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GAS CHROMATOGRAPHY ON MONOLAYERS OF DERIVATIVES OF PORPHYRINS AND CROWN ETHERS

E. V. ZAGOREVSKAYA and N. V. KOVALEVA*

Laboratory of Adsorption and Chromatography, Chemical Department, M. V. Lomonosov State University of Moscow, 117234 Moscow (U.S.S.R.)

SUMMARY

The adsorption and gas chromatographic properties of graphitized thermal blacks and carbochromes, modified with monolayers of derivatives of porphyrins and crown ethers, have been investigated. Retention volumes, differential heats of adsorption and specific interaction energies have been determined for adsorbates of different classes. The adsorbents obtained are selective towards different classes of organic compounds. The chromatographic and adsorption properties of the modified adsorbents depend on the nature of the complex-forming metal and of the substituents in the modifying substances.

INTRODUCTION

Adsorptive modification of graphitized thermal carbon blacks (GTBs) and carbochromes (mechanically more stable) has been widely used to obtain adsorbents for gas chromatography (GC)¹.

Adsorption on a flat adsorbent surface (*e.g.*, on the graphite crystal basal face), is determined by the geometry of the adsorbate molecule; thus such adsorbents can be used to separate geometrical and structural isomers. However, the number of substances that can be successfully separated on GTB and carbochromes is limited, since, first, they constitute practically non-specific adsorbents and, secondly, the energy of the non-specific interactions between the molecule and the GTB surface is high, which hinders the separation of high-molecular-weight substances. It is therefore of interest to use them as supports for non-volatile substances with different functional groups, capable of specific interaction with the components of a mixture. When the modifying substances are deposited in quantities that do not exceed a dense monolayer, they are firmly retained on the GTB surface, changing its chemical nature and, in many cases, reducing the specific interaction energy, without markedly changing the surface geometry.

The present work is as continuation of a series of investigations on the adsorptive modification of GTBs¹⁻⁹, specifically with sodium salts of the sulphoacids of copper and cobalt phthalocyanine⁶. Here, porphyrin derivatives, readily soluble in organic solvents, were used as modifying substances: ethioporphyrin (H₂EP) and its

complexes with Cu (CuEP), Ni (NiEP) and VO (VOEP)¹⁰; tetra(*p*-methoxyphenyl)-porphyrin (H₂TMPP) and its complex with cobalt (CoTMPP). Crown ethers were also used for modification (see Fig. 1).

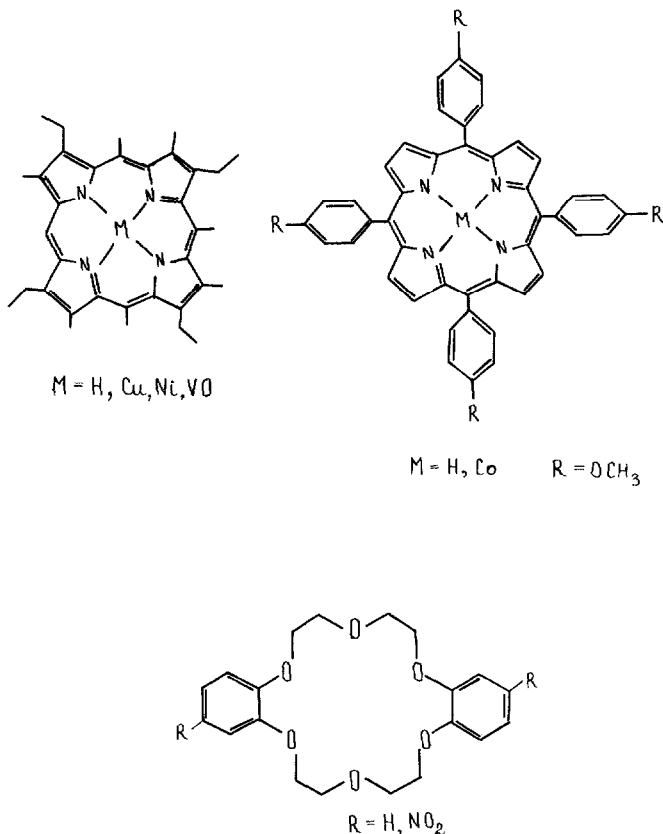


Fig. 1. Structural formulae of modifying substances.

