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A STUDY OF VARIABLE DIAMETER COLUMNS IN PREPARATIVE GAS CHROMATOGRAPHY

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SUMMARY

The operation of the variable diameter columns in the preparative gas chromatography has been studied. It has been shown that such columns are more efficient than those of constant diameter. To explain this effect the influence of the carrier gas flow rate and pressure upon the HETP and criterion of separation has been studied.

INTRODUCTION

In a great number of reports[1-6] concerning preparative gas chromatography, attention has been drawn to the increase of the height equivalent per theoretical plate (HETP) with an increase of column diameter and exactly the same unit load (*i.e.* the same sample volume per unit of cross-section or per cubic centimetre of sorbent) arising from the additional enlargement of the chromatographic band. Consequently, finding out methods for maintaining the efficiency of a separation after increasing the column diameters can be considered as one of the main tasks in preparative gas chromatography.

In considering this problem, a number of scientists[2,7-10] have made use of different redistributors (baffles, rings etc.), which made it possible to reduce the expansion of the chromatographic bands to some extent and, thereby, to increase the efficiency of the preparative columns. The results, obtained by PHILLIPS[11], of using columns of variable diameters in liquid chromatography, were taken as a basis. We decided to examine the possibility of using similar columns to increase the efficiency of the separation in preparative gas chromatography. Columns of such a type were used by WALKER[12] and FRISONE[9] for micropreparative separations as well as for defining mixtures. For instance, WALKER used columns of variable dimensions ranging from 100 to 600 cm in length and from 0.3 to 0.9 cm in diameter. In WALKER's work[12] attention is drawn to the great advantage of such columns when compared to columns of constant diameter.

Nevertheless, VERZELE[13] after having carried out an experiment with a great number of columns of variable diameters, achieved no advantage.

Up to now there is no common opinion in the literature about the possibility of increasing the efficiency of separation by such a method.

It was assumed that changes in the diameter of sections along the length of a sorbent would naturally cause changes in the distribution of the pressure of the carrier gas flow along the whole length of the column as well.

It is known[14-20] that pressure changes in a column greatly affect the efficiency of a separation, but data concerning this question are on the whole related to the analytical version. That is why FOWLIS et al.[17] proposed to work with a higher pressure than atmospheric at the inlet of the column. They carried out their experiments using an analytical column of 180 cm in length and 0.4 cm in diameter.

EXPERIMENTAL

We studied a series of columns of variable diameters and of approximately the same length (480–560 cm) containing sorbents of different volumes (1000–2200 cm³). The columns under test were made up from sections 100–120 cm in length and 0.6, 1.2 or 2.6 cm in diameter.

The diameters of the sections in the columns decreased along the length from the inlet to the outlet. The list of columns of variable diameters, which have been studied by us is given in Table I.

TABLE I

SORBENT VOLUME (V, cm³), MEAN CROSS-SECTIONAL AREA (S, cm²), VOLUME OF SAMPLE BEING INTRODUCED (V, ml) AND QUANTITIES CHARACTERISING THE CARRIER GAS FLOW RESISTANCE FOR COLUMNS OF VARIABLE DIAMETER

Dimensions of columns of variable diameter (size in cm)	V (cm³)	S (cm²)	V (ml)	$\bar{a}_0$ (cm/sec)	ΔP	j
500 × 1.2	550	1.13	0.08	0.74	1.06	0.64
480 × 2.6	2170	5.31	0.3	1.57	0.55	0.774
(120 × 2.6) + (400 × 1.2)	990	2.09	0.13	4.62	1.26	0.59
(240 × 2.6) + (300 × 1.2)	1530	2.99	0.17	3.68	1.13	0.62
(360 × 2.6) + (200 × 1.2)	1850	3.82	0.22	3.05	1.10	0.62
(360 × 2.6) + (200 × 0.6)	1680	3.51	0.20	3.99	1.83	0.49
(240 × 2.6) + (300 × 0.6)	1290	2.52	0.14	5.29	2.12	0.45

All the experimental data were obtained using a PACh V-04 preparative gas chromatograph constructed with a detector of the katharometer type for obtaining data on thermal conductivity. In all cases the temperature of thermostatic control was kept at 64°.

