GAS CHROMATOGRAPHY WITH OTC IN PARALLEL

M.Eng.

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GAS CHROMATOGRAPHY WITH OPEN TUBULAR COLUMNS IN PARALLEL

by

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ABSTRACT

Gas chromatographic columns composed of bundles of open tubular columns (OTC) were prepared and tested. For example, one bundle consisted of 5 OTC, each 440 cm long, 0.0165 cm in diameter, and coated with a film of squalane. A coating process was developed to yield columns that gave coherent peaks. The mixing in the dead volumes of the chromatography instrument contributed to the coherence of the peaks.

A derivation was given of a general equation relating the second moment of the peak from a bundle to the second moment of the peak from the "mean" OTC and the variances of the length and diameter of the ensemble of tubes in the bundle. As an example, the coefficients of the equation were estimated for a specific bundle of OTC. In this example, it appears that the increase of the HETP due to the variabilities of length and diameter is not excessive. Des colonnes de chromatographie gazeuse composées de groupes de colonnes capillaires ouvertes ont été fabriquées, et étudiées. Par exemple un groupe se compose de cinq colonnes capillaires de 440 cm de long, 0.0165 cm de diamètre et revêtues d'une couche mince de squalane.

RESUME

Le mode de revêtement a été étudié afin que les colonnes donnent des pics cohérents.

Les mélanges qui se produisent dans les volumes morts de l'instrument de chromatographie contribuent également à la cohérence des pics.

Une équation mathématique a été établie entre le second moment du pic d'un groupe de colonnes et les variables suivants: second moment du pic moyen des colonnes, la variance de la longeur et la variance du diamètre de l'ensemble des tubes.

Les coefficients de l'équation ont été determinés pour un des groupes de colonnes. Dans cette exemple il apparait que l'acroissement de la hauteur équivalente à un plateau théorique, due aux variations de longueur et de diamètre des tubes est modérée.



#### ACKNOWLEDGEMENTS

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#### NOMENCLATURE

Longitudinal diffusion in gas-phase (Golay Eq.,  $cm^2/s$ ) Permeability of column (cm<sup>2</sup>) Base width of ith peak (cm;s) Concentration of vapor solute in gas-phase, from single OTC  $(\frac{g}{cm^3}; \frac{gmole}{cm^3})$ Resistance to mass-transfer in gas-phase (Golay Eq.,  $s/cm^2$ ) Resistance to mass-transfer in stationaryphase (Golay Eq., s/cm<sup>2</sup>) Percent concentration of stationary-phase in coating solution (by mass; by volume) Concentration of vapor solute in gas-phase, from bundle of OTC  $(\frac{g}{cm^3}; \frac{gmole}{cm^3})$ Column inside diameter (cm; micron) Film thickness (micron) Diffusivity in gas-phase  $(\frac{cm^2}{s})$ Diffusivity in liquid-phase  $\left(\frac{Cm^2}{s}\right)$ Outlet Volumetric flow rate (cm<sup>3</sup>/min) Volumetric flow rate at any cross-section in the column (cm<sup>3</sup>/min) Mean volumetric flow rate  $(cm^3/min)$ 

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	i -	-			,
	Fc	۲			Corrected volumetric flow rate (cm <sup>3</sup> /min)
	HETP	(or	H)		Height equivalent to one theoretical plate
		3	L		(cm)
	j			Ø.	Pressure correction factor
. •	к				Capacity ratio
	L				Column length (cm)
•	m	•			Mean retention time (s)
	n				Number of theoretical plates
t	no				Modified number of theoretical plates
	N				Number of columns
	N <sup>*</sup>		ı		Number of column's that contribute to a
	l	•			particular retention time
	P <sub>i</sub>				Inlet pressure (atm absolute)
	Po				Outlet pressure (atm absolute)
	Р	1			Pressure at any point in the columr (atm
	*	. ~		-	absolute)
	Ē.				Mean pressure (atm absolute)
ł	P W				Partial pressure of water at ambient
			r 3		temperature (atm absolute)
	Pa				Ambient pressure (atm absolute)
	ΔP				Pressure differential along column (atm)
•	đ	,		•	Concentration of solute in stationary-phase
	۲				$\left(\frac{g}{cm^3}; \frac{gmole}{cm^3}\right)$
	rc			١	Column inside radius (cm; micron)

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Cylindrical coordinates  $(r, \Theta, z)$ Standard deviation of peak from single OTC (Cm) Variance of peak from bundle  $(cm^2)$ s<sup>2</sup> Variance of peak from single OTC  $(cm^2)$ Absolute temperature of carrier gas  $(^{\circ}K)$ Absolute temperature of column (<sup>O</sup>K) Absolute ambient temperature (<sup>O</sup>K) \* Time coordinate Inert time (s)  $t_r$ Retention time (s) Outlet linear velocity (cm/s) Linear velocity at any point in the column (cm/s)Mean linear velocity Volume coordinate Volume of stationary-phase in column (cm<sup>3</sup>) Volume of gas-phase in column  $(cm^3)$ Corrected retention volume (cm<sup>3</sup>) R Gas hold-up (cm<sup>3</sup>) Μ Parameter of distribution (length or diameter, cm) Mass of stationary-phase in column (g) Peak width at half height (cm;s) Distance from inlet of column, cm Density of carrier gas (g/cm<sup>3</sup>)

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Density of stationary-phase  $(g/cm^3)$ Ratio of gas to liquid volumes in column Partition coefficient Absolute viscosity of carrier gas  $(\frac{g}{cms})$  or mean value of distribution of lengths or diameters (cm)

Variance of distribution of lengths or diameters  $(cm^2)$ 

Note:

ρ<sub>s</sub>

γ

ß

σ

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This table lists only the most important and most used symbols. Those which do not appear in the table are defined in the Text or Appendix, where they are introduced.

# GLOSSARY OF ABBREVIATIONS

OTC - Open Tubular Column

GC - Gas Chromatography

GLC - Gas-Liquid Chromatography

TCD - Thermal Conductivity Detector

FID - Flame Ionization Detector

OPGV - Optimum Practical Gas Velocity

FCV - Flow Control Valves

HETP - Height Equivalent to a Theoretical Plate

#### INTRODUCTION

a) The use of Open Tubular Columns (OTC) in Gas Chromatography (GC) has had an increasing acceptance since they were introduced in 1956 by Golay<sup>(1)</sup>. They have a special advantage over packed columns, in the analysis of complex mixtures and separation of isomers (2), but have inherently some important limitations, one of which is the very small sample sizes they can handle without an apreciable loss in their efficiency. This, in turn, poses a limitation upon the choice of detector, which is usually a Flame Ionization Detector (FID), as conventional Thermal Conductivity Detectors (TCD) do not have the required sensitivity to respond adequately to such small samples. Note that, for some applications, a relatively large sample size is required (trace analysis, collection of components, coupling with auxiliary techniques for component, identification). Single OTC are not practical for these applications.

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One approach to overcome this problem is the use of larger diameter OTC<sup>(3)</sup>, as they still have higher efficiencies in comparison to packed columns, even though their efficiency is smaller than that of OTC with smaller diameters. Besides, if FID are used, the larger sample capacity of these columns allows the detection of very small concentrations. This could be of special interest to air pollution studies, <sup>(4)</sup> as determinations of concentrations in the range 0.01-1 ppm are of interest, both in atmospheric and laboratory photochemical investigations. Again, OTC of small diameter have not found much application in air pollution studies, as they cannot accept the sample sizes needed for trace analysis, without serious overloading and loss of resolution. The use of larger diameter OTC in trace analysis is not widespread, and this again is due to their sample capacity, which is naturally larger than that of OTC of smaller diameter, but still not adequate for many cases.

A serious improvement over the use of OTC with large diameter would be the use of OTC of small diameter, but with a large increase in the acceptable sample size. One way of increasing the sample size in smaller diameter OTC is by increasing the surface of retentive material within the column, and this is usually done by etching the inner column surface with a caustic solution, prior to depositing the retentive material.<sup>(5)</sup> The original method was proposed by Mohnke and Saffert, who used an aqueous armonia solution to form a film of SiO<sub>2</sub>, and some modifications of these methods were proposed.<sup>(6)</sup> While this may prove successful to improve the sample capacity of OTC, it is not the solution that we are

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looking for, as we would like to increase the sample capacity by some orders of magnitude, and chemical methods for treating the glass surface cannot produce such large improvements.

3

The approach that was taken here was to use small diameter (i.e., high efficiency) OTC, in parallel. Provided this could in practice be successfully done, any number of OTC could be used, and so the increase in the sample capacity would have the limits of reasonability, which in an epoch of high technology are no longer yesterday's limits. With this in mind, there would be no loss of efficiency as compared to single OTC of the same diamter, the problem of sample size would be overcome, and this could be a powerful tool for air pollution studies, as well as for complex separations (where OTC are usually employed) where it would be of interest to collect the separated components.

But there are more problems connected to the use of single OTC. Usually, OTC of small diameter operate with a splitting system, by means of which only a fraction of the injected sample and of the carrier gas pass through the column. Unless the splitter is carefully constructed, hydrodynamic perturbations may produce fractionation of the sample, i.e., the composition of the vapor going through the column is neither the same as that vented nor

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the same as that entering the splitter<sup>(7)</sup>. With the use of bundles of OTC, a splitting system will no longer be necessary, so this problem does not arise. Another important point when using OTC of small diameter, is that the dead volumes should be kept as low as possible, because asymmetry and broadening of the peaks will develop. Again, the use of bundles of OTC will allow the possible dead volumes to have a much less important role relative to one OTC (of the same diameter as each one in the bundle).

At this point, the reader may be interested to note the remarks made by  $Golay^{(1)}$  (the inventor of OTC) on the use of OTC in parallel:

... "I would not recommend capillaries (i.e., OTC) as a source of sample separation for even microanalysis. There I believe we need packed columns of large diameter, because if we used capillaries, it would be quite a job to put capillaries together in parallel which would be like each other"...

The potential advantages of a kind of chromatographic column that is composed of a bundle of parallel OTC led to the formulation of the following research problems:

1. To make bundles of OTC.

2. To determine the effect of the variability of OTC . parameters on the performance of the bundle of OTC. 3. To prepare and demonstrate a practically useful bundle of OTC.

This thesis is a report of research on these problems.

b) This report is organized in such a way that only the fundamental steps are integrated in the main text, while all the auxiliary research is reported in the Appendix. The basic theory of OTC must be known to understand the operation of OTC, and this is the reason why it was included in the text. The reader who is familiar with this theory may go directly to Chapter 2.

c) An extensive bibliographic search was done on the subject of OTC in parallel, and none was found. In a personal letter written to L.S. Ettre\*<sup>(8)</sup>, his answer on the subject was:

"...I don't know any literature which would deal with your subject..."

We think this is a new field in GC research, worthwhile of further exploration, as the potential advantages of using OTC in parallel are certainly very large.

\*Dr. L.S. Ettre, presently at Perkin Elmer Corporation, Norwalk, U.S.A., is well known by the important contributions that he made to the field of OTC, and is often cited in this report.

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All the equations, figures and tables referred to
 as (iA), where i is a number, are the Appendix equations,
 figures and tables.

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#### CHAPTER 1

### THEORY OF OPEN TUBULAR COLUMNS

#### 1.1 Introduction

Gas-Chromatography (GC) comprises all chromatographic methods in which the moving phase is gaseous. In this project, the stationary-phase is liquid, at the operating temperatures, and the appropriate term is then Gas Liquid Chromatography (GLC).

For the injection of one absorbed component and one inert, the schematic diagram shown in Fig. 1 applies. GLC is linear and non-ideal, as the isotherm is considered to be linear and as longitudinal diffusion and departures from equilibrium take place.

### 1.2 Basic Theory.

There are two excellent books that deal almost exclusively with OTC, those by Ettre<sup>(2)</sup> and Kaiser<sup>(9)</sup>. Only the parts that are directly related to this project will be presented here. There are three main parts in which this study may be divided: flow, mass transfer and column parameters as related to its efficiency. Special attention is focused on each one of these in turn, as they are all extensively used during this work. A reader familiar with the theory of OTC may follow directly to Chapter 2.



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Detector Response (Schematic)

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a) Flow in OTC

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The appropriate system of coordinates to derive the Equation of Motion and the Continuity Equation is cylindrical coordinates. From the Navier-Stokes equations, the following system results:

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(1)

(4)

 $\frac{\partial P}{\partial r} = \frac{1}{3} \mu \frac{\partial^2 u}{\partial z \partial r}$ 

 $\frac{\partial P}{\partial z} = \frac{-\rho u \partial u}{\partial z} + \frac{4}{3} \mu \frac{\partial^2 u}{\partial z^2} + \mu / r \frac{\partial u}{\partial r} + \mu \frac{\partial^2 u}{\partial r^2}$ (2)

The Continuity Equation is:

$$\frac{\rho \partial u}{\partial z} + \frac{u \partial \rho}{\partial z} = 0$$
(3)

Due to the fact that the gas is compressible, a step approach to a solution is taken<sup>(7)</sup>. For the mean crosssection velocity, the solution is the well known Hagen-Poiseuille equation:

 $\bar{u} = \frac{P_i - P_o}{8\pi L} r_c^2$ 

Assuming  $\overline{u}$  to be a function of the length along the column (i.e., of z), we get:

$$z/L = \frac{P_{i}^{2} - P_{i}^{2}}{P_{i}^{2} - P_{o}^{2}}$$
  
F is the flow rate at the cross-section at

If F is the flow rate at the cross-section at the distance z from the entrance, then:

$$z/L = \frac{(P_{i}P_{o})^{2} - (F_{o}/F)^{2}}{(P_{i}/P_{o})^{2} - 1}$$
(6)

This solution gives a pressure gradient that increases along the column length, confirming that expansion is taking place. Another way of correcting to Hagen-Poiseuille flow is based on the conversion of kinetic energy, which gives:

$$P_{i} - P_{o} = \frac{8\mu u L}{r_{c}^{2}} + \frac{m(\rho u^{2})}{2}$$
(7)

where m is an adjustable parameter, probably 2.2. (10)

The first approach is used in most GC literature, and will be the one followed here.

For the cases where the flow is measured at the outlet of the column (i.e.,  $F_{O}$ ), corrections must be applied to obtain the mean volumetric flow rate ( $\overline{F}$ ). Two corrections are usually made, the first accounting for the partial we pressure of water when using a bubble flowmeter, and the second accounting for the expansion within the column.

10

(5)

corrections yield:

$$F_{c} = F_{o} \frac{T_{c}}{T_{a}} \frac{(^{a}L - P_{w})}{P_{a}}$$
(8)

where  $P_{w_{a}}$  is the partial pressure of water at ambient temperature  $T_{a}$ , and  $P_{a}$  is the ambient pressure. For the mean volumetric flow rate, we have:

$$\vec{\mathbf{F}} = \mathbf{F}_{\mathbf{C}} \mathbf{j}$$
 (9)

where j is the pressure gradient correction factor, given by:

$$j = \frac{3}{2} \frac{({}^{P}i/{}^{P}o)^{2}-1}{({}^{P}i/{}^{P}o)^{3}-1}$$
(10)

From (9), it follows that:  $\bar{u} = u_{0}j$ 

One way of testing the uniformity in the diameter from tube to tube, in a bundle of OTC, is by applying the same pressure differential to all the tubes and checking the flow through each tube. For this case, the following expression was employed: <sup>(11)</sup>

 $\Delta p \Phi = (\mu/B_{O}) L \bar{u} \qquad (11)$ where B<sub>O</sub> is the permeability of the column, defined by:

$$B_{0} = \frac{r^{2}}{\frac{c}{8}}$$
(12)

12

and  $\phi$  is given by:

$$\phi = \frac{(P_{i}/P_{o})^{2} + 2(P_{i}/P_{o}) + 1}{(P_{i}/P_{o})^{2} + (P_{i}/P_{o}) + 1}$$
(13)

For the cases where the flow rate is not actually measured, but calculated from the retention time of an inert, the following expressions hold:

 $\bar{\mathbf{u}} = \underbrace{\mathbf{L}}_{\bar{\mathbf{t}}_{m}} \tag{14}$ 

and

$$\overline{\mathbf{F}} = \pi \mathbf{r}_{\mathbf{C}}^2 \overline{\mathbf{u}} \tag{15}$$

As pointed out by Ettre, <sup>(11)</sup> the error involved is very small, using the second method as compared to the actual measurement of  $F_0$  and afterwards correcting to get  $\overline{F}$ .

### b) Mass Transfer in OTC

The first order conservation equation for GC (DeVault Equation) is: (7)

$$\frac{\partial c}{\partial z} + \frac{A\partial c}{\partial V} + \frac{D\partial q}{\partial V} = 0$$
 (16)

where:

( )

c - concentration of solute (vapor) in gas-phase
 (gmole/cm<sup>3</sup>)
g - concentration of solute in liquid-phase (gmole/g)
D - mass of stationary-phase per unit length (g/cm)
A - volume of gas-phase per unit length (cm<sup>3</sup>/cm)
V - retention volume (cm<sup>3</sup>)
For a linear isotherm and a linear impulse input, the

solution is:

$$7 = z (A+D\beta')$$
 (17)

where  $\beta' = q/c$  is the partition coefficient, related to  $\beta$  by:

 $\beta = \beta' \rho_{s} \tag{18}$ 

Putting z=L, we have  $V=V_R^O$  (corrected retention volume), LA= $V_M^O$  (gas hold-up), DL=W<sub>s</sub> (weight of stationary phase). Thus:

$$V_{\rm R}^{\rm O} = V_{\rm M}^{\rm O} + \beta' W_{\rm S}$$
 (19)

The capacity ratio is defined as the mass of solute in the stationary phase divided by the mass of solute in the gas phase. As:

it follows that:

 $\gamma K = \beta$ 

(21)

(20)

which is an important relation when comparing geometrically

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different columns that operate with the same phases and same solute. The corrected retention volume is related to the retention time by:

 $v_r^{O} = t_r \bar{F}$  (22)

From here, we have:

$$t_r = t_m(1+K)$$
 (23)

This relation between the retention times of the absorbed component and the inert will be extensively employed.

The shape of the GC peaks is affected by many factors, but the simplified Gaussian shape may be derived from mass transfer considerations. Fick's first law of diffusion states that the quantity of material diffusing per unit time and unit area in the direction of diffusion, is proportional to the concentration gradient, i.e.: (18)

$$\frac{\partial N}{\partial t} = -D \frac{\partial C}{\partial t}$$
(24)

where N is in (mole/area) and c is in (mole/volume). D is the diffusion coefficient.