Porphyrins are structural analogues of phthalocyanine¹¹. Just like phthalocyanines, they have a planar structure, but, in contrast, they are readily soluble in organic solvents due to their lower crystal lattice energy. The high solubility and their high thermal stability makes possible their use as modifying substances by means of adsorption from solutions.

Porphyrin derivatives, specifically their metal complexes, play an important part in many biological catalytic and other processes. That is why much attention has recently been given to ascertaining their structure and the influence exerted by the metal and the substituents in the pyrrole rings up their properties¹¹.

Dibenzo-18-crown-6 is a crystalline substance, readily soluble in various organic solvents, including chloroform. It is thermally stable, subliming without decomposition at 380°C¹². As a mobile phase applied to Chromsorb W, it was shown¹³ to be highly selective towards chlorophenols.

The object of the present work was to investigate the influence of the complex-forming metal and substituents on the interactions of these compounds with substances of different classes.

EXPERIMENTAL

By means of adsorption from solutions², the modifying substances were deposited in quantities corresponding to a monolayer on the surface of GTB and carbochrome. Thermal black TG-10 was used, treated in a stream of argon for 4 h at 3000°C. The specific surface area of GTB is 8.4 m²/g (measured by thermal desorption of nitrogen). The carbochrome EPT-5¹⁴ was obtained by depositing pyrocarbon on TG-10.

To characterize the adsorption and chromatographic properties of modified GTB, the specific retention volumes, $V_{m,1}$, and the differential molar internal energies, $-\Delta u_1$, were obtained for a small (zero) sample, and the contributions of the specific interaction energy, $-\Delta u_{\text{spec}}$, to the overall adsorption energy were estimated for substances of different classes, according to the classification in ref. 1. The $-\Delta u_1$ values were determined from the $\lg V_{m,1}$ vs. $1/T$ dependence. The $-\Delta u_{\text{spec}}$ values were found from the dependence of $-\Delta u_1$ on polarizability, as the difference between the $-\Delta u_1$ for a given substance and that for an *n*-alkane with the same polarizability¹⁵. The monolayer capacity was estimated by three methods: from adsorption from solutions, from the dependence of $V_{m,1}$ on the amount of modifier applied to GTB and from the Van der Waals dimensions of the molecules of the modifying substances tightly packed on the GTB surface⁷. In all cases, similar results were obtained: the monolayer capacity for these substances amounted to about 0.7–0.8 mg/m².

A Tsvet-I chromatograph with a flame ionization detector was employed. Glass columns (100 cm × 0.2 cm) were used. The carrier gas (helium) flow-rate was 30 ml/min, and the size of the adsorbent pellets was 0.25–0.5 mm. In some experiments, narrow fractions with grain sizes of 0.20–0.25 mm were used.

RESULTS AND DISCUSSION

Modification with porphyrin derivatives

Table I shows the $V_{m,1}$ values on the unmodified and the modified GTB. As is seen the retention volumes of almost all the adsorbates on the modified samples

TABLE I
SPECIFIC RETENTION VOLUMES, $V_{m,1}$ (cm³/g), AT 70°C ON UNMODIFIED GTB AND GTB MODIFIED WITH MONOLAYERS OF PORPHYRIN DERIVATIVES

Adsorbent	<i>n</i> -C ₆ H ₁₄	<i>n</i> -C ₇ H ₁₆	(CH ₃) ₂ CO	(C ₂ H ₅) ₂ O	C ₃ H ₇ OH	CHCl ₃	CCl ₄	C ₆ H ₆
GTB	76.8	285	2.6	8.7	7.1	8.2	16.4	40.6
GTB-H ₂ EP	9.1	17.9	2.2	2.1	2.5	5.2	3.6	3.5
GTB-CuEP	11.6	33.6	4.9	2.5	2.2	5.2	4.9	6.4
GTB-CoEP	6.7	16.3	5.9	3.1	8.1	8.7	6.1	7.9
GTB-H ₂ TMPP	75.5	270	7.4	9.8	11.4	20.2	59.0	48.1
GTB-CoTMPP	75.5	270	7.5	9.8	11.4	20.2	59.0	48.3

were less than those on unmodified GTB, which is probably associated with a decrease in the concentration of non-specific molecular interaction centres. The samples modified with H₂TMPP constitute an exception: retention volumes of *n*-hydrocarbons on these samples remained almost unchanged compared with those unmodified on GTB. This may be explained by the structure of the modifier: the four phenyl substituents are almost perpendicular to the plane of the porphyrin ring¹¹, and it is possible that a part of the GTB surface remains free and accessible to the adsorbate molecules.

