A study of mobile phase mass transfer (zone dispersion) in packed beds of non-porous spheres is undertaken in two parts. The first is a literature study of zone dispersion in non-sorbing systems. Over 750 data observations from 18 research teams in chemistry and engineering are gathered and plotted together. The line of best fit through the points is seen to agree very well with that predicted by the coupling theory in chromatography and the mixing cell model in engineering. The research parameters used by the various investigators are correlated and examined as to their contribution to zone dispersion.

The second part is an investigation of mobile phase zone dispersion in sorbing systems and its dependence on the column capacity ratio. For this purpose a high pressure chromatograph is constructed. It is made to work up
to 6000 lbs/in$^2$ and the outlet pressure is variable up to that of the inlet pressure. A micro ionization cross-section detector is built to be pressurized with the column up to the maximum pressure. It has a volume of 11.8 microliters.

Normal hydrocarbon homologues are used as samples and data series of reduced plate height versus reduced velocity are obtained at constant linear velocity. This procedure separates the mobile phase mass transfer term (dependent on reduced velocity) from the stationary phase mass transfer term (dependent on linear velocity). The stationary phase mass transfer term is subtracted out and the data points are fitted by least squares to three models proposed in the literature. All fit the data well but only a simple coupled equation extrapolates to the expected value at a reduced velocity of zero.

Three expressions for the dependence of the mobile phase mass transfer term on the column capacity ratio are investigated. It is found that the best results are obtained using the expression of Knox and Saleem (based on the mal-distribution of stationary phase) in conjunction with the simple coupled equation.

It is found that the onset of turbulence in this
system occurs at a reduced velocity of 100 to 120 (Reynolds number of about 30), suggesting that the flattening of the plate height curve is due either to turbulence or coupling and turbulence together.
Mobile Phase Mass Transfer in Chromatographic Beds of Impermeable Spheres

by

John Robert Cluff

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MOBILE PHASE MASS TRANSFER IN CHROMATOGRAPHIC
BEDS OF IMPERMEABLE SPHERES

THEORY

Introduction

The two most basic phenomena of chromatography are
1. The separation of the components of a sample into individual zones.
2. The spreading out or dispersion of the zones as the separation progresses.

A sample which contains only a few components can most easily be separated by attention to phenomenon 1, that is, a judicious choice of the stationary and mobile phases can always separate two or three components. In reality, however, the situation becomes more complex since samples tend to be multicomponent. An example is ordinary gasoline, which may have as many as two hundred components. In such a case attention to phenomenon 1 becomes useless since a combination of conditions to separate some components will just as surely obscure others. By giving attention to both phenomena, however, a greatly improved separation can be obtained as shown
in Figure 1.

Chromatogram A of Figure 1 shows a typical separation in which some components are well-separated and others are only very poorly resolved. Chromatogram B shows the same mixture eluting in the same time but with greatly reduced zone dispersion. All of the components are well resolved. Two things may be noted with chromatogram B. First, it would be possible to analyze a much more complex sample since there is room between the existing peaks for several other components (although the possibility of overlap increases). Second, it would also be possible to obtain a faster analysis of the existing sample since the peaks shown could be pushed much closer together before they would overlap.

Either possibility is desirable and illustrates the necessity of studying zone dispersion in an effort to understand its mechanisms.

The measure of zone dispersion in a chromatographic system is given as

$$H = \frac{d\sigma^2}{dL}$$

(1)

where $d\sigma^2$ = incremental variance

$dL$ = incremental length of column

$H$ is called "height equivalent to a theoretical plate"
Figure 1  Poor and Good Resolution
(HETP) for historical reasons. A more workable expression is

$$H = \frac{\sigma^2}{L} \quad (2)$$

where sufficient homogeneity of the column is assumed.

It is a fortunate property of the variance that it is additive. Thus the variances from various dispersion mechanisms can be summed to yield a total variance.

$$\sigma^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \ldots \quad (3)$$

The only restriction is that the variances of the separate mechanisms not be interactive.

In 1956 van Deemter, Zuiderweg and Klinkenberg proposed an equation to explain the dispersion of a chromatographic zone:

$$H = A + B/v + Cv \quad (4)$$

where $A$, $B$, $C$ = constants

$v$ = linear mobile phase velocity

The constant $A$ arises from the fact that in a randomly packed column the flow paths which molecules follow may be tortuous or direct and thus may cause a molecule to either lag behind or get ahead of the mean of the zone, both of which will increase dispersion. The $A$ term is thus called
the multiple-path term. The length of the flow path, be it tortuous or direct, is a function of the particle size and is written

\[ A = 2\lambda dp \]  

where \( \lambda \) = constant  
\( dp \) = particle diameter

The \( B \) term arises from the fact that molecular diffusion will also contribute to zone dispersion. It is written

\[ B = 2\gamma Dm \]  

where \( \gamma \) = tortuosity factor  
\( Dm \) = molecular diffusion coefficient of the sample in the mobile phase

The tortuosity factor is the ratio of the direct-line distance between two widely separated points in a packed column to the length of the route a molecule must travel between the points going in and out and around the particles. The \( B \) term is inversely proportional to velocity since the higher the velocity the less time there is for diffusion to occur and is thus important only in low velocity regions.

The \( C \) term is called the "resistance to mass transfer" from the recognition that anything less than in-
stantaneous mass transfer of solute molecules in a column will cause zone dispersion. It was seen quite early in the study of chromatography (11) that a C term could arise both in the mobile and stationary phases but at the time columns were commonly made with a thick coating of stationary phase. Such a coating would cause the stationary phase C term, $C_s$, to be many times greater than the mobile phase term, $C_m$, so that $C_m$ was often dropped from the van Deemter equation.

$C_s$ is written as

$$C_s = q \frac{k}{(1+k)^2} \frac{d_f^2}{D_s}$$

(7)

where

$q$ = a configuration factor
$k$ = column capacity ratio
$d_f$ = thickness of stationary phase film on support
$D_s$ = molecular diffusion coefficient of the sample in the stationary phase

The individual terms will be dealt with in more detail as needed.

Zone dispersion due to the $C_s$ term arises from the fact that a molecule of the sample in the mobile phase is moving ahead of the zone center while a molecule momentarily sorbed on the stationary phase lags behind the zone center, both situations causing dispersion.
It can be seen from Eq. 4 that the magnitude of \( C_s \) is dependent on the square of the film thickness, \( d_f \). Modern chromatography columns often bear a very light loading of stationary phase, which greatly reduces the magnitude of \( C_s \) to the point that \( C_m \), the mobile phase \( C \) term, becomes important (21,36).

\( C_m \) is written as

\[
C_m = \frac{\omega d_p^2}{D_m}
\]  

(8)

where \( \omega \) = constant

Mobile phase zone dispersion occurs in a column because of the variety of flow paths. This is counteracted by lateral diffusion from one path or regime to another. The fact that the counteracting diffusion is not instantaneous gives rise to the \( C_m \) term.

**MOBILE PHASE DISPERSION IN NON-SORBING SYSTEMS**

It has been customary when studying mobile phase dispersion to use a non-sorbing system since then \( C_s = 0 \) and \( C_m \) can be studied directly.

The study of separation has largely been the domain of chromatographers. Zone dispersion on the other hand
has interested researchers from many disciplines. Chemical engineers have been foremost in this interest since many chemical engineering processes involve the passage of a zone through a bed of particles. Civil and petroleum engineers as well as soil scientists find that a packed column can serve as a model for the movement of ground water through soil or gravel or the movement and displacement of petroleum through sands and other materials.

As suggested by Edwards (14), the study of these investigations by chromatographers can be enlightening since the problem is observed from a variety of viewpoints. In addition, despite its importance to chromatographers, there have been comparatively few studies of mobile phase dispersion with the goal of elucidating the fundamental mechanisms of flow and dispersion.

It has become apparent that the explanations and models of flow of earlier days as represented by Eq. 4 are oversimplified. A case in point is the finding of Hawkes (28) that the tortuosity factor, \( \tau \), of Eq. 6 is not a constant as has long been assumed but is flow dependent.

A study of zone dispersion and flow phenomena needs
to be undertaken to provide a truer picture or a more accurate model. This is becoming important as the trend in both gas and liquid chromatography turns toward higher pressures and velocities and flow enters regimes quite different from those of past experience.

Scientists and engineers are interested in finding dispersion in a packed bed as a function of flow velocity. For this purpose several functions of dispersion and velocity are used. Among engineers the velocity is usually incorporated into the Reynolds number

$$\text{Re} = \frac{v d \rho}{\eta}$$

(9)

where $\rho$ = density of the mobile phase
$\eta$ = viscosity of the mobile phase

The interstitial velocity, $v$ (the same $v$ as in Eq. 4), is the time-averaged velocity, defined as

$$v = \frac{L}{t_0}$$

(10)

where $L$ = length of column
$t_0$ = elution time of unretained sample

The interstitial velocity is related to the superficial velocity, $v_s$, by $\epsilon$, the void fraction of the bed.

$$v_s = \epsilon v$$

(11)
The quantity $\eta/\rho$ is called the kinematic viscosity and is the term more often used by engineers.

Chromatographers commonly use reduced velocity, $\nu$, as a velocity term.

$$\nu = \frac{v d_p}{D_m} \tag{12}$$

The use of the Reynolds number as a velocity function is for the most part tradition and it has been pointed out (4,13,34) that there is no evidence that dispersion is dependent on kinematic viscosity. The Reynolds number may be a useful parameter, however, in studying dispersion as a function of turbulence since it is a measure of the onset and degree of turbulence.

The great advantage of using the reduced velocity as a velocity function is that by dividing out the effect of molecular diffusion, data from systems in which the mobile phase is a gas and those in which it is a liquid can be correlated on the same coordinates. This is advantageous since the very low molecular diffusivity of liquids leads to high reduced velocities while gaseous systems give low reduced velocities.

Although an effective dispersion coefficient is sometimes used as a direct value for dispersion, the more com-
mon representation in engineering is the Peclet number,

\[ \text{Pe} = \frac{v d_p}{D} \]  

(13)

where \( D \) = axial dispersion coefficient

The axial dispersion coefficient, \( D \) (or often \( E \) in the literature), should not be confused with \( D_m \) or \( D_s \), the coefficients of molecular diffusion in the mobile and stationary phases respectively. The latter two are measures of dispersion due only to random molecular motion. The former is a measure of dispersion from all sources including molecular diffusion, flow and sorption-desorption kinetics, if any. In this work the term diffusion will relate only to \( D_m \) or \( D_s \) and the term dispersion only to \( D \).

The Peclet number is preferred over direct dispersion values since it is dimensionless but its usage is contested since its original application was to heat transfer and its use in mass transfer is by analogy due to the similarity of the two processes. Renaming the mass-transfer Peclet number the Bodenstein number has been suggested (30,47) but its usage has not been extensive.

Chromatographers commonly use reduced plate height, \( h \), as a measure of dispersion:
The only advantage of $h$ over $Pe$ is that $h$ is directly proportional to $D$ while $Pe$ is inversely proportional to $D$. $h$ is thus easier to visualize since minimum $h$ corresponds to minimum dispersion and vice versa.

Reduced plate height and reduced velocity are related to the Peclet and Reynolds numbers as follows:

$$h = \frac{H}{d_p} = \frac{2D}{v \cdot d_p} \quad (14)$$

$$\mathcal{V} = \frac{Re \cdot \gamma}{D_m \cdot \Omega} \quad (15)$$

Some engineering researchers (5,24,71) have arrived at expressions equivalent to reduced plate height for their work.

As stated before, there has been a great amount of work done on zone dispersion in fields other than chemistry. At times this has been recognized (14,31) but little time has been spent in any organized effort to gather everything together.

The work that has been done on dispersion is of two
types. The first is the purely theoretical work. This involves setting up dispersion models based more or less on physical reality and then solving the resulting differential equations. The second type of work involves the first approach but in addition attempts experimental verification of the model and equations. The difference between the two is that in the second approach boundary conditions are set and assumptions are made sufficient to allow tractable solutions applicable to the experimental data. In the first approach the equations and models tend to be large, cumbersome and complex. It yet remains for someone to gather all the theoretical dispersion equations in existence in the hope of some sort of synthesis.

