SOME EFFECTS OF SECTIONAL COLUMN PACKING IN LARGE DIAMETER GAS CHROMATOGRAPHY COLUMNS

By

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CHAPTER I

INTRODUCTION

Chromatography is a term used for separations achieved by sample transport in a moving phase and selective retardation of that sample's components by a stationary phase. Chromatographic separations are classified by the phases used to achieve separation. The moving phase, for sample transport, may be a liquid or a gas. The stationary phase, for separation of sample components, may be a solid or a liquid.

Gas chromatographic separations are those in which the moving phase is a gas. Further classification is dependent on the stationary phase used. Use of a solid stationary phase is termed gas solid chromatography (G. S. C.); and use of a liquid stationary phase, gas liquid chromatography (G. L. C.).

The two types of gas chromatographic separation are further subdivided into classes depending on the type of separation achieved. There are three such types; elution development, frontal analysis, and displacement. In elution development, the components are selectively retarded and emerge from the column as separate bands. For frontal analysis, the sample is continuously fed to the column. The least retarded component emerges first, followed by a mixture of the least and second least retarded components. The composition of the emerging gas stream varies in this manner until the last component emerges. The column effluent now contains all the components in the sample, diluted

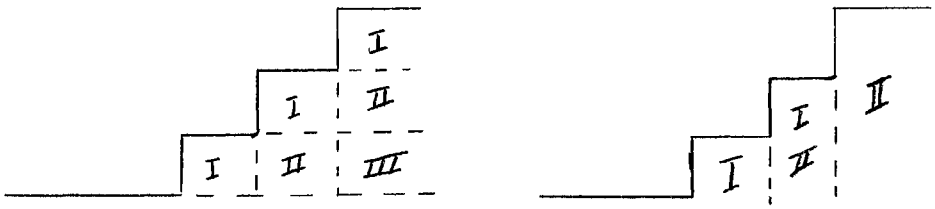
by the gaseous moving phase. In the displacement method, the sample is first placed on the column and then a moving phase more strongly adsorbed than any sample component is introduced. The sample components are then forced from the column as the moving phase desorbs and replaces them on the stationary phase. Examples of chromatograms obtained by each method are shown in Figure 1.

Gas chromatographic apparatus consists of the following basic units:

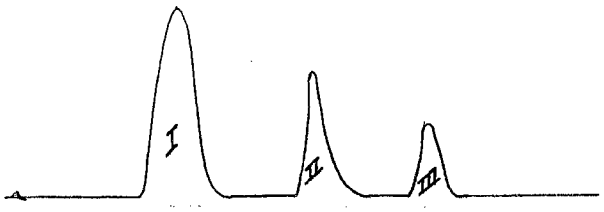
1. the carrier gas supply (moving phase)
2. the sample injection port
3. the column (containing the stationary phase)
4. the detector (which signals the presence of an emerging component).

A block diagram of the apparatus is shown in Figure 2.

The carrier supply may be regulated to give the desired flow of moving phase. The carrier passes through the injection port and then carries the sample across the stationary phase contained in the column. The sample components then pass through the detector, which signals their presence. Usually a recording is made of the detector's signal from the time of sample injection through elution of the last component of the sample. Qualitative identification of components is made on the basis of the time required to elute the component. Quantitative analysis is based on the integrated detector response or upon the maximum response to the passage of a sample component. The recording made of detector response is a chromatogram. The area under a peak traced on the recording corresponds to the integrated detector response, while measurement of peak height corresponds to determination of the maximum



Frontal Analysis Chromatogram Displacement Chromatogram



Elution Chromatogram

Fig. 1. Chromatogram Types.

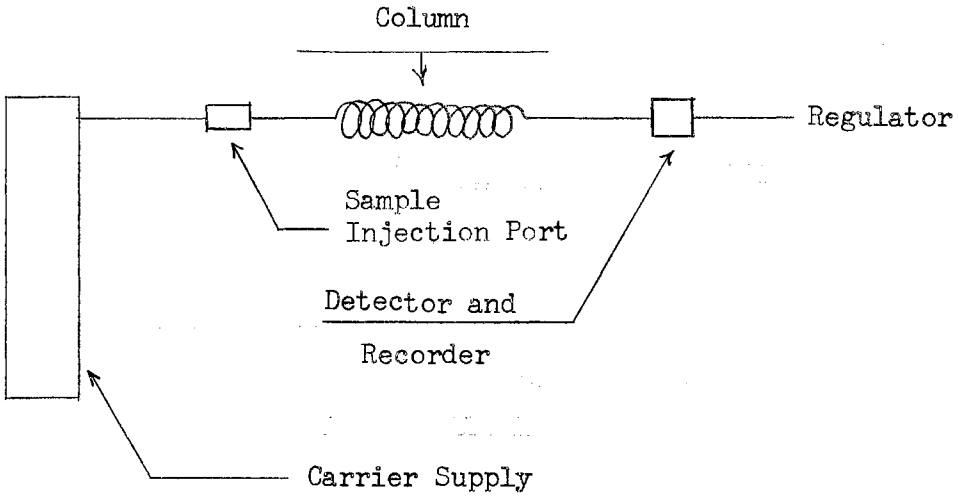


Fig. 2. Block Diagram of Chromatograph.

response occurring during the passage of the maximum component concentration through the detector.

COLUMN EFFICIENCY

Gas chromatography is capable of performing a very large number of separations. Variations in types of separation media and in techniques provide seemingly endless possibilities. The key to the versatility of gas chromatography is the column. A change of the liquid phase in a column may result in the separation of entirely different types and classes of compounds. As properties of column materials become better known, the choice of a column for a specific separation becomes easier. For comparison of separating efficiencies of different columns, an analogy of chromatographic columns to distillation columns has been employed. In this manner, a method of describing column efficiency in terms of theoretical plates exhibited toward a specific component and under specified conditions was developed.

Efficiency is expressed in this method as N, the number of theoretical plates, or as H.E.T.P., the height equivalent to a theoretical plate. The equation relating the two is

$$\text{H.E.T.P.} = L/N \text{ where}$$

L = column length

N = number of theoretical plates

Solutes, or sample components, in a chromatographic column may be described theoretically by an approximation to the binomial distribution and also Poisson distribution. Both theories yield the equation

$$N = 16\left(\frac{x}{y}\right)^2$$

when $\underline{x}$ and $\underline{y}$ are measured in the same units. In this equation $\underline{x}$ is the distance from the origin of the chromatogram to the point of maximum elution (i.e., to the peak) and $\underline{y}$ is the width of the peak at the base line. Both are, therefore, units of time which is represented by distance on the recording or chromatogram.

In the curve representing a normal distribution, tangents at the points of inflection intercept the abscissa at two points a distance of four standard deviations apart. One standard deviation is

$$\frac{x}{N^{\frac{1}{2}}}$$

The width of a peak approximating a normal distribution determined in this manner would be

$$y = \frac{4x}{N^{\frac{1}{2}}}$$

Solving for $\underline{N}$, the number of theoretical plates yields

$$N = 16\left(\frac{x}{y}\right)^2$$

This graphical method of calculating column efficiencies, which has been approved by the Gas Chromatograph Committee, is illustrated in Figure 3.

PREPARATIVE SCALE CHROMATOGRAPHY

Preparative gas chromatography is the use of a gas chromatographic separation to prepare relatively large quantities of highly purified compounds. It differs from analytical chromatographic separations in several aspects. In preparative gas chromatography, it is not necessary to separate all sample components; it is necessary only to separate the desired component from the remainder of the sample. In

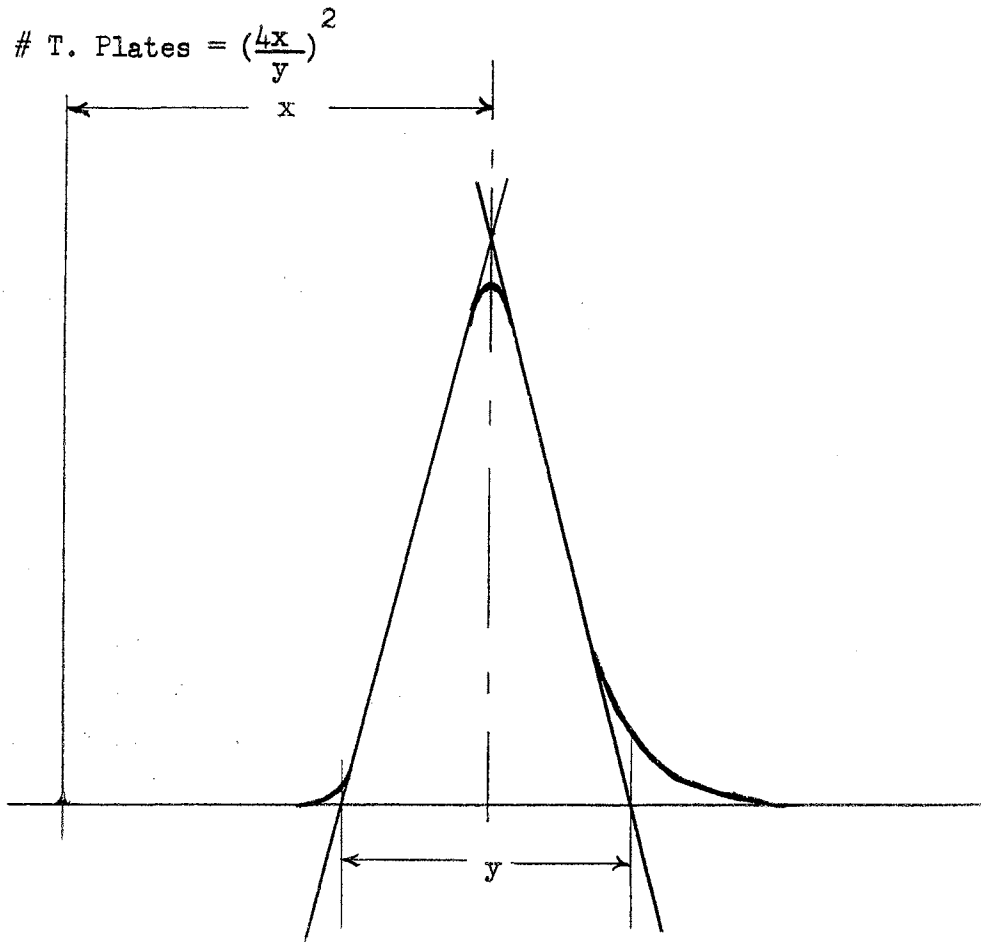


Fig. 3. Theoretical Plate Calculation.

preparative work, it is necessary to collect the desired component, while in analytical work, the eluted components are usually exhausted into the atmosphere after passage through the detector. In preparative work, quantitative data may not be necessary on each run. This in many cases eliminates close control of parameters affecting sensitivity, qualitative calibration, peak shape and sample introduction. Such control is necessary only when a parameter affects resolution to such a degree that the desired compound is mixed with another component of the sample. Incomplete resolution can be tolerated to some extent (but at a loss in efficiency) by collecting only the portion of the peak not mixed with the unresolved compound.

