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Short columns for gas chromatography

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Abstract - Gas chromatographic columns, which have internal diameter 1-4 mm, but are not longer than 25-30 cm, could be used in the analytical practice if the packing has a highly spread surface. Untreated and modified silica gel was utilized for this purpose in order to obtain columns with different polarity. It is shown the influence of the column length, internal diameter and particle size of packing on the efficiency, retention volumes, relative retention etc.

INTRODUCTION

The column is the simplest, but most important part, of the apparatus for gas chromatography and design of the column has attracted the attention of many specialists. Although various types of column have been proposed (e.g. open tubular, SCOT, PLOT, WCOT, wide bore or micro-packed) for most applications the usual form of packed columns has not undergone much change-apart from a reduction in size for some purposes.

There are three ways in which it is possible to reduce the size of a packed column (ref. 1-13), i.e. by reducing its internal diameter, its length or both internal diameter and length. The internal diameter of micropacked columns can be reduced below 1 mm, but high inlet pressures are required. Very little systematic work has been carried out with shortened columns of normal diameter (i.e. 2-4 mm). Columns of this type are sometimes used in combination with capillary columns (ref. 14-16): in all cases, high inlet pressures have been required to obtain low values of HETP. The work reported here has been carried out with columns of internal diameter 1-4 mm and length 25-30 cm. The columns were packed with middle-sized graded packing and normal inlet pressure was used.

The measurements shown in the following were carried out with untreated, and modified with hexamethyldisilazane, wide pore silica gel, whose specific surface was $S = 217\ m^2/g$.

INLET PRESSURE

The decrease of the particle size, in order to obtain better efficiency leads to an increase of the inlet pressure. It is desirable however to maintain it as low as possible to avoid the need of gas line reconstruction. The data show (Table 1), that the inlet pressure of the columns under investigation is a linear function of the column length.

This result is in agreement with the expression (ref. 17):

$$\Delta P = B\eta\omega L/d_p^2$$

where ΔP is the difference between the inlet and outlet pressures of the column, η is the viscosity of the gas-carrier, ω is the flow rate, d_p is the particle diameter and B is constant. If the upper limit of the inlet pressure expressed as inlet/outlet pressure ratio, is 2.5-3, it could be seen from the data that it is possible to work even with finer particles of the packing.

The dependences between the inlet pressure and internal column diameter and mean particle diameter of packing are not linear. They show that for a 20 cm columns with diameter 2 mm and grain size 63 - 71 μm the ratio P_i/P_o is below 2, which allows to make a further optimization of the column.

TABLE 1. Column characteristics

L cm	d_c mm	d_p μm	P_i/P_o	HETP mm	V_N cm^3
10	2	63 - 71	1.4168	0.42	7.7
15	2	63 - 71	1.4734	0.36	10.6
20	2	63 - 71	1.7237	0.32	14.1
25	2	63 - 71	1.7923	0.40	18.6
20	2	90 - 100	1.4622	0.42	10.0
20	2	80 - 90	1.4692	0.38	12.4
20	2	71 - 80	1.6984	0.32	14.1
20	2	63 - 71	1.7237	0.32	14.8
20	1	63 - 71	2.3348	0.32	10.2
20	2	63 - 71	1.7237	0.32	14.1
20	3	63 - 71	1.4504	0.41	27.5
20	4	63 - 71	1.3140	0.57	29.6
20*	4	80 - 90	1.2410	0.49	46.1
20*	4	71 - 80	1.3230	0.54	44.5
20*	4	63 - 71	1.3661	0.48	45.2
10**	2	90 - 100	1.2133	0.53	7.6
15**	2	90 - 100	1.2961	0.55	14.2
20**	2	90 - 100	1.3803	0.45	19.3
25**	2	90 - 100	1.4236	0.54	24.8
90	2	80 - 90	2.5890	1.65	67.8
90***	2	150 - 180	1.4390	0.54	44.1

*Unmodified silica gel, column temperature 130 °C.
**Modified silica gel, coated with 9.84% squalane, column temperature 60 °C.
***Chromosorb W/HP, coated with 10% squalane, temperature 60 °C.
The unmarked columns were investigated at 60 °C.