The $V_{m,1}$ values of substances capable of interacting specifically with the functional groups of the modifying substances (molecules in groups B and D)^{1,16} decrease less than in the case of *n*-hydrocarbons, or even increase on samples modified with VOEP, H₂TMPP and CoTMPP.

Table II shows the $-\Delta u_1$ values for some adsorbates on unmodified GTB and on modified samples. For all the adsorbates on modified samples the $-\Delta u_1$ values are considerably lower than on unmodified GTB. This is explained by the screening of the surface of the GTB and a decrease in the concentration of the non-specific intermolecular interaction centres upon modification.

TABLE II

$-\Delta u_1$ AND Δu_{spec} . (kcal/mol) ON GTB AND MONOLAYERS OF PORPHYRIN DERIVATIVES DEPOSITED ON GTB

Adsorbent	<i>n</i> -C ₆ H ₁₄ C ₆ H ₆		(CH ₃) ₂ CO			C ₃ H ₇ OH				
	$-\Delta u_1$	$-\Delta u_1$	$-\Delta u_{\text{spec}}$	$\frac{-\Delta u_{\text{spec}}}{-\Delta u_1}$	$-\Delta u_1$	$-\Delta u_{\text{spec}}$	$\frac{-\Delta u_{\text{spec}}}{-\Delta u_1}$	$-\Delta u_1$	$-\Delta u_{\text{spec}}$	$\frac{-\Delta u_{\text{spec}}}{-\Delta u_1}$
				(%)			(%)			(%)
GTB	10.2	9.8	—	—	8.3	—	—	8.1	—	—
GTB-H ₂ EP	7.6	6.4	—	—	8.5	1.2	14	6.7	2.5	37
GTB-CuEP	6.2	5.8	0.58	10	5.2	1.8	35	6.7	3.2	48
GTB-VOEP	7.3	6.8	1.6	24	6.7	3.5	52	8.3	5.2	63
GTB-H ₂ TMPP	9.6	9.1	1.2	13				7.8	2.8	36
GTB-CoTMPP	9.6	9.1	1.2	13				7.8	2.8	36

Estimation of the $-\Delta u_{\text{spec}}$ value showed that the monolayers of the ethio-porphyrin derivatives are characterized by a large contribution of molecules in groups B and D to the overall $-\Delta u_1$ value. When these values are compared the rôle of the complexing agent is clearly manifested, just as in the case of V_{rel} . This is most evident for molecules of groups B and D on NiEP and VOEP. The contribution of the specific interaction energy to the overall adsorption energy on H₂EP for acetone is 14% and for propanol is 37%, whereas on VOEP these values are much higher, amounting to 52% for acetone and more than 60% for propanol.

The H₂TMPP and CoTMPP monolayers deposited on GTB have the same adsorption properties with respect to compounds of different classes. The action of the cobalt ion is not manifested. This is probably associated with a special structure of these molecules. The Co²⁺ joined by four covalent bonds to the nitrogen atoms of the pyrrole rings is screened by four phenyl rings situated perpendicular to the

