AN ABSTRACT OF THE THESIS OF

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Title: ___The obstructive factor in gas chromatography___

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(Dr. Stephen J. Hawkes)

The study of the obstructive factor by Hawkes (11) showed a rela-
tion between the obstructive factor and velocity using a continuous
method. Later, Bowers and Hawkes (12) developed a similar method with
some improvements in the apparatus and found out that the obstructive
factor was not flow dependent. This study uses Bowers and Hawkes'
apparatus with some changes and restudies the relationship between
the obstructive factor and velocity with unretained gases on glass
beads. The dependence of the obstructive factor on velocity was veri-
fied. The effects of diffusion coefficients and the particle-to-column
diameter ratios on the obstructive factor-velocity relationship were
investigated. The results are consistent with Hawkes' hypothesis (11)
that values of γ at low velocities are averages over tightly packed and
loosely packed domains while at high velocities they are weighted in
favor of the loosely packed domains where there is more flow. However,
no explanation has been found for Bowers and Hawkes' results.

The Obstructive Factor

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by

Pornpan Thumneum

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

LIST OF SYMBOLS

A	=	eddy diffusion contribution to plate height
B, $\bar{B}$	=	longitudinal molecular diffusion term in plate height equation
C_g, $\bar{C}_g$	=	gas phase resistance to mass transfer term
C_l	=	liquid phase resistance to mass transfer term
D, D_m, D_g	=	diffusion coefficient in mobile fluid
D_{go}	=	diffusion coefficient in carrier gas at outlet pressure
d	=	diameter of a local domain
d_c	=	column diameter
d_p	=	particle diameter
f	=	Giddings compressibility factor
H	=	plate height
$\hat{H}$	=	apparent plate height
j	=	James - Martin compressibility factor
L, l	=	length of a column
l_T	=	length of a tortuous path
P_i	=	inlet pressure
p_o	=	outlet pressure
r	=	column radius
t_d	=	diffusion time
t_m	=	time spent by molecule in mobile phase
t_r	=	retention time
v	=	linear velocity

$\bar{v}$	=	average linear velocity
v_o	=	outlet velocity
$W_{\frac{1}{2}}$	=	width at half height of a recorded peak
γ	=	obstructive factor
σ_t	=	standard deviation of zone, in time unit
σ_t^2	=	variance of zone, in time unit
σ_x	=	standard deviation of zone, in length unit
σ_x^2	=	variance of zone, in length unit
ω	=	ill-defined geometric constant

THE OBSTRUCTIVE FACTOR IN GAS CHROMATOGRAPHY

I. INTRODUCTION

J. Calvin Giddings (1) has written a part about the obstructive factor in chromatography; it said "--- γ is essentially a structural constant and thus independent of the particular mobile phase or solute being considered. However, there is very likely a slight velocity dependence to γ----. The theory of γ's velocity dependence has not been worked out; as things stand now, we must assume that the velocity effect is negligible."

There are two experimental methods to determine the value of the obstructive factor:

- Static method and
- Dynamic method

When a static method or theoretical model is used to determine the value of the obstructive factor, γ , in a bed of randomly packed solid spheres, the value of 0.60 $\pm$ 0.02 is obtained (2-5). If a dynamic method is used, the value of 0.73 $\pm$ 0.02 is obtained for the value of γ (6-10).

Because of the discrepancy between the values of γ obtained by using a dynamic and a static method, the flow dependence of the obstructive factor was investigated by Hawkes (11). He found that the obstructive factor is clearly flow dependent. For the column packed with beads, the γ has a value of 0.60 $\pm$ 0.02 at zero velocity (by extrapolation) and 0.73 $\pm$ 0.02 at higher velocities.

Later, Bowers and Hawkes (12) repeated the work on flow dependence of the obstructive factor. They improved the system to solve the problems on the back diffusion and significantly skewed peaks which Hawkes had experienced in his previous work (11). No effect of gas flow or velocity on the variation of γ was found. γ remained constant at 0.74$\pm$0.02 over a velocity range from 0.1-8.0 cm/sec.

The value and interpretation of γ are still doubtful. The theory of γ's velocity dependence has not been worked out. In books or calculation, generally they just assume that the velocity effect is negligible and use the value of 0.60 for most non-porous densely packed materials and use the value of 0.74 for porous materials.

To obtain some more information on the relationship between γ and velocity, I compare the two experiments which showed the obstructive factors are flow sensitive by Hawkes (11) and the obstructive factors are not always flow dependent (12) one by one, as follows:

flow dependent	not always flow dependent
- column length 730 cm	- column length 736.6 cm
- column diameter	- column diameter
1/4 in. O.D.	1/8 in. O.D.
3/16 in. I.D.	1/18 in. I.D.
- diameter of glass beads	- diameter of glass beads
50/60 mesh	60/80 mesh
- $d_p/d_c = 0.06$ or $d_c/d_p = 17$	- $d_p/d_c = 0.15$ or $d_c/d_p = 7$
- nitrogen (N_2) sample	- methane (CH_4) sample
- helium (He) carrier gas	- helium (He) carrier gas
- at 50° C	- at 50° C
- obtained significantly skewed peaks	- used post- and pre- columns No skewed peaks
- varied velocity from 0.1-8.0 cm/sec	- varied velocity from 0.1-8.0 cm/sec

I conclude from the above comparison that the samples and the particle-to-column diameter ratio might have some effect on the γ - velocity relationship. My experimental system was set up like Bowers and Hawkes' system (12) because it produced unskewed and accurate peaks, with some changes, and I was able to obtain good results. The γ was determined by a dynamic and a static method while varying velocity, sample and particle-to-column diameter ratio.

II. THEORY

A. BACKGROUND

In gas chromatography, when an infinitely thin slice of a gas B spreads by diffusion into another gas A the concentration profile of B in A after a finite time (t) is gaussian and the rate of spreading is given by the equation 1.

$$d\,\sigma_x^2/dt \;=\; 2D_g \qquad (1)$$

where σ_x is the standard deviation of the gaussian concentration profile, measured as a distance. D_g is the diffusion coefficient of gas B in A. Equation 1 holds for axial diffusion in a uniform empty tube.

But if the tube is packed with obstructing, but not sorbing, material, diffusion is hindered and the rate of spreading is given by the equation 2.

$$d\,\sigma_x^2/dt \;=\; 2\,\gamma\,D_g \qquad (2)$$

where γ is called the "Obstructive Factor" (1) and γ is less than unity.

The obstructive factor is the factor that indicates the degree to which diffusion is hindered by the packed material. When D_m is the diffusion coefficient for solute in the mobile phase and D is the effective diffusion coefficient

$$\gamma \;=\; D/D_m \qquad (3)$$

The value of γ probably ranges from 0.4-0.9 when all types of chromatographic materials are taken into account.

