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ABSTRACT

Development of a Thermal Modulator for On-Line Monitoring Volatile Organic Compounds

**by
Yun Chen**

A thermal desorption modulator is made from a short segment of thin tubing containing an adsorbent or a chromatographic stationary phase. A carrier gas containing the analyte is introduced into the analytical column through the modulator which acts as a sample trap. Rapid electrical heating of the modulator releases a "concentration pulse" of the analyte and this serves as an injection similar to that from an injection valve. The modulator also acts as a sample preconcentrator and can be used to make repetitive injections every few seconds. In this research, the mechanism of thermal desorption modulator was studied and was used in continuously monitoring volatile organic pollutants.

**A THERMAL
DESORPTION MODULATOR FOR
CONTINUOUS MONITORING OF VOLATILE ORGANIC COMPOUNDS**

by
Yun Chen

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Submitted to the Faculty of
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APPROVAL PAGE

**A Thermal
Desorption Modulator for
Continuous Monitoring of Volatile Organic Compounds**

by
Yun Chen

Dr. Somenath Mitra, Thesis Adviser
Assistant Professor of Chemical Engineering,
Chemistry, and Environmental Science, NJIT

Dr. Barbara B. Kezbekus, Committee Member
Professor of Chemistry, Associate Chairperson
of the Department of Chemical Engineering,
Chemistry, and Environmental Science, NJIT

Dr. Leonard Dauerman, Committee Member
Associate Professor of Chemical Engineering,
Chemistry, and Environmental Science, NJIT

BIOGRAPHICAL SKETCH

Author: Yun Chen

Degree: Master of Science in Environmental Science

Date: January, 1993

Undergraduate and Graduate Education:

- Master of Science in Environmental Science, New Jersey Institute of Technology, Newark, NJ, 1992
- Bachelor of Science in Medicine, Fujian Medical College, Fuzhou, Fujian, P. R. China, 1984

Major: Environmental Science

Position Held:

Research Assistant 5/91 -8/92

Department of Chemistry, Chemical Engineering, and Environment Science,
New Jersey Institute of Technology, Newark, New Jersey

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CHAPTER 1

INTRODUCTION

1.1 Background

In order to achieve higher productivity, lower environmental emissions and waste reduction, a subdiscipline of analytical chemistry - process analytical chemistry (PAC) has emerged. The goal of PAC is to continuously provide quantitative and qualitative information about a chemical process. Such information is also important in monitoring environmental emissions, and meeting regulatory requirements (1).

In a traditional industrial environment, samples are taken from a process or waste stream, and transported to a central laboratory for analysis. On the contrary, PAC analyzers are located in or right next to the process. They attempt real-time (or near real-time) chemical analysis. Analytical results are critical for monitoring and regulating environmental emission as well. In traditional methods, analysis is done hours, or often days after a sample is collected. PAC analyzers are designed to eliminate the delay between sampling and analysis. Usually, PAC involves two critical steps: (1) the measurement of process parameters and (2) the conversion of the measurement data to process information. This information is then used to document, correct, and improve process performance. In general, PAC provides higher quality information very rapidly about what is going in the process or what kind of pollutants are being released on a continuous basis.

A variety of analytical instruments are used in PAC, including spectroscopic and chromatographic techniques. Among spectroscopic instruments, process infra-red spectrophotometers have found wide applicability. Previous IR analyzers were nondispersive, dual-cell correlation devices with microphone detectors. Recently, the Fourier transform infrared (FT-IR) has been modified to serve as continuous on-line analyzer. Commercial manufactures have begun to offer instruments designed

specifically for on-line process analysis. Another trend that has enhanced the on-line use of FT-IR is the development of improved methods for continuous sampling (2). In addition, the use of FT-IR has become more attractive with the advent of personal computers that allow near real-time data analysis. Although, the process is highly sensitive and selective, still, it does not generate information rapidly enough for feedback control.

In the ultraviolet-visible (UV-vis) area, technological developments have made scanning versions of these instruments far more rugged and reliable. Three key developments are the adaptation of single-beam techniques are the use stored baselines rather than mechanically switching between reference and sample compartments; the use of concave holographic grating that yield acceptable stray light rejection in a single monochromator and eliminate the need for collimating mirrors; and the introduction of photodiode array that eliminate mechanical scanning of the grating (2). The current generation of UV-vis spectrometers based on these principles are quite cost-effective and reliable. These advancement in UV-vis has made it possible to be used in continuous on-line analysis.

Mass spectrometers (MS) are also becoming more widely used instruments in continuous on-line analysis (3). For instance, applications for mass spectrometers include: ratio control for production of ethylene oxide, ammonia or methanol; material-balance control in various processes; distillation column optimizations; monitoring of trace impurities in chemicals, industrial gases, and semiconductor products; atmospheric monitoring in nuclear plants. The nature of mass spectrometry makes it possible to provide a definitive analysis very fast.

Also, photometers can be applied for continuous on-line analysis such as measurement of chlorine or fluorine in air, phenol in water, and NO_x and SO₂ in fluegas. The instrument compares the intensities at the two wavelengths, and from this calculates the concentration of the specific chemical.

On the other hand, although the liquid chromatographs (LCs) are not as popular as GC, they are useful in the analysis of high-boiling point compound polymers. The examples are the measure of styrenes, nitrated aromatic, organic acids etc. The stationary phase may be an adsorbent packing, a gel, an ion-exchange resin, or another liquid. IR, UV and MS can be used as detectors.

1.2 Continuous Monitoring of VOCs

It is well known that volatile organic compounds (VOCs) such as aromatic and halogenated organics are toxic, mutagenic, and carcinogenic. Therefore, in recent days, much efforts have been made to sample and analyze trace levels of these compounds (part per billion to parts per million). Sampling and analysis of VOCs in air are done either using whole air samplers or sorbent tubes. In the whole air sampling devices, such as tedlar bags and canisters (EPA method T014), a couple of liters of the sample are collected and then brought back to the lab for analysis. In the sorbent based method, (EPA method T01, EPA method 5) the sample is passed through a cartridge containing of one or more adsorbents, where the VOCs are trapped. The VOCs are recovered by thermal desorption or solvent extraction for analysis.

The above mentioned methods are effective in VOCs measurement, but can not be used in continuous on-line analysis. Although micro-sensor technology has provided some possibilities for real-time monitoring, specific sensors are not available to identify and quantitate the wide range of compounds. One has to rely on chromatographic separation techniques because compound specific sensors to analyze the wide range of VOCs are unavailable. Recently, automated GC systems have been designed for air analysis and semi-continuous basis. However, in all these devices the sample should flow through a sorbent tube for a period of time and then the sorbent tube is thermally desorbed for GC analysis (4)(5). Usually, a cycle time of several hours is encountered.

Continuous on-line GC analysis is important to make injection automatically and repeatedly. In chemical industries, sample valves have been used in process gas chromatography where injections from a sample stream can be made intermittently onto a GC column. Sample valves withdraw just a small amount of sample from the sample stream for GC injection, usually between a few microliters to a couple of milliliters. The sensitivity is low because a small injection results in a small detector signal. Excessive band broad and poor chromatographic resolution occurs if larger sample quantity is injected. Therefore, in environmental monitoring, it is difficult to analyze the low VOCs concentrations. In order to develop effective continuous monitoring device, we not only need an automated injection device, but also a sample preconcentrator.

CHAPTER 2

RESEARCH OBJECTIVE

The object of this research is to develop a gas chromatography system for continuous monitoring of volatile organic compounds(VOCs). The system need to be able to monitor trace concentration levels commonly encountered in air samples. In this research a thermal desorption modulator will be used as an injection devices. The modulator will also be used as a sample concentrator and its characteristic will be investigated.

CHAPTER 3

LITERATURE REVIEW

In conventional chromatography a sample is injected once for analysis, however, in some applications it is necessary to make many repetitive injections (6). A typical example is in process gas chromatography where injections are made intermittently to analyze a process stream. Other applications include pyrolysis GC and correlation (or multiplex) chromatography. Sample valves have been used exclusively in these application, because they can be automated to make repetitive injections. Recently thermal desorption modulators have emerged as an alternate injection device and a few papers have been published in this field.

A modulator is made from a short length of thin tubing containing an adsorbent or a chromatographic stationary phase. A short segment of a fused silica capillary column can also be made into a modulator by coating it externally with an electrically conductive paint. The construction of a fused silica modulator is shown in Figure 1. Modulator is designed in such way that it can be heated and cooled rapidly by a sharp pulse of electric current either through the walls of metallic tubing or through a coat of electrical paint. The carrier gas containing the sample can be introduced into column through the modulator. This is shown in Figure 2. As the stream containing the sample flows into the modulator, the sample components are adsorbed onto the stationary phase. When the electric current is switched on, the adsorbed components are released as a "concentration pulse" which act as injection or modulation. The column and the detector treats the "concentration pulse" just like an injection from an injection port or a valve and a chromatogram can be obtained corresponding to the modulation. The modulator is somewhat similar to an adsorbent or a cryogenic trap (7) used in various chromatography applications. While a modulation makes a series of injections (or modulations), a conventional cryogenic/sorbent trap normally preconcentrates a sample

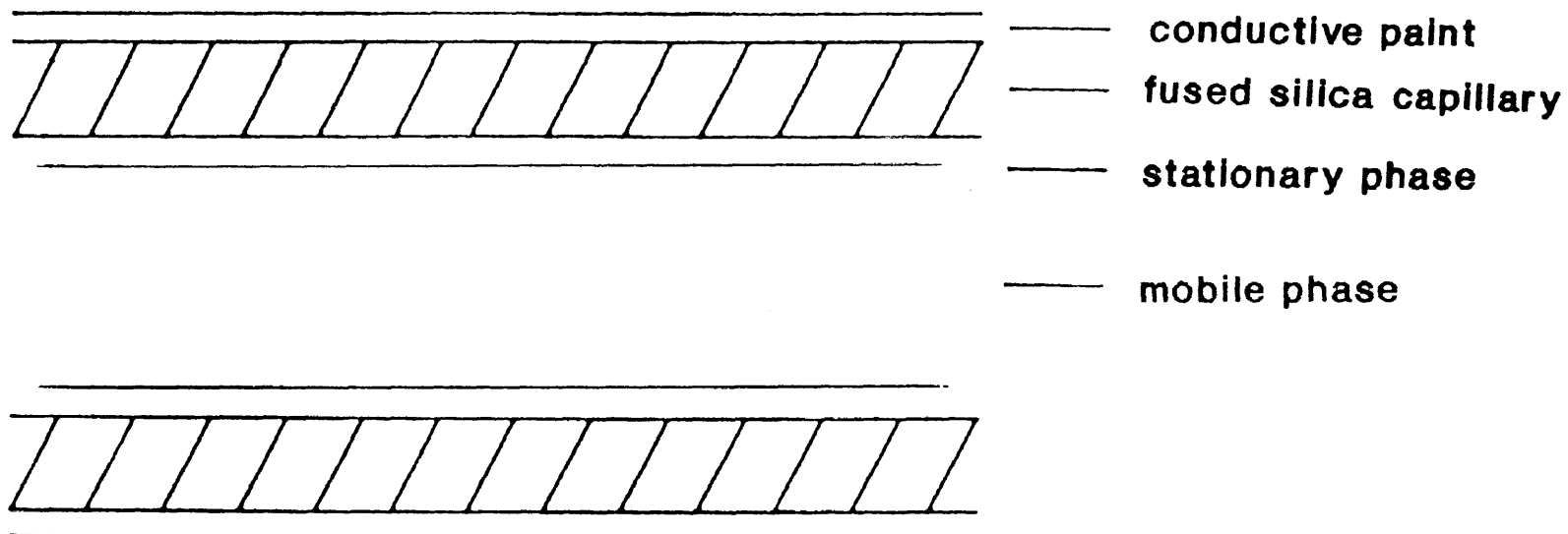


Figure 1. Construction of fused silica modulator.

