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COMMENTS ON VAN DEEMTER PLOT IN HIGH SPEED COUNTERCURRENT CHROMATOGRAPHY

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ABSTRACT

An inaccuracy in the computation of the linear mobile phase velocity rendered the whole content of a recently published article, Q.Z. Du, P.D. Wu, Y. Ito, *J. Liq. Chromatogr. & Rel. Technol.*, **23(19)**, 2929 (2000), erroneous. Since the stationary phase volume was given, the correct mobile phase velocity values were computed and the new values for the Van Deemter plots of three compounds are listed. It is concluded that the 1.5 mL/min flow rate, corresponding to the minimum of the Van Deemter plots, or the maximum efficiency, does not justify calling the technique High Speed CCC since three hours are needed to develop the chromatogram.

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INTRODUCTION

In a recent work¹ titled: "Van Deemter Plot in High Speed Countercurrent Chromatography with a Fixed Volume of Stationary Phase," Du et al. used the classical Van Deemter equation:

$$H = A + B/u + Cu \quad (1)$$

to investigate solute band broadening observed in a hydrodynamic CCC machine at different flow rates. In the Van Deemter equation, H is the height equivalent to a theoretical plate, in cm, u is the mobile phase linear velocity, in cm s^{-1} , A , B , and C are three constants. A , in cm, expresses the broadening contribution due to different possible paths that the solute molecules can follow. B , in $\text{cm}^2 \text{s}^{-1}$, represents the band broadening contribution due to longitudinal diffusion and C , in s, is the contribution of the kinetic of the solute transfer from the mobile phase to the stationary phase and vice versa. Three different solutes were used. They were epigallocatechin gallate (EGCG), gallic acid (GCG), and epicatechin gallate (ECG).

The aim of these comments is to rectify serious inaccurate statements found in this article.

FLOW RATE AND LINEAR VELOCITY

It is essential to have the correct value of the linear mobile phase velocity in order to derive significant A , B , and C constants in the Van Deemter equation. The linear velocity, u , is dependent on the flow rate, F , the column length, L , and the mobile phase volume, V_m , present in the chromatographic column:

$$u = FL / V_m \quad (2)$$

Unfortunately, in the cited work,¹ the stationary phase was ignored and the inside tubing volume, V_c , was used in Eq. 2 in place of V_m . Since the stationary phase volume was 22 mL, the V_c volume was 54 mL, it is easy to calculate the mobile phase volume, $V_m = 32$ mL. The stationary phase retention factor is $S_f = 41\%$. This inaccuracy introduces a systematic bias of $\sim 40\%$ by default in the whole set of u values used in Ref. 1. Table 1 lists the correct u values along with the plate number corresponding to the experiments exposed in Ref. 1.

The consequences of this inaccuracy on mobile phase flow rates are that the fitted parameters are dramatically changed. Table 2 lists the A , B , and C parameters obtained using the method presented in Ref. 2. Figure 1 shows the experimental points plotted with the fitted Van Deemter curves. The comparison of the correct values, listed in Table 2, with the published values shows the dramatic

Table 1. Linear Mobile Phase Velocities and Peak Plate Numbers at Different Flow Rates

F	u	EGCG		GCG		ECG	
		H	N	H	N	H	N
mL/min	cm/s	cm	Plates	cm	Plates	cm	Plates
16	8.33	36.70	27	41.5	24	51.67	19
12	6.25	28.42	35	33.5	30	38.98	26
8	4.17	22.72	44	25.3	39	32.40	31
4	2.08	15.47	65	17.7	56	21.99	45
3.2	1.67	12.62	79	15.9	63	19.50	51
2	1.04	11.01	91	14.3	70	18.22	55
1	0.52	12.08	83	15.2	66	20.47	49
0.5	0.26	12.35	81	15.7	64	22.73	44

The H values, in cm per theoretical plate, come from Ref. [1].

consequences that a change in the set of u values may have on the fitted A, B, and C parameters. The A parameter is no more a constant. It depends on the distribution coefficient, K, as well as the B and C values. However, the plot A versus K is certainly not linear (Figure 2). The regression coefficients obtained for the plots of B and C versus K are indicated in the figure. These variations are in accordance with that encountered in several chromatographic models, such as the plug flow model with axial dispersion.³ But, it should be noted that three points are not enough to draw any strong conclusion.

