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Non-Gaussian Theoretical Plate Number in Chromatography

ZHANG DALI[1,*], KE JIAJUN[2] and LU LIZHU[2]

[1]Biochemical Engineering College, Beijing Union University, Beijing, P.R. China
[2]Institute of Process Engineering, Chinese Academy of Science, Beijing, P.R. China

*Corresponding author: Tel: +86 10 67373943, E-mail: dali@buu.edu.cn

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Non-Gaussian theoretical plate number is the theoretical plate number of the non-Gaussian peak (*viz*. tailing peak). Gaussian theoretical plate number is the theoretical plate number of the Gaussian peak, *viz*. usual "theoretical plate number": n, $n = (t_R/\sigma)^2$, (I). According to the plate theory, the conditions contained in deriving eqn. I include linear ideal chromatography, Gaussian elution curve, large plate number and large partition ratio. These conditions should be the condition for the application of eqn. I. However, the normal chromatographic peaks are tailing peaks; thus, calculating the theoretical plate number of the tailing peak using eqn. I would evidently transgress the condition of eqn. I. Further using the theoretical plate number calculated from tailing peak to discuss the problems of nonlinear or non-ideal chromatography would lead farther against the application of eqn. I. Thus, researching and resolving the calculation of the theoretical plate number of the tailing peak is important. In this paper, a formula of non-Gaussian theoretical plate number was derived based on the plate theory. In the derivation, the slip mechanism was introduced into the plate theory, so that the non-Gaussian theoretical plate number is also called the theoretical plate number of the slip mechanism or slip plate number for short. The new model of the plate theory containing the slip mechanism was discussed and the laws of variation of both the Gaussian theoretical plate number and the slip plate number were compared.

Keywords: Chromatography, Plate theory, Theoretical plate number, Tailing peak, Slip mechanism.

INTRODUCTION

The theoretical plate number of a peak with Gaussian distribution can be calculated with the following equation:

$$n = (t_R/\sigma)^2$$

The plate number calculated with the equation can thus be named Gaussian theoretical plate number, wherein "Gaussian" means that the corresponding elution curve is Gaussian distribution. According to plate theory, when the peak shape is a symmetrical Gaussian distribution, the theoretical plate number could be very large and chromatographic process should be linear ideal chromatography. When the plate number is very large, both the velocity of solute partition between two phases and the velocity of mass transfer are very high. That is, the Gaussian theoretical plate number is engendered by the above given mechanism. Thus, when the problem of non-ideality or non-linearity in chromatography is discussed, non-Gaussian theoretical plate number should be utilized, instead of the Gaussian theoretical plate number. Obviously, the above discussion is a self-evident principle.

Although a number of non-Gaussian elution curve equations have been proposed and studied[1,2], the problem of calculating the non-Gaussian theoretical plate number has not been solved yet. To date, the Gaussian theoretical plate number, as well as the corresponding plate height concept, is still used in investigating non-ideal chromatography. In spite of a number of research findings obtained by this kind of research[3-9], significant attention should be given to discriminate Gaussian chromatography from non-Gaussian chromatography.

Gaussian chromatography: Chromatographic peak, whether it is experimental or whether it is theoretical, is simplified to the Gaussian peak and the theoretical or applied researches are dependent on the Gaussian theoretical plate number or corresponding theoretical plate height.

Non-Gaussian chromatography: The whole information of experimental elution curve is more importance. The experimental or theoretical chromatographic peaks are not artificially simplified to the Gaussian peaks and the non-Gaussian theoretical plate number is used.

In gas chromatography and high performance liquid chromatography, the solute chromatograms generally provide three pieces of important basic information *i.e.*, solute retention time (or retention volume), peak area and peak shape. Since normal elution curves of chromatography are smooth line, the peak shape mainly includes peak asymmetry and peak width.

The peak shape has very important position in the application of chromatography, such as in qualitative analysis and in drug test by chromatography. Under the same chromatographic condition, the retention time and peak shape of the sample should be identical with that of the standard substance. If their retention time is the same, but their symmetry of peak is different, the sample and standard substance are not the same substance. Thus, differentiating Gaussian chromatography from non-Gaussian chromatography is important.

Differentiating Gaussian chromatography from non-Gaussian chromatography also has important theoretical significance. Gaussian chromatography simplifies the experimental elution curve to the Gaussian curve, hence, a great deal of information of experiment is lost, which would restrict the depth and scope of chromatographic research and application.

To date, several chromatographic studies belong to Gaussian chromatography. The formation of the research mode of Gaussian chromatography has historical origins. In the early days of modern chromatography, the detector system and the data recording and processing system have not been highly developed, which made that investigators have difficulty in precisely and conveniently recording and processing experimental data. As a result, the chromatographic peak had to be predigested into simpler Gaussian peak. The representative personages and events were Martin and Synge[10] and their plate theory.

Martin and Synge[10] supposed that the difference in partition ratio between two phases of different solutes leads to their separation. They analyzed and calculated the solute distribution in their assumed plates where the mobile phase flowed past in a pulsation way. They proved that solute distribution among the plates can be described using binomial distribution[10].