Generally, in practice, the measurement of σ_x^2 as a function of

length is not possible. An elution method must be used to obtain the

time variance, σ_t^2 of the eluted band rather than the length variance

σ_x^2. Since $\sigma_x / \sigma_t = v$, a constant linear velocity, diffusional spread-

ing is given by

$$d\ \sigma_t^2/dt = 2D_g/v^2 \quad \text{(empty tube)} \tag{4}$$

$$d\ \sigma_t^2/dt = 2\gamma D_g/v^2 \quad \text{(packed tube)} \tag{5}$$

B. THE INTERPRETATION OF γ

When the solute moves along the packed column, diffusion will then

occur in each of the interstitial flow channels.

Giddings (1) has explained that these channels have two main char-

acteristics which hinder diffusion:

1. The channels zig-zag through the material in a tortuous manner.

This prevents the diffusion of molecules along the shortest direct path.
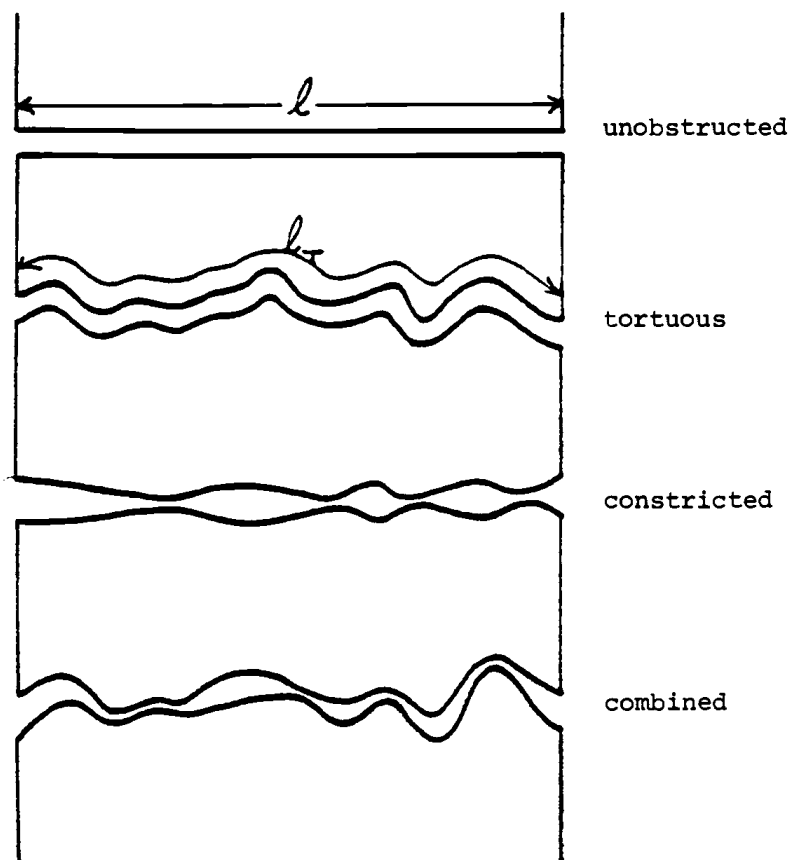
See figure I.

2. The channels alternately vary from wide to narrow. The narrow

constrictions slow diffusion. See figure I.

Hence, there are two factors which hinder diffusion through chromato-

graphic materials:

Tortuosity and Constriction

The tortuous path slows diffusion by increasing path length. The con-

stricted path creates "traffic bottlenecks" at random points, that slow

diffusion. The combined path provides both kinds of hindrances.

In a packed bed the situation at first appears more complex than

figure I since there are no channels with clearly defined walls. How-

ever, the concepts of tortuosity and constriction are still valid if we

define a diffusion path in an analogous way to a stream line in a flow-

From (1) page 244

FIGURE I: The nature of tortuous and constricted paths in a chroma-
tographic packing.

ing mobile phase. We define a "diffusion path" as a path through the column which is always in the direction of the maximum concentration gradient and consequently normal to successive surfaces of equal concentration. These diffusion paths are analogous to stream lines which are normal to isobaric surfaces. But stream lines will generally pass around porous particles, diffusion paths may pass through them as well as around them. The diffusion paths in a packed bed will be tortuous and any bundle of such paths will be constricted and expanded to that their envelope will be similar to figure I.

C. EQUATIONS FOR CALCULATIONS

The height equivalent to a theoretical plate has been given by Van Deemter, Zuiderweg, and Klinkenberg (13) in a form that reduces to

$$H = A + \overline{B}/\overline{v} + \overline{C}_g \overline{v} + C_l \overline{v} \tag{6}$$

where A is the eddy diffusion term, $\overline{B}$ is the longitudinal diffusion term at the average pressure in the column, $\overline{C}_g$ is the gas phase resistance to mass transfer term at the average pressure in the column, C_l is the liquid phase resistance to mass transfer term, and $\overline{v}$ is the average carrier gas velocity at the average pressure in the column.

In gas chromatography, working with uncoated glass beads, the $C_l \overline{v}$ term can be excluded. Thus,

$$H = A + \overline{B}/\overline{v} + \overline{C}_g \overline{v} \tag{7}$$

Giddings (14-15) has proposed the alternative form of the equation in which the eddy diffusion term A, is coupled with part of the gas phase resistance to mass transfer, $\overline{C}_g$

$$H = \frac{1}{1/A + 1/\overline{C}_g\overline{v}} + \overline{B}/\overline{v} + \overline{C}_g\overline{v} \qquad (8)$$

Consider the term $1/(1/A + 1/\overline{C}_g\overline{v})$; rapid diffusion in the gas phase probably makes the term $\overline{C}_g\overline{v}$, where $\overline{C}_g$ is inversely proportional to the gaseous diffusion coefficient, significantly smaller than A at velocities near the optimum. This term, $1/(1/A + 1/\overline{C}_g\overline{v})$, then, approaches $\overline{C}_g\overline{v}$ in value. With this approximation

$$H = \overline{B}/\overline{v} + \overline{C}_g\overline{v} \qquad (9)$$

The plate height H of a uniform column is proportional to variance σ^2.

$$H = \frac{\sigma^2}{L} \qquad (10)$$

From equation 9, we will first consider the contribution to the plate height made by longitudinal molecular diffusion. The spreading of a zone due to molecular diffusion in the mobile phase can be calculated from the equation

$$\sigma^2 = 2Dt_d \qquad (11)$$

where t_d is the diffusion time of the time period over which diffusion occurs, D is the diffusion coefficient.

