

## Note

### New method for estimation of the parameters in the Van Deemter equation

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Received January 10th, 1978)

The first test usually performed on a chromatographic column is to ascertain its efficiency, which can be obtained from a knowledge of the constants in the Van Deemter equation. This evaluation is important in order to establish the influence of these parameters on the efficiency of the column; further, it is fundamental in several theoretical considerations, such as the determination of thicknesses of liquid films and tortuosity factors.

The methods used hitherto<sup>1</sup>, which we shall call "the usual method of calculation", consists in making a series of linear extrapolations in order to obtain two parameters and a series of calculations to obtain the third. It is a long and tedious methods, it is not very accurate and one cannot simultaneously take into account all the data.

The Van Deemter equation has the form:

$$h = A + Bu^{-1} + Cu \quad (1)$$

where  $h$  and  $u$  indicate the HETP and the linear flow-rate of the carrier gas, respectively, and  $A$ ,  $B$  and  $C$  are the parameters to be determined. On the basis of eqn. 1, many experimental points are needed in order to make significant linear extrapolations and calculations. The estimation of  $A$  and  $C$  requires measurements at high linear flow-rate of carrier gas, whereas that of  $B$  requires measurements at low flow-rate.

In this paper, we shall show how the normalized-curves method<sup>2</sup> can conveniently be applied to establish the values of  $A$ ,  $B$  and  $C$ .

#### METHOD OF NORMALIZED CURVES

This method was introduced by Sillén<sup>2</sup> and has hitherto been applied to studies of equilibria in solution. According to this method, the experimental points, plotted in suitable form, are compared with a family of theoretical curves; by superposing the two plots, the best coincidence between points and curve is established, and, on the basis of the best fit, the values of the parameters can be found.

The logarithmic form of eqn. 1 is:

$$\log h = \log A + \log (1 + BA^{-1}u^{-1} + CA^{-1}u) \quad (2)$$

In eqn. 2, there are three parameters to be determined, so that three mathematical positions are necessary. We need a family of curves of equation:

$$y = \log(1 + a + la^{-1}) \quad (3)$$

The  $y$  values are calculated at fixed  $l$  values from arbitrary  $a$  values; the  $y$  values can also be obtained by using a very simple computer program.

By plotting  $y$  against  $\log a$ , the family of curves shown in Fig. 1 was obtained; from Fig. 1, it can be seen that the value of  $l$  influences the shape of the curve, whereas the values of  $a$  and  $y$  fix its position.