USING LOGARITHMS

The work finishes showing plots of log H versus log u and stating, "Figure 3 shows the plot of log H versus log u, indicating a linear correlation between

Table 2. Van Deemter Coefficients for the Table 1 Data Set and Solutes Retention Volumes and Distribution Coefficients

Solute	EGCG	GCG	ECG
A (cm)	6.1	8.8	10.6
B (cm ² s ⁻¹)	1.5	1.7	3
C (s)	3.7	3.9	4.8
Vr (mL)	56	85.5	164
K	1.1	2.35	6.0

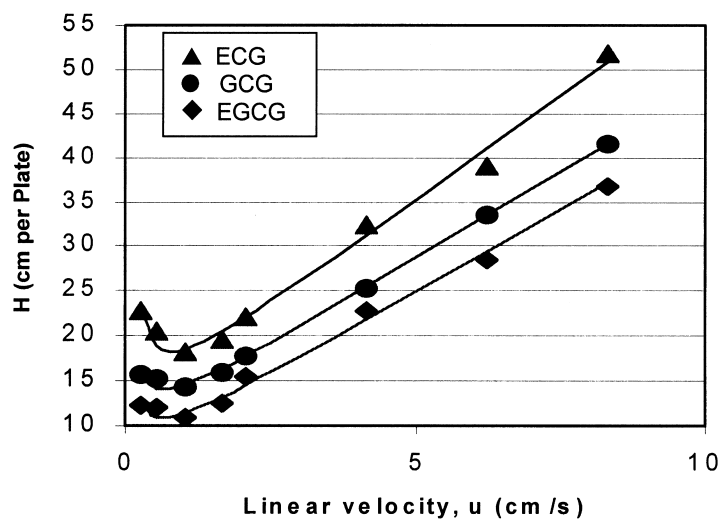


Figure 1. Van Deemter plots for the experimental data of Ref. 1 and the u values of Table 1. The lines correspond to equation 1 with A , B and C values of Table 2.

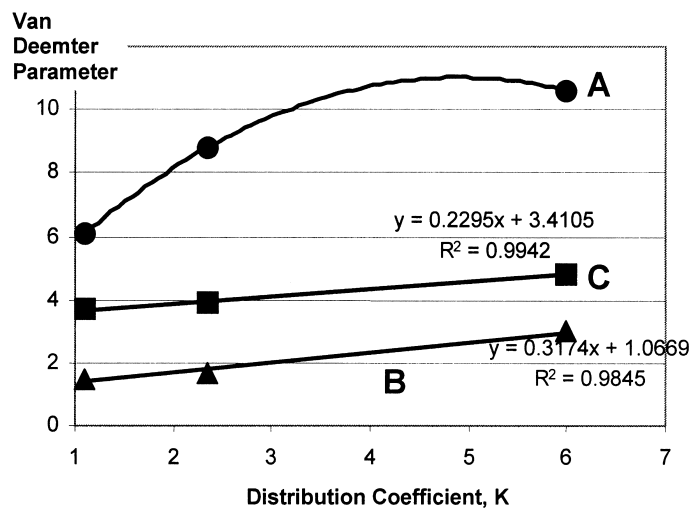


Figure 2. Van Deemter coefficients A , B and C plotted versus the solute distribution coefficients.

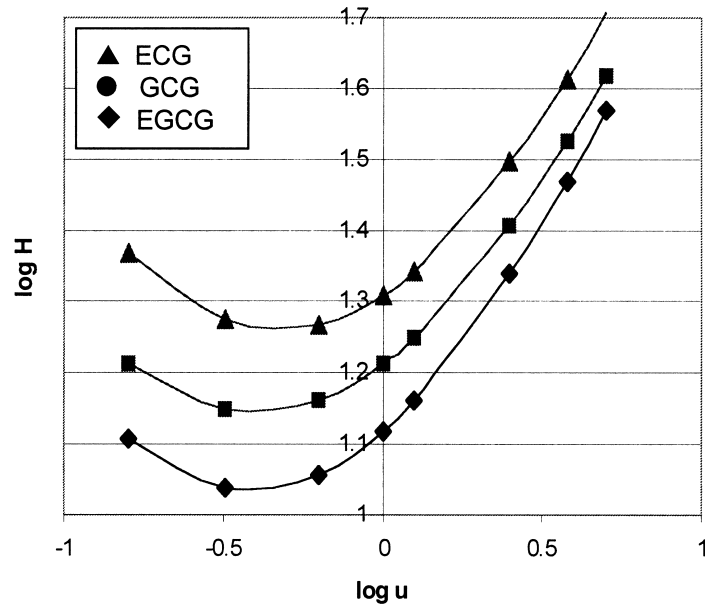
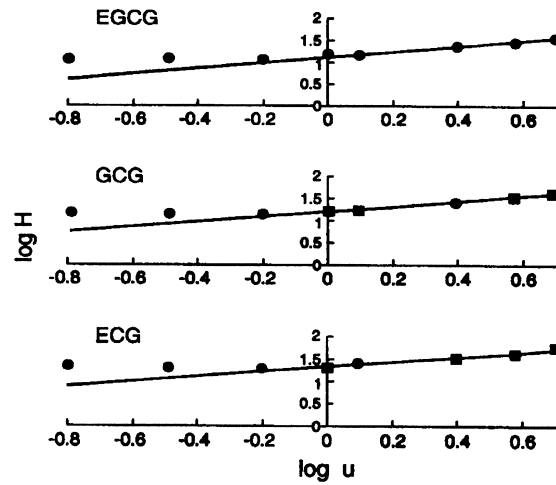


