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EFFECT OF GRAIN DIAMETER AND UNIFORMITY OF ADSORBENT GRANULES ON THE EFFICIENCY OF GAS CHROMATOGRAPHIC COLUMNS OF VARIOUS DIAMETERS

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SUMMARY

The effect of sorbent grain diameter and granule uniformity on the efficiency and resolving power of columns of various diameters has been studied. It is shown that for columns of small diameter the grain size has a significant effect on efficiency and resolving power, while for columns of large diameter non-uniformity of the sorbent granules is of greater importance.

INTRODUCTION

The fundamental cause of the spreading of chromatographic bands in columns of large diameter is the effect of filling the columns with non-uniform sorbents[1–3]. The distribution of sorbent particles over the cross-sectional area of preparative-scale columns has been studied[4,5], and it has been shown that when columns were filled with sorbent with non-uniform grains, large particles were located near the walls and smaller particles at the centre.

Thus, when using columns of large diameter in preparative gas chromatography, one of the main problems is the sorbent uniformity when filling such columns. The application of special techniques when filling preparative-scale columns does not completely solve the problem [6,7], and in this case the uniformity of the sorbent granules is perhaps of great importance. Many workers[6–14] have shown (even in preparative-scale columns), that it is expedient to use fine-grained sorbents which satisfy the requirements for the spreading of chromatographic bands.

EXPERIMENTAL

The effect of grain diameter and grain uniformity has been studied on the efficiency of columns of various diameters. The experiments were carried out using a PACh-04 preparative chromatograph with a thermal conductivity detector and hydrogen as the carrier gas. A light distillate of straight-run gasoline was used as the

test mixture. Columns of 0.6, 1.2 and 2.6 cm diameter, consisting of U-shaped sections 3 m in length, were studied.

Narrow uniform sorbent fractions of 0.2–0.3, 0.4–0.5, 0.5–0.6, 0.6–0.7 and 0.7–0.8 mm and two non-uniform fractions (I and II) were studied. Fraction I included only two grain sizes, 0.2–0.3 and 0.7–0.8 mm, in equal proportions by volume. Fraction II included grains of all the sizes under test (0.25, 0.45, 0.55, 0.65, 0.75 mm) in equal proportions by volume. Both fractions I and II have an average composition corresponding to a fraction of 0.5–0.6 mm.

All the experimental data were obtained using TZK-M adsorbent (diatomite from the Zikeevskii Quarry) treated with a 2% solution of sodium carbonate (on weight of sorbent) and modified with 5% of liquid paraffin related to adsorbent activity.

Narrow adsorbent fractions were prepared in the following manner. The starting adsorbent was screened into fractions and narrow fractions of untreated TZK-M adsorbent were treated, according to the technique of Kudryavtseva *et al.*[15], with a 2% solution of sodium carbonate, dried, heated at 800–900° and then modified with liquid paraffin in an amount corresponding to its activity. After each operation, the narrow fraction was separated from the dust formed. The final narrow fractions obtained were filled into the columns and compacted manually by tapping in vertical and horizontal directions. The volume of sample injected into a column with a hypodermic syringe was proportional to the cross-sectional area of the columns and equal to 0.15 ml/cm^2. In order to ascertain the effects of grain diameter and grain uniformity on the efficiency of columns of different diameters, we studied the dependence of the height equivalent to a theoretical plate (HETP; H, cm) and resolution ($K_1 = 0.5R$) on linear flow-rate of the carrier gas and the volume of sample injected.

RESULTS AND DISCUSSION

Of the three terms of the classical Van Deemter equation

$$H = A + B/u + Cu$$

the first term, $A = 2\lambda d$, is the most uncertain. This term[1] is independent of the nature of the material being analyzed, the stationary liquid phase used, the nature of the adsorbent or the operating conditions of a column, and it characterizes only the column packing, in terms of its geometric properties.

A depends on two parameters, (1) the non-uniformity of filling the columns with sorbent and (2) the sorbent grain diameter. The λ value depends on grain diameter, grain geometry, and on the column diameter. The value of this term can be lowered when globular particles (which have a uniform shape) are used, because in this case it is possible to produce the densest packing. It has also been stated[14] that it is not possible to obtain such a dense and uniform packing of a column when small rather than large particles are used. Therefore the λ value, as a measure of non-uniformity of filling a column, will increase as the grain diameter decreases. Thus, when the grain diameter of adsorbent decreases, A should, on the one hand, decrease as a function of the grain diameter, while on the other hand it should increase as a function of the λ value, which will increase with decrease in grain diameter.