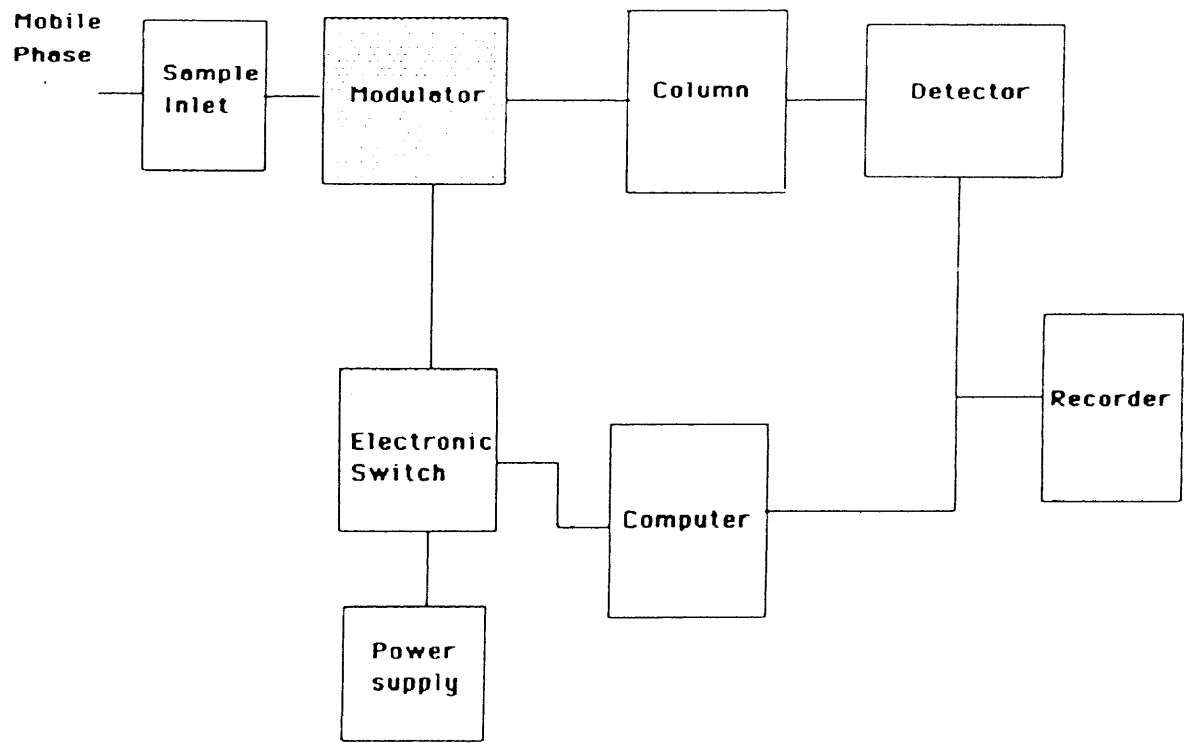


Figure 2. Schematic diagram of the modulation system

or sharpens an injection. However, a modulator needs to trap only a part of the sample flowing through it to make an injection (8). By modulating the temperature of the modulator, its capacity factor is modulated, which in turn modulates the concentration of the sample flowing through it. The modulator is operated by a computer or an electronic switch. The duration of electrical heating as well as the interval between modulation are controlled. It is important that each modulation drives out all the sample from the modulator and no sample should be accumulated within it. So enough energy should be supplied to the modulator to desorb all the sample. The time for which the modulator is heated (pulse duration) along with the current through the modulator controls the energy input.

3.1 Mechanism of Thermal Desorption Modulator

The mechanism of a modulator has been published by Mitra and Phillips (9). The modulator may be conceptualized as a short GC column. So, the velocity v , at which a sample migrates through a modulator is given by:

$$v = u / k + 1 \quad (3.1)$$

where u is the mobile phase velocity, k is capacity factor. The capacity factor is defined as the ratio of the number of sample molecules in the stationary phase to that in the mobile phase (9). A typical modulation has a positive part and a negative part (10). A positive peak is due to the desorption of sample when modulator is heated. A negative peak results from the reabsorption when modulator is cool. When the modulator is hot, the capacity factor is close to zero and sample migrates at the speed of mobile phase. So, the time required to produce the positive part is t_+ :

$$t_+ = b / u \quad (3.2)$$

where b is the length of the modulator. The negative part is generated when the modulator is cold and the capacity factor is greater than zero. So the sample migrates slowly and the time required to produce the negative part t_- is:

$$t_- = (k + 1) b / u \quad (3.3)$$

It is evident from Equation 3.3 that t_- is larger than t_+ . From Equation 3.2 and Equation 3.3, the ratio of the peak height of the negative part to that of the positive part is given as follows:

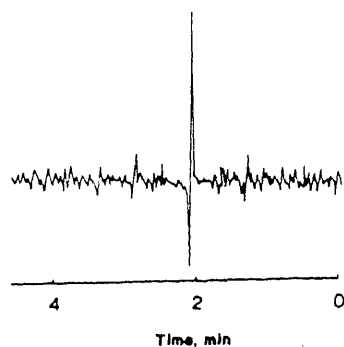
$$h_- / h_+ = 1 / k + 1 \quad (3.4)$$

where h_- and h_+ are the height of the negative and the positive peak. From the Equation 3.4, it is seen that as the capacity factor of the modulator increases, the ratio of the height of the negative part to that positive part decreases. The effect of capacity factor on peak shape is presented in Figure 3(a-c). It is seen that with increases in capacity factor, the negative part become relatively shallower and eventually merges with the base line. At this point, the peak shape resembles that of a normal chromatogram.

The rate of sample migration (Equation 3.1) is inversely proportional to $(k+1)$ of the sample in the modulator. So the sample residence time increases with capacity factor and the modulator traps sample for a larger period of time t_- . Consequently, larger the t_- larger is the amount of sample that can be accumulated in the modulator, and the larger is the signal obtained at the detector from each modulation .

The modulator is designed to make an injection at a certain interval. The modulation efficiency is defined as the ratio of modulated sample to total sample passing through it (9). Let t_i be the time interval between two injections. A previous paper by Liu and Phillip (11) predicted modulation efficiency as follows. If $t_i > t_-$ the modulation efficiency was expressed as:

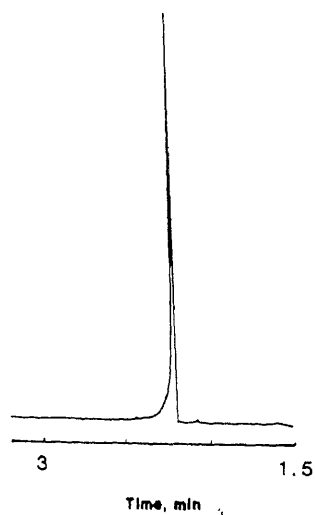
$$M = (t_i - t_h) / t_i \quad (3.6)$$



(a). capacity factor = 5, Iso-butanol was used at a modulator temperature of 80°C



(b). capacity factor = 500, Octane was used at a modulator temperature of -2°C



(c). capacity factor = 11400, Isobutyl alcohol was used at modulator temp. of -6°C

Figure 3. Response of Supelcowax modulator at different capacity factor

where t_h is the time period during which the modulator is too hot to retain the sample. Minimizing the heating time such that $t_h = t_+$ and substituting Equation 3.2 into Equation 3.6, the Equation 3.6 was rewritten as follows:

$$M = (t_i u - b) / t_i u \quad (3.7)$$

thus in this region modulation efficiency is independent of capacity factor, although t_+ did depend upon capacity factor. When $t_i = t_+$, the modulation efficiency was expressed as follows:

$$M = (t_- - t_h) / t_- \quad (3.8)$$

If $t_h = t_+$, by substituting Equation 3.2 and Equation 3.3 into Equation 3.8:

$$M = k / 1 + k \quad (3.9)$$

in this case, the modulation efficiency increases with capacity factor.

When $t_i > t_+$, the modulation efficiency can be expressed as:

$$M = (t_- - t_h) / t_i \quad (3.10)$$

Let $t_h = t_+$, and by substituting Equation 3.2 and Equation 3.3 into Equation 3.10, then

$$M = k b / t_i u \quad (3.11)$$

Here, the modulation efficiency is inversely proportional to the time interval between electric pulses. The modulator should be designed for the highest modulation efficiency. The situation described in Equation 3.11 should be avoided (11).

3.2 Other Types of Modulators

Thermal desorption modulators do not work in HPLC because the retention depends upon the strength of the mobile phase. However, TDM developed for Supercritical Fluid Chromatography(SFC) are quite interesting (12). Compared to GC, the mechanism of supercritical fluid modulator is more complicated. In SFC, the capacity factor varies with pressure (or density) and temperature (12-15). Retention in SFC is expressed as (14):

$$\log k = - 0.43 H_s / R T - \log B + 0.43 H_m / R T \quad (3.12)$$

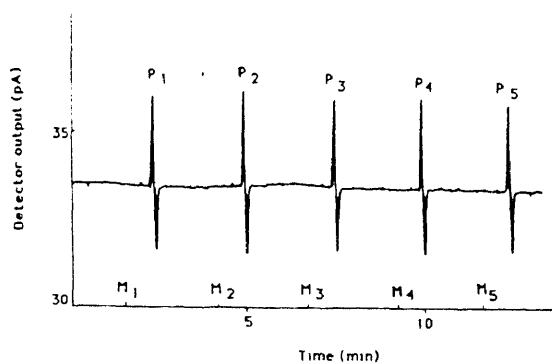
where k is the capacity factor, H_s and H_m are the heats of solution of the solute in the stationary and mobile phase respectively, T is the absolute temperature, B is the ratio of the volume of mobile phase to the volume of the stationary phase, and R is the universal gas constant. For a nonswelling stationary phase, H_s remains constant with temperature and H_m is directly proportional to density at a given temperature.

At higher temperature and constant pressure, retention in SFC is similar to GC, i.e., when the temperature increases the capacity factor decreases. The first two term of Equation 3.12 play an important part in this GC-like behavior. On the other hand, at lower temperatures, retention in SFC is similar to LC, i.e., the capacity factor decreases with the increase of the solvent strength. Since increasing the temperature, decreases the density, the solvent strength decreases and the capacity factor increases. Last term in Equation 3.12 contribute toward this LC-like behavior.

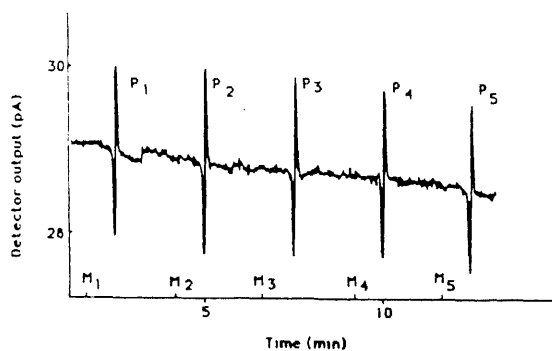
The GC-like and LC-like behavior is reflected in the modulator operation and are demonstrated in Figure 4(a-c). At 150°C (Figure 4a), the response of the SFC modulator is similar to that of a GC, i.e., as the modulator is heated, the capacity factor drops to zero and the sample desorbs to produce a positive peak. As the modulator current is turned off, the capacity factor increases, the sample readsorbs onto the stationary phase and a negative peak is obtained.

At low temperature ($t < 108^\circ\text{C}$), the opposite phenomena is observed. As the modulator is heated, the density of the supercritical phase drops and the solvent strength decreases. As a result, the capacity factor increases, the analytes transfer to the stationary phase and a negative peak is seen at the detector. When the modulator cools down, the density of mobile phase increases, so that the analytes retransfer to the mobile phase, this is seen as a positive peak at the detector. A modulation peak in this region resembles Figure 4b.

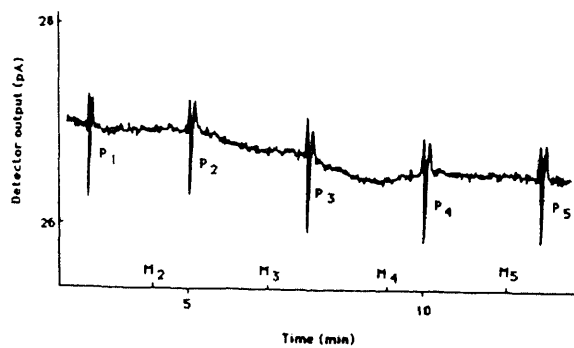
Figure 4c shown the peak shape in the region where there is a transition from the LC-like to GC-like behavior. In this example, temperature is between 105 and 110°C.



(a). modulator and column at 150°C.



(b). modulator and column at 75°C.



(c). modulator and column at 108°C

Figure 4. Response of SFC modulator at different temperature. five consecutive modulations were made at intervals of 2.5 min., M_x ($x=1-5$) represents the modulations and P_x ($x=1-5$) represents the corresponding peaks.

A small peak first resulted from thermal desorption. This was followed by a large negative peak with contributions from both sample readsorption and sample transfer to the stationary phase due to the increased capacity factor. The area of the negative peak also roughly equalled that of the positive peak. The peak shape here is a combination of Figure 4a and 4b.

Some other types of modulators have also been reported. A photochemical modulator that can modulate photochemically reactive components in a sample stream has been reported (16). Photochemical mechanisms include photodesorption, photodecomposition, photochemical reactions of the sample. A source of visible light causes photochemical reaction to occur within the modulator. Yet other modulators depend upon the chemical properties of both the samples passing through and the modulator packing. A thermal decomposition modulator (17) operates like a TDM, except by modulating the temperature of the modulator a thermally labile substance is decomposed and this is seen as a vacancy (or a negative peak) at the detector. A chemical modulator that selectively modulates methanol in a stream of hydrocarbons also has been developed (18). An Electrochemical modulators (19) that modulate the potential of an electrochemical cell placed at the head of a LC column have been developed for electroactive compounds. In general, the purpose of some of the specific modulators is to remove the required sample signal from other signals present in the sample.

3.3 Application of Thermal Desorption Modulators

3.3.1 Thermal Desorption Modulator as an Injection Device

A properly designed thermal desorption modulator acts as an excellent injection device. It can make reproducible injections, it is rugged and it exhibits long term stability (10). It has several advantages over a valve. Unlike an injection valve, it acts as a sample preconcentrator, thus much lower detection limits are obtained using modulators than

valves. Moreover, there is no dead volume or moving parts in a modulator, so precision and fast response time are obtained.