Research has proved that binomial distribution can describe various kinds of distributions of solute in column, such as leading, tailing, or Gaussian distribution. However, Martin and Synge[10] changed the binomial distribution into poisson distribution and then into normal distribution. After which, the solute distribution in the column was regarded as a Gaussian distribution and the elution band was regarded as a Gaussian band. A formula of theoretical plate number was derived from the above result. The calculation of the theoretical plate number only needs two data, namely, retention time and half band width (or standard deviation), which are relatively easy to determine. Owing to the great influence of Martin and Synge's research[10], their research is the real beginning of the research mode of Gaussian chromatography.

The closely related concepts which are the theoretical plate number and Gaussian peak became extremely important in many researches. As indicated by practice, the concepts of plate number and plate height provide new method or tool for chromatographic research. For instance, Van Deemter *et al.*[11] proposed the rate theory, which is based on summing up former research experiences[12-14]. In the derivation of Van Deemter equation, all the band broadenings caused by several influencing factors are considered to be of Gaussian function. By this treatment, the effects of the several influencing factors can be added in the form of variance and then the theoretical plate height can be used to discuss related problems. Thereafter, Giddings and the others improved the Van Deemter equation[15-23], but still adopted Van Deemter's train of thought.

The formula of theoretical plate number is obtained after the elution curve derived from the binomial distribution is simplified to Gaussian curve and the partition ratio (k) is supposed to be large. Therefore, the formula of theoretical plate number only suits the special condition that peak shape must be a Gaussian peak and 'k' must large, it does not suits all kinds of peak.

To solve the deviation of practical tailing peak from theoretical Gaussian peak, on one hand, the experimental condition could be adjusted to change the chromatographic peak into the Gaussian peak before the calculation of theoretical plate number. Obviously, this method is troublesome and difficult. On the other hand, by developing and promoting non-Gaussian chromatography, one uses a new theoretical plate number formula that suits all kinds of practical peak.

Propelled by modern high technology, the present detector system and the data recording and data processing system of the chromatographic instrument have been fully renewed and updated to satisfy the demand that researchers can precisely and conveniently record and process experimental data. Therefore, the research mode of Gaussian chromatography should be updated into non-Gaussian chromatography. The Gaussian elution curve equation of the plate theory should be updated into a new equation that can fit the experimental result nicely. The theoretical plate number should be updated into the new theoretical plate number of the non-Gaussian chromatography.

In this paper, a new elution curve equation of the non-Gaussian chromatography was derived from the binomial distribution of the plate theory and then, from which a new theoretical plate number formula of the non-Gaussian chromatography is derived. The formula is also called the plate number formula of the slip mechanism.

Fig. 1 shows the comparison between the five plate numbers discussed in this paper. Great difference exists between the theoretical plate number (Gaussian theoretical plate number) and slip plate number (non-Gaussian theoretical plate number) and the different laws of their variation are showed evidently. The theoretical plate number decreases with the increase in flow rate of the mobile phase, which accords with the law of rate theory. The slip plate number increases with the increase in flow rate of the mobile phase, which corresponds with the law of classical plate theory, because the increase in flow rate causes the symmetry of peak to increase.

The rate theory can not explain the phenomenon that the increase in flow rate causes the symmetry of peak to increase, because it does not have the concept that describes the asymmetry of peak. On the contrary, the plate theory integrates the asymmetry of peak with the plate number. The cause that the increase in flow rate makes the symmetry of peak increase is deemed by authors to be the fluid dynamics effect caused by the flow of the mobile phase. The classical plate theory and the rate theory neglect the effect of fluid dynamics of the mobile phase, which will be discussed in another paper.

The research in this paper is based on the experiment of gas-solid chromatography. In the experiment, the interaction between the solute and stationary phase is the physical adsorption of solute on the surface of the stationary phase (GDX-101).

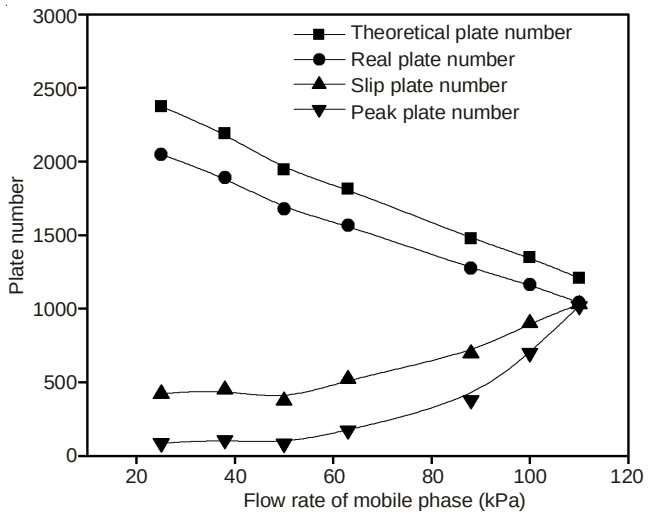

Fig. 1. Chromatographic properties of *n*-hexane as solute. *The flow rate of mobile phase is expressed by kPa: gage pressure of the carrier gas at the inlet of the column

Thus, this paper suppose that solute in adsorption state can be driven forward by mobile phase, namely, slips on the surface of stationary phase, which means that the first adsorption layer can slip on the surface of stationary phase. Furthermore, the second adsorption layer can slip on the first adsorption layer. The two "slip" all affects the plate number concerned. It is the slip mechanism. Slip mechanism is unlike plate theory and the others, because they believe that the solute in adsorption state does not move ahead with the mobile phase and the solute only in desorption state can move together with the mobile phase. Thus, the plate of plate theory is fixed, whereas the plate of slip mechanism is mobile.