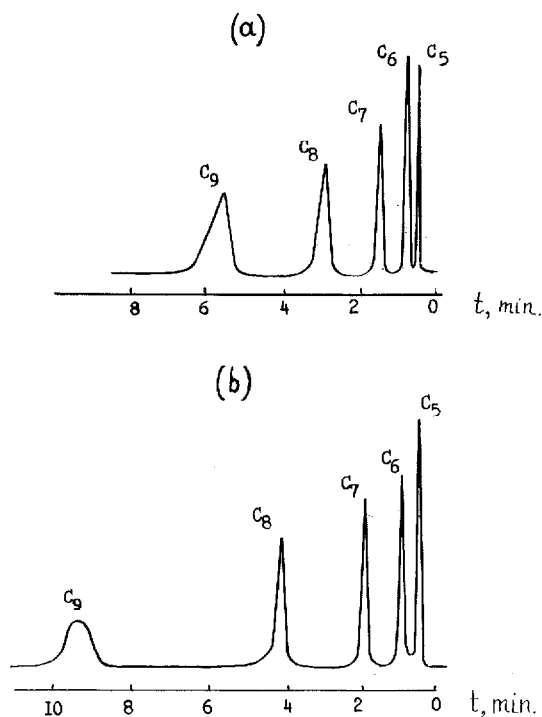


Fig. 2. Separation of *n*-hydrocarbons (C₅-C₉): (a) on GTB, at 150°C, 1 m × 2 mm column, carrier-gas (helium) flow-rate 40 ml/min; (b) on GTB modified with CuEP monolayer, at 65°C, 1 m × 1.2 mm column, carrier-gas (helium) flow-rate 20 ml/min.

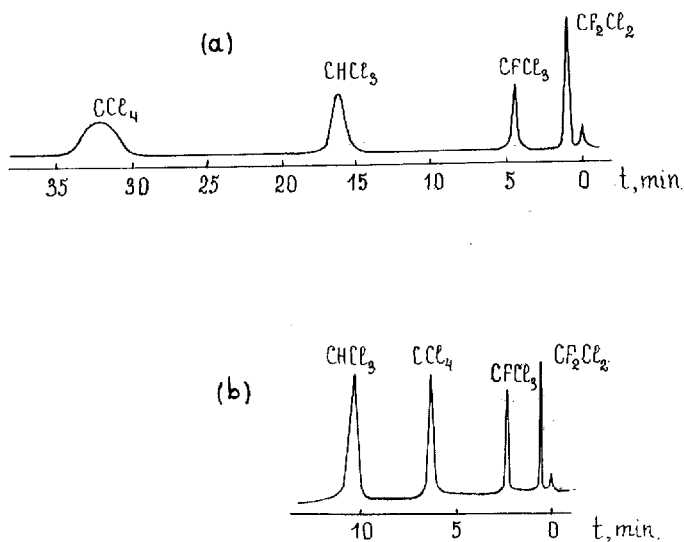


Fig. 3. Separation of chloro/fluoro methanes derivatives: (a) on GTB; (b) on GTB modified with EP monolayer, at 40°C, 1 m × 2 mm column, carrier-gas (helium) flow-rate 20 ml/min, electron-capture detector.

plane of the porphyrin ring¹¹. Specific interactions of these molecules with the B and D groups molecules seem to be caused by the presence of the π -electron density of the phenyl rings and by the presence of the OCH₃ groups.

The molecules of porphyrin and its derivatives have a complex electron structure and conjugation system. When complex compounds are formed with a metal ion the latter becomes an equal participant in this conjugated system, and affects all the properties of these molecules¹¹.

From previous studies¹⁻⁶ it is clear that the selectivity towards the components of mixtures is determined by the ratio of the contribution of the specific interaction

