

## 모멘트법에 의한 SCOT 컬럼의 유효이론단 높이의 계산

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(접수 1976. 11. 26)

### Calculation of SCOT Column HETP Values by Means of Moments

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(Received November 26, 1976)

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#### 요 약

Support Coated Open Tubular (SCOT) 컬럼에서 일어나는 물질전달 현상을 3개의 편미분 방정식으로 나타내고 Laplace domain에서 그 해를 구한 다음 유효이론단의 높이를 수식으로 유도하였다. 크로마토그램에 대하여 평균치를 중심으로 하는 이론적인 2차 모멘트를 계산하고 그 결과를 크로마토그래피의 이론에 적용함으로써 최종 연관식을 유도하였다. 이 연관식으로 계산된 값과 대표적인 실험치를 대비하여 본 연구에서 제시하는 확산(dispersion) 모델이 SCOT 컬럼의 물질 전달현상을 나타내는데 적절한 것임을 입증하였다.

#### Abstract

The Laplace domain solution of three coupled partial differential equations descriptive of the mass transfer phenomena that occur within a Support Coated Open Tubular (SCOT) Column is used to derive an expression for the Height Equivalent to a Theoretical Plate (HETP) for any SCOT Column. The final correlation is developed by calculating the theoretical second moment about the mean for a chromatogram and using this result in traditional chromatographic theory to construct the desired expression. Typical experimental values and those calculated from the correlation derived in this work are presented as a verification of the proposed dispersion model employed to describe the mass transfer phenomena within this dynamic system.

#### Introduction

While the introduction of the Support Coated Open Tubular (SCOT) column in gas chromatography is still a fairly recent event, its use in achieving chemical separations of relatively

complex samples has created a great deal of interest. Few theoretical studies pertaining to this subject are available to supplement the increasing number of studies oriented toward practical applications. The introduction of the thin porous layer characteristic of the SCOT

column greatly complicates the mathematical description of this separation/identification system. One of the goals of this research was to formulate a sound mathematical description of the flow conditions that prevail within a SCOT column so as to contribute to the fundamental knowledge available on this subject.

The use of mathematical modeling techniques has been employed in many studies in the traditional areas of packed and open tubular column chromatography. Physical and chemical properties of various samples and support materials used in chromatography, such as gaseous and liquid diffusivities, surface areas of porous supports, and thermodynamic properties such as heats of vaporization, equilibrium constants and boiling points, have all been calculated from various relations developed from the theoretical solution of a mathematical model proposed for each column geometry. In most cases, the validity of a proposed model can be verified by using the relationships developed from the model to calculate parameters such as those previously mentioned and by comparing those theoretical values to experimental values. The calculation of theoretical HETP (height equivalent to a theoretical plate) values for chromatographic columns presents a good example of a theoretically correlated value that is often compared with experimental values to verify both the validity and the applicability of the particular mathematical modeling techniques employed. This work will use a theoretical correlation for HETP values derived from the mathematical description of a SCOT column and the use of moments to show the applicability of the correlation by comparing theoretical values to experimentally determined values and values calculated through the use of correlations developed independent of this work.

While chromatography has received its great-

est interest since the early 1940's when Martin and Synge<sup>13)</sup> were awarded the Nobel Prize for their work in liquid-liquid chromatography, a tremendous amount of literature has been published over the last three decades. The first theoretical analysis of a chromatographic column was made by Wilson<sup>19)</sup> in 1940. The mathematical theory of chromatography has been made more precise by such authors as Lapidus and Amundson<sup>12)</sup>, van Deemter, *et al.*<sup>18)</sup> whose expression for HETP is one of several packed column correlations, and Golay<sup>4,6)</sup> for open tubular column HETP correlations. Correlations developed by these authors have resulted from mathematical models characterized by the inclusion of a finite mass transfer resistance and the use of a convective flow model involving the solution of one or more partial differential equations and the boundary conditions descriptive of the particular geometry employed.

The use of moments for correlating the theory of mathematical models for packed column chromatography to experimental data has been demonstrated by Kucera<sup>11)</sup>. He lists the first five moments in terms of mass transfer coefficients, distribution coefficients, diffusivities and flow terms. Work by Grubner<sup>9)</sup> and Masamune and Smith<sup>14,15)</sup> closely followed Kucera's modeling techniques. The calculation of dispersion coefficients by means of moments has been accomplished by Horn<sup>10)</sup>. However, the use of moments in SCOT column modeling has seldom been used.