THEORY

Slip mechanism

Elution curve equation: Slip mechanism suppose: In the chromatographic column, the motion of solute propelled by the mobile phase comprises at least two processes: slip motion and Martin-Synge partition motion. The slip motion is the mechanical migration of solute adsorbed at the surface of the stationary phase and is caused by the flow of mobile phase. The Martin-Synge partition motion is the ceaseless solute partition between the first and the second adsorption layers (or even the second and third adsorption layers, similarly hereinafter) on the surface of the stationary phase, accompanied with slip motion. It causes the distribution of solute in the column to conform to the binomial distribution rule. This kind of solute partition in the slip mechanism is called the Martin-Synge partition because it develops from the solute partition between two phases in the plate theory.

Given that the mass fraction of the solute in first adsorption layer is x, the mass fraction of the solute in second adsorption layer is y and the partition ratio is k, then

$$k = x/y$$

The flow of the mobile phase through the interstice among the particles of the stationary phase should be similar to the flow of liquid through the capillaries, *viz*. flow velocity gradient exists in the perpendicular direction of the flow. Thus, the velocity gradient of solute slip motion exists between the first and the second adsorption layers. The Martin-Synge partition motion in the velocity gradient would change the original aggregation state of the solute entering the column, which would make the distribution of the solute in the column conform to the binomial distribution rule. Obviously, this hypothesis mainly uses the plate theory for reference.

$$\text{Binomial distribution: } {}^{n}A_{p} = C_{n}^{p} x^{n-p} y^{p} \quad (1)$$

When n is large enough, the binomial distribution approximately obeys the normal distribution that $\mu = ny$ and $\sigma^2 = nxy$ (DeMoivre-Laplace theorem). Eqn. 1 can be changed into the density function of the normal distribution: eqn. (2).

$$f(p) = \frac{1}{\sqrt{2\pi}\times\sigma}\exp\left(-\frac{(p-\mu)^2}{2\sigma^2}\right) \approx \frac{1}{\sqrt{2\pi}\times\sqrt{nxy}}\exp\left(-\frac{(p-ny)^2}{2nxy}\right) \quad (2)$$

In eqns. 1 and 2, n is the number of times of Martin-Synge partition that occurred until certain time in the chromatographic process and p is certain position in the normal distribution or binomial distribution. Eqn 2 can express the elution curve after properly changing its variables. Suppose, the column outlet is at the qth plate and the column plate number is q. As plate theory has done, q is substituted for the p in eqn. 2. Because n increases continually in the chromatographic process, n should become the variable of the equation. Suppose at column outlet, solute is desorbed from the second adsorption layer and simultaneously flows out with mobile phase. Finally, when eqn. 2 is used for describing the elution curve, it should be expressed as eqn. 3:

$$f(n) = \frac{y}{\sqrt{2\pi}\times\sqrt{nxy}}\exp\left(-\frac{(q-ny)^2}{2nxy}\right) \quad (3)$$

Owing to the existence of slip motion of solute in the chromatographic process, the effect of the slip motion on Martin-Synge partition should be considered, thus eqn. 3 should be corrected for slip motion. After the correction, the plate number should changes, either increase or decrease. Let us suppose c is the decrease in plate number owing to the effect of slip motion. (The supposition is reasonable, because the following researches will prove that the c is positive and the plate number calculated by using the corrected equation generally is smaller than the plate number calculated by using the equation in which the slip motion is not considered).

Correction for the effect of slip motion: c is subtracted from the terms that relate to the plate number in eqn. 3. The corrected result is as follows. (Absolute value signs are added to eqn. 4 because the terms concerned should not be a negative value.)

$$f(n) = \frac{y}{\sqrt{2\pi}\times\sqrt{|ny-c|x}}\exp\left(-\frac{\left[(q-c)-(ny-c)\right]^2}{2|ny-c|x}\right) \quad (4)$$

$$f(n) = \frac{y}{\sqrt{2\pi}\times\sqrt{|n-c/y|yx}}\exp\left(-\frac{(q-ny)^2}{2|n-c/y|xy}\right) \quad (5)$$

Let $c_y = c/y$ (6)

$$f(n) = \frac{y}{\sqrt{2\pi} \times \sqrt{|\ n - c_y\ |xy}} \exp\left(-\frac{(q - ny)^2}{2|n - c_y|xy} \right) \quad (7)$$

