



## Acknowledgments

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## Introduction

### Objectives of This Work

The birth of liquid chromatography at the beginning of this century provided a powerful means of separating many types of mixtures into individual components. However, after its initial development by Tswett (1), the technique remained nearly unchanged until the late 1960's when the current wave of interest was initiated. The primary factors effecting renewal of interest in developing liquid chromatography were:

1. A growing need for separation of materials too thermally labile and too nonvolatile to be handled by gas chromatographic techniques.
2. The availability of high pressure pumping equipment and better means of detection.
3. The presence of a large volume of separations theory and experience developed in the field of gas chromatography.

One of the major requirements in the analytical use of liquid chromatography is a sensitive detector which continuously monitors the chromatographic column effluent. Because the micro-adsorption detector introduced in 1967 appeared to have potential as a universal detector, it was chosen as the subject of the work presented here. Specifically, the objectives of this work were:

1. To evaluate a micro-adsorption detector for use in liquid chromatography.
2. To evaluate a micro-adsorption detector for use in gas chromatography.



3. To investigate the micro-adsorption cell as a tool for screening chromatographic systems, for use in adsorption studies, and as a micro-calorimeter.

### Development of Liquid Chromatography

Chromatography is defined as the separation of the components of a mixture due to differences in their distribution between two immiscible phases, one stationary and one mobile. The stationary phase will selectively retard the sample components and the mobile phase will transport them through the column.

Depending upon the processes involved in the distribution, the nature of the phases and the geometry of the system, the general process can be subdivided into several areas. Referring to Figure 1, it can be seen that a major distinction is made between systems where the mobile phase is gaseous and those where it is liquid. The former, gas chromatography, can further be subdivided depending upon the nature of the stationary phase.

If the stationary phase is a liquid distributed as a thin film on an inert solid support, the classification gas liquid chromatography (GLC) is used. In this case, the distribution is referred to as a partitioning of the sample components between the gas and liquid phases. If the stationary phase is a solid, the process is called gas solid chromatography (GSC) and the distribution is due to adsorption. In both cases the geometrical form of the stationary phase is a bed of small diameter particles packed tightly in a glass or metal tubular column.

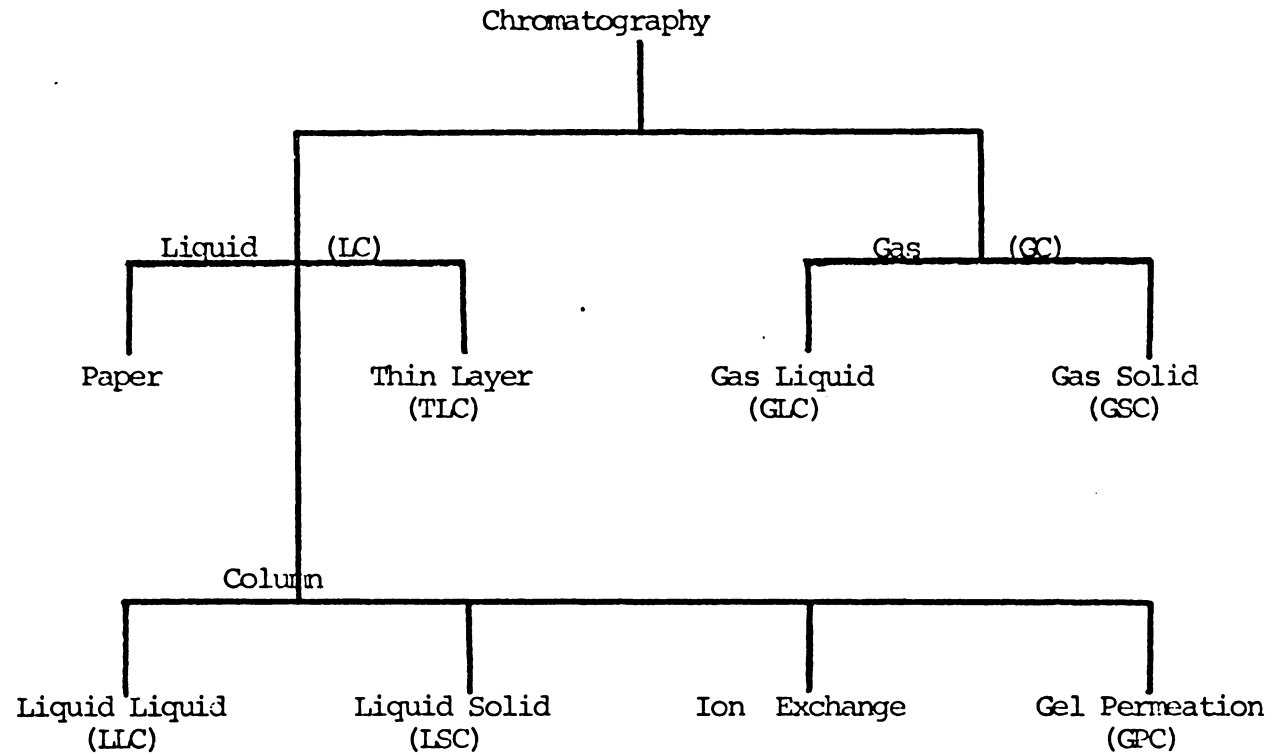


Figure 1. Major Subdivisions of Chromatography

When the mobile phase is a liquid the geometrical form of the stationary phase may be either planar or columnar. Both paper and thin layer chromatography (TLC), utilize the planar geometry. In paper chromatography the sample partitions between a flowing organic solvent and water trapped in the cellulose fibers of the paper. Sample adsorption on the cellulose itself is a minor effect. In TLC the stationary phase is an adsorbent, frequently silica gel, bonded to glass, plastic or metal plates. A liquid phase passes over the adsorbent carrying the sample components with it.

The columnar liquid chromatographic processes include ion exchange, gel permeation (GPC), liquid liquid (LLC), and liquid solid chromatography (LSC). Ion exchange chromatography utilizes attraction and interchange of ions between the stationary phase and the sample. The stationary phase normally used in ion exchange chromatography consists of a resin matrix with reactive end groups such as tertiary amino or sulfonic acid groups, which can participate in the interchange of ion.

The mechanism in GPC is the selective diffusion according to molecular size into small pores of the stationary phase. The stationary phase is a hydrophobic porous gel such as obtained by the polymerization of styrene with divinylbenzene. Gel filtration is another version of separation according to molecular size. It uses a hydrophilic stationary phase, such as cross-linked dextran and an aqueous mobile phase.

Both liquid liquid and liquid solid chromatography utilize packed columns of stationary phases, analogous to GLC and GSC.

Liquid chromatography was first reported as an adsorption process

by the Russian botanist Tswett in 1906 (1). Prior work by Day (2) had attributed the observed separation of petroleum fractions to a capillary phenomenon. Tswett however correctly described the adsorption process, invented the elution technique of washing continuously with fresh mobile phase and also coined the term, "Chromatography." Small wonder that he is considered the father of chromatography.

Since its introduction by Tswett liquid chromatography has been used in essentially the same form for difficult separations of complex mixtures. Liquid chromatography, particularly LSC, is widely used to separate and purify many types of organic compounds. Gravity feed supplies the pressure for the mobile phase, and fairly wide columns, 1 to 10 cm. i.d., are used. Fractions are collected and analyzed by auxiliary techniques.

With the introduction of gas chromatography (3,4,5) interest in liquid chromatography declined and few developments were made between 1954 and 1966. Gas chromatography was more rapid, more precise and more sensitive. The development of gas chromatographic theory pointed the way to more efficient column separations: use smaller diameter particles packed tightly into narrow tubes. A logical reason for the lack of development in liquid chromatography was the versatility of gas chromatography which was successfully applied to a wide range of organic and inorganic compounds. In addition high pressure pumping systems and sensitive, continuously recording detectors were not available for liquid chromatography until recently.

Eventually, however, the limitations of gas chromatography were reached. The separation by gas chromatography demands that the sample

be volatile and temperature stable. Many larger molecules, particularly biological molecules, are not suitable for gas chromatographic analysis. Liquid chromatography demands only that the sample be soluble. In theory liquid chromatography can be applied to all high molecular weight compounds, organic, inorganic, covalent or ionic. In practice it may be difficult to find a combination of stationary and mobile phases which selectively retard the sample, but do not interact with each other.

As the need arose to analyze trace quantities of steroids, nucleic acids, amino acids and similar biological molecules, it was only natural to turn to liquid chromatography.

As indicated earlier the knowledge of how to improve column efficiency was readily available from gas chromatography. High efficiency columns should be made from small diameter particles packed tightly into narrow columns. These columns have high resistances to flow and require inlet pressures of several thousand psi. The major hardware requirement for high performance liquid chromatography is high pressure systems. Of course sensitive continuous recording detectors with small internal volumes are also required for convenience and easy quantitation.

An example of the progress made in decreasing analysis time and improving column performance is shown by the comparison of the separations listed in Table I. At the time of publication each paper represented an advance in high performance liquid chromatography. The analysis time is decreased drastically, at the expense of high pressure. The rate of generating theoretical plates is increased one thousand fold and the sample size has decreased five orders of magnitude.

TABLE I

## COMPARISONS OF SELECTED LIQUID CHROMATOGRAPHIC SEPARATIONS

<u>DATE</u>	<u>1951 (7)</u>	<u>1967(6)</u>	<u>1969(8)</u>
Analysis Time Hrs.	50	3	0.1
Column Diameter mm	9	2	1
Packing Diameter microns	50	20	0.5 (Film)
Column Inlet Pressure, psig	20	30	2400
Theoretical Plates developed per second	0.005	0.3	4
Sample Size, gms	$10^{-3}$	$10^{-6}$	$10^{-8}$

The first publication by Moore and Stein (7) was the separation of amino acids by ion exchange methods. It illustrated the feasibility of handling complex thermolabile samples by LC. The second paper by Huber (6) illustrates high resolution by using high pressure. The analysis time is greatly reduced, and the results are comparable to GLC for the first time. The final paper by Horvath and Lipsky (8) illustrates another break-through in speed and resolution by the use of thin films bonded onto hard core glass beads (pellicular beads).

The problem of a suitable detector is still a major deterrent to the more universal use of liquid chromatography. To be compatible with the high performance LC columns available today, a detector should have sufficient sensitivity to detect solute quantities of the order of  $1 \times 10^{-9}$ . In addition it should have a linear dynamic range of one thousand and should respond to a wide range of chemical types. An internal volume of about 10 microliters, a low noise level and modest cost are also desirable.

No single liquid chromatographic detector can satisfy all of the above requirements, but several useful detectors are available today. The most common LC detector is an ultra-violet photometer. It has good sensitivity for many compounds, however it is limited to substances which absorb in the UV region. Recent designs have decreased internal volume to 8 microliters with nanogram sensitivity for strongly absorbing substances. Absorbance is usually measured at 254 nanometers, a wave-length absorbed by many biological compounds. Other detectors which have been used include differential refractometer (9), conductometric (10), ultrasonic (11), microwave (12), flame ionization (13),

and gas density balance (14) detectors.

In 1967 Hupe and Bayer (15) described a micro-adsorption detector for general use in liquid chromatography. This detector measures the heat evolved when a solute adsorbs on an adsorbent. It was theorized that any solute which could be separated in a column could be detected by using the identical column packing material as the adsorbent in the detector cell. If the solute and column packing interacted sufficiently to separate the compound, this same system should generate a temperature rise in the detector cell.

Commercial models of this detector are offered in Europe and the United States. A number of reports cite the use of this detector in the analysis of carbohydrates, lipids, and amino acids (16, 17, 18, 19, 20). All of these publications have come from the Varian laboratories however and there have been limited publications from other users. The flow sensitivity, approximately 10 microvolts for a 10 ml/hr change in flow rate at the 30 ml/hr level, and the temperature sensitivity, 10 microvolts change for a differential of  $3 \times 10^{-5}$  °C, require good temperature and flow control.

It is hoped that the results reported here will add to the current understanding of this detector, point out some major limitations and increase its utility as a research tool in gas and liquid adsorption studies. Also reported is its use as a micro-calorimeter, with the capability of measuring temperature differentials of  $5 \times 10^{-5}$  °C.



## Experimental

The experimental portion of the work can be conveniently divided into two major categories:

- (1) The description and requirements of the principal components.
- (2) The operation of the system and collection of data.

### Equipment

In this work the important pieces of equipment utilized included the micro-adsorption detector, a gas chromatograph, a pumping system, a calibration apparatus, a strip-chart recorder, a digital data logger, and a computer.

#### A. Micro-adsorption Detector (MAD)

The basic components of the MAD are shown diagrammatically in Figure 2 and an exploded photograph is shown in Figure 3. This model was purchased from Varian Aerograph, Walnut Creek, California.

The detector consisted of two matched, 100,000 ohm thermistors, each mounted in a 2.5mm diameter orifice in a 34 mm diameter, 4 mm thick, Teflon disc. These were held in a stainless steel housing having 1/8 inch Swagelock fittings. The cavities around the thermistors were packed with a non-adsorbing material in the upper or reference cell, and an adsorbing material in the lower or sensing cell. The two sections were separated by 400 mesh platinum wire screens.

The detector was attached directly to the outlet of the chromatographic column and the column effluent passed directly from the column into the reference cell. Here the reference thermistor sensed only the

temperature of the flowing stream. As the effluent passed into the sensing cell, the solute adsorbed on the packing material with the release of heat and a consequent increase in temperature of the liquid stream. The temperature differential between the reference and sensing thermistors was measured by means of a Wheatstone bridge.

The two thermistors formed opposing legs of a Wheatstone bridge circuit shown schematically in Figure 4. As the solute concentration increased, adsorption increased, the temperature differential increased, and the unbalance of the bridge produced a peak. As the solute band passed, the concentration decreased; desorption of the solute occurred, resulting in a lower temperature and a negative peak. The result was a positive peak for adsorption and a negative peak for desorption. An example of a MAD chromatogram is shown in Figure 5, along with a chromatogram from an UV photometer detector. The UV chromatogram was run separately and is included to illustrate the difference in peak shape obtained with the MAD and other detectors. Since, for a given substance and a given cell path length the UV detector response is a function of concentration, it follows the concentration of the sample as it comes into the cell. The UV response increases to a maximum, and then returns to the original baseline as the sample band passes out of the detector cell. This is the concentration profile common to all gas chromatographic detectors. The micro-adsorption detector response however is a function of the temperature change of the mobile phase. The temperature increases as the sample band enters the cell. As the maximum concentration is reached, adsorption is at a maximum. After the maximum concentration is seen, adsorption decreases and at some later time, de-

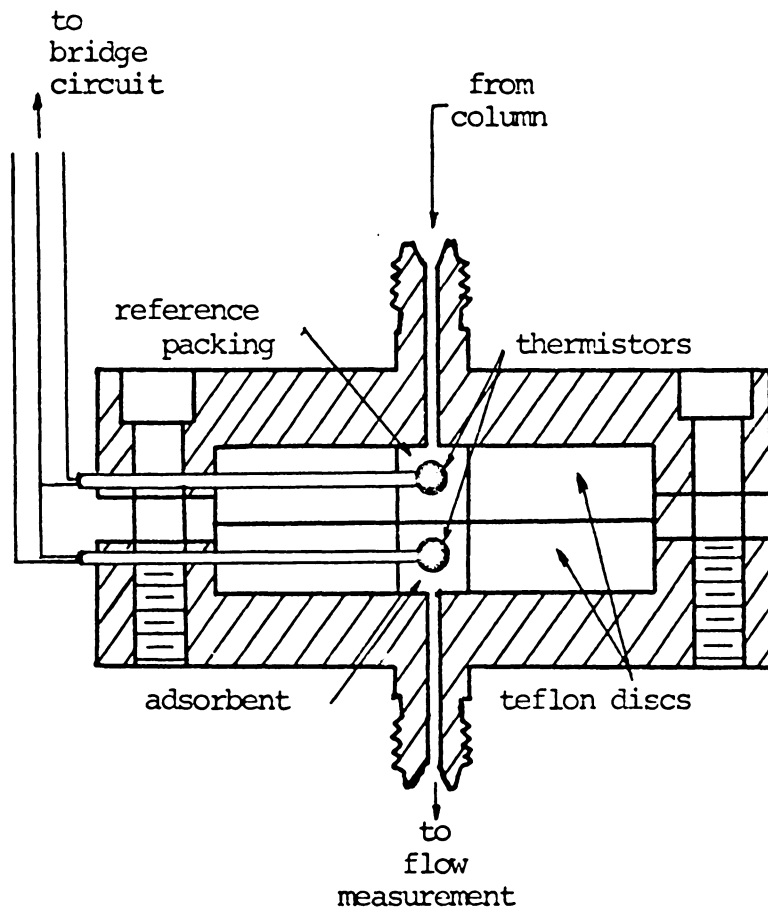


Figure 2. Schematic Diagram of Micro-Adsorption Detector

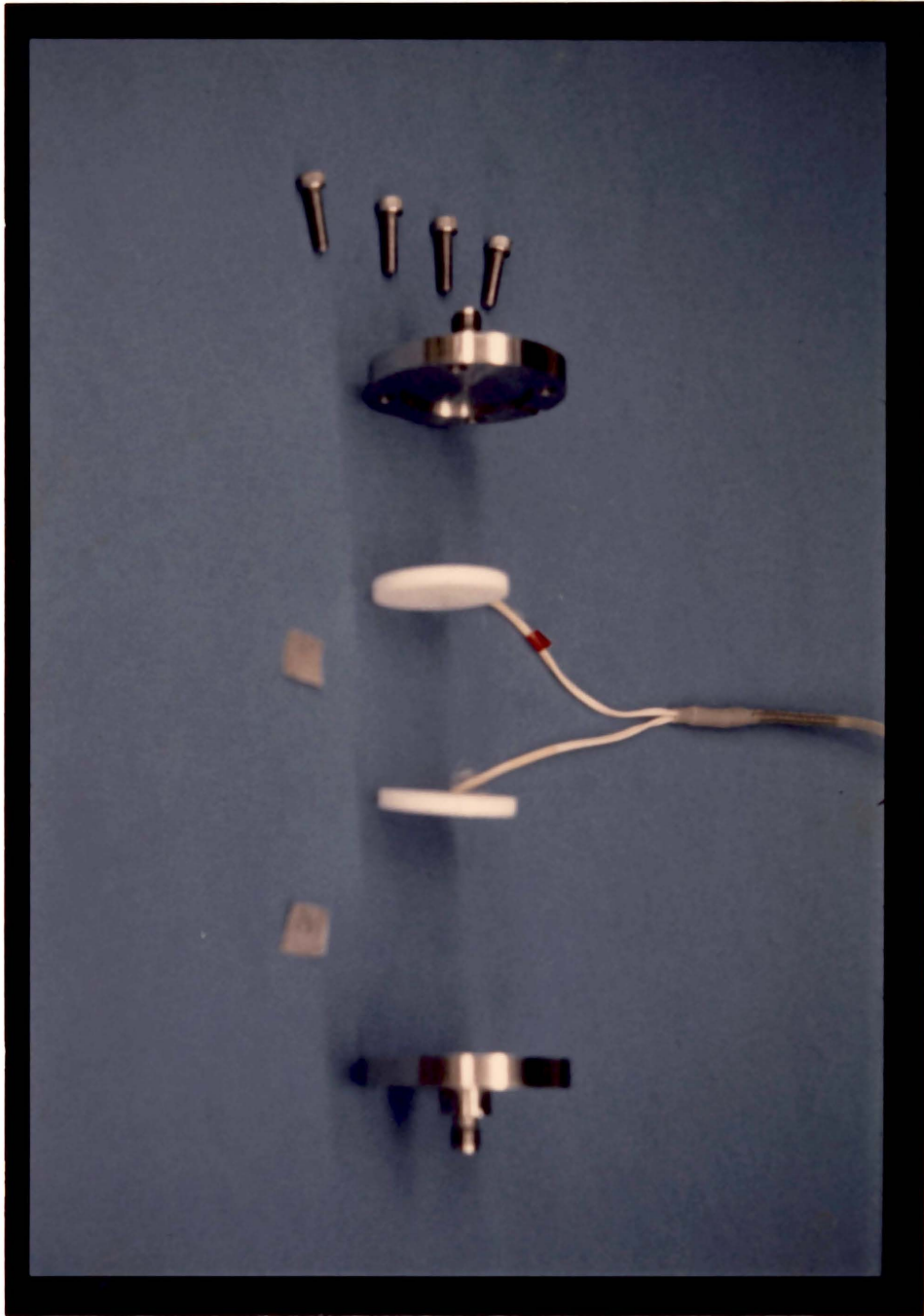


Figure 3. Photograph of Micro-Adsorption Detector Components

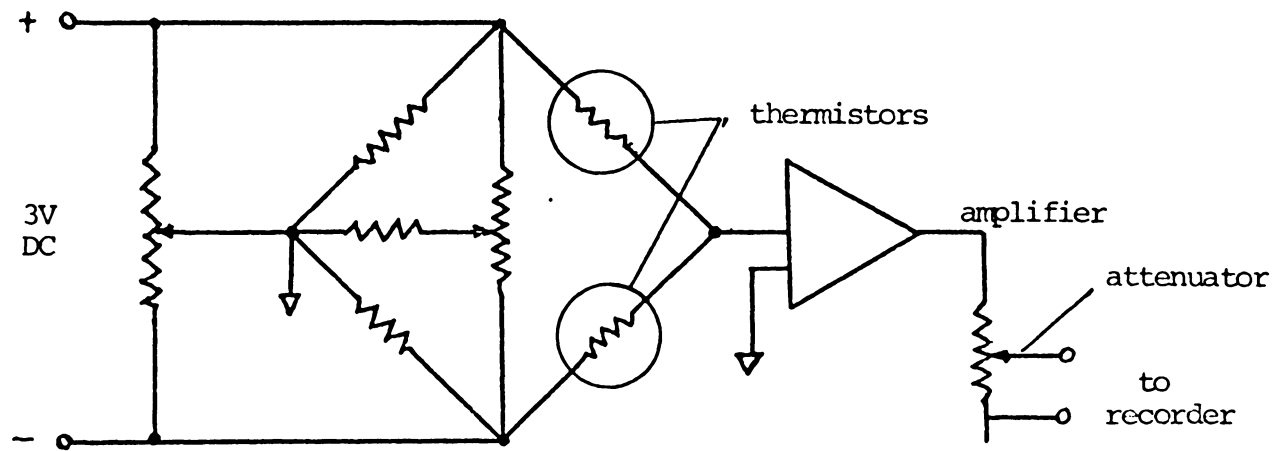


Figure 4. Schematic Diagram of Micro-Adsorption Detector Bridge Circuit

sorption begins. It seems important to clarify here what our results have shown about the beginning of desorption. With very small sample sizes, and most adsorbents the desorption begins immediately after the maximum concentration. Desorption however is a separate process from adsorption, in an overloaded situation, desorption may be very slow, and may not cause a decrease in temperature for several seconds, even minutes after the maximum concentration. In this case the peak shape, due to temperature differences will return to the original baseline, but will not record a negative temperature difference until desorption starts. Thus the backside of the positive peak can reflect two mechanisms which will return the peak to the baseline, less net adsorption, and/or desorption. It seems important to point out these phenomena early in this work, since there is considerable confusion about the mechanisms responsible for the peak shape observed. The desorption process is normally a slower process than adsorption, and may continue for several minutes. The result is a broadening and tailing of the observed peak. This detector contribution to band broadening is a major limitation to the analytical use of the MAD as a general purpose LC detector.

#### B. Pumping System

Since the MAD can detect temperature differentials of  $5 \times 10^{-5}$  °C, a thermostated environment and constant flow rate of the mobile phase are essential for stable operation.

Thermostating was provided by immersing the detector in a stirred two liter water bath in an insulated container. Liquid transfer lines

were encased in rubber tubing.

Two methods of pumping the mobile phase were tried. The first method was the pump supplied with the micro-adsorption system. This consisted of a 450 ml. solvent reservoir fitted with a dip-tube. Gas pressure from a cylinder is applied to the top of the liquid forcing it up through the dip-tube and through the column and detector. Nitrogen and helium were used. While this method was inexpensive and could supply a constant flow rate it had three disadvantages:

- (1) The flow rate was difficult to regulate.
- (2) The capacity of the reservoir was finite, in this case 450 milliliters, and the system equilibrium was upset at each filling.
- (3) At operating pressures of over 100 psig the driving gas dissolved in the mobile phase, coming out of solution when the pressure decreased and causing pulses in the detector signal.

It has been reported that by minimizing the gas solvent interface, this method can be used successfully to 1000 psi (40).

The second method, and that finally used, was a Model D-018 Milton Roy Mini-Pump used in a system shown schematically in Figure 6. The pump was a positive displacement piston pump with 1/8 inch diameter sapphire piston, stainless steel body, Teflon seals, and double sapphire ball check valves on suction and discharge sides. The pump delivery was variable from 10 to 240 ml/hr using a cam drive and micrometer adjustment of the pump stroke. Maximum deliverable pressure is 1000 psig.