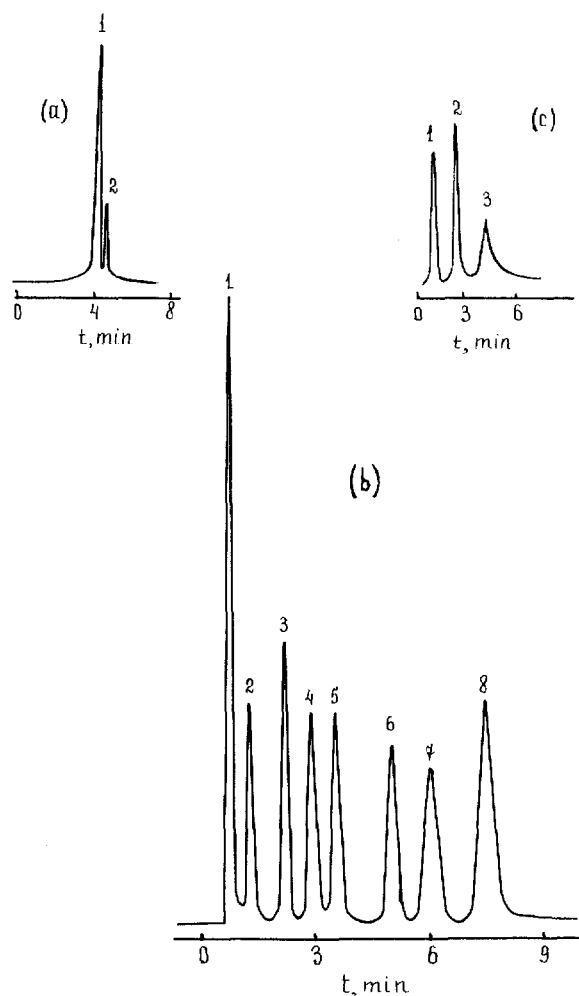


Fig. 4. Separation of oxygen-containing compounds. (a) On GTB modified with VOEP monolayer; 1 m \times 2 mm column, carrier-gas (helium) flow-rate 30 ml/min, at 65°C. Peaks: 1 = cyclohexanol; 2 = cyclohexanone. (b) On GTB modified with CuEP monolayer; details as in (a). Peaks: 1 = CH₃OH; 2 = C₂H₅OH; 3 = *iso*-C₃H₇OH; 4 = *n*-C₃H₇OH; 5 = *tert*-C₄H₉OH; 6 = *sec*-C₄H₉OH; 7 = *iso*-C₄H₉OH; 8 = *n*-C₄H₉OH. (c) Peaks: 1 = CH₃COOH; 2 = C₂H₅COOH; 3 = (CH₃)₂CHCOOH, details as in (a).

energy to the overall adsorption energy and the overall adsorption energy. A decrease in the overall adsorption energy of *n*-hydrocarbons on GTB modified with ethioporphyrin and its metal complexes makes it possible to separate them on these adsorbents at temperatures considerably lower than in the case of unmodified GTB (Fig. 2).

Since the planar structure of the surface of GTB remains after modification with ethioporphyrin and its complexes, the modified adsorbents, as well as unmodified GTB, can be used to separate structural isomers¹⁰. The ethioporphyrin monolayer deposited on GTB is selective to the separation of hydrocarbon halide derivatives. Fig. 3 illustrates the separation of chloro/fluoro methane derivatives on unmodified GTB and on GTB modified with ethioporphyrin. A decrease in the energy of dispersive interaction on a modified sample results in a decrease in the analysis time for these compounds, and a considerable contribution of chloroform molecules to the overall adsorption energy results in carbon tetrachloride being eluted much sooner than chloroform on this adsorbent.

The high selectivity of GTB modified with VOEP towards oxygen-containing compounds makes it possible to separate cyclohexanol and cyclohexanone (Fig. 4a). These compounds have similar molecular weights, similar molecular structures and on GTB are eluted as one peak at all temperatures.

More selective with respect to the separation of alcohols and acids are GTBs modified with ethioporphyrin or its copper complex; their specific interaction with alcohol molecules is much weaker than in the case of GTB modified with VOEP (Fig. 4b, c).

TABLE III

SPECIFIC RETENTION VOLUMES, $V_{m,1}$ (cm³/g), OF SOME CHLORINE-CONTAINING HYDROCARBONS ON CARBOCHROME MODIFIED WITH A MONOLAYER OF DIBENZO-18-CROWN-6

Column temperature (°C)	α -HCH	γ -HCH	Aldrin	Heptachlor	DDE
200			290.2	314.1	
205			241.9	281.5	
210			205.9	223.0	
215			175.0	187.1	
220			149.3	157.8	
225			130.3	138.2	
230	65.6	102.2	111.9	117.8	
235	58.9	87.1	84.1	88.1	
240	52.8	74.2	72.1	76.2	
245	46.2	63.3			
250	42.1	54.4			657.4
255					550.6
260					464.4
265					405.9
270					338.7
275					288.2
280					242.3
285					212.2
290					178.5

TABLE IV

$V_{m,1}$ (cm³/g) AND $-\Delta u_1$ (kcal/mol) ON THE UNMODIFIED AND THE MODIFIED CARBOCHROME

Adsorbate	Dipole moment (D)	Carbochrome		Carbochrome + dibenzo-18-crown-6	
		$V_{m,1}$ (230°C)	$-\Delta u_1$	$V_{m,1}$ (230°C)	$-\Delta u_1$
α -HCH	2.20	82.4	16.6 \pm 0.4	65.6	11.5 \pm 0.3
γ -HCH	2.89	143.0	16.8 \pm 0.4	102.2	13.0 \pm 0.4
Aldrin	—	150.7	15.2 \pm 0.3	111.9	14.0 \pm 0.4
Heptachlor	—	180.8	17.6 \pm 0.5	117.8	15.1 \pm 0.4
DDE		550.1*			

* At 285°C.

