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ABSTRACT

FAST GAS CHROMATOGRAPHY FOR INDUSTRIAL HYGIENE ANALYSIS AND MONITORING

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Industrial hygienists and chemists often rely on gas chromatography (GC) as the separation method during analysis of volatile organics. Although GC is an effective method of analysis, its usefulness is often limited by analysis times of several minutes or more. However, GC can be a much faster method of separation and analysis. If equipment and operating conditions are optimized for speed, many simple separations can be achieved in as little as a few seconds.

Two fast GC systems were developed for use in industrial hygiene and environmental applications. One was designed for analysis of organic vapors, and the other for analysis of liquids. Both systems featured a gas cooled and resistively heated cold trap inlet that produced injection bands with widths of 15 to 25 ms. Separation was achieved with 2 to 5 meter lengths of 0.25 mm i.d. capillary column. Flame ionization detectors were used with the detector signal directed to a custom built, fast responding electrometer and a PC-based data system.

This study shows that simple liquid mixtures of aromatics and aliphatics could often be separated in ten seconds or less. During replicate analyses, relative standard deviations for peak area were 1 to 10 per cent, and relative standard deviations for retention time were less than 1 per cent. Dilute solutions, with concentrations below 50 ug/ml, could not be analyzed due to the poor signal to noise ratios associated with fast responding electrometers.

To validate the fast GC as a vapor monitoring system, a side-by-side comparison was made with conventional GC. Test atmospheres containing benzene, toluene and o-xylene were measured at various concentrations and at humidities ranging from 10% to 80%. At concentrations ranging from 100 ppm to 1 ppm or lower, the fast GC improved retention times by a factor of 50 relative to the conventional system with no loss of precision or accuracy. Changes in humidity were shown to have no effect on the performance of the instrument.

FAST GAS CHROMATOGRAPHY FOR

INDUSTRIAL HYGIENE ANALYSIS AND MONITORING

by

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TABLE OF CONTENTS

LIST OF FIGURES

Figure

LIST OF TABLES

Table

LIST OF APPENDICES

Appendix

CHAPTER 1

INTRODUCTION TO FAST GAS CHROMATOGRAPHY

Industrial hygienists and environmental chemists often rely on gas chromatography (GC) as the separation method during measurement and analysis of volatile organics in air. Although a large number of GC based methods have been described, most fit into one of two general categories. The first category includes methods that involve collection of the sample in a liquid or on solid adsorbent, which is then sent to a laboratory for analysis. The second method involves the use of direct inlet GC systems that can be taken to the field and allow a small volume of air to be placed directly on the column.

Most routine monitoring for volatile organics in the work place is done using the methods which involve sample collection followed by laboratory analysis. These techniques generally involve three basic steps. First, contaminants are collected on a solid adsorbent material such as activated charcoal. Collection may be achieved either passively, using diffusion to move the contaminants to the adsorbent, or actively, using a pump.

Collected materials are then eluted into a small volume of liquid solvent, which is usually CS_2, and the solution is analyzed using GC (1). Procedures based on this general approach have been developed for a large number of compounds and are endorsed by federal agencies including OSHA and NIOSH (2,3).

A chromatogram showing the results obtained with this type of analysis is presented in Figure 1, which is taken from the OSHA Analytical Methods Manual (3).

Despite the requirement for laboratory analysis these are the most widely used monitoring techniques in industrial hygiene. Much of their popularity can be attributed to the requirement for integrated sampling during compliance monitoring and on the use of time-weighted averages in setting of exposure standards. In addition however, these techniques do have some advantages over most other methods. One advantage is that they allow extremely low concentrations of contaminant to be detected and quantified. Laboratory analysis is also useful where potential exposures involve either complex or poorly defined mixtures. In these cases, samples collected on solid adsorbents can be analyzed, and unknown contaminants identified, using techniques such as GC-MS or GC-FTIR.

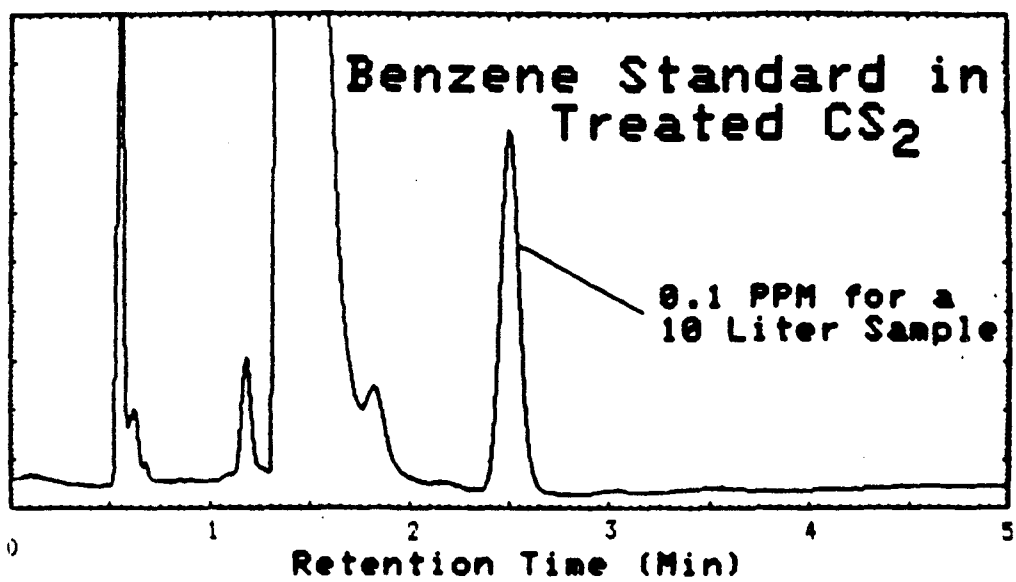

Fig. 1. Conventional Packed Column Chromatogram of benzene in CS_2. From OSHA Analytical Methods Manual.

Along with these advantages, laboratory analysis also involves a number of disadvantages. Most important is the requirement for samples to be sent off-site, and the potentially long delay that may be involved. Once the sample arrives at the laboratory, a typical analysis may involve a thirty minute to eight hour elution followed by GC separation which can require retention times ranging from a few minutes to more than 30 minutes. The elution step requires no special equipment and can usually be run as a batch process, which allows many samples to be prepared at the same time. The GC separations however require relatively expensive equipment and are usually run sequentially, one sample at a time.

In a large industrial laboratory where thousands of samples are run each year, these long separation times represent a significant cost and can result in unacceptably long sample turn around times. Under these conditions, optimization of the chromatographic system for maximum speed would be expected to produce significant cost savings, and may result in more rapid return of results to the industrial hygienist in the field.

As an alternative to sample collection and laboratory analysis, a number of real time, or direct

reading instruments have been developed for industrial hygiene applications. Some of the most common ones include portable total hydrocarbon analyzers which are based on measurement of the current developed by flame or photoionization of contaminated air (4). While these devices have proven valuable in many work environments, they are non-specific and do not allow the user to identify the material being detected. More specific real time detectors have also been developed. However, these instruments often suffer from interferences or are capable of detecting only a limited number, or a single class, of compounds (5).

As a compromise between laboratory analysis and direct reading instruments, portable direct inlet GC systems have also been developed. These allow a small sample of the test atmosphere to be placed directly onto the column. Direct inlet GC eliminates the need for, and long delay associated with, laboratory analysis and can provide more specific information than can be obtained with most direct reading instruments.

The design of direct inlet GC systems varies with the manufacturer and the application. However, the basic concept is the same as that used in process control systems, and is illustrated in Figure 2. Work place air is drawn into a sampling loop of known volume using a

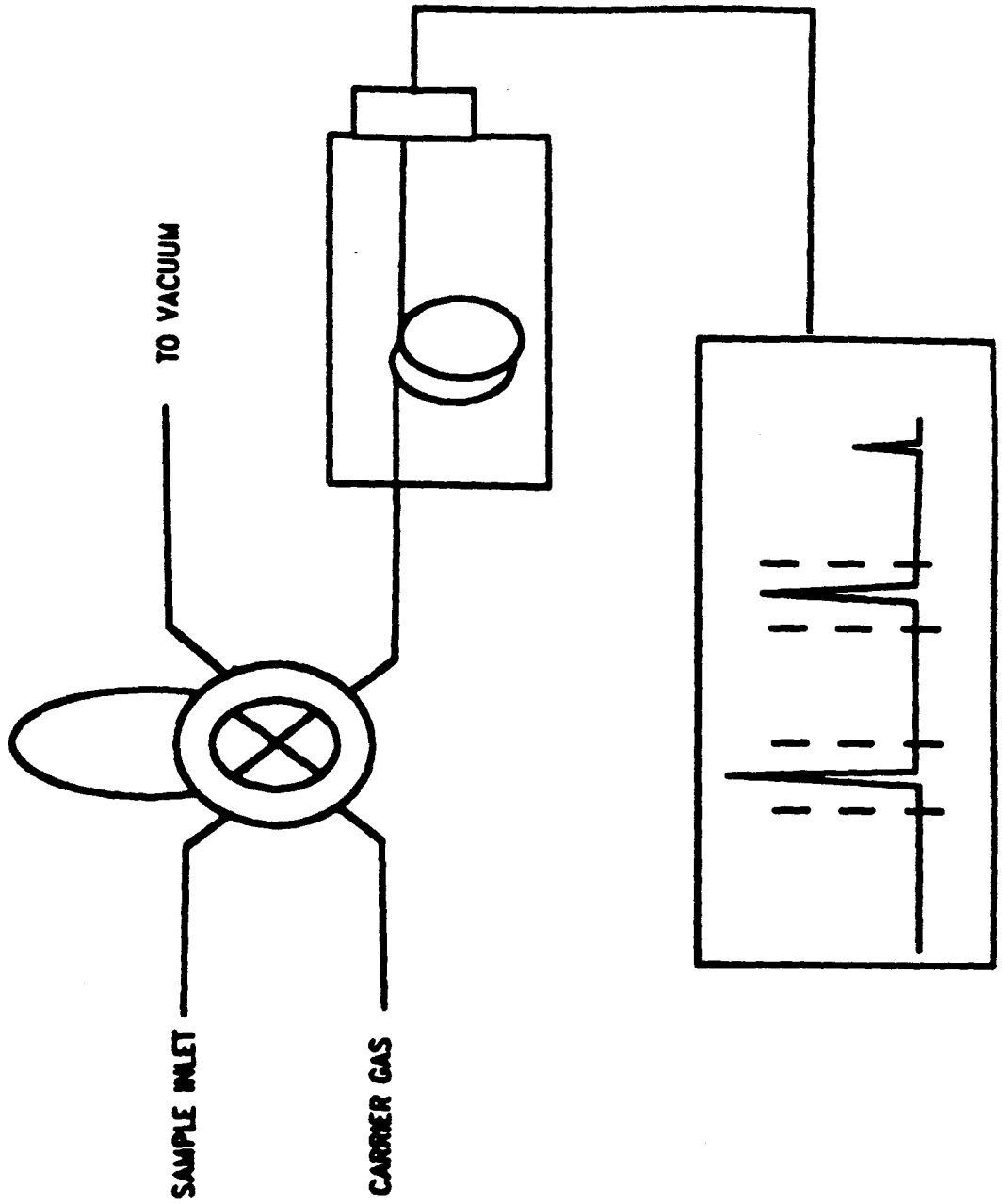

Fig. 2. Schematic diagram of a typical direct inlet GC system.

vacuum pump. A rotary valve, or similar switching device, is then used to place the sampling loop into the carrier gas stream. The air that was previously trapped in the sampling loop is swept directly onto the column for separation and analysis. In some cases the system may feature a single inlet, as shown in Figure 2. In other applications, a single GC is connected to a network of sampling lines that allows samples to be sequentially collected and analyzed from as many as 20 different locations.

Direct inlet GC systems and GC based sampling networks are extremely flexible and can be used to monitor most volatile organics at concentrations well below the ppm level (6). In addition, if used properly, direct inlet GC systems can provide the hygienist or chemist with information concerning the concentration and possible identity of specific compounds in a mixture.

The major disadvantage of direct inlet GC is the slow response of these instruments relative to other direct reading instruments. Direct inlet GC normally involves retention times ranging from one or two minutes up to as much as 20 minutes. In a sampling network that includes 15 to 20 sample collection points, these long analysis times can easily result in cycle times that exceed one hour. Direct inlet GC therefore does not

provide "real-time" results and may not be appropriate for monitoring in some situations involving potential exposures to highly hazardous materials or for monitoring in areas where short term exposure limits apply.

As in laboratory analysis of liquid samples, the development of high speed systems for direct inlet GC could provide a significant advantage over conventional systems. A decrease in retention time to a few seconds would allow direct inlet GC to provide near real-time results and would make this technique valuable in many applications where GC is currently considered too slow to be useful.

Gas chromatography is currently one of the most widely used and well developed techniques in analytical chemistry. However, most chromatographers are not aware that it is potentially an extremely fast method of separation. Usually GC systems are configured for ease of use, or are optimized for high levels of resolution with relatively little emphasis being placed on analysis time. If the equipment is optimized for speed rather than maximum resolution, and if operating conditions are carefully controlled, many simple separations can be achieved in as little as a few seconds. The potential of gas chromatography for this type of high speed separation was first demonstrated by Desty, who in 1965 published

chromatograms showing the separation of 15 components in less than two seconds (7,8).

Although increasing the speed of analysis always involves a loss of resolution, this may be an acceptable trade-off for many industrial hygiene applications. Often industrial hygiene samples consist of relatively simple mixtures, which do not require a high level of separation efficiency. In general, it should be possible for many of these separations that are currently achieved using packed column systems, to be completed on a fast GC system with a 10 to 100 fold improvement in retention time and no significant loss of resolution.

The theory and practice of fast gas chromatography has been studied by a number of laboratories. As is discussed on the following pages, the the primary requirement of these systems is the development of an appropriate inlet. Inlet systems designed for fast GC must be capable of placing the sample on the front of the column as an extremely narrow band. Although a number of potentially useful inlets have been described, few if any have been carefully evaluated, and none appear to be appropriate for routine industrial hygiene applications.

A large part of the work described in this thesis involves the development, testing and validation of a

high speed inlet system. The design is based on the the use of a gas cooled and electrically heated capillary cold trap or cryo-focusing system, and is an extension of the earlier work of Ewells and Sacks. The details of the design and theory are presented in Chapters 2 and 3. Briefly, the idea is that vaporized sample can be condensed as a narrow band on the inside wall of a cold metal tube. Once the sample is collected, the tube can be rapidly heated and the sample will be re-vaporized as a narrow plug. The trap is cooled by a flow of cold nitrogen gas and is heated resistively by running a current through the metal tube. The thin walls of the tubing present a small cross sectional area and a high electrical resistance. The high resistance, along with the small thermal mass, allows the trap temperature to increase very rapidly. In theory the system should allow reinjection to be completed in a few milliseconds.

The cold trap is placed between the primary inlet system, which can be any standard capillary GC inlet, and the column. This allows a sample which enters the trap as a wide diffuse band to be focused and placed on the column as a small well defined plug. This reduction in inlet band width is essential to the success of high speed separations. The basic design of the cold trap system is presented schematically in Figure 3.

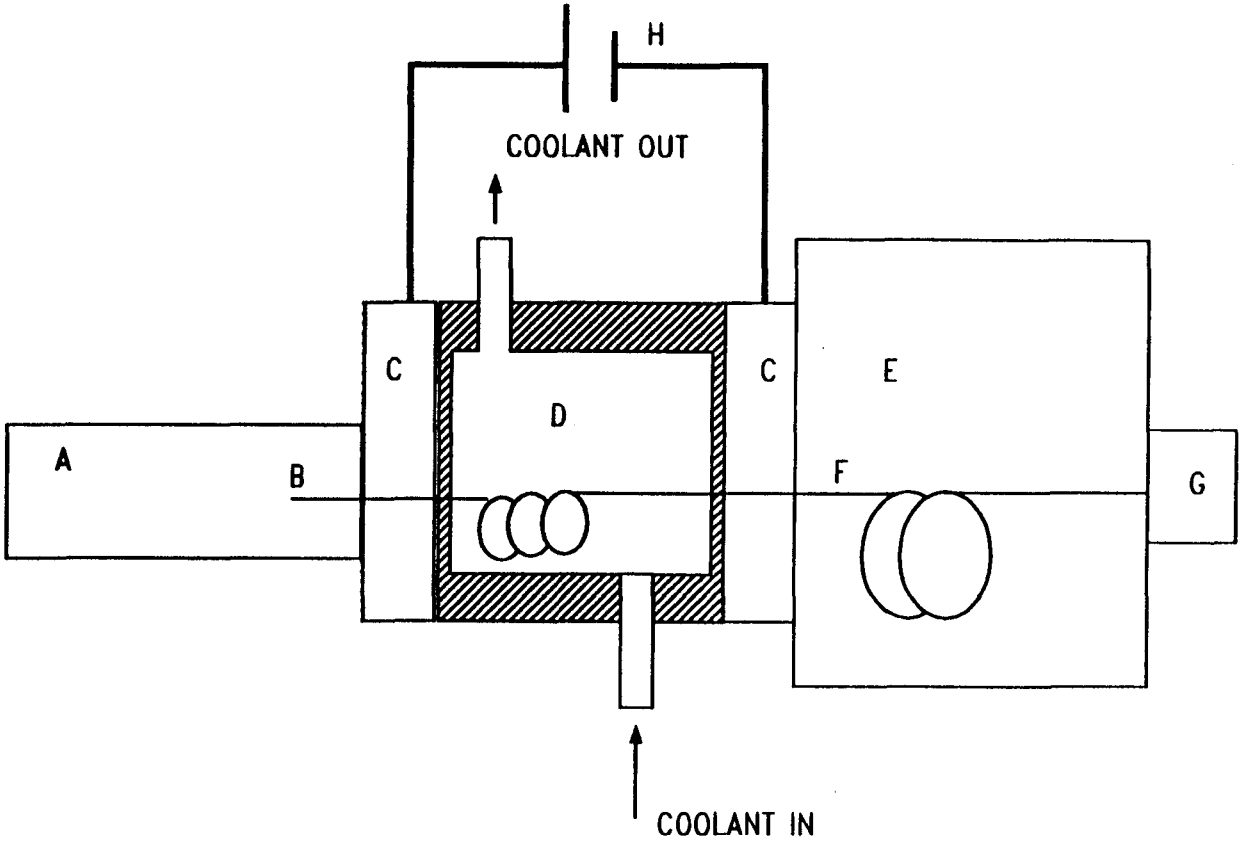

Fig. 3. Schematic diagram of a resistively heated cold trap inlet that could be used to reduce injection band widths. A; conventional inlet, B; cold trap tube, C; electrodes, D; cold trap chamber, E; GC oven, F; GC column, G; detector, H; power supply.

Research Objectives

The research described in this thesis was undertaken with the objective of testing the following hypothesis;

A fast GC system can be developed that will perform many important industrial hygiene separations 10 to 100 times faster than conventional GC systems.

In order to test this hypothesis, a number of specific goals were identified. These goals included the following;

1. Design an improved cold trap inlet suitable for use with both liquid and gas samples of the type that have significance in the field of industrial hygiene.

2. Develop and assemble a complete fast GC system featuring the improved cold trap inlet, automated injection, capillary columns, fast electronics, PC based data aquisition and analysis and computer controls.

3. Conduct a systematic evaluation of the fundamental operating characteristics of the cold trap. This includes studies of the trap heating and cooling

characteristics, injection band widths, trapping and reinjection efficiency and reproducibility.

4. Evaluate the chromatographic performance of the fast GC for the analysis of simple liquid samples that have significance in the field of industrial hygiene.

5. Evaluate the performance the fast GC system for analysis of simple mixtures of volatile organic vapors that have significance in the field of industrial hygiene.

Background

The hypothesis of this work has both a theoretical and an experimental basis. Since its introduction in the 1950s GC has become one of the most widely used and thoroughly studied techniques in analytical chemistry. The chromatographic process is well understood and is best described by the kinetic theory developed by van Deemter, Golay, Giddings and others (9 - 13). This well developed theory allows the chromatographic process to be modeled, and can be used to predict conditions that will provide maximum separation speed under a defined set of conditions.

In the early 1960s Desty and his co-workers predicted that small diameter open tubular columns could be used to achieve extremely rapid GC separations. They confirmed their hypothesis by developing a high speed GC, and publishing chromatograms that show the separation of 15 components in less than 2 seconds. Since the initial work of Desty, a number of other researchers have also developed fast GC systems and have demonstrated that high speed separations are possible (14 - 17). Despite the fact that Desty's original work was published over 20 years ago, fast GC systems are still not used on a routine basis. The reason for this is a lack of practical high speed equipment.

Fast GC places unusual demands on the chromatographic system, especially the inlet. In order to develop a high speed GC system that might be useful for industrial hygiene applications, these demands must be identified and instruments that can meet these demands must be developed. The equipment requirements for a fast GC system and the theoretical limits on the performance of such an instrument are discussed along with the relevant chromatographic theory in the following sections.

Chromatographic Resolution

The quality of a chromatographic separation is most simply expressed as the resolution (R), which is dependent on both distance between the center of adjacent peaks and on the peak widths as shown in equation 1.

$$R = \frac{2(Tr_1 - Tr_2)}{Wb_1 + Wb_2} \qquad (1)$$

Here Tr_1 and Tr_2 represent the retention times and Wb_1 and Wb_2 represent the base widths of the two peaks. For well shaped, Gaussian peaks, a resolution of 1.5 provides complete baseline separation, and a resolution of 1.0 is considered adequate for most analytical applications (18). Resolution can also be related to the characteristics of the chromatographic system and the materials being separated by the equation:

$$R = \frac{1}{4} (N)^{1/2} \left(\frac{a - 1}{a} \right) \left(\frac{k}{k + 1} \right) \qquad (2)$$

In this equation "a" represents the relative retention, or the ratio of adjusted retention times for the two peaks,"k" refers to the partition ratio of the second component and "NE" represents the number of effective theoretical plates. The partition ratio is defined as the amount of solute in the stationary phase divided by the amount in the mobile phase and is

dependent on the solute partition coefficient and on the phase volume ratio of the column. The effect of partition ratio on performance is discussed below.

Equation 2 indicates that resolution increases with relative retention and partition ratio, and as the square root of number of theoretical plates. The number of effective theoretical plates, NE in equation 2, is related to the number of theoretical plates, by the formula:

$$NE = N\left(\frac{k}{k+1}\right)^2 \qquad (3)$$

These relationships are valuable because they allow resolution to be related to the number of theoretical plates developed, which in turn can be related to basic operating parameters by the kinetic theory.

Since resolution is dependent on both the distance between peaks and on the width of the individual peaks, the time required to achieve a given level of resolution can theoretically be minimized by either increasing the rate at which the two solute bands separate, or by reducing the peak width and the required degree of separation. In practice, the speed at which two solute bands separate is largely determined by the relative

retention and the partition ratio, which are dependent on the physical and chemical properties of the solutes and the column coating. These factors are not easily manipulated, and in most cases improvements in the speed of analysis are more readily achieved through careful control of the factors that affect peak width.

Kinetic Theory

Peak width is dependent on column efficiency which can be expressed as the number of theoretical plates developed by the system. The key to successful high speed separations is to maximize the efficiency of the chromatographic system, and to thereby minimize the degree of separation needed to achieve good resolution.

The kinetic theory provides the best description of the chromatographic process and the various factors that affect final peak width. This theory, which is discussed in a number of excellent books and review articles (19-21), provides a useful framework for discussion of strategies that can be used to minimize peak width and retention time.

As it applies to open tubular columns, the kinetic theory is summarized by the well known Golay equation:

$$HETP = \frac{A}{U} f_1 f_2 + BU \frac{f_1}{f_2} + CU \qquad (4)$$

Here HETP represents the height equivalent to a theoretical plate, an expression of separation efficiency adopted from distillation technology. The number of theoretical plates developed by a column is calculated as the product of HETP and the column length (L).

$$N = \frac{L}{HETP} \qquad (5)$$

In general, the number of plates developed by a column serves as an indicator of how well it will separate similar compounds. The height equivalent to a theoretical plate is therefore an inverse expression of column efficiency with smaller HETP values indicating a greater number of plates and increased column efficiency. Small values of HETP, or large values of N, indicate that minimal band broadening occurs on the column, resulting in narrow peaks and better resolution.

The HETP can also be determined by direct measurement from a chromatogram, in which case it is defined as the ratio of peak width relative to the retention time (18). Since a well shaped peak is near

Gaussian, the peak width can be expressed in terms of variance, or the square of the standard deviation. This allows the various factors that contribute to band broadening to be studied independently, and their individual contributions added together to produce the overall HETP value. The A, B and C terms of equation 4 represent the three factors that contribute most significantly to band broadening on the column: longitudinal diffusion, resistance to mass transfer in the gas phase and resistance to mass transfer in the stationary phase. The U term represents the average linear velocity of the carrier gas.

As is discussed in a number of review articles, each of the factors that contributes to band broadening on the column can be related to basic operating conditions such as column diameter and film thickness as well as to physical properties of the carrier gas, the stationary phase coating the column and the materials being analyzed.

The first term in equation 4, "A", represents longitudinal diffusion, which is described by the Einstein equation:

$$A = 2D_g \qquad (6)$$

Here D_g represents the molecular diffusion coefficient of the solute in the carrier gas and is expressed in units of cm^2 per second.

As indicated by equations 4 and 6, the contribution of longitudinal diffusion to HETP varies inversely with carrier velocity and directly with diffusivity. This would seem to indicate that low diffusivity gases, such as nitrogen, would be preferred as the carrier. For fast GC systems, which utilize high carrier velocities and produce short retention times, however, it can be shown that the "A" term actually contributes very little to overall peak broadening, and in most cases can be disregarded.

The second factor, "B" in equation 4, represents resistance to mass transfer in the mobile or gas phase. Band broadening attributable to this factor is represented by the equation:

$$B = \frac{r^2(1 + 6k + 11k^2)}{24D_g(1 + k)^2} \qquad (7)$$

where r is the column radius.

Equations 4 and 7 indicate that peak broadening due to resistance to mass transfer in the mobile phase can be

minimized by selecting small diameter columns, operating at low carrier velocities and by selecting high diffusivity carrier gases such as helium and hydrogen. The choice of carrier gas and velocity indicated by the "B" term is the opposite of that indicated by the "A" term. The proper choice is therefore dependent on the relative importance of the "A" and "B" terms. As noted earlier, longitudinal diffusion is not a significant factor in high speed chromatography and the best choice is a high diffusivity carrier gas as indicated by equation 7.

The third major factor that contributes to on-column band broadening is resistance to mass transfer in the stationary phase, "C" in equation 4. This factor is represented by the equation:

$$C = \frac{2kd_f^2}{3(1+k)^2 D_l} \qquad (8)$$

Here d_f represents the thickness of the stationary phase film and D_l represents the molecular diffusion coefficient of the solute in the stationary phase. As indicated by equation 8, "C" increases as the square of the film thickness and is inversely related to the stationary phase diffusion coefficient. It follows that selection of a column with a thin stationary phase of

high diffusivity will minimize the value of "C". If thin film capillary columns are selected, "C" will have a value significantly less than "B", and in most cases will have little impact on the overall column efficiency.

As indicated by equation 4, carrier velocity, "U", interacts with the "A", "B" and "C" terms to play a major role in determining both column efficiency and analysis time. A graphic representation of the Golay equation, Figure 4, shows that there is an optimum velocity, U_{opt}, that will result in a minimum value of HETP, and the maximum number of theoretical plates.

While operation at U_{opt} might be expected to produce maximum resolution, it will usually result in very long retention times. For fast GC systems, obtaining the maximum number of plates available from a given column is not the primary consideration, and efficiency is better expressed as the number of effective plates developed per second.

As carrier velocity is increased above U_{opt}, retention times are decreased and resolution is sacrificed, but the number of plates developed per unit time may actually increase. The carrier velocity producing the greatest number of theoretical plates per unit time can be predicted and has been defined as the

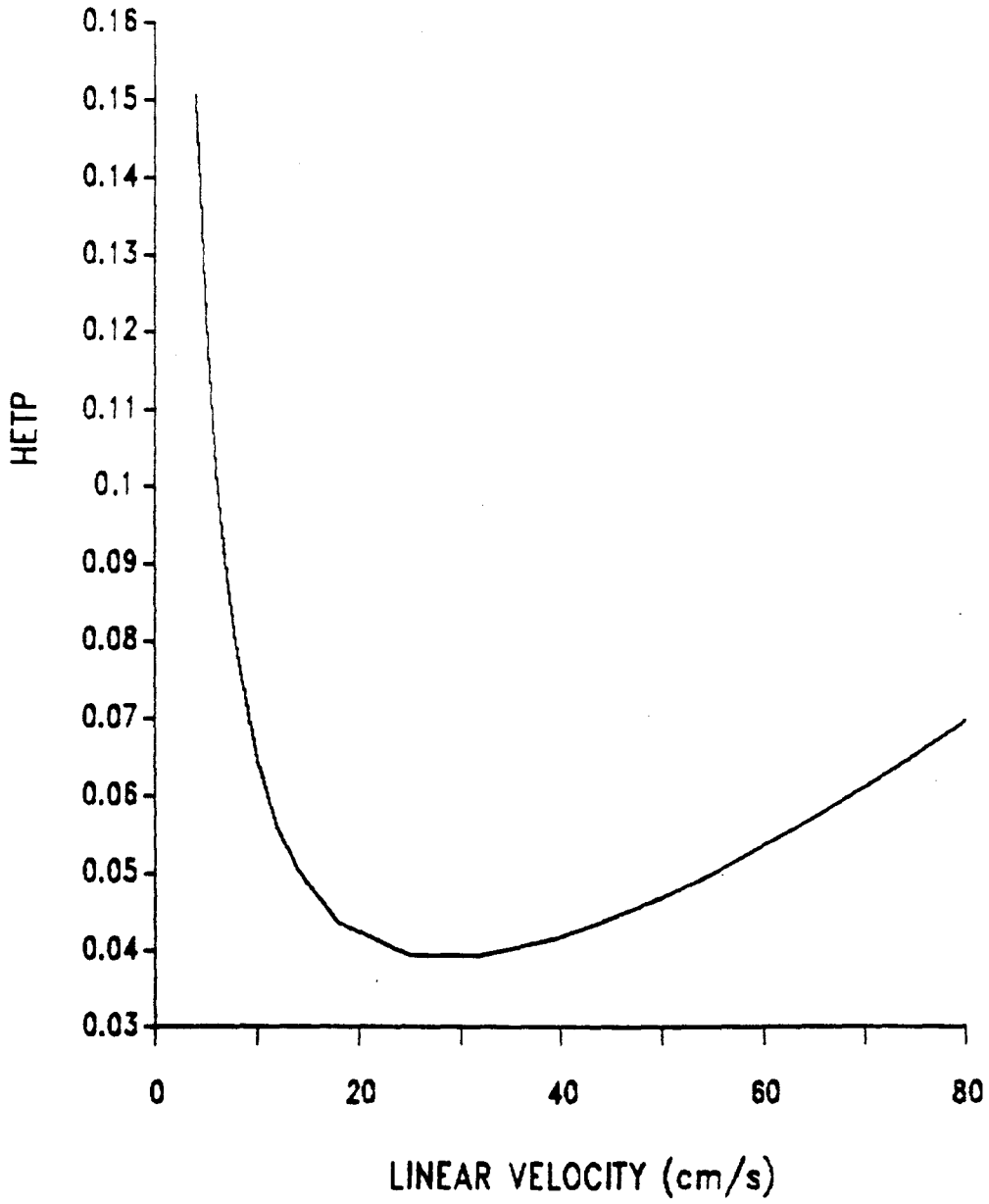

Fig. 4. Golay plot showing the effect of carrier velocity on column efficiency. Conditions are 40 m X 0.53 mm column with a 2 um stationary phase, D_l=5 x 10^{-5} cm^2/s and D_g=0.3 cm^2/s.

optimum practical gas velocity, OPGV (22). The rate at which resolution is lost with increases in velocity, and the value of the OPGV are mainly dependent on the magnitude of the two resistance to mass transfer terms, "B" and "C" in equation 4, and on the pressure correction factors f_1 and f_2. The values of these terms are reflected in the slope of the line extending to higher velocities. In order to allow increases in the carrier velocity with minimal loss of resolution, operating conditions that result in small values of "B" and "C" should be selected. Again, this can be done by using small diameter, thin film columns and by using high diffusivity carrier gases such as hydrogen and helium.

In recent years, open tubular fused silica columns with diameters as small as 0.1 mm and bonded stationary phases as thin as 0.1 um have become commercially available. These columns are generally well suited for use in fast GC systems.

Effect Of Pressure Drop

The f_1 and f_2 terms included in equation 4 are the Giddings-Golay (23) and Martin-James (24) correction factors. These were introduced to compensate for the compressibility of the carrier gas. Their values are calculated from the following equations:

$$f_1 = 9/8 \left[\frac{(P^4-1)\ (P^2-1)}{(P^3-1)^2}\right] \qquad (9)$$

$$f_2 = 3/4 \left[\frac{(P^2-1)}{(P^3-1)}\right] \qquad (10)$$

where P is defined as the ratio of inlet pressure, P_i to outlet pressure P_o.

$$P = \frac{P_i}{P_o} \qquad (11)$$

For columns with short lengths or large diameters, or for columns operated at low linear velocities, the pressure drop is small and the correction factors can generally be ignored. For high speed systems, especially those using small diameter columns, the pressure corrections are a necessary part of the kinetic theory.

Graphically the effect of the pressure corrections is to introduce a non-linear component to the Golay plot which, at high carrier velocities, causes the the value of HETP to increase faster than would otherwise be predicted. In practice, this non-linearity means that there is an optimal combination of column length and carrier velocity that should produce the highest level of

resolution possible with any given retention time. A column that is longer than the optimum will produce a larger pressure drop which will result in a loss of efficiency. Use of a shorter column will also result in less efficiency due to the decreased opportunity for exchange between the stationary and mobile phases. The effect of column length on performance, and the possibility of improving separation speed by "tuning" column length has been explored by other members of our group as well as by other laboratories.

Partition Ratio Effects

Partition ratio, k, plays an important role in determining both the value of HETP and the resolution that can be obtained with a given chromatographic system. The partition ratio is dependent on the phase volume ratio of the column, the operating temperature and the distribution ratio of the material being studied. The distribution ratio is an equilibrium constant defined as the concentration of analyte in the stationary phase divided by the concentration in the mobile phase. The factors affecting partition ratio, and its effect on peak width and resolution are complex, and are not immediately evident. For example the relationship between k and "B", shown graphically in Figure 5, indicates that the highest efficiency would be expected with k values near zero.

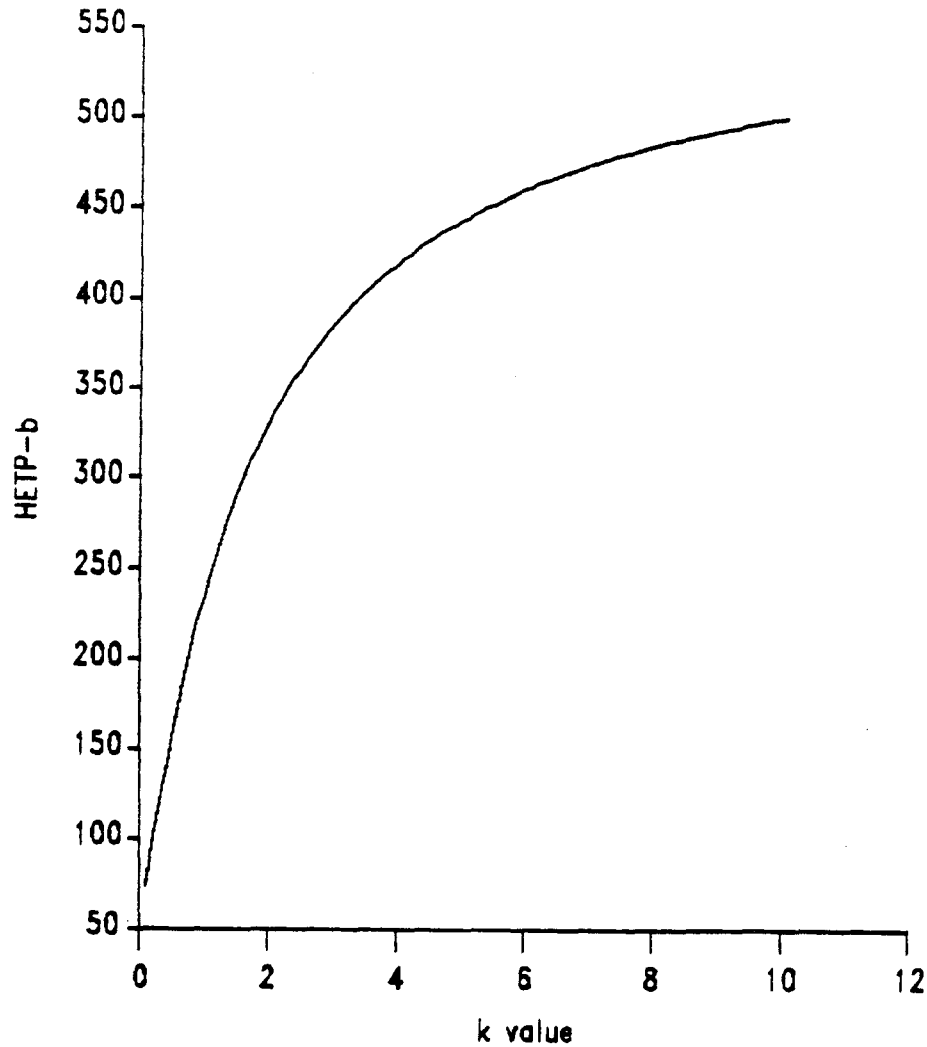

Fig. 5. Effect of partition ratio (k) on the Golay equation "B" term, resistance to mass transfer in the mobile phase. Assumes a 0.25 mm i.d. column, an average linear velocity of 100 cm/s, D_g=0.3 cm^2/s.

However, in practice such low k values indicate that a solute is poorly retained and generally result in poor separation, as indicated by equation 2 and Figure 6.

Although no single value of k can be identified as the optimum under all conditions, the work of several authors indicates that values ranging from about 1.5 to 3 should be used if possible (25-27). In the studies described here, k values ranged from less than 1 to about 10. For the more volatile solutes, optimal k values could not be achieved with thin film columns. Although the k values could have been decreased by use of sub-ambient oven temperatures, the necessary equipment was not available. Some experiments therefore required the use of columns with slightly thicker stationary phases than would otherwise have been selected. Although the system efficiency is expected to be better with thinner stationary phases, the partition ratios produced with the thin film columns were often too low to be useful.

