Flaked capillary columns with crown ether complexes for gas-liquid chromatography

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Flaked capillary columns with an OV-101/CE-Na_3PO_4 hydrophobic-hydrophilic sorbent have been suggested. This sorbent provides for the analysis of polar and nonpolar substances, including amines and aminoalcohols, in aqueous and organic solvents. The efficiency of new columns was demonstrated for the analysis of 25 organic substances of various classes.

Key words: gas chromatography; flaked capillary columns; OV-101; crown ether complexes; aqueous solutions.

The unique structure and properties of crown ethers allowed them to be used as selective phases in chromatography.[1] In gas chromatography (GC) individual crown ethers were used for separation of *n*-alkanes, aliphatic alcohols, nitrogen-containing compounds, and phenols.[2,3] However, there are several restrictions caused by their insufficient thermal stability and low efficiency of GC-columns.[3–5]

Highly efficient stable glass and silica fuse columns with a wide temperature range for analysis were obtained by the method of chemical immobilization of mono- and polycrown ethers or polysiloxanes containing crown ethers as substituents on substrates.[5–8] A wide range of organic compounds in organic solvents were analyzed on such columns;[1,4–9] however, they were not used for analysis of aqueous solutions. Data on the use of crown ether complexes with metal salts as stationary phases in GC are scarce.[1]

We have established previously that additions of Na_3PO_4 and KF salts to stationary phases favor separation of primary and secondary amines due to the weak donor-acceptor interaction with salts.[10] Melts of $KF \cdot 2H_2O$ were used as stationary phases in GC for analysis of aqueous solutions of organic compounds.[11]

The purpose of this work is to prepare flaked capillary columns containing, as sorbents, complexes of crown ether with trisodium phosphate and nonpolar stationary phases immiscible with them, and to study the possibility of using flaked columns for the analysis of polar and nonpolar organic substances in aqueous and organic solvents.

Experimental

Glass capillaries were treated with 3 mL of 1 % aqueous HF solution under 3 atm of pressure; then the acid was displaced with nitrogen, and the columns were subsequently washed with distilled water and methanol. The layer of $Na_3PO_4 \cdot 12H_2O$ was applied to the inner surface of the capillary by the method of a hexane plug,[12] using a saturated salt solution in methanol; then the column was blasted with nitrogen and thermostated for 1 h at 250 °C in the helium flow.

The OV-101/CE-Na_3PO_4 flaked columns containing the complex of crown ether with OV-101 were prepared as follows. The OV-101 stationary phase (Serva, 26 mg) was dissolved in 5 mL of freshly distilled chloroform. Solutions of crown ethers (10 and 40 % with respect to the amount of OV-101) were prepared by dissolution of 2.6 and 10.6 mg, respectively, of dibenzene-18-crown-6 in 5 mL of freshly distilled methylene dichloride. The solutions of OV-101 and crown ether were combined and used for applying the sorbent on the capillary walls using a the static high-pressure method.[12] Columns were conditioned in the helium flow at programmed temperature

Table 1. Parameters of flaked glass capillary columns with OV-101/CE-Na_3PO_4

Parameters of the column	Number of the column			
	1	2	3	4
Inner diameter/mm	0.3	0.31	0.31	0.31
Length/m	30	40	37.5	34
Thickness of the film of the phase/μm	0.2	0.2	0.2	0.2
Number of theoretical plates (for C_{17} at 120 °C)	56850	93720	68012	57120
Capacity factor *k* (for C_{17} at 120 °C)	22.4	25.37	21.15	22.0
[Crown ether]/[OV-101] (%)	10	40	40	40
Crown ether/Na_3PO_4 (mol mol^{-1})	1 : 2.5	1 : 1.5	1 : 1	1 : 1

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from 100 to 250 °C with velocity of 6 °C min^{-1}, and stored in an isothermal regime at 250 °C for 30 min. Parameters of the OV-101/CE-Na_3PO_4 columns are given in Table 1.