There are several approaches to the large scale preparation of pure components by gas chromatography. Commercial instrumentation is available and is based primarily on two methods of attack or upon a combination of these. One is the use of multiple identical columns arranged so that each column receives a portion of a single large sample injection, separates the components, and elutes them into a common manifold. Each column must elute the same component into the manifold at the same time to prevent mixing or loss. Another method uses automatically repeated injections and separations on an analytical scale. Small samples must be used to prevent overloading the column and, thus, much more time is required for production of a given amount of a pure compound. Automation for this type of preparative gas chromatography usually involves a cycle arranged so that the desired peak is collected; others are vented to the atmosphere and the last peak activates the mechanism for injection of the next portion of the sample.

There are disadvantages to both of these methods. In the use of multiple columns, each column must be identical to the others in the group in order to elute a specific compound at the same time the other columns do. This condition is difficult to achieve due to many parameters involved. Each must receive a proportional amount of sample, separate the components identically, and elute them at the same time. In the case of an impurity eluted close to the compound of interest, some mixing may occur in the exhaust manifold.

Automated analytical scale separations usually are dependent upon a relay activated by detector response to an emerging component. The relay activations are arranged in a cycle to vent undesired components, collect those desired, and reinject new sample upon completion of the run. In addition to problems normally encountered in setting up such a system and maintaining it in satisfactory operating condition, there are other problems created by factors inherent to the practice of gas chromatography. Baseline drift, spurious electrical noise, change in column temperature, and sample composition change are a few items--all possibly causing activation of the relay and erroneous advancement of the cycle. Thus an impurity could be collected in previously collected pure compound and the desired compound vented.

A single column, capable of handling large quantities of sample, would more efficiently produce pure compounds. If desirable it could be used in conjunction with the previous methods. Such a column must be capable of handling the desired sample volume and still resolve at least the compound or compounds of interest. Under identical conditions of temperature and pressure an increase in sample volume results

in a directly proportional increase in the column volume occupied by the sample. This increase, in a fixed diameter column, results in a wider zone occupied by a component of the sample. When such zones overlap, resolution is incomplete and the column is overloaded. Increasing column volume by increasing its length is not as practical as increasing the diameter of the column, for the volume of a cylinder changes much more rapidly with diameter than with length. An increase in volume furnishes more of the separation medium to handle the increased sample volume and if this were the only consideration, should yield a separation comparable to an analytical scale apparatus.

Unfortunately, however, the use of large columns in preparative chromatography has been hindered by high degree of loss of resolving power with increasing diameter. In most cases this loss is not accounted for by the factors normally associated with larger sample volumes, such as incomplete or slow vaporization of liquid samples.

CHAPTER II

HISTORY

The principles of chromatography were utilized as early as 1512 by Brunschwig (4). He described a method of purifying ethyl alcohol by passing the alcohol through a sponge soaked in olive oil to separate the spirits and the moisture. After repeated trials, the method disappeared from use during the 15th and 16th centuries (32).

In 1903, Tswett (36) passed a solution containing pigmented compounds through a column filled with a substance that selectively adsorbed and desorbed the compounds. The colored compounds emerged from the column as separate bands according to their varying degrees of adsorption. Tswett named the technique chromatography, from the Greek words chrom and graphien, with the meanings "color" and "to write," respectively.

The possibility of utilizing a gaseous moving phase was first mentioned in 1941 by Martin and Synge (33) in a paper describing a system of liquid-liquid chromatography. The principles of gas-liquid chromatographic separations were described in this paper. No experimentation was carried out, however, until 1952 when James and Martin (30) performed a separation using a gaseous moving phase. They separated a mixture of fatty acids in a column containing a silicone oil supported on kieselguhr. The quantitative aspects of the analysis were carried

out by an automatic titration device. The technique was now established, but it was little used for several years due to difficulty in the qualitative and quantitative determination of the eluted components.

The technique gained rapid general acceptance when, in 1954, Ray (34) introduced the katharometer as a detector. This detector had previously been used by Phillips as a detector in displacement gas chromatography. Many other detectors have since been developed and a high degree of sensitivity is possible.

Column parameters were observed and column theory developed. Some major contributors in this area are Giddings, Golay, DeWet, and Pretorius. Giddings' (15, 16, 17, 18) work is primarily with the theoretical aspects and authentic models describing processes involved in separations in gas chromatographic columns. Golay (23, 24) is generally credited with the concept of capillary or open bore columns in which the liquid phase is coated on the column walls, while DeWet and Pretorius (7, 8) studied the effect of various parameters upon column efficiency. As was mentioned earlier, a method of measuring column efficiency was established and is now in common use. The number of theoretical plates exhibited by a column is representative of its efficiency. The Poisson and binominal distribution theories make possible calculation of the number of theoretical plates in a column from measurements of retention time and peak width as taken from the recording or chromatogram. The solute is specified, as are conditions of temperature, carrier flow, and sample size. This method of determination of column efficiency was recommended as the definition of theoretical efficiency by the Gas Chromatography Committee (6).

PREPARATIVE SCALE CHROMATOGRAPHY

James and Martin (30) predicted that the usable sample size could increase proportionally with the cross sectional area of the column. This prediction was verified by DeWet and Pretorius (9).

Attempts to prepare chromatographically pure compounds in quantity were made. Evans and Tatlow (11) reported the use of a three centimeter by sixteen foot column to separate isomers of nonafluorocyclohexane in quantity, although the boiling points of the compounds differ by only one degree centigrade. Evans reported the separation of as much as 250 grams of mixture in a large diameter column.

Automation was introduced for repeated injection, separation and component collection of small samples on analytical scale apparatus. Ambrose and Collerson (1) used a clock mechanism for alternate injection and collection of hydrocarbons. However, column temperature and flow rate had to be controlled so that retention times would not vary. Atkinson and Tuey (2) eliminated this problem by using a system of electrically controlled valves activated by the deflection of a recorder as a sample component entered the detector. Felton (12) also reported the use of an auto-cycling instrument using an eccentric cam to close a microswitch at recorder deflection.

An apparatus for preparative use involving utilization of multiple columns was reported by Johns, et al. (31). The instrument used eight columns, either in parallel or in series. In 1962, Giddings (14) showed theoretical basis for a continuous separation performed on a revolving column. The separation media was contained between the walls of two concentric cylinders. This type of column design is referred

to as the annular ring type. The sample is continuously injected through a fixed stationary injection port. Rotation of the column and continuous injection would give separation and elution of sample components in bands resembling the stripes of a barber pole.

In 1964, Albert (3) reported encouraging results from preliminary tests using a number of columns fitted to the perimeter of a rotating disc. Sample feed and effluent removal were continuous. Taramasso (35) reported the use of a rotating unit containing thirty-six columns 2.4 meters in length. This apparatus was used for separation of pinenes, pentadienes, and purification of 2,5-dimethylhexa-2-4-diene and n-hexane.

Giddings (19) developed the theory of performance of large diameter columns and described expected losses in efficiency due to non-uniform liquid loading and cross-sectional velocity gradient. He developed a generalized non-equilibrium theory of plate height in large scale gas chromatography (20) and experimentally verified portions of his theories (21).

Gordon, Kirge, and Pretorius have reported theoretical studies of preparative chromatography concerning the effects of column diameter (28), column length (25), carrier flow velocity (26), and stationary phase (27).

Many investigations of large diameter columns have been carried out. Huyten and coworkers (29) investigated the efficiency of large diameter columns and the influence of various methods of packing. They reported that a narrow range of mesh size is necessary for highest efficiency; also, that the carrier flow near the walls of the column is

higher than elsewhere in the column. This causes axial speeding of component bands which results in a lower number of theoretical plates, due to the corresponding increase in peak width. Increased packing density was reported to decrease both axial and radial diffusion.

Golay (22) showed that a higher flow velocity at the column wall could be attributed to an average open pore space at the wall equal to half the average particle diameter. He concluded that efficiency was affected largely only when the column diameter was much greater than the height equivalent to a theoretical plate. Golay showed theoretically that the efficiency of a large diameter column would be improved if the inner wall was roughened. He also recommended the use of mixing regions to handle variations of band width caused by varying velocity profile. Huyten (29) confirmed the latter by connecting large diameter columns with short sections of empty tubing. Frisone (13) inserted probes in a large diameter column and showed experimentally that the loss in separating efficiency was due largely to uneven velocity profiles. He attempted to reduce the axial band velocity gradient by placing doughnut shaped pieces of filter paper in the column. The openings in the papers decreased uniformly toward the outlet end of the column.

Wright (37), in 1963, reported the use of a large diameter column with highly increased efficiency resulting from internal modifications. Internal radial fins running parallel to the column axis were reported to create the effect of multiple interconnected columns, giving a more uniform pressure and mutual equilibrium through lateral diffusion.

Carel and Perkins (5) report the use of large scale preparative

chromatography to supplement distillation and in some cases perform separations of which distillation is not capable. The large diameter columns used are packed in sections with a sintered metal disc or frit being provided as a bottom for each section.

CHAPTER III

SCOPE OF INVESTIGATION

The purpose of this investigation was to determine the effect of column sectioning on the efficiency of large diameter columns.

The decrease of column efficiency with increasing cross-sectional area has been attributed to uneven velocity profiles and the resultant band-spreading. In even packing, the wall effect described by Golay, and channeling contribute to band spreading. The magnitude of the wall effect is further increased in large diameter columns by the tendency of the larger particles to move toward the wall during filling of the column.

It was believed that packing a large diameter column in sections of suitable lengths with open spaces at the top of each section would result in more even packing distribution and provide a region between sections where radial concentration gradients could be diminished. Most important of all, however, sectional packing should minimize the formation and attenuation of channels produced by the flow of gas through weak points in the packing. Without the spaces provided by the sectional packing, a channel started at the bottom of the column might readily extend itself through the full length of the column.