3.3.2 Using of Modulators in On-Line Analysis

Most on-line GC techniques adopt intermittent sampling using a sample valve to make injections into the GC (21). A thermal desorption modulation can be used in process gas chromatography instead of a sample valve (20,22). The equivalent of an injection is made internally by modulating the temperature of the modulator. Modulators can be used for sample introduction into a GC from a process stream and can provide unattended GC operation. This method has the potential advantage over sample valves in term of faster operation, smaller band width and lower detection limit.

An on-line analysis technique using TDM (thermal desorption modulation) has been reported for monitoring H_2S produced in a hydrodesulfurization reaction (20). In a typical experiment, a few milligrams of a organo-sulfur compound was hydrodesulfurized by linearly increasing the temperature of the reactor. The evolving H_2S was analyzed using the modulator and a GC with thermal conductivity detector. A typical profile of H_2S evolution from a hydrodesulfurization reaction is given in Figure 5. In this case, the modulations were made at a regular intervals and corresponding to each modulation, H_2S peak was seen at the detector. The peak area was directly proportional to the average concentration of H_2S in the reactor effluent stream. It can be seen that first sign of H_2S was seen at 488K. As the temperature increased, the rate of H_2S evolution increased due to the increase in reaction rate. H_5 is maximum peak after which the rate of H_2S evolution began to decrease as the sample in the reactor was consumed. The modulator in this case was made from a 0.2 mm I.D. tubing with chromosorb stationary phase.

The reproducibility of the modulator was evaluated using a standard containing 100 ppm H_2S in He. For 20 modulations, the relative standard deviation was less than

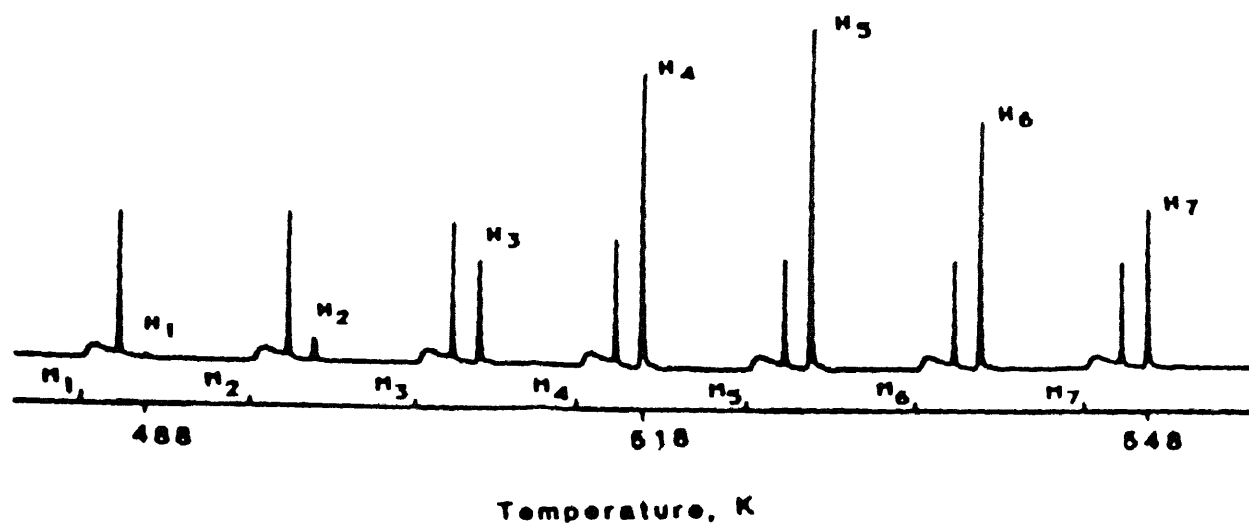


Figure 5. H₂S evolution profile from the hydrodesulfurization. M_x (x=1-7) represent the modulations and H_x (x=1-7) are the resulting H₂S peak.

+1%. The peaks which resulted from these pulses were identical in duration and peak shape.

3.3.3 Application in Fast Chromatography

Gas chromatography is probably the fastest known separation method. Nevertheless, a single GC separation normally requires several minutes or more, the cycle time for a multipoint sample may easily exceed an hour. This type of apparatus is not suitable for applications where real time, or near real-time monitoring is required.

If the gas 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 theory was first demonstrated by Desty (23), who in 1965, showed that it was possible to separate 15 components in 2 sec. Since Desty's initial work, several publications have discussed both the theoretical and practical aspects of fast gas chromatography (24-30).

The theoretical potential of capillary column for high-speed analysis is well known. Separation efficiency and speed of analysis can be significantly improved by decreasing the capillary column diameter (31,32). Generally speaking, the height equivalent to a theoretical plate (HETP) is directly proportional to the column diameter. Thus, the required number of plates can be achieved by using a shorter column and consequently number of plates per second. This in turn can significantly reduce analysis time (33,34).

The major barrier preventing application of high-speed techniques has been a lack of a suitable injection technique. For fast GC to be successful, the peak widths must be kept as narrow as possible. In particular, extra-column band broadening caused by 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 GC, peak widths usually are measured in seconds or tens of seconds. In fast GC, peaks

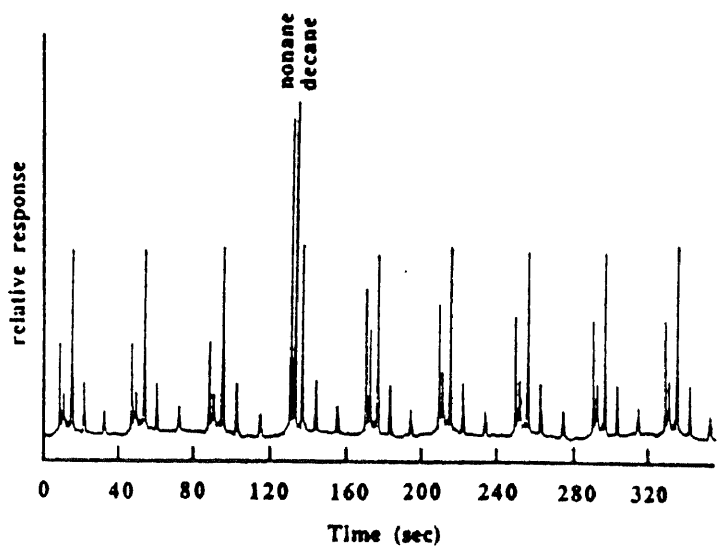
are much narrower, often 50 msec or less. In order to produce a final peak this narrow, the initial band width produced by the inlet should be no more than about 20 msec (35).

Conventional GC inlets that use a syringe for injection and a splitter typically produce initial band width of 50 to 100 msec, and are clearly inadequate for high-speed separation. Gas injection systems, using a rotary valve and sample loop, are likely to produce even wider injection bands, often measuring 1 to 10 sec. and more. However, A decrease in the column diameter from 250 μm to 50 μm requires that the injection volume be reduced by more than two orders of magnitude and the input band should be of the order of a few milliseconds for narrow-bore column(100 μm -5 μm) application. The requirements of very small injection (nanoliter to picoliter) and sharp input band are difficult to meet for most conventional injection devices and often result in sample loss and poor reproducibility.

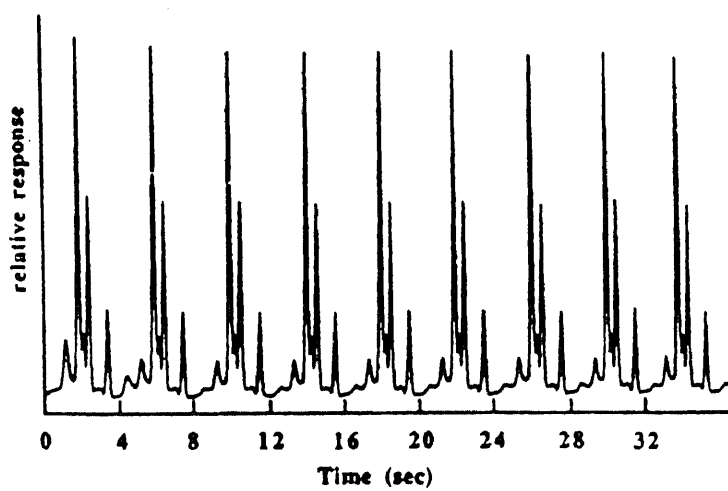
On-column thermal desorption modulator has been used as a sample introduction device for narrow-bore, high-speed gas chromatography (11,36-38). The modulator is an integral part of the column so that the generated concentration pulse are compatible with the column diameter. By using on-column thermal desorption modulator and narrow-bore column, the chromatograms have been generated in a few seconds.

Figure 6(a) shows a series of chromatograms monitoring a simulated process stream subjected to a sudden disturbance. The five hydrocarbons are separated within 30s. A 40-sec repetition period is usually appropriate. The first three chromatograms in Figure 6(a) are identical because the stream was not disturbed by any external causes during that time period of time. After the elution of the third chromatogram, nonane and decane were introduced to the stream through the injection port. The concentration changes for these two components were immediately noticeable after their introduction [chromatogram 4 in figure 6(a)].

Figure 6(b) shows a series of high-speed chromatograms monitoring a simulated process stream. Five components are monitored with a repetition period of 4s. A 1.00m



(a). modulator response when an additional sample was introduced into a steady stream



(b) modulator response to a steady stream

Figure 6. High speed chromatogram

long and 50 μm i.d. column which had a separating power of a 5m and 0.25 mm i.d. column was used in the analysis.

Using thermal modulation for sample introduction allows a smaller diameter column to be used in process stream analysis. Smaller diameter columns are shorter and faster than larger diameter columns resulting in higher speed and resolution.

3.3.4 Application in Correlation or Multi-input Chromatography

In conventional chromatography, sample is injected into the head of column in the GC (same as HPLC or SFC) column and the different sample compounds separate as they migrate down the column. To prevent overloading of the stationary phase and to obtain good resolution only a small volume (few microliters to 2 ml) is usually injected. A large amount of analyte is wasted when it is present in a large volume of gas or liquid. e.g. only .02% of the sample is actually used when 1 μl is injected from a 5 ml solution of the analyte. The signal generated is proportional to the amount of analyte that passes through detector. Therefore, a loss of sample is equivalent to decrease in signal to noise (S/N) ratio and this would lead to poor sensitivity.

Multi-input chromatography is a variation of conventional chromatography (9,10,39-42). Limited work has been published on MIC and it is referred to as correlation chromatography (39-42) or multiplex chromatography (9,10). Unlike conventional chromatography, here, a series of injection are made into the column in rapid succession. Corresponding to each injection, a chromatogram is obtained. The peaks from different chromatograms overlap at the detector such that the detector output cannot be directly interpreted. However, using mathematical techniques such as Cross-Correlation or Fourier Transform the chromatogram can be elucidated from the detector output.

The difference between conventional chromatography and MIC is similar to that between scanning IR and FTIR. The convoluted detector output in multiplex

chromatography is analogous to the time domain spectra (or interferogram) in FTIR from which the IR spectrum is computed. Analogously, in MIC the chromatogram is recovered from the convoluted output.

The advantage of MIC is to increase signal to noise ratio. Since injections are made so frequently, sample passes through the detector almost continuously. As a result, quantity of sample that passed through the detector per unit time is much larger than in conventional chromatography. This is equivalent to a higher sample throughput, which results in a higher signal to noise ratio(S/N).

Sample valves have been used for making injection in the past. Modulators have proven to be excellent injection devices for multiplex chromatography. They are much faster than valves and exhibit lower sensitivity.

3.3.5 Application in Multidimensional Chromatography

Separation capability of a chromatographic system increases when two columns of different characteristic placed in series. This is known as two-dimensional gas chromatography. Coupled columns can either have different polarities in stationary phases or work at different temperatures. Usually, only required parts of eluent leaving the first column are transferred into the second column. The first column just provides with a rough separation, while the second column provides samples with major separation. It has been proved that this heart cutting technique has some limitation in applications where the analysis of the entire sample is required.

Recently, a different and significant more powerful technique, i.e., a comprehensive two-dimensional gas chromatography technique, has been developed for making the second column fast enough to produce at least one complete chromatography each signal peak elutes from the first column. The key point of this technique is that a high-speed separation in the second dimension is needed. As mentioned before, the on-line thermal desorption modulator is a simple and excellent

injection device for high-speed gas chromatography. Liu et al. (43) have used a thermal desorption modulator to inject the eluent from the first column onto the second one. In this case the two columns have different stationary phases. The components that cannot be separated on the first column can be separated on the second column. An example of a two dimensional chromatogram is presented in Figure 7. Figure 7 shows a contour plot of 14 component mixture separated with the two dimensional gas chromatography. The vertical axis is retention time on the first column and the horizontal axis is retention time on the secondary column. The pair of substances, p-xylene and cyclohexyl chloride, provide a clear example of improved resolution due to two-dimensional operation. These two components of the sample have identical retention on the first column ($t_R=89s$), but are almost base-line separated on the second column. On the second column, nonane, cyclohexyl chloride, o-xylene, and styrene overlap significantly but are separated on the first column before entering the second.