In this work a correlation of all the experimental results of the second approach is undertaken. Data from as many researchers as possible were gathered and evaluated and reduced to common parameters. As far as is known the research was exhaustive. Not all data that were uncovered in literature searches, however, were found to be useable and some had to be excluded for various reasons. Only data from systems of packed beds of hard, non-porous, non-sorbing spheres were used. In addition, reasonable annotation of experimental conditions was necessary to allow the
MOBILE PHASE ZONE DISPERSION IN SORBING SYSTEMS

As stated above, studies of mobile phase zone dispersion have with few exceptions been undertaken in non-sorbing systems to eliminate the effect of the $C_s$ term. This can be done on the assumption that $C_m$ is independent of any effects of the sorption-desorption process. If this were not so $C_m$ would be different in sorbing than in non-sorbing systems.

It is known from the work of Golay (23) that in open tubular (capillary) columns the $C_m$ term is dependent on the interaction of the sample with the stationary phase, namely,

$$C_g = \frac{1 + 6k + 11k^2}{24(1 + k)^2} \frac{r^2}{D_g}$$  \hspace{1cm} (17)

where

- $k$ = column capacity ratio
- $r$ = internal radius of column
- $C_g$ = gas-phase mass transfer coefficient
- $D_g$ = gas-phase molecular diffusion coefficient

A note on subscripts is needed. The subscript $m$ refers to the mobile phase and makes no distinction as to whether it is a gas or a liquid. Likewise the sub-
script s refers to stationary phase without other qualifications. When the subject is specifically gas-liquid chromatography the subscript g (gas) is identical to m and l (liquid) is identical to s. Eq. 17, for example, is specific for gas-liquid chromatography.

The column capacity ratio is defined as

\[ k = K \frac{V_l}{V_g} \]  \hspace{1cm} (18)

where

- \( K \) = partition coefficient
- \( V_l \) = total volume in column of liquid (stationary) phase
- \( V_g \) = total volume in column of gas (mobile) phase

\( K \) (known as Big K) is a well-known thermodynamic quantity and is the ratio of the amounts of a substance partitioned between two phases. \( k \) (known as Little k) is a parameter dependent on column conditions. Both are dependent on temperature and (to a lesser extent) pressure and are, of course, unique for any sample-stationary phase combination.

In practice \( k \) is determined by

\[ k = \frac{t_r - t_0}{t_0} \]  \hspace{1cm} (19)

where
- \( t_r \) = total retention time of sorbed sample
- \( t_0 \) = total retention time of unsorbed (inert) sample
Thus a substance eluting in twice the time of an unretained peak has a $k$ of unity and $k$ may vary from zero to infinity.

The dependence of $C_g$ on $k$ in Eq. 17 was not obtained by Golay from experimental results but was derived mathematically. Such a derivation is impossible in a packed column because of its complexity but Golay noticed the similarity between the open-tubular process and the telegrapher's equation in information theory and solved this equation to obtain the $C_g$ and $C_\ell$ terms exactly.

Eq. 17 suggests that there should also be a dependence of $C_g$ on $k$ in packed columns. There has been little work on this however. Littlewood in 1964 (49) predicted theoretically that $C_g$ should be independent of $k$ but his qualification was the absence of non-equilibrium in the column. Giddings (19) has also examined the problem theoretically and concluded that for non-porous particles the principle contribution to the mobile phase $C$ term is probably due to interchannel velocity variations over short ranges and gives the expression

$$C_m = (0.62 - 0.18) \frac{1}{1 + k} \frac{d_p}{D_m}^2 \quad (20)$$

Knox and Saleem (45) considered the problem with a
different model and arrived at the expression

\[ C_m = \left( \frac{k}{1 + k} \right)^2 \frac{d_p^2}{D_m} \]  

(21)

The usual method for obtaining \( C_m \) data from sorbing systems is to vary the diffusivity of the mobile phase by varying the nature of the carrier gas. Using helium and nitrogen is the most common method (49,58,62). The data from the two systems are then solved as simultaneous equations to obtain the \( C_m \) term. The \( C_s \) term is assumed to be constant since it contains no term dependent on the mobile phase. The drawback of this method is that it only allows an approximately 3.5-fold variation in reduced velocity which arises from the difference in the molecular diffusivity of the sample in the two carrier gases.

An alternative method is to vary the diffusivity of the sample in the carrier by varying the column pressure since \( D_g \) is inversely proportional to pressure (12). This approach, however, involves some intricate pressure calculations as well as assumptions to obtain useful data. In both approaches it is often the case that the coefficients of the van Deemter equation are found by fitting the whole equation to the data by a least squares method (9, 22,38,39).
A third approach is the one used for this work. As given in Eq. 4 the van Deemter expression is

$$H = A + B/v + C_m v + C_S v$$  \hspace{1cm} (22)$$

Expanding the terms gives

$$H = 2 \lambda d_p + \frac{2 \gamma D_m}{v} + \frac{(\omega d_p^2 v}{D_m} + \frac{k}{(1 + k)^2} \frac{d_f^2 v}{D_s}$$ \hspace{1cm} (23)$$

Dividing through by $d_p$, the particle diameter, gives

$$\frac{H}{d_p} = 2 \lambda \frac{D_m}{v} + \frac{2 \gamma D_m}{d_p} + \frac{(\omega d_p^2 v}{D_m} + \frac{k}{(1 + k)^2} \frac{d_f^2 v}{D_s d_p}$$ \hspace{1cm} (24)$$

Since $h = H/d_p$ and $\nu = v d_p/D_m$, Eq. 24 rearranges to

$$h = 2 \lambda \frac{\gamma}{\nu} + (\omega \nu) + \frac{C_S}{d_p} v$$ \hspace{1cm} (25)$$

which is the van Deemter equation in reduced form with the exception of the last term.

As has been pointed out (45), there has never been a theory of $C_S$ which is not of the form

$$H = C_S v$$ \hspace{1cm} (26)$$

If a method can be found to vary $\nu$ continuously (rather than discreetly as with the He-N$_2$ method) while
holding \( v \) constant a plot of \( h \) vs. \( \nu \) would yield a line of slope \( \omega \) whose extrapolated intercept (to \( \nu = 0 \)) will be \( C_s v/d_p \). In practice if a chromatograph is constructed so that inlet and outlet pressure can be varied independently with flow rate being the dependent variable, \( \nu \) and \( v \) can, within limits, be varied independently. Since

\[
v = \frac{L}{t_0}
\]  

(27)

t_0 \text{ can be held constant while column pressure is varied.}

This is seen by

\[
D_g = D_g^* \frac{P_{\text{atm}}}{p}
\]

(28)

where \( D_g^* \) = gaseous molecular diffusion coefficient at one atmosphere pressure and column temperature

\( P_{\text{atm}} \) = atmospheric pressure

\( p \) = average column pressure

Since

\[
\bar{p} = \frac{p_0}{j}
\]

(29)

where \( p_0 \) = outlet pressure

\( j \) = James-Martin compressibility factor,

\[
3 \left( \frac{P^2}{2} - 1 \right)
\]

\[
2 \left( P^3 - 1 \right)
\]

where \( P = p_i/p_o \), the ratio of inlet to outlet pressure

the expression for reduced velocity becomes
Thus by varying column inlet and outlet pressures while keeping \( t_0 \) constant \( \mathcal{V} \) can be varied (by varying \( \bar{p} \)) without changing \( v \). This approach has not been attempted nor suggested before and as mentioned offers a simple method for continuously varying the parameter of choice.

In the foregoing sections it was assumed that the total plate height of a chromatographic system is the direct sum of the plate heights due to the various mechanisms. That is, considering only mobile phase contributions to \( h \),

\[
h = 2\lambda + \omega \mathcal{V}
\]  

(31)

It has become apparent, primarily through the work of Giddings, that these terms are not independent but "couple" in some way to reduce \( h \) below that of the sum of the individual terms. Giddings gives the expression (18, p.52ff):

\[
h = \frac{1}{\frac{1}{2\lambda} + \frac{1}{\omega \mathcal{V}}}
\]  

(32)
The underlying physical phenomena resulting in coupling are somewhat difficult to visualize. It can best be seen as follows. The random walk model is a common exercise in elementary statistics and describes the transformation of a delta function to a binomial and ultimately to a gaussian distribution. It is applicable to a simple theory of zone dispersion in chromatography. Two things to come out of it are that the variance of a random walk distribution is proportional to the number of steps but increases with the square of the step length. One may imagine a packed bed with molecules moving through it. If the molecules move through it so rapidly that there is no time for lateral diffusion out of a given streampath each molecule will elute in the minimum number of steps corresponding to maximum step length and \( h \) will be at a maximum. At very low reduced velocities lateral diffusion will occur very often and the step length will be very short leading to a very small \( h \). In between these two extremes the two mechanisms couple to an extent determined by the velocity. In short, at high \( \nu \), Eq. 32 becomes

\[
h = 2 \lambda \quad (33)
\]

and at low \( \nu \).
The classical theory of chromatography predicts that \( h \) will increase indefinitely with \( \nu \) and that \( \lambda \) is a constant term which will give a finite \( h \) even at \( \nu = 0 \).

In an effort to base Eq. 32 on a more realistic model Giddings proposed (18, p.40ff) that there were several distinct regions in a packed bed over which nonequilibrium and thus diffusion could occur such that (18, p.55)

\[
h = \sum_{i=1}^{n} \frac{1}{2 \lambda_i} + \frac{1}{\omega_i \nu} \tag{35}
\]

for which he gave \( n = 5 \). Knox extended the summation logically to an integral (41)

\[
h = \int \int f(\lambda, \omega) \frac{d}{2 \lambda} + \frac{d}{\omega \nu} \tag{36}
\]

but at this point the expression loses most of its tractability.

In an effort to correlate theory with experimental data it has been proposed from time to time that \( h \) need not be a linear function of \( \nu \). This has led to the conclusion that (35,40,45,67,68)

\[
h = \omega \nu^x \tag{37}
\]
where $x$ is less than unity.

This has also been included in the coupling equation by (32,45)

$$h = \frac{1}{\frac{1}{2\lambda} + \frac{1}{\omega x}}$$

(38)

The inclusion of the exponent in Eqs. 37 and 38 is empirical and does not arise from any proposed model.

A plot of $h$ versus $\nu$ at constant linear velocity, $v$, using the classical van Deemter equation would appear as Figure 2A. Figure 2B is the same plot using the coupled van Deemter equation. It can be seen that at high velocities the curve levels off as it approaches the limit of $h = 2\lambda$. At high velocities however there is the possibility of turbulence and its effect cannot be disregarded.

The usual measure of turbulence is the Reynolds number defined in Eq. 9. For this work, however, $v$ must be replaced by a reduced velocity so that the Reynolds number becomes

$$Re = \frac{\nu D_m^* \rho^*}{\eta}$$

(39)

where $\rho^*$ = density of the carrier gas at one atmosphere and column temperature

Although the onset of turbulence in open tubes is
Figure 2 Reduced Plate Height vs Reduced Velocity \((h \text{ vs } \nu')\) at Constant Linear Velocity \((v)\)
well known as a function of the Reynolds number the situation with packed columns is less certain. The best that can be said is that between Reynolds numbers of one and ten turbulence may start and at a Reynolds number of 100 it is probably fully developed. It depends, of course, on the nature of the packing particles. Turbulence is expected to start earlier in columns of particles with rough exteriors, such as diatomaceous earths, and later with smooth particles, such as glass beads. In a well-designed chromatograph the onset of turbulence can be determined through the use of the flow resistance parameter, $\phi$, (29)

$$\phi = \frac{4}{3} v \frac{\eta L}{g}$$

(40)

where $g = \frac{(P^2 - 1)^2}{(P^3 - 1)} P_0$

In laminar flow inertial forces are proportional to viscous forces. In turbulent flow inertial forces increase more rapidly and flow resistance increases (18,p. 217ff). For this work $v$ must be replaced by a $\nu$ term in Eq. 40 and it becomes

$$\phi = \frac{4}{3} \frac{\eta L}{g} \frac{\nu D_m^* P_{atm}}{d_p P_0}$$

(41)

A plot of $\phi$ versus $\nu$ will yield a straight line
of slope zero in the laminar flow region. In turbulent flow, however, $\phi$ decreases with increasing turbulence.