Fick's second law, which is a conservation law, is:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial r^2}$$

A particular solution to this equation is:

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(25)

$$c = \frac{M}{t} \exp\left(\frac{-z^2}{4Dt}\right)$$

where M is a constant. Considering m\* to be the total mass of material diffusing, we have:

$$M = \frac{m^*}{2\sqrt{\pi D}}$$
(27)

and so:

$$c = \frac{m^*}{2\sqrt{\pi Dt}} \exp\left(\frac{-z^2}{4Dt}\right)$$
(28)

which is the equation for a Gaussian curve, with:

$$w_h = 2.35s$$
 (29)

where s is the standard deviation and  $w_h$  is the peak width at half height.

c) Column Efficiency and Related Parameters

The number of theoretical plates (n) is the usual parameter that expresses the efficiency of one column, and is given by:

n = 5.54 
$$\left(\frac{t_r}{w_h}\right)^2$$
 (30)

This expression is only valid for K large, i.e., for  $t_r^{>>t_m}$ . For the early peaks, the modified expression is:

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(26) ~
The Height Equivalent to One Theoretical Plate is, by definition:

 $n_{o} = 5.54 (\frac{K}{K+1}) (\frac{t_{r}}{w_{h}})^{2}$ 

$$HETP = \frac{L}{n}$$
(32)

Golay<sup>(1)</sup> developed an expression for the HETP, considering the independent effects of longitudinal diffusion in the gas-phase, and  $\phi f$  non-instantaneous equilibrium in both phases. It is as follows:

HETP = 
$$\frac{2D_{g}}{\overline{u}} + \frac{1+6K+11K^{2}}{24(1+K)^{2}} \frac{r_{c}^{2}}{D_{g}} + \frac{K^{3}}{6(1+K)^{2}} \frac{r_{c}^{2}}{\beta^{2}D_{l}}$$
(33)

where  $D_g$  and  $D_g$  are the diffusivities in the gas-phase and stationary phase, respectively, and the other variables have the previous meaning. This expression neglects the resistance at the interface between phases, <sup>(12)</sup> which is usually negligible. Briefly, Equation (33) is usually writen as:

HETP = 
$$B_{\overline{u}}$$
 +  $(C_g + C_{\ell})\overline{u}$ 

where  $C_g$  and  $C_l$  are the resistances to mass transfer in both phases, and B is the term that accounts for the longitudinal diffusion in the gas phase.

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(31)

(34)

It is of interest to have the minimum value for HETP, which will provide the maximum number of theoretical plates, for a fixed column length. This is given by:

 $HETP_{min} = 2 \left[ B \left( C_g + C_{\ell} \right) \right]^{\frac{1}{2}}$ (35)

In practice,  $n_{max}$  is never achieved. For a long OTC the value of the optimum linear gas velocity, for which HETP has the minimum value, is very small to be well controlled and to give reasonable analysis times. For a short column, this value is too high, and implies large pressure differentials along the columns, with the associated problems of leak-proof pressure connections. Usually; long columns are used, and so work is done above the optimum value for  $\bar{u}$ , at a velocity close to the optimum practical gas velocity (OPGV), for which the longitudinal diffusion term in the gas-phase, i.e., the term B on Golay Equation, becomes very small in comparison with C<sub>q</sub> and C<sub>k</sub>. In this case:

# $HETP = (C_{a} + C_{b}) u$ (36)

There are three parameters of special importance when dealing with the efficiency of OTC. These are the column diameter, the film thickness and the sample size. C.1 Influence of the Column Diameter on the Performance of OTC .

When working at OPGV, HETP is proportional to  $r_c^2$ , and so columns of the smaller diameter should be preferred. For the cases where the resistance in the liquid-phase may be neglected, i.e.,  $C_l = 0$ , then HEPT is proportional to r and again columns of the smaller diameter are preferred. The practical limits of reducing the diameter of OTC seems to be connected to two problems. The first is the permeability of the column (Equation 12), which decreases with the square of the diameter. Pressure differentials would then have to be too high to overcome the resistance in a very small diameter column. The second reason, and probably the limiting reason when using single OTC, is the decrease in the surface area of retentive material with a decrease in the diameter, and thus a decrease in the sample size. Both these problems may be overcome by using a bundle of OTC, as the flow resistance may be compared to an electrical resistance in parallel, and as the increase in the number of OTC may well surpass the effect of the decrease in the film thickness in the individual columns.

C.2 Influence of the Film Thickness (df) on the Column Performance

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If we assume the retentive material to form a uniform film, deposited over all the column length, with a constant thickness  $d_{f}$ , it follows that:

 $\gamma = \frac{r_c}{2d_f}$ (37)

For a given system of solute, stationary and gasphases, and at a certain column temperature,  $\beta$  is constant. So, for a given column (i.e.,  $r_c$  fixed), a decrease in  $d_f$ will decrease K, and this in turn will decrease the resistance to mass transfer in the liquid phase, with a consequent reduction in the analysis time. Because of the reduction of sample size with a reduction in  $d_{f}$ , usually a range of  $d_f$  is used, between 0.6-1.5  $\mu$ , while  $d_f$ greater than 2.5  $\mu$  are unstable.<sup>(2)</sup> Again, we see that using a bundle of OTC would be advantageous, as a very thin film could be formed, with its inherent advantages, and the number of OTC would be the variable to be controlled in order to solve the sample size problem.

The coating technique has a definite influence on the film thickness. At present, there are two coating techniques available, the static method and the dynamic method. In the first, the column is filled with the solution of the stationary phase, usually in an organic solvent, and then it is slowly fed into an oven, at a

constant rate, for controlled evaporation of the solvent. This method was first introduced by Golay, and has the remarkable advantage of permitting an easy determination of the mean value of  $d_f$ , knowing the concentration of coating solution and the dimensions of the column, by using:

$$\gamma = \frac{V_{q}}{V_{s}} = \frac{100 - c_{s}}{c_{s}}$$
(38)

where  $c_s$  is the volumetric percent concentration of coating solution. With the use of Equation (37), we get  $d_f$ . With this method,  $d_f$  increases with increasing diameter (the other variables being constant), and in practical columns the concentrations used are less than 2 per cent. <sup>(1)</sup>

In the dynamic coating method, the column is filled with solution, normally one order of magnitude more concentrated than in the static method, and then the bulk of the solution is displaced by forcing an inert gas through the column at a constant speed. In order to overcome expansion effects the flow rate of the gas must be varied. In contrast with the static method,  $d_f$  increases with a decrease in  $d_c$ , keeping the concentration of coating solution and the linear velocities constant. <sup>(2)</sup> The determination of  $d_f$  is no longer simple. It requires weighing the column prior to coating and after coating, determining the amount of coating in the column, or collecting the leftover liquid-phase solution and comparing this

volume with the initial volume, the difference being the volume of coating solution inside the column (assuming no solvent evaporation). These methods are not very rigorous (specially the first one), due to the difference in magnitude of the compared terms. A better way would be to use two methods, for cross-checking.

A variation of the dynamic method is referred to as the coating plug method,  $^{(13)}$  and some empirical equations exist for the necessary volume of coating solution. This method was not used, due to the extremely small volumes of solution that would have to be used.

C.3 Influence of the Sample Capacity on the Column

Overloading of OTC, i.e., injection of samples larger than a certain threshold value, will decrease the efficiency of the columns, and the peaks will become broader and asymmetric.  $^{(2,9)}$  There are three ways of considering this threshold value. One is the concept of maximum permissible sample size,  $^{(14)}$  as the maximum amount that can be injected into a column without more than 10% loss of efficiency:

$$v_{K} = a_{k} v_{eff} \sqrt{n}$$

(39)

where  $V_k$  is the volume of vaporized sample exclusive of carrier gas,  $V_{eff}$  is the effective volume of one theoretical plate, and  $a_k$  is a parameter. Actually, as discussed by Ettre, <sup>(3)</sup>  $a_k$  cannot be assigned a fixed value, in agreement with the conclusions of Klinkenberg. <sup>(15)</sup> The limiting value of  $a_k$  is calculated, when not available, for the maximum number of theoretical plates, and

$$v_{\text{eff}} = \frac{V_{\text{g}}}{n} + \beta \frac{V_{\text{s}}}{n} = \frac{V_{\text{g}}}{n} (k+1).$$
 (40)

So, V<sub>k</sub> may be calculated by:

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$$V_{k} = a_{k} \frac{\pi Lr_{c}^{2}}{\sqrt{n}}$$
 (k+1) (41)

Another way is to think that the amount of material that can be injected is limited by the volume of one theoretical plate, i.e., to  $V_{eff}$ .

The third way is to calculate the mass of sample by: (9)

$$B^* = 0.05 \text{ Md}_c^3 (K+1)10^{-6}$$
 (42)

where  $d_c$  is in mm and M is the solute molecular weight and B\* is in grams. From this, knowing the operating conditions of temperature and pressure, the volume of vapor may be calculated. As  $a_k$  cannot be assigned a constant value, even for each particular system, the last method was the one used. Overloading of the column results in non-linearity in the peak height, while overloading of the detector results in non-linearity of the peak area. It is most advisable to work in the linear regions of both column and detector, as asymmetry and broadening will develop as a consequence of overloading.

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#### CHAPTER 2

#### DESCRIPTION OF EXPERIMENTAL APPARATUS AND ITS MODIFICATION

2.1 Introduction

Fig. 2 shows the most basic parts of any GC system. Sometimes, a collector is used after the detector, but in the case of OTC (at least of small diameter), this is not done, due to their small sample capacity.

2.2 Modification of the GC System

Originally, the unit was provided with a TCD, coupled to a bridge circuit and amplifier. Because of the small sample capacity of OTC, a more sensitive detector was needed, and the TCD was substituted by a FID. This FID was a dual flame type, and required a source of compressed air and a source of compressed hydrogen.

The recorder had a maximum chart speed of 4 inch per minute. The injections were done by standard Hamilton syringes, gas-tight, provided with a Chaney Adapter (in order to deliver pre-determined quantities of the gaseous sample, with little error). Various bubble-flowmeters were used, their cross-section depending on the magnitude of the flows to be measured. In addition to the flow control valves (FCV) of the base oven module, two other



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Gas Chromatography System (General)

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FCV were used, in order to provide the right flows of carrier gas reaching the detector. This particular FID works with a minimum flow rate of carrier gas of about 40 ml/min, which is impossible to achieve with small diameter OTC, at reasonable inlet pressures, and so, a make-up line had to be added to the system. This detector is of the dual flame type, which implies that a comparative column is necessary. Instead of using a second column and working with the FCV provided on the base oven module, a direct connection of the carrier gas cylinder to the FID was employed, with one of the other FCV. This arrangement proved simpler than a parallel column, as OTC are very fragile, and it is safer to use them as the lower column (position in the oven), so they can rest on the bottom of the oven, avoiding unnecessary tensions. If a parallel column had been used, it would have had to be removed every time that the experimental column was removed. This would have been troublesome and would have risked the breakage of the experimental column.

Due to the presence of the make-up line, when it was connected to the column exit, measurements of flow rates through the column had to be made using the retention times for the inert component. As mentioned before, the

error involved is very small. When the make-up line was not connected, the bubble flowmeters could be used. Fig. 3 is a schematic flow diagram, and Fig. 4 shows the general setup used.

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Principle of the Dual Flame Ionization Detector a) The flames in a FID, produced by the combustion of H<sub>2</sub> in air, contain an appreciable concentration of free electrons, resulting from ionization, and this gives them an electrical conductivity, which for the case of H<sub>2</sub> flames is very small. But when organic vapors are present, this conductivity increases, and this increase is a signal to the electrometer, which converts it into an appropriate signal to the recorder. (16,17) The mechanism of ion formation is not very well understood, (7) as the temperature of the flame is not sufficient to produce the observed number of ions by equilibrium processes. An explanation based upon ionization from heated particles (e.g., of carbon), <sup>(18)</sup> is not adequate. <sup>(19)</sup> The most probable explanations are of two types. (20,21,22) Chemi-ionization reactions may take place, and pairs of species react together in the flame, one (at least) of the reaction products being an ion. These ions are unstable, and degrade their excess energy by collisions. If this degradation is sufficiently slow, their concentration

### FIGURE ·3

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## Flow Diagram (Schematic)

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### FIGURE 4

Gas Chromatography System

1. Oven Base Module

2. Flame Ionization Detector

3. Oven Temperature Programer-Controller

4. Electrometer

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5. Chart Recorder

#### FIGURE 5

Flame Ionization Detector

1. Flow Control Valves for H<sub>2</sub>

2. Flow Control Valves for Air

3. Connections to Electrometer

4. On-Off Valves for H<sub>2</sub>

5. Flame Stacks

6. Hydrogen Line

7. Air Line

8. Oven Cabinet



in the flame will be high. Another possibility is that electrons created by some primary process, possessing energy well above their equilibrium values, cause further ionization upon colliding with neutral molecules. In the FID used in this project, the conductivity of the flames is measured between one electrode and the metal jets. These detectors are mass-flow sensitive, and the responses are measured in terms of the current given for a certain mass-flow of vapor, e.g., coulombs per gram. They are linear over a wide range of mass-flow rates, and a dommon range is from about  $10^{-14}$ g/s to  $10^{-7}$ g/s (of organic material), but the linearity over such a large range must be suspect. <sup>(7)</sup> Fig. 5 shows the FID used in this project.

b) Importance of the Dead Volumes

When using OTC, the connections of the column to both injection port and detector must be kept as small as possible, in order to avoid spreading and asymmetry of the peaks. (2,9) This is well illustrated by comparing the peaks given in Figs. 6-8-10, all obtained with the same chart speed of 1"/min, and with the same amount of gaseous solute, in this case propylene. The column was not coated, and so these peaks are representative of the air peaks. The length of the column was  $\approx$  700 cm and the

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inside diameter was 0.22 mm. The pressure differential across the column was 40 psi and the flow through the column was 9 ml/min, measured at the outlet. The operating temperature was  $293^{\circ}$ K and approximately 1µl propylene was injected in each case. Figure 6 shows the original peak, i.e., the peak obtained with the original connections. The width at half height is  $\approx$  30 s.

The connection from column to detector was modified, and Fig. 7 shows a diagram of the new connection. Figure 8 shows the peak obtained, which is very similar to the previous one, again with  $w_h \approx 30$  s, but the tailing was reduced.

The next step was the modification of the injection port. An examination of the injection port showed that a large dead volume existed, creating the possibility of slow mixing between the gaseous solute and the carrier gas, prior to entering the column. Figure 9 shows the adapted design for the injection port, and Figure 10 shows a typical peak obtained with this new system.

The basic difference between the two designs is the relative position of the carrier gas and the solute. In the original design, the carrier gas enters upstream of the solute (an extremely large needle should be necessary in order to avoid this), while in the new design it enters downstream (with conventional needles). Besides, the dead

FIGURE 6

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Detector Response for Propylene, Using Single Uncoated OTC

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Modified Connection Column-Detector, with the Make-Up Line



Detector Response for Propylene, Using Single Uncoated OTC



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FIGURE 9

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### Modified Injection Port

FIGURE 10

Detector Response for Propylene, Using

Single Uncoated OTC

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FIG.9



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volume was also reduced substantially. The new injection port produced a peak which is 85% narrower than the first ones, but it still had considerable tailing. The total dead volume present in a GC system is the sum of the various volume contributions from the system. The modifications explained above contributed to the reduction in the dead volumes of the connections of the column to the detector and to the injection port and, to some extent, to the reduction of the injection port dead volume. But the remaining dead volume of the injection port and the detector dead volume, which is inherent to its construction, may well be a significant part of the total dead volume. This hypothesis is investigated later in this chapter. Another factor which may contribute to the spreading is the overload of the column, and this sample size effect is discussed below.

Figure 13 is a photograph of the connection of the column to the detector, showing the line for the make-up / gas and Figure 14 is a photograph of the modified injection port.

c) Importance of the Sample Size

A l µl injection of propylene was the smallest direct injection that could be made. In order to inject a smaller amount through the column, a splitting system

was designed, and its diagram is shown on Fig. 11.

Due to the large difference in diameters between the Nylon tubing and the needle connected to the column, and due to the presence of the needle valve, any practical splitting ratio is achieved. Although this splitter is not a warranty against fractionation of the sample, it was sufficient for the purposes of this project, and produced a typical peak shown in Fig. 12, for an injection of propylene of 10  $\mu$ l and splitting ratio of l:190, and the same chart speed as before, i.e., l"/min.

This peak represents an improvement of about 92% over the first two peaks (Fig. 6-8) and of about 50% over the peak shown in Fig. 10. It can be seen that the tailing was also dramatically reduced. Based on the ratio of flows through the column and through the vent, the splitting ratio was 1:190, which means that  $\sim$  0.05 %1 of propylene went through the column. Using Equation 42,  $B^* = 2.24 \times 10^{-8}$  $T_{z}$  and mean pressure of the column (p=2.36 atm). This means that an injection ten times less would not overload the column, and would probably produce a narrower peak with less tailing, but that would have required working at the high sensitivity region of the FID, with all the stability and background noise problems associated with it. Through Fig. 6-8-10-12, we can see the importance of both dead volumes and sample size on the obtaining of narrow

peaks with single OTC, specially of small diameter (2).

Although the total dead volume is the sum of the dead volume contributions from the different components of the GC system, the same is not true for the total broadening. The broadening is usually expressed in terms of standard deviations, and the standard deviation produced by several independent factors will be less than the sum of the standard deviation produced by each factor. So, the factor that gives the largest individual broadening is the most important one. For the column tested, the mean velocity (as corrected for pressure drop) is 158 cm/s. As the column has no coating:

$$\frac{s_{L}^{2}}{T} = \frac{2D_{g}}{\overline{u}} + \frac{r_{c}^{2}\overline{u}}{24 D_{g}} , \text{ where } s_{L} \text{ is the}$$

standard deviation in distance units. The diffusivity of  $CH_4$  in helium at room temperatures may be estimated from Gilliland Equation, to be  $\sim 0.6 \text{ cm}^2/\text{s}$ . So,  $s_L^2$  is of order  $10^{-2}$  cm. But for the peak shown in Fig. 12, assuming it is Gaussian,  $s_L$  is of order 10 cm, which gives  $s_L^2$  of order 1. From these results, we conclude that the end effects have a great importance, adding the main contribution to peak spreading. So, no reliable data may be taken on peak spreading due to columns

FIGURE 11

### Splitting System

FIGURE 12

Detector Response for Propylene, Using Single Uncoated OTC Ι.



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using this GC system, be it from coated or uncoated columns (the end effects on peak broadening from coated columns are discussed in Chapter 4), and no values of HETP or n may then be calculated from the experimentally otbserved values of  $w_h$ .

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### FIGURE 13

Partial View of Column-Detector Connections

1. Column

2. Make-Up Line

3. Comparative Column

4. Connection Column-Detector

### FÌGURE 14

Injection Port

1. Original Injection Port

2. He Line

3. New Injection Port

4. Oven Cabinet



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FIG. 13



#### CHAPTER 3

#### EXPERIMENTAL TECHNIQUES

3.1 Preparation of the Column

a. Drawing - The method used was introduced by Desty<sup>(23)</sup> and Kreyenbuhl<sup>(24)</sup>, almost simultaneously. The material used was Pyrex tubing,  $d_{ext.} = 6.9$  mm and  $d_{int.} =$ 3.0 mm and, in principle, any diameter smaller than this one could be obtained, just by adjusting the relative speeds of the two drawing motors. These motors, as well as the controllers and the furnaces are shown in Fig. 15.

