

CHROM. 7820

MOMENT ANALYSIS OF NON-LINEAR GAS CHROMATOGRAPHY BY COMPUTER SIMULATION

KIYOSHI YAMAOKA and TERUMICHI NAKAGAWA

Faculty of Pharmaceutical Sciences, Kyoto University, Kyoto (Japan)

(Received June 24th, 1974)

SUMMARY

Solute retention and column efficiencies for non-linear gas chromatography are discussed from the viewpoint of the statistical moments. Non-linearity of the distribution isotherm is reflected in the material-balance equation according to plate theory, and the solution for the equation required to calculate the statistical moments is obtained by a numerical integration of the system. The Runge–Kutta–Gill method is used for the computer simulation because of its good stability and convergence against the simple finite-difference approximation for a partial differential equation. The time interval, Δt , for the numerical integration is chosen by comparison with the analytical solution of a linear chromatographic system, then applied to the computer simulation. From the results thus obtained for the statistical moments, the effects of the non-linearity of the distribution isotherm on solute retention and column efficiency are discussed.

INTRODUCTION

It is important in analytical discussions on a chromatographic system to know whether or not the system is described by a linear material-balance equation. Linear chromatography, in which the distribution isotherm is of the Henry type and the carrier-gas flow-rate is independent of gas-phase solute concentration, has been analytically treated^{1,2} by the effective use of a convolution integral and a Laplace transform. Also, equations for the statistical moments of the breakthrough curve have been successfully developed for various types of linear chromatography^{3–10} with or without ideal properties and instantaneous equilibrium. On the other hand, it is so complicated and difficult to obtain the analytical solution for a non-linear material-balance equation, that quantitative explanations with use of statistical moments are not given to non-linear chromatographic problems. DeVault¹¹, dealing with a non-linear ideal and instantaneous equilibrium chromatography with a rectangular solute input, and Houghton¹², followed by Haarhoff *et al.*¹³ (who reduced the non-linear material balance to a parabolic equation), have explained the concentration profile of a non-linear chromatographic curve without making use of statistical moments. The analytical solutions described in those

papers, however, are too complicated to permit calculation of the plate height or even the retention time. Another way to tackle the problems of non-linear chromatography involves use of a large-scale electronic computer, which can carry out the numerical integration of such a system. Computer simulation has been used in two ways; in one, based on the so-called rate theory, the material balance is described by partial differential equations, and in the other, based on the plate theory, it is described by difference differential equations. Funk and Houghton¹⁴, and Dunckhorst and Houghton¹⁵, according to the first way, and Sakodinsky *et al.*¹⁶ according to the second, have obtained theoretical chromatograms incorporating the effect of non-linearity of the distribution isotherm. Their results were reasonable enough to explain the experimental trends of non-linear chromatography, but unsatisfactory for quantitatively expressing the column efficiencies, because no account was taken of the statistical moments that give more detailed information about non-linearity effects. This paper presents an attempt to interpret profiles of solute retention and column efficiency with respect to the non-linear distribution isotherm according to the moment-analysis method.

NON-LINEAR CHROMATOGRAPHIC SYSTEM DESCRIBED BY PLATE THEORY

Non-linear and instantaneous-equilibrium chromatographic systems have been described by the following iterative ordinary differential equation on the basis of plate theory¹⁷

$$dC_i/dt = \frac{u}{\Delta z} \frac{C_{i-1} - C_i}{1 + \frac{1}{\varepsilon} \partial C_{s,i} / \partial C_i} \quad (1)$$

where $i = 1, 2, \dots, N$ and where C_i and C_{i-1} represent the solute concentrations in the mobile phases of the i th and the $(i-1)$ th plates, respectively, and $C_{s,i}$ represents the solute concentration in the stationary phase of the i th plate. The linear velocity of the mobile phase is represented by u , ε is the volume ratio of the two phases, Δz is the plate length along the column direction, and N is the total number of plates. Although there appears to be no explicit description of the longitudinal diffusion in eqn. 1, it is obvious that Δz is concerned with the diffusion phenomenon. Now, we consider the following initial and boundary conditions as

$$C_i(0) = 0, \text{ and } C_0(t) = m \delta(t) \quad (2)$$

respectively, where m is a solute amount in a unit of the Dirac delta function, $\delta(t)$; this means a pulse-like introduction of a solute into a column. For linear chromatography, the term, $(1/\varepsilon) \partial C_{s,i} / \partial C_i$ in eqn. 1 (which is called the distribution ratio) becomes constant. In this paper, we deal with the case where the non-linear isotherm is expressed in the form

$$C_{s,i} = \frac{\beta C_i}{1 + \alpha C_i} \quad (3)$$

where a and β are constants depending on the curvature of the isotherm and the sorption capacity of the stationary phase, respectively.