According to the property of binomial distribution, the relationship of q (plate number of column) and y is as follows:

$$q = n_R y \quad (8)$$

In eqn. 8, n_R is the number of times for Martin-Synge partition until solute distribution peak (solute maximum concentration) arrives at the column outlet. Eqn. 8 is substituted in eqn. 7 to obtain eqn. 9.

$$f(n) = \frac{y}{\sqrt{2\pi} \times \sqrt{xy|\ n - c_y\ |}} \exp\left(-\frac{((n_R - n)y)^2}{2xy|n - c_y|} \right) \quad (9)$$

Eqn. 9 can be called the plate equation of elution curve because the variable in the equation is n, which is the number of times of Martin-Synge partition of solute in the plate. In usual chromatogram, abscissa is t, the elution time and the ordinate is the detector response. Thus, eqn. 9 needs to be changed to time equation of elution curve, [f(t)], which is more easy to use.

a is the unit conversion factor, a factor to change partition times (n) into elution time (t). The a is the number of times of Martin-Synge partition per unit time. The terms that relate to partition in eqn. 9 are multiplied by a and divided by a simultaneously.

$$f(an/a) = \frac{y}{\sqrt{2\pi} \times \sqrt{xy|an/a - ac_y/a|}} \exp\left(-\frac{((an_R/a - an/a)y)^2}{2xy|an/a - ac_y/a|} \right) \quad (10)$$

Given: $n_R/a = t_{nR}$ (11)

According to eqn. 11, the meaning of t_{nR} is time that solute distribution peak moves and arrives at the column outlet. In fact, t_{nR} is different from retention time t_R and slightly larger than t_R.

Given: n/a = t. Obviously, the t is elution time.

Given: $c_y/a = c_t$ (12)

The c_t is the apparent slip factor (ordinarily, $0 < c_t < t_R$), where the larger its value is, the greater the loss of plate number is.

$$f(an/a) = \frac{y}{\sqrt{2\pi} \times \sqrt{axy|\ t - c_t\ |}} \exp\left(-\frac{ay(t_{nR} - t)^2}{2x|t - c_t|} \right) \quad (13)$$

In eqn. 13, the variable has changed from n to t, so the equation is not normalized function, but original f(n) is normalized. If the time eqn. f(t) need to be normalized, it is easy to prove that

Normalized f(t) = Af(an/a).

Thus, the normalized equation f(t) is as follows:

$$f(t) = af(an/a) = \frac{\sqrt{ay/x}}{\sqrt{2\pi} \times \sqrt{|\ t - c_t\ |}} \exp\left(-\frac{(ay/x)(t_{nR} - t)^2}{2|t - c_t|} \right) \quad (14)$$

Let, $ay/x = B$ (15)

The area of chromatogram peak = A and the base line is Y. When eqn. 14 is used to real peak, it can be expressed as follows:

$$f(t) = Y + \frac{A\sqrt{B}}{\sqrt{2\pi} \times \sqrt{|\ t - c_t\ |}} \exp\left(-\frac{B(t_{nR} - t)^2}{2|t - c_t|} \right) \quad (16)$$

Normalization of elution curve function: For the plate equation of elution curve, A_n is the peak area of the n abscissa.

$$A_n = \Sigma f(n_i)(\Delta n_i) \quad (17)$$

For the time equation of the elution curve, A_t is the peak area of the t abscissa.

$$A_t = \Sigma f(t_i)(\Delta t_i) \quad (18)$$

When the abscissa is changed from n to t, the area of the peak should not change, $A_n = A_t$. Thus, the terms that relate to the number of times of the partition in eqn. 17 are multiplied by a and divided by a, simultaneously. The a is the number of times of Martin-Synge partition per unit time. Therefore, $\Delta n_i/a = \Delta t_i$.

$$\begin{aligned} A_n &= \Sigma f(n_i)(\Delta n_i) \\ &= \Sigma f(an_i/a)(a\Delta n_i/a) \\ &= \Sigma a\ f(an_i/a)(\Delta n_i/a) \\ &= \Sigma a\ f(an_i/a)(\Delta t_i) \end{aligned} \quad (19)$$

Given that $A_n = A_t$ is required, eqns. 18 and 19 are compared; then the following can be obtained:

$$f(t_i) = a\ f(an_i/a),$$

namely, $f(t) = a\ f(an/a)$.

Theoretical plate number of slip mechanism: Eqn. 16 is the elution curve equation of the slip mechanism. If $c_t = 0$, that is, the solute slip motion is not considered or neglected, the slip mechanism model is changed to the plate theory model and eqn. 16 is changed to the elution curve equation of the plate theory, namely, eqn. 20.

$$f(t) = \frac{A\sqrt{B_0}}{\sqrt{2\pi} \times \sqrt{t}} \exp\left(-\frac{B_0(t_{nR} - t)^2}{2t} \right) \quad (20)$$

The B in eqn. 16 is changed to B_0 in eqn. 20 to show the model variations.

Eqn. 20 expresses a slight tailing peak, but its tailing degree is generally exceeded by real peaks.