If the solute molecules are migrating through the column with the distance L, traveling with the average mobile phase velocity $\overline{v}$ then the time spent in reaching L is

$$t_m = L/\overline{v} \qquad (12)$$

From equation 11

$$\sigma^2 = 2Dt_d$$

So, $$\sigma^2 = 2D_m t_m \qquad (13)$$

From equation 12 and 13

$$\sigma^2 = 2D_m L/\overline{v} \qquad (14)$$

where D_m is the diffusion coefficient in the mobile phase.

In packed columns, there are the tortuosity and constriction factors, and an obstructive factor γ is applicable. Thus,

$$\sigma^2 = 2\gamma D_m L/\bar{v} \tag{15}$$

From equation 10 and 15

$$H = 2\gamma D_m/\bar{v} \tag{16}$$

Second we will consider the contribution to the plate height made by the gas phase resistance to mass transfere term. The plate height is always (except for the transcolum effect) approximately proportional to the particle size d_p squared and to velocity $\bar{v}$, and inversely proportional to the mobile phase diffusion coefficient D_m.

$$H = \omega d_p^2 \bar{v}/D_m \tag{17}$$

where ω is essentially constant. Combining two terms to obtain the equation of plate height,

$$H = 2\gamma D_m/\bar{v} + \omega d_p^2 \bar{v}/D_m \tag{18}$$

or

$$H = 2\gamma D_{go}/v_o + \omega d_p^2 v_o/D_{go} \tag{19}$$

where D_{go} is the diffusion coefficient of sample in carrier gas at outlet pressure, v_o is the outlet velocity.

D. THE ROLE OF PRESSURE GRADIENTS

In a gas chromatographic column, the gas flows in the narrow interstices between the particles of packing, which offer resistance to flow and thus, because of the finite viscosity of the gas, there is a pressure gradient along the length of the column. Any gas packet within a column containing significant pressure gradients will physically expand as it passes down the column by an amount over and above that due to ordinary plate-height spreading.

Giddings, Seager, Stucki and Stewart (14) have analysed this effect and corrected the equation of plate height. The final result is

$$H = 2\gamma D_{go} j f / \bar{v} + \omega d_p^2 \bar{v} f / D_{go} j \tag{20}$$

where $\qquad j = 3((p_i/p_o)^2 - 1)/2((p_i/p_o)^3 - 1)$

$$f = j^2((p_i/p_o)^2 + 1)/2$$

$$v_o = \bar{v}/j$$

$\bar{v}$ is the average velocity, p_i is the inlet pressure, p_o is the outlet pressure.

III. EXPERIMENTAL WORK

The gas chromatograph consisted of a coiled copper column with 1/8-inch outside diameter and 1/18-inch inside diameter packed with glass beads. To ensure a consistent environment, post- and pre- columns 182.9 cm in length packed with the same size glass beads as in the column were placed between the reference side of the detector and the injection port, and after the sample side of the detector to atmosphere as was done by Bowers and Hawkes (12). The instrument was placed in a 50±0.5° C oil bath, and a 762 cm empty tube coiled copper column was placed before the detector to ensure the constant temperature of 50° C of the helium carrier gas before the gas entered the column. A sample was injected through an injection port of minimal dead volume with the Hamilton gas-tight syringe. The detector was a Carle microkatharometer detector and peaks were recorded on an Esterline-Angus E1105 recorder. A general scheme of the apparatus used in this study is shown in figure II.

The helium gas from the gas tank flowed through the empty tube, the gas pressure was measured by the gas pressure gauge. Before entering the temperature equilibrium column, the helium carrier gas passed through a two-way tap. The two-way tap was using to alternate the helium carrier gas flow to the temperature equilibrium column or a dummy column. The dummy column consisted of a empty copper tube with an adjustable valve. The temperature equilibrium column was connected to the reference side of the detector. The helium gas at 50° C from the temperature equilibrium column would pass through the pre-column and
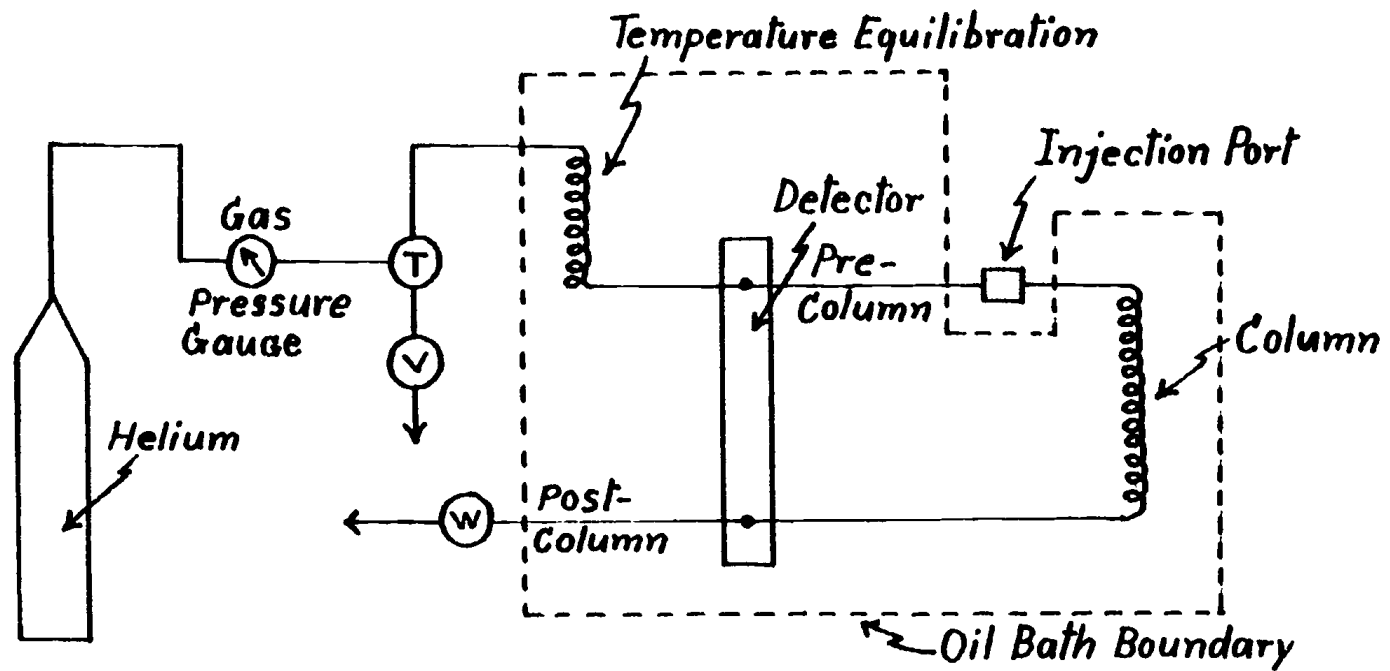
FIGURE II: Diagramatic scheme of the apparatus

T = two way tap, V = needle valve,

W = one-way tap.

injection port, samples were swept through the column, detected by the detector, passed the post-column and on to atmosphere. The dummy column and the one-way tap on the post-column were used in Knox and McLaren's arrested elution method.

