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CONTRIBUTION TO THE THEORY OF GAS CHROMATOGRAPHY AND TO THE COMPUTATION OF THE HETP VALUE

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SUMMARY

Results of our investigations on theoretical and practical problems of programmed flow gas chromatography and the data of the paper of fundamental importance by COSTA NETO, KÖFFER AND DE ALENCAR made it possible to solve the problem of the new approximation.

In the new approximation of general validity, the plate and rate theories approximating the gas chromatographic processes, are amalgamated into a harmonic unity. Derivation of the new equation makes the numerical computation of the coefficients possible either traditionally or by means of computers.

Until now, processes occurring in the gas chromatographic columns have generally been approached in two ways: either by the plate theory or by the kinetic, *i.e.* the rate theory.

The plate theory was introduced by MARTIN AND SYNGE¹ to describe chromatographic processes. This theory has been developed further by MAYER AND TOMPKINS² to determine the number of theoretical plates necessary for a suitable separation. The stepwise procedure adopted by them was extended by GLUECKAUF^{3,4} to cover conditions of real, continuous flow. The kinetic or rate theory describes the kinetics of the process, and the VAN DEEMTER, ZUIDERWEG AND KLINKENBERG⁵ equation, which describes the process, is widely used and accepted.

We have no intention of dealing with the plate theory or the VAN DEEMTER equation⁶, or with papers and theories suggesting different modifications, *e.g.* the work of KAMBARA^{7,8,14}, but we wish to point out that many workers including ourselves have attempted to find a better approximation and description of real processes, primarily to clear up the effect of factors having an influence on the HETP value.

Though the coefficients of the VAN DEEMTER equation may be determined graphically or by other approximation methods^{9,15}, factors influencing the HETP value could not be investigated unambiguously, on account of errors peculiar to the approximation methods. Because of this last circumstance, we have developed an approximation-equation which uses simple mathematical means numerically determining the coefficients of the approximation-equation.

Results of our investigation on theoretical and practical problems of programmed flow gas chromatography¹⁰⁻¹², and the data of the paper of fundamental impor-

tance by COSTA NETO, KÖFFER AND DE ALENCAR¹³ made it possible to solve the problem of the new approximation.

In the course of the theoretical derivation, it became evident that the two different approximations (plate and kinetic theory, respectively) can be amalgamated harmoniously in the new equation which is of general validity and describes the processes in either packed, open tubular or capillary columns.

THEORETICAL

On the basis of GLUECKAUF's equation⁴ n can be expressed by:

$$n = 16 \left(\frac{t_N}{w} \right)^2 \quad (1)$$

where:

n = number of theoretical plates

t_N = net retention time of the component (min)

w = peak width of the component (min).

This expression can be substituted into the well-known fundamental equation for the HETP value:

$$\text{HETP} = \frac{L}{n} = \frac{L}{16} \left(\frac{w}{t_N} \right)^2 \quad (2)$$

where:

HETP = height equivalent to a theoretical plate (cm)

L = length of the column (cm).

Next, using the two fundamental theorems¹⁰⁻¹², obtained by investigating theoretical and practical problems of programmed flow gas chromatography, equation (2) may be rewritten, according to one of the fundamental theorems, as:

$$w = m_1 \Psi + b_1 \quad (3)$$

where:

m_1 = slope of the straight line (ml)

ψ = flow rate factor of the carrier gas (min/ml)

b_1 = axial section Y of the straight line (min).

By definition, the flow rate factor of the carrier gas is¹²:

$$\Psi = \frac{1}{F^2} (F + C^x) \quad (4)$$

where:

F = flow rate of the carrier gas (ml/min)

C^x = constant depending on the quality of substance (ml/min).

According to the other fundamental theorem:

$$t_N = m_2 \cdot \frac{1}{F} \quad (5)$$

where m_2 is the slope of the straight line (ml).