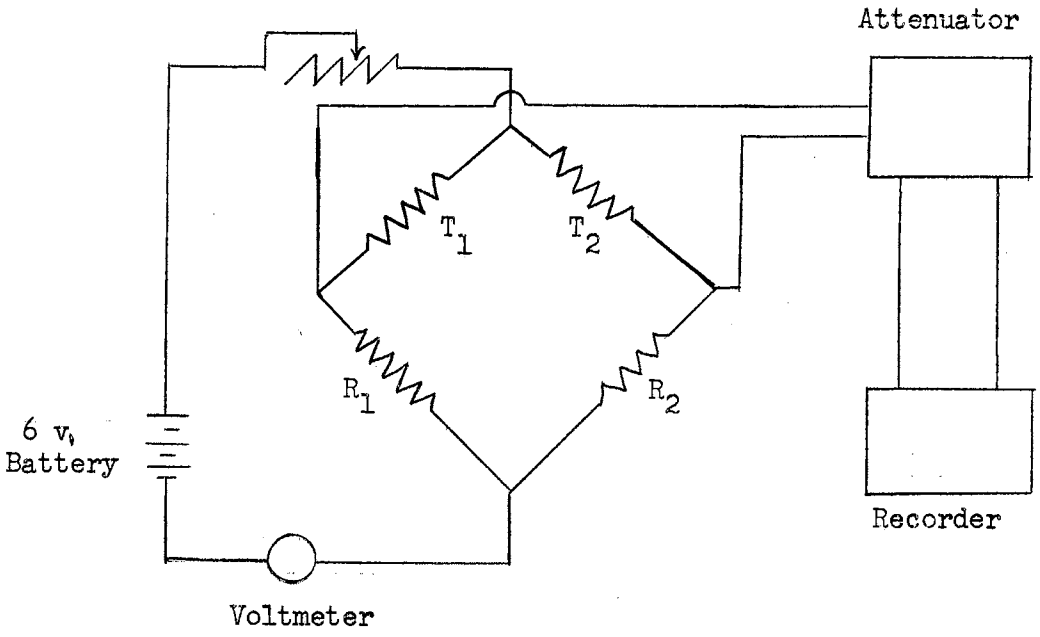
CHAPTER IV

APPARATUS

The chromatograph used in this investigation was designed by Dr. Paul Arthur. It was machined and assembled by the Chemistry-Physics machine shop. The detector was a thermal conductivity cell equipped with a matched pair of Gow-Mac thermistors of 5000 to 6000 ohms resistance. The thermistors were arranged in series with fixed resistances in such a way as to form a Wheatstone bridge circuit. A 6-volt automobile battery provided a d.c. power source for the bridge. The d.c. voltage created by unbalance of the bridge was attenuated by circuitry designed by Dr. Arthur and the resulting signal was recorded on a Sargent 1-millivolt, 1-second recorder. The detector circuitry is shown schematically in Figure 4.

Two columns were used. Both were packed with ground Johns Manville C-22 firebrick, 20-30 mesh, coated with a Nujol liquid phase. The analytical column was 1/4" o.d. copper tubing, 6 feet in length. The preparative column was a 3-inch i.d. brass tube, 6 feet long. Both will be described in more detail later.

The carrier gas system consisted of a N_2 gas cylinder, a Matheson pressure regulator, the chromatographic column, the detector, a flow splitter, and a soap bubble flow meter. The flow splitter was used to send a fraction of the total effluent from the preparative column

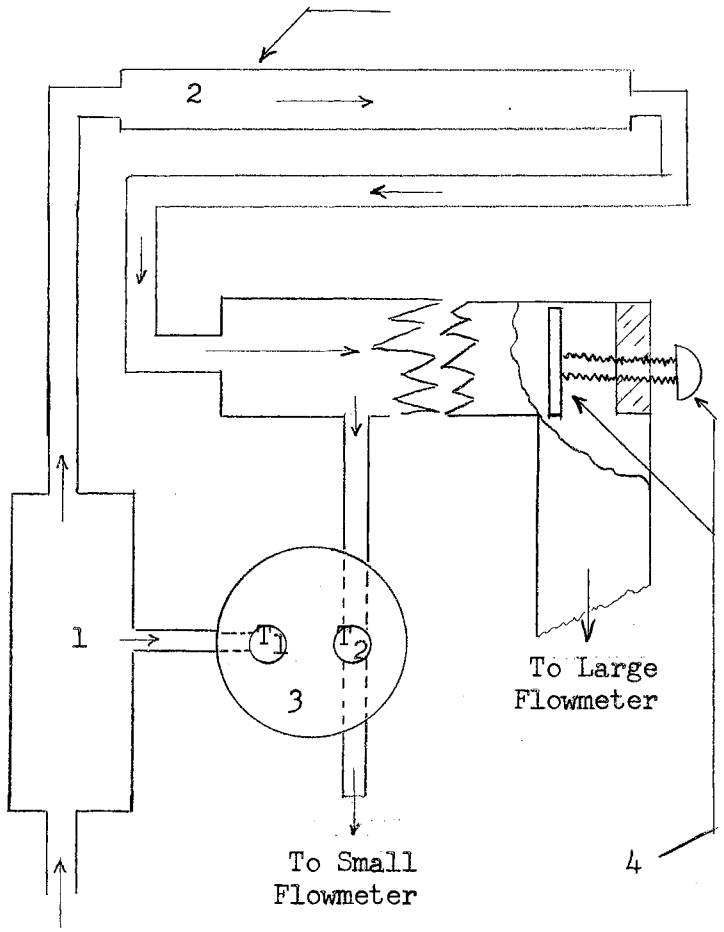


T_1; T_2 Thermistors

R_1; R_2 Resistors

Fig. 4. Detector Electronic Schematic.

through the sensing side of the detector. A flow schematic of the detector is presented in Figure 5. Injection ports for the analytical and the preparative column were fitted with replaceable silicone rubber septums for syringe injection. The column oven for the preparative column was a 6 x 1 x 1-ft. upright insulated metal box, supported by a wooden frame and fitted with a door for access to the column. Heater controls and thermocouple connections were mounted on the outer metal shell. The top end of the oven was removable to provide greater access to the column. The heater for the oven containing the detector and the analytical column was coiled nichrome wire wound on a firebrick frame, while the preparative column was heated by nichrome wire wound around the column in two sections. Powerstats controlled the current to both heaters. Iron-constantin thermocouples located at the center and the upper and lower ends of the preparative column and on the injection port block provided preparative column temperature readout. The voltages of these junctions were read against a similar junction in an ice water bath. A 1-milliliter and a 10-milliliter Hamilton syringe were used for sample injection. Further description of the apparatus is included later.



1. Chamber
2. Column
3. Detector
4. Restrictor and
   Adjusting Screw

Fig. 5. Detector Flow Schematic.

CHAPTER V

EXPERIMENTATION AND DISCUSSION

Apparatus Problems. The purpose of this investigation was to determine the effects of sectional column packing on the efficiency of the resulting column. Consequently, the column, the sampling system, and carrier flow control are of primary interest and need to be described in greater detail.

The preparation and arrangement of the analytical column presented no special problems. It was coiled to fit into the detector oven and all of the gas passing through this column was passed through the sensing side of the detector. The injection port for this column was heated to a slightly higher temperature than was the column, but no unusually high temperature was required to volatilize the small samples of benzene employed.

The preparative scale column created several problems. It and its oven, due to size, could not be made integral parts of the detector control chassis as could the analytical column; consequently, the separate units had to be connected by thermally insulated tubes. The height of the column and its oven made it difficult to keep them at a uniform temperature at the levels needed. The injection port posed special heating difficulties due to the large samples it was required to vaporize. Then, too, a much greater volume of carrier was required

to maintain the velocity of the gas through the column at the same rate as through the analytical column. Not all of this gas could be passed through the sensing side of the detector without increasing both the pressure and velocity of the gas through the detector to unacceptable levels.

Early experiments showed that a single winding of heater from the top to the bottom of the preparative column caused the upper section to maintain a higher equilibrium temperature than the lower section; consequently, the heater was divided into two sections, each separately controlled. A higher power setting for the lower section made it possible to maintain uniform column temperature over the full length of the brass column.

A third power control supplied current to the sampling block and its injection port. Owing to the large sizes of sample to be employed, the sampling block was designed so it would have a large enough heat capacity to volatilize the sample without significant cooling of the block. Slow volatilization of the sample would create a broader, more dilute sample band in the column and greatly distort and broaden the elution peak.

The column was mounted on the injection block by bolting together flanges with which each was provided. Preliminary runs showed that the lead wire rings first used to gasket the joint could not maintain a gas-tight seal. The lead gaskets were therefore replaced with a commercial asbestos-copper gasket which proved satisfactory. The column was capped at the upper end by connections made in the same manner (see Figure 6).

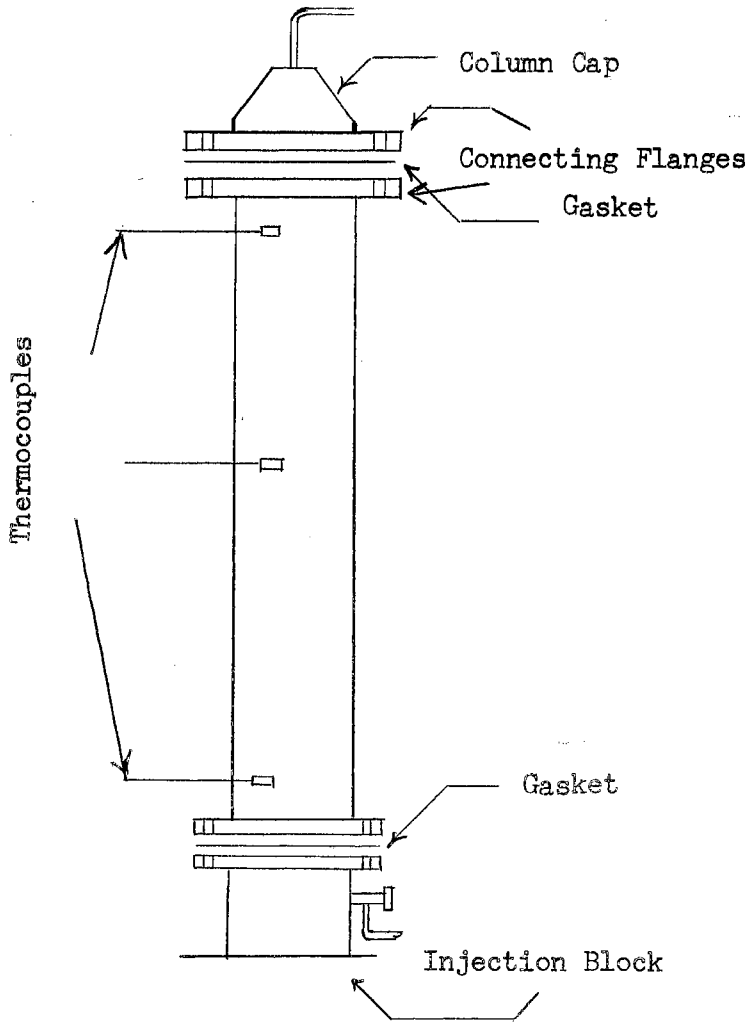


Fig. 6. Preparative Column.