Degassing of the mobile phase was accomplished by passing the mobile

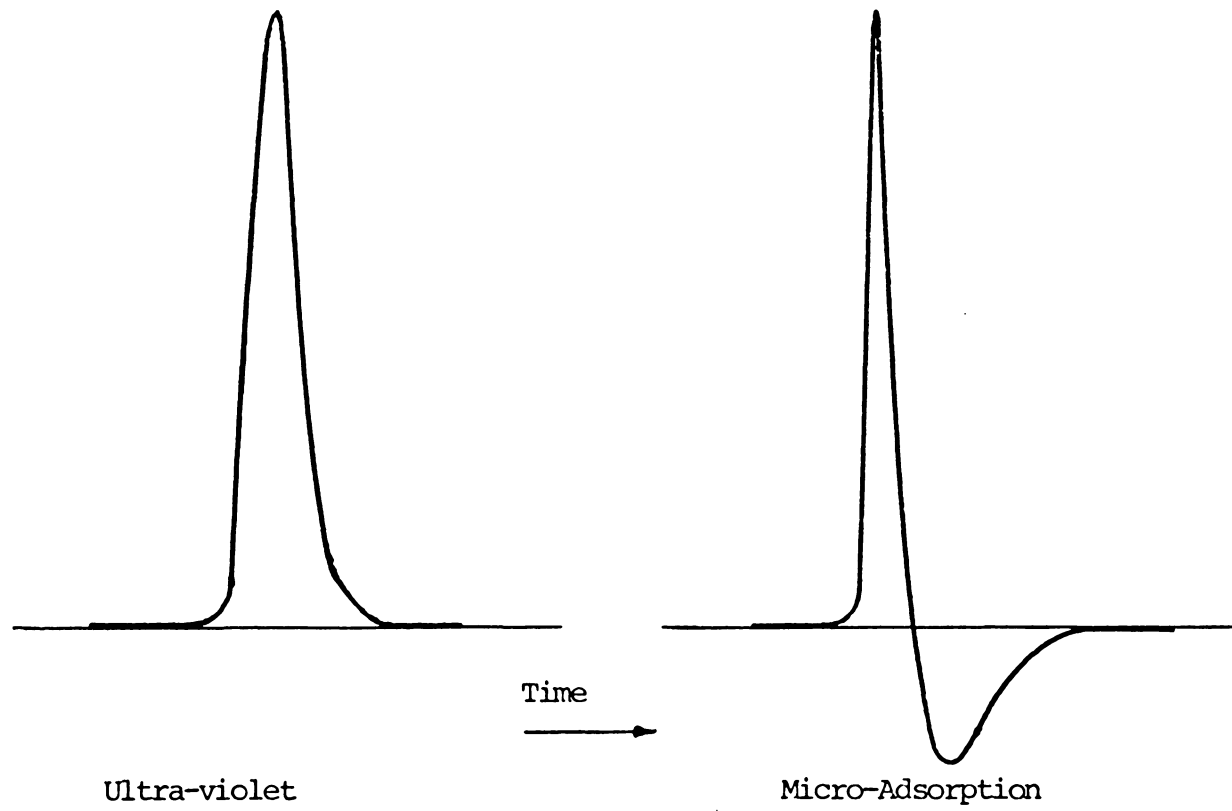


Figure 5. Comparison of the Shapes of Typical Response Curves From Ultra-Violet and Micro-Adsorption Detectors



phase through a heated stainless steel block between the mobile phase reservoir and the suction side of the pump. Off-gas from the degasser was returned to the solvent reservoir which operated under atmospheric pressure. Since trace amounts of water in the mobile phase deactivate the detector adsorbent and cause considerable loss in sensitivity, the mobile phase had to be thoroughly dried. Drying was accomplished by passing the pump discharge through a bed of 60/200 mesh silica gel (Fisher grade 950) contained in a section of 3/8 inch diameter stainless steel tubing four feet long fitted with sintered stainless steel filters on each end. The silica was activated by heating for 48 hours at 140°C. It was changed every 48 hours although no decrease in detector sensitivity was observed after 60 hours of operation.

The pressure fluctuated about 10% of maximum pressure per stroke resulting in an unacceptable noise level in the MAD output signal. This pressure oscillation was damped by filling the pressure pump reservoir half full of mobile phase and feeding the discharge from the drying column into the connection originally intended for gas pressurization. In this manner the mobile phase vapor acted as a buffer against the pump stroke and damped the pressure fluctuation. The noise level was reduced from 50 microvolts to less than 5 microvolts. This was consistent with the noise level generated by our temperature control and did not warrant more effort on our part.

### C. Calibration Apparatus

To calibrate the response of the MAD with the temperature generated in the adsorption cell, it was necessary to supply accurately known amounts of temperature change. This was accomplished by passing accurate-

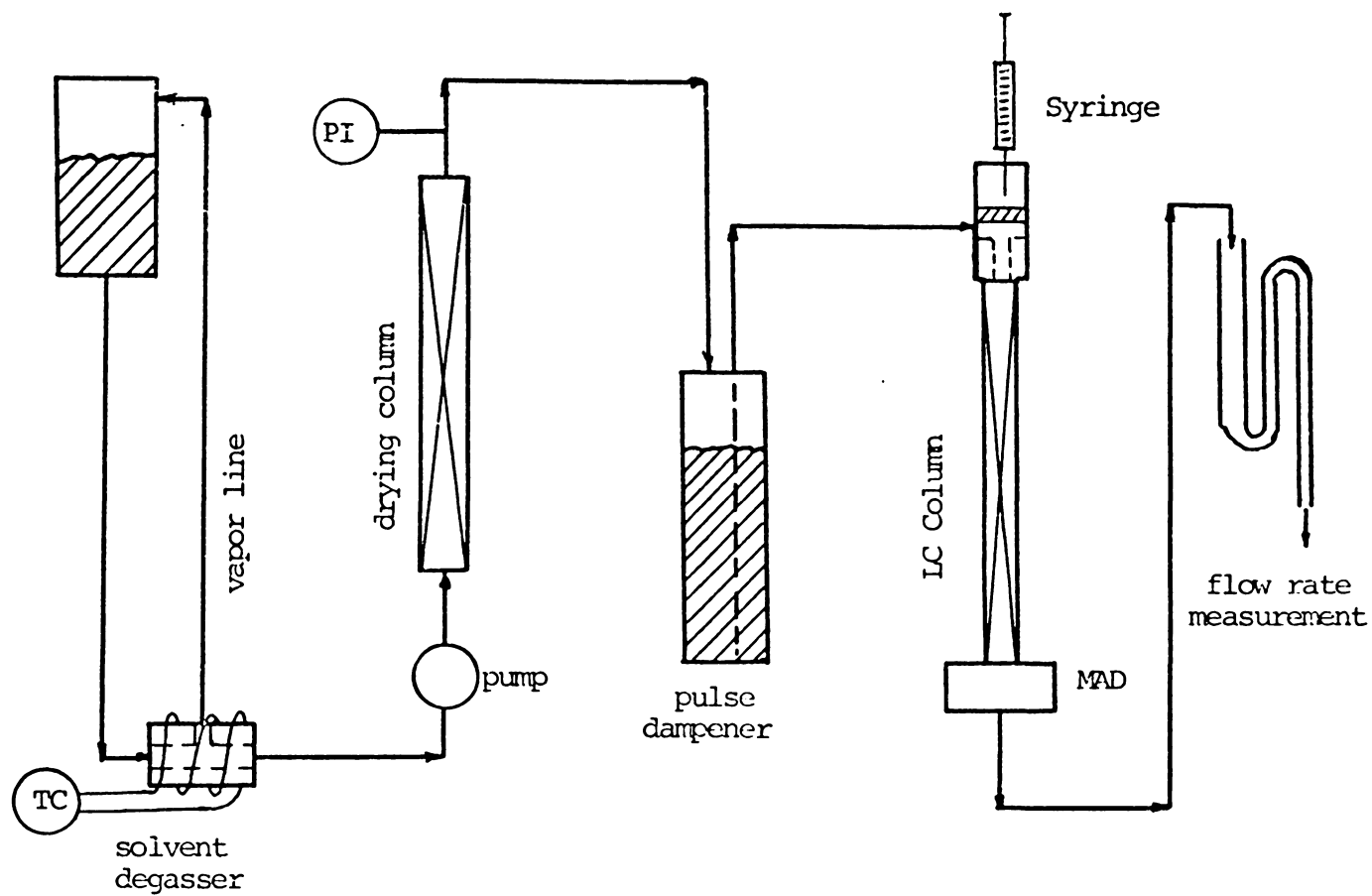


Figure 6. Flow Diagram of Liquid Chromatographic System

ly known currents through a precision resistor mounted between the two thermistors. A diagram of the calibration apparatus is shown in Figure 7 and an exploded photograph illustrating location in the detector is shown in Figure 8.

The calibration apparatus consisted of a 1.5 megohm resistor, a battery power supply, and a 10 turn variable resistor for control of the voltage across the resistor. The resistor was mounted in teflon discs identical to those holding the thermistors. The resistance and voltage were measured using a Keithley Model 160 digital multimeter, with accuracies of  $\pm 0.0004$  megohms and  $\pm 0.05$  volts respectively.

#### D. Data System

The output signal from the MAD was recorded on a Westronics Model LD11AD, 1 millivolt, dual pen recorder with disc integrator. When the system included use of the Gow-Mac gas chromatographic unit its output was recorded on the second pen of the same recorder.

In addition to the analog recorder a digital data logger was employed in runs studying peak areas. The MAD analog signal was fed in parallel to the recorder and to a Keithley Model 160 digital multimeter. The output from the multimeter was a digitized millivolt signal, which was converted to hard copy as printed output and ASCII coded punched paper tape. The interface between the multimeter and a Teletype printer and punch was designed and built by the Chemistry Department Electronics Shop. The digitized data were then read from the paper tape into the Digital PDP 8/I computer and processed. The list of focal programs used in this study is found in the Appendix and is followed by the individual programs.

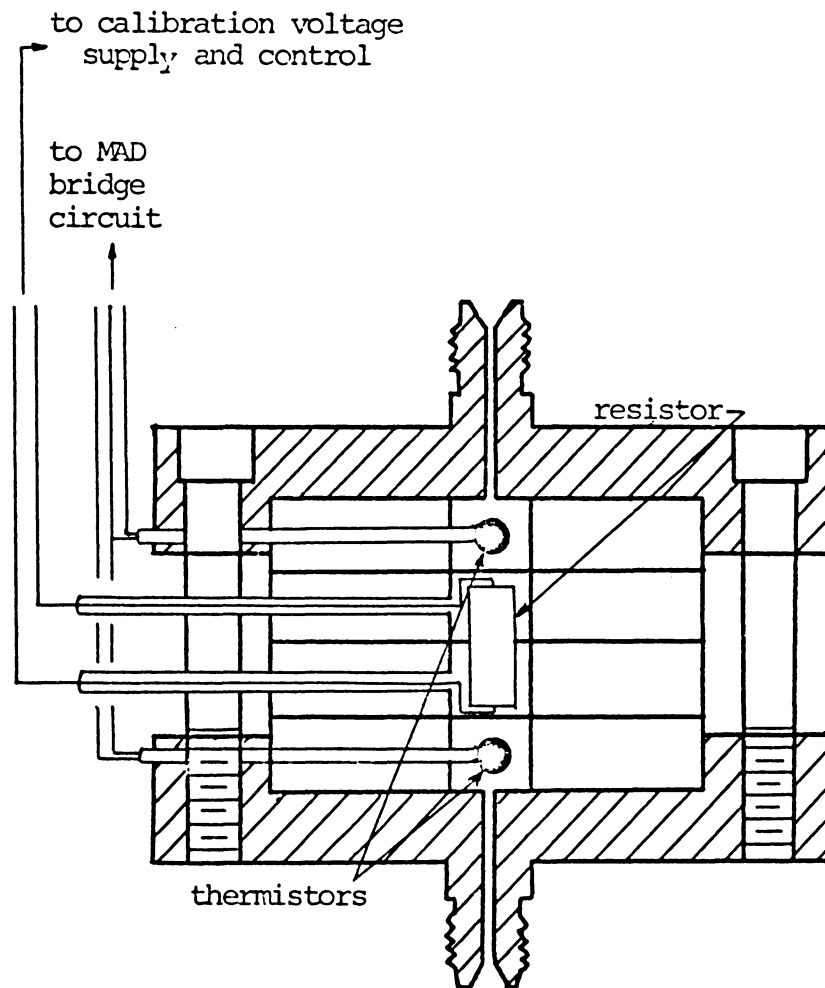


Figure 7. Schematic Diagram of Micro-Adsorption Detector  
With Calibration Apparatus in Place

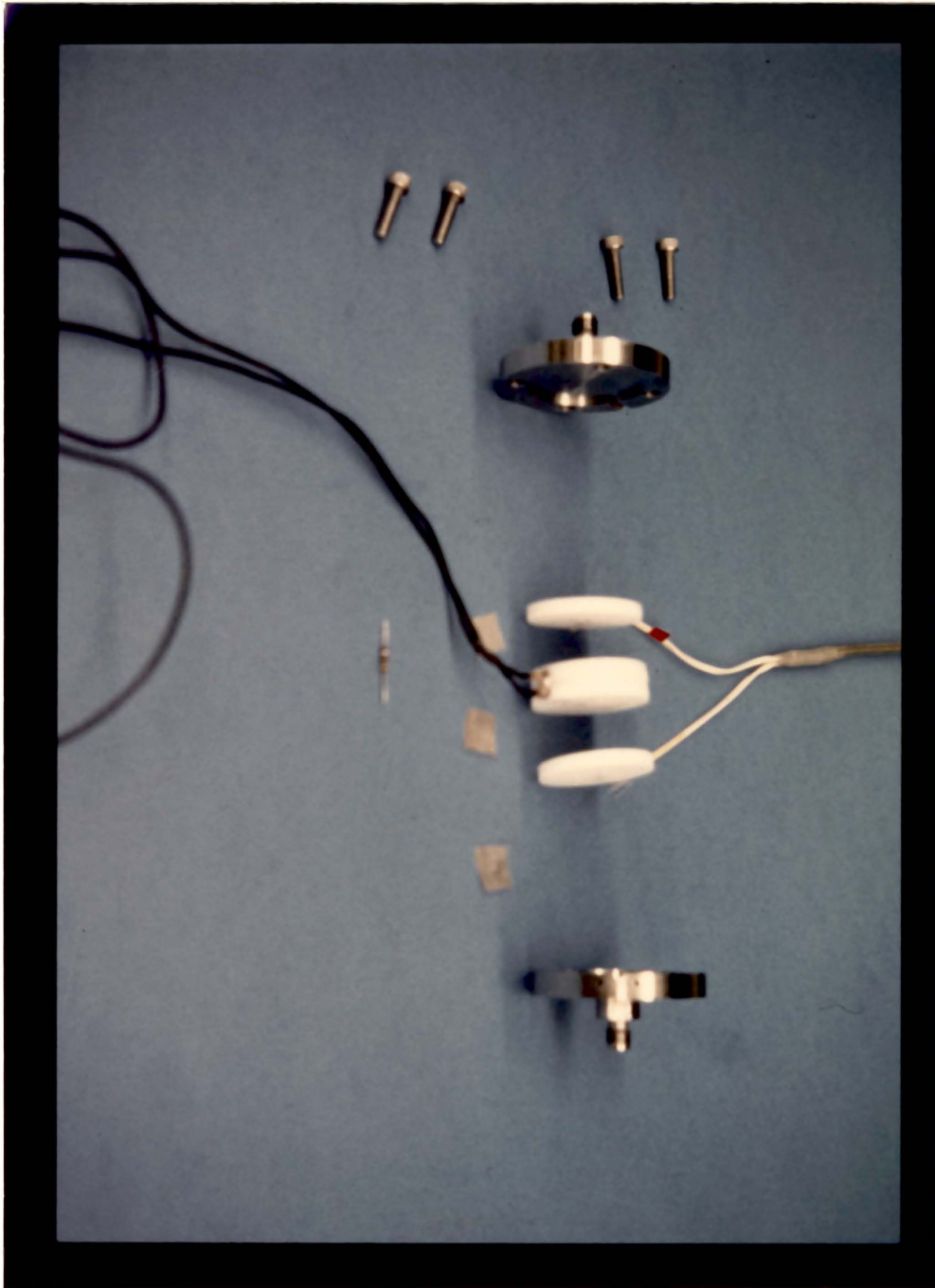


Figure 8. Photograph of Micro-Adsorption Detector Showing Placement of Calibration Apparatus

### Systems Operation

The mobile phase used in this work was benzene. It was chosen primarily because it can serve as a solvent for a wide range of samples. It is also readily available and inexpensive.

The solutes, (listed in Table II) were chosen to represent a range of chemical types, physical sizes, shapes, and properties.

To minimize adulteration of the samples with water, the liquids were handled in two milliliter vials fitted with a Teflon coated silicone elastomer septum. A one millimeter hole was drilled in the screw cap so that a syringe could be inserted through the septum and liquid withdrawn. Each undiluted solute was placed in a vial approximately half full of 60/200 mesh silica gel (Fisher 950) which had been activated at 140°C for several days. In preparing a benzene solution the sample was withdrawn with a syringe and transferred to a preweighed, dry 25 ml volumetric flask which was purged with dry nitrogen. Benzene, dried over silica, was added to the weighed sample. The flask and contents were weighed again. Several dry two milliliter vials were filled simultaneously so that one standard solution was sufficient for all of the studies.

Gaseous samples were prepared in a similar manner except that bottles of 250 milliliter capacity were dried and purged with helium several hours before injecting silica dried liquid samples and sealing with a serum cap.

Sample dilutions were selected such that a 10 microliter sample of liquid gave approximately seventy-five percent full scale recorder deflection at an attenuation of 64 (48 millivolts). In all cases this

exceeded the linear range of the detector. This was essential to determine the upper limit of the linear range. The lower limit, minimum detectable quantity, was defined as that sample size which produced a signal two times the noise level.

The adsorbents investigated were porous glass beads manufactured by Corning Glass and obtained from Varian Aerograph; Corasil II, a porous silica marketed by Waters Associates; Zipax, a solid silica bead with a porous surface manufactured by E. I. duPont; Sil-X, an experimental porous silica developed by Nester Faust Corporation; and Sterling FT, a graphitized carbon manufactured by the Cabot Corporation. The packing for the reference cell in all cases was non-porous glass beads manufactured by the 3M Company. Photomicrographs of these materials are shown in Figures 9 to 14.

A number of differences are apparent in the photomicrographs. The Corning glass beads and the Sil-X silica particles with surface areas of 237 and 275  $\text{m}^2/\text{gm}$ , respectively are both quite crystalline in appearance and range widely in size. Their non-uniform sizes allowed these materials to pack more tightly than regular sized particles. Solutes were more strongly adsorbed than with the other packings used. The large surface areas were also indicative of a high degree of porosity.

The 3M and Corasil beads had surface areas of 0.088 and 17.8  $\text{m}^2/\text{gm}$ , respectively and were nearly uniformly spherical with a relatively narrow range of sizes and much lower porosity. The 3M beads have a smooth surface at the magnification used, and were inert as an adsorbent. No interaction with solutes was observed in this study, confirm-

TABLE II

## List of Compounds used as Solutes

## Alcohols

- Methanol
- Ethanol
- n-Propanol
- n-Butanol
- n-Pentanol
- n-Heptanol
- n-Octanol

## Ketones

- Acetone
- Methyl Ethyl Ketone
- Methyl iso-Butyl Ketone

## Benzoate Esters

- Methyl Benzoate
- Ethyl Benzoate
- Butyl Benzoate
- Benzyl Benzoate

## Substituted Benzenes

- Toluene
- Xylene
- Ethylbenzene

## Hydrocarbons

- n-Hexane
- n-Heptane
- n-Octane



ing their usefulness as an inert reference material. The Corasil beads appeared to have a rough surface and of course a much higher surface area than the 3M beads. They were not as strong an adsorbent as the Corning or Sil-X packings.

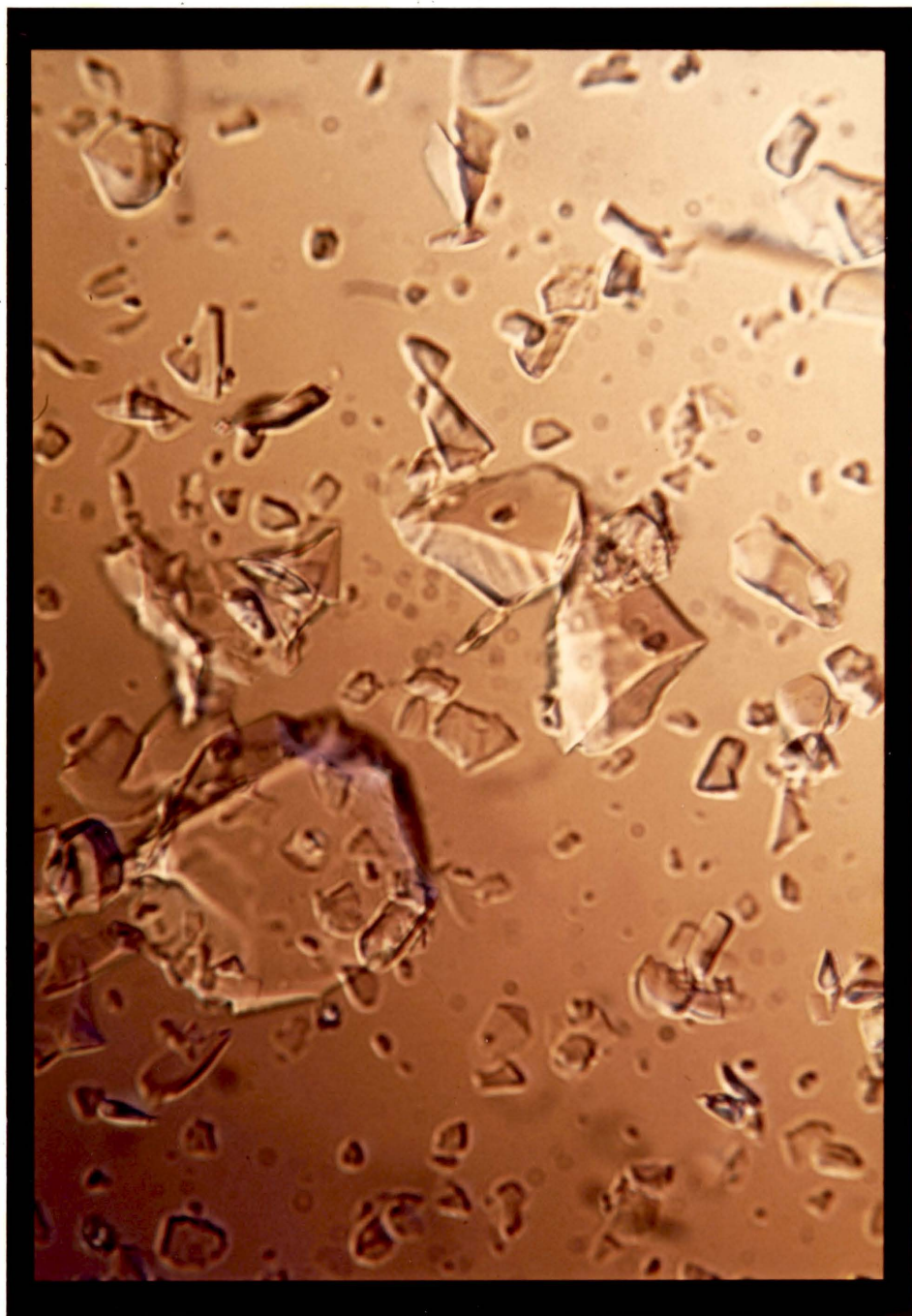
The Zipax particles were spherical, had a surface area of  $0.96 \text{ m}^2/\text{gm}$ , and were the weakest of the siliceous adsorbents. Adsorbent activity correlated well with the surface areas measured by the BET method. The measurements were made by Dr. J. P. Wightman, Chemistry Department, Virginia Polytechnic Institute and State University.

The Sterling FT carbon was irregular in both size and shape, with a surface area of  $12.1 \text{ m}^2/\text{gm}$ . The carbon was not as strong an adsorbent as the siliceous material.

