THE DETERMINATION OF HETP AND COLUMN EFFICIENCY FOR AN ANNULAR PREPARATIVE-SCALE GAS-LIQUID CHROMATOGRAPHIC COLUMN

by

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I. INTRODUCTION

Preparative-scale gas-liquid chromatography is a relatively new separation technique. Analytical-scale chromatographs are used extensively in research and quality control. Over 60,000 units are in use throughout the world.

Gas-liquid chromatography utilizes differences in adsorptivities of the components of a gaseous mixture to accomplish a separation. The mixture is swept through a bed of packing by an inert carrier gas. The packing is coated with an adsorbent liquid phase. The attractive forces between the liquid phase and the components of the sample mixture are different for each component. The larger this difference, the more easily the separation is attained. The weakly adsorbed components pass through the packed column faster than the components which are strongly adsorbed. Weakly adsorbed components are therefore the first to exit from the column.

Gas-liquid chromatography can be superior to other separation techniques when separating materials such as isomers. While isomers have boiling points which are fairly close, their adsorptive properties on a specific liquid phase may be significantly different.

The excellent separating ability of the gas-liquid chromatograph, led investigators to visualize preparing small amounts of ultra-pure materials using this technique. However, serious difficulties have hampered development of preparative-scale units. Poor separating efficiencies have plagued scale-up efforts.
Variations in the carrier gas velocity in large-diameter columns is the main reason for poor efficiencies. This variation in carrier gas velocity causes widening of the sample bands which causes poor separation.

Several design approaches have been used to combat this problem. The most successful has been the use of disc-and-doughnut type baffles which periodically remix and redistribute the fluid stream. Efficiencies as high as fifty per cent have been achieved with this method. This figure represents the performance of a preparative-scale column relative to that of an analytical-scale column. By comparison, typical efficiencies for unbaffled preparative-scale columns are about fifteen per cent.

The object of this investigation was to design, build, and test a preparative-scale chromatographic column which contained a blocked-off center tube, thus forming an annular space for the packing.
II. LITERATURE REVIEW

This section contains published information which is pertinent to this project.

Development of Chromatography

Chromatography was first employed by Tswett\(^{20}\) in 1906. He separated plant pigments in a packed column. Since he obtained discrete bands of colored material, he termed the method chromatography (literally, color writing). Tswett's discovery went unnoticed until 1931. Kuhn, Winterstein, and Lederer\(^{77}\) rediscovered chromatography by duplicating Tswett's method and using it to separate plant carotene into its components. Martin and Synge\(^{79}\) formalized many of the principles of gas-liquid and paper chromatography in 1941. Paper chromatography proved so successful in medical and biological applications that Martin and Synge received the Nobel Prize in 1952\(^{70}\). James and Martin\(^{67}\) refined the principles of gas-liquid chromatography around 1950, and demonstrated its use as an analytical tool. Analytical-scale gas-liquid chromatography has grown widely in use since this work. By 1968, there were more than 60,000 units in service.\(^{21}\)

The general term chromatography refers to several types of separations based on adsorptive and/or molecular size properties.\(^{71}\) The most important are: gas-liquid, liquid-liquid, gas-solid, paper, and gel permeation chromatography. In this study, we are concerned with gas-liquid chromatography.
Definition of the Process

Gas-liquid chromatographic separations are based on differences in physical and/or chemical affinities of the components of a gaseous mixture for a liquid surface. This liquid surface is provided by coating the liquid onto an inert solid support material. The support material is usually crushed firebrick of a mesh size between twenty and two hundred. The combination of liquid coating and solid support is referred to as the packing. The packing is placed in a column. This is usually done by vibrating the column while the packing is poured into the top. Analytical-scale columns generally have diameters between three and seven millimeters.

The flow system of a typical analytical-scale chromatograph is shown in Figure 1. An inert (carrier) gas, frequently helium or nitrogen, is continuously passed through the column. After the column has attained the desired temperature, the mixture to be separated is injected. Sample sizes usually range between one and five microliters. The vaporizing section into which the sample is injected contains a heat source which aids in quickly vaporizing the mixture. The mixture is swept through the bed by the carrier gas. Differences in adsorptive properties cause different components to be adsorbed at different rates. Components that are weakly adsorbed by the liquid phase pass through the column rapidly. Strongly adsorbed components pass through the column slowly. The carrier gas transports the separated sample through a detector. The detector is usually a thermal conductivity cell or a flame ionization detector.
FIGURE 1. FLOW DIAGRAM FOR A TYPICAL GAS-LIQUID CHROMATOGRAPH
The signal from the detector is recorded on a moving-strip recorder. The record thus obtained is called a chromatogram, and can be analyzed quantitatively.

Advantages of Gas-Liquid Chromatography Compared to Other Separation Processes

In any separation, the ease of separation depends on a physical or chemical difference in the properties of the substances to be separated. Gas-liquid chromatography utilizes the difference in adsorptivities of the components of a mixture to accomplish a separation. For this reason, gas-liquid chromatography can separate mixtures which can not be easily separated by other techniques.

In distillation, the ease of separation depends upon differences in component boiling points. The closer the boiling points, the more difficult the separation becomes. In an organic chemical reaction, isomeric products almost always result. The boiling points of isomers are usually within five degrees Fahrenheit of each other. This can make separation by distillation difficult.

Even the slight structural differences of two isomers often result in significant differences in their adsorptive properties. For isomer separation then, gas-liquid chromatography is frequently superior to distillation.

In liquid-liquid extraction, the separation depends upon differences in solubilities of the components of a mixture in a
solvent. Extraction products consist of two streams. One stream contains the purified product and the other contains the extracted component(s) plus the solvent. Since the solvent is usually too expensive to throw away, it must be distilled out of the resulting mixture. Compounds which are very soluble in one another sometimes have fairly close boiling points. Therefore, this distillation may be difficult. If a suitable liquid phase could be found, gas-liquid chromatography would be superior to liquid-liquid extraction. This would also replace a two-step separation with a one-step separation, thus reducing capital cost.

Development of Preparative-Scale Chromatography

Preparative-scale chromatography is a scale-up of an analytical unit so that much more material can be processed. This means that the process could be utilized to replace distillation, extraction, or absorption for some separations. Many preparative-scale chromatographic designs have been attempted since James' and Martin's work in 1950. Serious technical problems have delayed the development of this potentially useful technique. The biggest problem is the non-ideal flow pattern encountered by many workers in large chromatographic columns. Several techniques have been patented. Baddour and co-workers have developed and marketed an industrial scale unit. Units of this type have processed from 115,000 to 1,840,000 pounds annually. For an easy separation, the cost per pound of feed can be as low as three cents.
For a very difficult separation, this cost can range as high as fifteen dollars per pound of feed. The capital costs range between $85,000 and $246,000.\textsuperscript{(109)}

In spite of these advances, the efficiencies of preparative-scale columns remain invariably lower than those of analytical units.\textsuperscript{(109)}

**Problems in Preparative-Scale Chromatography**

Attempts to develop efficient and economical preparative-scale chromatographic processes have met with several problems.

**Capacity.** One limitation of any process equipment is the maximum amount of material that can be processed. With techniques such as distillation and extraction, the designer is forced to cope with problems such as non-ideal mixing, large heat requirements, and structural requirements.\textsuperscript{(52)} Since gas-liquid chromatography is a batch process, rather severe limitations are present.\textsuperscript{(123)} For a given separation, there is a minimum time lapse between injections, or batches. This time lapse must be provided to prevent overlap of products exiting from the column.\textsuperscript{(18)} Consider the chromatographic separation of two components, A and B. If A is weakly adsorbed onto the liquid phase while B is strongly adsorbed, A will pass through the column quicker than B. The next injection must be timed so that the A in the second injection will not overtake the B in the first injection. Thus, we are faced with a limitation which is inherent in the process itself. If all components of a sample pass through the column quickly, we can inject new feed at fairly fast intervals.
However, if one of the components passes through the column much slower than the others, the throughput will be greatly reduced.\(^{(63)}\)

Temperature programming has been used in analytical-scale units to combat this problem. After the first components exit from the column, the temperature is raised steadily until the slow-moving components are "burned out" of the column.\(^{(64)}\)

**Sample Vaporization.** In a preparative-scale chromatograph, it is natural to try to use as large an injection as possible. The maximum injection size is dictated by column loading considerations.\(^{(10)}\) The mixtures to be separated are often in the liquid state at room temperature. Since the mixture must be vaporized, we are faced with large heat requirements. The sample must be vaporized as quickly as possible so that it will enter the column as a narrow band, or slug, of material. If this is not done, a longer column is required for the separation.\(^{(83)}\)

This problem has been solved by using a heat reservoir in the vaporization chamber.\(^{(84)}\) It is heated to five to twenty degrees Fahrenheit above the column operating temperature. When the sample is injected, the heat stored in the heat reservoir becomes available to help vaporize the sample.

**Product Recovery.** After the separated material leaves the column proper, the individual components must be recovered without loss of purity. This is usually done by passing the product stream through a condenser which condenses the vaporized sample out of the inert carrier gas.\(^{(85)}\) The carrier gas is usually a non-condensable gas. The problem is to collect each fraction separately. A typical solution
is to route the flow to one of several condensers by using a series of
time-actuated valves. One component is collected in each condenser.\(^{(86)}\)

**Carrier Gas Requirements.** When a preparative-scale unit is
designed, the large carrier gas requirements become important,
economically.\(^{(87)}\) To keep costs as low as possible, it is usually
desirable to compress and recycle the carrier gas stream. The
carrier gas must be cleaned to prevent a buildup of impurities.\(^{(88)}\)
This may be done by passing the stream over a bed of solid adsorbent
such as activated carbon.\(^{(89)}\)

**Non-Ideal Flow in Gas-Liquid Chromatographic Columns.** Analytical
chromatographic columns usually have parabolic velocity profiles.\(^{(23)}\)
Radial diffusion in these small diameter columns is chiefly responsible
for the flat elution front. Radial diffusion compensates for the
non-idealities in small diameter columns because the distances over
which the material must diffuse are very short.\(^{(24)}\)

Non-equilibrium effects are present in small diameter columns,
however. There are four main causes of non-ideal behavior or poor
efficiencies in these columns. Giddings\(^{(25)}\) has listed these effects
as: (1) the transparticle effect, (2) the short-range interchannel
effect, (3) the long-range interchannel effect, and (4) solvent
maldistribution.\(^{(53)}\) These effects are all deviations from
equilibrium in gas-phase mass transfer.

The transparticle effect develops when diffusion occurs between a
stagnant gas region and a rapidly moving gas stream.\(^{(26)}\) This
situation arises in gas-liquid chromatographic columns because part of
the mobile phase can enter the pores of the solid packing. Equilibrium can never be established between these regions.

The short-range interchannel effect occurs because the flow channels in the packed bed vary greatly in diameter and length. Hence, interstitial gas velocities in neighboring channels vary significantly. Nonequilibrium diffusion occurs because of this velocity difference.\(^{(27)}\)

The variation in cross-sectional area of the flow channels is random. Variations in average gas velocity exist between different sections of packing in the same cross-section. Nonequilibrium diffusion among these sections is termed the long-range interchannel effect.\(^{(28)}\) This effect was first postulated by Golay.\(^{(54)}\)

Non-ideal behavior is also caused by solvent maldistribution.\(^{(55)}\) When a sample is injected into a chromatographic column, it is difficult to insure even distribution over the bed of packing. If the sample is not evenly distributed, radial concentration gradients cause poor separation to result. This nonequilibrium effect can be important if the column is close to being overloaded. Overloading occurs when so much sample is injected that the first section of the column is saturated with part of the sample. The remaining sample is then swept past this region without being adsorbed and desorbed. Therefore, the component elution bands are widened significantly.

These effects could cause poor efficiencies in analytical columns. Fortunately, they tend to nullify each other, with the exception of solvent maldistribution.\(^{(29)}\) Solvent maldistribution can be eliminated
by keeping sample injections at acceptably small sizes.\(^{(56)}\) This is the reason analytical columns usually have flat elution fronts.

HETP (height equivalent to a theoretical plate) is the typical measure of efficiency for packed columns.\(^{(124)}\) The HETP concept is utilized for developing quantitative relationships which incorporate the non-idealities discussed above. An ideal column has a plate height equal to zero. In other words, a packing height of zero is required to accomplish a separation equivalent to one theoretical stage, or plate. Low HETP values correspond to good column efficiency, while high HETP values correspond to poor column efficiency.