The sampling block was machined from brass. The cone-shaped interior below the column flange was designed to reduce turbulence and dead volume where volatilized sample might remain and slowly mix with the carrier before entering the column. The best results would be to have the vapor enter the column as a slug; any slow mixing would cause peak broadening of the same type previously mentioned. The cone-shaped interior of the column cap was necessary for the same reasons.

To prevent condensation of the sample, all points between the injection port, the column, and the detector were maintained at a temperature above the boiling point of the sample. All of the flow path inside the oven could easily be kept at above the minimum due to heat from the column and injection port heaters. Conduction of oven heat by the 1/4-inch copper connecting tubing was sufficient to keep its temperature above the sample's boiling point. This was aided by the fact that the portion of the connecting tubing between the column oven and the detector oven was insulated to reduce the effect of drafts and ambient temperature changes.

Due to the large volume of gas required to operate the preparative column, a conventional calibrated burette-type soap bubble flowmeter could not be used. Consequently, a large soap bubble flowmeter was made from a 3" diameter x 3' long glass tube. This flowmeter will be described in detail later.

To correlate preparative column data to analytical column data, the flow rate of the preparative column had to be reasonably well controlled and adjustable to a given desired value. If the linear velocity of the gas passing through the columns was the same, then retention times for a common packing and sample should for equivalent ef-

ficiency, be approximately the same. Retention volumes would also be in the ratio of the cross-sectional areas for such columns of the same length. The last relationship was utilized to determine the flow rate desired for the preparative column. Operational parameters such as temperature and flow rate were optimized using the analytical scale column. The volume flow rate for the preparative column was then calculated from the cross-sectional area relationship to give the same linear velocity in both columns. This flow rate was assumed to be optimum for the large column and indications from a few runs at higher and lower flow rates appeared to verify this. The point was not extensively investigated, however.

In order to prevent possible detector damage and variations in detector response that might be caused from passing all the preparative column effluent through the sensing side of the detector, the flow was split as previously described and the flow rate through the sensing side of the detector was adjusted to the same value as for the total effluent from the analytical column runs. The flow control and flowmeter shown in Fig. 7 was constructed in order to obtain the desired flow control and measurements conveniently.

Column Packing. The solid support for the packing material was prepared from Johns Mansville C-22 firebrick. For early experiments, the brick was first broken up with a hammer, then loaded into a Waring food blender in which the brick particles were reduced to the proper size. The sieves chosen, 20 and 30 mesh, were used by hand and by mechanical shaking. The portion passing through the 30 mesh sieve was discarded, the fraction collected between the 20 and 30 mesh screens was retained

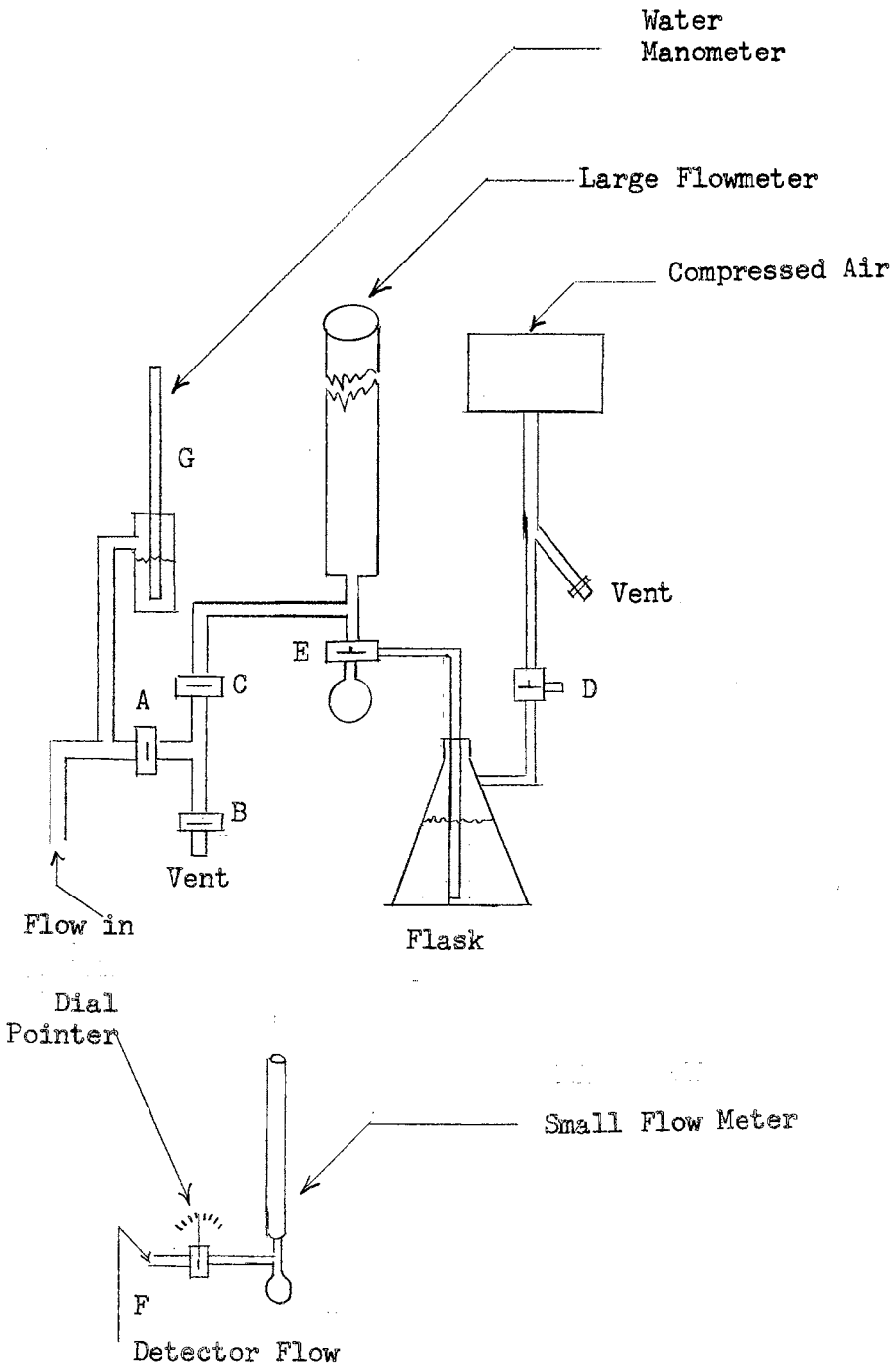


Fig. 7. Flow Control and Measurement Apparatus.

for liquid phase treatment, and the fraction not passing through the 20 mesh sieve was returned to the blender.

The first packing prepared was acid-washed to lessen its activity and decrease possible tailing of chromatographic peaks. About one gallon of the seived firebrick was placed in a three-gallon plastic container. Distilled water was added until the packing was just covered. A 1 N solution of hydrochloric acid was slowly added until the container was nearly full, then the contents were gently agitated for uniform exposure to the acid solution.

When all visible evidence of reaction ceased, the container was allowed to stand for another half hour. The acid solution was decanted and the container filled with distilled water as a rinse. The packing was gently stirred and the water decanted. This rinse procedure was followed until tests of the decanted water with Hydrion paper showed no acidity. The packing material was then treated with a solution of 1N sodium hydroxide and rinsed in the same manner.

After the final rinse, the material was air dried. Many fines, (very small particles) were observed in the dry packing. Some possibly remained due to inadequate sieving and others were probably formed when the softened packing was agitated during the washing procedure. Fines are harmful to column performance and attempts to remove them were made. In the first procedure, small portions of the packing were added to a three gallon container partially filled with water and the mixture was stirred until nearly all the particles were suspended. When this mixture was allowed to stand, the heavier, larger particles settled to the bottom first and the fines were removed by decanting the water

while they were still in suspension. The remaining packing was then again air dried. This method worked relatively well but due to the length of time required to treat all of the packing material (about 5 gallons), it was abandoned and the remaining packing was simply re-sieved.

The packing material was coated with a liquid substrate as described later and used to pack both the analytical and the preparative column. The experiment required that the large diameter column be repacked several times. When this was done, however, performance deteriorated rapidly and repeated runs with identical column set-ups indicated definitely that the packing material was changing. Investigation showed that the proportion of fines in the packing material was increasing rapidly presumably because the material was subjected to mechanical forces such as those incurred in packing the column.

An attempt was made to salvage as much as possible of the prepared packing by removing the fines. Previously described methods were unsuitable due to the liquid phase now on the material. To separate the particles without harming the liquid phase, an apparatus for air-separation was constructed. In this apparatus, the packing was poured into a fan-driven stream of air which carried the smaller, lighter particles some distance along the length of a box-like chamber and thus removed the fines. Size grading was apparent, but even the largest particles were not retained by a 30-mesh screen. Further investigation showed that all of the packing material (originally a 20-30 mesh cut) would pass through a 70-mesh sieve, the finest mesh sieve available.

In the belief that the acidic and basic washes the firebrick par-

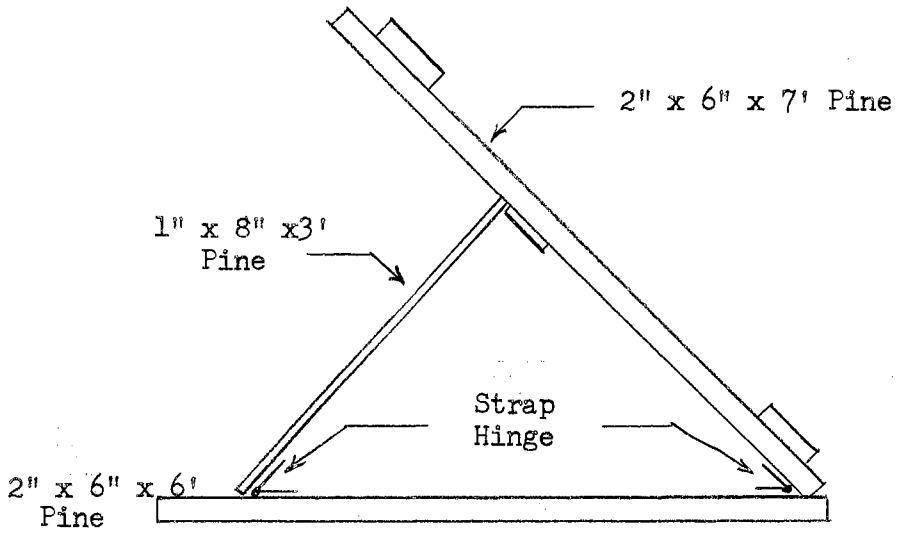
ticles had been subjected to had lowered its mechanical strength, it was decided that the raw untreated brick would be employed. More firebrick was crushed, ground, and sieved as before and then was coated with the liquid phase. Upon testing, it was found that this packing could withstand the necessary handling without creating excessive fines.