It has been pointed out (41) that at fully developed turbulence dispersion will become independent of velocity, a conclusion also arrived at by the coupling theory. This does not mean that the constant $h$ reached at high velocities in the coupled region is the same value as the constant $h$ at fully-developed turbulence. This will be brought up in a later section.
THE CHROMATOGRAPH

To accomplish the goals set out in the previous section it was necessary to build a suitable chromatograph. Such a chromatograph must meet the following requirements:

1. It must withstand high pressures.

2. It must have a system to vary inlet and outlet pressures independently.

3. It must have a suitable detector with low volume, good sensitivity, fast response and the ability to be pressurized with the column.

4. It must have an injection system that will function at high pressures, have a well-defined pulse shape and have either a negligibly small or a precisely measureable pulse width.

5. It must be precisely temperature-controlled.

These goals were accomplished with the chromatograph described in this section.

Preliminary calculations showed that the experimental work for this thesis could probably be done without exceeding pressures of 2000 lbs/in$^2$. For safety and also to accommodate subsequent work on the apparatus this figure was tripled and the chromatograph was built to withstand pressures up to 6000 lbs/in$^2$.

Figure 3 is a diagram of the chromatograph as con-
Figure 3  Chromatograph  Dashed lines indicate elements below board
constructed. All components used are guaranteed by their manufacturers to have working pressures of 6000 lbs/in\(^2\) or greater.

All tubing used is type 316 stainless steel (Tube-sales, Los Angeles, Calif.) in either 1/4-inch outside diameter by .120-inch inside diameter, 1/8-inch o.d. by .069-inch i.d. or 1/16-inch o.d. by .007-inch i.d. as indicated in Figure 3.

All fittings and connectors are also of type 316 stainless steel and were obtained from either Crawford Fitting Co., Solon, Ohio (Swagelok) or Hoke Mfg. Co., Cresskill, N.J. (Gyrolok).

The entire chromatograph is constructed on a piece of 3/4-inch plywood 19 inches by 12 inches which is sealed against moisture by several coats of urethane resin. The plywood board sits atop a constant temperature water bath (Model TE3, Techne, Princeton, N.J.). Some of the components of the chromatograph, notably the column and the carrier gas heating coils, are mounted below the plywood board so that they extend into the water bath and are thus held at a constant temperature. The manufacturer of the water bath guarantees not more than \(\pm 0.1^\circ C\) variation at any one point in the bath and not more than \(\pm 1^\circ C\)
variation over the length of the bath. The plywood board on top of the water bath probably improves its ability to hold a constant temperature somewhat.

**Pressure-Regulating System**

The carrier gas to the chromatograph comes from a commercial gas cylinder and is reduced to the desired column inlet pressure by means of a two-stage self-venting valve made of stainless steel (Model 3062A, Matheson, East Rutherford, N.J.) and capable of delivering gas at pressures up to 5000 lbs/in².

The outlet pressure of the chromatograph is regulated by two type 316 stainless steel fine metering needle valves (Model SS-2S, Nupro, Cleveland, Ohio) connected in series. It is possible to regulate the outlet pressure with only one needle valve but it would be difficult, especially at high pressures, to adjust the pressure very finely. If two are mounted in series the largest pressure drop occurs over the first valve and little pressure drop over the second with the result that the first valve acts as a coarse adjustment and the second valve as a fine adjustment. This is found to work quite well in practice. The pressure drop across the length of the column can be
routinely adjusted to a precision of ± 0.5 lbs/in².

**Pressure Measuring System**

Nearly all chromatographs, if they possess pressure measuring devices at all, rely on gauges in which pressure is translated to dial readings strictly by mechanical means. All such gauges are more or less imprecise and inaccurate. This is due to mechanical friction of the linkages, no means of calibration and the simple problem of size--most dial faces are too small to be read with any degree of accuracy.

For these reasons it was decided to use electronic pressure transducers to measure pressures. The heart of such a transducer is a metal foil whose thickness depends on the pressure range to be measured. Gas pressure displaces the foil and the displacement is sensed electromagnetically and translated to a meter reading.

Two transducers are used on the chromatograph. One is an absolute transducer (Model P2A, Pace Wiancko, North Hollywood, Calif.) which measures pressures above 0 lbs/in² gauge pressure. It is connected by means of a tee to the carrier gas line just before the line connects to the top of the column and thus measures inlet pressures. The
other is a differential pressure transducer (Model KP15, Pace Wiancko, North Hollywood, Calif.) one side of which is connected to the column outlet between the detector and the outlet pressure regulating valves (see Figure 1). It thus measures the differential pressure between the inlet and outlet of the column which is the column pressure drop. The outlet pressure is obtained by subtracting the differential pressure from the inlet pressure.

The signal from the two transducers is read by means of a transducer indicator (Model CD25, Pace Wiancko, North Hollywood, Calif.). By means of the transducer indicator the signal from the absolute pressure transducer can be read to a precision of ± 4 lbs/in$^2$ and the differential transducer to ± 0.5 lbs/in$^2$.

The accuracy of the transducers depends on their calibration. With the equipment available it was possible to calibrate both transducers to an accuracy of ± 5 lbs/in$^2$. Greater accuracy could be obtained by using more sophisticated pressure standards.

**Injection System**

Due to the high pressures used in the chromatograph the usual injection systems would be unworkable on this
apparatus, notably the use of any septa or sliding sample loops sealed with O-rings is eliminated. The only devices that can withstand high pressures and be gas tight are high pressure valves. This is the device that was used.

As the gas comes from the storage cylinder it passes through a seven-micron filter (Model SS-4F-7, Nupro, Cleveland, Ohio) and splits at a tee connector. One branch of the tee passes through a cross connector, past a capillary bleed on a tee connector, through an on-off valve (Model 3TS4-A, Whitey Research Tool Co., Emeryville, Calif.) and a 1/4-inch to 1/16-inch tube reducing connector, past a second capillary bleed and finally onto the column (see Figure 3).

A six inch section of 1/4-inch tubing is capped on one end and attached vertically down from the union cross to act as a reservoir for the liquid sample. The capillary bleed following it is a short length of 1/16-inch o.d. by .007-inch i.d. tubing silver soldered into a 1/4-inch tube which is connected to a union tee. The second capillary bleed is about ten feet of the same size 1/16-inch tubing connected directly to a 1/16-inch union tee.

The liquid sample in the reservoir has sufficient vapor pressure that the tubing between the sample reser-
voir (union cross) and the on-off valve is quickly saturated with sample vapor. The first capillary bleed was pinched and filed until it had a very low flow rate but enough to keep a constant forward flow across the sample reservoir and prevent sample vapor from diffusing back to the inlet tee and entering the column through the other branch.

If some sample does diffuse back to the tee and onto the column two things may happen. If the diffusion is irregular, anomalous peaks will show up on the output trace. If the diffusion is constant an increase in ionization current will be observed that will set a new baseline but will consequently reduce the sensitivity of the detector to the sample.

No spurious peaks were observed indicating that no irregular diffusion occurs. If constant diffusion occurs so that a new baseline is set, the baseline before and after an analytical peak should be different since the sudden passage of helium across the sample reservoir should interrupt the steady diffusion onto the column. No sudden change in baseline was observed after an analytical peak indicating that if there is back-diffusion onto the column it is negligible.
The other branch (see Figure 3) consists of about 16 inches of 1/16-inch o.d. by .007-inch i.d. tubing, about ten feet of 1/4-inch precolumn and the tee connectors leading to the pressure transducers. It connects with the top of the column at the same place as the first branch.

When the on-off valve is closed there is no flow through the first branch and all the carrier gas goes through the second branch. The .007-inch i.d. capillary acts as a choke and the length was calculated so that at the pressures and flow rates normally used the inlet pressure undergoes about a 1% reduction. The carrier gas that reaches the column is thus at a lower pressure than the gas behind the on-off valve, which is normally closed.

To calculate the length of capillary necessary to cause such a pressure drop one uses the Kozeny-Carman and Poiseuille equations for packed and open columns, respectively. For packed columns the Kozeny-Carman expression is

$$v_o = \frac{r_p^2}{45 \eta l_a} \left( \frac{\epsilon}{1 - \epsilon} \right)^2 \frac{p_i^2 - p_o^2}{2 p_o}$$

(42)

and for capillary columns the Poiseuille equation is

$$v_o = \frac{r_c^2}{8 \eta l_c} \frac{p_i^2 - p_o^2}{2 p_o}$$

(43)
where \( v_0 \) = outlet velocity \\
\( r_b \) = radius of particle \\
\( \varepsilon \) = porosity of packed column \\
\( \gamma \) = viscosity of gas \\
\( L_a \) = length of packed column \\
\( L_c \) = length of capillary \\
\( P_i \) = inlet pressure \\
\( P_o \) = outlet pressure \\
\( r_c \) = internal radius of capillary \\

The term \( \frac{P_i^2 - P_o^2}{2 P_o} \) is the pressure drop expression for a compressible gas and is found by integrating Darcy's law over the proper limits

\[
v = K \frac{dp}{dx}
\]

(44)

where \( K \) = constant \\
\( dp \) = incremental pressure drop \\
\( dx \) = incremental length of column

However for small pressure drops

\[
\frac{P_i^2 - P_o^2}{2 P_o} = \Delta p = P_i - P_o
\]

(46)

Also since the volume flow rate through a tube is the velocity times the cross sectional area of the tube the Kozeny-Carman and Poiseuille equations can be further rearranged. The volume flow rate through the column must equal that through the capillary. Equating the two expressions and rearranging yields
\[ L_c = \frac{5.625 \cdot r_c^4 \cdot L_a \cdot \Delta P_{\text{cap}}}{r_a^2 \cdot r_b^2 \cdot \Delta P_{\text{col}}} \left( \frac{1 - \epsilon}{\epsilon} \right)^2 \]  

(46)

where \( r_a \) = internal radius of packed column

Substituting the proper values will give the length of capillary needed.

The arrangement at the column inlet is shown in Figure 4. It consists of a Swagelok union elbow connecting the carrier gas line to the top of the column. A hole was drilled through the elbow coaxial with the column tubing and a length of 1/16-inch tubing was inserted. This was silver soldered into position and connected to the tubing leading from the on-off valve.

The carrier gas flows continuously through the inlet tubing (after undergoing a pressure drop through the capillary choke) onto the top of the column. A small part of the gas also flows through the inlet fitting and the 1/16-inch tubing and out the capillary bleed (see Figure 4). As the on-off valve is opened the gas behind it at a higher pressure than that at the top of the column and laden with sample vapor is forced through the inlet capillary onto the top of the column. When the valve is closed the sample remaining in the inlet capillary is immediately forced back through the capillary bleed insuring a sharp
Figure 4 Detail of Injection System
cutoff and preventing sample from slowly diffusing onto the column.

A microswitch (Robertshaw-Fulton, Columbus, Ohio) is mounted near the valve handle so that it is activated by a metal tab on the handle. The switch opens and closes a circuit consisting of a 45-volt battery (Model M30, Burgess, Freeport, Ill.) connected across a 22-megohm resistor. A Universal Digital Instrument (Model EU-805, Heath, Benton Harbor, Mich.) is used to time the length of the input pulse, that is, the length of time the valve is open as sensed by the microswitch. Its inputs are connected across the resistor so that the timer starts as the IR drop increases across the resistor and stops as the IR drop decreases.

