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EFFECT OF COLUMN LENGTH ON HETP IN GAS CHROMATOGRAPHY

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SUMMARY

The effects of column length and pressure difference on HETP were studied on the basis of our previous theory in which the kinetic role of diffusion and the pressure drop along the column were taken into consideration. If one postulates a uniform linear velocity distribution in the column, the number of plates should be proportional to the column length. The theoretical prediction that the complicated relationship between HETP and column length is considerably affected by the pressure difference was studied and confirmed experimentally.

INTRODUCTION

The familiar Van Deemter equation[1,2] was derived under the assumption of a uniform mobile phase velocity[3], so that the application of the theory in gas chromatography has presented several problems owing to the lack of knowledge of the compressibility of the gas phase. The modifications of the Van Deemter theory were reviewed in detail by Walker and Palframan[4]. If there were a uniform linear velocity distribution of carrier gas along the column, the plate number should be proportional to the column length. In our previous papers[5,6], in which we considered what we shall hereafter call KOS theory, a new equation for the height equivalent to a theoretical plate (HETP) was derived from the kinetic viewpoint, in which the pressure dependence of the diffusion coefficient in the gas phase and the non-uniform velocity distribution along the column were dealt with mathematically. With varying gas flow-rates, the validity of KOS theory was confirmed experimentally[6]. The remarkable dependence of HETP on column length has already been discussed by Halász *et al.*[7], and later Novák and Boček[8] interpreted the problem in terms of the mean absolute pressure. The aim of the present study was to obtain a clear understanding of the effect of column length on the column efficiency.

THEORETICAL

Let H be the HETP, n the number of plates of a column of length l, D^* the diffusion constant under unit pressure, w the permeability coefficient and p_i and p_0

the inlet and outlet pressures, respectively. According to KOS theory, the HETP is given by

$$H = \frac{l}{n} = \frac{9\,D^{*}\,l}{2\,w} \cdot \frac{(p_i^4 - p_0^4)}{(p_i^3 - p_0^3)^2} + \frac{3\,w\,F_s^2\,\beta^2}{2\,\alpha\,F\,K^2\,l} \cdot \frac{(p_i^2 - p_0^2)^2}{(p_i^3 - p_0^3)} \tag{1}$$

where F and F_s are the volume fractions occupied by the mobile and stationary phase, respectively, K the distribution coefficient, α the rate constant of dissolution or adsorption and β is given by

$$\beta = 1 + \frac{F_s}{K F} \tag{2}$$

The flow rate, v, of carrier gas is given by the well known Darcy equation:

$$v = q\,u_0\,p_0\,F = \frac{w\,q\,F\,(p_i^2 - p_0^2)}{2\,l} \tag{3}$$

where q is the proportionality factor and u_0 is the outlet linear velocity.

Eqn. 1 can be rearranged into

$$\frac{1}{n} \cdot \frac{(p_i^3 - p_0^3)^2}{p_i^4 - p_0^4} = \frac{9\,D^{*}}{2\,w} + \frac{3\,w\,F_s^2\,\beta^2}{2\,\alpha\,F\,K^2} \cdot \frac{(p_i^2 - p_0^2)(p_i^3 - p_0^3)}{(p_i^2 + p_0^2)} \cdot \frac{1}{l^2} \tag{4}$$

From the technical viewpoint, it may be more exact and reasonable to employ the weight, W, of the packed material in the tube instead of the nominal column length. With a column of a uniform inner diameter, the weight of packed material may be considered as the effective column length. Thus, one has

$$l = kW \tag{5}$$

where k is a proportionality factor.

EXPERIMENTAL

The columns employed had the nominal lengths of 1.0, 2.0, 1.5, 2.5 and 3.0 m; the latter three columns were made by combinations of the first two columns and a 0.5-m column. The stainless-steel columns were U-shaped tubes of 4 mm I.D. The column packing was 25% (w/w) dinonyl phthalate on 60–80-mesh Shimalite. The amount of packed material in each column was weighed before and after the experiment. The weight loss was found to be within 0.3%. The mean value thus obtained gave the value for W in eqn. 5.