The columns were filled with TZK adsorbent (diatomite from the Zikeevskii Quarry) treated with a 2% solution of sodium carbonate and modified with 5% of liquid paraffin, the particle size of the sorbent being 0.2–0.4 mm. Hydrogen was used as carrier gas. A light distillate of straight-run gasoline of constant composition, received from the Novo-Gorkovskii refinery, was used as the test mixture. All the characteristics of separation were related to the peaks of n-pentane and isopentane

and the same specific volume of the sample related to 1 cm^3 of sorbent (Table I) was used in each case. The volume velocity of the carrier gas was measured at the column outlet with a flowmeter.

In order to compare columns of variable diameter, the dependence of the height equivalent per theoretical plate (HETP or H cm) and resolution value ($K_1 \simeq 0.5\,R$) on the mean linear velocity of the carrier gas flow have been studied.

The values under consideration were calculated according to well-known formulae.

In order to calculate the mean linear velocity of the carrier gas flow, the mean cross-sectional area of columns of variable diameter have been calculated according to the following formula:

$$S = \frac{\sum_{i=1}^{n} S_i L_i}{\sum_{i=1}^{n} L_i} \tag{1}$$

where $S_i =$ the cross-sectional area and $L_i =$ the length of every section.

The mean linear flow velocity at the outlet of the column was calculated according to the formula:

$$\bar{a}_o = v_o / \bar{S} \tag{2}$$

where $\bar{a}_o =$ the mean linear flow velocity; and $v_o =$ the measured volume velocity of the flow.

At the outset of our examination of columns of variable diameter, we expected a better efficiency on such columns as compared with the columns having just the same diameter as has been stated above, but the experimental data did corroborate this supposition.

Unexpectedly, after having achieved the velocity corresponding to the minimum of the function $H(\bar{a}_o)$, when using columns of variable diameters (see the plots), any subsequent increase in velocity at the outlet did not give any increase in the efficiency, i.e. there was a plateau of function $H(\bar{a}_o)$, where the efficiency did not depend on the flow velocity, moreover, the minimum of the curve $H(\bar{a}_o)$ shifted to the region of large velocities. A similar plateau of velocities for the function $H(\bar{a}_o)$ has not been observed in this region of velocities (Fig. 1a) for columns of constant diameter.

This phenomenon is of great value in that it allows one, while not decreasing the efficiency of preparative chromatographic columns, to work with large velocities, and thus to increase the productivity of such a column by diminishing the time of separation.

If we consider the van Deemter equation with the correction for the pressure drop in the column:

$$H = A + B'/\bar{a} + C_j\bar{a} \tag{3}$$

then the presence of plateau velocities for the function $H(\bar{a}_o)$ may be explained by a decrease in the C_j term in the above equation corresponding to a decrease in the j correction which, as can be seen from Table I, is smaller for columns of variable
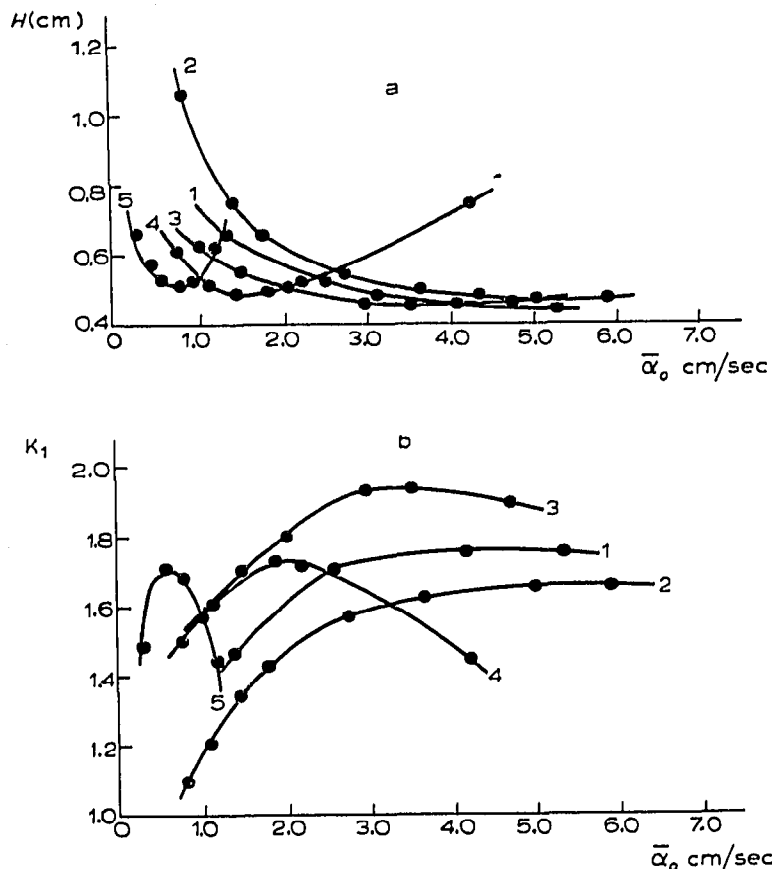
Fig. 1. Dependence of (a) height *(H)* equivalent per theoretical plate and (b) resolution value *(K₁)* on mean linear velocity *(ā₀)* of the carrier gas flow for columns of variable diameter with a constant ratio of the diameters of the sections. Columns sizes in cm: 1 = (240 × 2.6) + (300 × 1.2); 2 = (120 × 2.6) + (400 × 1.2); 3 = (360 × 2.6) + (200 × 1.2); 4 = (480 × 2.6); 5 = (500 × 1.2).

diameters than for columns of constant diameters. As the James–Martin correction for compressibility only accounts for the final pressure, it would be of great interest to consider the value of local velocity and local pressure along the length of a column of variable diameter. KEULEMANS[16] gives a formula whereby it is possible to calculate pressure at any point of a column of constant diameter:

$$P_x^2 = P_i^2 - X/L \ (P_i^2 - P_o^2) \tag{4}$$

where P_x = the pressure at any point; X = the distance from the beginning of the column to the point under consideration; L = the total column length; and P_i and P_o = the pressure at the inlet and outlet, respectively.

But this formula cannot be used for columns of variable diameters.

Using DARSI's[21] equation:

$$V = - \frac{KS}{\eta} \cdot \frac{dP}{dX} \tag{5}$$

we have derived a formula from which the pressure can be calculated for the junction

point of the sections and then at any point in such a column:

$$P_c{}^2 = \frac{P_i{}^2 \cdot \dfrac{S_1}{l_1} + P_o{}^2 \cdot \dfrac{S_2}{l_2}}{\dfrac{S_1}{l_1} + \dfrac{S_2}{l_2}} \qquad (6)$$

where P_c = the pressure at the junction of the two columns; P_i and P_o = the pressure at the inlet and outlet of columns of various diameters, and S_1; l_1; S_2; l_2 = the respective cross-sectional areas and lengths of the first and the second sections.

For calculating local velocities (a_x) of the carrier gas flow at any point in a column of various diameters a well known correlation has been used:

$$a_x P_x S_x = a_o P_o S_o \qquad (7)$$

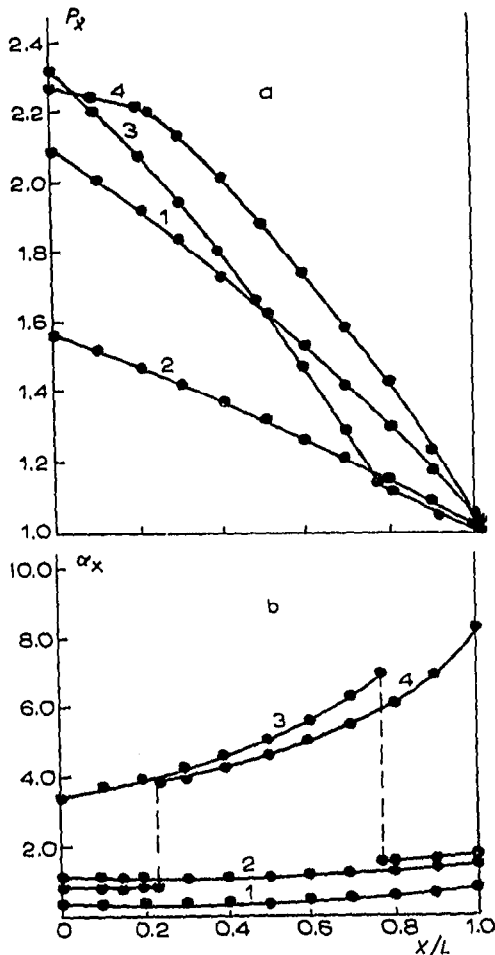The alteration of local pressures and local velocities at different points in

Fig. 2. Distribution of local (a) pressure (P_x) and (b) linear velocity (a_x) of carrier gas flow in columns of variable diameter. (X/L = ratio of the distance from the beginning of the column to any point X to the total length). Sizes of columns in cm: 1 = (500 × 1.2); 2 = (480 × 2.6); 3 = (400 × 1.2) + (120 × 2.6); 4 = (120 × 2.6) + (400 × 1.2).

columns of constant and variable diameters, which have been calculated according to the above formulas (4), (6) and (7), are shown in Figs. 2a and b.

Such alterations in local pressures and velocities have been obtained for all the columns considered.

Let us consider the comparison of the efficiency and the resolution value for columns of variable diameter and for columns of constant diameter.

Figs. 1a and b show correlations for the efficiency and the resolution value which are the functions of the mean linear flow velocity of the carrier gas for columns of variable diameters, where the ratio of the lengths of the sections as well as the total sorbent volume are altered while the ratio of their diameters is maintained constant. Fig. 1a shows that the function $H(\bar{a}_0)$, for columns of variable diameter, has a plateau of velocities where the efficiency does not depend upon the velocity and is the same in this region for all the columns under consideration, whereas the resolution value decreases with the decrease in diameter at the end of the first section length (Fig. 1b).

The results given above have been fully corroborated when a series of columns of various diameters but having a different ratio of section diameters ($d_k = 2.6$ cm and $d_k = 0.6$ cm) was studied.

In addition, a series of columns of variable diameter, where the total length of the bed and the ratio of the section lengths have been constant, but where the ratio of their diameters and the total volume of sorbent have been altered, have been considered. The efficiency of such variable diameter columns was found to be the
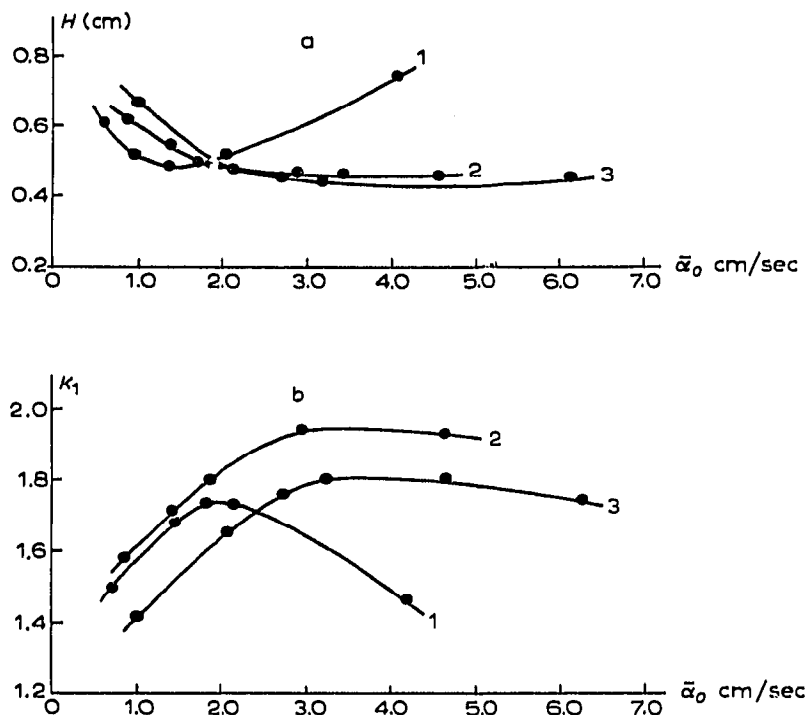