The liquid phase chosen was a mineral oil commercially distributed under the name Nujol. It was dissolved in ligroin, Skelly Solvent F. The appropriate weight of solid support was placed in a container with the calculated weight of Nujol dissolved in the solvent. The weights of Nujol and packing were chosen to make the Nujol weight 15%. Enough solvent was used to cover the solid support and fill the container several inches higher than the solid. The mixture was stirred at once, then again at intervals until the liquid solvent was gone. The still moist packing was spread on cloth supported several inches above a laboratory table, permitting air to pass through the packing and more rapidly and evenly dry it. The analytical column was packed by attaching a small funnel to the end of a 3/10" by 6" copper tube. The other end of the tube was plugged with glass wool. The tube was then filled by pouring small amounts of packing into the funnel and vibrating the column. When column vibration no longer caused the packing to settle, the funnel was removed and a glass wool plug was inserted in this end. The column was then coiled to fit the chromatograph oven.

Packing the large diameter column uniformly and reproducibly presented several problems not present in packing the small column. The

preparative column had to be packed and unpacked, without damage to the packing material, many times during the course of the experiment. Its size and weight prevented it from being mechanically handled in the same manner as the analytical column.

With these considerations in mind, the equipment shown in Fig. 8 was constructed. The column was suspended from the top of the preparative column oven by a hanger that bolted to the column mounting flange and left the top end of the column open. A screen was placed in the bottom of the column and about 100 cc. of packing material was poured into the suspended column. The suspended column was then tapped lightly to settle the packing and then more packing was added and the tapping repeated. To obtain consistent effects from vibration of the column, a set procedure was used each time the column was packed. After each addition of packing material, the column was vibrated by using the tapping block and striking it lightly with a hammer. The column was tapped eight times with a 90° rotation of the striking point after each blow. The striking point was at approximately the level of the last addition of material. A weighted line was lowered into the column until the weight touched the surface of the packing and the length of this line to the surface was used to determine the point of insertion of the separators. For example, when runs were made with two separators, the column was divided into three equal sections, each two feet long. The first separator was placed in the six-foot long column when the line showed four feet remaining to be packed. The second separator was inserted when two feet of column remained unpacked. This divided the column into three equal sections.



Packing Removal Column Mount

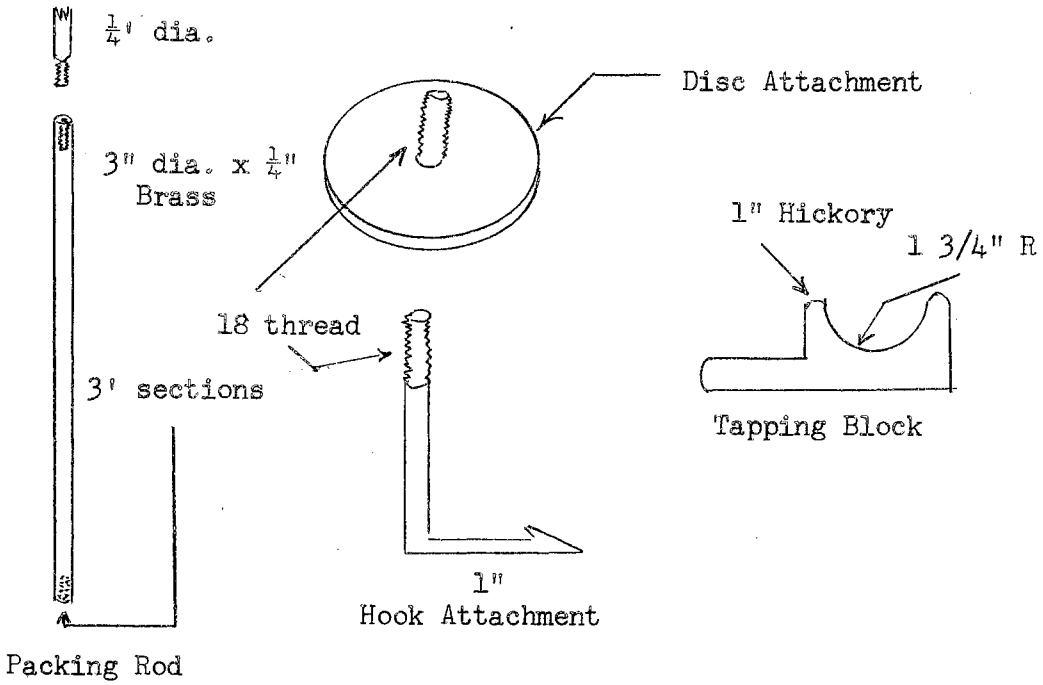


Fig. 8. Column Packing Equipment.

The rod and attachments shown in Fig. 8 were used to insert and remove the circular screens and the separator. The circular metal disc was used to level the screens in the column and position them at right angles to the column wall, thus preventing the screens and separator from becoming wedged in the column at an angle. The hook attachemnt was sometimes used to help position screens in the column, but was primarily designed to be inserted in the small wire loops attached to the center of the screens. The screens and separators, shown in Fig. 9 could easily be removed in this manner during the unpacking of the column. A flashlight was used to light the interior of the column during manipulation and positioning the separators and screens.

When the column was filled, it was tapped four times on the top and bottom flanges, with a 90° rotation of the striking point. A more rapid, lighter tapping was applied around the column at intervals, corresponding to the center of sections. More material was then added to fill the column and tapping at the flanges repeated in the same manner previously described. Packing material was then added to fill the column flush with the top, a circular screen cover was placed in the end, and the column was mounted in the oven. Early tests showed that pouring packing material from a beaker into the large diameter tube resulted in a mound forming in the center of the column. It was observed that, during subsequent additions of material, larger particles tended to roll down the sides of the mound and to the outside of the column while smaller particles lodged on or near the peak at the center of the column. This resulted in a radial particle size gradient. Larger particles at the outer edges of the column would cause a

radial velocity gradient with higher velocities at the column walls, due to the larger space between the particles near the wall. This would be in addition to the higher flow at the wall created by larger spacing between particles in contact with the wall and the smaller particle-to-particle spacings. The radial velocity gradient thus produced creates zone or band spreading in the column and the resulting loss of plates for the column.

To provide a more uniform packing distribution, the material was poured down the edges of the column with a circular motion of the beaker as the column was filled. This procedure and the vibration of the column is believed to have minimized the radial particle size gradient. After the column was packed with fresh material, it was conditioned by heating it to 150°C. and passing a slow flow of heated nitrogen through it for a period of 72 hours. The objective of this treatment or conditioning was removal of all traces of the liquid phase solvent and any other material in the column that was volatile at 150°C. Thus, when the column was lowered to 100°C for sample runs, there would be no bleeding or contamination from the packing material.

To unpack the column with the least possible damage to the packing material, the stand shown in Fig. 8 was constructed. The column was removed from the oven and placed on the lowered rack. It was than fastened to the rack and raised to the position illustrated in the figure. The cover screen was removed and the packing material collected. The rod and the hook attachment previously described were used to remove subsequent separators and permit collection of the packing material in each section of the column. The flashlight was used

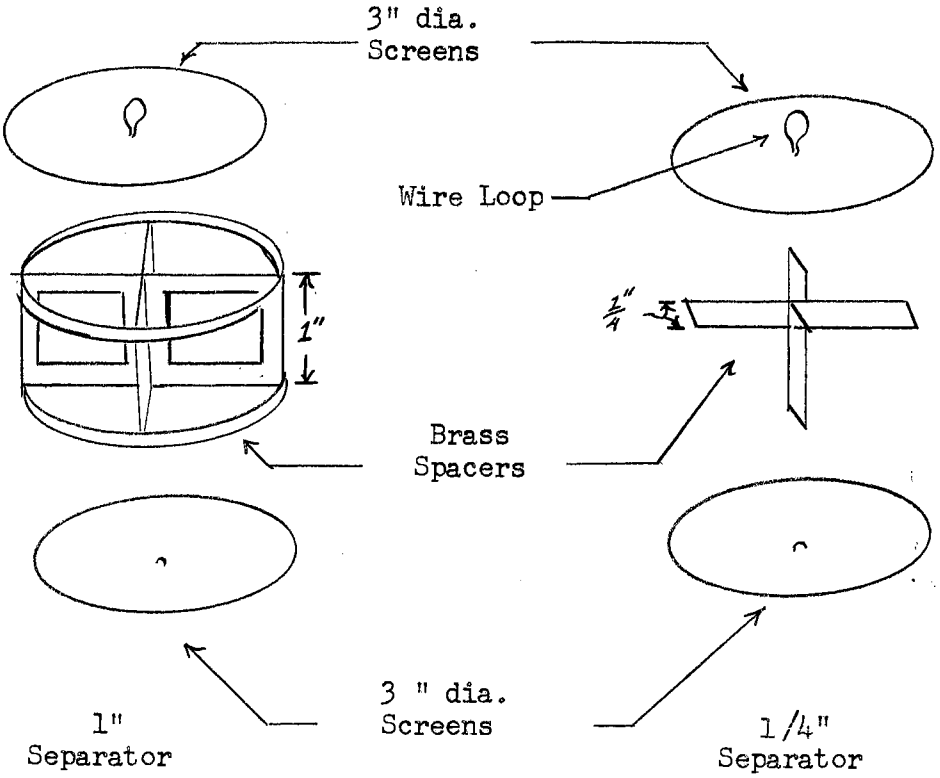


Fig. 9. Screens and Separators.

to aid in removal of the separator sections by the rod and its hook attachment.

Operational Procedure. Flow rate through the analytical column was determined by passing all the column affluent into a soap bubble flowmeter. The bubble meter was volume calibrated between two marks, and the time required for a soap bubble to pass between the marks was recorded on a stopwatch. The flow rate in milliliters per minute was then calculated. Flow was adjusted to the desired value by changing the pressure at the output stage of the cylinder pressure regulator.