Equations (3) and (5) have first of all to be transformed, in order to have the linear velocity of the carrier gas instead of its flow rate:

$$w' = m_1' \varphi + b_1' \quad (6)$$

where:

- m_1' = slope of the straight line (cm)
 φ = linear velocity factor of the carrier gas (sec/cm)
 b_1' = axial section Y of the straight line (sec)
 w' = peak width of the component (sec)

By definition, the linear velocity factor of the carrier gas is:

$$\varphi = \frac{1}{u^2} (u + C^{xx}) \quad (7)$$

where:

- u = linear velocity of the carrier gas (cm/sec)
 C^{xx} = constant depending on the quality of the substance (cm/sec).

Equation (5) can be transformed for the linear velocity of the carrier gas as:

$$t'_N = m_2' \cdot \frac{1}{u} \quad (8)$$

where:

- t'_N = net retention time of the component (sec)
 m_2' = direction tangent of the straight line (cm).

Substituting the respective parts of equations (6) and (8) into equation (2):

$$\text{HETP} = \frac{L}{16} \left(\frac{m_1' \varphi + b_1'}{m_2' \cdot \frac{1}{u}} \right)^2 \quad (9)$$

On substituting the value of φ from equation (7), rearranging the equation and applying all possible reductions, we obtain:

$$\text{HETP} = \frac{L}{16} \left(\frac{b_1'}{m_2'} u + \frac{m_1'}{m_2'} + \frac{m_1' C^{xx}}{m_2'} \cdot u^{-1} \right)^2 \quad (10)$$

After squaring and arranging the equation according to diminishing powers of u :

$$\begin{aligned} \text{HETP} = \frac{L}{16} & \left[\left(\frac{b_1'}{m_2'} \right)^2 u^2 + 2 \left(\frac{b_1'}{m_2'} \right) \left(\frac{m_1'}{m_2'} \right) u + \left(\frac{m_1'}{m_2'} \right)^2 + 2 \left(\frac{b_1'}{m_2'} \right) \left(\frac{m_1' C^{xx}}{m_2'} \right) + \right. \\ & \left. + 2 \left(\frac{m_1'}{m_2'} \right) \left(\frac{m_1' C^{xx}}{m_2'} \right) u^{-1} + \left(\frac{m_1' C^{xx}}{m_2'} \right)^2 u^{-2} \right] \quad (11) \end{aligned}$$

If we now introduce the symbols:

$$A = \frac{L}{16} \left[\left(\frac{m_1'}{m_2'} \right)^2 + 2 \left(\frac{b_1'}{m_2'} \right) \left(\frac{m_1' C^{xx}}{m_2'} \right) \right] \quad (12)$$

$$B = \frac{L}{8} \left[\left(\frac{m_1'}{m_2'} \right) \left(\frac{m_1' C^{xx}}{m_2'} \right) \right] \quad (13)$$

$$C = \frac{L}{8} \left[\left(\frac{b_1'}{m_2'} \right) \left(\frac{m_1'}{m_2'} \right) \right] \quad (14)$$

$$D = \frac{L}{16} \left[\left(\frac{m_1' C^{xx}}{m_2'} \right)^2 \right] \quad (15)$$

$$E = \frac{L}{16} \left(\frac{b_1'}{m_2'} \right)^2 \quad (16)$$

equation (11) can now be written in a new but conventional form as:

$$\text{HETP} = A + \frac{B}{u} + Cu + \frac{D}{u^2} + Eu^2 \quad (17)$$

Equation (17) is a new equation of general validity describing gas chromatographic processes, incorporating the HETP value, and is suitable for following the processes occurring in any kind of column. There are fundamental differences between equation (17) and the well-known VAN DEEMTER equation because of the more general character of the approximation, though concordant features can also be observed, especially with respect to the 2nd and 3rd terms of the equation. There is a definite difference both in the interpretation and value of the first term, and in the fact that the new, general equation incorporates two terms with coefficients D and E , which take into account diffusion and represent better the mass transfer conditions respectively, and thus improve the approximation.