Two parameters are of interest when drawing OTC: the length and specially the inside diameter of the capillary. The length may be easily controlled by drawing into a Harger length than what is needed, and then breaking the capillary to the appropriate length. But the diameter must be obtained at the drawing system, and a close control of the diameter is necessary, for it will affect the thickness of the retentive film in the column and the flow rate through the column. As pointed out by Kaiser, <sup>(9)</sup> if a pinch occurs in an OTC, it will be as if the diameter of the column were reduced to the diameter of the pinch, i.e., the flow rate will be controlled in large amount by the diameter of the pinch. In order to establish the

### FIGURE 15

System for OTC Preparation

1. Capillary

2. Pyrex Tubing  $\sqrt{\frac{1}{4}}$  0,D.

3. Drawing Furnace

4. Drawing Pre-Furnace

5. Coiling Furnace

6. Coiling Motor

7. Upper Drawing Motor

8. Lower Drawing Motor

9. Controller for Lower Drawing Motor
 10. Potentiometer for Drawing Furnace
 11. Controller for Upper Drawing Motor
 12. Potentiometer for Pre-Furnace

13. Potentiometer for Coiling Furnace


confidence limits of the drawing procedure, an experiment on the stability of the motors was conducted, followed by an experiment on the uniformity of the diameter.

Comparing Figure 16 with Figure 17, we see that the speed of the upper drawing motor is more uniform than that of the lower motor. This is probably due to the difference in the speeds of the motors. Some slip may have occurred between the revolution counter and the shaft at the higher speed of the lower motor.

To test the uniformity of the diameter, a coil of capillary tubing several meters long was drawn. The initial part, for which the drawing conditions were not at steady state, was discarded. The remainder of the coil of tubing was cut into sections 10 cm in length and the diameters of the ends of each section were measured by means of a microscope. Figure 18 shows that diameters of the order of 120  $\mu$  may be controlled to within ±2 per cent.

b) Cleaning of the Column Tubing

Cleaning is necessary prior to coating. Usually, various organic solvents are used, e.g., methylene chloride, chloroform, acetone, methanol, hexane, diethyl ether. Hollis<sup>(25)</sup> recommends the following order of solvents: pentane, methylene chloride, acetone, diethyl ether, and the







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FIGURE 18

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Uniformity of OTC Diameter (Uncoated)



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solvent of the stationary phase. This was the method originally used in this project, but it is very time , consuming, and so a simpler method was tried, using acetone, diethyl ether and the solvent of the stationary-phase. The cleaning is important for two reasons: first, because it is necessary to remove particles that are inside the capillary and may cause its clogging and secondly, because this cleaning changes the wettability of the glass. As discussed by Nečasová and Tesařík, <sup>(26)</sup> the interfacial tensions of glass, stationary liquid and solvent affect the mode in which the film of the stationary phase is deposited on the columns. Table 1 shows the critical surface tensions of Pyrex glass subjected to different treatments.

If a homogeneous coating of the glass capillary surface is to be obtained, then the surface tension of the coating solution should be lower than the critical surface tension of the glass. The surface tension of squalane is 29.5 dyne/cm, <sup>(26)</sup> and as only the solution phases whose surface tensions are lower than the critical surface tension of glass can form an uniform film on the capillary wall, cleaning the tubes with organic solvents, e.g., acetone may not be sufficient. As an approximation, the surface tension of a mixture may be calculated by:

 $y = y_1 x + y_2(1-x) = y_2 + (y_1 - y_2) x$  (43)



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# Critical Surface Tension of Pyrex Glass

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TABLE 1*
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Washed with acetone  $28.0\pm.5$  (dyne/cm) Cleaned with chromic  $H_2SO_4$   $44.0\pm1.0$ Etched with NaOH 32-34Carbonized (according to Grob) 41

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\*From Nečasová and Tesařík<sup>(2,6)</sup>

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where y is the surface tension of the mixture,  $y_1$  and  $y_2$ are the surface tensions of components 1 and 2, i.e., of the stationary-phase and its solvent, and x is the mass proportion of component 1 in component 2.

For example, a common concentration of a solution for the dynamic coating method is a 10 per cent by mass. For this solution, we have:

> $y_2 = 23.3 \text{ dyne/on}$  $y_1 = 29.95 \text{ dyne/cm}$ x = 0.10

So,  $y = 23.97 \, dyne/cm$ .

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Comparing this value with those given in Table 1, we find that cleaning the glass tubing with acetone is sufficient when the coating solution is 10 per cent squalane in acetone. The limiting concentration is seen to be around 70 per cent, using the additive expression (Equation 43). Actually, for concentrations as low as 20 per cent of squalane in acetone, uneven coatings were observed. Accumulations of squalane were distributed through the columns. These accumulations were large enough to be seen without a microscope, but not large enough to fill the column at any point. No accumulations were observed when the concentration of squalane was decreased to 15 per cent. However, the absence of accumulations of squalane does not

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necessarily mean that a coation was uniform on a microscopic scale.

The method of etching the glass with NaOH was also tried, but it is lengthy and cumbersome, and the simpler method of cleaning the tubes with organic solvents was used in this project.

c) 'Elimination of Secondary Adsorption Effects (Conditioning)

The poor wettability of glass surfaces with organic liquids has been recognized for many years as a key problem in the preparation of highly efficient and stable glass capillary columns.<sup>(27)</sup> Some exceptions are liquid-parafins, e.g., squalane (2,6,10,15,19,23-hexamethyltetracosane), which spread on the high-energy glass surface, but even in this case, the active-sites of the glass may produce nonuniformities, and this is usually overcome by using chlorosilanes or other compounds that will block the activesites of the glass. A quaternary ammonium compound was used (trioctadecylmethylammonium bromide) as discussed by. Metcalfe and Martin. (28) This considerably improves the performance of OTC, for many substances, including hydrocarbons. This compound is available under the name of Gas-Quat-L, from Lachat Chemical Company Laboratories. In the case of glass OTC, Metcalfe and Martin suggest the

precoating of the column with the quaternary solution, prior to coating with the stationary-phase. As acetone does not easily dissolve this quaternary compound, a solution of it in methylene chloride was used, prior to coating the column with the solution of squalane in acetone.

#### d) Coating of OTC

As already mentioned, squalane was the stationary This is a conventional GC phase, widely phase used. available and used for many purposes. The solute was a gaseous hydrocarbon (n-heptane), so this stationary phase is appropriate. Both of the two coating techniques discussed were used. For single, OTC only the static method (1) was used, because it provides an easy determination of the film thickness, assuming that a uniform film is formed, and because the necessary equipment was available. The principal part of this equipment is the oven, which is shown on Fig. 19. It is important that air bubbles are not trapped inside the tubing, as flash vaporization will occur, destroying the film. These bubbles were avoided by simply plugging the tube end with epoxy resin, after the coating solution was in the column, and while some drops of the coating solution were still coming out from the tube. The column was then fed into the oven shown in Figure 19. The important variables to be controlled were the oven

temperature, the speed of feeding and the concentration of the coating solution. For the solvent acetone (normal boiling point of 56.5°C) a temperature of  $70^{\circ}$ C and low speeds were used.

The static method was not satisfactory for bundles of OTC~ (See Chapter 3 of the Appendix). The pinch roller could not be used with the bundles of OTC, because it " would break one or more of the tubes. For this reason, bundles were fed into the oven by hand. The resulting nonuniform speed of feeding was probably one of the reasons that the static coating technique produced poor results with bundles.

The dynamic coating method is simpler and quicker than the static method, as it involves only one motor connected to a syringe, which in turn is connected to the column by some appropriate tubing. The variables to be controlled are the linear velocity of coating solution and its concentration. Due to the unsatisfactory results obtained with the static method this was the method used for bundles of OTC. Figure 20 shows the schematic sequence of steps involved in the preparation of single OTC as well as in the preparation of bundles of OTC, using in this last case the dynamic method. In both methods, the coating solution was filtered prior to entering the column. After all these steps, the columns are not ready to

## FIGURE 19

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Coating Oven (Static Coating)

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Oven
Feeding Motor
Thermometer

4. Pinch Roller

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FIGURE 20

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Step by Step Single OTC or Bundle

Preparation (Schematic)



work, as they need to be further conditioned to evaporate the remaining of the solvent and any other low-boiling substances that may be present. This was done by leaving them overnight in the GC oven, with a slow flow of carrier gas, at  $120^{\circ}$ C. The maximum operating temperature recommended for squalane is  $150^{\circ}$ C, <sup>(29)</sup> as the vapor pressure of squalane will become appreciable and the stationary phase will blow off rapidly at higher temperatures. The final conditioning process was monitored by the baseline stability. When the baseline was stable, the column was ready for operation.

3.2 Connections

a) Connection of Single OTC to GC apparatus

Single tubes were connected by means of Nylon tubing between the extremities of the column and the injection line and detector line. P Epoxy resin was used to hold the connections together, and Fig. 21 is a schematic diagram of the connections.

b) Combination of Single Tubes to Form a Bundle

In the preparation of bundles of OTC, care must be taken in order to fill the spaces between the tube with an appropriate material, e.g., epoxy resin. Otherwise leaks will occur. After this is done (Fig. 22), the connections

of the bundle to the GC system were made by means of connections similar to those in Fig. 21.

When more than  $\sim$  5 columns are used in a bundle, it becomes difficult to put them in parallel, and so partial bundles were made, and afterwards assembled into the final bundle. With this approach of the partial bundles, many long columns may be put in parallel, without the danger of breaking them.



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Connection of OTC to Injection Port

or to FID (Detailed)



Bundle Connection to Single Line



#### CHAPTER 4

#### EXPERIMENTAL RESULTS IN COATED COLUMNS

4.1 Introduction

With coated OTC, for an approximate determination of the inert retention time,  $CH_A$  was used. Methane actually is slightly absorbed, and at the temperatures used, i.e., ambient temperature, the partition-coefficient of methane may introduce a definite error. But the columns used were not long OTC, and so one assumption is that  $CH_4$ is representative of an inert component. Three different methods for calculating the actual t are given in the Appendix of Ref. (2). Propylene was abandoned in favor of n-heptane, to represent an absorbed component, and this is because of the very small  $\beta$  value (partition coefficient) of propylene. As discussed by Littlewood, (7) the partition coefficients ( $\beta$ ) of the C<sub>1</sub> to C<sub>4</sub> hydrocarbons are very small, so that a very long OTC would be needed to separate Usually, OTC coated with a solid propylene from methane. support are used for light hydrocarbon analysis. The system for sample preparation is shown in Fig. 23 together with a section of the splitting system. No attempts were made to use the OTC at the optimum flow-rate, as this project is not concerned in achieving the best performance from

the OTC, but the operational variables for each column are listed in every experiment. For comparative purposes, only the pressure differential was set constant, and this will be seen later, in Chapter 6.

### 4.2 Coated Single OTC

As discussed previously, when using single OTC, the static coating method was used. Here, the variables to be controlled are the concentration of coating solution, the temperature of the oven and the feeding speed of the OTC into the oven. After some trials the temperature of the oven was set at 70°C for the solvent acetone, and low feeding speeds were used, such that the feeding operation was carried overnight. The concentration of coating solution was determined by the thickness of film desired, which was usually between 0.6-1.5  $\mu$ . The smaller the d<sub>e</sub> (film thickness), the smaller the contribution to the peak broadening there will be, but this decreases the sample size. In this method, the closure of one end of the OTC is necessary, while the other end enters the oven. This was achieved by immersing one end of the OTC into a very small cup full of epoxy resin, while some drops of the coating solution were still coming out from that end of the OTC, after the motor that drives the coating syringe was disconnected. With this approach, no air bubbles were

### FIGURE 23

Sample Preparation System

1. Vent Line

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2. Needle Valve

3. CH<sub>4</sub>-Heptane System

4. Syringes

5. CH<sub>4</sub> Line

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6. Heptane or Heptane-Acetone System

7. Flowmeter Liné

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FIG.23

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, 。 、 、 、 予 trapped in the OTC, and so, no flash vaporization occurred. Assuming that the volume of stationary phase,  $V_g$ , is deposited as a film of uniform thickness, the thickness,  $d_f$ , may be calculated using Equation 37:

$$d_{f} = r_{c}V_{s}/2V_{g} = r_{c}V_{s}/2(\pi r_{c}^{2}L-V_{s})$$

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Two columns of different length and diameter were used. Their chafacteristics are given in Table 2, together with the results obtained for  $CH_4$  and n-heptane injections. All calculations are based on formulas given in Chapter 1.

The HETP min may be calculated by:

$$METP_{min} = 0.57 r_{c} (K small)$$
(44)

$$HETP_{min} = 1.9 r_{C} (K \text{ large})$$
(45)

The values are taken directly from Equation (35). It is easily seen, whether using (44) or (45), that these columns are very far from operating at the optimum conditions. With a very small film thickness as in case B or A, the resistance to mass-transfer in the liquid-phase should be very small, and Equation (33) may be approximated by:



TABLE 2

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Experimental Results in Two Coated Single OTC

· ,	Table 2	,
······	A	<u> </u>
P <sub>i</sub> (atm)	2.63	3.72
P <sub>o</sub> (atm)	~ 1	, ∿1
F(ml/min)	2.4	.0.12
ū(cm/s)	105	26 "
L(CM)	∿ 720	∿ 230
d <sub>c</sub> (µ)	220	100
c <sub>s</sub> (%vol)	0.8	°0.4
, d <sub>f</sub> (u)	~ 0.4	∿ 0.1
t <sub>m</sub> (s)	6.84	· 9.00 · ·
t <sub>r</sub> (s)	30.45	28.00
K	3.45	2.11
(w <sub>h</sub> (s)	∿ 3.7	∿ 5.5
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HETP  $\sim \frac{2 \overline{D}_g}{\overline{u}} + 0.27 r_c^2 \frac{\overline{u}}{\overline{D}_g} = \frac{0.52}{\overline{u}} + r_c^2 \overline{u}$ 

with  $D_g = 0.26 \text{ cm}^2/\text{s.}$ 

Using this simplified equation to compute HETP, the value for column A is 0.018 cm and for column B is 0.021 cm, which are about two orders of magnitude smaller than those calculated from the data of Table 2, by Equation (32). The peak spreading observed for uncoated columns and discussed in Chapter 2 suggests that mixing in the dead volumes of the inlet port and detector is the major cause for this difference. Microscopic non-uniformity in the coating could be another cause.

Figures 24 and 25 show the actual chromatograms obtained with both columns, with a chart speed of 4"/min.

4.3 Coated OTC Bundles

Attempts were made to use the static coating technique to produce bundles of OTC that operated satisfactorily, i.e., that produced single peaks for each component. As may be seen in Chapter 2 of the Appendix, the bundles produced single peaks for non-absorbed components, i.e., the differences in diameter (and length) from column to column were not sufficient to produce individual peaks for

FIGURE 24

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Detector Response for CH4 and n-Heptane,

on Single Coated OTC



Detector Response for CH<sub>4</sub> and n-Heptane, on Single Coated OTC



FIG. 24



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individual columns. With coated bundles, the same behaviour should be expected for  $CH_4$ , as it behaves as a quasi-inert, and this was indeed verified, even for the static coating technique. But for the absorbed n-heptane, a different picture develops, and various peaks appear from different columns; and this subject is treated in Chapter 3 of the Appendix.

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Using the dynamic coating method, care must be taken on the linear speed of the coating solution, and on the concentration of this coating solution. Upon the first problem, opinions seem divided, <sup>(2)</sup> as some experimenters use very small velocities ( $\sim$  1 cm/s), while others use larger velocities  $(\sim 10 \text{ cm/s})$ . Due to the expansion of the gas (inert) that is pushed through the column in order to remove the solvent, as the interface gas-liquid moves along the column, it is obvious that the inlet pressure should vary (if the outlet is constant), in order to obtain an approximately constant velocity through the whole process, i.e., until the last drop of solution leaves the The effect of expansion is very importnat, as column. it may produce a non-uniform film thickness, and this is especially true at the last parts of the column, i.e., near the column outlet. In this project, very small velocities were used, varying between 2 and 2.5 cm/s through the whole process, for each bundle prepared.

The choice of small velocities was made because small diameter OTC were used in the bundles, and very large inlet pressures are necessary for pushing the viscous coating solution through these columns. Small variations in the velocity of the gas-liquid interface may be appreciable when working at low velocities, although this becomes less significant at higher velocities. Despite the drawback of variations at low velocities, bundles of OTC that produced a unique relationship peak-component could be made this way, and this is described below.

## a) "In Parallel" Bundle Preparation

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In this approach, a long OTC was prepared (uncoated), and then broken into columns of the appropriate length, to make up the bundles. The coating technique (together with all the auxiliary cleaning and conditioning steps), was then applied to the tubes in parallel. Two bundles of different length were made this way, from columns of the same diameter. For the injection, only n-heptane was used, and so, if the length difference was sufficient, only two peaks should develop. Instead of 2 peaks, 4 . appeared, and it will be seen that this was because of contamination of n-heptane with acetone, used to clean the flask from where n-heptane was taken. Each bundle had 4 columns, and they were broken one by one, until the last

column of the longer bundle remained, giving two peaks. In order to confirm that it was in fact contamination and not malfunctioning of the bundles, the single OTC described in Table 2 (column A) was used, and again two peaks were obtained. Table 3 describes the characteristics of both bundles and the results obtained are discussed according. to the number of columns involved.

With (8, 7, 6, 5) columns, the chromatograms were like the one shown in Fig. 26, while with (4, 3, 2, 1) columns, i.e., only the columns of bundle G, the chromatograms were like the one shown in Fig. 27.

By the careful measurement of the retention times, and looking at Fig. 26, we see that there are four peaks, two of them superimposed.

The retention times obtained are shown in Table 4, obtained for an inlet pressure of 2.63 atm.

Now, we define M, as:

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$$M_{i} = \frac{t_{i}}{t_{1}} - 1$$
 (46)

i.e., we are normalizing with respect to the first peak. (M<sub>i</sub> is not the capacity ratio, K<sub>i</sub>, because the first peak is not an inert peak). With this approach, we get Fig. 28.

