AN ABSTRACT OF THE THESIS OF

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Title: FAST GAS CHROMATOGRAPHY

Abstract approved: Redacted for privacy
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Porous silica microparticles designed for modern liquid chromatography have proven effective in gas chromatography. Columns of 20-60 cms gave plate heights as low as $3.3d_p$, Rs^2/L of 900 m^{-1}, $Rs/t^{1/3}$ of 8.7 $sec^{-1/3}$, for successive hydrocarbons, and performance speeds of 500 N_{eff}/sec or 2400 N/sec. Inlet pressures up to 70 atms were needed using hydrogen as a carrier gas. Other than a specially designed injector and a high speed recorder, nothing out of the ordinary was used to handle these pressures and speeds.

The particles as received were too retentive for fast chromatography and gave asymmetric peaks. A coating of fluorosilicone oil overcame both problems but other coatings were less effective. Bonded phases proved less satisfactory on both counts and also gave substantially less efficient columns and greater flow resistance. Selectivity of the silica was found to vary between manufacturers and between different batches of silica from the same

manufacturer. Column efficiency and flow resistance were sharply dependent on physical properties of the particles. The most efficient packing was clearly spherical particles of 5-10 micron diameter with narrow size distribution, pore diameters about 500 Å, BET surface areas of 25-50 m^2/g with surfaces modified with trifluoropropyl silicone.

A six component hydrocarbon sample was separated in 33 seconds with a resolution of four for the most difficult pair. A similar mixture was separated in 2.6 seconds with minimal resolution. Performance was limited by end effects and by available pressure so that much better performance can be expected from longer columns and higher pressures.

The theory of small particle packed columns was refined to include the pressure dependence of the mobile phase diffusion coefficient. Analysis time and resolution were found to increase in proportion to $d_p^{-1/2}$ for decreasing d_p with column length held constant. However, when resolution is held constant and the column length decreased in proportion to d_p a concomitant decrease in analysis time was found. These proportionalities are totally different for HPLC due to the incompressibility of the carrier.

A literature study of different types of columns and methods used to make comparisons between them was undertaken. Experimental data on over 50 columns were compiled and added to a previously published review of over 40 columns. Columns were compared using the functions $Rs/t^{1/3}$,

N_{eff}/t, Rs^2/L, PI and the PP as indicators of column performance. The functions $Rs/t^{1/3}$ and N_{eff}/t seemed to be the most useful criteria for comparing column performance. The data clearly shows that packed columns constructed for the thesis out-performed all other packed columns previously made. Open tube columns were faster than packed columns when tube radius was considered equivalent to d_p. However the packed column may be preferred to the open tube column at very small tube radii (equivalent to small d_p) since they are easier to make and operate. Greater performances are indicated when small particle silica is used for liquid solid chromatography than for bonded phase chromatography and gell permeation chromatography. Porous layer bead packings when used for gas chromatography can offer 3-4 times the N_{eff}/t than of conventional porous packings.

Fast Gas Chromatography

by

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LIST OF SYMBOLS

Symbol	
B	logitudinal diffusion term in plate height equation
B_1	B measured at one atm. pressure
C	mass transfer term equal to $C_s + C_{m1}$
C_{m1}	resistance to mass transfer in the gas phase, measured at one atm. pressure
CP	conventional packed column
C_s	resistance to mass transfer in the stationary phase
D_{m1}	gas phase diffusion term measured at one atm. pressure
d_p	particle diameter
f	Giddings' compressibility factor, $9(P^4 - 1)(P^2 - 1)/8(P^3 - 1)^2$
FGC	fast gas chromatography
GC	gas chromatography
$\hat{H}$	measured plate height
H_e	contribution to $\hat{H}$ from end effects
HPLC	high performance (or pressure) liquid chromatography
HSGC	high speed gas chromatography
j	James-Martin compressibility factor, $3(P^2 - 1)/2(P^3 - 1)$
k	column capacity ratio
k°	specific permeability constant for column
L	column length
LC	liquid chromatography
N	number of theoretical plates
N_{eff}	number of effective theoretical plates

List of Symbols -- continued

Symbol	
P	ratio of inlet to outlet pressure, P_i/P_o
p	pressure
Δp	pressure drop, $P_i - P_o$
P_i, P_o	inlet and outlet pressure, respectively
PI	performance index
PLB	porous layer bead column
PP	performance parameter
Rs	resolution
r_T	internal radius of open tube column
SCOT	support coated open tube column
SPPC	small particle packed column
T	temperature
t	time
Δt	retention time difference between any two peaks in the chromatogram, usually between adjacent peaks then $t = t_{R2} = t_{R1}$ or $t_{s2} - t_{s1}$
t_m	time spent in the mobile phase
t_R	uncorrected retention time, $t_R = t_s + t_m$
t_s	time spent in the stationary phase
$\bar{u}$	time averaged linear velocity
u_o	velocity at column outlet
w	baseline width of peak, measured at the baseline where the tangents to the peak intersect the baseline
w_{ave}	average w for two adjacent peaks
WCOT	wall coated open tube column

List of Symbols -- continued

Symbol	
α	relative retention time ratio
η	coefficient of viscosity
ϕ	resistivity to flow
ω	coefficient of mobile phase mass transfer term, $C_{ml} = wd_p{}^2/D_{ml}$

Subscripts

(for peak and time identification)

x	pertaining to component x, the first component of a difficult pair
y	pertaining to component y, the second component of a difficult pair
z	pertaining to component z, the last component of a difficult pair
1,2	pertaining to components 1 and 2 the first and second components of a pair, most likely not the difficult pair, used to compile Table 3

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FAST GAS CHROMATOGRAPHY

I. INTRODUCTION

R. P. W. Scott made a statement (95) at the Fifth International Symposium on Gas Chromatography held at Brighton, England in 1964, that for the most part is true today; he said, "... the vast majority of work today is being carried out with packed columns, giving between three and ten thousand theoretical plates and perhaps to a lesser extent with capillary columns giving fifty or sixty thousand plates. Four years ago Purnell and Quinn, Desty _et al._, and Cummings and myself produced gas chromatographic separations in a few seconds. To my knowledge less than a dozen workers are employing equipment operating at these speeds ..." Little has been done to improve the speed of gas chromatographic separations since that statement was made and practically nothing to improve the design of the gas chromatographic packed column. In fact, only recently has the technique taken great strides forward with the commercial manufacture of small bore glass open tube columns (glass capillaries) and the availability of several commercial instruments capable of operating them. Other significant developments in column technology have been made by Halasz and Heine (45, 46) who fabricated several new column types and classified columns into six different groups. Unfortunately their classification scheme, coupled with inadequate parameters to measure overall column performance and unfair column type comparisons has been detrimental to the advancement of packed column technology. This is because their classification scheme based on column performance has not been used for the sake of nomenclature (38) or for the purpose of directing where improvements in column technology could be made but as the final word in arguments as to which column type is better than another. To make matters worse many of the comparisons have been unfair. For example, in Ettre and March's paper (26) an 8 foot long, 80-100 mesh Chromosorb W packed column with 2,100 effective plates ($\hat{H}$ of 7 dp) was compared to a 150 foot, .010 inch open tube column with 48,000 effective plates ($\hat{H}$ of 2.6 r_T). The column capacity ratio of methyl oleate, the test solute, was 58 on the packed column and 5.1 on the open tube column; later we will show that the optimum range for the column capacity ratio is 1-6. From their experimental results concluding statements like the following were made,

> ...In other words, while it takes over 30 minutes to get a base line resolution on the 8-ft-long packed column, the same can be achieved in a few minutes on the open tubular columns...

and

> ...This type of relative evaluation clearly shows that in the same analysis time, the open tubular columns gave a much better resolution than the packed column..."

Statements similar to these founded on equally poor comparisons have been made by others (24, 25, 44-46).

Thus developments have been made in the design of new column types and significant improvements made in the fabrication of open tube columns and instruments but, overall, very little to improve the speed of gas chromatographic separations and almost nothing to improve the conventional packed column -- it is today essentially as it was 25 years ago. With computers and microprocessors becoming more prevalent in laboratories and gas chromatography being applied to a greater number of disciplines for the purpose of analyzing complex samples, many of which have several hundred constituents, both the packed column and the speed of the technique need to be improved.

This thesis reports on the construction and usefulness of a high speed gas chromatograph capable of operating at pressures more than ten times that of commercial gas chromatographs. The instrument was specifically designed to efficiently operate columns packed with particles 10 microns in diameter. By using these columns, plate heights as low as 3 d_p were obtained and performance speeds up to 500 effective plates per second generated, enabling analyses that normally take many minutes to be done in a few seconds. Chromatograms of volatile mixtures completed in a few seconds are really not practical for routine analytical GC, although it may be of use to process control GC, but the real importance of the achievement is that if analogous gains in separation speed are realized for complex mixtures then chromatograms that normally take hours could be done in minutes. Unfortunately since only a gas sampling valve was used, complex samples could not be injected and the supposed gain in speed proven. However, fair and objective comparisons between data obtained on columns fabricated for this research and data obtained on a variety of column types chosen from the chromatographic literature indicates that gains of this magnitude are possible.

The design of the column is important in any chromatograph but here it was crucial and much had to be learned about column design. In this respect the research was highly successful since our objectives of learning how to pack and modify microparticle silica, and to understand the relationships between the physical properties of the silica and its performance were achieved. As this was the real goal of the research and the building of the instrument secondary, it follows that the project as a whole was a success. Furthermore with our point made to the chromatographic community and with the data contained herein adequate to provide direction for future work, the instrument now seems expendable. In fact this author strongly recommends that it be disassembled and future work done with a newly designed instrument.

The accomplishments of one's work are certainly important but also important is an awareness of what has not been accomplished. The title of the thesis, "Fast Gas Chromatography," applies since the major use of microparticle columns would be to increase the speed of the technique, and the main impetus of the work has been in that direction. However, true fast gas chromatography implies minimum time chromatography and to achieve this all the chromatographic variables should have been optimized. Such was not done in this work because of instrumental limitations and an inadequate range of commercially available microparticle packings from which to choose. The difficulties of injecting samples against high carrier gas pressures are well known; the task becomes even more difficult when the sample valve is heated. For this reason all experiments were done at room temperature and variation of one of the most important chromatographic variables had to be foregone. Enough pressure could not be generated to efficiently operate a column packed with 5 micron particles. If such could be done the analysis time could be decreased even further since theory developed in this thesis suggests that if the particle diameter is decreased a concomitant decrease in analysis time should be observed. The decrease may be even greater if chromatographic parameters are optimized that are not optimized here. In short, this work, like most scientific endeavors raised more questions than it answered.

II. THEORY OF FAST GAS CHROMATOGRAPHY

A. Background

High speed high resolution gas chromatography probably dates from the work of Scott (96) in 1958. Long columns of small internal diameter were packed with particles of 75-100 microns and operated under 14 atm. pressure to yield performance speeds of 10 effective plates per second, and a remarkable chromatogram for the time. Shortly thereafter Purnell and Quinn (91) and Kieselbach (56) produced fast chromatograms by carefully optimizing some of the parameters that control resolution and analysis time. Desty in his classic works (19, 20) was the first to demonstrate the great potential of open tube columns in HSGC. He operated his 35 micron bore open tube column at 14 atm. to do difficult analyses in a few seconds with performance speeds of up to 2,000 effective plates per second. Even today his chromatograms stand as the fastest ever produced. Myers and Giddings (87, 88), like Scott (96), worked with long columns (87) and even smaller particle diameters (88) (down to 2μ) which required pressures up to 170 atm. to operate. Although it is evident that they were limited by their packing technique and a crude injection system they produced 63 effective plates per second. More recently, others (11, 15, 50, 53) have used conventional packed small bore columns ("micropacked columns" (11, 15, 53)) to increase analysis speed. Using columns of this nature, Cramers et al., (15) have been able to produce 23 effective plates per second on particles as large as 180-200 microns. Huber, Lauer, and Poppe (50, 72) coupled small bore tubes with small particles to obtain 38 effective plates per second: they also were the first to efficiently operate a column packed with particles smaller than the usual mesh scale in GC, obtaining a plate height of about $3d_p$.

This thesis describes the design and construction of a high speed gas chromatograph capable of successfully operating columns packed with totally porous spherical microparticles of silica and the modification of the particles to make them amenable for high speed gas separations. Such columns have been in operation in high performance liquid chromatography, HPLC, since about 1972 (58, 78) and have resulted in the rapid growth of that technique (79).

B. Fundamental Equations

The following equations are basic to column chromatography and discussions of their usefulness can be found in any of the popular chromatographic textbooks (30, 74, 93).

$$k_x = t_{sx}/t_m \tag{1}$$

$$\alpha_{yx} = t_{sy}/t_{sx} = k_y/k_x \tag{2}$$

$$Rs = \Delta t/W_{ave} \tag{3}$$

$$N_y = 16(t_{Ry}/W_y)^2 \tag{4}$$

$$\hat{H}_y = L/N_y \tag{5}$$

These terms and all other terms in this thesis, are defined in the list of terms section at the beginning of the thesis. The parameters defined by Eq. (1-5) are measured from the chromatogram as demonstrated in Fig. (1). Another very useful expression for resolution follows from Eq. (3, 4)

$$Rs = \left(\frac{N_y}{16}\right)^{\frac{1}{2}} \left(\frac{\alpha-1}{\alpha}\right) \left(\frac{k_y}{1+k_y}\right) \tag{6}$$

obtained by assuming in Eq. (3) that $W_{ave} \simeq W_y$ (i.e. neighboring peaks of equal width and gaussian in shape) and eliminating W_y between Eq. (3, 4) expressing Δt as $t_{sy} - t_{sx}$ and t_{Ry} as $t_m + t_{sy}$ and converting the time expressions to column capacity ratios and relative retention times. Equation (6) states that the resolution of a given solute pair is a function of the column's efficiency N, its selectivity for the pair, and retentivity of the stationary phase for the pair. Other equations necessary for the development of the thesis but requiring a more lengthy discussion are the equations that describe the flow of mobile phase through packed and open tubes, and a general plate height equation.

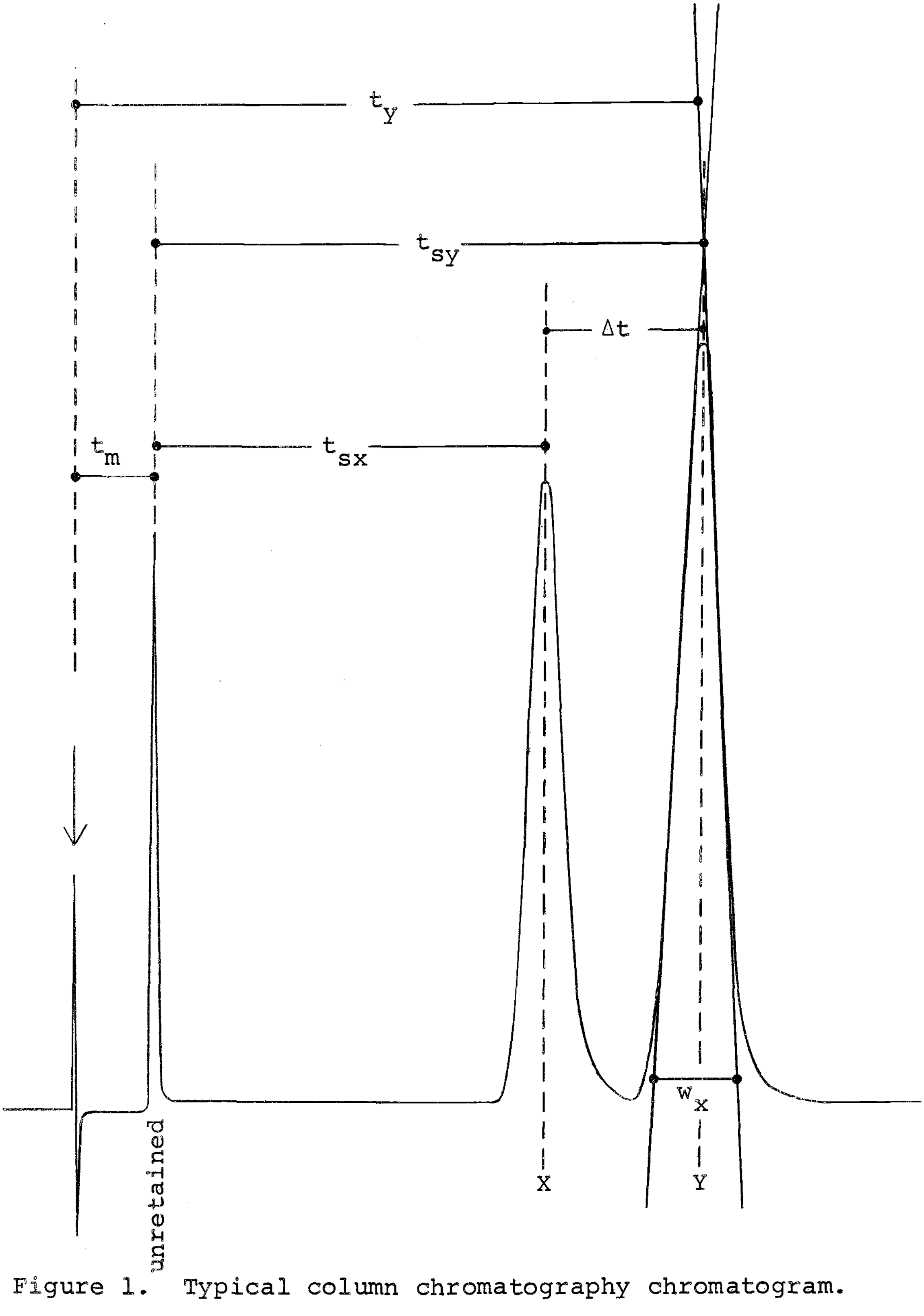


Figure 1. Typical column chromatography chromatogram.

The Flow Equations

The velocity of a fluid at any point, i, in a column is a function of the pressure gradient and inversely proportional to the fluid viscosity, η. This is stated mathematically as Darcy's Law

$$u_i = - \frac{K^\circ}{\eta} \left(\frac{dp}{d_i}\right) \tag{7}$$

For a liquid mobile phase the solution of Eq. (7) is immediate but for a gas there are velocity gradients as well as pressure gradients along the column axis and Boyle's Law must be introduced into Eq. (7) before it can be integrated for the velocity. When this is done Eq. (8) results

$$u_o = \frac{K^\circ}{\eta L} \frac{p_o(P^2-1)}{2} \tag{8}$$

assuming laminar flow and an ideal gas. The outlet velocity is of little importance in gas chromatography while the time average linear velocity is of paramount importance. The two are interrelated through the James-Martin compressibility factor j.

$$\bar{u} = u_o j \tag{9}$$

Entering the correct expressions for u_o and j in Eq. (9) and substituting d_p^2/ϕ for K° gives a more usable equation for the velocity in terms of the column parameters

$$\bar{u} = \frac{3d_p^2}{4\eta L\phi} \frac{p_o(P^2-1)^2}{(P^3-1)} \tag{10}$$

when P is greater than 6, Eq. (10) can be written much more simply as

$$\bar{u} = \frac{3\ d_p^2\ P_i}{4\eta L\phi} \tag{11}$$

without committing an error greater than 5% or without violating the ideal gas law assumption. In fact, for the usual conditions of gas chromatography and even for pressures much higher than were attained in this thesis the ideal gas law is valid (82).

The following flow equation for open tubes was developed in a manner similar to that which led to Eq. (10)

$$\bar{u} = \frac{3\ r_T^2}{32\eta L} \frac{p_o(P^2-1)^2}{(P^3-1)} \tag{12}$$

Equation (12) is known as Poiseulle's Equation and is accurate to only 10-30% (47) for the narrow open tubes usually employed in gas chromatography because of variations in r_T and because of deviations from the assumed parabolic flow profile.

General Form of the Plate Height Equation

There are a great number of plate height expressions in the literature, many of them are very complex, but none of them adequately describes the true physiochemical processes that take place in a packed column. However for our purpose the apparent plate height can be expressed in a general form as

$$\hat{H} = \frac{B_1 f\ j}{\bar{u}} + C_s\ \bar{u} + \frac{C_{ml}\ f\ \bar{u}}{j} + H_e \qquad (13)$$

This equation is identical to that used by Giddings (33) and, if coupling is assumed to be complete, by others (39, 55), except they omitted the end effects term, H_e. It has been included here as a reminder that a very efficient column can be offset by zone spreading from the injection device, connecting tubing and fittings, detector dead volume, and response time of detector, amplifier and recording system. Adequate theory exists (103) so that a numerical value could be assigned to H_e but in practice it is difficult to apply this theory to real situations. For the most part the B_1 and C_s terms of Eq. (13) are well understood and all theories (30, 74) are in accord on their make-up. In contrast little is known about the C_{ml} term of Eq. (13). Quite often it is simply written as $\omega d_p^2/D_{ml}$ and this will be done here because we are more interested in how C_{ml} is related to d_p than to other parameters: however, since C_{ml} is the dominant term in packed columns with light loadings of stationary liquid and in columns where adsorbent packings are used, more should be said about it. The term mathematically represents flow inequalities in the column and mass transfer in both moving and stagnant regions of the mobile phase, therefore it will strongly depend on the nature of the packing material, the inner diameter of the column and the packing technique. The dependence on flow inequality should be reflected in the multiplier ω and Giddings (30) has identified five regions of possible flow inequality in packed columns and for this reason ω is sometimes replaced with

$$\sum_{i=1}^{5} \omega_i \ .$$

Knox (66) has found that the term is also retention dependent. Not being able to understand the nature of the mobile phase mass transfer term is probably another reason why gas chromatographers are moving to the more mathematically describable column types, like the open tubes.

Recently Knox (64) and Halasz (48) defined a well packed column as one with a minimum plate height of 1.5-3d_p (64) or about 4d_p (48). Based on theoretical principles Giddings (30) indicated that the best packed column will have a plate height of about 1-2p_d, the step length from the random walk model. We shall therefore conclude that a column with a plate height of 3-4d_p is well packed and efficient.

C. The General Analysis Time Equation

The derivation of a general analysis time equation, one which would be a function of all the column variables and applicable to unprogrammed systems, requires solving four equations. The first equation is for the elution time of the last component

$$t_z = \frac{L}{\bar{u}}(1+k_z) \tag{14}$$

The second equation describes $\hat{H}_y$, in terms of separation variables, for the most difficult pair to separate in the mixture. It follows from Eq. (5, 6)

$$\hat{H}_y = \frac{L}{16Rs^2}\,\frac{(\alpha-1)^2}{\alpha^2}\,\frac{k_y^2}{(1+k_y)^2} \tag{15}$$

The actual choice of the difficult pair is not straightforward. A preliminary run will reveal a pair with minimal resolution but optimization of the chromatographic variables to improve the resolution of this pair may result in the overlap of another pair. This will more often be true for complex mixtures and in practice will usually be solved empirically. The third equation required for the derivation of a general analysis time equation is for $\hat{H}$ as a function of the column variables and will depend on the column type used but be of the general form of Eq. (13).

Fourthly one of the basic flow equations, Eq. (10-12), is needed.

Solving Eq. (15) for L and eliminating that variable in Eq. (14) gives

$$T_z = 16Rs^2 \frac{\alpha^2}{(\alpha-1)^2} \frac{(1+k_y)^2}{k_y^2} (1+k_z) \frac{\hat{H}}{\bar{u}} \qquad (16)$$

which is the fundamental analysis time equation that one finds in the literature. Variations of Eq. (16) can usually be traced back to how the author treated $\hat{H}/\bar{u}$. For example, Purnell (91) and others (19, 97, 98) greatly simplified Eq. (16) by operating their open tube columns well above the Van Deemter optimum so $\hat{H} = C\bar{U}$ and by working with two component systems where $k_z = k_y$. Giddings (33), on the other hand, used the full expression for the plate height (Eq. 13) and the velocity (Eq. 10) keeping all the pressure terms in these equations: the equation he derived for analysis time was very complex. Other treatments of Eq. (16) were between these two extremes (4, 65, 100-102).

D. Theory of Small Particle Packed Columns in Chromatography

Examination of Eq. (16) reveals that analysis time is proportional to $\hat{H}/\bar{u}$ and to Rs^2. Since the retention variables are independent of particle diameter then a decrease in the particle diameter is going to change analysis time through its effect on Rs and $\hat{H}/\bar{u}$. The relationships that determine the extent of these changes will now be worked out. One should mention at the outset that the relationships between particle diameter and Rs, $\hat{H}$, $\bar{u}_{opt}$ and $p_{i(opt)}$ are different for liquid and gas chromatography.

The packing materials investigated in this research had particle diameters ranging from 7-20μ and therefore the pressure drop required to operate any column at its optimum velocity, $\bar{u}_{opt}$, was always greater than 6 so that Eq. (11) is valid and the full definition of j reduces to $3p_o/2p_i$. The particles were made of silica, they were either used by themselves, with adsorbed stationary phases or with bonded silanes. When packings of this nature are used for chromatography Giddings (30) showed rather convincingly that the stationary phase mass transfer term contributes negligibly to Eq. (13). The work of Knox (22, 55) also supports this hypothesis. Indeed, this is the underlying principle for using small particle packings in chromatography. If $Cs > C_{ml}$ in Eq. (13) then the high inlet pressure required to operate the column would be wasted, since a larger particle diameter could be chosen (one where $Cs \simeq C_{ml}$) and the inlet pressure reduced without the analysis time or plate height being significantly affected.

