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PLASMA MODIFICATION OF ADSORBENTS OF DIFFERENT CHEMICAL NATURES WITH ELECTRON-DONOR MOLECULES

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SUMMARY

Adsorbent supports of different chemical natures, *i.e.*, thermal carbon black and silochrome (a macroporous silica adsorbent), have been modified with planar pyrene molecules which exhibit donor properties. The effect of exposure of the modified adsorbents to a high-frequency low-temperature plasma (HLP) on the retention parameters has been investigated by gas chromatography. It is shown that the HLP treatment modifies the surface properties of the adsorbents, which is manifested in an increased contribution of the electrostatic interaction to adsorption. The modified adsorbents have been applied to the separation of certain multicomponent mixtures.

INTRODUCTION

At present much attention is given to modification of inorganic adsorbents by adsorption of thin layers of organic molecules or macromolecules on their surfaces. This helps to extend the range of adsorbents featuring different surface chemistry and thus the range of compounds that can be analyzed by gas chromatography (GC)^{1,2}.

Macroporous silicas and carbon blacks are most commonly used as adsorbent supports^{1–5}. The retention on such supports when coated with small quantities of a modifying agent is determined by some combination of the properties of the support and those of the modifier. Modifiers having a planar structure and different chemical nature, including polynitro compounds and transition metal phthalocyanates^{4,5}, have been most widely used for modification of adsorbents.

The possibility of using low-temperature plasma for improving the properties of packing materials for chromatographic columns was investigated previously^{6–8}. It was shown that it is possible to control the sorbent selectivity, render the chromatographic bands more symmetric and increase the speed of analysis.

In this work we have used GC to investigate the surface properties of adsorbents prepared by modification of TG-10 thermal carbon black and silochrome with planar pyrene molecules, which are electron donors, and by exposure to a high-frequency low-temperature plasma.

TABLE I
METHOD OF PREPARATION OF SAMPLES

Sample No.	Preparation method
I	Non-graphitized thermal carbon black TG-10
II	TG-10 + 0.6 mg/m ² pyrene
III	Sample II exposed to HLP for 1 s (by the procedure of ref. 7)
IV	Silochrome C-80
V	Silochrome C-80 + 0.6 mg/m ² pyrene
VI	Sample V exposed to HLP for 30 min under steady conditions
VII	Sample V treated by HLP for 1 s

EXPERIMENTAL

The homogeneous macroporous silica adsorbent Silochrome C-80 (Stavropol Plant for Chemicals, Stavropol, U.S.S.R.) and non-graphitized thermal carbon black TG-10, specific surface areas of 105 and 10 m²/g respectively*, were used as adsorbent supports. The quantity of pyrene adsorbed from a solution in benzene was adjusted so as to form about a monolayer, as calculated from the van der Waals radii of the modifier molecules distributed over a plane surface, *e.g.*, ≈ 0.6 mg/m². Samples modified with pyrene and treated with a high-frequency low-temperature plasma (HLP) were also investigated^{6,7}.

In Table I the numerical notation and method of preparation of each sample are listed.

The chromatographic behaviour of molecules of groups A, B and D (according to Kiselev's classification^{1,9}), including hydrocarbons, halogen-, oxygen- and nitrogen-containing compounds, was studied. The retention volumes, V_g (per gram of adsorbent), and the relative retention volumes, $V_{rel} = V/V_{n\text{-alkane}}$, were determined on a Tsvet-102 chromatograph equipped with a flame ionization detector and a glass column (0.5–1.0 m \times 1–2 mm I.D.). Helium was used as the carrier gas. The adsorbent particle size was within 0.16–0.2 and 0.25–0.3 mm.

RESULTS AND DISCUSSION

Tables II and III give the retention volumes of the different organic molecules on all the adsorbents investigated.

For both kinds of investigated adsorbates, *i.e.*, those capable only of non-specific (dispersion) interactions or of specific, chiefly electrostatic, interactions, the retention volumes decreased on going from the unmodified to the pyrene-modified TG-10 samples. The lowest values were obtained on TG-10 carbon black coated with a monolayer of pyrene and treated with HLP (sample III, Tables I and II).

