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THEORY OF OPEN-TUBE CHROMATOGRAPHY: AN EXACT PROOF OF GOLAY'S EQUATIONS

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SUMMARY

A proof is given of Golay's equations for chromatography in an uncoated (or thinly coated), open-tubular column. The new derivation is exact and it is thus shown that it is not necessary to neglect some terms in the appropriate equations, as has been done in previous proofs. Furthermore, the proof is given for the situation where the rate of adsorption on to and desorption from the tube walls is not considered to be infinitely fast as was previously discussed. The effect of comparatively slow equilibration of material between the flowing medium and the tube wall is to increase the width of a peak, but not to change the average degree of retention.

INTRODUCTION

The theory of chromatography in an open tube was considered by Golay in 1958¹ and his proof is reproduced in many textbooks on chromatography. The problem is a special case of the theory of dispersion of material in a medium flowing in a tube which has been studied for a variety of circumstances; originally by Westhaver² for the concentration of a potassium isotope by countercurrent electromigration and later by a number of authors whose papers have been reviewed recently³.

In Golay's treatment, the appropriate differential equation and boundary condition are manipulated and it is then asserted that certain terms are comparatively small and they are therefore neglected. While investigating a related but more complex problem⁴ (the dispersion and chromatography of hydrogen atoms in a flown gas⁵) it has been found that it is not necessary to make these approximations and that Golay's ultimate equations can be proved exactly. This paper sets out the exact proof with one additional complication. In the proof below we do not assume, as did Golay, that the equilibration of material between the carrier and the stationary walls is instantaneous, but allow it to occur at a finite rate. This adds an extra term to Golay's equation for the peak width, which tends to zero as the rate of equilibration tends to infinity.

The equation which governs this problem, and from which Golay begins his treatment, is the general diffusion equation

$$\frac{\partial f}{\partial t} = \nabla \cdot (D \nabla f) - v \cdot \nabla f, \quad (1)$$

where ∇ is the differential operator, f is the local and instantaneous concentration of the material being transported, D is the diffusion coefficient, and v the velocity of the medium at the particular point in the column. In the present paper, as in Golay's treatment, we consider a circular column in which there is streamline (Pouisseulle or laminar) flow with no "slip" of the boundary layer along the tube wall.

We also assume, as did Golay, that the pressure is constant along the column (*i.e.* the gas viscosity coefficient is tending to zero) and consequently the diffusion coefficient and average velocity of the carrier is constant. This will certainly not be the case in open-tube chromatography, where a drop of one atmosphere pressure across a long column of 100 m is common. But, because the fractional drop in pressure over a one metre length of the column is small, it is believed that the results for a constant pressure model can be applied to the situation of a pressure drop with good approximation.

The column is a cylinder, and the cylindrical coordinates r , θ and z are used. It is assumed from the outset that the concentration of material is independent of the azimuthal angle θ . It can be shown⁴ that, if this is not the case initially it will rapidly become so. Thus, $f \equiv f(r, z, t)$. In the new coordinates and making all the assumptions given above eqn. 1 becomes

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial z^2} + D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial f}{\partial r} \right) - 2v_o \left(1 - \frac{r^2}{r_o^2} \right) \frac{\partial f}{\partial z}, \quad (2)$$

where r_o is the column radius, and v_o is the average velocity of the carrier. The expression $2v_o [1 - (r^2/r_o^2)]$ gives the variation of velocity across the column from zero at the walls to $2v_o$ at the centre.