Under the above stated conditions Eq. (13) can be written as

$$\hat{H} = \frac{3\ B_1\ f\ p_o}{2\ p_i\ \bar{u}} + \frac{2\ C_{ml}\ f\ \bar{u}\ p_i}{3\ p_o} + H_e \qquad (17)$$

The optimum velocity and its relation to the particle diameter can be found by differentiating Eq. (17) with respect to velocity but first the variable p_i and its dependence on $\bar{u}$ must be accounted for by taking cognizance of Eq. (11). When this is done and when $\omega d_p^2/C_{ml}$ is substituted for C_{ml} then as shown in Appendix A the optimum plate height $\hat{H}_{opt}$ is given by

$$\bar{u}_{opt}\ \alpha\ (d_p/L)^{\frac{1}{2}} \qquad (18)$$

and the pressure required to maintain that optimum velocity by

$$P_{i(opt)}\ \alpha\ d_p^{-3/2}\ L^{\frac{1}{2}} \qquad (19)$$

The effect of d_p on $(\hat{H}/\bar{u})_{opt}$ can now be established by entering Eq. (18, 19) into Eq. (17) for $\bar{u}$ and p_i to get

$$(\hat{H}/\bar{u})_{opt}\ \alpha\ (d_p\ L)^{\frac{1}{2}} \qquad (20)$$

Several interesting relationships and conclusions can be seen by close examination of Eq. (11, 15-20). First high inlet pressure *per se* does not lead to a significant increase in plate height since only f of Eq. (17) increases with pressure (P_i $\bar{u}$ also increases with pressure but since their product is in opposing terms of Eq. (17) only the position of $\hat{H}_{opt}$ with respect to velocity is affected and not its magnitude) and no more than 12½% of the column's efficiency (the maximum range of f) is lost in going from a velocity requiring a negligible pressure drop to a velocity requiring a high pressure drop (34). Second, the above equations are applicable in two cases of practical interest in chromatography:

1. Particle diameter is decreased and column length is held constant -- resolution increases.

   Solving Eq. (15-17, 20), as in Appendix A, shows

   $$t_z \propto d_p^{-\frac{1}{2}} \tag{21}$$

   Hence for a reduction in particle diameter with column length held constant and operation at the van Deemter optimum both the analysis time and resolution increase with $d_p^{-\frac{1}{2}}$. Furthermore the pressure required to operate the column at its' optimum velocity will increase in proportion to $d_p^{-3/2}$ as dictated by Eq. (19).

2. Particle diameter and column length are decreased -- resolution constant.

   This is the more usual case as exemplified by current trends in liquid chromatography. If the velocity is always at the van Deemter optimum then under the constraint of constant resolution, analysis time will decrease with the particle diameter,

$$t_z \propto d_p \qquad (22)$$

Since resolution is constant, this decrease must come from a decrease in $(\hat{H}/\bar{u})_{opt}$ (Eq. 16) which according to Eq. (20) is proportional to $(d_pL)^{\frac{1}{2}}$. In order to keep resolution constant, column length is decreased with the particle diameter which can be seen by entering Eq. (15) and Eq. (18) into Eq. (20) to get

$$L \propto Rs^2\ d_p \qquad (23)$$

Thus $(\hat{H}/\bar{u})_{opt}$ decreases with d_p and so does the analysis time. The situation is quite different for LC where it has been shown (81) that for the same constraints analysis time decreases with the square of the particle diameter. This is a direct result of the mobile phase diffusion coefficient in LC being pressure independent because of the incompressibility of the carrier. Consequently all the pressure terms of Eq. (13), j and f, become unity for LC which eventually leads to the optimum velocity increasing with decreasing diameter and therefore a far greater decrease in $\hat{H}/\bar{u}$ and the analysis time than in GC. However, this greater decrease is paid for by a far greater increase in inlet pressure for a proportional decrease in particle diameter.

Equation (19) shows that $p_{i(opt)}$ is only proportional to d_p^{-1} (since L has to be decreased to keep Rs constant) where in LC $p_{i(opt)}$ is proportional to d_p^{-3} (81), again because $\bar{u}_{(opt)}$ increases with decreasing d_p rather than decreasing with $d_p^{\frac{1}{2}}$ as in GC.

E. Optimization of the Chromatographic Parameters

In the simplest of routines, optimization of an instrumental parameter is usually done by adjusting one particular parameter, while holding the others constant, until the desired response in an objective variable has been obtained. Quite often the procedure has to be iterated because optimization of a new parameter may shift the optimum of a previously optimized parameter. The objective variables for chromatography considered here are resolution and analysis time, (maximum throughput or sample size have not been considered). The adjustable or controllable parameters, which require optimization if maximum resolution or minimum analysis time are to be achieved, are temperature, inlet pressure (or velocity) choice and amount of stationary phase, choice of mobile phase, particle diameter and column dimensions and type. Optimization of all these parameters would, at first glance, seem impossible or at best a formidable task and indeed optimization of them would be formidable if it were not for the fact that many of them affect the resolution and analysis time monotonically. Inlet pressure, particle diameter, column dimensions and type are of this category. Secondly, some parameters have been thoroughly investigated by other researchers or optimization of them for GC is straightforward. For example, the choice of mobile phase is of moderate importance in GC with sound theoretical (33,43) and experimental (12, 76, 98) evidence indicating hydrogen as the carrier of choice for FGC. Consequently, for the knowledgeable chromatographer only three parameters, temperature, and the choice and the amount of stationary phase, require special attention in GC.

Optimization of the chromatographic parameters for this investigation was even easier. Instrumental limitations and commercial availability of the packing materials greatly restricted the range of the controllable variables. In the end this meant the sample had to be chosen so that the fixed or greatly restricted chromatographic parameters were about optimal.

Temperature

Temperature affects every one of the variables of the chromatographic system including some that are not normally considered as variables such as the column diameter and the detector sensitivity. Raising the temperature of a gas chromatograph decreases the partition coefficient, increases the solutes' diffusion rate in both phases and increases the gas phase viscosity. Consequently every temperature is going to have a set of optimum parameters, such as column length and amount of stationary phase, which will give the maximum resolution or minimum time that can be achieved at that temperature. However the true maximum in resolution or minimum in time can only be attained by optimizing all parameters, including temperature. Most papers on minimum time chromatography have ignored the effect temperature has on the optimum set of conditions. Many investigators simply chose to optimize their own list of parameters under isothermal conditions and only four (49, 92, 94, 97) have considered the temperature effect into their optimization schemes. Because of instrument design and uncertainty in coiling and heating small particle columns we too, disapointingly, were not able to optimize temperature or even operate above room temperature. However our objective of producing fast chromatograms was still accomplished since a volatile sample was chosen and the choice and amount of stationary phase was selected to partially compensate for a non-optimum temperature.

Choice and Amount of Stationary Phase

The choice of stationary phase is the most important parameter in GC and most often is the easiest to optimize. Slight differences in the structure of a stationary phase can alter the solute-stationary phase interactions in such a way that resolution could be greatly enhanced or reduced. The ability of a stationary phase to interact differently with the constituents of a mixture in such a way as to effect a separation is termed the "selectivity" and is manifested in the relative retention time, α, which appears in both Eq. (16, 17). To date there are at least 200 different stationary phases (84) from which the chromatographer can choose, but if his choice is based on the number of different interactions (or intensities of the interactions) then only about a dozen (83) really exist. Several excellent papers have been published on how to chose the best stationary phase (9, 27, 74, 75); they all require at least a rudimentary understanding of solute-stationary phase interactions.

The amount of stationary phase is expressed in several ways depending upon the nature of the support and the state of the stationary phase. For the conventional packed column using a granular support with a liquid stationary phase coated on it, the amount of stationary phase is usually expressed as percent stationary phase by weight of the packing. With open tube columns it is termed the film thickness and is given in microns or angstroms; it is also done this way when thin films of stationary phase are adsorbed onto a support normally used as an adsorbent. Lastly, when the stationary phase is a solid adsorbent the amount is expressed as surface activity given in meters squared of adsorbent surface per gram of adsorbent.

The amount of stationary phase and k are directly proportional under the same set of experimental conditions. Therefore next to making the correct choice as to the stationary phase required for the analysis, the amount of stationary phase is of equal importance with temperature in GC. The column capacity ratio is defined by Eq. (1) and enters the analysis time equation, Eq. (16), explicitly through $(1 + k_y)^2(1 + k_z)/k_y^2$ and implicitly through $\hat{H}$. The exact dependence of $\hat{H}$ on k is known only for open tubes and was thoroughly discussed by Scott and Hazeldean (98). In general, $\hat{H}$ will be a slowly increasing function of k when the amount of stationary phase is low and certainly when C_s is negligible. Without a doubt the biggest effect of k on analysis time will come from the $(1 + k_y)^2(1 + k_z)/k_y^2$ dependence. This function will take on very large values at both high and low values of k_y, tending to infinity as k_y approaches zero and having its minimum value between k_y of 1-2 depending on the relative retention time of component z to component y.

Purnell and Quinn (91) were the first to investigate the effect of k on analysis time for both $k_y = k_z$ and the more usual case of $k_z > k_y$. They found that $k_y = 2$ represented a definite upper limit for fast analyses on open tube columns being near 2 when $k_y \simeq k_z$ and close to one when $k_z > k_y$, i.e. the mixture contains a high boiling component.

Others have found similar results; Ayers, Loyd and de Ford (4) concluded that the optimum k_y for a packed column was between 2-3 but that the minimum was shallow and could be extended to a range of 1-6 without significantly increasing the analysis time. This fact was also borne out by Knox (63) who found k_y's in the range of 2-6 optimal for packed columns but 2-3 optimal for open tubes. The general range of 1-6 for optimum k_y is also supported by computer optimizations and other theoretical calculations. The computer optimizations of Smuts and Pretorius (102) found the range 2-4 optimum for packed columns while that of Hawkes' (49), for open tubes, found a much lower 0.1-1.0 range, but he unlike the others had high boiling components in his mixture and this would shift the optimum k_y to lower values, a conclusion confirmed by the theoretical calculations of Giddings (31, 33). Lower partition coefficients also shift the optimum capacity ratios to lower values (33). This arises from a compromise with the mass transfer rate; at low values of the partition coefficient it would be necessary to use large amounts of stationary phase to get higher column capacity ratios and this would slow mass transfer from the stationary phase. The necessary compromise leads to lower optimal values of the column capacity ratio with lower stationary phase loads for slightly soluble samples.

In summary, for 2-component mixtures the optimum range for k_y will be from 2-3 but the range could be extended to

1-6 without greatly increasing the analysis time. Widely spaced components in the mixture or mixtures with very low partition coefficients will shift the optimum column capacity ratios to lower values.

The choice and amount of stationary phase will be thoroughly discussed in the experimental and the results and discussion sections of this thesis.

Inlet Pressure, Particle Diameter and Column Length

These parameters are quite logically discussed under the same heading since they affect the analysis time and resolution in a monotonical manner and are related through the flow equations. Decreasing d_p necessarily requires higher inlet pressures and usually smaller column lengths but the rewards are smaller values of the plate height and greater resolution and/or shorter analysis times. Hence, the absolute minimum in analysis time for a chromatograph and the smallest d_p that can be used are governed by the maximum operating pressure of the chromatograph. This concept was first formulated by Knox (63, 65) although others have touched on it (19, 30, 49, 98, 102) and is known as the pressure limited case of minimum time chromatography.

Commercial gas chromatographs usually have pressure capabilities of only 30-60 psi and thereby limit the particle size to about 100-125 microns (120-140 mesh). On the other hand modern liquid chromatographs can generate up to 8000 psi and have no trouble operating columns packed with the 5 micron particles that are commercially available. In fact quite often in LC 5 micron columns are operated at pressures well above $p_{i(opt)}$ using column lengths much longer than necessary partially to offset the increase in $\hat{H}$ from operating above $\bar{u}_{opt}$ and partially to compensate for poor plumbing, large injection volumes and a slow detector response. The reverse has been done in the theoretical computer optimization schemes of Hawkes (49) and Smuts and Pretorius (102); both have let their computer searches reach values of d_p or tube radius (in the case of open tubular columns) such that the optimal column length for their hypothetical separations are smaller than what one would care to connect to an injector-detector system.

The consequences of using smaller d_p's than what the chromatograph has pressure for are two fold. First, the velocity may be so slow that $C\bar{u}$ is negligible in comparison to $B/\bar{u}$ so that $\hat{H}$ is higher than if larger particles were used allowing for a greater velocity and a better compromise between $B/\bar{u}$ and $C\bar{u}$. Second, the column length could be reduced to the point where the chromatograph's maximum pressure is supposedly enough to operate the column. However, this column length may be too small to connect to the chromatograph or so short that there is little resolution Eq. (15), but most likely H_e of Eq. (13) will dominate and nullify the advantages of using small particles.

The chromatograph built for this work had a maximum pressure capability of 1000 psi. This was enough pressure to operate columns of 30-60 cm in length packed with 10 micron spherical silica particles. With columns shorter than 30 cm or packed with 5 micron particles instrumental end effects (probably speed of the sampling value) dominated the plate height.

III. EXPERIMENTAL

When a separation fails it is for one of two reasons; either the apparatus was poorly designed and offsets the separating power of the column or the proper column was not chosen, it was either not selective or not efficient enough for the separation at hand. Therefore when one designs a chromatograph much attention should be paid to the construction of both.

A. Construction of the Apparatus

Detector

In order for a detector to be acceptable for the kind of work done here it would have to meet four specifications. The detector would have to be sensitive, have a fast response time, be easy to maintain, and have a low dead volume without sacrificing any of the above. The only detector which can easily meet these requirements is the flame ionization detector (FID).

Commercial FID's, available at the time, were unacceptable from several standpoints. First, they all had long insulated signal conductor cables which would increase the input capacitance of the measurement system and it's response time. Second, they all had their detector jets mounted in such a way that the dead volume between the column and the flame was more than 100 microliters. Third, the purchase and modification of a commercial detector might have been more costly than a house-built model without a guarantee of success. For these reasons it was decided to design and build a FID for the chromatograph. This necessitated a thorough literature search to find the optimum design and operational variables. To this author's surprise, these variables only moderately effect the detector's sensitivity. As shown by Bradley and Falconer (7) who, using materials such as a modified Swagelock T, a No. 22 stainless syringe needle, a 35 mm film can and a blob of silver solder, built a FID having a sensitivity only an order of magnitude less than the best FID of the day (13). However, if that order of magnitude of sensitivity is required then it becomes important to optimize the detector variables and to understand their interplay.

Optimum Design Variables

The design variables are jet internal diameter, collector shape and position from the jet, and design of the collector and signal cable so as to minimize input capacitance and contamination of the insulator. Generally detector sensitivity increases with decreasing jet internal diameter although Gill and Hartman (35) found a maximum response for jet ID's of about .020" and slightly smaller responses for smaller jet diameters while larger ID's gave significantly lower responses. Smaller internal diameter jets are easily extinguished by the column effluent and reduce the dynamic linear range of the detector, large ID's lead to soot formation and require frequent cleaning. It is primarily for these latter reasons why commercial FID's have jet diameters from .02-.03".

Many sizes and shapes of electrode-collector systems have been studied (18, 21, 35, 89), the best system is where the jet is one electrode and the other is either a rod,a variously shaped flat piece of metallic gauze, a loop or cylinder suspended above the jet. With this type of arrangement the suspended electrode is called the collector even though the jet will collect one type of charge. The size and shape of the collector and its distance from the jet will determine the necessary polarizing voltage and the linearity of the detector. All shapes described above will work (36) if properly used but the most versatile is a cylindrical collector of about 5-10 mm in diameter (21, 3, 85) 3-5 cm in length (36) and extending a few inches below the jet tip (21). This type of electrode system gives rise to the best electric field; it completely encompasses the flame such that any charge formed in the flame is essentially trapped in a faradaic cage (21).

The collector and signal conductor cable should be designed to minimize input capacitance and contamination of the insulator. Contamination of the cable insulation can be greatly reduced by simply keeping the insulation away from the flame and exhaust gases; providing good ventilation to the detector is also a help. Input capacitance can be kept minimal by using cables of short lengths and insulated with a material having a low dielectric constant; choosing the insulator is important because the stray capacitance will be decreased by a factor equal to the dielectric constant. The dielectric constant is the smallest for a vacuum but dryair at 1 atm pressure is about as good, teflon is twice that of air while glass is 5-10 times that of air, other common insulators fall between the values for teflon and glass.

Optimum Operational Variables

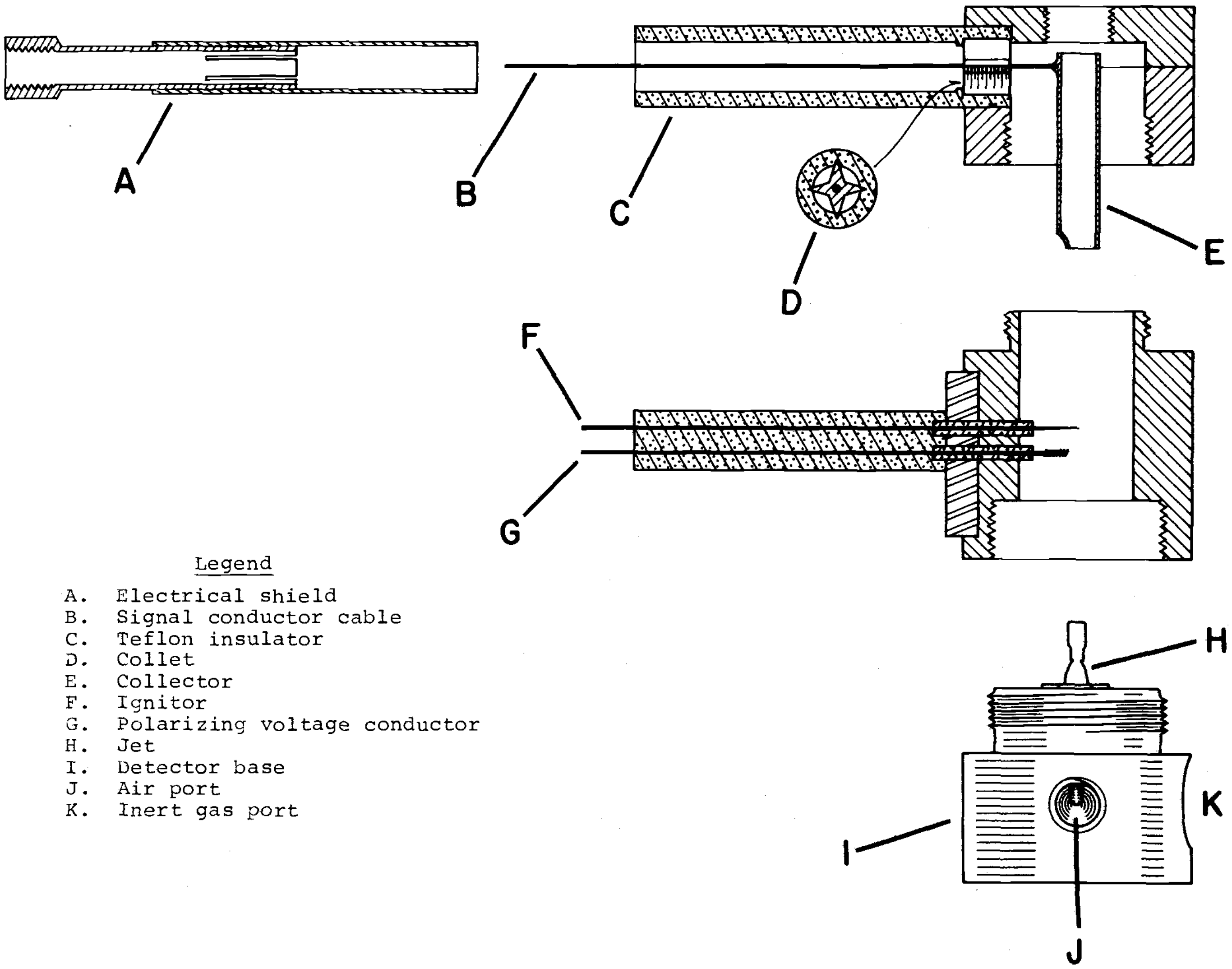
The operational variables are polarizing voltage, hydrogen flow, air flow, and carrier gas flow (usually nitrogen or helium as the carrier gas, although not in this work). The FID is relatively insensitive to operating variables; as long as there is a flame and a polarizing voltage a response will be obtained. However, a 2-3 fold increase in response and improved linearity will be obtained if the operational variables are in the optimum neighborhood.

A polarizing voltage of a few volts is sufficient to reach the plateau region of the current-voltage curve, with submicrogram/sec sample flow rates, but several hundred volts may be required for larger sample sizes. The minimum voltage required to reach the plateau region, the region where 100% ion collection is guaranteed, will depend on the detector design but usually polarizing voltages of 100-300 volts (84, 104) will be more than adequate to ensure 100% ion collection yet low enough to avoid electron multiplication. The polarizing voltage (either - or +) is best applied to the jet (104) and the electrometer circuit operated at ground potential; this will reduce stray capacitance and noise.

Most any hydrogen flow rate will give a good response (85, 104) if adequate air and inert gas are supplied but typically hydrogen flow is from 20-60 mls/min with very high hydrogen flows (200 mls/min or more) avoided because the collector may be heated giving rise to thermionic emission. Inert gas flow to the FID is not only a consequence of column flow but is necessary if maximum detector response is to be reached. The optimum inert gas flow is 1-1.5 times the hydrogen flow (85, 104) with ratios near 1.5 required for the higher hydrogen flow rates. Any air flow above 200-300 mls/min will support combustion and give good detector response (104), air flows as high as 2500 mls/min have been used (18) without serious loss in response.

Design and Operation of the Detector

The details of the flame ionization detector design are shown in Fig. (2-4). The detector has many of the optimum features outlined in the beginning of this section. The



Legend

A. Electrical shield
B. Signal conductor cable
C. Teflon insulator
D. Collet
E. Collector
F. Ignitor
G. Polarizing voltage conductor
H. Jet
I. Detector base
J. Air port
K. Inert gas port

Figure 2. Exploded view of flame ionization detector. Cross hatched areas are stainless steel. Dotted areas are Teflon.

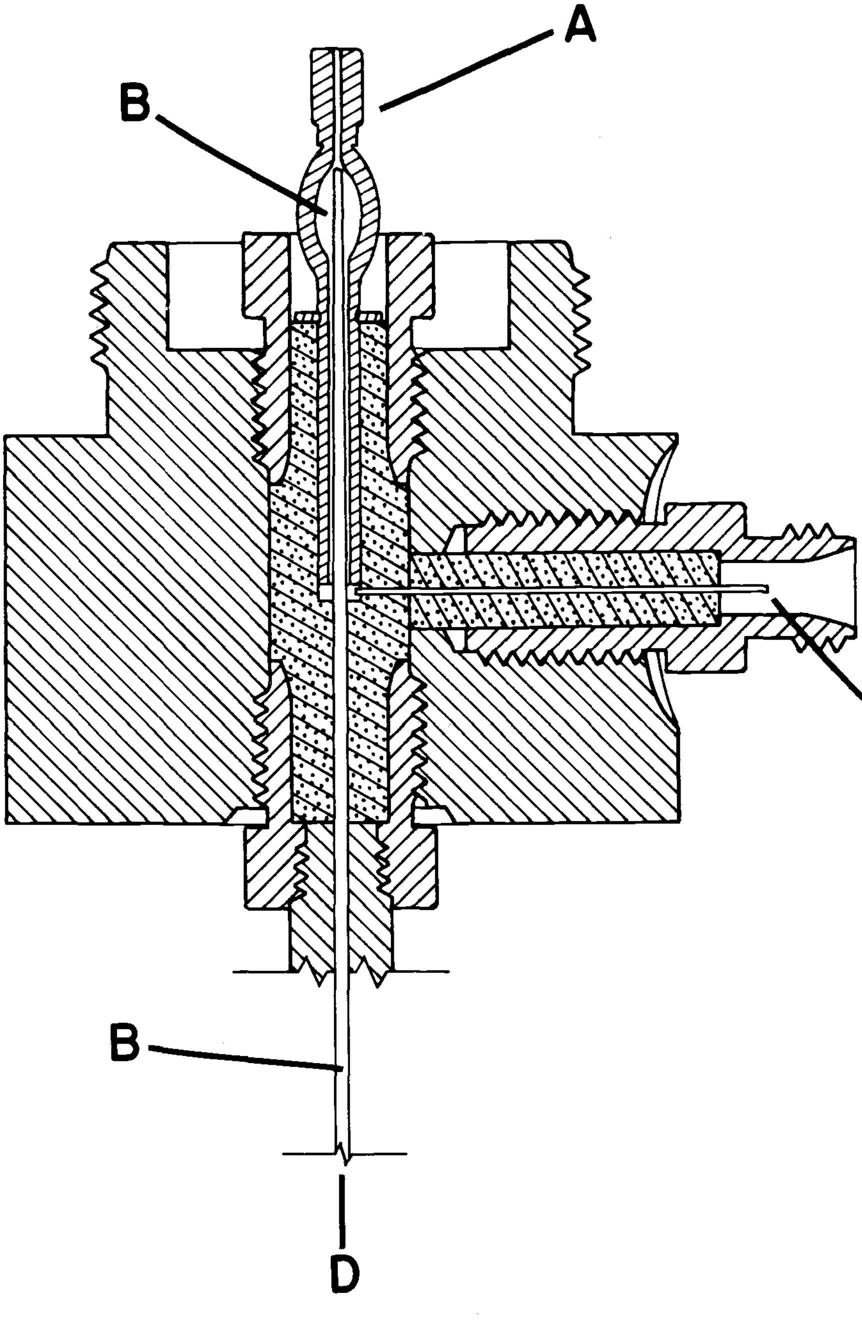


Figure 3. Detector base. Cross hatched areas are stainless steel. Dotted areas are Teflon. A. Jet; B. Splitter capillary; C. Inert gas line restrictor; D. To splitter - column assembly.

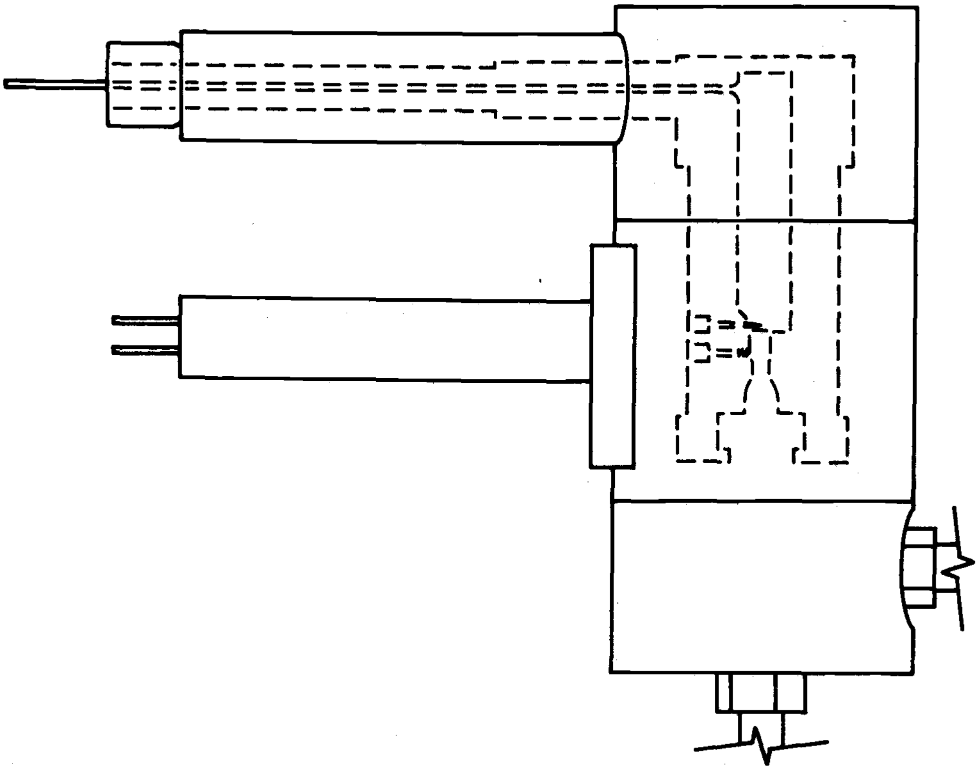


Figure 4. Assembled view of detector.

collector-signal conductor assembly shown in the top part of Fig. (2) is about five inches long when together and has air as the insulator between the shield and the signal conductor. The cylindrical collector E is suspended over the jet H and extends a few millimeters below the jet's tip, which can be seen from assembled view of the detector in Fig.(4), it is held in place by a small star shaped collet D which has been pressed into Teflon as shown in Fig. (2). The signal conductor cable B is shielded by a stainless steel tube A which slides into the cylindrical Teflon insulator C and is concentric with the cable.