Carbochrome modified with crown ether derivatives

Dibenzo-18-crown-6 and dinitrodibenzo-18-crown-6 were deposited on the carbochrome surface in amounts of 0.7 mg/m², following the procedure described⁹. The adsorption properties of carbochrome are similar to those of GTB, but the mechanical strength of its pellets is much higher¹⁴. To characterize the adsorption

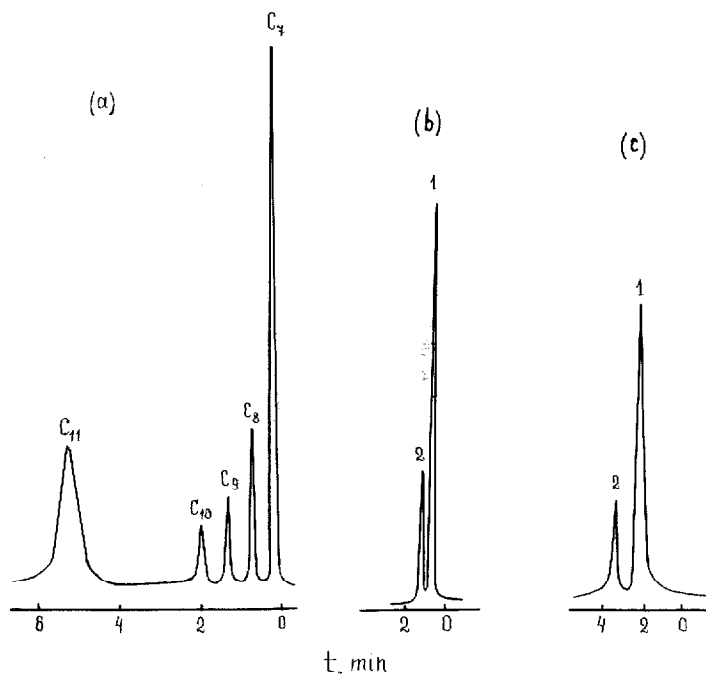
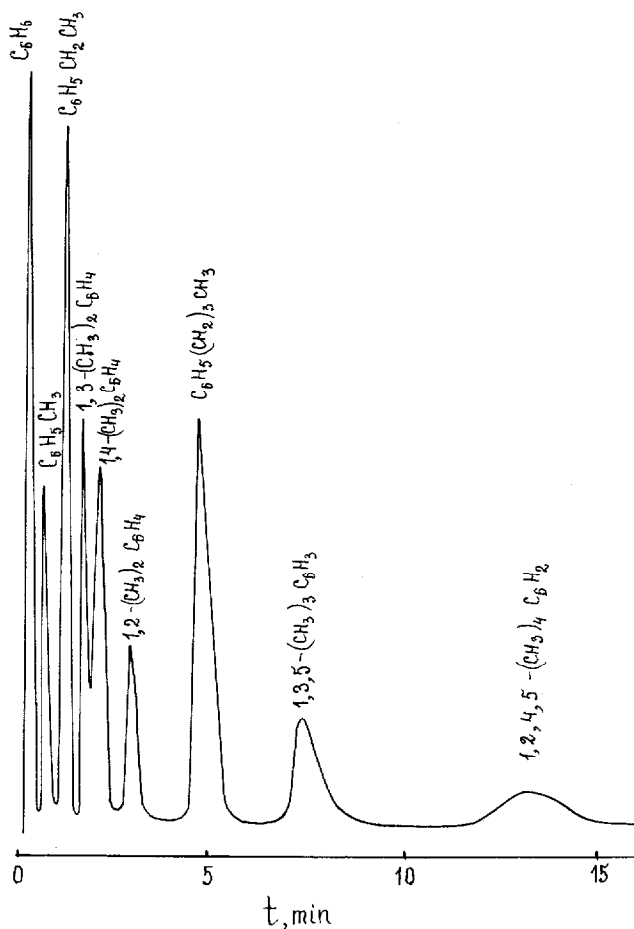


Fig. 5. (a) Separation of *n*-hydrocarbons on GTB modified with dibenzo-18-crown-6; 50 cm \times 1.5 mm column, carrier-gas (helium) flow-rate 15 ml/min. (b) Separation of 1,2-dimethylnorbornane (1 = *endo*; 2 = *exo*) on GTB modified with dibenzo-18-crown-6 at 48°C; other conditions as in (a). (c) Separation of 1,2-dimethylnorbornane on GTB at 140°C; 100 cm \times 4 mm column, carrier-gas (helium) flow-rate 30 ml/min.

