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THE HETP OF AN UNRETAINED COMPONENT OF FLUID FLOW IN A COILED ROUND PIPE

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SUMMARY

When Poiseuille flow occurs in an open-tubular curved pipe, the secondary currents created by centrifugal forces within the primary current cause a lowering of the HETP of the primary current for samples carried along.

An expression is developed for the first approximation of this effect, which is represented by a term proportional to the fourth power of the primary flow. The calculations are made for the less involved case of a circular pipe with retentionless walls, and serve to show that, while measurable effects can be expected for relatively high flow-rates, the effect is negligible in the case of the relatively slow flows of liquids at which optimal chromatographic separations are obtained.

INTRODUCTION

The height equivalent to a theoretical plate (HETP) is a useful concept in both gas and liquid chromatography because, when this HETP, dimensionally a length, is multiplied by the distance travelled by an injected sample, it gives the incremental variance of the spread of that sample which has occurred during that travel. The HETP of a sample which can be retained by the walls of an open-tubular column is somewhat higher than when its affinity for the retaining layer is absent, up to $\sqrt{11}$ times higher for walls with an infinite retaining power, which is the practical case in distillation processes. However, while the mathematical handling of the unretained sample can be readily extended to the case of retained samples, this extension would introduce additional manipulations which would burden uselessly a discussion aimed at the analysis of the effect of secondary currents, an analysis that is already tedious, even if without fundamental difficulties. That is why this study has been limited to the case of unretained samples, and has been limited also to the derivation of the first term of the presumably infinite series which would give with substantial rigor the reduction of the HETP of the sample due to secondary currents.

DISCUSSION

We consider a curved tubular column, that is a curved hollow pipe of circular cross-section and radius r_0 . The X axis is that of the pipe and the Y and Z axes,

normal to it and to each other, are oriented horizontally and vertically respectively. The pipe is curved downward within an X - Z plane with a radius of curvature r_1 , so that centrifugal forces due to the stream velocity are directed upward, in the Z direction. The stream velocity, v , is given at any point by the expression

$$v = 2v_0 \left(1 - \frac{Y^2 + Z^2}{r_0^2} \right) \quad (1)$$

where v_0 designates the average stream velocity in the X direction, so that the forces per unit volume are given by

$$f_x = 0, f_y = 0, f_z = \frac{\rho v^2}{r_1} = \frac{4\rho v_0^2}{r_1} \left(1 - \frac{Y^2 + Z^2}{r_0^2} \right)^2 \quad (2)$$

where ρ designates the specific weight of the fluid.

A first task will be the determination of the secondary flow due to the non-uniformity of f_z .

We note at the outset that if we can neglect the fluid compressibility the laplacian of the components v_y and v_z of this secondary flow must vanish, i.e.:

$$\frac{\partial v_y}{\partial Y} + \frac{\partial v_z}{\partial Z} = 0 \quad (3)$$

and we shall look for a velocity potential φ such that

$$v_y = \frac{\partial \varphi}{\partial Z}; v_z = -\frac{\partial \varphi}{\partial Y} \quad (4)$$

so that eqn. 3 shall be satisfied identically.

Next we consider the viscous forces which relate these velocity components to the tensions τ_y , τ_z respectively normal to the XZ and XY faces of a cube, and the shear tension τ tangential to these forces. We have, classically, with viscosity μ

$$\mu \left(\frac{\partial v_y}{\partial Y} - \frac{\partial v_z}{\partial Z} \right) = \tau_y - \tau_z \quad (5a)$$

and

$$\mu \left(\frac{\partial v_y}{\partial Z} + \frac{\partial v_z}{\partial Y} \right) = \tau \quad (5b)$$

while these tensions are related to f_y and f_z by

$$\frac{\partial \tau_y}{\partial Y} + \frac{\partial \tau}{\partial Z} + f_y = 0 \quad (6a)$$

and

$$\frac{\partial \tau_z}{\partial Z} + \frac{\partial \tau}{\partial Y} + f_z = 0 \quad (6b)$$