The elution curve equations of plate theory that are analogous to eqn 20 include the equation in reference[24], which variable is the elution volume of mobile phase and the equation in reference[25], which contains infinite series.

When eqns. 16 and 20 are used to fit the same elution curve, their f(t), which are the experimental data to be used for fitting, are same correspondingly; hence, the two equations can be made equal.

$$\frac{A\sqrt{B}}{\sqrt{2\pi} \times \sqrt{|t - c_t|}} \exp\left(-\frac{B(t_{nR} - t)^2}{2|t - c_t|} \right) = \frac{A\sqrt{B_0}}{\sqrt{2\pi} \times \sqrt{t}} \exp\left(-\frac{B_0(t_{nR} - t)^2}{2t} \right)$$

if $t = t_{nR}$,

$$\frac{A\sqrt{B}}{\sqrt{2\pi} \times \sqrt{|t_{nR} - c_t|}} \exp\left(-\frac{B(t_{nR} - t_{nR})^2}{2|t_{nR} - c_t|} \right) =$$

$$\frac{A\sqrt{B_0}}{\sqrt{2\pi} \times \sqrt{t_{nR}}} \exp\left(-\frac{B_0(t_{nR} - t_{nR})^2}{2t_{nR}} \right)$$

Exponent property: exp (0) = 1.

$$\exp\left(-\frac{B\left(t_{nR}-t_{nR}\right)^2}{2\left|t_{nR}-c_t\right|}\right)=\exp\left(-\frac{B_0\left(t_{nR}-t_{nR}\right)^2}{2t_{nR}}\right)=1$$

As a result,

$$\sqrt{B}/\sqrt{\left|t_{nR}-c_t\right|}=\sqrt{B_0}/\sqrt{t_{nR}}$$

$$B = B_0|1\text{-}c_t/t_{nR}| \quad (21)$$

According to eqn. 15, B= ay/x and is substituted in eqn. 21.

$$ay/x = \left(ay/x\right)_0\left|1\text{-}c_t/t_{nR}\right| \quad (22)$$

Both sides of the equation are multiplied by t_{nR}:

$$at_{nR}y/x = \left(at_{nR}y/x\right)_0\left|1\text{-}c_t/t_{nR}\right| \quad (23)$$

According to eqs. 11 and 8, $n_R = at_{nR}$, $q = n_R$ y.

$$q = at_{nR}y \quad (24)$$

Given that $(1/x) = (1/x)_0$ and $q = at_{nR}y$, the following can be obtained from eqn. 23:

$$q = q_0\left|1\text{-}c_t/t_{nR}\right|. \quad (25)$$

In eqn. 25, q is the column plate number of the slip mechanism, originating from eqn. 16 and q_0 is the column plate number of the plate theory, originating form eqn. 20.

The formula of the real plate number in the plate theory is as follows[25]:

$$n_0 = 5.54\left(t_R/W_{1/2}\right)^2\left(k/(1+k)\right)$$

This formula is obtained after the treatments that simplify the elution curve into Gaussian curve. Therefore real plate number n_0 implies that the peak is Gaussian peak.

The elution curve of eqn. 20 is a tailing peak, but its tailing degree is very low, so that suppose $q_0 \approx n_0$.

$$q_0 \approx n_0 = 5.54\left(t_R/W_{1/2}\right)^2\left(k/(1+k)\right) \quad (26)$$

In reference[25], the expression of the elution curve of the plate theory was changed from discrete function into the continuous function containing infinite series by means of mathematics and then its characters were investigated in detail using a computer calculation. This research proves that the plate number of plate theory (q_0) is very close to real plate number (n_0) in value.

Eqn. 26 is substituted in eqn. 25; eqn. 27 can be obtained:

$$q = 5\ 54\left(t_R/W_{1/2}\right)^2\left(k/(1+k)\right)\left|1\text{-}c_t/t_{nR}\right| \quad (27)$$

$W_{1/2}$ stands for the peak width at half-height and k is the partition ratio.

Peak plate number: q is the column plate number and c is the loss of plate number due to the effect of slip motion. The (q-c) should be the plate number which is reflected by real peak. It can be called peak plate number and expressed as q'.

$$q' = q\text{-}c \quad (28)$$

According to eqn. 6, $c = c_y$ y. According to eqn. 12, $c_y = ac_t$. According to eqn. 24, $ayt_{nR} = q$; we can obtain eqn. 29.

$$c = c_y\ y = ac_t y = (c_t/t_{nR})(ayt_{nR}) = (c_t/t_{nR})q \quad (29)$$

Eqn. 29 is substituted in eqn. 28, which gives eqn. 30.

$$q' = q(1\text{-}c_t/t_{nR}) \quad (30)$$

Eqn. 27 is substituted in eqn. 30, thus eqn. 31 can be obtained.

$$q' = 5.54\left(t_R/W_{1/2}\right)^2\left(k/(1+k)\right)\left|\ 1\text{-}c_t/t_{nR}\right|(1\text{-}c_t/t_{nR}) \quad (31)$$

Generally, $0 < c_t < t_{nR}$, where eqn. 31 can be simplified into eqn. 32:

$$q' = 5.54\left(t_R/W_{1/2}\right)^2\left(k/(1+k)\right)(1\text{-}c_t/t_{nR})^2 \quad (32)$$

In fact, eqn. 4 has the term (q-c), but the term disappears in later equations.

