Modification of the polytrimethylsilylpropine adsorption layer in open capillary columns

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Modification of adsorption open capillary columns coated with polytrimethylsilylpropine (PTMSP) was experimentally studied. The modification of PTMSP by solvents (chlorobenzene, pentanol) and hot ethanol improves (up to 40%) the efficiency of capillary columns with a slight (3—7%) decrease in the retention factor.

Key words: gas adsorption capillary chromatography, efficiency of capillary columns, retention values, polytrimethylsilylpropine, hydrocarbons C_1—C_4.

We have recently proposed to use the membrane material polytrimethylsilylpropine[1] (PTMSP) as a chromatographic adsorbent for open capillary columns.[2,3] The obtained results are of theoretical and practical interest, especially for the separation of gaseous hydrocarbons; however, open capillary columns with PTMSP suitable for separating gaseous hydrocarbons and other compounds are characterized by comparatively high values of the height equivalent to theoretical plate (HETP).

Based on the concepts[2,3] about the mechanism of retention of volatile sorbates by the PTMSP adsorption layer, the modification of the initial PTMSP can increase the pore diameter and the concentration of open pores in the surface layer and thus improve the parameters of mass exchange of the sorbates between the polymer layer and gas phase.

The modification of the PTMSP layers in capillary columns is based on the following main concepts: (1) preparation of the PTMSP adsorption layer containing some amount (~20%) of organic volatiles with a higher boiling point than that of the main solvent; (2) fast increase in the temperature of the column for the quasi-"explosion" liberation of the PTMSP layer from the modifying substance due to which one could expect the expansion of the polymer pores and an increase in the number of open pores.

It was of interest to study the following methods for improving the efficiency of capillary columns: (1) modification of PTMSP (swelling) at contact with ethanol (including washing of the layer with hot ethanol),[4] (2) coating the column with the PTMSP layer containing chlorobenzene, and (3) coating the column with the PTMSP layer containing pentanol. After the PTMSP layer was put on the inner walls of the capillary column, volatile modifying components were removed from the adsorption layer by a fast increase in the temperature followed by flashing with the carrier gas.

The purpose of this work was to study the possibility to modify the PTMSP adsorption layer in open capillary columns to increase the rate of mass exchange between the gas phase and PTMSP layer under the conditions of gas chromatography.

Experimental

The chromatographic parameters of PTMSP were studied on fused silica columns (column length 16—19 m, internal diameter 0.215—0.25 mm) coated with the PTMSP layer (0.22—0.28 μm). The internal surface of the columns was caoted with the PTMSP adsorption layer by the dynamic method[5] from a 4% solution of PTMSP in $CHCl_3$. The thickness of the obtained PTMSP adsorption layer was determined by the weight method.

Procedures for modification of open capillary columns coated with the PTMSP layer. Method *A* (treatment with EtOH at room temperature). A column (16.5 m × 0.25 mm) with the PTMSP adsorption layer (0.23 μm) prepared by the method described above was considered as the initial column. The column was filled with EtOH and kept for ~1.5 h at ~20 °C, then EtOH was removed from the column under a small nitrogen pressure. Then the column was placed in the chromatograph thermostat heated up to 150 °C. After 5 min, the column was connected with a source of the carrier gas, and helium was passed through it (3 atm at the inlet) for 30 min at 150 °C.

Method *B* (treatment with EtOH at an elevated temperature). The initial column (17 m × 0.23 mm) with the PTMSP layer (0.28 μm) was modified by washing with EtOH (3 mL) at 60 °C. Then the column was dried and conditioned for 30 min in a helium flow (3 atm) at 150 °C.

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Method *C* (modification with chlorobenzene). A column (17.5 m × 0.23 mm) with the PTMSP layer (0.23 μm) modified with chlorobenzene was prepared introducing PTMSP (with $CHCl_3$) as a solvent. The concentration of chlorobenzene was 20% of the amount of PTMSP. When the PTMSP layer with chlorobenzene was put on the internal walls of the capillary, the column was placed for 5 min into the chromatograph thermostat heated to 200 °C. After this, the column was connected with a source of the carrier gas and conditioned for 30 min in a helium flow (3 atm) at 150 °C, and then its chromatographic parameters were measured (initial column). After measuring the chromatographic parameters, the obtained column was again modified by washing with EtOH (according to method *B*) and conditioned, and its chromatographic parameters were measured again.

Method *D* (modification with pentanol). A column (18 m × 0.25 mm) with the PTMSP adsorption layer (0.22 μm) was prepared similarly to method *C*; however, *n*-pentanol (20% of the weight of PTMSP) was used instead of chlorobenzene. After measuring the chromatographic parameters of the prepared column, which was considered as the initial one, it was repeatedly modified by washing with hot (60 °C) EtOH using method *B*, and the chromatographic parameters were measured again.