#### Liquid Chromatographic Operation

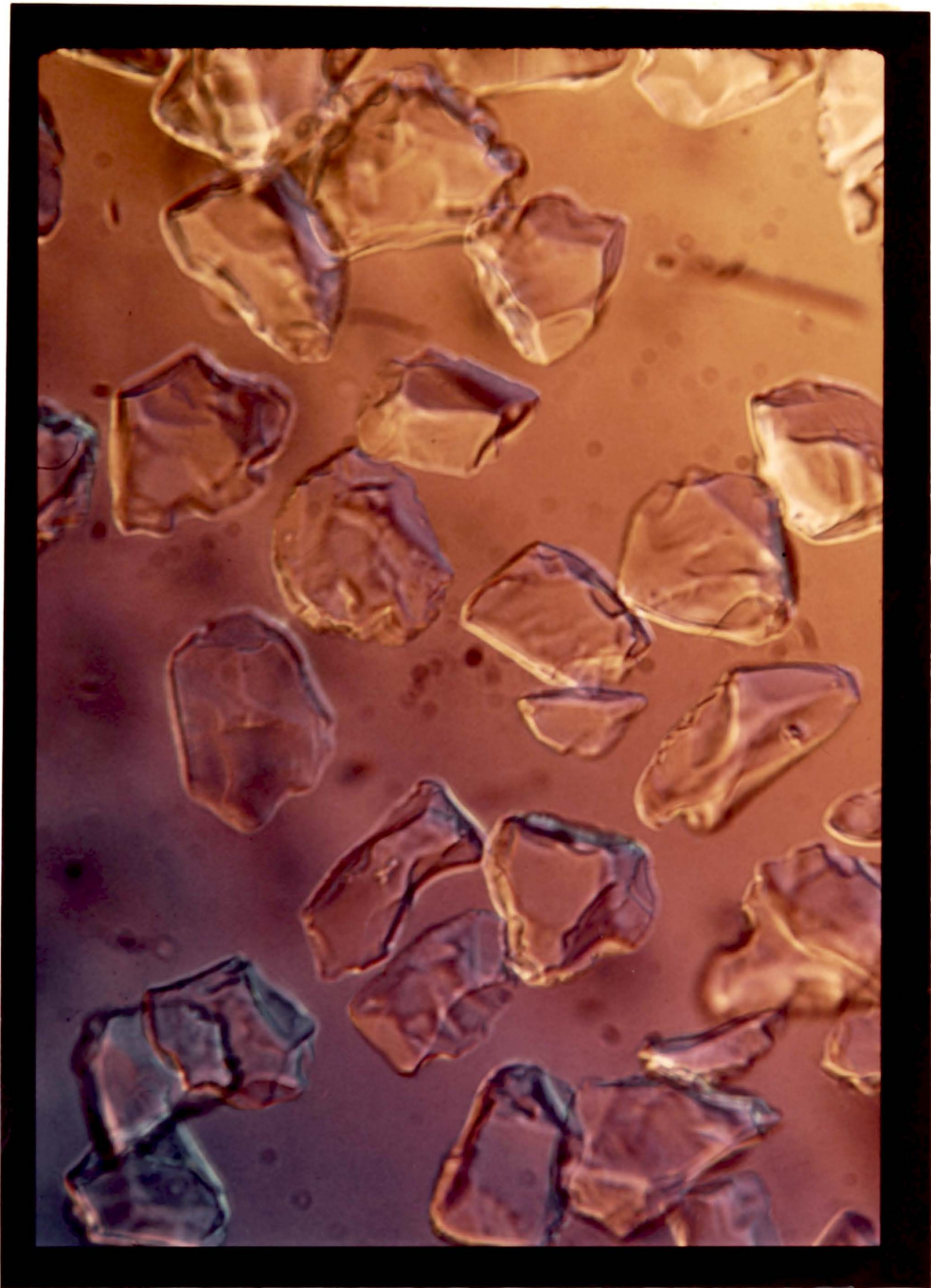
Runs to determine the linear dynamic range and sensitivity of the MAD were made with benzene as the mobile phase and samples of benzene solutions of each of the solutes prepared as previously described. Sample solutions varied from 0.1 to 10 microliters representing solute concentrations of  $10^{-4}$  to  $10^{-6}$  molar. Injections smaller than one microliter were made with a one microliter Hamilton syringe. Samples from 1 to 10 microliters were injected with a 10 microliter Hamilton syringe.

Flow rates of the mobile phase were measured at the discharge from the MAD using a siphon-dumped measured volume, and timed with a stopwatch. The average dump volume was 6.18 ml with a standard deviation of 0.0098 ml.



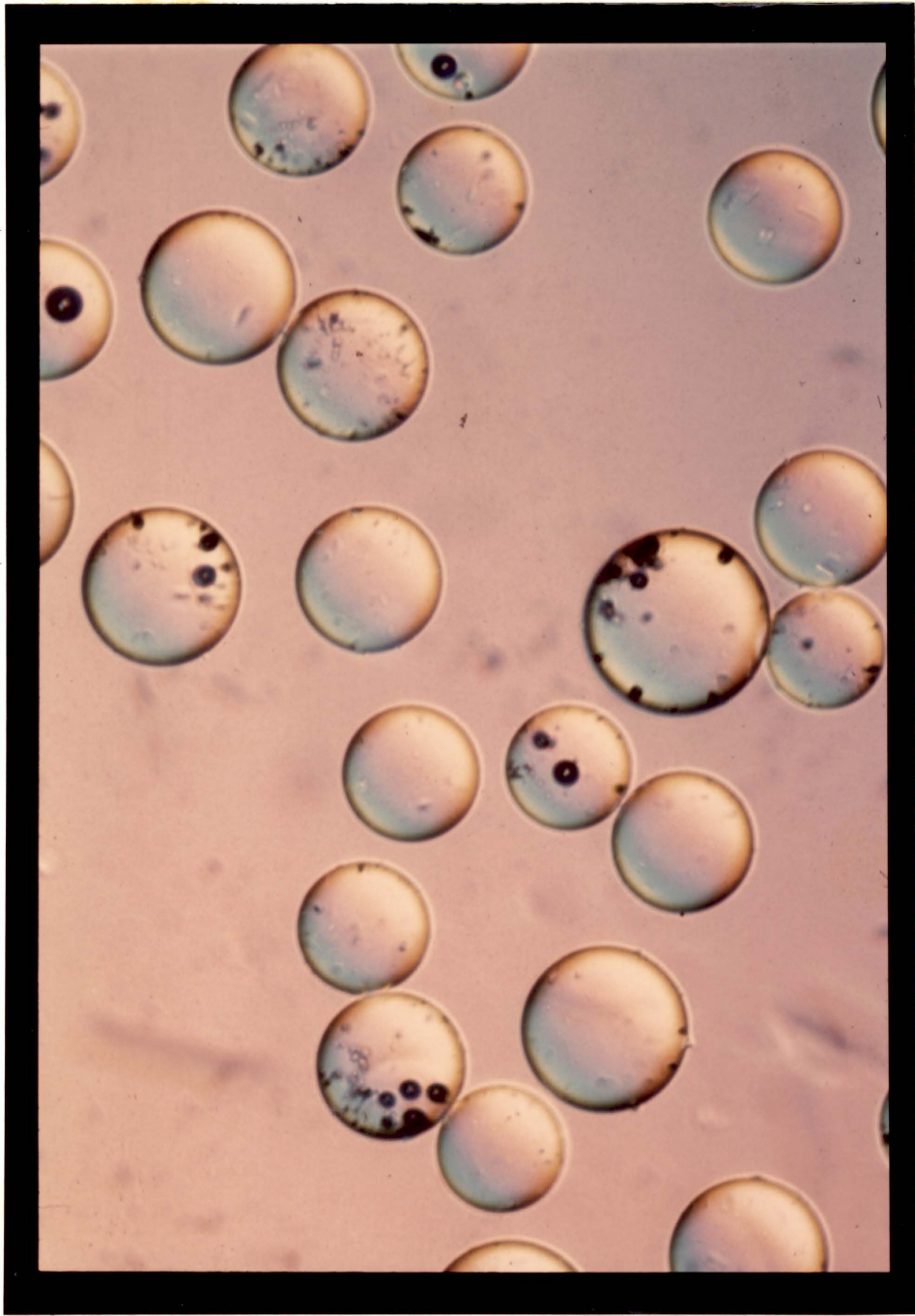
← 0.10 mm →

Figure 9. Photomicrograph of Porous Glass Beads  
(Corning Glass Co.)



┆———— 0.10 mm. ———┆

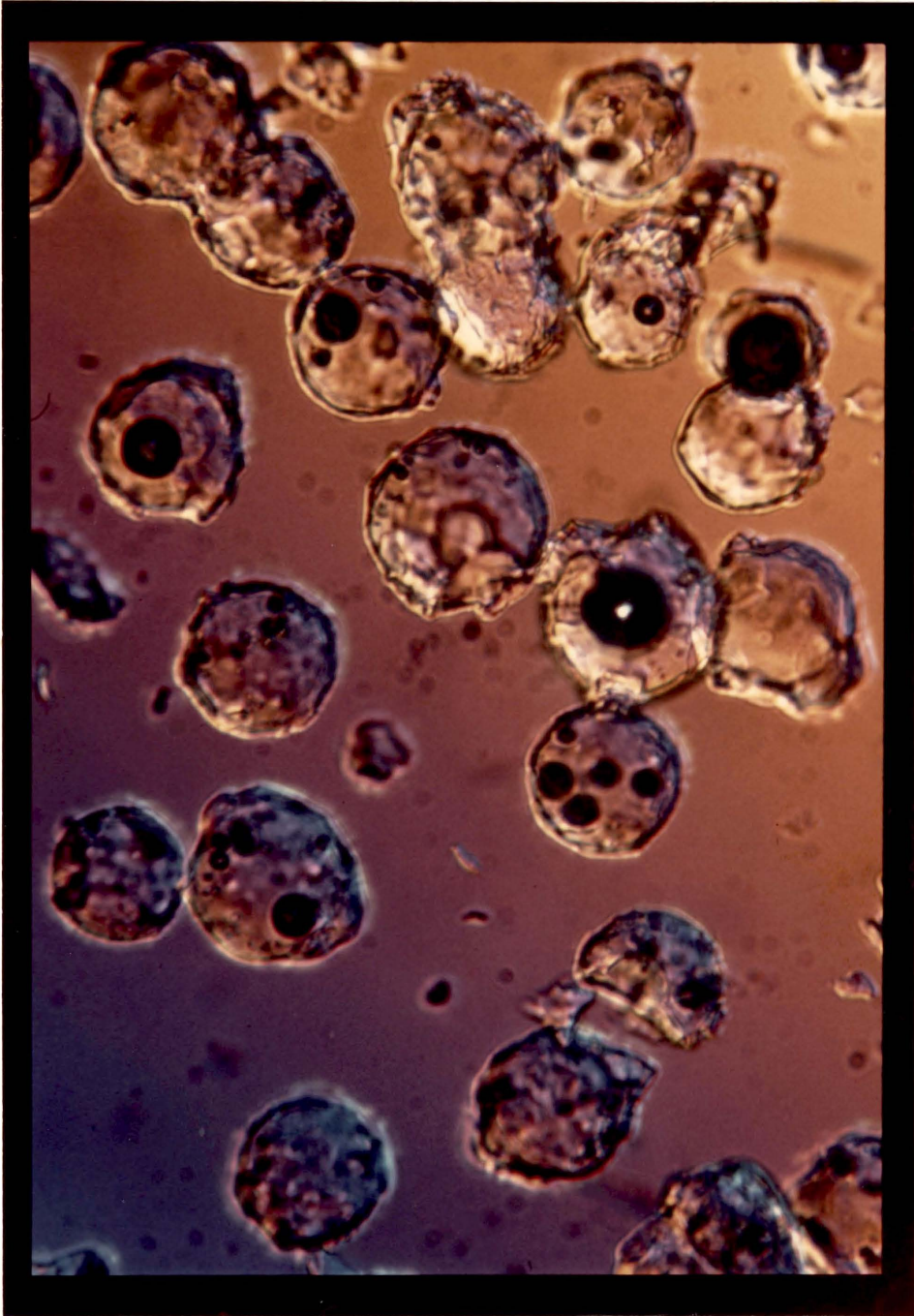
Figure 10. Photomicrograph of Sil-X (Nester/Faust Co.)



← 0.10 mm. →

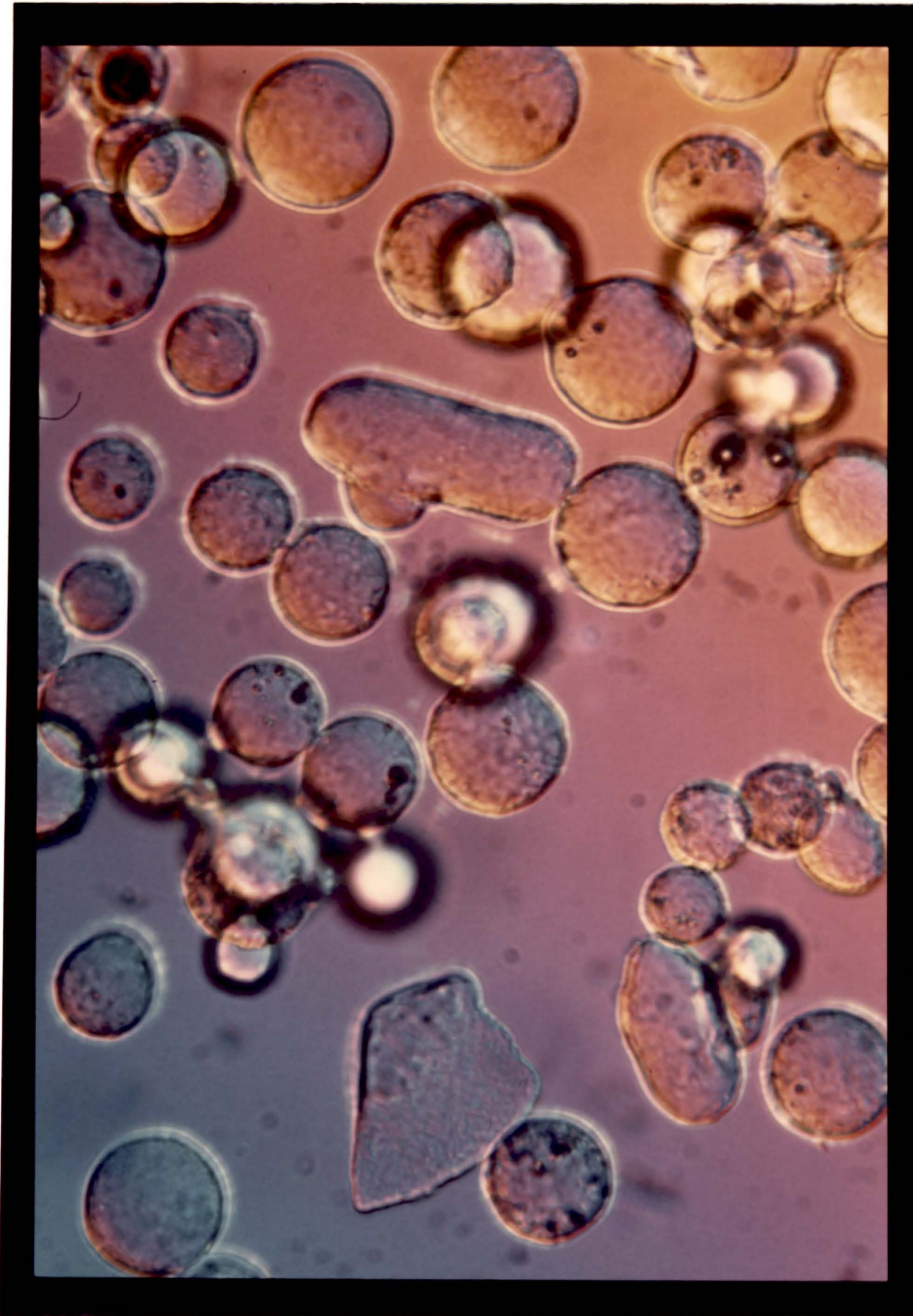
Figure 11. Photomicrograph of Smooth Glass Beads  
(3M Co.)





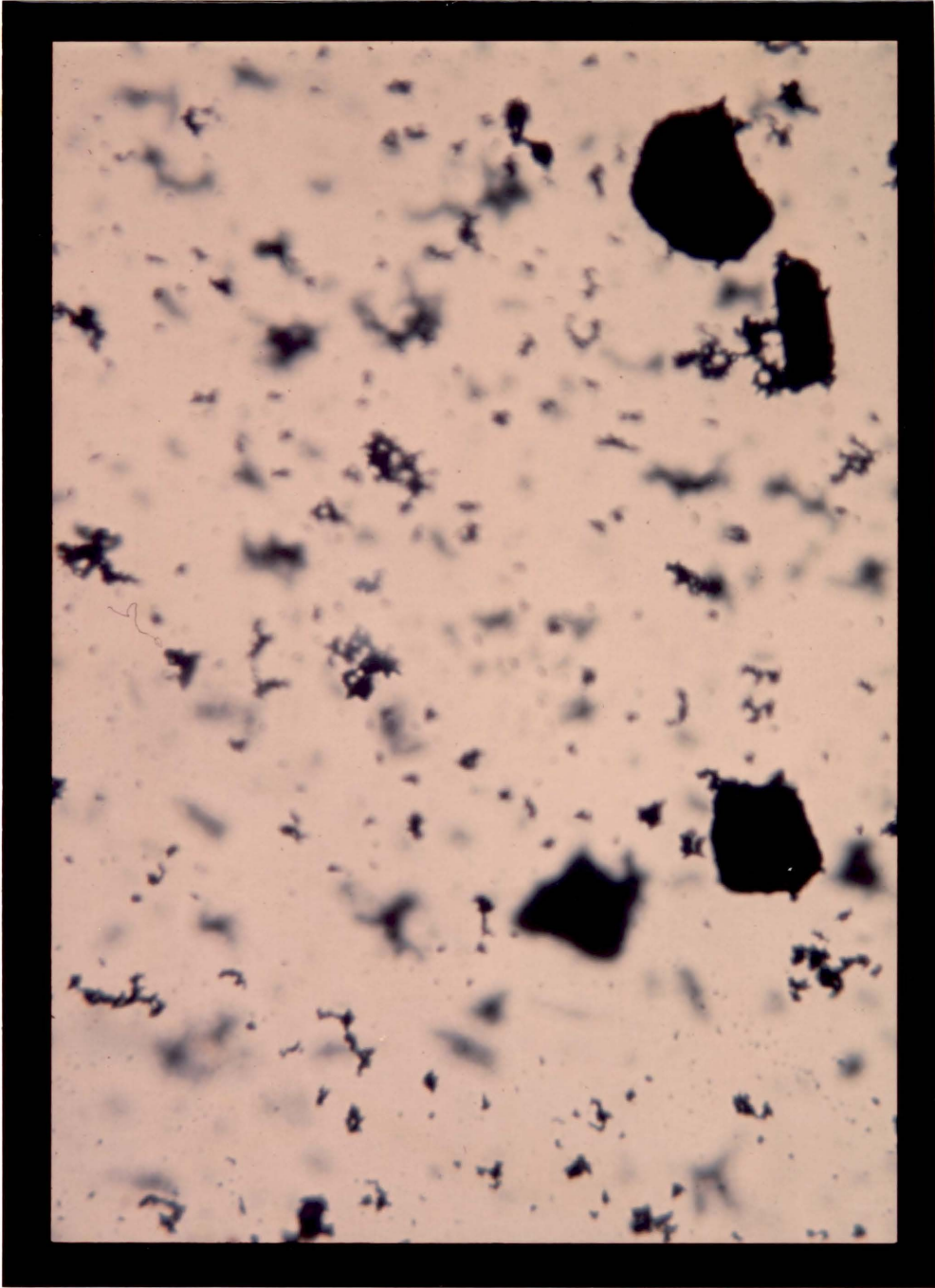
← 0.10 mm. →

Figure 12. Photomicrograph of Corasil II  
(Waters Associates)



┆———— 0.10 mm. ———┆

Figure 13. Photomicrograph of Zipax  
(E.I. duPont deNemours)



← 0.10 mm. →

Figure 14. Photomicrograph of Sterling FT Carbon  
(Cabot Corp.)



The linear dynamic range and sensitivity measurements were performed with no chromatographic column; the injection port was connected to the detector by an unpacked 6 inch length of 1/16 inch outside diameter stainless steel tubing. The empty tubing produced solute peaks of equal retention time and equal diffusion effects.

In addition to the above detector runs, several runs were made to investigate separations on the various materials used as adsorbents. In these the columns consisted of 20 centimeter long sections of 1/8 inch diameter stainless steel tubing packed with the stationary solid phase, or stationary liquid phase on a solid support. The column packing technique was to plug the discharge end of the column with glass wool (approximately 1/4 inch) and then add small portions of packing material equivalent to about 2cm. of column length. Vigorous tapping of the column on the bench-top was carried out for one minute between each addition. A 1/4 inch plug of glass wool was fitted into the top of the tightly packed column. The length of the glass wool plugs was not reported in the column length.

#### Gas Liquid Chromatographic Operation

The detector was also evaluated as a potential gas chromatographic detector. Two modes of operations were employed in the gas chromatographic investigations. In the first runs, the Gow-Mac Model 69-500 gas chromatograph was operated at a temperature high enough (95°C) to rapidly elute all samples. Thus the sample band spent a minimum of time in the column and suffered a minimum of broadening. In this manner the response of the MAD to the solute vapor in helium carrier gas



was studied.

The second mode of operation was to operate the GLC unit at a temperature which permitted differential retention of the solutes. In this way it was possible to study the correlation between the magnitude of the detector signal and the retention time of a solute by the same sorbent when utilized as a gas chromatographic column packing.

The purpose of these runs was to demonstrate the utility of the MAD in quickly and conveniently screening column packings and in predicting separation results from detector response.

All gas chromatographic column packings were prepared by the pan coating method (21) using chloroform as solvent; the three foot long, 1/8 inch diameter columns were packed with vibration and tapping. Each end was plugged with glass wool.

Injection of liquid samples into the gas chromatograph was made with a 10 microliter syringe; gas samples were injected with a 100 microliter Hamilton gas tight syringe.

#### Method of Response Measurement

The methods of measuring a typical gaussian gas chromatographic peak and their relative precisions are summarized by McNair and Bonelli (21); however, the MAD output was a non-gaussian peak and these methods were not directly applicable. The MAD response was a more complex curve containing both positive and negative portions, and consequently no data existed on the relative precisions of measurement techniques. To determine the most practical and precise means of measurement a series of runs were made at various solute concentration levels. The outputs

were analyzed from manually measured peak heights, from peak areas measured with a disc integrator, and from computer integration of the off-line digitized data.

The system used for this study consisted of acetone as solute and benzene as the mobile phase with Corning porous glass beads as adsorbent in the sensing cell. This system gave a strong, well defined, reproducible signal. The output signal was recorded on a strip-chart recorder with disc integrator. It was also digitized and recorded as printed copy and punched paper tape. Data points were taken at one second intervals, a positive peak consisting of a minimum of twenty points.

Referring to Figure 15 the positive peak height was defined as the vertical distance from A to B; negative peak height as the distance from A to C, and total peak height as the distance from B to C. The total positive peak area was defined as the area above the baseline and the negative peak area was defined as that area below the baseline. Total peak area was taken as the sum of these two areas.

Mechanically there was an advantage in measuring total peak height rather than either positive or negative heights, as it was easier to determine the peak maximum and minimum than it was to extend the baseline. Accuracy in measuring the longer distance should also be better, particularly for small peaks.

The positive and negative peak heights and widths were measured manually from the chromatogram. The areas were determined from the disc integrator and by computer integration of the punched tape data using a Digital Equipment Corporation model PDP 8/I computer and a Simpson's rule integration procedure given in Appendix I. The standard

deviations of ten replicate runs were compared at each concentration level and tested for their statistical significance, using Fischer's F test. The data are summarized in Tables III and IV. Table V defines the F ratio and rejection region for the statistical comparisons. The calculated F ratios and the statistical significance and confidence levels are given in Tables VI and VII.

### Calibration

Calibration of the MAD was made using the calibration apparatus previously described and applying from zero to sixty-seven volts to the 1.5 megohm resistor. This procedure gave temperature differentials from below the minimum detectable limit, about  $5 \times 10^{-5}$ , up to 0.3 °C.

The MAD output signal was allowed to stabilize for five minutes without voltage applied and then a two minute interval was recorded on punched paper tape. Data were collected at the rate of one point every ten seconds. Voltage was then applied and the output allowed to stabilize again. A five minute, one data point per 10 seconds, record was collected on tape. Following this, the voltage was switched off, a stable baseline was attained, and another two minute recording of the baseline was taped. A typical calibration curve is shown in Figure 16. Return to the original baseline was a good check on both the temperature and flow stability of the system.