RESULTS AND DISCUSSION

Relations among five plate numbers: Eqn. 32 can be written in the following form.

$$X = 5.54\left(t_R/W_{1/2}\right)^2\left(k/(1+k)\right)(1\text{-}c_t/t_{nR})(1\text{-}c_t/t_{nR})$$

$$\underline{\quad A \quad}\ \underline{\quad B \quad}\ \underline{\quad C \quad}\ \underline{\quad D \quad}$$

In the equation, X = peak plate number, q'. If term D = 1, X = slip plate number, q; if C = D = 1, X = plate number of plate theory, q_0 and real plate number, n_0; if B = C = D = 1, X = theoretical plate number, n. This is the relationship existing among the five plate numbers. In addition, t_R and t_{nR} are very close in value and t_R can replace t_{nR} in calculation and vice versa.

Discussion about five plate numbers

Plate theory plate number, q_0: The q_0 corresponding elution curve is the tailing peak. Only after the elution curve equation is fitted to the chromatographic peak, q_0 can be calculated with the fitted parameters in the equation. When using eqn. 20, q_0 can be calculated with the following equation:

$$q_0 = B_0t_{nR}(k/(1+k) \quad (33)$$

Because the tailing degree of the elution peak of eqn. 20 is very small, large error may exists in the fitting, *i.e.*, the fitting curve cannot fit the chromatographic peak well.

The value of q_0 closely approximates the real plate number n_0, which calculation is very simple (eqn. 26).

Real plate number, n_0: n_0 can be calculated using eqn. 34 and peak fitting is not needed, for the elution curve equation has been simplied to the Gaussian function and the peak shape is already given. However, only few of chromatographic peaks are Gaussian.

$$n_0 = 5.54\left(t_R/W_{1/2}\right)^2\left(k/(1+k)\right) \quad (34)$$

Theoretical plate number n: The n calculation is more simple.

$$n = 5.54\left(t_R/W_{1/2}\right)^2 \quad (35)$$

Supposing k in eqn. 34 is large, $[k/(1+k)] \approx 1$ and eqn. 35 is obtained. However, only few of chromatographic peaks are Gaussian.

Theoretical plate number of slip mechanism, q: The q corresponding elution curve equation (Eqn. 16) can describe the peaks with different degrees of tailing or leading. In calculating q, the fitting of chromatographic peak is needed, to find the values of the parameters in the equation. By using either eqn. 27 or the following equation, q can be calculated:

$$q = Bt_{nR}(k/(1+k) \quad (36)$$

Eqn. 36 is obtained from the equations in section elution curve equation and does not relate to eqn. 34 and 35, but the

results of the two methods are same, which indicates that both eqn. 27 and 36 are all right.

Eqn. 27 shows the relationship of q, n and n_0. n and n_0 are the theoretical plate numbers that the given elution curve is Gaussian, so the term $|1-c_t/t_{nR}|$ shows the deviation of the theoretical plate number of the tailing peak from that of the Gaussian peak. The deviation relates to the apparent slip factor, c_t.

As the A shows in Fig. 2, the theoretical plate number of column, q_0, is 100; these theoretical plates are fixed according to plate theory. According to the slip mechanism, the first adsorption layer, which corresponds to the plate of the plate theory, and the second adsorption layer can be pushed forward by mobile phase and slip on surface of the stationary phase; thus, the plate of the slip mechanism is moveable.

Owing to the forward slippage of the plates, the solute peak (solute maximum concentration) has come to the outlet of column, but the solute peak just moves to the plate that corresponds to the 50th of the fixed plates (B in Fig. 2), so the theoretical plate number of the slip mechanism is 50.

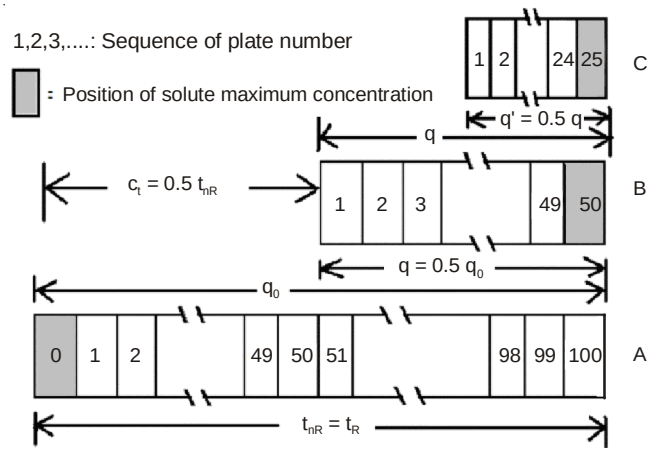

Fig. 2. Diagrammatic sketch of the plate number. Suppose $c_t = 0.5\ t_{nR}$, then $|1-c_t/t_{nR}| = 0.5$; by eqn. 25, $q = 0.5\ q_0$; by eqn. 30, $q' = 0.5\ q$

Fig. 1 shows that the slip plate number increases with the increase in flow rate of the mobile phase. This is the effect of fluid dynamics of mobile phase. The flow of mobile phase can accelerate the velocity of Martin-Synge partition. The increase in the velocity of mobile phase can cause the frequency of Martin-Synge partition to increase by the rule of exponent. When the velocity of flow increases, the number of times of Martin-Synge partition in column still increases, though the retention time of solute decreases. Therefore, slip plate number increases.