TABLE V

RELATIVE RETENTION VOLUMES, RELATIVE TO ISOCTANE, $V_{m,1}/V_{m,1}(\text{i-C}_8\text{H}_{18})$

Adsorbate	GTB	Dibenzo-18-crown-6	Dinitrodibenzo-18-crown-6
<i>n</i> -Nonane	4.3	4.5	2.2
<i>n</i> -Decane	16.3	7.0	4.7
<i>m</i> -Xylene	1.5	2.7	2.8
<i>n</i> -Heptanol	1.6	2.3	3.3
Phenol	0.3	0.9	3.0
Aniline	0.4	0.5	1.9

Fig. 6. Separation of aromatic hydrocarbons on carbochrome modified with dibenzo-18-crown-6; 1 m \times 1.2 mm column, carrier-gas (helium) flow-rate 16 ml/min.

properties of the modified adsorbents, the retention volumes (Table III) were determined for different adsorbates at five to ten temperatures on a small (zero) sample. The differential molar heats of adsorption were calculated from the $\log V_{m,1}$ vs. $1/T$ dependences. Table IV compares the specific retention volumes and heats of adsorption for some adsorbates on the unmodified and the modified carbochrome: the order of retention of these substances is the same. However, the modification of the carbochrome surface with dibenzo-18-crown-6 resulted in a decrease in the specific retention volumes and adsorption heats for all the substances investigated. As in the case of GTB modification with porphyrins, this is caused by a decrease in the number of adsorption centres and in the dispersive interaction energy.

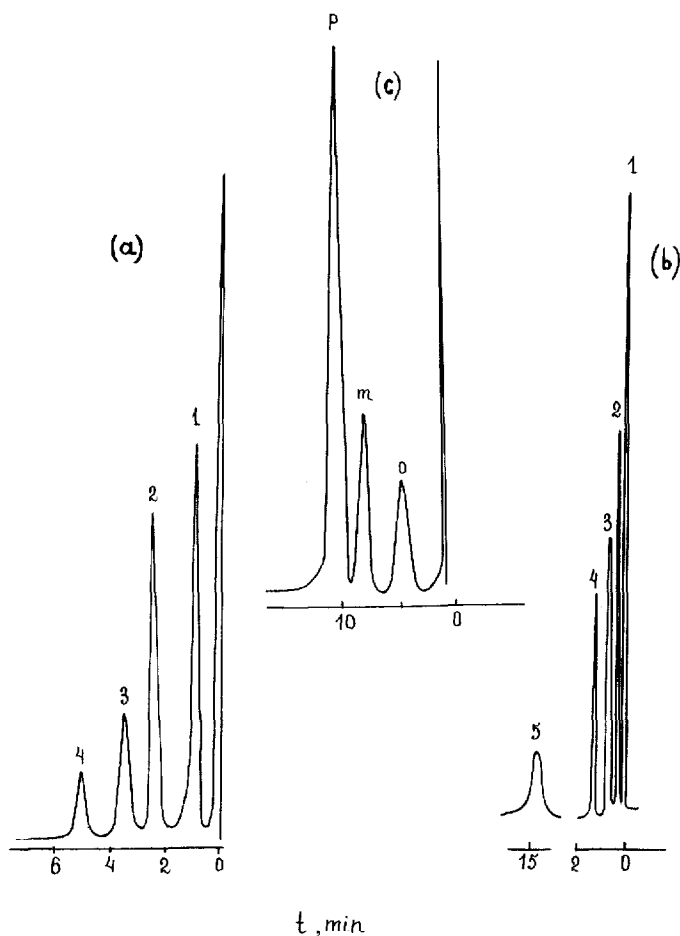


Fig. 7. Separations of chlorine-containing compounds (1 = α -HCH; 2 = γ -HCH; 3 = aldrin; 4 = heptachlor; 5 = DDE) (a) on carbochrome at 260°C, (b) on carbochrome modified with dibenzo-18-crown-6 at 200°C; 100 cm \times 1.2 mm column, carrier-gas (helium) flow-rate 14 ml/min. (c) Separation of isomers of chloronitrobenzene (*o*-; *m*-; and *p*-) on carbochrome modified with dibenzo-18-crown-6 at 80°C; 40 cm \times 1 mm column, carrier-gas (helium) flow-rate 20 ml/min.