The value of the resistor was checked before and after a series of calibration runs and spot checked during the runs. Its resistance did not change. The applied voltage was checked before and after each run and at maximum temperature differential. Calibrations were made with

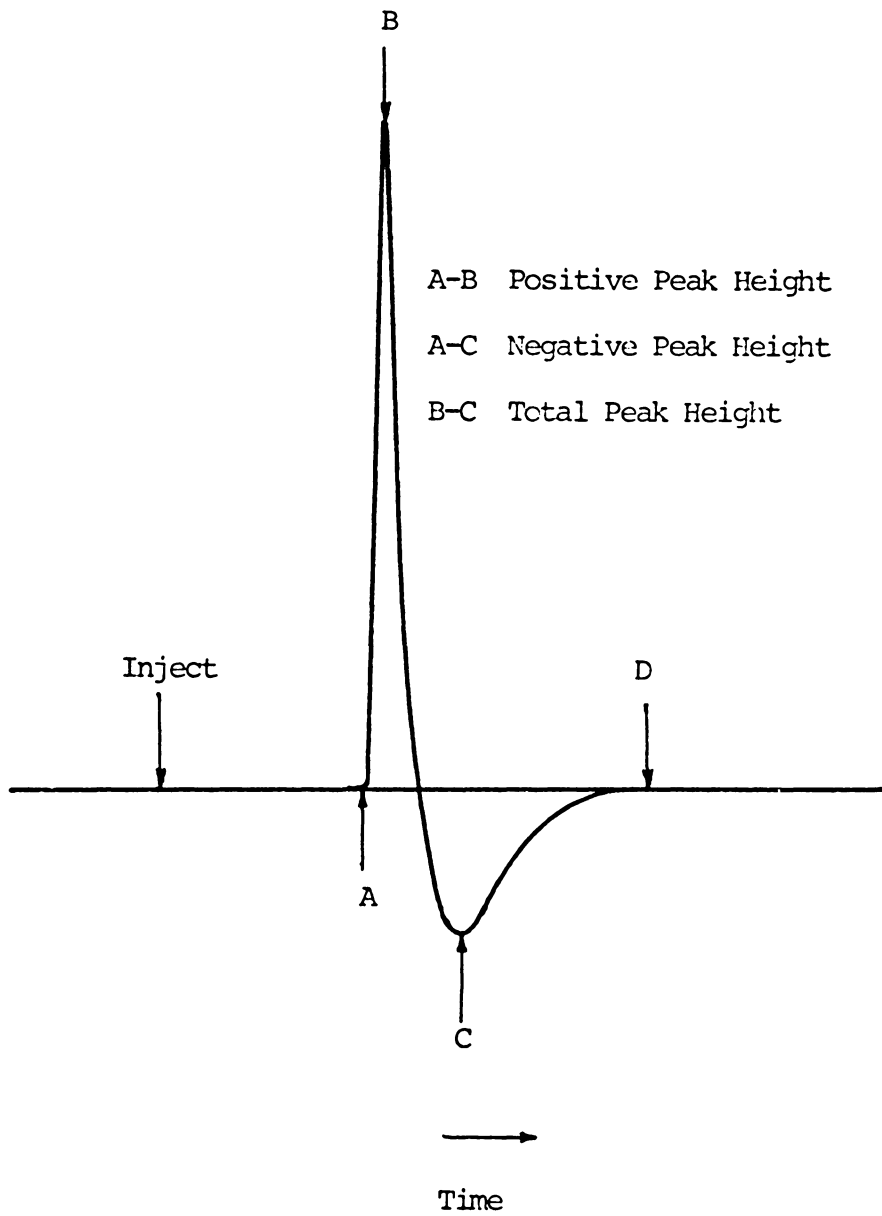


Figure 15. Definition of The Regions of The Response From  
A Micro-Adsorption Detector

TABLE III

STANDARD DEVIATION FOR PEAK HEIGHT MEASUREMENTS, % RELATIVE

SAMPLE SIZE MG'S.	DATA SYSTEM	PEAK HEIGHTS		
		POSITIVE	NEGATIVE	TOTAL
0.79	RECORDER	3.0856	9.1638	3.1954
	COMPUTER	2.7288	9.7187	3.1952
1.19	RECORDER	5.5911	13.2521	5.6214
	COMPUTER	5.2786	2.1851	5.7394
1.58	RECORDER	1.9476	8.4972	2.2260
	COMPUTER	2.4185	2.2439	2.0060
1.98	RECORDER	5.0327	9.1830	4.2439
	COMPUTER	2.3882	7.7339	2.5120
2.97	RECORDER	2.9225	12.3253	3.3240
	COMPUTER	3.1576	6.1318	3.0722
3.95	RECORDER	4.4656	13.0294	5.0732
	COMPUTER	5.1389	7.1276	4.7399

TABLE IV

STANDARD DEVIATION FOR PEAK AREA MEASUREMENTS, % RELATIVE

SAMPLE SIZE MGMS.	DATA SYSTEM	PEAK AREA		
		POSITIVE	NEGATIVE	TOTAL
0.79	RECORDER	9.9530	39.0274	16.2485
	COMPUTER	2.0119	13.2696	3.4860
1.19	RECORDER	6.7305	38.5247	13.8658
	COMPUTER	5.2897	20.2160	4.9829
1.58	RECORDER	7.0492	33.8367	8.1119
	COMPUTER	4.6363	6.4338	4.0263
1.98	RECORDER	5.8538	16.7015	9.3940
	COMPUTER	2.6578	16.4249	2.5926
2.97	RECORDER	8.0935	43.6230	20.5830
	COMPUTER	3.0256	12.3903	2.2819
3.95	RECORDER	7.4113	65.7130	20.3820
	COMPUTER	6.7913	9.9008	5.6288

TABLE V

DEFINITION OF F RATIO AND REJECTION REGION  
FOR STATISTICAL COMPARISONS TABULATED IN  
TABLES VI and VII

F - RATIO

$$F = S_1^2 / S_2^2$$

$S^2$  = Sample Variance

REJECTION REGION FOR HYPOTHESIS

$$H: \sigma_1^2 = \sigma_2^2$$

$$F \leq F_{(\alpha/2)}(V_1, V_2)$$

$\sigma^2$  = Variance

$\alpha$  = Confidence Level

V = Degrees of Freedom

TABLE VI

## F RATIO FOR PEAK HEIGHT COMPARISONS

SAMPLE SIZE GMS.		PEAK HEIGHT		
		POSITIVE	NEGATIVE	TOTAL
0.79	F RATIO	1.2786	0.8891	0.9800
		NS	NS	NS
1.19	F RATIO	2.1219	36.7813	0.9593
	LEVEL	NS	S 0.9995	NS
1.58	F RATIO	0.6435	14.3399	1.2314
	LEVEL	NS	S 0.9995	NS
1.98	F RATIO	4.4408	1.4099	2.8543
	LEVEL	S 0.975	NS	S 0.925
2.97	F RATIO	0.8566	4.0536	1.1706
	LEVEL	NS	S 0.975	NS
3.95	F RATIO	0.7551	3.3417	1.1456
	LEVEL	NS	S 0.96	NS

NS = Not Statistically Significant

S = Statistically Significant



TABLE VII

## F RATIO FOR PEAK AREA COMPARISONS

SAMPLE SIZE GMS.		PEAK AREA		
		POSITIVE	NEGATIVE	TOTAL
0.79	F RATIO	24.4735	8.6502	21.7256
		S	S	S
	LEVEL	0.9995	0.997	0.9995
1.19	F RATIO	1.6190	3.6315	7.7402
		NS	S	S
	LEVEL		0.90	0.975
1.58	F RATIO	2.3117	27.6593	4.0591
		S	S	S
	LEVEL	0.90	0.9995	0.975
1.98	F RATIO	4.8510	1.0340	13.1290
		S	NS	S
	LEVEL	0.975		0.9995
2.97	F RATIO	7.1557	12.3956	81.3641
		S	S	S
	LEVEL	0.998	0.9995	0.9995
3.95	F RATIO	1.1909	44.0583	13.1118
		NS	S	S
	LEVEL		0.9995	0.9995

three mobile phase flow rates using porous glass beads as adsorbent, and with one flow rate using Cabot's Sterling FT graphitized carbon as adsorbent.

Computer programs were written to process the punched paper tape data on the PDP-8/I computer (22). The baseline data were analyzed for consistency by calculating a mean and variance for the baseline both before and after power was applied to the calibration resistor. A mean and variance were also calculated after equilibration with power applied. These values were compared using a Student's "t" distribution to ascertain whether there was a statistical difference between the means (23, 24, 25). If the difference was statistically significant, it was used as the detector response (peak height) in calibration calculations; if the difference was not statistically significant, no calculation was made.

The temperature increase in the mobile phase was calculated using measured voltages, resistance, flow rates, and literature or handbook values of physical properties such as density, and specific heat. Equations used are defined in Figure 17. The temperature differential, and millivolt response per degree temperature differential were calculated for each calibration point.

#### A Screening Tool for Chromatographic Systems

The MAD can be useful in predicting the relative elution of compounds from a column containing a particular stationary phase. The detector response is a measure of solute/sorbent interaction and can thus be used to predict the time required to elute the sample.

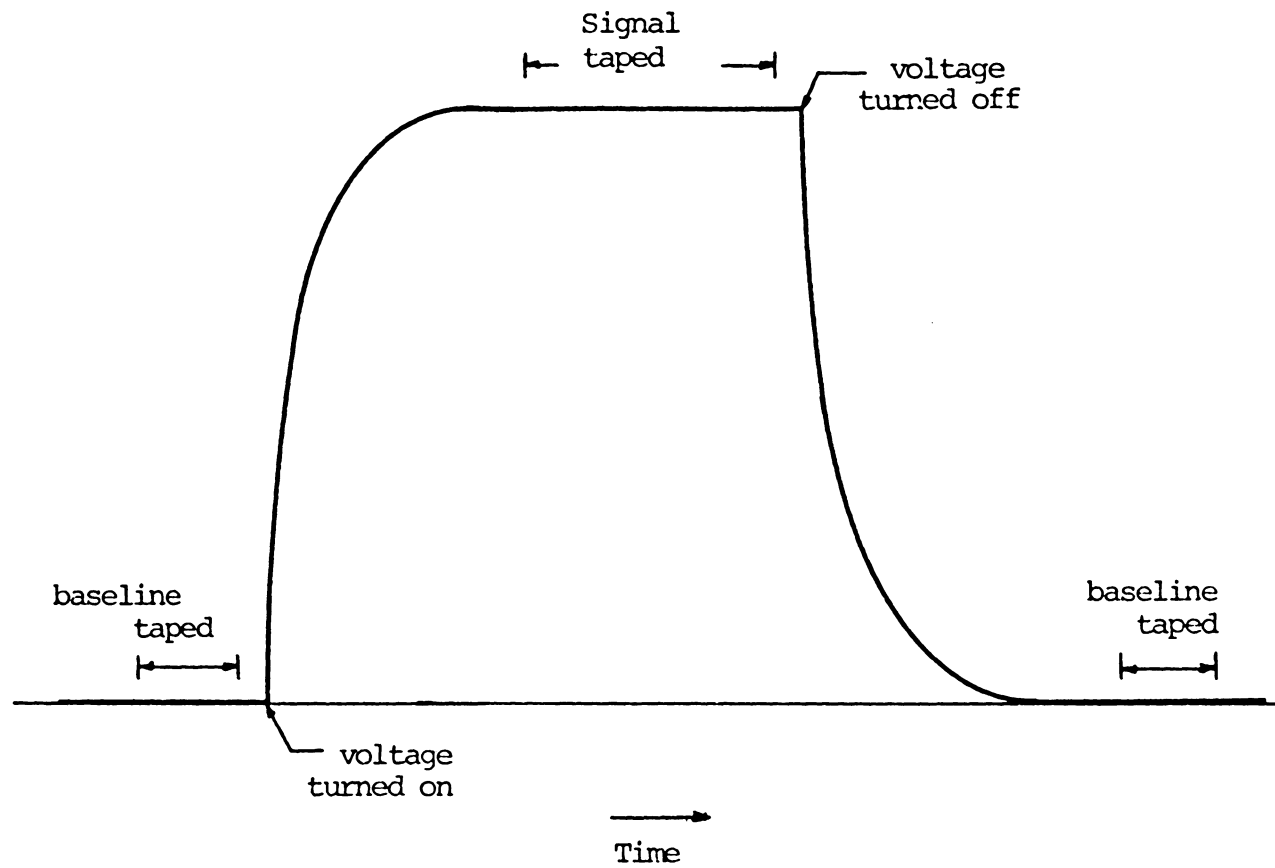


Figure 16. Typical Calibration Curve

$$\text{Power} = P = I^2 R = \frac{E^2}{R} \quad \text{Watts}$$

$$P = \frac{E^2}{R} \quad (0.239) \quad \text{Cal/Sec} \quad (1)$$

$$\text{Heat Rate} = H = (\text{F.R.}) (d) (C_p) (T) \quad \text{Cal/Sec} \quad (2)$$

Equating (1) and (2) :

$$(0.239) \frac{E^2}{R} = (\text{F.R.}) (d) (C_p) (T)$$

$$T = \frac{(0.239) (E^2)}{(R) (\text{F.R.}) (d) (C_p)}$$

P = Power, Watts

E = Electrical Potential Diff., Volts

I = Electrical Current, Amperes

H = Heat Rate of Mobile Phase, Cal/Sec

F.R. = Flow Rate of Mobile Phase, cc/Sec

d = Density of Mobile Phase, GMS/CC

C<sub>p</sub> = Sp. Heat of Mobile Phase, CAL/GM-°C

T = Change in Temperature of Mobile Phase °C

Figure 17.

Method of Calculating  
Thermistor Temperature Differentials  
From Calibration Data

The separation of benzene and cyclohexane was studied on gas chromatographic columns packed with three per cent loadings of Apiezon-L, 1,2,3 tris (2-cyanoethoxy) propane, and didecyl phthalate. These liquids were chosen to illustrate non-polar, polar and intermediate solvent behavior. Each of the three foot long, 1/8 inch diameter stainless steel columns was conditioned over night at 110°C with a helium flow rate of 20 milliliters per minute. After conditioning, the columns were connected to the thermal conductivity detector, and the retention times of benzene and cyclohexane were determined at a flow rate of 30 milliliters per minute. The effluent from the gas chromatograph was connected directly to the MAD. Thus the MAD was used as a second gas chromatographic detector with the stationary phases in the columns used as packings in the measuring side of the MAD. The GC injection port was maintained at 85°C; the columns were run at 35°C. The Apiezon-L column was also run at 95°C to elute both peaks rapidly and minimize the band broadening due to long retention times.

The detector responses of seven steroids were studied using Zipax, Corasil, Sil-X, porous glass beads, and 1% 3, 3', oxydipropionitrile on Zipax as sorbents in the MAD. The responses with Zipax (surface area of 0.96 m<sup>2</sup>/gm) were very small. Total peak heights of 5-10 mm; with 1% stationary phase on Zipax the total peak heights were greater, 40-220 mm; with the other three adsorbents, responses were universally very large. Corasil, with a surface area of 17.8 m<sup>2</sup>/gm gave responses of 300-500 mm total peak height, and the Sil-X, and porous glass beads with surface areas of 275 and 237 m<sup>2</sup>/gm respectively gave responses of 600-900 mm total peak height. When these materials were used as column

packings, benzene being the mobile phase, Zipax gave almost no retention for the steroids, and no differences in retention times. However, Corasil, Sil-X, and the porous glass beads retained the solutes to such an extent that no peaks were obtained. The 1% 3, 3' oxydipropionitrile on Zipax separated some components of the mixture. Some of these chromatograms are those shown in Figure 18.

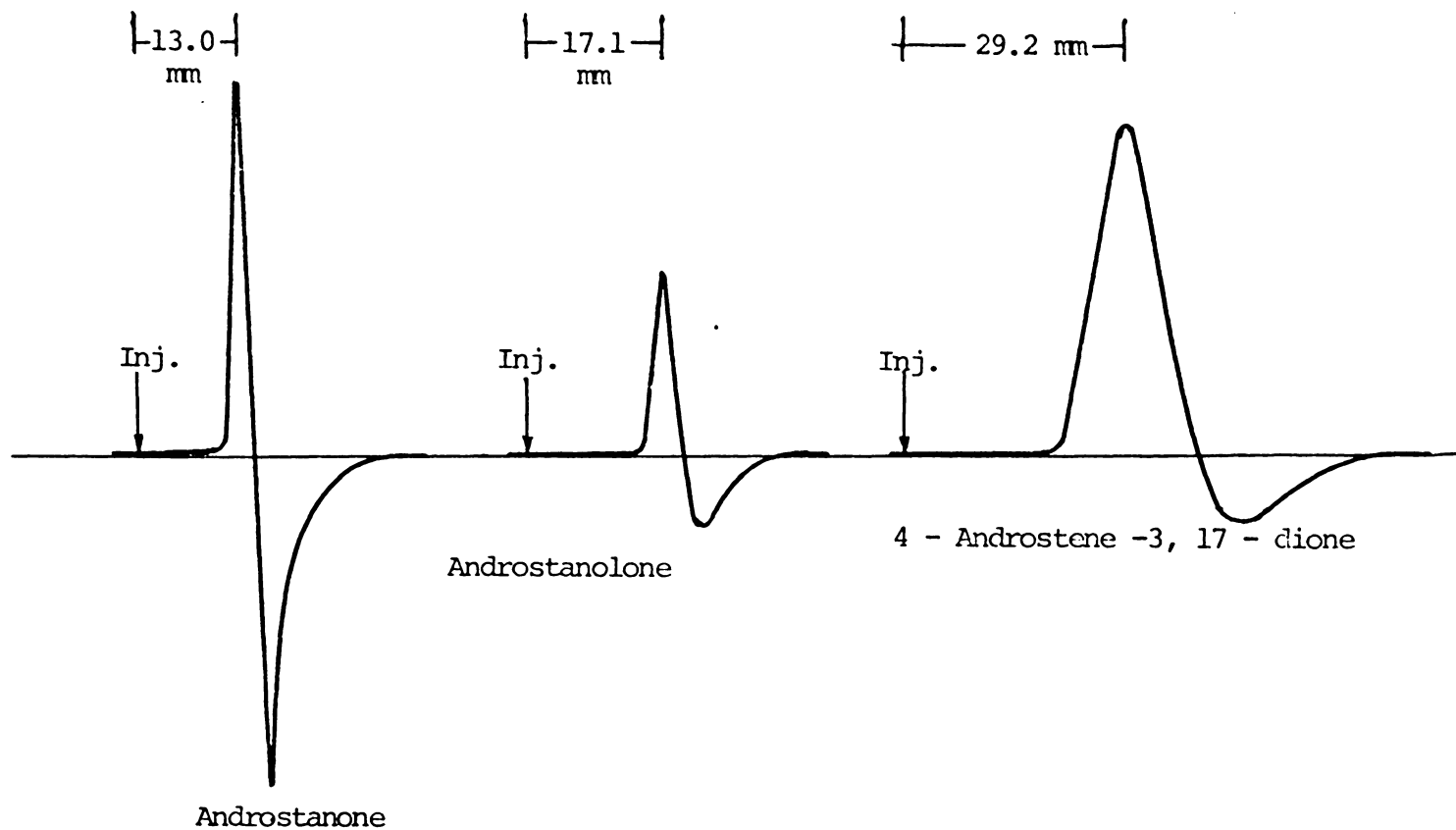


Figure 18. Chromatograms of Free Steroids  
 Column: 1/8" x 20 cm., 1% 3, 3' oxydipropionitrile on Zipax  
 Eluant: benzene

## Results and Discussion

The results of this work can be divided into the following principle sections:

1. Evaluation of the MAD as a liquid chromatographic detector.
2. Evaluation of the MAD as a gas chromatographic detector.
3. Calibration of the MAD response.
4. Potential use of the MAD as a tool for screening chromatographic systems.
5. Use of the MAD as a micro-calorimeter in adsorption studies.

### The MAD as a Liquid Chromatographic Detector

In evaluating the MAD as an analytical instrument, guidelines presented by Huber (20) as to sensitivity, stability, linear range and minimum detectable quantity were considered in addition to the problem of the degree of resolution necessary in using an adsorption detector. The results of the study to determine the method for measuring the MAD response have been summarized in Tables III to VII (Pages 38 - 42). This study showed:

1. Digitized, computer processed, off-line positive and negative peak areas are statistically more precise than areas obtained from the recorder.
2. There is no statistically significant difference between the precision of digitized off-line positive peak heights and areas, and total peak heights and areas.
3. Positive peak height, total peak height or positive peak area show good correlation with sample size; negative peak height



and negative peak area show much less correlation.

The results of work to establish the minimum detectable quantity, linear dynamic range, noise level, and selectivity are summarized in Table VIII and Figures 19 to 26. Data points on the curves have been omitted to reduce crowding. Each line represents a linear least squares fit of a minimum of five points with five replicates per point. Typical 95% confidence limits are shown for illustrative purposes for the methanol curve in Figure 19.

The minimum detectable quantities shown in Table VIII were established as that level which would be required to produce a signal equal to twice the noise level at maximum sensitivity (27); this signal represents a response of 7mm. in Figures 19 to 26. The maximum quantity for which the response was linear was obtained graphically. The linear dynamic range was defined as the ratio of this maximum to the minimum detectable quantity.

The tabulated data illustrate several points:

1. The micro-adsorption detector has good sensitivity, as shown by the minimum detectable quantities;  $3 \times 10^{-10}$  moles for acetone,  $5 \times 10^{-10}$  moles for methanol. This sensitivity is comparable to, or better than, the U.V. photometer detector and better than all other reported detectors.
2. The detector performance is a function of the solute/solvent/adsorbent systems, and all three must be specified for valid comparisons.
3. The linear dynamic range,  $10^2$ - $10^3$ , is good as compared to other liquid chromatographic detectors,  $10^2$  for UV and differential

TABLE VIII

## LINEARITY OF THE MICRO-ADSORPTION DETECTOR

ADSORBENT: POROUS GLASS/MOBILE PHASE: BENZENE

Solute Class	LINEAR RANGE		LDR <sup>(c)</sup>
	Minimum (a)	Maximum (b)	
Ketones	Moles	$1.0 \times 10^{-6}$	$10^3$
	Grams	$5 \times 10^{-5}$	$10^3$
Alcohols	Moles	$7 \times 10^{-7}$	$10^3$
	Grams	$7 \times 10^{-5}$	$10^3$
Benzoate Esters	Moles	$3 \times 10^{-6}$	$10^3$
	Grams	$4 \times 10^{-4}$	$10^3$
Hydrocarbons	Moles	$6 \times 10^{-5}$	$10^2$
	Grams	$5 \times 10^{-3}$	$10^2$
Substituted Benzenes	Moles	$6 \times 10^{-5}$	$10^2$
	Grams	$8 \times 10^{-3}$	$10^2$

(a) Represents minimum detectable quantity.

(b) Maximum of linear range.

(c) Linear dynamic range.

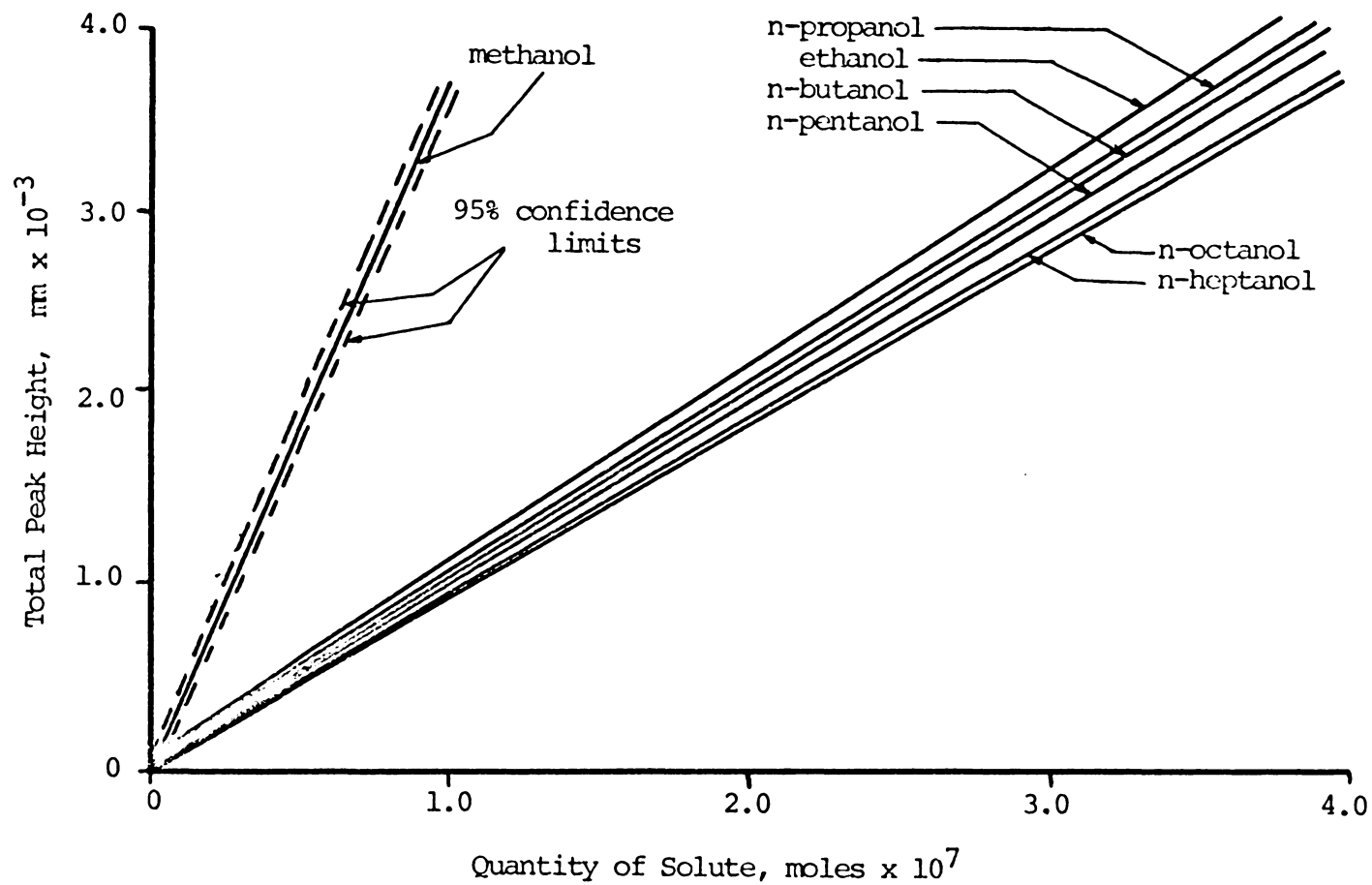


Figure 19. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Porous Glass Beads; Eluant: Benzene



Figure 20. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Porous Glass Beads; Eluant: Benzene