Eqns. 4 and 5 together give

$$2\mu \cdot \frac{\partial^2 \varphi}{\partial Y \partial Z} = \tau_Y - \tau_Z \tag{7a}$$

and

$$\mu \left(\frac{\partial^2 \varphi}{\partial Z^2} - \frac{\partial^2 \varphi}{\partial Y^2} \right) = \tau \tag{7b}$$

From eqn. 6 we deduce

$$\frac{\partial^2 (\tau_Y - \tau_Z)}{\partial Y \partial Z} + \frac{\partial^2 \tau}{\partial Z^2} - \frac{\partial^2 \tau}{\partial Y^2} + \frac{\partial f_Y}{\partial Z} - \frac{\partial f_Z}{\partial Y} = 0 \tag{8}$$

and, with eqn. 7

$$\mu \left(\frac{\partial^4 \varphi}{\partial Y^4} + \frac{\partial^4 \varphi}{\partial Z^4} \right) = \frac{\partial f_Z}{\partial Y} - \frac{\partial f_Y}{\partial Z}$$

or, since $f_Y = 0$

$$\frac{\partial^4 \varphi}{\partial Y^4} + \frac{\partial^4 \varphi}{\partial Z^4} = \frac{1}{\mu} \cdot \frac{\partial f_Z}{\partial Y} = \frac{16 \rho v_0^2}{\mu r_1} \cdot \frac{Y}{r_0^2} \cdot \left(\frac{Y^2 + Z^2}{r_0^2} - 1 \right) \tag{9}$$

It will be convenient to normalize eqn. 9 by writing

$$Y = r_0 y; Z = r_0 z \quad \text{and} \quad \varphi = \frac{\rho v_0^2 r_0^3}{525 \mu r_1} \cdot \psi \tag{10}$$

where the factor 1/525 was introduced to avoid fractional terms in the eventual expression for ψ .

We introduce further the boundary condition that the velocities vanish at the tube wall, where $y^2 + z^2 = 1$; i.e., we have for ψ

$$\frac{\partial^4 \psi}{\partial y^4} + \frac{\partial^4 \psi}{\partial z^4} = 8400 y (y^2 + z^2 - 1) \tag{11a}$$

and

$$\frac{\partial \psi}{\partial y} = \frac{\partial \psi}{\partial z} = 0 \quad \text{at} \quad y^2 + z^2 = 1 \tag{11b}$$

It can be verified by inspection that these three conditions are satisfied by

$$\psi = y (y^2 + z^2 - 1)^2 \cdot (9y^2 + 13z^2 - 39) \tag{12}$$

We must now calculate the HETP while taking into account the secondary flow with the normalized potential ψ . Toward this purpose we recall first that the

diffusion of a sample carried by a gas or a liquid can be represented by a convolution of elementary diffusion processes, and that the eventual result of an indefinite number of such convolutions can be represented by a gaussian distribution.

If we have a telegraph line, with continuously distributed series resistance r , and shunted capacitance c , the diffusion of any electrical charge placed on this line would be governed by the equation

$$\frac{1}{r} \cdot \frac{\partial^2 v}{\partial X^2} = c \cdot \frac{\partial v}{\partial t} \quad (13)$$

and we know that this equation would be satisfied by, e.g.

$$v = \frac{e^{-\frac{rcX^2}{4t}}}{\sqrt{t}} \quad (14)$$

Likewise, we shall postulate that the sample distribution after a certain time has become gaussian with respect to X , except of course that it has travelled a distance $v_0 t$ in that time, and that there is a shift $E(Y, Z)$ between the peaks of the gaussian distribution in the various locations within the pipe cross-section, the distributions near the pipe center, where travel is faster, leading the distributions near the pipe wall, and diffusing gradually toward the wall, while the lagging distributions near the wall diffuse eventually toward the pipe center to be picked up by the higher velocity of the stream. Mathematically, we are postulating a concentration of the form:

$$C = \frac{e^{-\frac{[X - E(Y, Z) - v_0 t]^2}{4kt}}}{\sqrt{t}} \quad (15)$$

where k represents the unknown dynamic diffusion constant of the sample, connected to the HETP, h , by the relation

$$\text{Variance} = 2 k t = h L = h v_0 t$$

or

$$h = \frac{2k}{v_0} \quad (16)$$

where L is the distance travelled in time t .