The details of the detector base are shown in Fig. (3). The internal diameter of the jet is .020 inches, and was purchased from Varian Aerograph (part No. 02-000634-00). The capillary tube coming from the splitter and carrying a fraction of the column effluent is clearly shown in Fig. (3) to have penetrated most of the jet. This reduced the dead volume in the detector from just over a 100 μl to less than 20 μl with half of this dead volume being swept out by the inert gas flow entering through the restrictor (C of Fig. 3).

Another unique feature of this FID is the manner in which the flame is lit. Most FID's have a hot wire ignitor which can cause noise or interfere with the collector but this detector's ignitor (shown in Fig. (2, 4)) operates off the polarizing voltage and once the flame is lit it can be removed.

Splitter

Columns operated under high pressure drops and having relatively large internal diameters will give high outlet volume flow rates. If the carrier is inert, and the detector is an FID, the high volume flow rate will extinguish the flame, if the gas is active like hydrogen, a vigorous flame is produced giving a high background current or the possibility of melting the collector. The most convenient way to handle the problem of high column outlet flow rates is to install a splitter between the column and the detector and only send a fraction of the column effluent to the detector. The obvious disadvantage of this is loss of sample and an increase demand on detector sensitivity.

The details of the splitter design are shown in Fig. (5). The split ratio was varied by changing the capillary i.d. or by packing the coupler with glass beads of a different diameter. The range of split ratios that this method offers and the mathematics for calculating the split ratio are the subject of Appendix B.

The Electrometer and Recording System

Basically an electrometer, as used here, is a very high-impedance operational amplifier functioning as a linear current-to-voltage converter. Because fast current measurements of no more than a few microamperes (the upper current level of the detector) were to be made, the offset current

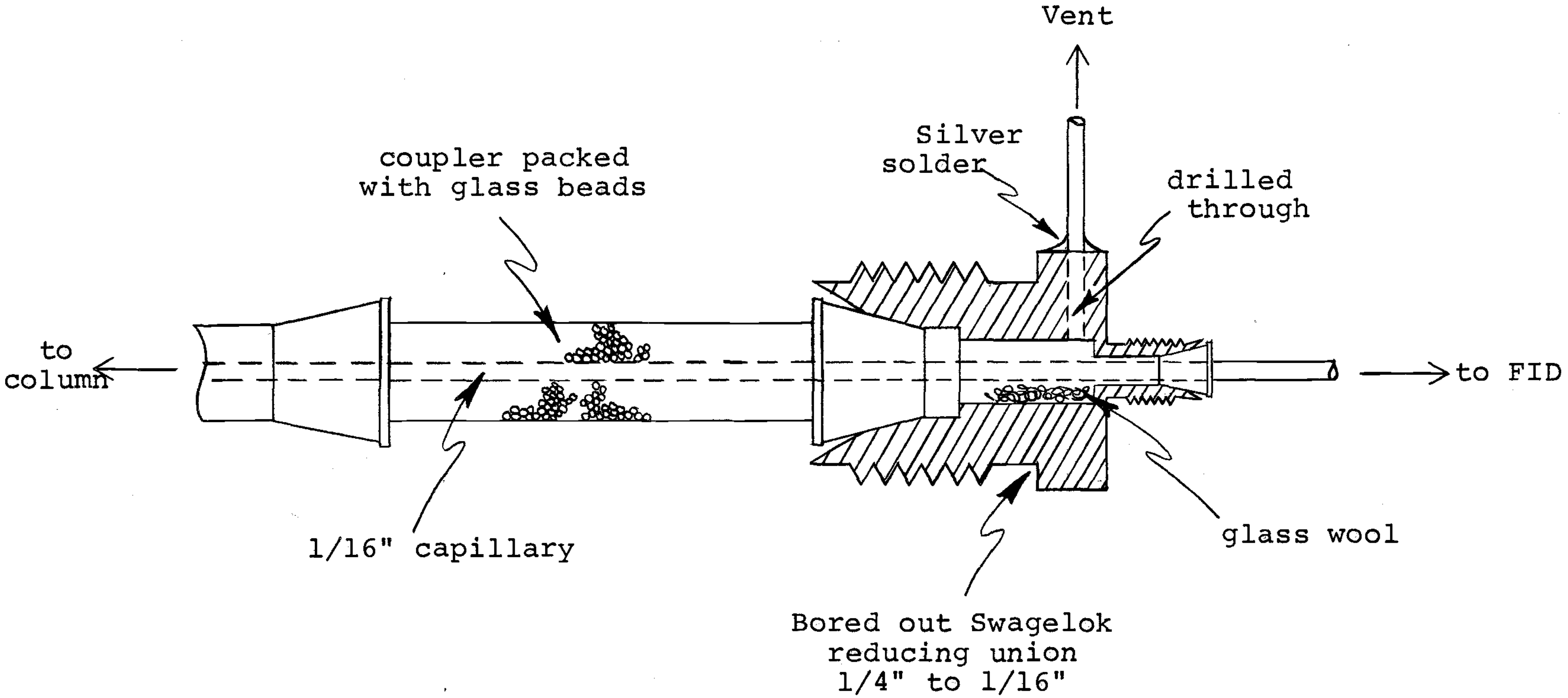


Figure 5. Details of the Splitter.

of the electrometer had to be small and the gain set to give a wide bandwidth. The electrometer circuit in Fig. (6) fulfills these requirements. The first amplifier is an Analog Devices 310K electrometer (Analog Devices, Cambridge, MA) with an input impedance of 10^{11} ohms, an offset current of 10^{-14} amperes, and a bandwidth, at unity gain, of 2 KHz. Because the frequency response of this amplifier is poor (about 10 Hz at a gain of 100 or 40 dB), a relatively low valued feedback resistor was used in the feedback loop; if gain was required it was given with the cascading Model 118 operational amplifier (Analog Devices) which had a crossover frequency of 1.5 MH_z. Every effort was made to reduce stray capacitance, leakage current and noise pickup in the electrometer circuit. Metal film resistors were used everywhere except in the attenuation section, the feedback capacitor was a polystyrene capacitor having a leakage resistance greater than 10^{14} ohms, and each lead of the power supply (Analog Devices Model 904) was decoupled with one microfarad tantalum capacitors. The modular amplifiers and power supply were mounted on a printed circuit board and the works placed in a metal box which acted as a shield. Ground loops were avoided by connecting the shields of the recorder, electrometer, and FID signal conductor to the noninverting input of the first amplifier (86).

The output voltage of the circuit in Fig. (6) is given by

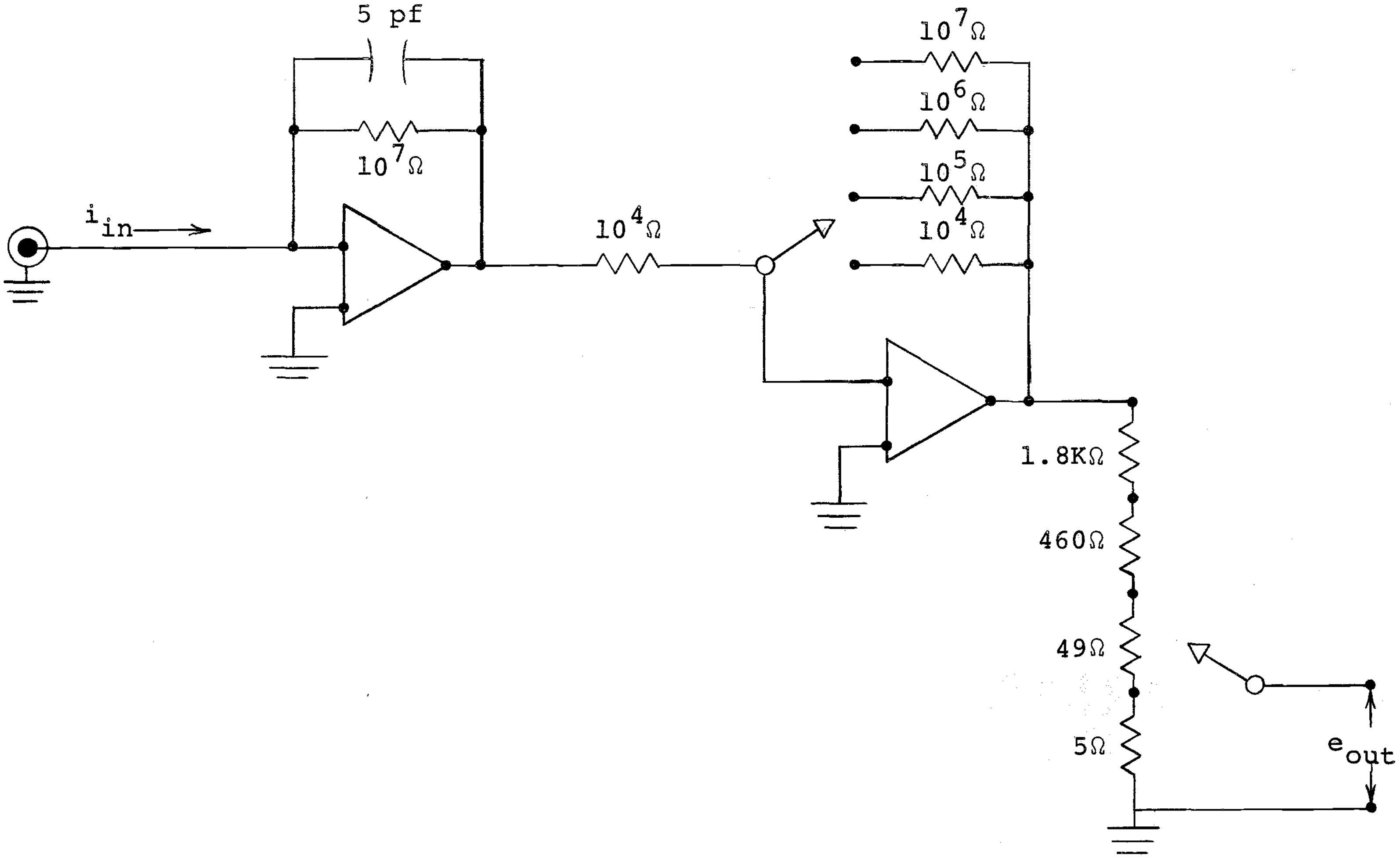


Figure 6. Electrometer circuit.

$$e_{out} = i_{in} \times 10^7 \times \frac{\text{Gain}}{\text{Attenuation}} \qquad (24)$$

Every chromatogram in this thesis was recored with gain = attenuation = 1 (gain was never used, attenuation was used when data was collected for a van Deemter curve) then the output voltage is equal to $i_{in} \times 10^7$. Since most peaks of the chromatograph were one-half to full scale response of the recorder (1/2 - 1 MV) the peak currents produced by the detector were from 5×10^{-11} to 10^{-10} amperes. Hence the need for a well designed measurement system.

The Injection System

The biggest obstacle to the successful implementation of the principles developed in this thesis is the injection system; it is a problem which has never been satisfactorily solved in gas chromatography. The approach taken here parallels the design of sample valves used for HPLC. Some of these valves can be operated at 7000 psi and 80°C without leaking or distoring the input pulse.

Sample Valve Development

The details of the sample valve are shown in Fig. (7-11), the valve was developed over many years of work and many failures. The mistakes that were made in previous valve designs have been noted below, along with the corrections which have led to an overall improved valve design.

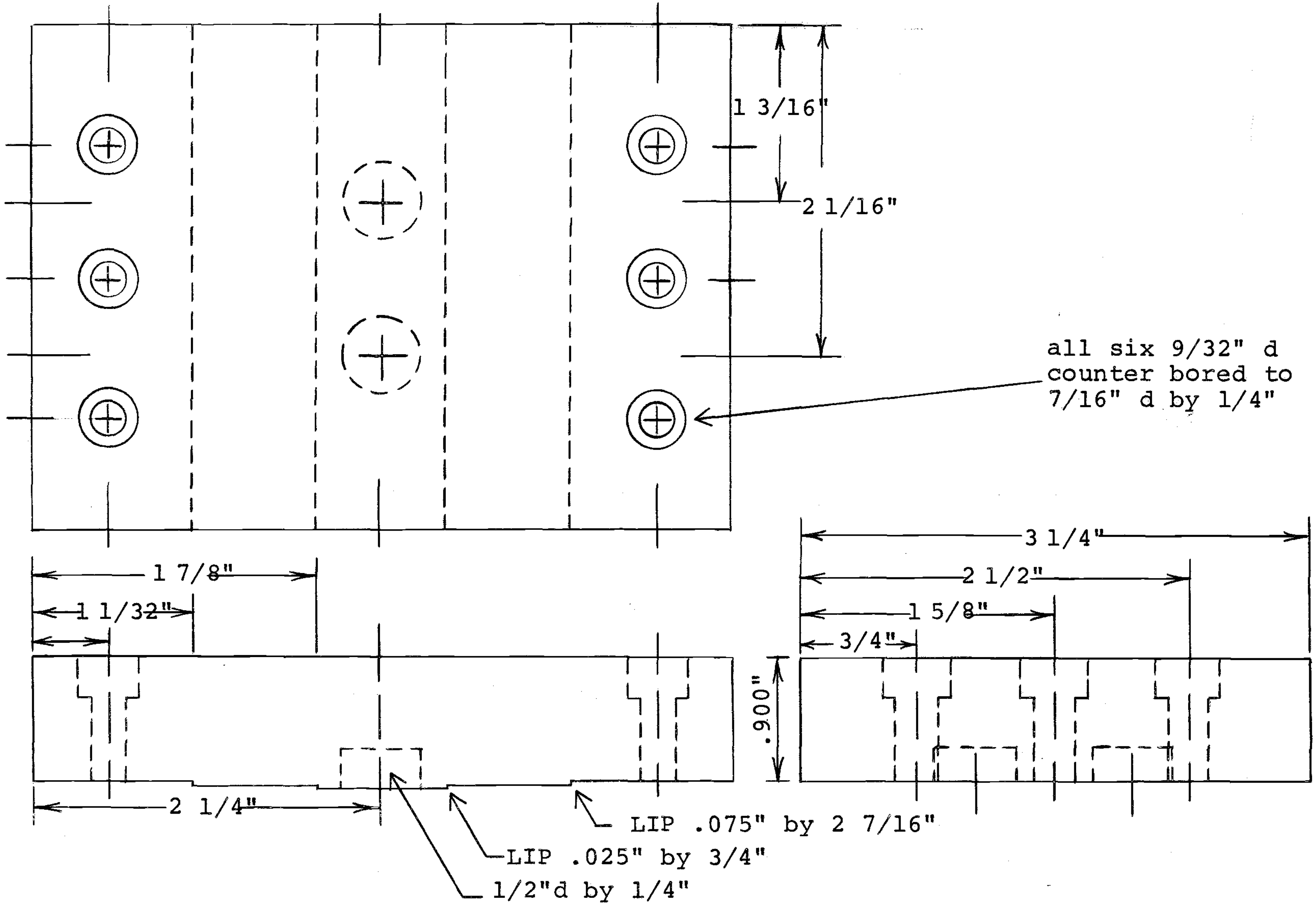
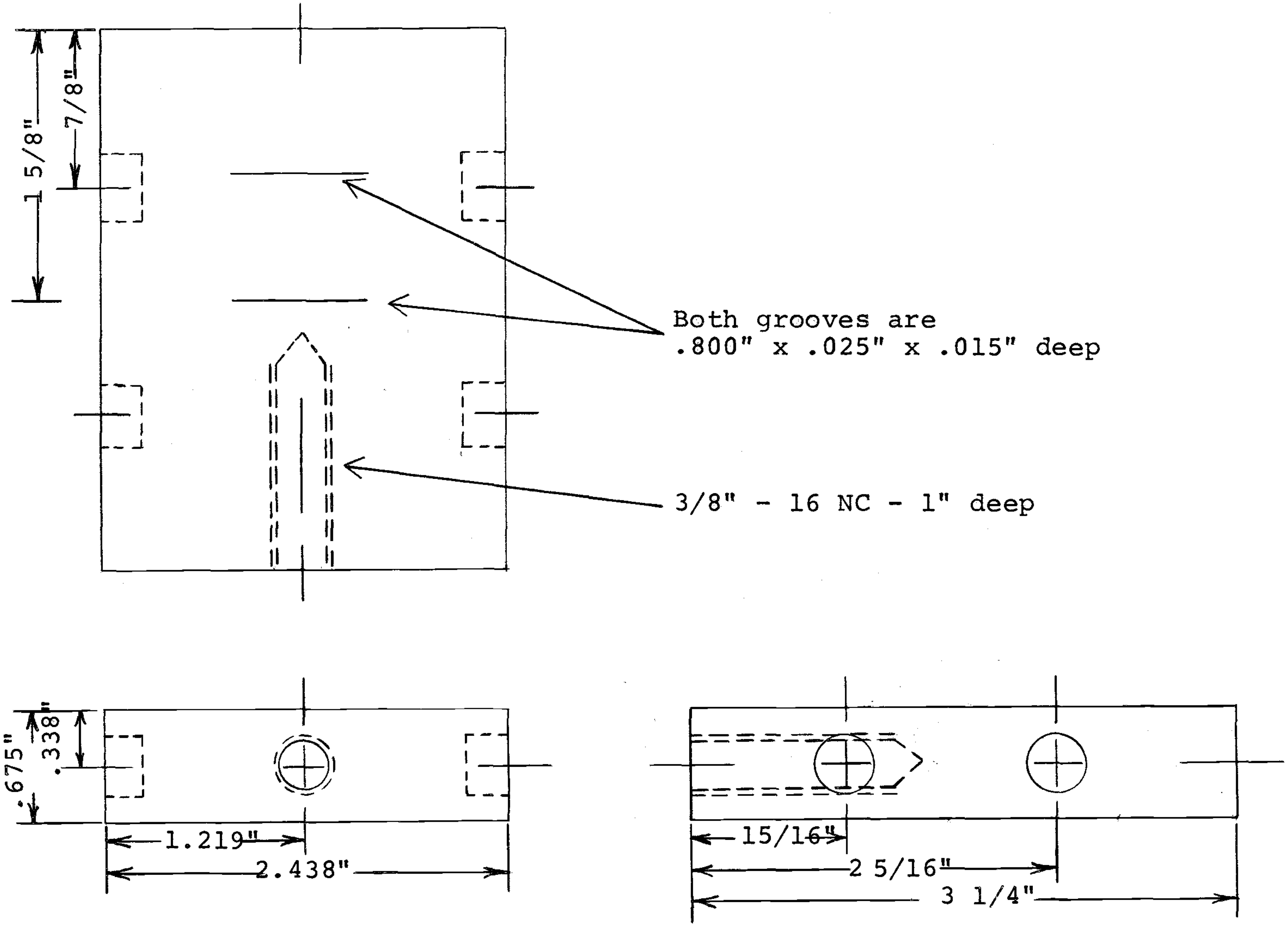


Figure 7. Valve cover.



Both grooves are .800" x .025" x .015" deep

3/8" - 16 NC - 1" deep

Figure 8. Tool steel slide.

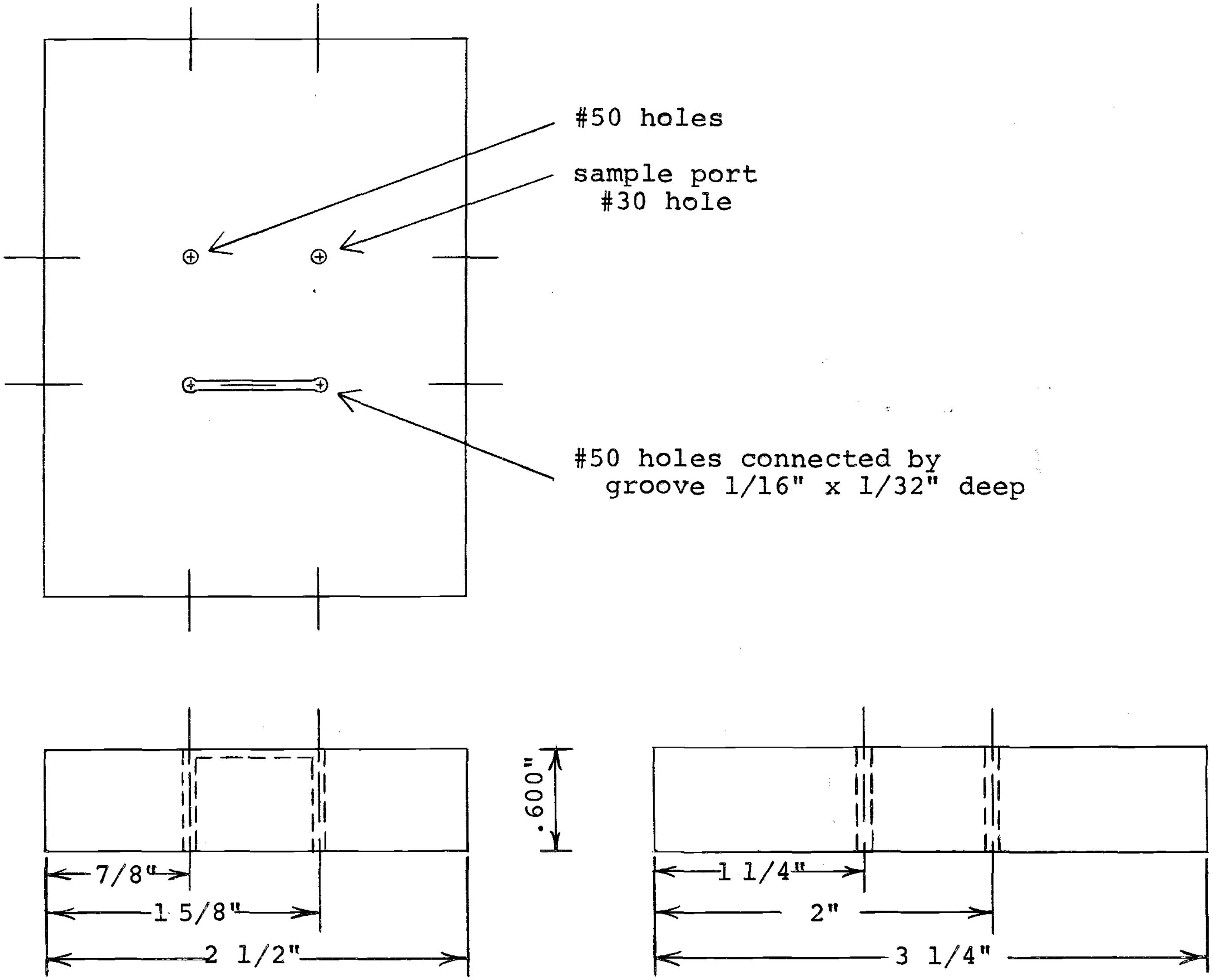
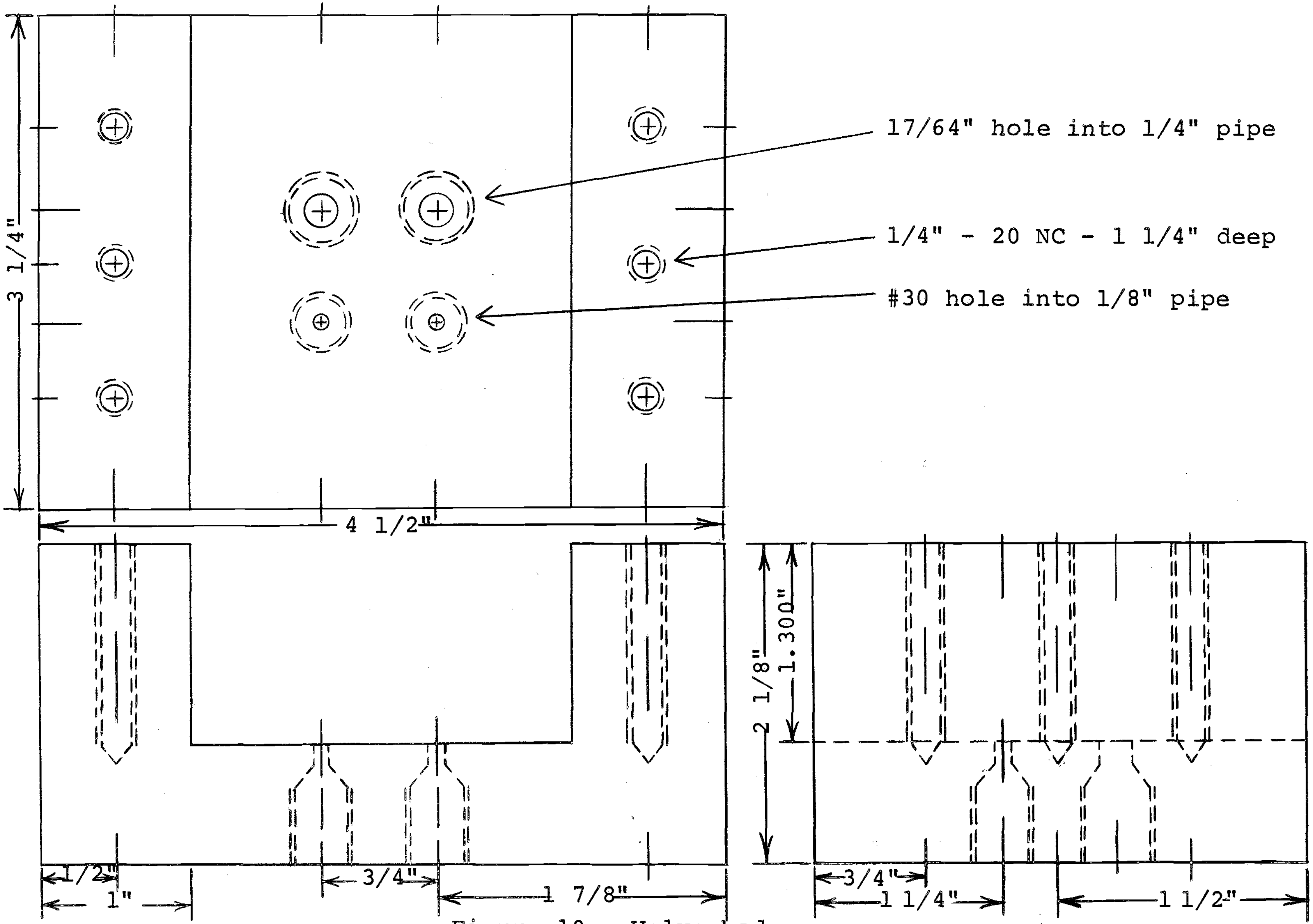


Figure 9. Cadmium oxide filled Teflon seal.