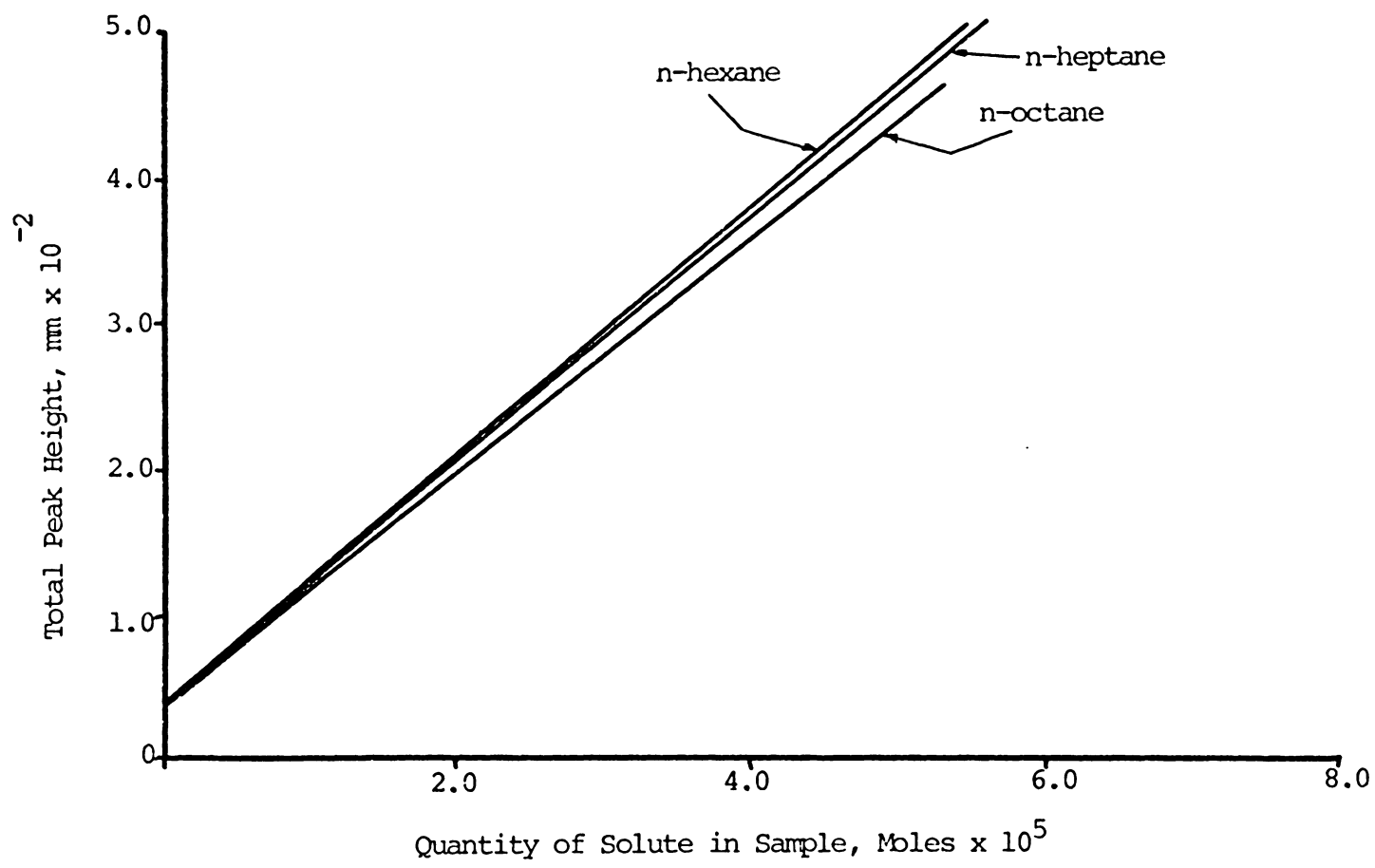


Figure 21. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Porous Glass Beads; Eluant: Benzene

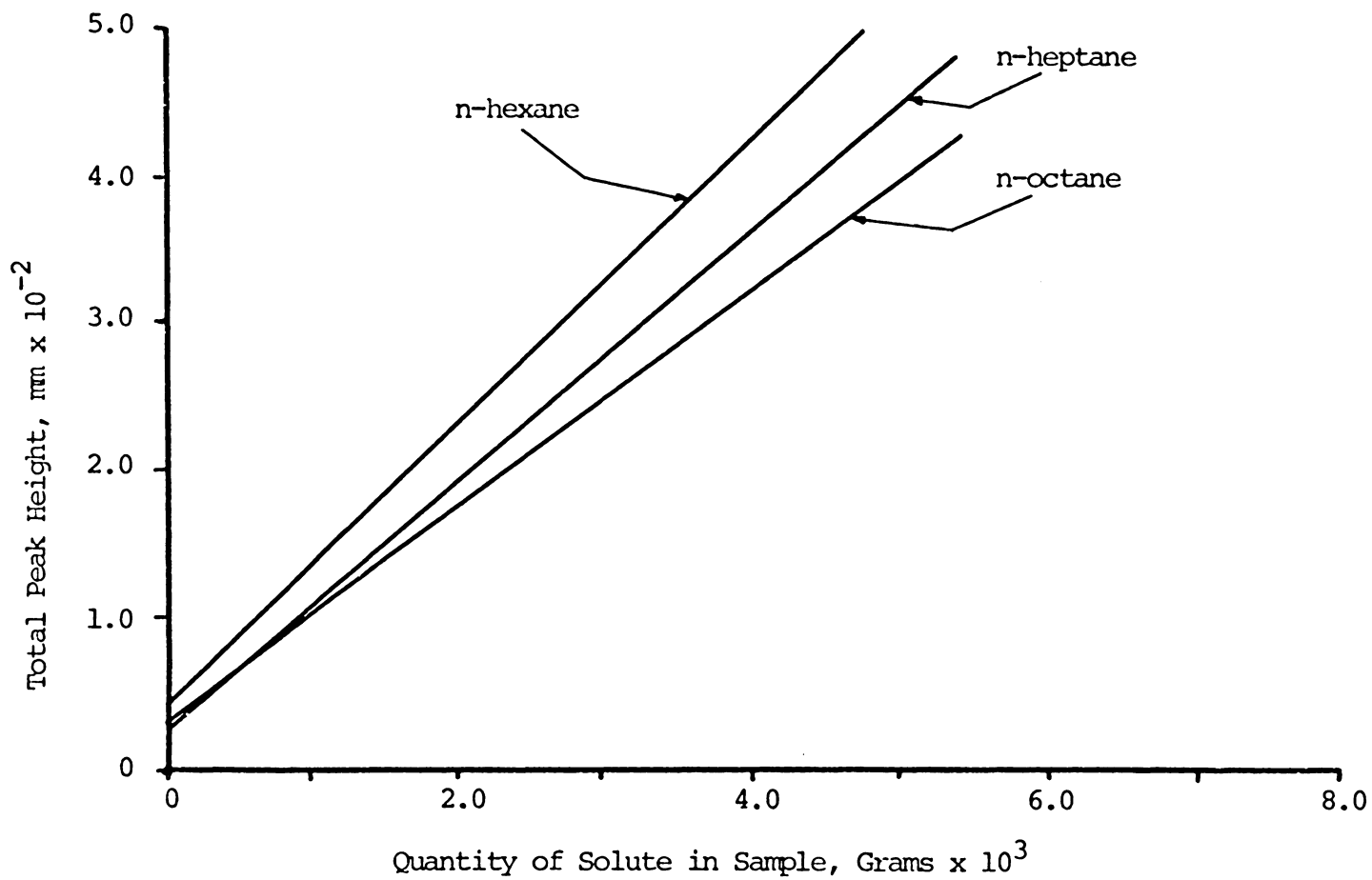


Figure 22. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Porous Glass Beads; Eluant: Benzene

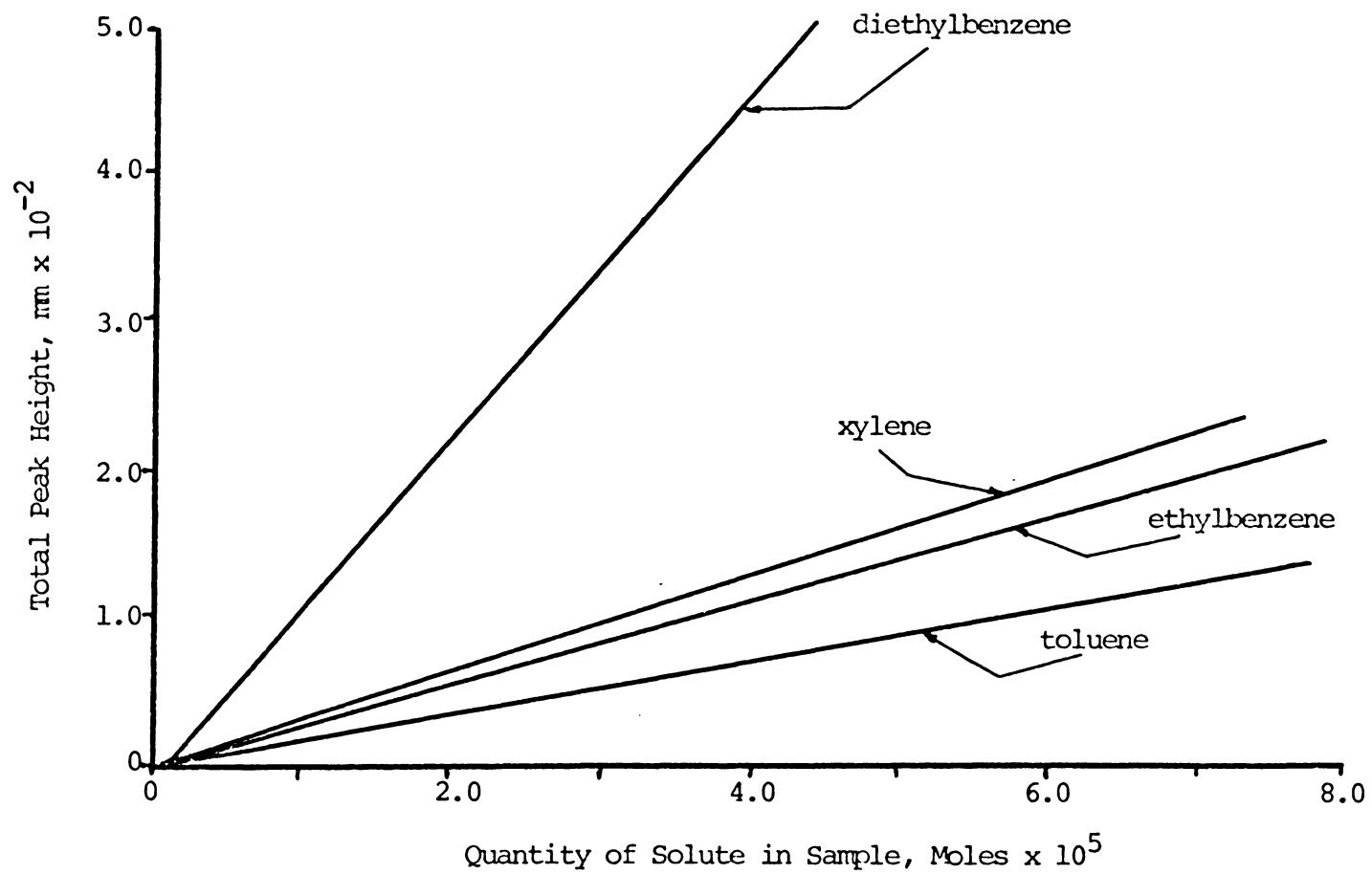


Figure 23. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Porous Glass Beads; Eluant: Benzene

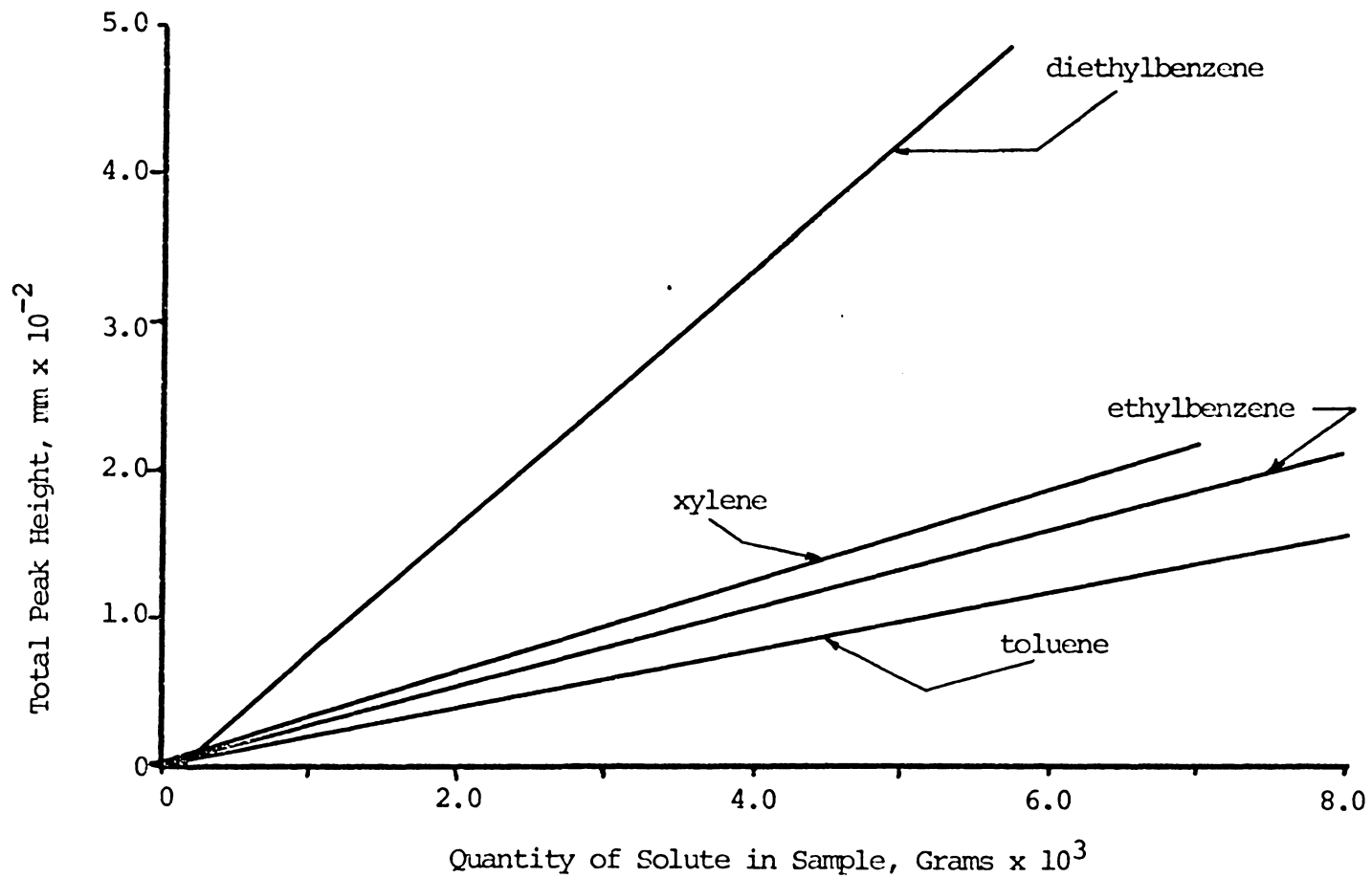


Figure 24. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Porous Glass Beads; Eluant: Benzene



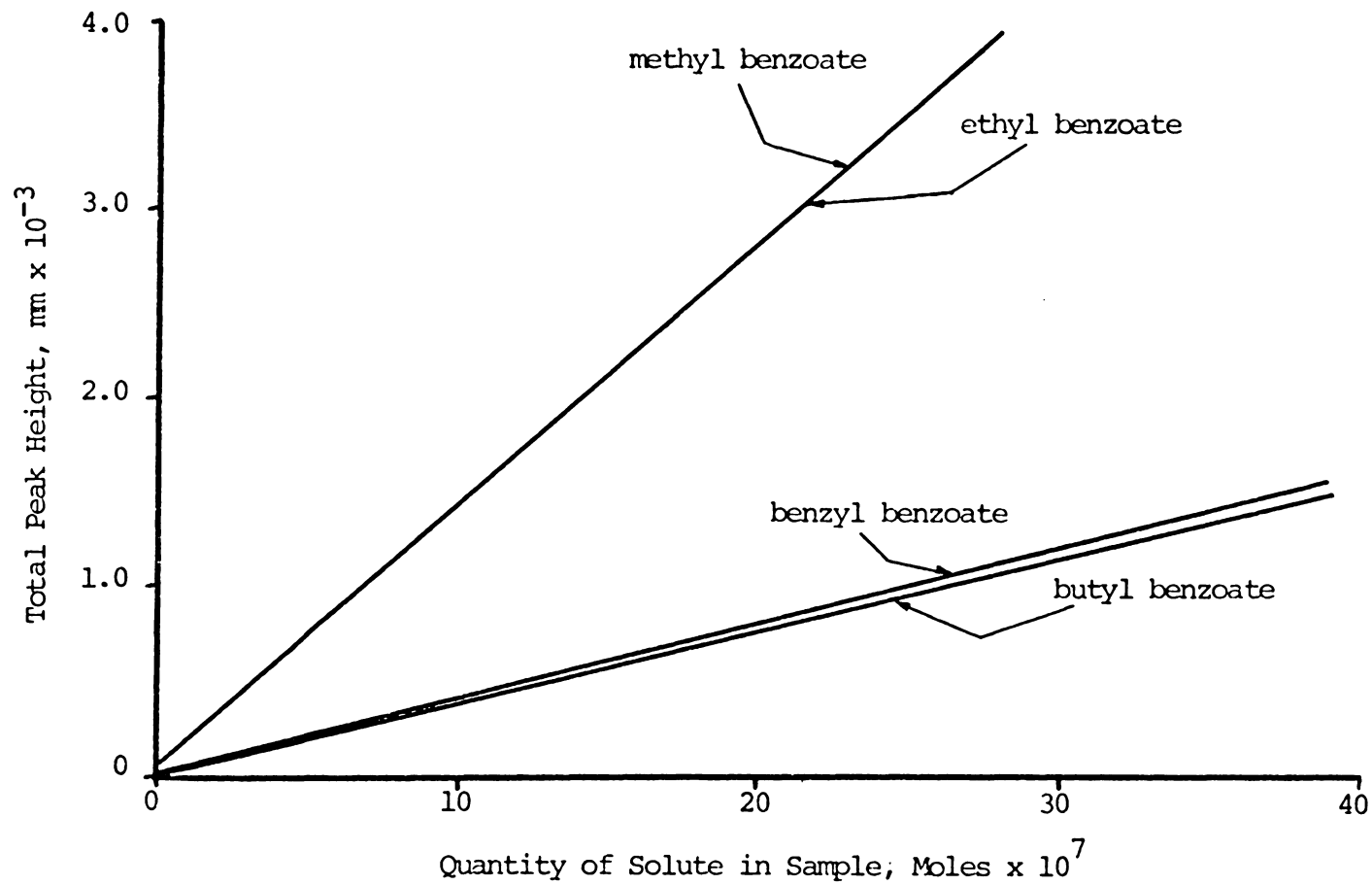


Figure 25. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Porous Glass Beads; Eluant: Benzene

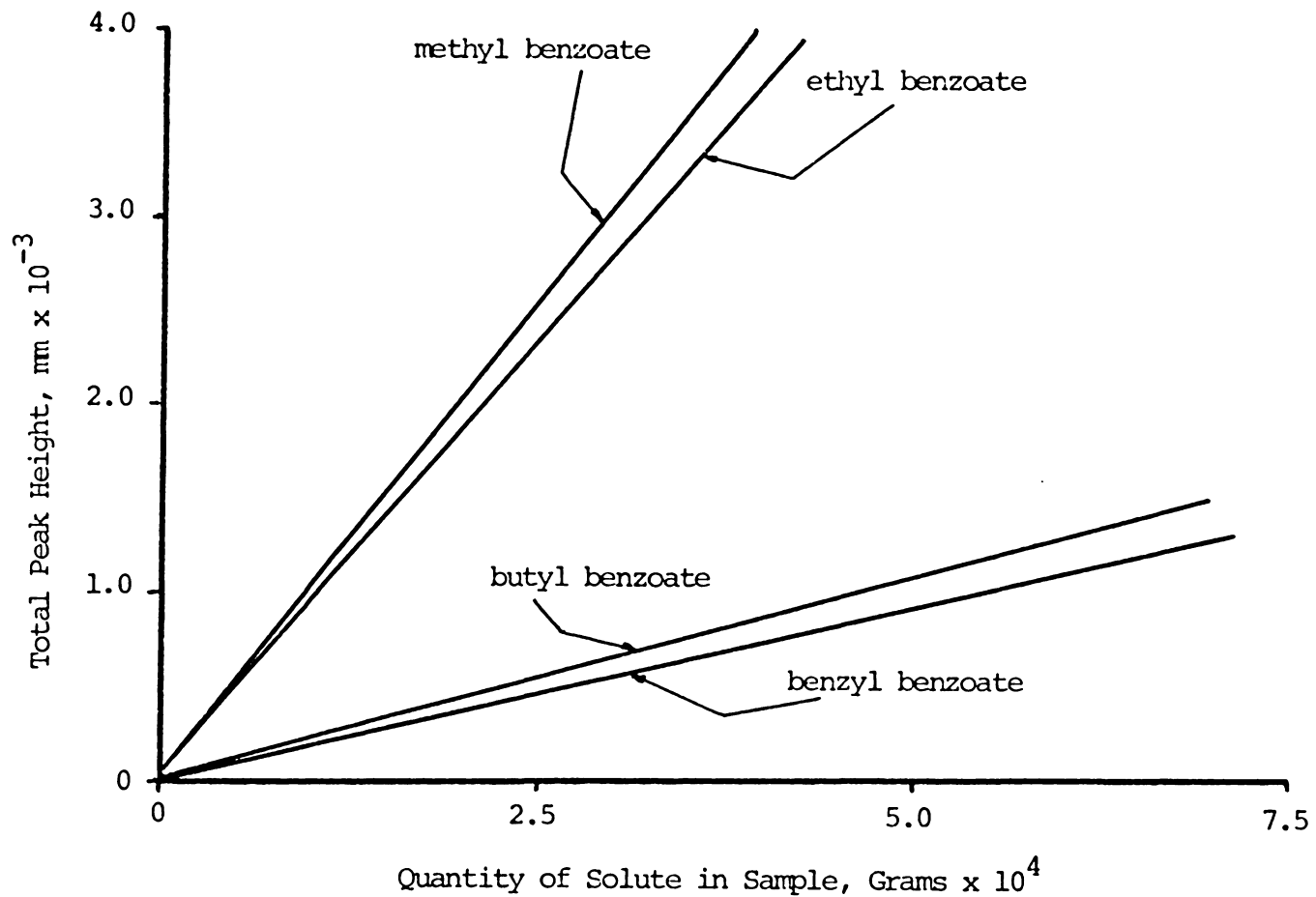


Figure 26. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Porous Glass Beads; Eluant: Benzene

refractometer (28) but poor compared to established gas chromatographic detectors; for example  $10^4$  for thermal conductivity, and  $10^6$ - $10^7$  for flame ionization detectors (29).

4. Peak shape poses major problems in analyzing mixtures of several components (see page 60 for discussion).
5. The response of the detector is universal and can be approximated if the response characteristic of the chemical class to which the compound belongs is known, for example the response curve for alcohols as shown in Figure 19, or for the hydrocarbons as shown in Figure 21. As shown in Figure 19 it would be possible to estimate that  $1 \times 10^{-7}$  moles of an alcohol would give a response of approximately  $1 \times 10^3$  mm, total peak height.

The detector response is dependent on the adsorbent type and solute functional group. For example  $2 \times 10^{-8}$  moles of methanol give a total peak height of 750 mm with porous glass (surface area,  $237 \text{ m}^2/\text{gm}$ ) as the adsorbent, and only 180mm with graphitized carbon (surface area,  $12.1 \text{ m}^2/\text{gm}$ ) as the adsorbent. This indicates a fourfold greater interaction energy of the hydroxyl of the methanol with the porous glass than with the carbon. As an example of function group influence consider Figures 19 and 25. It can be seen that  $1 \times 10^{-7}$  moles of ethanol will give a response of 1000mm while  $1 \times 10^{-7}$  moles of ethylbenzoate will give a response of 150 mm, total peak height.

In addition, Figure 19 shows that the molar response of the normal alcohols from ethanol through heptanol could very nearly be represented by a single line; the same can be said for the normal hydrocarbons in Figure 21, three of the four substituted benzenes in Figure 23, and two

pairs of benzoate esters in Figure 25. The weight responses can also be represented by linear, but divergent lines, as shown in Figures 20, 22, 24, and 26.

These data demonstrate that the adsorption measured is dependent primarily on the functional groups, and to a lesser extent on the arrangement of the groups in the molecules (30). While these effects have been discussed before, the present treatment presents a more quantitative and thorough analysis than previously found in the literature. As an example, consider the substituted benzenes, Figure 23. While toluene, xylene, and ethylbenzene have slopes reasonably close together, the slopes increase with the amount of hydrocarbon character, and approach the slope of the hydrocarbon curves, Figure 21. The slope of the diethylbenzene line is greater than that of the hydrocarbon lines. This can be explained by considering that there are two hydrocarbon moieties in the diethylbenzene molecule and the interaction energy for a mole of diethylbenzene would be expected to be greater than that for a mole of hydrocarbon.

The effect of side chain length is shown in Figure 25 where the ester linkage is the most active entity. The smaller methyl and ethyl groups appear to have much less effect on the adsorption interaction than the larger butyl and benzyl groups. This represents a steric hindrance effect; the larger groups prevent close approach to the adsorbent surface.

The peak shape represents a severe limitation for use as a general purpose detector. As shown in Figure 15 (page 37) the MAD output signal consists of a positive adsorption peak, and a negative desorption

peak. This imposes a drastic requirement for the resolution of a closely spaced pair of peaks. For two gaussian curves, a resolution of 1.5, as defined in Figure 27, represents baseline separation of the peaks (31). If the width of the MAD negative peak is fifty per cent greater than that of the positive peak, a column resolution of 3.75 is required to show MAD baseline separation from the following peak. This assumption of the negative desorption peak width being 150% of the adsorption peak is conservative and can be exceeded by large sample sizes. The result is that the column must be 6.25 times as long to compensate for the existence of the negative peak. This assumes resolution is proportional to the square root of column length. This is a severe limitation to use of the MAD. Figures 18 (page 48) and 28 (page ) show chromatograms of free steroids, androstanone, androstanolone, and 4-androstene -3, 17-dione separated on a column of 1% 3, 3<sup>1</sup> oxydipropionitrile on Zipax. The failure to completely elute the negative desorption peak of one component, prior to elution of the following adsorption peak results in a complex chromatogram which is meaningless for quantitative analysis (Figure 28, page ).