This conflict illustrates the difficulties that can develop in attempting to optimize a system for maximum speed. Often the conditions that are expected to produced optimal results for one component of the mixture produce poor results for other components. In conventional GC this problem is overcome through the use of temperature programing which allows the operator to

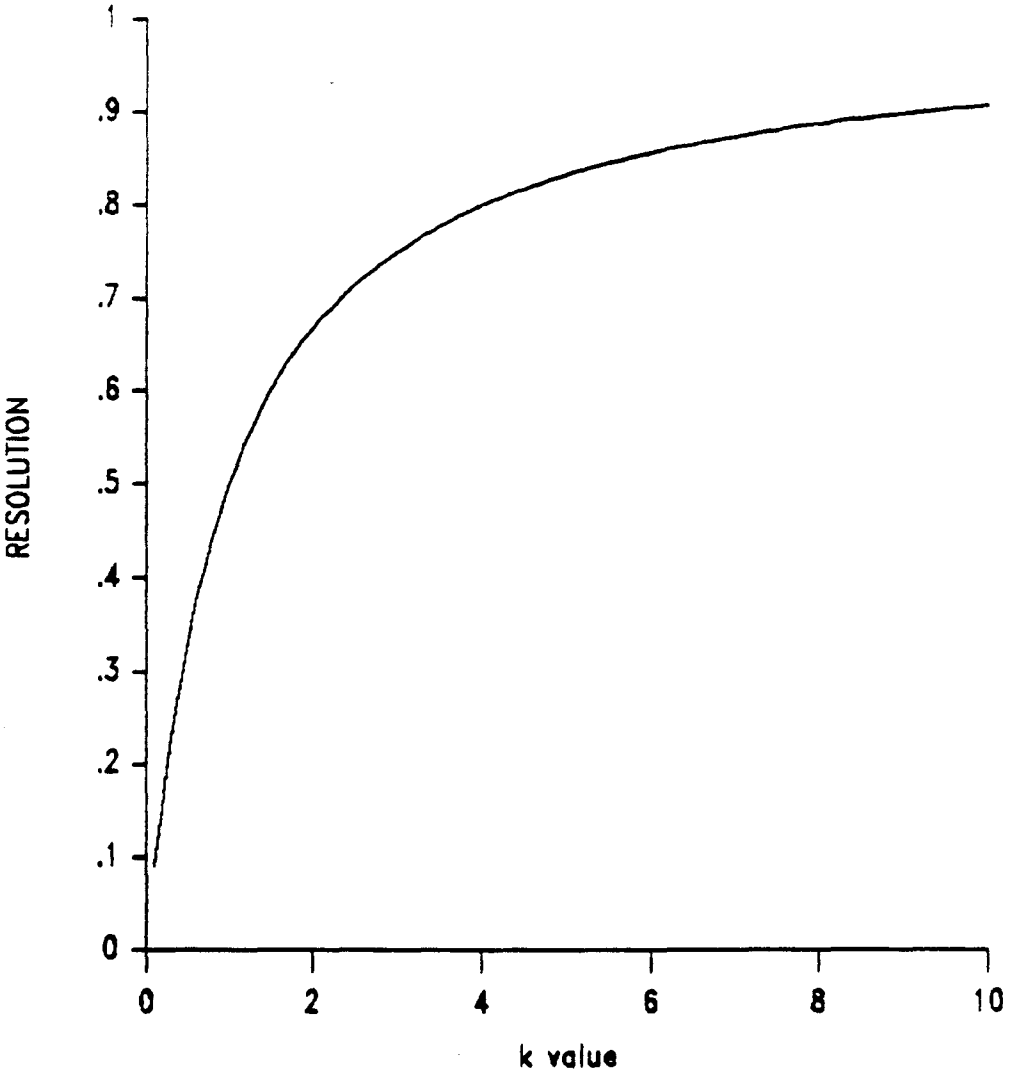

Fig. 6. Effect of partition ratio (k) on resolution if the number of plates and the relative retention are held constant.

adjust k values during the analysis. Temperature programing is not practical for fast GC systems, so each analysis is limited to a narrow range of boiling points.

In many cases, factors other than speed, such as column loading, limits of detection or injector performance limitations also have to be considered. In almost all cases it is necessary that some compromises be established that will produce adequate separation and best overall performance.

Extra-Column Considerations

The Golay equation, as presented earlier, provides an accurate description of on-column band broadening in open tubular column GC. This equation considers only column efficiency and assumes that extra-column factors, such as the initial band width produced by the injection system, do not contribute significantly to final peak width. While this is usually a valid assumption for conventional speed GC, it is not necessarily true for high speed operation.

Under conditions that are used for high speed separations, overall system efficiency is often significantly less than column efficiency. In order to

correct for this, Gaspar (28) introduced a fourth term to produce a modified Golay equation of the form:

$$HETP = \frac{A}{U} f_1 f_2 + BU \frac{f_1}{f_2} + \frac{CU}{f_2} + DU^2 \qquad (12)$$

Here the D term represents all extra-column factors that contribute to the final width of the peak and is defined as:

$$D = \frac{t^2}{(1 + k)^2 L} \qquad (13)$$

with t representing the time constant of the instrument, or the sum of all extra-column contributions expressed in seconds.

Most significant among the extra-column factors are the width of the initial injection band, peak broadening due to dead volumes or unswept areas in the detector, and peak distortion caused by slow responding electronics. As indicated by the modified Golay equation, 12, the contribution of extra-column factors to final peak width increases with the square of carrier velocity. At the high velocities used in fast GC, the extra-column factors can become the major contributor to band broadening, and are usually the limiting factors that determine the maximum speed of analysis.

The importance of extra-column factors in fast GC, and the effect they have on overall system efficiency is illustrated in Figure 7, which shows Golay plots for column efficiency and system efficiency under conditions that are selected for high speed operation. The difference between the two plots represents the loss of efficiency that can be attributed to extra-column factors. The figure was generated assuming a stationary phase film thickness of 0.25 um, a column length of 3 m and a diameter of 0.25 mm. The diffusion coefficients are taken from published values for benzene. A fixed value of 100 ms, which is typical of values measured for convention capillary GC, was assumed for the D term. As indicated by a comparison of the two Golay plots, the extra-column factors could account for over half of the total peak width at the high velocities that are often used in fast GC.

The importance of extra-column factors in high speed operation can also be illustrated by a comparison of peak widths obtained with conventional and fast GC. In conventional GC, peak widths measured at half height, are usually expressed in terms of seconds or tens of seconds. In high speed GC, peaks are always much narrower, and in many cases may be less than 50 milliseconds. A conventional capillary GC inlet using a "T" type splitter

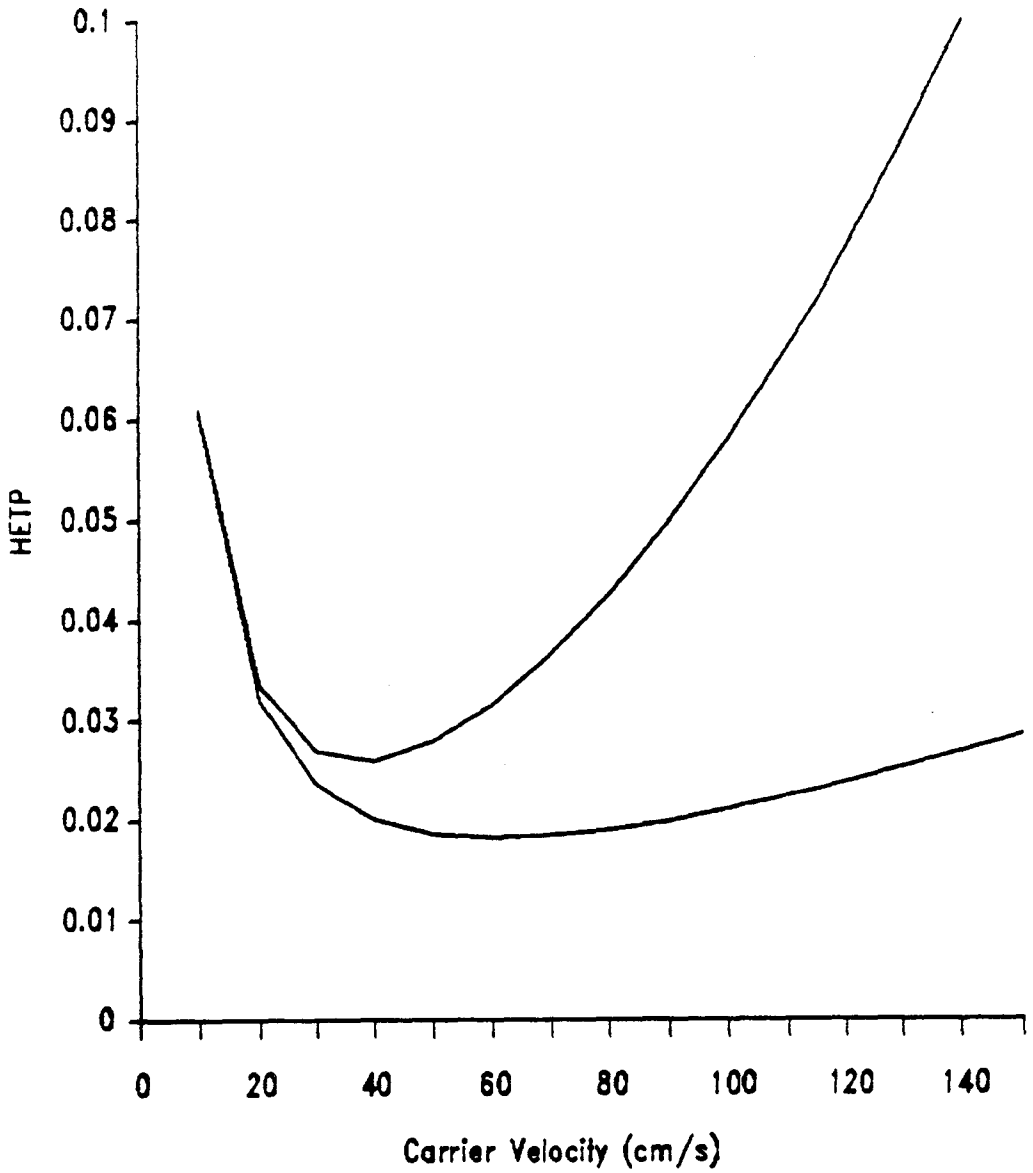

Fig. 7. Golay plots showing the difference between column efficiency, shown on the lower trace, and system efficiency, shown on the upper trace. Assumes a 3 m X 0.25 mm column with a .25 um stationary phase, D_g=0.3 cm^2/s and D_l=5 x 10^{-5} cm^2/s.

typically produces an initial band width of 50 to 100 milliseconds (29). Other types of inlets such as gas sampling loops produce even wider injection bands, often 1 second or more in width. While these initial band widths do not contribute significantly to final peak width for conventional GC, they are clearly unacceptable for a high speed system.

In addition to the wide injection band produced by conventional GC systems, band broadening is also caused by dead volumes. Many detectors, especially those that use a closed cell such as thermal conductivity detectors (TCD) or photoionization detectors (PID), are likely to have large dead volumes, or unswept areas, that contribute significantly to final peak width. The effect of detector dead volumes can be minimized by adding large volumes of makeup gas. However, this may have detrimental effects on limits of detection (30). Dead volumes are much less of a problem with open cell devices such as FIDs in which the column can be moved close to the base of the flame.

Final peak width can also be affected by factors outside the actual flow path, such as the electrometer and data system response times. The electronics used in most gas chromatographs are designed to minimize noise rather than to have short response times. Many

commercial systems, especially those designed for packed column use, have response times that exceed 200 milliseconds and are not capable of accurately tracing peaks as narrow as those produced by fast GC systems.

In order to perform fast GC successfully it is important that the system be designed to address each of these sources of extra-column band broadening. A useful high speed GC system therefore requires an inlet, capable of placing the sample on the front of the column as an extremely narrow band, a low dead volume detector and flow path, and fast responding electronics.

Computer Simulations

The kinetic theory has been tested and refined by many researchers. If reliable values are provided for the various constants such as the diffusion coefficients and gas viscosity, these equations have been shown to provide an accurate description of the chromatographic process. This has made it possible to develop mathematical models that can be used to predict the performance of a GC system under various sets of conditions.

Several authors have used models of this type to predict conditions that might be optimal for specific

applications. Because of the complexity involved in deriving a solution to these equations, the most successful approach to modeling has been the use of micro-computer based programs. The first computer based models to be published were those of Ingraham who developed a set of computer generated Golay plots that illustrated the effects of changing various parameters such as column diameter and film thickness (31). This was followed by a series of more sophisticated and complete models developed by Jennings, Cramers and Leclercq that were intended to help the practicing chromatographer select optimal conditions, and which included some consideration of analysis time (32-34). The most complete model is that of Villalobos and Annino who developed a computer based model for optimization of capillary systems that considers column length, minimum analysis time and minimum detectability (35).

The work of Villalobos and Annino closely parallels research being done in our own laboratory by Sacks, Puig and Rankin. Their work is directed toward the development of a model for predicting the optimal conditions for time constrained separation of specific pairs of compounds (36). Although the model has not yet been completely validated, it does provide a useful tool for setting initial experimental conditions. Much of the work described in this thesis was conducted using

conditions that the model indicated should be near optimal.

For the work described here, the GC modeling program which was originally developed in BASIC by Sacks and Puig, was modified and adapted for use as a LOTUS 123 spreadsheet. The spreadsheet environment allowed the program to be easily modified and provided a powerful tool for graphing the relationships between various parameters of interest. The logic and algorithms used in developing the program are nearly identical to those used in the original program and are discussed elsewhere (36).

Some sample outputs from the computer model used in this work are presented in the following figures. Figure 8 illustrates the effect of extra-column band broadening and column length on the number of effective plates developed by a chromatogram of fixed retention time. In this case the number of effective plates is plotted versus column length with each line representing a different instrumental time constant. The analysis is constrained to a 10 second retention time on a 0.25 mm i.d. column with a 0.1 um thick stationary phase. The partition ratio was set at 2 and the diffusion coefficients were published values for benzene (37).

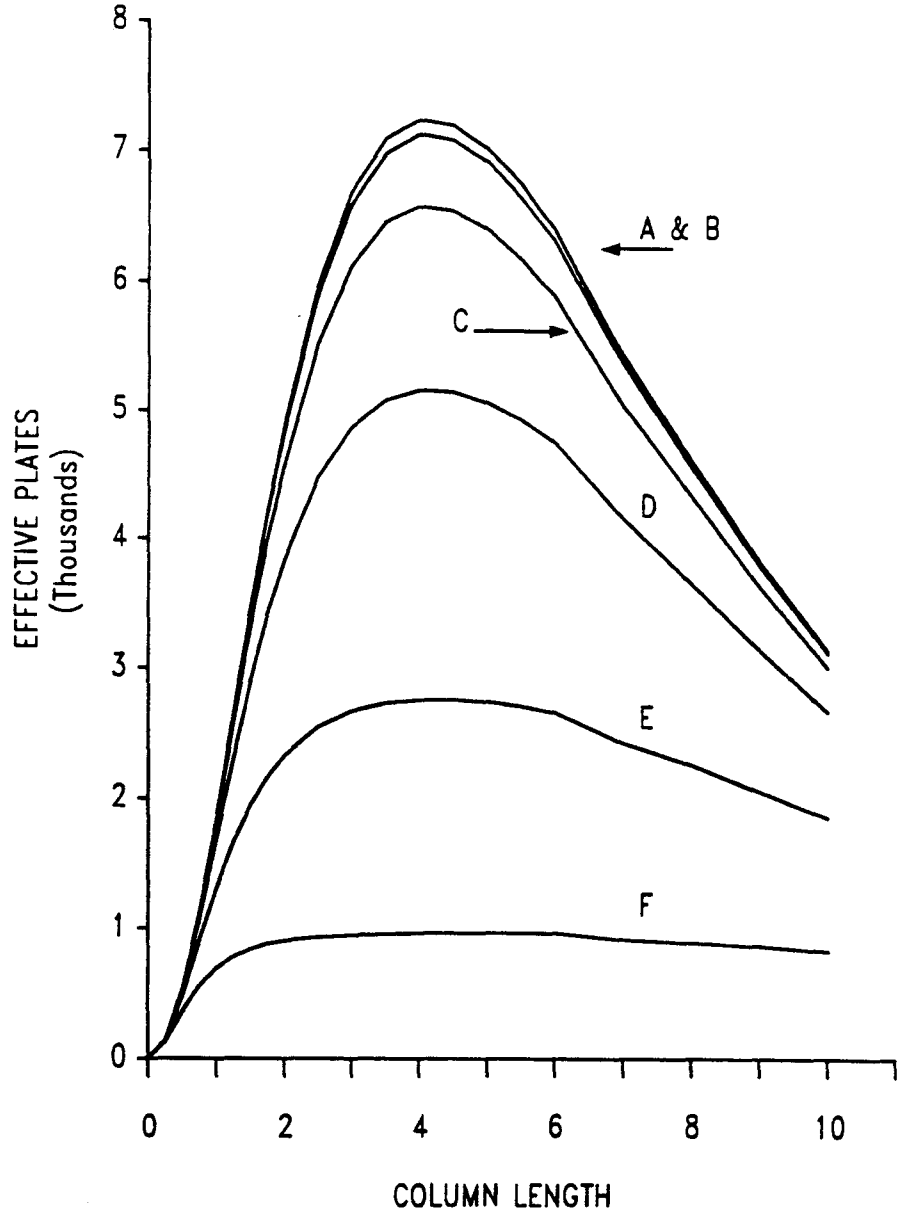

Fig. 8. Computer generated plot showing the number of effective plates developed at varying lengths of 0.25 mm i.d. column with a 0.1 um stationary film. Each line represents a different instrumental time constant. From top to bottom these are: 0, 10, 25, 50, 100 and 200 ms. Operating conditions are presented in the text. Assumes D_l=5 x 10^{-5} cm^2/s and D_g=0.3 cm^2/s.

The six lines, labeled A, B, C, D, E and F, represent time constants of 0, 10, 25, 50, 100 and 200 ms. Line A, with a time constant of 0, represents the column efficiency. The peak value of about 7300 plates at a length of about 4.2 meters shows the maximum number of theoretical plates that might be obtained if extra-column band broadening could be completely eliminated. This value is comparable to the number of theoretical plates developed by many packed column systems with retention times of 10 to 15 minutes or more (21). It follows that many simple industrial hygiene separations that are currently done on packed column systems could be done on a fast GC with retention times of 10 seconds if extra-column factors were sufficiently controlled.

The sharp rise from near zero to a peak at about 4 meters illustrates the effect of column length on performance. Selection of a column that is longer than the optimum requires the use of higher carrier velocities and increased inlet pressure, which degrades performance. The use of a column that is shorter than the optimum can cause an even more dramatic loss of efficiency.

Smaller diameter columns or shorter time constraints generally result in even sharper peaks, meaning that length tuning becomes even more important under those conditions.

Line B in Figure 8 shows the results that might be expected with the cold trap injection system. Based on the earlier results of Ewells and Sacks, the cold trap is expected to produce initial band widths of about 10 ms (38). For a 10 ms time constant, a maximum of about 7100 effective theoretical plates, or 97% of the maximum available from the column, is expected. Reduction of the injection band to less than 10 ms would only slightly increase the number of effective plates. It should be noted that resolution increases only as the square root of the plate number and small increases are not significant.

Lines D, E and F, represent results that might be obtained with syringe injection and a splitter system operated at various split ratios, or volumetric flow rates. At high flow rates it is possible to achieve a 50 ms injection band, shown as line D. This results in a maximum of about 5200 theoretical plates which corresponds to a 29% loss of efficiency. With a 100 ms band, which might be obtained with lower flow rate, the loss of efficiency is even greater at 63%, so that only 2700 theoretical plates would be expected. Line F shows the results that might be obtained with an injection band of 200 ms. This could represent a splitter operated at

low split ratios or a small dead volume gas sampling loop.

Although the loss of efficiency indicated by Figure 8 is fairly dramatic, the effect of extra-column band broadening is even greater at shorter retention times. All of the data in this figure represents losses that would occur for a peak with a 10 second retention time. The loss of efficiency would actually be much larger for any components of the mixture that were eluted earlier in the chromatogram. For components that were eluted in less than 5 seconds, the loss of efficiency could easily exceed 90%. This illustrates the importance of narrow injection bands for extremely fast chromatography.

Similar data are presented in Figure 9 for a system using a thicker, 0.5 um stationary phase. The thicker film results in an increase in resistance to mass transfer in the stationary phase and a five fold increase in k values at the same temperature. Together, these changes result in a much less efficient column and a significant loss of effective plates. Despite the loss of efficiency, the use of thicker films is sometimes necessary if oven temperature can not be reduced sufficiently or if overloading of some components becomes evident. Comparison of Figures 8 and 9 also shows the effect that film thickness and partition ratio have on

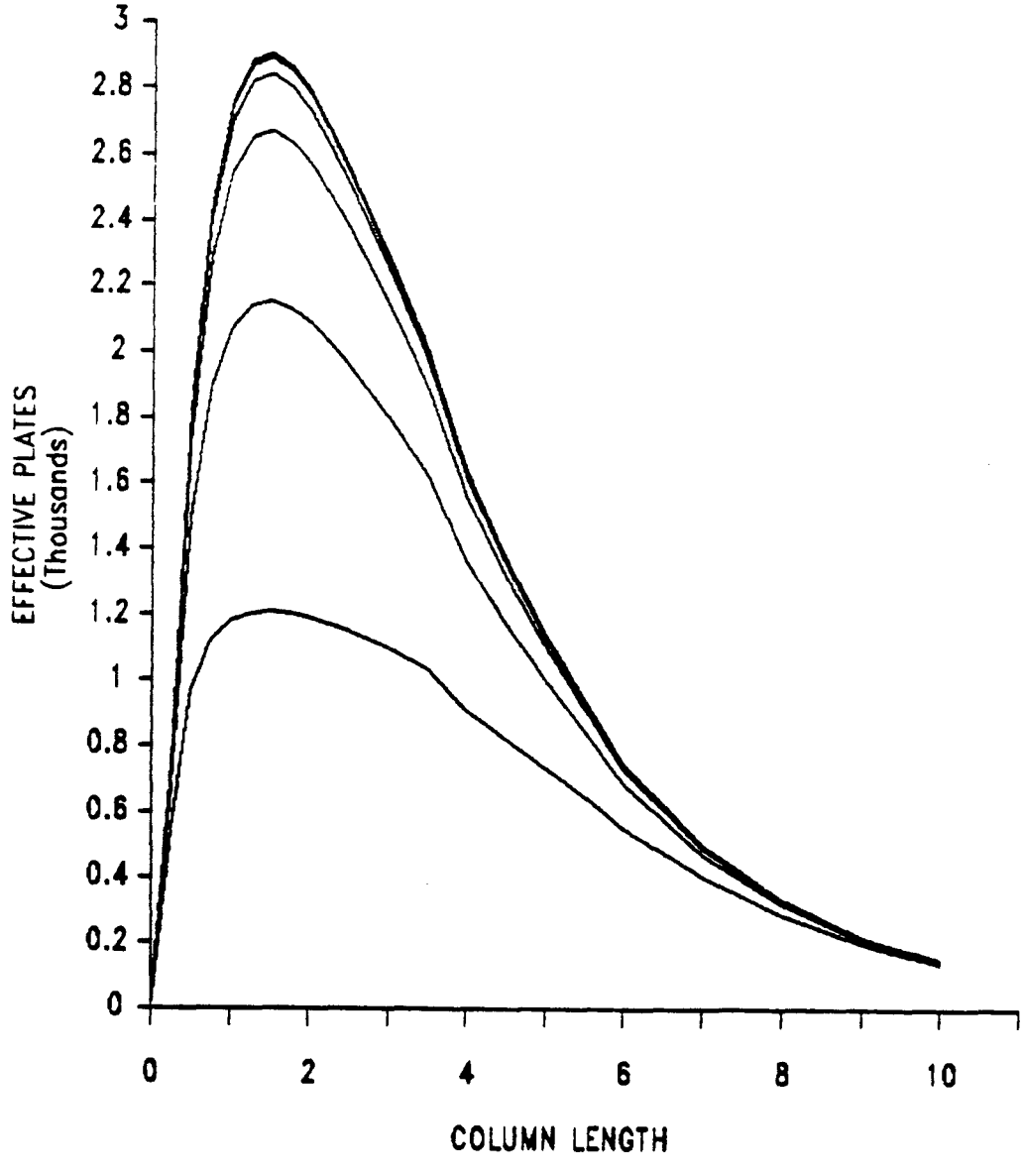

Fig. 9. Computer generated plot showing the number of effective plates developed at varying lengths of 0.25 mm i.d. column with a 0.5 um stationary film. Each line represents a different instrumental time constant. From top to bottom these are: 0, 10, 25, 50, 100 and 200 ms. Operating conditions are presented in the text. Assumes D_l=5 x 10^{-5} cm^2/s and D_g=0.3 cm^2/s and k value of 10.

optimal column length. In order to maintain the 10 second retention time with increased partition ratios, higher carrier velocities are required. The resulting increase in pressure drop degrades performance and pushes the optimal length to a lower value. Under the low efficiency conditions used to generate Figure 9, the effect of increased instrumental dead time is less apparent. Since column efficiency is lower under these conditions, the extra-column factors become relatively less important and the injection band width has less effect on the system. Under these conditions, use of a high efficiency inlet will not significantly increase separation efficiency.

Figure 10 illustrates the potential benefits of "microbore" columns with internal diameters of 0.1 mm. Other than column diameter, all parameters used to generate Figure 10 were the same as those used in Figure 8. It is clear that the smaller diameter column has the potential to produce better high speed chromatograms. However, these small diameter, thin film columns are much harder to handle, are easily overloaded and, due to the small volumetric flows, are more sensitive to dead volumes. The high efficiency of these small diameter columns also makes the system more sensitive to extra-column effects, and makes the use of an efficient injection system more critical. For routine applications

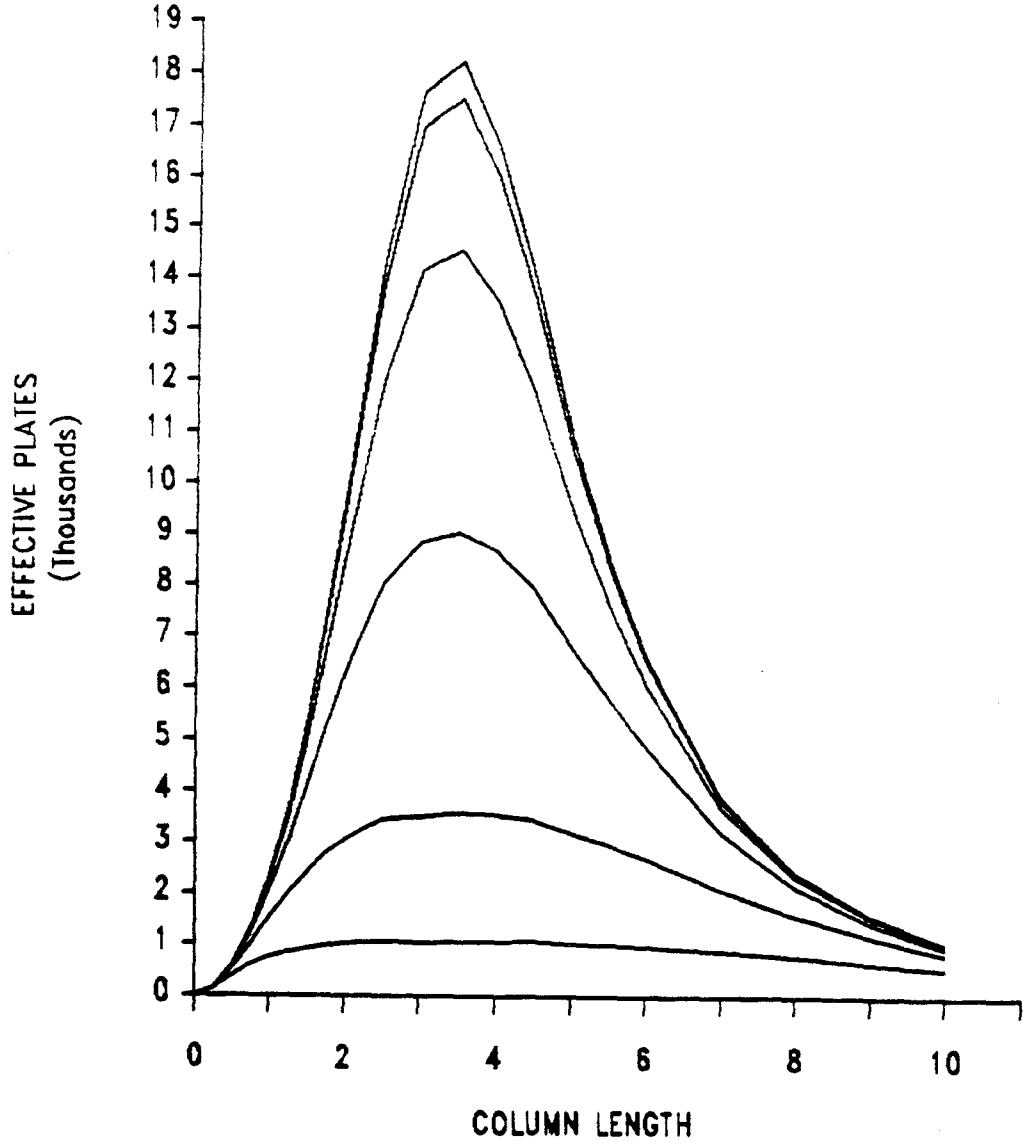

Fig. 10. Computer generated plot showing the number of effective plates developed at varying lengths of 0.1 mm i.d. column with a 0.1 um stationary phase. Each line represents a different instrumental time constant. From top to bottom these are: 0, 10, 25, 50, 100 and 200 ms. Operating conditions are presented in the text. Assumes $D_l=5 \times 10^{-5}$ cm^2/s and $D_g=0.3$ cm^2/s and k value of 2.

involving simple separations, the 0.25 mm columns appear to be the more practical choice.

Another application of the computer model is presented in Figures 11 and 12. In these figures resolution is plotted versus column length for a specified maximum retention time. Each line was calculated from a different partition ratio and represents a different compound in the mixture being separated. Retention times corresponding to the various k values are printed at the end of each line. Figure 11 shows the results obtained with a 0.25 mm i.d. column with 0.1 um stationary phase and k values ranging from 0.05 to 2.0. The resolution values are based on separation of two compounds with a relative retention of 1.1. The more highly retained materials will generally be better resolved on short columns, while the less retained materials will be better resolved on longer columns. In practice the majority of compounds are usually grouped toward the early part of the chromatogram, and the best overall performance is obtained by selecting column length based on the early eluting materials. From Figure 11, a column length of 5 to 6 meters would probably be the best choice under these circumstances.

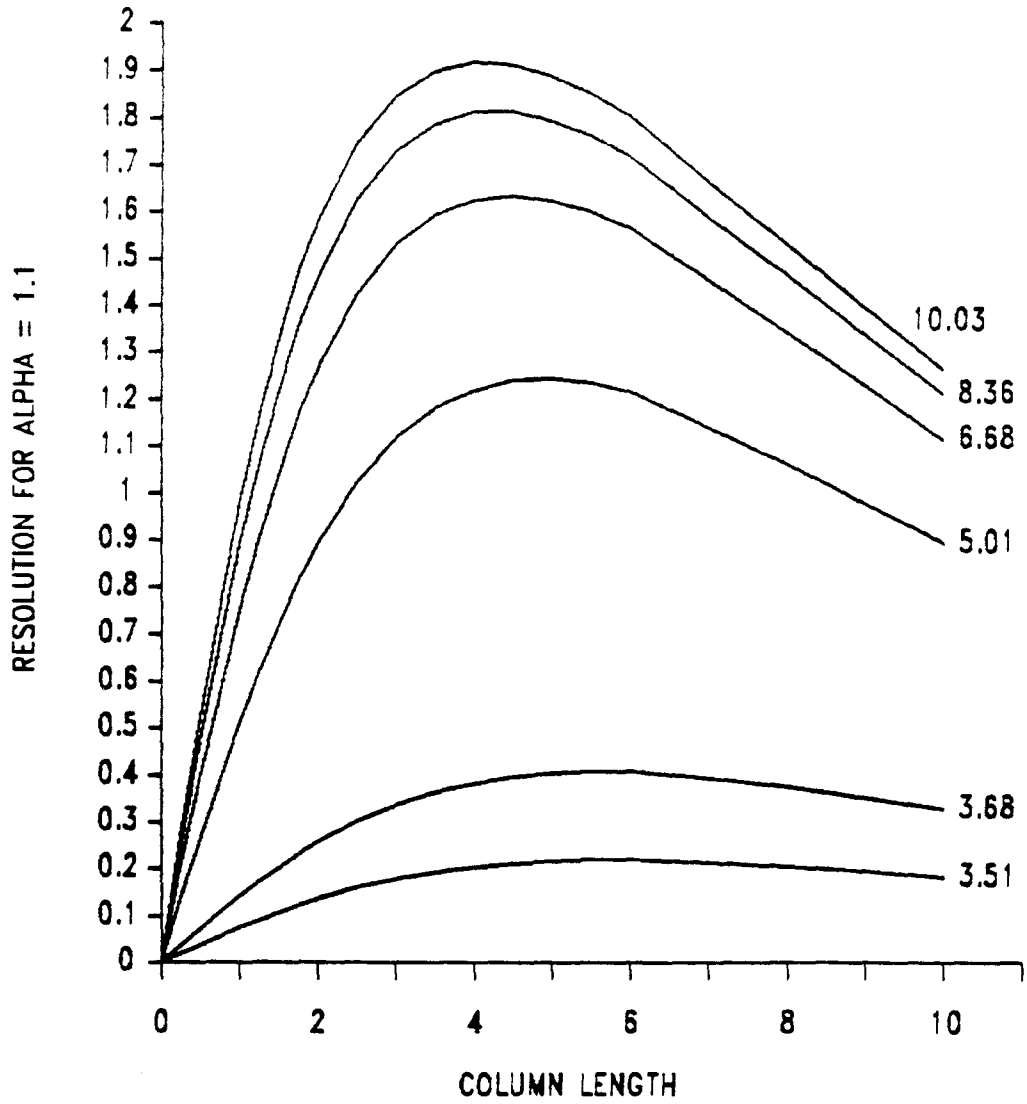

Fig. 11. Computer generated plot showing the resolution expected with varying lengths of 0.25 mm i.d. column and 0.1 um stationary phase. The analysis is constrained to a 10 second maximum with k values of 0.05 to 2.0. Each line represents a different k value or component of the mixture. Labels at the end of each line indicate the retention time for that component.

Figure 12 shows the results obtained with a 0.25 mm column having a 0.25 um thick stationary phase and k values ranging from 0.125 to 5. These figures illustrate the relationship between k value and resolution. The thicker film results in a loss of effective plates, however the increase in partition ratio that is expected at the same oven temperature may actually improve resolution for highly volatile materials. This situation does occur in the analysis of some compounds that are important in industrial hygiene. In order to get good separation of the low molecular weight chlorinated hydrocarbons, for example, it is necessary to use either subambient analysis temperatures or slightly thicker film columns. The thicker film columns also benefit from increased sample capacity, and are less likely to be overloaded by the increased sample volumes that may be needed for some analyses.

As these figures illustrate the choice of column is dependent on the application being considered. If there is a specific pair of compounds that is considered the most important, the column length and carrier velocity can be selected to maximize resolution for that pair. The column choice can be made based on the desired retention time and measured k values. Use of a longer column and higher velocity or a shorter column and lower velocity will degrade performance for the critical pair,

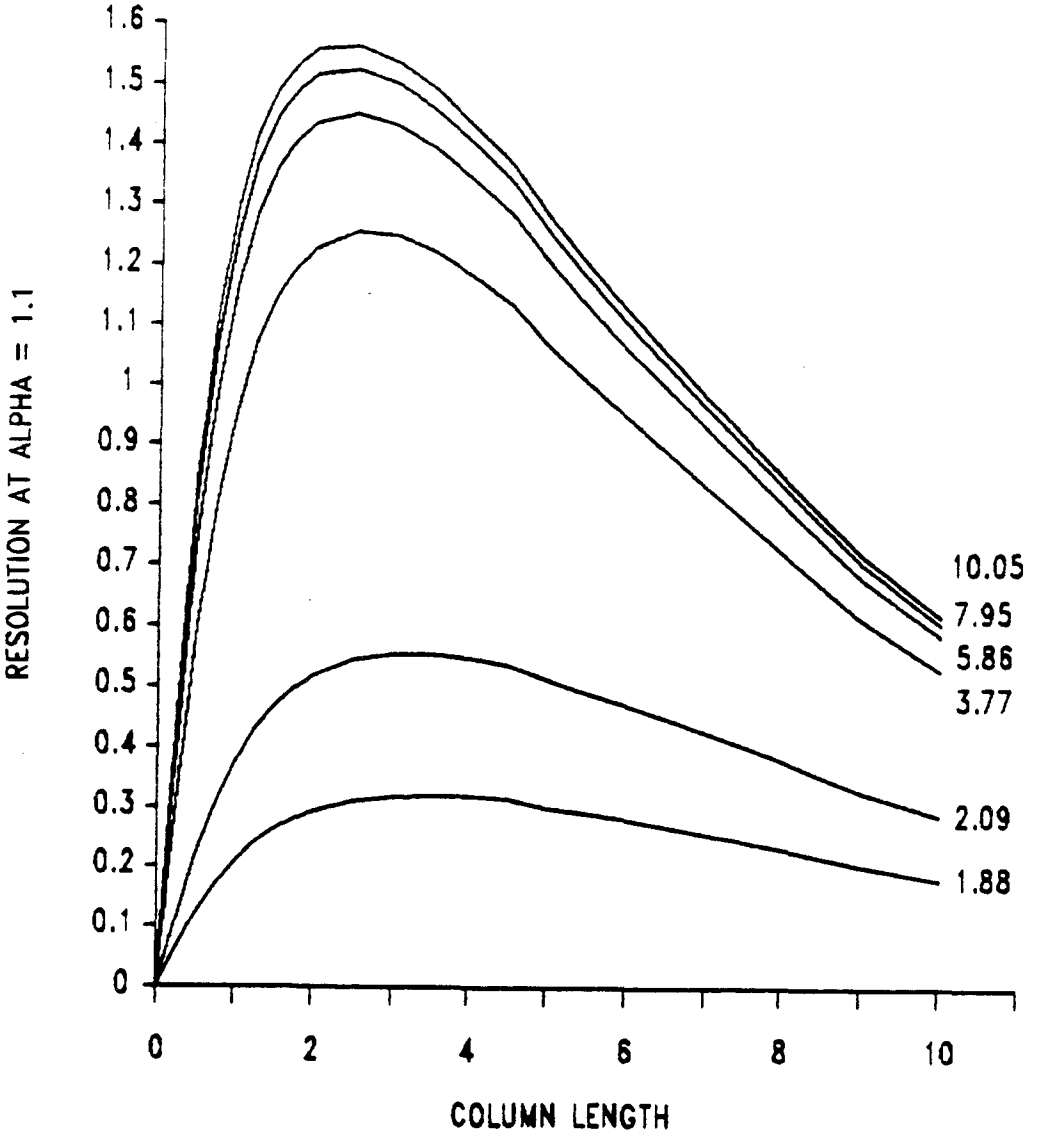

Fig. 12. Computer generated plot showing the resolution expected with varying lengths of 0.25 mm i.d. column and 0.25 um stationary phase. The analysis is constrained to a 10 second maximum with k values of 0.125 to 5.0. Each line represents a different k value or component of the mixture. Labels at the end of each line indicate the retention time for that component.

and possibly for other components of the mixture. In other cases it may not be possible to identify a single pair of compounds as the most important, and a length that gives good average performance will be selected.

The figures presented here also illustrate another restriction on fast GC. Without temperature programing, the range of k values that can be accommodated is fairly limited. This means that all the compounds of interest must have similar boiling points. While this is not a major restriction for most industrial hygiene samples, it may present a significant obstacle in other applications such as the analysis of extracts from water or hazardous waste.

In using the model to select a column and operating conditions for experiments described in this thesis, the following procedure was used. First a column diameter and film thickness were selected based on availability and past experience. Next a column length was selected using plots such as those shown in Figures 8 - 10. Since k values, and diffusion coefficients were initially unknown, estimates were made based on values from the literature or from past experience. A test mixture containing the materials of interest was then prepared and chromatographed at a series of different temperatures. The holdup time was measured using a

methane injection, and the k values and relative retentions were calculated. The measured values were used to re-calculate optimal column length and to investigate the effect of changes in film thickness. In most cases the pre-selected length and velocity were close enough to optimal conditions so that a change was not justified. The measured values, however, were recorded for use in selection of column parameters for future experiments.