Equation (17) due to the mathematical exactness of its coefficients (equations (12) to (16)) creates a new opportunity of investigating the factors which influence the HETP value, and at the same time allows one to follow gas chromatographic processes numerically.

On the basis of the relationships above, there are unambiguous answers to many questions, formerly unsettled. For instance whether the term A in the equation can or cannot be neglected; what is the relationship between the diffusion and mass-transfer processes for a given gas rate, etc. Our investigations in this respect are continuing.

The derivation of the equation and the method of computing the coefficients is published now, well before completing our investigations, in order to give other workers the chance to examine the coefficients influencing HETP value, or on the other hand, to evaluate critically both their derivation and equation (17).

EXPERIMENTAL

Numerical evaluation of equation (17), *i.e.* of its constants, is done in the following manner. The net retention time of the tested component is determined for five different linear velocity values of the carrier gas under stationary gas chromatographic conditions. Then, adopting the principle of the least squares¹¹ to the data obtained, a functional relationship between the net retention time and the reciprocal of linear velocity is obtained, so the linear functional equation (8) will be solved. The slope m_2' of this straight line is the first of the data necessary for the computations.

Next, the relationship between the peak width and the linear gas rate is determined with help of the chromatograms already determined for the net retention time and the linear gas velocity function. Writing equation (6) involves lengthy computations, based on our earlier publications on the determination of these coefficients¹², because of the substance constant figuring in the linear velocity factor, so possibly a computer should be used, so that these computations can be carried out easily. From equation (6), *i.e.* from the substance constant and the linear velocity factor the values of m_1' , b_1' and C^{xx} , necessary for the computations, are obtained.

The constants of equation (17) have then to be computed by means of the relationships (12 to 16), derived as discussed in the theoretical part.

The complete series of computations can also be carried out by a computer. The gas chromatographic programme necessary for programming the computer is as follows:

Related data of carrier gas rate-retention time (at a constant temperature and under unchanged gas chromatographic conditions), the relevant peak width, the inlet and outlet pressures of the carrier gas, together with the relevant t_M values are fed into the computer in dimensions corresponding to the equations. t_M stands for the gas hold-up time of the non-sorbed substance, in sec.

The computer is programmed so as to compute first the gas compressibility correction factor j by means of the well-known JAMES-MARTIN equation:

$$j = \frac{3}{2} \left(\frac{P^2 - 1}{P^3 - 1} \right) \quad (18)$$

where:

j = gas compressibility correction factor according to JAMES-MARTIN

$P = (p_i/p_o)$

p_i = inlet pressure of the carrier gas (in kp/cm²), or another pressure unit

p_o = outlet pressure of the carrier gas (in kp/cm², or another pressure unit).

After the evaluation of j , the net retention times have to be computed according to the well-known relationship:

$$t_N' = j(t_R^0 - t_M) \quad (19)$$

where:

t_R^0 = retention time of the component (sec).

Next equation (8) should be computed by applying the principle of least squares and the slope m_2' of the straight line so determined is printed out.

Then the substance constant, the slope and the axial section of equation (6) are determined on the basis of appropriate relationships. These m_1' , C^{xx} and b_1' values are also printed out.

Now that all the necessary data for further computations are stored in the memory of the computer, determination and printing out of the constants of equation (17), based on equations (12) to (16), can be carried out. After determining the coefficients, the corresponding linear velocities are co-ordinated to the corresponding constants, and equation (17) for the substance tested is printed out corresponding to the given gas chromatographic system. Finally a computer programme for the HETP value will be presented.

According to our experience, it is expedient to feed the computer a programme, which makes it automatically raise the linear gas rate values first by 0.5 (cm/sec) from the value of 0.5 cm/sec to 50.0 cm/sec in the equation, then by 5.0 cm/sec up to 100.0 cm/sec. In some instances, e.g. in high rate investigations, even higher values may be needed, these are advisably programmed separately. Of course, in this stage of the programme all HETP- u values have to be printed out. If the investigations are intended to examine factors influencing the HETP value, it is expedient to have all the computed data printed.