By introducing eqn. 3 into eqn. 1, we obtain

$$dC_i/dt = \frac{u}{\Delta z} \frac{C_{i-1} - C_i}{1 + \frac{1}{\varepsilon} \beta / (1 + \alpha C_i)^2} \quad (4)$$

Based on this equation, we carried out a computer simulation with use of the Runge-Kutta-Gill method.

As the explanation of general relationships between the statistical moments and the shape of a chromatogram, and of how to obtain the statistical moments from a Laplace-transformed solution for a basic material-balance equation, are well known³⁻¹⁰, these are not repeated here. The published results, which we cite here, are

$$t_r = M'_1 \quad (5)$$

$$H = L M_2 / (M'_1)^2 \quad (6)$$

$$H' = L^2 M_3 / (M'_1)^3 \quad (7)$$

$$H'' = L^3 (M_4 - 3 M_2^2) / (M'_1)^4 \quad (8)$$

$$M_0 = \sum_j f_j \quad (9)$$

$$M'_1 = \frac{1}{M_0} \sum_j t_j f_j \quad (10)$$

$$M_n = \frac{1}{M_0} \sum_j (t_j - M'_1)^n f_j \quad (11)$$

The quantities H' and H'' are the second and the third plate heights, respectively, which have been proposed previously^{8,10}. Both, as well as H , are independent of column length (L), and it is desirable that both should be close to zero for good column performance. An increase in the values of these quantities is ascribed to the broadening and tailing of a chromatographic peak. According to eqns. 9, 10 and 11, the statistical moments are numerically calculated by computing a digitized chromatogram^{18,19}. Using these relationships, we discuss below the profiles of an elution curve in non-linear gas chromatography. First, however, we shall consider a linear chromatographic system ($a = 0$ in eqn. 4) in comparison with a non-linear system. For the linear system, eqn. 4 has been solved under the conditions of eqn. 2, and the solution at the N th plate, $C_N(t)$, has been given as⁶

$$f(t) \equiv C_N(t) = m \frac{\left\{ \frac{u}{\Delta z(1+k)} \right\}^N}{\Gamma(N)} \cdot t^{N-1} \exp \left[- \frac{u t}{\Delta z(1+k)} \right] \quad (12)$$

where $f(t)$ is the output elution curve, $k = \beta/\varepsilon$ and N is related to the column length (L) by the expression

$$N = L/\Delta z \quad (13)$$

Substituting eqn. 13 into eqn. 12, and calculating the moments from the Laplace transform of eqn. 12 in a general way, the following relationships are obtained

$$t_r = \left(1 + \frac{\beta}{\varepsilon}\right) L/u \quad (14)$$

$$H = \Delta z \quad (15)$$

$$H' = 2\Delta z^2 \quad (16)$$

$$H'' = 6\Delta z^3 \quad (17)$$

It is noticeable that H , H' and H'' are all represented only by Δz , which will be used to check the accuracy of the numerical calculation in the following section.

Numerical calculation

To achieve the numerical solution for eqn. 4, eqn. 2 is approximated to the rectangular input form, viz.,

$$C_0(t) = \begin{cases} m' & (0 \leq t \leq \Delta t) \\ 0 & (\text{otherwise}) \end{cases} \quad (18)$$

where Δt is the time interval for the numerical integration, the value of which should be decided before the calculation. For this purpose, we compare the values of t_r , H , H' and H'' calculated according to eqns. 14–17 with those according to eqns. 5–8 combined with eqns. 9–11. In calculating the latter values, the skirt of a chromatographic peak less than 0.001 % of its maximum height was truncated. The results are listed in Table I, where the value of Δt is 0.1 and the values of β , u , ε , Δz , m' and a are chosen to suit the numerical calculations. It can be seen from Table I that the values obtained from eqns. 14–17 (Anal.) and those from eqns. 5–8 (Numeric.) are in good agreement with each other except for H'' . A difference between the values of H'' , however, may be insignificant considering the accuracy of the fourth central moment. Thus, 0.1 was adopted as the value of the time interval in the numerical calculation of non-linear eqn. 4.