It can therefore be assumed that the diameter of the sorbent grains will have a considerable effect on A. As the results showed, this assumption is true only for columns of small diameter. In Table I, values of A, B and C in eqn. 1 are given; these terms were calculated from the experimental data by the least-squares method using a computer. From Table I, it can be seen that for columns of 0.6 cm diameter, A increas-

TABLE I

VALUES OF TERMS A, B AND C, IN THE VAN DEEMTER EQUATION AND OF PENETRATION COEFFICIENTS (K_{pen}) FOR COLUMNS OF VARIOUS DIAMETERS, CALCULATED USING A COMPUTER

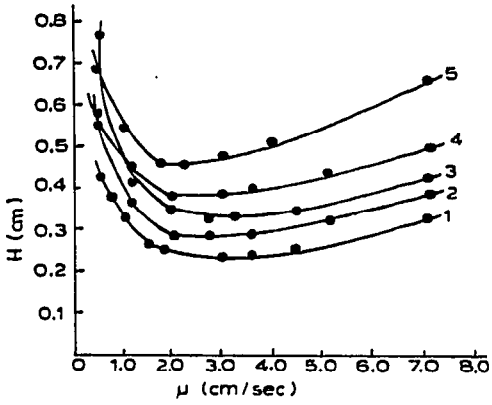
Column diameter (cm)	*Sorbent granule size (mm)*	A	B	C	$K_{pen} \cdot 10^7$
0.6	0.2–0.3	0.11	0.20	0.02	1.64
	0.4–0.5	0.17	0.19	0.03	2.28
	0.5–0.6	0.19	0.30	0.02	3.44
	0.6–0.7	0.28	0.13	0.03	8.47
	0.7–0.8	0.30	0.15	0.05	10.00
	Fraction I	0.18	0.15	0.03	1.93
	Fraction II	0.11	0.18	0.04	1.83
1.2	0.2–0 3	0.23	0.14	0.02	1.25
	0.4–0.5	0.22	0.15	0.04	1.30
	0.5–0.6	0.23	0.14	0.03	1.46
	0.6–0.7	0.19	0.19	0.06	1.51
	0.7–0.8	0.11	0.23	0.12	1.71
	Fraction I	0.19	0.15	0.07	1.93
	Fraction II	0.20	0.15	0.05	1.83
2.6	0.2–0.3	0.20	0.20	0.05	0.60
	0.4–0.5	0.22	0.21	0.05	1.17
	0.5–0.6	0.20	0.19	0.08	1.67
	0.6–0.7	0.05	0.31	0.14	2.04
	0.7–0.8	0.06	0.38	0.14	2.30
	Fraction I	0.56	0.17	0.29	1.08
	Fraction II	0.43	0.11	0.01	1.44

es with an increase in grain diameter, *i.e.*, in this instance A is influenced more by the grain diameter than by the λ value. However, for columns of 1.2 and 2.6 cm diameter, a decrease in A occurs with an increase in grain diameter, so in this instance A is influenced more by the λ value rather than by grain diameter.

Thus, when the column diameter increases, A and therefore the HETP are influenced more by the uniformity of filling a column with sorbent (λ value) than by the absolute value of the grain diameter.

One can represent the density of packing a column with sorbent in terms of the penetration coefficient (K_{pen}). Values of K_{pen} are given in Table I; as expected, they increase with increase in grain diameter.

According to the Van Deemter equation, the HETP increases with an increase in sorbent grain diameter, and this theoretical prediction is in good agreement with the experimental results. Plots of the dependence of efficiency on grain diameter for



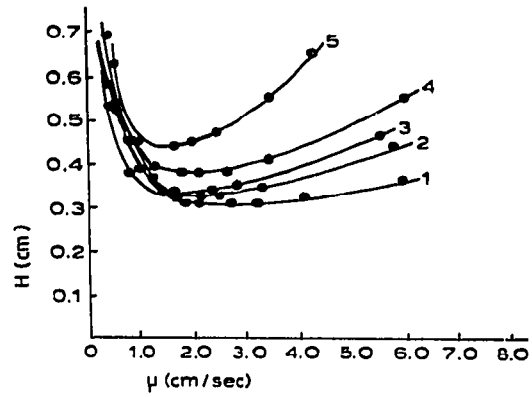


Fig. 1. Dependence of the HETP (H) on the linear flow-rate of the carrier gas (u) for columns of 0.6 cm diameter charged with sorbent fractions with uniform grains. Grain size: 1, 0.2–0.3; 2, 0.4–0.5; 3, 0.5–0.6; 4, 0.6–0.7; 5, 0.7–0.8 mm.