#### The MAD as a Gas Chromatographic Detector

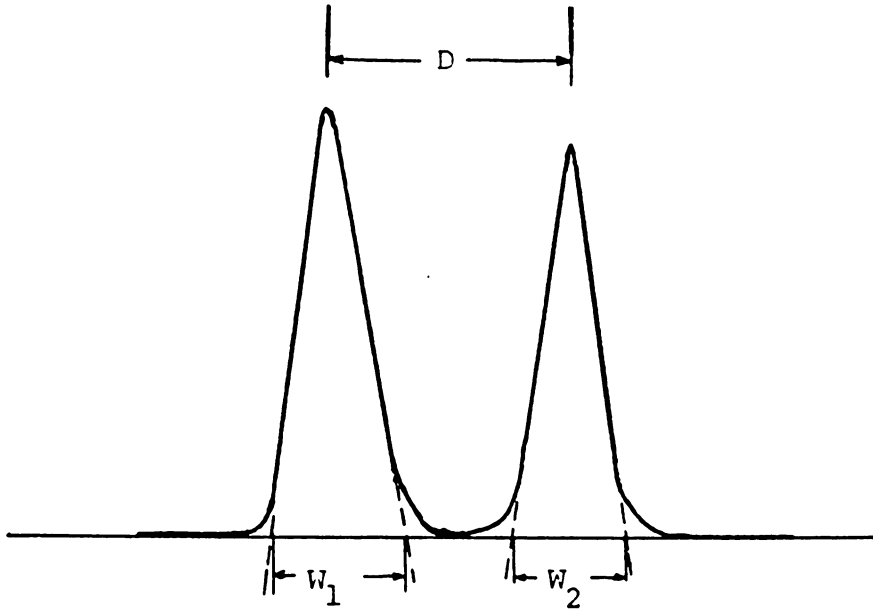
The evaluation of the MAD as a gas chromatographic detector was made with the same considerations of response characteristics as discussed for liquid chromatographic systems. The results of this work are summarized in Tables IX and X, and Figures 29 to 32. These data show that the minimum detectable quantities, linear dynamic ranges, and response curves are comparable to those obtained with the liquid chromato-

graphic systems investigated.

Minimum detectable quantities of the order of  $10^{-10}$  moles and linear dynamic ranges of  $10^2$ - $10^3$  which were determined for the MAD in use as gas chromatographic detector compare favorably with those found for thermal conductivity detectors, although lower than those obtainable with flame ionization detectors. These properties along with the ability to respond to any component which can be separated in the chromatographic column give the MAD potential as a detector in GC systems. In addition the proper choice of adsorbent can provide both specificity and selectivity in detecting compounds on the basis of their functional groups.

#### Calibration and Analysis of the MAD Response

The sensitivity and convenience of the micro-adsorption detector make its use as a micro-calorimeter very attractive. In order to interpret the MAD response, an analysis for the operations within the cell, and their relation to the output signal is necessary. Scott (32) has made an analysis of the heat flow in packed adsorption columns. However, he has neglected the amount of heat removed by the mobile phase. This may not be serious in the case of gaseous mobile phases, but certainly cannot be neglected when using a liquid mobile phase. Smuts, Van Niekerk, and Pretorius (33) have attempted an analysis of the MAD output, but conclude that "since the response deviates from the ideal in an unknown manner, it does not appear possible to devise a means of converting the observed signal to an ideal signal "which can be treated analytically." They present a means of circumventing the problem,



$$\text{Resolution} = R = \frac{2D}{W_1 + W_2}$$

Figure 27. Illustration of the Method of Calculating Resolution

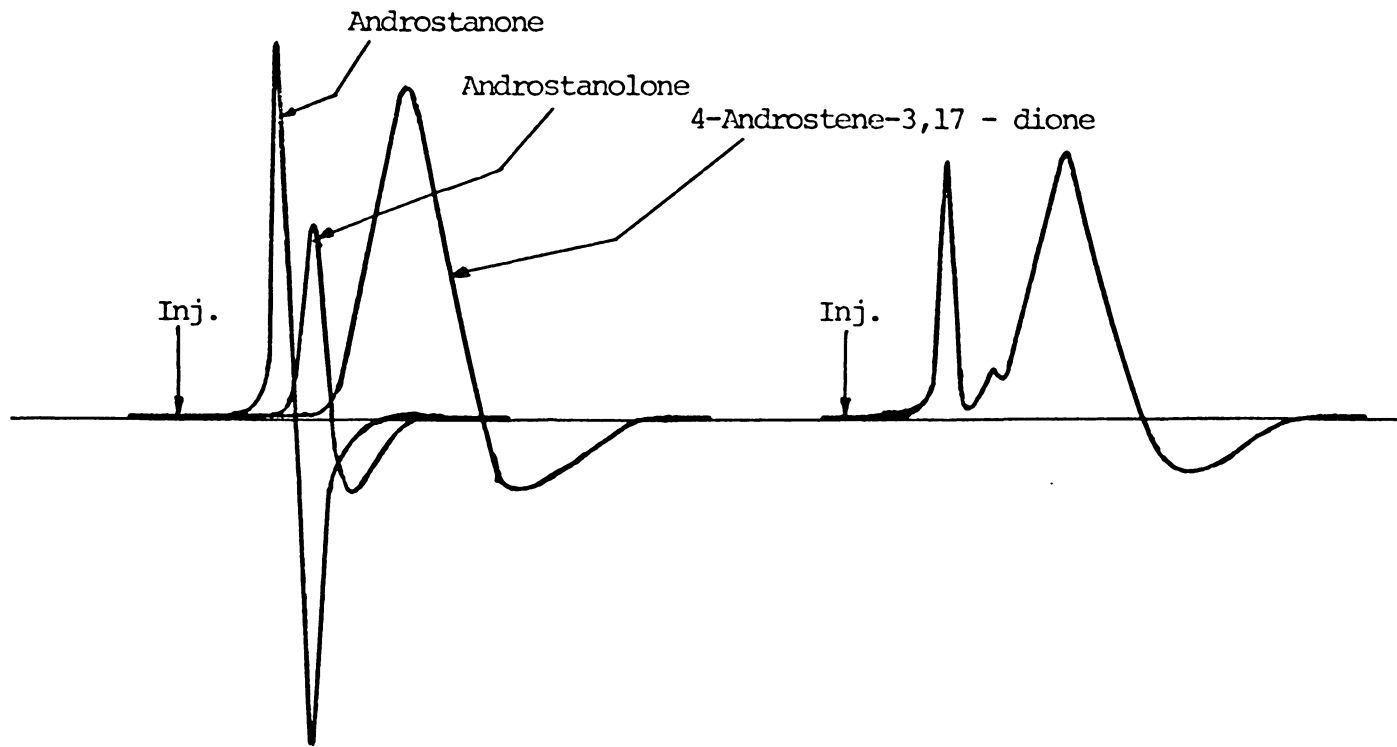


Figure 28. Comparison of Superimposed, and Actual Chromatograms Obtained Running a Mixture of Free Steroids



which is not germane to this work and will not be discussed here.

The calibration procedure, already presented, was devised to be utilized under dynamic conditions, and therefore accounts for both heat losses to the environment and heat removed from the cell by the mobile phase. Indeed, the calculation of temperature differentials between the thermistor beads depends on the amount of heat removed by the mobile phase.

Observation of the cell output signal during calibration reveals that the shape of the curve is that which would be predicted from a consideration of the heat transfer in a stream when a sudden constant heat flow is imposed (34). This means that the temperature differential begins to decrease instantaneously when heating is stopped and the flowing mobile phase rapidly cools the second thermistor bead to its initial temperature. Thus, even if no endothermic desorption were to occur, the mobile phase would bring the thermistors back to equilibrium.

Then the MAD was run in series with the GC unit, it was observed that if the GC and MAD curves were adjusted to account for the time lag caused by interconnecting tubing, the maximum of the GC curve, which represents the maximum solute concentration, corresponded to the maximum of the MAD positive peak. Applying these observations to the MAD response curve, Figure 15 (page 37), we can analyze the processes occurring in the adsorption cell under non-overloaded conditions. A component injected at I is first encountered by the adsorbent at A; adsorption occurs and an increase in temperature begins and continues until B is reached. At B, the maximum solute concentration has been reached,

TABLE IX

## LINEARITY OF THE MICRO-ADSORPTION DETECTOR

Adsorbent: Porous Glass Mobile Phase: Helium

Solute Class	Linear Range		LDR (c)
	Minimum (a)	Maximum (b)	
Ketones			
Moles	$4 \times 10^{-10}$	$4 \times 10^{-8}$	$10^2$
Grams	$2 \times 10^{-8}$	$2 \times 10^{-6}$	$10^2$
Alcohols			
Moles	$4 \times 10^{-11}$	$7 \times 10^{-9}$	$10^2$
Grams	$2 \times 10^{-9}$	$3.5 \times 10^{-7}$	$10^2$
Hydrocarbons			
Moles	$3.5 \times 10^{-10}$	$2 \times 10^{-7}$	$10^3$
Grams	$3 \times 10^{-8}$	$1.7 \times 10^{-5}$	$10^3$
Benzene			
Moles	$7.5 \times 10^{-10}$	$4.5 \times 10^{-7}$	$10^3$
Grams	$6 \times 10^{-8}$	$3.5 \times 10^{-5}$	$10^3$

- (a) Represents minimum detectable quantity.
- (b) Maximum of linear range.
- (c) Linear dynamic range.

TABLE X

## LINEARITY OF THE MICRO-ADSORPTION DETECTOR

Adsorbent: Carbon Mobile Phase: Helium

Solute Class	Linear Range		LDR (c)
	Minimum (a)	Maximum (b)	
Ketones	Moles	$2.5 \times 10^{-8}$	10
	Grams	$1.25 \times 10^{-6}$	10
Alcohols	Moles	$7.5 \times 10^{-9}$	10
	Grams	$3.5 \times 10^{-7}$	10
Hydrocarbons	Moles	$2 \times 10^{-7}$	$10^2$
	Grams	$2 \times 10^{-5}$	$10^2$
Benzene	Moles	$3.5 \times 10^{-7}$	$10^2$
	Grams	$3.0 \times 10^{-5}$	$10^2$

(a) Represents minimum detectable quantity.

(b) Maximum of linear range.

(c) Linear dynamic range.

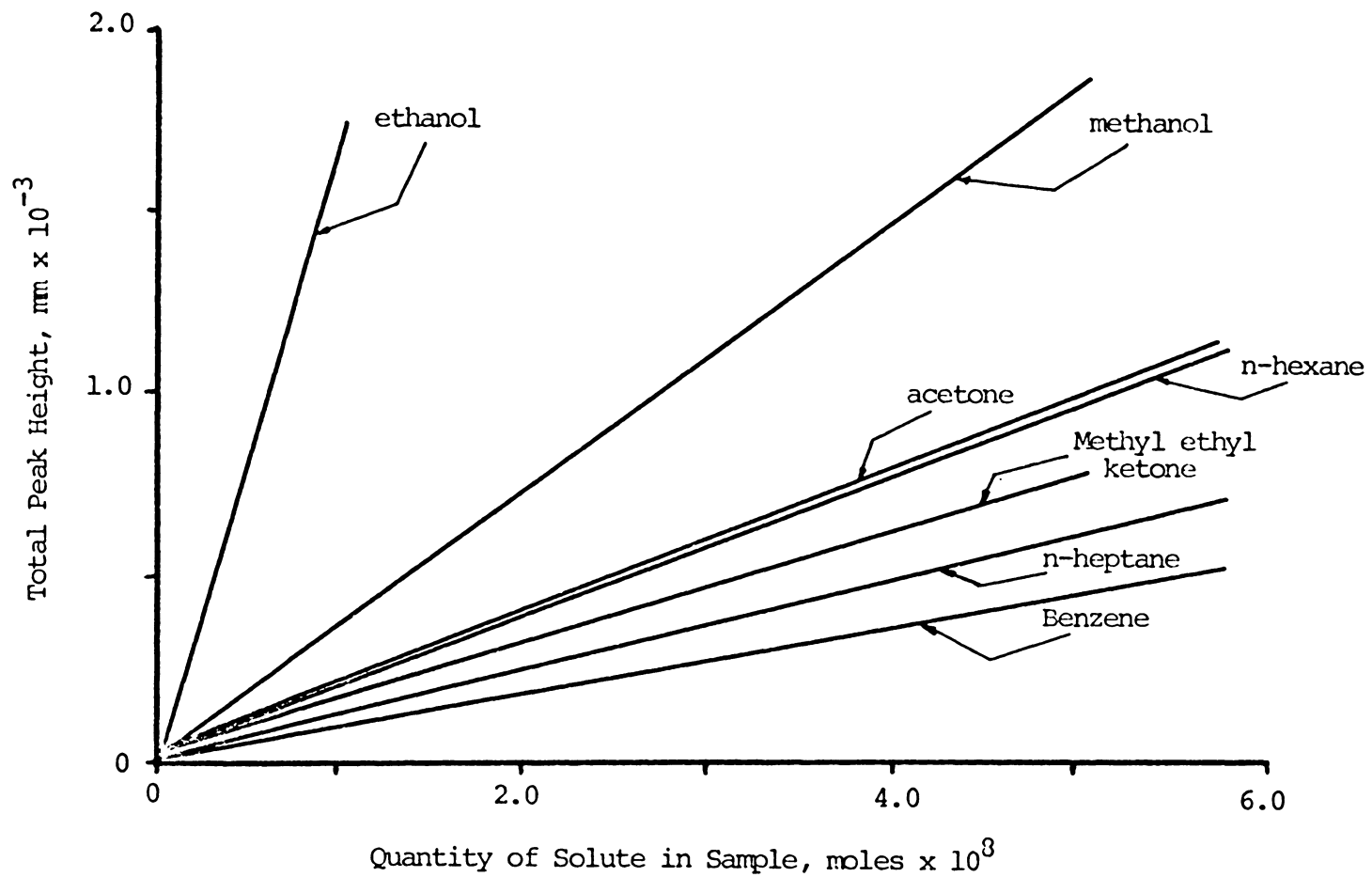


Figure 29. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Porous Glass Beads; Eluant: Helium

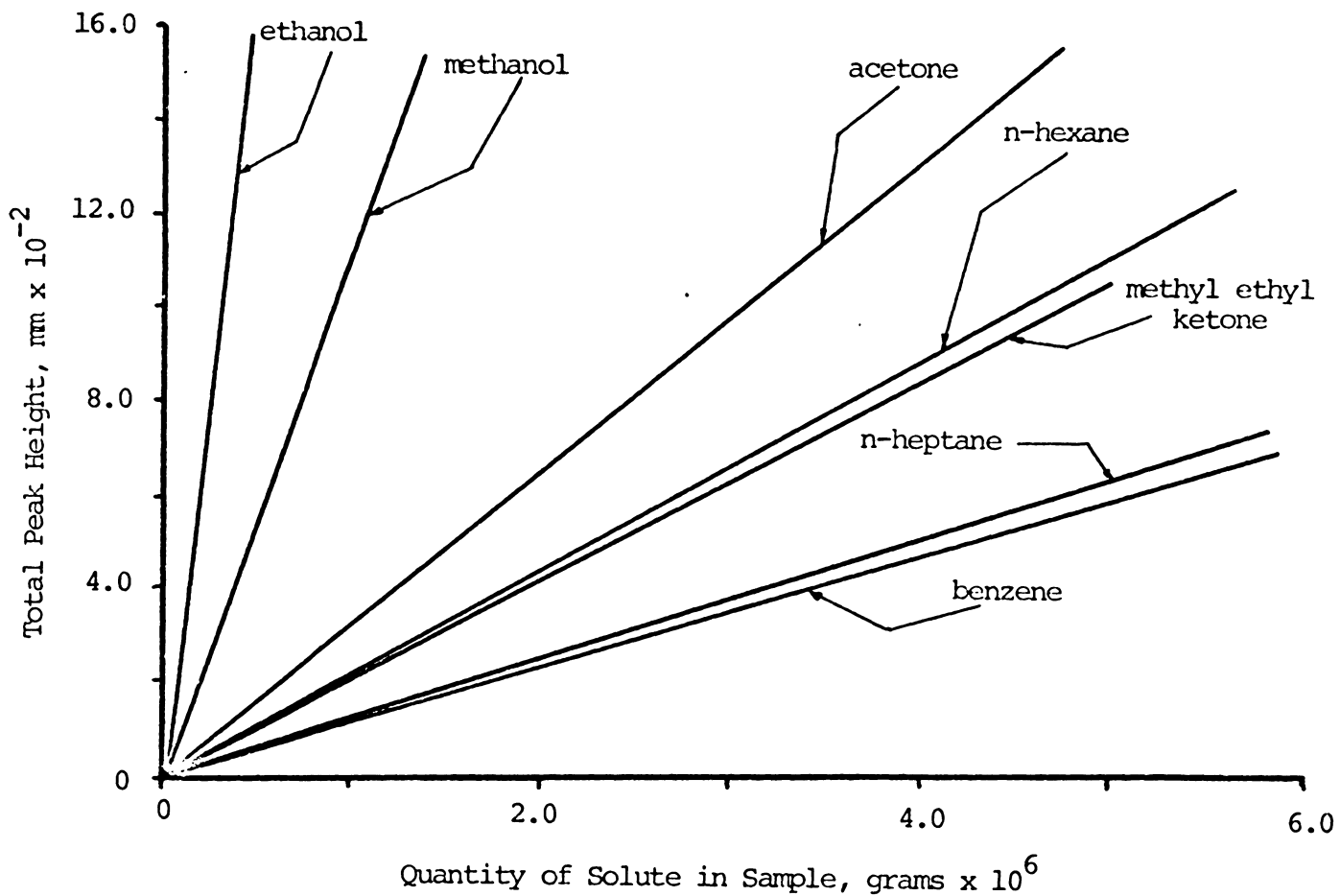


Figure 30. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Porous Glass Beads; Eluant: Helium

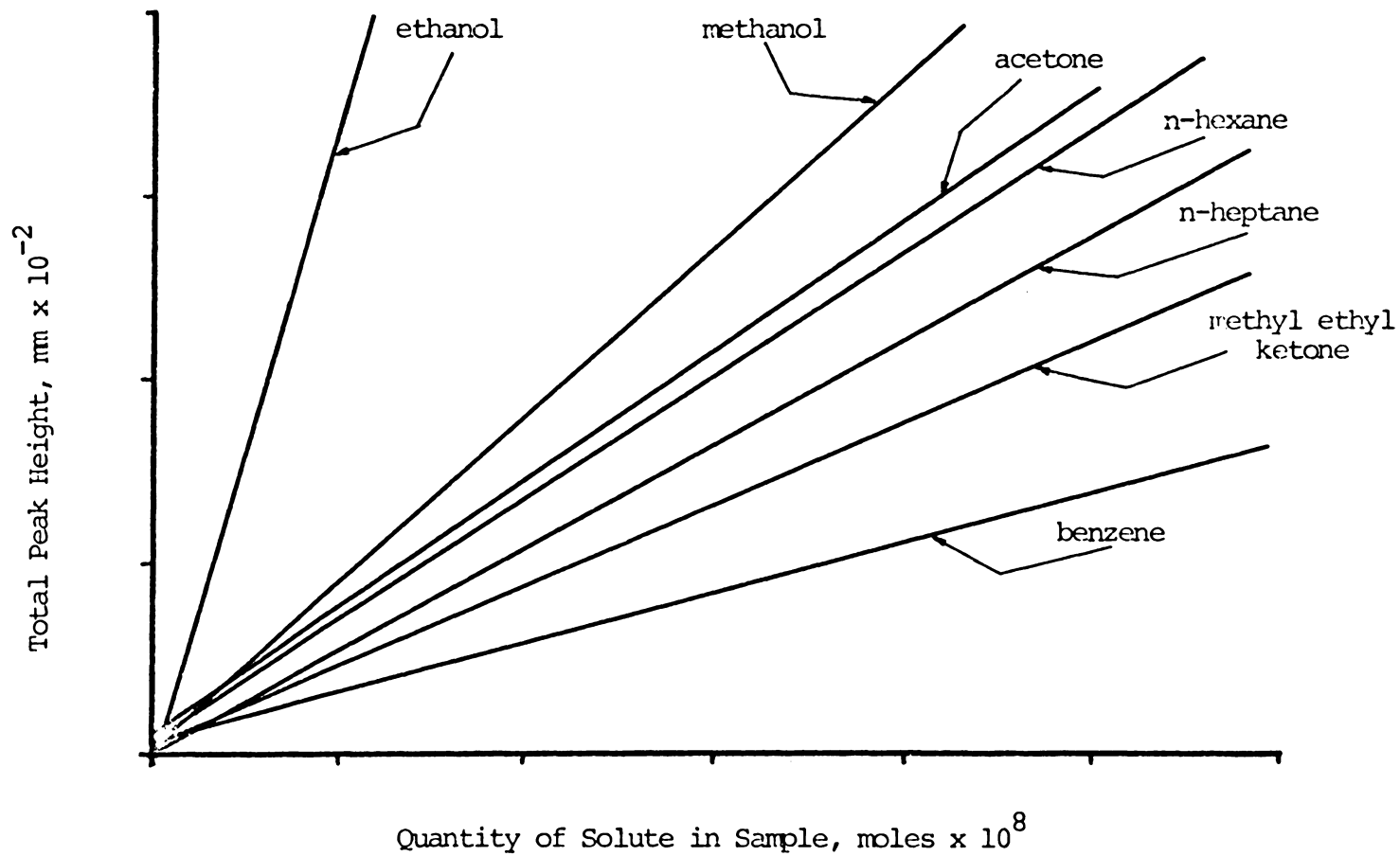


Figure 31. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Sterling FT carbon; Eluant: Helium

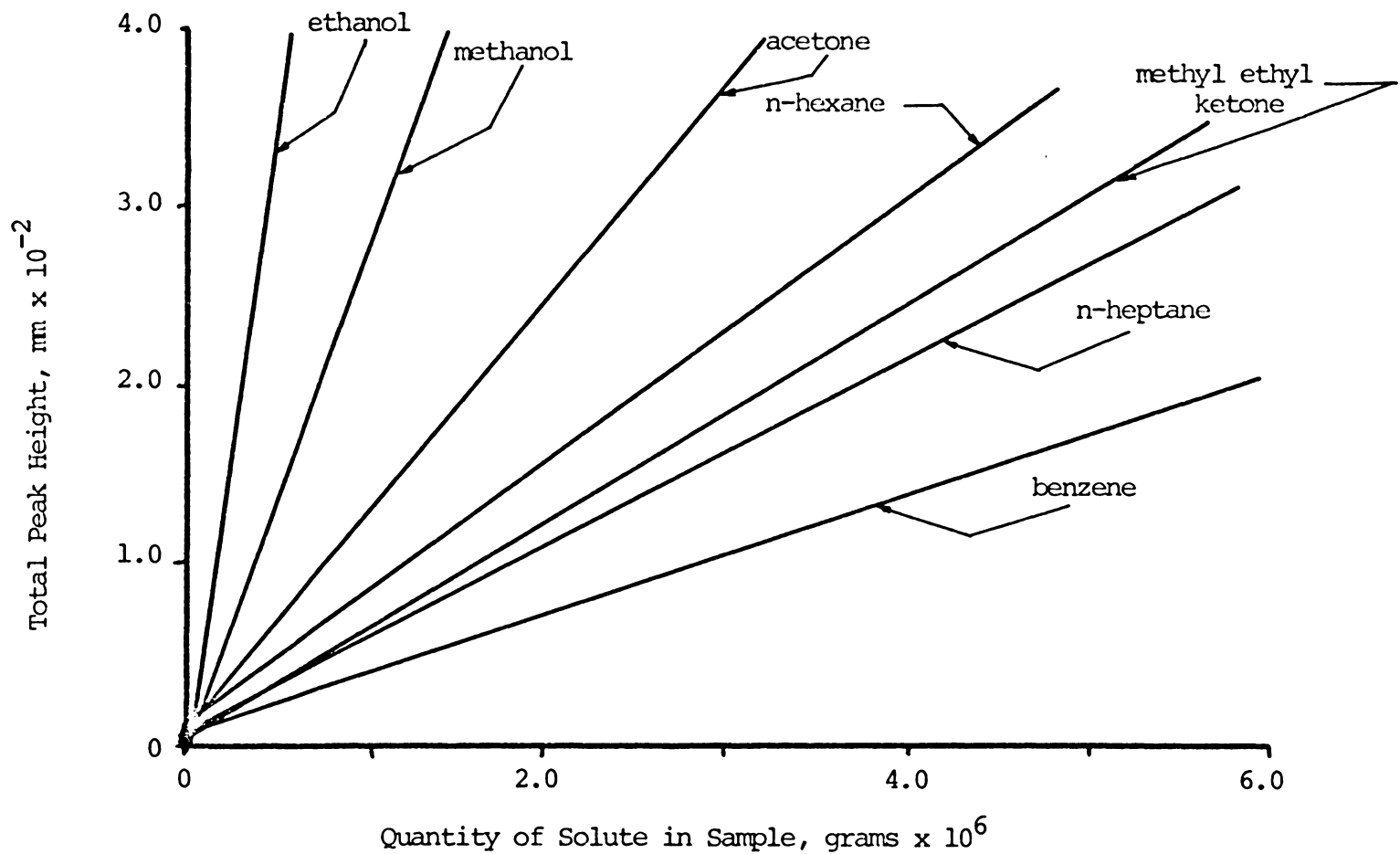


Figure 32. Response of the MAD as a Function of Quantity of Solute in Sample  
 Adsorbent: Sterling FT carbon; Eluant: Helium

and after this point net adsorption, as opposed to dynamic exchange of solute molecules in the interfacial layer, stops, and the temperature begins to decrease, since no heat is being supplied by adsorption. As the concentration of the solute decreases, desorption of the solute begins, and continues to point C. The negative temperature differential encountered prior to C is caused by the endothermic nature of the desorption process. Desorption is not complete at point C, but the maximum rate of desorption has been reached at this point. The ability of the environment to supply the heat necessary for desorption is just balanced by the heat uptake by the desorption process. At point D the desorption is completed, and the system re-equilibrates. The desorption curve differs entirely from the adsorption curve. The desorption process is dependent upon the ability of the environment to supply the heat for the endothermic reaction. The peak is not a derivative of the sample concentration profile. Two assumptions are vital to this analysis:

1. The adsorption occupies only a small fraction of the adsorption sites, and is therefore not influenced by the availability of sites.
2. Only physisorption is considered.