In addition to the well-known advantages (rapidity, exactness, etc.), computer investigations of this character have the great advantage that a general programme has only to be prepared once, and the changing gas chromatographic data merely have to be fed into this established general programme for each case.

To illustrate the above, instead of examples of individual character, the development of the functional curves for the VAN DEEMTER approximation equation

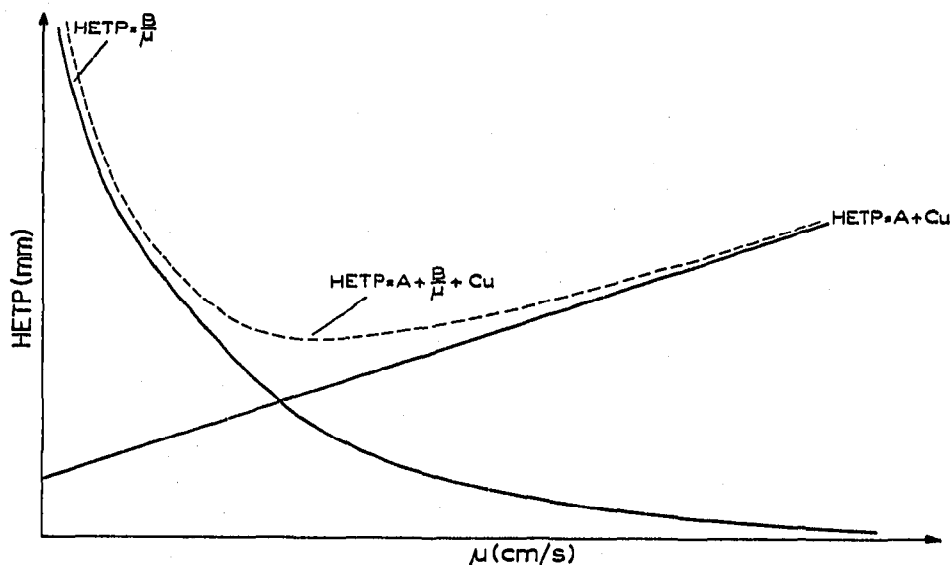


Fig. 1. General functional curve for the approximation by the VAN DEEMTER equation.

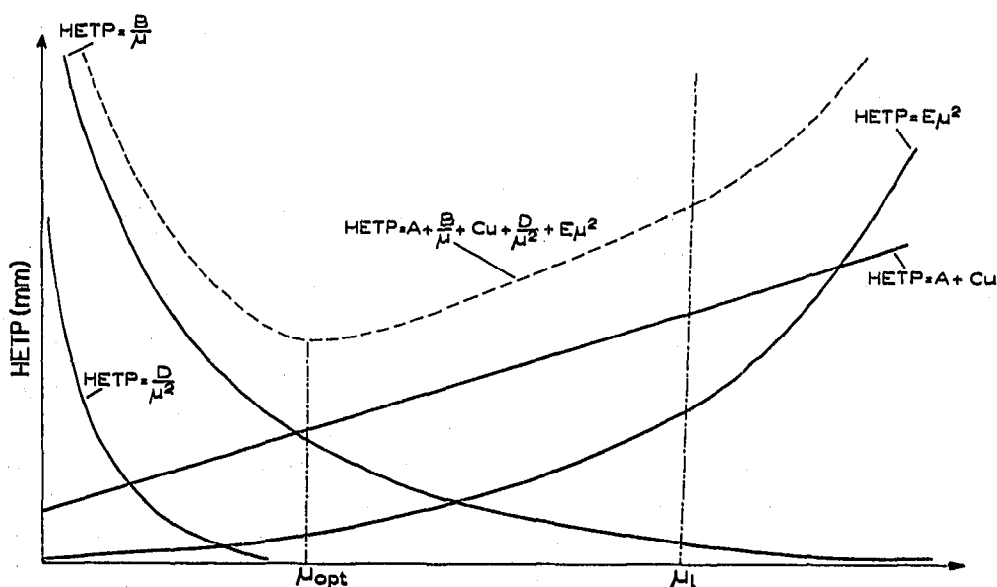


Fig. 2. General aspect of the functional curve for the approximation by equation (17).