The gas chromatograph used was a Hitachi Type KGL-2A instrument, equipped with a thermal conductivity detector.

The difference between the inlet and outlet pressures was measured by means of a pressure gauge and the outlet pressure was kept at atmospheric. The flow-rate of the carrier gas (helium) was measured with a soap-film meter and corrected for the water vapour pressure.

The column temperature was maintained at 78 ± 0.1°, at which value the chromatogram of benzene was a normal distribution curve. The HETP values for benzene were found to be independent of the sample size at levels below 0.8 µl, so a

0.6-μl sample of benzene was injected. The number of plates was calculated from the equation

$$n = 16 \left(\frac{a}{b}\right)^2 \quad (6)$$

where a and b are the peak distance from the starting line and the peak width at the baseline, respectively[9].

RESULTS AND DISCUSSION

The carrier gas flow-rate plotted against $p_i^2 - p_0^2$ for each column is shown in Fig. 1. From eqns. 3 and 5, it is clear that the slope of each line corresponds to

$$\frac{w\,q\,F}{2\,k\,W} \quad (7)$$

The constancy of wqF/k indicates the uniform packing in each column, as illustrated in Table I. The coefficient of variation is 2.7% and it was confirmed that there is no significant difference in packing performance among the five columns used.

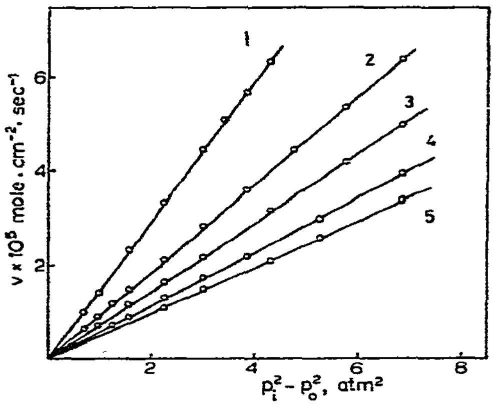

Fig. 1. Helium carrier gas flow-rate plotted against $p_i^2 - p_0^2$ for columns of various nominal lengths: 1, 1 m; 2, 1.5 m; 3, 2 m; 4, 2.5 m; 5, 3 m.

TABLE I

CONFIRMATION OF UNIFORM PACKING

Nominal column length, l (m)	*Weight of packed material, W (g)*	*Slope of straight line in Fig. 1 (μmole·cm^{-2}·sec^{-1}·atm^{-2})*	*wqF/k (mmole·cm^{-2}·sec^{-1}·g)*
1.0	7.01	14.86	0.208
1.5	10.43	9.41	0.196
2.0	13.84	7.30	0.202
2.5	17.00	5.75	0.196
3.0	20.59	4.95	0.204
		Mean:	0.201_2

TABLE II

EFFECTS OF COLUMN LENGTH AND PRESSURE DIFFERENCE ON PLATE NUMBER

The outlet pressure was kept at atmospheric. The results are mean values of four measurements.

Pressure difference (atm)	*Nominal column length (m)*				
	1.0	*1.5*	*2.0*	*2.5*	*3.0*
0.3	816	992			
0.4	915	1196	1339		
0.5		1443		1873	
0.6	962	1449	1869	2037	
0.8	957	1592	2053	2463	2778
1.0	895	1515	2247	2770	3268
1.1	855				
1.2	784	1439		2770	
1.3	761		2062		3390
1.4	667	1332			
1.5	629			2653	3448
1.6		1309	1894		
1.8		1111	1808	2469	3236
2.0		1068	1642	2415	3165
2.2			1577	2208	3021
2.4			1473	2012	2809
2.6				1969	2786
2.8				1930	2544

The number of plates measured with a series of columns of varying length is given in Table II. With increasing inlet pressure, the plate number first increases and then decreases.