The basic equation relating HETP for chromatographic columns to diffusion effects is given by Giddings\(^{(30)}\) as:

\[
HETP = A + \frac{B}{u_o} + C_0^o u_o + C_1 f u_o
\]

where \(u_o\) is the bulk flow velocity.

\(A\) represents the contribution to plate height due to eddy diffusion. Random flow patterns induced in packed columns by the irregular nature of the packing cause eddy diffusion.\(^{(31)}\) Some of the injected sample passes through the eddy region without contacting the liquid phase. This inefficient contacting decreases the separation per unit of packing. HETP is correspondingly increased. The equation which quantitatively expresses this effect is:

\[
A = \omega^2 \omega \lambda \frac{d_p}{\beta}
\]

\(^{(2)}\)
Where:
\[ \omega_\beta = \text{ratio of velocity difference inside and outside the eddy region to average flow velocity, dimensionless} \]
\[ \omega_\lambda = \text{ratio of average free distance available for molecular diffusion to particle diameter, dimensionless} \]
\[ d_p = \text{average particle diameter, length} \]

Eddy diffusion effects are associated with all the non-idealities listed above (transparticle, interchannel effects, etc.). Each non-ideality has a particular \( \omega_\beta \) and \( \omega_\lambda \). For example, in the short-range interchannel effect, Giddings has shown that \( \omega_\beta = 0.8 \) and \( \omega_\lambda = 1.5 \). For the transparticle effect, \( \omega_\beta \) is about unity and \( \omega_\lambda \) can be as high as 10,000. The specific values of \( \omega_\beta \) and \( \omega_\lambda \) are functions of eddy region velocity, bulk flow velocity, particle diameter of packing, and the particle size distribution within the bed. The total eddy diffusion term, \( A \), is then the sum of the individual eddy diffusion contributions.

In Equation (1), \( B \) is the longitudinal diffusion term. Longitudinal diffusion is a band-broadening effect caused by diffusion either in the direction of flow or opposite to it. The quantitative expression for this effect is:

\[ B = 2 \psi D_m \]  

Where:
\[ D_m = \text{molecular diffusion coefficient for the mobile phase, (length)}^2/\text{time} \]
\( \gamma \) = obstruction factor for diffusion through granular materials, dimensionless

The obstruction factor, \( \gamma \), is an empirical factor which accounts for the impedance of the packing on diffusion.\(^{37}\) \( \gamma \) equals unity for unpacked columns and must be less than unity for packed columns. It is usually 0.6 for porous, densely packed columns.\(^{38}\) This factor is a function of the tortuosity and area constrictions in the flow channels.

In Equation (1), \( C_0^g \) is the gas-phase mass transfer term. This term is the sum of the non-ideal effects discussed previously, such as the transparticle effect. Giddings\(^{40}\) has shown that these effects are additive. Therefore, \( C_0^g \) is given by:

\[
C_0^g = \sum_{i=1}^{l} C_{gi} \tag{4}
\]

Quantitative relationships have been developed for the individual \( C_{gi} \)'s. For approximately spherical packing material, the transparticle contribution is:

\[
C_{gi} = 2(1-\Phi R)^2 \frac{d_p^2}{60(1-\Phi)\gamma D_m} \tag{5}
\]

Where:

- \( C_{gi} \) = plate height contribution due to transparticle effect, time
- \( \Phi \) = fraction of mobile phase occupying interparticle space, dimensionless
- \( R \) = fraction of solute in mobile phase, dimensionless
\( \gamma = \) obstruction factor for diffusion within packing 
particles, dimensionless

\( D_m \) and \( d_p \) are as defined previously.

For most gas-liquid chromatographic columns, \( \gamma = 0.6 \) and \( R = 0.05 \). \( F \) is usually taken as 0.5. While the values of these factors are somewhat uncertain, and may vary from case to case, the above values usually yield fairly accurate results. With these values, Equation (5) becomes:

\[
C_{gI} = 0.1 \frac{d^2}{D_m} \tag{6}
\]

The plate height contribution for short-range interchannel 
effects, \( C_{gII} \), is given by:

\[
C_{gII} = \omega \frac{d^2}{D_m} \tag{7}
\]

\( D_m \) and \( d_p \) were defined previously and, for porous solids permeated 
with the mobile phase, \(^4\)

\[
\omega \approx 0.70(1-0.15R) \tag{8}
\]

Using the value of \( R \) given above as 0.05, we have \( \omega = 0.695 \).

Therefore, \( C_{gII} \) becomes:

\[
C_{gII} = 0.695 \frac{d^2}{D_m} \tag{9}
\]

For the long-range interchannel effect, Giddings' relationship 
is\(^5\) :
\begin{equation}
C_{gIII} = (6R^2 - 16R + 11) \frac{r_c^2}{24D_m} \tag{10}
\end{equation}

where \(C_{gIII}\) is the plate height contribution due to long-range inter-channel effects. The column radius is \(r_c\). \(R\) and \(D_m\) are as defined previously. This equation has been derived assuming a parabolic flow profile through the packed bed.\(^{(44)}\) Assuming, as before, that \(R = 0.05\), we have:

\begin{equation}
C_{gIII} = 0.426 \frac{r_c^2}{D_m} \tag{11}
\end{equation}

The fourth nonequilibrium effect is solvent maldistribution. This problem can be eliminated entirely by keeping the injection size small.\(^{(57)}\) Sample sizes for analytical columns range from one to twelve microliters per injection. If the sample size is kept within these limits, we may assume no contribution from solvent maldistribution and therefore \(C_{gIV} = 0.\)\(^{(45)}\)

Combining this fact with Equations (6), (8), and (11), \(C_g\) for analytical columns is then:

\begin{equation}
C_g^o = \sum_{i=1}^{4} C_{gi} = \frac{0.426}{D_m} (1.865 \alpha_d^2 + r_c^2) \tag{12}
\end{equation}

In Equation (1), \(C_1\) is the liquid-phase mass transfer term. This term is a function of adsorption and desorption rates, solute concentration in the gaseous phase, thickness of liquid phase film on
The expression for the overall contribution to plate height by liquid-phase mass transfer, $C_1$, is:

$$C_1 = \frac{2}{3} \left[ R (1-R) \right] \frac{d^2}{D_s}$$ (13)

Where:

- $d$ = average film thickness if liquid phase, length
- $D_s$ = molecular diffusion coefficient for stationary phase, (length)$^2$/time
- $R$ = fraction of solute in the mobile phase, dimensionless

$D_s$ includes the dependence upon temperature, pressure, and adsorption and desorption rates. Assuming again that $R = 0.05$, we have:

$$C_1 = 0.033 \frac{d^2}{D_s}$$ (14)

In Equation (1), $f$ is an empirical pressure correction factor given by:

$$f = \frac{3}{2} \left[ \left( \frac{P_i}{P_o} \right)^2 - 1 \right] \left[ \left( \frac{P_i}{P_o} \right)^3 - 1 \right]$$ (15)

where $P_i$ and $P_o$ are the inlet and outlet pressures of the column, respectively. The correction factor, $f$, is included in the equation because $C_1$ is calculated at the prevailing pressure in the column. $C_1$ must be corrected to the outlet pressure in order to be consistent with the other terms in Equation (1).

By substituting the relationships presented above into Equation...
(1), we have the following relationship for HETP:

\[
\text{HETP} = \omega^2 \omega \lambda d_p + 1.2 D_m / u_o + 0.426 (1.865 d_p^2 + r_c^2) u_o / D_m + 0.033 f_u d^2 / D_g
\]

This equation gives the total plate height in an analytical chromatographic column as a function of column and particle dimensions, bulk flow velocity, and properties of the carrier gas and sample components.

Another non-ideality arises when the diameter of a chromatographic column is increased to preparative-scale dimensions. This non-ideality is caused by radial variations in the carrier gas velocity. This variation is included in the HETP equation by adding a fifth contribution, \( C_{gV} \), to \( C_g \), the gas-phase mass transfer term. Giddings\(^{(39)} \) has developed a relationship for this contribution:

\[
C_{gV} = \Phi G^2 r_c^2 / 96 \gamma D_m
\]

Where:

\( G = \text{fractional velocity nonuniformity, } \Delta u / u_o \), dimensionless
\( D_m, r_c, \Phi, \gamma \), are as defined previously. By using \( \Phi = 0.5 \) and \( \gamma = 0.6 \) as above, we have:

\[
C_{gV} = 0.009 G^2 r_c^2 / D_m
\]

The variation in carrier gas velocity is illustrated in Figure 2. The effect of radial carrier gas velocity gradients is negligible in analytical-scale columns.\(^{(90)} \) In fact, column diameters can be increased to about 0.7 inches before \( C_{gV} \) becomes important.\(^{(65)} \)

Efficiencies as low as fifteen per cent have been found in
SAMPLE INJECTED

SAMPLE BAND BEGINS TO DISTORT AS SEPARATION BEGINS TO TAKE PLACE.

FIGURE 2. BAND BROADENING EFFECT IN PREPARATIVE - SCALE CHROMATOGRAPHIC COLUMNS
(iii) DISTORTION INCREASES AS SEPARATION IS COMPLETED.
(iv) DISTORTION OF BANDS IS COMPLETE.

FIGURE 2. BAND BROADENING EFFECT IN PREPARATIVE-SCALE CHROMATOGRAPHIC COLUMNS
unbaffled preparative-scale columns. Hargrave and Sawyer have demonstrated that the major cause of this efficiency loss is the variation in carrier gas velocity. They carefully compared a $\frac{7}{8}$-inch analytical column with a one-inch preparative-scale column. In the analytical column, $C_g^o$ was 0.76 seconds. Of this, 7.9 per cent was attributed to the radial variations in carrier gas velocity. In the preparative-scale column, $C_g^o$ was 4.8 seconds. The radial variation in carrier gas velocity accounted for 85.4 per cent of this term. This comparison was made with all other parameters equal or scaled up proportionately. Hargrave and Sawyer concluded that improved efficiencies in preparative-scale columns can only be obtained by improving the carrier gas velocity profile across the column.

**Existing Preparative-Scale Designs**

Various designs for preparative-scale chromatographs have been proposed. Several investigators have attempted to scale-up analytical columns to accommodate larger sample sizes by simply increasing the column diameter. Primarily, these attempts represent the earliest designs.

All of these attempts were frustrated because of the variations in carrier gas velocity across the column. Analysis of the poor column efficiencies obtained by direct scale-up have led to many different preparative-scale designs. Several important design approaches are described below.
Coupled Columns. Berg (7) has designed a unit for large-scale chromatographic separations by joining several columns of successively smaller diameter and volume. At the exit of each column, a Teflon insert is used to restrict the flow to capillary dimensions (approximately one millimeter). This design gives results superior to those of a preparative-scale column of comparable volume when the preparative-scale column has no flow-correcting devices. (8) This is because the Teflon inserts at the end of each column partially remix the sample passing through the system. (9)

Overloaded Columns. Verzele and co-workers (126) have explored the use of narrow-bore columns which are long enough to allow severe sample overloading. The theory is that a long, narrow column can process a sample that is much larger than a short, wider column of equivalent volume. (127) The disadvantages are that the efficiency of such columns is very low because of the sample overloading, and the holdup time is sharply increased. (91)

Multicolumn Arrays. One of the simplest approaches to obtaining greater throughput from chromatographic units is to use a multicolumn array. (93) With this method, good efficiencies can be maintained. A large sample can be split among the columns and processed as quickly and as efficiently as a small sample in one analytical column. (94)

There are two main disadvantages to this method: One is the development of an efficient manifold system to handle simultaneous injections and product collections. The second problem is trying to match a group of columns so that they have the same retention time characteristics. (95)
An extension of this idea is to mount the columns in a cylindrical rack and rotate them, injecting into each one in turn. This is an automatic mechanical way to achieve multiple injections. The problem of matching the retention time characteristics of each column remains.

Counter-Current Fluidized Bed Process. Until recently, the most successful chromatographic separation technique was that of Benedek and co-workers. This system uses a counter-current approach. The vaporized sample is introduced continuously at the bottom of the tower. The stationary phase (packing) falls down the length of the column by gravitational force. In a two component system, the more weakly adsorbed component exits from the top of the tower while the more strongly adsorbed component is carried out the bottom of the column.

The major disadvantage of this design is that it is only applicable to a two-component system. Also, additional processing equipment is required for handling the solid packing, which must be recycled to the top of the tower.