The first assumption is probably valid up to the limit of the linear response range and the reasonable linear dynamic range seems to verify it. Reproducibility of repeated runs verifies the second. If chemisorption were present, the irreversible chemical reactions would decrease the active sites available and decrease the detector response.

While the above analysis is applicable to non-overloaded condi-



tions, it is reinforced and elucidated by consideration of overloaded conditions. Referring to Figures 33 and 34 it can be seen that as larger samples are used the peak shape depends upon the sample size. The desorption peak width increases with sample size and the shape of the desorption peak changes. As the solute concentration reaches the level which represents overloading, no further net adsorption can occur, and the temperature differential between the reference and adsorption cells decreases. The mobile phase rapidly carries the heat away. If this concentration were maintained the system would re-equilibrate and the response curve would return to baseline, as indeed is shown, prior to desorption in the extreme case. If this concentration level were maintained, only a single positive peak would be obtained. The origin of the broadening of the desorption peak is the increased amount of solute to be desorbed, and the limitation is the rate at which heat can be supplied by the environment. The delay in the negative peak is attributable to the fact that net desorption will not occur until the concentration of solute in the mobile phase has decreased to a level which will permit desorption. That effective saturation of the adsorption sites is affected in the overload condition is indicated by the identical size and shape of the desorption peaks observed in the largest sample sizes.

No adequate description of the processes in the adsorption cell has been found in the literature, and certainly no attempt at a mathematical description has been found. From the complexity of the response signal, and the difficulties encountered in calibrating the negative peak, it would appear that Smuts, Van Niekerk, and Pretorius (33) are

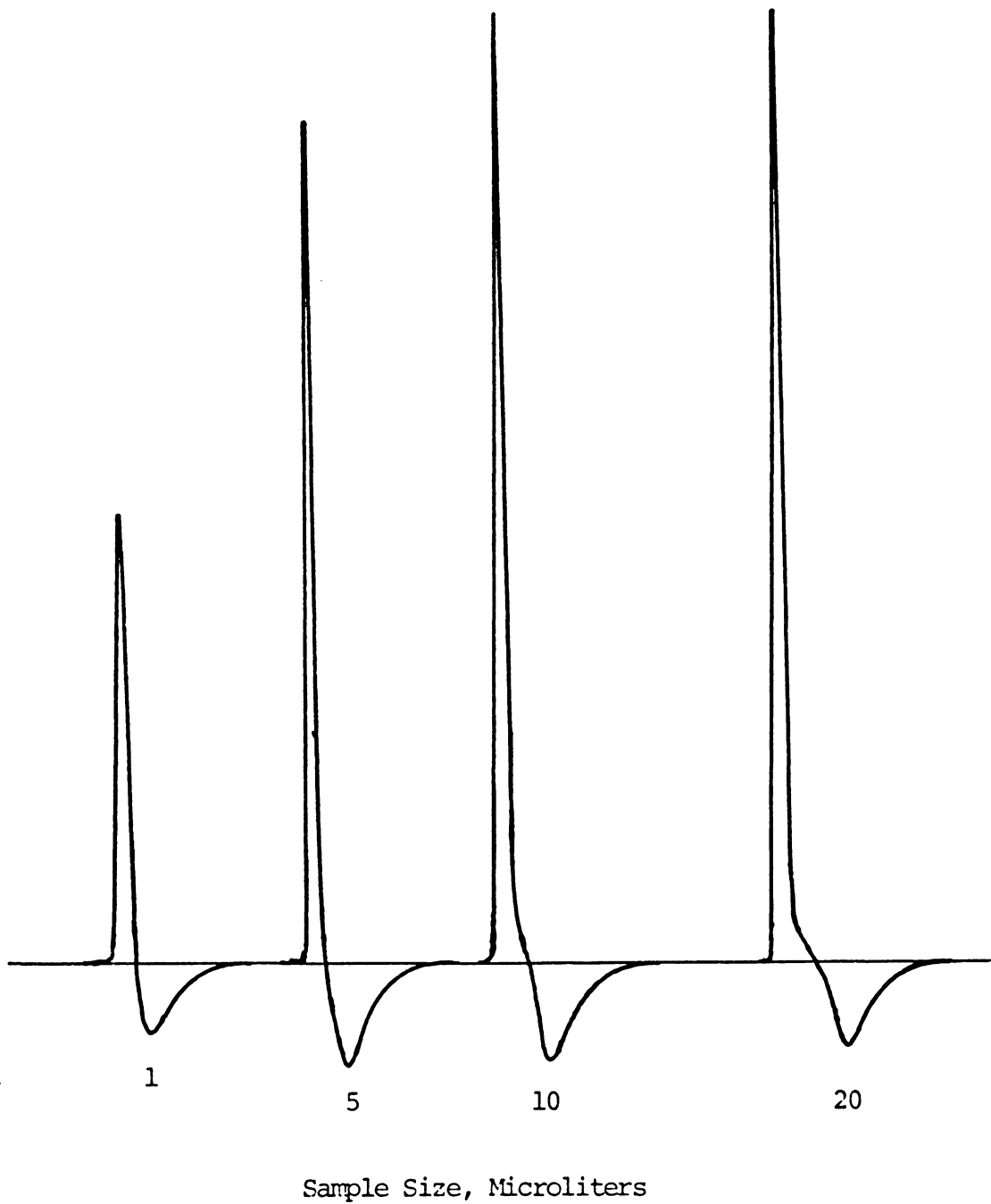
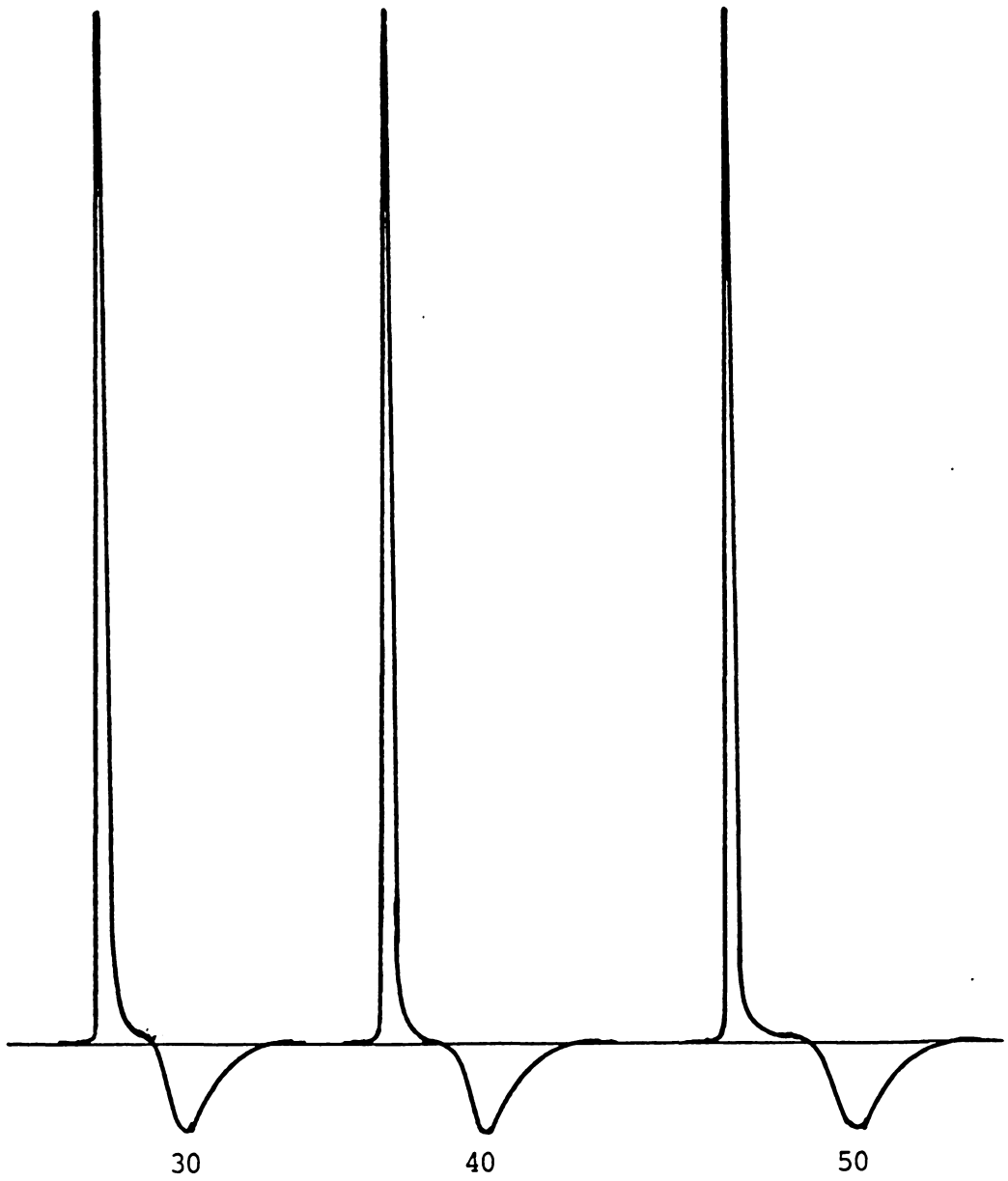


Figure 33. Peak Shape as Function of Sample Size  
(Continued on Figure 34)



Sample Size, Microliters

Figure 34. Peak Shape as a Function of Sample Size  
(Continued from Figure 33)

correct in saying that a mathematical description in the near future is unlikely.

#### The MAD as a Micro-Calorimeter

A series of runs were made using the MAD as a micro-calorimeter. The primary purpose was to establish whether the heats calculated were reasonable and in agreement with published experimental values. Data on adsorption of solutes using the liquid/solid systems and particularly the low concentration levels employed in this work were not found. While both Schay (35) and Kipling (36) discuss theories and give examples, no data are presented for systems comparable to those used here.

Values of heats of adsorption from benzene solution were calculated for some of the systems considered in this work. The method of calculation is outlined in Figure 35, and the data are tabulated in Tables XI to XIII. The calculations were made using the area of the positive peak up to the maximum, from points A to B in Figure 15, and assuming that this represented the passage of half the solute band through the detector. This is, in effect, assuming that the concentration band and positive peak maxima coincide. This assumption agrees well with the earlier reported GC data.

The tabulated values from MAD measurements are in the range 1 to 2 kcal/mol. Groszek (37) reports the adsorption of ethanol from n-heptane solutions using silica and carbon as adsorbents. From the data reported, values of about 3 kcal/mol can be calculated. The surface areas of Groszek's adsorbents were 300 m<sup>2</sup>/gm for the silica and 860 m<sup>2</sup>/gm for the carbon, which are significantly higher than the surface

areas of the adsorbents employed here. Although the surface areas and solvents are different, the preferential heats of adsorption are of the same order of magnitude.

It must be noted that the calculated heats are subject to error because of the steep slope and narrow width of the positive peak of the chromatogram. However, it can be seen that the calculated preferential heats of adsorption are consistent, with no obviously high or low values. These data are presented in anticipation that they may stimulate additional work.

In the area of adsorption of solutes from the vapor phase by graphitized carbon, the data of Kiselev and Yashin (38) were utilized. They report the differential heats of adsorption obtained from gas-chromatographic measurements extrapolated to zero concentration. The heats which were measured using the MAD are integral heats (39); however, at the solute concentration levels considered, these differential and integral heats of adsorption should be essentially identical.

The data for several solutes are presented in Table XIV, and the procedure for calculation of the heats of adsorption from chromatograms is outlined in Figure 35. Examination of the data reveals that the heats calculated from this work are consistently about 15% lower than those reported by Kiselev and Yashin. However, several differences exist in the two experiments. The Russian work was done using Cabot's Sterling FT graphitized thermal carbon black while the MAD work was done with Sterling MF as adsorbent. The principle difference is that the carbon black MF is graphitized at 3100°C and would have a more homogeneous surface than the FT which is graphitized at 2700°C. The

Y = ordinate of MAD chromatogram, mm

Y' = Y(d) (F.R.) (C<sub>p</sub>) (1/K) = Cal/Sec

X = abscissa of MAD chromatogram, mm

X' = X (1/CS) (C) = Sec

H = heat, Cal

$$= \frac{X'(Y') (3600) (d) (F.R.) (C_p)}{CS(25.4) (K)} = \text{Cal}$$

Referring to Figure 15, area under the curve from A to B represents half of the solute quantity, therefore:

$$\text{Cal/mol} = \frac{A(d) (F.R.) (C_p) (3600)}{K(m) (CS) (25.4)}$$

d = Density of mobile phase, Gms/cc

F.R. = Flow rate of mobile phase, cc/Hr

C<sub>p</sub> = Specific heat of mobile phase, Cal/Gm°C

K = Conversion factor, °C/mm  
Determined from calibration

CS = Chart speed, In/Hr

C = Conversion factor for chart speed  
3600 sec/Hr (1 in/25.4 mm)

m = moles of adsorbate

Figure 35. Method of Calculating Heat of Adsorption from MAD Chromatogram

TABLE XI

PREFERENTIAL HEATS OF ADSORPTION FROM BENZENE  
WITH SIL-X AND POROUS GLASS ADSORBENTS

ADSORBENT:		SIX-X
Adsorbate	Moles of Adsorbate	Heat of Adsorption kcal/mol
Acetone	$4.8 \times 10^{-7}$	1.05
Methanol	$2.4 \times 10^{-6}$	1.67
Ethanol	$5.2 \times 10^{-7}$	1.59
Hexane	$7.7 \times 10^{-5}$	1.42
Heptane	$6.8 \times 10^{-5}$	1.18
Androstanone	$4.5 \times 10^{-8}$	1.28
Androstanolone	$5.0 \times 10^{-8}$	1.34
4-Androstene-3, 17-dione	$4.0 \times 10^{-8}$	1.70

ADSORBENT:		POROUS GLASS
Acetone	$7.1 \times 10^{-9}$	1.61
Methanol	$8.8 \times 10^{-9}$	1.97
Hexane	$7.7 \times 10^{-6}$	1.74
Heptane	$6.8 \times 10^{-6}$	1.67
Androstanolone	$5.0 \times 10^{-8}$	1.25

TABLE XII

PREFERENTIAL HEATS OF ADSORPTION FROM BENZENE  
WITH CORASIL AND ZIPAX ADSORBENTS

ADSORBENT:		CORASIL
Adsorbate	Moles of Adsorbate	Heat of Adsorption kcal/mol
Acetone	$4.8 \times 10^{-7}$	1.68
Methanol	$2.4 \times 10^{-6}$	1.39
Ethanol	$5.2 \times 10^{-7}$	1.76
Hexane	$7.7 \times 10^{-5}$	1.19
Heptane	$6.8 \times 10^{-5}$	1.15
Androstanone	$4.5 \times 10^{-8}$	1.50
Androstanolone	$4.0 \times 10^{-8}$	1.61
4-Androstene-3, 17-dione	$4.0 \times 10^{-8}$	1.65
ADSORBENT:		ZIPAX
Acetone	$4.8 \times 10^{-7}$	1.26
Methanol	$2.4 \times 10^{-6}$	1.24
Ethanol	$5.2 \times 10^{-7}$	1.12
Androstanone	$4.5 \times 10^{-8}$	1.23
Androstanolone	$5.0 \times 10^{-8}$	1.23
4-Androstene-3, 17-dione	$4.0 \times 10^{-8}$	1.80



TABLE XIII

PREFERENTIAL HEATS OF ADSORPTION FROM BENZENE  
WITH CARBON ADSORBENT

ADSORBENT:

STERLING FT GRAPHITIZED CARBON

Adsorbate	moles of Adsorbate	Heat of Adsorption kcal/mol
Acetone	$4.8 \times 10^{-7}$	1.32
Methanol	$2.4 \times 10^{-6}$	1.40
Ethanol	$5.2 \times 10^{-7}$	1.21

differences in surface homogeneity would be reflected by differences in heats of adsorption.

Another possible reason for differences could be the methods used for measurements. If the differential heats in the Russian work were obtained at several concentration levels and then extrapolated to zero concentration, the result could well be a value somewhat greater than the MAD value. Unfortunately the experimental procedure used by Kiselev and Yashin is not described. From other publications of the same Russian group, it is probable that they used conventional gas chromatographic detectors and solute concentrations much higher than our samples.

The reasonable agreement of values from the two methods, and particularly the reproducible 15% lower value for our method support the use of the MAD as a micro-calorimeter. It is impossible to state at this time which method is more accurate. Certainly the sensitivity and simplicity recommend the MAD for additional work. Intuitively it would seem better to work with the very dilute solutions handled by the MAD system.

The small amounts of material which can be employed when using the MAD, its flexibility in handling both liquid and gaseous systems, and the wide range of adsorbents compatible with its operation, make the MAD quite attractive as a tool for use in adsorption studies, in addition to more general use as a micro-calorimeter.

TABLE XIV

## COMPARISON OF HEATS OF ADSORPTION

ADSORBATE	HEATS OF ADSORPTION kcal/mol			
	Moles x 10 <sup>8</sup> (MAD)	Q <sub>m</sub> (MAD)	Q <sub>k</sub> (Kiselev 38 )	Q <sub>m</sub> /Q <sub>k</sub>
Benzene	5.6	8.5	9.8	0.87
Acetone	1.4	7.4	8.3	0.90
Methanol	1.0	4.7	5.3	0.89
Ethanol	2.4	5.9	6.9	0.85
n-Hexane	6.1	8.7	10.4	0.83
n-Heptane	5.5	10.5	12.5	0.84

### The MAD as a Screening Tool for Chromatographic Systems

The potential use of the MAD in evaluating chromatographic systems results from three advantages of the M.A.D.:

1. The speed and convenience of changing the sensing cell packing.
2. The ability to use column packing material as adsorbent in the MAD.
3. The detector response being a function of adsorbent-adsorbate interaction, the same property which affects separation in the column.

The data which were accumulated to determine whether the MAD could be used as a screening tool for chromatographic systems are summarized in Table XV. These data show:

1. Gas chromatographic retention distances increase in the same order as the increase in MAD response.
2. The separation of two GC peaks (peak to peak distance) increases in the same order as the increase in difference in MAD response.

These results indicate that the MAD can be used for quickly and conveniently obtaining information for prediction of the interaction of solutes with column packing material. The column material can be either a liquid on a solid support, or a solid adsorbent.

The results to date have only been semi-quantitative. Efforts are continuing to establish a quantitative relationship. The method could be of considerable convenience in both gas and liquid chromatography where solute/solvent/adsorbent systems could be rapidly screened without the need to pack and equilibrate columns.

TABLE XV

## COMPARISON OF MAD RESPONSE AND RETENTION DISTANCES

Liquid Phase	TOTAL PEAK HEIGHT			Air	RETENTION DISTANCE		
	Cyclohexane	Benzene	Difference		Cyclohexane	Benzene	Difference
Apiezon-L	960	1680	720	1.5	10.4	11.8	1.4
Didecyl Phthalate	2000	3840	1840	1.8	24.8	35.3	10.5
1,2,3 Tris (2-Cyanoethoxy) Propane	140	2420	2280	1.8	3.0	17.9	14.9

## Conclusions

The results of the work with the micro-adsorption detector support a number of conclusions, which are summarized below:

1. The MAD has good sensitivity,  $3 \times 10^{-5}$  °C or  $3 \times 10^{-10}$  moles of acetone. To specify minimum detectable quantities, it is necessary to know solute, solvent and adsorbent. All three contribute to the signal generated.
2. The linear dynamic range,  $10^2$ - $10^3$ , is reasonable for an analytical detector in both liquid and gas chromatographic systems.
3. The detector response can be used in both qualitative and quantitative determinations. Precision of quantitative measurements, using total peak height, or positive peak area is good, about 4% relative.
4. The utility of the MAD as a general purpose chromatographic detector is severely limited by the peculiar peak shape. For modest sample size it requires a column resolution of at least 3.75 times greater than other detectors in order to avoid peak overlap. Under overloaded conditions, the detector cannot be used to quantitate mixtures.
5. It is possible to calibrate the MAD response in terms of temperature differential or amount of heat released as a result of adsorption.
6. The MAD can be used to quickly and conveniently screen chromatographic systems to aid in selecting proper solvent and station-

ary phase for effecting separations.

7. The sensitivity and small volume of the MAD make it extremely useful as a micro-calorimeter. It is particularly well suited to adsorption studies at adsorbate concentrations down to  $10^{-6}$  molar.

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## APPENDIX I

### LIST OF FOCAL PROGRAMS USED WITH THE PDP 8/1 COMPUTER

1. MAD Peak Evaluation
2. MAD Peak Integration
3. MAD Resistor Check
4. Average and Standard Deviation of Manually Entered Data
5. "F" Test For Statistical Significance of Two Variances
6. Average and Standard Deviation of Multiple Data Sets Entered From Punched Paper Tape
7. Student's "t" Test for Statistical Equivalence of Two Means
8. MAD Calibration
9. Linear Least Squares Line and Lack of Fit of Linear Line
10. Linear Least Squares Line and Confidence Limits of Line
11. Data Reduction for Linear Dynamic Range Data-Liquid Mobile Phase
12. Data Reduction for Linear Dynamic Range Data-Gaseous Mobile Phase
13. Calculation of Minimum Detectable Quantity and Linear Dynamic Range.

