A new type of capillary column for gas chromatography

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A new type of capillary column for gas chromatography was proposed. A sorbent layer (for example, stationary liquid phase) is supported on the internal capillary surface, and the internal (interstitial) volume is packed with nonporous large particles of a sorbent (particle diameter is 0.1—0.6 of the capillary internal diameter). The external surface of the particles can also be coated with the sorbent layer (for example, stationary liquid phase). The specific separation efficiency (number of separation) on the new type column is by 1.6—2.3 times higher than that of the initial classical capillary column.

Key words: capillary gas chromatography, packed capillary column.

A very low sorption capacity is the main disadvantage of capillary columns.[1—4] This requires special methods of introduction of microsamples (for example, flow separation), which impedes apparatus and has an unfavorable effect on determination of admixtures and quantitative parameters of analysis.

An increase in the thickness of the layer of the stationary liquid phase (SLP) or in the column diameter are the most popular methods for enhancing the sorption capacity of the columns[2,3,5] (Fig. 1). This enlarges the surface coated with the SLP layer and increases the amount of SLP per column length unit. However, these methods do not enhance substantially the capacity of the column because an increase in the thickness of the SLP layer by more than several microns or an increase in the column diameter by more than 0.5—0.9 mm results in a substantial diffusion of chromatographic zones and decreases the separation efficiency of the column.

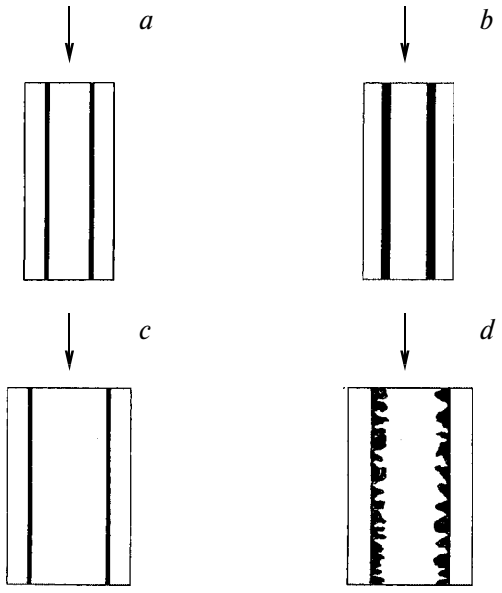

Fig. 1. Main types of capillary columns: classical capillary column (*a*), capillary column with the thick SLP layer (*b*), capillary column with the great diameter (*c*), and column with the enlarged surface of the internal walls and increased surface concentration of SLP on the column wall (*d*).

The most important parameter of a column, retention factor (k), depends on both the partition coefficient K and the phase ratio β [2]

$$k = K/\beta, \quad (1)$$

$$\beta = V_g/V_s = d_c/4d_f, \quad (2)$$

where V_g and V_s are the volumes of the mobile and stationary phases, respectively; d_c is the internal diameter of the column; and d_f is the thickness of the SLP layer.

The following generalized equation can be obtained from Eqs. (1) and (2):

$$k = 4Kd_f/d_c. \quad (3)$$

Thus, the k factor is proportional to the thickness of the SLP film (d_f) and inversely proportional to the internal diameter of the capillary column (d_c).

A possible, but nonaccomplished yet variant of increasing the SLP amount in the column by an increase in the internal surface of the column (which can already be achieved at the stage of preparation of the capillary) is presented in Fig. 1.

Another variant of solution of this problem is transition to packed capillary columns[6—10] and, in particular, the use of quartz capillaries[11] to prepare packed capillary columns. Quartz capillary columns with a fine-grain sorbent demonstrated a high specific capacity. However, a high resistance to the carrier gas flow restricts their wide use.

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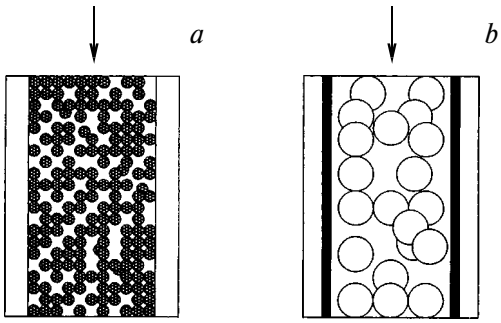

Fig. 2. Packed capillary columns: classical packed capillary column (quartz capillary packed with the packing sorbent) (*a*) and proposed hybrid of a classical capillary column, whose internal walls are coated with the SLP layer, and a packed capillary column (using the packing with the nonporous core) (*b*).