Difficulties were encountered in measuring the flow rate of the preparative column. The large volume of gas passing through the column, partially split to the sensing side of the detector, could not be accurately measured by the apparatus used for the analytical column. The flow measurement and regulation system previously mentioned (see Fig. 7) was used in the following manner. The pressure regulator was adjusted to approximately the same output pressure required for the analytical column. Stopcock B (see Fig. 7) was opened and the effluent allowed to vent directly to the atmosphere. Stopcock C was closed and stopcock E, with a T-flow configuration, was turned to open the flow meter to the water reservoir. This reservoir was a suction flask with the side arm connected to stopcock D. Stopcock D had a T-flow path with one arm open to atmosphere, another connected to the laboratory compressed air supply, and the third to the side arm of the suction flask. A piece of glass tubing was extended to the bottom of the reservoir, or flask, through the rubber stopper sealing the top of the reservoir. The end of the glass tubing was connected to one of the

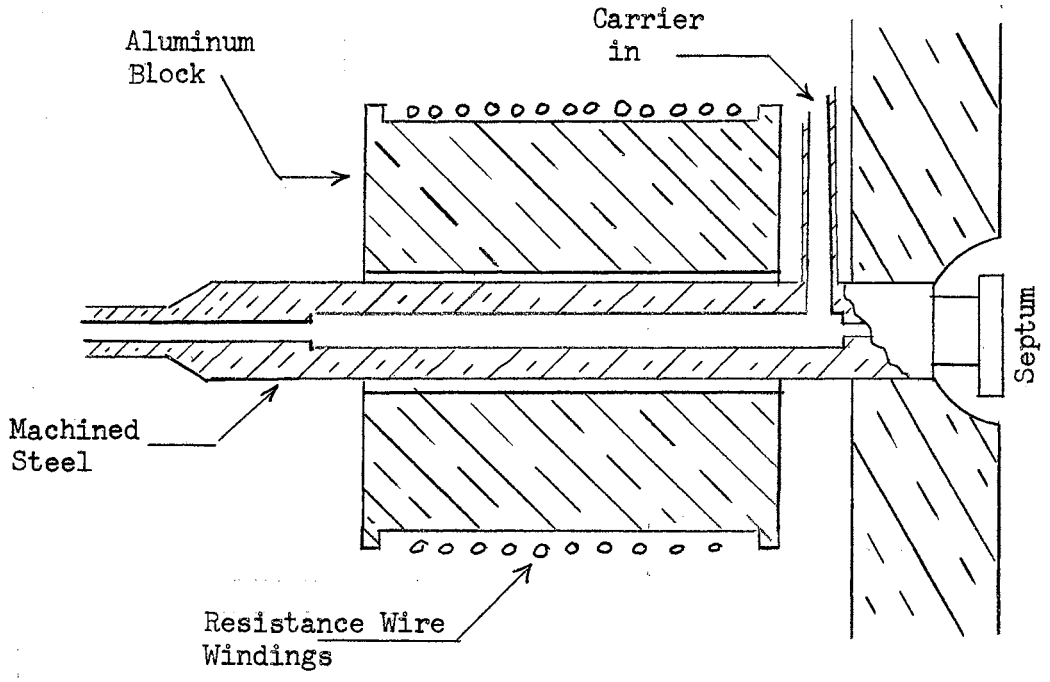
arms of stopcock E. This apparatus was constructed in order to fill the large flow meter with water to wet the glass walls. Previous attempts showed that the large diameter of the flow meter made it difficult to obtain a soap film that could traverse the length of the flow meter before breaking. The walls of the flow meter quickly became coated with a gummy film that increased the difficulty of maintaining a soap film. Filling and draining the flow meter before and after both wet the walls and removed the gummy film.

With stopcock E furnishing a flow path from the reservoir to the flow meter, stopcock D was rotated to open the laboratory air source to the reservoir. As air pressure increased in the reservoir, water was forced through the glass tubing to stopcock E and into the flow meter. When the flow meter was filled beyond the upper calibration mark, stopcock D was rotated to allow the compressed air and the back pressure from the reservoir to vent to atmosphere. As the air pressure in the reservoir dropped, the water in the flow meter drained back into the reservoir. When the flow meter had drained, stopcock E was rotated to provide a path for soap solution in the rubber bulb to the flow meter. Stopcock C was then opened and stopcock B closed, passing all of the effluent through the flow meter. Stopcock A was then used to adjust the flow to the desired value of five liters per minute. This value was determined from the optimum flow rate for the analytical colume and the ratio of the column's cross-sectional areas or volumes. When this flow was attained, stopcock C was closed and stopcock B opened to vent the effluent directly to the atmosphere. Stopcock F was opened, allowing a portion of the column effluent to pass through the

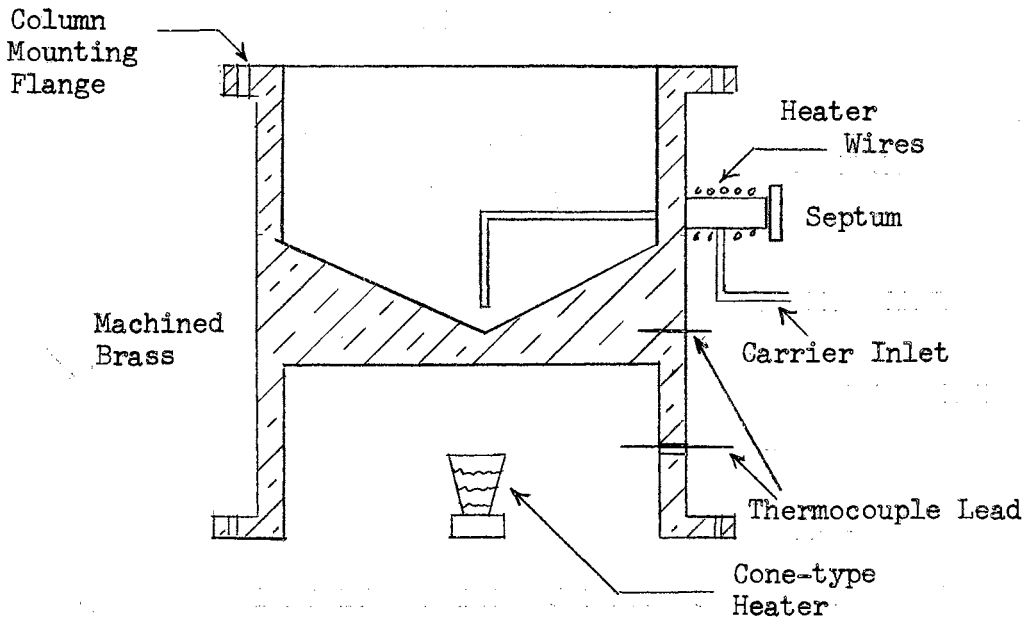
sensing side of the detector and through the small flow meter. The flow restrictor was utilized as a coarse adjustment for flow control through the detector, and stopcock F provided the final control.

Wire pointers were attached to stopcocks A and F and graduated dials were placed under the tips of these pointers. This provided a means of more rapid adjustment to desired values by providing a more sensitive indication of changes in the orifice as the stopcocks were adjusted. A water-filled manometer (G in Fig. 7) was attached to the detector effluent line ahead of stopcock F. It provided an indication of pressure in the line and of changes in back pressure produced as stopcock F was adjusted. This also aided in adjusting detector flow to the same value as was used for analytical column runs. This value was chosen as 20 milliliters per minute, as described later. Heater power was then switched on and powerstats were adjusted to apply voltage to their respective heaters.

The heater elements for the analytical column, its injection port, the carrier gas preheater, and the detector were all contained in the chromatograph control section and were relatively well evaluated. They required little adjustment after initial setting of power controls. A small secondary heater was cycled by an adjustable thermally activated switch to maintain a constant oven temperature. Thermocouples connected to a thermally calibrated meter furnished temperature indication for these sections of the chromatograph. All but the injection port were maintained at 135° C. The injection port was heated by resistance wire windings on an aluminum block, as shown in Fig. 10. It was operated at 150° C for sample vaporization.



Analyitical Column Injection Port



Preparative Column Injection Port

Fig. 10. Analytical and Preparative Injection Ports.

In addition to the split heating system for the large column, a heater was provided in the base of the column to heat the vaporizer and,by conduction, the sample inlet. This section was operated at temperatures ranging from 150° C to 175° C in order to vaporize the relatively large amounts of sample. The larger mass of metal in this sample inlet allowed satisfactory vaporization at only slightly higher temperatures than that required for operation of the analytical column injection port. Five iron-constantin thermocouples with a common ice-water bath junction as a reference were used for temperature indication of points in this system. Differences in potential between the reference and sensing junctions were evaluated by a calibrated potentiometer. The millivolt reading was then converted to centigrade degrees by values obtained from standard tables in the Handbook of Chemistry and Physics. One of the junctions was located in the air space above the base heater, one in the metal of the vaporizer, one at the lower end of the column, one at the column center, and one at the upper end of the column, as shown in Figures 6 and 10. Frequent adjustments were required to maintain a uniform column temperature throughout the length of the column. These variations were caused by the higher temperature required for the inlet and subsequent conduction to the lower column section and by convection currents in the large oven.

Normally, satisfactory conditions could be obtained by heating the inlet section to a temperature between 150° C and 175° C and adjusting power to the upper column section to 135° C. The lower section was then adjusted to a lower power setting to compensate for heat obtained

by conduction from the inlet section. Temperature readings along the column were taken frequently and required frequent power adjustments. Finally, however, the circuit was changed so each of the two sections of heater windings was controlled by a Fenwal thermoregulator opposite the section it controlled. After this, the three thermocouple readings along the column could be maintained within 1° or 2° of the desired 135° C value.

After temperature adjustment was stabilized, power was applied to the detector circuit. A 6-volt automobile battery supplied a stable d.c. voltage to the circuit. Applied voltage was adjusted by the variable resistance as shown in the detector circuit schematic in Figure 4 and was read from a d.c. voltmeter mounted on the front of the control chassis. Four volts was found to give optimum sensitivity and therefore was used for all runs.

After temperatures had equilibrated at chosen values, the flow rates were again checked and minor adjustments made when necessary. The recorder power was turned on and allowed to stabilize. When all components steadily maintained their proper operating conditions, samples were injected. A sample size of 1 microliter was selected for the analytical column. Injections were made by a Hamilton syringe. For the large column a sample size of 1 milliliter was selected and used. Injections were made from a 5-milliliter Hamilton syringe. The needle for this syringe was modified when it was observed that it frequently sliced a small disc from the septum and became plugged. This interfered with sample injection, even when only partial plugging occurred and created a gas leak when the syringe was removed from the

septum. The modification consisted of filling the tip of the needle with silver solder, smoothing it to a point and drilling a small hole in the side of the needle at a point just behind the solder plug. The recorder chart was switched on at the time of injection and retention times and peaks were recorded.

Data Treatment; Parameters. Repeated runs were made for each phase of the experiment. When the required number of runs had been completed, the chart was removed and the individual runs treated graphically to obtain the information required for the calculation of the number of theoretical plates. The required calculations have previously been discussed and the graphical treatment of the chromatogram is illustrated in Figure 3. Retention time and peak width were measured in units of distance along the x-axis of the recorder chart. Inches were arbitrarily chosen as the unit of distance for use in calculations of the number of theoretical plates.