Literature descriptive of SCOT column geometry has been minimal. First suggested by Golay<sup>7)</sup>, this idea was a compromise between a packed column and the standard open tubular column. The SCOT column, as suggested by Golay, contained a porous layer adhering to the smooth wall of an open tube. The layer was coated with the traditional stationary liquid

phase. Golay<sup>5,8)</sup> later extended his original work by deriving an HETP correlation suitable for SCOT column geometry. This study combined many of the concepts mentioned earlier to develop a more realistic mathematical correlation for SCOT column HETP calculations.

### A Three-Region Model of a SCOT Column

Because of the novelty and the complexity of the physical structure of the SCOT column, little work has been done on its theoretical description as has been mentioned earlier. An accurate mathematical description of this dynamic system must account for several chemical and physical phenomena. Considering the geometry of the system, three separate concentrations could be measured at any cross section of the column. The basic cylindrical shape of the center of the column suggests the use of cylindrical coordinates. A differential material balance of the bulk flow area taking into account longitudinal dispersion, convective transfer, and mass transfer from the bulk region to and from the liquid coated porous layer adhering to the wall, results in the following unsteady-state equation describing the change in concentration of the bulk material:

$$\partial\bar{C}/\partial t + \bar{u}\partial\bar{C}/\partial z - D_p\partial^2\bar{C}/\partial z^2 = N_c \quad (1)$$

The exclusion of any radial dispersion from this differential equation is based on the usual assumption that radial dispersion can be neglected in comparison to the axial dispersion when the ratio of the column diameter to length is small. Although the assumption depends on the flow regime (laminar or turbulent), because  $D/L$  is of the order  $10^{-5}$ , the existence of large radial gradients is unlikely. Also of interest in this equation is the inclusion of a dispersion coefficient to take into account both molecular diffusion and any velocity effects which may

influence the axial concentration profile. The use of such a dispersion model was first suggested in the work of Taylor<sup>16,17)</sup>. The use of this dispersion model will simplify the mathematical description of the transport processes, while still accounting for velocity effects normally occurring with a laminar profile. Since this work will be in the laminar flow region, the use of the Taylor-Aris<sup>3,16)</sup> solution for the effective axial dispersion coefficient will be appropriate where  $D_p$  can be determined from the following relation:

$$D_p = D_g + R^2\bar{u}/48 D_g \quad (2)$$

The approximate range of applicability of the Taylor-Aris solution was given by Anathakrishnan, *et al*<sup>1)</sup>. The criteria presented there was given in terms of the Peclet number; a minimum value of  $D_g t/R^2$  must be maintained. Because of the size of  $R$  in this study ( $10^{-2}$  centimeters), this group is always very large except at the entrance of the tube where  $t$  is small, thus demonstrating the validity of the Taylor-Aris solution to this application.

As is typically done in the theoretical analysis of chromatographic columns, the mass transfer rate in this differential balance is defined by the following linear equation:

$$N_c = -H_c (K_C\bar{C} - C) \quad (3)$$

where  $H_c$  is a mass transfer coefficient representing transfer of material between the bulk flow region and the porous layer region.  $K_C$  is a linear equilibrium constant defined by the relation:

$$C^* = K_C\bar{C} \quad (4)$$

Here,  $C^*$  is the equilibrium concentration in the porous layer, while  $\bar{C}$  represents the bulk flow region concentration.

A differential balance on the porous layer taking into account that no axial convection or dispersion can occur, results in the following equation:

$$\partial C/\partial t - D_{eff} (\partial^2 C/\partial r^2 + 1/r \partial C/\partial r) = N_n \quad (5)$$

This unsteady-state equation indicates that  $C$ , the concentration in the porous layer adhering to the column wall, can vary in the radial direction because of the effective molecular diffusion through the porous material and because of adsorption and desorption of material into and out of the liquid adsorbent which coats the porous support material. This last effect, represented by  $N_n$  in Equation (5), is again represented by the following linear equation:

$$N_n = -H_n (K_n C - n) \quad (6)$$

where  $H_n$  is a mass transfer coefficient representing transfer of material between the void volume in the porous layer and the liquid phase coating the support material.  $K_n$  is a linear equilibrium constant defined by the following relation:

$$n^* = K_n C \quad (7)$$

where  $n^*$  is the equilibrium concentration in the liquid phase coating the porous material.