Fig. 2. Dependence of the HETP (H) on the linear flow-rate of the carrier gas (u) for columns of 1.2 cm diameter charged with sorbent fractions with uniform grains. Grain size: 1, 0.2–0.3; 2, 0.5–0.6; 3, 0.4–0.5; 4, 0.6–0.7; 5, 0.7–0.8 mm.

columns of various diameters are shown in Figs. 1–3. It can be seen that the efficiency of chromatographic columns decreases with an increase in particle diameter. However, the influence of grain size on the efficiency of columns of various diameters decreases with an increase in column diameter. Thus, with a three-fold increase in grain diameter, the efficiency of columns of 0.6 cm diameter decreased by a factor of 1.8, the efficiency of columns of 1.2 cm diameter decreased by a factor of 1.4 and the efficiency of columns of 2.6 cm diameter decreased by a factor of only 1.2. The greater decrease in the efficiency of columns of small diameter compared with those of large diameter with an increase in grain diameter is, in our view, due to an increase in the effect of the wall boundary layer, the thickness of which is from half to three grain diameters. The gas carrier flow-rate in this layer is higher than in the centre of the column. In this instance, non-uniformity of the distribution of particles over the cross-

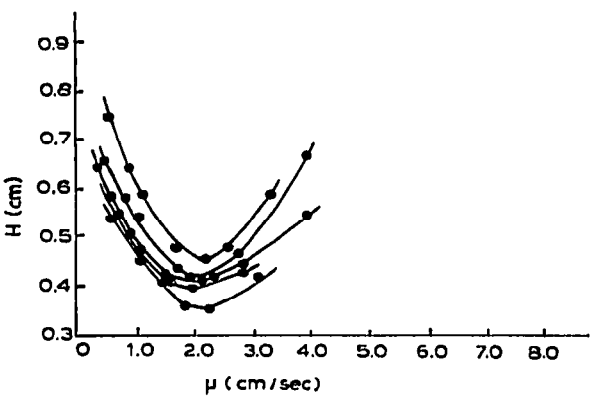
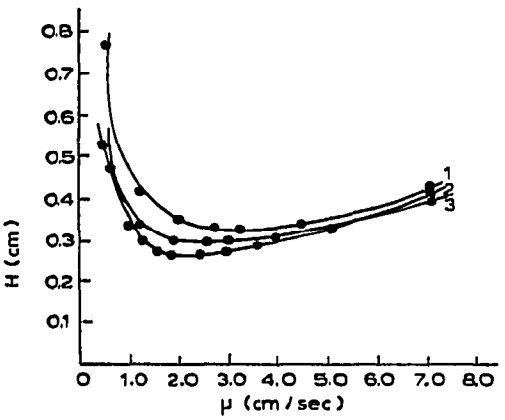


Fig. 3. Dependence of the HETP (H) on the linear flow-rate of the carrier gas (u) for columns of 2.6 cm diameter charged with sorbent fractions with uniform grains. Grain size: as in Fig. 1.

sectional area of the column, which causes the gas flow to be non-uniform, could not have occurred, because when packing the columns carefully screened uniform narrow particle fractions were used. Hence, the experimental results confirmed that the wall effect influences the efficiency of columns of small diameter (analytical columns) to a greater extent than the efficiency of those of large diameter (preparative columns).

In order to ascertain the effect of non-uniformity of sorbent granules on the efficiency of chromatographic columns of various diameters, we studied columns packed with a uniform fraction of grain diameter 0.5–0.6 mm and with the two non-uniform fractions, I and II.



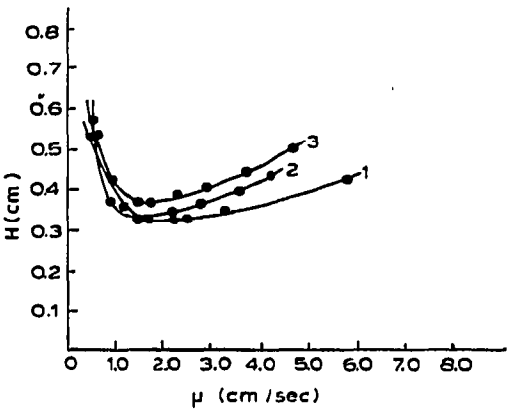


Fig. 4. Dependence of the HETP (H) on the linear flow-rate of the carrier gas (u) for columns of 0.6 cm diameter charged with sorbent fractions with non-uniform grains. Grain size: 1, 0.5–0.6 mm; 2, 0.25, 0.45, 0.55, 0.65, 0.75; 3, 0.25–0.75 mm.

Fig. 5. Dependence of the HETP (H) on the linear flow-rate of the carrier gas (u) for columns of 1.2 cm diameter charged with sorbent fractions with non-uniform grains. Grain size: as in Fig. 4.