Operational parameters, such as temperature and detector voltage, were selected from runs and observations made on the analytical column. Column temperature of 135° C showed no band spreading effects and no apparent column bleeding after the column conditioning previously mentioned. This temperature was sufficiently over the boiling point of the benzene used as a sample (80.09° C) so there were no problems of condensation of the vapor in the chromatographic system. This temperature was used as the column temperature for both columns. A higher temperature, 150° C, was selected at first for both injection ports in order to insure rapid vaporization of the liquid sample upon injection. This was satisfactory for both columns, although repeated

injections of large samples in the preparative column would drop the injection ports' temperature low enough for distortion of the chromatogram to occur. It was necessary to check injection port temperature on the large column after several consecutive injections; consequently, it was decided to operate this injection port between 150° and 175° C. When its temperature dropped to 150° C, a short wait was necessary to let the heater build the block's temperature above 150° C. No injections were made below 150° C and no sample vaporization effects were observed in the 150° C - 175° C range of operation.

Detector voltage was selected from observations made on analytical column runs. Sensitivity increased slowly between 1.0 and 2.5 applied volts, then rose rapidly from 2.5 to 3.5 volts. Response then tended to level off. The detector was operated on the plateau at 4 volts.

Samples of different volumes were run on both columns prior to selection of a sample size to be used during the experiment. The data is presented in Table I.

TABLE I

ANALYTICAL AND PREPARATIVE COLUMN PLATES

Analytical Column		Preparative Column	
Sample Size (Microliters)	No. of Plates	Sample Size (Milliliters)	No. of Plates
1	498.6	0.20	168.7
1	498.6	0.5	158.7
1	470.8	1.0	128.3
5	454.4	1.0	117.9
5	444.4	1.0	118.5
5	454.8	1.0	122.7
100	95.1	5.0	100.0
100	110.0	10.0	40.0

Sample sizes of 1 milliliter and 0.5 milliliter were selected for the preparative column runs as they were significantly large samples and still did not require excessively high injection port temperatures for repeated volatilizations; nor did they present mechanical injection difficulties as did the 5-milliliter and 10-milliliter samples. The time required for syringe injection of these larger volumes was of sufficient length to present problems in widening the on-column sample band even if the injection port maintained a temperature high enough for complete volatilization of the sample.

Several runs were made on the analytical column at different flow rates and a flow rate of 20 milliliters per minute was selected for the column. This flow rate gave a reasonable retention time for benzene and yielded relatively symmetrical peaks without excessive distortion from detector operation. The flow for the large column was determined from calculating the relative volumes of the columns. Since the columns were of the same length, volumes were proportional to the ratio of the cross-sectional areas of the columns. Using 3/16 inches as the inside diameter of the analytical column and 3 inches for the large column, the ratio of the cross-sectional area of the large versus the small column is

$$\frac{A_l}{A_s} = \frac{r_l^2}{r_s^2} = \frac{(3/32)^2}{(3/2)^2} = \frac{256}{1}$$

Multiplying this factor by the analytical column's flow rate yields a flow rate of 5120 ml/minute. A flow of 5 liters per minute was used. Selecting a preparative column flow in this manner gave both columns approximately the same linear carrier velocity.

The flow split to the detector from the preparative column was selected so the same velocity, 20 milliliters per second, went through the detector for both columns.

Systematic Experiments and Results. The investigation of effects of sectioning the column packing proceeded in the following manner. Six separators were provided for separating the packing into equal sections. The column was divided into two equal parts with one separator, repeated runs were made, then the column was unpacked. It was then repacked, two separators being used to divide it into three equal sections, and again several runs were made. This procedure was followed until the column was in seven equal sections and all six separators utilized. The repeated runs from each mode of sectioning comprised one series. Prior to each series, repeated runs were made on the column packed with no separator. These runs would indicate deterioration of column material due to loss of liquid phase or mechanical breakdown of the particles. Several initial runs were made on the analytical column to provide a measure of the effectiveness of the packing material prepared for use in the preparative column.

Loss of large column efficiency due to channels flowing through the material should be decreased by sectional packing, for open spaces between section should prevent the propogation, by gas flow, of channels started in the sections below. This should then result in an increase in the number of theoretical plates as separators decreased the possible length of channels. No obvious improvement, however, was observed during the course of the first series as summarized in Table II.

The number of theoretical plates indicated in the table is an

average taken from about ten runs made on each column packing mode.

TABLE II

SERIES I
(with 1" separators)

Sample Size	No. of Separators	Plates	Sample Size	No. of Separators	Plates
1 ml.	0	125.1	1 ml.	5	101.2
1 ml.	1	102.9	1 ml.	6	91.9
1 ml.	2	108.9	0.5 ml.	3	142.2
1 ml.	2	108.7	0.5 ml.	5	153.3
1 ml.	3	87.9	0.5 ml.	6	108.5
1 ml.	4	109.7			

It should be noted that the number of equal column sections exceeds the number of separators by one. Thus, where two separators are indicated there are three equal sections of column material. The packing made of two separators, or three sections, was repeated in this series to provide an indication of the reproducibility of the packing methods. The method is quite reproducible as indicated in Table II. The closeness of the two averages indicated tends to infer a falsely high degree of reproducibility, however. The range of values for each packing job is slightly higher than the difference in repeated packings of the same mode. Occasionally runs of different sample sizes were made to check on any changes in efficiency in other sample size ranges. These runs are averaged within the packing mode on which they were taken and are indicated in the table according to sample size.

In an attempt to help sweep the top and base cones of the column

cleanly, alcohol-washed steel wool was placed in the two cones and the packing mode of five separators was repeated. A further efficiency loss was indicated. Further runs were then made with the steel wool removed from the injection port cone. The effects produced are illustrated by the data in Table III.

TABLE III

STEEL WOOL EFFECT

Steel wool in both cones		Steel wool in top cone only	
Sample	Plates	Sample	Plates
1 ml.	110.8	1 ml.	90.9
1 ml.	108.9	1 ml.	91.9
1 ml.	98.7	0.5 ml.	108.8
1 ml.	96.4	0.5 ml.	124.1

As may be observed from comparison of the above table with Table I no benefits were derived; therefore, the steel wool was discarded for the remainder of the experiment.

The second series was run in the same manner as the first except that the height of the chamber created between sections by the separator was reduced to one-fourth inch. Data in Table IV for this series show the average values obtained for the sample sizes indicated.

In considering the data from series II, note the loss of efficiency in the unseparated column, or control. The number of plates dropped for 1-milliliter samples from 125 to 94. This was taken as an indication of packing material deterioration due to mechanical effects during repeated packings of the column. The series was continued with

0.5-milliliter injections. Theoretical plates for packing modes of 1 and 5 separators are of particular interest not only because of their high number but also because of the low values of adjoining packing modes. This is illustrated by Figure 11, a plot of theoretical plates versus the number of column sections.

TABLE IV

SERIES II
($\frac{1}{4}$" separators)

Sample Size	No. of Separators	No. of Plates	Sample Size	No. of Separators	No. of Plates
1 ml.	0	94.2	0.5 ml.	6	117.9
0.5 ml.	0	113.1	0.25 ml.	0	132.6
0.5 ml.	1	187.4	0.25 ml.	1	201.8
0.5 ml.	2	156.1	0.25 ml.	2	156.9
0.5 ml.	2	160.6	0.25 ml.	3	119.4
0.5 ml.	3	113.8	0.25 ml.	4	121.6
0.5 ml.	4	108.3	0.25 ml.	5	200.0
0.5 ml.	5	188.5	0.25 ml.	6	129.9

The entire series was then repeated as series III with the results shown in Table V.

The data again illustrates the pattern followed in series II. Note the rise in efficiency with 1 separator and with 5 separators. Packing modes of 4 and 5 were rerun to verify the sharp rise in efficiency.

A different approach was used in an attempt to separate the effect of the separators' providing mixing space and the effect of a section's length. A final series was run with the length of packing

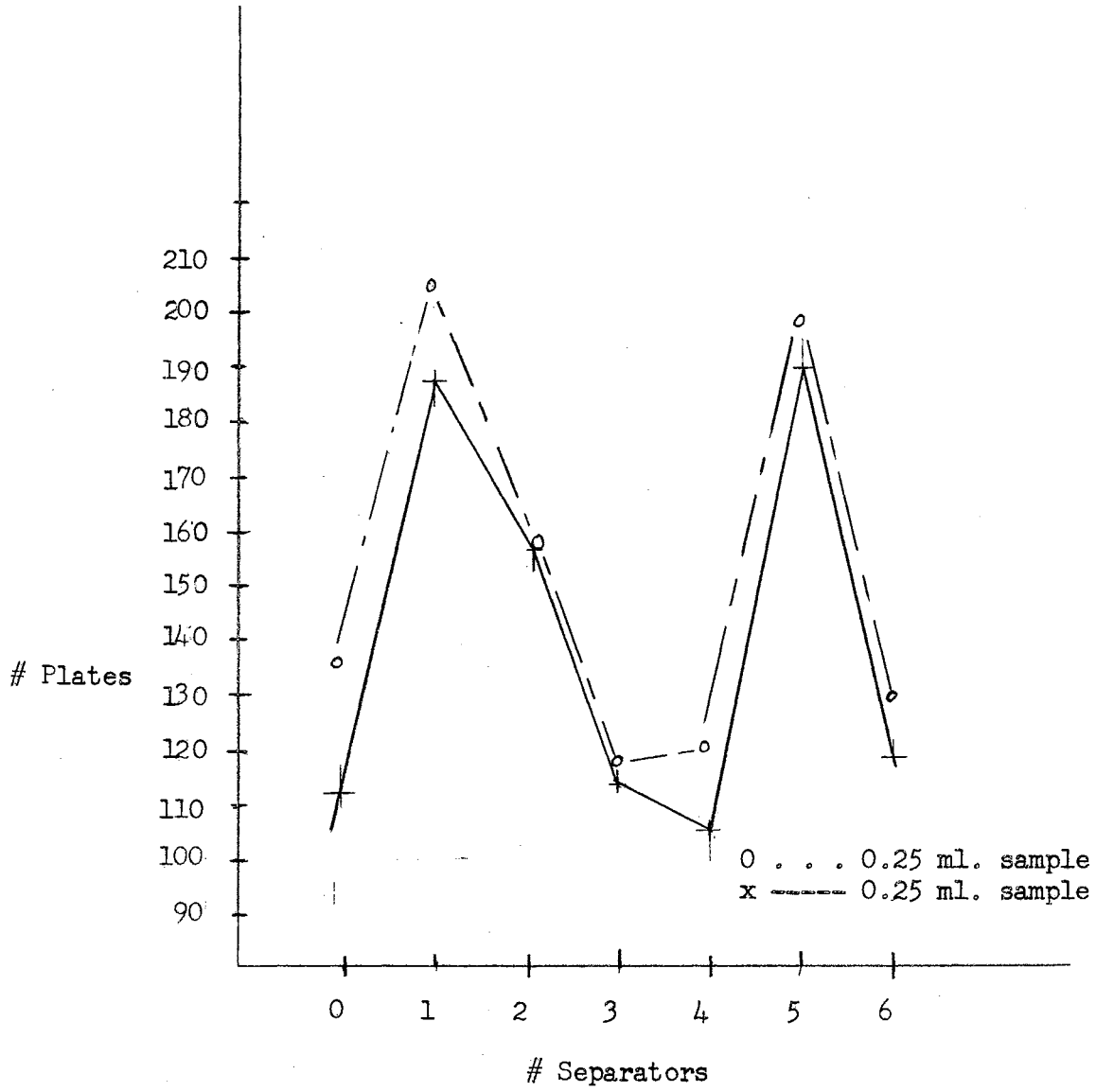


Fig. 11. Theoretical Plates vs. No. of Column Separators.

material successively shortened for each element of the series. This was intended to produce the effects of different column lengths, or column sections length with no mixing chambers being present in the column. The low values for theoretical plates resulting from the first attempt of this approach suggested solute band-spreading in the empty portion of the column. The theoretical plate number dropped to an average value of 73.8 plates for a $5\frac{1}{2}$' column material length.