Continuous Disc Chromatograph. A unique approach to eliminating the batch nature of chromatographic separations was developed by Sussman and Huang. Their apparatus consists of two thin solvent-coated circular plates. These plates are rotated with a constant angular velocity. The mixture which is to be separated is introduced continuously at the center of the rotating discs. The feed flows between the two plates to the outer rim. As the components are adsorbed onto and desorbed from the solvent coating, a separation will
occur. The different components in the feed will exit at different points on the rim of the discs.

Although this method is continuous, it has a limited capacity. The capacity depends on the spacing between the plates. The distance separating the plates is about fifty to seventy-five microns. Good separation and immediate response are characteristics of this system. It can not handle materials in the amounts necessary for it to become economically feasible as a replacement for more conventional separation processes.

Other Designs. Luft has patented a process similar to Sussman's except that the distance between the plates is much greater. Unlike Sussman's design, this space is filled with packing. As the chamber is rotated, the inlet valve near the center shaft admits first the sample and then the carrier gas. The separated sample is withdrawn from an exit valve near the outer edge of the device.

Strange, Charlton, and Yant have patented a device based on the same principle as Benedek. The difference is that the feed is introduced at some point near the middle of the column. Several patents have been awarded in the field of chromatographic separation.

Baffled Preparative scale Column. Baddour has patented an idea which does represent a new approach to chromatographic separation. It has proved to be the most important industrial-scale design thus far. This design is a large, packed chromatographic column with disc-and-doughnut type baffles mounted within it. These flow restrictions tend to level out the variation in carrier gas velocity discussed
earlier. The baffles, in effect, mix and redistribute the fluid streams.\(^{(112)}\) Using this approach, marked improvements in column efficiencies have been realized.\(^{(113)}\) Efficiencies as high as fifty percent have been achieved on these preparative-scale units.\(^{(114)}\) This efficiency figure is relative to an analytical column of the same length performing the same separation. This is a significant improvement over the fifteen per cent efficiencies obtained in previous work.\(^{(115)}\) The design is commercially available as a package unit from Abcor, Incorporated of Cambridge, Massachusetts.\(^{(22)}\)

**Annular Columns.** There have been at least two attempts to use annular columns in gas-liquid chromatographic separations. Hall\(^{(49)}\) has patented an annular column. Two cylindrical tubes of different diameters are mounted concentrically about a center shaft. The carrier gas and sample are introduced at the top of the annular space, which has been filled with packing. The entire apparatus is rotated while the carrier gas sweeps the sample through the packing. The separated sample and the carrier gas exit from the bottom of the column.

Nester/Faust Manufacturing Corporation\(^{(1)}\) has marketed a preparative-scale unit which uses an annular column. The unit includes a device for selecting any given peak and isolating it from the rest of the sample, as well as temperature programming and other typical features. Columns are available which have outer annular diameters of \(\frac{1}{2}\) and 3/4-inches. The 3/4-inch column is barely in the region where poor efficiencies have been experienced.
Giddings(47) has suggested that the use of annular columns might be the answer to the efficiency problems which have been encountered in preparative-scale work. Heat could also be supplied to the system from the inner column. This would help the heat transfer problems which have been encountered in preparative-scale chromatographs.(100)

**Column Efficiency**

The aim of workers in preparative-scale chromatography has always been higher efficiencies. Martin and Synge,(81) and other investigators(75,69) have reported efficiencies of about fifteen per cent for large-diameter chromatographic columns. The major cause of these low efficiencies is variation in carrier gas velocity across the column diameter. Many ideas have been tried in attempts to improve the efficiencies of preparative-scale columns. Several of these designs are mentioned in the previous section.

To date, the best preparative-scale efficiencies have been achieved through the use of disc-and-doughnut baffles.(116) Efficiencies as high as fifty per cent have been achieved on these columns. For a four foot diameter column, an HETP of 2.1 millimeters was found for the separation of α and β-pinene. An HETP of 1.05 millimeters was found for the same separation on a 1/4-inch analytical column.(117)

Figure 3 shows the relationship between HETP and column diameter for n-pentane at room temperature with nitrogen as the carrier gas. The packing is 30/40 mesh Silocel C 22 coated with silicone oil MC 200/200. The curve is taken from an article by Huyten, van Beersum,
Figure 3. Relationship of HETP to Column Diameter.
and Rijinders. (66) The graph shows that HETP increases rapidly with increases in column diameter above 0.7 inches.

**Analysis of Chromatographic Peaks**

The performance of any piece of process equipment must be determined by quantities measured experimentally. To determine the efficiency of the equipment, the data is compared with a similar unit or a theoretically predicted level of performance.

In gas-liquid chromatography, the data is usually a chromatogram such as that shown in Figure 4. Here, the ordinate is detector response and the abscissa is retention time. The retention time of any component is defined as the time between injection of the sample into the column and elution of the sample through the detector. The zero point on the abscissa represents the injection point.

Before any of the sample is eluted from the column, the response is a straight line, called the base line. When the sample passes through the detector, a peak is produced by the resistance change across the detector.

Two lines are drawn tangent to the inflection points on both sides of the peak. The distance between the injection point and the intersection of these two lines is called the retention time, $d$. The peak height, $h$, is defined as the vertical distance between this intersection and the base line. The peak width, $w$, is the distance between the two tangents at a point level with the base line. The distance between the tangents at one-half the peak height is called
Figure 4. A Typical Chromatogram
the peak width at half height, \( w_h \). These quantities have been chosen for convenience. They are also fairly easy to determine with a good measure of accuracy.\(^{(74)}\)

Although comparisons between peaks can be made with these quantities, plate theory is usually used.\(^{(125)}\) The number of theoretical plates is given by:

\[
NTP = \left(\frac{4d}{w}\right)^2
\]

Where:
- \( NTP \) = number of theoretical plates, dimensionless
- \( d \) and \( w \) are as defined above, usually measured in inches or centimeters.

This equation is recommended by the Gas Chromatography Committee.\(^{(19)}\)

Once the number of theoretical plates has been determined, the HETP may be obtained from:

\[
HETP = \frac{L}{NTP}
\]

Where:
- \( L \) = the total column length, inches
- \( HETP \) = the height equivalent to a theoretical plate, inches

A quantitative comparison between two columns of equal length performing the same separation, but with different cross-sectional areas may be made by comparing their HETP's. In this work, a preparative-scale unit is to be compared with an analytical-scale unit. For this comparison, an efficiency based on the HETP's of both units is usually used:
\[ \% E = \frac{\text{HETP}_a}{\text{HETP}_p} \times 100 \% \] (21)

Where:

\( \% E \) = per cent efficiency

\( \text{HETP}_a \) = height equivalent to a theoretical plate for the analytical-scale unit, inches

\( \text{HETP}_p \) = height equivalent to a theoretical plate for the preparative-scale unit, inches
III. EXPERIMENTAL

The experimental section contains all information relating to the plan of experimentation, procedures used, and the results of this study.

Plan of Experimentation

The following experimental plan was pursued throughout this investigation.

**Literature Survey.** The literature on gas-liquid chromatography was surveyed. Special emphasis was placed on preparative-scale work. A system for use in this investigation was selected from an article by King and co-workers. This article dealt with separation of high-boiling compounds present in crude oil. One of the compounds, 1-methylnapthalene, was chosen for this study. The operating conditions used by King were:

- **Temperature:** 419 degrees Fahrenheit
- **Pressure Drop:** 50 pounds per square inch
- **Carrier Gas:** helium
- **Carrier Gas Flow Rate:** 28 milliliters per minute
- **Column:** one-eighth inch outside diameter, six feet long, packed with 30/60 mesh Chromosorb W, onto which a liquid phase of 20 weight per cent Craig polyester succinate was coated.
Analytical Work. To minimize helium requirements for the preparative-scale column, tests were made on an analytical-scale column at various carrier gas flow rates. To minimize operating temperature, tests were made at various temperatures. Both minimums were considered passed when the peaks became extremely spread at the base and were no longer smooth curves.

After these conditions were determined, ten injections were made to determine average values for NTP and HETP for the analytical column. Four other sample sizes were selected and two injections were made at each sample size.

Preparative Work. A preparative-scale column was designed and constructed. This column had a circular piece of tubing inserted into its center. This center section was sealed off so that no gas flowed through it. The remaining part of the column interior was packed to a height of six feet, thus forming an annular space for the packing. The same carrier gas and packing were used as in the analytical-scale column. Temperature and pressure drop also remained the same. Sample size and flow rate were scaled-up by multiplying by a ratio of the cross-sectional areas of the two columns.

After construction of the preparative-scale unit, ten injections were made at the conditions listed above. From this data, average values of NTP and HETP were calculated for the preparative-scale column. The performance of the preparative-scale column was evaluated by comparing the HETP's of the two units. Four other sample sizes (corresponding to the four selected for the analytical unit) were selected and three injections were made at each sample size.
Method of Procedure

This section describes the methods of procedure used to obtain the average values of NTP and HETP for both the analytical and preparative-scale columns.

Preliminary Studies on the Analytical Column. The chemical system was selected following a literature survey. The system was chosen because of the high temperature involved in the separation (419 degrees Fahrenheit) and because the materials being separated were high molecular weight hydrocarbons. This makes the separation on a large scale important to the petroleum industry.

The flow rate given in the article was 28 milliliters per minute. It was desired to determine the minimum temperature and flow rate to keep the cost of the project at a minimum. Helium cost represented one of the major expenses of this investigation. The temperature was minimized so that the heaters for the large column could be as small as possible. Therefore, the first runs on the analytical unit were aimed at finding these minimums. The determination of minimum operating conditions is described in detail in the appendix. First, the minimum operating temperature was determined. This was done by successively lowering column temperature while maintaining the flow rate at approximately 15 to 20 milliliters per minute. When the 1-methyl-naphthalene peaks became shortened and spread at the base, and when the peaks were no longer smooth curves but were irregular in shape, the minimum was considered passed. After determining the minimum operating temperature, the minimum flow rate was found. This was done by
operating the analytical unit at the minimum temperature and lowering the flow rate until the peaks became irregular as described above.

**Comparative Studies on the Analytical Column.** After determining the minimum operating temperature and carrier gas flow rate, ten injections of practical grade 1-methylnaphthalene were made. From these injections, average values of NTP and HETP for the analytical column could be calculated. HETP values were also calculated for four other sample sizes, for which two injections each were made.

Practical grade 1-methylnaphthalene was used instead of ultra-pure material (as in the preliminary studies) because practical grade material was to be used in the preparative-scale unit. Since injections for the preparative-scale unit were about 800 times larger than the analytical injections, ultra-pure material was too costly to be used in the preparative-scale unit. Cost considerations thus dictated the use of a lower purity 1-methylnaphthalene.

During all the analytical tests, the following start-up and shut-down procedures were used:

**Start-Up Procedure.**
1. Turn on and adjust carrier gas flow rate.
2. Turn on power to chromatograph.
3. Adjust cell current to 20 milliamps.
4. Turn heaters to maximum output.
5. When temperature approaches the desired level, adjust heater output to the predetermined steady-state settings.
6. Turn on recorder.
7. After steady state has been reached (as indicated by a steady horizontal base line) readjust carrier gas flow rate and cell current.

8. Inject sample.

Shut-Down Procedure.

1. Turn off recorder.
2. Turn off heaters.
3. Turn off power to chromatograph.
4. When temperature in unit has decreased to room temperature, turn off carrier gas flow.

Comparative Studies on the Preparative-Scale Column. After the preparative-scale unit had been constructed, the column was packed and then heated to operating temperature on six different occasions. This "break-in period" was to insure that any excess liquid phase was removed from the packing. During these heating periods, a small flow of helium passed through the column.

Ten injections were then made on the preparative-scale column. From the chromatograms obtained from these injections, average values of NTP and HETP for the preparative-scale column were calculated. The performance of the preparative-scale column was then evaluated by comparision with the analytical-scale column through the use of Equation (21). Three injections each of four other sample sizes were made. HETP values were calculated for each of these sample sizes.

The following start-up and shut-down procedures were used for all runs on the preparative-scale unit:
Start-Up Procedure.

1. Turn on and adjust carrier gas flow rates through column and both sides of the thermal conductivity cell.
2. Turn on power to thermal conductivity cell.
3. Adjust cell current to 20 milliamps.
4. Turn power for all heating tapes to maximum output.
5. When temperature approaches the desired level, adjust heater outputs to the predetermined steady-state settings.
6. Turn on recorder.
7. After steady state has been reached (as indicated by constant temperature readings and a constant base line) readjust all flow rates and the cell current.
8. Inject samples.

Shut-Down Procedure.