We know that the concentration obeys the law

$$\frac{dC}{dt} - DA^2C = 0 \quad (17)$$

where D designates the (static) diffusion constant of the sample and in which it is to be understood that the time derivative is the absolute derivative, measured as one goes along with the sample. This absolute time derivative can be replaced by its expression in terms of the time derivative at any one point, $\partial C/\partial t$, and the concen-

tration gradients and velocity components at that point, and we re-write eqn. 17 thus:

$$\frac{\partial C}{\partial t} + v_x \cdot \frac{\partial C}{\partial X} + v_y \cdot \frac{\partial C}{\partial Y} + v_z \cdot \frac{\partial C}{\partial Z} - D \left(\frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2} + \frac{\partial^2 C}{\partial Z^2} \right) = 0 \tag{18}$$

When its expression from eqn. 15 is substituted for C in eqn. 18, fourteen terms are obtained, which come in three groups, each of which is equated to zero to satisfy eqn. 18. A first group of four terms share the coefficient

$$\frac{[X - E(Y, Z) - v_0 t]^2 e^{-\frac{[X - E(Y, Z) - v_0 t]^2}{4kt}}}{t^2 \sqrt{t}}$$

and when this group is equated to zero, the common coefficient can be dropped and we obtain the relation

$$k = D \left\{ 1 + \left[\frac{\partial E(Y, Z)}{\partial Y} \right]^2 + \left[\frac{\partial E(Y, Z)}{\partial Z} \right]^2 \right\} \tag{19}$$

A second group of six terms share the common coefficient

$$\frac{[X - E(Y, Z) - v_0 t] e^{-\frac{[X - E(Y, Z) - v_0 t]^2}{4kt}}}{t \sqrt{t}}$$

and when this group is equated to zero, this common coefficient can again be dropped and we obtain the relation

$$\begin{aligned} \frac{\partial^2 E(Y, Z)}{\partial Y^2} + \frac{\partial^2 E(Y, Z)}{\partial Z^2} &= \frac{v_0}{D} \left(2 \cdot \frac{Y^2 + Z^2}{r_0^2} - 1 \right) + \\ \frac{1}{D} \left[\frac{\partial E(Y, Z)}{\partial Y} \cdot v_y + \frac{\partial E(Y, Z)}{\partial Z} \cdot v_z \right] &= \frac{v_0}{D} \left(2 \cdot \frac{Y^2 + Z^2}{r_0^2} - 1 \right) + \\ \frac{1}{D} \left[\frac{\partial E(Y, Z)}{\partial Y} \cdot \frac{\partial \varphi}{\partial Z} - \frac{\partial E(Y, Z)}{\partial Z} \cdot \frac{\partial \varphi}{\partial Y} \right] & \end{aligned} \tag{20}$$

As to the remaining group of four terms, when equated to zero, it yields an expression identical to eqn. 10.

The general method followed from here on consists in first determining a suitable approximation for $E(Y, Z)$ from eqn. 20, then replacing the two squared derivatives of E in eqn. 19 by their average taken across the entire pipe cross-section. The physical meaning of these squared expressions is analogous to the $(1/r)(v/x)^2$ dissipation of energy in a telegraph cable. In the case of fluid flow in pipes it corresponds to the increase of entropy implied by the diffusion of the sample from regions of high concentration to regions of lower concentration, and the

approximation which consists in replacing these terms in eqn. 19 by their average is increasingly accurate for increasingly extended spreads of the gaussian distributions of the samples as the flow proceeds*.