GC analysis was performed on a Pye Unicam-104 chromatograph (England) rebuilt for capillary columns. Temperatures of a flame-ionization detector and an injector were kept equal to 220 and 200 °C, respectively. The chromatography was performed in an isothermal regime at 100 °C and programmed temperature from 80 to 200 °C with velocity of 4 °C min^{-1}. The splitting of gas-carrier helium at the opening of the column was 1 : 30. The volume of a sample of aqueous or pentane solutions of organic compounds was 0.3 μL. A sample was injected by a syringe (1 μL in volume, Scientific Glass Engineering, Australia).

n-Alkanes C_6—C_{17}, aromatic hydrocarbons, carbonyl- and S-containing compounds, aliphatic alcohols, nitrogen-containing compounds, and aminoalcohols were used as test compounds. Aqueous and pentane solutions with concentrations of test compounds of 0.05 and 0.5 % v/v, respectively, were analyzed. Retention parameters were determined in the form of the Kovac indices.

Results and Discussion

Methylsiloxane OV-101 and a complex of dibenzene-18-crown-6 with Na_3PO_4 were chosen for the preparation of glass capillary columns with hydrophobic-hydrophilic sorbents. Complexes of salts of alkaline metals with crown ether were uniformly distributed over the capillary surface. Hydrophobic-hydrophilic properties of the complex also provide the uniform distribution of nonpolar OV-101 siloxane over the surface of a capillary column. Thus obtained flaked capillary columns consist of the layers of trisodium phosphate, a complex of trisodium phosphate with crown ether, and OV-101 methylsiloxane. An additional experiment showed that these layers do not mix even on heating.

The parameters of four obtained capillary columns with flaked phases are presented in Table 1.

In order to elucidate the probable influence of the crown ether complex on the energy of the dispersion interaction of the sorbate and methylsiloxane, energetic contributions of methylene units of *n*-alkanes $\Delta G(CH_2)$ were compared for our OV-101/CE-Na_3PO_4 columns and the OV-101/KF column prepared according to the known method.[13] The values of $\Delta G(CH_2)$ calculated from the corrected retention times of *n*-C_{12}—C_{13} turned out to be similar for these columns: −1.93 and −1.97 kJ mol^{-1}, respectively. Therefore, the layer of the crown ether complex almost does not affect the energy of the dispersion interaction with OV-101.

Pentane and aqueous solutions of aliphatic and aromatic hydrocarbons were analyzed on flaked columns at programmed temperature (Fig. 1) and in the isothermal regime (Fig. 2). Solutions of amines and aminoalcohols were analyzed as well (Figs. 3 and 4). The analyses were performed at equal sensitivities of an amplifier of $5 \cdot 10^{-12}$ A, using equal volumes of samples of aqueous and pentane solutions. Concentrations of the compounds in water were 10-fold lower than in pentane. As seen from Figs. 1 and 2, areas of the peaks corresponding to hydrocarbons in aqueous solutions (see Figs. 1, *b*, 2, *b*) are greater than those of the corresponding peaks in pentane (see Figs. 1, *a*, 2, *a*). This increase is related