17/64" hole into 1/4" pipe

1/4" - 20 NC - 1 1/4" deep

#30 hole into 1/8" pipe

Figure 10. Valve body.

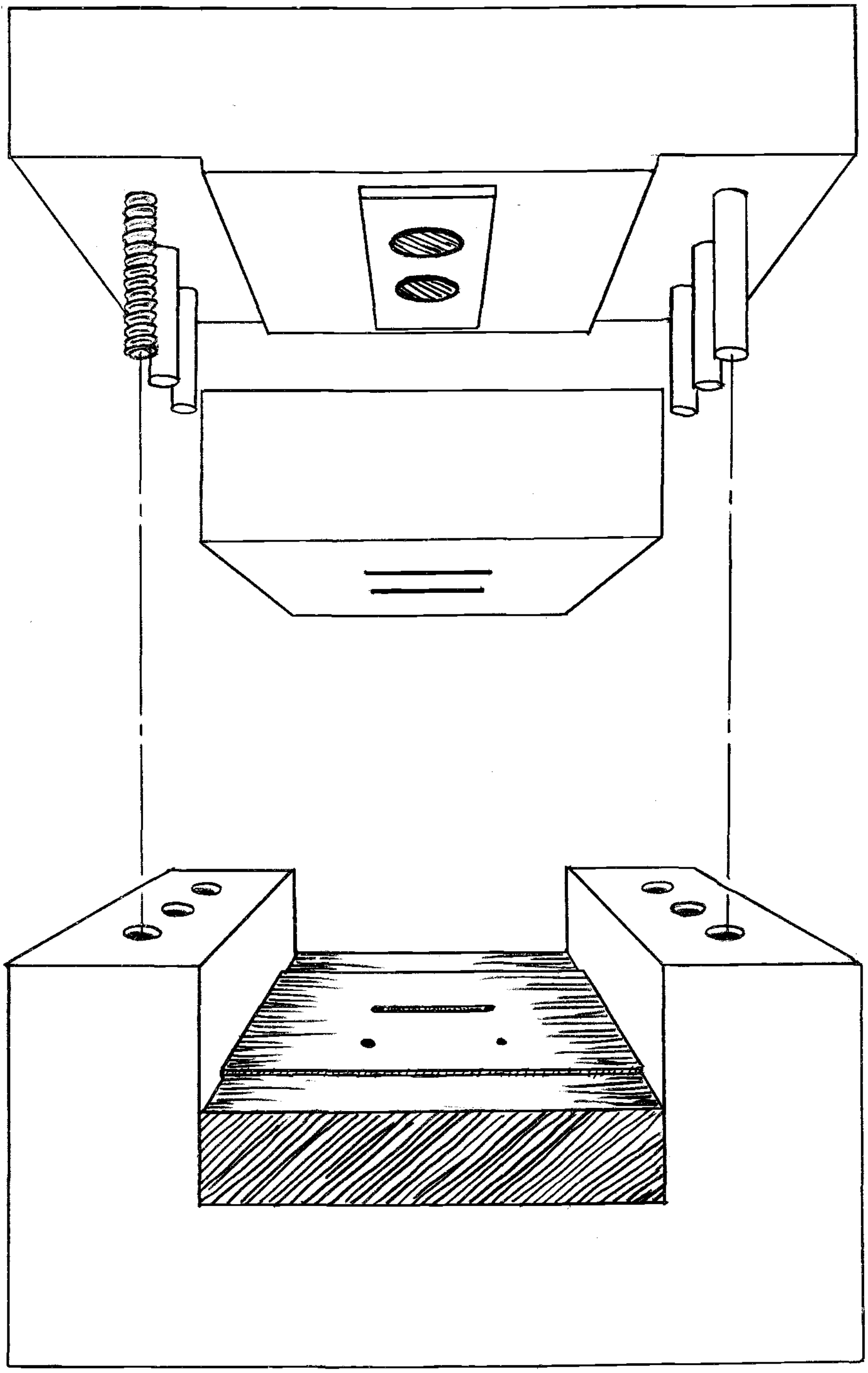


Figure 11. Exploded view of sample valve.

1) In the first valve design the Teflon seal was held in place within the valve body by set screws. Eventually these screws would work into the Teflon and the seal would move a little every time the slide was actuated, making injection onto the top of the column impossible. The problem was solved by encapsulating the Teflon seal in metal, the valve body and the two face plates (shown in Fig. 12)) did this nicely.

2) This first valve design was also plagued by an unequal sealing area around the valve ports. The distance between the sample ports and the column-pressure ports is 0.750 inches; all these ports should have at least this much distance between them and the atmosphere for a sealing area of $(3 \times .750)^2$ or about 5.1 square inches around the ports.

3) The Teflon seal shown in Fig. (9) is about 1.5 cm thick; if the column port going through this seal is not constructed properly a very large dead volume could be added in the worst possible place. Hence, considerable attention was given to the design of that port. The first approach was to drill a very small hole (#60 drill-.040") through the Teflon. This decreased the dead volume but it increased end effects by restricting the sample from entering the column and by creating such a

large diameter change that dead pockets formed at the head of the column trapping the sample and giving tailed peaks. The second approach was to mill out the bottom of the Teflon seal so the column could be inserted one centimeter into the bottom of the Teflon, cutting the samples traveling distance through the seal. This failed to work because the remaining half centimeter of Teflon between the column and the slide was not strong enough to hold the sealing force exerted by the column. Eventually the surface of the Teflon seal, just above the column port, became distorted causing the valve to leak. The dead volume problem was finally solved by drilling out the column port to the same internal diameter as the column and hand packing the port with the column packing material.

4. Different materials of construction were tried for both the seal and the slide. Seals were made of unfilled Teflon and Teflon filled with either graphite or cadmium oxide. The unfilled Teflon was much too soft for our purpose and reacted to stress by cold-flowing away from the stress, sometimes to the extreme that holes drilled through it were closed. The graphite filled Teflon (15% by weight, the Fluorocarbon Co., Sunnyvale, CA) worked far better, but with use the slide would extrude the

graphite from the Teflon causing it to build up between the slide and the seal, creating leaks. The cadmium oxide filled Teflon (12% by weight, the Fluorocarbon Co.) worked the best, on both accounts, and is the second major reason for the improved valve performance.

The first slides were machined from aluminum since it is inexpensive and easy to work with. The aluminum slides would work for 10 or 20 injections then they became so scratched they had to be removed and resurfaced. The major improvement to the valve has been to make these slides out of hardened tool steel (Timken Graph-Air Tool Steel, Timker Company-Steel Div., Canton OH). By doing this the maximum working pressure of the valve has been more than doubled and resurfacing is now done only a few times a year.

5. The surfaces of the Teflon seals, were trimmed in the mill using a technique called fly cutting. The purpose of this process was to put smooth flat surfaces on the seal, surfaces parallel to each other and to the slide. While this operation was an improvement over hand sanding it too had difficulties. Specifically, the cut on the Teflon was made while it was held lengthwise in a vise, the gripping force of the vise caused the Teflon to

bow so that more would be taken off in the middle than the sides (the additional amount taken off was estimated to be less than .001 inches). Hence there was a valley down the middle of the seal and most of sealing force exerted by the slide fell on the edges of the seal where it was needed least. The difficulty with the fly cutting process was never overcome, smooth flat surfaces on the Teflon seals were obtained in the following manner. After fly cutting, the seal was placed in the valve where the maximum load of the valve was placed on it. The slide was run back and forth across the seal several times then removed and surfaced using wet crocus cloth with either glass or stainless steel sheet as a backing. Sometimes the process had to be repeated 2 or 3 times and with some seals it never worked.

Design and Operation of the Sample Valve

The details of the sample valve design are shown in Fig. (7-11) and how it is mounted in the chromatograph is shown in Fig. (12). The valve was a slide type gas sampling valve consisting of an aluminum body and cover, Fig. (7-10), cadmium oxide filled Teflon seal, Fig. (9), and a tool steel slide, Fig. (8). The slide had been heat treated to a 65 Rockwell hardness and then surface ground to a better than 8 micro finish. Two V-shaped grooves on the slide aid in maintaining flow to the column when the valve is in sample pick-up position and in transporting samples to the column when the valve is thrust into sample inject mode. The seal to the column and the pressure port are made at the bottom of the CdO-filled Teflon seal, about 1.5 cm below the slide. The added dead volume was eliminated by drilling out the column port in the seal to the same internal diameter as the column and hand packing the seal with the column packing material. Eventually packing would work its way in between the seal and the slide resulting in destruction of the seal and requiring an occasional regrinding of the surface of the slide. Travel of the slide was 0.750 inches from the sample ports to the column-pressure ports. Movement of the slide was maintained by a 5" Power Dome air cylinder (Bellow-Valvair Div. of IBEC, Akron, OH) pressurized at 250 psi.

B. The Column

Nature and Choice of the Stationary Phase

Every year more microparticle packings are commerically available for the chromatographer to choose from. Most of these packings are positive centered adsorbents, usually silica or silica with bonded groups, and are tailored for use in the various modes of LC. The packings have a much higher BET surface area than conventional gas chromatographic supports and their adsorptive forces are always felt unless large amounts of stationary phase are put on them. However they come the closest to having the uniformity described by Kiselev (62). On the micro level the surface of the packings are uniform, consisting of a minimum of different adsorption sites. On the macro level the particle size, shape and pore distribution are all held within narrow limits (58, 60, 107). Furthermore, the high pressure slurry techniques used to pack them are reproducable and give very efficient columns; two attributes the hand packing techniques lack.

A broad number of microparticle packings exist from which to choose but generally a microparticle packing will come from one of three groups. The organic polymers or porous polymers were the first microparticle packings and are traditionally used for gel permeation chromatography (GPC), although larger particles have been used in GC for gas samples where it has been demonstrated that the polymers are much too retentive towards hydrocarbons. The next group of microparticle packings is the aluminas, which is not very popular with liquid chromatographers and is only available in some particle sizes with limited adsorption properties. Silica or silica with bonded organic groups are by far the most popular LC packings, they are commercially available in a wide range of particle sizes, having greatly different adsorption properties and, in the case of silica, can be modified in a number of ways (3, 6, 11, 40-42, 50, 57, 64, 67, 72, 80, 106). The variety of microparticle silica available and the wealth of information that exist on it made this packing the most logical choice to start our high speed work with.

The most popular procedures for modifying silica are bonding silanes (57, 67, 80, 106) and adsorbing stationary phases (11, 40-42, 50, 72). Both have been tried in this thesis using two silanes and a number of stationary phases on three commercial silicas. The silicas were donated by the following organizations: Spherisorb silica from Spectra-Physics, Santa-Clara, CA; LiChrospher Si500 silica from EM laboratories Inc., Elmsford, NY; and PSM 600 silica from Dupont, Wilmington, DE (my thanks to Dr. Dick Henry, Ted Abstander and Dr. J. J. Kirkland of the respective organizations). Most of the work was done on silica with adsorbed OV-210, Ohio Valley trifluoropropylmethysilicone oil (Ohio Valley Specialty Chemical, Inc., Mariett, OH) as a stationary phase, but packings with adsorbed Kel-F oil (Alltech Associates, Arlington Heights, IL) and triethyleneglycol and dinonylphthalate of technical purity were also investigated. Later we will show that the fluorosilicone oil worked the best and for this reason the silanes, 3,3,3-trifluoropropylmethyldichlorosilane from Silar Laboratories, Inc., Scotia, NY and trimethylchlorosilane from Pierce Chemical Co., Rockford IL were tried as bonding materials.

Column Construction, Packing, and Modification Procedure

The LiChrospher Si500, the Spherisorb silica and any bonded phase packings were packed at 6000 psi using the balanced-density slurry technique (78). The dispersing medium was 65% v/v methylene bromide/methanol, which, like all other solvents used here, were reagent grade and were used without further treatment. However, in time, the methylene bromide acquired a yellow color and had to be purified by passing it over 6-12 mesh silica gel: failure to do this caused corrosion of the stainless steel screens. The PSM 600 silica was packed at 7000 psi, using the high pressure stabilized slurry technique (60), out of 50% v/v chloroform/methanol. Both the balanced density and stabilized slurry techniques have been widely discussed in the literature (5, 8, 10, 14, 57-61, 64, 73, 110) and all agree that the important aspects of the techniques are:

1) the silica should be dried to remove adsorbed water. Drying can be done in a 150-200°C oven for two hours or overnight.
2) The dispersing medium should wet the packing. Alcoholic and/or halogenated solvents seem to do this the best.
3) The slurry should be vigorously shaken before it is placed in the packing reservoir. The shaking is

invariably done with an ultrasonic bath or probe.

4) The slurry should be pushed into the column as fast as possible which implies the application of high pressure.
5) The column packing assembly must be designed to allow a direct smooth delivery of the slurry into the column. When these suggestions are adhered to the packing of a column with 10 micron particles becomes easy, with practice; the packing of columns with particles of 5 or 3 microns is difficult and is more art than science.

Columns were 15, 20 or 25 cm lengths of cleaned 3.2 mm internal bore polished stainless steel tubing (Altex Scientific, Inc., Berkeley, CA). Columns were terminated, at the exit end only, with 1/4" diameter 10 stainless steel screens (Analabs, North Haven, CT). Longer columns were made by coupling shorter columns with a drilled out Swagelok union (Crawford Fitting Co., Solon, OH) and a 1/4" O.D. x 1/8" I.D., 1/8" thick aluminum seal which was packed in place at the time the lower column was packed. The packing reservoir consisted of one meter of the polishes bore tubing coupled to the column with a drilled out Swagelok union and an aluminum seal. The volume of this reservoir-column assembly was 9-10 mls, which fixed the slurry concentration at about 10% w/v, which is roughly optimal for these slurry methods (5, 110). Column packing pressure were generated with a Haskel double air head chromatography pump (Haskel Engineering and Supply Co., Burbank, CA).

Columns to be equilibrated with a stationary phase were attached to a Milton Roy controlled volume mini pump (Milton Roy Co., St. Petersburg, FL) and at least ten column volumes of a 1-3% w/w solution of the stationary phase in 55% v/v acetone-methanol was pumped through the column. All columns were dried by passing nitrogen through them at about 1 l/min for a minimum of two hours, before mounting in the high speed gas chromatograph.

Packings were bonded according to the procedure used by Majors (80) and were packed as described above.

C. The Chromatograph

The assembled chromatograph is shown in Fig. (12). Aside from a specially designed injection system and consideration of the design principles discussed in section III.A of this thesis there is nothing sophisticated about the chromatograph. Indeed, one should note that the only high speed instrumentation required is a fast recorder, A of Fig. (12).

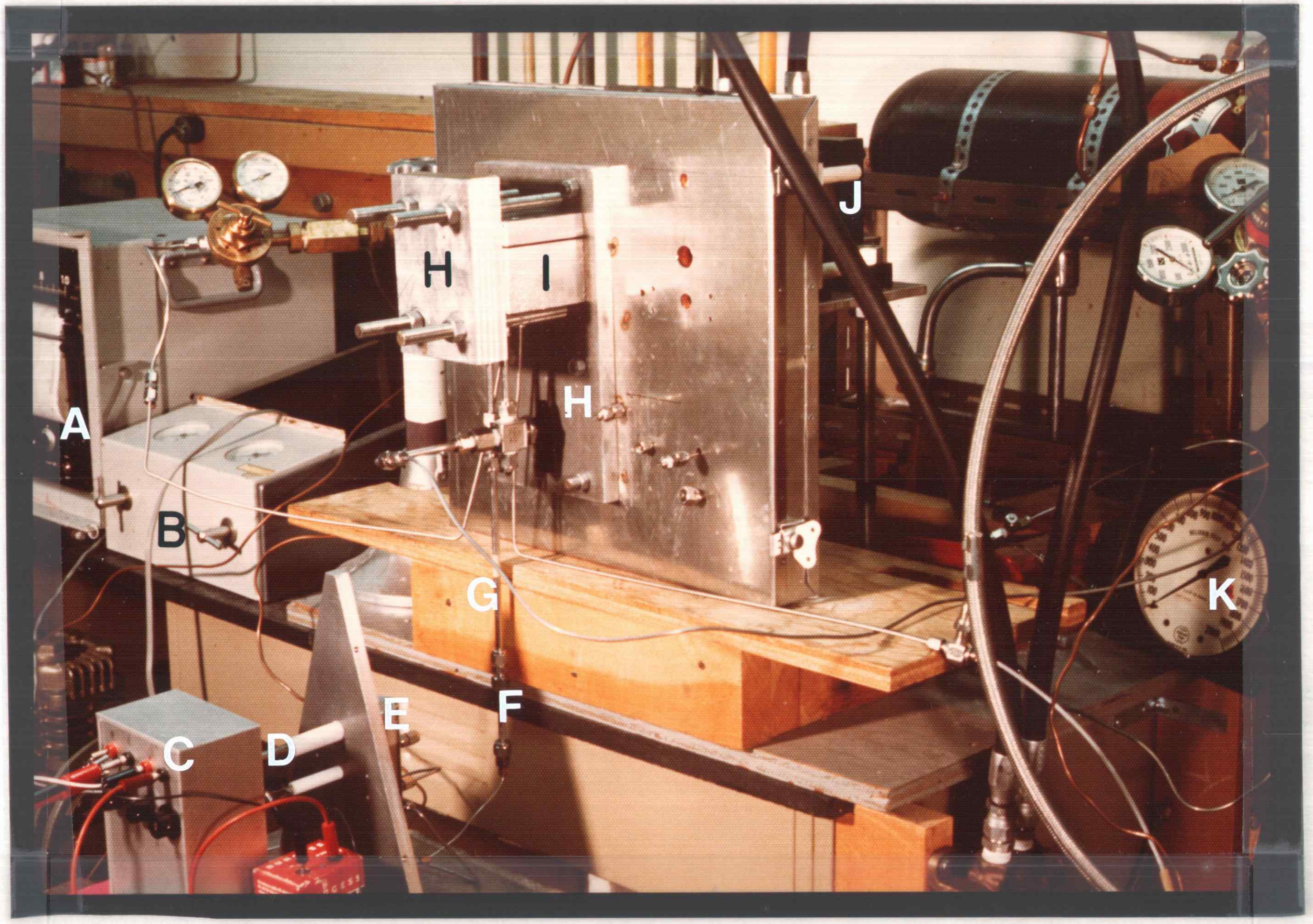


Figure 12. Chromatograph. A. Esterline angus high speed recorder; B. Manifold for detector gases; C. Electrometer (see Fig. (6)); D. Signal conductor cable (see Fig. (2)); E. Flame ionization detector (see Fig. (2-4)); F. Splitter (see Fig. (5)); G. Column; H. Valve face plates; I. Valve (see Fig. (7—11)); J. 5 inch air cylinder; K. Helicord test gage, 1/4% accuracy.

IV. RESULTS AND DISCUSSION

A. Surface Modification of the Silica

The silicas, as they were received, retained hydrocarbons far too strongly for fast chromatography. For this reason an investigation was undertaken as to which types of stationary phases would best modify the adsorbents and to answer the question whether bonding silanes would be preferred to adsorbing stationary phases. Table 1 shows data on 25 cm columns with various adsorbates on 10µ Spherisorb silica. From the table it is evident that OV-210 not only improved peak symmetry but also reduced the highly retentive nature of the silica. The Kel-F's seemed to have promise from the standpoint of reducing retention but the columns were low in permeability and gave poor peak symmetry. The reason for this became clear when the Kel-F #90 packing was examined; it was found to be inhomogeneous apparently as the result of the stationary phase not wetting the silica.

From the stationary phase study one has to wonder whether the way to get a more uniform layer of partitioning material and to further reduce retention would be to bond a fluoro containing silane, followed by exhaustive silanization with trimethylchorosilane. But from Table 2 and Figure (13) it is clear that adsorbing a stationary phase

Table 1. Effect of adsorbing stationary phases onto 10μ silica.

Spherisorb Silica Plus	$\bar{u}$ cm/sec	k_{C_5}	Symmetry Index C_6
---	13	38	3.9
TEG	10	31	1.7
DNP	12	30	2.3
OV-210	12	27	1.3
KEL-F #90	3.0	8	3.7 for C_5
KEL-F #10	11	30	---

Table 2. Effect of bonding silanes to 10μ silica.

	Lichrospher SI500 bonded with silanes	Lichrospher SI500 with adsorbed OV210	Spherisorb S10W with adsorbed OV210
L, cm	36	41	51
U, cm/sec	4.9	8.1	14
k_{c2}	0.33	0.21	0.79
k_{c3}	1.3	0.77	3.1
k_{c4}	3.9	2.4	9.8
H_{c3},	211	41	40
K°, $cm^2 \times 10^{-9}$	0.47	0.75	1.2

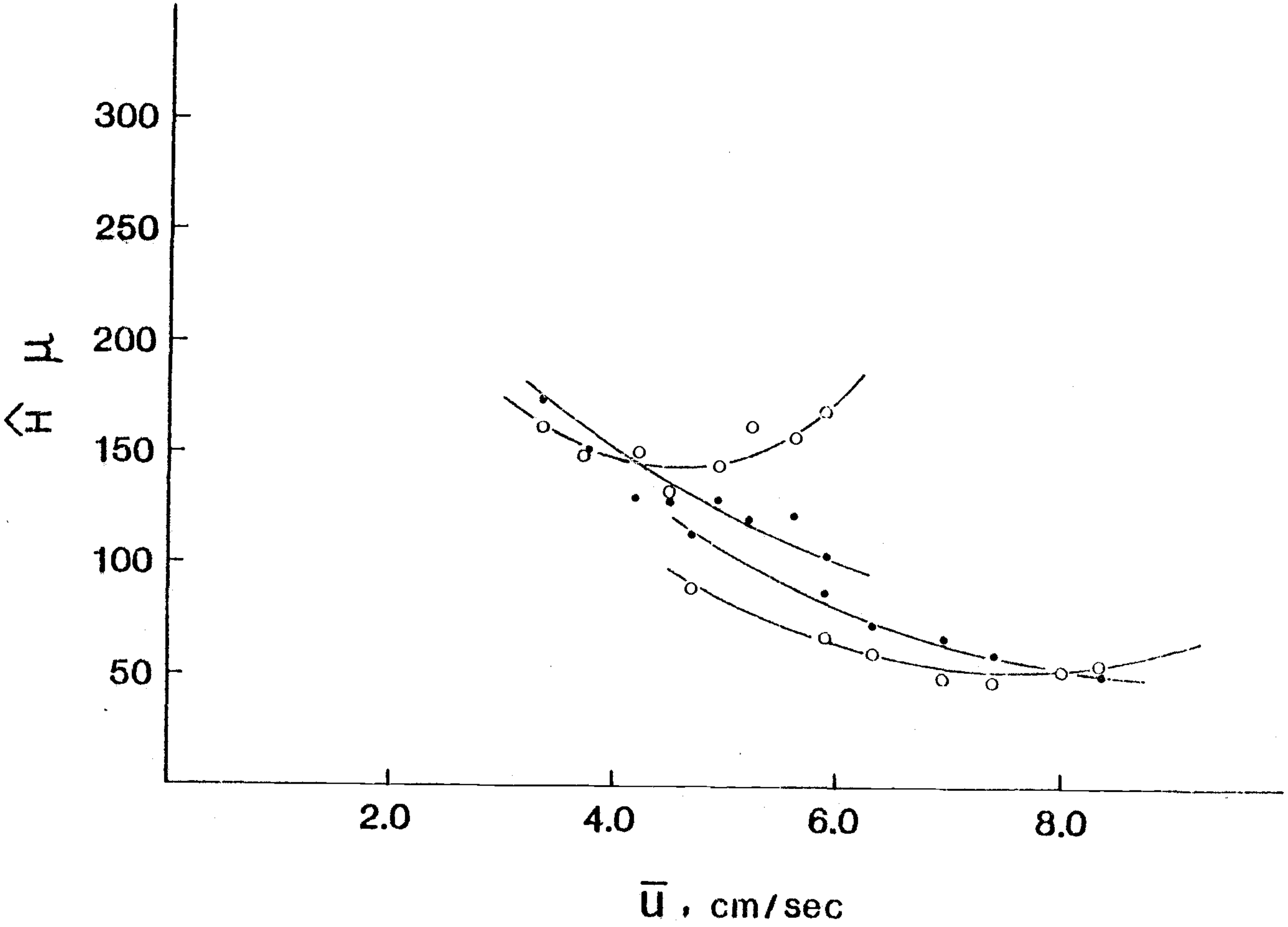


Figure 13. Upper plate height curve methane, k=0 (·) and ethane, k=0.33 (o) on 10μ LiChrospher Si500 bonded with 3,3,3 Trifluoropropylmethyldichlorosilane and Trimethylchlorosilane. Column length = 36 cm. Lower plate height curve for methane, k=0 (·) and ethane, k=0.21 (o) on 10μ LiChrospher Si500 with adsorbed OV-210. Column length = 41.5 cm.

worked better than bonding silanes. Both plate height and retention were higher while permeability was lower for LiChrospher Si500 bonded with 3,3,3-trifluoropropylmethyldichlorosilane and trimethylchlorosilane over LiChrospher Si500 with adsorbed OV-210. Higher plate heights were the result of a mass transfer term strongly dependent on retention and velocity as seen in Figure (13). Table 2 also shows the advantages of working with a packing having a very narrow particle size distribution. The permeability of Spherisorb is 50% greater than that of LiChrospher; however, because Spherisorb has four times the surface area of the LiChrospher Si500 it also gave four times the retention.