The experimental results for the function H (eqn. 1) plotted in Fig. 4–6 and the results in Table I corroborate the above supposition, in which we assumed that the spreading of chromatographic bands and therefore the decrease in the efficiency of columns of small diameter are largely influenced by the absolute value of the grain diameter (Fig. 1), but are not much influenced by non-uniformity of the granules (Fig. 4).

With an increase in column diameter, the HETP is adversely affected by the non-uniformity of the sorbent granules (Figs. 5 and 6) rather than by the absolute value of the grain diameter (Figs. 2 and 3). However, if the efficiencies of columns filled with non-uniform fractions I and II are compared, it can be seen that the columns filled with fraction II will be more effective; this is shown very clearly with the 2.6 cm diameter columns. This fraction consists of a wide range of grain size, but in general it is more uniform than fraction I and is better packed into columns. This is corroborated also by the values of A and the penetration coefficients (Table I), which define packing uniformity and packing density.

As expected, with an increase in column diameter, the resolution (K_1) and also the column efficiency are influenced by non-uniformity of the grains rather than by the absolute value of grain diameter.

From Fig. 7, in which the dependence of column efficiency on the specific

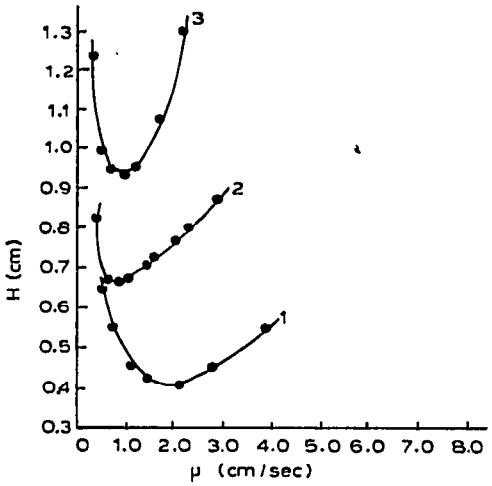


Fig. 6. Dependence of the HETP (H) on the linear flow-rate of the carrier gas (u) for columns of 2.6 cm diameter charged with sorbent fractions with non-uniform grains. Grain size: as in Fig. 4.

volume of the sample injected into the column is shown, it can be seen that non-uniformity of the grains, especially when using small amounts of sample, does not have a great effect on the HETP for columns of 0.6 and 1.2 cm diameter. With columns of 2.6 cm diameter, the HETP increases by a factor of 1.5 when a column charged with a uniform 0.5–0.6 mm fraction is replaced with a column charged with fraction II, and by a factor of 2 when the former is replaced with a column charged with fraction I. When a column charged with fraction I is replaced with a column charged with fraction II, the HETP increases by a factor of 1.5 times. These results confirm that, with columns of large diameter, grain uniformity is of great importance.

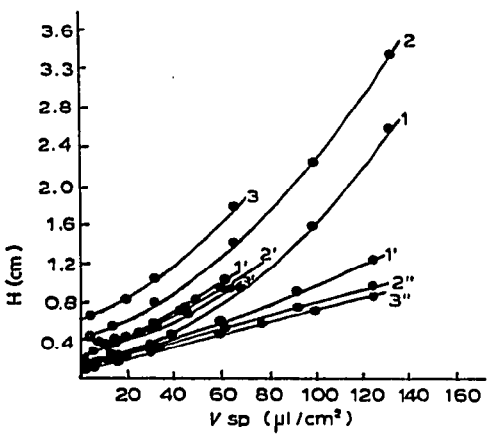


Fig. 7. Dependence of the HETP (H) on the specific volume of the sample injected into the column (V_{sp} ml/cm²) for columns of various diameters charged with sorbent fractions with non-uniform grains. Column diameter: 1, 2 and 3, 2.6 cm; 1′, 2′ and 3′, 1.2 cm; 1″, 2″ and 3″, 0.6 cm. Grain size: 1, 1′ and 1″, 0.5–0.6 mm; 2, 2′ and 2″, 0.25, 0.45, 0.55, 0.65, 0.75 mm (Fraction II); 3, 3′ and 3″, 0.25–0.75 mm (Fraction I).

CONCLUSIONS

The effect of grain diameter on the efficiency of the columns considered decreases with increase in their diameter, and therefore it is expected that for columns of large diameter (2.6 cm in this work) the grain size will not have a great influence on the column efficiency.

With an increase in column diameter non-uniformity of the sorbent granules adversely affects the spreading of chromatographic bands and therefore the efficiency. Consequently, for preparative columns of more than 1.2 cm diameter, sorbents with uniform grains should be used.

It has been found that where it is necessary to use fractions with non-uniform grains, it is desirable to use those with a wide range of grain size rather than those with grains of only two sizes that differ substantially from each other.

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