A mechanical switch has a good deal of contact bounce. This became evident in that the input levels on the Universal Digital Instrument to start and stop the timer had to be carefully set or only the contact bounce would be timed. It was necessary to catch the switch on the right bounce but once the levels were properly set the timer was quite reliable, having an estimated failure rate of less than 1%.

This injection system satisfies the necessary re-
quirements. The on-off valve has a teflon seat especially made for leak-free service. It has no discernable leakage at a pressure drop of 2000 lbs/in$^2$ to atmosphere. The input pulse can be accurately timed and the capillary bleed system assures sharp cutoff of the pulse. The input pulse is a plug of uniform vapor composition.

Originally a solenoid-acutated valve was used in place of the manual on-off valve. It had the advantage of a very short pulse width which is always desirable in a chromatographic system. A circuit to actuate it was constructed using a monostable multivibrator which would pulse the gate of a triac (a bidirectional silicon-controlled rectifier). The triac closed the circuit to the solenoid and kept it closed until the gate pulse was removed. The gate pulse could be set for any value from a few to several hundred milliseconds by means of a precision potentiometer on the multivibrator.

It was a good system but its weak point was that the solenoid valve would not seal leak-tight or near enough so to be useable. The valve came equipped with a nylon seat which did not seal very well at all. It was sent back to the manufacturer to have a softer teflon seat installed. This helped some but measured leakage rates were still at
best around 0.2 ml/sec and usually more which was too much for the capillary bleed to handle.

The problem was that solenoid-actuated valves can be made leak-tight at either low or high absolute and differential pressures but not at high absolute and low differential pressures, for example, a pressure of 1000 lbs/in\(^2\) on the inlet side of the valve with a pressure drop of 10 lbs/in\(^2\) across the valve. This is because the pressure differential itself is used to help seal the valve.

The solenoid valve system was reluctantly replaced after much effort had gone into it.

Detector System

For this chromatograph a detector was specially constructed because no commercial detectors are made which are suitable for this application. Of the three main types of gas chromatographic detectors--flame ionization, radiation and thermal conductivity--only a radiation detector satisfies the requirements of this study.

Theory

The simplest radiation detector is the ionization cross-section detector. It approaches most closely the
ideal detector since it detects all substances and is reliable, robust and linear in its response. Its only drawback is that it is not as sensitive as some other detectors but its mass sensitivity can be increased by decreasing the volume of the detector.

An ionization cross-section detector consists of a source of beta-radiation, an ionization chamber, a polarizing potential, a collector electrode (anode) and a method of measuring the current flow. If a potential is applied to such a system a current is measured which is that produced by the disintegration of the ionization source. As the potential is increased the current also increases until a point is reached at which all the beta particles are being collected at the anode. A further increase in potential will cause little increase in ionization current. This is seen in Figure 5, which is the current-voltage curve for the detector in this study. It can be seen that once the current plateau has been reached careful voltage stabilization is not necessary.

A light gas such as hydrogen or helium flowing through the cell will not increase the current greatly but if a substance such as a hydrocarbon is introduced into the chamber the beta particles will ionize the substance.
Figure 5: Current Voltage Curve for Detector
The ion pairs then migrate under the potential to opposite electrodes and an increase in current is observed.

The basis of ionization cross-section measurements has been described by Otvos and Stevenson (56). They note that the ionization cross-section of a molecule is very close to that of the sum of the cross-sections of the individual atoms and is almost completely independent of molecular bonds.

It is possible for an ionization cross-section detector to operate in different modes. For example, if ultra-pure helium is used as the carrier gas it is possible for the beta particles to excite the helium atoms to a metastable state. They then collide with sample molecules and ionize them. Commercially this is called a helium detector (argon detectors, using the same principle, are more common). It is fortunate for this study that the slightest impurities in the helium supply quickly quench any helium excitation. The helium used in this work was not sufficiently pure to cause difficulties.

Another problem is that strongly electrophilic samples may absorb the beta particles and the detector will act in the electron capture mode. There would then be a competition between increased and decreased ionization.
current. This was seen to occur with nitrogen at pressures greater than 1900 lbs/in$^2$. At these pressures the nitrogen appears as a negative peak while at lower pressures the peak is positive. Shoemake (64) also noted this occurrence with nitrogen. Other substances such as chloroform and similar electrophilic species yielded oddly-shaped peaks. Normal hydrocarbons gave well-shaped peaks at all pressures which is to be expected since they are not electrophilic.

Construction

In designing a detector there are many factors to consider. The first of these is probably the source of ionizing beta radiation. There are about 16 beta emitting isotopes which can possibly be used but of these only a few are practical. Table 1 lists these.

Originally it was felt that Ni$^{63}$ would be the best choice. Since this is a metal it could be shaped or formed into any configuration, for example, a rod down the center of a hollow cylinder. Ni$^{63}$ can only be purchased, however, as a salt in solution. This yielded two possibilities. One was to electroplate Ni$^{63+}$ onto an electrode surface and the other was to preform a piece on Ni metal and then
<table>
<thead>
<tr>
<th>Source</th>
<th>Half-Life</th>
<th>Energy (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^3$</td>
<td>12y</td>
<td>0.018</td>
</tr>
<tr>
<td>C$^{14}$</td>
<td>5770y</td>
<td>0.0156</td>
</tr>
<tr>
<td>Si$^{32}$</td>
<td>700y</td>
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</tr>
<tr>
<td>Ni$^{63}$</td>
<td>92y</td>
<td>0.067</td>
</tr>
<tr>
<td>Sr$^{90}$</td>
<td>28y</td>
<td>0.54</td>
</tr>
<tr>
<td>Ra$^{228}$</td>
<td>6.7y</td>
<td>0.055</td>
</tr>
</tbody>
</table>

Table 1  Possible Sources of Beta-Radiation
have it irradiated in an atomic reactor so that $\text{Ni}^{63}$ is produced by the reaction

$$\text{Ni}^{62} + n \rightarrow \text{Ni}^{63} \quad (47)$$

The first proposal was found to be economically unsound. It is possible to purchase $\text{Ni}^{63+}$ in solution but to keep concern with federal regulations to a minimum the activity of the solutions is quite low. Thus it would have been prohibitively expensive to buy enough isotope in solution to give the necessary activity.

The second proposal, although probably the best in theory, was not pursued on two accounts. First, a lengthy licensing procedure would have to be undertaken in order to receive an isotope of such high activity from a nuclear reactor. Second, the cost of such an irradiation could have been very high. The time necessary to irradiate a 3/64-inch diameter nickel rod to the desired activity was calculated to be on the order of several weeks. The abundance of $\text{Ni}^{62}$ is sufficient (3.66%) and the thermal neutron cross-section is quite large (15 barns) but due to self-shielding the irradiation time is long. Such an irradiation could not be carried out in the Oregon State University reactor since it is actually turned on only for short periods of time. A "swimming-pool" type reactor that runs
continuously would be necessary. A two week irradiation would be quite expensive although the possibility existed that a reactor run by the U.S. Atomic Energy Commission would do the irradiation gratis except for handling fees since this had at times been done in the past for educational purposes. Still it was felt best to explore other possibilities first.

Tritium is the isotope most commonly used as a source of beta-radiation in cross-section, argon and electron capture detectors. Because of its relatively short half-life and low particle energy it is not difficult to obtain with high activity. Its low energy radiation means that just about anything from paper on up can act as an effective shield. It is also relatively inexpensive. For these reasons tritium was chosen as the ionization source.

It has a few drawbacks. Most notable is that the tritium, which is occluded on a titanium film, has a finite loss rate. The detector in which it is mounted must therefore be carefully vented in order not to contaminate the room atmosphere. Due to its low energy it is not detectable by ordinary means (Geiger Mueller tubes) and so contamination checks become a laborious process.

It was not necessary to obtain an AEC license but
the Radiation Safety Committee of the University kept a rather close watch over the activities in the laboratory. They were particularly concerned with the temperature at which the detector was operated. Above 250°C the loss rate of tritium is very high but since the detector in this study was operated at only slightly above room temperature there was no problem.

Radiation detectors come in several shapes and sizes, the most common of which is the parallel plate configuration in which one wall of the ionization chamber is the emitting source and the opposite wall the collector electrode. This type suffers from the disadvantages of a large volume, unequal sample distribution within the cell and blind corners, to and from which the sample can move only by diffusion.

Much more useful is the cylindrical configuration in which the cell is an extension of the column and is itself one electrode. The second electrode is a rod along the axis of the cylinder. This eliminates blind corners and unequal sample distribution. Its only drawback is that if the diameter of the collector rod is much smaller than the diameter of the cylindrical emitter migrating ions may "pile up" at the collector. This is known as a space
charge and is evidenced by the recorder output of the chromatographic peaks dipping below the baseline (a momentary current decrease). The problem, if it occurs, can be overcome by changing the dimensions of the detector or, within limits, by increasing the bial voltage across the electrodes.

The cylindrical configuration is the one chosen for this work.

The detector cell is illustrated in Figure 6. The emitting source is a 40 millicurie piece of titanium tritide on a stainless steel foil backing with a specific activity of one curie/in² (Hastings Radiochemical Works, Friendswood, Texas). Since one curie is equal to $3.7 \times 10^{10}$ disintegrations per second and one amp is $6.24 \times 10^{18}$ electrons per second a 40 millicurie source will produce a base ionization current (due only to the collection of beta particles) of about $0.25 \times 10^{-9}$ amp.

The collector is a steel rod 3/64-inch in diameter. It is supported on the axis of the detector by two spacers made of ceramic-filled teflon (Canal Industrial Supply, Seattle, Wash.) which resists creep better than ordinary teflon. The spacers are, of course, grooved to permit passage of the carrier gas.
Figure 6  Detail of Cross-Section Detector
The whole detector is mounted in one arm of a 1/8-inch Swagelok union tee as shown in Figure 7. The tritium foil is stiff enough to stay in place when inserted. The collector electrode runs from the detector out the second arm of the tee where it is insulated from the tee body by a nylon tube. The carrier gas exits through the branch arm of the tee. The free volume of the ionization chamber is 11.9 microliters.

It is difficult to appreciate the dimensions of the cell but if one can imagine a piece of coat-hanger wire 1/8-inch long this is the approximate size of the ionization chamber. A piece of this wire 3/8-inch long is the total length of chamber plus spacers.

This cell is similar to one built by Lovelock, Shoemake and Zlatkis (50) having a volume of 8 microliters. Theirs, however, is able to operate only at atmospheric outlet pressure while the one for this work can operate at pressures compatible with the rest of the system. It has been found operational and leak-tight up to 2000 lbs/in² and will presumably withstand much higher pressures.

The cell was assembled in the Swagelok tee by Hastings Radiochemical Works, Friendswood, Texas.

Figure 8 illustrates the experimental setup of the
Figure 7  Detector Mounted in Fitting
Figure 8  Detector Circuit
detector. The bias voltage is supplied by a 45-volt battery (Model M30, Burgess, Freeport, Ill.). The electrometer is a Barber-Colman Model 5170-100 with field-effect transistor input. The recorder is an Esterline-Angus Model E1101S one millivolt recorder which has a full-scale response time of 0.2 seconds.

**Operation of the Chromatograph**

**Response Time**

The response of a system is determined in part by the time constants of the various components. The time constant of a detector is simply the volume of the detector divided by the volume flow rate of the gas through the detector. The detector volume in this case is about 0.012 milliliter and a representative flow rate for this apparatus is about 0.2 ml/sec giving the detector a time constant of about 60 milliseconds.

The time constant of the recorder is that time required to reach 63% of the final signal in response to a step input. Since the recorder has a full-scale response time of 0.15 seconds its time constant is approximately 100 milliseconds.
The time constants of the electrometer are given by the manufacturer as a function of range. The range times the attenuation times $10^{-11}$ is the input current value necessary for full scale output voltage.