The chromatograms shown in Fig. (14-16) demonstrate the strong dependence the surface structure of the silica has on retention. The chromatograms in Fig. (15, 16) were obtained on different batches of the same silica, the one in Fig. (14) on a slightly different silica: each column was packed, equilibrated with stationary phase and dried in exactly the same manner. The saturated hydrocarbons in Fig. (15, 16) were eluted off both columns with the same retention times, as it should be. The PSM-600 silica retained the saturated hydrocarbons in Fig. (14) longer than the LiChrospher Si500 silica as one would predict from the differences in packing densities and surface areas of the silicas, a prediction which is straightforward.

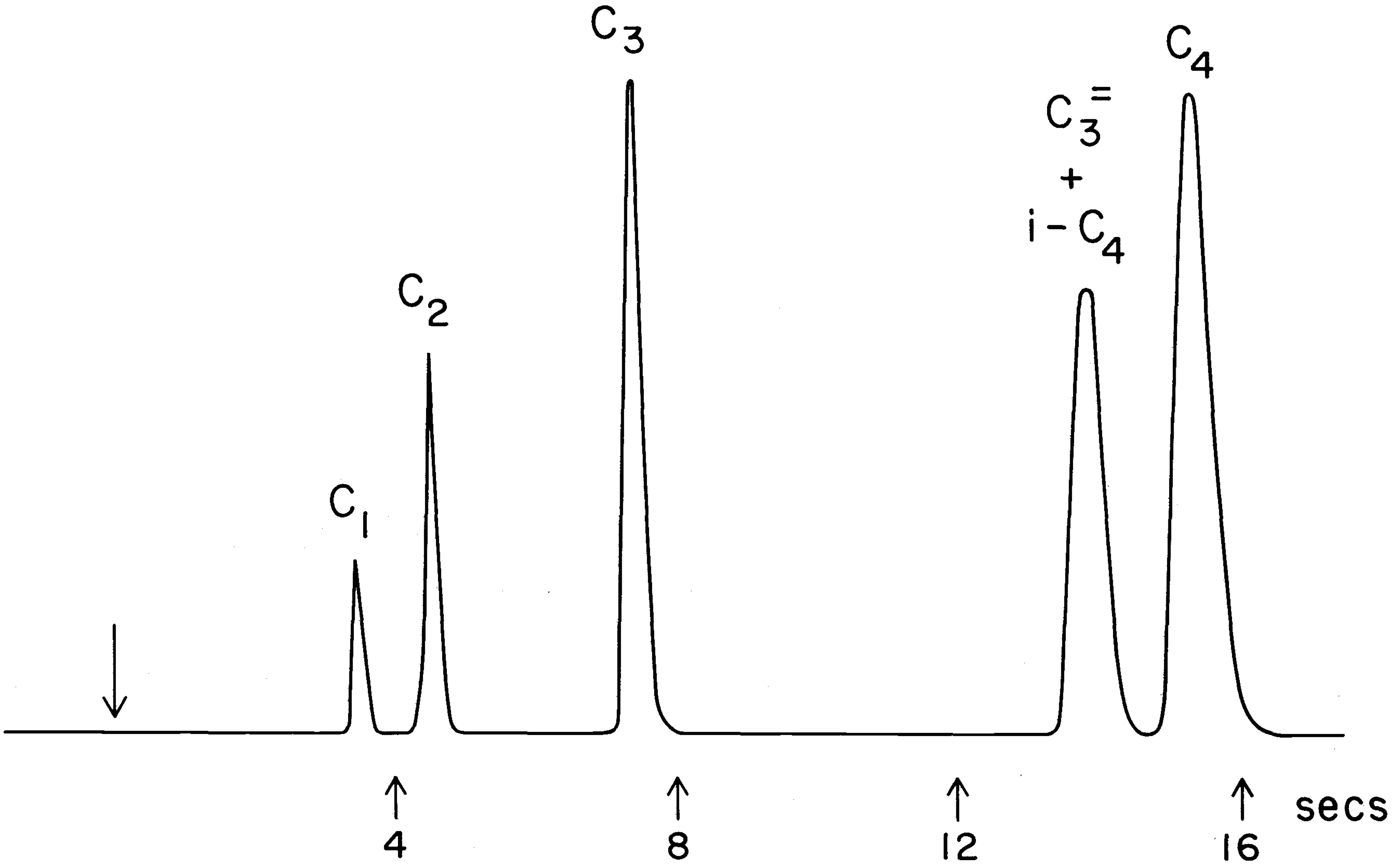


Figure 14. Hydrocarbon mixture on 26.5 cm of 7.1μ PSM-600 silica with adsorbed OV-210. P_i = 700 psi. $\overline{u}$ = 7.6 cm/sec. $\hat{H}$ (C_3) = 60μ.

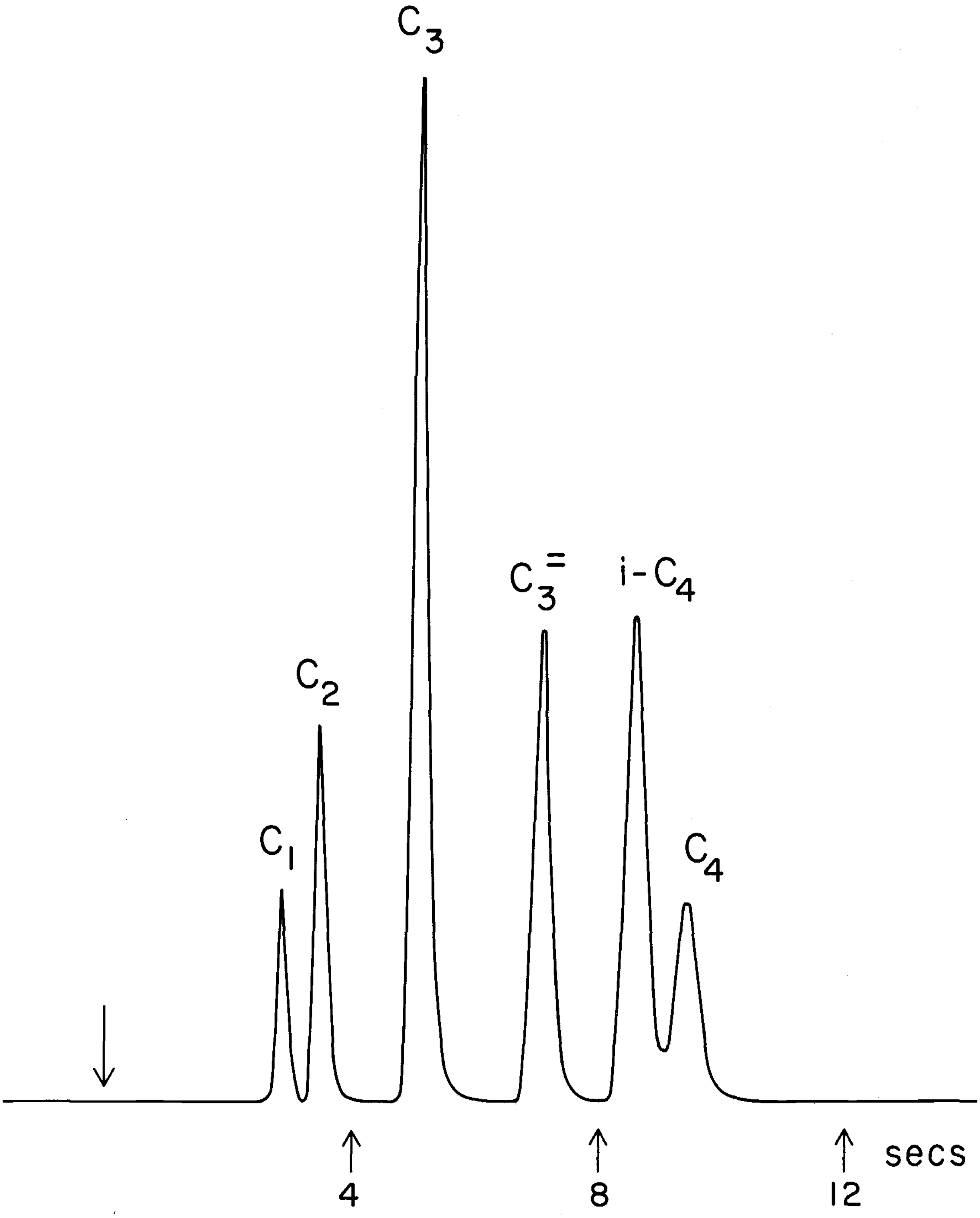


Figure 15. Hydrocarbon mixture on 21.5 cm of 10μ LiChrospher Si500, EM lot no. YE422 with adsorbed OV-210. P_i = 400 psi. $\bar{u}$ = 7.5 cm/sec. $\hat{H}$ (C_3) = 92μ.

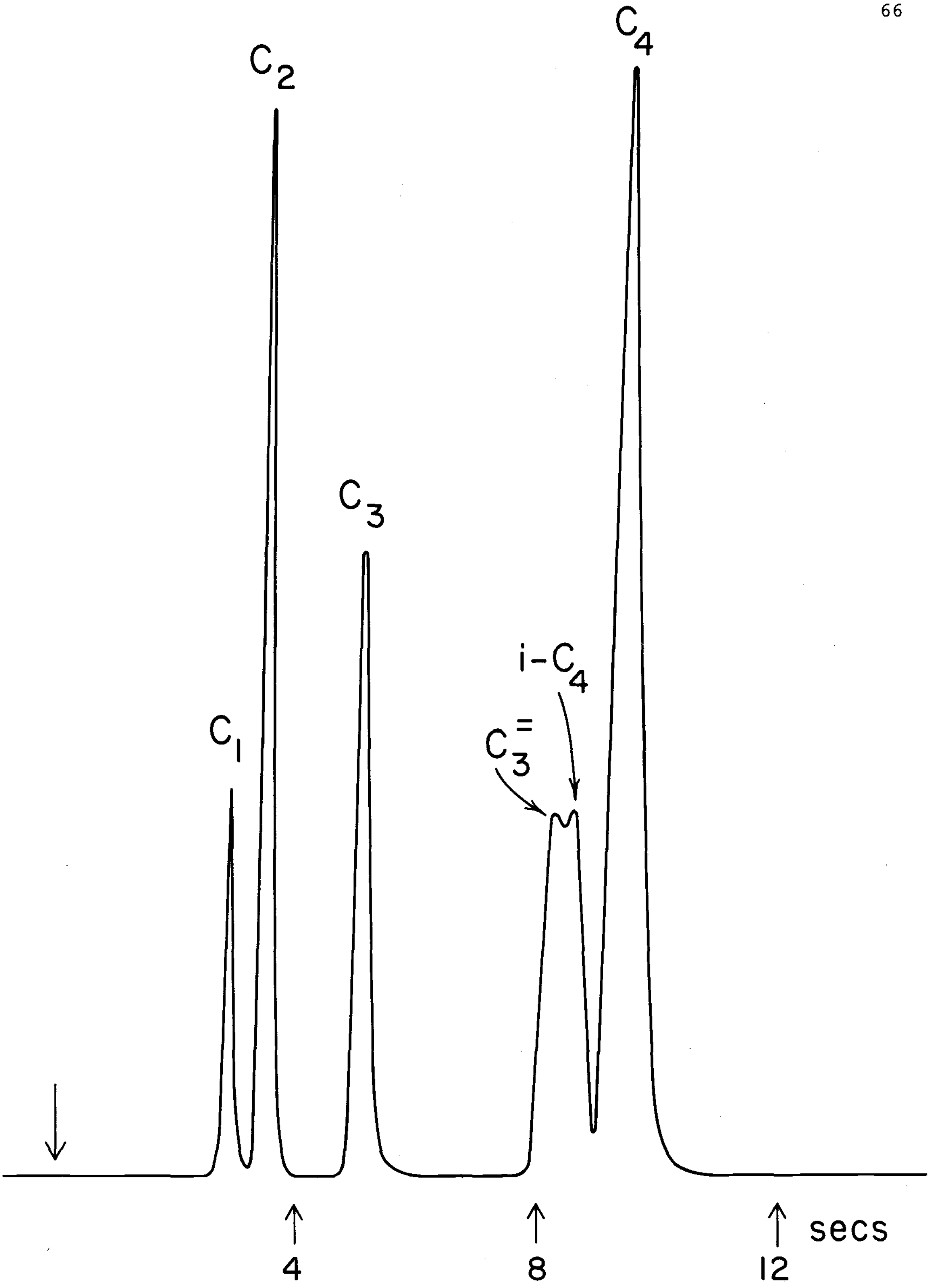


Figure 16. Hydrocarbon mixture on 21.5 cm of 10μ LiChrospher Si500, EM lot no. YE 461 with adsorbed OV-210. P_i = 500 psi. $\bar{u}$ = 7.5 cm/sec. $\hat{H}$ (C_3) = 76μ.

For example, when the PSM-600 silica has a surface area of 45 m^2/g, 5 m^2/g less than LiChrospher Si500 but a greater packing density (6.0 g/m as opposed to 4.8 g/m) then a hydrocarbon should be retained 6.0/4.8 x 45/50 longer on the PSM 600 silica for columns of equal length and operated at the same velocity. Hence for the propane peak in Fig. (14) one would expect a retention time of 5.1 x 6.0/4.8 x 45/50 x 26.5/21.5, or 7.1 seconds based on the retention time of the propane peaks in Fig. (15, 16); a value close to the observed retention time of 7.4 seconds. While the silicas are behaving predictably for the saturated hydrocarbons they are behaving unpredictably for unsaturated hydrocarbons. The propylene peak in Fig. (16) was retained a full second longer than in Fig. (15) which are chromatograms obtained on different batches of the same silica. The propylene was retained even longer on the PSM-600 silica which was used to obtain the chromatogram in Fig. (14). From the propylene peaks in Fig. (15, 16) one would predict a retention time for the propylene peak in Fig. (14) of 9.9 and 11.4 seconds respectively, well below the observed 13.9 seconds. With respect to resolution the column used to produce the chromatograms in Fig. (15) is preferred, from the standpoint of efficiency it would stand last.

A possible explanation for the variation of retention time of the unsaturated hydrocarbons on the silicas is different amounts of different adsorption sites from batch to batch and from one manufacturer to another. The surface of this synthetic silica is predominantely SiO_2 and SiOH groups and the BET method of measuring surface area probably does not discriminate between them, although chromatographically they behave differently. The SiOH group with its inherent strong dipole can, in addition to interacting by dispersion forces, induce a dipole in unsaturated molecules, like propylene, whereas the SiO_2 group by virtue of the nonbonding electrons on the oxygens, offers more dispersion interactions than a methylene group. Hence a variation in the ratio of these groups on the surface of silica could lead to a difference in retentivity for unsaturated hydrocarbons but not for the aliphatics.

B. Fast Gas Chromatography

The Performance of Microparticle Silica in Gas Chromatography

Several attempts were made by both slurry and hand packing techniques to successfully pack 20μ silica into an efficient column. Fig. (17) shows the plate height curve for 20μ Spherisorb packed by two techniques. The minima are at about $7d_p$ which are twice that for a well packed column. Despite the relatively high plate height for the slurry packed column it performed quite well, as one can see from the chromatograph in Fig. (18). Based on the

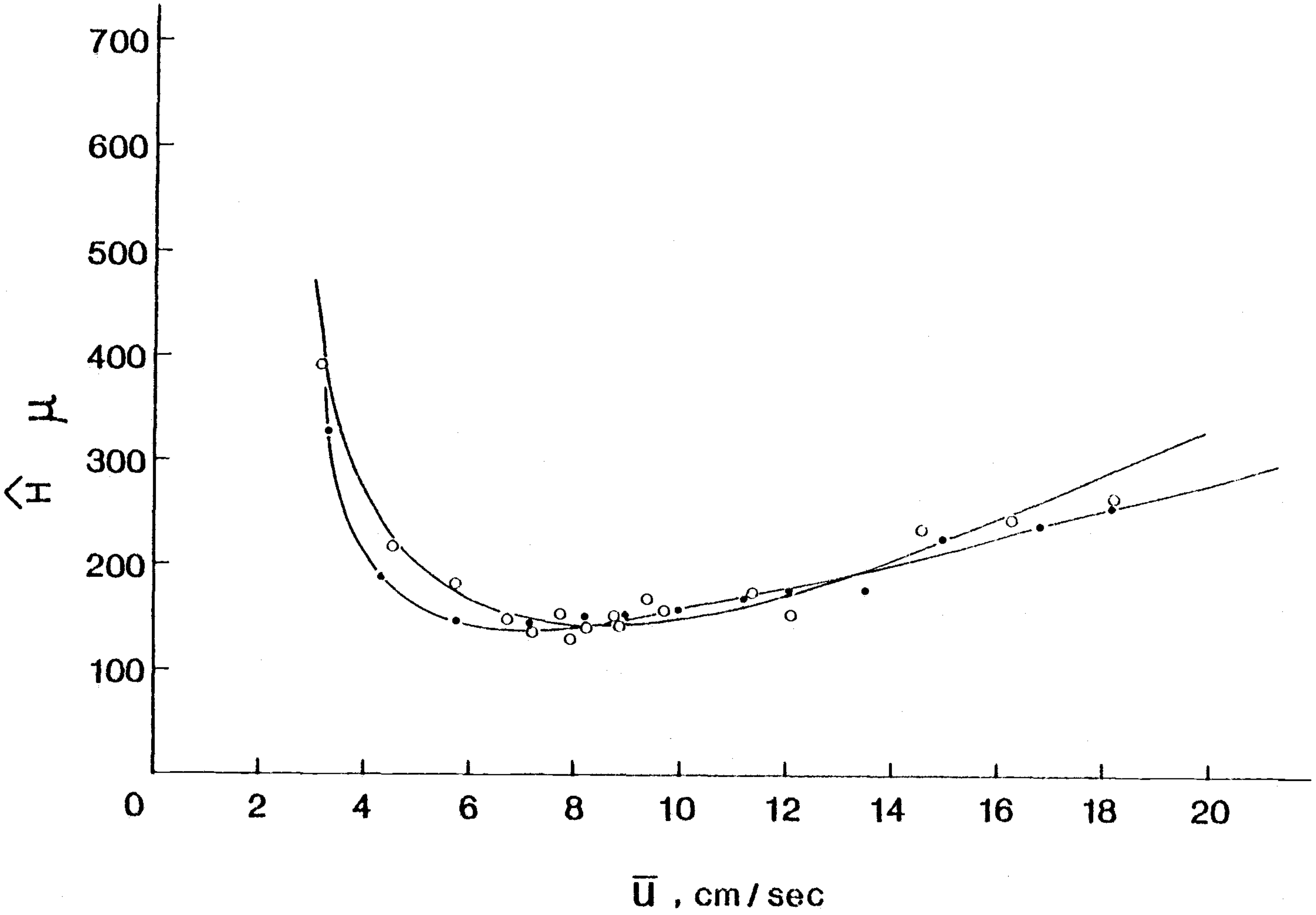


Figure 17. Plate height curve for methane (k=0) on 20μ Spherisorb with adsorbed OV-210. o = hand packed, · = balanced density slurry packed, column length = 58 cm.

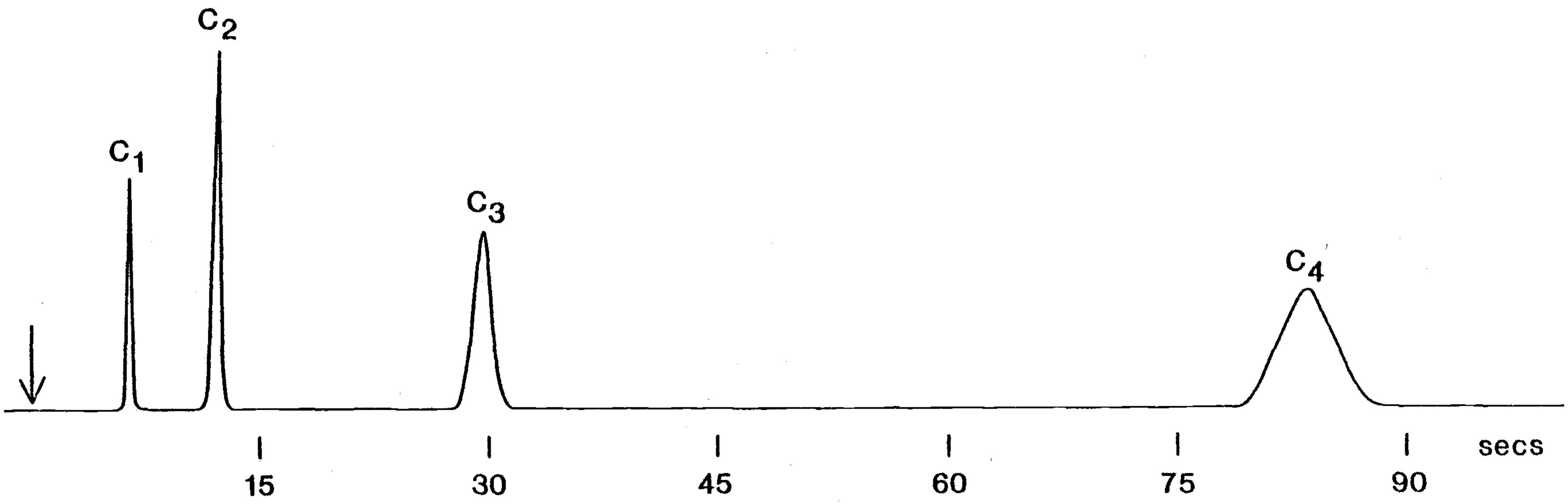


Figure 18. Saturated hydrocarbons on 58.0 cm of 20μ Spherisorb with adsorbed OV-210. p_i = 385 psi. $\bar{u}$ = 9.2 cm/sec.

propane peak the column had generated 85 N_{eff}/sec, 6500 N/m and gave a resolution of 12 for the ethane-propane pair.

It is interesting that the two packing techniques gave similar plate height curves, with minima at twice that for a well packed column. Hand packing techniques are known to be more difficult for smaller particles but with effort some (50, 55) have been able to hand pack particles as small as 30-40 microns. Conversely the high pressure stabilized slurry techniques work the best for small particles (5 or 10 micron) and give difficulty for larger particles since the settling rate of the particles in the various dispersing media is proportional to the square of the particle diameter. Hence the packing of an efficient 20μ column may be difficult since this particle diameter lies outside the range where both techniques are known to work. Little data can be found in the literature on 20 micron particles which in itself helps to support this conclusion.

Fig. (19, 20) are plate height curves obtained on 10μ Spherisorb and LiChrospher Si500 respectively. The ascending branches for the two solutes on Spherisorb were not obtained since the maximum working pressure of the valve was reached for that column at 14 cm/sec. Fig. (20) is indicative of how shallow the minimum of the plate height curves on these particles are in gas chromatography; the plate height increased only 50% over the velocity range

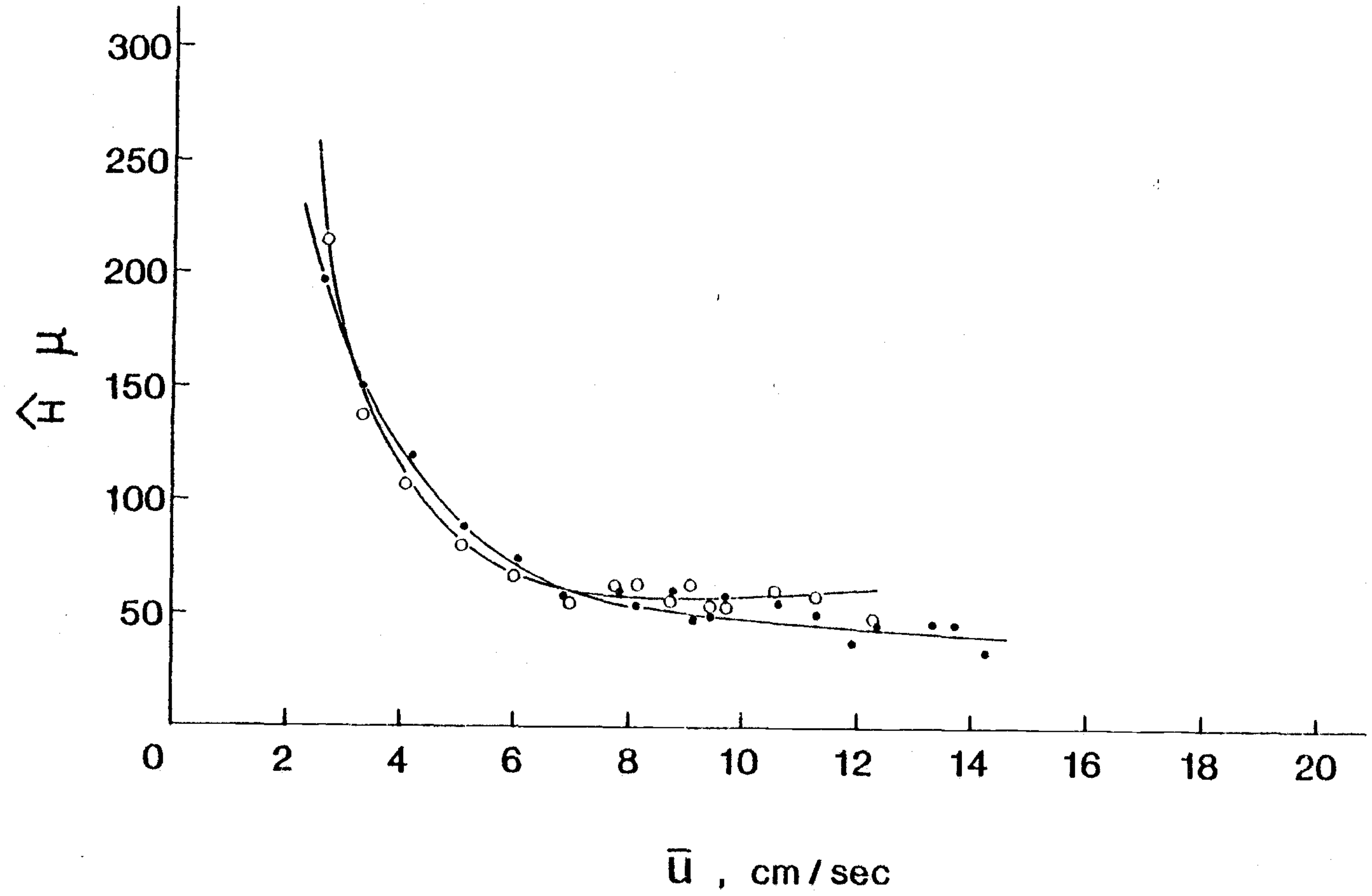


Figure 19. Plate height curve for ethane, k = 8.0 (·) and propane, k = 3.20 (o) on 10μ Spherisorb with adsorbed OV-210. Column length = 39 cm.