1. Turn off recorder.
2. Turn off all heaters.
3. Turn off power to thermal conductivity cell.
4. When the temperature has decreased throughout the system to room temperature, turn off carrier gas flow.

Results

The following tables give the calculated results for the tests on the analytical and preparative-scale units. Tables I and III give the NTP and HETP values for each run on the analytical and preparative-scale units. Tables II and IV give average HETP and sample size per
unit cross-sectional area values for the injections on both units. Table V gives the final results of the investigation. The data given in Tables II and IV is plotted in Figure 5.
<table>
<thead>
<tr>
<th>Injection Number</th>
<th>Sample Size, µl</th>
<th>NTP (dimensionless)</th>
<th>HETP (inches)</th>
</tr>
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<tr>
<td>A7-1</td>
<td>1.00</td>
<td>23.4</td>
<td>3.08</td>
</tr>
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<td>3.60</td>
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TABLE II

Average HETP and Sample Size Per Unit Cross-Sectional Area

From Tests for Analytical Unit

<table>
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<tr>
<th>Sample Size</th>
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<th>Average HETP</th>
</tr>
</thead>
<tbody>
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<td>0.12</td>
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<td>2.35 inches</td>
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</tr>
<tr>
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<td>1.67 inches x 10^2</td>
<td>3.00 inches</td>
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<tr>
<td>1.00</td>
<td>2.09 inches x 10^2</td>
<td>3.22 inches</td>
</tr>
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<td>Injection Number</td>
<td>Sample Size, ml</td>
<td>NTP Dimensionless</td>
</tr>
<tr>
<td>------------------</td>
<td>----------------</td>
<td>------------------</td>
</tr>
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<td>P1-2</td>
<td>0.5</td>
<td>9.15</td>
</tr>
<tr>
<td>P1-3</td>
<td>0.5</td>
<td>13.40</td>
</tr>
<tr>
<td>P1-4</td>
<td>0.5</td>
<td>11.87</td>
</tr>
<tr>
<td>P1-5</td>
<td>0.5</td>
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<td>P1-6</td>
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<td>12.30</td>
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<td>P1-7</td>
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<td>9.57</td>
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<td>P1-8</td>
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<td>13.50</td>
</tr>
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<td>P1-9</td>
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<td>P1-10</td>
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<td>15.29</td>
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<td>P1-11</td>
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<td>7.32</td>
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<tr>
<td>P1-12</td>
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<td>P1-13</td>
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<td>P1-14</td>
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<tr>
<td>P1-15</td>
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<tr>
<td>P1-16</td>
<td>0.7</td>
<td>16.40</td>
</tr>
<tr>
<td>P1-17</td>
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<tr>
<td>P1-18</td>
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<td>8.16</td>
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<tr>
<td>P1-19</td>
<td>0.1</td>
<td>11.14</td>
</tr>
<tr>
<td>P1-20</td>
<td>0.7</td>
<td>16.41</td>
</tr>
</tbody>
</table>
TABLE IV

Average HETP and Sample Size Per Unit Cross-Sectional Area
From Tests for Preparative-Scale Unit

<table>
<thead>
<tr>
<th>Sample Size</th>
<th>Sample Size Per Unit Cross-Sectional Area</th>
<th>Average HETP</th>
</tr>
</thead>
<tbody>
<tr>
<td>ml</td>
<td>inches $\times 10^2$</td>
<td>inches</td>
</tr>
<tr>
<td>0.1</td>
<td>0.24</td>
<td>6.44</td>
</tr>
<tr>
<td>0.3</td>
<td>0.73</td>
<td>9.45</td>
</tr>
<tr>
<td>0.5</td>
<td>1.21</td>
<td>6.06</td>
</tr>
<tr>
<td>0.7</td>
<td>1.69</td>
<td>4.33</td>
</tr>
<tr>
<td>0.9</td>
<td>2.18</td>
<td>6.11</td>
</tr>
</tbody>
</table>
### TABLE V

Results of Tests on Analytical and Preparative-Scale Units

**Analytical Unit:**
- Average Bubble Flowmeter Rise Time (min): 33.33
- Flow Rate (ml/min): 12.0

**Preparative-Scale Unit:**
- Average Bubble Flowmeter Rise Times
  1. 1.0 liter volume (sec): 5.86
  2. 400 ml volume (min): 7.00
- Total Flow Rate (l/min): 10.30

<table>
<thead>
<tr>
<th>Analytical Sample Size, µl</th>
<th>Preparative-Scale Sample Size, ml</th>
<th>Per Cent Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.1</td>
<td>36.5</td>
</tr>
<tr>
<td>0.35</td>
<td>0.3</td>
<td>33.4</td>
</tr>
<tr>
<td>0.58</td>
<td>0.5</td>
<td>58.2</td>
</tr>
<tr>
<td>0.80</td>
<td>0.7</td>
<td>69.3</td>
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<tr>
<td>1.00</td>
<td>0.9</td>
<td>52.7</td>
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</table>
Figure 5. HETP versus Sample Size per Unit Cross-Sectional Area for Tests on Analytical and Preparative-Scale Units
IV. DISCUSSION

In this section, discussions of previous work, the procedures used in this work, and the results of this work are presented. In addition, recommendations for future study and the limitations of this investigation are presented.

Discussion of Literature

The method for calculating HETP values for both the analytical and preparative-scale columns is presented in the literature review. This method entails drawing two tangents to the inflection points on the sides of a chromatographic peak. The ideal situation would be for the chromatographic peak to be tall, narrow, and symmetrical. Frequently, peaks are not ideal. This was the case in the present study. The peaks were not symmetric for either column because of tailing. Tailing is caused by impurities in the sample which have about the same retention time as the sample. Longitudinal (or axial) diffusion is another cause of tailing. When a low carrier gas flow rate is used, the sample band can widen due to longitudinal diffusion. Some of the sample material tends to lag behind the rest of the sample band, thus causing tailing. This behavior was especially pronounced in the analytical column data. This factor can lead to considerable inaccuracy in drawing the tangents to the peaks. It is always difficult to draw a tangent "by eye", and tailing makes the situation worse. It is
also difficult to estimate the error introduced by this method of analysis. The equation used to calculate the NTP's is:

\[ \text{NTP} = 4 \left( \frac{d}{w} \right)^2 \]  

(19)

Any error in measuring the retention time (d) or the width of the peak at the base (w) is compounded because the ratio of the two quantities is squared.

This method of analysis does have the advantage of being quick and easy. As noted in the literature review, it is recommended by the Gas Chromatography Committee.\(^{(19)}\) Most workers have used this method to obtain their HETP values. In spite of its disadvantages, this method of analysis was used in this study in order to conform to accepted practice.

**Discussion of Procedures**

The procedures for operating both the analytical and preparative-scale units are fairly standard procedures for gas-liquid chromatographs. With both units, steady state was reached by allowing the recorder base line and the temperature readings to become constant before any injections were made. There should have been no error introduced into the data by non-steady state conditions. Some shortcomings of the equipment did become apparent during operation, however.

**Sample Injection.** Inaccuracies were introduced into the data for both the analytical and preparative-scale units because of the necessary sample sizes and the calibrations on the syringes. A sample size of
three microliters was originally planned for the analytical unit. This was an arbitrarily selected number. This value, scaled-up for the preparative-scale unit, becomes 2.58 milliliters. Vaporization of a 2.58 milliliter sample would cause two problems. The high pressure resulting from vaporization of the 2.58 milliliter sample would cause severe leaks in the system. It was also hard to read the syringes accurately and to make the preparative-scale injections rapidly.

A ball-type check valve was installed in the feed line to prevent back flow when the sample was vaporized. However, the vaporization of a 2.58 milliliter sample would cause pressure in the column and flow lines. This would result in recurrent leaks in the system. This would also tend to burst (1) the septum in the injection port, or (2) the epoxy resin which sealed the thermocouple wells. Because of these problems, the sample sizes were lowered to a maximum of one milliliter for the preparative-scale unit.

Another problem derived from the syringes used to inject the samples. The large syringe which was used for the preparative-scale injections was calibrated in divisions of two-tenths of a milliliter. Therefore, the sample sizes for the preparative-scale unit were selected as 0.1, 0.3, 0.5, 0.7, and 0.9 milliliters. The corresponding analytical unit sample sizes were then 0.12, 0.35, 0.58, 0.81, and 1.05 microliters. The syringe used with the analytical unit was calibrated in divisions of one-tenth of a microliter. Considerable error could be introduced in the data by trying to reproduce these sample sizes exactly.
Another problem with the sample injections was the length of time required to empty the syringe after it was inserted into the septum. It took about four to five seconds to complete an injection on the preparative-scale unit. This time lapse could cause the sample to enter the column in a wider band than would be desired.

**Flow Control.** The metering valves functioned well everywhere except in the main product line from the preparative-scale column. This valve had to be replaced with another valve which had a much coarser needle. The three degree pitch on the original needle valve caused the valve to clog with the high-boiling impurities in the practical grade 1-methylnaphthalene. These materials collected on the needle of the metering valve and made it impossible to obtain the required flow rate through the preparative-scale column. The replacement valve had good flow control characteristics at the flow rate used in this study. However, its characteristics would not allow it to be used to study a very wide range of flow rates. Its operating range was approximately nine to eleven liters per minute.

**Discussion of Results**

The following section contains a discussion of the results obtained in this investigation. The investigation entailed comparisons of the performance of an analytical-scale chromatographic column with that of a preparative-scale column.
Tests on Analytical-Scale Column. Table I and Figure 5 show that the data taken using the analytical column had good reproducibility at each sample size tested. Variations in HETP were somewhat more pronounced at the larger sample sizes. For example, Injections A7-1 and A7-2 (made at a sample size of one microliter) had HETP's of 3.08 and 3.36 inches, respectively. The difference in HETP for this pair of injections is 0.28 inches. For Injections A7-6 and A7-7 (made at a sample size of 0.35 microliters) had HETP's of 3.18 and 3.13 inches. The difference in HETP for this pair of injections is 0.05 inches. All the analytical data substantiated the fact that variations in HETP were greater for the larger sample sizes than for the smaller sample sizes. This result was expected since tailing is more pronounced for larger sample sizes. Tailing in chromatographic peaks is caused by impurities present in the sample. Figure 6 shows that tailing makes the tangent on the downward side of the peak much harder to draw accurately. Since tailing is more pronounced at the higher sample sizes, more variation in retention time and peak width measurements would be expected. This would be reflected in the data, and this is the case. Another reason for this variation in the HETP values was the graduations on the syringe used with the analytical column. This was mentioned in the discussion of procedures. Some of the variation in HETP was probably due to inaccuracy in the size of the injections. However, the analytical data was very good as far as reproducibility is concerned.

In Figure 5, the lower curve is a plot of HETP versus sample size per unit cross-sectional area for injections on the analytical column. This curve is practically horizontal, indicating that in the range of
sample sizes used in this investigation HETP is not very dependent upon sample size. Although the literature has no data of this type for 1-methylnaphthalene, this is not an unusual result. At these low sample sizes, several investigators have reported the same type of dependence of HETP upon sample size for many different compounds and systems.\(^{63,72,84}\)

The main difference in the analytical data of this investigation and typical data reported in the literature is the magnitude of the HETP's. HETP's as low as 0.04 inches have been consistently reported for various systems and separations.\(^{16,79,84}\) The HETP's obtained in this investigation from the analytical column varied between 2.32 and 3.81 inches. This range of values is unusually high for a good analytical column. The chief reason for these high HETP values is probably broadening of the sample band in the vaporization chamber. The vaporization chamber was a section of tubing four inches in length with an inside diameter of 3/4 of an inch. Since the samples used were one microliter or less in size, and the flow rate was so low (twelve milliliters per minute), there was ample opportunity for the sample band to widen after it was vaporized. When the vaporized sample entered the column, it was already spread out. The high HETP values resulted. During the preliminary tests at higher carrier gas flow rates, the peaks were considerably narrower than those tests at lower flow rates. For example, at a flow rate of 19.2 milliliters per minute and an operating temperature of 302 degrees Fahrenheit, an HETP of 0.518 inches was obtained at a sample size of three microliters. This is a good indication that the above explanation is valid.
Tests on Preparative-Scale Column. Table III and Figure 5 show more spread in the HETP's at sample sizes of 0.3 and 0.5 milliliters on the preparative-scale column than in the analytical column data. However, for sample sizes of 0.1 and 0.7 milliliters, the variances are about equal. The reason for the spread in the HETP data at two sample sizes but not at the other two lies in the injections themselves. The syringe used for the preparative-scale tests had a small diameter needle. However, the inside diameter of the cylinder of the syringe was much larger than the needle. When the needle was inserted through the septum, the pressure in the column forced the plunger out about one-half inch. The needle was hard to push in and, since the injections were done by hand, the time to inject the samples varied. This would affect the width of the sample band entering the column. Consequently, the peak widths would vary from injection to injection because of the difference in sample band widths. This factor caused the HETP variations for sample sizes of 0.3 and 0.5 milliliters. This problem was not present in the HETP data for sample sizes of 0.1 and 0.7 milliliters.