The rate of change of  $n$  with time can be described by the following expression:

$$N_n = -\partial n/\partial t \quad (8)$$

Since Equations (1), (5), and (8) represent time dependent concentrations, the following initial conditions describing the initial concentrations in each of the three regions are appropriate:

$$\bar{C}(z, t) = 0 \quad \text{for } t \leq 0 \quad (9)$$

$$C(r, t) = 0 \quad \text{for } t \leq 0 \quad (10)$$

$$n(t) = 0 \quad \text{for } t \leq 0 \quad (11)$$

Equation (5), which has a second order partial differential as its highest order derivative, can be solved only if two radial boundary conditions can be obtained from physical considerations of the SCOT column geometry. The first of these boundary conditions comes from the symmetry of the porous layer and the physical boundary of the tube wall. This boundary condition can be written as follows:

$$\partial C/\partial r|_{r=R_2} = 0 \quad (12)$$

Here  $C$  is again the concentration in the gaseous void volume of the porous material.  $R_2$  is the internal radius of the tube extending completely through the porous layer to the stainless steel wall. Physically, this condition satisfies the requirement that no mass can be transported farther than  $R_2$  distance from the center line of the tube in a radial direction because of the physical boundary created by the tube wall.

The second radial boundary condition required for the solution of Equation (5) can be obtained by equating the flux of material in the direction normal to the surface of the porous layer ( $J_R$ ) to the diffusional flux of material into this porous layer. This results in the following relation:

$$J_{R_1} = -D_{eff} \left. \frac{\partial C}{\partial r} \right|_{r=R_1} \quad (13)$$

By defining  $a_p$  as follows:

$$a_p = (\text{Surface available for mass transfer on the external surface of the porous layer}) / \text{Unit volume of column} \quad (14)$$

and by realizing that the rate of influx of material into the porous material at  $r=R_1$  must also be equal to the rate of mass transfer through the available area open to mass transfer into the porous liner, Equation (13) can be extended to the following general relation:

$$J_{R_1} = -D_{eff} \left. \frac{\partial C}{\partial r} \right|_{r=R_1} = N_c/a_p$$

The solution of Equation (1), which also contains a second order partial differential term as its highest order term, will require two axial boundary conditions. Since the SCOT column employed has a very large  $L/D$  ratio, and  $L$  is itself very large, the following axial condition is suggested for one of the two necessary conditions:

$$\bar{C}(z, t) = 0 \quad \text{at } z = +\infty \quad (15)$$

In most general form, this study was based on the evaluation of SCOT column performance using pulse tracer techniques. Therefore, the boundary conditions at  $z=0$  will be those corresponding to the introduction of a pulse injection at  $z=0$ . This condition then becomes:

$$\bar{C}(z, t) = C_0 \quad \text{for } t_0 < t \leq t_1, \quad z=0 \quad (16)$$

and

$$\bar{C}(z, t) = 0 \quad \text{for } t > t_1, \quad z=0 \quad (17)$$

This completes the specification of both initial and boundary conditions necessary to determine a solution for the problem represented by Equations (1), (5), and (8).

Having derived the mathematical expressions that describe the transport properties that occur within the SCOT column, one would normally proceed to the solution by methods of applied mathematics. However, the complexity of solving three-coupled unsteady-state partial differential equations of the type previously described has prevented a determination of an analytical solution in the time domain. The validity of this model for SCOT columns, as well as other useful correlations for characterizing the performance of a SCOT column can be verified by the solution of these three coupled equations in the Laplace domain. The following property of the Laplace transformation allows one to determine the theoretical statistical moments for any mathematical model as long as  $C(s, z)$  can be obtained and the following limit exists:

$$\int_0^\infty t^k C(t) dt = (-1)^k \lim_{s \rightarrow 0} d^k \bar{C}(s, z) / ds^k \quad (18)$$

where

$$\int_0^\infty t^k C(t) dt = \mu_k \quad (19)$$

and

$$M_k = k\text{-th moment} = \mu_k / \mu_0 \quad (20)$$

In order to obtain  $\bar{C}(s, z)$ , the transformation of Equations (1), (5), and (8) into the Laplace domain must be performed. Using traditional