Although the computer model has not been thoroughly validated, it does serve as a useful laboratory tool. In cases where peak performance is desired, some experimental adjustments of column length, carrier velocity and oven temperature would probably be required. In order to test the model more thoroughly, experimental data comparing the actual performance to predicted performance are needed. This would require that data concerning each of the parameters, such as diffusion coefficients and column coating efficiency, be available.

Conclusions

Results of the computer based modeling done in our laboratory, and by other groups, indicates that by selecting high efficiency columns and using equipment that will minimize extra-column band broadening, the

resolution available with fast GC systems should be adequate for many routine applications. This conclusion is supported by a number of publications that have demonstrated fast GC separations (14-17, 39, 40). While no commercial system is capable of performing as a fast GC, a number of manufacturers now produce components that are suitable for use in high speed GC systems, or that can be adapted to that application. High efficiency open tubular columns, low dead volume fittings, and low dead volume detectors are now readily available. High speed electrometers and analog to digital converters are also available or can be built. Recent advances in microcomputer technology and the appearance of a wide variety of data aquisition and analysis software have also made the application of fast GC systems to routine industrial hygiene applications more feasible.

The primary barrier to routine use of fast GC in industrial hygiene appears to be the continuing lack of suitable injection systems.

In order to meet the objectives of this thesis, it was first necessary to develop and validate a high speed inlet system that would be suitable for industrial hygiene applications. The development and testing of the cold trap inlet and other basic components is discussed in Chapter 2. The final design and performance

characteristics are presented in Chapter 3. Chapters 4 and 5 present data collected during the validation of the system with vapor and liquid samples. In both cases the samples are mixtures of aromatics similar to those that might be found in an industrial environment. Conclusions and recommendations for further development of fast GC systems are presented in Chapter 6

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CHAPTER 2

INSTRUMENT DEVELOPMENT

If extra-column band broadening is sufficiently reduced, the separation efficiency available from modern capillary columns will allow many simple analyses to be completed in as little as a few seconds. As was discussed in Chapter 1, several factors that contribute to extra-column band broadening can be identified. The most important factors are usually:

1. The initial band width produced by the injector
2. The response time of the electrometer
3. Dead volumes in the detector
4. Dead volumes in the column connections

For the GC system used in these experiments, dead volume in the detector was minimized by the use of a FID, which is an open cell detector. In addition, keeping the number of column connections at a minimum, and using commercially available low dead volume unions helped minimize dead volumes outside the detector. Under these conditions the dead volumes could be neglected and the major concerns became the injector and

electrometer. A discussion of the development, optimization and initial testing of these two components is presented in this chapter.

Introduction

The width of the initial injection band is usually the major contributor to extra-column band broadening. Therefore, one of the keys to routine use of fast GC in industrial hygiene is the development of a practical and reliable inlet system that can minimize initial band width.

In his original work with fast GC systems, Desty minimized initial band width by using an inlet splitter operated at high volumetric flow rates and by driving the syringe plunger with a rubber mallet (1). Although his system was unsophisticated, it did allow his research group to publish some of the first and best high speed chromatograms.

Following Desty's initial research in this area, a number of laboratories described more sophisticated high speed inlet systems. Each of these placed sample on the front of the column as an extremely narrow band, sometimes with a width of 1 ms or less.

Jonker, Poppe and Huber in 1982 described a packed column fast GC system that used a modified rotary valve as the inlet (2). No sampling loop was used, and only the internal volume of the rotor valve, about 1.5 ul, could be injected. Although no measurement of initial band width was reported, final peak widths of about 10 ms were obtained, indicating a high level of injection efficiency.

A series of papers by Wade, Gaspar, Annino and others described the development of high speed inlet systems based on the use of fluid logic gates, or Dean's switches (3-5). While the designs varied, the idea was that a narrow, well defined plug of sample could be injected by momentarily redirecting the flow of sample vapor from a vent to the stream of carrier gas. The flow switching was controlled by pressure pulses, and required no mechanical valves or other moving parts. Fluid logic injectors are reportedly capable of producing injection band widths of 10 ms or less. However, these systems are quite sensitive to pressure fluctuations, and therefore may not achieve the reproducibility necessary for measurement of trace environmental contaminants.

More recently, Tijssen described a mechanical inlet system that was capable of producing injection bands with widths of 1 ms or less (6). The system was based on what was essentially a sliding needle with a vent that quickly moved past the open end of the GC column. As the open vent moved past, a small plug of sample vapor entered the column. The reproducibility of the system, and its potential for routine applications, have not been well documented.

While each of the inlet designs described by these authors is well-suited for research purposes and may be useful in some applications, their value in routine environmental or industrial hygiene applications is questionable. None of the designs has been thoroughly tested, and each is limited in the type and size of sample that it can handle. In each case the sample must be a gas, and due to the small sample size, should be fairly concentrated. These inlet systems could probably be interfaced with a heated injection port for liquid analysis. However, in most cases, this has not been done and it would require that the injection and flow switching mechanisms be closely coordinated to avoid sampling variability. An additional limitation of these systems is that they lack any type of pre-concentration mechanism which would allow analysis of dilute gases or vapors.

Another solution to the requirement for extremely narrow injection bands is the use of a cold trap. Although cold traps have received only limited attention as fast GC inlets, they have been used extensively in other applications including the collection of organic vapors from ambient air (7-10). A cold trap allows sample that is introduced by conventional injection methods to be collected and concentrated in a small area. If the trap temperature is rapidly increased, the collected sample can be revaporized and placed on the column as a narrow, concentrated band.

Expanding on the earlier work of Hopkins and Pretorius (11), Ewells and Sacks developed a gas cooled and electrically heated cold trap inlet that could produce injection bands with widths of less than 10 ms (12, 13). Their inlet design featured an open tubular, stainless steel cold trap with an internal diameter of 0.5 mm. The trap was enclosed in a Teflon sheath and cooled by a continuous flow of cold nitrogen gas. Samples were introduced into a standard injection port and splitter using a syringe. The cold trap was located between the splitter and the column, and was placed inside the oven. Following trapping, the focused sample was revaporized by running a short pulse of current from a transformer through the trap tubing.

More recently, van Es et al described a very similar fast GC system that used a section of the capillary column as a cold trap (14). In their design, an extremely small diameter, 0.05 mm i.d., capillary column was used for the separation. The front of the column was threaded through an aluminum clad, fused silica capillary which acted as the heating element. The aluminum clad capillary and front section of the column were cooled by a flow of nitrogen gas. Heating for reinjection was achieved by running an electric current from a transformer through the aluminum coating on the outer capillary. Although the performance characteristics of the system were not thoroughly documented, the authors claim that injection bands as small as 1 ms could be produced.

Cold trap systems appear to have a number of advantages over other types of high speed inlets. Primary among these is the capacity for collection and concentration of dilute vapors from a large volume of air or other gas. These systems can be combined with most conventional inlets and allow a wide variety of sample types, including both gases and liquids, to be analyzed.

Although achieving reproducible, efficient, high speed injection was the greatest difficulty in the development of a fast GC system, the response time of the electrometer and data system was also a consideration. Conventional GC systems usually produce peaks that are at least a few seconds wide and do not require fast responding electronics or data systems. Manufacturers often take advantage of this slow response time and use various filtering mechanisms to remove high frequency noise from the detector signal. For example, HNU Systems standard electrometer uses a low pass filter to eliminate noise with frequencies above 3 HZ (15). This approach to signal processing produces a very low background with good signal to noise ratios, and minimizes the need for for low noise detection devices. These systems typically have response times of about 200 to 250 ms, which is much too slow for fast GC applications.

The time constant, or sampling rate, of the data recording system is another potential problem. Many analog devices, such as chart recorders, convert signal intensity to a mechanical response and are too slow for use with fast GC systems. While digital signal processing can be accomplished at extremely fast rates, many analog to digital converters are not designed for high speed data aquisition. For example, most dedicated

chromatography integrators are designed to sample at less than 20 Hz, a speed which is adequate for conventional systems but is not appropriate for fast GC. Even PC based chromatography work stations, such as those sold by Nelson Analytical, are usually limited to a maximum sampling rate of about 40 Hz.

The importance of electrometer response time in high speed GC was explored in some detail by Gaspar et al (16). In their initial studies of extra-column band broadening, they estimated that inadequate electrometer response speed could account for as much as 85% of total band broadening for very short retention times. For the narrow peaks developed by their system, sigma equal to 30 ms, even a response time of 15 ms was too slow, and resulted in significant peak broadening. As a general rule, peak distortion is avoided only if the response time of the electrometer is 10% or less of the rise time for the sharpest peak (15).

As Gaspar noted, it is relatively easy to build a fast electrometer with a response time of less than 1 ms. Fast responding electrometers, however, are extremely sensitive to noise that originates either in the detector or in other electronic components. Since efficient injection and column operation requires small sample loads, the electrometer sensitivity and

amplification must be maximized and the noise problem is compounded. In order to minimize noise problems, the sample must be enriched or the noise must be eliminated at the source.

The work described in this thesis was, for the most part, done with a cold trap injection system based on the work of Ewells and Sacks. For purposes of comparison, data were also collected using a conventional inlet splitter. Manual sample injection was used in both this study and by Ewells. In this study, some injections were also made with a Hewlet Packard HP-7673A auto-injector. The HP-7673A was used because it is capable of making highly reproducible liquid injections with volumes as small as 0.5 ul. In addition the dwell time of the needle is very short, approximately 20 ms, so it should not contribute significantly to the width of injection bands produced by the splitter.

The electrometer used for most of these studies was essentially identical to that developed by Ewells and Sacks. In some cases a 60 Hz filter was added. However, since the effect on narrow peaks was not well defined, the filter was only used on a limited basis.

The data recording system used by Ewells, and in the earliest stages of this work, was a Nicolet digital oscilloscope capable of sampling at over 1 kHz. This was later replaced with a PC based system featuring a Data Translation DT2801 analog to digital converter with a maximum sampling speed of over 10 kHz.

Preliminary Design Considerations

Following Ewells' initial work with cold trap injection, a new fast GC system was assembled. This new system was based on the earlier design, but included a number of changes that were made with the hope of improving overall chromatographic performance and ease of use. The major improvements that were included in this first prototype are listed here.

1. The trap tube was replaced, first with a stainless steel tube of smaller diameter, and later with a custom drawn nickel tube.

2. The trap was redesigned and moved outside the oven to make cooling easier, and to prevent the trap from affecting oven temperature.

3. The cold trap sheath and electrodes were redesigned to simplify replacement of the trap tube, improve

electrical contact and minimize the number of column connections.

4. The transformer based heater system was replaced with a small, low voltage, capacitor discharge power supply featuring a digital control capability.

5. The column was replaced with a high efficiency 0.25 mm i.d. fused silica capillary column (Quadrex).

6. The injector was replaced with a Varian injection port and SGE splitter system featuring a glass lined stainless steel injection chamber. These were mounted in a custom made, heated, aluminum injection block and attached to the side of the GC.

7. The oven and FID were replaced with a Varian 3700 GC for improved temperature control and detector performance.

8. The pneumatic systems were redesigned to provide continuous digital display of flows and pressures, and to allow independent control of the flow rate and split ratio.

9. The digital oscilloscope was replaced with a PC based data aquisition, analysis and control system.

One of the major advantages this design has over those of Pretorius and Hopkins, Sacks and Ewells or van Es is the use of a small, low voltage capacitor discharge power supply. The power supply was originally developed by J. Foulke of the University of Michigan Department of Industrial Engineering, and was later refined by Prototype Design Company of Ann Arbor Michigan.

The original system featured 16, 1000 uF 100 volt capacitors and 8 107 uH inductors arranged to form 8 LC sections. The design was later modified to provide 30% greater capacitance at a maximum charge of 75 to 80 volts. The system also features a 60 Hz sustainer and pre-heat circuit which prevents the trap from cooling too rapidly, and in addition, can be used to keep the trap warm between chromatograms.

The design is intended to produce a rectangular current pulse with a width of 5 to 10 ms, which is expected to heat the trap to reinjection temperatures in 10 ms or less. A schematic diagram of the heater circuit, and some examples of the voltage waveforms it produces are presented in Figure 13.

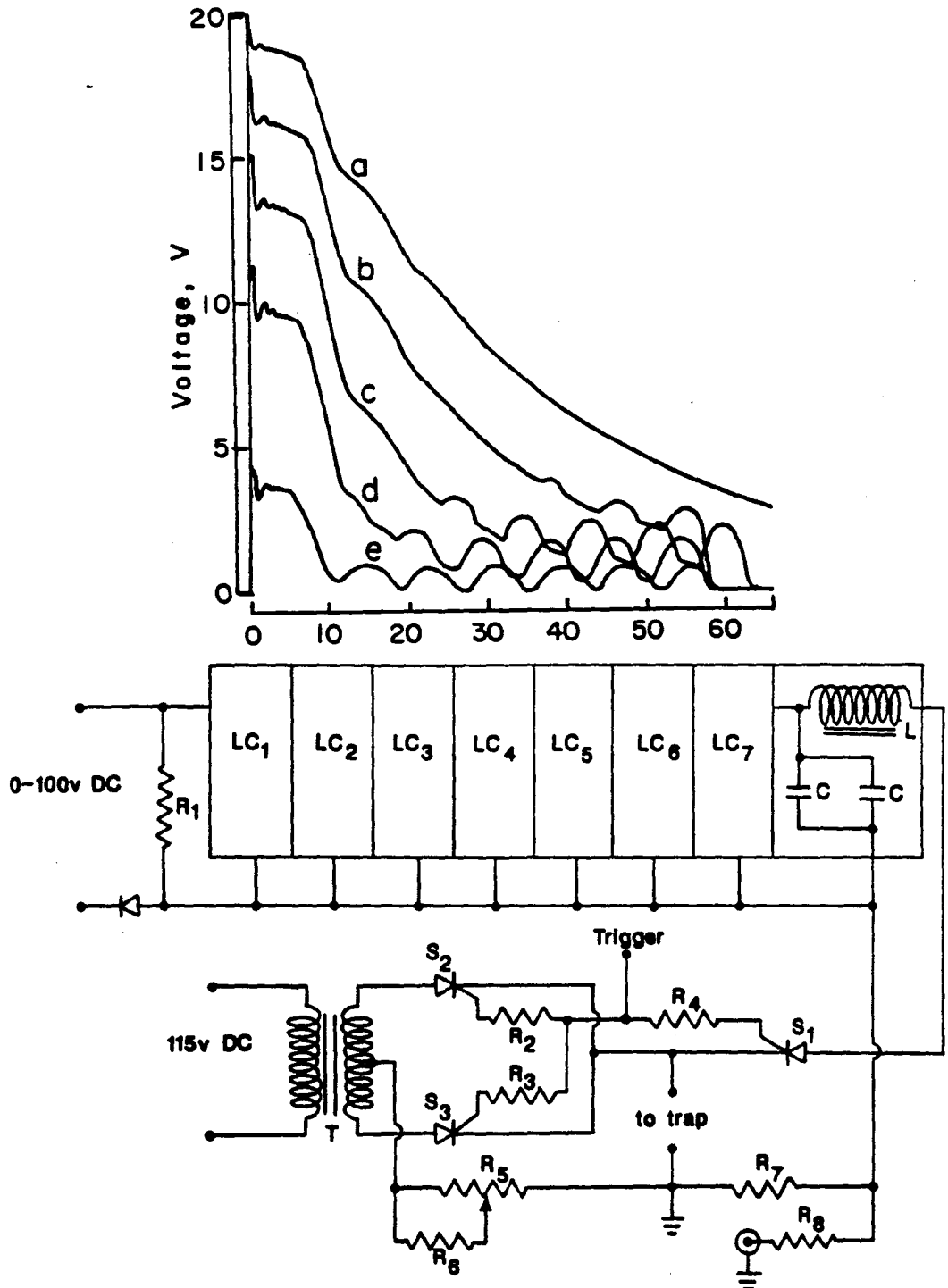

Fig. 13. Trap heater circuit and voltage waveforms for a series of 23 volt discharges. A high current pulse from the LC discharge circuit is delivered through S_1. A low sustainer and preheat current is delivered through S_2 and S_3. The discharge current is monitored as the voltage across R_7. C; capacitors, L; inductors, S_1; SCR (35 A, 200 V), $S_{2,3}$; SCR (8 A, 50 V), T; 6.3 V CT. The inset was produced with steel trap tubing of varying length. A; 40 cm, B; 20 cm, C; 10 cm, D; 5 cm, E; 2 cm.

Following the modifications listed above, the system was used to produce a number of high speed chromatograms, an example of which is shown in Figure 14. These chromatograms, which were made using neat mixtures of simple hydrocarbons, demonstrated the capabilities of the system. While the fast GC was shown to be capable of producing qualitatively good chromatograms, the capacity for quantitative analysis had not yet been evaluated.

Preliminary quantitative tests of the system revealed that although separation efficiency and ease of use had been improved over earlier designs, a number of design and performance problems remained. Specific problems included a lack of repeatability, poor durability and inadequate trapping and reinjection efficiency.

The remainder of this chapter presents a discussion of the experiments that were run to test the fast GC system. A number of design changes that were implemented to improve performance are also described. A complete report on the final system design, and a study of its basic operating characteristics are presented in Chapter 3.

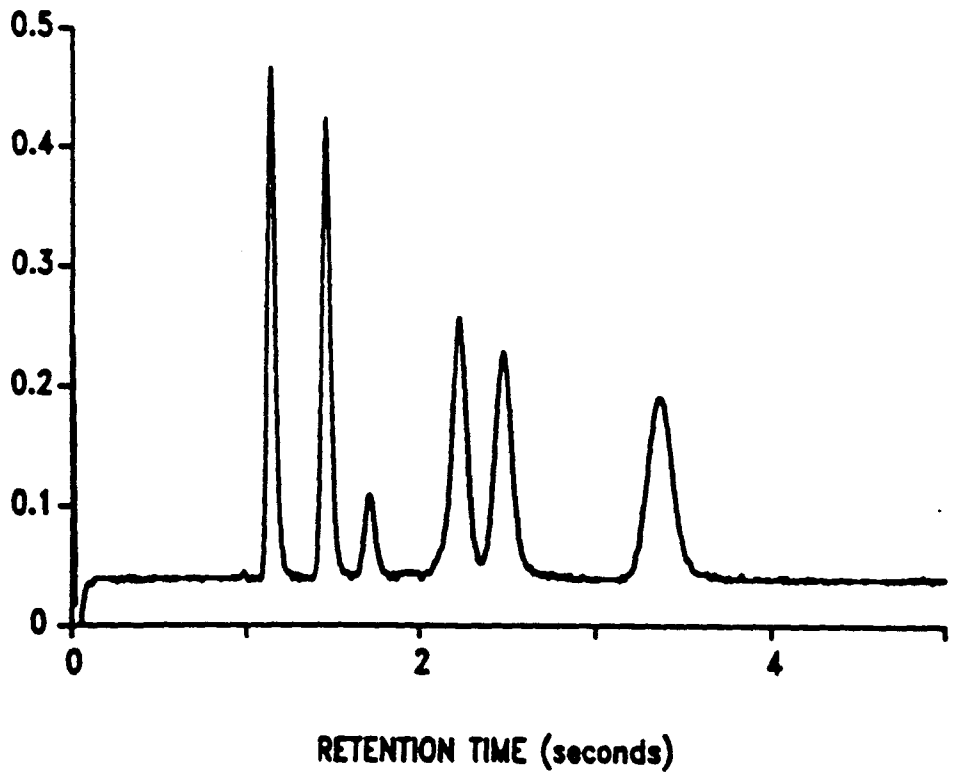

Fig. 14. Fast gas chromatogram produced with the cold trap inlet. Major peaks are: Benzene, Toluene, O-Xylene, M-Xylene and O-chloro-Toluene. Separation was achieved with a 2 m X 0.25 mm column with a 0.1 um stationary phase and a carrier velocity of approximately 220 cm/s.

Experimental

Experiments were designed to evaluate four aspects of system performance that were believed to present potential problems: repeatability, sample recovery, injection band width and trap durability. In order to achieve this, three basic sets of experiments were planned. The first set of experiments was intended to assess the performance of the inlet system in terms of heating rate and maximum attainable temperature. The second set of experiments was designed to evaluate the fast GC performance in terms of quantitative chromatographic parameters, such as peak area reproducibility. The third set of experiments was designed to test the performance of the system in terms of instrumental time constants. The procedures used in each set of experiments are described in the following paragraphs. While conducting these experiments, trap durability was also evaluated.

Trap Temperature Measurements

Sample recovery and trap durability were both expected to be dependent on the trap temperature profile during the trapping and reinjection cycle. Previous estimates of trap temperature and heating rate were based on calculations made from published values for

resistivity and heat capacity. For the experiments described here a series of actual temperature measurements was required.

In order to make these measurements, small (30 or 36 gauge) thermocouples were spot welded to the approximate center of the trap tubing. The output from the thermocouples was directed to a high speed differential amplifier built specifically for this application. The amplifier output was directed to the DT2801 Analog to Digital converter and sampled at a rate of either 400 or 1000 Hz. The system was calibrated against a thermocouple-based digital thermometer and the calibration was verified by measuring the temperatures of ice water and boiling water.

The trap tubing, with the attached thermocouple, was then installed in the cold trap system and simulated trapping and reinjection cycles were run at varying voltages. Three replicates were run at each voltage. Because the welding process occasionally created small holes in the trap tubing, actual chromatograms were not usually collected during the temperature measurement experiments. In order to detect any artifacts that might be attributed to the quality of the thermocouple or the weld, each tube was tested with three different thermocouples.

Chromatographic Performance

Sample recovery and peak area repeatability were evaluated by comparing results obtained with cold trapping and reinjection to results obtained under identical operating conditions, but without use of the cold trap. In most cases the test mixture was toluene in carbon disulfide at a concentration of 1 mg/ml. In some experiments an alternate test mixture containing hexane was used.

Because of the difficulty involved in obtaining good high speed chromatograms without the cold trap, these experiments were generally conducted under conditions that resulted in relatively long retention times. This allowed good peak shapes to be obtained, and peak areas to be measured accurately, even without trapping. Peak areas measured from the non-trapped chromatograms could then serve as controls.

The procedure used in these experiments was to first heat the injection port and cold trap to 275 ^{o}C and make a series of syringe injections, as in conventional GC. A set of three to five chromatograms was collected at each of several injection volumes. Peak areas were then measured and the average and

standard deviation were calculated so that a calibration curve could be established that would relate peak area to the mass of the injected sample.

Once a calibration curve was established, the trap was cooled to -90 ^{o}C and a second set of data was collected, but this time with trapping and reinjection. A series of samples was run with varying reinjection voltages and peak areas were measured. The peak areas obtained with trapping and reinjection were then compared to the areas that were expected based on the earlier calibration.

The effective trapping temperature of -90 ^{o}C was established by monitoring the FID response during syringe injection. If any baseline elevation was observed, this was taken as evidence of incomplete trapping or breakthrough, and the trap was cooled to a lower temperature.

Inlet Performance and Time Constant Evaluation

In order to compare performance of the cold trap to the conventional inlet splitter, a series of peak width measurements was made. For these experiments, the column was replaced with a 25 cm long transfer line

made from 0.2 mm i.d deactivated fused silica tubing. During evaluation of the splitter, the cold trap was removed and the splitter outlet was connected directly to the FID with the transfer line. A similar configuration was used during evaluation of the cold trap. In this case however, the the splitter was connected to the cold trap with one piece of fused silica tube, and the transfer line was used to connect the the cold trap to the FID.

All liquid injections were made with the Hewlett Packard autoinjector and vapor injections were made with a gas-tight syringe. The injector temperature was set at 250 ^{o}C, the oven at 170 ^{o}C and the FID at 190 ^{o}C. Because of the low flow resistance produced by the short transfer line, the flow rate was much higher than normal at 10 ml/min, which produced linear velocities of about 900 cm/s.

Peak widths were measured at the base, and instrumental time constants were calculated using the modified Golay equation that was discussed in Chapter 1. Based on the high oven temperature and lack of a stationary phase, the partition coefficient was assumed to be zero. In addition, the small pressure drop allowed the pressure correction factors to be

eliminated. These simplifications allow the Golay equation to expressed as:

$$H = \frac{2D_g}{U} + \frac{d_c^2 U}{96D_g} + \frac{T^2U^2}{L}$$

The value of H can be calculated from measurements of peak width, W_b, using the equation:

$$H = \frac{(W_b * 0.25)^2}{L}$$

A sample calculation is is presented as Appendix A.

Since contributions of other extra-column factors are believed to very small, the calculated time constants were interpreted as a measure of injector performance.

Results and Discussion

Trap Durability

In her earlier work with transformer based cold trap inlet systems, Ewells reported few problems with trap durability. During her preliminary work with capacitor discharge heating circuits, however, she suggested that the improved performance that these

systems provide might come at the expense of trap durability. Intensive use of the cold trap and capacitor discharge heating system developed for this project revealed that there was in fact a severe problem with trap breakage.

In order for the inlet to be useful for routine analysis, the trap should require little or no maintenance and should have a useful lifetime of at least several thousand heating and cooling cycles. Trap durability with the prototype inlet developed for this project was highly variable, but was generally unacceptable. While some traps lasted for as many as four to five hundred firing cycles, others failed after fewer than one hundred.

Inspection of failed traps revealed that breakage occurred most frequently at the point of connection to the upstream electrode. At least four processes may have contributed to the problem:

1. Mechanical stress due to thermal expansion: Thermal expansion of the trap during the re-injection cycle is significant. Because the trap was held rigidly at both ends, the trap would bow in the center. This repeated bending of the trap

tube at the edge of the electrode appears to have eventually lead to breakage at that point.

2. High point resistance resulting in over-heating at the electrode: Poor electrical contact between the electrodes and the trap tubing may produce a high point resistance and hot spots that melt or weaken the trap tube. Poor contact could result from electrode corrosion and/or from inadequate matching of the trap tube to the electrode blocks.

3. Work-hardening of the trap tube: Certain metals, such as the high carbon steels, have a tendency to work-harden, or become brittle, when exposed to repeated heating and cooling. This process was probably a major factor that contributed to the poor durability of stainless steel traps.

4. Over heating resulting from a lack of temperature monitoring and control capability: Early work with the fast GC system was done without the benefit of a trap temperature monitor. It is likely that the trap lifetime was reduced by excessive, and inadvertent, overheating of the trap tubing. This is especially true at the upstream electrode which was continuously heated with a heating cartridge to a temperature of 150 ^{o}C to avoid sample condensation in that area.

In response to the durability problem, a number of changes were made in the inlet design and in the choice of trap materials.

In order to allow the trap tube to expand and contract with a minimum amount of mechanical stress, spring loaded electrodes were developed. These allowed the trap to slide in a longitudinal direction as the length of the tubing changed, but still maintained a solid electrical contact. The design, which is illustrated in Figure 27, featured a copper-beryllium strip that held the trap tubing in place without making a rigid connection. The length of the trap chamber was also decreased by about 30%, which allowed the trap tubing to be coiled slightly, thereby providing additional dampening of length changes.

In order to improve electrical contact and reduce resistance at the point of connection, the shape of the groove in the lower electrode was changed from a "V" to a semi-circle to increase the contact area. In addition the electrodes were plated with nickel to reduce surface corrosion.

Temperature Measurement and Trap Tubing Selection

The success of the fast GC project was expected to be highly dependent on the performance of the trap heater system. The heating rate and the maximum attainable temperature are especially important, and are at least partly determined by the characteristics of the trap tubing. Therefore, careful testing and selection of trap tubing was an important part of the project.

Selection of a thin walled tube made from a high resistivity metal would be expected to provide the most rapid and efficient heating. However, thin wall tubing is also expected to be the most fragile. While the characteristics that affect heating were the primary consideration in selection of the trap tubing, other factors that might affect durability, such as the malleability or ductility, coefficient of thermal expansion and susceptibility to work-hardening were also considered. Materials were selected for testing on the basis of their physical properties, which are listed in the manufacturers literature, as well as on the basis of availability in the form of thin wall capillary dimension tubing.

Unfortunately cost considerations did not allow testing of some materials that might be well suited to

this application. For example, Nichrome, an alloy of nickel and chromium, appears to have excellent characteristics. This alloy, which is used as the heating element in stoves and ovens, has a very high electrical resistivity, a small coefficient of thermal expansion and is resistant to work-hardening. Unfortunately Nichrome was not available in the form of capillary tubing, and could not be custom drawn, except in large quantities.

Only a limited number of metals were available. However, based on the suppliers specifications, some of these were expected to perform better than the stainless steel which was used by Ewells, or the nickel that was used in some of these early experiments. The materials that were obtained and tested for suitability as trap tubing included several varieties of steel, nickel, platinum, titanium, Monel-400 and a 30% copper - 70% nickel alloy. Some of the important characteristics of the sample tubes are listed in Table 1.

Evaluation of the sample traps was based on temperature measurements made during a series of heating and cooling cycles. Durability during the testing cycle was also considered.

TABLE I

PROPERTIES OF EXPERIMENTAL TRAP TUBES

METAL	THERMAL[1] EXPANSION	ELECTRICAL[2] RESISTIVITY	ELONGATION[3] %	TENSILE[4] STRENGTH	WORK HARDEN
Copper-Nickel	9.0	225	40	55	NO
18% Nickel	9.0	173	40	58	NO
Monel 400	8.7	307	40	75	NO
Type 316 Steel	9.0	445	50	85	YES
Titanium	5.8	331	28	70	NO
Nickel	7.9	75	45	65	NO

1. Per cent increase in length for a 100 ^{o}C increase in temperature.
2. Expressed in ohms.
3. Elongation is expressed as the per cent increase in length at the point of breakage. This a measure of the material's ductility.
4. Expressed relative to a standard material.

A typical data file collected during a trap heating cycle is shown in Figure 15. This particular data set was collected using a nickel trap tube identical to those used in the prototype inlet, and a 50 volt reinjection pulse. The thermocouple output is labeled "B" and shows the temperature rising over a time span of about 30 ms. Tracing "A" shows the current flow, which rises and drops rapidly over a span of only about 5 to 10 ms. The current spike is stretched on the downward slope by a sustainer current which was designed to prevent the trap from cooling before the sample was completely cleared.

In this case the initial temperature was -50 ^{o}C and the actual temperature rise, shown here on an arbitrary scale, was about 50 degrees. Because the thermocouples used in these experiments had a significant lag time, they were probably not capable of accurately tracking the temperature rise. The heating rates shown here should therefore be considered as minimum values. The cooling rate was found to be relatively slow, and it was possible to make accurate determinations of peak temperature and to make an estimate of the temperature change profile during the remainder of the reinjection cycle. It should be noted that the apparent heating rate and the maximum temperature are both highly

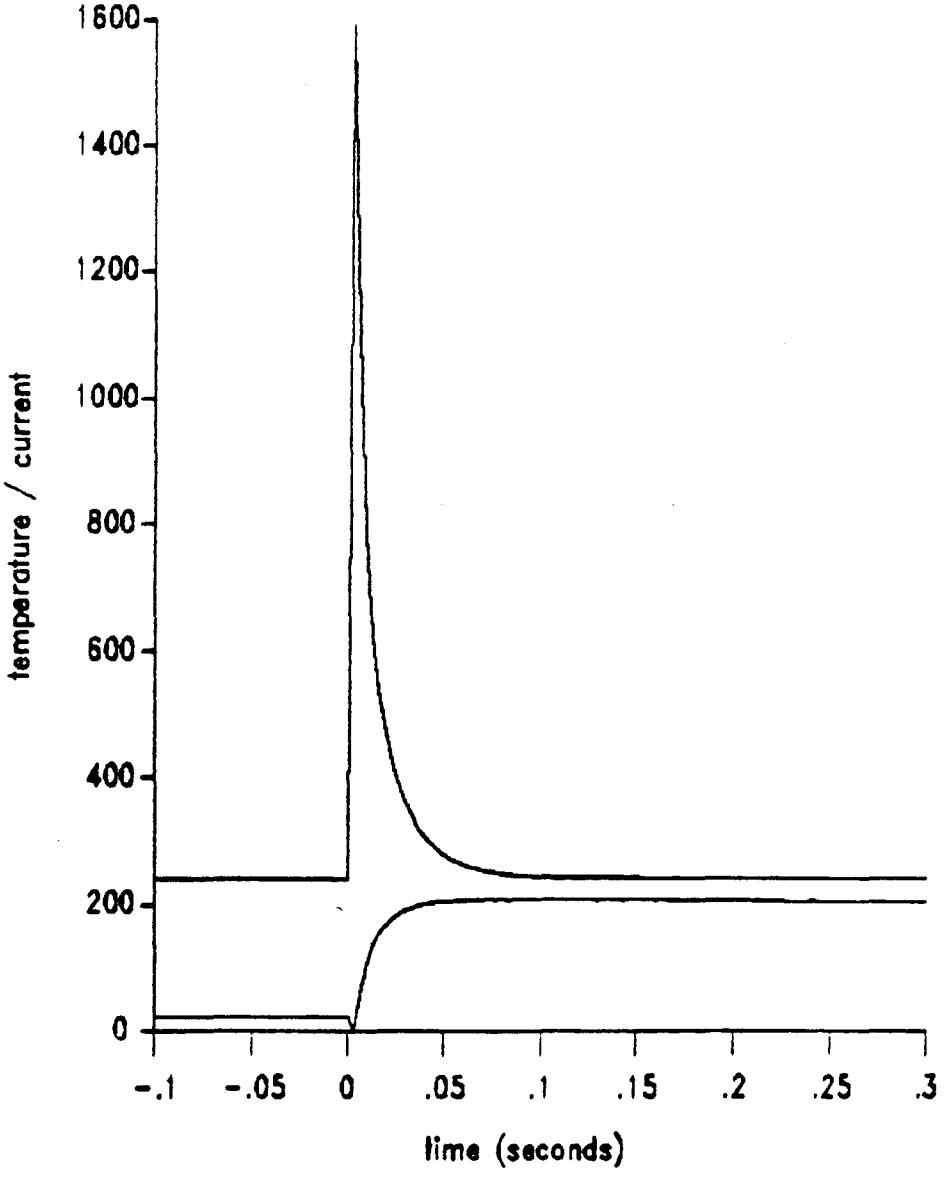

Fig. 15. Current and temperature profile during one heating cycle. The upper trace shows the current and the lower trace shows the thermocouple signal. Units on the vertical axis are arbitrary. The trap material was nickel and the actual temperature increase was about 50 ^{o}C.

reproducible, with temperature peaks varying by only a few degrees from one heating cycle to the next.

Figure 16 illustrates a complete data set for the nickel trap with initial temperatures of -50 ^{o}C and initial capacitor charges of 33 to 60 volts. As expected, higher initial voltages produce higher maximum temperatures and faster heating rates. Although data on the effect of starting temperature is not presented in this figure, it should also be noted that the initial temperature has a greater effect on heating characteristics than might be anticipated. Starting 50 degrees colder for example, will result in a loss off more than 50 degrees from the peak temperature. This can be attributed to the fact that lower temperatures produce lower electrical resistivity and hence decrease the heating efficiency. This is an important consideration because many compounds require temperatures as low as -150 ^{o}C for efficient trapping. From starting temperatures that cold, the nickel tubing could not be heated to temperatures higher than about 75 ^{o}C.

Figure 17 shows a similar data set, but compares the heating profiles of different types of tubes tested under similar temperatures and reinjection voltages. These data seem to indicate that, on the basis of

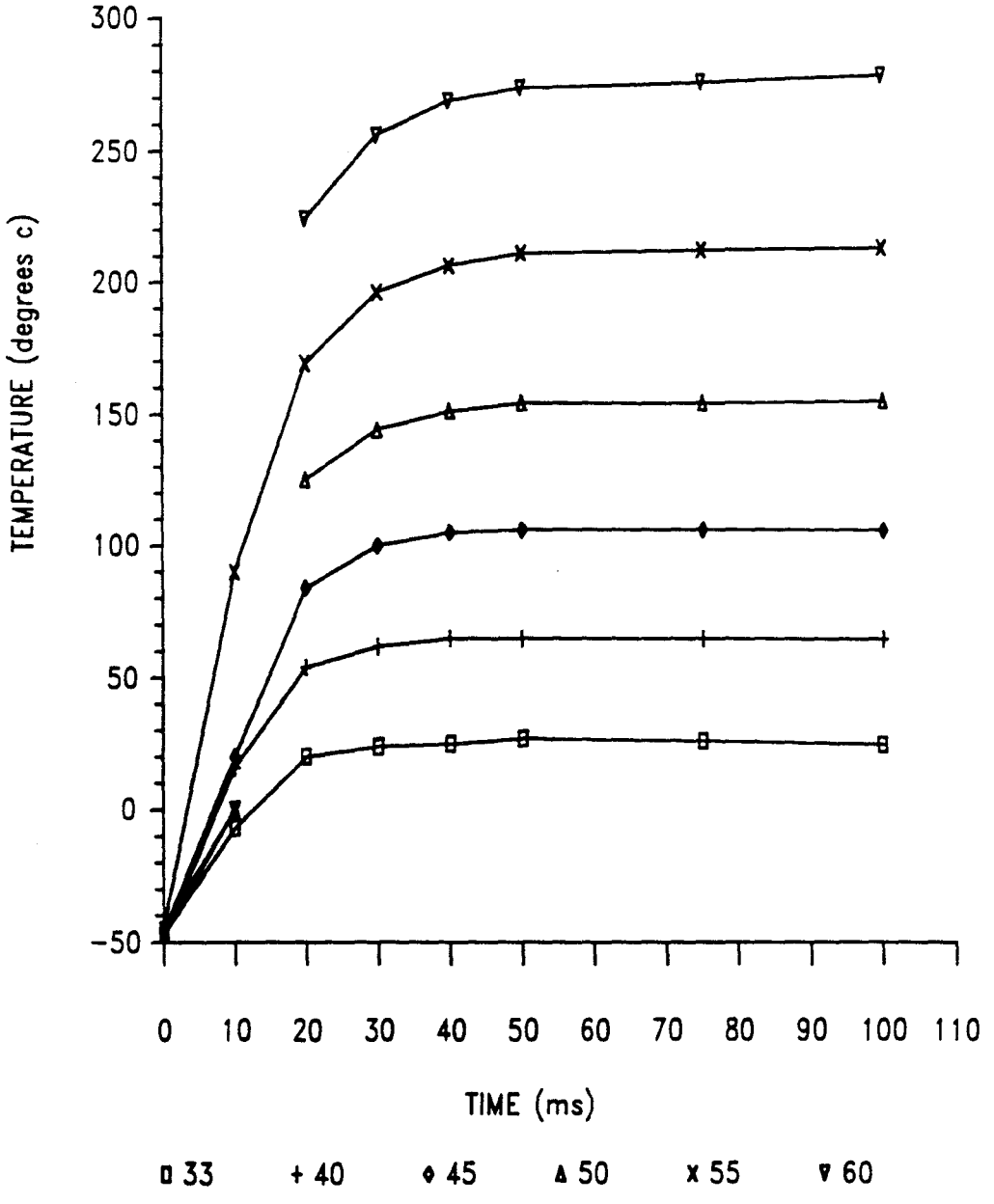

Fig. 16. Trap temperature profiles for heating cycles initiated at different capacitor voltages using a nickel trap tube.