Over the entire first column elution time of 154 seconds, 77 chromatograms were generated from the second column. Many more peaks can fit into this chromatogram than could be fit into a one-dimensional chromatogram generated on either column individually. The measured peak capacity was 15.3 for the first column and 15.2 for the second column. The theoretical two-dimensional peak capacity in Figure 7 is thus 233, the product of peak capacities on the two dimensions.

These results shows that speed two dimensional gas chromatography closely resembles GC/MS. This method has many advantage, such as high speed, high power to separate complex mixtures, and more reliable identification of substances through two independent retention time. With the application of a thermal desorption modulator the experiments could be done in an automated manner.

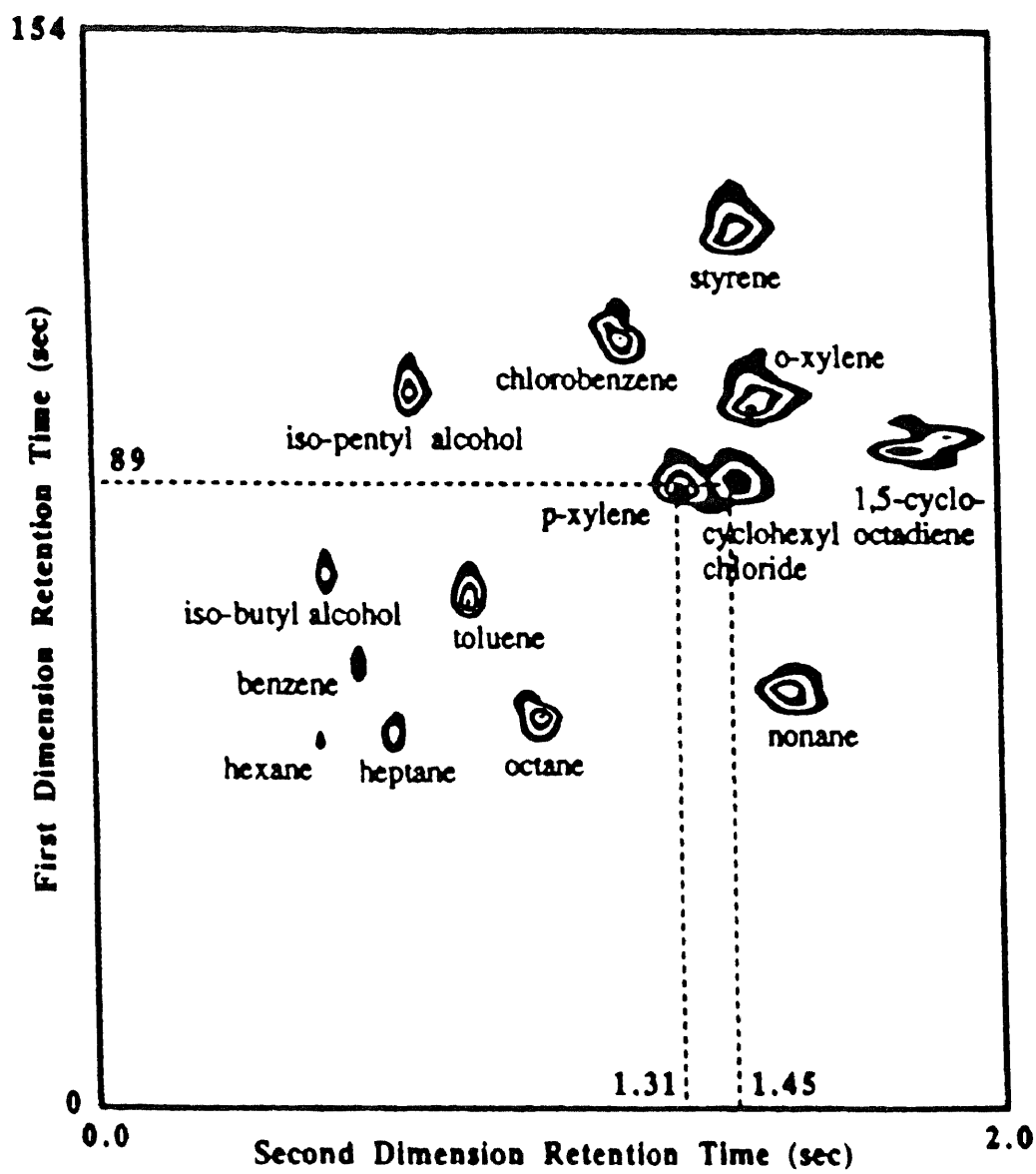


Figure 7. The two dimensional gas chromatogram.

CHAPTER 4

EXPERIMENTAL

4.1 Instruments

The experimental system used is shown in Figure 8. The VOCs stream was generated by entraining the analytes from a diffusion tube onto a flow of nitrogen. A Hewlett - Packard 5890 series 2 gas chromatography equipped with an FID was used in this study. Typical flowrates for FID were: air 400 ml/min, hydrogen 30 ml/min and nitrogen make up gas 25 ml/min. the detector temperature was 250°C. The carrier gas was nitrogen. A 0.53 mm i.d. and 30m long fused silica column from J & W scientific with a 3.0 µm thick stationary phase (Duraboned-624) was used in these experiments. In same experiments, a spit / splitless injection port was also used. The split ratio was 100 to 1 and injection port temperature was 250°C.

Modulators were made with fused silica as well as stainless steel tube. The stainless steel modulator were made from a short length of thin stainless steel tube (23 gauge, 0.33 mm i.d., from Hamilton Inc., Reno, NV) containing an absorbent e.g. Carbotrap C, Chromosorb 100/120, Carboseive 3, Chromosorb 60/80 (purchased from Supelco Inc.). Length of stainless steel modulator was 13 cm. The other type of modulator was constructed from a pieces of 0.53 I.D. deactivated fused silica capillary tubing using one of the above an absorbents. The external conductive layer in the fused silica modulator was made by painting with an electrically conductive paint (Loctite Corporation). A stable conductive layer was obtained by applying multiple layers of the paint on the modulator and drying it with a heat gun after each application. The electrical resistance of the modulator was between 1-3 ohm. Length of fused silica modulator was 6-6.5 cm. To make electrical contact, two pieces of wire tightly wrapped at the end points of the modulator. The construction of fused silica modulator is shown in Figure 1. This modulator was heated by passing current through the

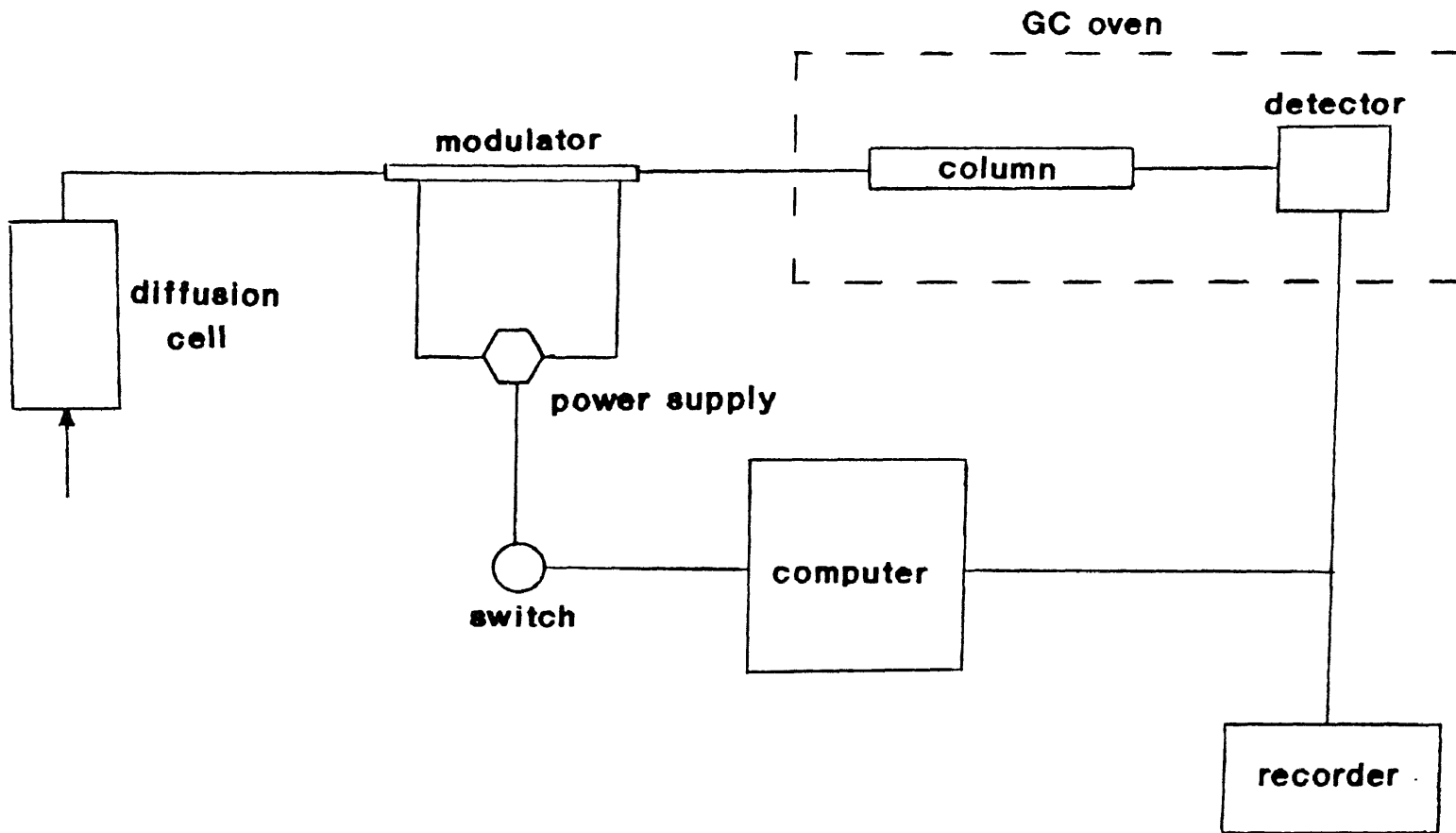


Figure 8. Schematic diagram of the experiment system.

electrical paint. The stainless steel modulators were heated by passing current directly through the wall of the tubing. The thin walled, small diameter tubes have low thermal mass and can be heated and cooled very rapidly.

The modulation efficiency and t_r of the modulator depended upon the temperature of the modulator. The modulator was cooled to sub-zero temperature to attain higher modulation efficiency and t_r . For low temperature operation, the modulator was placed on the oven and connected to detector using deactivated fused silica. Modulator was cooled to the required temperature using cryogenic coolant hardware for operation with liquid nitrogen. Extra care was taken to make sure that there was no unheated portion of the modulator with stationary phase inside.

A Variac was used as the power supply, and two 10 ohm parallelly connected power resistors were placed in series with the modulator to control the current through it. A microprocessor controlled electronic switch (built in-house) that could turn on the modulator current at a prespecified intervals for a fixed period of time was used to turn the current on. The interval between injections was anywhere between 5 sec to 300 sec. The duration for which the current was turned on was between 100 to 1000 msec.

The injections were also controlled by the personal computer (IBM compatible). This computer was interfaced to the GC through analog to digital converter (DAS8-PGA, Metrabyte Corp., Elmwood Park, NJ). Computer programs were written in Quick Basic. The interval between the pulses and the duration of the pulse could be changed by adjusting particular variables in the program.

The data acquisition was done using HP 3396A integrator or a Das - 8PGA Analog to Digital Converter (Metrabyte Corp.) and an IBM compatible personal computer.

4.2 Sampling

Analytical grade hexane, p-xylene, benzene etc. were used in this study. A steady stream containing VOCs was generated by diffusing a controlled amount of these

analytes from a diffusion capillary into a flow of N_2 (44). The schematic diagram of the diffusion cell is shown in Figure 9.

The liquid was placed in a melting point capillary of 0.165 mm diameter. A smaller diameter fused silica capillary (diameter 0.25 mm, 0.050 mm, 0.025 mm) was connected on top of it to reduce the effective diffusion cross-sectional area. The sample diffused up the capillary tube onto a flow of N_2 . The diffusion rate depends upon the cross sectional area of the capillary and the height from the liquid surface to the top of the capillary. The rate of diffusion of the sample into the gas stream at any given time can be calculated by the Equation 4.1 (44):

$$S = Xp A / 2 L \quad (4.1)$$

where S is rate of diffusion, in grams/sec. X is a constant for the liquid at the given temperature and has a unit of cm^2/sec , p is density of liquid. A is cross section area of the capillary in cm^2 and L is depth of the liquid meniscus below the capillary mouth, (cm). The value of X was experimentally determined for each compound and at each temperature. This was done by running N_2 through the diffusion cell and measuring L periodically. A plot of L^2 vs. time give a straight line with X as the slope.

4.3 Reagents

Analytical standards of hexane, benzene, ethanol, toluene, p-xylene from Fischer Scientific were used as samples for the experiments. Carrier gas was pre-purified N_2 and for the flame ionization detector, prepurified H_2 and breathing quality air were used.