The rather laborious task of solving eqn. 20 can be eased by normalizing $E(Y, Z)$, as was done previously for φ , and writing

$$E(Y, Z) = \frac{v_0 r_0^2}{D} \cdot e(y, z) = \frac{v_0 r_0^2}{D} \cdot e \quad (21)$$

This last expression, together with eqn. 10, permits eqn. 20 to be re-written thus:

$$\frac{\partial^2 e}{\partial y^2} + \frac{\partial^2 e}{\partial z^2} = 2(y^2 + z^2 - 1) + \sigma \left(\frac{\partial e}{\partial y} \cdot \frac{\partial \psi}{\partial z} - \frac{\partial e}{\partial z} \cdot \frac{\partial \psi}{\partial y} \right) \quad (22)$$

where σ is a dimensionless quantity:

$$\sigma = \frac{\rho v_0^2 r_0^3}{525 D \mu r_1} \quad (23)$$

and where ψ is defined by eqn. 12 as formerly.

As we shall be interested in the cases where σ is rather small, a sufficient approximation for the solution of eqn. 22 can be obtained by writing

$$e = e_0 + \sigma e_1 + \sigma^2 e_2 \quad (24)$$

e_0 , e_1 and e_2 are then given by the successive solutions of

$$\frac{\partial e_0}{\partial y^2} + \frac{\partial^2 e_0}{\partial z^2} = 2(y^2 + z^2 - 1) \quad (25a)$$

$$\frac{\partial e_1}{\partial y^2} + \frac{\partial e_1}{\partial z^2} = \frac{\partial e_0}{\partial y} \cdot \frac{\partial \psi}{\partial z} - \frac{\partial e_0}{\partial z} \cdot \frac{\partial \psi}{\partial y} \quad (25b)$$

$$\frac{\partial^2 e_2}{\partial y^2} + \frac{\partial^2 e_2}{\partial z^2} = \frac{\partial e_1}{\partial y} \cdot \frac{\partial \psi}{\partial z} - \frac{\partial e_1}{\partial z} \cdot \frac{\partial \psi}{\partial y} \quad (25c)$$

and e as given by eqn. 24 will be correct to within terms in σ^3 , etc.

* At the 1964 International Gas Chromatography Symposium in Brighton¹, Golay pointed out what appeared to be a Maxwell Demon-like paradox in chromatography, namely that with increasingly large separation times vanishingly small energies were required to separate different kinds of molecules, thereby decreasing the entropy of the system with vanishingly small effort. The refutation of this paradox appears to be that while in truth the separation of different molecules spells a decrease in entropy, this decrease is obtained at the expense of the higher increase of entropy which takes place as the various groups of molecules spread in the carrier fluid while separating from each other, a spread which is gratefully accepted for the sake of the information revealed by the essential separation of the different groups. This constitutes a situation in which the concepts of the entropy of the information theorist and the entropy of the thermodynamicist become closely connected.

To eqn. 25 will be added the boundary condition that the gradient of e normal to the pipe wall, which has no retention capacity for the sample molecules, also vanishes, *i.e.*

$$y \cdot \frac{\partial e}{\partial y} + z \cdot \frac{\partial e}{\partial z} = 0 \quad \text{for } y^2 + z^2 = 1 \tag{26}$$

It can be verified by inspection that eqn. 25a and 26 are satisfied by

$$e_0 = \frac{1}{8}(y^2 + z^2)(y^2 + z^2 - 2) \tag{27}$$

with

$$\frac{\partial e_0}{\partial y} = \frac{1}{2}y(y^2 + z^2 - 1) \tag{28a}$$

and

$$\frac{\partial e_0}{\partial z} = \frac{1}{2}z(y^2 + z^2 - 1) \tag{28b}$$

The solutions for e_1 and e_2 from eqns. 25b and 25c, with the condition 26 and with ψ given by eqn. 12, become increasingly laborious, but without difficulty. The solution for e_1 is given by the eleventh degree odd polynomial defined by

$$3360e_1 = \sum_{i=0}^5 \sum_{j=0}^i (-1)^i A_{ij} y^{2(i-j)} z^{2j+1} \tag{29}$$

where the coefficient of e_1 is designed to insure that all A_{ij} values are integral numbers which are given in Table I.