Laplace transformation techniques, Equations (1), (5), and (8) become:

$$s\bar{C} + \bar{u}d\bar{C}/dz - D_p d^2\bar{C}/dz^2 = \bar{N}_c \quad (21)$$

$$s\bar{C} - D_{eff} (d^2\bar{C}/dr + 1/r d\bar{C}/dr) = \bar{N}_n \quad (22)$$

$$s\bar{n} = -\bar{N}_n \quad (23)$$

These equations must be solved with the following transformed relations:

$$\bar{N}_n = -H_n(K_n\bar{C} - \bar{n}) \quad (24)$$

$$\bar{N}_c = -H_c(K_c\bar{C} - \bar{C}) \quad (25)$$

$$\left. \frac{\partial \bar{C}}{\partial r} \right|_r = R_2 = 0 \quad (26)$$

$$\left. \bar{J}_{R_1} = -D_{eff} \frac{\partial \bar{C}}{\partial r} \right|_{r=R_1} = \bar{N}_c / a_p \quad (27)$$

$$\bar{C}(s, z) = 0 \quad \text{for } z = +\infty \quad (28)$$

and

$$\bar{C}(s, z) = e^{-st_0} (1/s - e^{-sz}/s) C_0 \quad \text{for } z=0$$

where  $\varepsilon = t_1 - t_0$  (29)

This transformation has now altered the mathematical complexity by replacing the problem of solving three coupled partial differential equations with the problem of solving three coupled ordinary differential equations.

The actual solution of these three equations in the Laplace domain and the evaluation of the limits as  $s$  approaches zero in order to obtain the desired statistical moments is impossible unless a simplifying assumption is incorporated into the solution. This assumption involves neglecting any radial concentration gradient that may appear in the porous layer on physical grounds. Calculations as well as actual observance of the porous layer within the SCOT column show this layer is very small. The capacity of this layer to accept tracer material depends on the volumetric amount of liquid phase coating the porous support material. However, since the porous layer itself is very small, the amount of liquid phase available to accept tracer material is small. Therefore, the flux of tracer into the porous region must also be small. Since this flux can be defined as

$$N_A = -D_{eff} \partial C / \partial r \quad (30)$$

$\partial C / \partial r$  must be small to account for the size of  $N_A$ . Since the driving force for the mass transfer phenomenon between the bulk flow region and the porous layer void volume, as well as that between the porous layer void volume and the liquid coating on the support material, is the difference in concentrations  $\bar{C}$ ,  $C$ , and  $n$ , the assumption that  $C$  varies only slightly across the porous layer allows the replacement of  $C(r, t)$  with  $C_{AVE}(t)$ . This assumption permits the mathematical solution for  $\bar{C}(s, z)$  from Equations (21), (22), and (23). The mathematical techniques employed were relatively straightforward although cumbersome and lengthy. The resultant expression for  $\bar{C}(s, z)$  is:

$$\bar{C}(s, z) = e^{-st_0} (1/s - e^{-sz}/s) C_0 \exp \left\{ (\bar{u}/2D_p - \frac{1}{2} \sqrt{\bar{u}^2/D_p^2 - 4(\beta-s)/D_p}) z \right\} \quad (31)$$

where

$$\beta = \frac{\alpha^2 a_p K_C D_{eff} \Delta R^2 H_C}{2R_1 H_C - \alpha^2 a_p D_{eff} \Delta R^2} \quad (32)$$

$$\alpha^2 = (1/D_{eff}) (s^2 + H_n s + H_n K_n s) / (H_n + s) \quad (33)$$

and  $\Delta R = R_2 - R_1$

The use of this expression for determining statistical moments has been accomplished. Generally, the first and second moments, and the second central moment are the highest moments that can accurately be used for correlation of experimental data. The following relationships are appropriate for determining these moments:

$$\mu_0 = -C_0 \varepsilon \quad (34)$$

$$\mu_1 = (C_0 \varepsilon / 2) \left\{ \varepsilon - 2L/\bar{u} + L a_p \Delta R^2 (K_C + K) / R_1 \bar{u} \right\} \quad (35)$$