The column was packed by bouncing and vibrating method and terminated with gauze screens to avoid undesirably large instrumental spread and peak asymmetry. The post- and pre- columns were placed with the same size of glass beads as in the column to avoid peak asymmetry. The light paraffin oil was used in the bath instead of water because it is less corrosive liquid. The O-ring between the detector and the adaptor is Teflon, therefore, it does not soften in warm solvent.

A. CONTINUOUS ELUTIONS

A typical experiment was carried out as follows. A gas sample was injected into the column and eluted in the normal way without arresting gas flow. The time of passage along the column, t_r, is the total elapsing between injection and detection. The average velocity was obtained from $\bar{v} = L/t_r$, L is the length of the column. $W_{\frac{1}{2}}$ was measured from recorded peaks. H was calculated from $H = LW_{\frac{1}{2}}^2/5.546t_r^2$. The obstructive factor, γ, was calculated from equation 20.

$$H = 2\gamma D_{go}jf/\bar{v} + \omega d_p^2 f\bar{v}/D_{go}j$$

The inlet pressure was varied to obtain velocities from 0.1-17 cm/ sec (0.1-25 cm/sec in one case). The valve of ω was determined using high velocities as in the previous work (11). To study the effect of the diffusion coefficient on the obstructive factor - velocity relationship, methane and argon gases were used as samples. The diffusion coeffcient of methane in helium at 50° C is 0.7682 cm^2/sec (16). The

diffusion coefficient of argon in helium at 50° C was calculated to be

0.8453 cm^2/sec using the value of 0.7335 cm^2/sec at 25° C and correcting

for temperature by proportion to T$^{1.77}$ (17). To study a particle-

to-column diameter ratio effect on the obstructive factor-velocity

relationship, the 1/8-inch O.D., 1/18-inch I.D. copper columns, post-

and pre- columns were packed with 60-80 mesh glass beads, 25-35 mesh

glass beads and 80-100 mesh glass beads. In this case the sample was

methane only.

B. ARRESTED ELUTIONS

To study static spreading, Knox and McLaren's arrested elution

technique (2) was used. A band of methane was eluted about half way along

the column (figure II), by turning the two-way tap, T. After a delay of

1 to 20 minutes the flow was reconnected to the column and the peak eluted.

According to equation 5, a plot of σ_t^2 against delay time t should

be a straight line with the slope of $2\gamma D_{go}/v_o^2$. The σ_t^2 was obtained

from $\sigma_t^2 = W_{\frac{1}{2}}^2/5.546$. The outlet velocity, v_o, was obtained from $\bar{v}$ by

applying the James-Martin pressure correcting factor, knowing the

pressure drop across the column, $v_o = \bar{v}/j$. The obstructive factor,

γ was calculated from the slope of σ_t^2-t plot.

C. CORRECTION FOR INLET AND OUTLET PRESSURE OF THE COLUMN

To correct the effect of pressure gradient on the plate-height

spreading, the James-Martin compressibility factor j and the Giddings

compressibility factor f were applied to the equation of plate height

(equation 20). This corrected the effect of pressure gradient along

the column. But in this experimental system there were pre- and post-

columns which were packed with the same size glass beads as the column,

thus there were pressure gradients in the pre- and post- columns. Hence, the gas pressure measured with the gauge before the gas entered the pre-column must be corrected to give the inlet pressure of the column, and the atmospheric pressure that the post-column was leading to must also be corrected to the outlet pressure of the column. Littlewood (18) has derived an equation for the pressure at any point in the column.

$$\frac{x}{1} = \frac{p_i^2 - p^2}{p_i^2 - p_o^2} \qquad (21)$$

x is the length at any point in the column, 1 is the total length of the column, p_i, p_o are the inlet and outlet pressure of the column respectively, p is the pressure at the length x.

Applying equation 21 to the pre- and post- column problems in order to calculate the inlet and outlet pressure of the column, the following equations were obtained:

$$\frac{L_{pre}}{L_{pre} + L_{col} + L_{post}} = \frac{p_m^2 - p_i^2}{p_m^2 - p_{atm}^2} \qquad (22)$$

$$\frac{L_{pre} + L_{col}}{L_{pre} + L_{col} + L_{post}} = \frac{p_m^2 - p_o^2}{p_m^2 - p_{atm}^2} \qquad (23)$$

L_{pre}, L_{col}, L_{post} are the length of the pre-column, column itself and post-column respectively. p_m is the pressure measured at the pressure gauge. p_{atm} is the atmospheric pressure. The inlet pressure of the column, p_i and the outlet pressure of the column, p_o were calculated from equation 22 and 23 respectively.

To check the deviation of calculated p_i, p_o from the real measured p_i, p_o of the column, the system at the injection port was removed and

a manometer was connected directly to the inlet of the column. Let the gas flow and keep the oil bath at 50° C, read the real inlet pressure from the manometer. The average percentage of deviation of calculated p_i from measured p_i at several gas flows was $-(2.00\pm0.01)$%. If the measured p_o was assumed to be smaller than the calculated p_o about 2%, the ratios of p_i/p_o were the same in both calculated and measured pressures. This resulted in no change in the values of H and Y on both cases. In this experiment, the calculated p_i, p_o were used because it was more convenient.

IV. RESULTS AND DISCUSSION

A. PERFORMANCE CHECK - OPEN TUBULAR COLUMN

The performance of the system was evaluated using an open tubular column, for which plate height could be calculated directly from theory (19, 20). A 731.5 cm long, 1/8-inch O.D., 1/18-inch I.D. copper tube was used as a column in this study. Methane is a sample and helium as a carrier gas.

From the Golay theory of capillary column performance (19), which gives, for an unretained component,

$$H = 2\gamma D_{go}/v_o + r^2 v_o/24 D_{go} \tag{24}$$

where r is the radius of the tube, D_g is 0.7682 cm^2/sec at 50° C for CH_4.

With the expressions derived by Giddings (14) the modification of equations (24) is as follows:

$$\hat{H}/f = 2\gamma D_{go} j/\bar{v} + r^2 \bar{v}/24 D_{go} j \tag{25}$$

where $\hat{H}$ is the apparent plate height obtained from the emergent peak width and retention time, and f is Giddings compressibility factor.

Performance data for the open tubular column are shown in table I. The value of γ agrees with the theory that the value of the obstructive factor of the open tubular column is unity. γ value seems to be stable over the 4-21 cm/sec velocity range.