Experiments were conducted on an LKh-8MD modified gas chromatograph (plant "Khromatograf," Moscow) with a flame-ionization detector (FID) using helium as the carrier gas. Retention times were measured using an I-02 modified integrator (plant "Mikroprovod," Chisinau, Moldova) with a resolution of 0.1 s. The volume of the analyzed sample was ~10 μL of a mixture of hydrocarbon gases C_1—C_4 (2—3 vol.% of each component in N_2), the flow split of the carrier gas was 1 : 100, and the sensitivity of the FID was $20 \cdot 10^{-12}$ A per whole scale. The chromatographic parameters (retention factor *k* and HETP) were measured at 40 °C and a linear flow rate of the carrier gas of 35—40 cm s^{-1}, which is optimum for this group of sorbates.

Table 1. Influence of different methods* of modification of the PTMSP adsorption layer on the chromatographic parameters of columns

Sorbate	HETP/mm		ρ (%)	*k*		λ (%)
	I	II		I	II	
Methane	0.37	0.35	−5.4	—	—	—
	0.37	**0.38**	**2.7**	—	—	—
	(0.36)	(0.36)	(0)	—	—	—
	[0.48]	[0.46]	[−4.2]	—	—	—
Ethylene	0.33	0.32	−3.0	0.082	0.072	−12.2
	0.32	**0.31**	**−3.1**	**0.096**	**0.093**	**−3.1**
	(0.31)	(0.30)	(−3.3)	(0.093)	(0.092)	(−1.1)
	[0.41]	[0.40]	[−2.4]	[0.086]	[0.085]	[−1.1]
Ethane	0.32	0.33	3.0	0.127	0.115	−9.4
	0.31	**0.30**	**−3.2**	**0.152**	**0.147**	**−3.3**
	(0.31)	(0.30)	(−3.3)	(0.151)	(0.146)	(−3.3)
	[0.41]	[0.41]	[0]	[0.134]	[0.134]	[0]
Propylene	0.46	0.43	−6.5	0.463	0.447	−3.5
	0.39	**0.40**	**2.6**	**0.576**	**0.553**	**−4.0**
	(0.50)	(0.40)	(−20.0)	(0.575)	(0.549)	(−4.5)
	[0.50]	[0.50]	[0]	[0.496]	[0.489]	[−1.4]
Propane	0.66	0.59	−10.6	0.649	0.622	−4.2
	0.50	**0.48**	**−4.0**	**0.809**	**0.77**	**−4.8**
	(0.73)	(0.56)	(−23.3)	(0.812)	(0.768)	(−5.4)
	[0.72]	[0.64]	[−16.7]	[0.698]	[0.681]	[−2.4]
Isobutane	1.92	1.63	−14.6	2.74	2.65	−3.3
	1.20	**1.06**	**−11.7**	**3.43**	**3.24**	**−5.5**
	(2.22)	(1.32)	(−40.5)	(3.51)	(3.25)	(−7.4)
	[2.00]	[1.67]	[−16.5]	[2.97]	[2.87]	[−3.4]
Butane	1.22	1.05	−13.9	3.63	3.52	−3.0
	0.72	**0.69**	**−4.2**	**4.56**	**4.30**	**−5.7**
	(0.97)	(0.81)	(−16.5)	(4.66)	(4.30)	(−7.7)
	[1.11]	[0.97]	[−12.6]	[3.94]	[3.80]	[−4.3]

* The results obtained by methods ***A***, ***B*** (emphasized by bold), ***C*** (in parentheses), and ***D*** (in brackets) are presented; I, initial columns; II, modified columns.

Results and Discussion

The change in the main chromatographic parameters (HETP, retention factor *k*) of the modified capillary columns compared to the initial columns is the most important measure of efficiency of the modification methods used. The relative change in the HETP value was used for the quantitative estimation of different modification methods

$$\rho = [(\mathrm{HETP})' - (\mathrm{HETP})_0]/(\mathrm{HETP})_0 \cdot 100\%$$

as well as the relative change in the retention factor

$$\lambda = (k' - k_0)/k_0 \cdot 100\%,$$

where the parameters with stroke are used for the modified column.

The results of measuring the chromatographic parameters of the columns (Table 1) reflect the efficiency of the studied modification methods. First, all used modification methods result in a substantial decrease in the HETP values and a slight decrease in the retention factor *k* (mainly by 3—7%). Second, the enhancement of the efficiency of the column (a decrease in the HETP values) is most pronounced for hydrocarbon gases of the C_3 and especially C_4 group (to 40%); for lighter hydrocarbons, a decrease in HETP is insignificant (3—5%) but not critical because the absolute HETP values for light gases are quite satisfactory. The additional treatment of the column with hot EtOH decreases the HETP values by still more 10—20%. In connection with this positive result, the possibility of using several different methods of treatment in sequence for the modification of the PTMSP layer should be mentioned.

Thus, the methods proposed for modification allowed us to enhance noticeably the chromatographic parameters of the adsorption capillary column coated with PTMSP, which is associated, most likely, with an increase in the rate of interphase mass exchange of the sorbates.

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