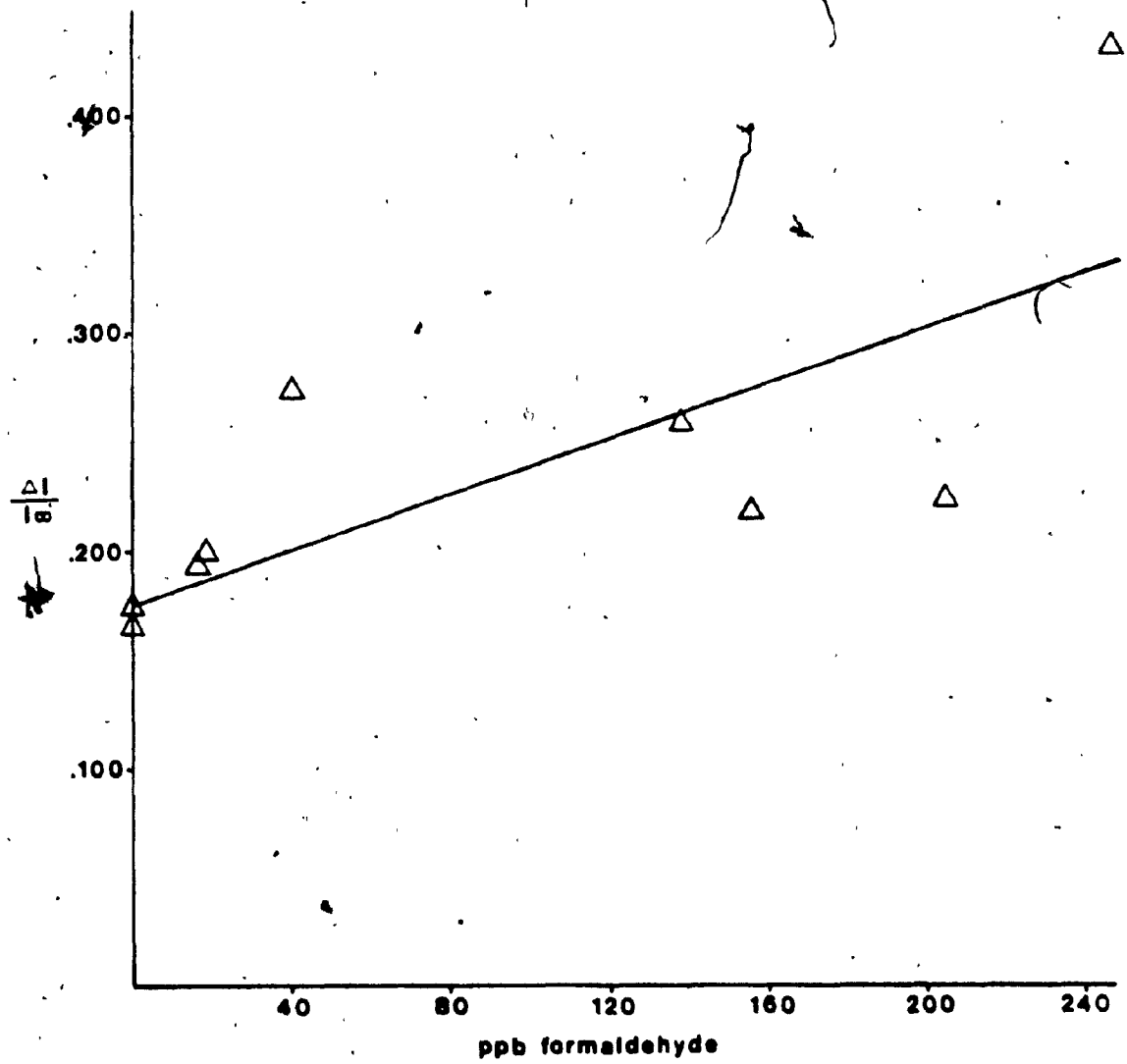


Figure 18. Results from the thermal lens experiment using gaseous formaldehyde samples.

Even with the large errors present, the flow system does demonstrate the feasibility of using LTL to measure ppb concentrations of formaldehyde in air in sample volumes as low as 15 liters. Unfortunately it does not allow the determination of a true detection limit for the LTL though .