Note that, for the last four columns, as they were from the longer bundle, peak No. 1 was not present, and

TABLE 3

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Coated Bundle Characteristics

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Detector Response for Acetone and n-Heptane, for Two Coated Bundles of Different Lengths

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# FIGURE 27

Detector Response for Acetone and n-Heptane,

for One Coated Bundle


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FIG.26



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Experimental Results in Two Coated Bundles of OTC

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N	8	7	6	5	4	3	2	1
t <sub>l</sub> (s)	6.83	6.05	6.58	6.00	-	-	<b></b>	
t <sub>2</sub> (s)	15.30	12,.77	14.41	13.68			<b></b>	-
t <sub>3</sub> (s)	17.55	15.06	17.17	16.32	17.00	15.50	16.20	16.40
t <sub>4</sub> (s)	48.36	40.78	44.09	37.62	41.21	38.24	41.00	40.15

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Table 4

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### FIGURE 28

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# Normalized Retention Times for Two Coated Bundles

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t, was calculated as follows:

$$t_{1} = t_{4} \times \left(\frac{t_{1}}{t_{4}}\right) = 0.15 t_{4}$$
(47)  
(8,7,6,5, columns)

We always have, of course,  $M_1 = 0$ . We can see from here that each bundle contributes to 2 peaks (one is acetone and the other n-heptane), and the chaotic results obtained with the static coating technique, shown in the Appendix, Chapter 3, do not appear when the dynamic coating technique is used. Figure 29 shows the chromatogram obtained from column A, and no measurements were made here.

In order to check the assumption that the dead volumes of the connections between the bundle and the GC instrument are a cause of the increase in the width w<sub>h</sub> as the number of columns decreases, here those dead volumes were changed 2 times during the runs. The original connection was kept until only 3 columns were connected, and then the connections were changed for the smallest one that was possible to achieve. Then, two more runs were made (with 3 and 2 columns respectively), and when only one column was in, the connections were again changed, trying to keep them the smallest possible. The results are shown in Fig. 30, for peak No. 4, which is an n-heptane peak. The sample size was kept proportional to the number of

FIGURE 29

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Detector Response for Acetone and n-Heptane

for Single Coated OTC



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FIGURE 30.

Variation of Peak Width at Half Height, with

the Number of Columns

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OTC employed.

The arrows indicate where a change in the connections occurred, and it is seen that  $w_h$  drops when this is made, and it drops approximately to the mean value of  $w_h$  for 5 and more columns.

The conclusion that may be taken from this is that the connections of the columns to the detector and the injection port have a definite role in the spreading of the peaks.

#### b) "In Series" Bundle Preparation

Another way to prepare a bundle of OTC is by preparing a long OTC, coated, and then breaking it into the columns that will form the bundle. The results of using bundles prepared in this way gives some information about the uniformity of film thickness obtained by using the dynamic coating technique. Table 5 shows the bundle characteristics and the results obtained, with injections of acetonemethane, as the same sampling as before was used. Again, we are not interested in the actual performance of the bundle, but in achieving a unique relation peak-component, and this was in fact obtained, as may be seen from the chromatogram shown in Fig. 31.

### TABLE 5

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## Experimental Results in Coated Bundle

\_("In Series" Preparation)

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· Bundle F						
Ŷ	-					
N _ •	5					
L ( Cm)	∿ <b>4</b> 40					
d <sub>c</sub> (μ)	165					
c <sub>s</sub> (% mass)	10					
t <sub>l</sub> (s) .	5.64					
t <sub>2</sub> (s)	14.40					
M	1.55					
w <sub>h</sub> (s)	∿7.44					
P <sub>i</sub> (atm)	2.63					
Po (atm)	`^					
	2.					

Table 5

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Detector Response for Acetone and n-Heptane for Coated Bundle, Prepared by the "In-Series" Techniques

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FIGURE 32

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Bundle of OTC, Installed in the GC System



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#### 4.4 Conclusions

A method was developed for preparing bundles of OTC. This method is a solution to the first of the research problems listed in the Introduction.

The first criterion of a useful combination of GC column and instrument is the existance of a unique relationship between peak and component, i.e., the coherence of the peaks in a chromatogram. The second criterion is the separating power of the combination, which may be quantified as the reciprocal of the apparent HETP of the column. The mixing that occurs in the dead volume associated with the inlet, connections, and detector of the GC instrument affects both of these criteria. By smoothing the irregularities in a peak due to the differences in the characteristics of the individual tubes in a bundle 'of OTC, mixing can make GC peaks coherent. However, this is only achieved by a reduction of the separating power of the combination of column and instrument. The optimum amount of dead volume would give both coherent peaks and maximum separating power.

Bundles of OTC that were prepared using the dynamic coating technique satisfied the criterion of peak coherence while those prepared by the static coating technique did not (see Chapter 3 of the Appendix). The separating power of the combination of column and instrument for an optimum dead volume was not determined. The separating power that was demonstrated using columns giving coherent peaks would not have been adequate for most analytical purposes, but it would be suitable for some preparative and process control applications. In this qualified sense, the third research problem listed in the Introduction has been solved.

#### CHAPTER 5

#### MATHEMATICAL MODEL

#### 5.1 Introduction

The second of the three research problems listed in the Introduction is to determine the effects of the variabilities of OTC parameters on the performance of a bundle of OTC. In this chapter, we will derive an equation that relates the dispersion of a coherent concentration pulse in the gas issuing from a bundle of OTC to the variabilities of the parameters of the columns comprising the bundle. The coefficients of the equation will be discussed in Chapter 6.

#### 5.2 Derivation of the Mathematical Model

Assumptions: 1) The peaks from individual OTC are Gaussian in shape, and so Equation (54) applies for the concentration profile, where m and s<sup>2</sup> are the first and second moments and both are functions of the parameters length and diameter.

 $c = \frac{1}{s\sqrt{2\pi}} \exp \left[-(t-m)^2/2s^2\right]$  (54)

2. The parameters length and diameter are independent, normally distributed on the bundle, i.e.:

$$p(w) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ - (t-m)^2 / 2s^2 \right]$$
 (55)

where w stands for L or d.

3. For a Guassian distribution of diameters, if the peaks emerging from the individual OTC are Gaussian in shape, the composite peak will also be Gaussian.<sup>(30)</sup>

A mass balance gives:

$$c_{T}(t,L,d_{c}) = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p(L) p(d_{c}) c(t,L,d_{c}) F(L,d_{c}) dL dd_{c}}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p(L) p(d_{c}) F(L,d_{c}) dL dd_{c}}$$
(56)

where c<sub>T</sub> is the concentration profile from the bundle, and F is the flow rate.

For simplification of notation, let  $w_1 = L$  and  $w_2 = d_c$ . Expanding  $F(w_1, w_2)$  as a Taylor's series, about the mean values  $w_1 = \mu_1$  and  $w_2 = \mu_2$ , we get:

$$F(w_{1},w_{2}) = \overline{F} + \sum_{i} \frac{\overline{\partial F}}{\partial w_{i}} (w_{i} - \mu_{i}) + \sum_{i} \sum_{j} \frac{\overline{\partial 2_{F}}}{\partial w_{i} \partial w_{j}} (w_{i} - \mu_{i})$$

$$(w_{j} - \mu_{j}) \quad i=1,2 \text{ and } j=1,2 \quad (57)$$

where the variables that have a bar over them are evaluated at the mean values for  $w_i$ , i=1,2. Now, we recall two properties of the moments of a Gaussian distribution, namely:

$$\int_{-\infty}^{\infty} p(w_i) dw_i = 1 \qquad (58)$$

and

$$\int_{-\infty}^{\infty} p(w_i) (w_i - \mu_i) dw_i = 0$$
(59)

Applying these relations (57, 58, 59), it is easily seen that equation (56) resolves into:

$$c_{T}(t,L,d_{c}) = \frac{\int_{\infty}^{\infty} \int_{\infty}^{\infty} (w_{1}) p(w_{2}) c(t,w_{1},w_{2}) F(w_{1},w_{2}) dw_{1} dw_{2}}{\overline{F} + \sum_{i} \frac{\overline{\partial^{2} F}}{\partial w_{i}^{2}} \sigma_{i}^{2}}$$

$$(60)$$

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Doing the Taylor's expansion of  $c(t, w_1, w_2)F(w_1, w_2)$  around  $w_1 = \mu_1$  and  $w_2 = \mu_2$ , we get:

$$c(t, w_{1}, w_{2}) F(w_{1}, w_{2}) = \overline{c(t)F} + \sum_{i} \left( \frac{\overline{\partial c}}{\partial w_{i}} \overline{F} + \overline{c} \frac{\overline{\partial F}}{\partial w_{i}} \right) .$$

$$(w_{i} - \mu_{i}) + \sum_{i} \sum_{j} \left[ \frac{\overline{\partial^{2} c}}{\partial w_{i} \partial w_{j}} \overline{F} + \frac{\overline{\partial c}}{\partial w_{i}} \frac{\overline{\partial F}}{\partial w_{j}} + \frac{\overline{\partial c}}{\partial w_{j}} w_{j}} + \frac{\overline{\partial c}}{$$

i=1,2; j=1,2

(61)

Again, using Equations (58, 59), we get:

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$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} [w_{1}) p(w_{2}) c(t, w_{1}, w_{2}) F(w_{1}, w_{2}) dw_{1} dw_{2} = \frac{1}{c(t)F} + \sum_{i}^{\infty} \left[ \frac{\partial^{2} c}{\partial w_{i}^{2}} \overline{F} + 2 \frac{\partial c}{\partial w_{i}} \frac{\partial \overline{F}}{\partial w_{i}} + \overline{c} \frac{\partial^{2} F}{\partial w_{i}^{2}} \right] \sigma_{i}^{2}$$

$$(62)$$

So, finally Equation (56) becomes:

$$\frac{1}{c_{T}(t)} = \frac{1}{\frac{\overline{c}(t)F}{\overline{c}(t)F} + \sum_{i} \frac{\overline{\partial}^{2}c_{i}}{\overline{\partial}w_{i}^{2}} \overline{F} + 2 \frac{\overline{\partial}c_{i}}{\overline{\partial}w_{i}} \frac{\overline{\partial}F}{\overline{\partial}w_{i}} + \overline{c} \frac{\overline{\partial}^{2}F}{\overline{\partial}w_{i}^{2}} \sigma_{i}^{2}}{\overline{F} + \sum_{i} \frac{\overline{\partial}^{2}F}{\overline{\partial}w_{i}^{2}} \sigma_{i}^{2}}$$
(63)

The peak broadening is related to the second moment of the peak, because of assumptions 1 and 3. Let  $s^2$  be the second moment for the individual OTC column peak evaluated for certain values of the parameters  $w_i$ , i.e., of length and diameter. Let  $s_T^2$  be the second moment for the peak from the bundle of OTC columns. So,

$$\overline{s_{T}^{2}} = \int_{-\infty}^{\infty} \overline{c_{T}(t)} (t-\overline{m})^{2} dt \qquad (64)$$

and

$$\overline{s^2} = \int_{-\infty}^{\infty} \overline{c}(t) (t-\overline{m})^2 dt \qquad (65)$$

We recall here that while m is function of  $(w_1, w_2)$ , m is not a function of them, because it is evaluated for fixed values of  $w_1$  and  $w_2$ , namely  $w_1 = \mu_1$ , i.e., the mean values of  $w_1$ . Now using Equation 63, we get:



$$+\sum_{i}\int_{-\infty}^{\infty}\left[\frac{\partial^{2}c}{\partial w_{i}^{2}} \overline{F} + 2\frac{\partial c}{\partial w_{i}}\frac{\partial \overline{F}}{\partial w_{i}} + \overline{c}\frac{\partial^{2}F}{\partial w_{i}^{2}}\right]\sigma_{i}^{2}(t-\overline{m})^{2}dt$$

$$= \frac{\overline{F} \ \overline{s}^{2} + \int_{-\infty_{i}}^{\infty} \sigma_{i}^{2} \left(\frac{\overline{\partial^{2}c}}{\partial w_{i}^{2}} \ \overline{F} + 2 \ \overline{\frac{\partial c}{\partial w_{i}}} \ \overline{\frac{\partial F}{\partial w_{i}}} + \overline{c} \ \overline{\frac{\partial^{2}F}{\partial w_{i}^{2}}}\right) (t-\overline{m})^{2} dt}{\overline{F} + \sum_{i} \ \overline{\frac{\partial^{2}F}{\partial w_{i}^{2}}} \sigma_{i}^{2}}$$

$$(66)$$

Using the following relations:

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$$\frac{\partial c}{\partial w_{i}} = \frac{\partial c}{\partial s} \frac{\partial s}{\partial w_{i}} + \frac{\partial c}{\partial m} \frac{\partial m}{\partial w_{i}}$$
(67)

$$\frac{\partial c}{\partial s} = \left[\frac{(t-m)^2 - s^2}{s^3}\right] c \qquad (68)$$

$$\frac{\partial c}{\partial m} = -\frac{(t-m)}{s^2} c \qquad (69)$$

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we get:

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$$\frac{\partial c}{w_{i}} = \left[\frac{(t-m)^{2}-s^{2}}{s^{3}}\right] c \frac{\partial s}{\partial w_{i}} - \left[\frac{(t-m)}{s^{2}}\right] c \frac{\partial m}{\partial w_{i}}$$
(70)

and:

$$\frac{\partial^{2} c}{\partial w_{i}^{2}} = c \left[ \frac{(t-m)^{2}-s^{2}}{s^{3}} \frac{\partial s}{\partial w_{i}} + \frac{m-t}{s^{2}} \frac{\partial m}{\partial w_{i}} \right]^{2}$$

$$+ c \left[ \frac{(t-m)^{2}-s^{2}}{s^{3}} \frac{\partial^{2} s}{\partial w_{i}^{2}} + \frac{m-t}{s^{2}} \frac{\partial^{2} m}{\partial w_{i}^{2}} \right]$$

$$+ c \left[ \frac{(t-m)^{2}-s^{2}}{s^{3}} \frac{\partial^{2} s}{\partial w_{i}} + \frac{m-t}{s^{2}} \frac{\partial^{2} m}{\partial w_{i}^{2}} \right] (\frac{\partial s}{\partial w_{i}})^{2} + \frac{1}{s^{2}} (\frac{\partial m}{\partial w_{i}})^{2} \right] (71)$$

Substituting Equations 67 through 71 in Equation 66, and letting  $M_i$  represent the ith moment about the mean we get:

 $\overline{\mathbf{s}_{\mathrm{T}}^{2}} \left( \overline{\mathbf{F}} + \sum_{i} \frac{\overline{\partial^{2} \mathbf{F}}}{\partial \mathbf{w}_{i}^{2}} \sigma_{i}^{2} \right) = \overline{\mathbf{F}} \overline{\mathbf{s}}^{2} + \sum_{i} \sigma_{i}^{2} \left[ \left( \frac{\overline{\partial \mathbf{s}}}{\partial \mathbf{w}_{i}} \right)^{2} \right]$ 

$$\cdot \left(\bar{F} \frac{\overline{M_{6}}}{s^{6}} - 5\bar{F} \frac{\overline{M_{4}}}{s^{4}} + 2\bar{F} \frac{\overline{M_{2}}}{s^{2}}\right) + \left(\frac{\overline{\partial^{2} s}}{\partial w_{1}^{2}}\right) \left(\bar{F} \frac{\overline{M_{4}}}{s^{3}} - \bar{F} | \frac{\overline{M_{2}}}{s} \right)$$

$$+ \left(\frac{\overline{\partial m}}{\partial w_{i}}\right)^{2} \left(\overline{F} \frac{\overline{M_{4}}}{s} + \overline{F} \frac{\overline{M_{2}}}{s^{2}}\right) + 2 \frac{\overline{\partial s}}{\partial w_{i}} \frac{\overline{\partial F}}{\partial w_{i}} \left(\frac{\overline{M_{4}}}{s^{3}} - \frac{\overline{M_{2}}}{s}\right)$$

$$+ \frac{\overline{\partial^2 F}}{\partial w_i^2} \overline{M_2}$$

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as the odd moments of a Gaussian distribution are zero. Also, for a Gaussian distribution, we have:

(73)

(72)

(74)

(75)

 $M_4 = 3s^4$ 

 $M_{6} = 1.5s^{6}$ 

 $M_2 = s^2$ 

So, the final expression becomes:

$$\overline{\mathbf{s}_{\mathrm{T}}^{2}} \left( \overline{\mathbf{F}} + \sum_{i} \frac{\overline{\partial^{2} \mathbf{F}}}{\partial \mathbf{w}_{i}^{2}} \sigma_{i}^{2} \right) = \overline{\mathbf{F}} \overline{\mathbf{s}}^{2} + \sum_{i} \sigma_{i}^{2} \left[ 2\overline{\mathbf{F}} \left( \frac{\overline{\partial \mathbf{s}}}{\partial \mathbf{w}_{i}} \right)^{2} + 2\overline{\mathbf{F}} \overline{\mathbf{s}} \left( \frac{\overline{\partial^{2} \mathbf{s}}}{\partial \mathbf{w}_{i}} \right)^{2} + 4\overline{\mathbf{s}} \frac{\overline{\partial \mathbf{s}}}{\partial \mathbf{w}_{i}} \left( \frac{\overline{\partial \mathbf{F}}}{\partial \mathbf{w}_{i}} + \overline{\mathbf{s}}^{2} \frac{\overline{\partial^{2} \mathbf{F}}}{\partial \mathbf{w}_{i}^{2}} \right) \right]$$

$$(76)$$

To better understand Equation 76, we recall that the bar over a symbol indicates that the variable is to be evaluated for the (possibly hypothetical) mean OTC in a bundle, i.e. an OTC having the mean diameter and length. The variables m and s refer to a chromatographic peak. For Gaussian peaks,  $m = t_r$  and  $s = 0.425 w_h$ , where  $w_h$  is the peak width at half height. The symbols  $w_1$  and  $w_2$  are aliases for L and  $d_c$  that permit the equation to be written more compactly by using subscripts. The variances of L and  $d_c$  for the OTC in a bundle are  $\sigma_1^2$  and  $\sigma_2^2$ .

The development of this expression depended on the assumption of Gaussian distributions and the approximation of the functions F and cF by truncated Taylor series. This approximation should be appropriate in view of the narrow distributions that are desired for L and  $d_c$ . Equation 76 is a general expression of the effect of the variability of OTC parameters on the performance of a bundle of OTC and, as such, is a part of the solution to the second research problem listed in the Introduction.

#### CHAPTER 6

AN APPLICATION OF THE MODEL

6.1 Introduction

As Golay (1) observed, the difficulty in making a practical chromatographic column from a bundle of OTC lies in putting"... capillaries together in parallel which are like each other". There is no hope of making all of the OTC in a bundle exactly alike, but the variabilities of column parameters about their means may be measured and controlled to some degree. In the previous chapter there was derived a quantitative relation that gives the spreading of the coherent peak from a bundle as a function of the variances of the diameter and the length of the OTC in the bundle. There is no question that the width of a peak from a bundle of OTC is greater than the width of the peak from a single OTC in the bundle. The question to be answered is, "How much is the peak width increased by realizable variances of OTC diameter and length?" The purposes of the research reported in this chapter and to provide estimates of the coefficients in Equation 76 of Chapter 5 and give a rough, tentative answer to our question concerning the increase in peak width.