The relationship between HETP and flow-rate obtained with various column lengths is shown in Fig. 2. The shift of the curve towards lower HETP values with increasing column length can be seen. The effect of inlet pressure, at a constant outlet pressure of 1 atm, on the number of plates of each column is shown in Fig. 3 and is in good agreement with eqn. 4.

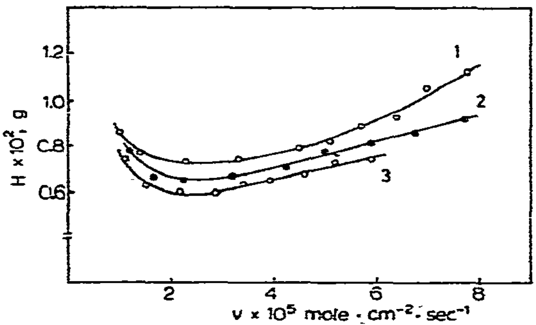

Fig. 2. HETP *versus* flow-rate curves. Column length: 1, 1 m; 2, 2 m; 3, 3 m. The HETP, expressed in terms of length, is converted into the weight of packed material according to eqn. 5. Sample: 0.6 µl of benzene. Stationary phase: 25% (w/w) dinonyl phthalate on 60–80-mesh Shimalite. Temperature: 78 ± 0.1°.

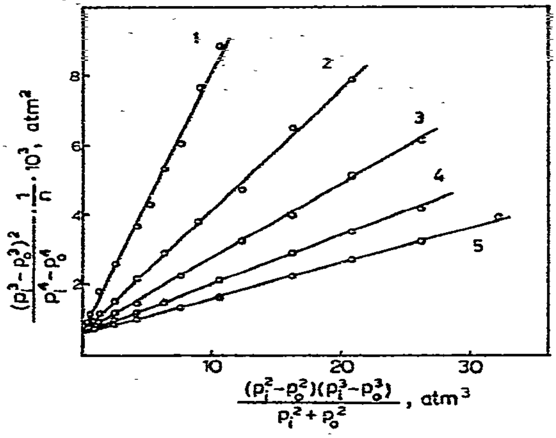

Fig. 3. Dependence of HETP on inlet pressure at a constant outlet pressure of 1 atm, as shown by eqn. 4. Column lengths as in Fig. 1.

The good reproducibility of the data was confirmed as follows. With the 1-m column, a duplicate measurement was carried out with varying pressure differences, and it was found that there was no significant difference between the two sets of corresponding data.

It is predicted from eqn. 4 that the slopes of the lines in Fig. 3 are a function of column length. The plot of the slopes of these lines against W^{-2} showed good proportionality, as shown in Fig. 4. This result clearly demonstrates the validity of eqn. 4.

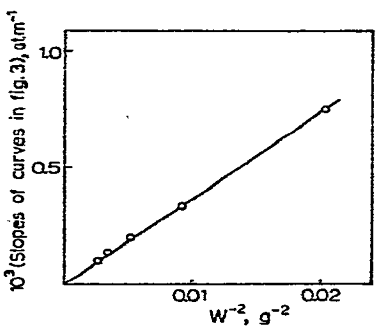

Fig. 4. Slopes of the lines in Fig. 3 plotted against W^{-2}.

Halász *et al.*[7] and Novák and Boček[8] have also reported the dependence of HETP on column length. They have discussed the problem on the basis of the classical Van Deemter equation with some additional modifications. HETP is plotted against the mean carrier gas velocity, $\bar{u}$, which is obtained from the following equation:

$$\bar{u} = \frac{l}{t_0} \tag{8}$$

where t_0 is the retention time of the unretained solute, such as air. It is found that at high flow-rates, the HETP is shifted towards higher values as the column length increases.

As t_0 is very short, an exact estimation of $\bar{u}$ is difficult. One can measure the outlet flow-rate more directly, accurately and easily, so that it seems more reasonable to establish the column efficiency in terms of outlet flow-rate, as shown by eqn. 3, than by means of the linear velocity.

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