TABLE I
VALUES OF A_{ij}

i	j					
	0	1	2	3	4	5
0	4634					
1	7866	8298				
2	7945	17150	9205			
3	4011	13545	15057	5523		
4	819	4116	7434	5796	1659	
5	5	205	770	1130	745	185

When the derivatives of e_1 obtained from eqn. 29 and Table I are substituted in eqn. 25c, that relation, together with eqn. 26 serves to calculate e_2 , which is then given by a polynomial of the form

$$55440e_2 = \sum_{i=1}^9 \sum_{j=0}^i (-1)^i a_{ij} y^{2(i-j)} z^{2j} \tag{30}$$

TABLE II
VALUES OF a_{ij}

i	j	0	1	2	3	4	5	6	7	8	9
1	2943457264	2066267456									
2	5319159069	10115440146	4747720509								
3	5606223690	18015232770	19187363430	6780966510							
4	4054621098	18523865976	31332475020	23330654424	6467424282						
5	2089775358	12368734290	28679079660	32767493220	18523807830	4156435338					
6	701345337	5204545038	15519981015	24114159300	20747862135	9418517262	1278033113				
7	134501169	1271481981	4778909289	9563786925	11188153515	7723126719	2929777851	472946199			
8	10973885	152903640	746562460	1894548040	2857758750	2679713960	1543340540	502674360	71204365		
9	16925	6142275	45414900	149005500	282154950	337387050	261132900	127881900	36253125	4556075	

where again the factor 55440 serves to insure that the α_{ij} values are integral numbers, which are given in Table II.

With the values thus obtained for e_0, e_1 and e_2 , we are in a position to evaluate the average value of the constant term and of the term in σ^2 of $(\partial e/\partial y^2 + \partial e/\partial z)^2$ taken over the pipe cross-section. This value will be, according to eqn. 24

$$\overline{\left(\frac{\partial e}{\partial y}\right)^2 + \left(\frac{\partial e}{\partial z}\right)^2} = \overline{\left(\frac{\partial e_0}{\partial y}\right)^2 + \left(\frac{\partial e_0}{\partial z}\right)^2} + \sigma^2 \left[\overline{\left(\frac{\partial e_1}{\partial y}\right)^2 + \left(\frac{\partial e_1}{\partial z}\right)^2} + 2 \cdot \overline{\frac{\partial e_0}{\partial y} \cdot \frac{\partial e_2}{\partial y}} + 2 \cdot \overline{\frac{\partial e_0}{\partial z} \cdot \frac{\partial e_2}{\partial z}} \right] \quad (31)$$

as the term $2\sigma(\partial e_0/\partial y \cdot \partial e_1/\partial y + \partial e_0/\partial z \cdot \partial e_1/\partial z)$ vanishes because e_0 and e_1 are of different parity. An expression giving the average value of $y^{2m}z^{2n}$ over the pipe cross-section is obtained by changing over to polar coordinates:

$$y = r \cos\varphi; z = r \sin\varphi$$

and we have

$$\begin{aligned} \overline{y^{2m}z^{2n}} &= \frac{1}{\pi} \iint y^{2m}z^{2n} dydz = \frac{1}{\pi} \iint r^{(2m+2n+1)} \cos^{2m}\varphi \sin^{2n}\varphi drd\varphi = \\ &= \frac{(2m)!(2n)!}{2^{(2m+2n)}m!n!(m+n+1)!}; \quad x^2 + y^2 < 1 \end{aligned} \quad (32)$$

This expression serves to calculate the right-hand side of eqn. 31 and we obtain

$$\overline{\left(\frac{\partial e_0}{\partial y}\right)^2 + \left(\frac{\partial e_0}{\partial z}\right)^2} = \frac{1}{48} \quad (33a)$$

$$\overline{\left(\frac{\partial e_1}{\partial y}\right)^2 + \left(\frac{\partial e_1}{\partial z}\right)^2} = \frac{1}{3360^2} \cdot \frac{2^3}{11} \cdot 5959687 \quad (33b)$$

and

$$2 \left(\overline{\frac{\partial e_0}{\partial y} \cdot \frac{\partial e_2}{\partial y}} + \overline{\frac{\partial e_0}{\partial z} \cdot \frac{\partial e_2}{\partial z}} \right) = - \frac{1}{3360 \cdot 55440} \cdot 2^3 \cdot 3 \cdot 5959687 \quad (33c)$$