B. THE OBSTRUCTIVE FACTOR AND VELOCITY

The variation of obstructive factor with velocity was studied on 735.4 cm long copper coiled column, 1/8-inch O.D., 1/18-inch I.D.,

TABLE I: Performance data on open-tubular column, 731.5 cm long, 1/8-inch O.D., 1/18-inch I.D., He carrier, CH_4 sample.

P_i (p.s.i.)	——	16.5655	18.4384	21.4234
P_o (p.s.i.)	——	15.0884	15.4384	16.2657
P_i/P_o	——	1.0979	1.1718	1.3171
j	——	0.9527	0.9189	0.8578
f	——	1.0007	1.0021	1.0062
t_r (sec)	172.7500	100.4375	58.7500	34.7844
$\bar{v}$ (cm/sec)	4.2344	7.2831	12.4511	21.0301
$W_{\frac{1}{2}}$ (sec)	9.0751	4.0381	1.8273	0.7357
H (cm)	0.3640	0.2132	0.1276	0.0702
γ	1.0001	1.0498	1.0907	1.0076

CH_4 sample, He carrier gas. The value of ω was determined to be 1.2

(11) The relation is shown in figure III. The obstructive factor is

clearly flow dependent. This result agrees with Hawkes' work (11).

The obstructive factor at zero velocity, achieved by extrapolation, is

0.60 in agreement with the static determinations (2,3,4,5). The highest

value of γ is 0.74 in agreement with the dynamic determinations (7,8,9,10).

Hawkes (11) had explained that 'This dependence lies in the fact

that the lowest flow resistance is offered by gaps or wide paths in the

packing structure, especially at the walls, where γ is greatest.

Accordingly more sample flows through regions of high γ, and the value

of γ is weighted by this effect. At low or zero flow this is offset by

diffusion between domains of low and high γ.' To quantitatively com-

pute the maximum of γ, he used the consideration that the maximum value

of γ will be obtained when escape from a domain by flow is faster than

by diffusion. This may be roughly estimated when

$$\frac{\bar{v}d}{D} > \frac{4}{3} \tag{26}$$

where $\bar{v}$ is the velocity that 1/3 of the material at a point source at

the center of domain diffuses out of it before the source has moved

1/3 of the distance to the domain boundary. d is the diameter of

domain. D is the diffusion coefficient of the sample in mobile fluid.

If the domain is the comlumn cross-section d = 1/18 inch, the velo-

city at which γ will reach the maximum value would be 7 cm/sec. From

the experiment, the flattening point on the γ-$\bar{v}$ curve is about 7 cm/

sec, this agrees very well with the estimated velocity.

Another part of the experiment to study the γ - velocity depen-

dence, Knox and McLaren's arrested elution method (2) was applied at

each velocity step. The data is shown in table II.

Column: 1/8-in. O.D., 1/18-in. I.D., 735.4 cm long

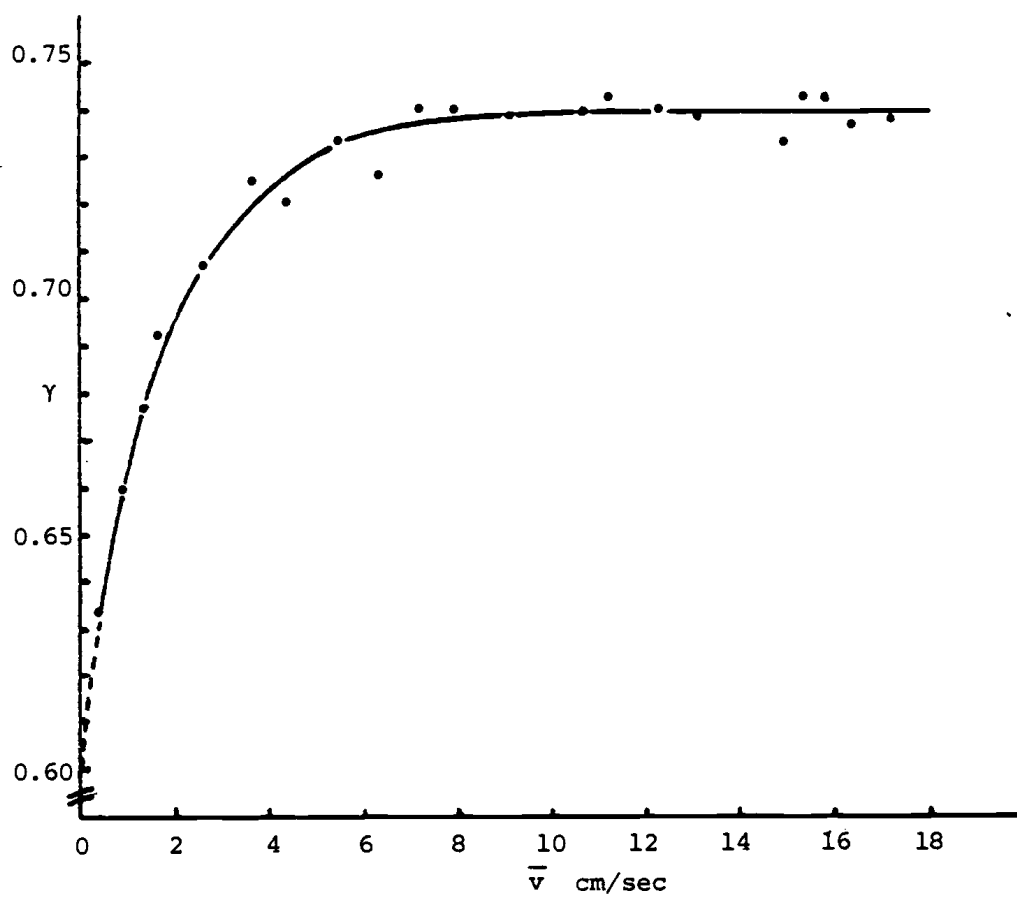Packing: 60-80 mesh glass beads

Sample: CH_4

Carrier gas: He

FIGURE III: Variation of obstructive factor with velocity, $\bar{v}$.

TABLE II: Arrested elution; column 736.6 cm long, 1/8-in. O.D., 1/18-in. I.D., sample-CH_4, carrier gas-He, D_{go} of CH_4 = 0.7682 cm^2/sec at 50° C, particles-60-80 mesh glass beads.

$\bar{v}$(cm/sec)	v_o (cm/sec)	γ
2.2840	2.5085	0.6300
3.0591	3.4507	0.6320
3.9908	4.6011	0.6064
4.8070	5.6413	0.6087
6.8771	8.3693	0.3207
8.8084	10.9482	0.2905

From the data it seems to be that the static method could be applied when the velocity was low or the pressure drop across the column during the elution was low. With large pressure drop the gas velocity did not reach its stationary value before the peak was eluted, thus σ_t was overestimated and an excessively low value of the obstructive factor was obtained. But at low velocity the obstructive factor value agrees with the value from the continuous elution.