Part 3E : Calculation of the Sublimation Rate Constant

As an aside from the main theme of this project, the sublimation rate constant for the formaldehyde pellets was determined using the data from the temperature vs. weight loss experiments. Plotting the log of weight loss per minute against 1/T in degrees Kelvin, the Arrhenius factor A and the "activation energy" Ea were obtained. Using these values in the Arrhenius expression ;

$$k_{sub} = A\ e^{-Ea/RT} \qquad (6)$$

the sublimation constant k_{sub} was evaluated for the range of 20^{o} - 80^{o} C. The deviation in the values in table XXI become more apparent in figure 19. The pellets that were not purified before use (table XI values), understandbly showed a larger variation than the dried pellets.

Table XXI

% WEIGHT LOSS / MINUTE	log (% LOSS MIN^{-1})	TEMPERATURE (kelvin)	$(T)^{-1}$
from table XVII			
.00175	- 2.76	295.0	.00338
.00203	- 2.69	303.0	.00330
.00321	- 2.49	313.0	.00319
.00627	- 2.20	323.0	.00310
.00746	- 2.13	333.0	.00300
.01950	- 1.71	343.0	.00292
.03873	- 1.41	353.0	.00283
from table XI			
.00243	- 2.61	294.5	.00340
.00298	- 2.52	304.5	.00328
.00255	- 2.59	314.5	.00318
.00421	- 2.38	324.5	.00308
.0128	- 1.89	334.5	.00299
.0213	- 1.67	344.5	.00290
.0541	- 1.27	354.5	.00282

Parameters

Average pellet weight	- .05 grams
Flow rate	- 500 ml/min
Air pressure	= ambient
Intercept (a)	- 5.23
Slope (b)	- 2387 K
Correlation coefficient	- .9469

$$k_{sub} = A\, e^{-Ea/RT}$$

intercept (a) = 5.23 = log (A)