In this work, we performed experimental estimation and considered challenges for the use of packed capillary columns of a new type (Fig. 2). As compared to the known columns (see Fig. 2, *a*), the columns of this type have three substantial distinctive features. The SLP layer is placed on the internal surface of the capillary. A nonporous material is used as a sorbent (support), and large particles, whose diameter is comparable with the column diameter, are used as a packing. The use of large particles ($d_s/d_{col} \approx 0.2$—0.6, where d_s is the diameter of sorbent particles) allows a substantial decrease in the resistance of the column to the gas flow. This solution provides a noticeable enhancement of the capacity of the column with respect to SLP, especially when the phase is supported on large particles. A sharp increase in the height equivalent of a theoretical plate (HETP) can also be avoided because a nonporous (or surface-porous) sorption material characterized by high mass exchange rates is used as a packing. In addition, the free volume of the column decreases and, as a result, the retention factor k increases.

In the proposed combination of packed and capillary columns, the SLP layer on the column wall decreases the edge effect. A decrease in the gas volume of the column by packing with a coarse-grained material is a new method for increasing the retention factor k. This method is used for the first time.

Experimental

The main parameters of two columns were studied: an open capillary column (CC) with a large diameter (10 m×0.53 mm, SE-30 as SLP, thickness of the linked liquid phase 0.5 μm) and a packed capillary column, which was prepared by packing of a part of the above described column (1.42 m×0.53 mm) with glass balls. Thus, the packed capillary and open capillary columns were combined (PCC). Glass balls (fraction 0.100—0.125 mm) designed for packing of the capillary column with the SLP layer on the walls was preliminarily washed with 5% HCl, water, and acetone and dried at 150 °C for 1 h. Then the surface of the glass balls was silanized using a reagent available from Serva.[12] The direct chromatographic experiments on a classical packed capillary column showed that, under the chosen experimental conditions, the glass balls manifest a low adsorption capacity.

Chromatographic parameters were measured on an LKhM-8MD gas chromatograph (5th model, Khromatograf plant, Moscow, Russia) with a flame-ionization detector. The chromatograph was modified at the Laboratory. The temperature of the column was 70 °C, and helium was used as the carrier gas. The pressure at the inlet of CC was varied from 0.06 to 0.20 atm, and that at the inlet of the packed capillary column (PCC) was 0.7—2.2 atm.

Results and Discussion

The change in HETP with the linear carrier gas flow rate is presented in Table 1 for two columns: a classical gas liquid column (CC) and a similar shorter column, whose interstitial volume is packed with silanized glass balls (PCC). For CC the optimum gas carrier flow rate (*i.e.*, the rate for the minimum HETP value) was ~20 cm s^{-1} at HETP of 0.44—0.55 mm, and that for PCC was ~9.1 cm s^{-1} at HETP of 0.55—0.78 mm.

Thus, a decrease in the free volume of the column by the packing with a low sorption capacity results in a noticeable (by ~25—60%) increase in HETP and the shift of the optimum rate to low linear gas carrier flow rates (from 20 to 9 cm s^{-1}), which can likely be explained by an increase in the resistance to mass transfer.

The retention factor k and especially the number of separations TZ, which reflects both the equilibrium and kinetic characteristics of the chromatographic process, are very important parameters of a chromatographic column.

The retention factors k and number of separations TZ are presented in Table 2 for two capillary columns: CC and PCC. For all studied compounds, using PCC, the retention factor increases by 2.22—2.26 times. Such a high and almost similar for all compounds increase is explained by the fact that a decrease in the gas volume of

Table 1. HETP as a function of the linear carrier gas flow rate (u) for the classical column and packed capillary column and various sorbates

u/cm s^{-1}	HETP/mm			
	n-C_6H_{14}	n-C_7H_{16}	n-C_8H_{18}	n-C_9H_{20}
	Classical column			
8.5	0.77	0.75	0.73	0.73
11.6	0.65	0.63	0.61	0.61
16.4	0.52	0.50	0.50	0.55
20.0	0.44	0.45	0.48	0.55
28.9	0.60	0.58	0.55	0.60
	New type of packed capillary column			
7.1	1.01	1.05	0.96	0.92
9.1	0.55	0.63	0.72	0.78
11.2	0.68	0.65	0.76	0.85
15.9	0.85	0.85	0.84	0.96
21.0	0.91	0.95	1.00	1.07