This differential equation has to be solved in conjunction with a boundary condition which for Golay's treatment, assuming rapid equilibration, was

$$-D \frac{\partial f}{\partial r} = \frac{r_o k'}{2} \frac{\partial f}{\partial t}, \quad (3)$$

where k' is a constant which was assumed to be the ratio of the amount of material on the tube wall to that in the carrier. Golay solved eqn. 2 with the condition given in eqn. 3 by manipulating the equations and using his insight into the problems to neglect certain terms, which he asserted were small. He finally obtained the correct results that the average velocity (v_{av}) of the material is given by

$$v_{av} = \frac{v_o}{1 + k'} \quad (4)$$

and the rate of increase of the mean-squared width of the peak of material is equal to

$$\frac{2D}{1 + k'} + \frac{r_o^2 v_o^2}{24D} \cdot \frac{1 + 6k' + 1(k')^2}{(1 + k')^3} \quad (5)$$

BOUNDARY CONDITION FOR FINITE RATES OF EQUILIBRATION

It is first necessary to obtain the boundary condition that is appropriate when adsorption and desorption are not fast. Let k_a be the rate of adsorption per unit area per unit concentration in the carrier near the surface, k_d the rate of desorption per unit area per unit surface concentration, and f_s the surface concentration. By Fick's law the flux of molecules near the surface is equal to $-D(\partial f/\partial r)$ and so at $r = r_0$

$$-D \frac{\partial f}{\partial r} = k_a f - k_d f_s. \quad (6)$$

The change of surface concentration will be equal to the same quantity;

$$\frac{\partial f_s}{\partial t} = k_a f - k_d f_s \quad (7)$$

Elimination of f_s from eqns. 6 and 7 gives

$$D \frac{\partial^2 f}{\partial r \partial t} + k_a \frac{\partial f}{\partial t} + k_d D \frac{\partial f}{\partial r} = 0. \quad (8)$$

This is the boundary condition that we seek. As will be shown later this boundary condition becomes identical to that used in Golay's derivation and eqn. 8 becomes eqn. 3 as k_a and k_d become large in the rapid equilibration limit.

EQUATIONS FOR THE MOMENTS

Eqn. 2 is difficult to solve because the variables are not separable. We therefore turn to the method of moments, first used by Aris⁶ in this context for a similar but simpler problem. We define the p th moment of the distribution of the injected material, c_p , by

$$c_p(r, t) = \int_{-\infty}^{\infty} f(r, z, t) z^p dz \quad (9)$$

We will be interested in the zeroth, first and second moment given by $p = 0, 1$ and 2 in eqn. 9. These will respectively give information about the total amount of material, its average flow-rate, and its average width. It should be noted that the moments, c_p , depend on the radial coordinate r . They refer to the distribution of material in longitudinal elemental filaments inside the column.

We also define moments averaged over the column cross-section, m_p , by

$$m_p(t) = 2\pi \int_0^r c_p(r, t) r dr \quad (10)$$

m_o will be the total amount of material in the column, which will expect to be constant. m_1/m_o will give the average distance of the material along the tube and will give information about chromatographic retention. m_2/m_o will give the mean-squared distance of the material from the beginning of the column and thus $[m_2/m_o - (m_1/m_o)^2]$ will give the mean-squared distance of the material from its average position, *i.e.* the mean-squared width of the peak.

The calculation is carried out as follows. Equations are obtained for the moments c_p and solutions for c_o , c_1 and c_2 are found. The moments m_o , m_1 and m_2 are then calculated from the solutions for c_o , c_1 and c_2 . To obtain equations for the moment c_p , both the differential eqn. 2 and its boundary condition (eqn. 8) are multiplied by $z^p dz$ and integrated from $-\infty$ to $+\infty$ to give, respectively

$$\frac{\partial c_p}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_p}{\partial r} \right) + 2v_o \left(1 - \frac{r^2}{r_o^2} \right) p c_{p-1} + D p (p-1) c_{p-2} \quad (11)$$

and

$$D \frac{\partial^2 c_p}{\partial r^2} + k_a \frac{\partial c_p}{\partial t} + k_d \frac{\partial c_p}{\partial r} = 0 \quad (12)$$

Eqn. 11 was obtained using integration by parts and also assuming that $f(r, z, t) \rightarrow 0$ as $z \rightarrow \pm \infty$. Equation 11 is a general equation for the moments c_p , which must be solved in conjunction with its boundary condition¹³. The most general solutions are quite complex, but a full analysis shows that only parts of the solutions are important even a very short time after injection of the material on to the column⁵. These are the solutions that are practically important and that are given below.