$$\mu_2 = (C_0 \varepsilon) \left\{ 2L D_p / \bar{u}^3 [1 - a_p \Delta R^2 (K_C + K) / R_1 + a_p^2 (\Delta R^2)^2 (K_C + K)^2 / 4R_1^2] + \varepsilon^2 / 3 + (L/\bar{u}) [1 - a_p \Delta R^2 (K_C + K) / 2R_1] + (L/\bar{u}) \frac{[2R_1^3 H_C^4 H_n^3 a_p \Delta R^2 K + R_1^2 H_C^3 H_n^2]}{2R_1^4 H_C^4} \right\}$$

$$\frac{a_p^2 (\Delta R^2)^2 (H_n + H_n K_n)^2}{H_n^4} + (L/\bar{u}^2) [1 - a_p \Delta R^2 (K_C + K) / R_1 + a_p^2 (\Delta R^2)^2 (K_C + K) / 4R_1^2] \quad (36)$$

and

$$M_2^* = (2L D_p / \bar{u}^3) \left\{ 1 - a_p \Delta R^2 (K_C + K) / R_1 + a_p^2 (\Delta R^2)^2 (K_C + K)^2 / 4R_1^2 \right\} + \varepsilon^2 / 12 + (L/\bar{u}) \frac{[2R_1^3 H_C^4 H_n^3 a_p \Delta R^2 K + R_1^2 H_C^3 H_n^2]}{2R_1^4 H_C^4} + \frac{a_p^2 (\Delta R^2)^2 (H_n + H_n K_n)^2}{H_n^4} \quad (37)$$

where  $K = K_C K_n$ .

For practical applications, these equations for theoretical statistical moments are too cumbersome. Unknown variables contained within these relationships are 1) the two mass transfer coefficients  $H_n$  and  $H_C$ , 2) the two equilibrium constants  $K_C$  and  $K_n$ , 3) the product  $a_p \Delta R^2$ , and 4) the dispersion coefficient  $D_p$ . In order to reduce the complexity of the moment relationships, several simplifications may be introduced.

First, by earlier definition,  $H_C$  represents the rate of mass transfer across the boundary between the bulk flow region and open areas available for stagnant diffusion into the porous layer, and  $H_n$  represents the rate of mass transfer across the film boundary between the stagnant gas pockets within the porous material and the surface of the liquid phase coating the porous support material. However, van Deemter<sup>18)</sup> has demonstrated that resistance to mass transfer in chromatography is located almost entirely in the liquid phase. Also, Ettre<sup>3)</sup> relates that, for columns with high values of  $\beta$  (ratio of the total volume of gas in the column to the total volume of stationary phase in the column), the resistance to mass transfer in the liquid phase is large when compared to the resistance in the gas phase. For the three-region model, this is equivalent to stating that the rate of mass transfer into the liquid phase dominates

mass transfer effects in the gaseous regions, or  $H_C$  is much greater than  $H_n$ . Employing this fact in the previous moment the relation for the second central moment yields:

$$M_2^* = (2LD_p/\bar{u}^3) \{1 - a_p \Delta R^2 (K_C + K)/R_1 + a_p^2 (\Delta R^2)^2 (K_C + K)^2 / 4R_1^2\} + \varepsilon^2 / 12 + L/\bar{u} (a_p \Delta R^2 K / R_1 H_n) \quad (38)$$

Further simplification of Equations (35) and (36) is possible by combining classical chemical equilibrium theory with the theory of chromatography. The equilibrium relationships represented by Equations (4) and (7) can be combined to give:

$$n^* = K_n K_C \bar{C} \quad (39)$$

By defining the product of the two equilibrium constants as  $M = K_n K_C$ ,

$$n^* = M \bar{C} \quad (40)$$

In the theory of chromatography, the partition process, associated with partition columns (columns in which the stationary phase is held either by a solid support material or by the column wall), is defined by the partition coefficient ( $K$ ), and is equal to the equilibrium ratio of the concentrations of the sample in equal volumes of both the stationary phase and the gas phase. The capacity ratio ( $k$ ) in the theory of chromatography is defined as the equilibrium ratio of the amounts of sample in the stationary and gaseous phases of the column. The partition coefficient and the capacity ratio are related by the  $\beta$  value. These factors are related by the following relation:

$$K = \beta k = \text{Concentration in Liquid Phase} / \text{Concentration in Gas Phase} \quad (41)$$

By comparing Equations (39) and (40), it is evident that  $K$  and  $M$  are equivalent forms. Since  $\beta$  is a physical characteristic of the column being used, and  $k$  can be obtained by correlations involving resolution times in chromatography, the value of  $K$  is obtainable.