$\therefore A = 1.7 \times 10^5$ %loss min^{-1}

slope (b) = - 2387 K = -Ea/2.303 R

$\therefore$ Ea = 46 kJ mole^{-1}

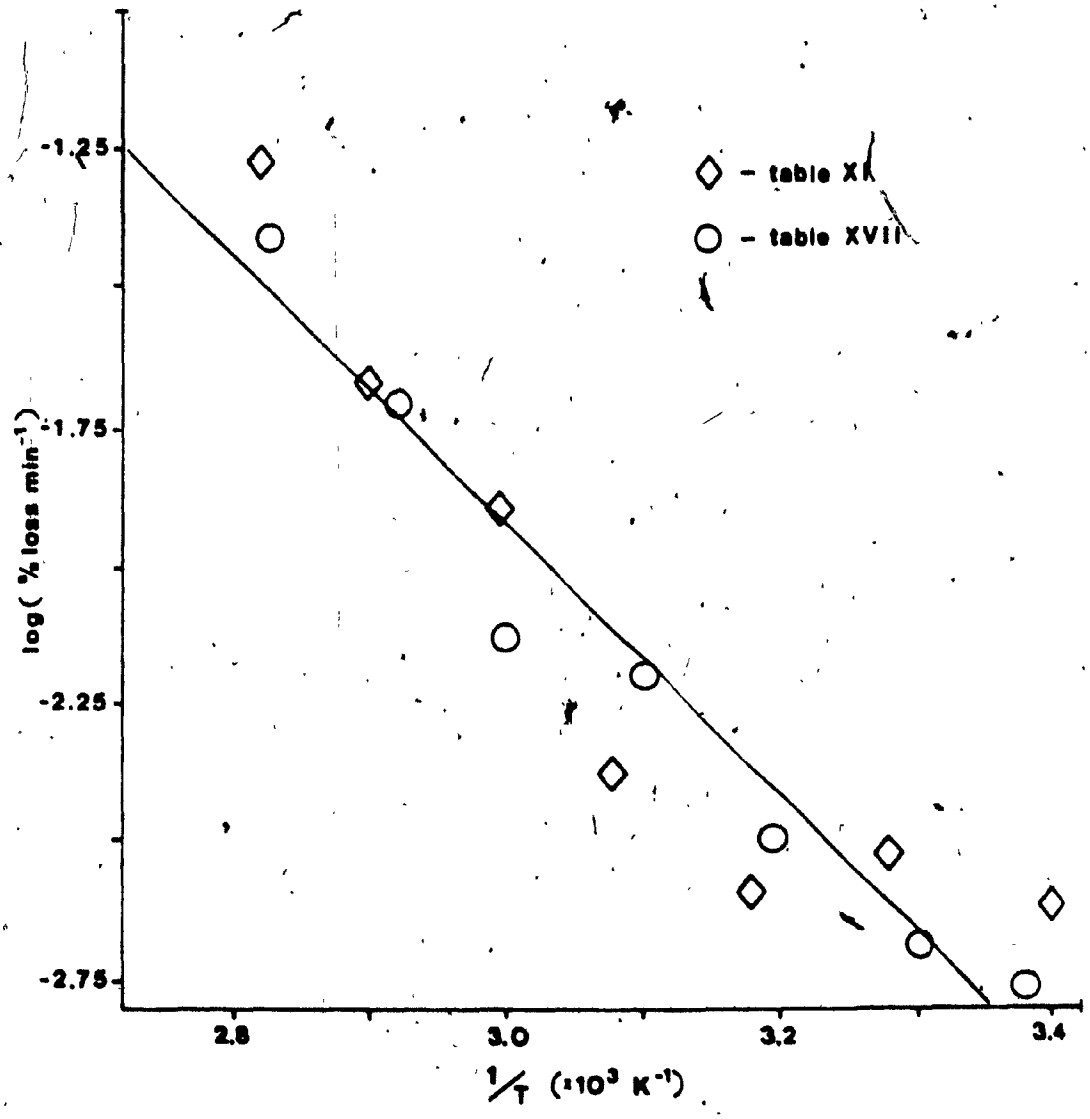


Figure 19. Determination of the rate constant for the sublimation of formaldehyde.

Table XXII lists the various k values for the range of temperatures used in the experiments.

Table XXII

TEMPERATURE (° C)	k_{sub} (% weight loss min^{-1})
20	1.1×10^{-3}
30	2.0×10^{-3}
40	3.6×10^{-3}
50	6.2×10^{-3}
60	10.3×10^{-3}
70	16.8×10^{-3}
80	26.5×10^{-3}

Part 3F : Construction of a LTL spectrometer

At the present moment no commercial design exists for a LTL spectromenter. It has been shown that LTL is capable of competing with GC and HPLC methods of formaldehyde analysis. Until a commercial instrument is accessible to the average analyst at a competitive cost however, chromotography will continue to be the best method of analysis.

As an epilogue to this project, a design is proposed for the construction of a LTL spectrometer. When suggesting a design for a thermal lens device, two factors must be kept in mind. Since allignment of the laser beam through the optical components and with a second beam, (if a dual laser system is used) is crucial, vibrations must be eliminated.

The distance between the focussing lens, sample cell and detector must be carefully chosen to achieve optimization of the thermal lens effect.

Figure 20 is a schematic design of a possible dual laser LTL spectrometer. To facilitate allignment of the lasers, fiber optics (a) are used to bring the laser beam into the optical train. The choice of fiber optic and the collimating lens (b) used to enter the beam into the fiber and collimate it afterwards would be dependent on the wavelength of the laser beam chosen.

The use of fiber optics allows for several interesting possibilities. Since there is a minimal power loss when light passes through fiber optics, the length of the fiber can be chosen arbitrarily. Thus the situation could arise where the laser source could be in a different location than the spectrometer. A second interesting possibility is that if one were to use a fiber optic bundle, one could theoretically drive more than one spectrometer with a pair of lasers.

The design of the spectrometer is modeled after Ishibashi et. al., as was our experimental setup. The probe beam is not focussed before passing through the sample cell (h), while the pump beam passes through a focussing lens (d) before reaching the cell.