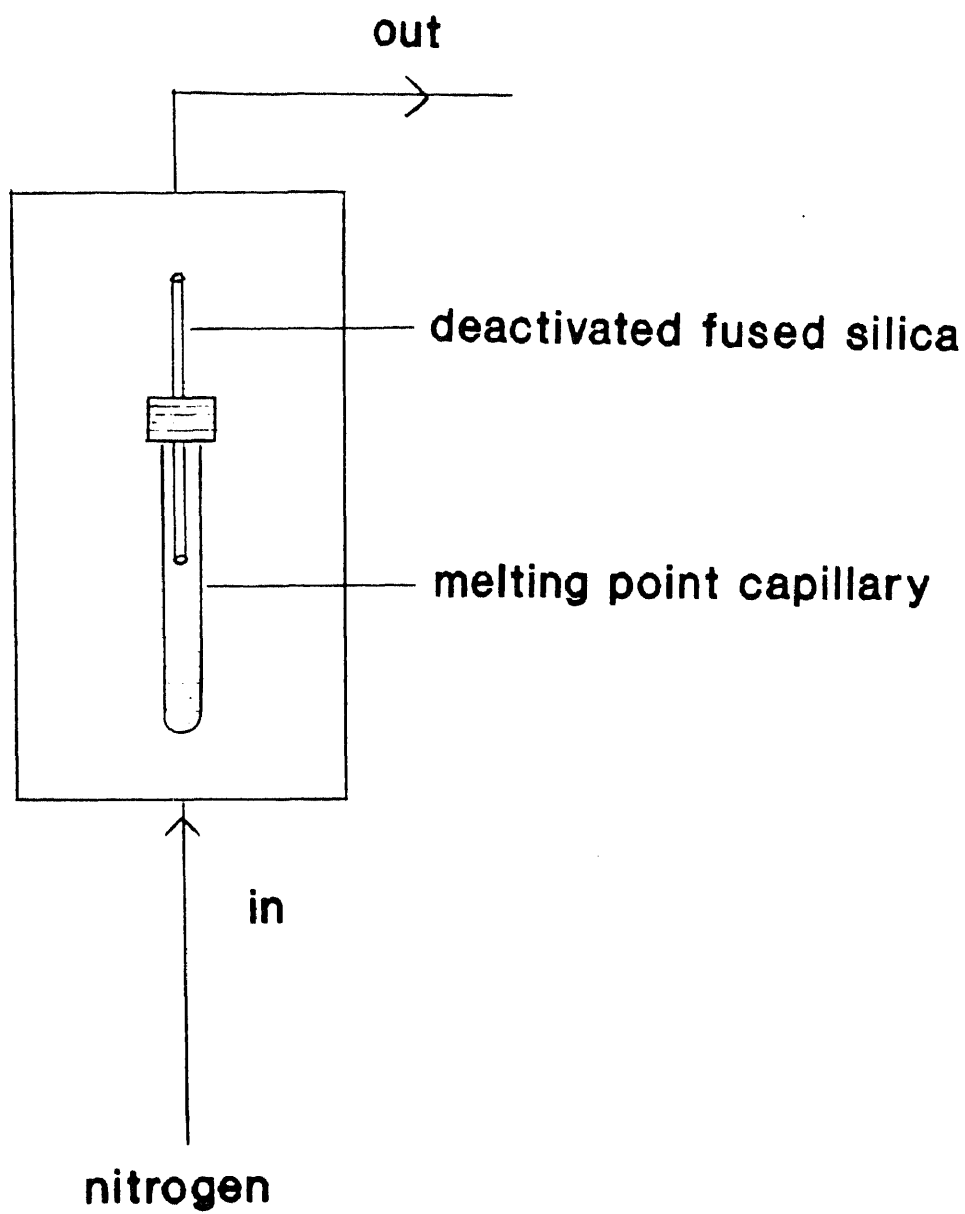


Figure 9. Diffusion dilution cell

CHAPTER 5

RESULTS AND DISCUSSION

Automatic sample introduction is the most important feature in on-line chromatographic techniques. When using modulator, the equivalent of an injection is made internally by modulating the temperature of the modulator, and hence the modulator can be used for sample introduction into the GC from a process stream. Modulator can be a substitute for automatic valves, that are commonly used in process gas chromatographs. Faster operation, lower detection limit and shorter band width are some of the advantageous a modulator has over a sampling valve.

Since signal generated by the modulator is directly proportional to the amount of the analyte flowing through, it ought to be applicable in quantitative analysis.

The modulator is the central operating component in the analytical system. Several operating parameters, such as modulator temperature, pulse duration (for how long the modulator current is turned on), modulation interval (i.e. at what frequency the modulation are made) need to be optimized for proper functioning of the modulator.

5.1 Modulation Efficiency

A modulator operation may be compared to a sorbent trap which tend to hold all of the analysis from a sample. However, a modulator traps only a fraction of the sample for short period of time in proportion to the concentration of the sample flowing through it. In effect, the modulator modulates the concentration of the analytes flowing through it rather than trapping the sample. In order to obtain a large signal at the detector, the modulator should accumulate as much sample as possible before making an injection. Another reason for doing this is that the untrapped sample breaks through the modulator and contributes to the background at the detector.

Trapping or modulation efficiency of the modulator is defined as the fraction of the incoming sample retained by the modulator before an modulation is made:

$$\text{Modulation efficiency (m)} = \frac{\text{sample retained}}{\text{sample passed through}} \quad (5.1)$$

The retention mechanism in a modulator is similar to that of a GC column. There is an equilibrium between the concentration of the sample in the stationary and the mobile phase. The modulations are normally made at fixed intervals of time (referred to as modulation interval). So modulation efficiency can be written as:

$$m = t_- c_s / t_i c_t \quad (5.2)$$

where, c_s is the amount of sample in the stationary phase, c_t is the amount of the sample flowing into the modulator, t_i is modulation interval, and t_- is time required for the sample to migrate through the modulator. When a sample enters the modulator, it distributes between the stationary and mobile phase. So, Equation 5.2 may be written as:

$$m = t_- c_s / t_i (c_s + c_m) \quad (5.3)$$

here, c_m is the amount of sample in the mobile phase. The above equation can be rearranged to:

$$m = (t_- / t_i) K / (K + 1) \quad (5.4)$$

where K is the capacity factor defined as the ratio of the moles of a solute in the stationary phase to the moles in the mobile phase. If the modulations are made very frequently such that $t_i < t_-$, then the modulator accumulates sample only for t_i and equation 5.4 becomes:

$$m = K / (K + 1) \quad (5.5)$$

Thus in this case m depends only upon K and does not change with the modulation interval t_i . Equation 5.5 indicates that a greater sample capacity factor results in a

higher modulator efficiency. If modulation interval is large and $t_i > t_r$ then modulation efficiency is given by equation 5.4 and m is inversely proportional to t_i .

The modulation efficiency can be computed from the modulator response such as in Figure 10. The sample retained by the modulator is proportional to the area under curve AED. The total sample flowing into the detector is equal to the area ABCD. So, the modulation efficiency is:

$$m = \text{area AED} / \text{area ABCD} \quad (5.6)$$

The modulation efficiency as a function of modulation interval is presented in Figure 11(The data of Figure 11 are shown in table 1). These experiments were performed at 35°C and 15°C and using hexane as the sample and t_r of 36 sec and 110 sec were obtained at these temperature. From Figure 11, it is seen that when modulation interval is less than t_r , as predicted by Equation 5.5, the modulation efficiency is constant and is at its highest value(74% at 35°C and 86% at 15°C). When the interval is further increased and higher than t_r , the modulation efficiency begins to drop exponentially.

5.2 Factors Effecting the Modulator Response

t_r is an important characteristic for a modulator which is given in by Equation 5.3. For a specific analyte and a stationary phase of modulator, the value of t_r depends upon capacity factor which depends upon temperature, . Maximum modulation efficiency (corresponding to the flat portion of Figure 11) and t_r are plotted as a function of temperature in Figure 12(The data of Figure 12 are shown in table 2). The experiments in Figure 12 was performed using a Carbotrap C fused silica modulator and hexane as the sample. It is found that as temperature increased, the modulation efficiency decreases as well as t_r decreased. This is expected because according to Equation 5.5 modulator efficiency is proportional to t_r . The decrease in modulation efficiency and t_r