C. THE OBSTRUCTIVE FACTOR AND DIFFUSION COEFFICIENT

Methane (D_g = 0.7682 cm^2/sec at 50° C) and argon (D_g = 0.8453 cm^2/ sec at 50° C) samples were studied on the same column and packing; 735.4 cm long, 1/8-in. O.D., 1/18-in. I.D., 60-80 mesh glass beads packing, He carrier gas, ω value was 1.2, using the continuous elution method. γ was calculated using equation 20.

Plots of γ and $\bar{v}$ of both samples are shown in figure IV. At zero or very low velocities, γ values of both samples are

Column: 1/8-in. O.D., 1/18-in. I.D., 735.4 cm long

Packing: 60-80 mesh glass beads
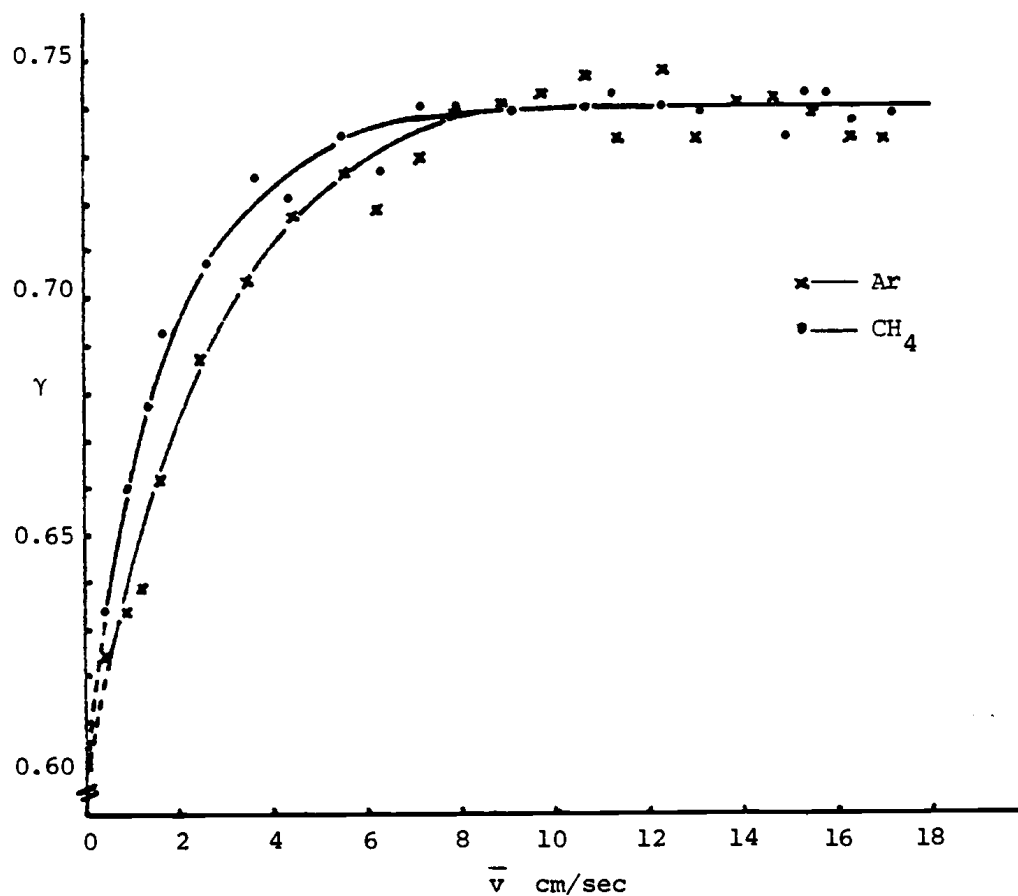
Samples: CH_4, Ar

Carrier gas: He

FIGURE IV: Variation of obstructive factor with velocity, $\bar{v}$.

Compare between CH_4 and Ar samples.

about 0.60, and at high velocities are about 0.74. By using $\overline{v}d/D > 4/3$

(equation 26), the maximum value of γ will be obtained at $\overline{v} = 8$ cm/sec,

this agrees well with the experimental flattening point. But between

the minimum and maximum values of γ, there is difference in γ on

argon's and methane's curves. At the same velocity, the value in the

case of argon as a sample is smaller than in the case of methane as a

sample. This can be explained that at the same velocity, with higher

diffusion coefficient, sample has more chance to diffuse into more

tightly packed regions of the column before it will be swept through

the gas flow.

D. THE OBSTRUCTIVE FACTOR AND THE PARTICLE-TO-COLUMN DIAMETER RATIO

Three columns were studied in this case; 1/8-in. O.D., 1/18-in.

I.D. columns packed with 25-35 mesh (ω value was 1.3), 60-80 mesh (ω

value was 1.2) and 80-100 mesh glass beads (ω value was 1.3), methane

sample, He carrier gas. The particle-to-column diameter ratios (d_p/d_c)

were varied from 0.1 to 0.4. See table III.

TABLE III:

column	column diameter cm.	packing mesh range	particle diameter cm.	diameter ratio d_p/d_c
1	0.1411	25-35	0.061	0.43
2	0.1411	60-80	0.021	0.15
3	0.1411	80-100	0.016	0.12

The relation between the obstructive factor and velocity at each particle-to-column diameter ratio is shown by figure V.

The minimum value and maximum value of γ are the same for all particle-to-column diameter ratios. $\gamma_{min.} = 0.60$ and $\gamma_{max.} = 0.74$. But the γ values in between were different at the same velocity.

It is generally accepted that a direct proportionality exists between plate height and particle diameter (22, 23). In 1964 Sternberg and Poulson (21) studied the particle-to-column diameter ratio effect on band spreading. According to the modified Van Deemter equation, equation 7

$$H = A + \overline{B}/\overline{v} + C_g\overline{v}$$

they found that the effect of the particle-to-column diameter ratio on the eddy diffusion term, A, is negligible within experimental error. On the longitudinal diffusion term, B, the smaller particle-to-column diameter ratio causes the lower value of B. This agrees with Kieselbach's work (24) and Norem's work (20) (the higher d_p/d_c causes the higher B value). The B coefficient covers a range of only 15%, the variations in the particle-to-column diameter ratio affect only the gas phase mass transfer, C_g.

Theoretical treatments (1,25) predict a quadratic dependence of C_g upon the particle diameter, d_p.

$$C_g = \omega d_p^2 /D_g \tag{27}$$

where ω is the geometric constant. Sternberg and Poulson have found that the values of ω are strongly dependent upon the particle-to-column diameter ratio; for glass beads, this dependence extends well into the range of particle and column diameters normally employed

Column: 1/8 in. O.D., 1/18-in. I.D.,

653.3 cm, 735.4 cm, 728.2 cm long.