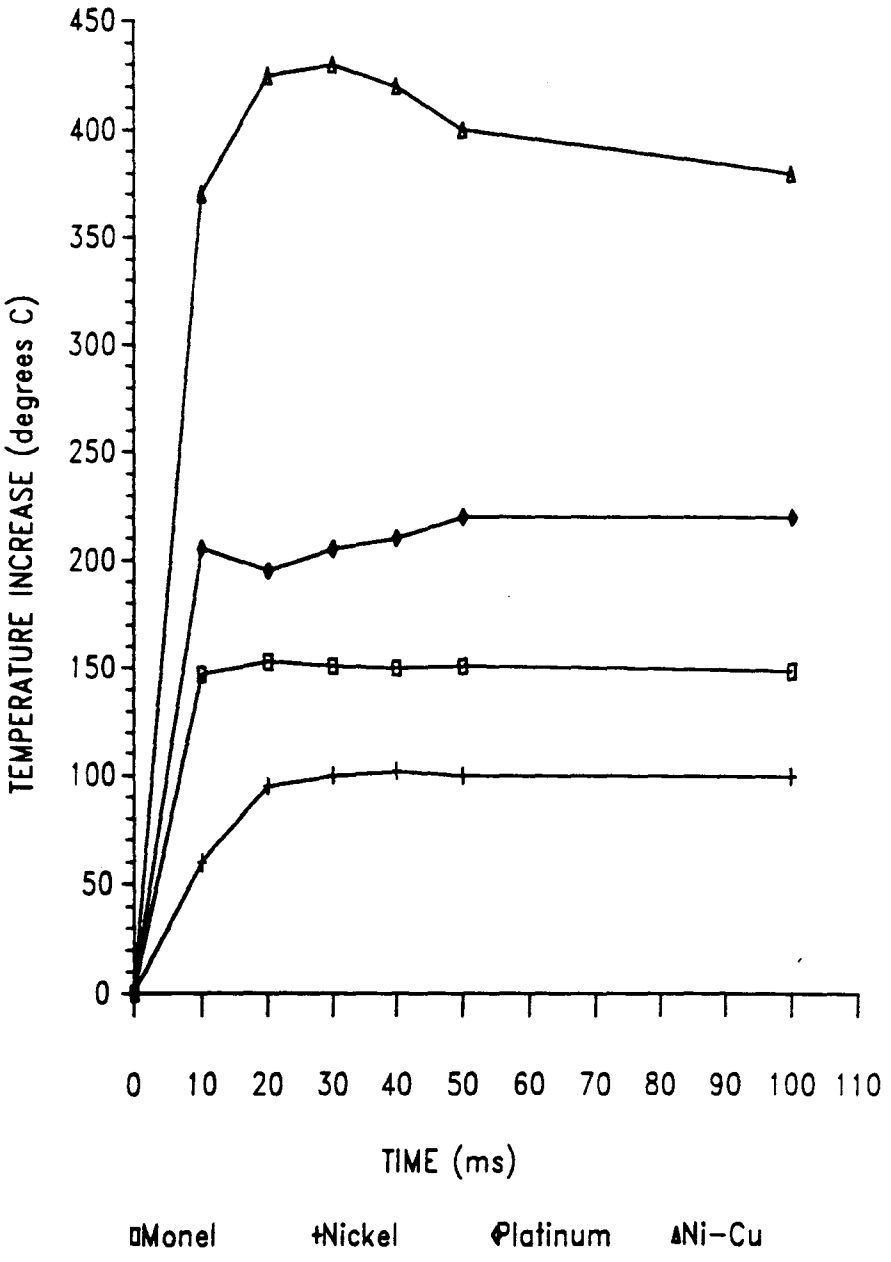

Fig. 17. Trap temperature profiles recorded with a 45 volt reinjection pulse and trap tubes made of four different materials.

heating characteristics alone, the nickel tube would be the least acceptable choice and that the copper-nickel alloy would be the best. As discussed earlier however, factors other than heating characteristics must also be considered. For example, titanium and steel were found to heat rapidly. However these materials work-harden and break quickly, and were therefore eliminated from consideration.

Nickel was found to be durable, and is believed to be relatively inert, but it is difficult to heat because of its low resistivity. Platinum, Monel-400 and the copper-nickel alloy were all acceptable in terms of heating and durability. Platinum was eliminated from consideration because of its excessive cost. Monel-400 was chosen as the best overall trap material, and was used for experiments described in the following chapters. Monel-400 was chosen over the copper-nickel alloy mainly because it was was available with a 0.25 mm i.d, which matched the column diameter, and because it was slightly more durable. The copper-nickel alloy heated most effectively would probably also have been an acceptable choice.

The data collected during these tests show that with proper selection of tubing, the capacitor discharge circuit is capable of heating the trap from -150 ^{o}C to

+150 ^{o}C or hotter in less than 20 ms. At maximum voltages, temperatures in excess of 200 ^{o}C were recorded. Most materials of industrial hygiene significance are relatively volatile and should be easily vaporized by this system. Other, less volatile compounds, such as those found in many soil or water extracts may not be effectively vaporized, however, and would be difficult to analyze.

In addition to improving trap heater performance, the changes in trap design and tube material produced a significant increase in trap durability. Although trap lifetime has not been the subject of a well controlled study, breakage of the Monel-400 trap was not a significant problem during the experiments described in later chapters. In fact the cold trap described in Chapter 3 was used for several months and was fired well over 1000 times without any failures.

Trapping and Reinjection Efficiency

Early work with the cold trap system indicated that effective trapping could be achieved at temperatures of -50 ^{o}C. These early studies were conducted with neat samples or with simple mixtures of C5 through C9 hydrocarbons and common aromatics. Attempts to trap and reinject more dilute solutions of these same compounds

in CS_2 revealed a need for much colder trap temperatures. Although the temperature required for effective trapping varies with the type of sample, many CS_2 solutions were found to require temperatures of -90 ^{o}C or colder. Preliminary experiments indicate that for some samples, especially those containing highly volatile materials or chlorinated hydrocarbons, even lower temperatures would be required. For example, quantitative trapping of a mixture of dichloromethane and tetrachloroethane required trap temperatures of -150 ^{o}C or colder.

Although no general rules concerning the required trap temperatures could be established, it appears that the choice of solvent, and possibly the melting point of the materials under study, are important considerations. For example, aromatics, which freeze at relatively high temperatures are generally trapped at -50 ^{o}C. Chlorinated alkanes with similar boiling points, but lower melting points, are often difficult to trap, and may require temperatures of -150 ^{o}C or colder. In addition, highly volatile solvents, such as CS_2, tend to reduce trapping efficiency for mixtures.

The degree of cooling necessary to trap different samples is therefore highly variable and is not easily predicted. In most cases an effective trapping

temperature can only be established through trial and error.

Experimentation with the original trap design revealed a minimum sustainable temperature of about -75 ^{o}C. In order to achieve lower temperatures and better trapping efficiency, a number of design changes were implemented. First, a flow restriction was added to the coolant line downstream of the liquid nitrogen reservoir. This allowed pressure to develop in the cooling coil and resulted in the formation of liquid nitrogen in the cooling line. A small amount of liquid nitrogen then sprayed into the trap for more effective cooling.

In order to provide more uniform temperatures, the chamber design was also altered, as illustrated in Fig 27. The cold trap was divided into upper and lower chambers that were separated by a baffle. Coolant entered the upper chamber where the liquid nitrogen vaporized. The cold nitrogen gas then moved through the baffle into the lower chamber which held the actual trap tubing.

Using this system, trap temperatures as low as -175 ^{o}C could be achieved. For the experiments described here, the new trap design was used with trapping

temperatures of -90 to -120 ^{o}C. Under these conditions, no breakthrough of the test sample, 1 mg/ml toluene in CS_2, was observed.

Once quantitative trapping had been established, reinjection efficiency became a major consideration. In order to optimize limits of detection and avoid memory effects, it is important that all of the sample be reinjected with a single heating pulse.

Studies of re-injection efficiency with the original trap design revealed problems with sample recovery and peak area reproducibility. In earlier studies it was assumed that reinjection efficiency was 100% if a second pulse produced no peaks. Results obtained in these experiments revealed that this was not necessarily true. Even when a second pulse produced no peak, the peak areas obtained with the first pulse were found to be significantly smaller than those obtained without use of the cold trap.

The poor reinjection performance of the early trap design is illustrated in Figures 18 - 20. Figure 18 shows a set of chromatograms made with a stainless steel trap and a simple mixture of toluene in CS_2. The bottom chromatogram shows the results obtained without trapping. In this case there is a large solvent peak

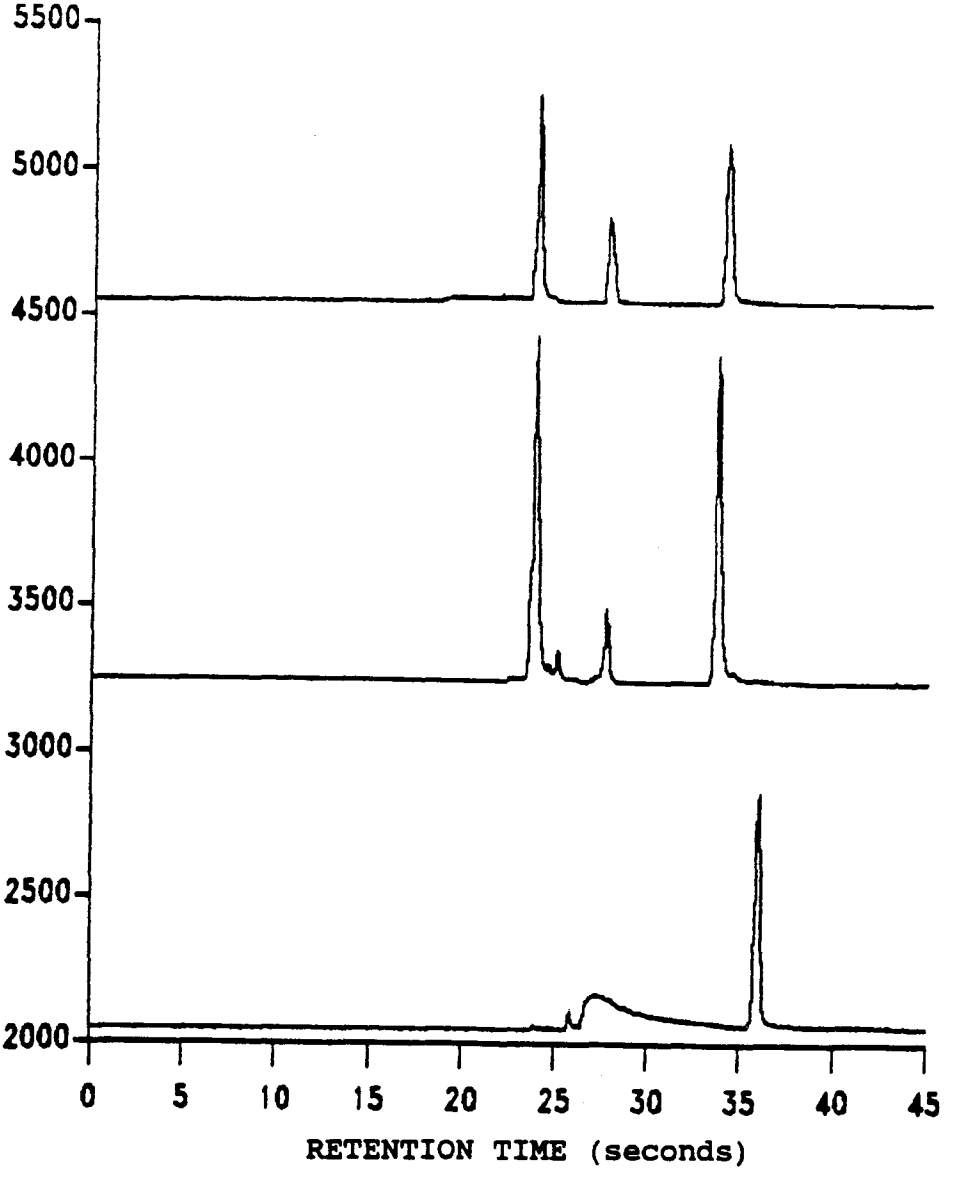

Fig. 18. Chromatograms showing the effect of trapping and reinjection. The lower chromatogram was made without trapping, the center one with a 45 volt reinjection and the upper one with a 60 volt reinjection. The column was 5m X 0.25 mm and had a 0.1 um stationary phase. The sample is Toluene in CS_2.

which shows a significant amount of tailing. This is followed by a well defined toluene peak. The center chromatogram shows the results obtained with cold trapping and a 45 volt reinjection pulse. Under these conditions, the solvent appears as a series of sharp peaks. The top chromatogram, which was made with cold trapping and a 60 volt reinjection, shows the same three peaks, but the toluene peak and the first solvent peak are both smaller.

Using the early trap design, with a nickel trap tube, performance was worse than with steel. Often less than 50% of the original sample could be recovered. Even with multiple heating cycles, a great deal of material was left on the trap. This was confirmed by shutting the coolant flow off and allowing the trap temperature to rise over a period of several minutes. As the trap temperature slowly increased, the heater circuit could be fired and the residual sample would appear as a series of peaks.

The poor reinjection efficiency of the design that featured a nickel trap was attributed mainly to the low electrical resistivity of the tubing, and to inadequate capacitance and/or voltage in the original power supply. When the capacitance of the power supply was later increased by 30%, and the trap tubing was replaced with

the higher resistance Monel 400, much higher recoveries became possible.

As expected, sample recovery was also found to be highly dependent on reinjection voltage. Low voltages produced insufficient heating, and resulted in low sample recoveries. High voltages however were also found to result in poor sample recovery, with maximum efficiency occurring at only a narrow range of voltages. Peak area reproducibility was also found to be unacceptable, with relative standard deviations for peak area exceeding 30%.

Figure 19 presents data on recovery efficiency at varying voltages. In this case, peak area relative to that measured from untrapped chromatograms, is plotted versus reinjection voltage. Each point represents the average area measured from three chromatograms and the three horizontal lines represent the average plus or minus one standard deviation for peak areas measured from chromatograms made without trapping. As reinjection voltage is increased, peak size also increases until a maximum value is reached at about 45 volts. As reinjection voltage is increased further, peak areas decrease. With different sample types and trap materials, the peak recovery occurs at different

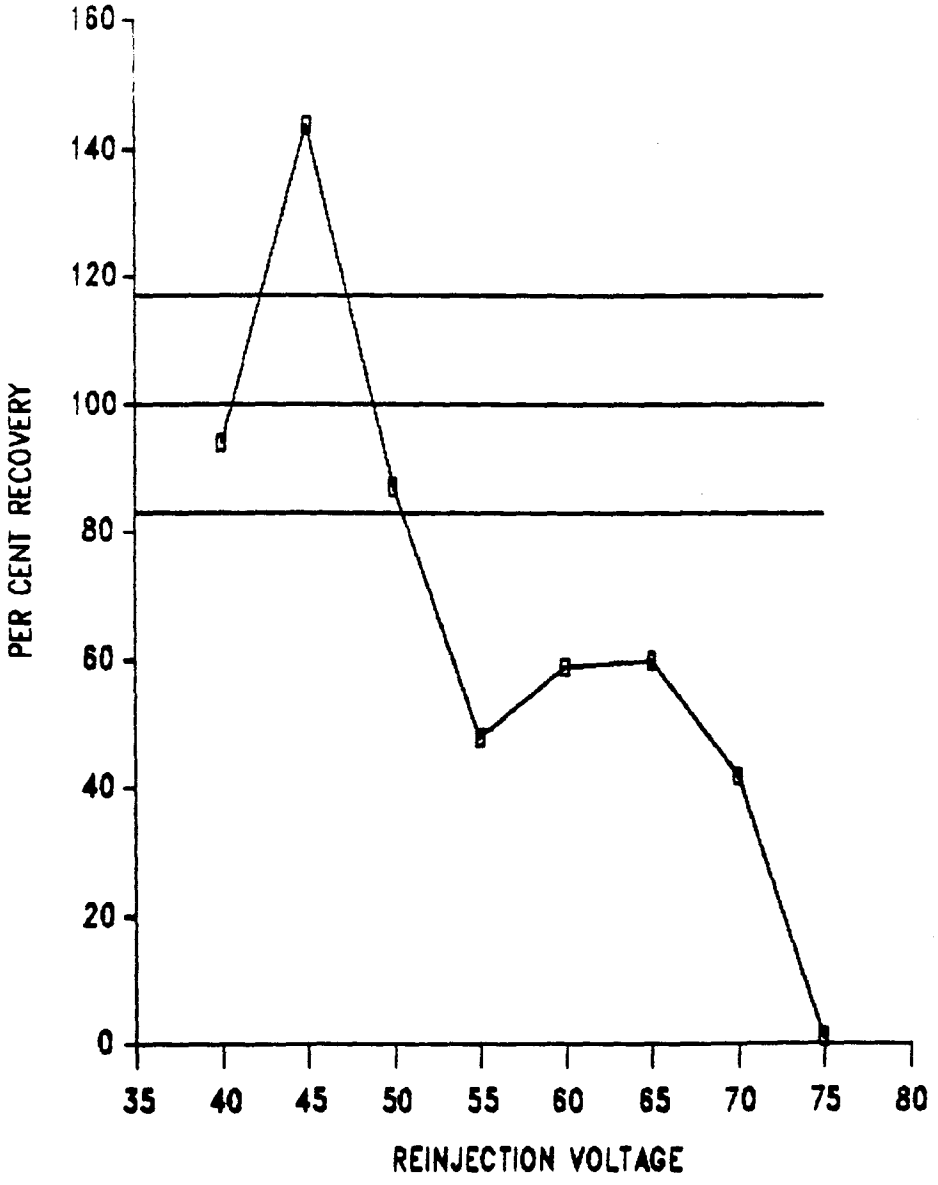

Fig. 19. Effect of reinjection voltage on sample recovery for samples of toluene in carbon disulfide.

voltages. This is illustrated by comparison to results presented in Chapter 3.

Two hypotheses were developed to explain the poor quantitative performance of the prototype system. First, it is believed that high reinjection temperatures can lead to over-heating and sample pyrolysis. This hypothesis was supported by the fact that as injection voltage was increased, the size of the toluene peak decreased, and new early eluting peaks appeared. The identity of these new peaks was not established, but, it seems likely that they represent smaller, more volatile compounds that were formed by fragmentation of the toluene. An example of this behavior is presented in Figure 20, which shows a series of chromatograms made with neat injections of toluene at increasing reinjection voltages. The pyrolysis problem points out the importance of having a reliable temperature monitoring system. The second hypothesis that was developed to explain the systems poor quantitative performance was based on the lack of a pressure and/or volume buffer between the injection port and the cold trap. It is believed that the rapid expansion of the trapped sample and carrier gas during the heating cycle may have forced a momentary flow reversal, and pushed part of the sample back into the splitter. In order to

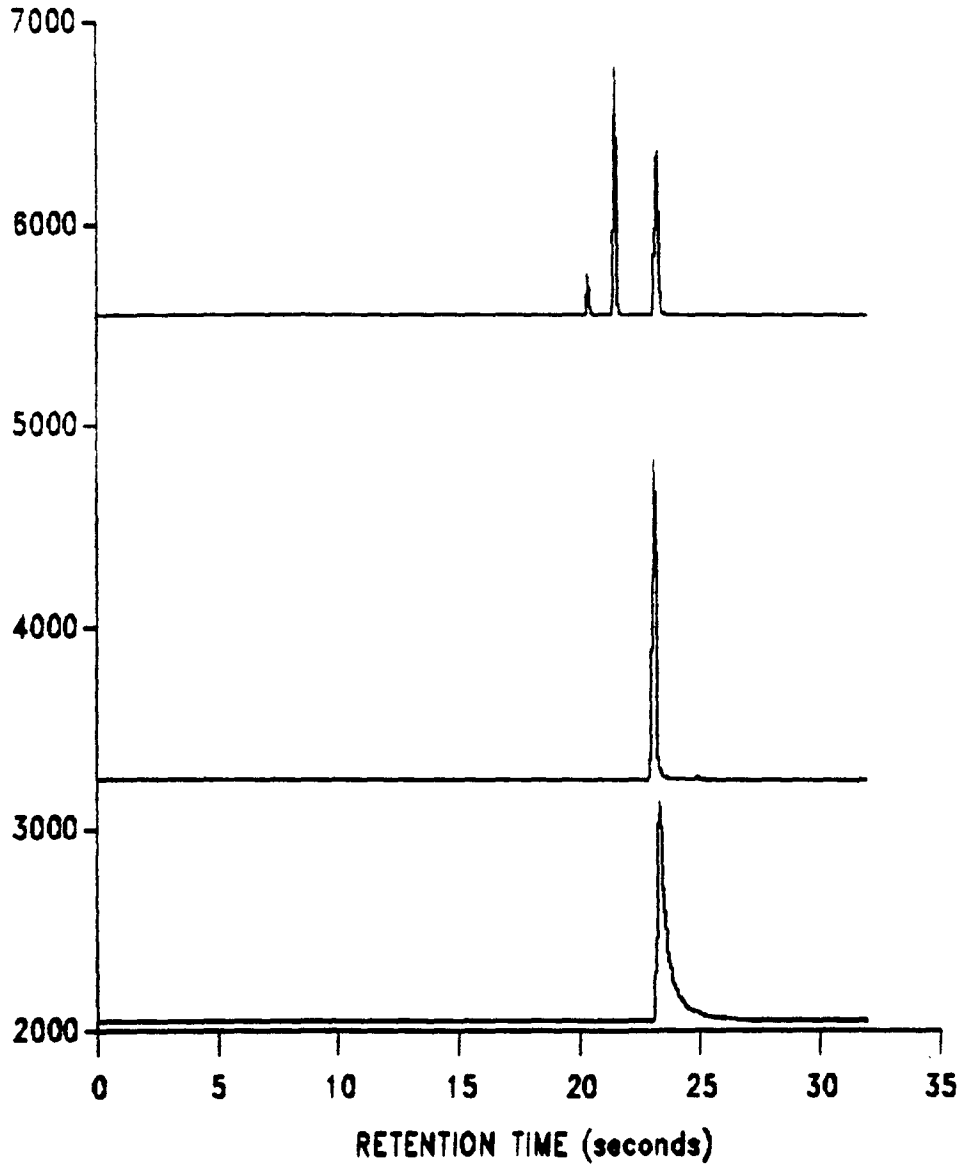

Fig. 20. Comparison of trapped and untrapped chromatograms using neat toluene injections. The lower chromatogram was made without trapping, the middle one with a 40 volt reinjection and the top one with a 68 volt reinjection. The column was 5m X 0.25 mm and had a 0.1 um stationary phase.

test this hypothesis, a 20 cm buffer column was installed between the injection port and the cold trap.

Initial tests with the buffer column installed revealed a significant improvement in performance with peak areas increasing and maximum recovery being achieved at a wider range of voltages. Addition of the buffer column also improved reproducibility, with the relative standard deviations for peak area decreasing to between 5 and 10%, which is equivalent to that achieved without trapping. Despite the addition of the buffer column, high reinjection voltages still produced some sample loss, which was presumably attributable to over heating and pyrolysis.

It should be noted that under some conditions, the maximum sample recovery appears to be significantly greater than 100%, with the average values falling above the 95% confidence interval for untrapped samples. Recoveries greater than 100% are believed to result from changes in the flow pattern and split ratio that occur when the vaporized sample hits the cold trap. As the sample condenses out of the carrier gas, the decreased vapor pressure alters the split ratio and draws more sample into the buffer column. This hypothesis was not carefully tested. However, a similar effect has been reported in the literature. This interpretation is also

consistent with the fact that a longer buffer column decreased the magnitude of the effect.

Complete data on trapping and reinjection efficiency with the Monel 400 trap, the buffer column and a higher capacitance power supply are presented in Chapter 3, along with a complete description of the final trap design.

Injector Performance Evaluation

In addition to studies of trap temperature, sample recovery and repeatability, data were also collected concerning injection band widths. Although the cold trap is important as a method of vapor collection, it's primary role in fast GC is to reduce the instrumental time constant by minimizing the width of the injection band. For retention times of less than about 10 seconds to be practical, the instrumental time constant must be no greater than about 15 to 20 ms, and would preferably be 10 ms or less. The major contributor to the instrumental time constant with this GC system is believed to be the inlet, although other factors such as the electrometer response time also contribute.

In order to assess the effectiveness of the high speed inlet, injection bands produced with the splitter

system were compared to those produced with cold trapping and reinjection.

The band width produced by a splitter system can be affected by several factors including the injection port temperature, the carrier gas flow rate, the volume of the injection, the volatility of the sample and the injection method. For small volumes of highly volatile materials, or for gas injections, it is expected that the carrier flow rate will determine the injection band width. As carrier flow rate is increased, the time required to sweep the injection port is reduced, and the injection band is expected to become more narrow. For large injection volumes, or for low volatility materials, the time required for sample vaporization may be the limiting factor. In other cases the injection technique or the skill of the operator may be the most important consideration. The auto-injector for example, is expected to be more reproducible than manual injection, and was used to make all the liquid injections for this set of experiments.

In these experiments the performance of the splitter system was highly variable, and was found to be dependent on a number of factors. The most important considerations were the carrier gas flow rate, the

choice of test compound or mixture and the injection volume.

The relationship between carrier flow rate and the width of injection bands produced by the splitter system is illustrated in Figures 21 and 22. In each case the instrumental time constant, which is assumed equal to the injection band width, is plotted versus the flow rate measured at the splitter outlet. Since the flow rate through the transfer line was maintained at 10 ml/min in all experiments, the split ratio is equal to one tenth the split flow.

Figure 21 illustrates the effect of flow rate on band widths obtained with neat injections of hexane. The upper tracing shows the results obtained with a series of 2.5 ul injections and the lower tracing shows the results obtained with a series of 0.5 ul injections.

As expected, the injection band width decreases with increases in the flow rate of the carrier. This is especially clear at the lower flow rates. At the highest flow rate tested, a 0.5 ul injection of neat hexane produced an initial band width of about 75 ms. At lower flow rates the band width increased to a maximum of about 120 ms.

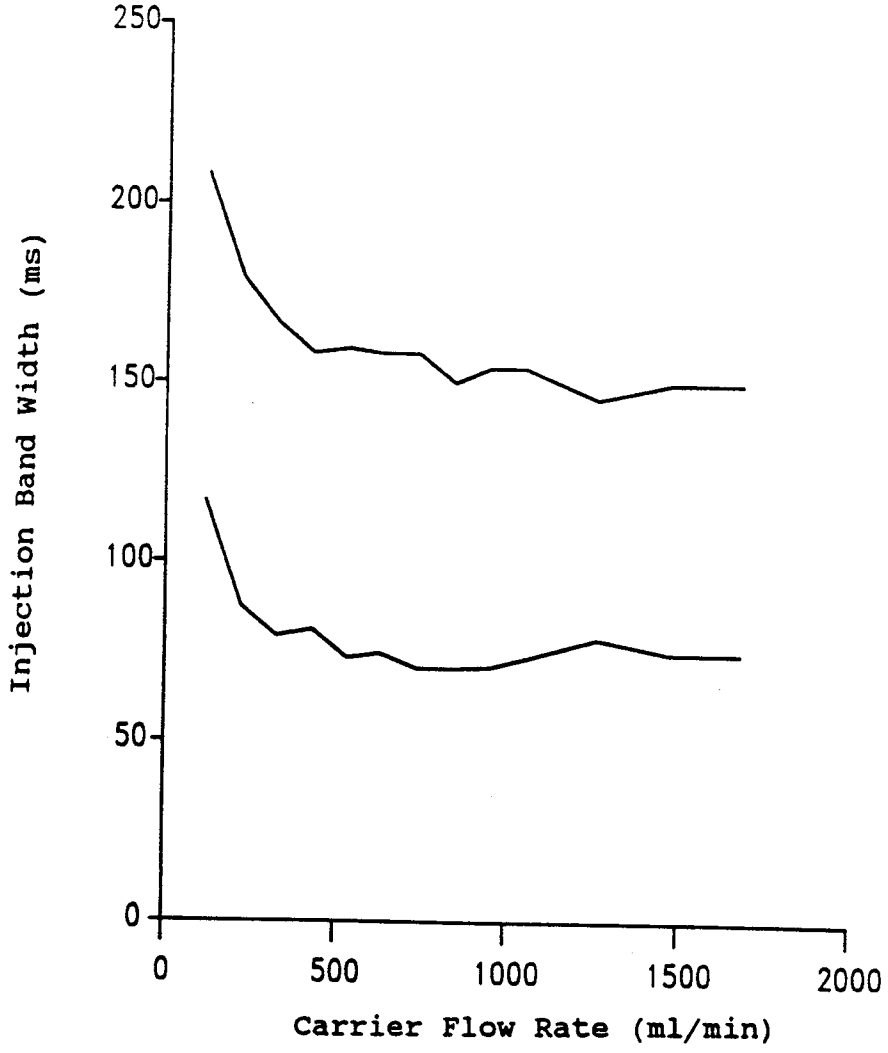

Fig. 21. Effect of carrier flow rate on injection band width produced by a splitter. The sample was neat Hexane and the column flow was 10 ml/min. Upper trace; 2.5 ul, lower trace; 0.5 ul.

As figure 21 also illustrates, larger injection volumes generally produce wider injection bands. This may indicate that the time required for evaporation of the sample is an important consideration. This interpretation is supported by data presented in Figure 22. Here injection band width is plotted versus split flow for a series of injections made with a 1% solution of hexane in CS_2. Once again the smaller injection volumes produce smaller injection bands. In addition however, comparison of Figures 21 and 22 shows that the more volatile 1% solution produces significantly smaller injection bands than the neat samples. The importance of sample volatility was also supported by results obtained with neat injections of Dichlorobenzene. Although a complete data set was not obtained, the higher boiling dichlorobenzene consistently produced wider injection bands than hexane.

As Figure 22 illustrates, under optimal conditions using liquid samples, the splitter system can generate initial band widths of 30 to 35 ms. The splitter should therefore be capable of producing chromatograms with acceptable levels of resolution and retention times of 10 to 15 seconds or more. With larger injection volumes, or less volatile samples, it is probably not possible for the splitter to produce narrow injection bands or to achieve good high speed separations.

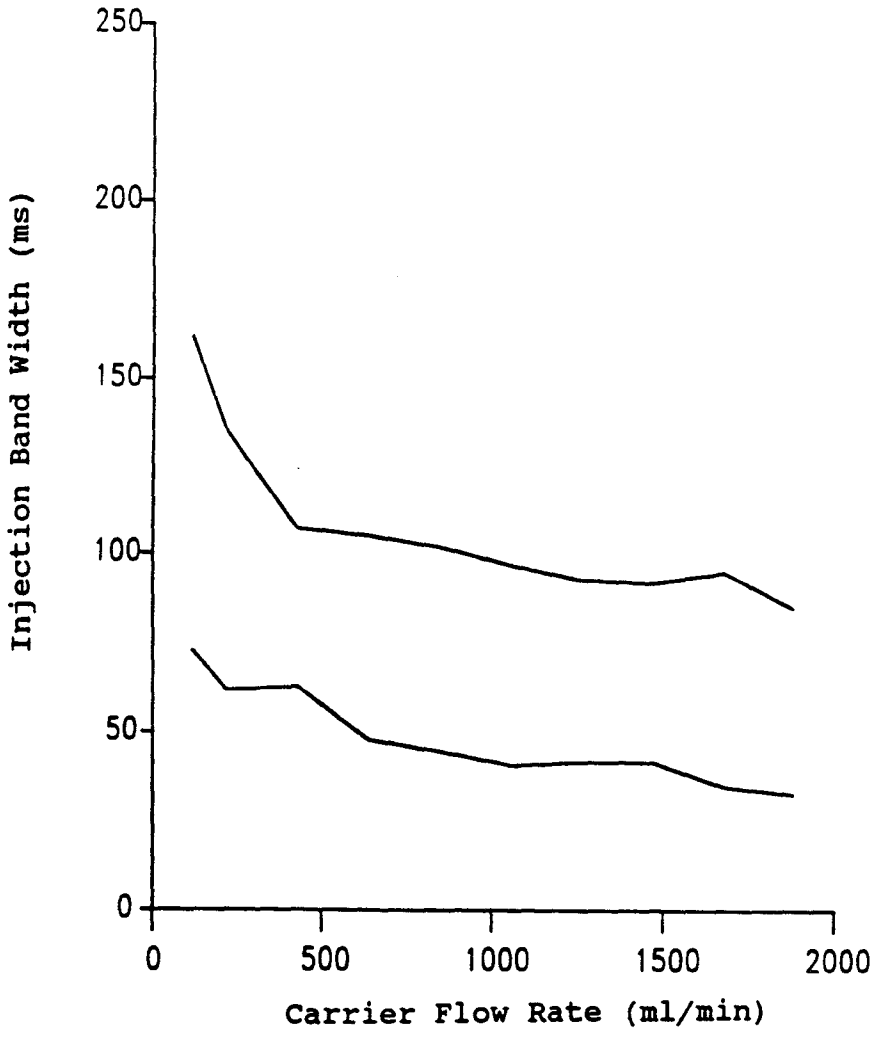

Fig. 22. Effect of carrier flow rate on injection band width produced by a splitter. The sample was 1% Hexane in CS_2 and the column flow was 10 ml/min. Upper trace; 2.5 ul, lower trace; 0.5 ul.

Despite the possibility of producing narrow injection bands, operation of a splitter at such high carrier flow rates may not be practical. Since flow rate through the column is independent of the carrier flow rate, increases in carrier flow increase the split ratio and decrease the amount of material entering the column. At the maximum tested flows, the high split ratio would reduce the volume of sample entering the column to less than 10 nl. Because of the poor signal to noise ratios produced by the fast electrometer, a 10 nl sample will generally be inadequate for trace environmental analysis. In addition to the small sample size, some literature reports indicate that splitters perform erratically and suffer from increased non-linearity under these conditions.

A similar set of data was also collected using the cold trap system and is presented in Figure 23. Cold trap performance was expected to be highly dependent on trap loading. Therefore the instrumental time constant is plotted against the volume of sample entering the column rather than against split flow. Data was collected using varying split ratios and injection volumes of 1% Hexane in CS_2. In this figure, the upper tracing shows the results obtained without trapping and the lower figure shows the results obtained with the

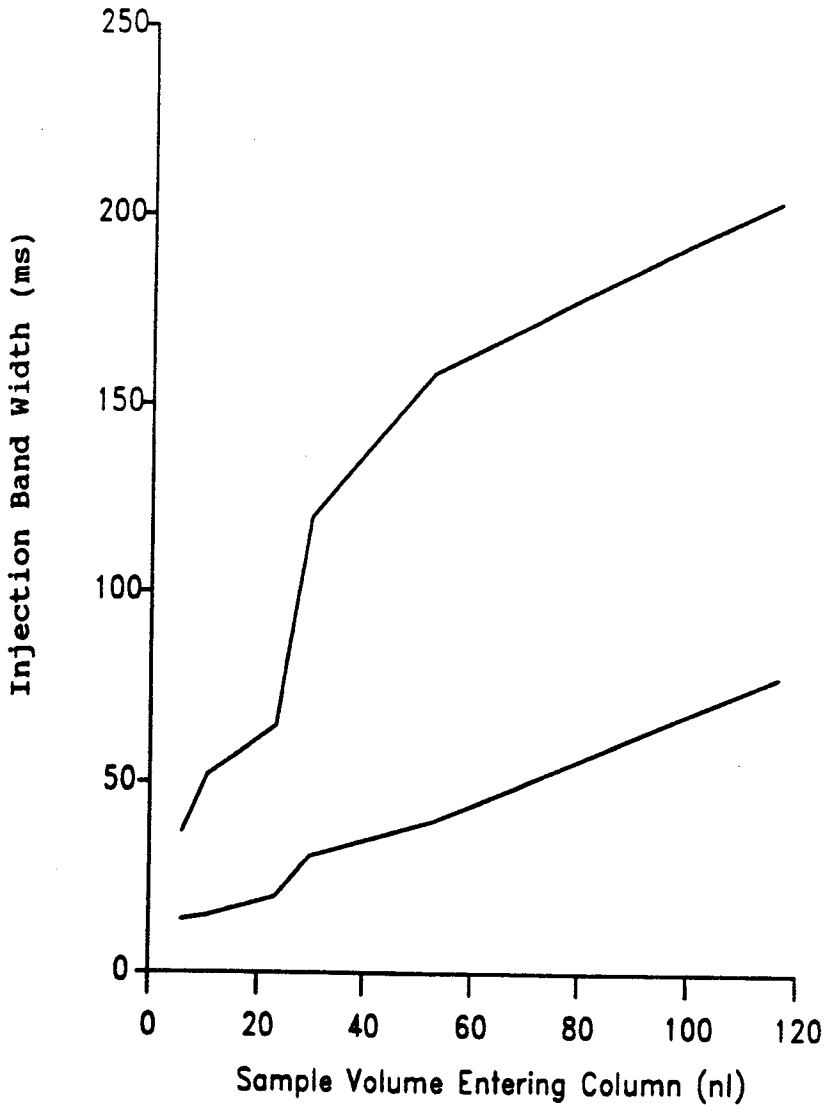

Fig. 23. Effect of sample volume on injection band width produced by the cold trap inlet (lower trace), and the splitter (upper trace). Sample is 1% hexane in carbon disulfide. Sample volume was adjusted by changing injection volume and split ratio.

cold trap. In all cases trapping was achieved at -90 ^{o}C and reinjections were made with a 50 volt pulse which produced peak temperatures of about +90 ^{o}C. As with the splitter system, the injection band width produced by the cold trap was highly dependent on sample volume, or in this case trap loading. For large injection volumes of 1% hexane, the cold trap system produced significantly more narrow injection bands than the splitter system. In addition the minimum band size produced by the cold trap was about half that produced by the splitter. In these experiments, a minimum band width of about 15 ms was obtained.

In order to determine the minimum band size that the cold trap would produce with even lower sample loading, injections were made using a gas tight syringe and 50 ppm toluene vapor in nitrogen. Trapping was again conducted at a temperature of -90 ^{o}C and the reinjection charge was set to 60 volts. Under these conditions, the minimum injection width was determined to be about 20 ms, which is not significantly different than that achieved with liquid injections. This may indicate the sample load was no longer the limiting factor.

In order to determine the effect of reinjection temperature on band width, a series of tests was run

with initial capacitor charges of 50, 60 and 65 volts. The results indicate that reinjection band widths are not decreased by increased reinjection voltage, and may in fact be slightly increased. Data was not collected at capacitor charges below 50 volts because the reinjection efficiency was expected to be less than 100%.

Results presented here indicate that the minimum instrumental time constant for the fast GC system ranges from about 15 to 25 ms depending on the sample size and type. This is barely fast enough to meet the criteria for 5 to 10 second chromatograms. The minimum time constant achieved with the cold trap was better than that achieved with the conventional splitter and auto-injector. In addition, the cold trap produced much smaller time constants for large sample sizes.

The fact that the time constant was somewhat larger than the anticipated 10 ms may indicate that some factor other than injection band width is important in determining the overall time constant, or it may indicate that the cold trap is simply not as efficient as was hoped. The measured band widths of 15 to 25 ms are however fairly consistent with the heating rates that were discussed earlier.

In addition to producing smaller injection bands the cold trap has a number of advantages over most conventional inlets. For liquid samples, the cold trap improves signal to noise ratios and limits of detection by increasing the volume of sample that can be introduced at minimum band widths. This also allows lower split ratios to be used, which should improve splitter linearity and reproducibility. In addition, use of the cold trap makes band width independent of injection port temperature. This allows lower injection port temperatures to be used which results in less septum bleed and may minimize degradation of some thermally labile samples. Despite these potential advantages, fast GC analysis of dilute liquid environmental or industrial hygiene samples is expected to be difficult.