Peak plate number (q'): Peak plate number is the plate number which peak shape reflects. In calculating q', the fitting of the chromatographic peak is needed, to obtain the values of parameters in the elution curve equation and then the q' can be calculated by either the following or eqn. 32.

$$q' = B(t_{nR}-c_t)\ [k/(1 + k)] \quad (37)$$

Eqn. 37 is obtained from the equations In section elution curve equation and does not relate to eqn. 34 and 35, but the results of the two methods are same, which proves that both eqn. 37 and 32 are correct.

According to the slip mechanism, relative slip motion exists between the second adsorption layer and the first adsorption layer. Martin-Synge partition just takes place in the two adsorption layers.

The relative slip motion could make the contributing plate number become small. When the velocity of relative slip motion does not match with the velocity of Martin-Synge partition, a part of the column plates will not take effect, namely these plates will be lost. The loss of plate number c is relative loss to slip plate number q (C in Fig. 2). It is caused by non-matched velocity of the relative slip motion.

Fig. 1 shows the peak plate number increases with the increase in flow rate of the mobile phase. It is also the effect of fluid dynamics of the mobile phase.

$$q' = q(1-c_t/t_{nR}) \quad (30)$$

In eqn. 30, when $c_t = 0$, $q' = q$. This is an optimum state, *viz*., the velocity of relative slip motion perfectly matches with the velocity (or frequency) of Martin-Synge partition.

As shown in Fig. 1, at low velocity of the flow, the difference between q' and q is large. It is because the velocity of the relative slip motion can not perfectly matches with the velocity (or frequency) of Martin-Synge partition, namely, comparatively speaking with the perfect match, the velocity of the relative slip motion is too fast and the velocity (or frequency) of Martin-Synge partition is too slow. As a result, in comparison with the perfect match, the number of times of Martin-Synge partition in column decreases greatly. The number of times of Martin-Synge partition in the perfect match should be q/y.

As shown in Fig. 1, at high velocity of flow, the difference between q' and q lessens. It is because the match degree becomes better. The increase in velocity of flow causes the velocity (or frequency) of Martin-Synge partition to increase by the rule of exponent, but the velocity of relative slip motion to increase by the rule of linearity, so that the match between them meliorate. As a result, the difference in number of times of partition between q and q' diminishes and peak plate number largens.

Indicated by the above discussion, the hypothesis in slip plate number: column plate is moveable and the velocity of the relative slip between the first and the second adsorption layers perfectly matches with the velocity (or frequency) of Martin-Synge partition. The hypothesis in peak plate number is different from slip plate number, because it farther considers that whether the velocity of the relative slip can matches with the velocity (or frequency) of Martin-Synge partition.

Peak plate number and symmetry of peak: Peak plate number is consistent with the symmetry of peak, *viz*. peak plate number is inversely proportional to the asymmetry of the peak. General chromatography workstation can provide asymmetrical degree of peak. Thus, the peak plate number, q', is inversely proportional to the asymmetrical degree of peak, ADP.

$$ADP \propto k_1/q'$$

The asymmetrical degree of peak is defined as the area ratio of the back part to the forepart for a peak, when a vertical line across the highest point of a peak is the boundary. Therefore, for Gaussian peak, ADP = 1 and q' is very large. The above equation is revised as follows:

$$ADP \propto k_1/q' + 1$$

$$ADP = k_1/(q' + k_2) + 1 \quad (38)$$

Fig. 3 shows the relationship between the asymmetrical degree of peak and peak plate number. Fig. 3 represents a system of gas-solid chromatography. The sample is a mixture of five solutes. The determinations were done under five velocities of flow. Chromatography workstation N2000 can show the asymmetrical degree of each peak and can also export the chromatogram in the text format. With the data of elution curve in the text format, the elution curve equation (eqn. 16) is fitted to each peak through software Origin 6 and the parameters in the equation can be gotten and thus the peak plate number can be calculated.

The experimental spots in Fig. 3 is fitted with eqn. 39 and the results is the solid curve (fitted curve) and $k_3 = 1.05$, $k_1 = 21.4$, $k_2 = 18.6$, $R^2 = 0.987$, $Chi^2 = 0.00062$.

$$ADP = k_1/(q' + k_2) + k_3 \quad (39)$$

The above result should confirm the positive correlation between the peak plate number and symmetry of the peak.