Also, making the appropriate simplifications

as outlined previously and solving for  $M_2$  from Equation (20), the following result is obtained for the theoretical variance as predicted from the proposed model:

$$M_2 = \{ (2LD_p/\bar{u}^3) [1 - a_p \Delta R^2 (K_C + K)/R_1 + (a_p \Delta R^2)^2 (K_C + K)^2 / 4R_1^2] + \varepsilon^2 / 3 + (L/\bar{u}) (a_p \Delta R^2 K / R_1 H_n) + (L/\bar{u}) [1 - a_p \Delta R^2 (K_C + K) / 2R_1] + (L^2/\bar{u}^2) [1 - a_p \Delta R^2 (K_C + K) / R_1 + a_p^2 (\Delta R^2)^2 (K_C + K)^2 / 4R_1^2] \} \quad (42)$$

Application of Equation (20) to determine  $M_1$  results in the following expression:

$$M_1 = \{ \varepsilon / 2 - L/\bar{u} + a_p \Delta R^2 (K_C + K) / 2R_1 \bar{u} \} \quad (43)$$

Of great interest in analyzing the performance of a chromatographic column is the determination of the HETP associated with a particular column and its stationary phase. By definition, HETP is:

$$H = \sigma^2 / L \quad (44)$$

or in terms of temporal variance,

$$H = L \tau^2 / t_r^2 \quad (45)$$

Therefore, by employing Equations (45) and (38), the following expression for the theoretical value of HETP can be obtained:

$$H = (L/t_r^2) \{ (2LD_p/\bar{u}^3) [1 - a_p \Delta R^2 (K_C + K)/R_1 + (a_p \Delta R^2)^2 (K_C + K)^2 / 4R_1^2] + (L/\bar{u}) (a_p \Delta R^2 K / H_n R_1 + \varepsilon^2 / 12) \} \quad (46)$$

Then, by substituting the chromatographic relation

$$t_r = t_m (1 + k) \quad (47)$$

where  $t_m$  is the elution time of a non-adsorbent material; i. e.,  $t_m = L/\bar{u}$ , and  $k$  is the capacity ratio discussed earlier, Equation (46) becomes:

$$H = \{ 2D_p / (1 + k)^2 \bar{u} \} \{ 1 - a_p \Delta R^2 (K_C + K) / R_1 + (a_p \Delta R^2)^2 (K_C + K) / 4R_1^2 \} + \{ \bar{u} / (1 + k)^2 \} (a_p \Delta R^2 K / R_1 H_n) + \bar{u} \varepsilon^2 / \{ 12 t_m (1 + k)^2 \} \quad (48)$$

Although this expression represents the HETP as produced by a finite width pulse, most expressions for HETP in chromatography are

based on and impulse type injection. For this case, the  $\epsilon$  (pulse width) that appears in Equation (48) approaches zero and results in the following simplified relation for HETP for an impulse type injection:

$$H = (1+k)^{-2} \left\{ (2D_p/\bar{u}) (1 - a_p \Delta R^2 (K_C + K) / R_1 + (a_p \Delta R^2)^2 (K_C + K)^2 / 4R_1^2 + \bar{u} a_p \Delta R^2 K / R_1 H_n) \right\} \quad (49)$$

### Experimental Equipment and Results

The experimental data necessary to calculate the actual HETP values for comparison to the predicted theoretical values was taken by using a Perkin-Elmer Model 990 Gas Chromatograph. The unit was factory equipped with both dual flame ionization detectors and the standard hot wire thermal conductivity detector. The carrier gas employed was helium. The actual separation device used was a fifty foot, 0.02 inch diameter SCOT column. The support material coated to the wall was diatomaceous earth with an uncoated surface area of six square meters per grams of material. Since ethanol was selected as the sample, Carbowax 1540 was used as the liquid phase to coat the solid support material. The SCOT column was fabricated to provide a beta factor of 50.