TABLE I

VALUES OF M'_1 , H , H' AND H'' FOR $\Delta t = 0.1$ SEC IN LINEAR CHROMATOGRAPHY
Values of parameters were $\beta = 100$, $u = 5.0$ cm/sec, $\varepsilon = 10.0$, $\Delta z = 1.0$ cm, $m' = 1.0$ and $L = 50$ cm.

	M'_1 (sec)	H (cm)	H' (cm ²)	H'' (cm ³)
Anal.*	110	1.00	2.00	6.00
Numeric.**	108	1.04	2.07	3.89

* According to eqns. 14–17.

** According to eqns. 5–11.

DISCUSSION

Among the parameters involved in eqns. 4 and 18, we shall now consider α , m' , and Δz , and discuss the solute retention and the column efficiencies in terms of M'_1 , H , H' and H'' as functions of α , m' and Δz .

Effect of non-linearity of distribution isotherm

Non-linear distribution isotherms can be specified according to the value of α ; for example, $\alpha > 0$, $\alpha = 0$ or $\alpha < 0$ correspond to isotherms of the Langmuir, Henry and anti-Langmuir types, respectively. In Figs. 1 and 2, the effect of the non-linearity on M'_1 , H , H' and H'' is shown as a function of α . The plot of M'_1 versus α , showing a monotonic decrease (Fig. 1), indicates that an increase in α gives rise to a linear decrease in solute retention, which corresponds to a substantial decrease in the sorption capacity of the stationary phase; increase in the value of α has the reverse effect on H , H' and H'' , as can be seen in Figs. 1 and 2. It is noteworthy that H passes through a minimum value at $\alpha \approx -15$, and H' and H'' also cross the zero-line near this value. These results suggest that a slightly negative deviation of the isotherm from the Henry type may be desirable to ensure good column efficiencies, but a positive or excessively negative deviation is undesirable. It is interesting to compare this conclusion with the experimental observation that a plot of plate height (H) against column temperature exhibits a minimum at a temperature somewhat lower than the boiling point of the solute²⁰. On the other hand, it is well known that the solute distribution is a function of the column temperature and that the latter should not be excessively lower or higher than the solute boiling point in a gas chromatographic experiment. In this connection, there may be a slight deviation of the distribution isotherm from the Henry type to the anti-Langmuir type if the column temperature is somewhat lower than the solute boiling point; the reverse may be true for a Langmuir isotherm.