Fig. 3. Dependence of (a) height (H) equivalent per theoretical plate and (b) resolution value (K_1) on mean linear velocity ($\bar{a}_0$) of the carrier gas flow for variable diameter columns having different ratios of section diameter. Sizes of columns in cm: 1 = (480 × 2.6); 2 = (360 × 2.6) + (200 × 1.2); 3 = (360 × 2.6) + (200 × 0.6).
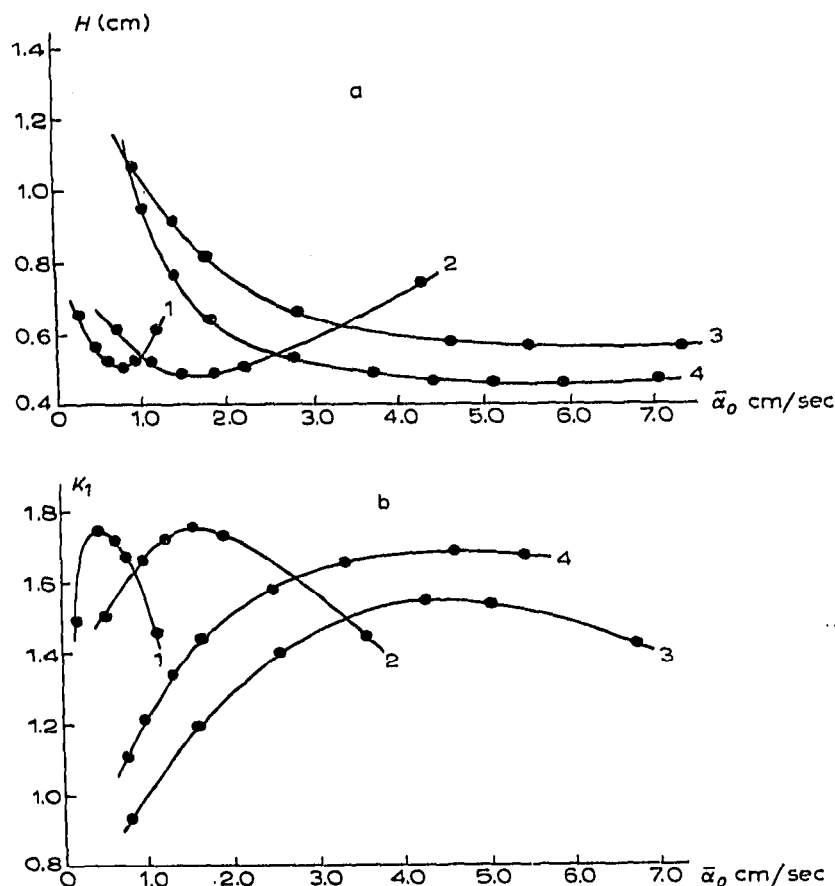
Fig. 4. Dependence of (a) height (H) equivalent per theoretical plate and (b) resolution value (K_1) on mean linear velocity ($\bar{a}_0$) of the carrier gas flow for variable diameter columns the sections being added in different orders in the chromatographic scheme. Sizes of columns in cm: 1 = (500 × 2.6); 2 = (480 × 2.6); 3 = (400 × 1.2) + (120 × 2.6); 4 = (120 × 2.6) + (400 × 1.2).

same for all columns (Fig. 3a), but the resolution value decreases with the decrease of the diameter of the final section (Fig. 3b).