HETP data for the preparative-scale column has a much greater dependence on sample size than the HETP data for the analytical column. In Figure 5, the average HETP values for sample sizes of 0.1, 0.5, and 0.9 milliliters are 6.44, 6.06, and 6.11 inches respectively. A maximum in the curve of 9.45 inches is observed at a sample size of 0.3 milliliters. A minimum of 4.33 inches is observed at a sample size of 0.7 milliliters. There has been no data published in the literature for preparative-scale columns with which to compare this data.
The fact that HETP decreased between sample sizes of 0.3 and 0.7 milliliters is probably explained by axial diffusion. After the sample has been vaporized and is traveling through the column, the sample band is widened by axial diffusion. Axial diffusion is diffusion of the sample band in the direction of bulk flow or opposed to it. This widening of the sample band causes an increase in HETP. This increase in HETP should be more pronounced at smaller sample sizes. The data reflects this because HETP decreases as sample size increases from 0.3 to 0.7 milliliters.

HETP starts increasing above sample sizes of 0.7 milliliters. This is probably caused by overloading in the vaporization section and/or the column itself. Only one injection was made at a sample size of 0.9 milliliters. This was because the septum bulged out severely after the first injection. It was feared that repeated injections might burst the septum. This indicated that the vaporization chamber and/or the column might be overloaded. The boiling point of 1-methylnaphthalene is 472 degrees Fahrenheit. The vaporization chamber was heated to approximately 301 to 306 degrees Fahrenheit. At the larger sample size, immediate vaporization of the sample may not have occurred because of the relatively low temperature. This would widen the sample band which would increase $C_{gIV}$ as mentioned in the literature review. This, in turn, would have increased HETP. Even if the vaporization chamber vaporized the 0.9 milliliter sample as rapidly as the other samples, the column could have been overloaded due to the larger sample. When a column is overloaded, the first layers of packing have adsorbed all of the sample they can. The rest of the sample is carried past these
saturated layers of packing without being adsorbed. The sample band is widened, and HETP is increased. Overloading, in the vaporization chamber and/or the column, probably explains the higher HETP at a sample size of 0.9 milliliters.

For a 0.1 milliliter sample size HETP is 6.44 inches. HETP then rises to a maximum of 9.45 inches at a sample size of 0.3 milliliters. This behavior is explained by examining Equation (1). A is the contribution to plate height due to eddy diffusion. From Equation (2), we see that it is independent of the concentration of solute (sample) in the gaseous phase. $C^0_g$ is the contribution to plate height due to gas-phase mass transfer. It is equal to the sum of five contributions. Solvent maldistribution ($C_{gIV}$) can be neglected because of the low sample size. From Equation (17) we see that $C_{gV}$ is independent of solute concentration in the gas phase.

In Equations (5), (7), (8), and (10), R is the fraction of solute in the mobile phase. As R is decreased, $C_{gI}$ and $C_{gII}$ are increased. As R is decreased, $C_{gIII}$ is decreased. Examination of the equations for $C_{gI}$, $C_{gII}$, and $C_{gIII}$ shows that $C_{gIII}$ decreases with R more rapidly than $C_{gI}$ or $C_{gII}$ increase as R decreases at low sample sizes. Therefore, $C^0_g$ is almost constant with changes in R at low sample sizes.

Therefore, the two major terms affecting HETP in Equation (1) are $B/u_0$ and $C_1u_0$. B is the contribution to plate height due to longitudinal diffusion. This effect is diminished by the fact that B is divided by the bulk flow velocity, $u_0$. $C_1$ is the contribution to plate height due to liquid-phase mass transfer. The effect of $C_1$ is increased because
it is multiplied by the bulk flow velocity, \( u_0 \). In the earlier
discussion of longitudinal diffusion, it was explained how this effect
caus \( \text{d} \) a decrease in HETP between sample sizes of 0.3 and 0.7 milli-
liters. This effect would certainly be more pronounced at a sample
size of 0.1 milliliters. However, in the case of the lower sample
size, the size of the liquid-phase mass transfer term \( (C_1) \) would be
very small. This is because there is not as much sample material
present. Consequently, there is less diffusion within the liquid-filled
pores of the solid packing. The molecules of the sample material
would not have to diffuse very far at all through the liquid phase to
find an active site for adsorption. \( C_1 \) in the case of the 0.1 milli-
liter sample is probably very close to zero. Therefore, even severe
longitudinal diffusion can not increase plate height very much. As the
sample size is increased, \( C_1 \) would become larger because more sample
material would be present. The sample molecules would have to diffuse
further into the liquid phase to find active sites for adsorption. As
explained earlier, as sample size is increased still further, longi-
tudinal diffusion effects decrease rapidly causing HETP to decrease in
spite of an increase in \( C_1 \).

Comparison of Tests on Analytical and Preparative-Scale Units.
The shape of the curves in Figure 5 for both the analytical and prepar-
ative-scale units have been discussed. Regardless of shape, however,
it is apparent that at every sample size tested, the analytical column
yielded lower HETP values than the preparative-scale column. This is a
good indication that \( C_{GV} \) in Equation (17) has not been kept as low in
the preparative-scale tests as in the analytical tests. This was as expected. This column does show definite improvement over the fifteen per cent efficiencies reported in unbaffled preparative-scale columns which do not utilize an annular space to hold the packing. This is reflected in the efficiencies listed in Table V. The lowest efficiency was 33.4 per cent. The efficiencies at 0.5, 0.7, and 0.9 milliliter preparative-scale sample sizes are 58.2, 69.3, and 52.7 per cent, respectively. The three efficiencies are all higher than the fifty per cent efficiency of Abcor's baffled column.

The same effects which caused the shape of the HETP versus sample size curve in Figure 5 are no doubt present in the analytical column. They are certainly not as pronounced, however. Before a comprehensive picture of the performance of the preparative-scale column can be formed, a great deal more data must be taken.

Another difference in the analytical and preparative-scale data was the peaks themselves. Figures 6 and 7 show typical chromatograms for the analytical and preparative-scale units, respectively. The analytical peak is shorter and wider at the base than the preparative-scale peak. The analytical peak's retention time was also much greater. The method used to calculate the HETP's for both columns did not take this into account. The main reason for differences in retention times is probably a difference in packing density. Several investigators \(^{(32, 63, 92)}\) have shown that the method of packing can make significant differences in the number of plates in a given length of column. This is because the packing densities are different due to different packing
techniques. The preparative-scale column had a packing density of 16.96 pounds per cubic foot. It was packed by slowly pouring packing into the column while constantly tapping the column with a rubber hammer; the analytical column was purchased prepacked. There is no data available on its packing density. The chromatograms indicate that the analytical column must have been packed tighter than the preparative-scale column. This conclusion is pointed out because the retention times were much greater for the analytical tests than for the preparative-scale tests. This, in turn, would allow more time for axial diffusion which accounts for the spreading in the analytical peaks.

Recommendations

The following are recommendations for changes in the apparatus used in this investigation and for further studies.

Flow Control. As mentioned in the discussion of procedures, the valve which controlled the main flow through the preparative-scale column does not have sufficient control to allow a study of various flow rates in the system. It is therefore recommended that a control valve with a flow rate of one to thirty liters per minute be installed in the unit before further tests are attempted.

Temperature Measurement. The accurate measurement of temperature in various parts of the preparative-scale system is important for determining steady state. Therefore, thermocouples were used for temperature measurement in the column itself. In the flow lines, thermometers were used. Several thermometers were broken during the
work on the preparative-scale unit. Thermal expansion of the brass fittings in which the thermometers were mounted caused some breakage. Accidentally hitting the thermometers while replacing fittings caused more breakage. It is therefore recommended that thermocouples be installed in the flow lines as well as in the column to eliminate this breakage problem.

**Sample Injection.** Sample size is a major variable in any gas-liquid chromatographic system. The possible inaccuracies in the data because the syringes were hard to read accurately has been mentioned in the discussion of procedures. It is recommended that a syringe which is calibrated to one hundredth of a milliliter be obtained for use with the preparative-scale unit. A more accurate syringe would also be desired for the analytical unit.

**Injection Port.** To allow much larger sample sizes to be studied on the preparative-scale unit, the injection port must be modified to stand higher pressures. The simplest solution would be to place a coarse screen in front of the septum. This screen would take most of the pressure and would probably eliminate the possibility of bursting the septum during sample vaporization.

**Column Packing Density.** It is recommended that additional packing should be purchased and another analytical column be prepared. This column should be packed so that it has the same packing density as the preparative-scale column. A more valid comparison could then be made between the analytical and preparative-scale columns.
System Studied. One of the major drawbacks in this investigation was the high cost of the helium carrier gas. One solution to this problem would be the selection of a different system which uses a less expensive carrier gas such as nitrogen.

Recycle and Clean-Up System. Another solution to the helium cost problem would be to compress and recycle the carrier gas. The present system could thus be retained. If an appropriate compressor could be found in the department's supplies, the recycle system would be inexpensive to install. The recycled carrier gas must be cleaned of the sample material before being reused. This could be accomplished by using cold water condensers and product traps.

Further Studies. The preliminary data taken in this investigation indicates that further studies of the system should be conducted. Further studies should include determination of column performance at: (1) higher sample sizes, (2) several different flow rates of carrier gas, and (3) several higher operating temperatures.

Limitations

The following are limitations imposed on this investigation.

System Studied. This investigation was limited to one system: that of King and co-workers. The system was selected because it was of industrial importance and because it required high temperature (above 250 degrees Fahrenheit) to perform the separation.
Operating Conditions. Tests were made at one set of operating conditions. The temperature used was 300 degrees Fahrenheit. The flow rate was 12.0 milliliters per minute for the analytical unit and 10.30 liters per minute for the preparative-scale unit. The current to the thermal conductivity cell was twenty milliamps. A fifteen percent sensitivity was used for the chromatograph.

Sample Size. It was found that a sample size of 2.58 milliliters on the preparative-scale column caused leaks and burst the septum. Therefore, it was arbitrarily decided to limit the injections on the preparative-scale column to a maximum of 0.9 milliliters. Sample sizes of 0.1, 0.3, 0.5, 0.7, and 0.9 milliliters were injected on the preparative-scale column. The corresponding sample sizes used on the analytical column were 0.12, 0.35, 0.58, 0.80, and 1.00 microliters.
V. CONCLUSIONS

The chromatographic system studied in this investigation consisted of 1-methylnaphthalene injections with helium carrier gas and a liquid phase of Craig polyester succinate coated onto crushed firebrick. The operating temperature was 300 degrees Fahrenheit. Two columns were tested: The analytical column had an inside diameter of 0.061 inches. The preparative-scale column had an annular space for the packed section. Its outer diameter was 2.075 inches and its inner diameter was 1.050 inches. The carrier gas flow rates were 0.012 and 10.30 liters per minute for the analytical and preparative-scale columns, respectively. Investigation of this system led to the following conclusions:

1. Efficiencies of 36.5, 33.4, 58.2, 69.3, and 52.7 per cent relative to the analytical column were calculated for preparative-scale injections of 0.1, 0.3, 0.5, 0.7, and 0.9 milliliters, respectively.

2. HETP for the preparative-scale column was very sensitive to variation in sample size in the range from 0.1 to 0.9 milliliters.

3. HETP for the analytical column was not sensitive to variation in sample size in the range from 0.12 to 1.00 microliters, as was expected from data in the literature.
VI. SUMMARY

The purpose of this investigation was to design, build, and test a preparative-scale column which contained a blocked-off center tube, thus forming an annular space for the packing.

The chromatographic system for this study consisted of 1-methyl-naphthalene injections with helium carrier gas and a liquid phase of Craig polyester succinate on crushed firebrick. The analytical column had an inside diameter of 0.061 inches. For the preparative-scale column, the outer diameter was 2.075 inches and the inside diameter was 1.050 inches. The operating temperature for both columns was 300 degrees Fahrenheit. The flow rates were 0.012 and 10.30 liters per minute for the analytical and preparative-scale columns, respectively.