For gas samples, the cold trap is clearly superior to conventional gas sampling loops or to the use of gas tight syringe injection. During vapor analysis, the cold trap allows materials collected from a large volume of gas and be introduced as a narrow injection band. During gas or vapor analysis the total mass of material collected on the trap is small, thus allowing the injector to function with maximum efficiency. The materials of interest, however, are likely to be the major components and will be present at a relatively

high concentration. This sample enrichment capability results in a good signal to noise ratio and appears to be the major advantage of the cold trap system.

The cold trap may also be useful in applications were retention time measurements are especially important. The rapid heating capability and the computer control system allow the injection time to be precisely controlled so that retention times can be measured with great accuracy and precision.

Even for vapor samples at moderate to high concentrations where sample enrichment is less important, the cold trap should produce much better injection profiles than most conventional inlets. This is illustrated in Figure 24, in which the lower tracing shows the injection band produced by a gas tight syringe and splitter system, and the upper tracing shows that produced by the cold trap. In both cases, the sample is 1 ml of 50 ppm toluene vapor in nitrogen and the split ratio is about 100:1. As this figure illustrates, the cold trap produces a much sharper injection band, which is expected to result in better high speed chromatograms.

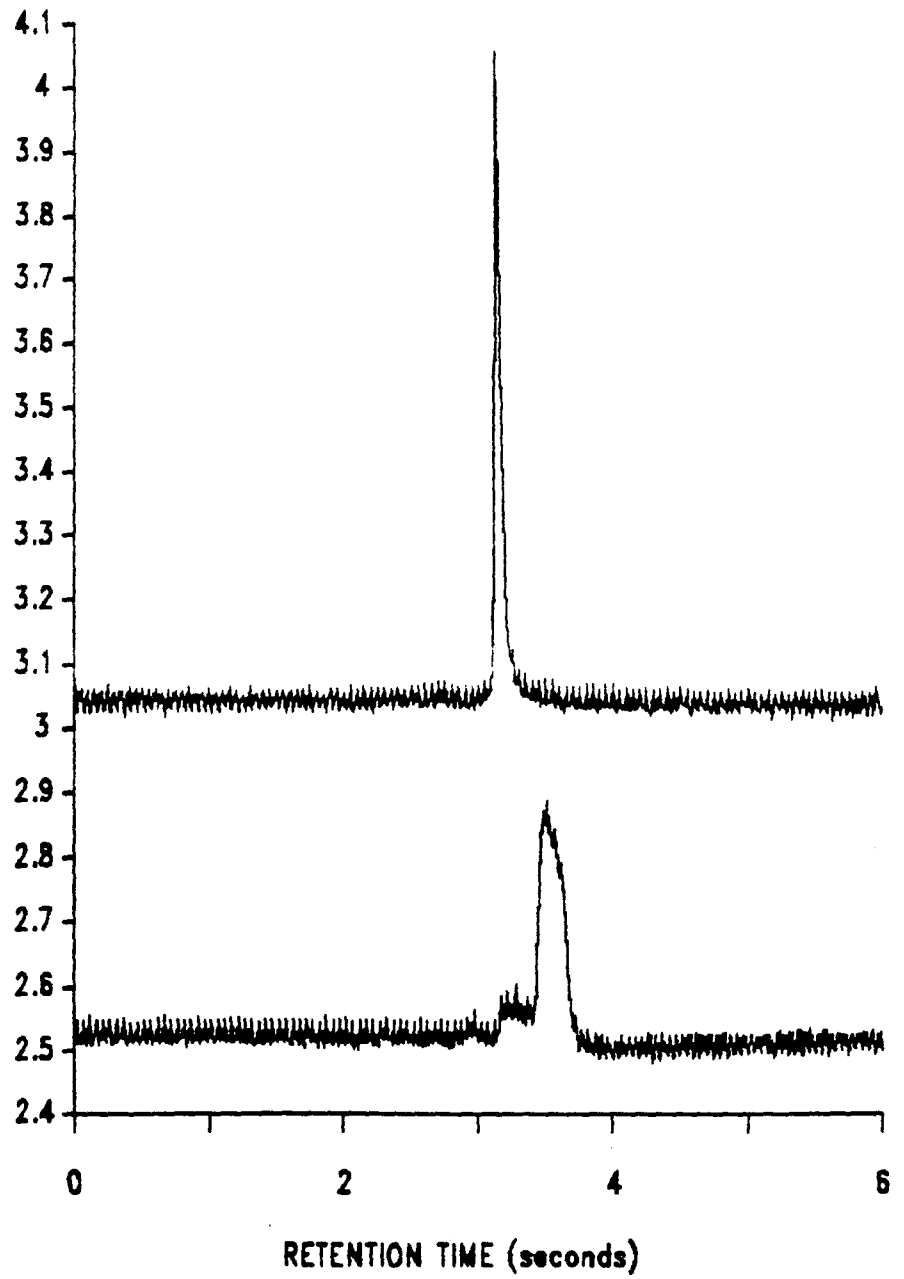

Fig. 24. Comparison of injection bands produced by the cold trap (top) and by gas tight syringe injection (bottom). Each sample is a 1 ml volume of 50 ppm toluene in nitrogen. The column was 0.25 mm i.d. uncoated fused silica, and was operated at approximately 500 cm/sec.

Electrometer Evaluation

The electrometer used for this project was built by the electronics shop at The University of Michigan Chemistry Department, and is essentially identical to that described by Ewells. The time constant was not measured but was previously reported to be less than 1 ms.

The importance of such fast response is illustrated by Figure 25. Here the upper tracing shows a high speed chromatographic peak recorded with the fast electrometer. The lower tracing shows a peak produced under identical conditions, but this time recorded with the standard Varian 3700 electrometer, which has a response time of 200 to 250 ms. It is apparent that the slow response of the Varian electrometer produces significant peak distortion and would be unacceptable for high speed chromatography.

The short time constant, and the necessary lack of filtering, make the fast electrometer extremely sensitive to 60 Hz or higher frequency noise. This is also illustrated in Figure 25. For applications where response speed could be sacrificed, a 60 Hz low pass filter was available. However, the performance characteristics of the filter, and its potential effect

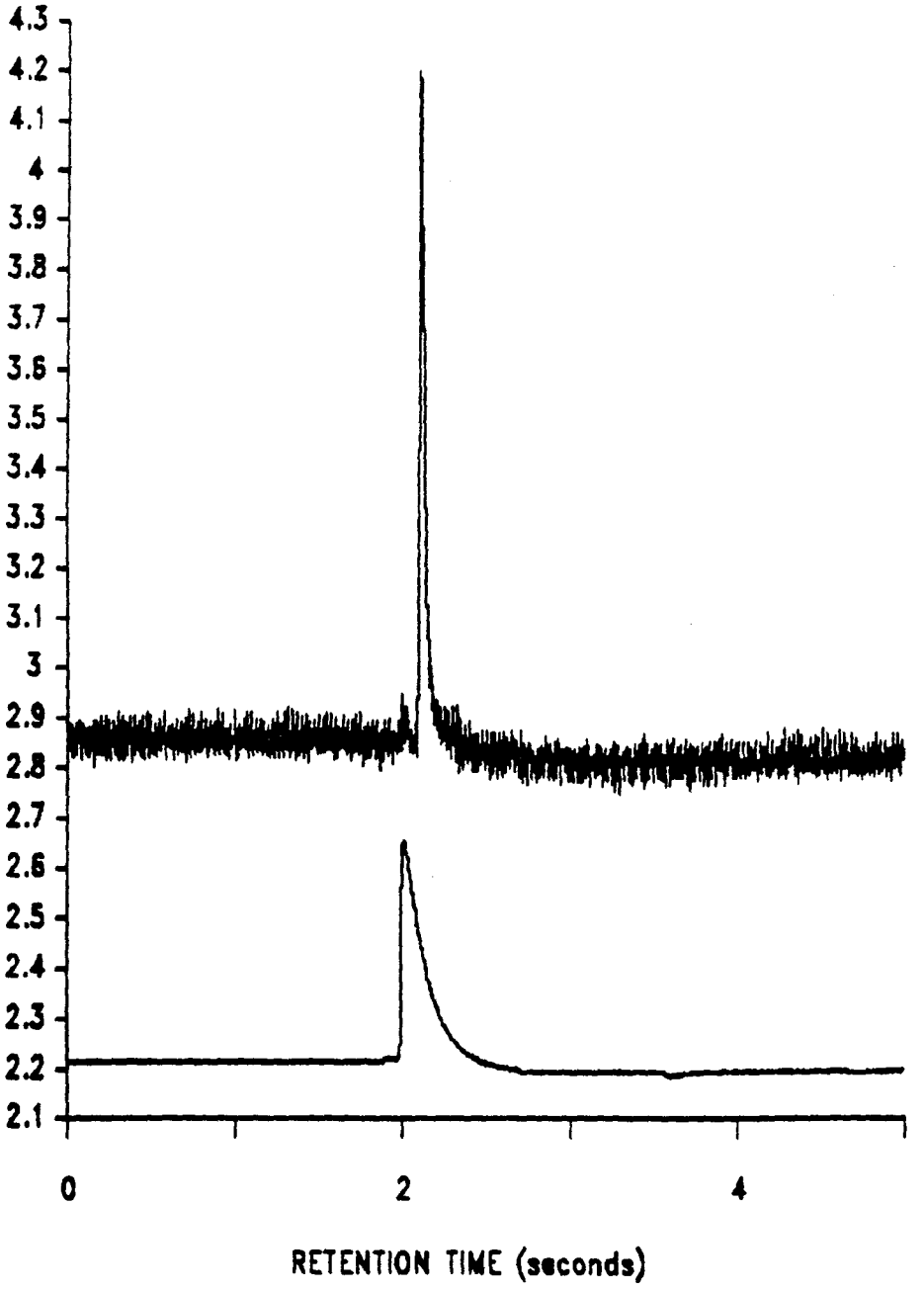

Fig. 25. Comparison of fast chromatograms recorded with high speed (top) and conventional (bottom) electrometers.

on peak shape were not well documented, so it was not used during actual data collection. Under conditions that produced relatively wide peaks, with base widths greater than about 250 ms, the A/D conversion rate was set to 60 Hz, which effectively removed 60 cycle noise. For narrow peaks, this lower sampling rate results in too few points per peak for accurate integration, and is not an acceptable solution to the noise problem.

The background noise levels and the effect of various filtering mechanisms are illustrated in Figure 26. Tracing "A" shows the signal produced by the fast electrometer with no filtering and with an A/D sampling rate of 400 Hz. Tracing "B" shows the background signal recorded with the 60 Hz filter and a sampling rate of 400 Hz. Tracing "C" shows the signal recorded without the filter, but at a sampling rate of 60 Hz. The significant reduction in amplitude in tracings "B" and "C" relative to tracing "A", indicates that the background noise has a strong 60 cycle component. For purposes of comparison, tracing "D" shows the background signal produced by the Varian 3700 electrometer.

Because the noise recorded with the fast electrometer originates in the detector and other components of the fast GC, and because digital or analog filtering will affect peak shapes, the noise problem may

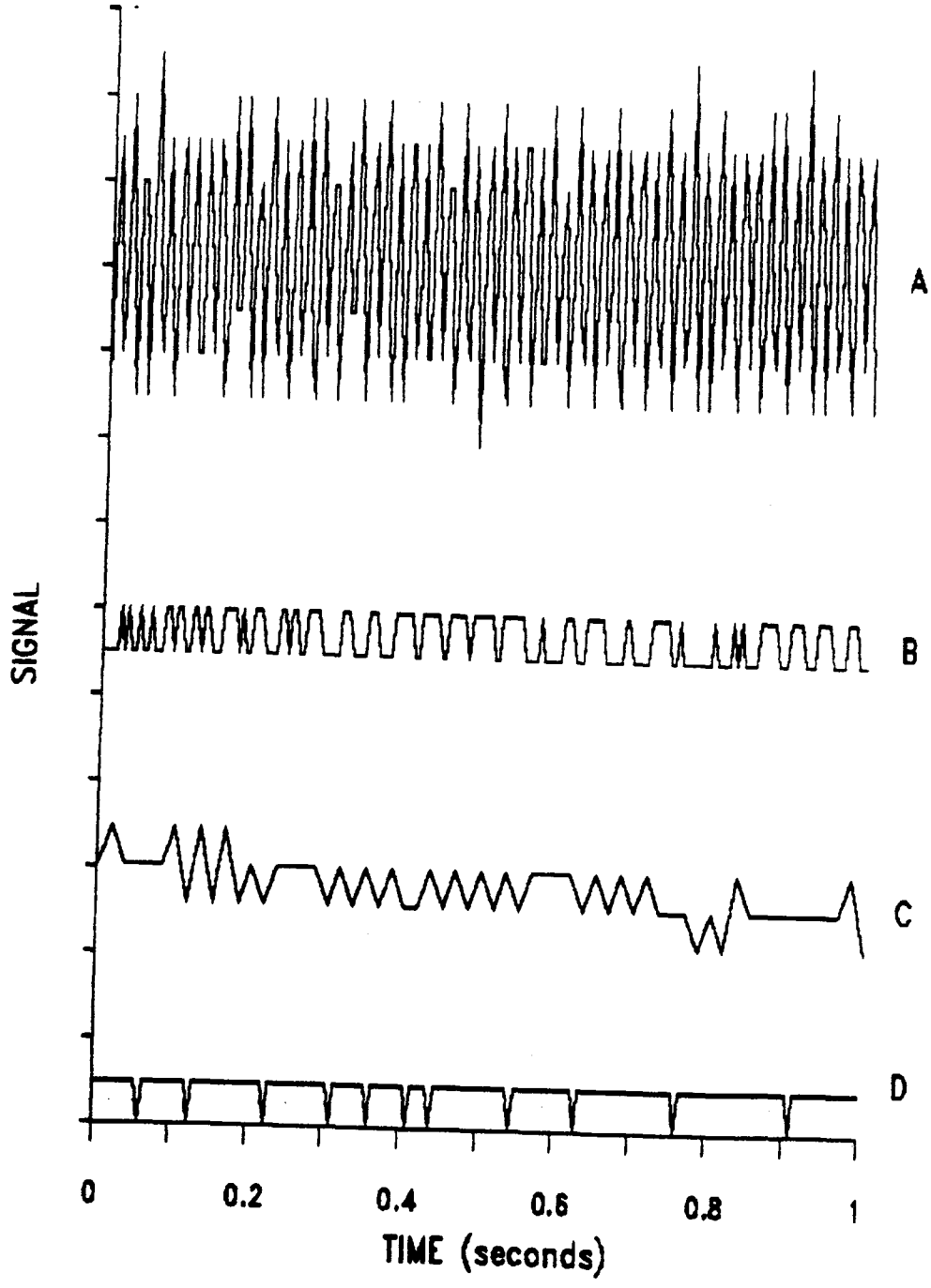

Fig. 26. Comparison of background noise levels picked up by different data systems. A; unfiltered at 400 Hz, B; filtered at 400 Hz, C; unfiltered at 60 Hz, D; Varian electrometer at 400 Hz.

be very difficult to overcome. This presents a significant problem for analysis of dilute liquids. At the levels of amplification necessary for the analysis of liquid industrial hygiene or environmental samples, the signal to noise ratio will probably be at least 1 to 2 orders of magnitude worse than that obtained with conventional systems. Combined with the limitations on sample size which are imposed by the injection system and by the thin film columns, this loss of signal may make very high speed analysis of some liquid samples difficult.

Conclusions

The early design of the fast GC was shown to be inadequate for quantitative analysis or for analysis of dilute solutions. The major problems were:

1) lack of durability
2) poor trapping efficiency
3) inadequate heating capacity for reinjection
4) poor reproducibility
5) lack of temperature monitoring capability and
6) poor signal to noise ratios.

Each of these problems was investigated and, if possible, corrected by the design changes described in this chapter.

Following these changes, preliminary testing indicated that high speed, quantitative analysis of some samples should be possible with retention times of 5 to 15 seconds.

The minimum instrumental time constant for cold trap injections is estimated at about 15 to 25 ms depending on the type of sample being analyzed. This level of performance can be matched by the splitter system, but only with extremely high split ratios and small injection volumes.

Sensitivity of the electrometer to noise originating in the detector or other electronic components of the GC was found to be a significant problem. In conjunction with the need for small sample volumes, the high levels of background noise may make fast analysis of dilute liquid samples impossible. However, extension of retention times to 30 to 45 seconds may allow the use of electrometer filtering and would also allow larger samples to be injected. Under these conditions, moderately fast analysis of dilute liquid samples, either with or without cold trapping,

may be feasible. A low noise detector and/or an electrometer with adjustable filtering may be of great benefit for this application.

A complete description of the improved cold trap design, and an evaluation of its basic operating characteristics is presented in Chapter 3.

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CHAPTER 3

FAST GAS CHROMATOGRAPHY WITH A GAS COOLED AND ELECTRICALLY HEATED COLD TRAP INLET

Gas chromatography (GC) is often used in industrial laboratories for routine, repetitive analysis of simple mixtures. For some of these applications, such as process monitoring and control and certain types of environmental monitoring, the use of 2 to 5 m capillary columns operated at high linear velocities of 150 to 200 cm/s offers the possibility of extremely short analysis times. While the potential for fast separations has been demonstrated several times in the last twenty years, limitations in available equipment, especially inlet systems, have prevented general application of high speed techniques.

In 1965, Desty provided an early demonstration of fast GC when he reported the separation of as many as 15 components in less than 2 seconds (1). Since then, a number of studies have appeared which discuss both the theoretical and practical aspects of high speed GC (2-6). Many of these studies have emphasized the importance of minimizing instrumental contributions to band broadening

and the use of inlet systems that can produce a narrow injection band. With retention times of ten seconds or less, the peak width at half height is often fifty milliseconds or less. Under these conditions, a major problem can be extra-column band broadening caused by the inlet. Successful high speed GC requires an inlet that produces an initial band width of no more than about 20 ms. Conventional syringe injections, using an inlet splitter, typically produce injection band widths of 50 to 100 ms which is clearly inadequate.

A useful high speed inlet system must also be precisely controlled to allow accurate measurement of retention times. For retention times of a few seconds, the time measurements should be accurate to within a few milliseconds. Such accuracy cannot be easily achieved with most injectors, and requires that the inlet and data collection system be automated to provide a reliable zero time reference.

While Desty's work showed that fast separations are possible, the injection method, which involved striking a syringe plunger with a rubber mallet, was not practical for routine applications. Reasonably good high speed chromatograms can be obtained with a conventional "T" type splitter if it is operated at high enough split ratios (7), but it is difficult to obtain acceptable

reproducibility and to avoid discrimination effects. In response to this problem a number of alternate methods of high speed injection have been developed.

Among the designs that have been successfully tested are mechanical systems including a modified six port rotary valve (8) and a piston driven sliding valve which acts as a high speed splitter (9). Other approaches, including the use of high speed fluidic logic gates (5, 10-12) have also been demonstrated.

Previous reports from our laboratory (13, 14) described a cryo-focusing, or cold trap and re-injection system, that meets the requirements for a fast GC inlet, and can also act as a concentrating device for the analysis of dilute vapors or gases. The design, which expands on the innovative work of Hopkins and Pretorius (15), features a metal capillary cold trap that is cooled by a continuous flow of cold nitrogen and is resistively heated using a current pulse from a capacitor discharge power supply.

In this report, we describe extensive re-design and improvements to the prototype inlet system that result in increased trapping efficiency, better analytical performance and enhanced reliability. Data concerning the trap heating characteristics, trapping and

reinjection efficiency, and chromatographic performance are also presented.

Experimental Section

Description of the Cold Trap

The cold trap, which has been extensively redesigned since our earlier publication (14), is shown schematically in Figure 27. As in the earlier design, a conventional heated inlet port and splitter was used for syringe injection of liquid samples. The inlet splitter was connected to a 50 cm long untreated fused silica or nickel capillary which served as a buffer between the inlet and the cold trap. The buffer column was enclosed in an aluminum chamber and heated to prevent sample condensation in this area. The buffer column was not used in earlier designs.

A low dead volume union connected the outlet of the buffer to a 9 cm long, 0.25 mm i.d. metal capillary which acted as the actual cold trap. A slight coil in the metal capillary allowed for changes in length associated with temperature changes occurring during the trapping and reinjection cycle. The cold trap was enclosed in the lower half of a small, two-chambered Teflon box. A flow of cold nitrogen entered the upper chamber and then moved

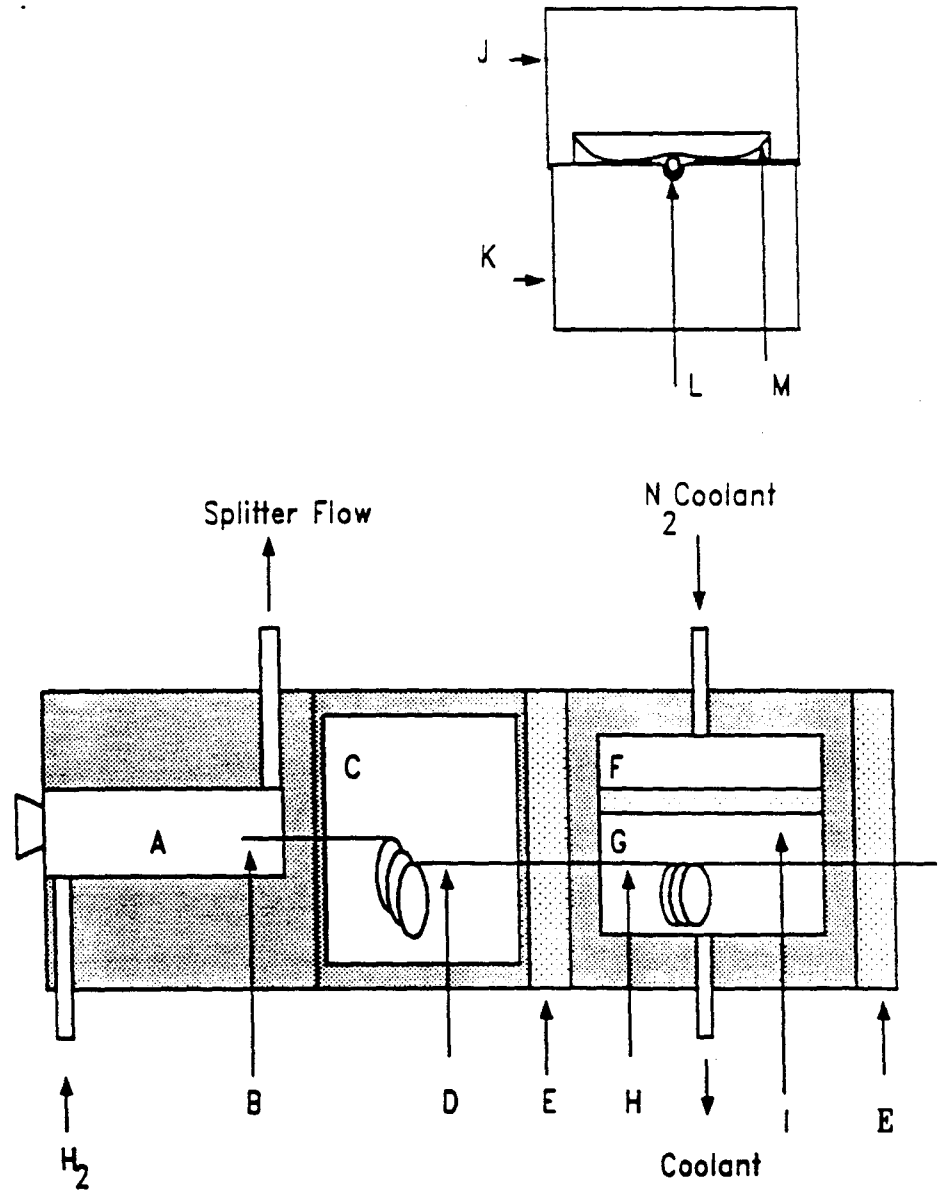

Fig. 27. Diagram of the high speed inlet system and electrode block. A, injection port; B, split point; C, buffer chamber; D, buffer tube; E, electrode; F, upper chamber of the cold trap; G, lower chamber of the cold trap; H, trap tube; I, baffle; J, upper block; K, lower block; L, trap tube; M, spring.

through a baffle into the lower chamber to cool the interior of the box. This baffled two chamber design was developed to minimize problems with non-uniform cooling, and is an important improvement since the earlier publication (14).

The nitrogen was cooled by running it through a coil of copper tubing immersed in liquid nitrogen. After passing through the liquid nitrogen bath, the cooling line was reduced from 1/4 inch i.d. to 1/16 inch i.d. to allow pressure to develop in the cooling coil. This pressurization resulted in the formation of a small amount of liquid nitrogen inside the cooling line, which then sprayed into the upper chamber of the Teflon box and provided more efficient cooling than could have been achieved with a similar system operated at atmospheric pressure. The trap temperature was controlled by adjusting the nitrogen pressure. The coldest achievable temperature was -190 ^{o}C.

At each end of the Teflon box, the cold trap was connected to a 3 cm wide copper block which served as an electrical contact. Each electrode was constructed from an upper and lower block (Figure 27, cross-sectional view). The trap tubing was set in a small groove cut in the upper surface of the lower block and was held in place by a thin phosphor-bronze strip anchored in the

upper block. Each electrode was heated by a 150 watt heating cartridge to prevent sample condensation outside the cold trap. These redesigned electrodes have also been added since the previous publication.

The power supply used to heat the trap for reinjection was a capacitor discharge system similar to that described earlier (14). Improvements since the earlier publication include the addition of a preheat circuit that allowed the operator to maintain the trap at an elevated temperature, and an increase in duration of the sustainer pulse from 50 ms to about 300 ms.

Operating Conditions and Chromatographic Equipment.

All chromatograms were collected isothermally at 40 ^{o}C using a 5 m long, 0.25 mm i.d. fused silica column with a 0.1 um bonded methyl silicon stationary phase (Quadrex). The carrier gas was hydrogen, which was supplied at flow rates of 4 to 5 ml/min to produce linear velocities of about 140 to 175 cm/s. The injector, trap buffer and upstream electrode were heated to 175 ^{o}C, and the downstream electrode was maintained at 75 ^{o}C. A flame ionization detector was used in all experiments, with the column moved close to the base of the flame to minimize the effective dead volume. The test mixture contained hexane (5.0 mg/ml), benzene (6.6 mg/ml),

heptane (5.1 mg/ml) and octane (5.3 mg/ml) and was prepared in high purity CS_2 provided by The Dow Chemical Company. Samples, which in most cases were 1 ul in volume, were introduced with a 5 ul syringe (Hamilton). Chromatographic data was collected at frequencies ranging from 60 to 400 Hz depending on the peak width. The fast electrometer-amplifier has been described elsewhere (13). Computer hardware included an 80286/287 based personal computer and a Data Translation DT2801 analog to digital converter. Data acquisition was controlled using Labtech Notebook (Laboratory Technologies), and the data was analyzed using software developed in our laboratory.

Trap temperatures were measured using 36 gauge type J thermocouples (Omega) spot welded to the trap tubing. The thermocouple output was amplified with a high speed differential amplifier built in-house, and then sent to the analog to digital converter and sampled at 500 Hz.

Results And Discussion

Extensive use of the cold trap described in our earlier papers revealed problems in durability and performance that required modifications to the design of the cold trap.

The design of the electrodes, shown as the inset of Figure 27, is especially important in determining trap life. These electrodes must provide a low resistance electrical pathway, but must not clamp the trap tubing too tightly. Poor electrical contact between the electrodes and the trap tubing produces high point resistance and hot spots that tend to melt or weaken the trap tubing. Poor contact can result from surface corrosion or from inadequate matching of the groove in the electrode surface to the diameter of the trap tubing. In order to minimize resistance due to surface corrosion, the electrodes were plated with nickel and were cleaned regularly. If the electrodes clamp the trap too tightly, mechanical stresses are introduced which also tend to shorten trap life. The pressure from the phosphor-bronze spring was carefully adjusted for the best performance.

The choice of trap material also affects durability and reinjection performance. While the electrical characteristics and chemical activity of the trap tubing must be the primary considerations, the malleability or ductility, the coefficient of thermal expansion and susceptibility to work hardening were also considered. An ideal material would have high electrical resistivity, low chemical activity, a low coefficient of thermal expansion, would be highly malleable and would be resistant to work-hardening. A number of materials,

including stainless steel, nickel, platinum, Monel 400, and an alloy of thirty per cent copper - seventy per cent nickel were considered for use as trap tubes. Although platinum appeared to have the most desirable characteristics, the cost was considered prohibitive, and the work reported here was done using a trap made of Monel 400. Stainless steel, which was used in the earlier studies, is the least expensive and most readily available material. It is, however, the least desirable choice because of its tendency to work-harden and become brittle. In addition, steel is often considered an inappropriate material for GC applications because of its surface activity.

Another important factor affecting trap durability is the choice of trap dimensions, especially the wall thickness. Increasing wall thickness will increase the strength and durability, but the decreased electrical resistivity and increased thermal mass make rapid heating and cooling more difficult. For a trap made of hard-tempered Monel 400, an internal diameter of 0.25 mm and a wall thickness of 0.18 mm provided a good combination of strength and performance.

In addition to the design changes made to improve durability, other modifications were implemented to enhance performance. The buffer column was added in

front of the cold trap to prevent the sample from being forced backwards into the splitter chamber by the rapid expansion of the carrier gas when the trap tube was heated.

The addition of a preheat circuit allowed the system to be conveniently run either with or without trapping, and allowed the operator to heat the trap between chromatograms. This minimized problems with accumulation of contaminants from the carrier gas. In addition, increasing the duration of the sustainer pulse was found to improve the efficiency of reinjection for some high boiling compounds.

Trap Temperature Measurements

In order for the high speed inlet to function effectively, the trapped sample should revaporize quickly to form an injection band with a width of no more than about twenty milliseconds. The power supply must therefore be capable of raising the trap temperature from -150 ^{o}C or colder to +150 ^{o}C or hotter within that time span. In addition, the power supply must be sufficiently controlled to avoid overheating which could pyrolyze thermally labile components of the sample mixture or damage the trap.

Figure 28 shows the trap temperature during heating cycles that were initiated at various reinjection voltages. Interference from the discharge of the capacitors prevented temperature readings over the first several milliseconds, a problem which was more severe at higher voltages. Each data point on the graph represents the average reading from five heating cycles and has a relative standard deviation of less than +/-10 ^{o}C.

At an initial capacitor charge of 40 volts (D), the trap temperature increased from -170 ^{o}C to a peak of -50 ^{o}C in 12 ms. Charging the capacitors to a higher initial voltage resulted in both faster heating and higher maximum temperatures. At an initial charge level of 55 volts (A), which was the maximum used in these experiments, the trap reached a peak temperature of nearly 200 ^{o}C in about 20 ms.

Because the thermocouple response may involve a significant lag, the true heating rate is believed to be somewhat faster than that indicated. The cooling rate, however, was slow relative to thermocouple response times, so peak temperature measurements are thought to be accurate. Despite the response lag inherent in thermocouple based temperature measurements, the data presented here indicates that the trap does heat quickly

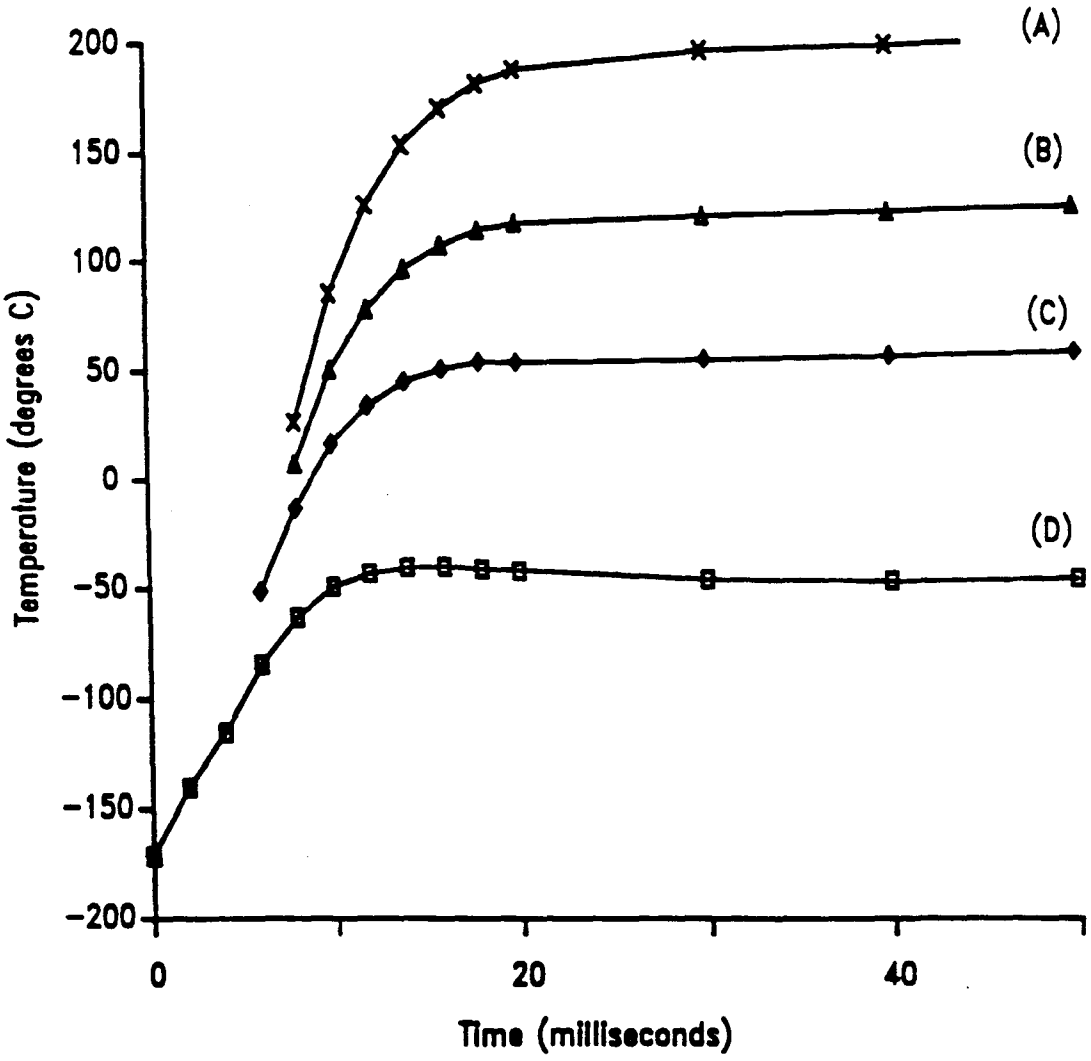

Fig. 28. Trap temperature profiles during reinjection at various voltages. A, 55 V; B, 50 V; C, 45 V; D, 40 V.

enough to produce injection bands with widths of 20 ms or less.

Trapping and Reinjection Efficiency

Cold traps have been used in GC for many years (16-19). In most cases the cold trap is made from a relatively long loop of uncoated fused silica or glass tubing which is sometimes filled with a packing material. Cooling is usually accomplished by submerging the trap in a liquid nitrogen bath during the trapping cycle. Even under optimal conditions, the efficiency of open tubular capillary cold traps has been questioned (19). Since the short, open tubular trap used in these experiments is likely to be less efficient than some other designs, a careful evaluation of trapping efficiency was considered necessary.

To test the trapping efficiency, syringe injections were made at varying trap temperatures and the FID response was monitored for any elevation of the baseline which would indicate sample breakthrough. In order to allow small amounts of breakthrough to be detected, the volume of the injections was increased to 3 ml and the concentration of the test components was tripled. The trap was cleaned between injections by heating it to 200 ^{o}C.

Figure 29 illustrates the results of the breakthrough experiment. Tracing A was obtained with a trap temperature of +150 ^{o}C to show the chromatogram that would be obtained under these conditions with zero trapping efficiency. Tracing B shows the chromatogram obtained when the trap temperature was dropped to 0 ^{o}C. The sample was not efficiently trapped, but there was a noticeable increase in retention times and deterioration of the chromatogram. Tracing C shows the chromatogram obtained at a trap temperature of -50 ^{o}C. Under these conditions the sample was temporarily retained and then gradually released, producing a general elevation of the baseline. When the FID response was monitored beyond the time shown in the figure, the baseline continued to rise for three to four minutes, and then dropped back to the starting level. Tracing D shows the chromatogram obtained when the trap was cooled to -100 ^{o}C. At temperatures this low, or lower, there was no detectable breakthrough.

While these results seem to contradict some of those of Graydon and Grob (19), the discrepancy can be explained by considering the choice of test materials and the duration of the trapping cycle. Graydon, using open tubular traps operated at liquid nitrogen temperatures, reported trapping efficiencies as low as 14% for some

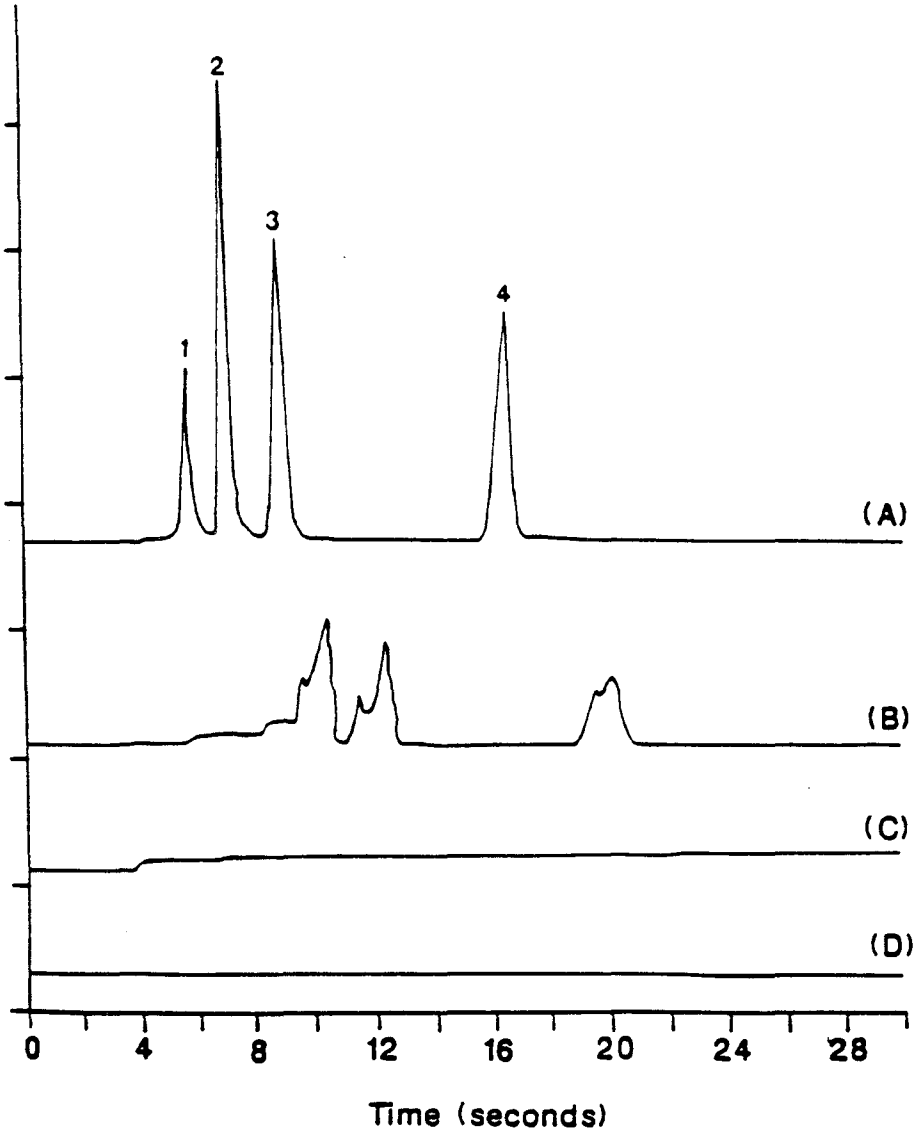

Fig. 29. Chromatograms showing the extent of breakthrough at various trap temperatures. A, 150 °C; B, 0 °C; C, -50 °C; D, -100 °C. Peak identities are: 1) hexane 2) benzene 3)heptane and 4) octane.

highly volatile compounds. For materials with boiling points similar to those used here, however, trapping efficiencies were greater than 90%. Most of the materials our laboratory is interested in can be effectively trapped at temperatures of -125 to -100 ^{o}C. More volatile materials may be difficult or impossible to trap under these conditions. Trapping behavior is not easily predicted, and in most cases an effective temperature must be experimentally determined for each type of sample.