## 1. MAD Peak Evaluation

C-8K MODV 11-219

```

01.01 T "MAD PEAK EVALUATION--ABRVD--05/10/71---STAFFORD" !
01.03 A "DATE OF THIS CALCULATION " DD; A "/" MM; A "/" YY; T !

02.01 C DATA INPUT AND CALCULATIONS
02.02 A "RB" RB; A " RE" RE; A " CM" CM; A " MK/HR" M; T !
02.03 S CP=0; S SN=0; S ST=0; S PS=0; S NS=0; S TS=0
02.04 S AS=0; S QA=0; S RS=0; S N=RB; S R(N)=N
02.05 S SA=0; S SQ=0; S SS=0; S SP=0
02.06 A "SAMPLE SIZE-UL " SS; T !!!
02.07 IF (RE-RB+9)2.15, 2.15, 2.09
02.09 S RO=R (N)+9
02.11 IF (RO-R(N) 2.70, 2.15, 2.15
02.15 T %8.04, "RUN NO." R(N); A "
02.20 A " PH " PH; A " PW " PW; A " PC " PC; T " CP "
02.21 S CP=(PC-PW*CM)*AN
02.22 T CP; T !
02.25 A " NH " NW " NW; A " NC " NC; T " CN "
02.26 S CN=(NW*CM-NC)*AN; T CN; T !!!
02.27 S CT=(PH+NH)*AN; S CA=CP+CN
02.31 S CV=CA/2.0
02.40 S SP=SP+(PH*AN); S SN=SN+(NH*AN); S ST=ST+CT
02.45 SAT=AN*AN; S PS=PS+(PH*PH*AT); S NS=NS+(NH*NH*AT)
02.46 S TS=TS+(CT*CT); S SA=SA+CP; S SQ=SQ+CN; S SS=SS*CA
02.47 S AS=AS+(CP*CP); S QS=QS+(CN*CN); S RS=RS+(CA*CA)
02.60 S N=N+1
02.61 S R(N)=N
02.65 IF (RE-N)w.80, 2.11,2.11
02.70 T "2.09 QUIT"
02.75 QUIT
02.80 T "!!!!!!!!!!!!!!!!!!!!!!"
02.85 T "RB" RB, " RE" RE, " SAMPLE SIZE-UL" SZ, !

03.01 C DATA OUTPUT
03.03 S NN=RE-RB+1; S ND=NN-1
03.05 T "TOTAL NO. RUNS THIS CALCULATION"; T NN, !!
03.07 S SP=SP/NN
03.10 T "AVG POSITIVE PEAK HEIGHT-MM"; T SP, !
03.12 S PS=FSQT(PS-NN*SP*SP)/ND)
03.15 T " STD DEVIATION-MM" PS, !
03.16 S RL=PS*100/SP; T " REL STD DEV-%" RL, !
03.17 S SN=SN/NN;
03.20 T "AVG NEGATIVE PEAK HEIGHT-MM" SN, !
03.22 S NS=FSQT(NS-NN*SN*SN)/ND)
03.25 T " STD DEVIATION-MM" NS, !
03.26 S RL=NS*100/SN; T " REL STD DEV-%" RL, !
03.27 S ST=ST/NN

```

Cont. on next page

## 1. MAD Peak Evaluation (Cont.)

```

03.30 T AVG TOTAL PEAK HEIGHT-MM" ST,  !
03.32 S TS=FSQ((TS-NN*ST*ST)/ND)
03.35 T "   STD DEVIATION-MM" TS,  !
03.36 S RL=TS*100; ST; T "   REL STD DEV-%" RL,  !
03.37 S S=SA/NN
03.40 T "AVG POSITIVE PEAK AREA-COUNTS" SA,  !
03.42 S AS=FSQ((AS-NN*SA*SA)/ND)
03.45 T "   STD DEVIATION-COUNTS" AS,  !
03.46 S RL=AS*100/SA; T "   REL STD DEV-%" RL,  !
03.47 SQ=SQ/NN
03.50 T "AVG NEGATIVE PEAK AREA-COUNTS" SQ,  !
03.52 S QS=FSQ((QS-NN*SQ*SQ)/ND)
03.55 T "   STD DEVIATION-COUNTS" QS,  !
03.56 S RL=QS*100/SQ; T "   REL STD DEV-%" RL,  !
03.57 S SS=SS/NN
03.59 T "AVG TOTAL PEAK AREA-COUNTS" SS,  !
03.60 S RS=FSQ((RS-NN*SS*SS)/ND)
03.65 T "   STD DEVIATION-COUNTS" RS,  !
03.66 S RL=RS*100/SS; T "   REL STD DEV-%" RL,  !
03.70 T "GOTO 2.01?"
03.80 QUIT
*
```

## 2. MAD Peak Integration

```

Ø1.14 T "MAD PEAK INTEGRATION-ABRVD--Ø5/1Ø/71----STAFFORD", !
Ø1.15 C USING SIMPSON'S RULE
Ø1.16 C INPUT DATA FROM PUNCHED PAPER TAPE
Ø1.17 A " DATE OF THIS CALCULATION " DD; A MM; A YY; T !!
Ø1.2Ø T " USING: MM/Ø.ØØ1MV=Ø.2286" !
Ø1.3Ø A " CHT. SP. IN/HR " CS; T !!
Ø1.32 T !!!!!!!
Ø1.34 C DATA INPUT
Ø1.35 A "RUN NO. " RN; T !
Ø1.4Ø S PK=1
Ø1.45 T !; A " NO. OF DATA PTS. " N; A " ATTN " AN; T !
Ø1.5Ø *; F I=1, N; A G(I);
Ø1.51 *;
Ø1.6Ø T !; T "INITIAL DATA PT" G(1);
Ø1.65 T !; T "FINAL DATA PT " G(N); T !

Ø2.Ø5 C INTEGRATION CALCULATIONS
Ø2.2Ø S MV=Ø.2286
Ø2.25 S NN=N; S DX=CS*25.4/36ØØ
Ø2.3Ø IF (NN-2)2.4Ø,2.45,2.35
Ø2.35 S NN=NN-2; GOTO 2.3Ø
Ø2.4Ø S NT=1; GOTO 2.5Ø
Ø2.45 S NT=Ø.Ø; S N=N-1
Ø2.5Ø S S4=Ø.Ø; S K=N-1; F I=2,2,K; S S4=S4+G(I)
Ø2.55 S S2=Ø.Ø; S K=N-2; F I=3,2,K; S S2=S2+G(K)
Ø2.6Ø IF (NT)2.65,2.65,2.75
Ø2.65 S XT=G(1)+G(N); S TP=(DX/2)*(G(N)+G(N+1))
Ø2.7Ø S N=N+1; GOTO 2.8Ø
Ø2.75 S XT=G(1)+G(N); S TP=Ø.Ø
Ø2.8Ø S AR=(MV)*((DX/3)*((4*S4) + (2*S2) + XT) + TP)
Ø2.82 S RA=AN*AR
Ø2.85 IF (PK-1)3.11,3.11,3.25

Ø3.Ø5 C DATA OUTPUT AND INDEXING
Ø3.11 T !!!; T "RUN NO. " RN; T !
Ø3.14 T "POSITIVE PEAK AREA, SQMM" AR; T !
Ø3.17 T "UNATTENUATED POS. PK AREA, SQMM" RA; T !
Ø3.21 IF (PK-1)3.34,3.34,3.27
Ø3.25 T !!!; T "RUN NO. " RN; T !
Ø3.27 T "NEGATIVE PEAK AREA, SQMM" AR; T !
Ø3.29 T "UNATTENUATED NEG. PK AREA, SQMM" RA; T !
Ø3.34 T "NO. DATA PTS THIS CALCULATION" N; T !
Ø3.4Ø F I=1, N+1; DO 3.45
Ø3.45 S G(I)=Ø.ØØØØ
Ø3.46 S N=Ø
Ø3.48 IF (PK-1)3.6Ø,3.6Ø,3.5Ø
Ø3.5Ø T !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!; T %2, DD,MM,YY; S RN=RN+1
Ø3.51 T !!!!!!!!!!!!!!!; T %8.Ø4, "RUN NØ. " RN; S PK = 1; GOTO 1.45
Ø3.6Ø T !!!!!!!!!!!!!!!; S PK=2; GOTO 1.45
Ø3.65 QUIT
*
```

## 3. MAD Resistor Check

C-8K MODV 11-219

```

01.03 T "MAD RESISTOR CHECK--05/11/71-----STAFFORD" , !
01.05 A "DATE OF THIS CALCULATION " DD; A MM; A YY; T !!!
01.45 C DATA INPUT
01.50 A "RUN NO. " RN; A "      NO. OF DATA PTS " N; T !
01.70 *; F I=1,N; A G(I)
01.75 *;

02.01 C CALCULATIONS
02.04 S SM=0; S SS=0
02.10 F I=1,N; S SM=SM+G(I)
02.20 F I=1,N; S SS=SS+G(I)*G(I)
02.30 S SM=SM/N
02.40 S SS=FSQT((SS-N*SM*SM)/(N-1))

03.05 C DATA OUTPUT AND INDEXING
03.10 T !!!, "RUN NO.
03.20 T "NO. DATA PTS" N, !
03.30 T "AVERAGE RESISTANCE--OHMS X E3"SM, !
03.40 T "STD. DEV. " SS, !
03.45 S SS=SS*100/SM
03.50 T "REL. STD. DEV., %" SS, !
03.60 QUIT
*
```

## 4. Average and Standard Deviation of Manually Entered Data

C-8K MODV 11-219

```

01.03 T "AVG. & STD. DEV.-MANUAL--5/12-71--STAFFORD" !
01.05 A "DATE OF THIS CALCULATION " DD; A MM; A YY; T !!
01.20 S RN=RB
01.30 S Q=1

02.01 C DATA INPUT AND CALCULATIONS
02.02 A "RUN NO. " RN; A " NO. PTS. " N
02.10 S SM=0; S SS=0; T !!
02.40 F I=1,N; T %2, I; T %8.04, " "; A G(I); T !
02.50 F I=1,N; S SM=SM +G(I)*G(I)
02.60 F I=1,N; S SS=SS +G(I)
02.65 S SM=SM/N
02.70 S SS=FSQT((SS-N*SM*SM)/(N-1))

03.05 C DATA OUTPUT AND INDEXING
03.10 T !; T "AVERAGE " SM, !
03.20 T "STD DEV "SS, !
03.25 S SS-SS*100/SM
03.30 T "REL STD DEV % " SS, !!!
03.50 S Q=Q+1; IF (Q-4)2.02,2.02,3.60
03.60 T !!!!!!!!!!!!!!!!!!!!!!!!!!!!!; T DD; T MM; T YY; T !!!
03.70 GOTO 1.30
03.90 T "1.10 QUIT", !
03.95 QUIT
*
```

## 5. "F" Test For Statistical Significance of Two Variances

C-8K MODV 11-219

```

Ø1.Ø3 T "F TEST FOR TWO VARIANCES--Ø5/13/71---STAFFORD",!
Ø1.1Ø A "DATE OF THIS CALCULATION " D; A M; A Y; T !!!
Ø1.25 S Q = 1
Ø1.35 C DATA INPUT AND CALCULATIONS
Ø14Ø A "RUN NO. " N; T!
Ø1.5Ø A "STD DEV (1) " S1; A" NO. PTS. " N1; T!
Ø1.6Ø A "STD DEV (2) " S2; A" NO. PTS. " N2; T!
Ø1.7Ø S R = (S1*S1) / (S2*S2)
Ø1.8Ø T "F RATIO " R; S R = 1/R: T"
Ø1.9Ø T "DF (1) "N1-1, " DF (2) " N2-1, !!!

Ø2.Ø1 C DATA OUTPUT AND INDEXING
Ø2.1Ø S Q=Q + 1; IF (Q-6) 1.5Ø, 1.5Ø, 2.3Ø
Ø2.3Ø T !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
Ø2.4Ø T %2, D, "/" M, "/" Y; T %8.Ø4, !!!
Ø.25Ø GOTO 1.25
*
```



6. Average and Standard Deviation of Multiple Data Sets Entered  
From Punched Paper Tape

C-8K MODV 11-219

Ø1.Ø3 T "AVG & STD DEV--MULTIPLE SETS-7/25/71-STAFFORD", !  
 Ø1.Ø4 C FROM PUNCHED PAPER TAPE  
 Ø1.Ø5 A "DATE OF THIS CALCULATION" DD; A MM; A YY; T !!  
 Ø1.15 S P=1  
 Ø1.2Ø A "RUN NO. ", RN; A" NO. DATA SETS", NS; T !  
 Ø1.3Ø SQ= 1

Ø2.Ø5 C DATA INPUT AND CALCULATIONS  
 Ø2.1Ø S SM=Ø ; S SS = 0/; T !!  
 Ø.217 A "NO DATA POINTS" DP  
 Ø2.2Ø \*; F I-1, DP; A G (I)  
 Ø2.23 \*;  
 Ø2.27 T !; A "USE DATA? Y= 1, N=2" UD; T !!  
 Ø2.3Ø IF (US-1) 2.33, 2.33, 3.5Ø  
 Ø2.33 F I-1, DP; S SM=SM + G (I)  
 Ø2.38 F I=1.DP; S SS=SS + G (I) \* G (I)  
 Ø2.5Ø S SM=SM/DP  
 Ø2.55 S SS=FSQT ((SS-DP\*SM\*SM) / (DP-1))

Ø3.Ø1 C DATA OUTPUT AND INDEXING  
 Ø3.Ø5 T "TUN " RN, ": SET" Q, ": NO. PTS" DP, !  
 Ø3.1Ø T !; T " AVERAGE "SM, !  
 Ø3.2Ø T "STD DEV "SS, !  
 Ø3.25 S SS=SS\*1ØØ SM  
 Ø3.3Ø T " REL STD DEV % " SS, !!!  
 Ø3.5Ø S Q = Q +1; IF (Q-NS) 2.1Ø, 3.6Ø  
 Ø3.6Ø S P=P+1; IF (P-1) 1.2Ø, 3.7Ø  
 Ø3.7Ø T !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!; T DD, MM, YY, !!!  
 Ø3.8Ø GOTO 1.15  
 Ø3.9Ø QUIT  
 \*

## 7. Student's "t" Test for Statistical Equivalence of Two Means

C-8K MODV 11-219

```

Ø1.Ø3 T "STUDENT'S T FOR H: MEAN 1-MEAN2-7/27/71-STAFFORD"; T!
Ø1.ØØ A " DATE OF THIS CALCULATION " DD: A MM: A YY: T!
Ø1.15 A "NO. CALCULATIONS/ PAGE" C;A" NO. SKIPS B" B; T.!'
Ø1.2Ø S Q=1
Ø1.45 C DATA INPUT
Ø1.5Ø A " RUN NO. " RN; T !
Ø1.55 A "MEAN (1) " M1; A" STD. DEV. (1) "S1
Ø1.56 " NO. PTS (1) " P1; T!
Ø1.6Ø A "MEAN (2) "M2; A" STD. DEV. (2) "S2
Ø1.66 A " NO. PTS (2) "P2; T !!

Ø21Ø C CALCULATIONS
Ø2.2Ø S M=Ø; S SS=Ø; S T=Ø
Ø2.3Ø S M=M1-M2
Ø2.35 S SS=((P1-1)*S1*s1)+((P2-1)*S2*S2)/(P1-P2-2)
Ø2.4Ø SM=FSQT(SS/P1 + SS/P2)
Ø2.45 S %T=M/SM

Ø3.Ø1 C DATA OUTPUT AND INDEXING
Ø3.Ø5 T "T " T; T !!!!
Ø3.15 S Q=Q+1; IF (Q-C) 1.5Ø, 1.5Ø, 3.4Ø
Ø3.4Ø S BB=1
Ø3.5Ø T !!!
Ø3.55 S BB=FF+1; IF (BB-B) 3.5Ø, 3.5Ø, 3.7Ø
Ø3.7Ø !!! ; T DD, MM, YY, !!!
Ø3.8Ø GOTO 1.2Ø
Ø3.9Ø QUIT
*
```

## 8. MAD Calibration

C-8K MODV 11-219

```

Ø1.Ø2 T "MAD CALIBRATION ---7/27/71--STAFFORD", !
Ø1.Ø5 A "DATE OF THIS CALCULATION " DD; A MM; A YY; T !!!
Ø1.1Ø C DATA INPUT
Ø1.3Ø A "OHMS " OH; A "          GMS/CC" D; A " CAL/GM=C CG; T !
Ø1.4Ø A "RB " RB; A "          RE' RE; A " ML/HR " M; T !!!
Ø1.5Ø S RN=RB
Ø1.6Ø S Q=1

Ø2.Ø1 C CALIBRATION CALCULATIONS
Ø2.Ø5 T %8.Ø4, "RUN NO. " RN; A" ATTN."AN; T !
Ø2.1Ø A "VOLTS: V' A" MV-SIGNAL" VS; A "BASELINE"VB; T !!
Ø2.2Ø S TD=(Ø.239*36ØØ*V*V)/(M*OH*D*C* G)
Ø2.3Ø S MD=(VS-VB)*AN)/(LØØØ*TD)
Ø2.4Ø S DM=228.6*MD/1ØØØ

Ø3.Ø5 C DATA PUTPUT AND INDEXING
Ø3.1Ø T %, "TEMP DIFERENTIAL-C" TD, !
Ø3.15 T "MV/DEG" MD; T" MM/DEG", DM; T !!!!
Ø3.5Ø S RN=RN+1; IF (RN-RE) 3.6Ø, 3.6Ø, 3.9Ø
Ø3.6Ø S Q=Q+1; IF (Q-5) 2.Ø5, 2.Ø5, 3.7Ø
Ø3.7Ø T !!!!!!!!!!!!!!!!!!!!!!!!!!!!!, DD, MM, YY, 111!!!
Ø3.75 GOTO 1.6Ø
Ø3.9Ø QUIT
*
```

## 9. Linear Least Squares Line and Lack of Fit of Linear Line

C-8K MODV 11-219

```

Ø1.Ø3 T "LINEAR LST SQUARES & LOF--8/7/71---SAFFORD",!
Ø1.Ø5 A DATE OF THIS CALCULATION" DD, MM, YY; T !!
Ø1.Ø6 C DATA INPUT
Ø1.1Ø A "RUN NO." RN; T !
Ø1.2Ø A "NO. DATA SETS" DS; A " NO. PTS/SET" DP; T !
Ø1.3Ø S RS=Ø=; S MS=Ø; S ES=Ø; S LS=Ø
Ø1.4Ø S C=1; S P=1; S PTS=DS*DP
Ø1.7Ø T "      I      " " T"      X(I)      " " T" Y (I)      " " T!

Ø2.Ø3 C LACK OF FIT ERROR CALCULATIONS
Ø2.Ø5 S EL=Ø; S E2=Ø; A " STIN" N; T !
Ø2.1Ø F I=P, P+(DP-1); T I;A" "X(I); A" " Y (I); T!
Ø2.2Ø F I=P, P+(DP-1); S E1=E1+Y(I)*Y(I)*N*N; S E2=E2+Ø(I)*N
Ø2.3Ø S ES=ES+EL=(E2*E2)/DP
Ø2.4Ø SP=P+DP
Ø2.5Ø S C=C+1; IF (C-DS) 2.Ø5, 2.Ø5, 3.Ø5

Ø3.Ø4 C LEAST SQUARES CALCULATIONS
Ø3.Ø5 S XS=Ø; S SX=Ø; S YS=Ø=; S SY=0/; S PR=Ø
Ø3.1Ø F I=1, PTS; S XS=SX+X(I); S SX=SX+X(I) 8X(I); S YS=YS+Y(I)*N
Ø3.2Ø F I=1, PTS; S SY=SY+Y(I) (Y(I) (N*N; S PR=PR+X(I)*Y(I)*N
Ø3.3Ø S M=(PR=(XS*YS)/ PTS)/ (SX-(XS*XS)/PTS)
Ø3.4Ø S B=YS?PTS-(M*XS)/PTS
Ø3.5Ø S RS=US*YS/PTS
Ø3.6Ø S MS=M*(PR=(XS*YS)/PTS0
Ø3.7Ø S LS=SY=RS-MS-es
Ø3.8Ø S EF=PTS-DS; S LF=PTS-EF-2
Ø3.9Ø S RF=(LS/LF)/(ES/EF)

Ø4.Ø5 C DATA OUTPUT AND INDEXING
Ø4.1Ø T !; T "SLOPE" M, !
Ø4.2Ø T "INTERCEPT " B, !
Ø4.3Ø T "LACK OF FIT F-RATIO" RF; T" DF" LF; T", "EF
Ø4.4Ø T !!!!!; T "1.1Ø QUIT"
Ø4.5Ø QUIT
*
```

## 10. Linear Least Squares Line and Confidence Limits of Line

C-8KMODV 11-219

```

Ø1.Ø3 T "LINEAR LST SQ. & CONF LIMS-8/1Ø/71-STAFFORD", !
Ø1.Ø4 A "DATE OF THIS CALCULATION"DD, M1, YY; T !!!
Ø1.Ø5 C DATA INPUT
Ø1.1Ø A "RUN NO." RN; T !
Ø1.2Ø A "NO. DATA PTS" PTS; T !
Ø1.3Ø S RS=Ø; S MS=Ø; S ES=Ø S LS=Ø; S RMS=Ø
Ø1.7Ø T " I          "; T"      X(I)          "; T " Y (I) "; T"
Ø1.71 T !
Ø1.8Ø F I=1, PTS; T I; A"  "X(I); A" "Y(I); A" "N(I)

Ø3.Ø5 C CALCULATINOF LEAST SWUARES SLOPE,
Ø3.Ø6 C INTERCEPT, AND CONFIDENCE LIMITS
Ø3.Ø8 S XS=Ø; S SX=Ø; S YS=Ø; S SY=Ø; S PR=Ø
Ø3.1Ø F I=1, PTS; S XS=SX+X(I); S SX=SSX+X(I)*X(I); S YS=YS+Y(I)*
Ø3.2Ø F I=1, PTS; S SY=SY+Y(I)*Y(I)*N(I)*N(I)
Ø3.25 F I=1, PTS; S PR=PR+X(I)*Y(I)*N(I)
Ø3.3Ø S M=(PR-(XS*YS)/PTS)/(SX-(SX*SX)PTS)
Ø3.4Ø S B=YS/PTS-(M*XS)PTS
Ø3.5Ø S MS=YS?PTS
Ø3.6Ø S RS=M*(PR-(XS*YS)/PTS)
Ø3.7Ø S LS=SY-RS-MS
Ø3.8Ø S ES=LS/(PTS-2)
Ø3.85 S YS-FSQT(ES/PTS)
Ø3.9Ø S DF=PTS-2
Ø4.Ø4 C DATA OUTPUT AND INDDXING
Ø4.1Ø T !; T "SLOPE" M, !
Ø4.2Ø T "INTERCEPT" B, !
Ø4.3Ø T "STD DEV" YH; T" DF" DF; T!
Ø4.4Ø T "CONFIDENCE LIMITS=±STD. DEV.*T(L=LEVEL/2) (DF))"
Ø4.5Ø T !!!!!; T" 1.1Ø QUIT"
Ø4.6Ø QUIT
*
```

11. Data Reduction for Linear Dynamic Range Data-Liquid Mobile Phase

C-8K MODV 11-219

```

Ø1.Ø3 T "LDR DATA REDUCTION-- 8/11/71--STAFFORD", !
Ø1.Ø5 A "DATE OF THIS CALCULATION" DD, MM, YY: T !!
Ø1.Ø6 D DATA INPUT
Ø1.1Ø A "ADSORBENT" AD: T !
Ø1.15 S P=;
Ø1.2Ø A "SOLUTE:" SO; A " MW" MW; A " NO. DATA SETS" NS; T !!
Ø1.25 S Q =1
Ø1.3Ø A "RUN NO." RN; A " ATTN: AN; T !
Ø1.4Ø A "US" UL; A " GMS/ML" C; A " MV/1-ØØØ" MV; T!

Ø2.Ø5 C CALCULATION
Ø2.1Ø S RE=AN*MV; S GF=(UL*C) / 1ØØØ; S MO-GM/MW

Ø3.Ø5 C DATA OUTPUT
Ø3.1Ø T%, "GMS SOLUTE" GM; T!
Ø3.2Ø T "MOLES SOLUTE" MO; T !
Ø3.3Ø T "RESPONSE, MV*E3" Re; T !!!!

Ø4.Ø5 C INDEXING
Ø4.1Ø S Q=Q+1;; IF (A-NS) 1.3Ø, 1.3Ø ,4.15
Ø4.15 S P=P+1; IF (p-2) 1.2Ø, 1.2Ø, 4.2Ø
Ø4.2Ø T% 2.00, !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!; T DD; T mm; T YY; T !!!
Ø4.3Ø GOTO 1.15
Ø4.4Ø QUIT
*
```

## 12. Data Reduction For Linear Dynamic Range Data Gaseous Mobile Phase

C-8K MODV 11-219

```

Ø1.Ø3 T "LDR DATA REDUCTION -PAIRS -LC/GC--8/26/71--STAFFORD", !
Ø1.Ø5 A "DATE OF THIS CALCULATION" DD, MM, YY; T !!
Ø1.Ø6 C DATA INPUT
Ø1.1Ø A "ADSORBENT" AD; A "          SOLUTE" SO; T !
Ø1.15 A " GMS/ML" C; A "          MW"   MW; T !!
Ø1.2Ø S Q=1
Ø1.3Ø A "RUN NO." RN; A " ATTN: AN; A " UL" UL; T !
Ø1.5Ø A "MV/1-ØØØ" M1; A " MV2/1ØØØ" M2; T !
Ø1.6Ø S MV=(M1+M2) / 2

Ø2.Ø6 C CALCULATIONS
Ø2.1Ø S RE=AN*MV; S GM=(UL*C)/1ØØØ; S MO=GM/MW

Ø3.Ø5 C DATA OUTPUT
Ø3.1Ø T%, "GMS SOLUTE" GM; T !
Ø3.2Ø T "MOLES SOLUTE" MO; T!
Ø3.3Ø T "RESPONSE, MV *E3" RE; T !!!

Ø4.Ø5 C INDEXING
Ø4.1Ø S Q=A+1; IF (Q-6)1.3Ø, 1.3Ø, 4.2Ø
Ø4.2Ø T% 2.ØØ, !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!; T DD; T MM; T YY; T !!!
Ø4.3Ø GOTO 1.1Ø
Ø4.4Ø QUIT
*
```

## 13. Calculation of Minimum Detectable Quantity and Linear Dynamic Range

C-8K MODV 11-219

```

Ø1.Ø3 T "MIN. DETECTABLE QUANT. & LDR--9/3/71--STAFFORD", !
Ø1.Ø5 A "DATE OF THIS CALCULATION" DD, MM, YY; T L
Ø1.Ø6 T "NOTE: INPUT DATA IN MM & MM/MOLE"; T !!
Ø1.Ø7 C DATA INPUT
Ø1.1Ø A "ADSORBENT" AD; T !
Ø1.13 S Q=1
Ø1.2Ø A "RUN NO." RN; A " SOLUTE" SO; A " MW" MW; T !
Ø1.3Ø A "SLOPE" M; A " MAX. SAMPLE" MX
Ø1.39 C CALCULATIONS
Ø1.4Ø T !; S MQ=7.Ø/M; S GQ=MQ*MW; S GX=MX*MW
Ø1.45 S MR=MX-MQ; S GR=GX-GQ
Ø1.46 C DATA OUTPUT AND INDEXING
Ø1.47 T "          MINIMUM          MAXIMUM          LDR"; T!
Ø1.5Ø T %, "MOLES;   "MQ; T "   "MX; T   "   "MR; T !
Ø1.6Ø T GRAMS;     " GQ; T "   "GX; T   "   " GR; T !!!!
Ø1.7Ø S Q=Q+1; IF (Q-7)1.2Ø,1.2Ø,1.8Ø
Ø1.8Ø T !!!!!!!!!!!!!!!!!!!!!!!!!!!!!; T % 2.Ø2, DD, MM, YY, !!!
Ø1.9Ø GOTO 1.1Ø
Ø1.95 QUIT
*
```



## EVALUATION OF A MICRO-ADSORPTION DETECTOR

### IN LIQUID AND GAS CHROMATOGRAPHY

By

David Todd Stafford

#### A B S T R A C T

A study was made with the objectives:

1. Evaluation of a micro-adsorption detector for use in liquid chromatography.
2. Evaluation of a micro-adsorption detector for use in gas chromatography.
3. Investigation of the micro-adsorption cell as a tool for screening chromatographic systems, in adsorption studies, and as a micro-calorimeter.

The micro-adsorption detector was found to have sufficient sensitivity to detect nanogram quantities of a component in either a liquid or gaseous carrier, and to have a linear dynamic range of  $10^2$ - $10^3$ . These qualities, combined with the selectivity of the detector indicate its usefulness in both liquid and gas chromatographic operations. The major limitation to its use is the characteristic adsorption/desorption response curve, which requires increased column lengths or resolution over other detectors such as the UV detector. In addition a semi-quantitative correlation between MAD response and chromatographic retention times indicates that the detector has significant potential as a screening tool for separation systems. By means of a calibration apparatus the detector response was characterized in terms of heat flux and temperature differential, and heats of adsorption were calculated at concentrations of  $10^{-4}$  -  $10^{-6}$  molar. These compared favorably with those literature values which were available close to these concentrations.

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