TABLE V

SERIES III
($\frac{1}{4}$" separators)

Sample Size	No. of Separators	No. of Plates	Sample Size	No. of Separators	No. of Plates
0.5 ml.	0	104.9	0.5 ml.	5	168.3
0.5 ml.	1	132.9	0.25 ml.	0	119.1
0.5 ml.	2	142.1	0.25 ml.	1	149.9
0.5 ml.	3	136.1	0.25 ml.	2	153.6
0.5 ml.	4	131.5	0.25 ml.	3	149.8
0.5 ml.	5	170.6	0.25 ml.	5	193.1
0.5 ml.	4	130.9			

Sea sand of the same mesh as the packing material was acid washed, dried, and packed in the column above the desired length of column material. This produced slightly better results with the number of plates for a $5\frac{1}{2}$' column increased to a value of 77.1.

Table VI contains the average number of plates observed for each column length of the packing material. In each case the remainder of the 6' column was packed with sand.

Adequate consideration of this data requires another unit for

column efficiency which incorporates column length. The height equivalent to a theoretical plate, or H.E.T.P., is such a unit and is calculated by dividing the number of theoretical plates of a column into its length. Table VI also gives H.E.T.P. values for series IV and the data is further illustrated by Fig. 12.

TABLE VI

SERIES IV

Sample Size	Column Length	Plates	H.E.T.P.	Sample Size	Column Length	Plates	H.E.T.P.
0.5 ml.	5.5 ft.	77.1	0.856 in.	0.25 ml.	5.5 ft.	85.3	0.774 in.
0.5 ml.	5.0 ft.	75.5	0.795 in.	0.25 ml.	5.0 ft.	86.1	0.697 in.
0.5 ml.	4.5 ft.	46.4	0.859 in.	0.25 ml.	4.5 ft.	50.6	0.937 in.
0.5 ml.	4.0 ft.	84.7	0.567 in.	0.25 ml.	4.0 ft.	92.8	0.517 in.
0.5 ml.	3.5 ft.	68.9	0.610 in.	0.25 ml.	3.5 ft.	87.0	0.483 in.
0.5 ml.	3.0 ft.	65.5	0.550 in.	0.25 ml.	3.0 ft.	73.4	0.490 in.
0.5 ml.	2.5 ft.	50.5	0.594 in.	0.25 ml.	2.5 ft.	62.6	0.479 in.
0.5 ml.	2.0 ft.	56.3	0.427 in.	0.25 ml.	2.0 ft.	76.6	0.314 in.
0.5 ml.	1.5 ft.	57.2	0.375 in.	0.25 ml.	1.5 ft.	63.2	0.285 in.
0.5 ml.	1.0 ft.	57.3	0.209 in.	0.25 ml.	1.0 ft.	65.1	0.184 in.

Keeping in mind that lower numerical values of H.E.T.P. indicate a higher efficiency, the data in Table VI shows noticeable rises in efficiency at column lengths, or section lengths, of 4' and 1'. This is illustrated by Fig. 12. From this data, it appears that efficiency gains are quite predominant for column packing lengths of 4' and 1'. This is corroborated by the data in Table IV. In Table IV, sharp rises in the number of theoretical plates occurred at packing modes of 1 separator and 5 separators. These packing modes are sections lengths of 3' and 1' respectively. Due to the physical length of the

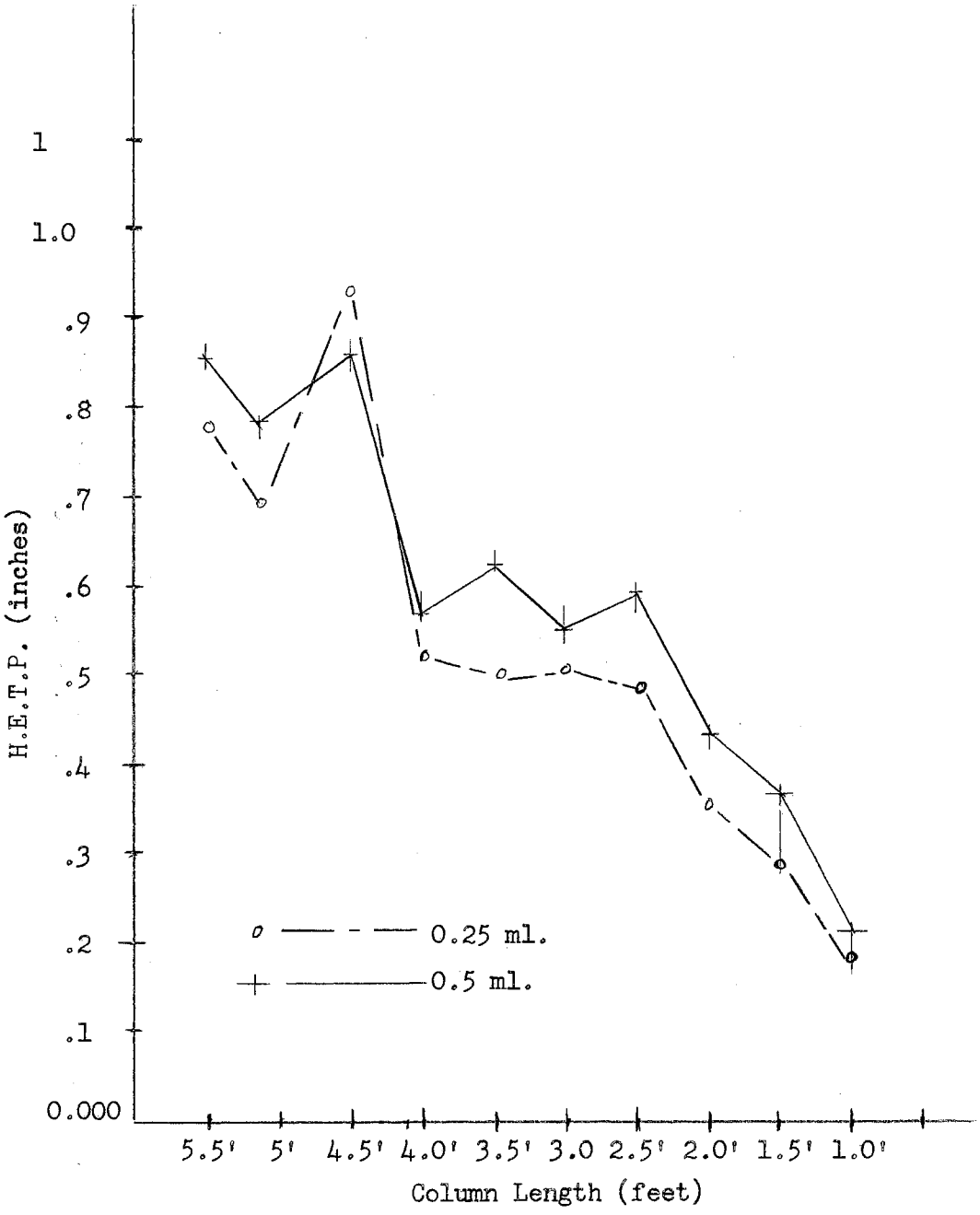


Fig. 12. H.E.T.P. vs. Section Length.

column and the desire to keep all sections equal in length, the sectional length of 3' from use of 1 separator was the closest to a 4' section used in previous series.

Additional verification of this efficiency increase was obtained by re-examination of the 4 and 5 separator packing modes and observation of the efficiency gain. Data from these reruns (actually, repetitions of series II and III packing modes) are presented in Table VII.

TABLE VII

RE-EXAMINATION OF 4 AND 5 SEPARATOR MODES

Sample Size (milliliters)	No. of Separators	Plates
0.5	4	130.2
0.5	5	211.0

These values correspond quite well with the data shown in Tables IV and V and verify the rise in theoretical plate number at this sectional length.

CHAPTER VI

SUMMARY

Results indicate that the efficiency of large diameter columns can be increased by sectioning column packing. In this experiment, the efficiency of a three-inch diameter column, packed with Nujol on firebrick, was doubled by sectioning the 6' column into sections 1' in length.

Apparently, two optimum section lengths existed. Sharp rises in the number of theoretical plates occurred at section lengths of 1' and 4'. This was verified in both cases by the method of using one column section and varying its length.

One optimum length might be explained as being due to the elimination of induced channeling. This is believed to be the cause of the high efficiency observed for the 1' sections. The second length showing a sharp efficiency rise (4') is not understood. Both efficiency rises were readily apparent in data from both methods of experimentation, discounting the theory that the separator space acted as a mixing chamber and reduced radial velocity gradient effects. However, the sand packed above the single section in the other method could act in somewhat the same manner.

The metal separators acting as heat conductors could also help reduce temperature gradients from column walls to the center of the column. This is also discounted due to observation of both efficiency increases during the second method of experimentation in which

only one (a single screen) separator was employed.

The second increase in efficiency is an optimum condition apparently produced, by section length, in one or more other variables, such as the change in velocity and pressure of the carrier as it passes through the column, or possibly mixing of irregular sample zone fronts produced by the radial velocity gradient.

Inconclusive evidence indicates that the 1/4" gap spacers were more efficient than the 1" spacers. This probably would vary with sample size and column diameter, especially the efficiency increase associated with reducing velocity gradient effects.

Further investigation should be made to determine the spacer volume effects by removing the spacer and packing the column in sections separated only by screens. Also, investigation should be made to determine and compare the effects of sectional packing on other diameter columns.

The effect of carrier velocity and pressure gradients along the length of the column could be investigated by packing the optimum section length at various positions in the column.

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