SOLUTIONS FOR THE MOMENTS c_o AND m_o

The equation for c_o is (eqn. 11)

$$\frac{\partial c_o}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial c_o}{\partial r} \quad (13)$$

and its boundary condition (eqn. 12), at $r = r_o$, is

$$D \frac{\partial^2 c_o}{\partial r^2} + k_a \frac{\partial c_o}{\partial t} + D k_d \frac{\partial c_o}{\partial r} = 0 \quad (14)$$

These equations are satisfied by

$$c_o = A \quad (15)$$

where A is a constant, independent of r and t . This shows that there is a solution where the total amount of material in a longitudinal filament in the open-tube column is constant and the same in all filaments of the same cross-sectional area. There is

therefore a steady-state solution where there is no net radial flow of material (although there is in fact radial flow at particular points in the column which averages to zero).

Application of eqn. 10 to the solution (eqn. 15) gives also

$$m_o = \pi r_o^2 A \quad (16)$$

and m_o , the total amount of material in the tube, is also as expected, a constant, independent of time.

SOLUTIONS FOR THE MOMENTS c_1 AND m_1

The equation for c_1 , obtained from eqn. 11 after substituting for c_o , is

$$\frac{\partial c_1}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_1}{\partial r} \right) + 2Av_o \left(1 - \frac{r^2}{r_o^2} \right) \quad (17)$$

and its boundary condition (eqn. 12), at $r = r_o$, is

$$D \frac{\partial^2 c_1}{\partial r \partial t} + k_a \frac{\partial c_1}{\partial t} + Dk_d \frac{\partial c_1}{\partial r} = 0 \quad (18)$$

As can be shown by substituting into both equations, a solution for c_1 is

$$c_1 = B + A \frac{v_o r_o^2}{8D} \left[\frac{r^4}{r_o^4} - 2 \left(\frac{1 + 2k'}{1 + k'} \right) \frac{r^2}{r_o^2} \right] + A \frac{v_o}{1 + k'} t \quad (19)$$

where B is another constant and k' is defined by

$$k' = 2k_a/r_o k_d \quad (20)$$

We shall show later that k' is identical to the normal chromatographic retention coefficient.

The moment m_1 can then be calculated using eqn. 10 to be

$$\frac{m_1(t)}{\pi r_o^2} = B - \frac{Av_o r_o^2}{24D} \cdot \frac{2 + 5k'}{1 + k'} + \frac{Av_o}{1 + k'} t \quad (21)$$

Using the boundary condition that $m_1 = 0$ at $t = 0$, then

$$B = \frac{Av_o r_o^2}{24D} \cdot \frac{2 + 5k'}{1 + k'} \quad (22)$$

and

$$m_1(t) = \pi r_o^2 \frac{Av_o}{1 + k'} t \quad (23)$$

and hence

$$m_1(t)/m_o = \frac{v_o}{1 + k'} t \quad (24)$$

as obtained by Golay. Using this value of B , the equation for c_1 becomes

$$c_1 = \frac{Av_o r_o^2}{24D} \left[3 \frac{r^4}{r_o^4} - 6 \left(\frac{1 + 2k'}{1 + k'} \right) \frac{r^2}{r_o^2} + \left(\frac{2 + 5k'}{1 + k'} \right) \right] + \frac{Av_o}{1 + k'} t \quad (25)$$