The experimental results were straightforward measurements of retention times for both the ethanol and air samples as well as the flow rates of carrier gas through the column and physical parameters such as column temperature, inlet pressure, etc. These measurements, in addition to the factory supplied column characteristics mentioned earlier, thus permitted the calculation of many of the parameters that appear in the HETP correlations developed earlier, i.e.  $R_1$ ,  $\bar{u}$ ,  $k$ , and  $K$ .  $H_n$ ,  $K_C$  and  $a_p \Delta R^2$  were calculated from independent experimental tests and other moment considerations.

HETP values from correlations produced by

Golay<sup>5,8)</sup> are presently the only numerical results available for comparison with values calculated from Equation (49). The Golay correlations were derived from the theoretical modeling of a gas sample flowing through an open tube and later modified to account for a thin porous layer adhering to the tube wall. However, the use of Golay's final HETP correlation for SCOT columns has been seldom used in chemical literature. *Table 1* presents the values of the HETP as calculated from the Golay correlation as well as from Equation (49). These results indicate the validity of the originally proposed three-region model as well as the applicability of the analytical results of the solution of these equations in the Laplace domain.

However, two discrepancies can be noted from the results listed in *Table 1*. First, while the differences in the HETP values calculated from Equation (49) and the experimental values are significantly less than the differences produced from a comparison of the experimental values and results calculated from Golay's correlations, several numerical results produced from Equation (49) are much larger than the equivalent experimental HETP values. It is felt that these relatively large errors due to experimental measurement errors resulting in inaccurate values for  $K$  and  $\bar{u}$ . Since both of these factors appear in the final HETP correlation, these errors could affect the final calculated HETP values. The second discrepancy in *Table 1* is noted when Golay's HETP values are compared to both experimental HETP values and HETP values calculate from Equation (49).

It is obvious that Golay's values are much smaller than either those values calculated from Equation (49) or experimental values. While no apparent reason for this phenomenon is evident, the failure of Golay's correlations to

Table 1. Experimental and theoretical values of HETP using impulse injection techniques.

Velocity (cm/min)	Temp.	HETP-Golay	HET-This Work	HETP-Exp.	% Error <sup>a)</sup>	% Error <sup>b)</sup>
1092	85 C	.836mm	4.37mm	4.04mm	79.3	8.2
1740	85 C	.493mm	3.21mm	5.09mm	90.3	37.0
2221	85 C	.417mm	3.66mm	6.71mm	93.8	45.4
1072	105 C	.801mm	4.20mm	4.57mm	82.5	8.1
1619	105 C	.567mm	6.08mm	5.59mm	89.9	8.8
2129	105 C	.435mm	6.36mm	6.85mm	93.7	7.2
650	125 C	1.290mm	3.83mm	4.80mm	73.1	20.2
1036	125 C	.844mm	3.57mm	3.89mm	78.4	8.2
1180	125 C	.763mm	2.28mm	4.42mm	82.7	48.4
1523	125 C	.608mm	4.40mm	5.28mm	88.4	16.7
1967	125 C	.443mm	5.12mm	6.21mm	92.9	17.6
2510	125 C	.385mm	7.60mm	7.75mm	95.0	1.9

a) % Error = (HETP-Exp. - HETP-Golay) / (HETP-Exp.) × 100

b) % Error = (HETP-Exp. - HETP-This Work) / (HETP-Exp.) × 100

accurately account for dispersional effects in the bulk flow region of the SCOT column during his modeling attempts could contribute to this error.