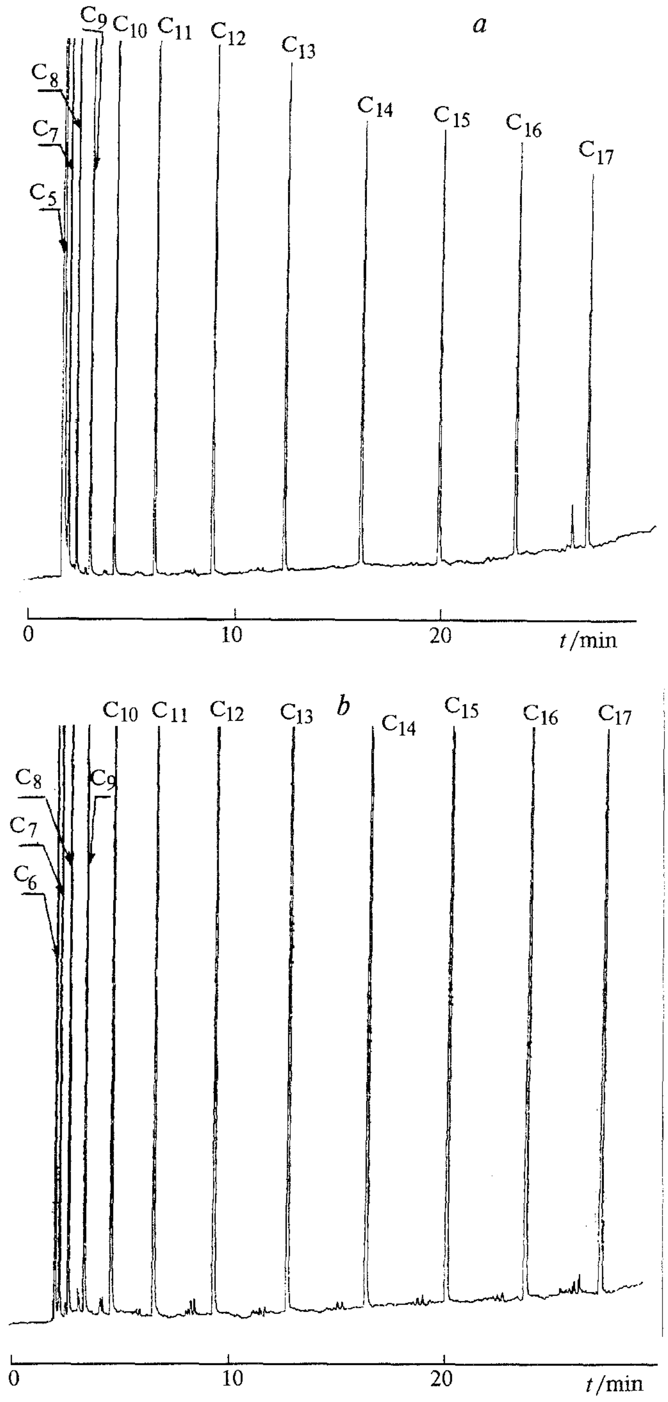

Fig. 1. Chromatograms of *n*-alkanes C_6—C_{17} on glass capillary column No. 1 with OV-101/CE-Na_3PO_4: pentane (*a*) and aqueous (*b*) solutions with concentrations of 0.5 and 0.05 % v/v, respectively. Temperature programming from 80 to 200 °C with velocity of 4 °C min^{-1}, T_{inj} = 200, T_{det} = 220 °C, V = 0.3 μL.

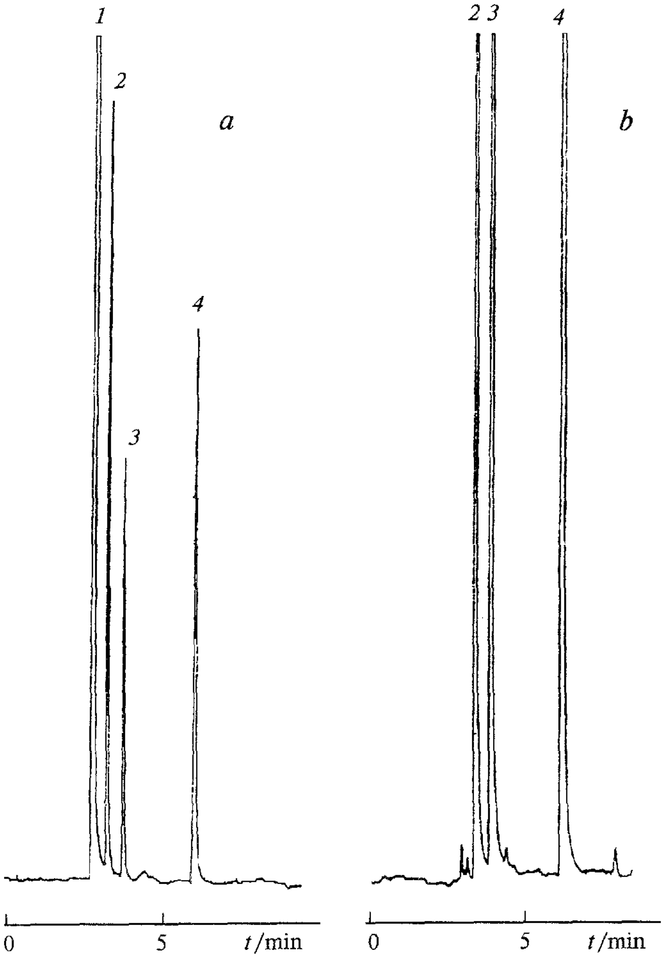

Fig. 2. Chromatograms of aromatic hydrocarbons on glass capillary column No. 2 with OV-101/CE-Na_3PO_4: pentane (*a*) and aqueous (*b*) solutions with concentrations of 0.5 and 0.05 % v/v, respectively. T_{col} = 100, T_{inj} = 200, T_{det} = 200 °C, V = 0.3 μL: *1*, pentane; *2*, toluene; *3*, *p*-xylene; and *4*, *n*-butyl benzene.