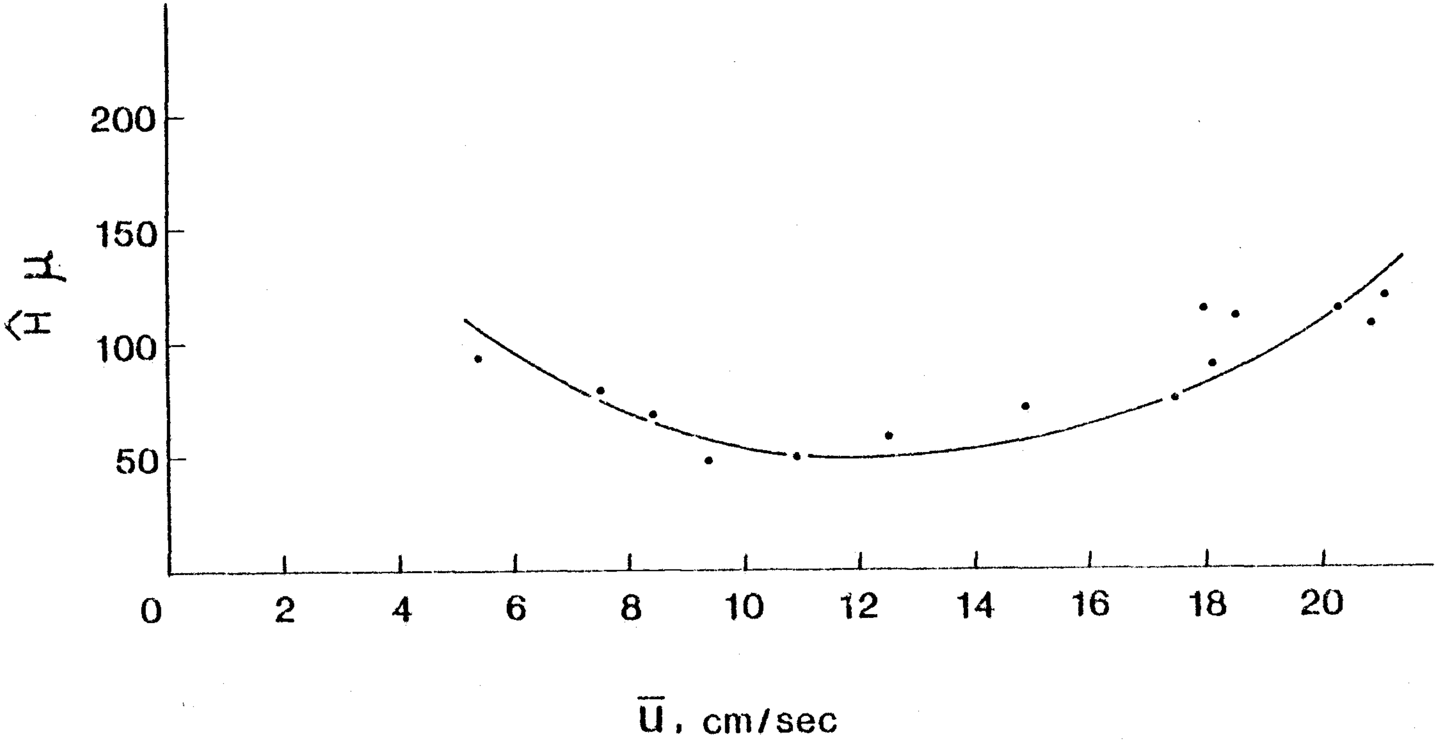


Figure 20. Plate height curve for propylene (k = 1.6) on 10μ LiChrospher Si500 with adsorbed OV-210. Column length = 21.5 cm.

from 7-17 cm/sec.

The high speed chromatograms in Fig. (21, 22) illustrate the performance one can obtain on 10μ silica in gas chromatography. The chromatogram in Fig. (21) was produced by the Spherisorb column in just 38 sec, the resolution between ethane and propane is 22, the plate count of the ethane peak is 30,000/m ($H = 3.3d_p$) which corresponds to 470 N_{eff}/sec or 2400 N/sec; an analysis speed that has not previously been attained on a packed column. The chromatogram in Fig. (22) further demonstrates this performance by showing the separation of a 6 component mixture in 33 seconds with a resolution of 4 between the most difficult pair. Equation (16) shows that resolution can be sacrificed to decrease the analysis time; this is demonstrated dramatically in Fig. (23). The analysis time to the butane peak in Fig. (22) is about 18 seconds but in Fig. (23) where the resolution is minimal it only is about 2.5 seconds.

If the sole interest is in the light hydrocarbons then, as the chromatogram in Fig. (22) demonstrates, LiChrospher Si500 with adsorbed OV-210 is an ideal packing. The most difficult pairs in the separation are propylene-isobutane and isobutane-butane with the column capacity ratio for isobutane equal to 2, which is in the optimal range for HSGC. Hence, the column is giving good selectivity and the right amount of retention towards the light hydrocarbons. However if higher paraffins are to be chromatographed then

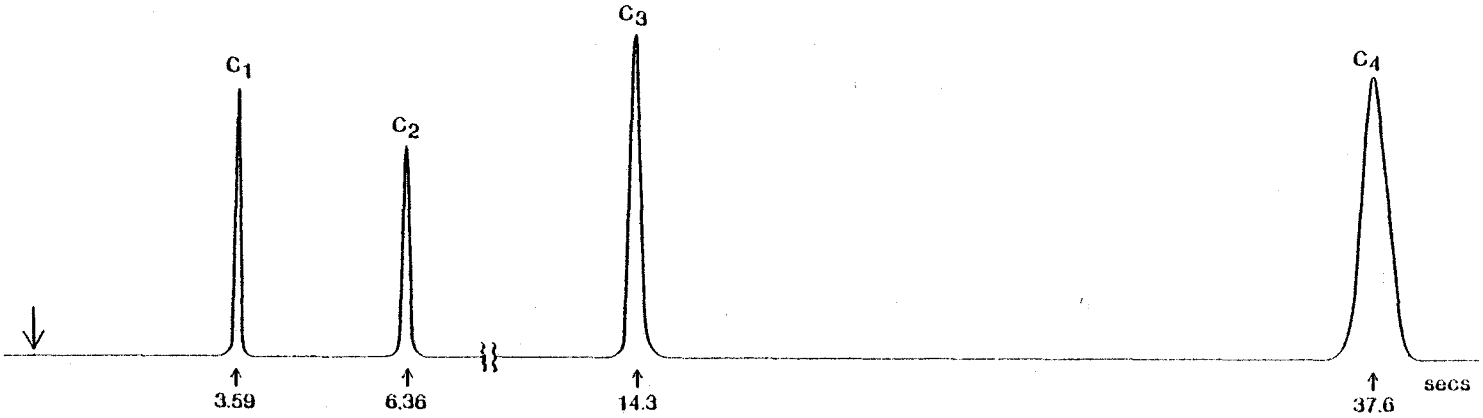


Figure 21. Saturated hydrocarbons on 51.0 cm of 10μ Spherisorb with adsorbed OV-210. p_i = 900 psi. $\bar{u}$ = 14.3 cm/sec.

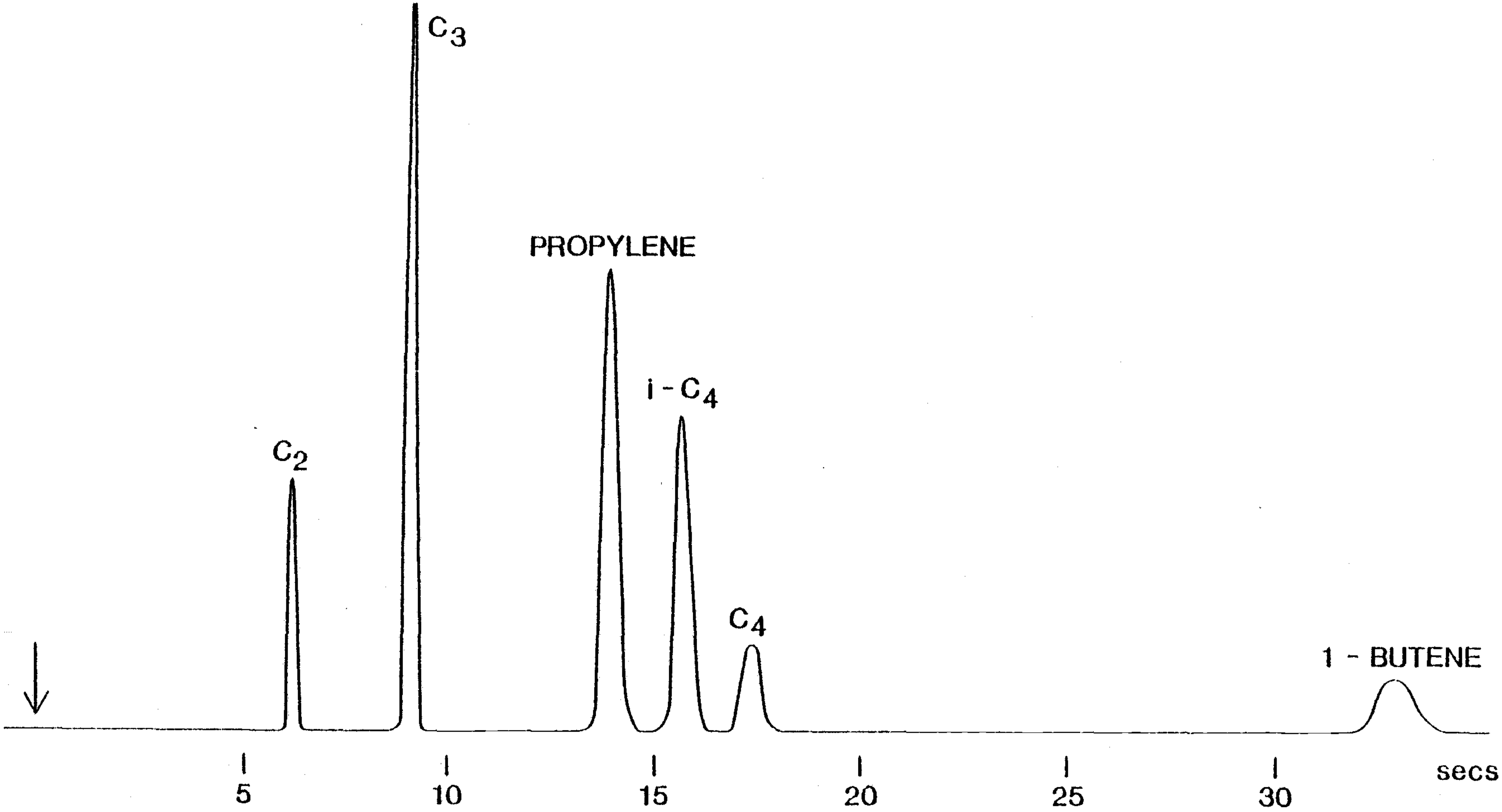


Figure 22. Hydrocarbon mixture on 41.0 cm of 10μ LiChrospher Si500 with adsorbed OV-210. p_i = 700 psi. $\bar{u}$ = 8.2 cm/sec.

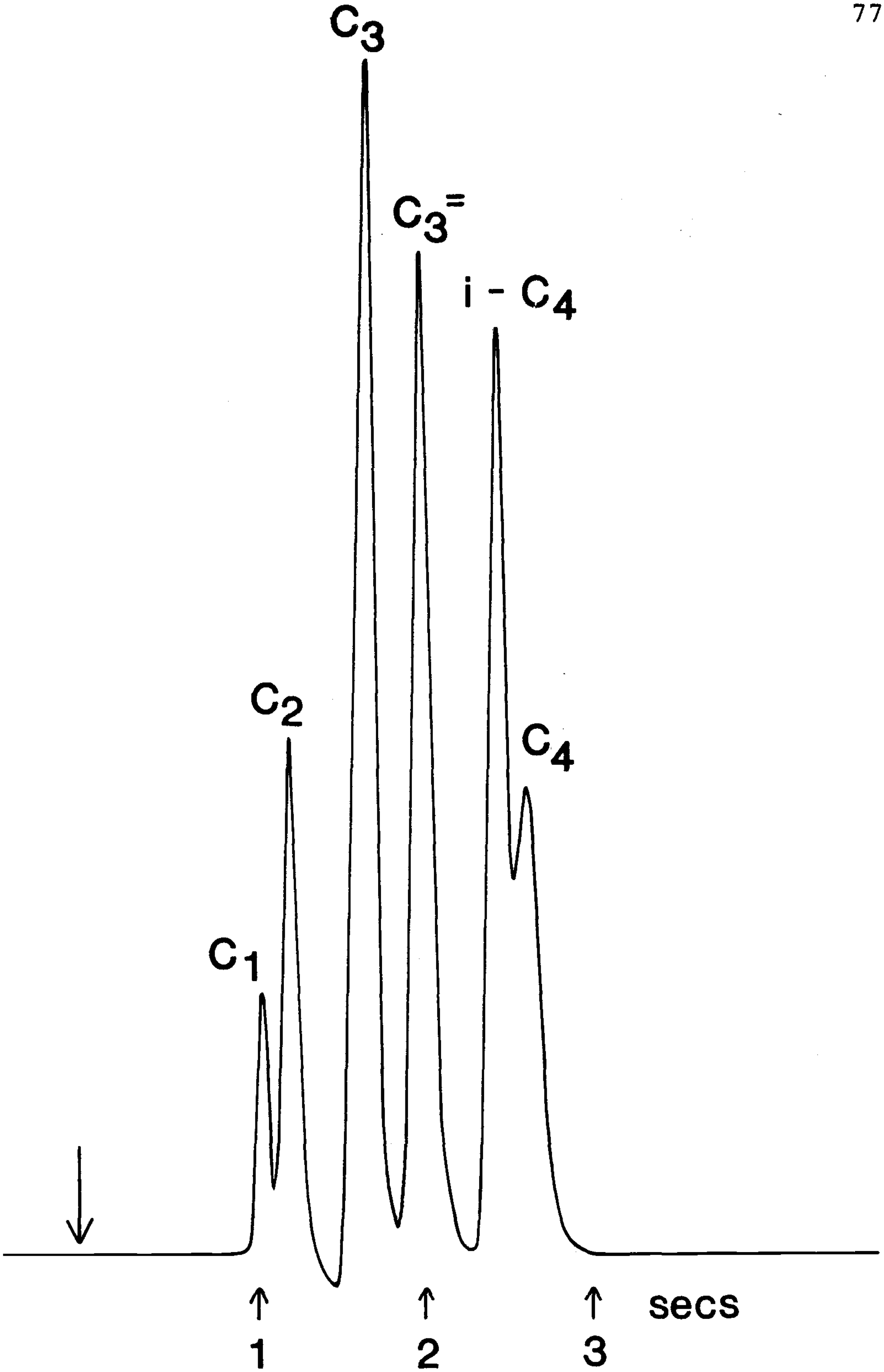


Figure 23. Hydrocarbon mixture on 21.5 cm of 10μ LiChrospher Si500 with adsorbed OV-210. p_i = 1250 psi. $\overline{u}$ = 21 cm/sec. t_z = 2.6 sec.

it is evident from Tables 1 and 2 that both Spherisorb and LiChrospher would be too retentive, even with adsorbed OV-210. The situation could be improved by using an adsorbent with a much lower surface area but for reasons stated later it would be more desirable to find a better stationary phase, i.e., one that could modify the activity of silica to a greater extent. Although OV-210 is inadequate, still the fluorosilicones seem to be the most desirable from this respect: the C-F bond with its high bond dipole moment but low bond polarizability makes it an excellent substrate for reducing the dispersion interactions of paraffins. Thus, a silicone oil containing a higher percentage of C-F groups would be promising from this respect.

Guillemin _et_ _al_. (41) varied the physical properties of 60 to 80 mesh porous silica beads and while using hexane as a probe monitored column efficiency. They found optimum efficiency with silica beads of surface area 25 m^2/g and pore radii of 200-800Å, although silicas with smaller surface areas and larger pore radii did well. Huber, Lauer and Poppe (50, 72) and Cirendini _et_ _al_. (11) used Spherosil XOC-005 which is a porous silica bead of low surface area (5 sq m/g) and large radius pores. While there is no doubt in the excellence of their data, silica of this type in particle diameters of 5 and 10 microns would be very difficult to pack. Slurry packing is made more difficult because low surface areas make the packing hard to wet, and to disperse, even with polar solvents. Large pore radii result in fragile packings that crush under normal slurry packing pressures. Ultimately silicas with physical properties like Spherosil XOC-005 might have to be slurry packed using pressures as low as 1000-2000 psi from methanol and upwards (8): the silica would most certainly have to be of a narrow particle dize distribution. It is possible that the forced draft-vibration techniques (11, 50) might work here, at least with 20 micron particles, but for smaller particles it would be difficult to implement. Porous silica beads like those of Kirkland's PSM-1500 or PSM-4000 silica might well be preferable in this area of GC. These particles are made by a process (60) different from the way most silicas are made (107) which apparently is the reason why they are mechanically stronger. The PSM-1500 and PSM-4000 have surface areas in the range of 10-20 m^2/g yet Kirkland (60) packs them at high pressures.

C. The Comparison of Column Types

The objective of this unit is to compare the data of this work with that of the literature. Primarily comparisons will be made between the conventional packed and the open tube columns and between small particle packed columns (SPPC) operated in liquid and in gas chromatography.

Finally, from the tabulated data a search will be made for verification of Eq. (18-22).

Functions Used to Measure Overall Column Performance

Many functions have been proposed for the job of indicating overall column performance; they can be loosely classified into three categories. The first consist of all functions which compare columns on the basis of analysis time or the speed of a separation, members of this group are N/t (87), N_{eff}/t (20), $N_{eff}/t^{2/3}$ (44), Rs/t (26), $Rs/t^{1/3}$ (44), SV/t (24, 25), t_{Ne} (45, 46) and SP (54). Next, is the group of functions which compare columns on the basis of resolving power; here belongs the resolution per time functions and the effective plates per time functions, as well as N_{eff}, EPN (51), TZ (52), SV (24, 25), SV/t (24, 25), SP (54) and Rs^2/L (31). Finally, overall column performance can be gauged by functions which measure the expenditure of some limited instrumental parameter, usually pressure, examples of this group are PP (45, 46), SPI or PI (37), ΔP_{ne} (45, 46), the critical inlet pressure (28, 29, 32, 33) and any consideration of pressure drop per plate number (23, 69). This last category of functions become relevant only when the instrument cannot generate enough pressure to operate the column efficiently.

If the two most important goals of chromatography are the achievement of a separation in a reasonable amount of time, then the most logical functions to choose to measure column performance are those of separability (TZ, EPN, SV, Rs, N_{eff}, etc.) as a function of time. These functions are certainly the most popular in the literature and we will emphasize them as did Guiochon (44) in his review of column types. Generally a conclusion reached by using one separability function as a function of time will not be altered by using another function of separability as a function of time. This author has tried most of the above separability per time functions to indicate overall column performance and for our purpose N_{eff}/t worked the best. However, since others are more popular and since we would like to assure a fair and objective comparison of column types we will also use TZ, Rs^2/L, Rs/t, N_2/t, PP and PI.

The number of effective theoretical plates was first defined by Purnell (90), where it was called the separating power, as

$$S = 16\ Rs^2 \frac{\alpha_{yx}^2}{(1 - \alpha_{yx})^2} \qquad (25)$$

The separating power is a measure of the resolving power of the column which accepts the selectivity as an important factor as well as the capacity to avoid dispersion of the zones. Desty *et al.* (20) called the separating power the number of effective theoretical plates and used the following equations as did others (45, 46) to define it

$$N_{eff\ y} = 16\left(\frac{t_{sy}}{w_y}\right)^2 = N\left(\frac{k_y}{1 + k_y}\right)^2 \qquad (26)$$

i.e. using the usual method of determing N except that the retention time is measured from the unretained peak instead of from the injection time (see Fig. 1). The number of effective theoretical plates becomes equal to the separating power when the zones are gaussian and when $w_x = w_y$. However Eq. (26) does not convey the same information about the column's ability to separate X from Y as does Eq. (25). While Eq. (26) does have a measure of the retentive power of the column (t_{sy}) it does not measure the columns, "separating power" which is incorporated into Eq. (25) through Rs and α_{xy}.

An expression for the number of effective plates per unit time can be derived for any pair in the chromatogram (for convenience let this be our X-Y pair) by entering Eq. (25) into Eq. (16), assuming $N_{eff} = S$ and $k_y = k_z$ to give

$$\frac{N_{eff\ y}}{t_y} = \frac{k_y^2}{(1 + k_y)^3} \ \frac{\bar{u}}{\hat{H}} \qquad (27)$$

Equation (27) indicates that if fair comparisons are to be made between and among column types using the function N_{eff}/t they must be made with the columns operated under their optimum conditions, i.e., operation in the neighborhood of the van Deemter minimum and with k_y from about 1-6.

Guidelines for Making Comparisons of Column Types

The operation of all column types under the same experimental conditions is impossible since each column type (and indeed different columns of a given type) demands a different set of experimental conditions for efficient operation. However, if each column is operated under optimum conditions and a series of test solutes chromatographed on them, then some useful data can be obtained which would allow us to make comparisons among different columns of a given type and between column types.

In GC the n-alkanes serve nicely as test solutes. Among the reasons given by Guiochon (44) are: they have relative retentions which are reasonably constant at a given temperature for two different adjacent pairs of alkanes on a given stationary phase and for the same adjacent pairs on different stationary phases. Thus, the influence of large variations in $\alpha/(\alpha-1)$ on analysis time and resolution is moderated to a large extent. Furthermore there is more data in the literature on this group of compounds than on any other.

In LC the situation is more complicated. A great variety of mobile as well as stationary phases can be used, samples can be ionic or molecular, they can have molecular weights of a few hundred or of several million, hence no series of test solutes exists for LC, as the n-alkanes do for GC, that can be chromatographed in all modes. However this should not stop one from making performance comparisons between the various modes of LC or between the techniques of liquid and gas chromatography. What it does indicate though is the need for some basic guidelines which, if followed, would enable columns in LC to be compared on a basis of performance or perhaps one could normalize the data for a key variable like α. Even then the job of making column comparisons in LC might have been very difficult if it were not for the fact that a large amount of today's LC is carried out on small porous particles of silica or silica based materials. This lends uniformity and consistency to all the modes of LC since the packing has a common structure and most likely a common packing technique (the high pressure slurry technique). Furthermore, silica of this type has been used in GC not only for this thesis, but in other works (11, 40-42, 50, 72) and this constitutes a bridge between the two techniques which could be used to make direct comparison between them. Thus, most of the data tabulated here is on small porous particles of silica with the LC data taken from the literature using the following guidelines:

1) Data was chosen so that the test solutes would have a relative retention time of about two and a column capacity ratio in the range of 1-6, the optimum range giving minimum time. However

interesting data with α's and k's outside these ranges was not discarded.

2) Solutes were chosen in a molecular weight range of 100-500 (except for GPC) and mobile phases chosen with a viscosity of 0.4-0.5 centipoise. Hence D_m will vary very little from column to column since it is proportional to the square root of the molecular weight but inversely proportional to the viscosity.

3) In GPC data was taken on polymers having a low molecular weight dispersion and then several molecular weight ranges were examined. The gel permeation data on the polystyrene standards were good for this.

The Relative Performance of Various Column Types

Halasz and Heine (45, 46) classified chromatographic columns into seven types based upon the column's permeability, phase ratio, and the nature of the stationary phase's support. For the most part their scheme will be retained here, even though only two of the five packed column types classified by them are prevalent today. These are the conventional packed column (CP), which still enjoys considerable use in both gas and liquid chromatography, and the porous layer bead column (PLB), invented to diminish the stagnant mobile phase mass transfer contribution to $\hat{H}$. The porous layer bead column seems to be more popular in LC than in GC but even there it is losing ground to the SPPC. Open tubular columns were classified by them into two groups; the conventional open tube column which we shall call the wall coated open tube column (WCOT) and the porous layer open tube column (PLOT), which we shall consider as a subgroup of the support coated open tube column (SCOT).

Since Guiochon's and Halasz' reviews (44-46) on the comparison of column types tremendous developments have been made in the synthesis of new packing materials and the fabrication of columns. The conventional packed column has been improved enormously; however the improvements, up to now, have been felt only in liquid chromatography where microparticles and the techniques for packing them are prevalent. If improvements in the gas chromatographic packed column have been made at all, they have been through the construction of small bore packed columns (called micropacked columns and by some packed capillaries) and the forced draft-vibration technique used to pack them. Developments also have been made in glass open tubular columns which have gained in popularity over the years. Glass drawing machines are commercially available and several workable methods exist for coating the glass tubes. Since these are the major improvement in column design that have taken place in the last ten years they have been favored in our search of the chromatographic literature. Guiochon in his review of column types (44) tabulated more data on open tubes and packed capillaries than on packed columns: here the opposite has been done.

The experimental data compiled in Table 3 is meant to be an extension of Guiochon's Table V (44) although unlike his table, it includes data from columns operated in LC. The experimental data in Table 3 represents data from 51 columns and includes all pertinent data for the calculation of the functions which will indicate overall column performance. Some of the key functions in Table 3 have been summarized in Table 4 for columns of interest.

Tables 3 and 4 demonstrate how inappropriate functions like the PP and PI are in measuring column performance. When they are blindly applied to the small particle packed columns operated in LSC the columns are ranked 10^2-10^3 times poorer than open tube columns operated in gas chromatography, whereas the other two categories of functions give a better assessment of their performance. The recent technological advances of liquid chromatography have made the operation of such columns possible, thus large values for the PP and the PI are almost irrelevant since pressures can be generated to operate them. Even though these parameters are many times inadequate to indicate column performance, the values listed in Table 3 for SPPC operated in GC are among the best ever obtained for packed columns.

Table 3. Experimental Data on Various Column Types.