## Nomenclature

$a_p$  Effective specific area (1/cm)  
 $C$  Gaseous concentration in porous layer (g-mol/cc)  
 $C^*$  Equilibrium concentration of  $C$  (g-mol/cc)  
 $\bar{C}$  Gaseous concentration of bulk flow region (g-mol/cc)  
 $\tilde{C}$  Porous layer concentration in Laplace domain (g-mol/cc)  
 $\tilde{C}$  Bulk Region concentration in Laplace domain (g-mol/cc)  
 $C_o$  Pulse height (g-mol/cc)  
 $D_g$  Gaseous diffusivity (cm<sup>2</sup>/min)  
 $D_p$  Axial dispersion coefficient (cm<sup>2</sup>/min)  
 $D_{eff}$  Effective gaseous diffusion coefficient (cm<sup>2</sup>/min)  
 $H_C$  Bulk to porous phase mass transfer

coefficient (1/min)

$H_n$  Porous to liquid phase mass transfer coefficient (1/min)

$J_{R_1}$  Flux of material at  $r=R_1$  (g-mol/cm<sup>2</sup>-min)

$k$  Capacity ratio

$K$  Product of  $K_n$  and  $K_C$

$K_C, K_n$  Linear equilibrium constants

$M$  Product of  $K_n$  and  $K_C$

$M_2^*$  Second central moment (min<sup>2</sup>)

$n$  Liquid concentration in liquid phase (g-mol/cc)

$n^*$  Equilibrium value of  $n$  (g-mol/cc)

$n$  Liquid concentration in Laplace domain (g-mol/cc)

$N_n, N_C$  Rates of mass transfer (g-mol/cc-min)

$N_A$  Molar Flux (g-mol/cc-min)

$r$  Radial distance from center-line (cm)

$R_2, R$  Tube radius (cm)

$R_1$  Average radius of bulk flow region (cm)

$s$  Laplace domain variable (1/min)

$t$  Independent variable, time (min)

$t_m$  Air peak time (min)

- $t_r$  Resolution time (min)  
 $\epsilon$  Peak width (min)  
 $\bar{u}$  Average bulk velocity (cm/min)  
 $z$  Independent variable, axial distance (cm)  
 $\alpha^2 = \frac{1}{D_{eff}} \frac{s + H_n + H_n K_n}{1 + H_n/s}$   
 $\beta = \frac{\alpha^2 a_g K_C D_{eff} \Delta R^2 H_C}{2 R_i H_C - \alpha^2 a_p D_{eff} \Delta R^2}$   
 $\mu_k$  Integral relation defined by Equation (19)  
 $c^2$  Spatial variance (cm<sup>2</sup>)  
 $\tau^2$  Temporal variance (min<sup>2</sup>)

### References

1. V. Anathakrishnan, W. N. Gill, and A. I. Banduhn, *AIChE J.*, **11** (1965), 1063.
2. R. Aris, *Proc. Roy. Soc. Lond.*, **A235** (1956), 66.
3. L. S. Ettre, "Open Tubular Columns in Gas Chromatography," Plenum Press, New York, 1965.
4. M. J. E. Golay, *Analytical Chemistry*, **29** (1957), 728.
5. M. J. E. Golay, *Analytical Chemistry*, **40** (1968), 382.
6. M. J. E. Golay, "Gas Chromatography," ed. R. P. W. Scott, Butterworths, Washington, D. C., 1960, pp. 139-43.
7. M. J. E. Golay, "Gas Chromatography," ed. D. H. Desty, Academic Press, New York, 1959, p. 36.
8. M. J. E. Golay, *Nature*, **199** (1963), 370.
9. O. Grubner, and D. W. Underhill, *Separation Science*, **5** (1970), 555.
10. F. J. M. Horn, "Calculation of Dispersion Coefficients by means of Moments", paper submitted to AIChE Journal, presented to 58th National AIChE Meeting, Dallas, Texas, 1966.
11. E. Kucera, *Journal of Chromatography*, **19** (1965), 237-248.
12. L. Lapidus and N. R. Amundson, *Journal of Physical Chemistry*, **56** (1952), 784.
13. A. J. P. Martin, and R. L. M. Synge, *Biography Journal*, **35** (1941), 1358.
14. S. Masamune and J. M. Smith, *AIChE J.*, **10** (1964), 246.
15. S. Massmune and J. M. Smith, *AIChE J.*, **11** (1965), 34.
16. G. Taylor, *Proc. Roy. Soc. Lond.*, **A219** (1953), 186.
17. G. Taylor, *Prcc. Roy. Soc. Lond.*, **A225** (195), 473.
18. J. J. van Deempter, F. J. Zuiderweg and A. Klinkenberg, *Chem. Eng. Sci.*, **5** (1956), 271.
19. J. N. Wilson, *J. Amer. Chem. Soc.*, **62** (1940), 1583.