The variability of column diameter or length influences

the dispersion from a bundle in several ways. For example, consider two OTC that have equal lengths but slightly different diameters. During the dynamic coating process, the pressure differences across the two tubes are equal, so the coating solution is displaced more rapidly from the tube having the larger diameter. This results in a difference in the thicknesses of the films deposited on the tube walls. The difference in film thickness means that the capacity ratios for the two tubes may be different. The tube having the larger capacity ratio will give a greater retention time, other things being equal. The difference in column diameters also influences the retention times directly. The pressure drops across the columns are equal during the elution of a peak, so the velocity of the carrier gas is greater through the column having the larger diameter. Thus, the tube having the larger diameter will give a smaller retention time, other things being equal. Both of these influences on the retention times of the peaks from individual OTC's are potential causes of an increase in the width of the peak from the bundle of OTC. A difference in the diameters of two columns will also cause them to give peaks having different widths. This may be seen by considering the effects of two different capacity ratios and velocities in the Golay equation, Equation 33. Although all of the

effects of the variability of column diameter are conceptually separable, they are difficult to separate in practice. We will only attempt to estimate the net effect of parameter variability on dispersion of the peak from a bundle of OTC.

In Chapter 2 it was shown that the peak spreading caused by end effects is too large to permit accurate measurement of the peak spreading in individual columns. Consequently, the Golay equation has been used to estimate the effect of variation in diameter or length on the peak widths of individual OTC's. The estimates of  $s^2$  that are obtained this way are too small, and the effect of this will be discussed below.

The value of the partition coefficient  $\beta$  of n-heptane was obtained from the data of Table 2. For Columns A and B, respectively,  $\beta$  equals 474 and 528. Kwantes and Rijnders (38) report values of  $\beta$  for n-heptane-squalane of 144, 73.5, and 36.5° at temperatures of 80, 105, and 135°C, respectively. An extrapolation of these data to 20°C gives  $\beta \approx 500$  at that temperature, a value that agrees with the mean of 501 for columns A and B. Values of  $d_f$  were calculated using  $\beta = 501$  and

 $d_{f} = \frac{Kr_{c}}{2\beta}$ 

The coefficients for Equation 76 were estimated from

one experiment on the influence of column length and two experiments on the influence of column diameter. Bundles of three columns were used in each of the experiments. The bundles were coated by the "in parallel" process using the dynamic coating technique. The sample sizes that were used were calculated from Equation 42. The pressure differences across the columns were approximately 1.6 atm in all three experiments.

#### 6.2 Influence of Length

Heptane and methane peaks were eluted at 20<sup>o</sup>C from a column consisting of 3 parallel OTC that had different lengths, but the same diameter. The characteristics of the three OTC and the measurements made during this experiment are shown in Table 6 and Figure 33.

Because the tubes were coated in parallel, the coating velocities were different for each one. The different velocities should lead to different film thicknesses, but the differences in the values of  $d_f$  shown in Table 6 are not as large as one might expect on the basis of Kaiser's (9) results.

For estimates of the coefficients in Equation 76, one needs relations between L and m and between L and s, the standard deviation of the concentration peak from a single OTC. Although the reported peaks are skewed, it

### TABLE 6

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## Experimental Results for the Experiment on the Influence of Length

			· · ·
Column designation	Ľ,	L <sub>2</sub>	L <sub>3</sub>
L(cm)	∿450	∿870	∿1620
d <sub>c</sub> (μ) ′	249	249	249
c (% mass)	10	10	10
t <sub>m</sub> (s)	3.23	10.66	38.31
t <sub>r</sub> (s)	6.75	31.69	103.75
К	1.09	1.97	1.71
d <sub>f</sub> (μ)	0.14	0.25	0.21
	$\sim$		0

Table 6

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Variation of Retention Times of n-Heptane

and CH4 with Column Length


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is assumed that the peaks issuing from the column are approximately Gaussian and that  $m = t_r$ , the retention time of the maximum concentration. The experimental data for m were correlated using a second degree polynomial:

 $m(sec) = -7.691 + 1.798 \times 10^{-2} L(cm) + 3.137 \times 10^{-5} L^{2} (cm^{2})$  (77)

Values of s<sup>2</sup> were calculated using the Golay Equation (Equation 33), HETP = s<sup>2</sup>/L, and (1+K) s(cm)=u(cm/sec)s(sec) (Equation 88A from Chapter 1 of the Appendix). For use in the Golay Equation, the diffusivity of n-heptane in squalane at 20°C was estimated to be 3 x 10<sup>-5</sup> cm<sup>2</sup>/sec by the method of Wilke and Chang (39). The values of s were correlated by

 $s(sec) = -0.0600 + 2.26 \times 10^{-4} L(cm) + 1.75 \times 10^{-8} L^{2}(cm^{2}).$ (78)

## 6.3 Influence of Diameter

Heptane and methane were eluted at 20<sup>o</sup>C from a column consisting of 3 parallel OTC that had different diameters, but the same length. Two columns were used in separate experiments. The first column was prepared using a coating solution of 10 per cent squalane in acetone, the same concentration that was used in the experiment on the influence of length. The second column was preprared using 15 per cent squalane in acetone as a coating solution. This second experiment was not necessary, strictly speaking, because there is no way that the concentration of the coating solution can vary from one tube to another in the "in parallel" version of the dynamic coating process. Nevertheless, it gives additional information on the effect of diameter on coating thickness and, together with the other experiment, shows the interaction between diameter and the concentration of the coating solution. It is of interest for these reasons.

The results of the two experiments are shown in Figure 34 and Table 7. The fact that the two sets of values for the retention time of an enert,  $t_m$ , do not agree, indicates that the flow rates were not the same in the two experiments. This may have been caused by an accidental change in the splitter.

Kaiser (9) correlates film thickness with tube diameter, solute concentration, and velocity of coating solution for different solvents. He shows that there is a critical velocity that gives the smallest value of  $d_f$ for fixed values of  $c_s$  and  $d_c$ . For velocities greater than the critical velocity, he presents a correlation that has the form

TABLE 7

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Experimental Results for the Diameter Influence Experiment

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Column designation	ב <sup>ת</sup> .		D	2	D <sub>3</sub>	·
L(Cm)	∿450		∿450		∿450	
d <sub>c</sub> (μ)	281		180		- 108	
		I	(			
c (% mass) s	10	15	IQ	15	10	15
t <sub>m</sub> (s)	4.20	3.20	9.83	7.23	22.09	15.58
t <sub>r</sub> (s)	` <b>9</b> .20	19.46	14.28	30.98	35.87	47.10
ĸ	1.19	5.08	0.45	<b>3.28</b>	0.62	2.02
d <sub>f</sub> (µ)	0.17	0.17	0.040	0.30	0.033	0.11
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Variation of Retention Times for n-Heptane and  $CH_4$  with Column Diameter, for Two Concentrations of

Coating Solution

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$$d_{f} = \frac{c}{d_{c}} (a'u_{s} + b').$$
(79)

For each bundle of columns, the coating velocities,  $u_s$ , are proportional to  $d_c^2$ , so that the form of the relation between  $d_f$  and  $d_c$  for the columns in a bundle should be

$$d_f = a d_c + b/d_c \tag{80}$$

where a and b are empirical constants. The values of  $d_f$ reported in Table 7 for the 15 per cent solution agree reasonably well with this relation, but the values for the 10 per cent solution do not. The critical velocity undoubtedly depends on the viscosity of the coating solution, so one explanation for the non-linearity of the  $d_f$  values for the 10 per cent solution is that the coating velocity in the smallest tube was below the critical velocity.

The data for m and  $s^2$  were correlated in the same way as in the experiment on the effect of length

> m(sec) = 96.3 - 0.715  $d_c(\mu)$  + 1.44 x  $10^{-3} d_c^2(\mu^2)$  (81)

and

$$s(sec) = 0.855 - 7.01 \times 10^{-3} d_c(\mu) + 1.49 \times 10^{-5} d_c^2(\mu^2).$$
  
(82)

## 6.4 An Example

In order to determine the effect of the variabilities of column parameters on peak spreading, we must evaluate the coefficients in Equation 76. The coefficients involve first and second derivatives of the empirical functions of L and d<sub>c</sub> that were developed in the previous two sections. It is assumed that the functions are smooth enough to be approximated by second degree polynomials. The operation of differentiating discrete experimental data magnifies experimental errors, so the results are only semiquantitative. In spite of this, some useful qualitative conclusions may be drawn.

The derivation of Equation 76 in the previous chapter used Taylor series expansions of  $F(w_1, w_2)$  and  $c(t, w_1, w_2) F(w_1, w_2)$  about specific values of  $w_1$  and  $w_2$ , i.e. specific values of L and  $d_c$ . Extrapolation of the empirical equations should be avoided, and the evaluation of the functions at an experimental point is to be preferred. The functions have been expanded around L = 450 cm and  $d_c = 249\mu$  which corresponds to column  $L_1$  in the length experiment and falls between columns  $D_1$  and  $D_2$  in the

diameter experiment.

From Equation 4, we obtain

$$F = \frac{\pi (\Delta P) d_{C}^{4}}{128 \mu L}$$
(83)

Then, from Equations 77, 78, 81, 82, and 83 we get the following values for L = 450 cm and  $d_c = 249\mu$ :

-	L Series W <sub>l</sub> = L	D Series $w_2 = d_c$
m, sec	6.75	7.60
s, sec	0.045	0.035
F cm <sup>3</sup> /sec	0.178	0.178
ds/dw <sub>i</sub> , sec/cm	$2.4 \times 10^{-4}$	4.3
$\partial s/\partial w_{i}^{2}$ , sec/cm <sup>2</sup>	$3.5 \times 10^{-8}$	$3.0 \times 10^3$
dm/dw <sub>i</sub> , sec/cm	0.046	28
<pre>∂F/∂w<sub>i</sub>, cm<sup>2</sup>/sec</pre>	$-4.0 \times 10^{-4}$	29
$\partial^2 F / \partial w_i^2$ , cm/sec	$1.8 \times 10^{-6}$	• 3500

The values of m and s for the two experiments should coincide. The differences are an indication of the experimental error. One might expect the value of  $\partial m/\partial w_2$  to be negative, but the increase in film thickness appears to be more important than the increase in u for

-- 75

increasing d<sub>c</sub>. By substituting these tabulated values into Equation 76, we obtain:

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$$\mathbf{s}_{\mathrm{T}}^{2} = \frac{0.178 \,\overline{\mathbf{s}}^{2} + 0.015 \sigma_{1}^{2} + 630 \sigma_{2}^{2}}{0.178 + 1.8 \times 10^{-6} \sigma_{1}^{2} + 3500 \sigma_{2}^{2}}$$
(84)

where  $\sigma_1^2$  and  $\sigma_2^2$  have dimensions  $cm^2$  and  $s_T^2$  and  $\overline{s^2}$  have dimensions sec<sup>2</sup>.

What are reasonable values for  $\sigma_1^2$  and  $\sigma_2^2$ ? From Figure 18,  $\sigma_2^2 = 6 \times 10^{-8} \text{ cm}^2$ . Actually, this estimate is more applicable to the variability of the diameter along the length of a tube. The variance of the apparent diameter within a bundle of tubes would depend on control of the drawing conditions over a longer period of time. Nevertheless, we will take the value from Figure 18 as a first estimate of an attainable value of  $\sigma_2^2$ . For OTC that are only a few meters long, the measurement and control of length is relatively easy, so a value of  $\sigma_1^2 = 0.003 \text{ cm}^2$  should be attainable.

The estimates of  $\sigma_1^2$  and  $\sigma_2^2$  lead to the conclusion that the second and third terms in the denominator of Equation 84 are probably negligible. The coefficient of  $\sigma_2^2$  would have to be more than two orders of magnitude larger before it would affect this conclusion. Therefore, the relation between  $s_T^2$  and  $\overline{s}^2$  may be written as

$$s_{\rm T}^2 \simeq \overline{s^2} + 0.084\sigma_1^2 + 3500\sigma_2^2$$
 (85)

The estimates of attainable values of  $\sigma_1^2$  and  $\sigma_2^2$  indicate that for a bundle of OTC in which the mean values were L = 450 cm and  $d_c = 249\mu$ , one could have

$$s_{\rm T}^2 \simeq \overline{s^2} + 5 \, {\rm x10}^{-4}$$
. (86)

Then, if  $\bar{s} \approx 0.040$  sec,  $s_T \approx 0.046$  sec and  $s_T/s = 1.15$ . This ratio corresponds to an HETP for the bundle that is 32 per cent larger than the HETP for the "mean" column of the bundle.

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Ninety per cent of the contribution to the coefficient of  $\sigma_2^2$  and over 99 per cent of the contribution to the coefficient of  $\sigma_1^2$  come from terms containing only  $\overline{F}$  and  $\overline{\partial m/\partial w_i}$ . The other terms involve the estimates of  $\overline{s^2}$  that were obtained from the Golay Equation. There are several reasons why these estimates of  $\overline{s^2}$  can be expected to be too small. For examples, non-uniformity in film thickness, interfacial transport resistance, and the curvature of the helical columns all contribute to an increase in  $\overline{s^2}$ . While the errors caused by estimating  $\overline{s^2}$  by the Golay Equation are significant, the terms involving  $\overline{s}$  and derivatives of  $\overline{s}$  in the coefficients

of  $\sigma_1^2$  and  $\sigma_2^2$  are relatively small. The major source of error in estimating  $s_T/\bar{s}$  is the error in  $\overline{\partial m}/\partial w_i$ , which comes from experimental errors in the measurement of m, errors in fitting the data by a polynomial, and the magnification of these errors by differentiation.

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In view of the uncertainty in the estimate of  $\partial m/\partial w_i$ , the true value of  $s_T/\bar{s}$  could easily be larger or smaller than 1.15. To the extent that  $\bar{s}$  has been underestimated by using the Golay Equation, the above estimate of  $s_T/\bar{s}$ is too large. For  $\bar{s} = 0.040$  sec, the sensitivity of the ratio  $s_T/\bar{s}$  to errors in the sum of the terms involving  $\sigma_1^2$  and  $\sigma_2^2$  in Equation 85 can be seen from the following comparison

$s_{\rm T}^2 - \overline{s^2}$ , $ {\rm sec}^2$		s <sub>T</sub> /s
$5 \times 10^{-4}$		1.15
$5 \times 10^{-3}$	t	2.0
$5 \times 10^{-2}$	e	5.7

Considering that possible underestimates of the terms involving  $\sigma_1^2$  and  $\sigma_2^2$  would be partially compensated by a very likely underestimate of  $\bar{s}$ , it seems likely that the ratio  $s_T/\bar{s}$  is less than 2. In this case, the ratio of the HETP of the bundle to the HETP of the "mean" OTC in the bundle would be less than 4. Columns consisting of such bundles of OTC would be suitable for preparative and some analytical applications. Whether columns for more demanding applications can be prepared from bundles of OTC remains an open question.

## 6.5 Conclusions

The conclusionspresented here are conditional on several assumptions and limitations:

- 1. The peaks are approximately Gaussian.
- 2. The distributions of L and d<sub>c</sub> in a bundle are approximately Gaussian and narrow.
- 3. The experimental values of m and the calculated values of  $\partial m/\partial L$  and  $\partial m/\partial d_c$  are approximately correct.
- 4. The estimates of realizable values of  $\sigma_2^2$  and  $\sigma_1^2$  are approximately correct.
- 5. The conclusions are limited to bundles for which the mean values are near L = 450 cm,  $d_c = 249\mu$ ,  $d_f = 0.15\mu$  and F = 0.18 cm<sup>3</sup>/sec.

With these reservations and limitations, we conclude that it is possible to prepare bundles of OTC for which the HETP will be less than four times the HETP of the mean column in the bundle. Furthermore, the control of end effects in instruments in which OTC bundles are used will be almost as important as the control of end effects for single OTC.

Given the conditions and limitations stated above Equation 84 provides a solution to the second research problem listed in the Introduction.

## CHAPTER 7

### SUMMARY

7.1 Conclusions

The preparation of bundles of OTC is reported by the static coating technique and by the dynamic coating technique, but coherent peaks were only obtained with this last method. Because of the presence of strong end effects, these coherent peaks do not mean that the response from each individual column of the bundle is similar enough to be analytically useful, so that the analytical usefulness of the bundles of OTC remains an open problem.

A mathematical model was developed, in which the broadening of the bundle peak is related to the broadening of the single OTC peak and the variances of the geometric characterics of the columns. This model can be a useful tool for the prediction of bundle performance, or for the prediction of construction requirements in order to meet a specified performance.

An application of the model was done, for a short range of lengths and diameters using the dynamic coating technique coupled with the "in-parallel" bundle preparation. This exemplifies how the model can be applied to any particular case and suggests that the increase in HETP

due to the variability of column length and diameter would not be excessive.

7.2 Original Contributions

OTC bundles were prepared that satisfied the first criterion of usefulness: they produced coherent peaks. The coherence of the peaks may have been helped by the end effects associated with the GC instrument.

A process for preparing bundles of OTC columns was developed.

A mathematical model was developed to relate the HETP (or peak width) of a bundle of OTC to the HETP of the "mean" OTC of the bundle and the variances of the length and diameter of the OTC in the bundle. An example was given showing how this model would be applied. The conditional conclusion was reached from this example that the HETP from a bundle would be less than four times the HETP of the "mean" OTC of the bundle.

7.3 Suggestions for Further Research

The conditional conclusion that the HETP from a bundle would be less than four times larger than the HETP of the "mean" column of the bundle should be tested experimentally. The apparatus that is used for this must have much smaller end effects than the apparatus used in this project. It would be interesting to produce and demonstrate and OTC bundle that would be useful as an analytical GC column.

Bundles of short, smaller diameter OTC could have interesting applications. It is suggested that the limitations on the production and use of compact bundles of OTC be explored.

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## INTRODUCTION

In the Appendix, the more important derivations, not provided in the text, will be made. Special attention is given to the diffusion in OTC, and to the flow through OTC.

The results of two sub-investigations that did not contribute to the main research objectives are also reported here. The first of these investigations was a study of flow in uncoated columns and the second was a study of the characteristics of an OTC bundle prepared by the static coating technique.