Figure 3. Plots of $\log H$ versus $\log u$. Top: verbatim of the Ref. 1 Figure 3 published plot; Bottom: plot with correct parameters (Table 2) and axis scale.

these two parameters when u is 1 cm/s or greater.” This is highly misleading. It is known that the logarithm function applied to any set of data produces a strong compression. A variation of one order of magnitude is converted in one log unit. If further compression is added using different scale for the X and Y-axis (Figure 3, top), any function can be linearized in the log-log space. Since the equation of the Van Deemter relation is known (Eq. 1), it is obvious that for high u values, the B/u term becomes small and H tends toward the Cu line. Figure 3 (bottom) shows the plots of $\log H$ versus $\log u$ in adjusted X and Y-axis. The compressed Van Deemter plot is apparent, when compared with Figure 1.

BAND BROADENING IN A CCC MACHINE

The importance of the stationary phase volume inside the CCC machine was pointed out early.^{4,5} Some results obtained with a variable stationary phase volume could be questioned.⁶ It remains interesting to see that, with a constant stationary phase volume, the behavior of a hydrodynamic CCC machine is classical. It should also be pointed out, that the low efficiency of the machine used

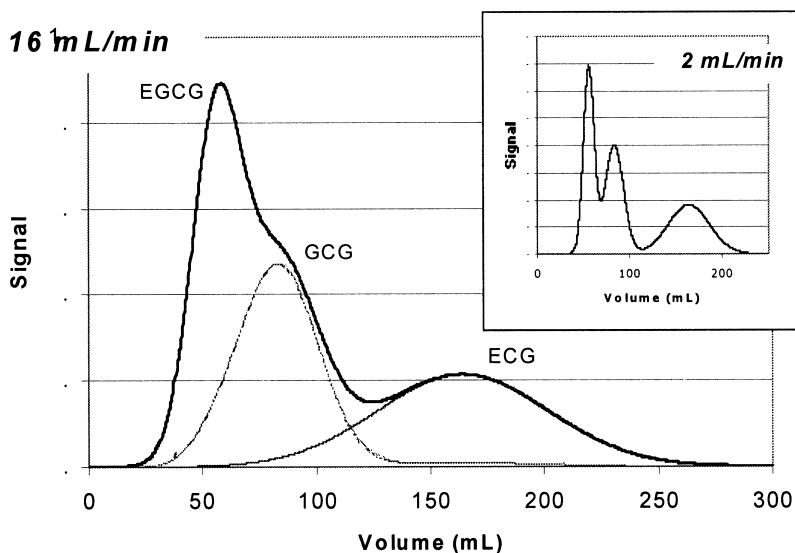


Figure 4. Reconstructed chromatograms using the data published in Ref. 1 at two different flow rates. Experiment duration: 19 min@16 mL/min and 125 min@2 mL/min.

(plate numbers are listed in Table 1) produced a broad peak. If the compounds were not injected one by one, the results listed might have a high uncertainty.

Figure 4 shows the chromatograms recalculated with the published data. At a 16 mL/min-flow rate, the peak efficiency measurement was not possible. At 2 mL/min (Figure 4, inset), the peak efficiencies were maximal and the measurement was accurate. The problem of the results exposed in Ref. 1 is, that it is shown that the maximum efficiency is obtained between flow rates of 1 and 2 mL/min, say about 1.5 mL/min. At this flow rate, the experiment duration is more than three hours to separate compounds with distribution coefficients of 6 (Figure 4). Is it still possible to say that this form of CCC is "High Speed?"

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