Several sample sizes were injected on both columns. Variation of HETP with sample size was determined. Preparative-scale column efficiencies were calculated from average HETP's at all sample sizes tested.

Efficiencies of 36.5, 33.4, 58.2, 69.3, and 52.7 per cent relative to the analytical column were calculated for preparative-scale injections of 0.1, 0.3, 0.5, 0.7, and 0.9 milliliters, respectively. HETP for the preparative-scale column was very sensitive to variation in sample size in the range from 0.1 to 0.9 milliliters. HETP for the analytical column was not sensitive to variation in sample size in the range from 0.12 to 1.00 microliters, as was expected from literature data.
VII. BIBLIOGRAPHY


3. ibid.


5. ibid.


7. ibid.

8. ibid.

9. ibid.


11. ibid.

12. ibid.


14. ibid, pp. 2-3.
15. ibid, pp. 48-51.
16. ibid, pp. 53-54.
17. ibid, p. 343.
18. ibid, pp. 4-14.
19. ibid, p. 67.
22. ibid.
24. ibid, p. 13.
25. ibid, pp. 42-43.
26. ibid, p. 42.
27. ibid.
28. ibid.
29. ibid, pp. 265-266.
30. ibid, p. 62.
31. ibid, pp. 49-61.
32. ibid, p. 49.
33. ibid, p. 51.
34. ibid, pp. 50-51.
35. ibid, pp. 60-61.
36. ibid, p. 60.
37. ibid, p. 35.
38. ibid, p. 36.
39. ibid.
40. ibid, p. 161.
41. ibid, p. 158.
42. ibid, p. 157.
43. ibid, p. 154.
44. ibid.
45. ibid, p. 142.
46. ibid, pp. 154-156.
49. ibid.
51. ibid, p. 1638.
52. ibid, p. 1634.
53. ibid.
54. ibid.
55. ibid.
56. ibid.
57. ibid, p. 1634.
58. ibid.
59. ibid, pp. 1634-1638.
60. ibid, p. 1638.
61. ibid.
64. ibid, p. 239.
65. ibid, p. 224.
66. ibid, pp. 235-237.
68. ibid.
69. ibid.
71. ibid, pp. 5-15.
72. ibid, pp. 58-103.
73. ibid, pp. 18-19.
74. ibid, pp. 15-17.
75. ibid, p. 108.
76. King, R. W., F. A. Fabrizio, and A. R. Donnell: Application of


80. ibid.

81. ibid, p. 1357.


84. ibid, pp. 337-345.

85. ibid, p. 350.

86. ibid.

87. ibid.

88. ibid, p. 331.

89. ibid, p. 337

90. ibid.

91. ibid, pp. 328-329.
92. ibid, pp. 328-329.
93. ibid, pp. 329-330.
94. ibid.
95. ibid.
96. ibid.
97. ibid.
98. ibid, p. 336.
99. ibid.
100. ibid, p. 355.
102. ibid.
104. ibid.
105. ibid.
106. ibid.
107. ibid.
109. ibid, p. 178.
110. ibid.
111. ibid, pp. 170-178.
112. ibid.
113. ibid.
114. ibid, pp. 170-178.
115. ibid.
116. ibid, p. 173.
117. ibid.
119. ibid.
120. ibid, p. 408.
121. ibid, p. 409.
122. ibid, pp. 436-437.
123. ibid, p. 452.
124. ibid, p. 319.
125. ibid.
127. ibid.
VIII. APPENDIX
This section contains the information required to reproduce the results of this work. It also contains a complete listing and description of all materials and apparatus used in this investigation. In particular, the preparative-scale column is described in detail on pages 89 through 94.

Data Tables

The following tables contain the data from the analytical and preparative-scale chromatographic units. Tables VI and IX give the temperatures, pressures, and other operating parameters. Tables VII, X, and XI give the bubble flowmeter rise time data. Tables VIII and XII give the sample size, retention time, and peak width for each injection.

Sample Calculations

This section contains examples of the procedures and calculations used in obtaining the results of this investigation from the data.

Cross-Sectional Areas of the Columns. The cross-sectional areas of the two columns were calculated so that carrier gas flow rates and sample sizes could be scaled-up for the preparative-scale column. Scale-up was based on equal loading per unit of cross-sectional area. For the analytical column, the outside diameter was 0.125 inches and the wall thickness was 0.032 inches. The inside diameter of the analytical column (D_{ia}) was, therefore:
TABLE VI

**Operating Parameters for Tests on Analytical Unit**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Temperature</td>
<td>302 °F</td>
</tr>
<tr>
<td>Room Temperature</td>
<td>84 °F</td>
</tr>
<tr>
<td>Flow Rate Temperature</td>
<td>84 °F</td>
</tr>
<tr>
<td>Inlet Pressure</td>
<td>40.4 psia</td>
</tr>
<tr>
<td>Outlet Pressure</td>
<td>14.5 psia</td>
</tr>
<tr>
<td>Variac Setting</td>
<td>78 %</td>
</tr>
<tr>
<td>Cell Current</td>
<td>20 ma</td>
</tr>
<tr>
<td>Chromatograph Sensitivity</td>
<td>15 %</td>
</tr>
<tr>
<td>Recorder Span</td>
<td>+ 40 to + 42 mv</td>
</tr>
<tr>
<td>Chart Speed</td>
<td>0.2 in./min</td>
</tr>
</tbody>
</table>
TABLE VII

Rise Time Data for Tests on Analytical Unit

Bubble Flowmeter Volume = 400 milliliters

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Start Time</th>
<th>Stop Time</th>
<th>Rise Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:00</td>
<td>33:17</td>
<td>33:17</td>
</tr>
<tr>
<td>2</td>
<td>0:34</td>
<td>33:57</td>
<td>33:23</td>
</tr>
<tr>
<td>3</td>
<td>0:45</td>
<td>34:05</td>
<td>33:20</td>
</tr>
<tr>
<td>4</td>
<td>1:49</td>
<td>35:10</td>
<td>33:21</td>
</tr>
<tr>
<td>5</td>
<td>2:31</td>
<td>35:51</td>
<td>33:20</td>
</tr>
</tbody>
</table>
### TABLE VIII

**Data From Chromatographic Tests on Analytical Unit**

<table>
<thead>
<tr>
<th>Injection Number</th>
<th>Sample Size, µl</th>
<th>Retention Time, inches</th>
<th>Peak Width, inches</th>
</tr>
</thead>
<tbody>
<tr>
<td>A7-1</td>
<td>1.0</td>
<td>2.30</td>
<td>1.90</td>
</tr>
<tr>
<td>A7-2</td>
<td>1.0</td>
<td>2.63</td>
<td>1.97</td>
</tr>
<tr>
<td>A7-3</td>
<td>0.90</td>
<td>2.57</td>
<td>2.17</td>
</tr>
<tr>
<td>A7-4</td>
<td>0.80</td>
<td>2.60</td>
<td>1.83</td>
</tr>
<tr>
<td>A7-5</td>
<td>0.80</td>
<td>2.47</td>
<td>1.55</td>
</tr>
<tr>
<td>A7-6</td>
<td>0.35</td>
<td>2.18</td>
<td>1.55</td>
</tr>
<tr>
<td>A7-7</td>
<td>0.35</td>
<td>2.13</td>
<td>1.48</td>
</tr>
<tr>
<td>A7-8</td>
<td>0.12</td>
<td>2.13</td>
<td>1.10</td>
</tr>
<tr>
<td>A7-9</td>
<td>0.12</td>
<td>2.08</td>
<td>1.10</td>
</tr>
<tr>
<td>A7-10</td>
<td>0.58</td>
<td>2.00</td>
<td>1.61</td>
</tr>
<tr>
<td>A7-11</td>
<td>0.58</td>
<td>2.00</td>
<td>1.50</td>
</tr>
<tr>
<td>A7-12</td>
<td>0.58</td>
<td>1.97</td>
<td>1.57</td>
</tr>
<tr>
<td>A7-13</td>
<td>0.58</td>
<td>1.98</td>
<td>1.50</td>
</tr>
<tr>
<td>A7-14</td>
<td>0.58</td>
<td>2.00</td>
<td>1.57</td>
</tr>
<tr>
<td>A7-15</td>
<td>0.58</td>
<td>2.03</td>
<td>1.55</td>
</tr>
<tr>
<td>A7-16</td>
<td>0.58</td>
<td>2.03</td>
<td>1.61</td>
</tr>
<tr>
<td>A7-17</td>
<td>0.58</td>
<td>2.00</td>
<td>1.58</td>
</tr>
<tr>
<td>A7-18</td>
<td>0.58</td>
<td>2.00</td>
<td>1.60</td>
</tr>
<tr>
<td>A7-19</td>
<td>0.58</td>
<td>2.00</td>
<td>1.60</td>
</tr>
</tbody>
</table>
### TABLE IX

**Operating Parameters for Tests on Preparative-Scale Unit**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temperature:</td>
<td>88°F</td>
</tr>
<tr>
<td>Flow Rate Temperatures:</td>
<td>88°F</td>
</tr>
<tr>
<td>(for both flowmeters)</td>
<td></td>
</tr>
<tr>
<td>Inlet Pressure:</td>
<td>39.7 psia</td>
</tr>
<tr>
<td>Outlet Pressure:</td>
<td>13.8 psia</td>
</tr>
<tr>
<td>Variac Settings (as per cent of line voltage)</td>
<td></td>
</tr>
<tr>
<td>Feed Preheater Line:</td>
<td>120</td>
</tr>
<tr>
<td>Sample Vaporizer:</td>
<td>115</td>
</tr>
<tr>
<td>Top of Column:</td>
<td>115</td>
</tr>
<tr>
<td>Second from Top of Column:</td>
<td>120</td>
</tr>
<tr>
<td>Third from Top of Column:</td>
<td>125</td>
</tr>
<tr>
<td>Bottom of Column:</td>
<td>125</td>
</tr>
<tr>
<td>Product Line:</td>
<td>120</td>
</tr>
<tr>
<td>Thermal Conductivity Cell Bath:</td>
<td>88</td>
</tr>
<tr>
<td>Recorder Span:</td>
<td>+40 to +42 mv</td>
</tr>
<tr>
<td>Cell Current:</td>
<td>20 ma</td>
</tr>
<tr>
<td>Cell Sensitivity:</td>
<td>15%</td>
</tr>
<tr>
<td>Chart Speed:</td>
<td>0.2 in./min</td>
</tr>
<tr>
<td>Temperature Readings (in degrees Fahrenheit)</td>
<td></td>
</tr>
<tr>
<td>Feed Line Thermometer:</td>
<td>306</td>
</tr>
<tr>
<td>Product Line Thermometer:</td>
<td>307</td>
</tr>
<tr>
<td>Cell Bath Thermometer:</td>
<td>305</td>
</tr>
<tr>
<td>Top Thermocouple:</td>
<td>303</td>
</tr>
<tr>
<td>Inside Middle Thermocouple:</td>
<td>302</td>
</tr>
<tr>
<td>Outside Middle Thermocouple:</td>
<td>302.5</td>
</tr>
<tr>
<td>Bottom Thermocouple:</td>
<td>301</td>
</tr>
</tbody>
</table>
TABLE X

Rise Time Data for Large Bubble Flowmeter

for Tests on Preparative-Scale Unit

Bubble Flowmeter Volume = 1.0 liter

Timer was reset to zero for each test.