The corresponding data in the table for the short columns could be compared with the data for columns with length 90 cm. One of them was packed with modified silica gel and the other was packed with packing squalane on Chromosorb W/HP. It is evident that practically the short columns have in most cases a normal pressure ratio not higher than 2.

The ratio d_p/d_c is an interesting column parameter. Fig. 1 presents the influence of this parameter on the pressure ratio. The line 1 shows the change of pressure ratio depending on the mean particle size, at constant column diameter 2 mm. The line 2 express the function of pressure ratio in the case of constant particle size 63-71 μm. Similar results are obtained for micropacked columns too (ref. 18). The cross point of the lines corresponds to the optimal value of the diameter ratio.

HEIGHT OF THEORETICAL PLATE (HETP)

The HETP in all cases under investigation are lower than 0.6 mm. Practically an efficiency of almost 3000 theoretical plates per meter could be achieved. HETP is independent of the column length, but depends on the column diameter. The last result for capillary packed columns was obtained from other authors too (ref. 5).

As is known uniform filling of the columns could be achieved if the ratio d_p/d_c is not higher than 0.5 (ref. 8, 19). For different type columns it is as follows: capillary packed columns - from 0.2 to 0.5; micropacked columns - lower than 0.2; usual packed columns - 0.03.

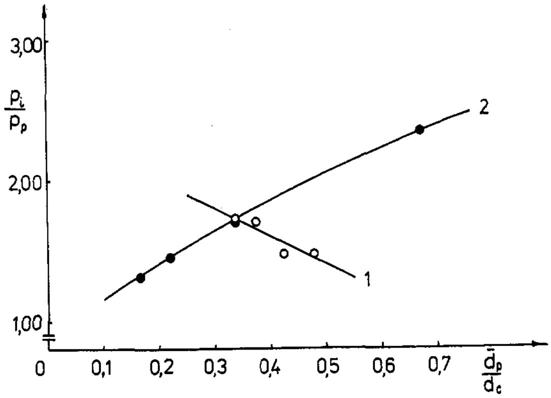

Fig. 1. Plot of P_i/P_o vs. d_p/d_c.

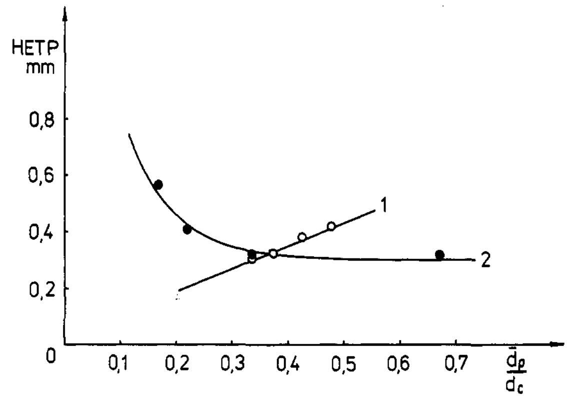

Fig. 2. Dependence of HETP on the diameter ratio.

It could be seen from curve 1 (Fig. 2) that the columns under investigation with constant column diameter (2 mm) but differing in the particle size of packing correspnds to the capillary packed columns. Curve 2 (Fig. 2) shows that HETP increases at the values of diameter ratio corresonding to 3 and 4 mm columns (constant particle size 63 - 71 μm). Since the ratio is favourable the decrease of plate height is due probably to the dry method of filling.

The long column (90 cm) packed with modified silica gel (80 - 90 μm) shows very high value of the HETP if it is compared with the values obtained for the short columns. The height of the theoretical plate for the column packed with squalane on Chromosorb W/HP however is almost equal to the HETP of the short columns with squalane coated on modified silica gel.