Along with the choice of test materials, the duration of the trapping cycle appears to be an important consideration. In some applications, the trapping cycle can last for several minutes or more. In those types of situations a slow, almost undetectable, loss of sample could be important. In the application described here, however, the trapping cycle normally lasts only 5 to 10 seconds. Because of the short trapping time, the total amount of material lost by slow release will be negligible, and trapping can be considered to be quantitative.

The overall efficiency of the trapping and reinjection process is also dependent on the behavior of the system during the heating cycle. Trapping at -160 ^{o}C followed by reinjection with a 35 volt pulse, resulted

in only 50 +/- 11% sample recovery. As the voltage was increased, the recovery efficiency and repeatability improved, reaching 100 +/- 7% at 50 volts, which corresponds to a maximum trap temperature of 110 to 120 ^{o}C. In this case, recovery is expressed as the sum of the areas for all peaks in the trapped chromatogram divided by the sum of the areas for all peaks in the untrapped chromatogram.

If reinjection voltage is increased further, recovery efficiency tends to decrease. This is believed to occur, at least in part, because rapid expansion of gases increases pressure in the trap tubing and forces some of the sample to flow backwards through the buffer column and into the splitter. This effect was more dramatic in earlier designs that did not use the buffer column. If reinjection voltages are increased to 65 volts or more, trap temperatures can rise to 350 ^{o}C or hotter. Under these conditions, late eluting peaks often become smaller as new, early eluting peaks appear. This is apparently caused by pyrolysis of the larger molecules.

The effect of reinjection voltage on the individual components of the sample mix was also investigated. Figure 30 shows the recovery efficiency for hexane, benzene and octane at initial capacitor charges ranging

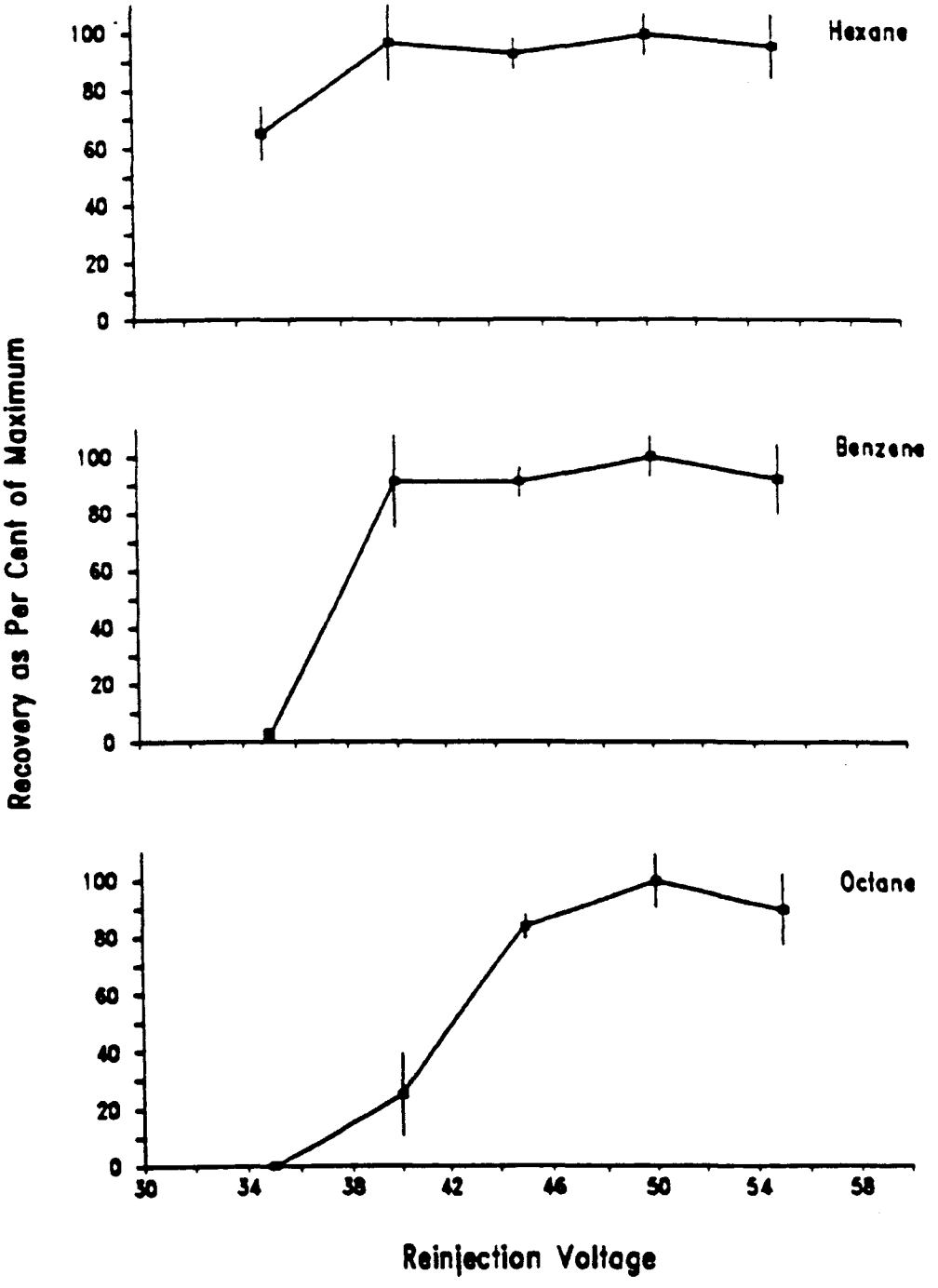

Fig. 30. Effect of reinjection voltage on recovery of the individual components of the test sample. Recoveries are expressed relative to the peak area measured at the most efficient reinjection voltage.

from 35 volts to 55 volts. Recovery is expressed as a percentage of the maximum recovery for that compound. Each data point represents the average of five injections with the error bars indicating plus or minus one standard deviation. As would be expected, the more volatile components of the sample are reinjected at lower voltages than are required for high boiling components. At 35 volts about 50% of the hexane is reinjected while less than 5% is the benzene and none of the octane is recovered. At 40 volts both the hexane and the benzene are recovered at efficiencies greater than 90%, while less than 30% of the octane is reinjected. As the initial capacitor charge is increased to 50 volts, all three components show maximum recovery. Reference to Figure 28 shows that this occurs at about 120 ^{o}C. This ability to selectively vaporize only certain components based on their boiling points, may be useful in cases where the operator wishes to analyze trace levels of a highly volatile component with minimal interference from a less volatile solvent or other components of the sample.

Chromatographic Performance

The effect of cold trapping on separation of the test mixture is illustrated in Figure 31. Tracing A represents the chromatogram obtained with manual

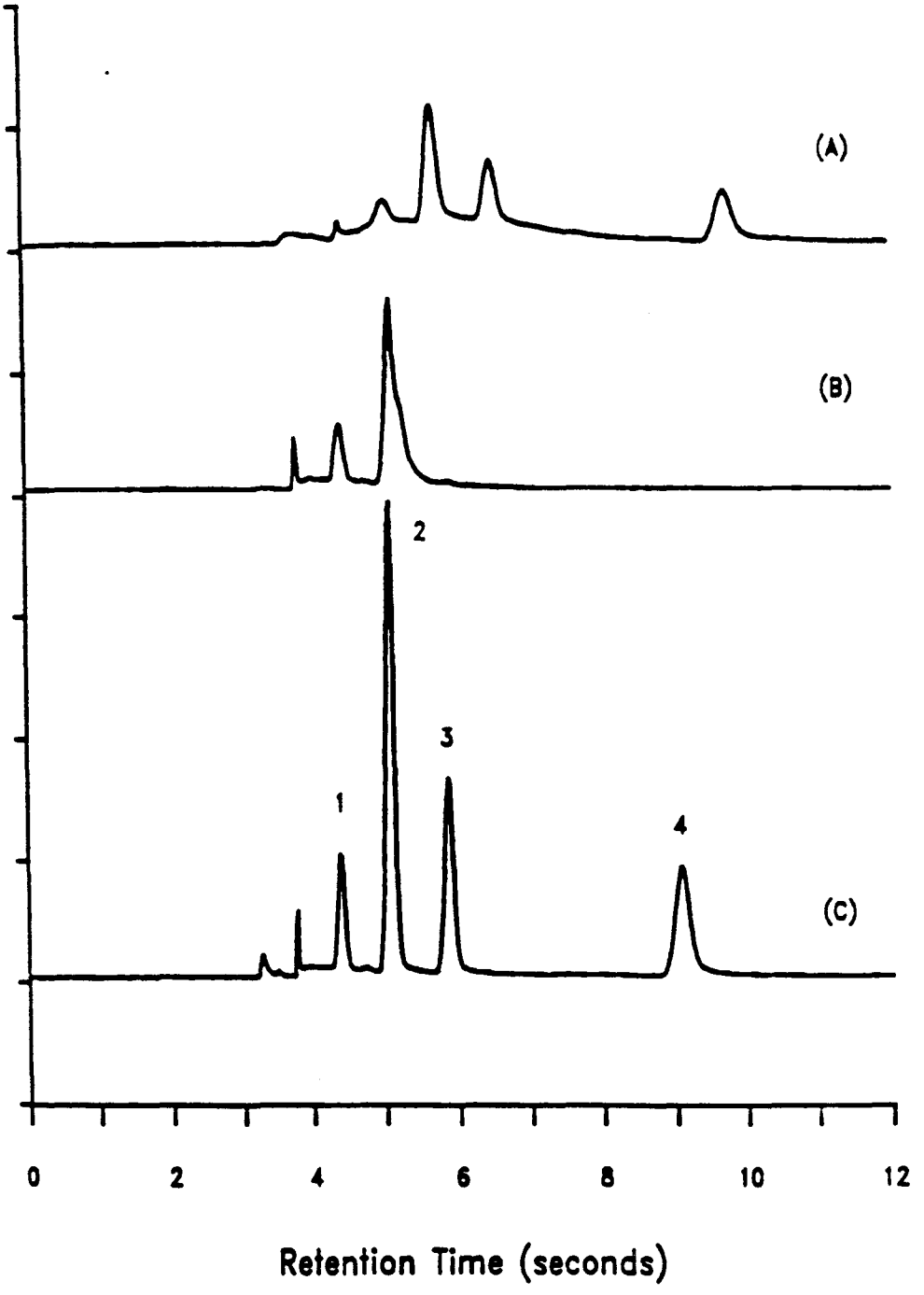

Fig. 31. Chromatograms of the test mixture made with and without the high speed inlet. A, manual injection without cold trapping; B, trapped and reinjected at 35 volts; C, reinjected at 50 volts. Peak identities are: 1) hexane 2) benzene 3)heptane and 4) octane.

injection and no cold trapping. For this chromatogram, the preheat circuit was used to hold the trap temperature at +150 ^{o}C during the injection process. Because the injection band produced by the syringe and splitter is very wide, the early peaks are poorly defined. There is also a general elevation and loss of stability in the baseline that can be attributed to evaporation of sample from the syringe needle as it penetrates the septum. Tracing B shows a chromatogram obtained when the injected sample was trapped at -160 ^{o}C and reinjected with a 35 volt pulse. Early peaks are somewhat sharper than those obtained without trapping and the baseline shows improved stability, but the less volatile components of the sample are left on the trap. Tracing C shows a chromatogram obtained when the sample was trapped under the same conditions, but reinjected with a 50 volt pulse. In this case, the frozen sample was quickly revaporized producing a well defined chromatogram with complete baseline separation for the materials of interest. The retention times for the four major peaks shown in tracing C are: hexane 4.37 s, benzene 5.05 s, heptane 5.83 s, and octane 9.05 s. Other smaller peaks represent the CS_2 solvent and unidentified contaminants.

The effect of cold trapping on the quality of high speed chromatograms can also be expressed as a decrease in peak width, or an increase in the number of

theoretical plates developed. For benzene, with a retention time of 5.05 s, cold trapping reduced the peak width at half height by about 40%, from 215 ms to 125 ms. The number of theoretical plates is increased from 3050 for the untrapped sample to 9040 for the trapped sample.

The effect of the cold trap on chromatographic performance is most dramatic when retention times are short and the sample concentration is relatively low. This is illustrated by a comparison of the manual injections shown in Figures 29 and 31. The chromatogram in Figure 29 is much clearer because the sample was more concentrated, and because the retention times are slightly longer. Under the conditions used to generate Figure 29, the cold trap would provide little improvement in resolution. Under conditions producing even shorter retention times, however, the advantage of the cold trap would become more apparent.

To be useful for routine quantitative analysis, the high speed inlet must not introduce any significant increase in the error associated with measures of sample mass or concentration. To test the system repeatability, the relative standard deviations for peak area were compared with and without trapping. Cold trapping was performed at -160 ^{o}C and reinjection was made with a 50 volt pulse. The results, presented in Table II, indicate

TABLE II

RELATIVE STANDARD DEVIATION OF PEAK AREA, RETENTION TIME AND RETENTION INDEX

	PEAK AREA		RETENTION TIME		RETENTION INDEX	
COMPOUND	CONTROL	TRAPPED	CONTROL	TRAPPED	CONTROL	TRAPPED
HEXANE	14	7	1.3	0.2	NA	NA
HEPTANE	11	7	1.2	0.2	NA	NA
BENZENE	11	7	1.0	0.2	0.25	0.02
OCTANE	14	9	0.7	0.2	NA	NA

that cold trapping introduces no measurable increase in variability for peak area. In fact, trapped samples seem to show less variability than the controls, probably because the improved peak shape results in less peak integration error.

Although retention time and retention index are not considered reliable identification tools in the analysis of unknown mixtures, they are often extremely useful in applications involving routine or repetitive analysis of samples from a known source. For these types of applications the precision with which retention time can be measured is often important. Since the heater circuit is controlled by the computer that is used for data collection, the digital signal used to trigger reinjection should serve as a reliable zero time reference and allow improved reproducibility of retention time data. To test the effect of the high speed inlet on retention time measurements, the relative standard deviations for chromatograms made using manual injections were compared to similar measurements made using the high speed inlet.

Although the precision achieved with manual injection is dependent on the skill of the operator, we found it difficult to achieve relative standard deviations of less than 1% for retention times of less

than 10 s. Using the computer controlled high speed inlet relative standard deviations of 0.2% were measured for retention times ranging from 5 to 10 s.

In addition to measuring retention times, the retention index was calculated for benzene. Because retention index is less affected by operator error, the relative standard deviations are smaller than those seen for retention time measurements. Again, however, the high speed inlet improved performance by one order of magnitude, bringing the relative standard deviation down from 0.25% to 0.02%.

Although the system must still be considered a prototype, the data presented here indicate that it can significantly improve chromatographic performance for retention times of less than 10 to 15 seconds. Higher plate numbers and greater resolution can be attained by optimization of the chromatographic conditions and use of smaller diameter columns. These strategies, which have been discussed by other authors (2,6), will allow the use of shorter retention times for some separations. Under these conditions the advantages of the cold trap over manual injection will become even more apparent.

Many simple GC separations which are currently performed using packed columns or non-optimized capillary

systems could probably be achieved much more quickly using a high speed inlet system similar to the one described here.

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CHAPTER 4

MEASUREMENT OF ORGANIC VAPORS AT SUB-TLV CONCENTRATIONS USING FAST GAS CHROMATOGRAPHY

Gas chromatography is often considered too slow a method to be useful for real time or near real time multi-point monitoring. If the chromatographic system is optimized for speed, however, it is possible to significantly reduce retention times. Recently our laboratory described a fast GC that allows many simple separations to be completed in 10 seconds or less. The system features a gas cooled, electrically heated, capillary cold trap that focuses the sample as an extremely narrow band at the front of the column. In the work described here the fast GC was used to measure the concentrations of benzene, toluene and xylene in test atmospheres generated in the laboratory. The measurements were then compared to simultaneous measurements made with a conventional GC. At concentrations ranging from 1 ppm to 100 ppm, the fast GC decreased retention times by a factor of 10 to 100 fold relative to the conventional GC, with no loss of precision or accuracy. These results indicate that it may be feasible to develop a high speed monitoring system based on a GC design similar to the one described here.

Introduction

Gas chromatography (GC) is currently used for ambient air monitoring in a number of industries. Often a centrally located GC is connected to a network of sampling lines through a multi-port valve and is used to sequentially analyze samples collected from various areas. Because a single GC separation normally requires several minutes or more, the cycle time for a multi-point sampler can easily exceed an hour. While this type of apparatus provides information on air quality at a relatively low cost, it may not be suitable for some applications where real time, or near real time, monitoring is required.

Gas chromatography, however, is potentially a much faster method of separation than is usually realized. If the chromatographic system is optimized for speed, rather than resolution, it is possible to achieve relatively simple separations in as little as a few seconds. The feasibility of performing such high speed separations was first demonstrated by Desty, who in 1965 separated 15 components in under 2 seconds (1). Since Desty's initial work, a number of publications have appeared that discuss both the theoretical and practical aspects of fast gas chromatography (2-8). While these studies have shown

that high speed separations are possible, the techniques they describe have generally been complex and have not been applied to routine environmental monitoring.

The major barrier preventing application of high speed techniques to routine analysis has been a lack of suitable equipment. For fast GC to be successful, the peak widths must be kept as narrow as possible. In particular, extra-column band broadening due to the injector, detector, and connectors must be minimized. The importance of preventing band broadening is illustrated by a comparison of final peak widths in conventional and fast GC. In conventional GC, peak widths are usually measured in seconds or tens of seconds. In fast GC, peaks are much narrower, often 50 milliseconds or less. It can be shown that in order to produce a final peak this narrow, the initial band width produced by the inlet should be no more than about 20 ms (9).

Conventional GC inlets using syringe injection and a splitter typically produce initial band widths of 50 to 100 ms, and are clearly inadequate for high speed separations. Gas injection systems, using a rotary valve and sampling loop, are likely to produce even wider injection bands, often measuring 1 to 10 seconds or more. Even for normal speed chromatography gas sampling systems

of this type may be inadequate, and often require that the sample be focused on the front of the column, or on a pre-column, to improve resolution and limits of detection (10).

In addition to the requirement for an extremely narrow injection band, a fast GC detector and the various connections must have extremely low dead volumes to minimize band broadening in those areas, and the electronics must have millisecond response times. In most cases, commercially available equipment is not able to meet these demands. Detectors that use a closed cell, such thermal conductivity, electron capture or photoionization detectors, are especially susceptible to peak spreading due to dead volumes, and are usually not appropriate for high speed applications. Flame ionization detectors have little or no dead volume, and if the column is moved close to the base of the flame, can be used for fast GC. While most FIDs can therefore be adapted to high speed GC, most electrometers are not capable of accurately tracing peaks as narrow as those developed by fast GC systems (11). Until recently, there was also a lack of affordable high speed data collection and processing systems. Advances in the area of personal computer technology have now made it feasible to collect and process data at rates that are adequate for fast GC applications.

A recent publication from our laboratory describes a GC that is capable of meeting the requirements of high speed analysis (12). The inlet system uses a metal capillary cold trap to focus and concentrate the sample before it enters the column. The trap is cooled by a continuous flow of cold nitrogen and is resistively heated for reinjection with a low voltage, high current pulse from a capacitor discharge power supply. Using the cold trap inlet with thin film capillary columns, a flame ionization detector (FID), and specially designed electronics we were able to analyze simple mixtures of liquids in less than 10 seconds. These experiments are also described in Chapter 3.

This instrument may also be useful as a direct air inlet and sampling system for monitoring organic vapors. For this application the cold trap is expected to serve both as a vapor collection device and as a high speed inlet. In this chapter, we report the results of a preliminary study concerning the application of high speed GC to the measurement of aromatic vapors at TLV and sub-TLV concentrations.

Experimental

Apparatus

The design of the fast GC is shown schematically in Figure 32. Various components of the system are described in the following paragraphs.

Samples were introduced using a motor driven six port valve (Valco) fitted with a 200 ul sampling loop. The outlet of the six port valve was connected to a 50 cm long buffer column made from 0.25 mm i.d. deactivated fused silica tubing (Quadrex). The buffer column was enclosed in an aluminum chamber which was heated to 75 ^{o}C to prevent sample condensation in that area. The downstream end was attached to a 15 cm long capillary cold trap made from 0.25 mm i.d. X 0.625 mm o.d. Monel 400 tubing. The trap tubing was coiled slightly to allow for length changes associated with heating and cooling, and was enclosed in a 9 cm long Teflon chamber. The chamber was cooled to -60 ^{o}C by a continuous flow of cold nitrogen gas. The nitrogen was cooled by running it through a copper coil submerged in liquid nitrogen.

At each end of the Teflon chamber, the trap tubing was clamped between two copper blocks which served as electrical contacts during the heating cycle. The copper blocks were heated to 100 ^{o}C with 150 watt heating

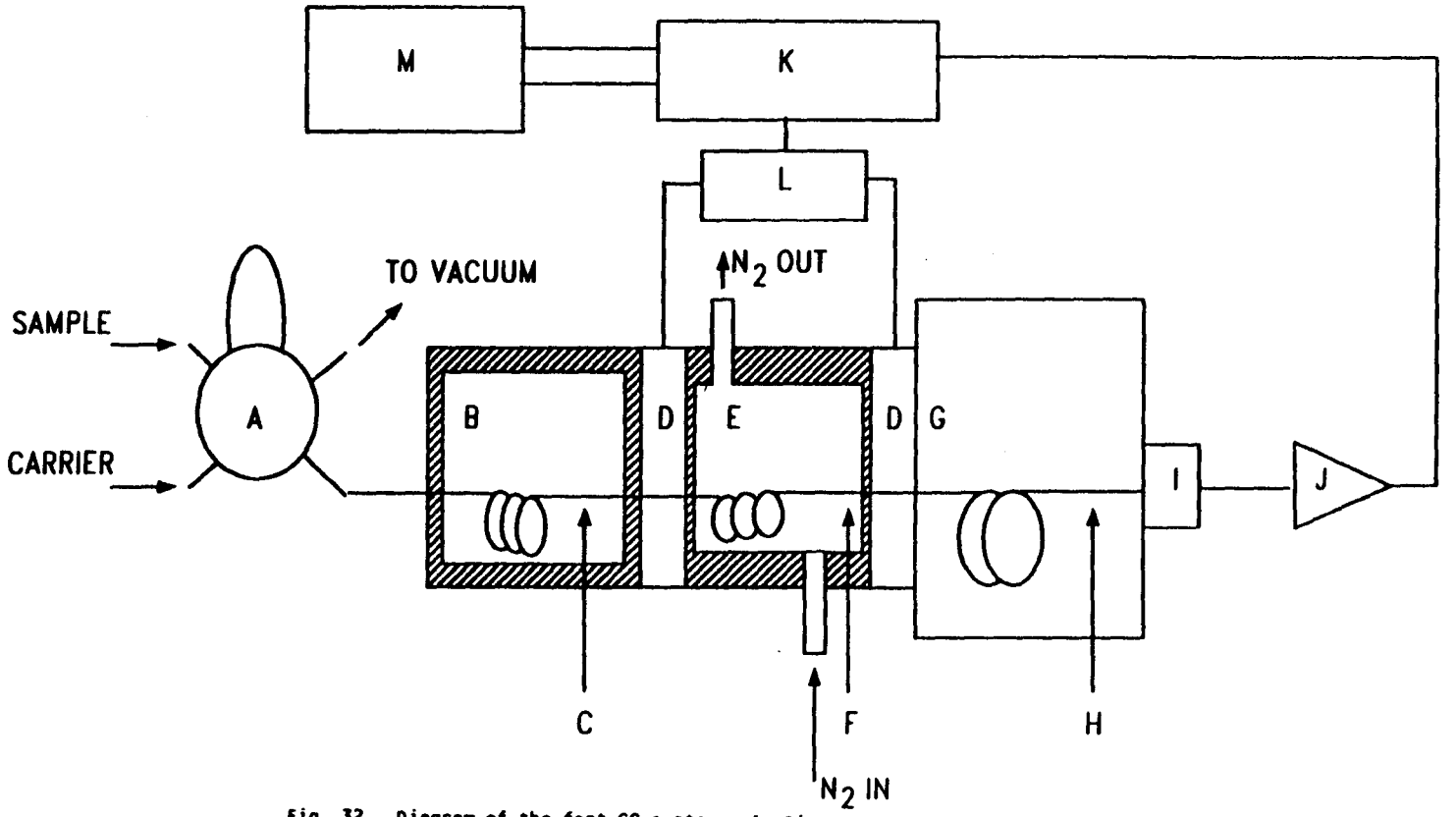


Fig. 32. Diagram of the fast GC system. A, Six port rotary valve; B, buffer chamber; C, buffer column; D, copper electrodes; E, cold trap chamber; F, cold trap; G, oven; H, capillary column; I, FID; J, electrometer; K, A/D converter; L, power supply; M, computer.

cartridges to prevent sample condensation outside the cold trap.

During the trapping cycle, which lasted for 15 to 30 seconds, sample vapors were collected by condensation on the inner wall of the trap tubing. The frozen sample was then rapidly vaporized to form a narrow injection band by running a short pulse of current through the trap tubing. The current was provided by a capacitor discharge power supply which is capable of raising the trap temperature by as much as 300 ^{o}C in less than 20 ms. The trap temperature was monitored by wrapping a 36 gauge type J thermocouple around the trap tubing. Details of the inlet system's design and performance characteristics have been published elsewhere and are presented in Chapter 3 (12).

The high speed inlet was mounted on an HNU model 301 GC. All separations were performed using isothermal analysis at the temperatures noted with the individual data sets. The column was a 5 meter long, 0.25 mm i.d. capillary, with a 0.1 um bonded methyl silicone stationary phase (Quadrex). Hydrogen was used as the carrier gas in all experiments, and was provided at a flow rate of 4 to 5 ml/min to produce linear velocities of 140 to 170 cm/s.

Peaks were detected using a standard HNU Systems FID with the column moved forward to the base of the flame to minimize the effective dead volume. The FID signal was directed to a fast electrometer - amplifier with a response time of 5 milliseconds. The high-speed electronics were developed specifically for this application by HNU Systems. Data was digitized and the entire system was controlled using a 12 bit analog to digital - digital to analog converter (Data Translation, DT2801) mounted in a 80286 based personal computer. Data was collected at a frequency of 400 Hz using Labtech Notebook software (Laboratory Technologies) and was analyzed using software developed in our laboratory.

The test atmospheres used in this study contained benzene, toluene and xylene at concentrations ranging from the TLV to one tenth the TLV. The relative humidity was adjusted to levels ranging from 10% to 80%.

The design of the vapor generator and monitoring system is shown schematically in Figure 33. The monitoring system has been described in detail elsewhere (13). In brief, the vapors were generated by slow introduction of a test mixture from a liquid reservoir into a fast moving stream of clean humidified air. The vapor concentration was controlled by adjusting the

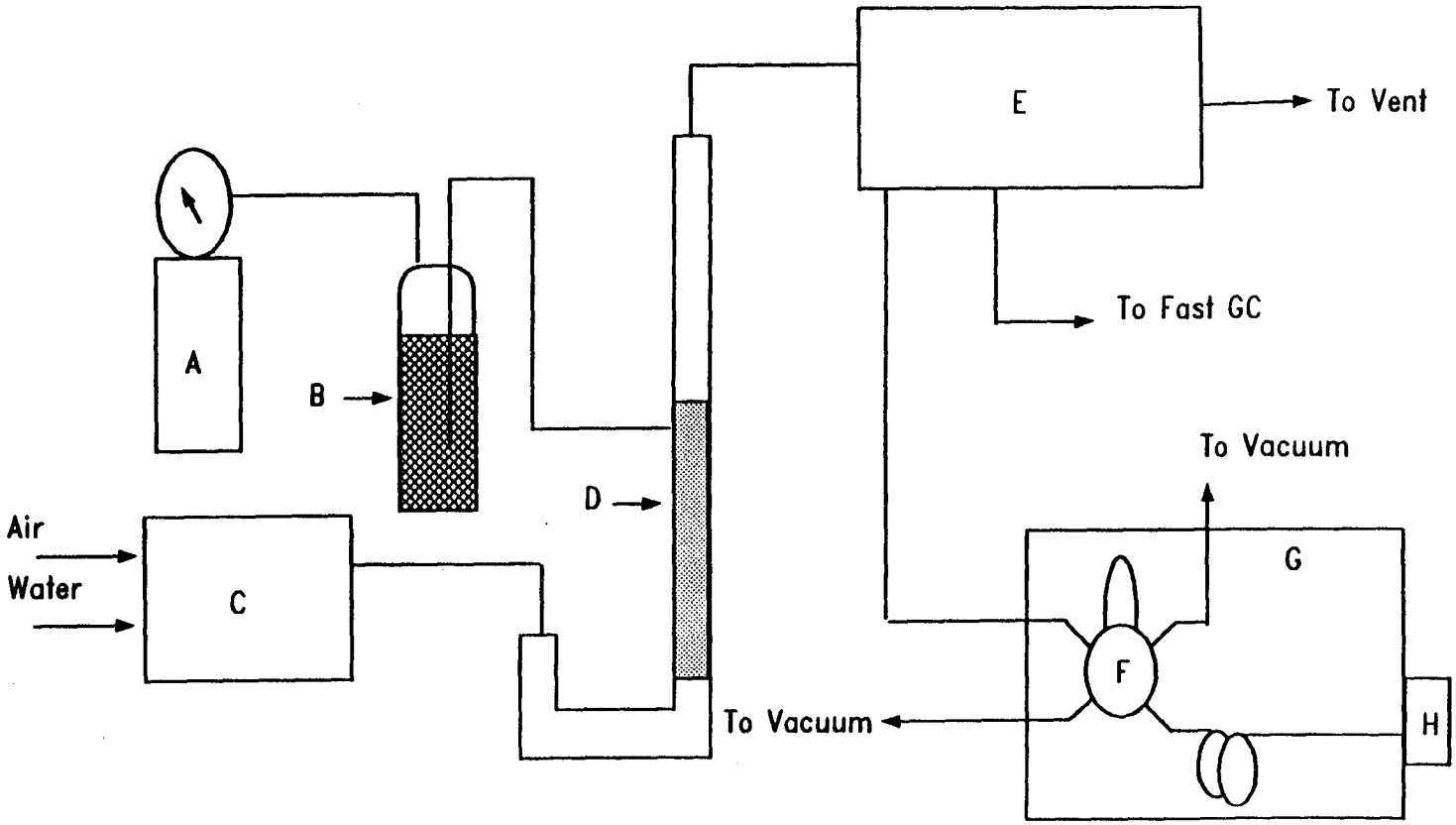


Fig. 33. Diagram of the vapor generator and test apparatus. A, Pressure regulated N_2 supply; B, test mixture reservoir; C, flow controller and humidifier; D, vaporization chamber; E, sampling chamber; F, rotary valve; G, conventional GC oven; H, FID.

relative flow rates of the air and the liquid test mixture.

The concentration of benzene, toluene and xylene was continuously monitored using a conventional GC vapor analysis system, featuring a Hewlett Packard 5890 gas chromatograph with a 30 m long, 0.32 mm i.d. capillary column and a DB-624 stationary phase. Peaks were detected using a FID. Samples were introduced through an electrically actuated capillary gas sampling valve (Valco) and were focused on a 1 ft long, 0.32 mm i.d. pre-column with Porapak Q packing. The temperature was programmed to increase from 60 ^{o}C to 150 ^{o}C during the analysis. Total analysis time was 6 minutes, and the time between successive samples was 10 minutes. Data from the conventional GC was collected and processed using an HP 3357 laboratory automation system. The conventional GC was calibrated using vapor injections from a set of static standards prepared in Saran bags.

Experimental Procedure

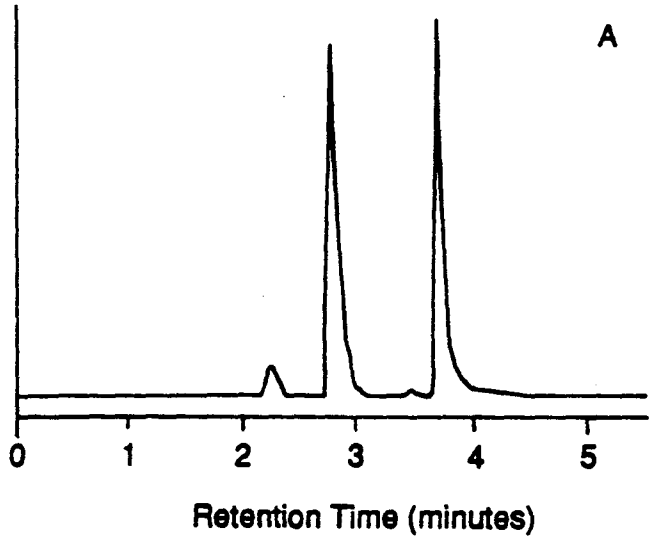
The vapor generator was adjusted to produce a test atmosphere containing benzene at approximately 10 ppm, and xylene and toluene at 100 ppm. After allowing the vapor concentration to stabilize, a series of simultaneous analyses were performed using both the

conventional GC and fast GC, thus allowing a side by side comparison of the two systems. The vapor concentration was then reduced in a step-wise manner and the experiment was repeated at various concentrations. Initial experiments were run at a relative humidity of 10%, and then repeated at relative humidities as high as 80%.

Results and Discussion

For a fast GC system to be useful in routine air monitoring, the quality of the analytical data should be comparable to that obtained with a standard GC. Among the important parameters considered in this study are the chromatographic resolution, the accuracy and precision of peak area and height measurements, retention time reproducibility and the effect of water vapor or other contaminants.

The initial consideration in this work was the quality and speed of the chromatograms that could be obtained. Figure 34 shows chromatograms made with the standard GC and with the fast GC at a vapor concentration equal to approximately one tenth the TLV for each component. The relative humidity was 10% in both cases. The conventional chromatogram shows retention times ranging from 2.5 minutes for benzene up to 3.7 minutes for o-xylene. The fast GC achieved a similar separation



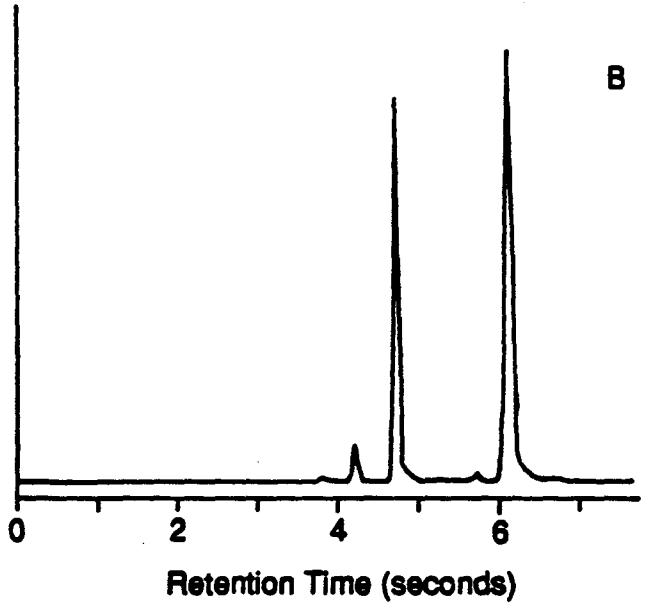


Fig. 34. Comparison of a conventional chromatogram (A) and a fast chromatogram (B) run under similar conditions. Peak identities and concentrations are; 1, Benzene 1 ppm; 2, Toluene 10 ppm; 3, O-Xylene 10 ppm.

with a maximum retention time of about 6 s. The distance between adjacent peaks in the high speed chromatogram is still relatively large, indicating that the retention times could have been made even shorter without a significant loss of resolution. In addition to the difference in retention times, the fast chromatogram shows considerably sharper peaks and less tailing. Other than those differences, the two chromatograms appear to be essentially identical. These results indicate that, for simple mixtures, use of the high speed chromatograph does not produce a significant loss in resolution.

In addition to producing adequate separations, a useful air monitoring GC system must also be accurate, and should have a linear response over a wide concentration range. In order to assess the fast GC's accuracy and linearity, peak areas were plotted against the vapor concentrations measured using the standard GC. The results, presented in Figure 35, show excellent agreement between the two systems at concentrations ranging from approximately the TLV to one tenth the TLV. Each point on the graph indicates the average, plus or minus one standard deviation for seven to nine high speed measurements, and three conventional measurements. The line represents the least squares line of best fit, and in each case has a correlation coefficient of 0.99 or better. As the dilution air flow was increased to reduce

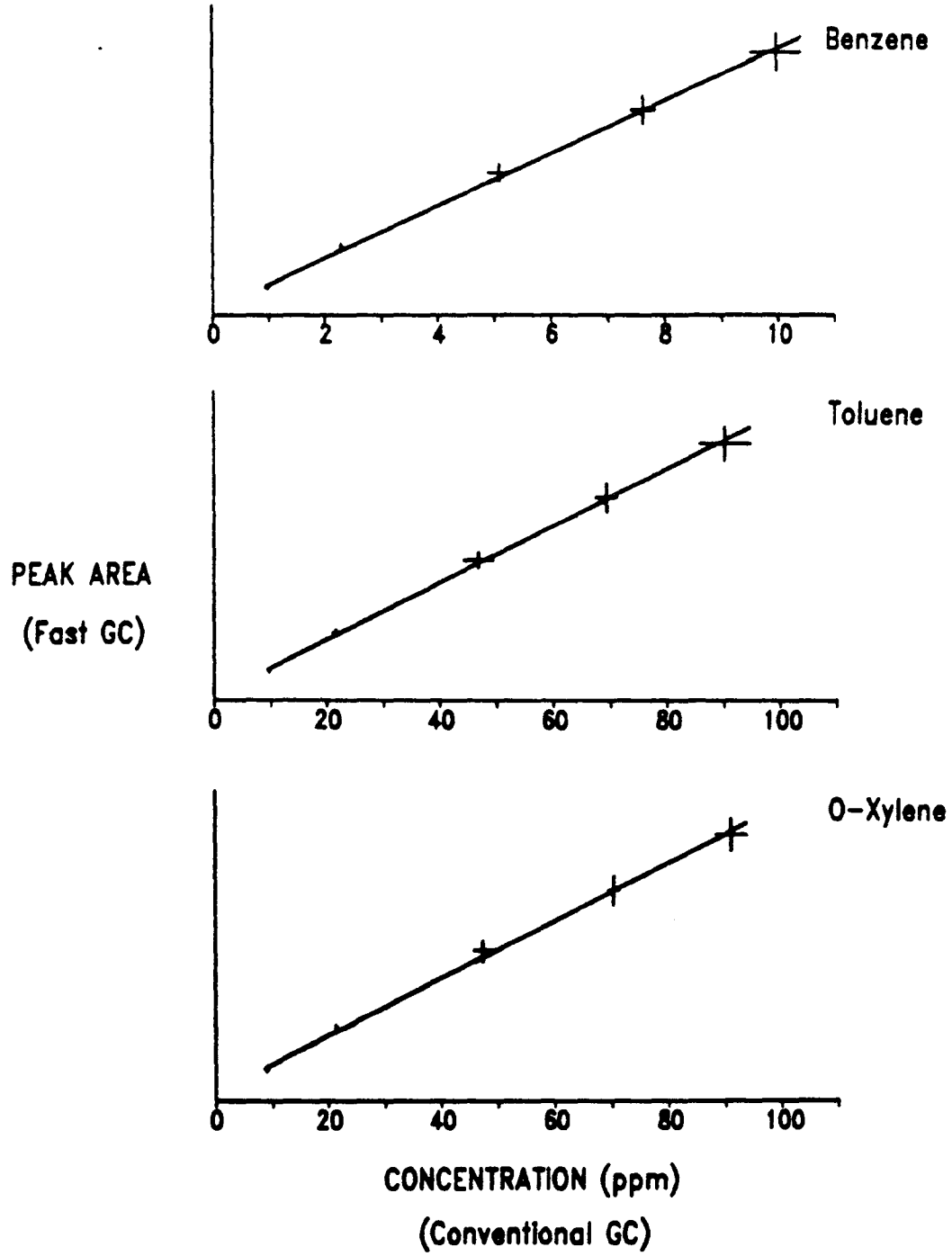


Fig. 35. Peak area measurements from high speed chromatograms (vertical axis) versus vapor concentration measured with conventional GC (horizontal axis). Error bars indicate one standard deviation.

the vapor concentrations to levels of about 50 ppb, the two methods continued to show excellent agreement. These data are not presented in the graph, however, because concentrations extended below the calibration curve established from static standards.