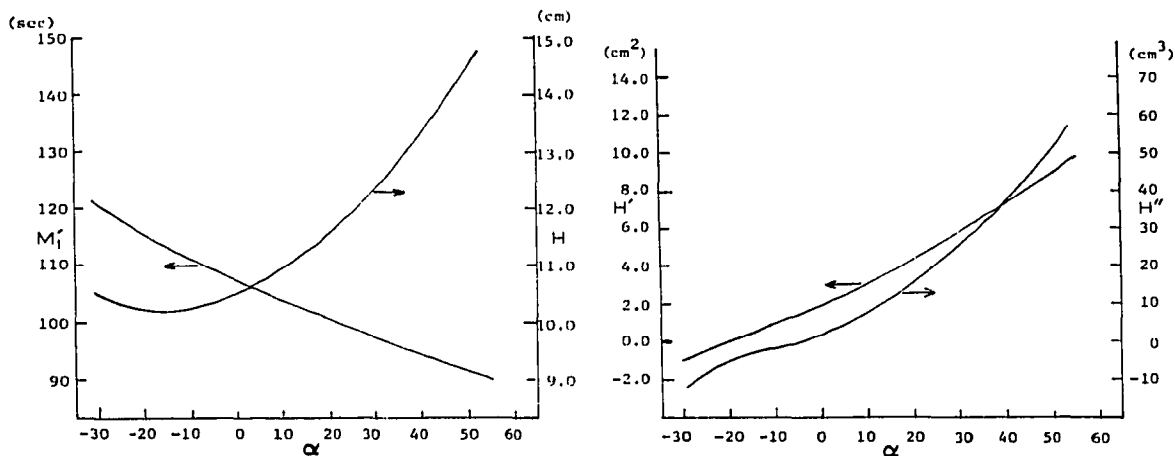


Fig. 1. Plots of M'_1 and H versus α . Values of the other parameters were: $\beta = 100$, $u = 50$ cm/sec, $\epsilon = 10.0$, $\Delta z = 1.0$ cm, $\Delta t = 0.1$ sec, $m' = 1.0$ and $L = 50$ cm.

Fig. 2. Plots of H' and H'' versus α . The values of β , u , ϵ , Δz , Δt , m' and L were as for Fig. 1.

Effect of sample amount

It is known that the sample amount does not affect M'_1 , H , H' and H'' in a linear chromatography, but it does affect their values in non-linear chromatography. As a part of our work, we have derived analytical expressions for M'_1 , H , H' and H'' in non-linear chromatography²¹, in which we found that M'_1 is a linear function of the solute amount. However, as it is difficult to deduce analytical expressions for H , H' and H'' in non-linear, non-ideal and instantaneous-equilibrium chromatography, computer simulation is employed to ascertain the effect of solute amount on these quantities. Such effect can be estimated by varying m' in eqn. 18, and Figs. 3 and 4 illustrate plots of M'_1 , H , H' and H'' against m' for a Langmuir-type isotherm ($\alpha = 10.0$). From these plots, it is found that a linear decrease in retention time accompanies an increase in the solute amount (which was predictable from previous results²¹), and that all three plate heights (H , H' and H'') increase with increase in the solute amount. Thus, as far as the solute amount is concerned, it is desirable to introduce as small an amount of sample as possible into the chromatographic column. This is also consistent with experimental trends.

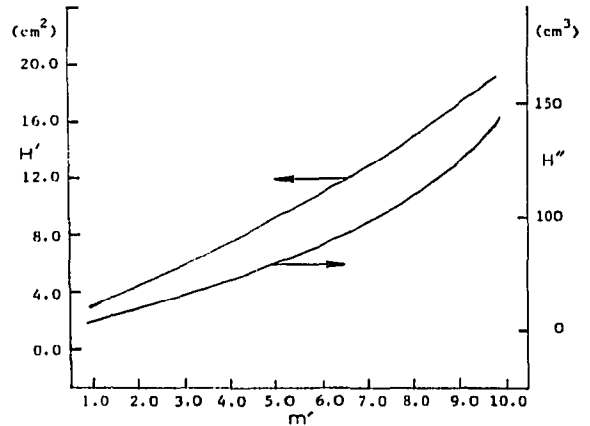
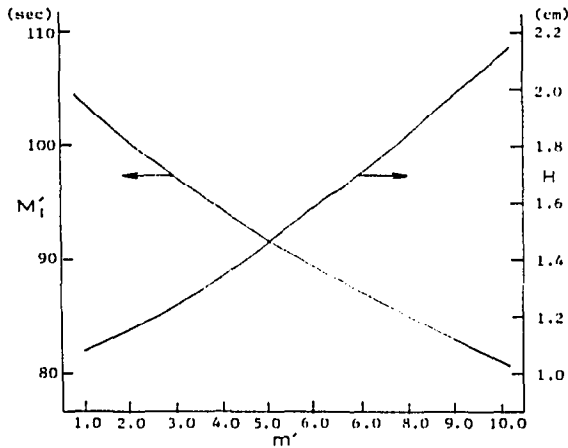


Fig. 3. Plots of M'_1 and H versus m' . Values of the other parameters were: $\alpha = 10.0$, $\beta = 100$, $u = 5.0$ cm/sec, $\varepsilon = 10.0$, $\Delta z = 1.0$ cm, $\Delta t = 0.1$ sec, $L = 50$ cm.

Fig. 4. Plots of H' and H'' versus m' . The values of α , β , u , ε , Δz , Δt and L were as for Fig. 3.