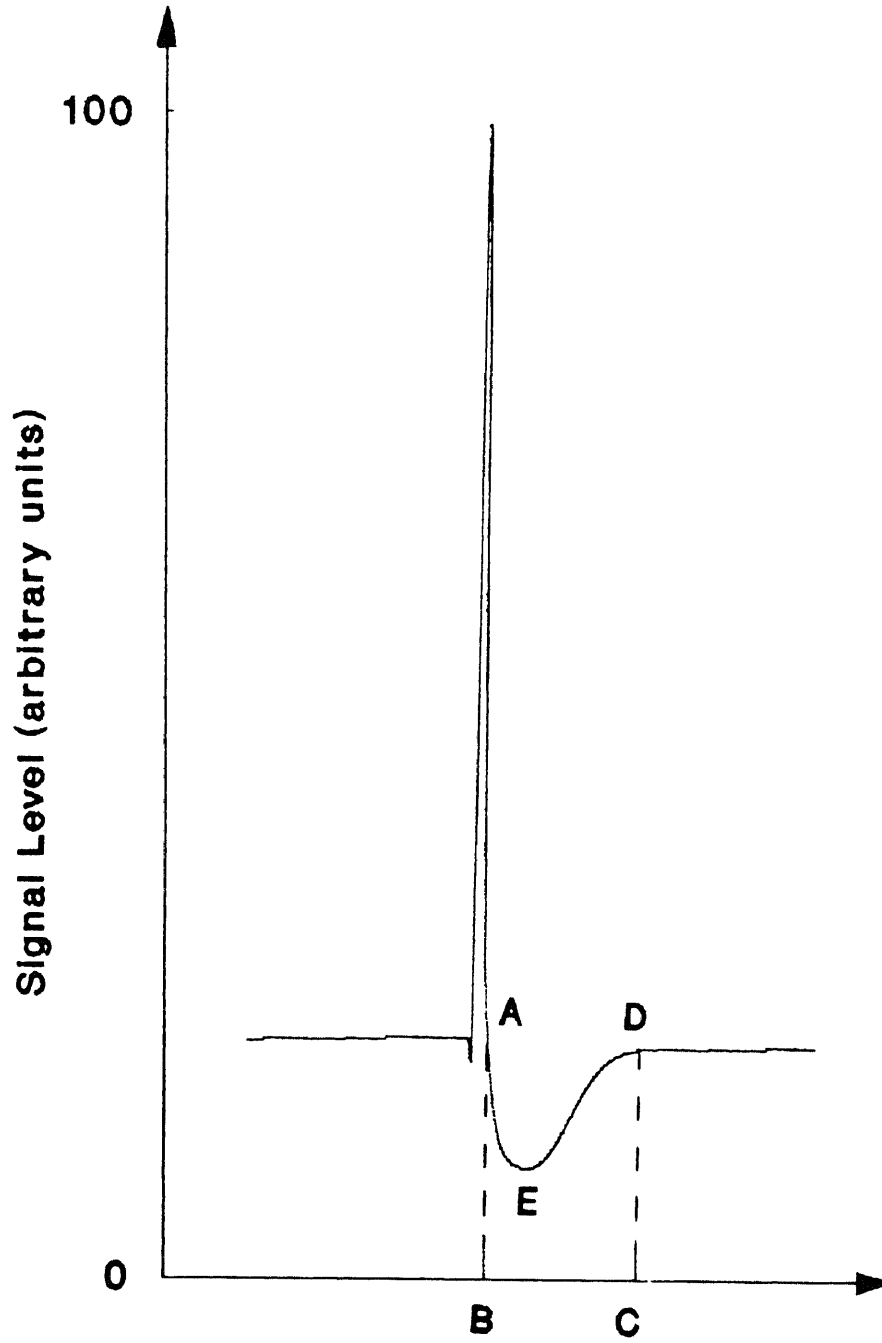


Figure 10. Typical modulator response

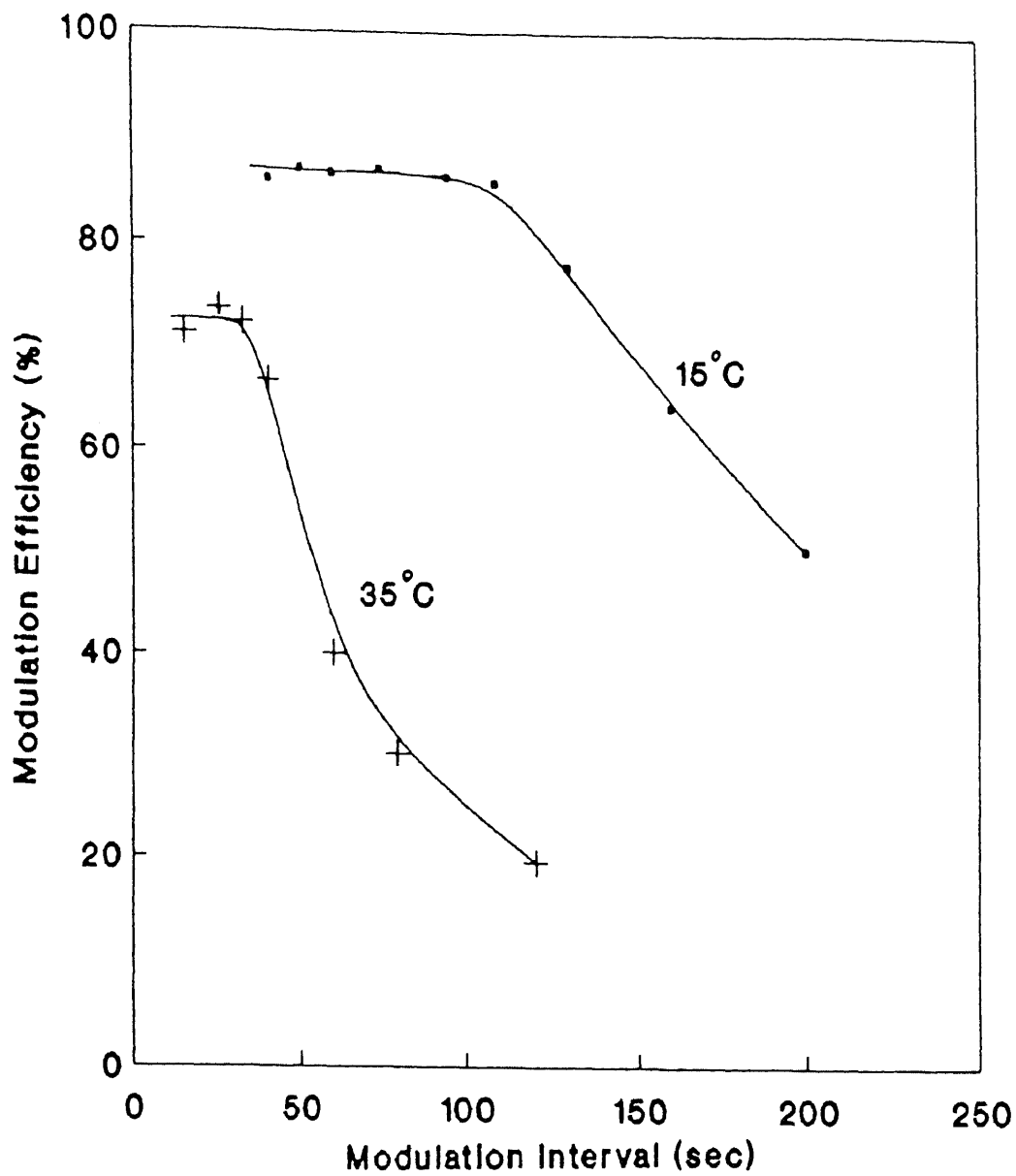


Figure 11. Variation in modulation efficiency as function of modulation interval. A 6 cm long fused silica modulator was used with hexane as the sample.

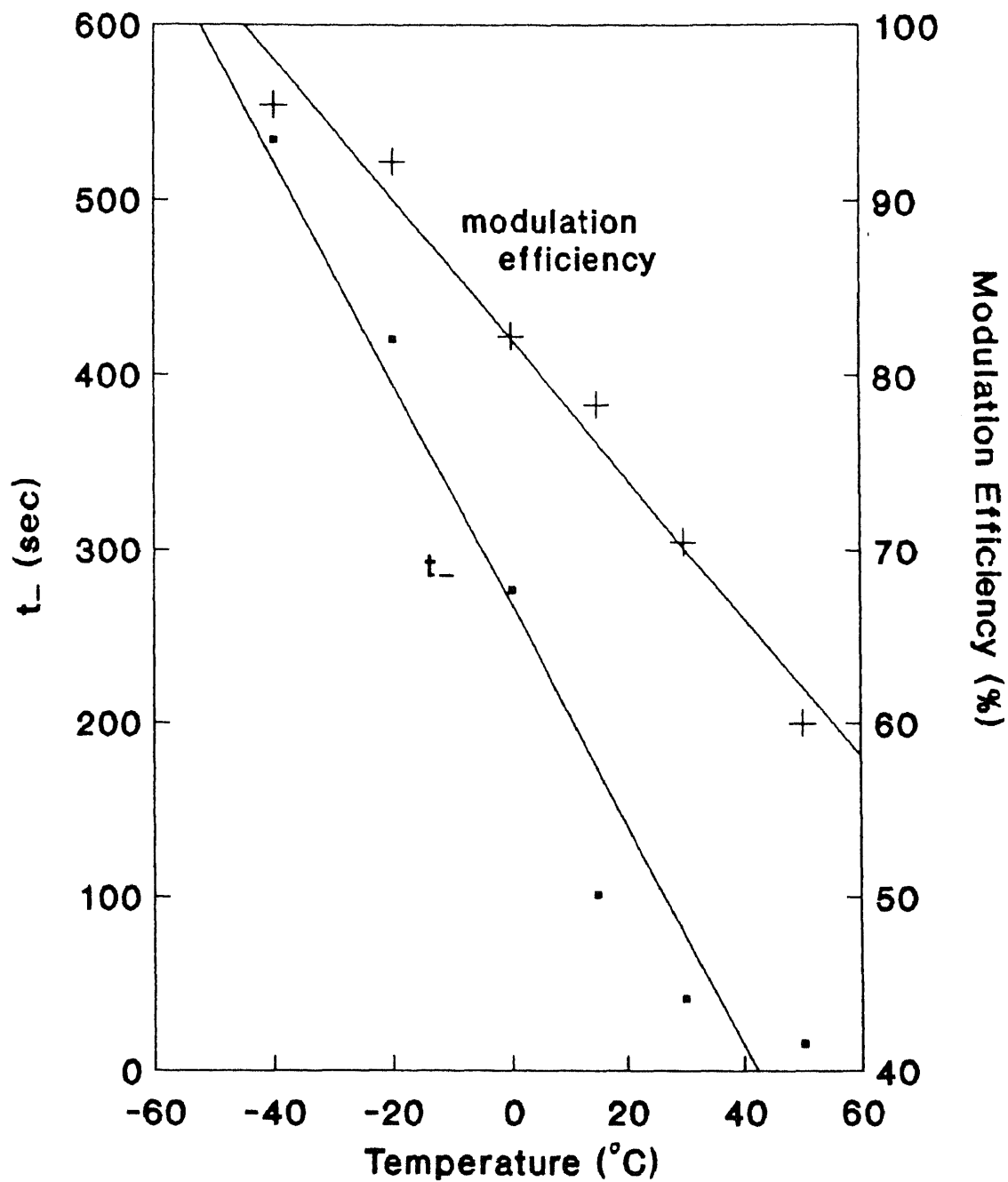


Figure 12. Variation in modulation efficiency and t_- as function of modulation temperature. Hexane was used as sample and a 6 cm long fused silica modulator was used.

with temperature may be approximated by linear relationship. When modulator temperature was at -40°C , the modulator efficiency was almost 100%.

5.2.1. Effect of Pulse Duration and Energy Input to the Modulator

In order to desorb the sample from the absorbent in the modulator, relatively high temperatures are needed. It is very difficult measure the actual temperature in the modulator and no attempts were made to do so. Current passing through the modulator and the pulse duration determines the total energy input. The time for which the power is to be delivered depends on the pulse duration while the ohmic heating rate depends on the current. The period of time for which the modulator is held hot (and the capacity of the modulator is zero) is another important factor that is also controlled by the pulse duration. The current through the modulator is controlled by controlling the voltage of the power supply, and by putting resistances in series with the modulator. Once these factors are set, the energy input depends solely on pulse duration.

Typical variation of modulator response with pulse duration is shown in Figure 13. Ethanol was used as sample. Peak height increased with increase in pulse duration until it reached a maximum beyond which it remained constant. At this point, enough energy was applied to desorb all the absorbed sample. For this particular modulator, 0.51 sec. is necessary for complete desorption of ethanol and 37 voltage power supply is used.

Similarly, if the pulse duration and the resistance are fixed, the energy input can be controlled by controlling the voltage across the modulator. Figure 14 shows relationship between modulator response and applied voltage. As the voltage was increased, signal amplitude was increased until it reached a maxima beyond which it remained constant.

5.2.2 Modulation Interval

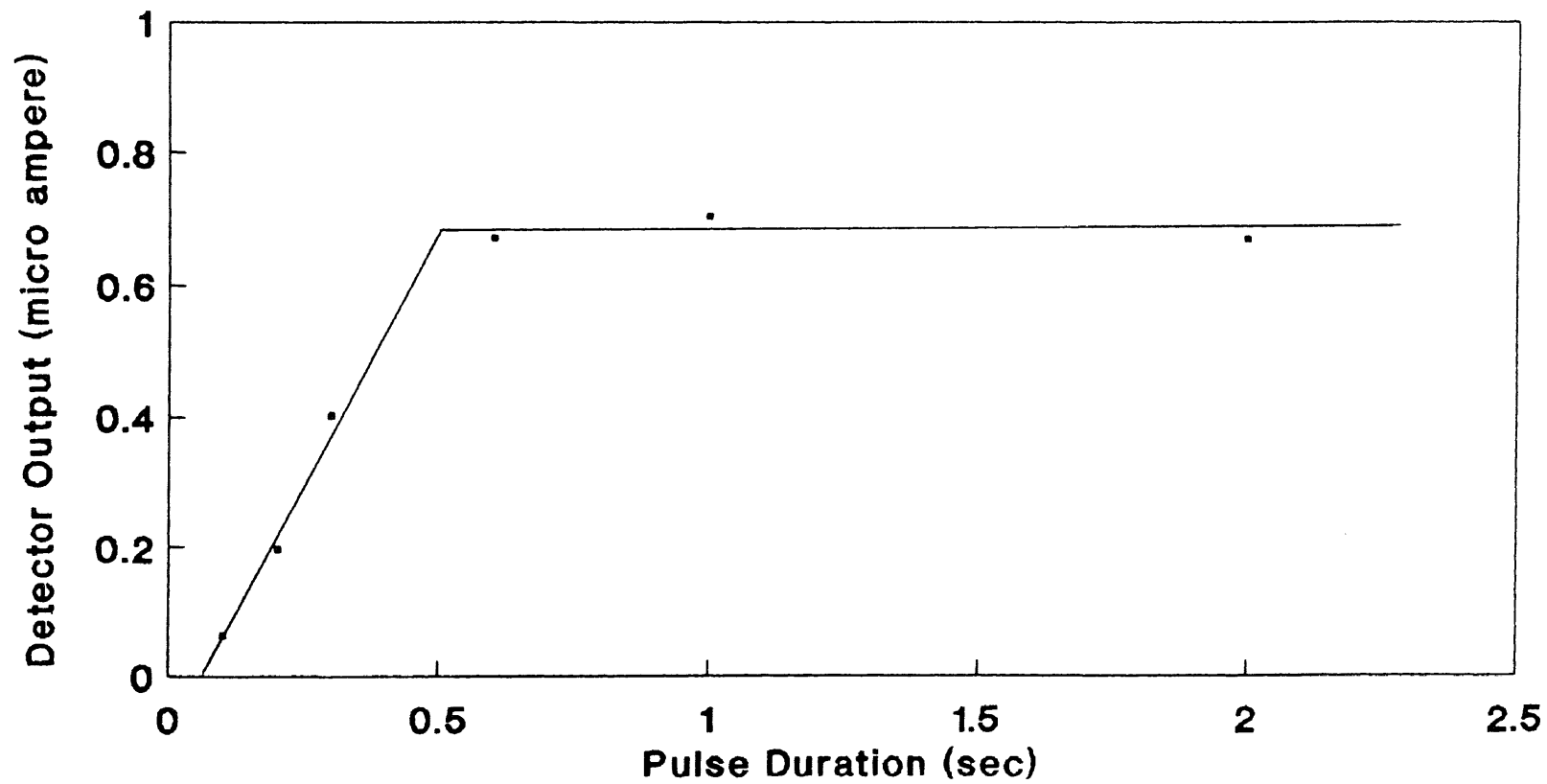


Figure 13. Response of Carbotrap C modulator as function of pulse duration when the applied voltage was 37.