RETENTION VOLUMES

The specific retention of benzene per unit packing surface has a constant value, as it was observed in the case of usual packed columns (ref. 20). The net retention volumes however change depending on the parameters connected with the total sorbent surface in the columns. It is interesting the dependencebetween the net retention volume per gram silica gel and particle sizes.It increases at the small particle sizes, which indicates some increase in the specific surface. The measurement of the specific surface by the method of the thermal desorption gave no difference in the specific surfaces of the size fractions. Probably the sensitivity of the method is not sufficient to show the change, while the retention is influenced from it.

RELATIVE RETENTION AND CAPACITY

The change in the relative retention, measured by the pair benzene/cyclohexane, is similar to the change of the retention volumes. The increase of the total surface of the packing leads to an increase of the relative retention. More interesting is the dependence of relative retention on the particle size. The highest values are obtained at the lowest particle sizes (Fig. 3).

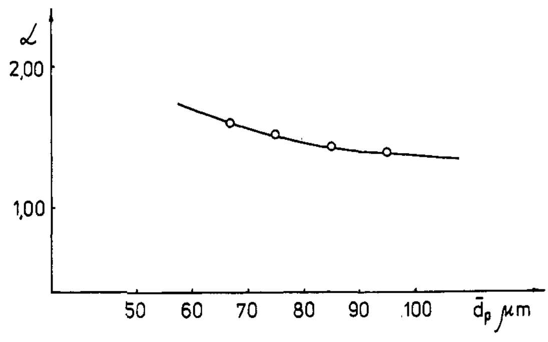

Fig. 3. Relative retention (cyclohexane/benzene) as a function of particle size.

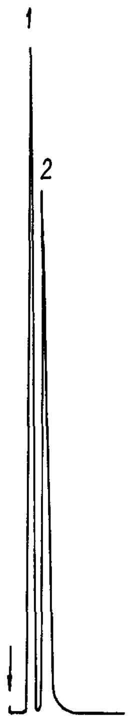

Fig. 4. Separation of mixture of cyclohexane (1) and benzene (2). Column 20 x 0.2 cm, 60°C, silica gel 63 - 71 μm (HMDS).

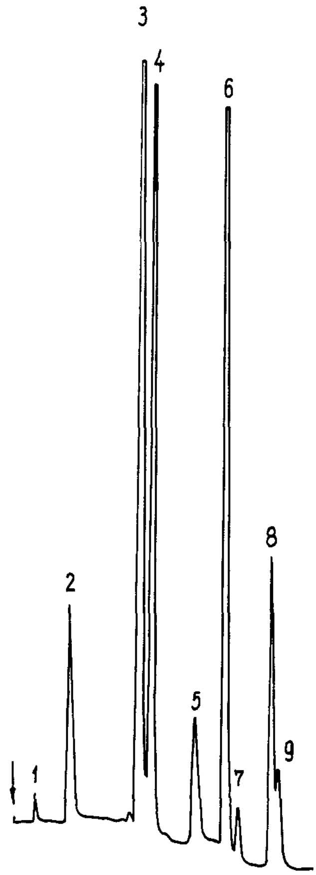

Fig. 5. Separation of mixture of n-pentane (1), cyclohexane (2), n-heptane (3), isooctane (4), n-octane (5), benzene (6), n-nonane (7), n-decane (8) and toluene (9). Column 20 x 0.2 cm, 50 - 120°C, 15°/min, silica gel 63 - 71 μm.

For the columns under investigation relative retention increases if column length, column diameter and particle diameter increase too. The values of the relative retention are between 1.40 and 1.70. The corresponding values on the column packed with squalane on Chromosorb W/HP and on the long column with unmodified silica gel are 1.27 and 1.72.
The values of the capacity, calculated for the columns under investigation are between 25 and 40. They are therefore close to the usual packed columns (k'= 5-100) and differ considerably from the packed capillary columns (k'= 0.1-5). For instance the column with squalane on Chromosorb W/HP has k' = 26 and the column with modified silica gel (90 cm) has k'= 67.