<table>
<thead>
<tr>
<th>Range</th>
<th>Time Constant</th>
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<tbody>
<tr>
<td>.1</td>
<td>500 msec</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>100</td>
<td>&lt;.1</td>
</tr>
<tr>
<td>1000</td>
<td>&lt;.1</td>
</tr>
</tbody>
</table>

Every effort was made to operate on as high a range as possible for two reasons. The first is on course to minimize the time constant. It was also found that on low ranges but high attenuation the solid-state devices in the electrometer, notably the input field-effect transistors, would saturate. This resulted in non-linear response and produced in many cases curiously flat-topped peaks. The problem was eliminated by using a higher range setting.

Range 10 was most often used with the result that the recorder contributed most to the time constant of the system, which is the usual case for a good chromatograph.

Since most of the peaks recorded had base widths of greater than four seconds and rise times of around two
seconds response time problems were not present.

**Noise**

The noise in the detector determines the lower limit of detection. The background current will have random fluctuations due to the stochastic variations in the ionization process and will also fluctuate due to pressure and temperature variations.

Shoemake (64) reports that the best theoretical noise level is about $10^{-13}$ amp which is associated with a base ionization current of $10^{-7}$ amp. This is the point at which temperature and pressure noise approximately equal random ionization noise. A larger or smaller ionization current will have greater noise level compared to the signal. Since the ionization current of this detector was found to be about $10^{-9}$ amp a smaller signal-to-noise ratio is expected.

As it turns out the greatest contribution to the noise in the system comes not from the above sources but from random static charges and/or stray capacitance and external vibrations. When the apparatus was first constructed it was found to be so sensitive that when the electrometer was at the proper settings to record peaks
a person moving anywhere in the room would send the recorder pen off scale. This problem was alleviated to a large extent by mounting the whole apparatus in a wire cage—a wood-frame "rabbit hutch" covered with hardware cloth. The whole thing is grounded to the metal-frame building. The only part not commonly grounded is the collector electrode in the detector, between which and ground there is infinite resistance.

The problem of vibration is a persistent one. A door slamming in the hall will cause the recorder pen to vibrate 3-4% of full scale while taking data. Mounting the water bath on two inches of foam rubber and securely fastening all free parts on the chromatograph helped some but the problem is likely to remain since the most troublesome vibrations are of low frequency and large amplitude, making them difficult to damp out.
OBSERVATIONS AND CONCLUSIONS

Mobile Phase Zone Dispersion in Non-Sorbing Systems

In gathering and correlating zone dispersion data from fields other than chemistry, not only are the results of value but also the various methods by which data were obtained. Table 2 lists the different research teams that have published zone dispersion data usable in this study. After each name the various physical parameters of their particular system are listed. Some seem rather cryptic but the explanation of the terms is in the text following.

To chromatographers a column is long and narrow, its length being several hundred to several thousand times its width. To most of the engineering world on the other hand a column is short and broad, its length to width ratio being less, usually much less, than 100. This leads to some considerations not covered in chromatographic literature.

Chromatographers are inclined to assume that once a bed is packed it is held in some sort of rigid array. In contrast, the phenomenon of fluidization is well known in engineering literature (6)—the fact that the particles in the packed bed may be displaced by the mobile phase. En-
<table>
<thead>
<tr>
<th>Investigator</th>
<th>Col. Dia. ((d_c)) Range (cm.)</th>
<th>Part. Dia. ((d_p)) Range (cm.)</th>
<th>Aspect Ratio ((d_c/d_p)) Range</th>
<th>Col. Length (cm.)</th>
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<td>16-39</td>
<td>61</td>
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<tr>
<td>2. Carberry &amp; Bretton (CB)</td>
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<td>.05-.5</td>
<td>7.6-76</td>
<td>92</td>
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<tr>
<td>3. Ebach &amp; White (EW)</td>
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<tr>
<td>4. Edwards &amp; Richardson (ER)</td>
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<td>.096-1.5</td>
<td>14-219</td>
<td>27-102</td>
</tr>
<tr>
<td>5. Evans &amp; Kenney (EK)</td>
<td>1.9-2.5</td>
<td>.2-.081</td>
<td>9.6-31</td>
<td>315</td>
</tr>
<tr>
<td>6. Harloman &amp; Rumer (HR)</td>
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<td>.96</td>
<td>145</td>
<td>84</td>
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<tr>
<td>7. Hiby (HI)</td>
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<td>5.6-180</td>
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<td>.050</td>
<td>36-64</td>
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<tr>
<td>9. Horne et al., liquid (HKML)</td>
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<td>.0397-.0598</td>
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<td>15.2(hex)</td>
<td>1.9</td>
<td>8</td>
<td>66</td>
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<tr>
<td>11. Kaizuma et al., gas (KMCC)</td>
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<td>.050</td>
<td>3.7-10</td>
<td>300</td>
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<td>.050</td>
<td>3.7-10</td>
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Table 2 Parameters for Non-Sorbing Dispersion Studies
<table>
<thead>
<tr>
<th>Part. Type</th>
<th>Mob. Phase</th>
<th>Tracer</th>
<th>Injection</th>
<th>Readout</th>
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</thead>
<tbody>
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<td>step, dynamic</td>
<td>point, conductivity</td>
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<tr>
<td>2. glass beads</td>
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<td>blue dye</td>
<td>pulse, static</td>
<td>integrated, photometric</td>
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<tr>
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<td>water</td>
<td>blue dye</td>
<td>sinusoidal, pulse, dynamic</td>
<td>integrated, photometric, relative</td>
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<tr>
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<td>argon</td>
<td>pulse, dynamic</td>
<td>integrated, ionization, absolute</td>
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<tr>
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<td>nitrogen,</td>
<td>H₂, He</td>
<td>pulse, dynamic</td>
<td>integrated, thermal conductivity, absolute</td>
</tr>
<tr>
<td>glass beads</td>
<td>argon</td>
<td>C₂H₄, Ar</td>
<td>dynamic</td>
<td></td>
</tr>
<tr>
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<td>.1% NaCl</td>
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<td>point, conductivity</td>
</tr>
<tr>
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<td>.028M ZnSO₄</td>
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<td>point, conductivity</td>
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<tr>
<td>8. glass beads</td>
<td>nitrogen</td>
<td>C₂H₄</td>
<td>pulse, dynamic</td>
<td>integrated, FID</td>
</tr>
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<td>acetone</td>
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<td>integrated, FID</td>
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<td>10. ceramic spheres</td>
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<td>point, conductivity</td>
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<td>integrated, ionization, relative</td>
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<td>helium</td>
<td>pulse, dynamic</td>
<td>integrated, thermal conductivity, relative</td>
</tr>
</tbody>
</table>

Table 2  Continued
gineering columns are commonly straight, vertically-mounted and large bore and the upward motion of the mobile phase may displace particles beyond a critical fluidization (bed expansion) velocity, which may be achieved at low Reynolds number (53). Indeed, fluidization is preferred for many applications and either the distinction between packed and fluidized beds is not considered to be of consequence or the study of dispersion in packed beds is done only as a preliminary step to the study of dispersion in fluidized beds (6,65). There has been no theoretical or experimental work on the presence or extent of fluidization in chromatography but it is a prospect to consider, not only for its detrimental effects but also for its possible usefulness. Edwards and Richardson (15) point out, for example, that in columns packed with particles of varying sizes channeling may occur as small particles, not rigidly held, are swept out of the way by the fluid stream.

The first seven columns of Table 2 list the physical parameters of the systems that were used. They are all self-explanatory except perhaps column three. The aspect ratio is the ratio of the diameter of the packing particle to the diameter of the column. Work has been done on this parameter by researchers who claim that its effect on zone
dispersion is important (33,43,44,70).

The last two columns describe the injection and read-out systems used. These are important in that they not only may affect the true dispersion in the bed but may also make their own additive contribution to the total variance of the system.

**Injection Systems**

Three methods of injection have been used for dispersion studies.

**Pulse Injection** is that normally used in chromatography. It consists of a pulse of sample of finite width but often of unknown shape. Mathematically analyzed by various models, it has been shown (5) that after a sufficiently long time, (which is generally much less than the elution time) the distribution of the solute molecules about the mean of the pulse is gaussian and the initial pulse width itself contributes negligibly to the total variance.

**Step Injection** can be viewed as an extended pulse injection where the width of the injection pulse is no longer negligible. The front of the pulse (breakthrough)
and the back (purge) assume during elution a sigmoidal shape and can both be analyzed for dispersion values. Ideally, both values should be the same.

**Sinusoidal Input** is accomplished by injecting two fluids onto the column in such a way that their concentrations vary in a sinusoidal manner. This is usually accomplished by passing the fluids through chambers whose volumes are varied in a sinusoidal manner. In the column as the two fluids disperse into one another the amplitude of each wave (but not the frequency) becomes less and the ratio of the amplitudes at two points in the column yields a measure of the dispersion between the two points. The basic theory of the frequency-response technique has been worked out by Rosen and Winsche (60). The full solution of the differential equation is complicated but approximations give an expression (51)

\[
\ln \left( \frac{A_1}{A_2} \right) = \left( \frac{d_P \Theta}{v} \right)^2 L
\]

(48)

where \( A_1, A_2 \) = amplitude at two points in the column
\( h \) = reduced plate height
\( d_P \) = particle diameter
\( \Theta \) = angular frequency
\( v \) = linear mobile phase velocity
\( L \) = distance between points 1 and 2
The advantage of this method is that it is essentially steady-state, which simplifies data acquisition.

**Readout Systems**

Engineers have recognized that to obtain a true measure of dispersion in a column it is not sufficient to measure a tracer at the column outlet and hope for an ideal input. This has led some to devise systems whereby the dispersion is measured at two points in a packed column removed from the column ends. Such an arrangement yields a relative readout while a one-detector setup gives an absolute readout. Insofar as the method of measurement does not perturb the system as it measures, the two-point relative system should give truer dispersion values. The need for removal of the measuring points from the column ends has seldom penetrated the chromatographic literature although it has been recognized in engineering (48). It would seem that the two-point system is superior for dispersion studies (26). Aris (1) has shown, for example, that even if a pulse has some arbitrarily odd shape, the difference in the variances measured at two points is the variance of the pulse arising from passage through the bed between the two points. This is important since in
chromatography pulses not only may have some odd shape and width but also may vary from one injection to the next.

Another problem that arises is defining true dispersion. In its simplest picture, axial dispersion in unretained systems consists of two effects—true molecular diffusion and flow phenomena. The latter arises from the fact that in a bed some flow paths are open while others are constricted and some are tortuous while others are direct. This has variously been termed convective diffusion, flow dispersion, eddy diffusion (But only in chromatography. Eddy diffusion means something quite different to an engineer.), etc. These flow phenomena are modified to varying extents by lateral diffusion between flow paths as discussed earlier under the coupling theory. Studies of packing structure (10, 25, 59, 66, 69) and flow profiles (29, 52, 63) have shown that mobile phase velocity across a column is not constant but varies with radial position. Such variations are ascribed to the "wall effect"—the perturbation of the packing structure due to the presence of the wall. It will cause dispersion due to velocity variations as with the flow phenomena described above but of a somewhat different nature since the velocity is known as a function of radial position while in flow phenomena the
velocity fluctuations are truly random. Researchers such as Cairns and Prausnitz (4) make a point of the fact that dispersion due to the wall effect should not be considered "true" dispersion since it is not a function solely of the packed bed (as with flow phenomena) but of the packed bed-column combination. Other researchers are either unaware that wall-effect dispersion exists or consider it with other dispersion mechanisms. Chromatographers have recognized this as, for example, Knox (43), who packed an "infinite" bed in which the dispersion of the tracer, injected at a point source, was measured downstream before it could disperse to, and thus be affected by, the wall layers.

The point manifests itself in the choice of detection method. A micro detector in the center of the bed will give a readout of tracer distribution independent of any velocity profile effects (point readout of Table 2). A detector that records a signal across the entire width of the column, on the other hand, will have an integrated readout which includes all mechanisms (integrated readout on Table 2).