(Fig. 1) and for the general approximation by equation (17) are presented, plotting also each component separately (Fig. 2).

DISCUSSION

This initial paper on our work in this field, concentrates on a new approximation of general validity, therefore no attempt has been made to discuss completely all the problems. Nevertheless some problems are outlined here and some of them even discussed.

One of these is the interpretation of the first term "A" of the equation, which is formulated in an entirely different manner from the former conventions, though it

must be stressed that the interpretation of the first term of the VAN DEEMTER equation must be incorporated in this new term, because it belongs there intrinsically. Up to now this term has been given much less attention, than justified by its effect on the process. There have even been opinions that its effect on the HETP value could be neglected, its value would be zero, etc. For instance $HETP_{min}$ values depend on this first term in each case in the same way as do diffusion and mass transfer factors.

In our opinion that part of the theory of capillary columns should also be re-considered according to the new approximation of general validity which is connected with this question, as this term has been neglected in the case of capillary columns, in the earlier interpretations.

Another problem of interest is that the functional curve for $HETP-u$, occurs in each case above the functional curve of the VAN DEEMTER equation. This is primarily due to the fourth and fifth term of the equation, adding their values to the corresponding function values. This, however, by no means contradicts practical experiences, which in general have higher values than expected according to the VAN DEEMTER equation.

The third problem to which we want to call attention is connected with the upper limit of interval used for gas chromatographic processes; this value is in general $P = 3.00-3.50$. In Fig. 2, the relative position of this upper limit has been indicated and the linear gas velocity (u_1) corresponding to this limit has been specially marked. In former approximations, there was no explicit theoretical basis for this empirical upper limit (Fig. 1), whereas the new approximation gives an unambiguous theoretical explanation for its development and position. Namely the new, fifth term (Eu^2), takes into account more exactly the mass transfer resistance, which has a decisive role here by bending upwards the hitherto straight line and lending a parabolic character to the functional curve by developing an inflexion along it. Practically this inflexion point may be considered as upper limit.

Last but not least, the dimensions of acceleration and of reciprocal acceleration of the 4th and 5th terms, respectively, of the new equation are to be noted as a fact also deserving further investigation. This investigation may yield useful data to complete the existing picture of the gas chromatographic process.

SYMBOLS

- n = number of theoretical plates
- t_N = net retention time (min)
- t_N' = net retention time (sec)
- w = chromatographic peak width (min)
- w' = chromatographic peak width (sec)
- HETP = height equivalent to a theoretical plate (cm)
- L = length of column (cm)
- m = slope of the straight line (ml)
- m' = slope of the straight line (cm)
- b'_1 = axial section Y of the straight line (sec)
- ψ = flow rate factor of the carrier gas (min/ml)
- φ = linear velocity factor of the carrier gas (sec/ml)
- F = flow rate of carrier gas (ml/min)

- b'_1 = axial section Y of the straight line (min)
 u = linear velocity of carrier gas (cm/sec)
 C^x = constant depending on the substance quality (ml/min)
 C^{xx} = constant depending on the substance quality (cm/sec)
 A, B, C, D and E = constants of equation (17)
 A = base factor of the gas-chromatographic system (cm)
 B = a factor to take into account diffusion processes (cm²/sec)
 C = a factor to take into account mass transfer processes (sec)
 D = a further factor to take into account diffusion processes (cm³/sec²)
 E = a further factor to take into account mass transfer processes (sec²/cm)

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