As is indicated by the error bars in Figure 35, peak area measurements made from the fast chromatograms also show a high level of precision. Relative standard deviations for peak area and peak height are presented in Table III.

For benzene concentrations ranging from 1 to 10 ppm and toluene and o-xylene concentrations ranging from 10 to 90 ppm, the relative standard deviations for peak area ranged from +/- 3% to +/- 7%. Relative standard deviations for peak height also ranged from +/-3% to +/- 7% and are presented in Table III.. These results compare favorably with peak area measurements taken from the conventional GC, which also produced relative standard deviations ranging from +/- 3% and to +/- 7%. Although these data must be considered preliminary, they indicate that the fast GC achieves precision comparable to the conventional GC. It appears likely that a fast GC system can meet NIOSH criteria for analytical methods, which require accuracy of +/- 25% with 95% certainty at

TABLE III

RELATIVE STANDARD DEVIATIONS OF PEAK AREA AND HEIGHT MEASUREMENTS

BENZENE			TOLUENE			O-XYLENE		
CONC. ppm	AREA %	HEIGHT %	CONC. ppm	AREA %	HEIGHT %	CONC. ppm	AREA %	HEIGHT %
10.0	7	6	90	7	6	91	6	4
7.6	6	6	69	7	6	70	7	4
5.1	5	6	47	6	5	47	7	5
2.3	4	4	22	3	3	21	4	3
1.0	7	5	10	5	6	9	7	7

concentrations between one half and twice the current permissible exposure limit (PEL) (14).

Although retention time is not a reliable indicator of peak identity in the analysis of unknowns, it is often used in air monitoring applications where the number of peaks is limited, and the composition of the mixture being chromatographed is well defined. The reproducibility of retention time data is therefore an important consideration for air monitoring applications. In order to determine retention time reproducibility, a series of twenty replicate chromatograms was run over a two hour period. Toluene and o-xylene, with average retention times of 4.58 and 5.91 s, both had relative standard deviations of +/-0.6%. Benzene, with an average retention time of 4.11 s had a relative standard deviation of +/-0.5%. These results indicate that retention time reproducibility is at least as good as, and in many cases better than, that obtained with a conventional system.

The final consideration in these preliminary tests of the fast GC, was the possibility that water vapor would have a negative impact on the systems performance. In many industrial environments water vapor is likely to present in the atmosphere at high concentrations. Because the high speed inlet uses a capillary dimension

cold trap, this was a considered to be a potential problem. If a large amount of water was collected with the sample, ice forming on the inner wall of the trap could conceivably slow the revaporization process and degrade chromatographic performance. It was thought possible that, in an extreme case, ice might even block the flow of carrier gas.

In order to test the effect of water vapor on the system performance, chromatograms were run at relative humidities ranging from 10 to 80%. Sample chromatograms obtained at 10% and 80% relative humidity are shown in Figure 36. The results indicate that water has little or no effect on the overall performance of the system. The lack of any humidity effect is probably explained by the extremely small volume of the sample injection. The chromatograms shown here were made with injection volumes of only 200 ul, which, at a relative humidity of 80% and a temperature of 25 ^{o}C, would contain about 4 ug of water. At this level, water is expected to act much like any the materials being analyzed, and has little or no effect chromatographic performance. If significantly larger sample volumes were used, it is possible that water would cause some difficulty. The results presented here, however, indicate that the instrument sensitivity is high enough so that significantly larger samples would

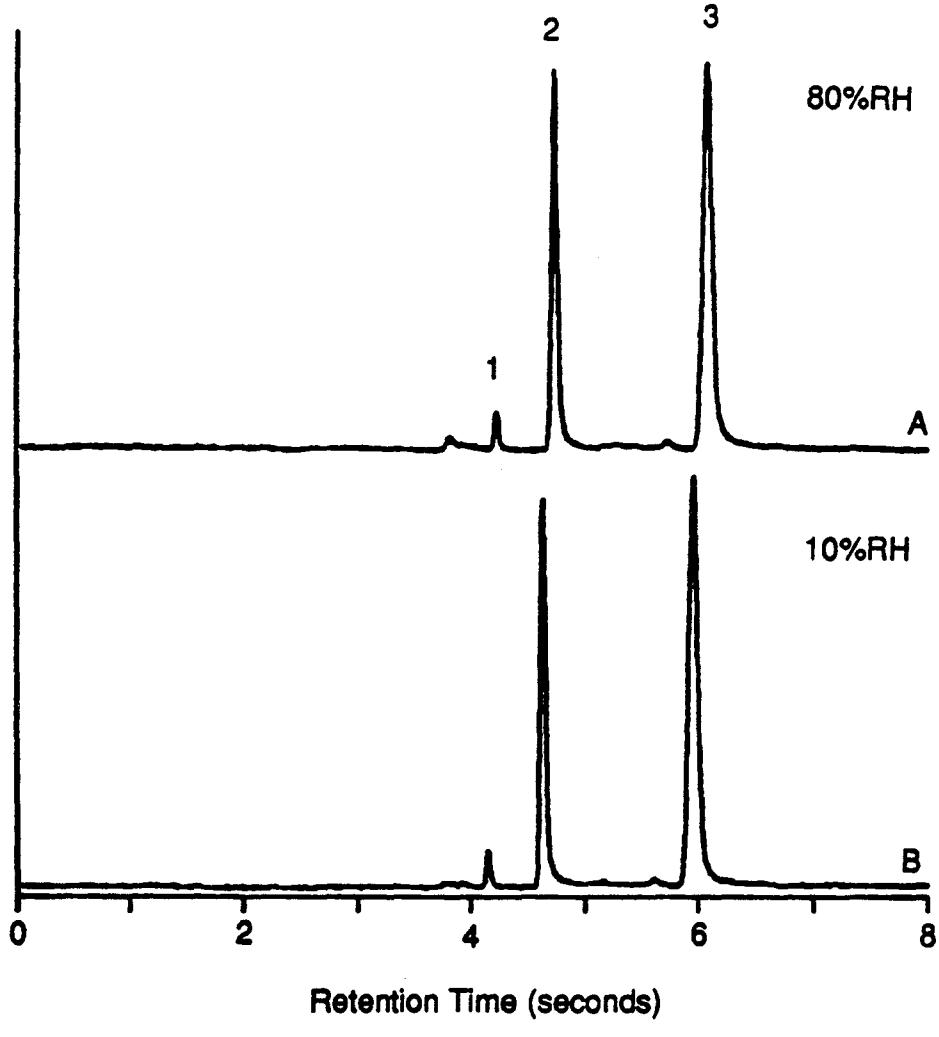


Fig. 36. Comparison of fast chromatograms run at 10% RH (A) and 80% RH (B). Peak identities are; 1, Benzene; 2, Toluene; 3, O-Xylene.

rarely be necessary for monitoring in most industrial environments.

Conclusions

Although the preliminary results presented in this paper are encouraging, there are a number of issues which have not yet been investigated. Among the potential limitations with the current design are the durability of the trap, the lack of a back-flush to remove high boiling contaminants, the potential for thermal decomposition of the sample, the requirement for liquid nitrogen cooling and a lack of efficient analysis software. In addition, other analytical concerns, such as the limits of detection and the long term stability have not yet been investigated.

Despite the need for further development, the results presented here do indicate that a high speed GC system may be useful for air monitoring in some work places. A system of this type would be especially appropriate where the hygienist is concerned with potential exposures to a limited number of volatile organics. In these situations, application of high speed techniques may significantly reduce the lag time between measurements for single point monitors, and the cycle time for multi-point monitors. This may allow GC

systems to be used as monitors in situations where the longer analysis time associated conventional GC is considered unacceptable.

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CHAPTER 5

FAST GAS CHROMATOGRAPHY OF DILUTE LIQUID SAMPLES

The most common type of chromatography in most industrial hygiene laboratories involves the analysis of dilute liquid samples. Usually the sample is collected from the atmosphere in a tube of solid adsorbent material such as activated charcoal. The adsorbent tube is then sealed and sent to a laboratory where the collected materials are eluted into a small volume (0.5 to 2.0 ml) of liquid solvent, which is usually CS_2. The mixture is analyzed by gas chromatography using a flame ionization detector (FID). Carbon disulfide is the solvent of choice in most analyses because it produces little response with a the FID, and because it has been shown to be effective in elution of many organics (1).

Typically the final mixture contains only a few compounds of interest and a few contaminants from either the original sample or from the solvent. The separation is often relatively simple and can be performed on a packed column system. In fact, most NIOSH and OSHA methods recommend, or at least provide an option for, packed column analysis (2, 3). This type of simple

separation should be a suitable application for fast GC. In a large industrial laboratory where thousands of these analyses are performed each year, even a 10 fold increase in analysis speed could provide significant cost savings.

One of the primary goals of this project was the development and validation of a fast GC system for liquid samples of the type that are common in industrial hygiene laboratories. Ewells' previous work with the fast GC was, for the most part, restricted to qualitative analysis of neat mixtures or of solutions at high concentrations (4). Research described in Chapters 2 and 3 formed the basis for attempts at quantitative analysis of dilute liquids, and included data on analysis of liquids at higher concentrations. In this chapter, data are presented concerning the testing and validation of the fast GC with samples more similar to those found in the field of industrial hygiene.

Experimental

All experiments described in this chapter were performed using a fast GC configuration very similar to that described in Chapter 3. However, some modifications were made to increase ease of use and to simulate the type of configuration that might be used during routine analysis.

The most important change was the addition of the Hewlett Packard HP-7673A auto-injector system to the Varian 3700 GC. For these experiments the auto-injector was mounted on the top of the Varian 3700 and injections were made through the standard injection port rather than through the custom made side mounted injector. The splitter outlet was connected to a 25 cm long 0.2 mm i.d. deactivated fused silica buffer column. The buffer column was attached to the trap tubing inside the oven and the trap chamber was placed against the inner wall. The coolant inlet was connected through a small opening in the oven wall, and the coolant exhaust was carried outside the oven by a short section of 1/4 inch o.d. polyethylene tubing. The trap chamber was heavily wrapped with electrical tape to avoid coolant leaks that might affect oven temperature.

In this configuration it was difficult to prevent the copper electrodes from contacting the metal walls of the oven, so the electrical contacts were instead made by wrapping and then soldering multi-strand copper wire around the trap tubing. In order to minimize electrical resistance, each connection was made with two pieces of 14 gauge multi-strand wire.

Separations were performed using a 5 meter long section of 0.25 mm i.d. column with a 0.1 um thick non-polar stationary phase (Quadrex). The carrier gas was hydrogen which was supplied at a volumetric flow rate of about 3 ml/min to produce an average linear velocity of approximately 100 cm/s and a holdup time of about 5 s. All separations were performed with an oven temperature of 60 ^{o}C, an injector temperature of 180 ^{o}C and a detector temperature of 190 ^{o}C.

All other hardware, including the detector, electronics, power supply and data system were identical to those described in Chapter 3. Data were collected at a sampling rate of 400 Hz with no digital or analog filtering, except as noted in the Discussion. All cold trapping was performed at temperatures of -120 to -90 ^{o}C, and all reinjections were performed at an initial capacitor charge of 55 volts. In order to minimize problems with contaminant accumulation on the trap tubing, the trap was heated to 200 ^{o}C between each analysis.

Test samples containing benzene, toluene, and o-xylene (Aldrich HPLC grade) were prepared in high purity CS_2 obtained from The Dow Chemical Company Health and Environmental Sciences Laboratory. Samples were prepared by first mixing each of the three target compounds in

equal volumes and then performing serial dilutions to obtain concentrations down to approximately 30 ug/ml. Each analysis was repeated three times with injection volumes of either 0.5 ul or 2.5 ul.

Results and Discussion

In order to be considered generally useful in an industrial hygiene laboratory the fast GC should, in most respects, be able to match the analytical performance of conventional packed column systems. Although the maximum number of plates, and hence the ability to perform difficult separations, is expected to be low, the limits of detection, linear range and repeatability should be similar to those obtained with conventional GC. The analytical performance of the fast GC system with liquid samples was investigated by performing a series of separations with standard solutions. The results of these tests are presented here.

Chromatographic Performance

Chromatographic performance, or the ability to separate similar compounds, may be considered the most basic measure of a GC system's usefulness. Several different expressions for chromatographic performance have been proposed, however, none has been universally

accepted (5). For the work described here, the number of effective plates developed was chosen as the most meaningful measure of performance. The number of effective plates can be easily calculated from the peak width and adjusted retention time, and is directly related to a systems ability to separate similar compounds (6). One of the goals in setting up a fast GC system is to try and select operating conditions that will produce the maximum number of plates without exceeding necessary constraints on retention time. It should also be noted however that small increases in plate number are not generally important, and that resolution increases only as the square root of the number of effective plates (7). For example, increasing the plate number from 200 to 2000 would result in a significantly better chromatogram, but a similar increase from 2000 to 4000 would produce relatively little improvement.

Optimized GC systems using extremely long open tubular columns may develop as many as one million effective plates. However, numbers this high are unusual. A more typical range of values for capillary GC systems might be 50,000 to 100,000 plates. Packed column systems are much more limited and often develop only a few thousand effective plates (8).

Despite the low number of effective plates, packed column systems are often adequate for the analysis of simple industrial hygiene mixtures. According to the theory described in Chapter 1, fast GC systems utilizing small diameter, thin film columns should be capable of developing a few thousand plates with retention times of 5 to 15 seconds. It should therefore be possible to increase the speed of many simple industrial hygiene separations by switching from packed column systems to a fast GC system similar to that described here.

In order to determine the efficiency of the fast GC system, a series of injections was made and the number of effective plates was calculated for each of the three test compounds. Typical chromatograms produced during this set of experiments are presented in Figures 37 and 38. Figure 37 shows a chromatogram produced with a 2.5 ul injection of sampling containing benzene, toluene and o-xylene, each at a concentration of 290 ug/ml. Figure 38 shows a similar chromatogram produced with smaller, 0.5 ul, injection of the same sample.

The average retention times for the three compounds were 6.6 s for benzene, 7.9 s for toluene and 11.8 seconds for o-xylene. The peak widths, measured at half height, for the 2.5 ul injection were 160 ms for benzene, 150 ms for toluene and 220 ms for o-xylene. These values correspond

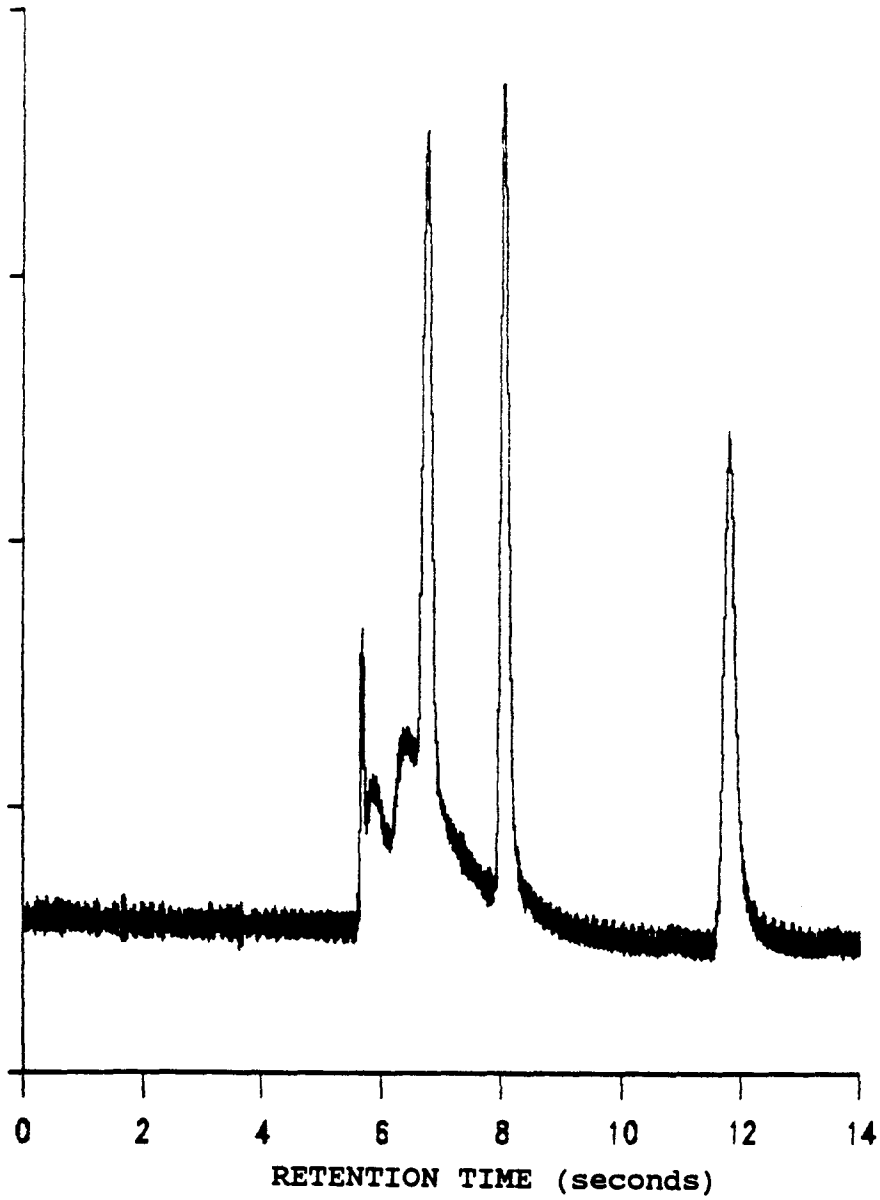

Fig. 37. Fast chromatogram showing separation of benzene, toluene and O-xylene in carbon disulfide. Volume was 2.5 ul and concentration was 290 ug/ml. The separation was performed on a 5 m X 0.25 mm column with a 0.1 um stationary phase at a linear velocity of about 100 cm/s.

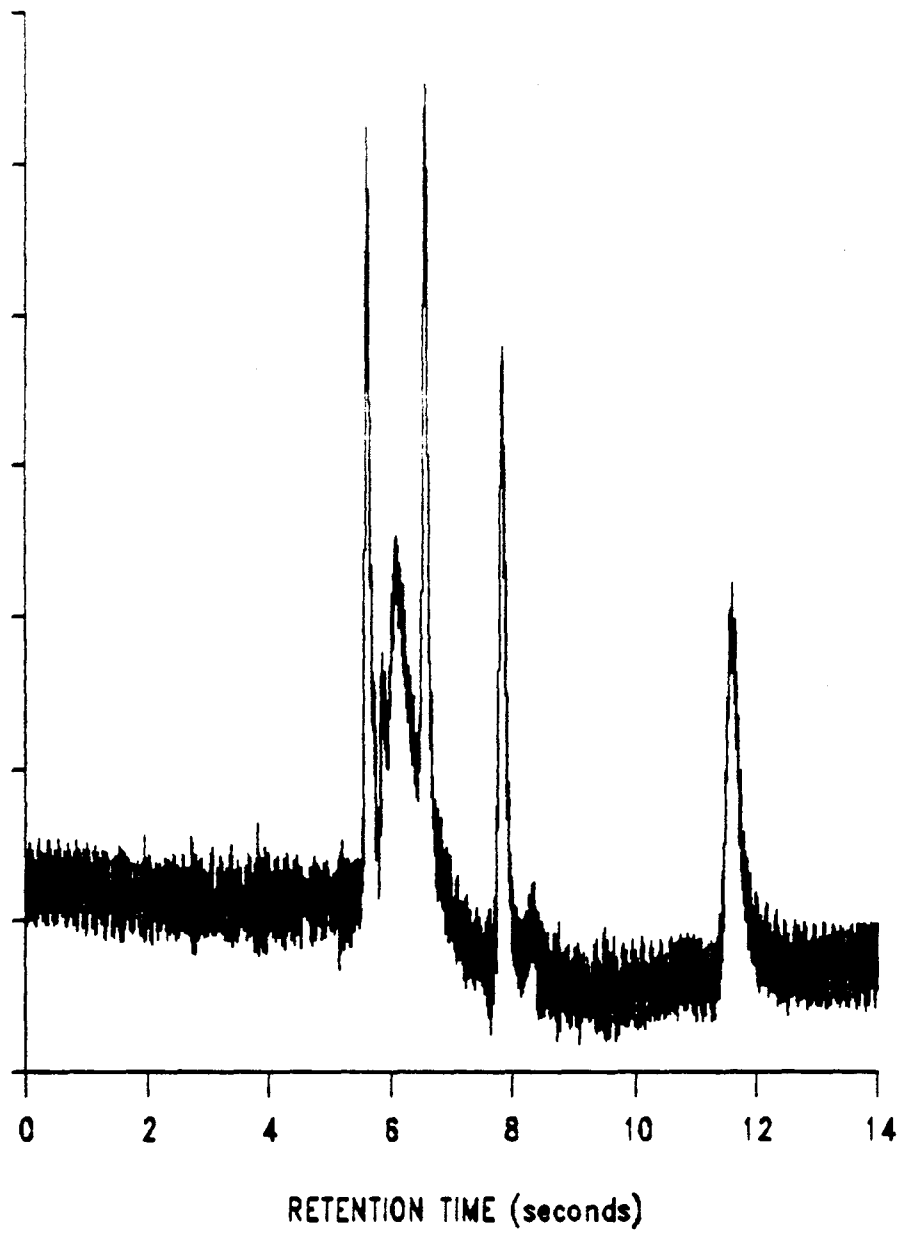

Fig. 38. Fast chromatogram showing separation of benzene, toluene and O-xylene in carbon disulfide. Volume was 0.5 ul and concentration was 290 ug/ml.

to effective plate numbers of 260 for benzene, 1500 for toluene and 4300 for o-xylene.

In general smaller sample volumes produce more narrow peaks and a higher number of plates. This is especially true for the peaks that elute first and is probably the result of more efficient injection band formation. For example, the 0.5 ul injection shown in Figure 38 produced 775 effective plates for benzene, 2300 for toluene and 5300 for o-xylene.

As these calculations illustrate, the number of effective plates developed is relatively small. Comparison to the number predicted by the computer model however, indicates that the system is functioning as expected. Figure 39 shows a computer generated plot that can be used to predict the number of effective plates expected for each peak under the conditions used in this experiment. The plot was generated using the spreadsheet model described in Chapter 1 and assumes an instrumental time constant of 20 ms.

For the 5 meter column used in this experiment, the model predicts plate numbers of approximately 900 for benzene, 2600 for toluene and 7800 o-xylene. In each case, the number of plates measured is only 10 to 20 per cent less than the number predicted by the model. Considering the

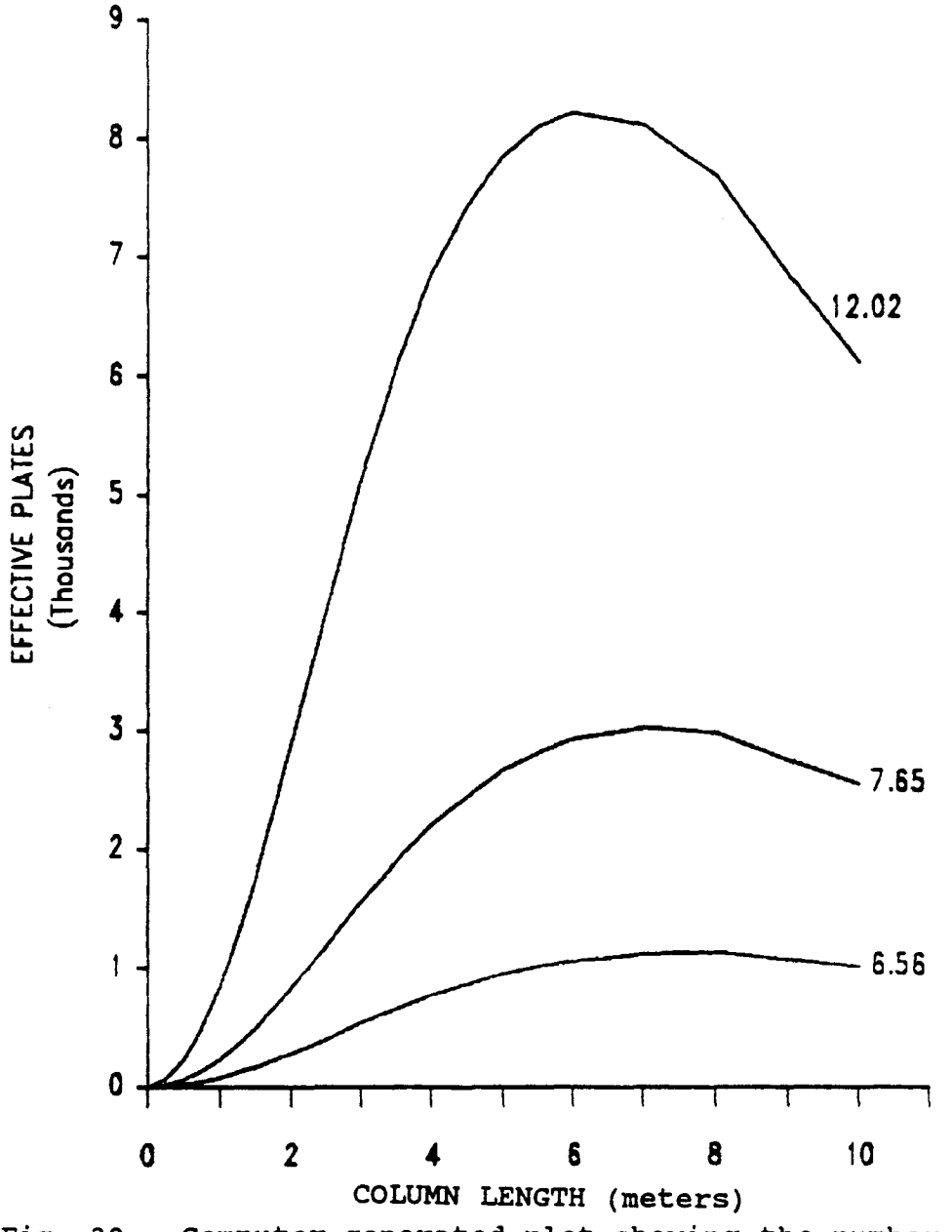

Fig. 39. Computer generated plot showing the number of effective plates expected under conditions used in these experiments. 5 m X 0.25 mm column with 0.1 um stationary phase. The numbers at the end of each line represent expected retention times and are based on measured k values of 0.2, 0.4 and 1.5.

fact that accurate values for column coating efficiency and diffusion coefficients are not available, the measured values are surprisingly close to those predicted from Figure 39.

The relatively low number of effective plates available from the system can be attributed to low partition coefficients, or k values that were obtained with the thin film column. The k values, which were measured at 0.2, 0.4 and 1.1, were well below the optimum value of 1.5 to 3. If k values are increased, either by operation at sub-ambient temperatures or through the use a thicker stationary phase, the number of effective plates could be increased significantly.

For example, Figure 40 shows the number of plates that could be expected if the film thickness were increased to 0.25 um. Under these conditions the number of effective plates would apparently double for benzene, and would increase by about 50% for toluene. The k value for o-xylene would then be increased well above the optimum, and the number of effective plates for that compound would be slightly decreased.

Partition ratios could also be increased through the use of lower operating temperatures. In theory, this would allow the k values to be adjusted upward, but would not

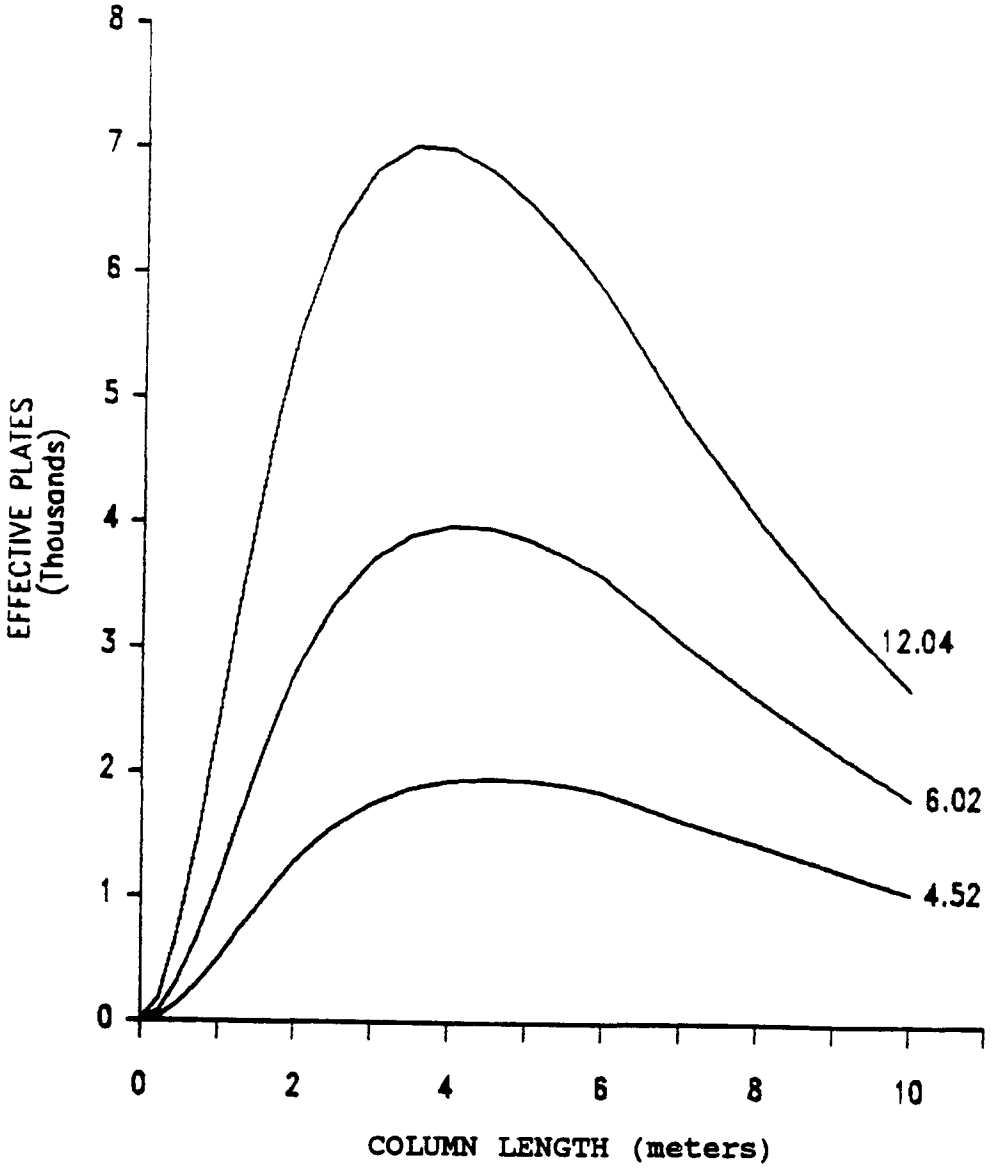

Fig. 40. Computer generated plot showing the number of effective plates expected with a 0.25 um stationary phase. The numbers at the end of each line represent expected retention times and are based on k values of 0.5, 1.0 and 3.0

require the use of the less efficient thicker film columns. Unfortunately, the Varian GC system can not maintain low enough temperatures without the addition of specialized sub-ambient cooling systems. In addition, at low temperatures, the thin film columns are more likely to suffer from sample overload problems.

The results presented here illustrate one of the major difficulties involved with developing applications for the fast GC system. If operating conditions are optimized for one compound, the resolution available in other areas of the chromatogram is likely to be very low. In this case, over 4000 plates are developed for o-xylene, while benzene is subjected to less than 1000 plates. The small number of plates available to the early peaks makes separation efficiency low and results in significant overlap between benzene, the solvent and the unidentified contaminants. If the system is optimized for benzene however, the later peaks will either be poorly resolved or will have much longer retention times.

In conventional GC systems, this problem is solved through the use of temperature programing. Since temperature programing of fast GC systems is not practical at this time, other solutions, such as flow programming may be needed (9).

In some cases, such as those involving the analysis of highly volatile materials, the situation might also be improved through the use of alternate solvents. Selection of a solvent that elutes after the materials of interest, and which is available with fewer impurities, may minimize problems with low resolution. Preliminary experiments with iso-octane (2,2,4-trimethylpentane) and dimethylformamide indicate that the use of higher boiling solvents is possible and may eliminate problems associated with overlap of the solvent with early peaks. It should be noted however, that solvents other than CS_2 will not be readily accepted by the industrial hygiene community without extensive testing.

The most practical method of improving resolution for early peaks may be to simply accept slightly longer retention times. Figure 41 shows the results of computer modeling that assumes a 0.25 um film thickness and a maximum retention time of 20 seconds. The eight second increase in maximum retention time is expected to produce a four fold increase in the number of effective plates for benzene, a three fold increase for toluene, and about a two fold increase for o-xylene. In most cases the increase in performance would probably be worth the slight loss of separation speed.

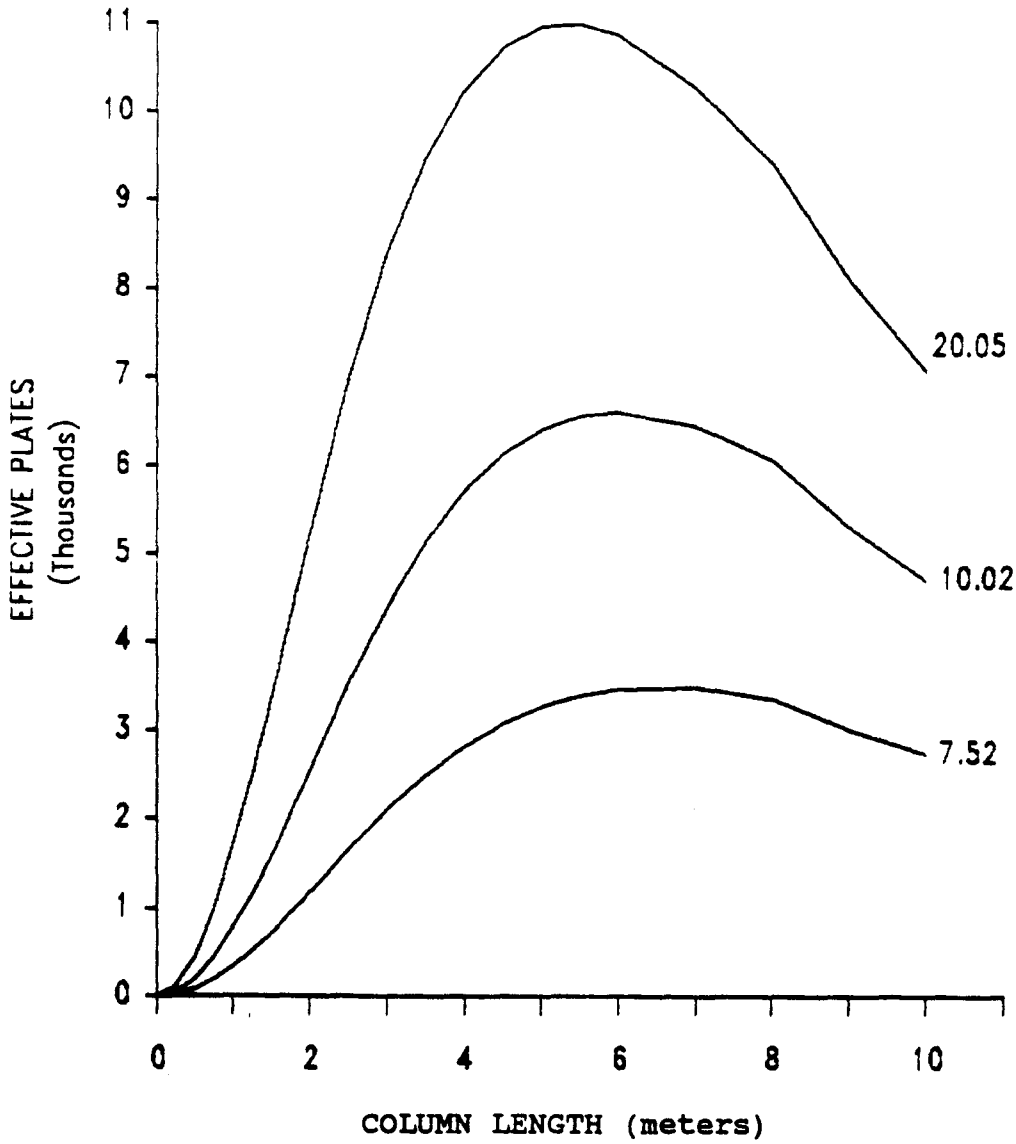

Fig. 41. Computer generated plot showing the number of effective plates expected under conditions used in these experiments, but with a maximum retention time of 20 seconds and thicker film. 5 m X 0.25 mm column with 0.1 um stationary phase. The numbers at the end of each line represent expected retention times and are based on k values of 0.5, 1.0 and 3.0

Linear Range And Limits Of Detection

In addition to meeting some minimum criteria for chromatographic efficiency, the fast GC should also have a linear response range and limits of detection similar to those of conventional GC systems. To test these aspects of performance, a series of analyses was run with varying concentrations and volumes of test compounds.

A calibration curve established from this data set is presented in Figure 42 where peak area is plotted versus the mass of the injected sample. In this figure, each point represents the average of three values and the line represents the best fit to a linear model, as calculated by the least squares method. The correlation coefficient exceeds 0.99 for all three compounds, indicating an excellent fit to the model.