On pyrene-modified silochrome (sample V; Tables I and III) the retention volumes are almost the same for compounds incapable (saturated hydrocarbons) or

* The specific surface areas of the adsorbents were determined from the low-temperature adsorption of krypton or by thermal desorption of nitrogen.

TABLE II

RETENTION VOLUMES, V_g , AT 100°C ON UNMODIFIED AND MODIFIED THERMAL CARBON BLACK

Adsorbate	TG-10 sample		
	I	II	III
<i>n</i> -Hexane	40.6	9.2	4.6
<i>n</i> -Heptane	184.6	29.0	12.3
Cyclohexane	13.0	6.1	3.1
Adamantane	245.6	112.1	58.4
Benzene	28.3	4.6	2.7
Toluene	169.6	16.6	8.6
<i>n</i> -Butanol	37.6	21.3	8.6
Cyclohexanol	170.2	74.7	36.3
Methyl ethyl ketone	20.3	8.8	3.1
Cyclohexanone	154.6	69.9	30.4
Diisopropyl ester	40.5	10.5	4.9
Ethyl acetate	24.8	10.2	4.4
Pyridine	97.0	39.1	18.8

capable of only weak specific interactions (alkyl- and halogenobenzenes) with the hydroxyls on the adsorbent surface and the aromatic rings of pyrene. However, for polar compounds (acetone, ethanol, nitrobenzene), the adsorption of which on a surface containing locally concentrated positive or negative charges is accompanied by a strong electrostatic interaction, the V_g values were larger. The exposure of a pyrene monolayer on silochrome to HLP (samples VI, VII; Tables I, III) causes a further variation of adsorption properties, *viz.*, a decrease in the retention volumes of hydrocarbons and substituted benzenes in comparison with unmodified silochrome. It was found that the exposure conditions do not affect the adsorption prop-

TABLE III

RETENTION VOLUMES, V_g , AT 120°C ON UNMODIFIED AND MODIFIED SILOCHROME

Adsorbate	Silochrome sample			
	IV	V	VI	VII
<i>n</i> -Octane	25	23	18	18
<i>n</i> -Nonane	48	45	33	33
<i>n</i> -Decane	89	86	60	61
Adamantane	70	67	46	48
Toluene	29	27	24	24
Ethylbenzene	53	51	44	44
Chlorobenzene	29	29	23	24
Bromobenzene	44	47	35	36
Nitrobenzene	480	570	430	430
Acetonitrile	57	62	65	66
Acetone	137	149	158	159
Ethanol	59	75	76	77

TABLE IV

RELATIVE RETENTION VOLUMES, V_{rel} (WITH RESPECT TO *n*-HEXANE), AT 100°C ON UNMODIFIED AND MODIFIED THERMAL CARBON BLACK

Adsorbate	TG-10 samples		
	I	II	III
Toluene	4.2	1.9	1.9
Cyclohexanol	4.2	8.1	7.9
Cyclohexanone	3.8	7.3	6.6
Ethyl acetate	0.6	1.1	0.9
Pyridine	2.4	4.5	3.6

erties of pyrene-modified silochrome. The V_g values of the small-sized and strongly polar acetone, ethanol and acetonitrile are increased. Therefore, in order to estimate the adsorption properties, we compared the relative retention volumes, V_{rel} . The results for certain adsorbates are presented in Tables IV and VI. The data show that modification of the surface of thermal carbon black with pyrene reduces the V_{rel} of aromatic hydrocarbons. The lower V_{rel} values for the adsorption of aromatic hydrocarbons on samples II and III are probably due to the repulsion between the π -electrons of these compounds and of pyrene adsorbed on the carbon black surface.

The π -electron density on the pyrene-modified carbon black surface makes a considerable contribution to the adsorption of molecules containing various functional groups (ketones, esters, alcohols, nitrogen-containing compounds) and increases the relative retention volumes. Treatment of the pyrene monolayer on thermal carbon black with HLP has an insignificant effect on the relative retention volumes of most compounds investigated.