<table>
<thead>
<tr>
<th>Test</th>
<th>Rise Time</th>
<th>Test</th>
<th>Rise Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sec</td>
<td></td>
<td>sec</td>
</tr>
<tr>
<td>1</td>
<td>5.6</td>
<td>7</td>
<td>5.8</td>
</tr>
<tr>
<td>2</td>
<td>5.8</td>
<td>8</td>
<td>6.0</td>
</tr>
<tr>
<td>3</td>
<td>5.8</td>
<td>9</td>
<td>5.8</td>
</tr>
<tr>
<td>4</td>
<td>6.0</td>
<td>10</td>
<td>6.0</td>
</tr>
<tr>
<td>5</td>
<td>5.8</td>
<td>11</td>
<td>5.8</td>
</tr>
<tr>
<td>6</td>
<td>6.0</td>
<td>12</td>
<td>5.9</td>
</tr>
</tbody>
</table>
TABLE XI

Rise Time Data for Small Bubble Flowmeter

for Tests on Preparative-Scale Unit

Bubble Flowmeter Volume = 400 milliliters

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Start Time</th>
<th>Stop Time</th>
<th>Rise Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min, sec</td>
<td>min, sec</td>
<td>min, sec</td>
</tr>
<tr>
<td>1</td>
<td>0:00</td>
<td>7:01</td>
<td>7:01</td>
</tr>
<tr>
<td>2</td>
<td>0:30</td>
<td>7:30</td>
<td>7:00</td>
</tr>
<tr>
<td>3</td>
<td>0:47</td>
<td>7:47</td>
<td>7:00</td>
</tr>
<tr>
<td>4</td>
<td>3:55</td>
<td>10:55</td>
<td>7:00</td>
</tr>
<tr>
<td>Injection Number</td>
<td>Sample Size, ml</td>
<td>Retention Time, inches</td>
<td>Peak Width, inches</td>
</tr>
<tr>
<td>------------------</td>
<td>----------------</td>
<td>------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Pl-1</td>
<td>0.5</td>
<td>0.93</td>
<td>1.04</td>
</tr>
<tr>
<td>Pl-2</td>
<td>0.5</td>
<td>0.81</td>
<td>1.07</td>
</tr>
<tr>
<td>Pl-3</td>
<td>0.5</td>
<td>0.97</td>
<td>1.06</td>
</tr>
<tr>
<td>Pl-4</td>
<td>0.5</td>
<td>0.93</td>
<td>1.08</td>
</tr>
<tr>
<td>Pl-5</td>
<td>0.5</td>
<td>0.97</td>
<td>1.12</td>
</tr>
<tr>
<td>Pl-6</td>
<td>0.5</td>
<td>0.92</td>
<td>1.05</td>
</tr>
<tr>
<td>Pl-7</td>
<td>0.5</td>
<td>0.82</td>
<td>1.06</td>
</tr>
<tr>
<td>Pl-8</td>
<td>0.5</td>
<td>0.88</td>
<td>0.96</td>
</tr>
<tr>
<td>Pl-9</td>
<td>0.5</td>
<td>0.88</td>
<td>1.02</td>
</tr>
<tr>
<td>Pl-10</td>
<td>0.5</td>
<td>0.89</td>
<td>0.92</td>
</tr>
<tr>
<td>Pl-11</td>
<td>0.3</td>
<td>0.73</td>
<td>1.08</td>
</tr>
<tr>
<td>Pl-12</td>
<td>0.3</td>
<td>0.73</td>
<td>1.07</td>
</tr>
<tr>
<td>Pl-13</td>
<td>0.1</td>
<td>0.78</td>
<td>0.93</td>
</tr>
<tr>
<td>Pl-14</td>
<td>0.1</td>
<td>0.75</td>
<td>0.90</td>
</tr>
<tr>
<td>Pl-15</td>
<td>0.7</td>
<td>0.82</td>
<td>0.80</td>
</tr>
<tr>
<td>Pl-16</td>
<td>0.7</td>
<td>0.77</td>
<td>0.76</td>
</tr>
<tr>
<td>Pl-17</td>
<td>0.9</td>
<td>0.96</td>
<td>1.12</td>
</tr>
<tr>
<td>Pl-18</td>
<td>0.3</td>
<td>0.75</td>
<td>1.05</td>
</tr>
<tr>
<td>Pl-19</td>
<td>0.1</td>
<td>0.71</td>
<td>0.85</td>
</tr>
<tr>
<td>Pl-20</td>
<td>0.7</td>
<td>0.82</td>
<td>0.81</td>
</tr>
</tbody>
</table>
Figure 6. Chromatogram of Injection A7-14 Using a Sample Size of 0.58 Microliters on the Analytical Unit
Figure 7. Chromatogram of Injection Pl-4 Using a Sample Size of 0.5 Milliliters on the Preparative-Scale Unit
The cross-sectional area of the analytical column \((A_a)\) is:
\[
A_a = \frac{\pi}{4} \, D_{ia}^2 \tag{22}
\]
\[
A_a = \frac{\pi}{4} \, (0.061)^2
\]
\[
A_a = 2.92 \times 10^{-3} \text{ in.}^2
\]

The outside diameter of the center section of the preparative-scale column \((D_{op})\) was 1.050 inches. The inside diameter of the outer section \((D_{ip})\) was 2.075 inches. The cross-sectional area of the preparative-scale column \((A_p)\) was:
\[
A_p = \frac{\pi}{4} \, (D_{ip}^2 - D_{op}^2) \tag{23}
\]
\[
A_p = \frac{\pi}{4} \, (2.075^2 - 1.050^2)
\]
\[
A_p = 2.52 \text{ in.}^2
\]

**Scale-Up Factor.** The carrier gas flow rate and sample size for the preparative-scale column were obtained by multiplying the analytical value by the ratio of the cross-sectional areas of the two columns. The scale-up factor \((SUF)\) was therefore:
\[
SUF = \frac{A_p}{A_a} \tag{24}
\]
\[
SUF = \frac{2.52}{2.92 \times 10^{-3}}
\]
\[
SUF = 861
\]
Analytical Flow Rate. The carrier gas flow rate was determined from the bubble flowmeter rise time data given in Table VII. The rise times were determined by subtracting the start times from the stop times. The average rise time was determined by adding the rise times and dividing by five, the number of tests. The average rise time \( t_{ra} \) was 33.33 minutes. The flow rate of carrier gas in the analytical column \( q_a \) is given by:

\[
q_a = \frac{V_a}{t_{ra}}
\]

where \( V_a \) is the volume of the bubble flowmeter used with the analytical column. \( V_a \) was 0.4 liters. Therefore, the carrier gas flow rate in the analytical column was:

\[
q_a = \frac{0.4}{33.33}
\]

\[
q_a = 0.012 \text{ liters/min}
\]

Preparative-Scale Flow Rate. The design flow rate through the preparative-scale column \( q_p \) was calculated from the following relationship:

\[
q_p = \text{SUF} \; q_a
\]

\[
q_p = (861) \; (0.012)
\]

\[
q_p = 10.33 \text{ liters/min}
\]

The actual flow rate was calculated by adding the flow rate through the thermal conductivity cell and the flow rate through the main exit line. Rise time data for the main exit line are given in Table X.
The timer was reset to zero for each test; consequently, the readings are the rise times. The average rise time \( t_{r1} \) was calculated as above to be 5.86 seconds. The volume of the flowmeter \( V_p \) was 1.0 liter. The flow rate through the large flowmeter was, therefore:

\[
q_1 = \frac{V_p}{t_{r1}} \tag{27}
\]

\[
q_1 = \frac{1.0}{5.86} \tag{60}
\]

where 60 is the conversion factor from seconds to minutes.

\[
q_1 = 10.24 \text{ liters/min}
\]

Rise time data for flow through the thermal conductivity cell are given in Table XI. The average rise time \( t_{r2} \) was calculated to be 7.00 minutes. The flow rate through the cell \( q_2 \) was, therefore, given by:

\[
q_2 = \frac{V_a}{t_{r2}} \tag{28}
\]

where \( V_a \) was 0.4 liters, as above. Therefore, we have:

\[
q_2 = \frac{0.4}{7.00}
\]

\[
q_2 = 0.06 \text{ liters/min}
\]

The total flow rate through the preparative-scale column \( q_p \) was:

\[
q_p = q_1 + q_2 \tag{29}
\]
\[ q_p = 10.24 + 0.06 \]
\[ q_p = 10.30 \text{ liters/min} \]

The difference between the design flow rate and the actual flow rate is:

\[
\% \text{ Difference} = \left( \frac{(q_p) \text{ desired} - (q_p) \text{ actual}}{(q_p) \text{ desired}} \right) \times 100\% \quad (30)
\]

\[
\% \text{ Difference} = \left( \frac{10.33 - 10.30}{10.33} \right) \times 100\% 
\]

\% \text{ Difference} = 0.29%

**Sample Size.** Because of the calibration on the syringe used for the preparative-scale injections, the sample sizes for the preparative-scale unit were selected for accuracy in injection. They were then scaled down to obtain the analytical injection sizes. For example, in Table XII, Injections P1-1 through P1-10 were made with a sample size of 0.5 milliliters. The corresponding analytical sample size was obtained from:

\[
SS_a = \frac{SS_p}{SU} \times 10^3 \quad (31)
\]

Where:

- \( SS_a \) = analytical sample size, \( \mu L \)
- \( SS_p \) = preparative-scale sample size, ml
- \( SUF \) = scale-up factor = 861, dimensionless
- \( 10^3 \) = conversion factor from microliters to milliliters
Therefore, we have:

\[ S_{S_a} = \frac{0.5}{861} (10^3) \]

\[ S_{S_a} = 0.58 \mu l \]

This is the value given in Table VIII for Injections A7-10 through A7-19.

**Calculation of NTP and HETP.** The same procedure for calculating NTP and HETP was used for both the analytical and preparative-scale data. In Table XII, Injection Pl-4, the retention time and peak width (measured from the chromatogram) are 0.93 and 1.08 inches, respectively. NTP is calculated from this data by Equation (19):

\[ \text{NTP} = (\frac{4d}{w})^2 \]  

(19)

Where:

- **NTP** = number of theoretical plates, dimensionless
- **d** = retention time, inches
- **w** = peak width at base, inches

For Injection Pl-4, we have:

\[ \text{NTP} = (4 \times 0.93/1.08)^2 \]

\[ \text{NTP} = 11.87 \]

HETP is then calculated from Equation (20):

\[ \text{HETP} = \frac{L}{\text{NTP}} \]  

(20)

Where:

- **HETP** = height equivalent to a theoretical plate, inches
- **L** = length of column, inches
NTP is as defined above. For Injection Pl-4, we have:

\[ \text{HETP} = \frac{72}{11.87} = 6.07 \text{ inches} \]

The NTP and HETP values for Injection Pl-4 are given in Table III. A similar calculation was carried out for each injection on both columns.

**Preparative-Scale Column Efficiency.** The efficiency of the preparative-scale column relative to the analytical column is calculated from Equation (21):

\[ \% \text{Eff} = \left( \frac{\text{HETP}_a}{\text{HETP}_p} \right) (100\%) \]

Where:
- \( \% \text{Eff} \) = per cent efficiency of the preparative-scale column relative to the analytical column
- \( \text{HETP}_a \) = average HETP of analytical column, inches
- \( \text{HETP}_p \) = average HETP of preparative-scale column, inches

\( \text{HETP}_a \) and \( \text{HETP}_p \) are the values calculated from corresponding sample sizes. For example, one efficiency was calculated using the average HETP's for an analytical sample size of 0.58 microliters and for a preparative-scale sample size of 0.5 milliliters. \( \text{HETP}_a \) was obtained by averaging the HETP's in Table I for Injections A7-10 through A7-19. \( \text{HETP}_p \) was obtained by averaging the HETP's in Table III for Injections Pl-1 through Pl-10. Therefore, we have:

\[ \% \text{Eff} = \frac{3.53}{6.06} (100\%) \]

\[ \% \text{Eff} = 58.2 \% \]

The efficiencies calculated for each pair of sample sizes are listed in Table V.
Materials

This section describes the materials used in this investigation.

**Helium.** Commercial Grade, 99.7 per cent minimum. Manufactured by Air Reduction Co., Roanoke, Virginia. Used as carrier gas in both units.

**1-Methylnaphthalene.** 99.3 per cent purity. 0.7 per cent 2-methylnaphthalene (impurity). Manufactured by and purchased from Chemical Samples Co., Columbus, Ohio. Used as sample material in analytical unit when locating the minimum operating temperature and optimum carrier gas flow rate.


**Packing.** Solid phase: 30/60 mesh Chromosorb W. Liquid phase: 20 weight per cent Craig polyester succinate. Manufactured by and purchased from Lawshe Instrument Co., Bethesda, Maryland. Used as packing material in the preparative-scale column.

Apparatus

This section describes the apparatus used in this investigation.

**Analytical Gas-Liquid Chromatograph.** Model 160, serial no. A22. Regulated temperature range: 95°F to 250°F, 115 v., ac, 350 watts, 60 cycles, single phase. Modified by addition of two 500-watt strip
heaters so that the regulated temperature was 95° to 450°F.

Detector: thermal conductivity cell containing two Fenwal Type G-112 thermistors rated at 6800 ohms at 25°C. Manufactured by Fisher Scientific Co., Chicago, Ill. Used to establish NTP and HETP for analytical column, and as primary measuring device for preparative-scale experiments.