## APPENDIX

## CHAPTER 1

## Theory of Open Tubular Columns

1.1 Flow in OTC

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In cylindrical coordinates, the components of Navier-Stokes Equation are: <sup>(31)</sup>

r-component:

$$\rho \left( \frac{\partial u_{r}}{\partial t} + u_{r} \frac{\partial u_{r}}{\partial r} + \frac{u_{\theta}}{r} \frac{\partial u_{r}}{\partial \theta} - \frac{u_{\theta}^{2}}{r} + u_{z} \frac{\partial u_{z}}{\partial z} \right) = -\frac{\partial p}{\partial r} - \left( \frac{1}{r} \frac{\partial}{\partial r} (r\zeta_{rz}) + \frac{1}{r} \frac{\partial \zeta_{r\theta}}{\partial \theta} - \frac{\zeta_{\theta\theta}}{r} + \frac{\partial \zeta_{rz}}{\partial z} \right) + \rho_{q_{r}}$$

$$(1A)$$

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z-component:

$$\rho \left( \frac{\partial u_{z}}{\partial t} + u_{r} \frac{\partial u_{z}}{\partial r} + \frac{u_{\theta}}{r} \frac{\partial u_{z}}{\partial \theta} + u_{z} \frac{\partial u_{z}}{\partial z} \right) = -\frac{\partial P}{\partial z} - \frac{\partial P}{\partial z} - \frac{\partial L}{\partial r} \left( r\zeta_{rz} \right) + \frac{1}{r} \frac{\partial \zeta_{\theta z}}{\partial \theta} + \frac{\partial \zeta_{zz}}{\partial z} + \rho_{g_{z}}$$
(2A)  
$$\zeta_{rr} = -\mu \left[ 2\frac{\partial u_{r}}{\partial r} - \frac{2}{3} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( ru_{r} \right) + \frac{1}{r} \frac{\partial u_{\theta}}{\partial \theta} + \frac{\partial u_{z}}{\partial z} \right]$$
(3A)

$$\zeta_{\theta \theta} = -\mu \left[ 2 \left( \frac{1}{r} \frac{\partial^{u} \theta}{\partial \theta} + \frac{u_{r}}{r} \right) - \frac{2}{3} \left( \frac{1}{r} \frac{\partial}{\partial r} (r u_{r}) + \frac{1}{r} \frac{\partial^{u} \theta}{\partial \theta} + \frac{\partial^{u} z}{\partial z} \right) \right]$$
(4A)

$$\zeta_{zz} = -\mu \left[ 2 \frac{\partial^{u} z}{\partial z} - \frac{2}{3} \left[ \frac{1}{r} \frac{\partial}{\partial r} (r u_{r}) + \frac{1}{r} \frac{\partial^{u} \theta}{\partial \theta} + \frac{\partial^{u} z}{\partial z} \right] \right]$$
(5A)

$$\zeta_{\mathbf{r}\theta} = \zeta_{\theta\mathbf{r}} = -\mu \left[\mathbf{r} \frac{\partial}{\partial \mathbf{r}} (\frac{\mathbf{u}_{\theta}}{\mathbf{r}}) + \frac{1}{\mathbf{r}} \frac{\partial^{\mathbf{u}} \mathbf{r}}{\partial \theta}\right]$$
(6A)

$$\zeta_{\Theta z} = \zeta_{z \theta} = -\mu \left( \frac{\partial^{\mathbf{u}} \theta}{\partial z} + \frac{1}{r} \frac{\partial^{\mathbf{u}} z}{\partial \theta} \right)$$
(7A)

$$\zeta_{zr} = \zeta_{rz} = -\mu \left( \frac{\partial^{u} z}{\partial r} + \frac{\partial^{u} r}{\partial z} \right)_{\mu}$$
 (8A)

The following assumptions are made: -two dimensional axisymmetric flow; -steady state flow; -no body forces.

These equations reduce to:

r-component:

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$$\frac{\partial p}{\partial r} = -\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r,\frac{2}{3}\mu,\frac{\partial^{u}z}{\partial z}\right) - \frac{1}{r}\frac{2}{3}\mu,\frac{\partial^{u}z}{\partial z} + \frac{\partial^{u}z}{\partial z}\left(-\mu,\frac{\partial^{u}z}{\partial r}\right)\right] \quad (9A)$$

z-component:

$${}^{\rho} u_{z} \frac{\partial^{u} z}{\partial z} = - \frac{\partial p}{\partial z} - \left[ \frac{1}{r} \frac{\partial}{\partial r} (-\mu r \frac{\partial^{u} z}{\partial r}) + \frac{\partial}{\partial z} (\frac{2}{3} \mu \frac{\partial^{u} z}{\partial z}) \right]$$
(10A)

Developing, they become:

$$\frac{\partial p}{\partial r} = \frac{1}{3} \mu \frac{\partial^2 u_z}{\partial z \partial r}$$
(11A)

$$\frac{\partial \mathbf{p}}{\partial z} = -\rho \mathbf{u}_{z} \frac{\partial^{\mathbf{u}_{z}}}{\partial z} + \frac{4}{3} \mu \frac{\partial^{2} \mathbf{u}_{z}}{\partial z^{2}} + \mu/r \frac{\partial^{\mathbf{u}_{z}}}{\partial r} + \mu \frac{\partial^{2} \mathbf{u}_{z}}{\partial r^{2}}$$
(12A)

For a small radius,  $\frac{\partial p}{\partial r} = 0$ . The Continuity Equation is:

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \rho u = 0 \tag{13A}$$

and for steady-state, div  $\rho u=0$ 

$$\overline{\nabla} \cdot (\rho \overline{u}) = \overline{u} \cdot \overline{\nabla} \rho + \rho \overline{\nabla} \cdot \overline{u} = 0$$
 (14A)

$$\overline{\nabla} \cdot \overline{u} = \frac{1}{r} \frac{\partial}{\partial r} (ru_r) + \frac{1}{r} \frac{\partial^{u} \theta}{\partial \theta} + \frac{\partial^{u} z}{\partial z} = \frac{\partial^{u} z}{\partial z}$$
 (15A)

so,

$$\nabla \overline{\nabla} \cdot \overline{u} = \rho \frac{\partial^{u} z}{\partial z}$$
(16A)

$$\bar{\nabla}_{\rho} = \frac{\partial \rho}{\partial r} \bar{g}_{r} + \frac{\partial \rho}{\partial z} \bar{g}_{z}$$
(17A)

where  $\overline{g}_i$  is the unit vector in direction i.

Because of the assumption that  $\frac{\partial p}{\partial r} = 0$ , it follows that  $\frac{\partial p}{\partial r} = 0$ , and the Continuity Equation becomes:

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$$\rho \frac{\partial^{\mathbf{u}} z}{\partial z} + \mathbf{u}_{\mathbf{z}} \frac{\partial \rho}{\partial z} = 0$$
(18A)

Substituting into the Equation of Motion (Equation 12A), we have:

$$\frac{\partial p}{\partial z} = u_z^2 \frac{\partial \rho}{\partial z} + \frac{4}{3} \mu \frac{\partial^2 u_z}{\partial z^2} + \mu r \frac{\partial^2 u_z}{\partial r} + \mu \frac{\partial^2 u_z}{\partial r^2}$$
(19A)

To solve this equation, a step approach is considered. First, we assume the velocity  $u_z$  to be just a function of the radial position. So, the equation reduces to:

$$\frac{\partial p}{\partial z} = \mu/r \frac{\partial^2 u}{\partial r} + \mu \frac{\partial^2 u}{\partial r^2}$$
(20A)

which is the Hagen-Poiseuille Equation. Integrating<sup>(32)</sup>, the solution is:

$$\mu_{z} = \frac{1}{\mu} \frac{dp}{dz} \frac{r^{2}}{4} + A \ln r + B$$
 (21A)

For r=0, u<sub>z</sub> must be finite . A=0

For r=r<sub>c</sub>, u<sub>z</sub> must be zero . B =  $-\frac{1}{\mu} \frac{dp}{dz} \frac{r_c^2}{4}$ .

So, the solution becomes:

$$u_z = \frac{P_i^{-P_o}}{4\mu L} (r_c^2 - r^2)$$
 (22A)

Averaging over the cross-section, we get  $\bar{u}\colon$ 

$$\bar{u} = \frac{\int_{0}^{2\pi} \int_{0}^{r_{c}} u_{z} r dr d\theta}{\int_{0}^{2\pi} \int_{0}^{r_{c}} r_{c}} = \frac{P_{i} - P_{o}}{2\mu L} \left(\frac{r_{c}^{2}}{4}\right) \quad (23A)$$

Some correction must be applied for compressibility. The most common way is by applying the compressibility correction factor j, and another way is the correction based on kinetic-energy conversion. (10)

# By the definition of retention time: $t_{r} = \int_{0}^{V_{r}^{0}} \frac{dV}{F}$ (24A)

so,

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$$t_{r}F_{o} = L(A+D\beta') \cdot \left[\frac{2}{3} \frac{\binom{r}{p}}{\binom{p}{p} - 1}\right] as PF = P_{o}F_{o}$$
(25A)

But  $t_r F_o = V_r^o$  (corrected retention volume).

(26A)

Then,

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$$v_R^o = jv_r$$

where

$$j = \frac{3}{2} \frac{\left(\frac{P_{i}}{P_{o}}\right)^{2} - 1}{\left(\frac{P_{i}}{P_{o}}\right)^{3} - 1}$$
(27A)

From here, it immediately follows that:

$$\overline{u} = ju_{0}$$
 (28A)

where  $u_0$  is the outlet linear velocity.

To get the pressure gradient along the column length, we introduce the permeability of the column, as:

$$B_{0} = \frac{r_{c}^{2}}{8}$$
 (29A)

So,

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$$\Delta p = p_i - p_o = \frac{\mu L \bar{u}}{B_o}$$
(30A)

From here, considering  $\overline{u}$  to be function of z, we have:

$$\frac{dp}{dz} = -\mu \frac{u}{B_0} = -\mu \frac{F}{\pi r_c^2 B_0} = -\mu \frac{P_0 F_0}{P B_0 \pi r_c^2}$$
(31A)

As the viscosity  $(\mu)$  does not depend on P, we have:

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$$\frac{dp}{dz} = \frac{k_1}{p}$$
(32A)

where

$$k_1 = \frac{-\mu P_0 F_0}{B_0 \pi r_c^2}$$
(33A)

Integrating we get:

$$z = \frac{p^2}{2k_1} + k_2$$
 (34A)

The boundary conditions are:

 $z = 0, P = P_i \text{ and } z = L, P = P_o$  $K_1 = \frac{P_o^2 - P_i^2}{2L}$  (35A)

and

so,

$$K_{2} = \frac{-P_{i}^{2}L}{P_{0}^{2}-P_{i}^{2}}$$
(36A)

The final relation becomes:

$$\frac{z}{L} = \frac{P_{i}^{2} - P_{i}^{2}}{P_{i}^{2} - P_{o}^{2}}$$
(37A)

This gradient agrees for the case of expansion, as it becomes steeper towards the end of the column, in order to accomodate the higher velocities encountered there. The kinetic energy correction is based on the fact that:

$$\Delta p = (\Delta p) \text{ frictional loss}^{+ (\Delta p)} \text{ kinetic energy}$$
(38A)

When a gas flows from a reservoir to a tube, its potential energy is partially consumed to overcome friction, and the other part is transformed into kinetic energy associated with the acceleration of the gas particles, as expansion is occuring. Let  $\Delta p_1$  be the additional pressure drop due to the conversion of kinetic energy. The potential energy corresponding to  $\Delta p_1$  is obtained by multiplying it by the volume flow rate. The kinetic energy of the gas discharged at the outlet of the tube is:

K.E. = 
$$\int_{0}^{r_{c}} \frac{u^{3}}{2\pi\rho} \frac{u^{3}}{2} r dr = \Delta p_{1} \overline{u} \pi r_{c}^{2}$$
(39A)

From Equations 22A and 23A,

So,

$$u = u_{max} \frac{r_c^2 - r^2}{(r_c^2)} = 2\overline{u} \frac{r_c^2 - r^2}{(r_c^2)}$$

 $\frac{1}{2} \frac{2\pi u^3}{2} \rho r dr = \pi \rho \bar{u}^3 r_c^2 = \Delta P_1 \bar{u} \pi r_c^2$ 

 $\Delta P_1 = \rho \bar{u}^2$ 

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(40A)

(41A)

Then,

$$\Delta P = P_{i} - P_{o} = \frac{8\mu \bar{u}L}{r_{c}^{2}} + 2\left(\frac{\rho \bar{u}^{2}}{2}\right) + (42A)$$

while experimentally, <sup>(10)</sup> a better correction was observed to be:

$$\Delta P = \frac{8\mu \bar{u}L}{r_{c}^{2}} + 2.2 \quad (\frac{\rho \bar{u}^{2}}{2})$$
(43A)

This pressure distribution is sketched in Fig. 1A.

 $P_d$  is the dynamic pressure,  $P_s$  is the static pressure and  $P_+$  is the total pressure (i.e.,  $P_d + P_s$ ).

From a to i, the gas is accelerated to a velocity  $u_{inlet}$ . The  $P_d$  is increased by  $(\frac{\rho u}{2})$ , while  $P_s$  drops by the same amount. In this section, the total pressure remains constant, and the friction is neglected because of the large cross-section of the tube from which the gas flows into the capillary. At the instant the gas enters the column, the velocity profile is not yet parabolic, but the kinetic energy is  $\rho \frac{\bar{u}^2}{2}$ . To obtain the parabolic profile,  $P_d$  must increase by this amount, while  $P_s$  decreases by the same amount. Now, the internal friction is appreciable, and P drops by y. This means that the pressure gradient measured in the column is higher than the predicted by Hagen-Poiseuille, by the amount  $(\rho \bar{u}^2 + y)$ , i.e., by  $m^* \rho \bar{u}^2$ , where  $m^*$  is usually 1.2.

FIGURE 1A

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Pressure Gradient Along Column Length (Schematic)



1.2 Transfer of Mass in Open Tubular Columns

The first order conservation equation (De Vault Equation) is here derived for a single absorbed component.

Let c be the molar concentration (per volume) in the gas phase, and q be the molar concentration (per mass) in the liquid-phase. A mass balance across dz gives:

$$\frac{\partial C}{\partial z} dz = \Delta C$$
 (44A)

Then, AcdV is the variation in moles of solute, in the gas-phase, across dz. Accounting now for the liquid-phase, another mass-balance (total) gives:

$$\frac{\partial c}{\partial z} dz dV = \frac{\partial c}{\partial V} A dz dV - \frac{\partial q}{\partial V} D dz dV \qquad (45A)$$

where A is the volume of gas-phase per unit length of column, and D is the mass of liquid-phase, also per unit length of column.

So, wè have:

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$$-\frac{\partial c}{\partial z} = A \frac{\partial c}{\partial V} + D \frac{\partial q}{\partial V}$$

which is DeVault Equation.

For a linear isotherm:

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(46A)

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(50A)

$$q = \beta' c$$
 (47A)

where  $\beta$  is the partition coefficient. So, Equation (46) becomes:

 $\frac{\partial C}{\partial z} + (A D \beta') \frac{\partial C}{\partial V} = 0$  (48A)

For an impulse input, i.e., for  $\delta(y) = 0$  and  $\delta(y) = 0$ 

 $\delta(y)$ dy=l, the general solution for DeVault equation is:

$$C = \delta \left[ V - z \quad (A + D\beta') \right]$$
(49A)

Considering infinitesimally small concentration, i.e., c+0, we have:

 $V = z (A+D\beta')$ 

and putting z=L, we arrive at:

$$V_{R}^{O} = L(A+D\beta')$$
 (51A)

1.3 Factors Affécting the Broadening of Peaks in GLC, using OTC

a) Effect of the Input Distribution

If we consider an input distribution, at the beginning
of the elution, the zone of vapor (a zone is a region in the column where the solute is present in detectable concentrations) takes the form of an infinitely narrow band. This ideality is not attained, as both the vapor and the sample injector cavity occupy a finite volume. The effect of this on  $V_{\rm p}^{\rm O}$  may be small, but noticeable.<sup>(7)</sup> Two extreme inputs may be considered. (33) In the first one, the vapor goes into the column as a compact plug of finite volume. within which the vapor concentration is uniform. The result is the superimposition of a Gaussian distribution and the plug of vapor, and the final distribution has the maximum point at the mid point of the input. The shape of the peak is both a function of the column operation and of the vapor introduction. In the case of linear isotherm and ideal chromatography, whatever the input distribution of a component, the output distribution will have exactly the same shape.<sup>(1)</sup> In the practical case of non-ideal linear. GC, every input distribution tends to be broadened out into a distribution that approaches the Gaussian distribution.

In the case of a plug type input, if the retention time is measured from the instant that the front of the plug enters the column, the retention volume measured to the maximum of the output distribution will be greater than the retention volume corresponding to a  $\delta$  function, by half of the width of the plug (measured in volume units).

$$V_{R}^{O} = V_{R \text{ correct}}^{O} + \frac{1}{2} V_{\text{plug}}$$
 (52A)

In the second extreme case of an input distribution, complete mixing occurs in the sample injector cavity, and the input will be a Poisson type distribution.

The real cases seem to lie between these two extremes, and the best practical input is a plug of pure vapor that enters the column undiluted by the carrier gas. In the introduction of liquid samples, below their boiling point, the vapor is necessarily diluted with carrier gas, and there is a period in which the sample is evaporating, and thus, the input distribution occupies a larger volume, particularly for the less volatile components, than, in the case of pure vapor injection. The width of this input can be described by  $v_{plug}$ , and retention volumes (measured) increase with the sample size.

## b) Effect of Finite Vapor Concentration

The DeVault Equation was derived for c+0, which is not the real case. A finite vapor concentration will produce an increase in  $V_R^0$  with a decrease in the sample size. At each point in the column, since there is a finite vapor pressure of solute, the partial pressure of carrier gas is less than for the case of c+0. This means that the carrier gas velocity is greater, where there is more vapor, in order to maintain the fixed mass flow rate along the column,

and this produces asymmetry in the peak, as the center of the zone (where c is larger) moves more rapidly than the edges. The increased flow rate inside a zone of vapor may be calculated as follows:

Let c' be the mole fraction vapor in the gas-phase. Then:

 $\mathbf{F} = \boldsymbol{\phi}(\mathbf{c}') \tag{53A}$ 

$$\frac{F(c')}{F(c'=0)} = \frac{1+K}{1+K(1-c')}$$
(54)

Let's assume now that  $c'_{max}^2$  is proportional to  $\frac{1}{z}$  (this is proved later), and let  $c'_{max}$  be the particular value of  $c'_{max}$  as the peak emerges from the column, i.e., for z=L.

$$C'_{max} = C'_{R_{max}} \left(\frac{L}{z}\right)^{\frac{1}{2}}$$
(55A)

By Equation (24A), we have:

$$t_{r} = (A+D\beta') \int_{0}^{L} \frac{Pd_{z}}{F_{0}P_{0}}$$
(56A)

But

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$$\frac{PF(z)}{P_{O}F_{O}} = \frac{1}{2}$$

(57A)

$$t_{R}^{*} = (A+D\beta') \int_{O}^{L} \frac{1}{F(z)} d_{z}$$
(58A)

Now

$$\frac{F(c')}{F(c'=0)} = \frac{1+K}{1+K \left[1-C'_{R_{max}}(\frac{L}{z})^{\frac{1}{2}}\right]}$$
(59A)

$$F(c') = \frac{(1+K)F(c'=0)}{1+K\left[1-C'_{R_{max}}\left(\frac{L}{z}\right)^{\frac{1}{2}}\right]},$$
 (60A)

So, we get:  

$$t_{R}^{*} = \frac{A+D\beta'}{F(c'=0)} \int_{0}^{L} \frac{1+K \cdot \left[1-C_{R_{max}}^{*} \left(\frac{L}{z}\right)^{1/2}\right] dz}{1+K} = \frac{L(A+D\beta')}{F(c'=0)} (1-2c_{R_{max}}^{*} \frac{K}{K+1})$$
(61A)

Finally, we reach:

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$$t_{r}^{*} = t_{r} (1 - 2C_{R_{max}}^{*} \frac{K}{1 + K})$$
 (62A)

A consequence of the finite vapor concentration is the viscosity of the peak. When the flow through the column is controlled by maintaining a  $\Delta P$  constant, the viscosity

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of the peak perturbs the flow rate in' proportion to the sample size, and usually these perturbations will appear in plots of  $F/F_0$  against z/L. The pertubations are expressed as:

$$\frac{\Delta F}{F} = -(\frac{X+22.4M}{V_R})W$$
 (63A)

where w is the weight of vapor retained in the column, and  $X = \frac{1}{\mu} \left( \frac{\partial \mu}{\partial C} \right)$  is the concentration coefficient of viscosity of vapor in the carrier gas. Usually, this error is less than 1%, and decreases with decrease in the sample size.