All detectors for gaseous systems in this study but one yield integrated readouts but trans-column equilibra-
tion due to molecular diffusion and stream-splitting is rapid enough in gaseous systems that integrated and point readout probably would yield the same values. That is, there is a wall effect but it is inseparable from other effects. This is not the case in liquid systems.

In column eight of Table 2 is also listed whether the sample was injected into a flowing stream (dynamic) or a stopped stream in which the flow was started after injection (static).

Column nine of Table 2 gives four main types of detectors that were used--electrical conductivity (conductivity), thermal conductivity, photometric and ionization (flame and radiation).

Correlation of Data from Non-Sorbing Systems

Over 750 data points from 18 different research teams were gathered and converted to $h - \nu$ values. These were plotted by computer on log-log coordinates. The individual points can be seen on Figure 9. In reduced velocity they extend over nine orders of magnitude which is the most comprehensive set of dispersion data yet assembled. To find a composite curve of best fit the data points were subjected to non-linear regression
Figure 9: Individual Data Points and Curve of Best Fit
analysis from library programs (*SIPS) at the Oregon State University Computer Center.

It would be ideal to be able to fit the points to a model equation to describe the behavior but none exists over the complete velocity range. As an alternative a quartic equation was used to allow for as many maxima and/or minima as necessary.

\[ h = c_0 + c_1 \nu + c_2 \nu^2 + c_3 \nu^3 + c_4 \nu^4 \]  

(49)

where \( c_n \) = constant unrelated to mass transfer C term

In order to represent the individual data groups coherently each set was subjected to non-linear regression analysis (*SIPS) to find the line of best fit. Each of these was fitted to the above quartic equation to allow the curve to best follow the course of the data points. This method may make the curves somewhat less reliable at the data extremes but any other method would require unwarranted judgements as to where the curve is "supposed" to go. The coefficients obtained for each curve are shown in Table 3.

Figure 10 shows the composite curve plus the curve for each set of data. The identification is the same as
<table>
<thead>
<tr>
<th>Name</th>
<th>$C_0$</th>
<th>$C_1$</th>
<th>$C_2$</th>
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Table 3  Coefficients of Dispersion Data Equations
Figure 10  Fitted Data from Non-Sorbing Systems
that found on Table 2. From this figure insight into several problems is made possible. With sufficient data points the composite curve becomes a fair estimate of the mean. Thus it is profitable to examine each individual data set to see if there is any correlation between the instrumental set-up used to obtain the data and the position of the individual curve relative to the composite—above, below or coincident. This is done in Table 4.

In the first column the method of detection—point or integrated—is compared. It is seen that all the data groups above and close to the line of best fit used integrated readout. All those using point readout lie below the composite. The three sets with integrated readout which lie below the line of best fit are from gaseous systems. This is good evidence that in some systems there is an increase in dispersion due to velocity-profile (wall) effects which is detected by integrated but not by point readout. It also indicates as stated previously that this may be unimportant in gaseous systems.

Column two of Table 4, giving the type of detector used, is inconclusive, mainly because it is so closely tied with column one. That is, all photometric detectors have integrated readout and all electrical conductivity detect-
### Methods of Detection

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<th>Input Signal</th>
<th>Injection</th>
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<td></td>
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<td>integrated photometric absolute pulse dynamic</td>
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<td></td>
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<tr>
<td>cb</td>
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<td>lg</td>
<td>integrated photometric relative sinusoid dynamic</td>
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<tr>
<td>hkml</td>
<td>integrated FID absolute pulse dynamic</td>
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</table>

<table>
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<table>
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Table 4 Correlation of Column Parameters
ors have point readout, etc.

Column three lists the systems with regard to relative or absolute readout. It is surprising that of the four systems with relative readout three show a greater dispersion than the mean. This is the opposite of what was predicted above. The fourth data set is gaseous while the other three are liquid and this may have some bearing especially when it is noted that all gaseous data lie below or close to the mean. This would indicate that in gaseous systems injection methods are rapid enough that their effect on the dispersion is negligible while in liquid systems the inclusion of an additional detector may perturb the system more than the injection system. Another possibility is that the liquid systems using relative readout also used integrated detector systems. This would mean that the increase in variance due to the velocity profile as seen by the integrated detector is greater than the decrease in variance obtained by using a two-point (relative) readout. This would be more comforting to accept but additional experimentation would have to be done to reach any conclusion.

In column four it seems as if there is no inherent advantage of pulse over sinusoidal method of input or vice
versa but it is seen that all systems with step input have dispersion values below the mean. This, however, is probably because they also all have point readout. The possibility exists, though, that a well-designed system for step input may give a sharper front upon injection than the average pulse input, but the problem then becomes one of system design rather than system choice.

Column five indicates whether the sample injection is static or dynamic. Although only four systems used static injection, three of these lie below the mean. Again this might be due to the fact that they all have point readout. The general opinion of chromatographers has been that static injection causes greater zone dispersion. This is indicated (rather weakly) in that the one static injection system not using point readout lies above the mean. Hiby (30), on the other hand, claims that static injection may lead to decreased zone dispersion.

The individual data points on Figure 9 show quite a bit of scatter. This is understandable considering the wide range of experimental variables. Column diameters vary 81-fold, particle diameters 370-fold and column lengths 58-fold. In view of this it is surprising that the composite curve comes so close to that predicted by
theory. The area from log \( \nu = -2 \) to 2 is that encountered in most chromatography. It is described by the classic van Deemter equation, Eq. 4. From log \( \nu = 2 \) to 4 the composite curve levels off as described by the coupling equation, Eq. 32. From log \( \nu = 4 \) to 7 the reduced plate height falls as turbulence increases until it reaches a constant value of log \( h = 0 \) \((h = 1)\). Theories have been advanced in engineering to predict the limiting Peclet number. The theories are based on a mixing cell model \((2, 3, 46, 55)\) where minimum dispersion corresponds to perfect mixing in the cell. The cell dimensions are referred to the particle diameter where the length of a mixing cell or height of a mixing unit is a multiple of the particle diameter. Thus perfect mixing is achieved when

\[
\text{length of mixing cell} = d_p \quad \text{(50)}
\]

Since \( h = H/d_p \) the final value of \( h = 1 \) at extremely high reduced velocities on Figure 9 bears out the mixing cell theory and indicates that in the mobile phase plate height cannot be reduced below the particle diameter, that point being perfect mobile phase mixing.

Nearly all the work done on packed beds has been on random beds. The possibility of using beds having an or-
dered packing structure has not been extensively investigated. Mickley, Smith and Korchak (52) have studied flow profiles in an ordered bed made of ping-pong balls but Jacques, Hennico, Moon and Vermeulen (34) are the only researchers to use ordered beds in dispersion studies. They packed their columns with ceramic spheres in tetragonal ($\varepsilon = 0.32$) and two types of orthorhombic arrangements ($\varepsilon = 0.38$ and 0.395). In comparison, the void fractions of their random beds were 0.40 to 0.41. Thus if one judges by void fraction the two orthorhombic types must be similar to random arrangements while the tetragonal arrangement is more closely packed. The tightest packing structure, for comparison, is the hexagonal close-pack with $\varepsilon = 0.26$.

A regular bed brings up several interesting problems. For one thing, there is no macroscopic multiple-path contribution to zone dispersion ($A$ in Eq. 4, $2 \lambda$ in Eq. 32) since all flow paths have the same length. There will be microscopic velocity variations since it is well known that in flow through any capillary or interstice the velocity close to the wall is near zero while that in the center of the stream is about twice the average velocity. But if the interstices are narrow lateral equilibration is
very rapid. This situation comes most closely to approxi-
mating the "bundle of capillaries" model, which has been
used to analyze packed beds in the past. This is fortunate
since the exact solution for a single capillary is known.
The gas-phase C term for a capillary is given in Eq. 17.

Using Eq. 32 as a model, from the above considera-
tions \( \omega \) would probably be smaller in ordered than in
random beds and the point \( h = 2\lambda \) would probably be reached
at higher reduced velocities. Turbulence would probably
cause a decrease in \( h \) before the point \( h = 2\lambda \) is reached.
In addition, in a tightly ordered bed, the length of a
perfect mixing cell would probably be less than the par-
ticle diameter and thus the limiting reduced plate height
at high reduced velocities would be less than unity.

This is borne out by the data of Jacques et al.(34)
as seen in Figure 10. The composite of their data lies a
factor of 2 (about 0.3 log units) below the mean. This
gives the length of a mixing cell equal to about 0.2 of
a particle diameter. This figure may be somewhat low due
to the point readout system used but it indicates the ad-
vantage that can be obtained in regular beds. This also
indicates, perhaps, the necessity for uniform random beds
to achieve low plate height.
It is interesting to note that while studying column packing and wall effects Knox suggested (41) that perhaps a polygonal column, such as hexagonal, might cause the particles to pack more uniformly, simply because there is no way possible to pack a uniform bed in a cylinder. He subsequently tried a hexagonal column (43) and found it to give larger reduced plate heights than a comparable cylindrical column.

**Mobile Phase Zone Dispersion in Sorbing Systems**

The apparatus described earlier was used to obtain data on mobile phase zone dispersion in sorbing systems.

**Column Construction**

The support particles used in this study were glass beads with a textured surface (GLC-100, Corning, Corning, New York) in mesh sizes 60/80, 80/100, 100/120 and 120/140. The textured surface results in a more uniform coating of stationary phase. In addition, the glass used in these beads is specially made to have a very low metal ion contamination.

The stationary phase was tri-o-tolyl phosphate (TOTP) (Eastman Chemical, Rochester, N.Y.), practical grade. The
stationary phase as received was dark yellow and smelled strongly of cresol contamination. Small aliquots were cleaned by dissolving approximately 5 ml of the TOTP in about 25 ml of ethyl ether (to reduce viscosity and density) and washing vigorously in a separatory funnel with 25 ml portions of 20% sodium hydroxide solution four or five times. The ether-TOTP layer was then washed with 25 ml portions of distilled water until the water layer showed a pH of seven on wide-range pH paper. The ether layer was allowed to evaporate at room temperature under a dry nitrogen stream. The TOTP left behind was pale yellow and had no odor.

The columns used were all 25 feet (760 cm) in length and made of 1/8-inch copper tubing with an internal diameter of 1/16-inch (Alaska Copper and Brass, Portland, Ore.).

The stationary phase was coated on the support beads by first making an accurate solution of TOTP in acetone. The desired amount of beads was weighed on an analytical balance and an accurate aliquot of TOTP in acetone was added. More acetone was added to distribute the stationary phase evenly and this was stirred until dry under a stream of nitrogen. For example 10.0 ml of a 20.0%
solution of TOTP in acetone added to 40.00 grams of glass beads gave a 0.05% loading, which was the loading most commonly used.

Since the column was so long a packing frame needed to be constructed. This was fabricated out of two two-by-fours each 12 feet long. These were fastened together end to end with metal braces. Lengths of thin-walled copper tubing two inches long and one inch in diameter were fastened the length of the frame 18 inches apart with their axes parallel to the length of the boards. The whole thing was mounted in one of the fire escapes of Weniger Hall between the first and fourth floors. The column was threaded through the short sections of tubing and packed by banging it up and down and sideways. The low loading on the beads allowed them to be free-flowing so packing was not difficult.

The ends to the column were closed by soldering very fine (about 400) mesh copper screen over the ends, a procedure requiring no little skill. The column was coiled circularly and mounted on the chromatograph so that it was immersed in the water bath.
Data Acquisition

In order to achieve a constant linear velocity at varying average column pressure both the inlet and outlet pressures had to be adjusted. This was done by first elevating the inlet pressure to the desired level and then adjusting the outlet pressure to give a constant inert peak time, \( t_0 \). For example, if the velocity to be maintained was 19.00 cm/sec and the column length was 760 cm then

\[
\frac{L}{v} = \frac{760 \text{ cm}}{19.00 \text{ cm/sec}} = 40.0 \text{ sec} \quad (51)
\]

Theoretically the pressure drop necessary to achieve the desired \( t_0 \) can be calculated from well known pressure equations (73) but in practice it was better to arrive at the correct pressure drop by trial and error. Once this was found it remained the same for work in the laminar region. For the above case, for example, a pressure drop of 70 lbs/in\(^2\) gave the desired \( t_0 \). The \( t_0 \) values in practice were held to \( \pm 0.2 \) seconds in the extreme and about 75% of the time this was held to \( \pm 0.1 \) second, introducing an error of 0.25% in the velocity, which is less than the normal errors found in chromatography.