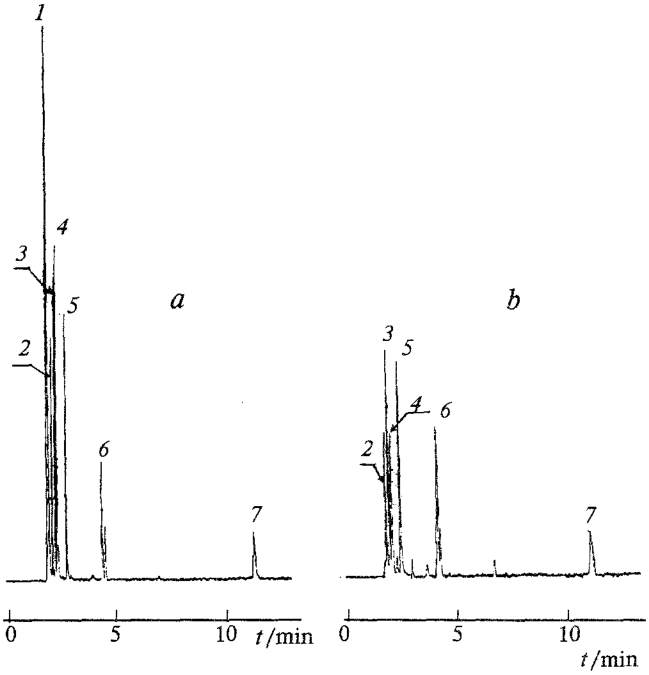

Fig. 3. Chromatograms of nitrogen-containing compounds on glass capillary column No. 3 with OV-101/CE-Na_3PO_4: pentane (*a*) and aqueous (*b*) solutions with concentrations of 0.5 and 0.05 % v/v, respectively. T_{col} = 100, T_{inj} = 200, T_{det} = 200 °C, V = 0.3 μL: *1*, pentane; *2*, pyridine; *3*, α-picoline; *4*, *n*-hexyl amine; *5*, 2,3-lutidine; *6*, methyl-*n*-octyl amine; and *7*, dimethyl-*n*-decyl amine.

to the existence of the aerosol preconcentration, because the analysis was performed under conditions that ensured the appearance of this effect.[14] The comparison of the peak areas of aqueous and pentane solutions in Figs. 3 and 4 shows that the effect of the aerosol preconcentration appears to a lesser extent in the analysis of such polar compounds as amines and aminoalcohols.

It is known that chromatographic separation of amines and aminoalcohols requires a special treatment of the column surface with alkali or salts of alkaline metals or application of an inorganic salt with a phase, which is capable of the donor-acceptor interaction with analyzed substances.[10] However, the GC analysis of aminoalcohols is also difficult in this case. These compounds are completely adsorbed on the columns containing individual crown ethers.[15] As seen from Figs. 3 and 4, both pentane and aqueous solutions of amines and aminoalcohols are well separated on the flaked columns containing the complex of crown ether with a salt of the alkaline metal and OV-101 as a phase. Thus, flaked columns make it possible to analyze aqueous solutions of aminoalcohols on a nonpolar phase. The absence of adsorption of aminoalcohols on the OV-101/CE-Na_3PO_4 columns confirms the assumption that dibenzene-18-crown-6 exists as a complex with trisodium phosphate and, therefore, does not form inclusion compounds with alcohols. Complete adsorption of amines and aminoalcohols was observed only on column No. 1 (see Table 1) with lower content of the crown ether complex with respect to the amount of OV-101.

Reproducibility and stability of the columns were evaluated from the values of retention indices of organic compounds of various classes. It is established that retention indices of the compounds studied on the columns with OV-101/CE-Na_3PO_4 are almost unchanged from column to column (Tables 2, 3). The values of retention indices of benzenes, O- and S-containing compounds on the columns with OV-101/CE-Na_3PO_4 and on the columns with OV-101 are very similar (see Table 2). This fact indicates that the existence of the layer of the complex of dibenzene-18-crown-6 with Na_3PO_4 does not affect the character of