A calibrated photodiode (g) is used to measure the power

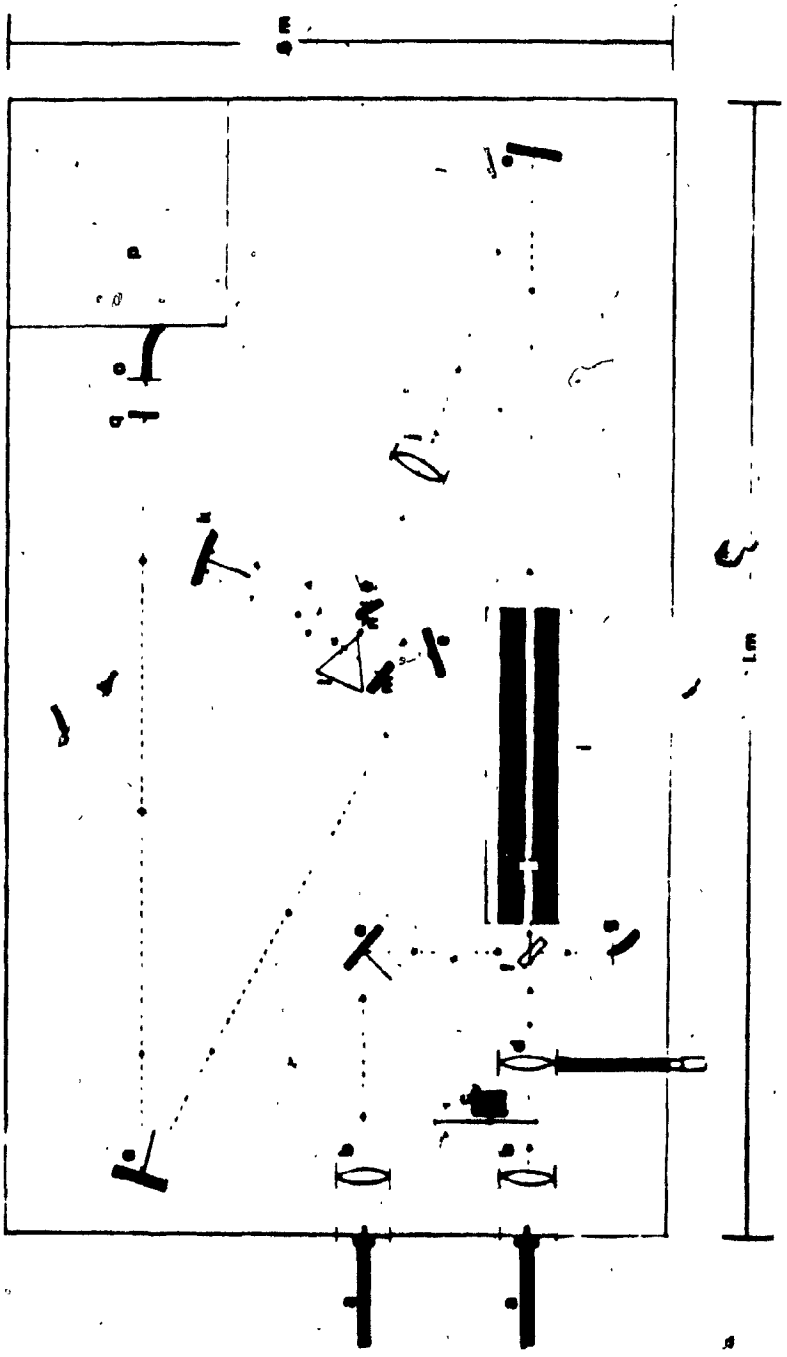


Figure 20. Schematic of a potential comercial LTL spectrometer.

of the pump beam from reflections off of the beam splitter (f). The cylindrical sample cell mount (h) was placed on a railing for a specific purpose. Papers have been published which have studied the use of LTL as a possible detection assembly for HPLC (52,53). To provide a spectrometer that could be adaptable to HPLC work, while still capable of being itself a means of analysis, provisions had to be made to allow for the placement of a flow through cell closer to the focussing lens (d) than would normally be found in a standard LTL system. For this same reason the focussing lens (d) must be interchangeable with other shorter focal length lenses .