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Column type	WCOT	WCOT	WCOT	SCOT	SCOT	SCOT	SCOT	SCOT	PC	PC
Type of chromatography	GLC	GLC	GLC	GLC	GLC	GLC	GLC	GLC	GLC	GLC
Column, L, cm	2000	2000	5500	3000	800	2000	3190	3000	1000	1000
id, mm	0.20	0.24	0.11	0.40	0.28	0.28	0.28	0.40	0.45	0.45
dp range,									80-100	125-160
dp (ave),										
Specific permability cm^2 x 10^9	12500^g	18000^g	3800^g	5000^g	24500^g	24500^g	24500^g	5000^g	630	1700
Mobile phase	N_2	N_2	Ar	N_2	He	He	He	N_2	N_2	N_2
Viscosity, centipoise^a	.021	.020	.024	.025	.023	.023	.023	.025	.019	.019
Stationary phase	OV-101	Carbowax 20 M	squalane	OV-225	SF-96	OV-101	OV-101	SE-30	squalane	squalane
Support properties	soft soda-lime glass	etched-lime soft glass	untreated pyrex glass	silanized Chromosorb and nonsilanized glass tubing	NaCl and pyrex glass	Na Cl + BTPPC and pyrex glass	NaCl + BTPPC and pyrex glass	Silanox 101	Chromosorb P	Chromosorb P
Packing procedure	static method	static method	equilibrated dynamic method	two-step dynamic static procedure	dynamic method	dynamic method	dynamic method	dynamic method	draws capillary equilibrates with sol. of st. phase	draws capillary equilibrates with sol. of st. phase
T, °C	100	85	50	220	100	100	100	220	50	50
Solute 1	n-C_{11}	n-C_{12}	n-C_6	n-C_{28}	n-C_{12}	n-C_{12}	n-C_{12}	n-C_{24}		
Solute 2	n-C_{12}	n-C_{13}	n-C_6	n-C_{32}	n-C_{13}	n-C_{13}	n-C_{13}	n-C_{28}	n-C_7	n-C_7
k_1, k_2	2.24, 4.25	1.73, 3.17	0.09, 0.23	1.32, --	--, 15.4	14, 26.2	--, 20.1	3.5, --	--, 2.2	--, 8.5
Relative retention time	1.90	1.83	2.6			1.87				
ΔP, atm	0.46^h	0.31^h		0.12^h	0.21^h	0.57^h		0.12^h	1.5	0.42
$\bar{u}$, cm/sec	13.9	13.9	9.9	8.0	28.1	30.0	34.1	7.5	4.6	3.6
t_{R2}, sec	756	600	683	860^k	468	1810	1970	1800^k	696	2640
N_1, N_2	10800, 10700	10800, 63500	S42000, 424000	37500, --	--, 20000	--, 63300	--, 109000	75000, --	--, 16300	--, 14200
$\hat{H}_1$, $\hat{H}_2$,	185, 187	185, 315	101, 130	800, --	--, 400	--, 316	--, 293	400, --	--, 620	--, 700
N_{eff2}^{b}	70100	36700	14800	12000^k	17600	58700	98900	45400^k	7700	11400
Rs^c	46.5	34.2	18.5^i	38^L	21.2	37.2	57.7	53^L		
TZ^d	38	28	15	31^L	17	31	48	44^L		
Rs^2/L, m^{-1}	110	58	6.3	48^L	56	69	100	94^L		
Rs/$t_{R2}^{1/3}$, sec$^{-1/3}$	5.1	4.1	2.1	4.0^{k,L}	2.7	3.1	4.6	4.4^{k,L}		
N_2/t_{R2}, sec^{-1}	142	106	621	44	43	35	55	42	23	5.4
N_{eff2}/t_{R2}, sec^{-1}	93	61	22	14	38	32	50	25	11	4.3
PP, atm·sec^e	0.0019	0.0043	0.103			0.0083			0.16^m	0.076^m
Pi, poise^f	0.22	0.44	1.39	1.7	0.48	0.29	0.25	0.31	49	19
Reference	(1) Table 1 Column #2	(1) Table 2 Column #8	(99) Table 5	(16) Column #13	(108) Table 1 Column #6	(108) Table 1 Column #9	(108) Table 1 Column #10	(16) Column #2	(70) Column #2	(70) Column #5

Table 3. (continued)

Column type	CP	CP	CP	CP	CP	CP	CP	CP	PLB	CP	CP
Type of chromatography	BPC	GLC	GLC	GLC	GLC	GLC	GLC	GLC	GLC	GLAC	GLAC
Column, L, cm	1500	30	75	150	150	150	150	600	150	58.0	26.6
id, mm	0.8	6.4	4.4	1.0	1.0	1.0	1.0	1.0	1.0	3.2	3.2
dp range,	180-200	125-149	88-105	30-35	63-71	120-140	200-250	50-60	30-40	16-24	5.4-8.8
dp (ave),										20	7.1
Specific permeability $cm^2 x 10^9$				3.9	25	42	710	20	21	3.4	0.48
Mobile phase	N_2?		H_2	N_2	N_2	N_2	N_2	He	He	H_2	H_2
Viscosity, centipoise[a]			.0088	.020	.020	.020	.020	.022	.022	.0088	.0088
Stationary phase	Porasil C/OPN	2% DC-200 oil	20% squalane	3.0% squalane	3.1% squalane	4.1% squalane	3.0% squalane	3.0% squalane	1.0% squalane	Spherisorb S20W with adsorbed OV-210	PSM-600 with adsorbed OV-210
Support properties	SA=75m^2/g d(pore)=300Å spherical	firebrick	firebrick	Spherosil XOC-005	Spherosil XOC-005	Spherosil XOC-005	Spherosil XOC-005	Spherosil XOC-005	Perisorb A	SA=200m^2/g d(pore)=80Å spherical	SA =45 m^2/g d(pore) = 330Å spherical
Packing procedure	forced draft vibration technique			forced draft vibration technique	forced draft vibration technique	forced draft vibration technique	forced draft vibration technique	forced draft vibration technique	forced fraft vibration technique	BDS packed	HPS packed out of 50% CH_3OH and 50% $CHCl_3$
T, °C	70		20	79	79	78	78	80	80	ambient	ambient
Solute 1			n-C_2	n-C_5	n-C_5	n-C_5	n-C_5	n-C_5	n-C_5	n-C_2	n-C_2
Solute 2	butadiene-1,3		n-C_3	n-C_6	n-C_6	n-C_6	n-C_6	n-C_6	n-C_6	n-C_3	n-C_3
k_1, k_2	--, 2.7	0.92, 1.5	0.6, 2	1.0, 2.2	1.0, 2.3	0.9, 2.1	0.7, 1.5	0.74, 1.72	2.16, 5.29	0.88, 3.4	0.31, 1.2
Relative retention time		1.7	3.3	2.2	2.3	2.3	2.1	2.3	2.5	3.9	3.9
ΔP, atm	2.5			24	7.3	4.0	0.71	27	15	11.9	54.0
$\bar{u}$, cm/sec	~ 4	18	56	2.5	5.2	5.0	7.5	3.3	6.8	5.8	8.8
t_{R2}, sec	960	4.3	5.5	192	95	93	50	495	139	44.4	6.5
N_1, N_2	--, 42000	750, 750	--, 160	15000, 15000	7500, 7500	3800, 3100	3300, 2500	35300, 35300	7100, 7100	3870, 3600	4840, 4470
$\hat{H}_1, \hat{H}_2$	--, 360	400, 400	--, 4700	100, 100	200, 200	390, 490	450, 600	170, 170	210, 210	150, 160	55, 60
N_{eff2}[b]	22000	280	70	7100	3600	1400	900	14100	5000	2160	1300
Rs[c]		2	1.5	14	11	6.9	5.0	18	12	10	6.9
TZ[d]		0.70	0.27	11	8.3	4.9	3.2	8.3	9.2	7.5	4.9
Rs^2/L, m^{-1}		13	3	130	76	31	1.7	50	92	190	180
$Rs/t_{R2}^{1/3}$, $sec^{-1/3}$		1.2	0.9	2.4	2.3	1.5	1.4	2.2	2.3	2.9	3.7
N_2/t_{R2}, sec^{-1}	44	180	30	78	79	33	50	71	51	81	690
N_{eff2}/t_{R2}, sec^{-1}	23	70	13	37	38	15	18	28	36	49	200
PP, atm·sec[e]				1.5	0.77	2.3	0.34	0.85	0.77	0.35[n]	6.1[n]
PI, poise[f]				220	140	500	50	150	170	260[n]	360[n]
Reference	(15) Figure 8	(56) Figure 7	(91) Figure 4a	(50) Figure 7	(50) Figure 4a	(50) Figure 3a	(50) Figure 2a	(72) Figure 1	(72) Figure 3	this work	this work

Table 3. (continued)

Column type	CP	CP	CP	CP	CP	CP	CP	CP	CP	CP
Type of chromatography	GLAC	GLAC	BPC	LSC	LSC	LSC	LSC	LSC	LSC	LSC
Column, L, cm	51.0	41.4	35.9	25	15	30	10	10	10	10
id, mm	3.2	3.2	3.2	3.2	2.4	4.2	4.5	4.5	4.5	9.5
dp range,	8-12	7.9-13.9	7.9-13.9	8-9						
dp (ave),	10	10	10		6.1	13.2	11	6	3.7	3.7
Specific permeability $cm^2 \times 10^9$	1.2	0.75	0.47	1.25	0.39	0.9	0.91[o]	0.23[o]	0.13[o]	0.70[o]
Mobile phase	H_2	H_2	H_2	50% H_2O saturated CH_2Cl_2	79.9% Hexane 20.0% CH_2Cl_2 1.3% IPA	Hexane	49.0% Hexane 50.0% CH_2Cl_2 1.0% IPA	49.0% Hexane 50.0% CH_2Cl_2 1.0% IPA	49.0% Hexane 50.0% CH_2Cl_2 1.0% IPA	49.0% Hexane 50.0% CH_2Cl_2 1.0% IPA
Viscosity, centipoise[a]	.0088	.0088	.0088	0.40	0.38	0.36	0.42	0.42	0.42	0.42
Stationary phase	Spherisorb S10W with adsorbed OV-210	LiChrospher Si500 with adsorbed OV-210	LiChrospher Si500 bonded with 3,3,3 trifluoropropyl-methyldichloro-silane and TMCS	porous silica microspheres	LiChrosorb Si60 silica	LiChrosorb Si100 silica	Partisil 10 silica	Partisil 5 silica	Partisil 3 silica	Partisil 3 silica
Support properties	SA=200 m^2/g d(pore)=80Å spherical	SA=50 m^2/g d(pore)=500Å spherical	SA=50 m^2/g d(pore)=500Å spherical	SA=250-350 m^2/g d(pore)=75Å	SA=366 m^2/g d(pore)=60Å irregular	SA=400 m^2/g d(pore)=100Å irregular	SA=400 m^2/g d=45Å irregular	SA=400 m^2/g d(pore)=45Å irregular	irregular	irregular
Packing procedure	BDS packed	BDS packed	BDS packed	aqueous charged stabilized	BDS packed	high viscosity slurry method	HPS packed out of CCl_4	HPS packed out of CCl_4	HPS packed out of CCl_4	HPS packed out of CCl_4
T, °C	ambient	ambient	ambient	27	ambient	ambient	ambient	ambient	ambient	ambient
Solute 1	$n\text{-}C_2$	$n\text{-}C_3$	$n\text{-}C_2$	benzyl alcohol	N,N-diethyl-p-amino azobenzene		m-nitroaniline	m-nitroaniline	m-nitroaniline	m-nitroaniline
Solute 2	$n\text{-}C_3$	$n\text{-}C_4$	$n\text{-}C_3$	3-phenyl-1-propanol	N-ethyl-p-amino-azobenzene	nitrobenzene	p-nitroaniline	p-nitroaniline	p-nitroaniline	p-nitroaniline
k_1, k_2	0.79, 3.1	0.77, 2.4	0.33, 1.3	4.7, 6.3	1.2, 4.1	--, 6	2.04, 2.41	1.99, 2.39	2.00, 2.37	1.79, 2.14
Relative retention time	3.9	3.1	4.0	1.3	3.4		1.18	1.20	1.19	1.20
ΔP, atm	57.8	47.6	40.8	44	91	246[p]	9.2	26	50	91
$\bar{u}$, cm/sec	13.7	8.1	4.9	0.50	1.0	2	0.195	0.141	0.154	0.148
t_{R2}, sec	15.0	16.9	16.8	365	48	105	175	239	218	212
N_1, N_2	10900, 12800	10100, 9380	2500, 1700	3730, 3330	2100, 3000	--, 2700	3100, 3100	6700, 6400	8100, 8300	13500, 13100
$\hat{H}_1$, $\hat{H}_2$,	47,40	41,44	140, 210	67, 75	70, 50	--, 110	32, 32	15, 16	12, 12	7, 8
N_{eff2}[b]	7290	4670	550	3000	1900	2000	1500	3200	4100	6100
Rs[c]	21	13	5.1	3.6	8.4		1.6	2.5	2.6	3.4
TZ[d]	17	10	3.3							
Rs^2/L, m^{-1}	900	400	72	52	480		26	62	67	120
$Rs/t_{R2}^{1/3}$, $sec^{-1/3}$	8.7	5.0	2.0	0.50	2.3		0.29	0.40	0.43	0.57
N_2/t_{R2}, sec^{-1}	850	560	100	9.1	63	26	18	27	38	62
N_{eff2}/t_{R2}, sec^{-1}	490	280	33	8.2	25	19	8.8	13	19	29
PP, atm·sec[e]	0.062[n]	0.19[n]	7.9[n]	1100	16		1600	1100	1300	960
PI, poise[f]	45[n]	96[n]	4300[n]	6300	9200	17000	2000	2000	2000	1700
Reference	this work	this work	this work	(58) Figure 3&4	(77) Figure 8b & 6 & Eq. 6	(2) Table IV Column #20	(110) Table IV	(110) Table V	(110) Table V	(110) Table VI

Table 3. (continued)

Column type	CP	CP	CP	CP	CP	CP	PLB	PLB	CP
Type of chromatography	LSC	LSC	LSC	LSC	LSC	BPC(RP)	BPC	BPC(IE)	BPC
Column, L, cm id, mm	25 3.2	10 2.8	12 4.6	99.5 8.0	9.5 5.0	12.5 5.0	100 2.1	100 2.1	15 2.2
dp range,							37-44	37-44	
dp (ave),	5	10	5	3.0	5.9	7.5	40.5		10
Specific permeability $cm^2 \times 10^9$	0.26	0.7	0.26	.201	.746	1.3	23.0	12.3	
Mobile phase	90.6% isooctane 8.2% CH_2Cl_2 1.2% IPA	H_2O saturated Hexane	isooctane	1% acetonitrile in C_6	1% acetonitrile in C_6	30% H_2O 70% CH_3OH	n-C_6 with 1% C_2H_5OH	0.01M aqueous citric acid-NaOH buffer (pH 3.0)	15% CH_2Cl_2 85% n-C_6
Viscosity, centipoise[a]	0.52	0.36	0.4	0.33	0.33	0.72	0.34	0.467	0.34
Stationary phase	LiChrosorb Si60 silica	LiChrosorb *Si100* silica	LiChrosorb *Si100* silica	Spherisorb S3W silica	Spherisorb S5W silica	*totally porous* silica with a short chain reverse phase	ETH Permaphase 1% by weight of polymerized silicone ether	AAX Permaphase polysiloxane containing quaternary ammonium chemically bonded	γ-isocyanatopropyl-methydichlorosilane bonded to LiChrosorb Si60 silica
Support properties	SA = 366 m^2/g d(pore) = 60Å irregular	SA = 400 m^2/g d(pore) = 100Å irregular	SA = 400 m^2/g d(pore) = 100Å irregular	spherical	SA = 200 m^2/g d(pore) = 80Å spherical	SA = 200 m^2/g spherical	Zipax	Zipax	SA = 366 m^2/g d(pore) = 60Å irregular
Packing procedure	BDS packed	HPS packed out of methanol and dioxane	HPS packed using CC14	slurry packed using CH_3OH	slurry packed using CH_3OH	BDS packed	dry packed using a mechanical device	dry packed using a mechanical device	BDS packed
T, °C	ambient	ambient	ambient	ambient	ambient	ambient	20	60	ambient
Solute 1	benzyl alcohol	phenetol				acetone	p-cresol	terephthalic acid	N,N-diethyl-p-amino-azobenzene
Solute 2	3-phenyl-1-propanol	nitrobenzene	anthracene	phenanthracene	phenathracene	2,6-xylenol	phenol	phthalic acid	N-ehtyl-p-amino-azobenzene
k_1, k_2	5.60, 6.81	1.5, 3.6	--, 1.7	--, 0.24	--, 1.50	0.9, 1.5	1.4, 2.4	1.94, 2.81	5.3, 8.9
Relative retention time	1.22	2.4				1.7	1.7	1.45	1.7
ΔP, atm	113	12	98.7	147	6.9		14	10.6	
$\bar{u}$, cm/sec	0.222	0.22	0.54	.094	0.216	0.16	1.0	0.26	0.6^P
t_{R2}, sec	864	189	60	1312	110	200	330	1420	248
N_1, N_2	11600, 10500	4200, 2500	--, 2100	--, 108026	--, 11648	7900, 6900	1800, 1900	2900, 2650	--, 370
$\hat{H}_1$, $\hat{H}_2$,	22, 24	24, 40	--, 57	--, 9.2	--, 8.2	16, 18	560, 520	340, 380	--, 410
N_{eff2}[b]	8000	1500	830	3985	4193	2500	950	1400	300
Rs[c]	3.7	8				6.1	2.8	2.9	3.3
TZ[d]									
Rs^2/L, m^{-1}	55	640				290	7.8	8.4	72
$Rs/t_{R2}^{1/3}$, $sec^{-1/3}$	0.39	1.4				1.0	0.41	0.26	0.53
N_2/t_{R2}, sec^{-1}	12	13	35	82	110	35	5.8	1.9	1.5
N_{eff2}/t_{R2}, sec^{-1}	9.3	7.9	14	3	38	13	2.9	1.0	1.2
PP, atm·sec[e]	1900	12				16	240	1000	
PI, poise[f]	4000	3200							
Reference	Authors Laboratory	(73) Figure 6A	(14) Figure 7	(8) From text	(8) From text	(64) Figure 5 & Table II	(67) Figure 1 & Eq (1) & Tables 1 & 3	(68) Figure 2 & Table 1	(80) Table VI Figure 4 Col XXIX

Table 3. (continued)

Column type	CP	CP	CP	CP	PLB	CP	CP	CP	CP	CP
Type of chromatography	BPC(RP)	BPC(IE)	BPC(RP)	LLC	LLC	GPC	GPC	GPC	HPSEC	GPC
Column, L, cm	15	10	25	15	100	25.0	25.0	25.0	25.0	25
id, mm	2.2	2.0	3.2	2.2	2.1	4.0	4.0	4.0	6.2	6.2
dp range,		7-11			16-40					4.5-7.5
dp (ave),	10	9	7	10	29	10	10	10	8.4	6
Specific permeability cm^2 x 10^9			0.48[p]		15.3					0.65[p]
Mobile phase	15% CH_2Cl_2 85% n-C_6	0.1N H_3PO_4 0.1N $NaNO_3$	12.5% H_2O 87.5% CH_3OH	isooctane	cyclohexane	THF	THF	THF	THF	THF
Viscosity, centipoise[a]	0.34		0.42	0.50	1.0	0.51	0.51	0.51	0.51	0.51
Stationary phase	octadecylsilane bonded to LiChrosorb Si60 silica	sulfonated benzylsilyl groups on silica	porous silica microspheres with C_{18} surface and silanized	33% ODPN on LiChrosorb Si60 silica	1% BOP	porous LiChrospher silica with silanized surface	porous LiChrospher silica with silanized surface	porous LiChrospher silica with silanized surface	PSM-40 with silanized surface	PSM-800
Support properties	SA = 366 m^2/g d(pore) = 60Å irregular	d(pore) ≈ 60Å spherical	SA = 200 m^2/g spherical	SA = 366 m^2/g d(pore) = 60Å irregular	Zipax	SA = 50 m^2/g d(pore) = 500Å spherical	SA = 50 m^2/g d(pore) = 500Å spherical	SA = 50 m^2/g d(pore) = 500Å spherical	SA = 351 m^2/g d(pore) = 61Å spherical	SA = 34 m^2/g d(pore) = 300Å spherical
Packing procedure	BDS packed	HPS packed	BDS packed	BDS packed	dry packed using a mechanical device	BDS paced	BDS paced	BDS paced	BDS paced	HPS paced out of 50% CH_3OH and 50% $CHCl_3$
T, °C	ambient	27.0	50	ambient	ambient	25	25	25	27	ambient
Solute 1	N-ethyl-p-amino-azobenzene	pyridine carbonitrile-3	pyrene	diphenylamine	m-cresol	PS 173	PS 51	PS10		
Solute 2		nicotinamide	chrysene	N-phenyl-naphthlamine	phenol	PS 98	PS 10	ethylbenzene	toluene	PS 51
k_1, k_2	--, 1.7	13.0, 25.0	5.7, 10	4.1, 8.2	4.7, 6.6	0.17, 0.33	0.57, 0.88	0.88, 1.09	--, 1.0	--, 0.38
Relative retention time		1.92	1.8	2.0	1.4	1.9	1.5	1.2		
ΔP			135		34				15.3	97.6
$\bar{u}$, cm/sec	0.6[p]	0.5	0.6	1	0.47	0.36	0.36	0.36	0.20	0.49
t_{R2}, sec	68	510	470	138	450	92.4	131	145	210	71
N_1, N_2	--, 220	--, 5000	1900, 2000	250, 260	--, 4000	230, 230	270, 690	690, 4000	--, 11000	--, 1500
$\hat{H}_1, \hat{H}_2$	--, 680	--, 20	130, 125	610, 570	--, 250	1100, 1100	930, 360	360, 63	--, 23	--, 170
N_{eff2}[b]	87	4600	1700	210	3000	13.9	151	1080	2750	110
Rs[c]		6.0	5.3	1.9	4.9	0.45	1.08	1.59		
TZ[d]										
Rs^2/L, m^{-1}		3.6	120	24	24	0.81	4.7	10		
$Rs/t_{R2}^{1/3}$, sec$^{-1/3}$		0.75	0.7	0.37	0.64	0.10	0.21	0.30		
N_2/t_{R2}, sec^{-1}	3.2	9.8	4.3	1.9	8.9	2.5	5.3	27	53	21
N_{eff2}/t_{R2}, sec^{-1}	1.3	9.0	3.6	1.5	6.7	0.15	1.15	7.46	13	1.6
PP, atm·sec[e]			750		1100					
PI, poise[f]										
Reference	(80) Table VI Column XIII	(106) Figure 4 & Table 2	(57) Figure 1A	(80) Table IV Column XXXV	(22) Figure 6	(105) Table III Column #5	(105) Table III Column #5	(105) Table III Column #5	(61) Table IV Column #2	(60) Table II & Figure 4

Table 3. (continued)

Column type	CP	CP
Type of chromatography	GPC	GPC
Column, L, cm	10	60^{r}
id, mm	7.8	7.8
dp range,	7.7-10.1	^{r}
dp (ave),	8.9	
Specific permeability $cm^2 \times 10^9$	1.2^{p}	1.2^{p}
Mobile phase	THF	THF
Viscosity, centipoise[a]	0.51	0.51
Stationary phase	PSM-1500	porous silica microspheres with silanized surface
Support properties	SA = 20 m^2/g d(pore) = 750Å spherical	spherical[r]
Packing procedure	HPS packed out of 50% CH_3OH and 50% $CHCl_3$	HPS packed out of 50% CH_3OH and 50% $CHCl_3$
T, °C	ambient	ambient
Solute 1		PS 390
Solute 2	PS 97	PS 97
k_1, k_2	--, 0.57	0.17, 0.29
Relative retention time		1.7
ΔP, atm	9.2	27.9
$\bar{u}$, cm/sec	0.21	0.11
t_{R2}, sec	75	700
N_1, N_2	--, 2300	4700, 10000
$\hat{H}_1$, $\hat{H}_2$,	--, 43	130, 60
N_{eff2}[b]	300	500
Rs[c]		1.8
TZ[d]		
Ts^2/L, m^{-1}		5.3
$Rs/t_{R2}^{1/3}$, $sec^{-1/3}$		0.2
N_2/t_{R2}, sec^{-1}	31	14
N_{eff2}/t_{R2}, sec^{-1}	4.0	0.7
PP, atm·sec[a]		3200
PI, poise[f]		
Reference	(60) Table II & Figure 4	(60) Figure 11

a. ambient temperature is considered 20°C, water saturated solvents are considered to have the viscosity of the hydrocarbon component, the viscosity of multi-component solvents are calculated by assuming the overall viscosity to be a linear additive function of the individual component viscosities.

b. $N_{eff_2} = N_2[k_2/(1 + k_2)]^2$

c. If the resolution was not stated then it was calculated from the published chromatograms, unless N was given for both solutes then Rs was calculated from

$$Rs = [t_{R2} - t_{R1}]x1.178/[t_{R1}(5.55/N_1)^{\frac{1}{2}} + t_{R2}(5.55/N_2)^{\frac{1}{2}}]$$

d. $TZ = \frac{Rs(z + 1)/z}{1.178} - 1$

The trennzahl with $Rs_{(z + 1)/z}$ the resolution of two adadjacent hydrocarbons with number of carbon atoms z and z + 1. The separation value and effective peak number may be calculated from the TZ, see reference (24).

e. The performance parameter as defined by Halasz (46)

$$pp = (\hat{H}_2^2\ S_{req}^2\ \eta/K°j' \cdot 10^6)(1 + k_2)^5/k_2^4$$

where $S_{req} = 36[\alpha/(\alpha - 1)]^2$ and j' is equal to 1 for LC and for GC where $P < 2$ otherwise $j' = j(P + 1)/2$.

f. the performance index,

$$PI = 30.7\ H_2^2\ \eta((1 + k_2)/(k_2 + 1/16))/K°$$

g. calculated $(r_T^2/8)$

h. calculated from $U_oNL/K°$ by assuming a small gas pressure drop.

i. calculated from their Eq. (2) after the error was corrected.

k. data is for the lower molecular weight hydrocarbon.

l. two consecutive alkanes would have a value of about 1/4 this.

m. assuming C_6 and C_7 would have a relative retention of 2.6 on squalane at 50°C.

n. to compare with N_2 values multiply by 2.

o. calculated from $\bar{u} = \Delta P\ K°/NLf$ where f is the total porosity, assumed equal to 0.83 for porous packings.

p. this velocity was calculated from his figures 3 and 4 and Table VI, and is more reasonable than the stated approximate 1 cm/sec velocity.

r. the 60 cm column is made from the following five columns: 10 cm PSM-50 (dp 5.9, SA 326, d(Pore)60), 15 cm PSM-300(dp 8.9, SA 87, d(Pore)257), 10 cm PSM-800 (dp 6.0, SA 34, d(Pore)300), 10 cm PSM-1500(dp 8.9, SA 20, d(Pore)750), 15 cm PSM-4000 (dp $\sim$ 6, SA 9, d(Pore) 3500.