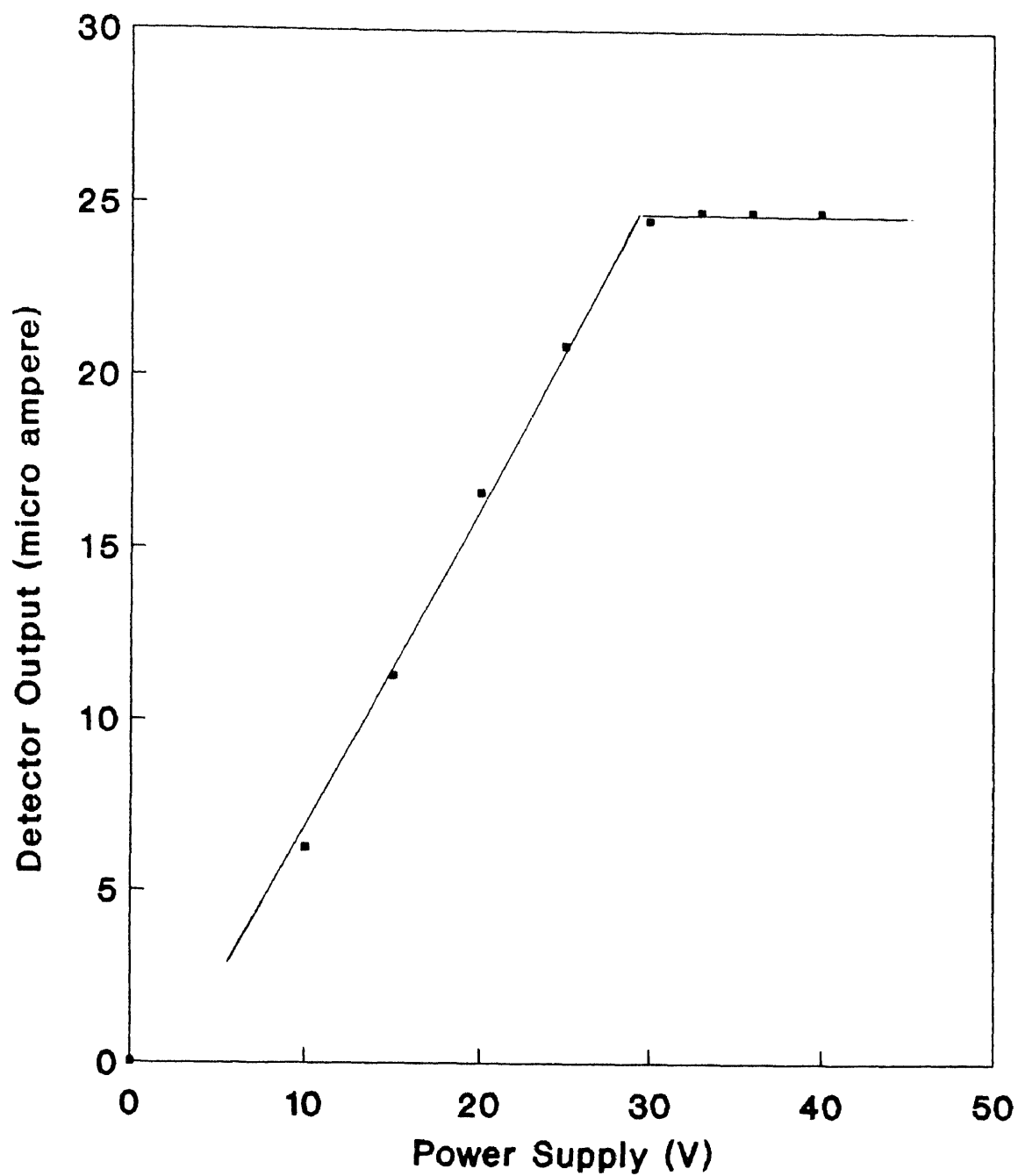


Figure 14. Response of Carbotrap C modulator as function of applied voltage at pulse interval of 0.51 sec.

At what frequency the modulator should be operated is an important factor to be taken into consideration. Making injections very often offers the advantage of obtaining informations more often, but may have other disadvantages such as lower sensitivity and not enough time for chromatographic separation. By operating modulator in the different modulation intervals, one can investigate the trapping characteristics of modulator. Typical response of the modulator as a function of modulator interval is presented in Figure 15. Here, ethanol was used as the sample. It is seen that the modulator response increased with modulation interval up to a point beyond which the response stayed constant. This maximum is obtained at a modulation interval equal to t_{r} . Beyond t_{r} , the sample begins to breakthrough and the response cannot be increased further by increasing the modulation interval. In the rising part of curve, the size of the modulation peak is directly proportional to the modulation interval. The maximum time for which the modulator can accumulate sample is the time required for the sample to migrate through the modulator, i.e. t_{r} .

5.2.3 The Effect of Modulator Temperature

As mentioned before, a lower modulator temperature results in a higher modulation efficiency and longer t_{r} . The results are in both Figure 12 and 16 (The data of figure 16 are shown in table 3). Higher modulation efficiency results in a larger fraction of the sample being trapped and consequently a larger desorption peak when the modulator is heated, i.e., higher sensitivity. For example, at modulation interval of 50 sec, the modulator response at -10°C is 2.1 times that at 35°C . Lowering temperature also has advantage of increasing t_{r} , i.e., we can trap sample for a longer period of time. For a continuously flowing sample, this means a larger sample accumulation in the modulator resulting in higher sensitivity and lower detection limit. Because of the above mentioned reasons, the maximum attainable response at -10°C is 6 times higher

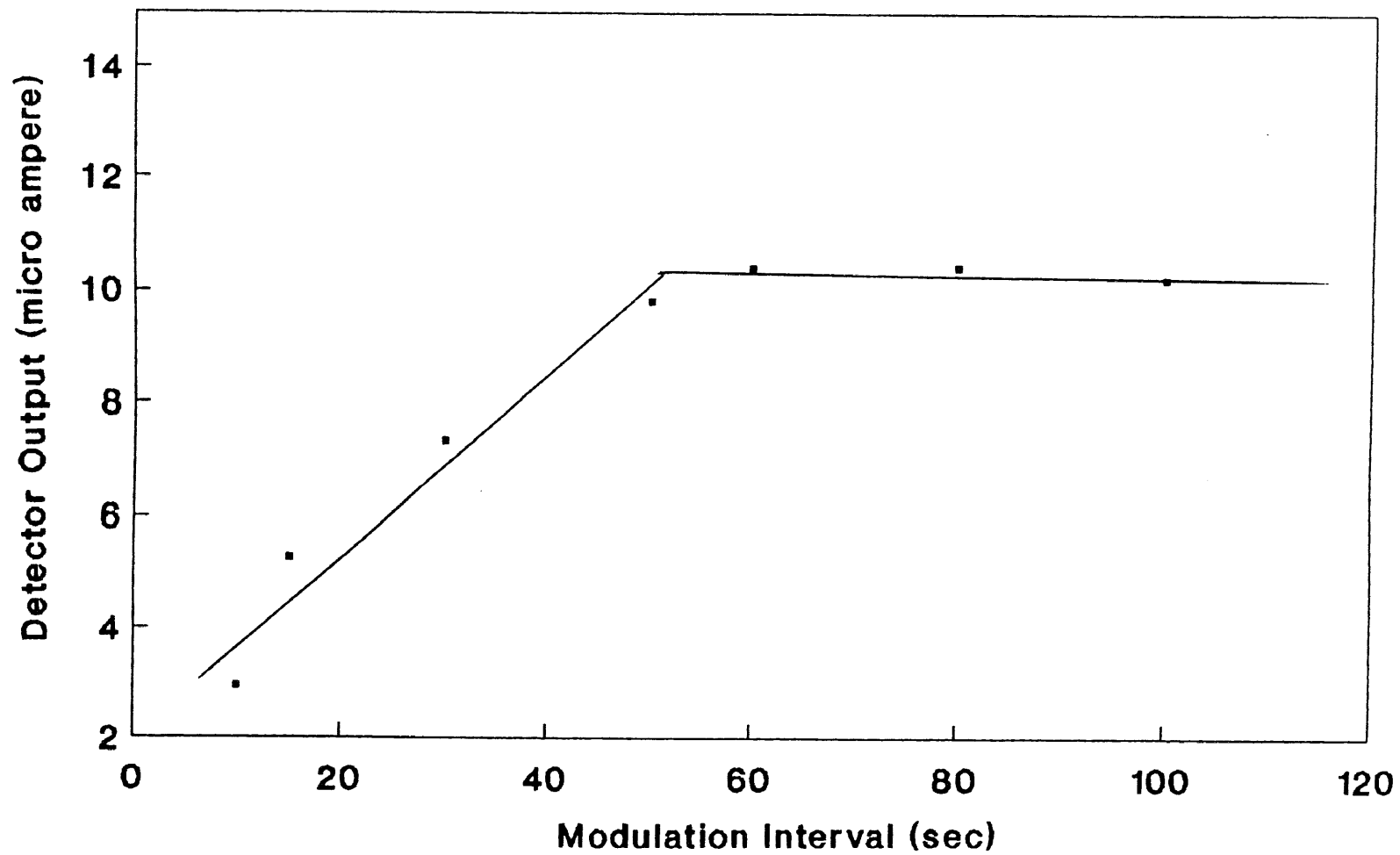


Figure 15. Response of Carbotrap C modulator as function of modulation interval

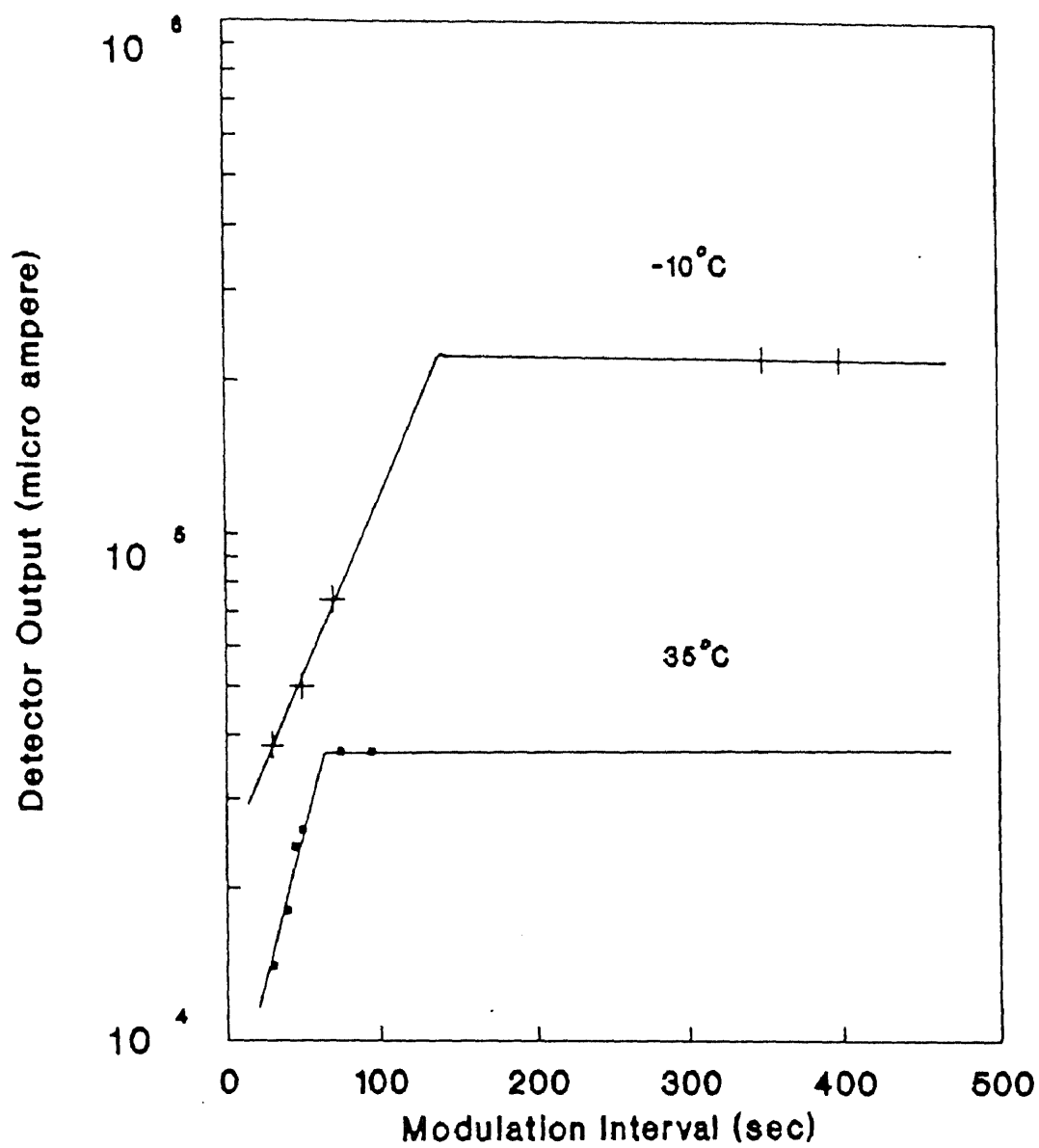


Figure 16. Variation of detector output as a function of modulation interval in difference temperature. Hexane was used as the analyte and a 5.5 cm long fused silica modulator was used.

than that at 35°C. In short, the increase in sensitivity at lower modulator temperature is observed whether the modulation interval is longer or shorter than t_{r} .

Lowering the temperature to very low values may cause the components to adsorb irreversibly in the modulator, and this may be a limitation. The modulator temperature should be optimized for the analytes of interest. For example in Figure 9, 23°C was appropriate temperature for the analyte of interest and subambient cooling was not required. However, sensitivity can be increased and detector limit can be decreased by subambient cooling of the modulator. Since the change in temperature results in a change in sensitivity, the modulator temperature should be controlled carefully. A change in modulator temperature would require recalibration of the system during extended periods of continuous operation.