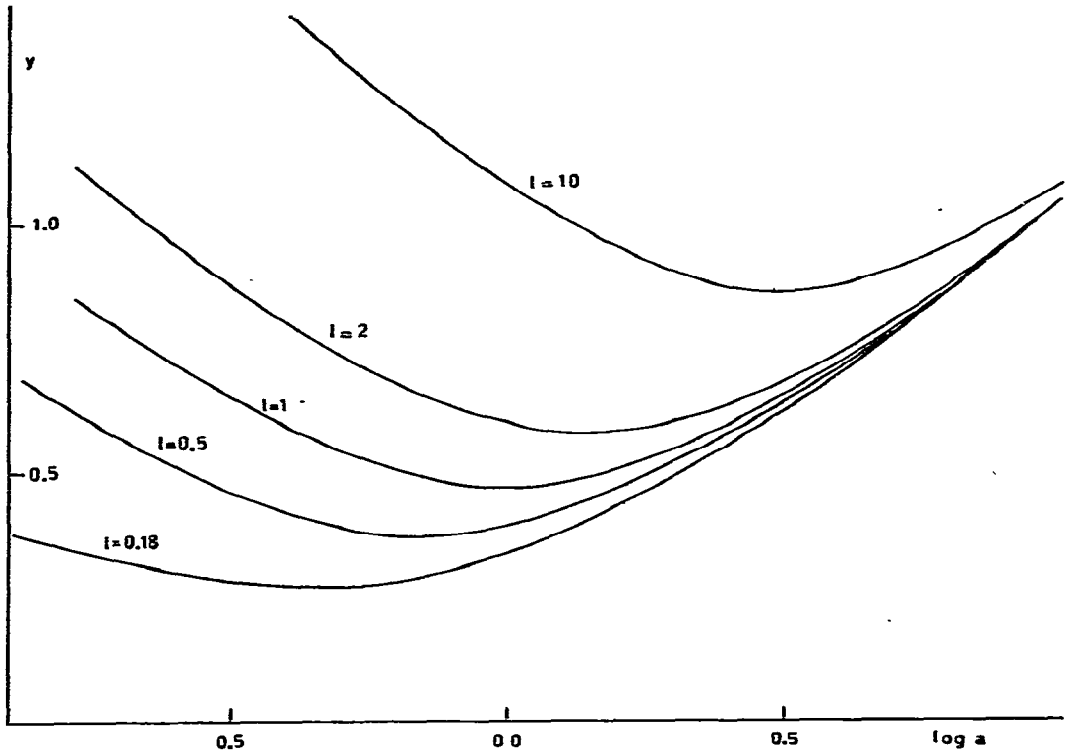


Fig. 1. Normalized curves of eqn. 3 for different values of  $l$ .

Comparison of eqns. 2 and 3 shows that:

$$\log h - y = \log A; a = uCA^{-1}; \text{ and } l = BA^{-2}C^{-1} \quad (4)$$

The experimental points plotted in the form  $\log h$  vs.  $\log u$  are superposed on the family of normalized curves of eqn. 3 and shown in Fig. 1. By moving the two plots parallel to both abscissa and ordinate and seeking the best fitting curve, the position of best concordance can be found. In this position, corresponding values

on the two axes of the graphs are read consideration also being given to the  $l$  value relative to the chosen curve. The parameters  $A$ ,  $B$  and  $C$  are obtained from these data and the number of mathematical positions (4). This approach was performed on a series of data obtained from measurements for various types of packed column.

In Tables I and II, column parameters and five sets of values obtained by the usual method of calculation are compared with those obtained by the proposed

TABLE I  
PARAMETERS OF COLUMNS USED

Columns 1, 2, 3 and 4 were packed with Carbopack C supporting 0.2% of PEG 20,000 and were operated at 55°, with  $n$ -pentane as test compound. Column 5 was packed with Corning glass spheres supporting 0.05% of SE-52 and was operated at 120°, with  $n$ -hexadecane as test compound.

Column No.	Length (m)	I.D. (mm)	Mesh size of support	Value of $K'$
1	1.08	1.0	195-203	25.2
2	1.08	1.5	100-120	24.6
3	1.08	2.0	60-80	25.4
4	1.08	1.0	203-247	25.0
5	1.80	3.0	80-100	23.1

TABLE II  
VALUES OF  $A$ ,  $B$  AND  $C$  DERIVED BY THE PROPOSED AND THE USUAL METHODS  
The packed columns used were as specified in Table I.

Column No.	$A$ (cm)	$B$ (cm <sup>2</sup> /sec)	$C$ (sec)
<i>Values obtained by usual method of calculation</i>			
1	0.010 ± 0.001	0.015 ± 0.002	0.00075 ± 0.00010
2	0.014 ± 0.0013	0.0277 ± 0.0025	0.0016 ± 0.00015
3	0.026 ± 0.0025	0.040 ± 0.005	0.0032 ± 0.0003
4	0.010 ± 0.001	0.011 ± 0.002	0.00075 ± 0.00003
5	0.008 ± 0.0035	0.123 ± 0.007	0.0076 ± 0.0004
<i>Values obtained by the proposed method</i>			
1	0.010 ± 0.001	0.022 ± 0.005	0.00074 ± 0.00005
2	0.014 ± 0.001	0.027 ± 0.003	0.0014 ± 0.0002
3	0.025 ± 0.001	0.038 ± 0.003	0.0030 ± 0.0002
4	0.009 ± 0.001	0.018 ± 0.004	0.00072 ± 0.00002
5	0.009 ± 0.002	0.121 ± 0.005	0.0073 ± 0.0003

method. As an example, Fig. 2 shows the trend of experimental points in a graph of  $\log h$  vs.  $\log u$  (see eqn. 2). The selected theoretical curve for the position of best fit is indicated.