The inert peak comes from air entering the sample
chamber when it is filled with liquid sample.

It was found that the pulse width if allowed to become excessively large could contribute to the width of the output peak, giving false dispersion values. It was also found that Sternberg's method (71) for subtracting the dispersion due to the input pulse from the total dispersion did not work for this system. This could be due to the failure of the method in going from theory to reality. More likely, when the sample valve is opened for a long time (a few hundred milliseconds) the sample enters the inlet fitting (see Figure 4) faster than the column flow rate allows and backs up into the tubing. When the valve is closed this sample is swept onto the column giving a much broader pulse than that indicated by the pulse timer.

A method to get around (but not eliminate) this problem was devised. If an input pulse is negligibly narrow compared to the output an increase or decrease in pulse width within the "negligibility" region will cause a proportional increase or decrease in peak height but not in peak width. Beyond this region pulse width may affect peak height for a time but ultimately only peak width will change with pulse width and a step input as described
earlier will result. A plot of peak width versus pulse width should show a region at low pulse width that gives a constant peak width. Operation within this region should give true dispersion values. Such a plot is shown as Figure 11, where peak width is the width of the peak at half its height ($w_{1/2}$, the half-width). It can be seen that there exists such a region of negligible pulse width. All analytical peaks had pulse widths within this region.

Analysis of Data

There are several methods for analyzing chromatographic peaks. Some methods are more suited to certain investigations than others. The most precise method of obtaining the true total dispersion of a peak is by moments analysis. The first moment of a concentration distribution (no restriction is placed on the shape of the distribution) is

$$m_1 = \frac{\sum t_i y_i}{\sum y_i}$$

(52)

where $t_i =$ time at point i on the horizontal (time) axis

$y_i =$ concentration (vertical) value at $t_i$

t_1 must be outside the limits of the concentration dist-
Figure 11 Pulse Width vs Peak Width
ribution (i.e., $y_1 = 0$). The first moment is called the mean of the distribution. The second moment is

$$m_2 = \frac{\sum t_i'^2 y_i}{\sum y_i} \tag{53}$$

where time is now taken around the first moment such that

$$t_i' = t_i - t_{m_1} \tag{54}$$

The second moment is the variance, $\sigma^2$, and the square root of the second moment is thus the standard deviation, $\sigma$.

Reduced plate height is obtained from

$$h = \frac{H}{d_p} = \frac{\sigma^2}{d_p L} \tag{55}$$

The second moment can be obtained from experimental data by direct application of Eq. 53.

Sternberg (71) has suggested a method that is somewhat easier. Since most peaks are tall and narrow, vertical displacement as in Eq. 53 can only be measured inaccurately. He suggests dividing a peak into horizontal rectangular segments such that the midpoint of the end of each segment is bisected by the peak trace at that point as in Figure 12. One then applies the formula
Figure 12  Integration Method of Sternberg
\[ \sigma^2 = \frac{\sum w_i^3}{12} \sum w_i^2 \]  

where \( w_i \) = width of each rectangular segment at its midpoint

A third method involves certain basic assumptions, namely that the peak being analyzed is gaussian. If the peak is gaussian, the width of the peak at half-height, \( w_{1/2} \), is a known function of the standard deviation of the peak. By application of elementary statistics and chromatographic theory

\[ h = \frac{L w_{1/2}^2}{5.54 t^2 d_p} \]  

where \( t \) = total elution time of peak

Eq. 57 is given without proof since it or related equations are derived in most chromatography texts (18, p. 24).

All three of these methods were tried. The moments method and that of Sternberg agreed fairly well with each other (within about 7%) but both disagreed with the half-width method, the latter being lower by about 15-20%. The method of Sternberg was found to be less tedious but if few rectangles were used (fewer than about 20) the second moment was found to vary with the height of the peak,
that is, with the number of rectangles. If a great number of rectangles were used it became largely independent of peak height but became about as tedious as the first method.

The discrepancy between the first two and the last method can be explained as follows. Cram (8) has noted that he has never observed a true gaussian peak as observed on his specialized apparatus and goes so far as to say that there is no such thing as a true gaussian peak. This is probably true. If one examines the area of a peak closely enough to the baseline one always can find some tailing. This does not contribute significantly to peak area but due to its distance from the mean adds quite a bit to the variance through the \( t_i^2 \) term in Eq. 53. It must be remembered, though, that there is a difference between a tailed peak and a skewed peak. The latter is definitely non-gaussian and results from non-linear sorption-desorption processes in the column. The tailed peak on the other hand is generally regarded as a gaussian peak with a tail added which can arise from adsorption on the support and other reasons (20). The usual criterion for a symmetrical peak is the Skewness, which is defined as the total half-width of the peak divided by twice the
half-width of the front half of the peak. A peak with a Skewness between 0.95 and 1.05 is considered symmetrical. Some error must be allowed in estimating the mode.

A sample of 20 of the peaks used in this study showed an average Skewness of 1.047, indicating that Eq. 57 should give a reliable measure of dispersion due to linear sorption-desorption kinetics and flow phenomena. Figure 13 shows a typical peak obtained with the apparatus used in this study.

It is interesting to note that for many years Eq. 57 has been applied to skewed peaks by doubling the half-width of the front half of the peak. This has been done on hope more than knowledge but some chromatographers seem prepared to believe that this is valid. However, anyone who has seen a strongly "fronted" peak due to column overloading would be skeptical.

To investigate mobile phase zone dispersion in sorbing systems three homologous hydrocarbons were used as the sample--n-hexane, n-heptane and n-octane. Hydrocarbons were used to minimize any kinetic effects such as chemisorption which might occur with more reactive and/or polar substances. The three homologues were used because in this particular system they gave k values in a region
Figure 13  Typical Chromatographic Peak
where various functions of $k$ are changing most rapidly.

Values of reduced plate height for various reduced velocities were obtained. These were fitted by a non-linear least squares method to the three equations proposed to explain the shape of the curves other than by the classic van Deemter equation.

Figure 14 shows four series of points. Curve 1 is that of n-octane run using a constant linear velocity, $v$, of 25.33 cm/sec. Curve 2 is of n-octane using $v = 19.00$ cm/sec. Curve 3 is of n-heptane at $v = 19.00$ cm/sec and Curve 4 is of n-hexane at $v = 19.00$ cm/sec.

Calculations were done by Eqs. 57 and 30. The normalized diffusion coefficients of the hydrocarbons in helium, $D_m^*$, were obtained from the sources listed as 0.2716 cm$^2$/sec for heptane (7), 0.2556 cm$^2$/sec for octane (7) and 0.5440 for hexane (17), all at 34.5°C. These were calculated from the values given by using the relationship $D \propto T^{1.75}$.

The curves were fitted to the simple exponential equation

$$h = C_0 + \omega \nu^x$$  \hspace{1cm} (58)

to the simple coupled equation
Figure 14 Data Points
\[ h = C_0 + \frac{1}{2\lambda} + \frac{1}{\omega \nu} \]  

(59)

and to the coupled exponential equation

\[ h = C_0 + \frac{1}{2\lambda} + \frac{1}{\omega \nu^x} \]  

(60)

In each case \( C_0 \) is a constant and does not refer to a mass-transfer C-term.

The points from Figure 14 plus the curves generated by each expression for reduced plate height are shown in Figures 15, 16 and 17. The curves themselves were generated and plotted by computer using 100 to 250 points for each curve, depending on its length.

Table 5 lists the values of the parameters for each of the four curves according to each of the fitted equations along with the residual sum of squares, which is a measure of the "goodness" of the fit. It is the sum of the squares of the distance of each point from the line and the smaller its value the better the fit. It is no indication of the verity of the function fitted to the points.

The significance of \( C_0 \), the intercept on the \( h \) axis, is that at a reduced velocity of zero \( C_m = 0 \) but since
Figure 15  Data Fitted to Eq. 58
Figure 16 Data Fitted to Eq. 59
Figure 17  Data Fitted to Eq. 60
\[ h = C_0 + \frac{C_0}{\omega \nu^x} \]

<table>
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<th>( 2\lambda )</th>
<th>( \omega )</th>
<th>( x )</th>
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\[ h = C_0 + \frac{1}{2 \lambda} + \frac{1}{\omega \nu} \]

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\[ h = C_0 + \frac{1}{2 \lambda} + \frac{1}{\omega \nu^x} \]

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<td>.0125</td>
</tr>
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Table 5  Coefficients of Fitted Equations
\( v \neq 0 \) (see Figure 2)

\[
C_0 = \frac{C_s v}{d_P} \tag{61}
\]

\( C_0 \) is thus a constant \((v/d_P)\) times the stationary phase mass transfer term. This is rather a leap of faith since the situation of zero reduced velocity at finite linear velocity is clearly imaginary, being only achieved by infinite diffusivity of the sample in the mobile phase. There is thus a minimum reduced velocity below which one cannot go at constant linear velocity, the point for this system being that at which the outlet pressure equals atmospheric pressure. Nevertheless it is permissible to extrapolate to zero reduced velocity. The difficulty here is that since the curve describing the data is non-linear one is somewhat uncertain about its behavior between the lowest data point and \( \nu = 0 \).

One measure of the suitability of a function to describe the model is the observation of the function beyond the limits of the data. That is, it should be able to correctly predict the course of the curve up to the boundary conditions of the model if it truthfully represents the model.

Figure 15 shows the data fitted to Eq. 58. The
equation fits quite well to the points within their range but the curve falls off rapidly below the last data point typical of exponential functions. This is a drawback of the equation but it must be noted that it was formulated from observations on liquid chromatography systems where the normal linear velocities produce reduced velocities between 100 and 10,000 (45) and its validity has only been assumed over short ranges (67). Thus it could only be described as fortuitous if the curve fit at low velocities. The low h-intercept, $C_0$, interpreted as a low $C_s$ term, gives a falsely high $C_m$ term. Table 5 shows that $\omega$ for Eq. 58 is several times higher than for the other two equations.

In Figure 16 Eq. 59 appears to be a good fit to the data and extrapolates in the expected manner to zero reduced velocity. This would be hoped for since the equation is modeled to account not only for moderately high but also low reduced velocities.

Figure 17 shows the curves fitted to Eq. 60. The behavior of the upper two curves is unexpected in that they both have a point of inflection between $V = 0$ and 50. A point of inflection is expected in a normal van Deemter curve with coupling due to the molecular diffusion $B$ term
This term has not been included in the expressions used here, however, so the appearance of points of inflection in the curve is a coincidence and indicates that Eq. 60 does not truthfully reflect the model beyond the limits of the data. No model for mobile or stationary phase mass transfer terms indicates such curves as the upper two on Figure 17.