As Figure 42 shows, the response of the system is linear over the tested range of 72 ng to 15 ug which, in these experiments, corresponded to a concentration range of 30 ug/ml to 30 mg/ml. Samples with concentrations higher than those tested would be extremely unusual in the field of industrial hygiene. However, they could probably be analyzed quite easily if necessary. Samples with concentrations lower than those tested are quite common in the field of industrial hygiene and would be very

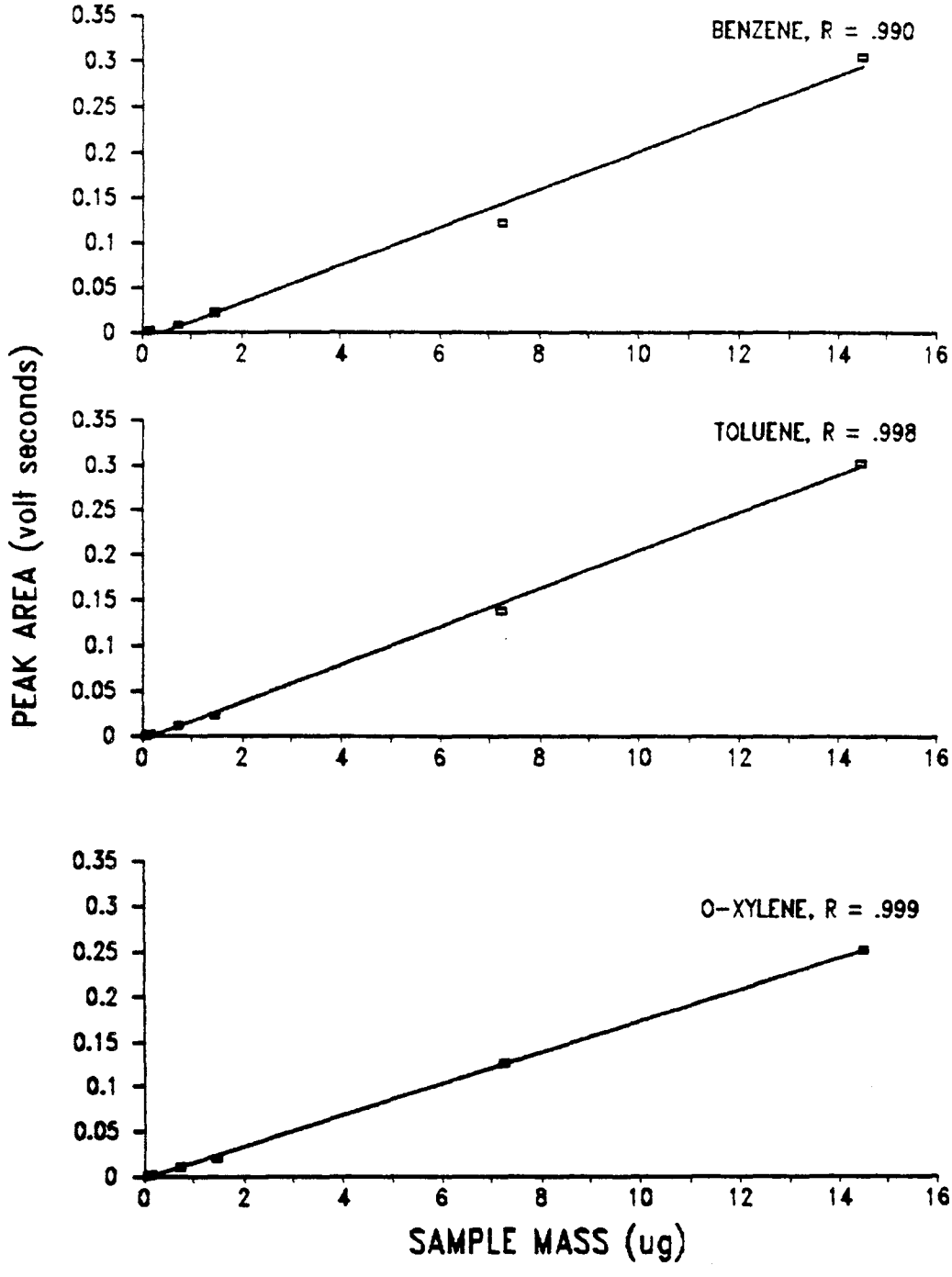

Fig. 42. Calibration curve for fast GC analysis of benzene, xylene and O-toluene in carbon disulfide.

difficult to analyze with the configuration used in these studies.

A sample chromatogram produced with a 2.5 ul injection of the most dilute test mixture is shown in Figure 43. This chromatogram illustrates many of the difficulties involved in fast GC analysis of dilute liquid samples. Under these conditions, the signal to noise ratio has deteriorated to the point where the system is approaching the limits of detection for both toluene and o-xylene. For this project, the limit of detection (LOD) was defined as the sample concentration that produced a peak height equal to the average plus three standard deviations of the background signal (10). Using this definition, the LOD was calculated to be 60 ug/ml. The limit of quantitation (LOQ), was defined as the sample concentration that would produce a peak height equal to the average background plus ten standard deviations (11). According to this definition, the LOQ was about 80 ug/ml. For purposes of comparison, concentration based limits of detection with conventional GC are often reported at about two to three orders of magnitude lower than the values determined here (12).

In order for the fast GC to useful in industrial hygiene analysis, it is not always necessary that the limits of detection be as good as those obtained with conventional

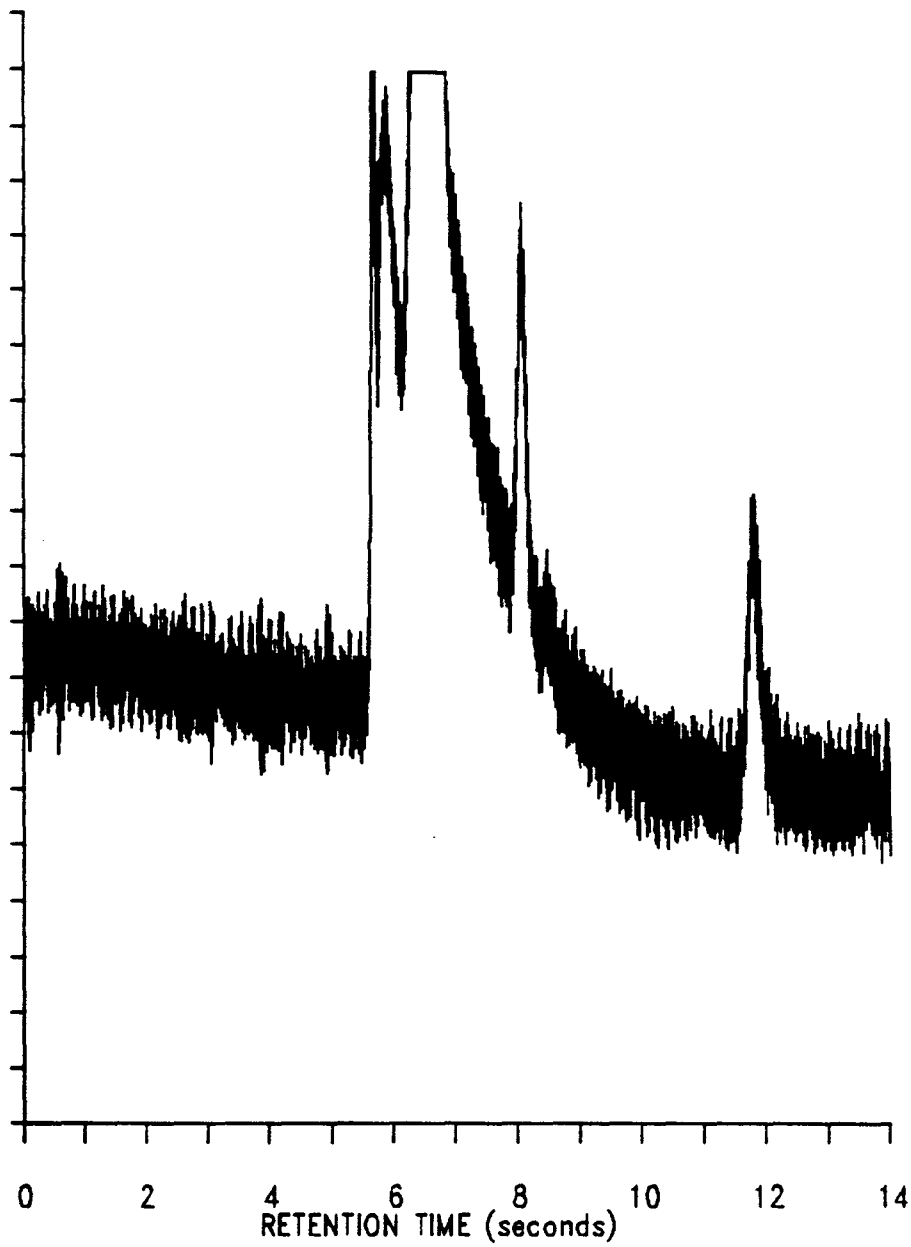

Fig. 43. Fast chromatogram showing high noise levels and solvent tail during separation of a dilute mixture (30 ug/ml) of benzene toluene and xylene in carbon disulfide.

systems. As a general rule, it should be possible to make measurements at one tenth the current PEL or TLV using accepted sample collection and elution techniques. This would require limits of detection of at least 3 ug/ml for benzene, 37 ug/ml for toluene and 44 ug/ml for o-xylene. The fast GC system used in these studies can therefore meet the requirements for toluene and o-xylene, which have relatively high TLVs, but could not meet the requirements for benzene.

Benzene is not seen in the chromatogram shown in Figure 43, and can not be analyzed at 30 ug/ml with the current system. The primary reason for this is the lack of good separation for early eluting materials. As discussed earlier, the benzene peak is not well separated from the solvent and/or contaminants, and tends to be obscured by those materials. The situation is aggravated by the fact that the fast electrometer used in these experiments has no zero off-set. Operation at high levels of amplification elevates the baseline and move the solvent "tail" off scale. The same kind of problem is anticipated during attempts to analyze any mixture containing highly volatile materials.

The situation could be improved through the use an improved electrometer with a adjustable zero. However, the basic problem of separating the solvent from the

materials of interest would still need to be addressed. The reasons for the poor separations and some possible solutions were discussed in the previous section.

In general, it appears that the linear range and limits of detection are barely adequate for some industrial hygiene or environmental applications, and would probably be considered inadequate for many others. It is likely however that limits of detection can be significantly improved.

If retention times are extended to a maximum value of 20 or 30 seconds, peak widths will increase and allow digital and/or analog filtering. A simple example of the improvement that can be achieved using these methods is presented in Figure 44. Here the upper tracing shows a chromatogram recorded with a 400 Hz sampling rate and no filtering. The lower tracing shows a similar chromatogram that was collected using a 60 Hz sampling rate, which provides a simple form of digital filtering. In addition the lower chromatogram was smoothed by application of a three point moving average with 1:2:1 weighting. Although more sophisticated methods, such as Savitsky-Golay smoothing (13), would be required for routine analysis, this example does demonstrate the potential improvements that might be obtained by

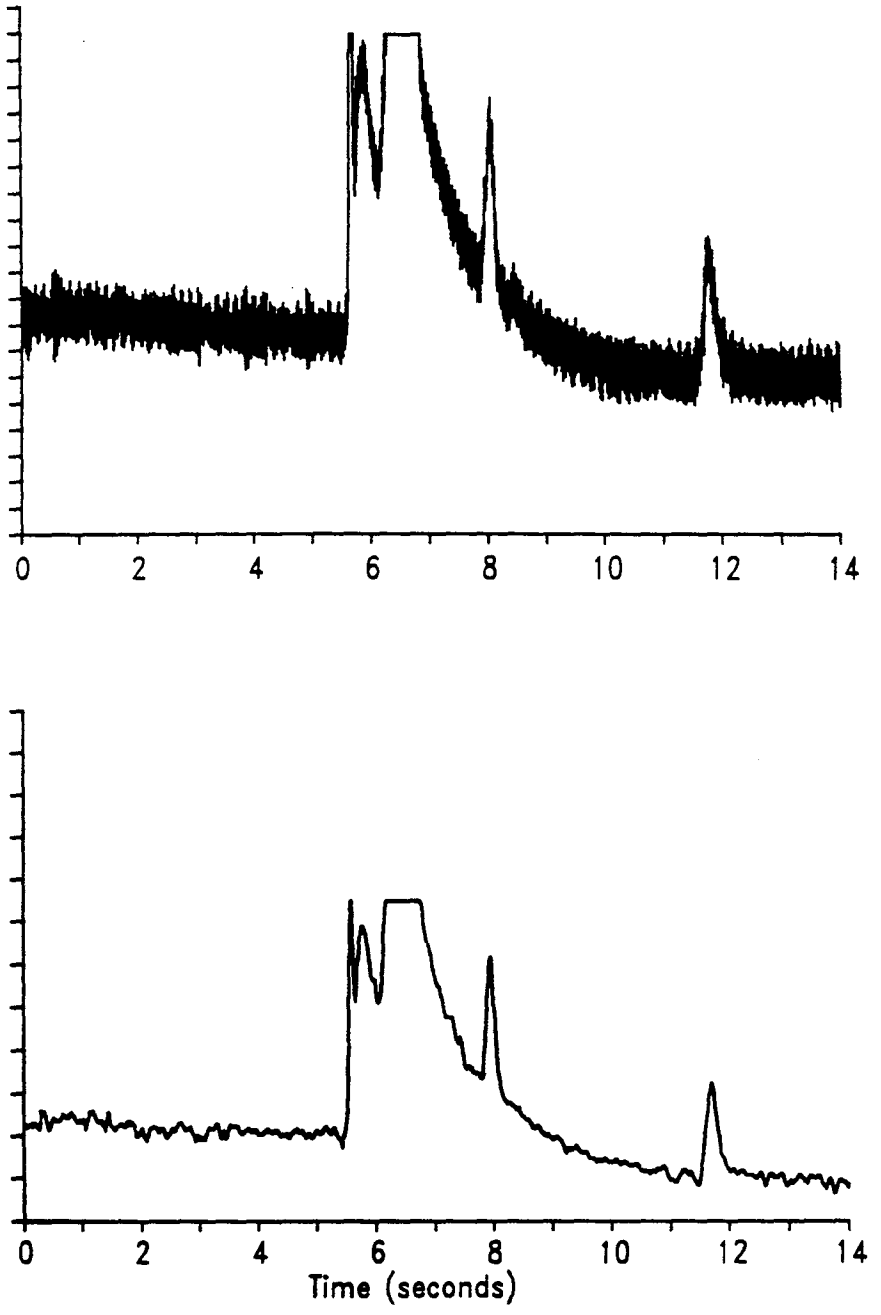

Fig. 44. Fast chromatogram showing the effect of noise reduction by application of a simple 60 Hz filter and signal averaging.

application of various analog and digital filtering or signal processing techniques.

Signal to noise ratio and limits of detection might also be improved by simply increasing the sample volume. As discussed in Chapter 2 however, this would likely result in an increase in the width of the initial injection band and would decrease resolution for the early peaks. Again, if slightly longer retention times are considered acceptable, the loss of injection efficiency would be less important.

Peak Area Repeatability

The final consideration in these experiments was precision, or repeatability of peak area measurements made with the fast GC system. Precision can most easily be expressed in terms of either the standard deviation or the relative standard deviation obtained from a series of replicate measurements. In most cases, conventional GC systems achieve relative standard deviations of 5 to 10 per cent or better, which is considered adequate for most analytical applications. Earlier experiments with concentrated liquids and with vapor samples indicated that relative standard deviations of 5 to 10 per cent could be expected with the fast GC.

For the experiments described in this chapter, precision was actually much better than that achieved in the earlier work. In most cases, triplicate chromatograms produced peak areas with relative standard deviations of less than 1%. The most obvious explanation for this improvement over earlier results is the addition of the Hewlet Packard auto-injector, although other factors such as the change in injector configuration may also have been involved.

Conclusions

Data presented in this chapter indicate that the fast GC system may be useful in the analysis of some liquid samples that have significance in the field of industrial hygiene. The instrument was shown to a have a linear response over a concentration range covering at least three orders of magnitude, and was also shown to allow precise measurement of sample mass. Application of the system to analysis of dilute samples will be limited by the relatively poor limits of detection and by the systems inability to separate low boiling constituents from CS_2 and from low boiling contaminants.

In the current configuration, the fast GC system was not able to match conventional systems in terms of signal to noise ratio or limits of detection, and could not be

used to measure solutes at concentrations less than about 50 ug/ml. The high background noise levels limit the usefulness of the system for many industrial hygiene applications. This problem results from the increased sensitivity of fast electrometers and amplifiers to 60 cycle or higher frequency noise. Because the peaks produced by the fast GC have a strong 60 Hz component, the use of analog or digital filters is not practical (14). Although data are not presented here, it is likely that the limits of detection could be improved by one to two orders of magnitude if retention times were extended and filtering mechanisms are applied. Noise levels might also be reduced, and the usefulness of the system extended, through the use better shielding, higher purity gases and through improved detector design.

In order for the fast GC to be useful in the analysis of highly volatile materials, the problem with poor separation from the solvent must also be addressed. Compounds with volatility equal to or greater than benzene, can not be easily separated from CS_2, which is the standard solvent for most industrial hygiene analyses. The use of alternate, high boiling, solvents is suggested as one solution. However, this would require an extensive series of validation tests.

The problem of poor separation efficiency for early peaks might also be addressed through the use of sub-ambient operating temperatures. Lower operating temperatures would produce increased partition ratios and would provide increased efficiency for high volatility materials.

In conclusion, the fast GC system was found to be a potentially valuable tool for the analysis of some liquid samples. The system is currently limited to the analysis of simple mixtures of moderate volatility materials. It is also limited to concentrations of about 50 ug/ml or higher. For samples that meet these requirements the increased speed of analysis may be significant and achieved without loss of accuracy or precision. Further, it is expected that relatively minor improvements and changes in the system configuration could extend the range of applications to cover many of the more common industrial hygiene and environmental analyses.

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The objective of this research project was to develop and validate a fast GC system that would allow many industrial hygiene separations to be completed 10 to 100 times faster than with a conventional GC. In order to achieve this objective, a number of steps, or specific aims were identified. Briefly stated, these were:

1. Develop an improved cold trap inlet system based on the earlier work of Ewells.

2. Develop a fast GC system and optimize for speed.

3. Conduct a systematic evaluation of the cold trap and fast GC operating characteristics.

4. Evaluate the fast GC performance with liquid samples similar to those found in industrial hygiene applications.

5. Evaluate the fast GC performance in the direct inlet mode, using a vapor mixture similar those found in many industrial environments.

Conclusions

The conclusions, as they relate to each of the specific aims are presented in the following five sections. These are followed by a summary of the overall project and by a set of recommendations for further development.

Inlet Development

As discussed in Chapter 2, the original inlet design proved to be inadequate for routine quantitative analytical work of the type that is common in industrial hygiene laboratories. Major problems with the performance of the inlet included poor repeatability, low sample recovery, and inadequate durability.

In order to improve analytical performance, the trap tube material was changed from steel to Monel-400, which was shown to have superior characteristics. In addition a buffer column was added between the injection port and the cold trap, and a thermocouple-based temperature monitor was added.

Trapping efficiency was improved by redesign of the trap chamber and nitrogen delivery system that allowed trap temperature to be sustained at -175 ^{o}C or colder.

Trap durability was improved by changes in electrode design, addition of a coil to the trap tube and through careful selection of trap materials and dimensions. Following these changes inlet performance was carefully evaluated and was shown to meet the requirements of this project.

Fast GC Development

While development, testing and characterization of the cold trap inlet was the key to a successful project, the development of other components was also necessary.

The cold trap inlet was interfaced with an improved splitter system for liquid injection and with a rotary valve and sampling loop for gas injections. The high speed inlet was then interfaced to a Varian 3700 GC and flame ionization detector that were used for the majority of the research. The Varian GC was also fitted with a Hewlett Packard autoinjector for use in analysis of liquids. A second system, based on an HNU model 301 GC, was assembled for use in vapor analysis.

The new systems also featured improved capacitor discharge power supplies. The power supplies were originally designed by Jim Foulke of the Department of Industrial Engineering and was later re-engineered and

built by Prototype Design Inc. of Ann Arbor. The final design was capable of heating the Monel-400 trap from -150 ^{o}C to +150 ^{o}C in less than 20 ms, and was computer controlled.

Both the Varian and HNU systems were fitted with high efficiency fused silica capillary columns from Quadrex. An internal diameter 0.25 mm and a non-polar stationary phase ranging from 0.1 to 0.5 um was used in all research. Columns were selected to give maximum efficiency possible while still avoiding practical problems such as sample overloading. Operating conditions and column lengths were selected on the basis of computer simulations.

Data aquisition and processing were both computerized, as were some of the control systems. In order to overcome the limitations found in most chromatography stations, data was collected using a Data Translation DT2801 analog to digital converter mounted in a 80286/87 based PC and LabTech Notebook software (Laboratory Technologies). Since Labtech Notebook is not capable of performing data analysis functions, a control and analysis system was devised using Labtech Chrom, Lotus 123 and a set of keyboard macros developed with Lotus Metro.

An independent data aquisition and analysis program was also developed using Microsoft complied basic (QuickBasic 4). This program performs data aquisition at rates up to about 200 Hz and allows the operator to manipulate the display, calculate retention times, peak areas and peak heights and print the chromatogram.

Fast GC Characterization

The cold trap inlet has been well characterized in terms of trapping and reinjection temperature. The overall chromatographic performance and trapping efficiency for a limited number of compounds has also been established.

Most testing was limited to common industrial solvents with relatively high stability and moderate volatility. The materials were selected for their significance in industrial hygiene applications and for ease of separation. With these simple mixtures, the fast GC system was able to meet the stated goal of a 10 to 100 fold improvement in analysis speed. The fast GC also was also found to match conventional systems in terms of peak area reproducibility. Retention time reproducibility was at least as good as, and often better than, that obtained with convention systems.

Trapping and reinjection efficiency for other types of materials is unknown at this time. Highly volatile materials, such as the Freons, are probably very difficult to trap, while low volatility materials may be difficult to re-vaporize as a narrow band. Increasing the heating power is expected to allow reinjection of high boilers, but may lead to reduced trap life and sample pyrolysis.

Although further studies of basic operating characteristics would be needed for many applications, the cold trap injection system and fast GC have been validated and shown to function for many samples of interest in the field of industrial hygiene.

Analysis of Liquid Samples

The initial objective of this research project was the analysis of liquid samples. Most liquid samples analyzed for industrial hygiene applications are dilute solutions which may contain the materials of interest at concentrations of a few micrograms per milliliter or less. The fast GC system developed in these studies is not useful for analysis of materials at concentrations less than about 50 ug/ml. While some industrial hygiene samples could be analyzed, the poor limits of detection

would not allow for measurement of most materials found in the atmosphere at sub ppm concentrations.

In order for the fast GC to be widely useful for analysis of liquid samples, the limits of detection should be improved by at least one to two orders of magnitude. It may be possible to achieve this through improved detector design or through changes in the inlet that would allow increased sample volume. A more practical solution might be to extend the retention times into the 15 to 45 second range. This would produce wider peaks and would allow either analog or digital filtering techniques to be applied

Liquid analysis is also complicated by the presence of impurities in the solvents. In order for fast GC to be widely accepted by the industrial hygiene community, adequate performance with CS_2 solutions is essential. Unfortunately CS_2 is one of the most difficult solvents to purify or to obtain in a high purity form. For conventional GC systems this is not usually a problem since the contaminants can be separated from the materials of interest fairly readily. With the fast GC system however, separation power is limited and it often difficult to separate the contaminants from the materials of interest. The ability to separate similar compounds is especially low for the first few seconds of the

chromatogram. Unfortunately, this is often the most heavily contaminated area.

Despite these limitations, the fast GC may prove useful for certain types of liquid analysis. If the materials of interest are at relatively high concentrations, approximately 50 ug/ml or higher, and if their boiling points are well removed from those of the contaminants, high speed analysis is possible. These conditions can occasionally be met for industrial hygiene or environmental samples, and in those cases the fast GC may be a very useful tool. In many other fields, such as process control, the poor limits of detection and solvent limitations may not present a problem. In those applications, the cold trap and fast GC systems may be extremely valuable.

Vapor Analysis

The initial tests of vapor analysis, presented in Chapter 4, were very successful. The fast GC matched conventional GC for resolution and reproducibility while increasing the speed of analysis by at least 50 fold. The poor limits of detection that were encountered during attempts to perform liquid analysis, were not a problem during vapor analysis. This can be attributed to the lack of solvent, and the relative enrichment of the

sample. The lack of a solvent allows heavier sample loading and improves the limits of detection. Although the limits of detection were not determined, vapor analysis was performed at concentrations of benzene in air as low as 50 ppb, which is sufficient for most industrial hygiene applications.

The results presented in Chapter 5 indicate that it should be possible to use a high speed system of this type in the development of a single point or multipoint monitoring system. A monitoring system based on the fast GC would be useful in many applications were conventional GC systems are considered too slow to be practical.

In conclusion, a fast GC system was developed and validated for use with some simple mixtures of the type that are important in the field of industrial hygiene. In its present configuration the fast GC is capable of producing high quality chromatograms 10 to 100 times faster than a conventional system. Poor limits of detection and inability to separate some low boiling compounds do impose some limits on use of the fast GC with liquid samples. These factors are not a significant problem during vapor analysis. Despite these limitations, the concept of fast GC using a cold trap inlet and high efficiency capillary columns was shown to be valid.

The fast GC developed for this project served as a useful research tool. With further development, a useful air monitor based on fast GC could be produced, and would offer some significant advantages over conventional instrumentation.

Recommendations For Further Research

Although the initial studies reported here have been successful, a variety of potential limitations still need to addressed before a practical instrument can be developed. Some of the possible objectives for future development are presented here.

Improving the Cold Trap and Heater Circuit.

The current cold trap design performed well for the experiments described in this thesis. However, for field applications the arrangement would be inconvenient and would likely require further improvement. The trap is difficult to install or replace. In addition, the cooling system is inefficient and requires a large volume of both liquid and gaseous nitrogen.

The durability of the trap itself may be a potential problem, and the durability of the capacitor discharge power supply is unknown.

A high priority should be the development of a more convenient, efficient, and durable cold trap. This would probably involve redesign of the trap chamber and electrodes, and testing of different trap tube materials. The materials tested for this work were generally those that were available at little or no cost, and may not represent the best possible choices.

In addition to the design changes discussed above, further development may be required to improve system performance with either high or low boiling compounds. The experiments conducted so far have concentrated on materials with intermediate volatility. Improved trapping efficiency may be required for high volatility materials and increased heating capacity may be required for those materials that are less volatile.

Improving Signal to Noise Ratios.

The greatest limitation on the use of fast GC appears to be the poor limits of detection. The primary problem is the sensitivity of the high speed electrometer to noise that is picked up from the detector and other

associated electronics. The signal to noise ratio might be improved by addition of filtering mechanisms to the electrometer or through the application of digital filtering techniques. However, either of these techniques may cause peak distortion and limit the amount of resolution that can be achieved with short retention times.

The presence of high frequency noise is a fundamental problem. Since most GC signals are low frequency, instrument manufacturers have probably not directed any significant effort to reducing high frequency noise. It may be possible to make some improvements through better shielding and design of the detector systems. For high speed GC to match conventional GC in limits of detection, this issue will need to be addressed.

One partial solution to the problem is the use of an electrometer with adjustable response time and filtering. This would allow the operator to "tune" the electronics and retention times for optimal performance under the conditions being used in that particular analysis. If limits of detection and high frequency noise became a problem, the analysis time could be extended and filtering could be added.

Signal to noise ratios might also be improved through the use of digital filtering techniques. One technique that is widely used in the field of chromatography is Savitsky-Golay smoothing. Although this technique must be applied carefully to avoid peak distortion, it can in some cases produce a significant improvement in signal to noise ratios. Other digital filtering techniques, such the Fourier transform are not used as often. However they have occasionally been applied to chromatographic data and may be useful.

The limits of detection could also be improved for specific applications by the development of new, or different low dead volume detectors. For example, development of a low dead volume electron capture detector would presumably improve limits of detection for halogenated materials, and a low dead volume PID might be useful for analysis of aromatics.

Develop High Speed Software.

Although the software used in this study was adequate for preliminary research, it is not well suited to field work, or for complete automation of the system. Data analysis speed is currently the limiting factor that sets the minimum analysis time. Production of a commercial instrument, or even field testing of the

current design would require improved software. The necessary technology is available and could be applied to this problem.

Development of Back-Flush and Sequential Sampling

The fast GC system developed for this project is best suited for use as a direct inlet vapor monitoring system. In some air monitoring applications it should be able to provide near real time results. To be useful in a field situation however, a number of additional capabilities will be required. For many applications a back-flush system will be needed to clear low volatility components off the column between chromatograms. An automated, sequential sampling system will also be required.

A prototype back-flush system was previously demonstrated and is currently under development and testing by other members of the research group. A sequential automated sampling system has not been developed, but could be adapted from a conventional system. The addition of these two components would greatly improve the prospects for using fast GC in the field.

Development of Alternate Detectors

The use of highly specific detectors could, in some cases, provide a significant improvement in analysis speed. If the detector responds only to the compounds of interest, then it is not necessary to separate those materials from other contaminants and retention time can be reduced. This approach to increased analysis speed may be especially valuable in the analysis of complex mixtures and may help solve the contaminant problem that was experienced during attempts at dilute liquid analysis.

The potential advantages of element specific detection in fast GC have been discussed, and are being studied by other members of the research group. Other types of detectors that might be useful in some applications include electron capture, photoionization and nitrogen phosphorus detectors. Each of these has the potential to be used in fast GC. However, a significant amount of development effort may be required to reduce dead volumes, increase response speeds and minimize noise.

APPENDICES

APPENDIX A

SPREADSHEET MODEL FOR PREDICTION OF CHROMATOGRAPHIC PERFORMANCE

The spreadsheet model used in this work was based on the BASIC program developed by Sacks and Puig. The program was transferred to the spreadsheet environment to make the program more flexible and to improve the graphing capabilities. Unfortunately the LOTUS COMMAND LANGUAGE is not well structured, and unless the reader is familiar with spreadsheet programs the listing may be very difficult to interpret.

The program opens with an input screen that allows the user to enter operating conditions including;

1. Column diameter
2. Diffusion coefficients in both phases
3. Stationary phase film thickness
4. Instrumental time constant
5. Outlet pressure
6. Relative retention for the critical pair
7. Maximum anticipated k value
8. Maximum acceptable retention time
9. k values of 5 or fewer other components

A printout showing the input screen with default values is included with the source code listing.

Based on the user responses concerning maximum k value and retention time, the required velocities are calculated for a variety of column lengths. Using the operator input, and literature values for viscosity of hydrogen, the predicted inlet pressures are calculated. As with the Sacks - Puig model, initial calculations are made without correction for compressibility. The error associated with gas compressibility is then determined and the inlet pressure is adjusted accordingly. This repeating cycle of error estimation and adjustment is repeated until the error is less than 2%. To increase the speed of the calculations, the inlet pressure is incremented exponentially.

In order to interpret the source code the reader must know the column labels that associated with each parameter. These are presented in the following list:

BG: Column Length

BI: Required Velocity

BK: Estimated inlet pressure without compressibility correction

BM: The ratio of inlet pressure to outlet pressure

BO: The actual flow expected to result from the ratio of inlet to out pressure. This calculation includes the correction for compressibility.

BQ: The ratio of expected flow relative to the desired flow.

BS: The F_1 pressure correction factor from the modified Golay equation.

BU: The F_2 pressure correction factor from the modified Golay equation.

BW: Golay "A" term for longitudinal diffusion.

BY: Golay "B" term for resistance to mass transfer in the gas phase.

CA: The Golay "C" term for resistance to mass transfer in the stationary phase.

CC: The Golay "D" term for instrumental time constant.

CE: The HETP or sum of "A", "B", "C", and "D".

CG: The number of theoretical plates.

CI: Resolution

CK: Holdup time

The program equations are presented on the following pages. The equations are followed by the general spreadsheet layout. The flow of the program recalculation on each page would be left to right. Columns marked with the error symbol are not errors, but have no current value. The input screen and the control macros are presented last.

BI: Uaim

```
(BG5*(1+MAXIMUM_k))/MAXIMUM_Tr
```

BK: Pin_est

```
@ROUND(Pout+((8*VISCOSITY*BI*BG)/R_SQUARED).0)
```

BM: Pratio

```
BK/Pout
```

BO: TRUE_FLOW

```
(0.9375*R_SQUARED*Pout)*((B5^2)-1)^2/((BM^3)_
     -1/(BG*VISCOSITY)
```

BQ: Utest

```
BO/BI
```

BS: F1

```
1.125*((BM^4-1)*(MB^2-1))/((BM^3-1)^2)
```

BU: F2

```
1.5*((BM^2-1)/BM^3-1))
```

BW: A Term

```
(2*CO*BS*BU)/BO
```

BY: B Term

```
BO*((DIAMETER^2)*BS/(CO*BU))*(((11*CURRENT_k^2)+_
     (6*CURRENT_k)+1))/(96*((CURRENT_k+1)^2))
```

CA: C Term

```
(1.5*(CURRENT_k/(CURRENT_K+1)^2)*(DF^2/DIFF_STAT))*BO
```

CC: D Term

```
(BO^2)*(EC^2)/(BG*(CURRENT_k+1)^2)
```

CE: HETP

```
CE+BW+BY+CA+CC
```

CG: THEOR. PLATES

```
BG/CE
```

CI: RESOLUTION

```
0.25*(@SQRT(CG))*(ALPHA-
1)/ALPHA)*(CURRENT_k/(CURRENT_k+1))
```

CK: HOLDUP

```
BG/BO
```

CM: COLUMN PRESSURE

```
(Pout/BU)/1013000)
```

CO: EFFECTIVE Dgas

```
DIFF_GAS/CM
```

CQ: EFFECTIVE PLATES

```
(CG)*(CURRENT_k/(CURRENT_k+1))^2
```

COLUMN DIAMETER:	.32	millimeters
CARRIER GAS:		
DIFFUSION-STATIONARY:	0	cm2/sec
FILM THICKNESS:	.1	micrometers
DIFFUSION - MOBILE:	.3	cm2/sec
EXTRA-COLUMN FACTORS:	10	milliseconds
OUTLET PRESSURE:	760	torr
RELATIVE RETENTION:	1.1	(alpha)

MAXIMUM k:	0	
MAXIMUM Tr:	0	seconds

FIRST k VALUE:	0
SECOND k VALUE:	0
THIRD k VALUE:	0
FOURTH k VALUE:	0
FIFTH k VALUE:	0
SIXTH k VALUE:	0

LENGTHS	possible column lengths to consider	U aim	U aim is the desired flow velocity	Pin est.
25		ERR		ERR
50		ERR		ERR
75		ERR		ERR
100		ERR		ERR
125		ERR		ERR
150		ERR		ERR
175		ERR		ERR
200		ERR		ERR
250		ERR		ERR
300		ERR		ERR
350		ERR		ERR
400		ERR		ERR
450		ERR		ERR
500		ERR		ERR
550		ERR		ERR
600		ERR		ERR
700		ERR		ERR
800		ERR		ERR
900		ERR		ERR
1000		ERR		ERR

PAGE 1

F1	F2	A term	B term
ERR	ERR	ERR	ERR
ERR	ERR	ERR	ERR

PAGE 2

C term	D term	HETP	Theor. Plates
ERR	ERR	ERR	ERR
ERR	ERR	ERR	ERR

PAGE 3

Column Pressure	Resolution	Holdup
ERR	ERR	ERR
ERR	ERR	ERR

```
\i        {for loops,1,2,1,increment}                    1


 /rvp in estimates~p in estimates~
 {goto}utest~{for counter,1,20,1,increment Pin}{calc}
 {if changes>0}{restart}{let changes,0}{branch \j}
 {branch return cell}

Counter         21

increment pin
/rv~test condition~
{if test condition<0.98}{branch increase Pin}
{if test condition>1.02}{branch decrease Pin}
{down}

increase {left 6}{edit}/@sqrt($test   STEP INCREMENT
   condition)~/rv~~{right 6}
{down}{let changes,1}

decrease {left 6}{edit}/@sqrt($test      STEP DECREMENT
   condition)~/rv~~{right 6}
{down}{let changes,1}


changes          0


counter2        21
rounding {edit}{home}@round({end},0)~{down}
```

```
\g      {calc}                          TURN OFF SCREEN
        {windowsoff}
        /cmaximum k~current k~          SET k VALUE
        {calc}
        {branch pcalc}                  GoTo Pressure calc.

        {goto}p in estimates~           Goto pressure and
                                         round off

        {for count,1,20,1,rounding}     Step through k
        {LET CURRENT K,frST K}          values and run
        {calc}                          the calculations
        /rvcurrent heetp~a range~
        {calc}
        {LET CURRENT K,SECOND K}
        {calc}
        /rvcurrent heetp~b range~
        {calc}
        {LET CURRENT K,THIRD K}
        {calc}
        /rvcurrent heetp~c range~
        {calc}
        {LET CURRENT K,FOURTH K}
        {calc}
        /rvcurrent heetp~d range~
        {calc}
        {LET CURRENT K,FIFTH K}
        {calc}
        /rvcurrent heetp~e range~
        {calc}
        {LET CURRENT K,SIXTH K}
        {calc}
```

DRAW GRAPHS:

\z	/rvcurrent heetp~f range~ {calc} {goto}ep21~ {windowson}/gvq{goto}z1~{goto}A28~/got	Draw the graph

APPENDIX B

SAMPLE CALCULATION FOR ESTIMATION OF INJECTION BAND WIDTHS

Injection band widths produced by the splitter and cold trap systems were estimated based on measurement of final peak widths produced under known conditions. In order to simplify the calculations, the column was replaced with a 25 cm long section of 0.2 mm i.d deactivated, uncoated, fused silica capillary tubing. This reduces the partition coefficient to zero and eliminates band spreading due to resistance to mass transfer in the stationary phase and greatly simplifies the calculation of initial band width. The calculations are also simplified by the small pressure drop produced with the short transfer line. Under these conditions, the two pressure correction factors have little effect and can be ignored.

Calculations were based on the modified Golay-Giddings equation:

$$H = \frac{A}{U} + (C_g * U) + (C_l * U) + (D * U^2)$$

Where the A, C_g, C_l and D terms are defined as:

$$A = 2DgF_1F_2$$

$$C_g = \frac{(11k^2 + 6k + 1)\, d_c^2}{96(1 + k)^2\, D_g} * \frac{F_1}{F_2}$$

$$C_l = \frac{2kd_f^2}{3(1 + k)^2\, D_l}$$

$$D = \frac{t^2}{(1 + k)^2 L}$$

Under the conditions discussed above, the C_l term and the two pressure corrections, F_1 and F_2, can be eliminated and the remaining terms can be simplified. The simplified forms used in these calculations are:

$$C_g = \frac{d_c^2}{96Dg}$$

$$D = \frac{t^2}{L}$$

The "A" and "D" terms are unaffected and the full equation becomes:

$$H = \frac{2D_g}{U} + \frac{d_c^2 U}{96 D_g} + \frac{t^2 U^2}{L}$$

All variables except "t" are known or can be calculated. For the calculations shown here, D_g was calculated by the method of Fuller, Schettler and Giddings, which is presented in Perry's Chemical Engineer's Handbook. A value of 0.63 cm^2/s was calculated for hexane at an oven temperature of 170 ^oC. The average linear velocity was calculated at 886 cm/s from the volumetric flow of rate 10 ml/min.

In order to calculate H, the width of the peak was measured at the base. This value was converted from seconds to centimeters using the average linear velocity of 886 cm/s. This value was divided by 4 and then squared to calculate the variance. Since "H" can be defined as the peak variance per unit length, the value of "H" was determined as the variance divided by 25. Filling in the values presented here, the "A" and "C_g" terms are found to be insignificant and the final equation becomes:

$$\frac{(W_b * 0.25 * 886)^2}{25} = 31,400 * t^2$$

A typical peak width for the splitter operated at very high split ratio would be about 100 ms or 0.1s. If this value is filled in for W_b, the value of t is calculated to be about 25 ms. Since other extra-column factors are believed to be very small, the calculated value of "t" was interpreted as the initial band width produced by the injection system.

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