Bubble Flowmeter. (2) See Figure 8. Both flowmeters were made from a piece of glass tubing with two-hole stoppers inserted into each end. At the bottom, one piece of glass tubing placed through the stopper carried the flow into the flowmeter. The other piece of glass tubing connected to a rubber squeeze bulb which was filled with a soap solution. When the bulb was squeezed, a bubble was introduced into the flowmeter. The gas flow carried the bubble up the column. One of the holes in the stopper at the top of the flowmeter contained a thermometer for measuring the temperature of the gas. The other hole contained a piece of glass tubing which allowed the gas to exit from the flowmeter. The glass tubing was connected to plastic tubing leading to an exhaust fan. The volumetric flow rate was determined by timing a bubble's rise through a known volume. The measured volume for the bubble flowmeter used with the analytical unit was 400 milliliters. The volume of the bubble flowmeter used with the preparative-scale column was 1,000
Figure 8. Schematic Diagram of Bubble Flowmeter
milliliters. All the glass tubing used in the flowmeters was Pyrex. The tubing was 1/8-inch outside diameter and the columns had ½ and one-inch inside diameters.

**Column, Analytical.** 1/8-inch outside diameter, 6 feet packed section, fitted with 1/8-inch Swagelok fittings. Made from stainless steel. Packed with 30/60 mesh size Chromosorb W. Liquid phase: 20 weight % Craig polyester succinate. Purchased prepacked from Lawshe Instrument Co., Bethesda, Maryland. Used with analytical chromatograph to obtain NTP and HETP values for comparision with preparative-scale column values.

**Column, Preparative.** Fabricated in the Chemical Engineering Shop, Virginia Polytechnic Institute. Refer to Figure 9. The column itself was made of black iron pipe 76 inches in length. The inside diameter 2.075 inches. A center tube (1.050 inches outside diameter) was placed in the column by welding three rectangular pieces of metal to each end of the outer pipe and the center tube. These braces were spaced 120 degrees apart. Thermocouple wells were installed in the column at the positions indicated in Figure 9. These wells were constructed of ½-inch outside diameter copper tubing, five inches in length. An iron-constantan thermocouple, made with 30-gauge wire, was placed in each well. The thermocouples were sealed into the wells with an Epoxy resin.

Reducers were used at both ends of the column. The inside diameter of the large end of these reducers was 2.275 inches and the small end was fitted with ½-inch pipe threads. A 90 degree elbow was connected
Figure 9. Preparative-Scale Column
to the bottom reducer. This was done to further constrict the diameter of the flow channel to fit \( \frac{1}{2} \)-inch outside diameter copper tubing.

A sintered metal plate was fitted into each of the two reducers using the following method: A section of threads was cut from another piece of two-inch pipe and threaded into the reducer. The sintered metal plate was then placed on the ledge formed by these threads. A Teflon gasket was placed on the plate. This entire assembly was then threaded onto the end of the column. The details of one of these assemblies are shown in Figure 10. The sintered metal plate at the column bottom supported the chromatographic packing. The plate in the top reducer supported a number of steel balls which acted as a heat reservoir to help vaporize the samples.

The column was packed by slowly pouring packing material into the top of the column while the column was vibrated by tapping with a rubber hammer. The packing density for the preparative-scale column was 16.96 pounds per cubic foot, or 0.272 grams per cubic centimeter.

The injection port was located directly above the entrance to the reducer at the top of the column. The injection port is illustrated in Figure 11. A short piece of \( \frac{1}{2} \)-inch pipe was used to connect the tee fitting to the reducer at the top of the column. The side leg of the tee was capped with a rubber septum and brass nut. The top leg of the tee was connected to the \( \frac{1}{2} \)-inch copper tubing by an elbow fitting. By using another tee fitting and a rubber seal, a thermometer was placed in the feed line immediately before the injection port. Another thermometer was placed in the exit line immediately preceding the
Figure 10. Reducer and Sintered Metal Plate Assembly
Figure 11. Injection Port
entrance to the constant temperature bath for the thermal conductivity cell. A ball-type check valve was also placed in the line preceding the column. This was to prevent back flow when the sample was vaporized.

After passing through the column the flow was split. Most of the flow went to the large bubble flowmeter. The remainder of the flow passed through one side of the thermal conductivity cell. Pure helium was passed through the other side of the cell. A flow diagram of the system is presented in Figure 12.

All of the parts used in the construction of the preparative-scale unit were supplied from stock in the Chemical Engineering Shop, Virginia Polytechnic Institute.


**Heating Tapes.** (2) Model 400, catalog no. 11-463-22. One tape was 3 feet in length with a power output of 120 watts at 115 volts. The other tape was 6 feet in length with a power output of 240 watts at 115 volts. Manufacturer unknown. Obtained from Fisher Scientific Co., Chicago, Ill. The 3 foot tape was used to heat the vaporizer section of the preparative-scale column. The 6 foot tape was used to heat the carrier gas feed line.
Figure 12. Flow Diagram for Preparative-Scale Unit
Recorder. Speedomax H Continuously Adjustable Zero. Catalog no. 3-961-000-186-6-360-0. Serial no. 62-54966-1-2. 120 volts, ac, 60 cycles. Chart speed: 0.2 inches/minute. Manufactured by Leeds and Northrup Co., Philadelphia, Penn. Obtained from Chemical Engineering Instrumentation Laboratory, Virginia Polytechnic Institute. Used to record chromatograms for both the analytical and preparative-scale units.

Strip Heaters. (2) resistance type HKL, serial nos. Z 69 and Z 70. 120 v., ac, 60 cycles, 500 watts. Manufactured by E.L. Winegand Co., Pittsburgh, Pa. Obtained from Chemical Engineering Shop, Virginia Polytechnic Institute. Used to augment heaters in analytical chromatograph for temperatures up to 450°F.


temperature at various points inside preparative-scale column, as indicated by iron-constantan thermocouples.

**Thermometers.** (3) Catalog no. 14-990D. Incremented in two degree graduations from +20 to +400 degrees Fahrenheit. Manufactured by Fisher Scientific Co., Chicago, Ill. Obtained from Chemical Engineering Stockroom, Virginia Polytechnic Institute. Used to measure temperature (1) in feed line just before injection port, (2) in product line just before entering temperature bath for thermal conductivity cell, and (3) in cell temperature bath.


**Tubing (Copper).** ¼-inch outside diameter. Manufacturer unknown. Obtained from Chemical Engineering Shop, Virginia Polytechnic Institute. Used for flow lines in preparative-scale unit.

**Tubing (Plastic).** ¼-inch outside diameter, type 44P. Manufactured by Imperial Supply Co., Inc., New York, New York. Obtained from Chemical Engineering Stockroom, Virginia Polytechnic Institute. Used to connect helium tanks to analytical chromatograph and preparative-scale unit.

**Valves.** (3) Metering type. Model B-2M. 1/8-inch Swagelok fittings, 3 degree pitch on needle, 100 psi (max.), 0.055-inch diameter orifice. Manufactured by Nuclear Products Company, Cleveland, Ohio. Purchased from Dibert Valve and Fitting Co., Richmond, Virginia. Used to control flow rate of carrier gas in the analytical unit and in the thermal conductivity cell of the preparative-scale unit.

Variacs. (8) Rheostat type 116, serial nos. 66324, 66325, 66378, 66379, 66380, 66411, 66442, and 66445. 120 v., ac, 50/60 cycles, 7.5 amps (max.). Manufactured by Superior Electric Co., Bristol, Conn., 1 kva (max.). Obtained from Chemical Engineering Stockroom, Virginia Polytechnic Institute. One was used to control the two 500 watt strip heaters which were installed in the analytical chromatograph for runs on the analytical and preparative-scale columns. The remaining seven variacs were used to control: (1) the four heating tapes on the preparative-scale column, (2) the heating tape which heated the vapor-ization chamber, (3) the heating tape which heated the feed line to the preparative-scale column, and (4) the heating tape which heated the product line.

**Determination of Minimum Operating Temperature and Carrier Gas Flow Rate for the Analytical Unit**

The method used for determining the minimum temperature and flow rate is discussed on page 34 in the method of procedure. The purpose of this section is to explain the results of the preliminary tests in greater depth.
Table XIII gives the quantitative results of the preliminary tests. During the period of testing on the analytical unit, it was found that both temperature and carrier gas flow rate affected HETP. This is reflected in the results in Table XIII and in Figures 13 and 14. From the two figures, it can be seen that both retention time and peak width are increased greatly as temperature and flow rate are decreased. It is clear that the peak in Figure 14 is unacceptable for use in the investigation because of its irregularities. The tangents are very inaccurate which are drawn on this chromatogram.

Carrier gas flow rate affected HETP more than temperature. This is illustrated by the first two values in Table XIII. An HETP of 0.758 inches was obtained with a temperature of 326 degrees Fahrenheit and a flow rate of 15.9 milliliters per minute. With the temperature decreased to 302 degrees Fahrenheit and the flow rate increased to 19.2 milliliters per minute, an HETP of 0.507 inches resulted. Even though the temperature was decreased 24 degrees, HETP decreased 33 per cent when the flow rate was increased by 3.3 milliliters per minute.

There are three facts which prevent comparison of these results with those of Table II on page 40. (1) The sample size in all the preliminary tests was three microliters. (2) These tests were made with 99.3 per cent 1-methylnaphthalene, while the tests in Table II were made with practical grade material. (3) None of the tests were made at both the same temperature and flow rate of the tests in Table II (302 degrees Fahrenheit and 12.0 milliliters per minute).
TABLE XIII

Average HETP Data for Preliminary Tests on Analytical Unit for Locating Minimum Operating Temperature and Carrier Gas Flow Rate

All injections were made with 99.3% 1-methylnaphthalene. Sample Size = 3.0 microliters Bubble Flowmeter Volume = 400 milliliters

<table>
<thead>
<tr>
<th>Injection Numbers*</th>
<th>Operating Temperature °F</th>
<th>Carrier Gas Flow Rate** ml / min</th>
<th>Average HETP inches</th>
<th>Average NTP dimensionless</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 (2)</td>
<td>326</td>
<td>15.9</td>
<td>0.758</td>
<td>95.0</td>
</tr>
<tr>
<td>A2 (2)</td>
<td>302</td>
<td>19.2</td>
<td>0.507</td>
<td>142.0</td>
</tr>
<tr>
<td>A3 (2)</td>
<td>280</td>
<td>14.5</td>
<td>1.420</td>
<td>50.7</td>
</tr>
<tr>
<td>A4 (2)</td>
<td>291</td>
<td>13.3</td>
<td>0.795</td>
<td>90.6</td>
</tr>
<tr>
<td>A5 (3)</td>
<td>302</td>
<td>8.4</td>
<td>1.045</td>
<td>68.9</td>
</tr>
</tbody>
</table>

* A 3, for example, indicates the day's tests on the analytical column. The number in parenthesis is the number of injections made that day with 1-methylnaphthalene.

** Flow rates were obtained as described in sample calculations by averaging several rise times and dividing the result into 400 milliliters.
Figure 13. Chromatogram of Injection A2-1 at a Temperature of 302 Degrees Fahrenheit and a Carrier Gas Flow Rate of 19.2 Milliliters per Minute
Figure 14. Chromatogram of Injection A3-2 at a Temperature of 280 Degrees Fahrenheit and a Carrier Gas Flow Rate of 14.5 Milliliters per Minute.
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ABSTRACT

The purpose of this investigation was to design, build, and test a preparative-scale column which contained a blocked-off center tube, thus forming an annular space for the packing.

The chromatographic system for this study consisted of 1-methyl-naphthalene injections with helium carrier gas and a liquid phase of Craig polyester succinate on crushed firebrick. The analytical column had an inside diameter of 0.061 inches. For the preparative-scale column, the outer diameter was 2.075 inches and the inside diameter was 1.050 inches. The operating temperature for both columns was 300 degrees Fahrenheit. The flow rates were 0.012 and 10.30 liters per minute for the analytical and preparative-scale columns, respectively.

Several sample sizes were injected on both columns. Variation of HETP with sample size was determined. Preparative-scale column efficiencies were calculated from average HETP's at all sample sizes tested.

Efficiencies of 36.5, 33.4, 58.2, 69.3, and 52.7 per cent relative to the analytical column were calculated for preparative-scale injections of 0.1, 0.3, 0.5, 0.7, and 0.9 milliliters, respectively. HETP for the preparative-scale column was very sensitive to variation in sample size in the range from 0.1 to 0.9 milliliters. HETP for the analytical column was not sensitive to variation in sample size in the range from 0.12 to 1.00 microliters, as was expected from literature data.