## c) Column Performance

In the text, the column performance comes expressed as the number of theoretical plates. A derivation of this concept will be given here, and thus justification of n as being regarded as the column performance indicator. The diffusion in OTC will also be examined.

The concept of column performance lies in the comparison of the width of the peaks with their retention parameter (volume, distance or time). The plate theory described in <sup>(7)</sup> will here be given.

## c.l) Plate Theory

Here, the column is divided into equilibrium zones, which are the theoretical plates. Although the HETP does not have the same meaning as for distillation, it is defined in the same way:

$$HETP = \frac{L}{n}$$
(64A)

The way in which the vapor is transferred by each incremental  $\delta V$ , will determine the way by which it is distributed along the column.

Let: <sup>*b*</sup> H = HETP

a = cross-sectional area occupied by gas-phase

- b = cross-sectional area occupied by liquid-phase
- $\beta$  = dimensionless partition coefficient =  $\beta' \rho_s$ at column temperature.

 $\delta V$  = incremental volume of carrier gas.

The weight of vapor, in the gas-phase, in one plate, is Hac, and its concentration in the stationary phase is  $\beta c$ . The weight of solute in one plate, in the stationary phase, is thus Hb $\beta c$ . So, the total weight of solute, per plate, will be Hc(a+ $\beta$ b). The passage of  $\delta V$  will remove from the plate the mass  $c\delta V$ . So, the proportion of vapor removed per plate (p) is:

$$P = \frac{\delta V}{H(a+\beta b)}$$
(65A)

but this doesn't take into account the vapor moved in from previous plates. Now, we make the assumptions that initially, all vapor was in the first plate, and that at time t, n incremental  $\delta V$  have eluted. By combinatorial analysis, the amount in plate r after n passages will be:  $\frac{n!}{r!(n-r)!} p^r(1-p)^{n-r}$ 

The mass distribution of vapor among plates, after the passage of  $n\delta V$  is:

$$w(n,r) = \frac{n!}{r!(n-r)!} p^{r} (1-p)^{n-r}$$
 (66A)

This is a binomial distribution, and as  $w \propto c$ , it is the equation of the peak in the column, as a function of n and r:

For this type of distribution, the mean is:

 $\bar{r} = np$  (67A)

and the variance is:

 $s^2 = np(1-p)$ 

 $\overline{r} = \frac{n\delta V}{H(a+\beta b)}$ 

(68A)

Actually, w(n,r) is the probability of success, in each trial. The width in a binomial distribution, increases as  $\sqrt{n}$ . So, taking into account Equations 65A and 67A, we get:

(69A)

which is the plate that bissects the area of the peak. Considering perfect symmetry this plate will be where  $c=c_{max}$ . As  $n\delta V=V$ , we get:

$$\overline{r} = \frac{V}{H(a+\beta b)}$$
(70A)

But TH is z, and so:

$$V = z(a+b\beta) \cdot V_R^O = L(a+b\beta)$$
(71A)

which is the same solution resulting from DeVault Equation (51A), with a=A and b $\beta$ =D $\beta$ '. As the variance s<sup>2</sup> increases the extent to which the distribution spreads from the mean, it is an indicator of the broadening. Usually, p is small ... (1-p) $\sim$ 1.

$$s_r^2 = \frac{n\delta V}{H(a+\beta b)} (1-p) \sqrt{\frac{V}{H(a+b\beta)}} = \bar{r}$$
(72A)

0

When  $V = V_R^O$ 

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 $s_r^2 = \frac{L(a+b\beta)}{H(a+b\beta)} = \frac{L}{H}$ . But  $\frac{L}{H} = n$ 

 $s_r^2 = n$ 

(73A)

$$\frac{\bar{r}^2}{s_r^2} = \frac{(V_R^0)^2 {}^{2} {}^{H^2} (a+b\beta)^2}{L/H} = \frac{L^2/H^2}{L/H} = \frac{L}{H} = n$$
(74A)

Usually, volumes or times are employed, and not distances. Multiplying Equation (74A) by

$$\frac{H^2(a+b\beta)^2}{H^2(a+b\beta)^2}$$

we get:

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$$(75A)^{2} = V_{R}^{0}$$
 (75A)

$$s_{r}^{2}H^{2}(a+b\beta)^{2} = s_{v}^{2}$$
 (76A)

So, again we get:

$$\frac{V_{R}^{O2}}{\frac{R}{2}} = n$$
(77A)

which in fact confirms that n is the appropriate indicator for column performance.

From the plate theory we can predict the peak shape:

In the case where  $\bar{r}$  is so large that  $\frac{1}{\bar{r}} \sim 0$ , which seems particularly true for OTC, as  $n \rightarrow \infty$ , the binomial distribution w(n,r) will approach a Gaussian distribution.<sup>(34)</sup>

(82A)

So, as  $n + \infty$ , we get:

$$w(r) = \frac{1}{s_r \sqrt{2\pi}} \exp \frac{-(r-\bar{r})^2}{2s_r^2}$$
 (78A)

But p must be small enough so that  $\bar{r}=np$  is finite as  $n \rightarrow \infty$ . Here, the quantity  $\frac{1}{s}\sqrt{2\pi}$  is a normalized quantity, so as to have the area of unity. Unnormalizing, for the concentration of vapor in the gas-phase, we get:

$$c(r) = \frac{w}{s_r \sqrt{2\pi}} \exp \frac{-(r-\bar{r})^2}{2s_r^2}, \text{ in } (\frac{\text{mass}}{\text{plate}})$$
(79A)

and

$$c(z) = \frac{w}{s_z \sqrt{2\pi}} \exp \frac{-(z-\overline{z})^2}{2s_z^2}, \text{ in } (\frac{\text{mass}}{\text{length}}) \quad (80A)$$

Because of symmetry of the peak, we can turn this immediately into volume units:

$$c(v) = \frac{w}{s_v \sqrt{2\pi}} \exp \frac{-(v-\overline{v})^2}{2s_v^2}, \text{ in } (\frac{\text{mass}}{\text{volume}}) \quad (81A)$$

We saw that  $c=c_{max}$  occurred at r=r. So,  $c_{max} = \frac{1}{s_v\sqrt{2\pi}}$ , assuming w=1. But  $s_v^2$  is proportional to V (Equation 72A), and thus:

 $c_{\max}^2 = \frac{1}{2}$ 

and the assumption we made before is now justified.

c.2) Broadening Factors and Column Variables

(a) Here, the ideal column will be taken as standard. The ideal column resolves in infinitesimal time, two vapors of relative retentions (i.e.,  $K_i/K_j$ ) infinitesimally close to unity, with a perfect resolution. It is obvious that real columns differ from the ideal column, as the zones of vapor will broaden during elution. The broadening factors add independent variances to an instantaneously introduced zone of sample, and they may be combined by the rule that applies in the addition of effects of independent sources of random error, <sup>(7)</sup> upon a distribution, i.e.,  $s_{total}^2 = \sum_{i} s_i^2$ . This approach fails when factors are interdependent, but on OTC, with linear isotherms, there are no such factors.

From Equation (71A), it follows that:,

 $s = (a+b\beta) s_z$ 

Equation (25A) may be written as:

$$t_{\rm p}F_{\rm j} = L(a+b\beta)$$

But we saw that  $F_0^{j=F}$ , where F is the volumetric flow rate corrected for the pressure gradient, but not accounting measurements from a bubble flowmeter. So,

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(83A)

(84A)

Equation (84A) is written as:

$$t_{p}F = L(a+b\beta)$$
 (85A)

and

$$F_{s_t} = (a+b\beta)_{s_z} = s_v \qquad (86A)$$

Now,  $a+b\beta=a(1+\frac{b}{a}\beta)=a(1+\beta/\gamma)$ , from Equation 20 of the text. But we also saw that  $\beta/\gamma=K$  (Equation 21 of text), and so:

$$Fs_{t} = a(1+k)s_{z} = uas_{t}$$
(87A)

From here, the following relation holds:

 $(1+k)s_{z}=\bar{u}s_{t}$ (88A)

But  $H = \frac{L}{n} = \frac{s_z^2}{z}$   $\therefore$   $s_z^2$  is proportional to H, and this signifies that each broadening effect adds something to HETP. Usually, the broadening of a peak is measured by the standard deviation s, rather than by  $s^2$ . As  $\sum_{i=1}^{n} (\sum_{i=1}^{n} \sum_{i=1}^{2} \sum_{i=1}^{1} \sum_{i=1}^{2} \sum_{i=1$ 

The different kinds of diffusion taken place in OTC, each one contributing to the total variance, are now going to be seen in detail.

b) Longitudinal Diffusion in the Gas-Phase From Fick's second law of diffusion, we get the particular solution given by:

$$C = \frac{m}{2\sqrt{\pi Dt}} \exp\left(\frac{-L^2}{4Dt}\right)$$
(89A)

with a variance of:

1

$$s_t = \sqrt{2Dt}$$

$$s_t^2 = 2Dt$$

If we call  $\ell$  a length coordinate, with a zero value at the peak maxima, then the elution of the vapor will not affect the diffusion, at these particular values of  $\ell$ .

From Fick's second law, we have:

$$\frac{\partial c}{\partial t} = D_g \frac{\partial^2 c}{\partial \ell^2}$$

With an initial input distribution as a  $\delta$  function, we have:

$$t=0, c=\delta(0)$$
 . .  $c(\ell,t) = \frac{1}{2\sqrt{\pi D_g t}} \exp(\frac{-\ell^2}{4D_g t})$  (93A)

(90A)

(91A)

(92A)

c(l,t) is then a Gaussian function of l, with mean at l=0and  $s_t^2 = s_l^2 = 2 D_g t$ . The effect of longitudinal diffusion on the stationary phase, accounted for in a similar expression, is certainly negligible, as typical values of  $D_l$  are about four orders of magnitude lower than typical values of  $D_g$ .

But we saw that  $s_z^2/z$  is proportional to HETP, and using now Equation 88A, we get:

$$s_{z}^{2} = \frac{2 D_{g}t}{1+K} = \frac{2 D_{g}V}{F(1+K)} = 2 D_{g} \frac{z}{1}$$
 (94A)

so,

€

$$s\frac{2}{z}/z = 2 \frac{Dg}{1}$$

and this is the first term in Golay Equation. Changing to volume units, we have:

$$s_{v}^{2} = \frac{2 D_{g} a(a+b\beta)V}{F} = \overline{a}^{2}(1+K) 2 D_{g} \frac{V}{F}$$
 (96A)

This type of broadening is symmetrical, so that the retention parameters are not affected, as long as measurements are taken at l=0, i.e., at the peak maxima.

**140** 

(95A)

c) Non-instantaneous Equilibration of Vapor

c.1) In ideal chromatography, the partition coefficient is a constant, only dependent on temperature, and the distributions in each phase are similar in shape, and are not functions of time. In non-ideal linear GC, the partition coefficient is not constant. In the front profile, i.e., the one that first meets the stationary phase,  $q/c<\beta'$ , i.e.,  $c>c_{equilibrium}$ . This implies that undissolved vapor in the gas-phase moves further along than it would in the ideal case. At the rear profile,  $q/c>\beta'$ , and vapor remains in the stationary phase more than ideally.

This deviation may be described by imputing a perturbation on the isotherm, so that the isotherm equation becomes:

 $q = \beta' cf(t)$ , where f(t) + l as  $t + \infty$  (97A)

The quantitative treatment will depend on f(t). Assuming:

$$f(t) = 1+k'e^{-k''t}$$

 $\frac{dq}{dt} = k^* (\beta' c - q)$ 

we have:

$$\mathbf{q} = \beta' \mathbf{c} \left[ \mathbf{l} + \mathbf{k'} \exp(-\mathbf{k''} \mathbf{t}) \right]^{\prime}$$

and:

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(100A)

(99A)

(98A)

(101A)

(102A)

This is equivalent to a first-order reaction between phases, with a rate constant of  $k^*$ .

The boundary conditions are:

q(0,z) = 0

and

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 $\mathbf{c} (\mathbf{V}, \mathbf{0}) = \delta (\mathbf{V})$ 

Recalling Equation (46A) (DeVault Equation), the solution becomes: (7)

$$c(V,z) = \frac{k^{*}}{F} \left(\frac{D\beta' z}{V - Az}\right)^{\frac{1}{2}} I_{1} \left[2 \frac{k^{*}}{F} \left[D\beta' z \left(V - Az\right)\right]^{\frac{1}{2}}\right]$$

$$exp\left[-\frac{k^{*}}{F} \left(D\beta' z - Az + V\right)\right]$$

$$(103A)$$

neglecting entry effects (i.e., a term containing  $\delta V$ ).

$$q(V,z) = \frac{\beta'k^*}{F} I_0 \left[ 2 \frac{k^*}{F} \left[ D\beta'z(V-Az) \right]^{\frac{1}{2}} \right]$$

$$exp\left[ -\frac{k^*}{F} \left( D\beta'z - Az + V \right) \right] \qquad (104A)$$

 $I_1$  and  $I_0$  are the Bessel functions of first and zero order of the imaginary argument iz<sup>(35)</sup>. When this argument is large, i.e., for z>10, we have:

$$[n(z) \sim \frac{\exp(z)}{(2\pi z)^{\frac{1}{2}}}$$

(105A)

So, Equation (103A) becomes:

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 $(D\beta'z - V-Az)^2$ 

To apply this expression to the actual chromatogram, we remember that for z=L, we have  $V=V_R^O$  (corrected retention volume). This gives:

 $c(V,z) \sim \frac{k^{\frac{1}{2}}}{(4\pi F)^{\frac{1}{2}}} \cdot \frac{(D\ddot{\beta} \cdot z)^{\frac{1}{4}}}{(V-Az)^{3/4}} \exp \left[ \frac{-k^{\star}}{F} \right]$ 

$$q(V) \sim \frac{k^{\frac{1}{2}}}{(4\pi F)^{\frac{1}{2}}} \cdot \frac{(V_R^0 - V_M)^{\frac{1}{2}}}{(V - V_M)^{3/4}} \exp \left[-\frac{k^*}{F}\right]$$

$$(\sqrt{v_{R}^{o}-v_{M}} - \sqrt{v-v_{M}})^{2}$$
 (107A)

Assuming the effective total width only a small fraction of its retention, which may be not true for the early peaks, we have  $V_R^O > V$ , and the following general relation holds:

$$(\sqrt{x} - \sqrt{x + \Delta x})^2 \gamma \frac{(\Delta x)^2}{4x}$$
 (108A)

Then, Equation (107A) will result in:

$$c(V) \sim \frac{k^{\frac{1}{2}}}{\left[4\pi F(V_{R}^{O}-V_{M})\right]^{\frac{1}{2}}} \exp\left[\frac{-k^{*}(V_{R}^{O}-V)^{2}}{4F(V_{R}^{O}-V_{M})}\right]$$
 (109A)

(106A)

But this is the expression for a Gaussian curve, with

 $s_{v}^{2} = \frac{2F(v_{R}^{0} - v_{M})}{k^{*}}$  (110A)

and

$$\bar{c} = v_R^0$$
 (111A)

So, the conclusion to be taken is that the result of a finite rate of mass-transfer is to broaden the  $\delta$  function input distribution, into an approximately Gaussian distribution, but with the same mean as before.

Converting  $s_v^2$  into distance units, we have:

$$s_z^2 = \frac{2K\bar{u}z}{(1+K)^2k^*}$$
 (112A)

where K is the capacity ratio of the column.

The following step is to determine k\*, as slow diffusion may take place in both phases, with different values for k\*.

c.2) Slow Diffusion of Vapor in the Stationary Phase Because of a certain resistance to mass transfer upon diffusion of the vapor solute to and from the interface, only at the interface holds the relation q=β'c. In the stationary-phase, at the front profile, q<β'c, while at the rear profile the reverse occurs. From the analogy,</li>

it is obvious that the effect of slow diffusion in the stationary-phase is equivalent to a first-order reaction (at the interface), and thus Equation 100A applies. The rate constant k\* is proportional to the area, the diffusivity, and inversely proportional to the film thickness  $(d_f)$ . The larger the volume of stationary-phase per unit length of column (i.e., the term b defined in pg. 132, part c.l, which is related to D by D=bp<sub>s</sub>), the more vapor must diffuse to increase the average concentration by a given amount, and so k\* is also inversely proportional to b.