Since the intercept of the $h - V$ curves, $C_0$, is known to be Eq. 61, calculations can be carried out on the term to determine the accuracy of the predicted curve. The two octane curves differ only in linear velocity, $v$, so they can be solved simultaneously. The upper curve has a velocity exactly $1/3$ higher than that of the lower curve. If three times the difference between their two intercepts, $C_0$, is subtracted from the lower curve the result should be zero. That is, the curve should intercept at $h = 0$ when the $C_s$ term is subtracted out. For the simple coupled expression, Eq. 59 (Figure 16) the actual result is 1.13. For the exponential coupled expression (Eq. 60) it is 2.16. This is probably an indication of the experimental error involved as well as the difficulty of extrapolating a curve. It is seen, however, that the simple coupled expression gives a value closer to zero.
It was given in Eq. 7 that

\[ C_s = q \frac{k}{(1 + k)^2} \frac{d_f^2}{D_s} \]  

(62)

q is a constant for the system, so knowing k and D_s it should be possible to calculate d_f, the film thickness, from the data of octane, heptane and hexane. It should be the same for all three since the same column was used. The values for the diffusivities of the hydrocarbons in TOTP were obtained from Nyberg (48, p.72) as octane, \(2.1 \times 10^{-6}\) cm\(^2\)/sec, heptane \(2.4 \times 10^{-6}\) cm\(^2\)/sec and hexane \(2.7 \times 10^{-6}\) cm\(^2\)/sec. The value of q is given (18, p.147) as 1/12 for glass beads where "puddling" around the contact points of the beads is assumed. The values of k are obtained from Eq. 19 as 1.1 for octane, 0.413 for heptane and 0.158 for hexane. Using

\[ d_f = \left( \frac{C_0 d_p D_s}{q \frac{k}{(1 + k)^2} v} \right)^{\frac{1}{2}} \]  

(63)

and using the values of C_0 from the simple coupled Equation d_f is found to be

- octane \(d_f = 2.62 \times 10^{-4}\) cm
- heptane \(d_f = 2.73 \times 10^{-4}\) cm
- hexane \(d_f = 3.46 \times 10^{-4}\) cm
The agreement between octane and heptane is fairly good but both differ from that of hexane. The reason for this is not clear. It can be seen on Figure 16 that the curve through the hexane data points is quite straight. If in reality there is a greater curvature the h-intercept would be lower than shown and the value of $d_F$ for hexane would be closer to that of the other two but no estimate can be given as to the magnitude. Certainly if the data for hexane could have been extended to higher reduced velocities some curvature would have been seen.

It was noted that when a fresh column was put on the chromatograph the reduced plate height measured on successive days would increase for the first several days and only reach a steady value after about ten days. This was probably due to a redistribution of the stationary phase. Due to the textured surface of the glass beads used the stationary phase was most likely deposited as a more or less uniform film. With ageing, however, the liquid would tend to puddle and change the $C_s$ term. It has been shown (18 p. 136-149) that the presence of a few deep narrow pockets of stationary phase will cause the plate height to increase markedly. This may have been the case as the stationary phase went from a thin film to
annuli at the contact points. This problem was noted on more than one column and was worse on columns packed with larger beads. It is interesting to compare this with the work of Knox and Saleem (45) on the maldistribution of stationary phase.

As noted before, three expressions have been formulated to explain the dependence of $C_m$ on $k$. Golay's expression, Eq. 17 (23), is derived and holds exactly for capillary columns. Its extension to packed columns may be warranted insofar as the packed column resembles a capillary or bundle of capillaries.

Giddings' expression, Eq 20 (19), is a modification of Golay's equation. He considered a packed bed to be made up of flow units consisting of a straight open region of relatively unimpeded flow surrounded by an annulus of particles comprising an area of restricted flow. The dependence of $C_m$ on $k$ in the first region reduces to Eq. 17 with the proper conditions and the second region has a lesser dependence on $k$. The two regions combined yield Eq. 20.

Knox and Saleem's expression, Eq. 21 (45), is of a different type. They consider that in any column it is unlikely that the stationary phase distribution is com-
pletely uniform. There will be regions, probably a few particle diameters wide, in which there is heavy loading of stationary phase alternating with regions in which there is light loading. Since by Eq. 18 \( k \) is dependent on stationary phase loading there will be regions in the packed bed where the sample surges ahead of the mean alternating with areas in which the sample lags behind the mean, all of which leads to zone dispersion. Knox and Saleem's analysis leads to Eq. 21.

All of these expressions lead to modification of a term previously thought to be constant, namely \( \omega \). This leads to the possible formulation

\[
\omega = f_n(k) \omega
\]  

(64)

where \( \omega \) is the \( \omega \) found in Eqs. 25, 58, 59 and 60 and \( \omega \) is a true constant. \( f_n(k) \) is

\[
f_1(k) = \frac{1 + 6k + 11k^2}{24 (1 + k)^2}
\]  

(65)

from Eq. 17,

\[
f_2(k) = 0.62 - 0.18 \frac{1}{1 + k}
\]  

(66)

from Eq. 20 and

\[
f_3(k) = \left( \frac{k}{1 + k} \right)^2
\]  

(67)
from Eq. 21.

If Eq. 64 is plotted as $f_n(k)$ vs. $\omega$ the slope should be $\omega$ if:

a. $\omega$ is a constant,

b. if there are no other mechanisms affecting the dependence on $k$ other than the $f_n(k)$ in question, and

c. if the model used to obtain $f_n(k)$ is actually a good representation of the processes occurring in the packed bed.

Such a plot is done in Figures 18, 19 and 20 for octane, heptane and hexane at $v = 19.00$ cm/sec. Figure 18 is the three functions of $k$ plotted for Eq. 58, the simple exponential equation. Figure 19 is the three functions plotted for Eq. 59, the simple coupled equation and Figure 20 is the three functions of $k$ plotted for the combination coupled-exponential equation, Eq. 60.

In Figure 18 it is seen that although none of the curves is straight through the three points there are no outlandish variations. Consider first Golay's $k$-function, Eq. 65. When $k = 0$ (unretained sample) $f_1(k) = 1/24$ and $\omega_1 = \omega_2/24$. The slope of the curve for $f_1(k)$ (which is $\omega_2$) is about 0.5 by least squares, which yields $\omega_1 = 0.02$. This is 10 to 30 times lower than values obtained for $\omega_1$ in unsorbing systems by other researchers (42,70).
Figure 18: $f_n(k)$ vs $\omega_j$ for Simple Exponential Equation
Figure 19 \( f_n(k) \) vs \( \omega_1 \) for Simple Coupled Equation
Figure 20  \( f_n(k) \) vs. \( \omega_1 \) for Coupled Exponential Equation
Considering Giddings' expression, the slope of $f_2(k)$ vs. $\omega_1$ is unity within expected error. At a $k$ of zero then $\omega_2 = 0.44$ which is similar to values obtained by other workers in unsorbing systems (42). If one solves $f_2(k)$ for $k$, which gives a unique solution since it is linear in $k$, it is found that $f_2(k) = 0$ at $k = -0.7$. If the curve of $f_2(k)$ is extrapolated to $f_2(k) = 0$ it intercepts the $\omega_1$ axis anywhere between -0.3 and -0.6. The point is imaginary of course since $k$ cannot be less than zero but it indicates that $f_2(k)$ and Eq. 58 give reasonable values.

Figure 20 shows the three functions plotted for the coupled-exponential equation, Eq. 60. The results lack significance. This is probably due to the fact that fitting such a curve is difficult. There are undoubtedly several minima in the 4-dimensional surface formed by Eq. 60. It is possible to set the initial starting points of the minimization program as close to the expected values as possible in the hopes of obtaining the best minimum and this was done with the data of n-heptane. It did not work so well with the others, however. For example, the theories of Eq. 60 indicate that the exponent to the term should be less than unity but this is the case only with
one of the data sets. The problem most probably lies in the complexities of curve-fitting rather than in the theory of the coupled-exponential function. This problem was partially sidestepped by Knox and Parcher (43) who fitted data from non-sorbing systems to Eq. 60 but specified arbitrarily that $x = 0.33$. Huber and Hulsman (32) set their value of $x$ at 0.5. No fitting has previously been done on Eq. 60 letting all constants vary and it appears from the present results that such a procedure gives anomalous results.

Figure 19 is the three $k$-functions plotted for the simple coupled equation (Eq. 59). Most apparent is the linearity of $f_3(k)$, Knox and Saleem's expression derived by considering the maldistribution of the stationary phase. The slope of the line (identified as $\omega_2$) is 0.397 with a correlation coefficient of 0.9999. This is undoubtedly better than the data warrants but it is satisfying to see such good agreement. This is a good indication that the mechanism which Knox and Saleem proposed is indeed a major contribution to the magnitude of the mobile phase mass transfer term in sorbed systems. Unfortunately it does not hold over the entire range of $k$ since at a $k$ of zero $f_3(k) = 0$, giving the incorrect conclusion that $C_m = 0$. 
More probable is the formulation

\[
(\omega)_1 = f_2(k)\omega_2 + f_4(k)\omega_2
\]

(68)

with the possibility that \( f_4(k) \) is unity for all values of \( k \). It could also be something akin to \( f_2(k) \). If it is unity then \( f_4(k)\omega_2 \) would be the \( \omega_1 \)-intercept, which for Knox and Saleem's curve is 0.0148, a value ten times lower than previous results (70). This does not mean that the value obtained here is unreliable. Most values of from the literature were obtained in the early days of the development of chromatographic theory, often without proper consideration or knowledge of the problems involved.

Golay's term, \( f_1(k) \), gives fairly good linearity and yields a slope of \( \omega_2 = 0.80 \) with a correlation coefficient of 0.996.

The same can be said for \( f_2(k) \) on Figure 19 as on Figure 18. The following conclusions may be drawn from the above:

1. It appears that the simple coupled equation for mobile phase peak dispersion describes the data in this study better than either a simple exponential or a coupled exponential equation. The failure of the latter may be due to the complexity of fitting such a function and
the possibility of multiple parameters of best fit.

b. Of the three functions of $k$ proposed on which $C_m$ may be dependent, the best appears to be that of Knox and Saleem although it does not go to the proper limit at $k = 0$. A possible remedy is the inclusion of an additive term representing the $\omega$ in an unsorbed system. The fact that their term produces consistent results even at very low $k$ may indicate the importance of good distribution of the stationary phase to obtain efficient columns.

In an earlier section the question of turbulence was brought up. Eq. 41 gave a function, $\phi$, that would indicate the onset of turbulence (29). A plot of $\phi$ vs. $\nu$ will be a straight line of slope zero in the laminar region and will have a negative slope in the turbulent region. Such a plot was made from the data of n-octane at $v = 19.00$ cm/sec. It is shown in Figure 21. As can be seen the curve is linear to about $\nu = 100$. Between $\nu = 100$ and 120 the onset of turbulence is indicated as a bend in the curve. Turbulence continues to develop out to the maximum reduced velocity used.

The onset of turbulence comes somewhat sooner than is normally expected in glass bead columns. This may be
Figure 21  Onset of Turbulence
due to the textured surface of the particles used. Observing the curves in Figures 17-20, one can see no abrupt change in the course of the curves due to turbulence. The onset of turbulence, however, certainly contributes to the flattening of the reduced plate height curve.

The ratio of reduced velocity to Reynolds number, \( \frac{\nu}{Re} \), is about unity for gases but is about 1000 in liquids. This means that an \( h - \nu \) plot is also approximately an \( h - Re \) plot for gases. For liquids, however, the reduced velocity must be divided by 1000 to obtain the approximate Reynolds number. This becomes significant when one observes Figure 10. There are a few curves in the area of \( \nu = 1 \) to 100 which appear to flatten off much earlier than the composite curve. These are gaseous systems which indicates that the flattening and downward trend of these curves is due to turbulence rather than, or combined with, coupling. The liquid systems on Figure 10, however, which achieve high reduced velocities at relatively low Reynolds numbers (Re = \( \nu/1000 \)) can probably attribute their flattening to coupling alone. This is essentially what Kaizu-}
An interesting and intriguing point was found in connection with the above. Many data points were taken while testing the chromatograph and optimizing experimental conditions. Most of this was done with heptane or octane. In nearly all the h - \( \nu \) curves which were run, as can best be seen on Figure 16, there is one data point around \( \nu = 100 \) to 120 that is somewhat below the composite curve. It is not far enough below to be startling. What was unusual was its persistence—it appeared on the same spot in nearly every curve. If it is not due to experimental error it is probably due to some process connected with the onset of turbulence. If this is true, the question is, why does the next point return to the expected line instead of continuing a downward trend? In order to investigate this many data points would have to be taken around this area in question and the time for this thesis did not permit such a digression. Nevertheless it is intriguing to speculate on its cause.
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