From Table II and Fig. 2, it can be seen that agreement between the values obtained by the two methods is good; thus, the validity of the proposed method is supported.

Eqn. 1 is of general validity and can be applied to all types of chromatographic columns. Sometimes, one of the three parameters is small and negligible with respect

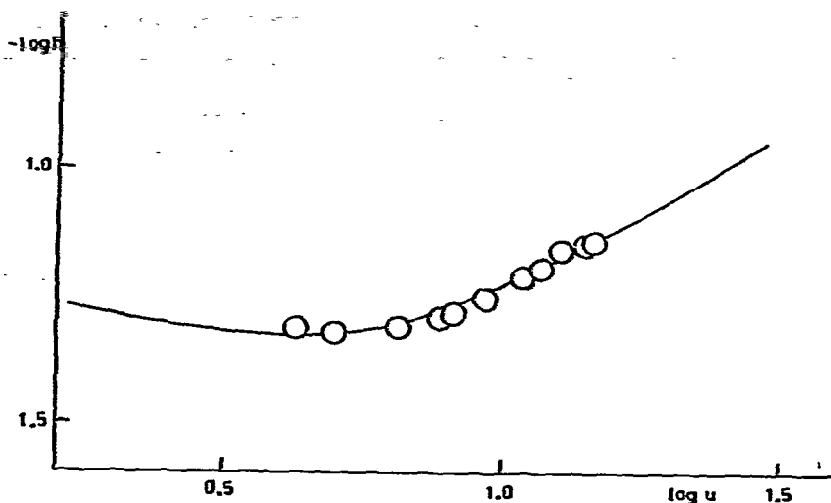


Fig. 2. The function  $\log h$  vs.  $\log u$ . The curve is the normalized one in the position of best fit.

to the others; in such instances, the proposed curve-fitting method is still applicable. If  $A$  is small with respect to the influence due to  $B$  and  $C$ , eqn. 1 approximates to

$$hu = B + Cu^2 \quad (5)$$

This occurs with wall-coated capillary columns, for which one can put  $A = 0$  without appreciable loss of accuracy.

To use the proposed method to establish the values of  $B$  and  $C$  in eqn. 5, we write this equation as

$$\log(hu) = \log B + \log(1 + CB^{-1}u^2) \quad (6)$$

The equation corresponding to the theoretical curve is:

$$y = \log(1 + a^2) \quad (7)$$

The curve of eqn. 7 can be established by allotting arbitrary values to  $a$  and plotting the corresponding  $y$  values against  $\log a$ .

The trend of experimental points (see eqn. 6) is similar to that expressed by eqn. 7, by plotting  $\log(hu)$  against  $\log u$  in eqn. 6 and  $y$  against  $\log a$  in eqn. 7.

By putting

$$\log(hu) - y = \log B \text{ and } a = u \sqrt{CB^{-1}} \quad (8)$$

We can compare experimental points with the theoretical curve of eqn. 7. The two plots are moved parallel to both abscissa and ordinate until the best fit is obtained. In this position, the corresponding values on the ordinate of the experimental and of the theoretical curves are read. On the basis of the number of mathematical

positions (8) and from the difference between the values read, the value of  $B$  is obtained. In the same position, the corresponding values of  $\log a$  and  $\log u$  are read. From these values,  $C$  can be calculated.

In contrast, for some chromatographic columns (for example, in liquid-liquid chromatography), parameter  $B$  in eqn. 1 is negligible and the expression becomes:

$$h = A + Cu \quad (9)$$

In this case also, a normalized curve can be found that fits the experimental points. The plot of  $\log h$  against  $\log u$  can be compared with a curve of equation:

$$y = \log(1 + u) \quad (10)$$

where

$$\log h - y = \log A \quad \text{and} \quad a = u(C/A)$$

The procedure used to establish the values of  $A$  and  $C$  is similar to that already explained. The two graphs are moved parallel to the two axes until the best fit is obtained. From the corresponding values and from the above number of positions,  $A$  and  $C$  can be calculated.