Due to the nature of fiber optics, the laser beam which is normally polarized loses its polarization after passing through the optic fiber. This precludes the use of a Nichol prism to reduce the intensity of the pump beam. Thus to prevent damaging the filter (q) which is designed to adjust the light intensity seen by the detector(o) (preventing saturation), a monochromator (e,j,k,l,m,n) is placed in the optical train.

The photodiode array detector (o) is linked to the supporting electronics (p) which can be interfaced with a computer for data averaging and fitting, or run alone. With the power being continuously monitored internally, any signal decreases due to power fluctuations can be corrected for electronically.

Figure 21 is a conceptual diagram of what a LTL

spectrometer might appear as. The actual frame would be extremely rigid and supported on vibration pads. The wavelength of light seen by the detector would be adjustable via the monochromator, to allow for a greater flexability in analysis wavelength choice.

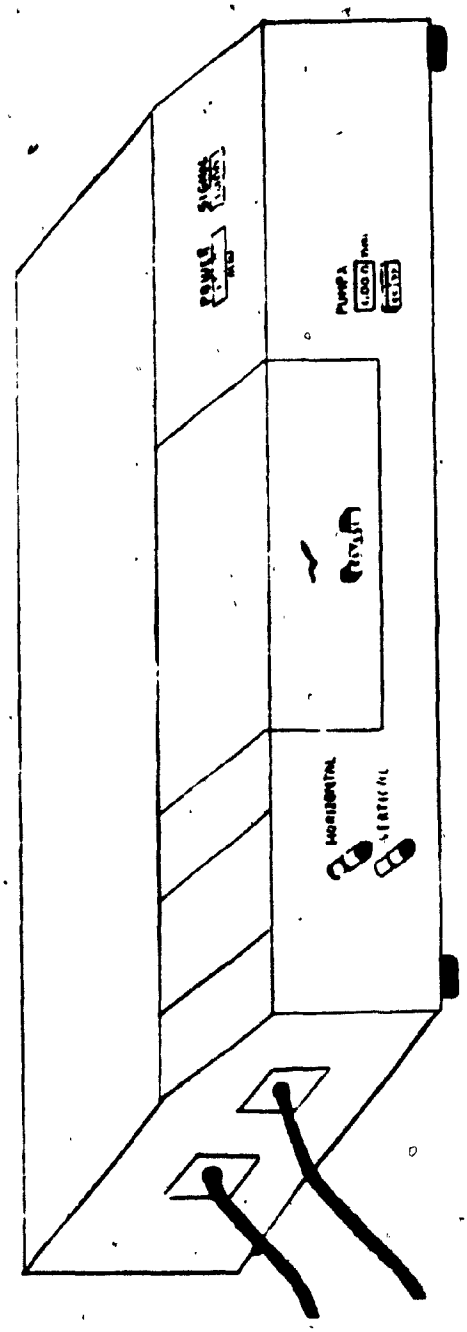


Figure 21. Conceptual diagram of an operating LTL spectrometer.

Part 4 Conclusion

From this study it is concluded that LTL is a feasible and competitive method of analysis for gaseous formaldehyde. It has been shown that the detection limit for formaldehyde is 5.6×10^{-7} M using the experimental set up described. It has also been shown that this detection limit can be improved upon by careful blank and sample preparation on a daily basis.

The flow system for production of formaldehyde in air samples has shown itself to be useful for demonstration purposes and has thus achieved its purpose. However it lacks the precision required to be a tool for quantitative calibration.

Although the LTL apparatus described in this study has demonstrated ppb detection capabilities, further work in this area should definately include a final calibration of the LTL spectrometer using gas samples generated by a precise system such as the permeation tube system.

A second area that requires further study and improvement is data aquisition and manipulation. The work in this study was greatly hampered by the fact that although a very unresolved signal was observable, the LTL data was inaccessible until the experiment had been completed and the averaging had been performed. Without knowledge of the signal intensity (i.e. $^{\Delta I}/_{I_\infty}$), it could not be determined whether or not the data was being stored correctly. This

lead to loss of data.

Finally, this study should be extended to other, gaseous organic pollutants. LTL has been amply demonstrated by this and other studies to be a sensitive method for trace analysis and the adaptation of standard absorption techniques and the development of new ones for these compounds to the LTL method should be attempted.

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