Packing: 25-35 mesh, 60-80 mesh, 80-100 mesh glass beads.
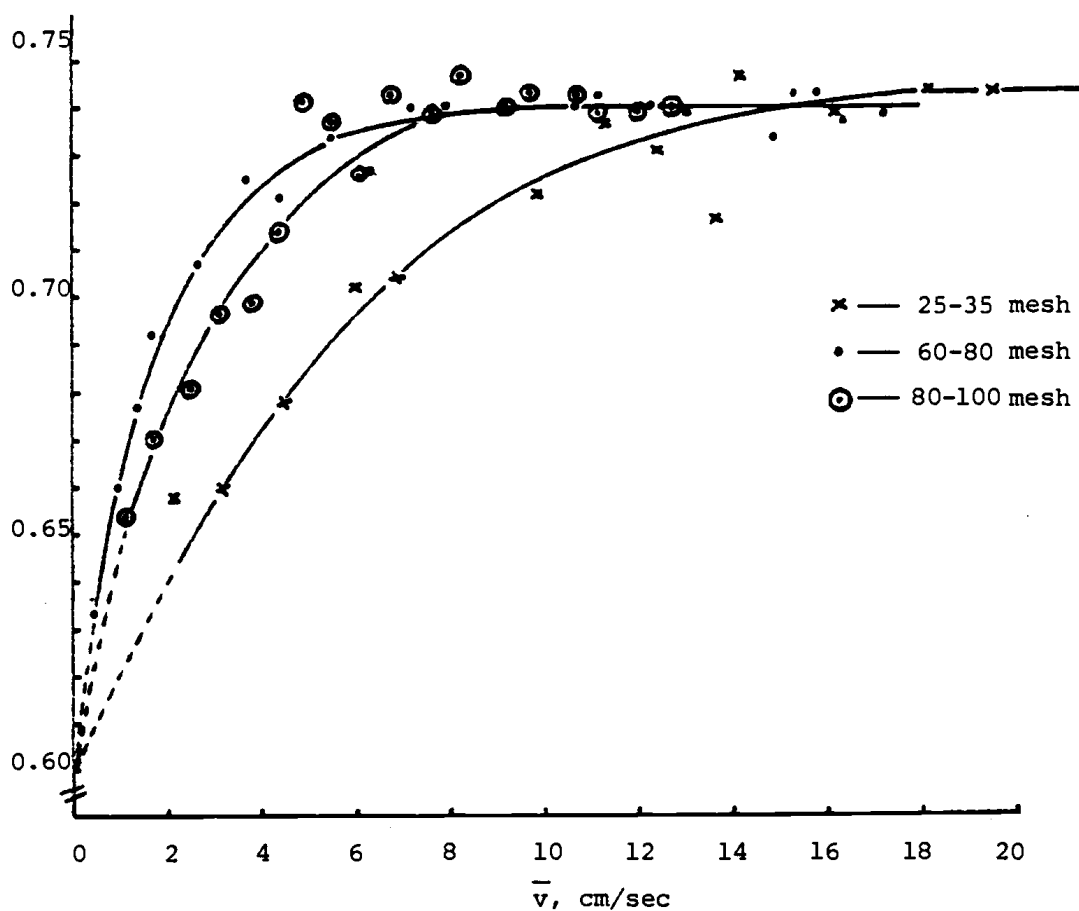
Sample: CH_4

Carrier gas: He

FIGURE V: Variation of obstructive factor with velocity, $\bar{v}$, among different d_p/d_c ratios.

$(d_p/d_c$; 1/5 to 1/50). With particles relatively large for the column,
ω becomes as small as 1/10 of its value for normal particle-to-column
diameter ratios. Sternberg and Poulson evaluated the value of ω using
the Van Deemter equation for plate height, expressed in the form

$$H/f = A + B/\bar{v} + C_g \bar{v} \tag{28}$$

The A value was negligible, the equation can be rewritten as

$$H\bar{v}/f = B + C_g \bar{v}^2 \tag{29}$$

and $H\bar{v}/f$ is a linear function of $\bar{v}^2$, with a slope C_g. From equation
27, ω value was calculated. For glass beads packing and $d_p/d_c = 0.423$,
ω value was 0.054. If this ω value of 0.054 (instead of the ω value
of 1.3 obtained by Hawkes' consideration (11)) was used to calculate
the value of γ from equation 20, the values of γ at high velocities
were greater than unity which is absurd. Hence, in this experiment
the ω value of 1.3 was used to calculate the γ values.

A possible explanation for the low value of Sternberg and Paul-
son's ω are that there might be coupling between ω and the A term. And
this ω value was the value over the long range of velocities. An
explanation for the higher ω value ($\omega = 1.3$) using Hawkes' consider-
ation at high velocities is that ω value was determined at the veloci-
ties which were not high enough to support the coupling theory.

From figure V, for $d_p/d_c = 0.12$ and $d_p/d_c = 0.15$ (within the
range normally employed) the points at which the ω value reached its
maximum are about at $\bar{v} = 7$ cm/sec. This agrees with the previous
explanation (equation 26) that it is more likely a long range effect,
the domain is the column cross section. For $d_p/d_c = 0.43$, the parti-
cle is about three times larger than in the other two columns. The

experimental flattening point is about 17 cm/sec. It seems to be that

the domain is about the size of a single particle (d_p), then the velo-

city would be 17 cm/sec. This agrees well with the experimental data.

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TABLE IV   (Appendix)   Individual Run Data

Column: 1/8-in. O.D., 1/18-in. I.D., 735.4 cm long
Packing: 60-80 mesh glass beads
Samples: CH_4 Carrier gas: He

Continuous elution

H (cm)	2.1888	1.0196	0.7115	0.5302	0.3373	0.2349	0.1862	0.1509	0.1299	0.1146
$\bar{v}$ (cm/sec)	0.4217	0.8996	1.2693	1.6804	2.5829	3.6204	4.4435	5.4798	6.2754	7.2209
j	0.9466	0.9011	0.8620	0.8287	0.7855	0.7380	0.7146	0.6881	0.6745	0.6587
f	1.0003	1.0031	1.0059	1.0086	1.0133	1.0193	1.0223	1.0263	1.0280	1.0307

H (cm)	0.1045	0.0929	0.0890	0.0810	0.0786	0.0735	0.0706	0.0651	0.0650	0.0642
$\bar{v}$ (cm/sec)	7.9503	9.0685	9.8176	10.7199	11.1981	12.2710	13.0738	14.9700	15.3059	15.6885
j	0.6502	0.6402	0.6346	0.6279	0.6241	0.6194	0.6167	0.6132	0.6113	0.6087
f	1.0317	1.0336	1.0344	1.0356	1.0362	1.0370	1.0375	1.0380	1.0384	1.0388