Table 4. Summary of some of the functions in Table 3 and Guiochon's Table V (44).

Function	Open tubes	Packed* columns (GC)	Micropacked columns	SPPC (GC)	SPPC (LC)
PP, atm · sec	.0019-.103		0.34-2.3	.062-7.9	12-1900
PI, poise	.022-1.7	5.5-1000[F]	50-500	45-4300	1700-17000
Rs^2/L, M^{-1}	1.5-110	2-13	4.1-130	72-900	4-640
$Rs/t_{R2}^{1/3}$, $sec^{-1/3}$	1.6-6.0	.44-1.60	1.4-2.4	2.0-8.7	.27-2.3
N_{eff2}/t_{R2}, sec^{-1}	3.8-2000	.26-70	15-38	33-490	1.38

*Includes all packed columns aside from the micropacked columns and the SPPC's.

[F] From Guiochon's Table XVIII (44).

The SPPC prepared for this work, out-performed all other columns listed in the combined tables (Guiochon's Table V and our Table 3) when ranked by the functions Rs^2/L and $Rs/t_{R2}^{1/3}$. This is clearly shown in Table 4 and while one would expect it for Rs^2/L it is encouraging to find values as high as 8·7 $sec^{-1/3}$ for $Rs/t_{R2}^{1/3}$. Such a value means that the column can give a Rs of 34 in one minute for two adjacent n-alkanes having column capacity ratios from 0.8-3.1. One should mention that these columns were very selective towards hydrocarbons having relative retention times of about four or twice that for most columns in the tables. However when the data is normalized to an α of two, the SPPC operated in GC give values for $Rs/t_{R2}^{1/3}$ of 1.3-5.8 which are still very good. One should further mention that Desty's open tube columns, considered by many to be the fastest columns ever made, listed in Guiochon's Table V were not included in any of the resolution functions comparisons since no resolution data was listed in Desty's work but only plate and effective plate numbers.

The number of effective plates per unit time as a measure of column performance was critically examined earlier; there it was also mentioned that this function seemed to do the job of comparing column performance the best. Figures (24, 25) show values of N_{eff2}/t_{R2} of Table 3 plotted against the parameter d_p (or r_T). The lines were drawn in as guides and are approximately the lines of best

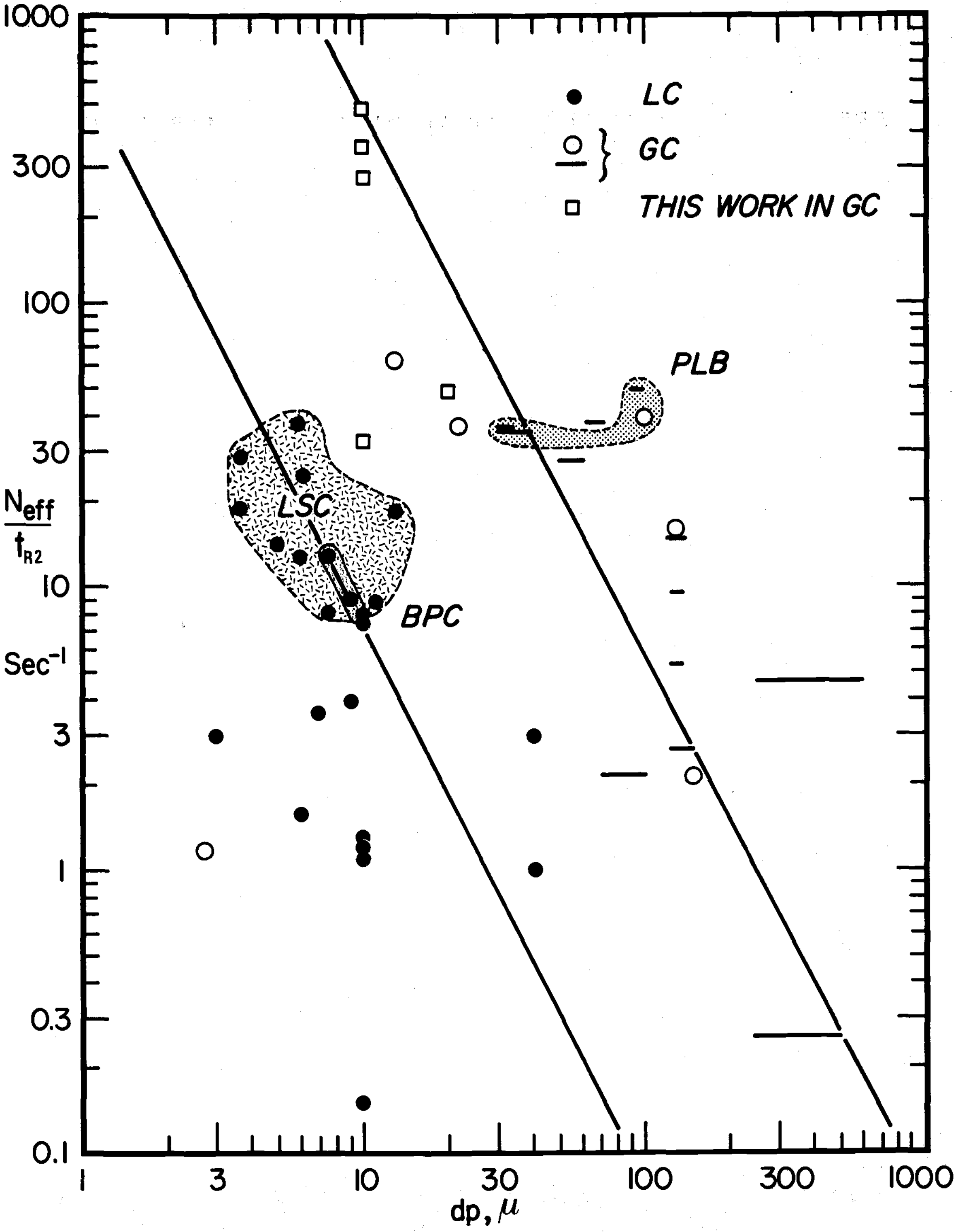

Figure 24 Relative Performance of GC and LC for Packed Columns of Various Particle Diameters

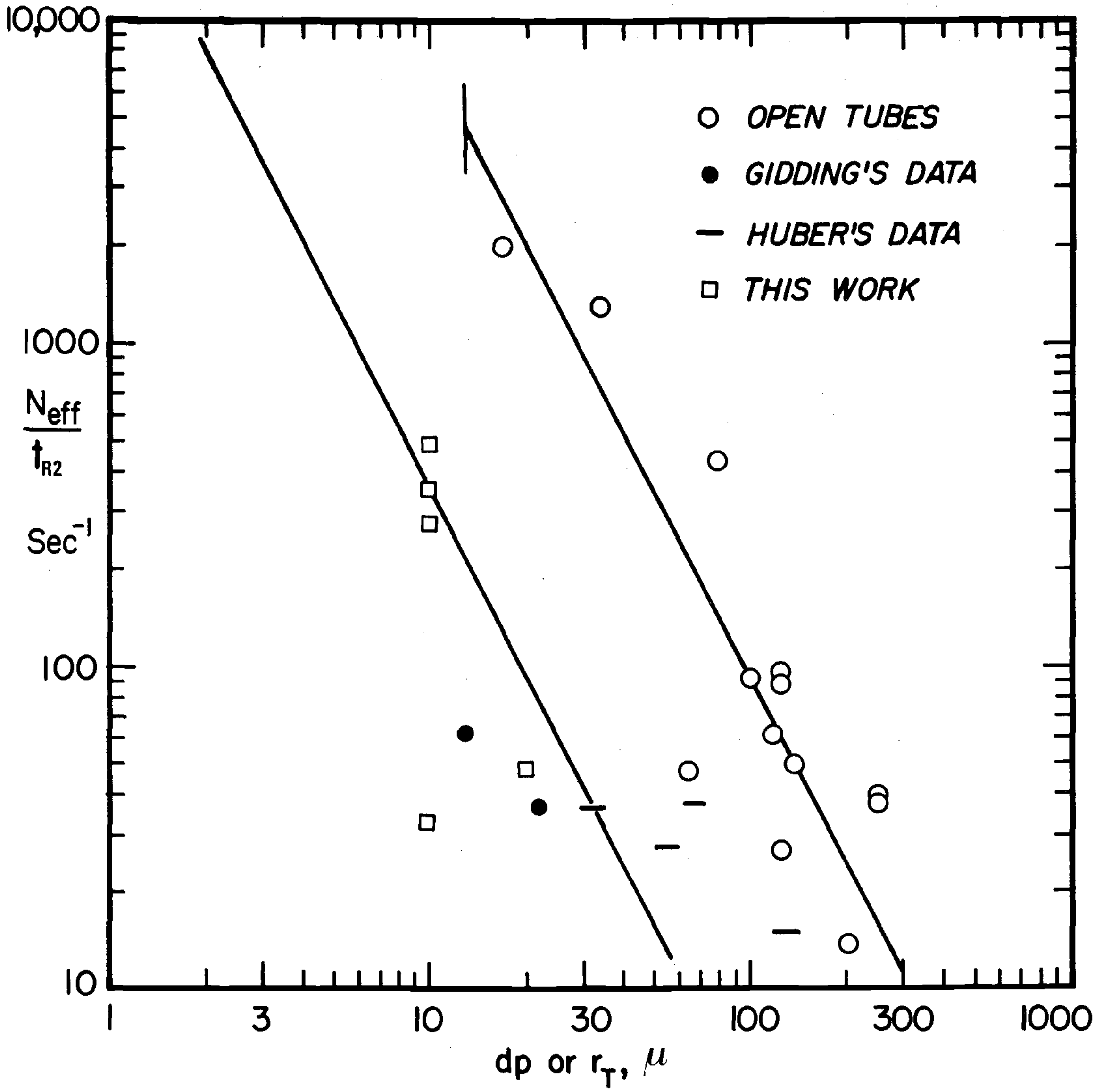

Figure 25 Relative Performance of Open Tube Columns and Packed Columns in GC for Various dp (or r_T).

fit with a slope of about 2. The figures indicate that, once again, the SPCC constructed for this work are the best packed columns so far made for GC when judged by the performance indicator N_{eff2}/t_{R2}. Figure (24) gives a good evaluation of the relative performance of packed columns when used in GC or in the various modes of LC. One can see from the figure that for an analysis which could be done by either gas or liquid chromatography, GC would be faster, owing to greater mass transfer in the mobile phase. The figure further indicates that GPC and BPC (included in here is ion exchange) fall short of the performance given by LSC (the larger shaded region in Fig. (24)). However, the performance of these modes of LC become equivalent to LSC when packings are used that have small organic groups bonded to their surface or when GPC packings are used for HPSEC (61). Proof of this is the small shaded region of Fig. (24) which holds data points from such packings and is inside the LSC region. Another interesting feature of Fig. (24) is the high performance that PLB columns offer gas chromatography. They give improved performance over columns packed with porous packings mainly because intraparticle sample trapping has been eliminated but also because porous layer bead packings pack better than conventional porous packings when tap-fill techniques are used. From Fig. (24) the PLB columns give 3-4 times the number of effective plates per second as CP columns having a packing of the same d_p

indicating they do deserve a place in high performance GC.

Figure (25) compares some of the best open tube columns with some of the best packed columns, including those of this work. The top three points on the open tube line are from Desty's work (20) on .0015, .003 and .005 inch diameter open tube columns respectively. The open tube line is terminated at r_T corresponding to a .001 inch (25 micron) diameter column since tubing of internal diameters smaller than this cannot be purchased from tube manufacturers. In contrast packed columns have been successfully packed and operated in LC using particles with diameters of 3 microns (8, 48, 100). However when the two types of columns are compared with d_p assumed equivalent to r_T the open tube columns out-perform the packed columns by more than an order of magnitude. Nevertheless the packed column may be favorable at small d_p (rather than using an equivalent r_T) when one considers the difficulties mentioned by Desty (17) in coating and operating such small diameter open tube columns.

Equation (7) shows that the velocity in a column is directly proportional to the specific permeability, K^o. The column's permeability can be an important parameter when the pressure of the instrument is limited, since the best possible use of the available pressure would be with the most permeable packing. In Fig. (26) the specific permeabilities listed in Table 3 have been plotted against the

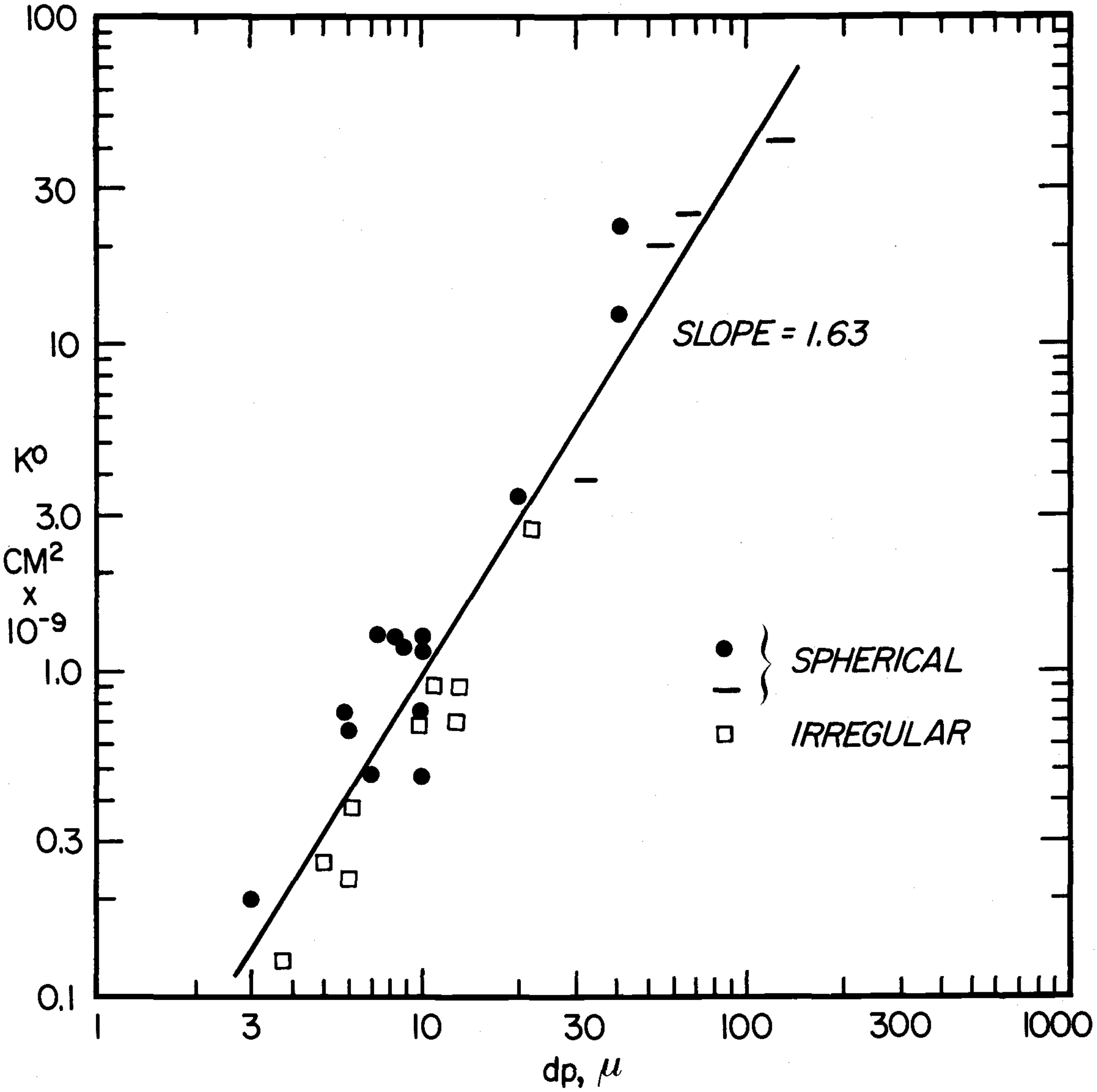

Figure 26 Permeability of Spherical versus Irregular Shaped Particles as a Function of Particle Diameter.

respective columns' particle diameter. The slope of the line of best fit is equivalent to what others have found (48, 77) but more importantly most spherical particle packings have permeabilities that lie above the line and all irregular shaped particle packings have permeabilities that lie below it. The few spherical particle packings which fall below the line are those which like LiChrospher Si500 have a large particle size distribution. Clearly what Fig. (26) is telling us, is that whenever pressure is the limited chromatographic variable one should choose a packing having spherical particles and a narrow particle size distribution.

Verification of the Theory

The data of Scott (96), Myers and Giddings (88), Huber et al. (50) and our own all suggest the dependence of $\bar{u}_{opt}$ on particle diameter that is indicated by Eq. (18). The dependence of $p_{i(opt)}$ on particle diameter as depicted by Eq. (19) was not proven here since particle diameter was not varied over a significant range. However the data of Huber, Lauer and Poppe (50) does prove the dependence. This can be seen by plotting log $p_{i(opt)}$ versus log d_p using the data from their Figures (2-4,7). The plot has a slope of -1.4 in good agreement with the theoretical value of -1.5. Examination of their data in Table 3 also shows that the resolution and analysis time for their columns of constant length increase with $d_p^{-1/2}$ as Eq. (21) suggest.

V. CONCLUSIONS

Obviously an instrument with a greater pressure capability would be desirable. Since this pressure could be used to operate longer columns packed with even smaller particles for faster analyses and more resolution. Ultimately the pressure limit will be determined by the cost of generating, storing and designing chromatographic equipment to handle the high pressures. Currently there seems to be a quantum jump in price when one tries to go much above 6000 psi. Indeed, eventually one will have to examine whether the resultant increase in separation speed from building and operating equipment to handle pressures of only a few thousand psi justifies the cost. However commercial manufacturers of gas chromatographs would not have to go to these pressures to realize an increase in separation speed. By increasing the working pressure of their chromatographs from 30-60 psi to 200-300 psi they could operate columns 1-2 meters in length, packed with 30-50 micron particles and experience a 3-5 fold reduction in analysis time over the exceedingly abundant 6 ft. 120-140 mesh packed column.

If high pressures and small particle packed columns are to be an effective tool in the analysis of complex mixtures, much work has to be done in equipment design. Foremost should be the construction of a reliable, easy to operate device that will inject liquid samples against high pressures much like the sample valves of today's liquid chromatographs. The chromatograph should operate at elevated temperatures and unlimited possibilities exist if SPPC are coupled with fast linear temperature programming. Post column splitters, while easy to design and construct, are a nuisance. They could be eliminated by using smaller bore tubing which might also improve column efficiency by increasing transcolumn equilibrium. There seems to be an endless number of packings that one could try but from considerations already mentioned the Zorbax (or PSM) silica from DuPont seems the best.

The field of chromatography is a highly developed one and while this author does not want to sound like he is in favor of closing the patent office, he does feel that there will be few major developments in chromatography in the years to come. Currently the greatest activity is in the area of chromatographic applications and techniques, of course, it is here where SPPC operated in both liquid and gas chromatography will have their use.

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APPENDIX A

Effect of Particle Diameter on Analysis Time

1. Effect of d_p on $\bar{u}_{opt}$ and $p_{i(opt)}$

We start by assuming that the column is operated with a high inlet pressure and that the stationary phase mass transfer term is negligible. Under such circumstances Eq. (11, 17) are valid. The variable p_i in Eq. (17) and its dependence on $\bar{u}$ can be accounted for by entering Eq. (11) for p_i in Eq. (17) to get

$$\hat{H} = \frac{9\ B_1\ f\ p_o\ d_p^2}{8\ \bar{u}^2\ \eta\ L\ \phi} + \frac{8\ C_{ml}\ f\ \bar{u}^2\ \eta\ L\ \phi}{9\ p_o\ d_p^2}$$

when $\omega d_p^2/D_{ml}$ is substituted for C_{ml} and 9/8, the high pressure limit of f, for f we obtain

$$H = \frac{81\ B_1\ p_o\ d_p^2}{64\ \eta\ L\ \phi\ \bar{u}^2} + \frac{\eta\ L\ \phi\ \omega\ \ \bar{u}^2}{p_o\ D_{ml}}$$

Taking the derivative of the above equation with respect to $\bar{u}^2$ yields

$$\frac{d\ \hat{H}}{d\ \bar{u}^2} = -\ \frac{81}{64}\ \frac{B_1\ p_o\ d_p^2}{\eta\ L\ \phi\ \bar{u}^4} + \frac{\omega\ \eta\ L\ \phi}{p_o\ D_{ml}}$$

Setting the equation equal to zero and solving for what is now $\bar{u}_{opt}$ gives Eq. (1A)

$$\bar{u}_{opt} = (d_p/L)^{1/2}\ \xi_o \qquad (1A)$$

where $\xi_o = \frac{3}{2}\left(\frac{B_1\ D_{m1}}{\omega}\right)^{1/4}\left(\frac{p_o}{2\eta\ \phi}\right)^{1/2}$.

The pressure required to maintain the optimum velocity can be calculated from an equation derived by substituting Eq. (1A) into Eq. (11) to yield Eq. (2A).

$$p_{i(opt)} = d_p^{-3/2}\ L^{1/2}\ \xi_1 \qquad (2A)$$

where $\xi_1 = (B_1 D_{m1}/\omega)^{1/4}\ (2p_o\ \eta\ \phi)^{1/2}$.

2. Effect of d_p on $(\hat{H}/\bar{u})_{opt}$

Equation (17) can be divided by $\bar{u}$ and H_e assumed negligible, C_{m1} set equal to $\omega d_p^2/D_{m1}$, f = 9/8 and operation at the van Deemter optimum assumed to give

$$\left(\frac{\hat{H}}{\bar{u}}\right)_{opt} = \frac{27\ p_o\ B_1}{16\ p_i\ \bar{u}^2} + \frac{3\ \ \omega d_p^2\ p_i}{4\ D_{m1}\ p_o} \qquad (3A)$$

Entering Eq. (1A, 2A) into Eq. (3A) gives the desired results

$$\left(\frac{\hat{H}}{\bar{u}}\right)_{opt} = (d_p\ L)^{1/2}\ \xi_2 \qquad (4A)$$

where $\xi_2 = 3B_1(\omega/B_1\ D_{m1})^{3/4}\ (\eta\ \phi/2p_o)^{1/2}$.

3. Effect of d_p on analysis time for decreasing d_p, column length constant - resolution increased.

Substituting Eq. (1A) into Eq. (4A) gives the dependence of $\hat{H}_{opt}$ on d_p as

$$\hat{H}_{opt} = d_p \, \xi_o \, \xi_2 \tag{5A}$$

By Eq. (15) the resolution is inversely proportional to the square root of the plate height hence it is also proportional to $d_p^{-1/2}$. When this relationship and that of Eq. (4A) are substituted into the analysis time equation, Eq. (16) we obtain

$$t_z \propto d_p^{-1/2} \; . \tag{6A}$$

APPENDIX B

Calculation of Approximate Split Ratio

We shall start by defining the following terms,

S = split ratio = $F_{o(cap)}/F_{o(cpl)}$

L_{cpl}, r_{cpl} = length and internal radius of the coupler

L_{cap}, r_{cap} = length and internal radius of the capillary

d_{cap} = outside diameter of capillary

K^o = the specific permeability and is defined by the Kozeny-Carmen equation (30) as $d_p^2\ \varepsilon^2/180(1-\varepsilon)^2$

ε = interparticle porosity of the glass bead packing.

Equation (12) can be written in terms of the outlet volume flow rate by entering Eq. (9) and multiplying both sides of the equation by r_{cap}^2 to get

$$F_{o(cap)} = \frac{\pi r_{cap}^4\ p_o\ (P^2 - 1)}{16\eta\ L_{cap}}$$

The equation for the volume flow rate of the coupler is derived by multiplying both sides of Eq. (8) by $\pi(r_{cpl} - d_{cap}/2)^2\varepsilon$ and making use of the above definitions to give

$$F_{o(cpl)} = \frac{\pi(r_{cpl} - d_{cap}/2)^2\varepsilon\ d_p^2\ \varepsilon^2\ p_o\ (P^2 - 1)}{360\ \eta\ L_{cpl}\ (1 - \varepsilon)^2}$$

From Fig. (3) one can see that the coupler and capillary have the same inlet pressure and approximately the same outlet pressure. Hence by dividing Eq. (1B) by Eq. (2B) the pressure terms will cancel and an equation for the split ratio will be obtained

$$S = \frac{r_{cap}^{4} \, L_{cpl} \, (1 - \varepsilon)^{2} \, 45}{2L_{cap}(r_{cpl} - d_{cap}/2)^{2} \, d_{p}^{2} \, \varepsilon^{3}} \qquad (3B)$$

In order to reduce dead volume and for experimental convenience, only d_p and r_{cap} of Eq. (3B) were allowed to vary and the other terms were fixed at the following values

$L_{cpl} = 7.9$ cm
$L_{cap} = 25$ cm
$r_{cpl} = 0.16$ cm
$d_{cap} = 0.16$ cm
$\varepsilon = 0.50$

Equation (3B) is very sensitive to ε, which for most packed columns lies between .38 and .42, but it is doubtful that the glass beads can be packed that tight around the capillary, if the actual value for ε was 0.45 instead of 0.50 the split ratio would be in error by 40%. Since we only were interested in increasing or decreasing the amount of column effluent sent to the detector this amount of error was acceptable. Inserting the numerical values for the above terms into Eq. (3B) gives

$$S = 2.26 \times 10^3 \, r_{cap}^4 / d_p^2 \qquad (4B)$$

Equation (4B) was used to calculate split ratios for two different capillary radii and particle diameters from 200-700 microns, the results are tabulated in Table (1B). By using such a splitter system the amount of column effluent sent to the detector could be easily varied 60 fold without significantly increasing the end effects.

Table 1B. Approximate split ratios for the splitter in Fig. (5). Calculated using Eq. (4B).

Approx. grade of glass beads	#6	#8	#9	#10	#11	#11
U.S. std. mesh range	20-30	30-40	40-50	50-60	60-70	70-80
Average d_p microns	710	500	360	270	230	190
S. 007" %	.28	.56	1.1	1.9	2.7	3.8
S .010" %	1.2	2.3	4.6	8.0	11	16