SOLUTIONS FOR THE MOMENTS c_2 AND m_2

The equation for c_2 , obtained from (eqn. 11) after substituting for c_o and c_1 , is

$$\begin{aligned} \frac{\partial c_2}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial c_2}{\partial r} + \\ + 4v_o \left(1 - \frac{r^2}{r_o^2} \right) \left\{ \frac{Av_o r_o^2}{24D} \left[3 \frac{r^4}{r_o^4} - 6 \left(\frac{1 + 2k'}{1 + k'} \right) \frac{r^2}{r_o^2} + \frac{2 + 5k'}{1 + k'} \right] + \frac{Av_o}{1 + k'} t \right\} + 2AD \end{aligned} \quad (26)$$

and its boundary condition, at $r = r_o$, is

$$D \frac{\partial^2 c_2}{\partial r \partial t} + k_a \frac{\partial c_2}{\partial t} + D k_d \frac{\partial c_2}{\partial r} = 0 \quad (27)$$

As can be shown by substitution, a solution for c_2 is the following

$$\begin{aligned} c_2 = C + A \left\{ \left(-\frac{1}{2} \frac{k'}{1+k'} + \frac{v_o^2}{2Dk_d} \cdot \frac{k'}{(1+k')^3} - \frac{v_o^2 r_o^2}{96D^2} \cdot \frac{3 + 16k' + 27(k')^2 + 20(k')^3}{(1+k')^3} \right) r^2 + \right. \\ + \left(\frac{v_o^2}{96D^2} \cdot \frac{5 + 19k' + 17(k')^2}{(1+k')^2} \right) r^4 - \left(\frac{5v_o^2}{144D^2 r_p^2} \cdot \frac{1 + 2k'}{1+k'} \right) r^6 + \left(\frac{v_o^2}{128r_o^4 D^2} \right) r^8 + \\ + \left(\frac{2D}{1+k'} + \frac{2v_o^2}{k_d} \cdot \frac{k'}{(1+k')^3} + \frac{r_o^2 v_o^2}{24D} \cdot \frac{5 + 20k' + 21k'^2}{(1+k')^3} \right) t - \\ \left. - \left(\frac{v_o^2}{2D} \cdot \frac{1 + 2k'}{(1+k')^2} \right) r^2 t + \left(\frac{v_o^2}{4D r_o^2} \cdot \frac{1}{1+k'} \right) r^4 t + \frac{v_o^2}{(1+k')^2} t^2 \right\} \end{aligned} \quad (28)$$

This is a complex function of both r and t , but m_2 can be calculated from it using eqn. 10 to be

$$m_2(t) - m_2(o) = \pi r_o^2 A \left[\frac{2D}{1+k'} + \frac{2v_o^2}{k_d} \cdot \frac{k'}{(1+k')^3} + \frac{r_o^2 v_o^2}{24D} \cdot \frac{1 + 6k' + 11(k')^2}{(1+k')^3} \right] t + \frac{Av_o^2}{(1+k')^2} t^2 \quad (29)$$

In this equation, all the constants independent of time have been lumped together in $m_2(0)$, the second moment of the peak when injected. The quantity $m_2/m_0 - (m_1/m_0)^2$, which gives the mean squared width of the pulse is thus given by its initial value plus the quantity

$$\left[\frac{2D}{1+k'} + \frac{2v_o^2}{k_d} \cdot \frac{k'}{(1+k')^3} + \frac{r_o^2 v_o^2}{24D} \cdot \frac{1+6k'+11(k')^2}{(1+k')^3} \right] t \tag{31}$$

Of the three terms in the square brackets, the first and last are identical to those obtained by Golay and given by eqn. 5.

THE CHROMATOGRAPHIC RETENTION COEFFICIENT, k'

So far the quantity k' has been defined by eqn. 20 in terms of k_a and k_d . In this section it will be proved that in a chromatography column k' is equal to the ratio of the amount of material adsorbed on the walls to that in the carrier. For a stationary gas in a closed tube, which has reached equilibrium it is easy to see that this is the case. The concentration will be uniform throughout the tube and the rates of adsorption will be equal at equilibrium and

$$k_d f = k_a f_s \tag{31}$$

In a column of length l the ratio of the total amount of material on the wall to that in the gas will be given by

$$2\pi r_o l f_s / \pi r^2 l f \tag{32}$$

which from eqns. 31 and 20 is equal to k' .