Effect of Δz

It is obvious from eqn. 13 that Δz , which is defined in eqn. 1 as a plate length along the column direction, is identical with the first plate height, H . This section shows the relationships between Δz and M'_1 , H , H' and H'' in a non-linear chromatographic system. To evaluate the dependence of these four quantities on change in the value of Δz , numerical calculations were carried out by computer integration of eqn. 4 ($\alpha = 10.0$) with Δz varying from 1.0 to 4.0. The results are listed in Table II, together with those given by eqns. 14–17, which are shown in parentheses. Table II indicates that M'_1 and H are almost uninfluenced by the non-linearity of the isotherm for each

TABLE II

DEPENDENCE OF M'_1 , H , H' AND H'' ON Δz

Values in parentheses are calculated according to eqns. 14-17. Values of parameters were $\alpha = 10.0$, $\beta = 100$, $u = 5.0$ cm/sec, $\varepsilon = 0.1$, $\Delta t = 10.0$ sec, $m' = 1.0$ and $L = 50$ cm.

Δz (cm)	M'_1 (sec)	H (cm)	H' (cm ²)	H'' (cm ³)
1.0	104 (110)	1.09 (1.00)	3.17 (2.00)	10.2 (6.0)
2.0	106 (110)	2.09 (2.00)	9.63 (8.00)	53.7 (48.0)
3.0	103 (110)	3.10 (3.00)	19.9 (18.0)	161 (162)
4.0	103 (110)	4.10 (4.00)	34.0 (32.0)	362 (384)

value of Δz , whereas H' and H'' deviate significantly from the values in parentheses. Thus, it is concluded that the higher moments are sensitive to the non-linearity of the distribution isotherm, but the lower ones are not. Such high sensitivity in the higher moments, especially H' , may be of use in examining the non-linearity of a chromatographic system.

REFERENCES

- 1 L. Lapidus and N. R. Amundson, *J. Phys. Chem.*, 56 (1952) 984.
- 2 J. J. van Deemter, F. J. Zuiderweg and A. Klinkenberg, *Chem. Eng. Sci.*, 5 (1956) 271.
- 3 E. Grushka, *J. Phys. Chem.*, 76 (1972) 2586.
- 4 M. Kubin, *Collect. Czech. Chem. Commun.*, 30 (1965) 1104.
- 5 E. Kucera, *J. Chromatogr.*, 19 (1965) 237.
- 6 O. Grubner and D. Underhill, *J. Chromatogr.*, 73 (1972) 1.
- 7 D. Underhill, *Anal. Chem.*, 45 (1973) 1258.
- 8 K. Yamaoka and T. Nakagawa, *J. Chromatogr.*, 100 (1974) 1.
- 9 D. A. McQuarrie, *J. Chem., Phys.* 38 (1963) 437.
- 10 O. Grubner, A. Zikanova and M. Ralek, *J. Chromatogr.*, 28 (1967) 209.
- 11 D. DeVault, *J. Amer. Chem. Soc.*, 65 (1943) 532.
- 12 G. Houghton, *J. Phys. Chem.*, 67 (1963) 84.
- 13 P. C. Haarhoff and H. J. van der Linde, *Anal. Chem.*, 38 (1966) 573.
- 14 J. E. Funk and G. Houghton, *J. Chromatogr.*, 6 (1961) 193.
- 15 F. T. Dunckhorst and G. Houghton, *Ind. Eng. Chem., Fundam.*, 5 (1966) 93.
- 16 K. I. Sakodinsky, L. V. Streltsov, V. Yu. Zelvensky, S. A. Volkov and I. N. Rozhenko, *Anal. Chem.*, 45 (1973) 1557.
- 17 S. W. Mayer and E. Tompkins, *J. Amer. Chem. Soc.*, 69 (1947) 2866.
- 18 K. Yamaoka and T. Nakagawa, *J. Chromatogr.*, 92 (1974) 213.
- 19 E. Grushka, M. N. Myers, P. D. Schuttler and J. C. Giddings, *Anal. Chem.*, 41 (1969) 889.
- 20 W. J. D. Wet and V. Pretorius, *Anal. Chem.*, 30 (1958) 325.
- 21 K. Yamaoka and T. Nakagawa, *J. Phys. Chem.*, 79 (1975) in press.