Hence for the left-hand side of eqn. 31 we have

$$\overline{\left(\frac{\partial e}{\partial y}\right)^2 + \left(\frac{\partial e}{\partial z}\right)^2} \approx \frac{1}{48} - 0.3839\sigma^2 = \frac{1}{48} (1 - 18.43\sigma^2) \quad (34)$$

and with eqns. 10, 19 and 21 for the diffusion constant, k :

$$k = D + \frac{v_c^2 r_0^2}{48D} (1 - 18.43\sigma^2) \quad (35)$$

Three remarks will be made about eqns. 33 and 35.

Firstly, for vanishingly small σ , eqn. 35 agrees, as it should, with the results of Westhaver² and Taylor³.

Secondly, the remarkable similarity between the right-hand sides of eqns. 33b and 33c, the second being, in absolute value, equal to exactly twice the first, suggest the existence of a generating function which, if found, could help derive the results above more expeditiously and, conceivably, generalize them to include higher even powers of σ . As for the prime number 5959687 which appears in both, no meaningful significance was found for it.

Thirdly, the right-hand side of eqn. indicates that no appreciable effect on k can be expected unless and until σ acquires values higher than 0.1.

In order to interpret this, σ will be re-written:

$$\sigma = \frac{48}{525} \cdot R_1 R_2^2 R_3 \approx 0.1 R_1 R_2^2 R_3 \quad (36)$$

where the three dimensionless ratios R_1 , R_2 and R_3 stand for the following respective quantities:

$$R_1 = \frac{D\rho}{\mu} \quad (37)$$

R_1 is the ratio of the diffusion constant D over the quantity μ/ρ , which has also the dimensions of a diffusion constant. In the case of gases, both quantities are of the order of magnitude of the product of the gas molecules' velocities by their mean free path, that is, for air, e.g., of the order of $0.3 \text{ cm}^2 \cdot \text{sec}^{-1}$. On the other hand, in the case of liquids, D can vary in the range from 10^{-5} to $10^{-7} \text{ cm}^2 \text{ sec}^{-1}$, while, in the case of water, e.g., μ/ρ is of the order of $0.01 \text{ cm}^2 \text{ sec}^{-1}$; i.e., the ratio R_1 can be expected to be found in the range from 10^{-3} to 10^{-5} .

$$R_2 = \frac{v_0}{v_{\text{opt}}} \quad (38)$$

R_2 is the ratio of the actual average stream velocity over the optimal velocity for minimal HETP, i.e., the velocity which minimizes the quantity:

$$h = 2 \cdot \frac{D}{v_0} + \frac{v_0 r_0^2}{24D}$$

and which is equal to

$$v_{\text{opt}} = \sqrt{48} \cdot \frac{D}{r_0} \quad \text{or} \quad v_{\text{opt}}^2 = 48 \cdot \frac{D^2}{r_0^2}$$

so that

$$48 R_2^2 = 48 \cdot \frac{v_0^2}{v_{\text{opt}}^2} = \frac{v_0^2 r_0^2}{D^2} \quad (39)$$

and finally:

$$R_3 = \frac{r_0}{r_1} \quad (40)$$

R_0 is the ratio of the pipe's inner radius to its radius of curvature, a quantity which can be expected in the range of 1/30 for cold-formed materials such as stainless steel, and possibly 1/10 in the case of glass capillaries tightly coiled while hot.

It will be readily verified that the right-hand side of eqn. 36 indeed represents the value of σ with the three R ratios as defined.

Since, therefore, values of σ of the order of 0.1 should be had before the secondary flow begins to affect the HETP, that is, since the product $R_1 R_2^2 R_3$ should be of the order of unity or larger, and since the product $R_1 R_3$ is, in the case of liquids, in the range 10^{-4} – 10^{-6} at best, secondary flow effects cannot be expected for stream velocities less than two or more orders of magnitude higher than the velocities which are optimal for liquid chromatographic separations.

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