5.2.4 On-Line Analysis

The operation of the continuous analysis system is demonstrated by continuously monitoring a stream containing benzene, toluene and p-xylene. The injection from a modulator was similar to that from an injection port or an injection valve. Figure 17 shows a series of chromatogram generated by making modulation every 150-s. The modulator here was a 6.5 cm long fused silica modulator packed with Carbotrap C modulator. Some of the characteristics of the chromatograms are presented in table 4. These results are an average of five measurements. An injection of the same standard was also made using the split injection port and the comparative results at the same retention time are also presented in table 4.

The relative standard deviation for retention time was 0.23% in modulator and 0.17% for the injection port. The peak height reproducibility from the modulator had a relative standard deviation 1.19%, which was better than that obtained by injection port (about 2% RSD). The terminal band length is measured as the length of the solute band emerging from the end of the column is expressed as:

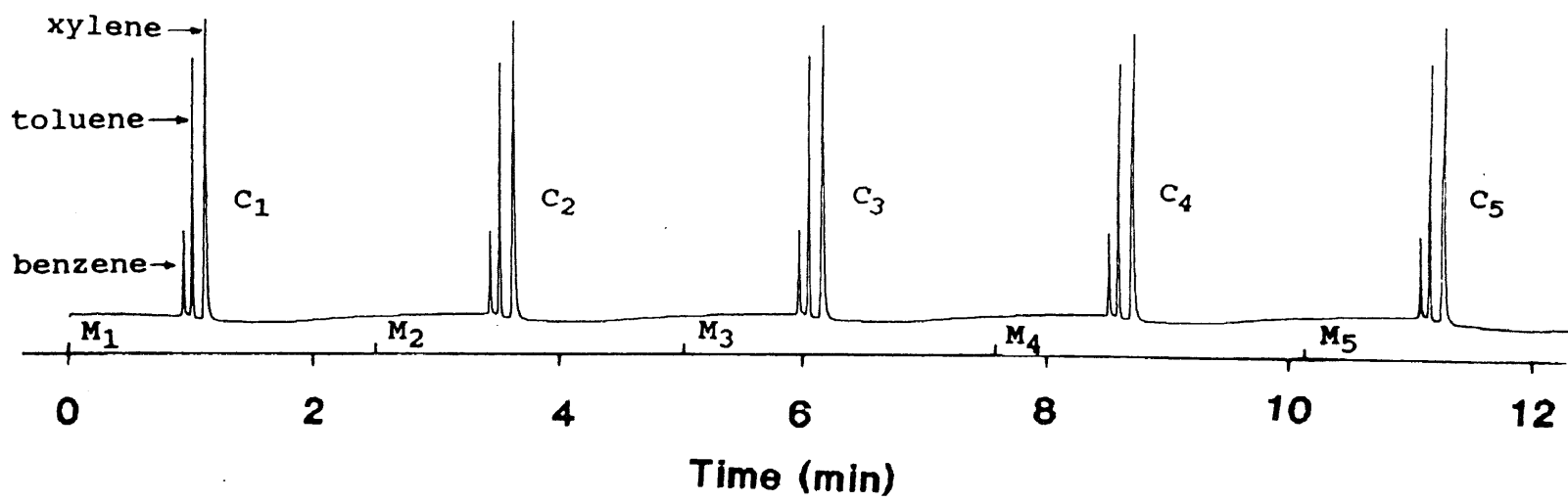


Figure 17. Continuous on-line analysis. A 6.5 cm long fused silica modulator was used and ppv_b levels of benzene, toluene and xylene were used as the samples

Table 4. Comparison of Modulator with Injection Port

Compounds	Modulator			Injection port		
	Benzene	Toluene	p-Xylene	Benzene	Toluene	p-Xylene
Retention Time (sec)	57.38	61.85	68.41	56.27	62.22	70.97
% RSD of Retention Time	0.22	0.23	0.20	0.13	0.17	0.16
% RSD of Peak Height	1.14	0.97	1.46	1.60	1.50	2.90
Band Duration *(sec)	0.76	0.78	1.12	0.80	1.00	1.20
Terminal Band Length* (mm)	385.09	365.74	475.62	411.30	467.02	490.38

*Measured at Half-Height.

%RSD - Percent Relative Standard Deviation

$$b = L W_b / t_R \quad (5.7)$$

where b is terminal band lengths, L is the column length, W_b is peak width measured at half height, and t_R is the retention time. The terminal band length is a useful measure of separating power because it is a real entity that is easily understood and is directly related to the column's band broadening process (45). At the same retention time, terminal band length of the peak generated by modulator was same what shorter than that from the injection port. This is to be expected, because the modulator has not only the same flow pattern as the column but also no dead volume. In previous fast chromatography studies (11) modulator were used to produce injection bands as short as 20-50 msec. The cooling and heating cycle of the modulator is very small and the frequency of injection is limited by the time required for separation in the column. Hence, in the optimized column conditions, we prefer to optimize the speed rather than efficiency.

5.2.5 Calibration Curves Using The Modulator

The linearity of the calibration curve is one of the important factors in on-line analysis. Concept of partition chromatography has been used in previous sections to explain the retention characteristics of modulators. The amount of sample trapped by the modulator depends upon the concentration of sample coming into the modulator. So a linear modulator response is expected. Calibration curves for hexane are shown in Figure 18 (the data are shown in table 5). Calibrating at two different modulator intervals, 40 sec ($< t_r$) and 400 sec ($> t_r$). Linear relationships between concentration and detector response were obtained in both cases. When t_r was above 40 sec, lesser amount of sample was trapped in the modulator and the sensitivity of analysis was lower although information was obtained more often. When modulation interval was 400 sec, more sample was accumulated for a longer time which increased the sensitivity. However, the maximum response was reached at modulation interval 59 sec (i.e. t_r) and the

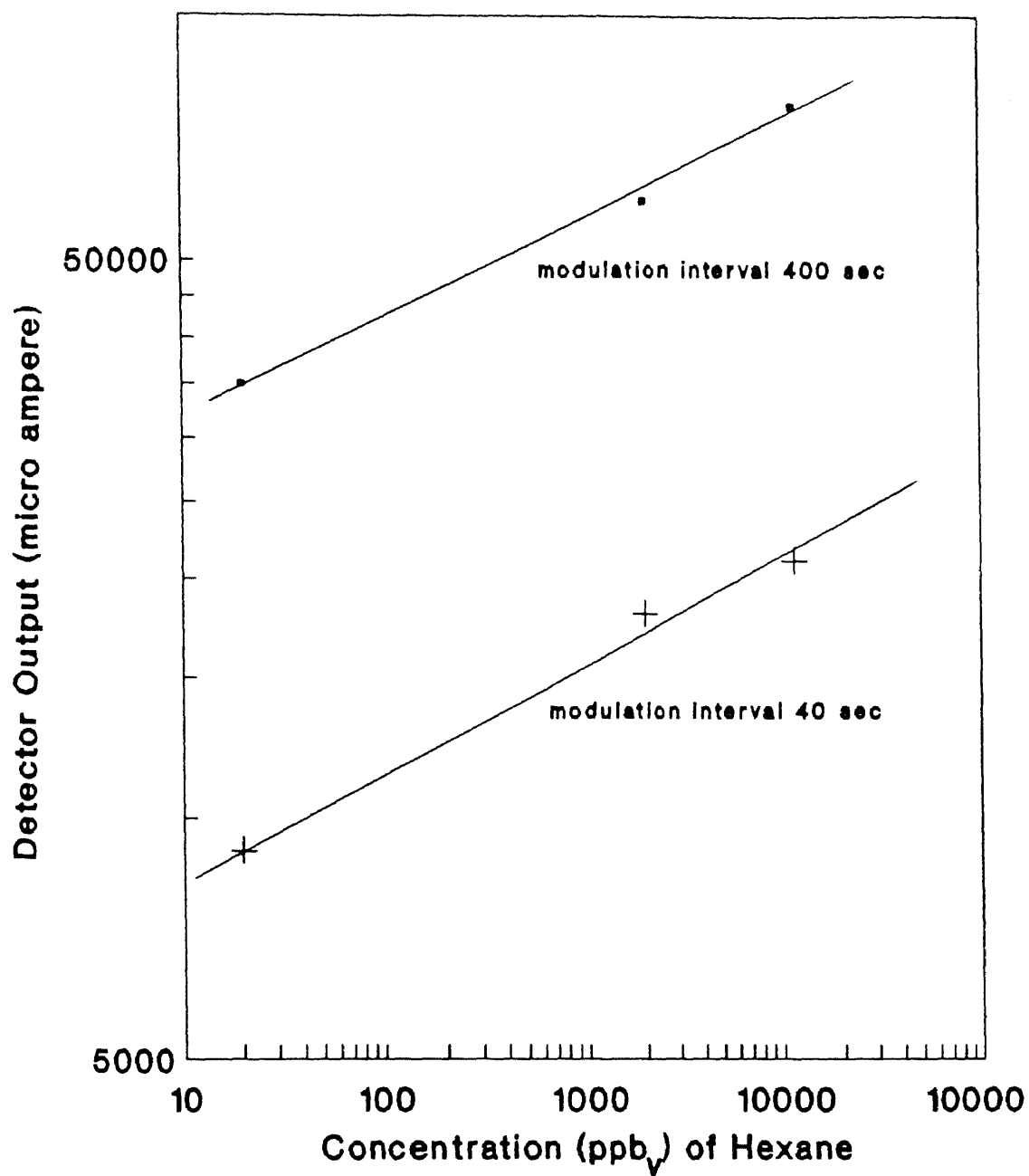


Figure 18. Plot of modulator response as a function of concentration. Hexane was used analyte and a 13 cm long stainless steel modulator at 23°C was used .

sensitivity could not be improved by raising the modulator interval from 59 sec to 400 sec. What is interesting is that linear relationship for calibration curves were obtained in the region $t_1 > t_0$ and in the region $t_1 < t_0$. This is important in analysis of multi-component samples which have components of widely differing volatility that are expected to have different t_0 value. In that case, irrespective of t_0 value, it is possible to obtain linear calibration curve for each compounds.

It is evident from the data presented so far that ppb_v levels of VOCs can be effectively analyzed using modulators. In the calibration curve of Figure 18, at 20 ppb_v the detector response was approximately 6000 uamps. A more than two order of magnitude lower signal can be easily measured by the detector. So it is anticipated that VOC stream with sub ppb_v concentration levels can analyzed using this method.

CHAPTER 6

CONCLUSION

In this research, thermal desorption modulator has been applied for real-time, on-line analysis of VOCs. The modulator parameters such as modulation interval, pulse duration, modulator temperature have been optimized. The modulator has proved to be effective in providing completely automated on-line analysis.

The thermal desorption modulator coupled with GC plays an important parts in continuous monitoring of trace levels VOC. The thermal desorption modulator not only serves as an automatic injection device but also as a sample preconcentrator. As a result, it can be used for analyzing low ppb_v levels of VOCs. A modulator is a very fast and responsive device because of its low thermal mass and the absence of any moving part, and capable of making injection very frequency.

Since the sample flow through the modulator is continuous, it can be termed as a continuous analysis device. On the other hand, in a classical injection valve the sampling is performed at discrete points in time, for example, every couple of minutes. If a large increase in concentration take place within this time, the valve may not be able to detect it. However, a modulator would integrate the sample for the two minutes and would produce a time averaged response.

In this research we investigated the characteristics of a thermal desorption modulator. Modulation efficiency of the modulator decreased with increase in modulator temperature and its decrease closely paralleled that of t_r . A lower temperature, longer is t_r , and higher modulation efficiency were encount. Modulation efficiency was also studied as a function of modulation interval. When modulation interval was less than t_r , the modulation efficiency was maximum value. As a result, the modulator sensitivity could be increased by lowing the temperature. When modulation interval is higher than t_r , it decreased exponentially.

APPENDIX

Table 1. Variation in Modulation Efficiency as Function of Modulation Interval

Modulation Interval	Modulation Efficiency(%)	
	15°C	35°C
15		71.15
25		73.51
32		73.23
40	85.93	66.62
50	86.99	
60	86.55	40.05
75	86.92	
80		30.18
95	86.22	
109	85.71	
120		19.57
130	77.72	
160	64.06	
200	50.25	

Table 2. Variation in Modulation Efficiency and t_{-} as Function of Temperature

Temperature	t_{-} (sec)	Modulation Efficiency
-40	534	95.38
-20	420	92.2
0	276	82.2
15	101	78.27
30	41	70.46
50	15	60.03

Table 3. Variation of Detector Output as a Function of Modulation Interval in Different Temperature

Modulation Interval	Detector output	
	35°C	-10°C
30	14000	38000
40	18000	
45	24000	
50	26000	50000
70		7400
75	3700	
95	3700	
350		220000
400		220000

Table 5. Concentration of Hexane vs. Detector Output

Concentration(ppb _v)	Detector Output	
	Modulation Interval 400 sec.	Modulation Interval 40 sec
20	35000	9100
1980	59000	18000
11600	77000	21000

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