Finally, columns of variable diameter having section lengths and diameters with the same ratio but only differing by the order in which the sections are introduced into the gas scheme of the chromatograph have been considered. From Figs. 4a and b it can be seen that there is a plateau of velocities for the function H ($\bar{a}_0$), where the efficiency does not depend upon the velocity, in both cases. Moreover, such a column is more efficient when the diameters of the sections decrease from the inlet to the outlet. Such a column also has a larger resolution value (Fig. 4b).

With regard to the plots of local pressure and velocity for all the columns of variable diameter (Figs. 2a and b) it may be assumed that formation of a plateau of velocities for the function H ($\bar{a}_0$), where the efficiency does not depend on the flow velocity of the carrier gas at the outlet of the column, is due to the sharp alteration in pressure at the junction of the sections created by the alteration of their diameters at these points. Furthermore, the larger the segment of the column, where the local velocity is left constant, the larger its efficiency and the resolution value.

When the ratio of the section lengths is the same, the ratio of their diameters

only affects the resolution value and has no effect on the efficiency of the columns (Figs. 3a and b).

In order to confirm previously quoted assumptions concerning the effect of pressure on the action of variable diameter columns additional experiments were carried out by introducing a gas resistor—a thin adjustable valve (throttle) at the outlet of the column.

To avoid the effect of the pressure drop along the column, an experiment was carried out on a short 120 cm × 2.6 cm column. Plots of efficiency against linear velocity of the carrier gas flow were obtained. The velocity was measured at atmospheric pressure after the throttle. The following columns were studied: (1) without the throttle; (2) with the throttle having a constant setting for the resistor; (3) with constant pressure at the outlet of the column.

On comparing the experimental data obtained, given in Figs. 5a and b, it may be seen that columns working under additional pressure at the outlet, are more
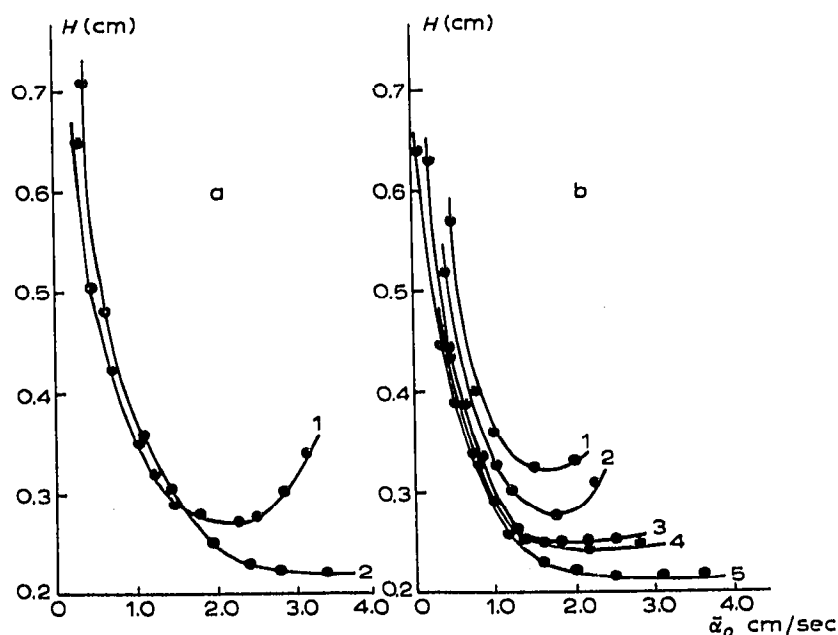