For a moving carrier we need to investigate the surface concentration as a function of z and t . It is given by eqn. 6 as

$$f_s = \frac{k_a}{k_d} f(r_o) - \frac{D}{k_d} \left(\frac{\partial f}{\partial r} \right)_{r=r_o} \tag{33}$$

Multiplying by dz and integrating between $\pm \infty$ gives

$$\int_{-\infty}^{\infty} f_s(z,t) dz = \frac{k_a}{k_d} c_o(r_o,t) - \frac{D}{k_d} \left[\frac{\partial f}{\partial r} \right]_{r=r_o} \tag{34}$$

The total amount of material on the surface is therefore given by

$$2\pi r_o \int_{-\infty}^{\infty} f_s(z,t) dz = 2\pi r_o \frac{k_a}{k_d} A \tag{35}$$

since $c_o = A$ is a constant. The ratio of this to the total amount of material in the carrier, m_o , (given by eqn. 16) is therefore $2k_a/r_o k_d = k'$, in a moving carrier also.

DISCUSSION

The equations for open-tube chromatography at constant pressure have been solved without approximation. The solution given is not the most general one, but it has been shown elsewhere⁴ that it is the only solution that is stable. The final expressions obtained both for the rate of elution and for the dispersion of material are basically those given correctly some time ago by Golay using an approximation method.

In this treatment, however, it has not been assumed that the rate of equilibration of material between the carrier and the surface is infinitely rapid. This has been found not to affect the degree of chromatographic retention, but increases the rate of dispersion (or spreading) of the peak. The rate of dispersion is given by eqn. 31 and contains three terms. The first, $2D/(1 + k')$, arises from longitudinal diffusion. The third term,

$$\frac{r_o^2 v_o^2}{24D} \cdot \frac{1 + 6k' + 11(k')^2}{(1 + k')^3} \quad (36)$$

represents dispersion due to the variation of velocity across the column, which is reduced by radial diffusion. The second term is a new one due to the finite rate of adsorption and is equal to

$$\frac{2v_o^2}{k_d} \cdot \frac{k'}{(1 + k')^3} = \frac{v_o^2 r_o}{k_a} \cdot \frac{(k')^2}{(1 + k')^3} \quad (37)$$

The effect arises from the variance of the time spent by molecules of the material on the surface. The more rapid absorption and desorption is for a given k' , the more times a molecule absorbs and desorbs as it passes through the column, and the closer is the time spent by that molecule on the surface to the average. Thus for rapid equilibration the term in eqn. 37 will disappear and eqn. 31 will resemble Golay's original expression (eqn. 5). At the same time the boundary condition given in eqn. 8 will reduce to Golay's boundary condition (eqn. 3).

Finally, it was shown that the ratio of the total amounts of material on the surface to that in the carrier is given by

$$k' = 2k_a/r_o k_d$$

for a moving carrier where k_a and k_d , the rate constants for adsorption and desorption, are defined in the section boundary condition for finite rates of equilibrium. This is in spite of the fact that the longitudinal distribution in the carrier varies with the radial parameter and is, in general, different again from that on the surface.

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REFERENCES

- 1 M. J. E. Golay, in D. H. Desty (Editor), *Gas Chromatography*, Butterworths, London, 1958, pp. 36–55.
- 2 J. W. Westhaver, *J. Res. Nat. Bur. Stand.*, 38 (1947) 169–183.
- 3 R. Aris, in W. E. Stewart, W. H. Harmon and C. C. Conley (Editors), *Dynamics and Modelling of Reactive Systems*, Academic Press, New York, 1980, pp. 1–35.
- 4 T. Boddington and A. A. Clifford, *Proc. R. Soc. London*, A389 (1983) 179–196.
- 5 A. A. Clifford, P. Gray, R. S. Mason and J. I. Waddicor, *Faraday Disc. R. Soc. Chem.*, 15 (1980) 155–160.
- 6 R. Aris, *Proc. R. Soc. London*, A235 (1956) 67–77.