Decreased retention makes it possible to perform chromatographic analysis at lower temperatures and within shorter periods of time (Figs. 5 and 6), which is very important in the case of chlorine-containing pesticides (Fig. 7), many of which are thermally unstable.

At the same time, carbochrome modification with dibenzo-18-crown-6 resulted in increased selectivity, especially with respect to substances capable of specific interaction with the modifier molecules (halogen and nitro compounds). On the non-specific carbochrome surface the values of the differential heat of adsorption, $-\Delta u_1$ for α - and γ -hexachlorocyclohexane (HCH) are the same, whereas on modified carbochrome the value for γ -HCH is 1.5 kcal/mol higher than for α -HCH. The incorporation of two nitro groups in the dibenzo-18-crown-6 molecule increases the selectivity with respect to substances with an excessive electron density (aromatic hydrocarbons, alcohols, anilines), as is seen from Table V where the relative retention volumes on the unmodified and the modified carbochrome are compared.

The results obtained have been used to find the optimum conditions for concentrating organochlorine compounds from the atmosphere^{1,2}.

REFERENCES

- 1 A. V. Kiselev and Ya. I. Yashin, *Adsorption Gas and Liquid Chromatography* (in Russian), Khimiya, Moscow, 1979, p. 287.
- 2 A. V. Kiselev, N. V. Kovaleva and Yu. S. Nikitin, *J. Chromatogr.*, 58 (1971) 19.
- 3 V. V. Vorontsov, N. V. Kovaleva, V. I. Rudas' and Yu. A. Eltekov, *Kolloidn. Zh.*, 35 (1973) 471.
- 4 V. V. Vorontsov, N. V. Kovaleva and V. I. Rudas', *Abstracts of Papers at All-Union Conference on Gas Chromatography, Tallin, 1969*, p. 48.
- 5 G. N. Bortnikov, I. A. Dolova, N. S. Vyazankin, N. V. Kovaleva, I. V. Rudas' and Ya. I. Yashin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1973) 577.
- 6 L. Yu. Gavrilina, A. V. Kiselev, N. V. Kovaleva, V. I. Zheivot and Ya. I. Yashin, *Chromatographia*, 10 (1977) 744.
- 7 L. Ya. Gavrilina, O. A. Yemelyanova, V. I. Zheivot, A. V. Kiselev and N. V. Kovaleva, *Kolloidn. Zh.*, 40 (1978) 639.
- 8 A. Berthold, N. V. Kovaleva, V. I. Zheivot, L. Ya. Gavrilina and V. M. Bubenshchikova, *Kolloidn. Zh.*, 44 (1982) 3.
- 9 J. Hille, M. Prochazka, L. Feltl, E. Smolkova-Keulemansova, A. V. Kiselev, N. V. Kovaleva and E. V. Zagorevskaya, *J. Chromatogr.*, 283 (1984) 77.
- 10 N. V. Kovaleva, A. V. Kiselev and E. V. Zagorevskaya, *Adv. Colloid Interface Sci.*, in press.
- 11 B. M. Berezin, *Coordination Compounds of Porphyrins and Phthalocyanine*, Nauka, Moscow, 1978.
- 12 E. V. Zagorevskaya, N. V. Ishenko, A. V. Kiselev and N. V. Kovaleva, *Adsorption Science and Technology*, in press.
- 13 A. Ono, *Analyst (London)*, 108 (1983) 1265.
- 14 T. B. Barmakova, A. V. Kiselev and N. V. Kovaleva, *Kolloidn. Zh.*, 36 (1974) 934.
- 15 R. M. Barrer, *J. Colloid Interface Sci.*, 21 (1966) 415.
- 16 A. V. Kiselev and Ya. I. Yashin, *Gas Adsorption Chromatography* (in Russian), Nauka, Moscow, 1967.