Fig. 5. Dependence of height (H) equivalent per theoretical plate upon linear velocity of carrier gas flow ($\bar{a}_0$) for columns of constant diameter (120 × 2.6 cm): (a) 1 = without throttle; 2 = with throttle; (b) with constant pressure at the outlet: 1 = 1.5 atm; 2 = 1.75 atm; 3 = 2.75 atm; 4 = 2.25 atm; 5 = 2.5 atm.

efficient than columns working at atmospheric pressure. Furthermore, there is an optimum outlet pressure at which the column has its greatest efficiency. The pressure in this case is 1.5 kg/cm² higher than atmospheric (see Fig. 5b curve 5).

The results obtained on the 120 cm × 2.6 cm column were fully corroborated on the longer 480 cm × 2.6 cm columns. From Figs. 6a and b it may be seen that the column outlet pressure affects the efficiency as well as the resolution value of the given mixture.
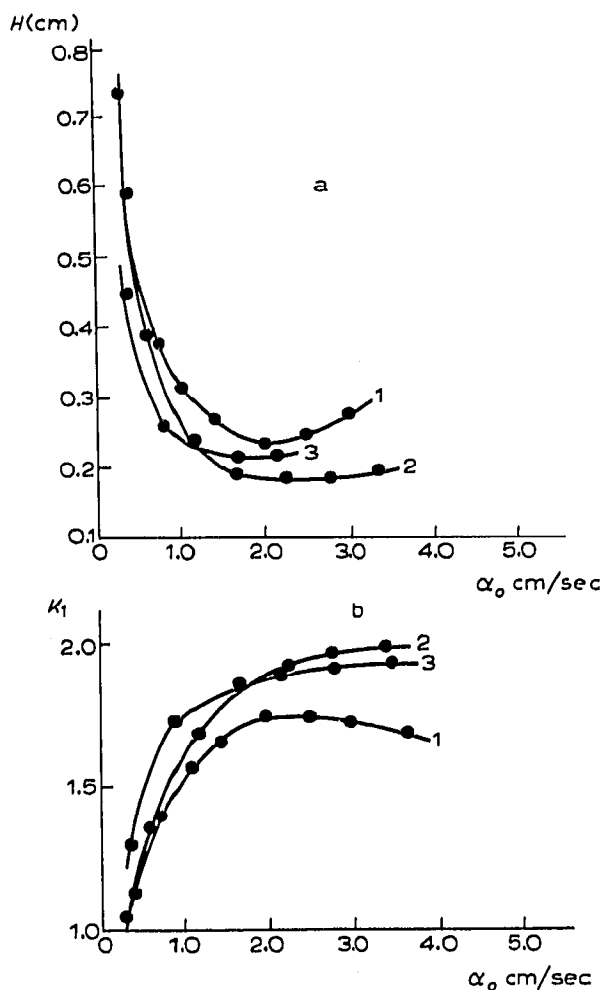
Fig. 6. Dependence of (a) height (H) equivalent per theoretical plate and (b) resolution value (K_1) on linear velocity of the carrier gas flow (a_o) for columns of constant diameter (480×2.6 cm): 1 = without throttle; 2 = with throttle set at a constant resistance; 3 = with constant pressure at the outlet.

CONCLUSIONS

1. A study of the effect of the carrier gas flow velocity and pressure upon the efficiency of columns of variable diameters has been carried out.

2. It was shown that when columns of variable diameter, as distinct from ordinary ones, are used the plot of the function H ($\bar{a}_o$) after reaching the minimum value for H value hardly changes on subsequent increase of the flow velocity ($\bar{a}_o$), in the region of velocities examined.

3. The distribution of local pressure and velocity along a column of variable diameter has been studied and a formula for calculating pressure at the junction of two sections has been derived.

4. It was shown that columns of large diameter acting at a higher outlet pressure than atmospheric are more efficient than similar columns working at atmospheric pressure. Moreover, there is an optimum value for the outlet pressure at which the efficiency of columns with a throttle is greatest.

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