In addition, according to eqn. 39, when the peak tailing is very serious, q' should be small, then $ADP \approx k_1/k_2 + k_3 \approx 2$. The area ratio of back part to the forepart for a peak is 2, which may be a limit of the slip mechanism. In other words, the most serious tailing peak which slip mechanism can describe is that the peak area ratio of the back part to the forepart is about 2.

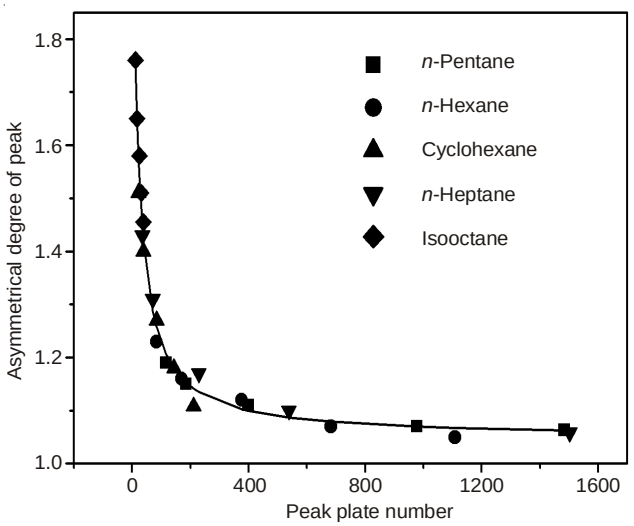

Fig. 3. Relationship between the asymmetrical degree of the peak and the peak plate number Shimadzu GC-14C chromatograph; Stationary phase: GDX-101; mobile phase: N_2; Flame ionization detector

Column plate number and symmetrical characteristic of peak: Whether the symmetry of real peak is considered, it has great influence on theoretical plate number. Several kinds of theoretical plate numbers for the peaks in Fig. 4 are listed in Table-1. It can be seen that theoretical plate number > real plate number >> slip plate number > peak plate number.

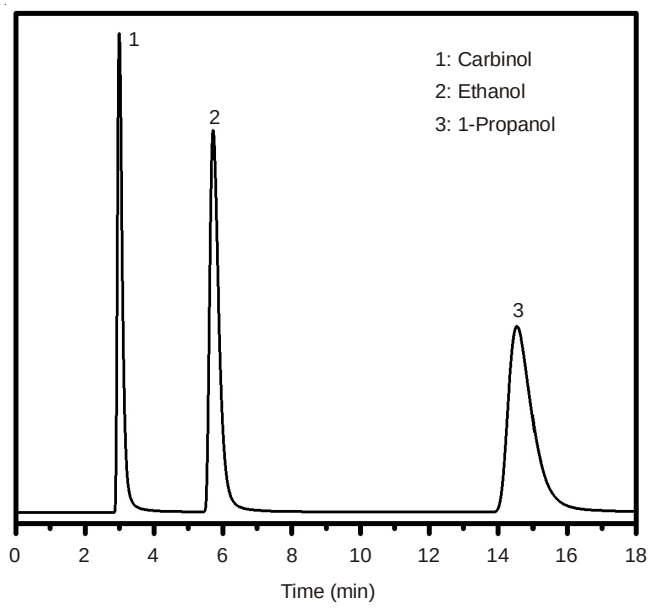

Fig. 4. Gas chromatogram Shimadzu GC-14C chromatograph; Chromatography workstation N2000; Stationary phase: GDX-101; mobile phase: N_2; 130 °C; 40 kPa; Flame ionization detector; 1: carbinol; 2: ethanol; 3: 1-propanol

These results indicate that when theoretical plate number is calculated, to select suitable calculating method would be very important, for different calculating methods will lead to greatly different or totally different results.

Notation

a	Number of times of Martin-Synge partition per unit time
A	Area of peak
ADP	Asymmetrical degree of peak,
B	ay/x
B_0	ay/x in eqn. 20 of plate theory model
c	decrease in plate number owing to effect of slip motion
c_t	c_y/a, apparent slip factor
c_y	c/y
k	Partition ratio
n	Theoretical plate number, Gaussian theoretical plate number
n_R	Number of times for Martin-Synge partition until solute distribution peak (solute maximum concentration) arrives at the column outlet.
n_0	Real plate number
q	Column plate number of slip mechanism, slip plate number
q_0	Column plate number of plate theory
q'	Peak plate number of slip mechanism
t	Elution time
t_R	Retention time

TABLE-1
CHROMATOGRAPHIC PEAK PROPERTIES

Solute	t_R	c_t	k	k/(1 + k)	1-c/t_{nR}	n	n_0	q	q′
Carbinol	2.96	2.82	1.36	0.58	0.047	2341	1351	63.9	3.0
Ethanol	5.7	5.39	3.52	0.78	0.054	2363	1840	100	5.4
1-Propanol	14.5	13.7	10.5	0.91	0.055	2183	1993	110	6.1

* Dead time: 1.27 min

t_{nR} Time that solute distribution peak moves and arrives at the column outlet.
$W_{1/2}$ Peak width at half-height
x Mass fraction of the solute in first adsorption layer
y Mass fraction of the solute in second adsorption layer
Y Base line
σ Variance of normal distribution

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