The higher values of the capacity allows work with the short columns without any splitter, which is very convenient.

CONCLUSIONS

The short packed columns could be used successfully in gas chromatography. Their advantages are as follows:

1. Low values of the height of theoretical plate;
2. Easy preparation and use;
3. Normal inlet pressure;
4. No splitter;
5. Economical and cheap.

Some disadvantages should be mentioned:

1. The dead volume of the gas line including the detector has to be small;
2. Need of closely size graded packing material;
3. The limited length of the column gives a relatively low total number of theoretical plates. In the case when the efficiency is not sufficient it is necessary to improve the separation by choosing selective packings.

SYMBOLS

d_c - column diameter;
d_p - particle diameter;
HETP - height equivalent to one theoretical plate;
k' - capacity of column;
L - column length;
P_i - inlet column pressure;
P_o - outlet column pressure;
V_N - net retention volume;
α - relative retention, the ratio of the adjusted retention volumes of cyclohexane and benzene.

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REFERENCES

1. J.F.K. Huber, H.H. Lauer and H. Poppe, J. Chromatogr. 112, 377-388 (1975).
2. H.H. Lauer, H. Poppe and J.F.K. Huber, J. Chromatogr. 132, 1-16 (1977).
3. R.J. Jonker, H. Poppe and J.F.K. Huber, J. Chromatogr. 186, 285-297 (1979).
4. V.G. Berezkin, L.A. Shkolina and A.T. Svyatoshenko, J. Chromatogr. 99, 111-122 (1974).
5. V.G. Berezkin, L.A. Shkolina, V.N. Lipavsky, A.A. Serdan and V.A. Barnov, J. Chromatogr. 141, 197-240 (1977).
6. A. Malik, V.G. Berezkin and V.S. Gavrichev, Chromatographia 19, 327-334 (1984).
7. V.G. Berezkin, A. Malik and V.S. Gavrichev, Zh. Anal. Khim. 39, 522-525 91984).
8. Th. Welsch, W. Engewald and J. Poerschmann, J. Chromatogr. 148, 143-149 (1978).
9. Th. Welsch, W. Engewald and J. Pörschmann, J. Prakt. Chem. 320, 493-496 (1978).
10. A. Di Corcia, A. Liberti and R. Samperi, J. Chromatogr. 167, 243-252 (1978).
11. M.N. Myers and J.C. Giddings, Anal. Chem. 38, 294-297 (1966).
12. Lu Peichang, Zhou Liangmo, Wang Chinghai, Wang Guanghua, Xia Aizu and Xu Fangbao, J. Chromatogr. 186, 25-35 (1979).
13. C.L. Guillemin, J. Chromatogr. 158, 21-32 (1978).
14. Jianying Zhang, Bingcheng Lin and Peichang Lu, Chromatographia 23, 487-491 (1987).
15. Fen Je, Bingcheng Lin and Lu Peichang, Chromatographia 23, 492-498 (1987). (1987).
16. Daixin Tong, Fangbao Xu and Peichang Lu, Chromatographia 23, 499-501 (1987).
17. J.C. Giddings, Dynamics of Chromatography, Part I. Principles and Theory, p. 350, Dekker, New York (1965).
18. J.A. Rijks, C.A. Cramers and P. Bocek, Chromatographia 8, 482-485 (1975).
19. I. Halasz and E. Heine in Advances in Chromatography 4, 215-226, Dekker, New York, (1967).
20. A.V. Kiselev, Yu.S. Nikitin, R.S. Petrova, K.D. Scherbakova and Ya.I. Yashin, Anal. Chem. 36, 1526-1533 (1964).