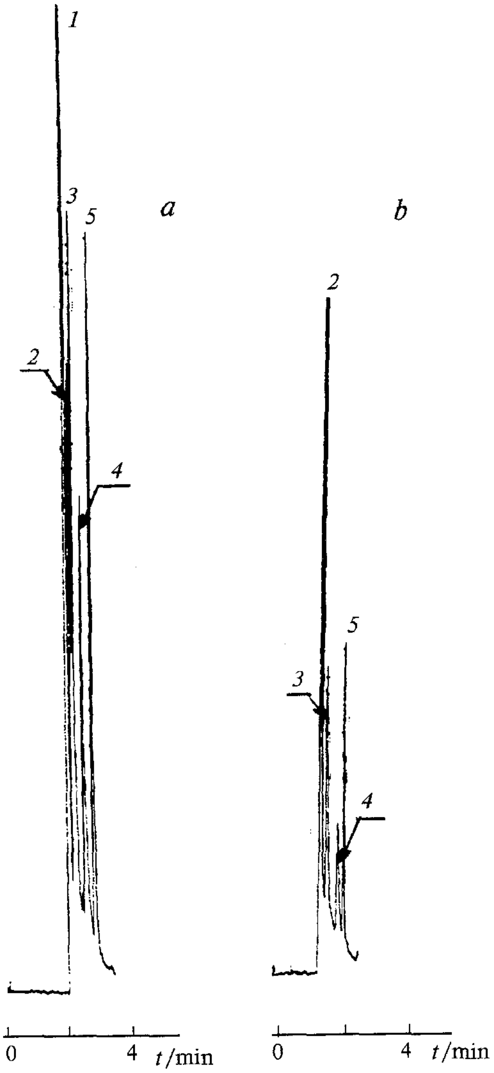

Fig. 4. Chromatograms of aminoalcohols on glass capillary column No. 3 with OV-101/CE-Na_3PO_4: pentane (*a*) and aqueous (*b*) solutions with concentrations of 0.5 and 0.05 % v/v, respectively. $T_{col} = 100$, $T_{inj} = 200$, $T_{det} = 200$ °C, $V = 0.3$ μL: *1*, pentane; *2*, ethanolamine; *3*, dimethylaminoethanol; *4*, aminobutanol; and *5*, diethylaminoethanol.

Table 2. Retention indices of organic compounds on glass capillary columns with OV-101/CE-Na_3PO_4 at 100 °C

Compound	Values of retention indices				
	Freshly prepared columns			After 30 days	Literature data[16,17] for OV-101
	2	3	4	2	
Toluene	768	775	765	766	766
p-Xylene	870	871	867	868	866
o-Xylene	897	896	890	891	888
n-Butylbenzene	1051	1048	1048	1046	1046
n-Amyl acetate	—	892	890	—	895
n-Heptyl acetate	1094	1093	1094	1094	1095
n-Hexane-1-thiol	913	911	911	910	910
Diisobutyl sulfide	993	989	991	991	—
Methyl-*n*-octyl ketone	1175	1177	1175	1173	1176
Amyl alcohol	753	755	750	754	756
Hexyl alcohol	856	850	850	855	858
Heptyl alcohol	957	953	953	957	957
Octyl alcohol	1058	1056	1056	1058	1061

Table 3. Retention indices of nitrogen-containing compounds on glass capillary columns with OV-101/CE-Na_3PO_4 at 100 °C

Compound	Retention indices		
	Freshly prepared columns		After 30 days
	3	4	3
Pyridine	737	739	735
α-Picoline	801	801	800
n-Hexyl amine	831	832	830
2,3-Lutidine	927	930	925
Methyl-*n*-octylamine	1088	1089	1085
Dimethyl-*n*-decylamine	1298	1298	1297

the dispersion interaction of the compounds analyzed with methylsiloxane.

Every day from 20 to 30 analyses of organic and aqueous samples were performed on the columns. Properties of the columns and retention indices were unchanged (see Tables 2, 3). Intense service during a month did not affect stability of the columns.

The formation of the complex of the sodium salt with crown ether provides a unified hydrophobic-hydrophilic surface and a uniform distribution on it of the OV-101 stationary nonpolar phase. Symmetric peaks in the analysis of aqueous solutions of polar compounds, including aminoalcohols, on the OV-101 nonpolar phase (the upper layer of the flaked sorbent) is likely to be related to the fact that the formation of the symmetric zone of a polar compound occurs in the second layer, the crown ether complex. Blurring of the formed zone of the hydrophilic sorbate is reduced to a minimum in the hydrophobic layer of methylsiloxane. This makes it possible to analyze aqueous solutions of aminoalcohols, amines, and other polar compounds on a nonpolar stationary phase.

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