Table 2. Comparison of the retention factor (k) and number of separations (TZ) for two capillary columns: classical (CC) and new type of packed (PCC)

Sorbate	k		$\frac{k(\text{PCC})}{k(\text{CC})}$	TZ		$\frac{TZ(\text{PCC})}{TZ(\text{CC})}$
	CC	PCC		CC*	PCC	
n-C_6H_{14}	0.23	0.52	2.26	1.14 (C_6/C_7)	2.62 (C_6/C_7)	2.30
n-C_7H_{16}	0.52	1.16	2.23	2.01 (C_7/C_8)	3.92 (C_7/C_8)	1.95
n-C_8H_{18}	1.15	2.55	2.22	2.85 (C_8/C_9)	4.50 (C_8/C_9)	1.58
n-C_9H_{20}	2.50	5.58	2.23	—	—	—

* Calculated value obtained for the column 1.42 m long, *i.e.*, for the initial CC with the same length as PCC.

the column increases the retention factor even when the packing with the "zero" sorption capacity is used. In addition, the number of separations for PCC increases by 1.6—2.3 times. This increase is especially pronounced for weakly retained compounds, for example, a hexane/heptane couple.

Thus, the introduction of a packing with the low sorption capacity into the CC with a great diameter enhances substantially its separation efficiency.

The low sorption activity of the packing was confirmed by independent chromatographic experiments. The retention factor due to the single sorption capacity of the packing is only 20—30% of the general retention factor of PCC. The sorption efficiency of the packing can be decreased or increased if necessary. Nonporous materials of different types (for example, mineral wool, inorganic or organic small balls or cylinders, wires, filaments, *etc.*) can be used as a chromatographic packing.

We have previously[13] advanced and experimentally substantiated to use sorbents with a very high mass exchange rate (for example, with the nonporous core and thin sorbent layer on the external surface) in capillary columns with fine-grain packing. It is also reasonable to apply sorbents of this type, but with a greater diameter (for example, 100—200 μm), in columns, which represent a hybrid of open and packed capillary columns.

References

1. M. L. Lee, F. J. Yang, and K. D. Bartle, *Open Tubular Gas Chromatography*, Wiley, New York, 1984.
2. J. V. Hinshaw and L. S. Ettre, *Introduction to Open-Tubular Column Gas Chromatography, Advanstar Communcations*, Cleveland, Ohio, 1994.
3. G. Guiochon and C. L. Guillemin, *Quantitative Gas Chromatography*, Elsevier, Amsterdam, 1988.
4. V. G. Berezkin and J. de Zeeuw, *Capillary Gas Adsorption Chromatopgraphy*, Huethig, Heidelberg, 1996.
5. K. Tesarik and K. Komarek, *Kapilarni Kolony v Plynove Chromatografii* [*Capillary Columns in Gas Chromatography*], SNTL, Praha, 1984 (in Czech).
6. I. Halasz and E. Heine, *Nature (London)*, 1962, **194**, 971.
7. I. Halasz and E. Heine, *Anal. Chem.*, 1965, **37**, 495.
8. H. V. Carter, *Nature (London)*, 1963, **197**, 684.
9. W. Virus, *J. Chromatogr.*, 1963, **12**, 406.
10. V. G. Berezkin, L. A. Shkolina, V. N. Lipavsky, A. A. Serdan, and V. A. Barnov, *J. Chromatogr.*, 1977, **141**, 197.
11. A. Malik, V. G. Berezkin, and V. S. Gavrichev, *Chromatographia*, 1984, **19**, 327.
12. *SERVA, Main Catalog 1991/92, Catalog N 35130, Silicon Solution SERVA*, 244.
13. V. G. Berezkin, A. Malik, and V. S. Gavrichev, in *Chromatography 85*, Eds. A. Kalasz and L. S. Ettre, Akademiai Kiado, Budapest, 1986, 429.

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