H (cm)	0.0627	0.0617	0.0593	0.0609	0.0607	0.0607
$\bar{v}$ (cm/sec)	16.3422	17.1272	20.1736	32.7804	36.9032	41.1214
j	0.6072	0.6052	0.5981	0.5952	0.5938	0.5866
f	1.0390	1.0393	1.0407	1.0411	1.0413	1.0426

Aressted elution
$\bar{v}$ = 2.2840 cm/sec, j = 0.8290

Delay time, t (min)	0	3	5	10	15	20
σ_t^2 (sec^2)	85.2980	117.2467	131.4461	196.3577	228.8389	284.9013

$\bar{v}$ = 3.0591 cm/sec, j = 0.7859

Delay time, t (min)	0	3	5	10	15	20
σ_t^2 (sec^2)	32.1353	42.6236	53.6535	88.2646	109.7828	129.9896

$\bar{v}$ = 3.9908 cm/sec, j = 0.7523

Delay time, t (min)	0	3	5	10	15	20
σ_t^2 (sec^2)	13.6477	18.0761	22.0662	36.6142	49.7611	59.6439

$\bar{v}$ = 4.8070 cm/sec, j = 0.7261

Delay time, t (min)	0	3	5	10	15	20
σ_t^2 (sec^2)	6.9555	8.5612	12.5530	19.1756	27.6128	34.4782

$\bar{v}$ = 6.8771 cm/sec, j = 0.6752

Delay time, t (min)	0	3	5	10	15	20
σ_t^2 (sec^2)	1.9414	2.5356	3.5381	5.2396	7.5998	9.5184

$\bar{v}$ = 8.8084 cm/sec , j = 0.6473

Delay time, t (min)	0	3	5	10	15	20
σ_t^2 (sec^2)	0.9905	1.2424	1.5230	2.6380	3.5907	5.0410

Column: 1/8-in. O.D., 1/18-in. I.D., 735.4 cm long
Packing: 60-80 mesh glass beads
Sample: Ar.   Carrier gas: He

Continuous elution

$\underline{H}$ (cm)	2.4481	1.1702	0.7784	0.6024	0.3753	0.2576	0.2049	0.1641	0.1416	0.1232
v (cm/sec)	0.4086	0.8288	1.2046	1.5539	2.4777	3.5176	4.4118	5.4550	6.2059	7.2164
j	0.9466	0.9011	0.8620	0.8287	0.7855	0.7380	0.7146	0.6881	0.6745	0.6587
f	1.0003	1.0031	1.0059	1.0086	1.0133	1.0193	1.0223	1.0263	1.0280	1.0307

$\underline{H}$ (cm)	0.1138	0.1023	0.0949	0.0882	0.0826	0.0790	0.0746	0.0722	0.0703	0.0677
v (cm/sec)	7.9155	8.8937	9.7203	10.6435	11.3438	12.3047	13.0629	13.8960	14.5601	15.4872
j	0.6502	0.6402	0.6346	0.6279	0.6241	0.6194	0.6167	0.6132	0.6113	0.6087
f	1.0317	1.0336	1.0344	1.0356	1.0362	1.0370	1.0375	1.0380	1.0384	1.0388

$\underline{H}$ (cm)	0.0655	0.0643	0.0624	0.0623	0.0624	0.0624
$\underline{v}$ (cm/sec)	16.3593	16.9881	20.0098	32.3598	40.9699	48.0310
j	0.6072	0.6052	0.5981	0.5952	0.5938	0.5866
f	1.0390	1.0393	1.0407	1.0411	1.0413	1.0426

Column: 1/8-in. O.D., 1/18-in. I.D., 653.3 cm long
Packing: 25-35 mesh glass beads
Sample: CH_4 Carrier gas: He

Continuous elution

$\underline{H}$ (cm)	0.4679	0.3328	0.2529	0.2125	0.1965	0.1715	0.1697	0.1686	0.1675	0.1722
$\underline{v}$ (cm/sec)	2.1914	3.1704	4.5031	5.9637	6.7986	9.8670	11.3126	12.4772	13.5874	14.0495
j	0.9846	0.9768	0.9667	0.9569	0.9509	0.9302	0.9215	0.9131	0.9060	0.9049
f	1.0001	1.0002	1.0004	1.0006	1.0008	1.0015	1.0019	1.0024	1.0027	1.0028

$\underline{H}$ (cm)	0.1777	0.1873	0.1933	0.2158	0.2407	0.3588	0.3904
$\underline{v}$ (cm/sec)	16.1833	18.0657	19.5306	22.8205	26.2176	40.3145	43.3487
j	0.8888	0.8782	0.8702	0.8369	0.8150	0.7664	0.7507
f	1.0038	1.0046	1.0051	1.0079	1.0101	1.0155	1.0175

Column: 1/8-in. O.D., 1/18-in. I.D., 728.2 cm long
Packing: 80-100 mesh glass beads
Sample: CH_4 Carrier Gas: He

Continuous elution

$\underline{H}$ (cm)	2.2909	1.4665	0.4878	0.3164	0.2550	0.2002	0.1748	0.1613	0.1430	0.1244
$\underline{v}$ (cm/sec)	0.3860	1.1033	1.6856	2.5024	3.0924	3.8453	4.4453	4.9068	5.4816	6.1794
j	0.9016	0.8297	0.7867	0.7396	0.7164	0.6901	0.6766	0.6609	0.6526	0.6425
f	1.0030	1.0086	1.0131	1.0189	1.0221	1.0259	1.0279	1.0303	1.0316	1.0332

$\underline{H}$ (cm)	0.1163	0.1031	0.0970	0.0873	0.0830	0.0770	0.0733	0.0692	0.0667	0.0636
$\underline{v}$ (cm/sec)	6.7499	7.6069	8.1899	9.1095	9.6895	10.5659	11.1659	12.0135	12.6256	13.4420
j	0.6371	0.6304	0.6266	0.6219	0.6193	0.6159	0.6139	0.6113	0.6099	0.6072
f	1.0341	1.0352	1.0358	1.0366	1.0370	1.0376	1.0379	1.0383	1.0386	1.0390

$\underline{H}$ (cm)	0.0817	0.0550	0.0541	0.0531	0.0500
$\overline{v}$ (cm/sec)	14.0541	16.9106	17.7267	18.1345	20.7869
$\dot{\jmath}$	0.6052	0.5981	0.5952	0.5938	0.5866
f	1.0393	1.0407	1.0411	1.0413	1.0426