Finally, if  $C$  is negligible with respect to  $A$  and  $B$ , eqn. 1 becomes:

$$h = A + Bu^{-1}$$

This case can be treated like the others, but the trend of the experimental points (graph of  $\log h$  against  $-\log u$ ) has to be compared with the normalized curve of equation:

$$y = \log(1 + a^{-1}) \quad (11)$$

putting  $\log h - y = \log A$  and  $a^{-1} = u^{-1}(B/A)$ .

Fig. 3 shows an example of the trend of the points on a graph of  $\log(hu)$  against  $\log u$  plotted for a capillary column, together with the normalized curve of eqn. 7 in the position of best fit.

## DISCUSSION

The aim of this work was to devise an alternative method for determining the parameters  $A$ ,  $B$  and  $C$  of the Van Deemter equation. The proposed method is simple, rapid and easy to use, and its validity is supported by the results shown in Table II and Figs. 2 and 3. Once the theoretical curves have been plotted, they are always immediately available, so that much time can be saved.

The method of fitting curves gives a comprehensive disposition of the experimental results, which is very difficult to achieve by the usual method of calculation, even if the least-squares technique is used.

Further, only a few well-spaced points are needed to select the position and

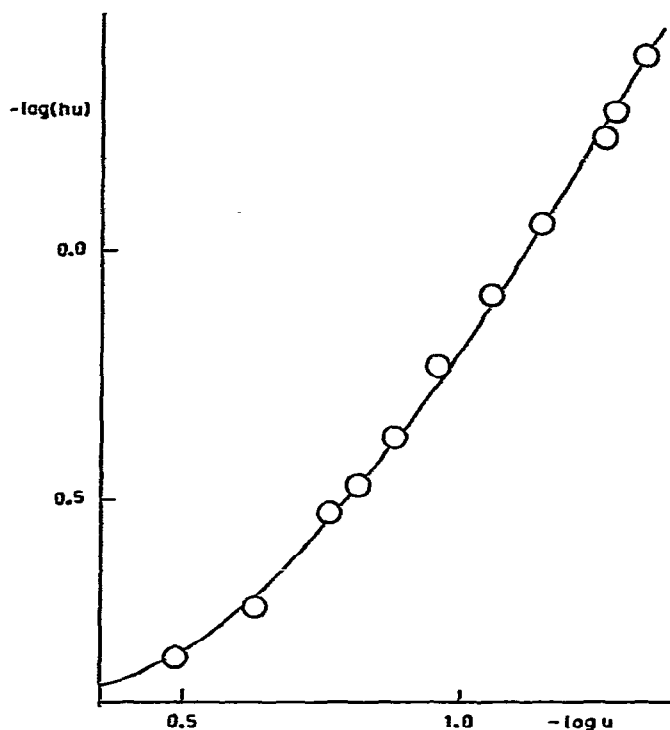


Fig. 3. The function  $\log(hu)$  vs.  $\log u$ . The curve is the normalized one in the position of best fit.

shape of the curve; this is an important advantage, as it means that fewer determinations of  $h$  and  $u$  have to be made; thus, time is also saved in performance of the measurements.

The accuracy of the values of  $A$ ,  $B$  and  $C$  is given by the maximum shift that still permits acceptable agreement between the experimental points and the curve. Further, when  $A$ ,  $B$  or  $C$  is negligible, the experimental points are compared with a single curve (from eqn. 7, 10 or 11, respectively), which can also be used to evaluate the accuracy of the measurements. The points must lie on this curve; those that do not are subject to experimental error.

It is probable that this method can also be applied in other types of chromatography.

#### ACKNOWLEDGEMENT

This work was supported by C.N.R., the Research Council of Italy.

#### REFERENCES

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