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$$k^{*} \propto \frac{\text{Area} \cdot D_{\ell}}{d_{f}b} = \frac{\text{Area} D_{\ell}^{\rho}s}{d_{f}D}$$
(113A)

The proportionality constant is obtained if  $k^*$  is determined by an even layer of  $d_f$ .

$$\frac{V_{g}}{V_{g}} = \frac{(r_{c}^{-d}f)^{2}}{r_{c}^{2} - (r_{c}^{-d}f)^{2}} \stackrel{\text{and}}{=} \frac{r_{c}}{2d_{f}}$$
(114A)

and

Area . 
$$d_f = b$$

 $k^{\star} = \frac{\pi^2}{4} - \frac{D_{\ell}}{d_{\epsilon}^2}$ 

The constant of proportionality is  $\pi^2/4$ .<sup>(36)</sup>

So, we have:

y proportional to

(116A)

Using Equation (110A), we get:

$$v = \frac{8}{\pi^2} d_f^2 F(V_R^0 - V_M) / D_{\ell}$$
(117A)

$$s_{z}^{2} = \frac{8}{\pi^{2}} d_{f}^{2} \frac{\bar{u}}{D_{g}} \cdot \frac{K_{z}}{(1+K)^{2}}$$
 (118A)

c.3) Slow Diffusion of Vapor in the Gas-Phase

Here, the problem is more complicated, as in addition to the lateral diffusion, gas streams in different parts of the cross-section move at different speeds, due to the velocity gradient. For OTC, this study may be characterized in 3 ways:

(a) Dispersion without Liquid-Phase

This was studied by Taylor <sup>(37)</sup>, in cylindrical tubes. The distortion of the initially planar flow profile (at time zero) into a parabolic one, will produce a very large variance in an initially compact distribution (averaged through the tube cross-section). This dispersion is counteracted by lateral diffusion, by which regions of greater vapor concentration in the front profile, will diffuse to the edges, while the reverse occurs at the rear profile. If the rate of lateral diffusion (independently of longitudinal diffusion) is fast, as compared to the gas flow, then:

$$s_z^2 = \frac{r_c^2 \bar{u}z}{24 D_q}$$

(b) Dispersion with Liquid-Phase and Instantaneous Mass-Transfer

Following Golay, (1) we have:

$$s_{z}^{2} = \frac{1+6K+11K^{2}}{(1+K)^{2}} \cdot \frac{r_{c}^{2}\bar{u}z}{24 D_{q}}$$
 (120A)

and we see that an extra term, which is function of the capacity ratio K, appears in comparison with Equation (119A). For K=0,  $s_{z}^{2}$  is a minimum, and thus, the presence of the stationary phase increases the variance due to viscous flow.

(c) Dispersion with Liquid-Phase and Non-instantaneous Mass-transfer

Again Golay<sup>(1)</sup> worked out this phenomena, and the expression for the variance is:

$$s_{z}^{2} = \frac{K^{3}}{6(1+K)^{2}} \cdot \frac{r_{c}^{2} - r_{c}^{2}}{\beta^{2} D_{\ell}}$$

"Now, we recall Equation (37), and we get:

$$s_{z}^{2} = \frac{2}{3} \frac{K}{(K+1)^{2}} d_{f}^{2} \frac{\bar{u}z}{D_{\ell}}$$
 (122A)

(119A)

(121A)

This equation is the same as Equation (118A), except for the constant  $\frac{2}{3}$ .

(d) Comparison of Magnitudes of the Variance's in OTC Dividing Equations (121A) and (120A), we get:

$$\frac{s_{(z)gas}^{2}}{s_{(z)liq}^{2}} = \frac{3}{48} \frac{r_{c}^{2}}{d_{f}^{2}} \frac{D_{\ell}}{D_{g}} \cdot \frac{1+6K+11K^{2}}{K}$$
(123A)

With OTC, K usually is small, frequently of order one. With this, we get:

$$\frac{s_{(z)gas}^{2}}{s_{(z)liq}^{2}} \sim \left(\frac{r_{c}}{d_{f}}\right)^{2} \frac{D_{\ell}}{D_{g}}$$
(124A)

Working with usual solutes and phases,  $\frac{D_{\hat{k}}}{D_{g}}$  is of order 10<sup>-5</sup>, while  $(\frac{r_{c}}{d_{f}})^{-2}$  is of approximately the same order. So:  $\int \frac{s_{(z)gas}}{2} \sim \text{ order 1}$  (125A)

For the peaks with large values of the capacity ratio (K),  $s^2 > s^2$ , (z)gas (z)liq.

(z) liq.

With very low values for K or with large values for  $\bar{u}$ , the peaks become asymmetrical, with sharp front profiles.

This is usually what happens with OTC, and may be readily seen by Equation (118A).

## (e) Golay Equation

If we assume the principle for summing variances, which is applicable to OTC, <sup>(7)</sup> then we may sum the variance given by Equations 94A, 120A, 121A, and we get:

$$s_{(z)}^{2} = \frac{2D_{g}z}{\bar{u}} + \frac{1 + 6K + 11K^{2}}{24(1+K)^{2}} \cdot \frac{\bar{u}r_{c}^{2}z}{D_{g}} z + \frac{K^{3}}{6(1+K)^{2}} \cdot \frac{\bar{u}r_{c}^{2}z}{\beta^{2}D_{\varrho}}$$

$$(126A)$$

which is the Golay Equation.<sup>(1)</sup> But HETP =  $\frac{s'(z)}{z}$ , and so:

$$HETP = \frac{2D_{g}}{\bar{u}} + \frac{1+6K+11K^{2}}{24(1+K)^{2}} \cdot \frac{\bar{u}r_{c}^{2}}{D_{g}} + \frac{K^{3}}{6(1+K)^{2}} \cdot \frac{\bar{u}r_{c}^{2}}{\beta^{2}D_{\ell}}$$

· (127A)

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This equation neglects the resistance to mass-transfer at the interface, which was treated by Giddings. (12)

(f) Variance Contribution due to the Input Distribution of Vapor

It was seen that the zone of vapor occupies a finite volume, at least equal to the volume of the pure

vapor, at the pressure  $P_i$ , but usually greater, because of dilution with the carrier gas.

Let  $s_I^2$  be the variance of the input-distribution,  $s_c^2$ be the variance due to the column. Then, the variance of the peak, produced by the column upon the input distribution

$$s_{t}^{2} = s_{I}^{2} + s_{c}^{2} = s_{I}^{2} + \frac{(v_{R}^{0})^{2}}{n}$$
 (128A)

from Equation (77A).

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In practice, a plate number (n<sup>\*</sup>) resulting from the combination column-input distribution is measured.

$$n^* = \frac{(V_R^0)_l^2}{s_t^2} < n$$
 (129A)

and so:

is:

\* 
$$\frac{n(v_R^0)^2}{ns_1^2 + (v_R^0)^2}$$
 (130A)

Equation (130A) shows the effect of the input distribution on the performance. From it, we get:



(131A)

and so:

$$\frac{s_{t}\sqrt{n}}{v_{R}^{o}} = \left[n \left(\frac{s_{I}}{v_{R}^{o}}\right)^{2} + 1\right]^{\frac{1}{2}}$$
(132A)

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We see from Equation (132A) that:

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$$\frac{s_{t}\sqrt{n}}{v_{R}^{o}} = \phi \quad \left(\frac{s_{I}\sqrt{n}}{v_{R}^{o}}\right)$$

It is seen that if

$$s_1 < \sim 0.2 \quad \frac{V_R^0}{\sqrt{n}} = 0.2 \ s_c$$

the effect of the input distribution on the column performance is negligible. For plug flow,  $V_{plug} = 3 s_{I}$ , and so:

$$V_{plug} < v 0.6 \frac{V_{R}^{o}}{\sqrt{n}}$$
 (133A)

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#### APPENDIX

## CHAPTER 2

Experimental Results in Uncoated Columns

4.1 Introduction

With columns that are not coated with the stationaryphase, the peaks obtained are representative of inert peaks. The gaseous solute was propylene or  $CH_4$ , due to the great response of the FID to small amounts of these compounds and due to their availability from previous experiments. In this chapter, studies are presented concerning the reproducibility of the retention times of linearity of the detector, and the uniformity of diameter from tube to tube.

4.2 Reproducibility of the Retention Times

Column characteristics:  $L \simeq 1180 \text{ cm}$ d<sub>c</sub> = 0.022 cm

For CH<sub>4</sub> injection, a sample size of 15  $\mu$ l was chosen, with splitting ratio of 1:190, which provides  $\sim$  0.08  $\mu$ l (NTP) through the column. For the seven injections made, the retention times are shown in Table 1A.

This gives a mean retention time of  $t_m = 45.7 s$ ,



"Air Peak" Times for CH<sub>4</sub> on Uncoated Column

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with the standard deviation of the mean = 0.27 per cent. The mean flow rate is  $\sim 0.6 \text{ ml/min}$ .

For propylene injection, a sample size of 10 µl was chosen, with the same splitting ratio of 1:190, which corresponds to  $\sim$  0.05 µl through the column. For the 25 injections made, the retention times are shown in Table 2A. This gives a mean retention time of  $\bar{t}_m = 45.4$  s, with the standard deviation of the mean = 0.18 per cent. The mean flow rate is  $\sim$  0.6 ml/min.

Conclusion: The retention times are reproducible to within one per cent.

4.3 Study of flow rate and pressure drop on uncoated bundle Bundle characteristics - Number of columns = 5

 $d_{c} = 0.0224.cm$  $L \simeq 190 cm$ 

It was mentioned before, that one way of testing the uniformity of the mean diameter from tube to tube in a bundle, is by checking the flow rate through the various columns, for a certain pressure differential along them. Equations (11, 12, 13, 14, 15) are used here, and the results are plotted graphically. Measurements were taken both with the make-up line connected and disconnected, but in the first case, the pressure at the outside of the column is not known, and is certainly greater than the



		- <u></u> ,			. <u></u>	<u></u>
Injection no.	1	2	3	4	5	ʻ <b>₋</b> ,≫ 6
t <sub>m</sub> (s),	45.2	45.4	45.4	,45.3	45.5	45.3
			,			
Injection no.	ŕ	8/	9	10	· 11	12
t <sub>m</sub> (s)	45.4	45.4	45.5	45.4	45.4	45.4
Injection no.	13	14	15	16	17/	18
t <sub>m</sub> (s)	45.4	45.4	45.5	45.5	45.5	45.5
<u> </u> ] .						~
Injection no.	19	20	21	22	23.	2.4
t <sub>m</sub> (s)	45.5	45.5	45.5	45.5	45.5	45.5
Injection no.	25		u			
t <sub>m</sub> (s)	45.5	, · · ·				1

Table 2A

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atmospheric pressure, although probably close to it.

a. Study of Flow Rate through the Columns

Here, the outlet of the columns was connected directly to a bubble flowmeter, and the outlet pressure is assumed to be  $\sim$  1 atm. Experiments were conducted with 5, 4, 3, 2 and 1 columns, and the flow rates were measured. Two corrections must be applied in order to obtain the mean flow rates, but we are interested in the relative effect, and as the same corrections would be applied in all cases of this experiment, they were not done. In Fig. 2A are shown the results obtained with the make-up disconnected. The pressure at the second stage of the tank was set at 40 psig.

The relation between the total flow rate and the number of columns is seen to be nearly linear. The total pressure drop, which is fixed, can be divided into the pressure drop across the column and the pressure drop in the other flow passages both upstream and downstream from the column. As the total flow rate increases, the pressure drop in the other flow passages increases and, as the total is fixed, the pressure drop across the column must decrease. The deviation from linearity in Figure 2A is attributed to this effect. This type of test does not appear to be a good substitute for the more laborious

testing of one tube at a time.

b. Study of Pressure Loss in the Columns

A study of the pressure loss on the columns was also made, with the make-up connected, i.e., under normal operation circumstances, and it was assumed that the pressure at the outlet of the columns is unknown, but the same through all experiments, i.e., independent of the number of columns tested. Further, due to the design of the connections between the column and detector and between the make-up line and the column, it may be assumed with little error that this pressure is approximately 1 atm.

If the tubes all had the same diameters, the value of  $B_0$ , from Equation 12, would be a constant and the right hand side of Equation 11 would be a constant times  $L^2/t_m$ . If  $P_0$  is constant, the left hand side of Equation 11 is a function of  $P_1$ . Equation 11 was solved for  $P_1$  and the results are shown in Table 3A. Figure 3A is a graph of  $\Delta P$  as a function of N and Figure 4A is a graph of  $F_{total}$ 

Again, the graph in Figure 4A is seen to be approximately linear. The departure from linearity is evidently due to the fact, shown in Figure 3A, that the pressure drop was not constant. This may also be due to an increase in pressure drop elsewhere in the flow path.

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FIGURE 2A

Total Flow Rate in Uncoated Columns in Parallel (Make-Up Line Disconnected)

# FIGURE 3A

Pressure Loss in Uncoated Columns in Parallel

(Make-Up Line Connected)



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	۴	۱ ۲	•	Table 3A				,
Ň	æ	t <sub>m</sub> (s)	ū(am/s)	F <sub>total</sub> ( <u>ml</u> )	¢∆p(atm)	ф.	P <sub>i</sub> (atm)	; j
5	÷	13.15	14.33	1.69	0.033	1.33	1.025	∿1 `
4		11.72	16.08	1.52	0.037	1.37	1.027	∿1
°3		11.14	16.92	1.20	0.039	1.34	1.029	_∿ <b>1</b> _
2		10.61	17.77	0.84	0.041	1.32	1.031	∿1
1		11.07	17.03	0,40	· 0.039	1.34	1.029	∿1

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In any case, this is not a satisfactory test procedure unless ' the pressure drop across the column can be held constant.

4.4 Study of Peak Broadening in a Column

The small differences in diameter that exist in the different columns of a bundle, affect not only the retention times for the inert peaks in the individual columns, but also the broadening of the peaks. In the case of uncoated columns, this is due to the longitudinal diffusion in the Figure 5A is a plot of  $w_h$  vs. N, and it may be gas-phase. seen that the width increases as the number of columns This is due to the increase in the ratio of decreases. dead volume to the volumetric flow rate. Changing the connections for the single column, minimizing its volume, produced point A in the graph. It must be kept in mind that if the connections' dead-volumes are minimized for a certain N, then they are no longer minimized as N decreases. So, referring to Chapters 2 and 4 of the text, the main contributions to peak spreading are from end effects, i.e., from the dead volumes of the detector, injection port, and connections.

4.5 Linearity of the FID with the sample sizes used Using Equation 42, and propylene as the gaseous solute, in Table 4A are the values of the maximum sample size B\*

(µl at operating T and  $\overline{P}$ ), for the various number of columns, and for K=0 (nonabsorbed component).

Experiments were conducted with 1, 2 and 3 columns, and the injections through them were respectively of 0.007  $\mu$ l, 0.015  $\mu$ l and 0.022  $\mu$ l, taking into account the splitting ratio calculated upon the flow rates through columns and through vent. The peak areas were measured, and Fig. 6A is a plot of these results.

We see that the FID responds linearly, at least if we keep the sample size below the value given by B\*. It is also seen that the sample size may be chosen to increase proportionally with the number of columns. This was the procedure followed throughout this project.

### FIGURE 4A

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Total Flow Rate in Uncoated Columns in Parallel

(Make-Up Line Connected)

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### FIGURE 5A

Variation of Peak Width at Half-Height in Uncoated Columns in Parallel

٩. flow rate, ml, min number of columns •1

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**(**)

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FIG 4A



FIG.5A

## TABLE 4A

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Theoretical Maximum Sample Size

According to Keulemans

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u .		
N ·	<u></u>	B <sup>*</sup> (µl)
5 <sup>′</sup>		0.1
4		0.08
3		0.06
2		0.04
1		0.02
		<u> </u>

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TABLE 4A

# FIGURE 6A

Variation of Peak Area with Sample Size,

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for Uncoated Columns



# APPENDIX

#### CHAPTER 3

Coated OTC Bundles Prepared Using the Static Coating Technique

Table 5A shows the bundle characteristics, as well as the results obtained for the case of 5 columns, where only one peak developed, i.e., the peaks coming out from individual columns overlapped, forming a single peak.

The experiment was started with the 9 columns and the sample size was kept proportional with the number of OTC in the bundle. The columns were removed (by breaking them) one by one from the bundle until only one of them remained. Table 6A shows the results obtained, and when more than one peak emerged (from n-heptane injections),  $w_h$  is not shown. Some peaks could be easily identified by their retention times relative to an inert (CH<sub>4</sub>), and an analysis was made on the distribution of the retention times for n-heptane, on this particular bundle.

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Again, we can see an increase in w<sub>h</sub> as the number of columns decreases. This is due to the important role of longitudinal diffusion in the gas-phase.in the dead volume of the connections bundle-GC apparatus as the total flow diminishes. Figure 7A shows the retention times

TABLE 5A ·

Experimental Results for Coated Bundle, by Static

Coating Technique (9 Columns)

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Number of columns*(N)	5
(L (cm)	∿340
₫ <sub>כ</sub> (μ)	∿196
c <sub>s</sub> (% vol)	2
a <sub>f</sub> (µ)	~1
P <sub>i</sub> (atm)	3
P <sub>o</sub> (atm) -	∿l
t <sub>m</sub> (s)	4.56
t <sub>r</sub> (s)	37.98
K 🔸	7.3
w <sub>h</sub> (s)	∿12.4
,	-
F(ml/min):N	1.35
*	

\* Initially, the bundle had 9 columns, but the results shown on Table 5A are for the case of 5 columns, because here only one peak appeared.

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TABLE 6A

Experimental Results on Coated Bundle, by Static

Coating Technique (Normalized Data)

Table 6A
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`` ' N	9	8	7	6	5	4	3	2	<b>1</b>
(just n-heptane) Schematic form of peaks	M	M	M	M	$\bigwedge$	$\nearrow$	$\bigwedge$	$\bigwedge$	$\bigwedge$
k <sub>l</sub>	6.50	6.33	8.52	8.25	8.33	7.38	7.32	7.27	6.94
, <b>k</b> 2	8.17	8.04	10.15	9.87	·	8.11	9.34	_/	_
k <sub>3</sub>	9.82	<sub>,</sub> 9 <b>.</b> 75		—		9.37			
w <sub>h</sub> (cm)	—				2.10	` <del></del>	_	3.50	6.40
h <sub>1</sub> (cm)	4.00	3.72	8., 36	17.45	13.40	4.35	10.83	11.7	8.00
h <sub>2</sub> (cm)	11.26	11.80	7.25	14.28		9.98	11.40		
h <sub>3</sub> (cm)	8.02	8.34	-	—	—	8.73	· · · · · · · · · · · · · · · · · · ·		 ·
b <sub>1</sub> (cm)	0.94	0.76	3.85	3.35	<b>.</b> 4.23	1.75	3.80	6.87	12.90
b <sub>2</sub> (cm)	3.38	3.30	3.34	2.74		4.18	4.00	. —	
b <sub>3</sub> (cm)	2.41	2.33				3.,66			^ <del></del>

Note: subscripts (1,2,3) refer to the first, second and third peaks, and

b<sub>i</sub> is an approximate measurement of the base width.

FIGURE 7A

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Variation of Capacity Ratio with Number of

Coated Columns in Parallel (Static Coating Method)

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(normalized) as related to the number of columns, and those that seem close enough to be produced by a single column are represented by the same symbol. The mean values for K, are also shown.

The strong lines are the mean values for  $K_i$ , while the dashed lines are correspondent to the peaks that are assumed to be present, but hidden by the other peaks. The numbers in circles, i.e., (n), represent the number of columns that are assumed to contribute to the peak that has the respective value of  $K_i$  mean. The distribution obtained, normalized to the peak that is assumed to be present over all runs, i.e., the peak from column 1, which has  $K_i$  mean = 13.7 is shown in Figure 8A. Here, N\* is the number of columns in the bundle that contributes to the particular value of  $K_i/7.13$ .

# FIGURE 8A

Number of Columns that Contribute to a Specific Normalized Capacity Ratio, for Coated Columns in Parallel (Static Coating Method)

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