Table V gives the asymmetry factors for the peaks of a number of adsorbates obtained on the unmodified carbon black TG-10 and on samples modified with pyrene under different conditions. Coating of the surface of thermal carbon black samples with a pyrene monolayer sharply reduces the asymmetry of the chromatographic peaks of a number of compounds whose molecules have the ability to undergo specific interactions with the adsorbent surface. Exposure of modified carbon black to HLP further improves the symmetry of the chromatographic peaks.

TABLE V

ASYMMETRY FACTORS OF PEAKS OBTAINED ON UNMODIFIED AND MODIFIED CARBON BLACK AT 100°C

Adsorbate	TG-10 sample		
	I	II	III
<i>p</i> -Xylene	3.6	1.5	1.0
<i>n</i> -Butanol	5.0	2.0	1.0
Cyclohexanol	10.0	5.0	2.0
Cyclohexanone	6.0	3.0	1.0
Pyridine	5.0	3.5	3.5

TABLE VI

RELATIVE RETENTION VOLUMES, V_{rel} (WITH RESPECT TO *n*-NONANE), AT 120°C ON UNMODIFIED AND MODIFIED SILOCHROME

Adsorbate	Dipole moment, μ (D)	Silochrome sample			
		IV	V	VI	VII
<i>n</i> -Decane		1.88	1.90	1.88	1.88
Ethylbenzene	0.59	1.11	1.20	1.37	1.37
Nitrobenzene	4.20	10.2	12.6	13.2	13.2
Acetone	2.85	2.9	3.3	4.9	4.9
Ethanol	1.69	1.2	1.8	2.3	2.3

For silochrome the change of the V_{rel} patterns is quite different (Table VI) from those observed for modified TG-10. The V_{rel} values for *n*-alkanes are the same on all silochrome samples. Yet, as is seen from Table VI, HLP causes an increase in V_{rel} of polar adsorbents and hence in the contribution of specific interactions in comparison with both unmodified silochrome and sample V. This is most apparent

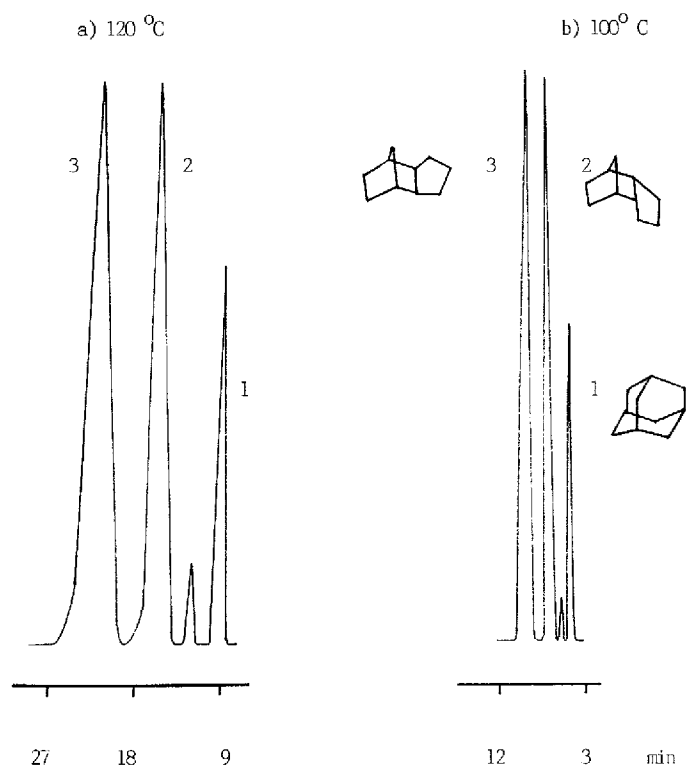


Fig. 1. Chromatograms of tricyclic hydrocarbons adsorbed on (a) unmodified TG-10 and (b) TG-10 modified with pyrene and treated by HLP (sample III, Table I). Peaks: 1 = adamantane; 2 = *endo*-trimethylenenorbornane; 3 = *exo*-trimethylenenorbornane. Column: 70 cm \times 0.2 cm.

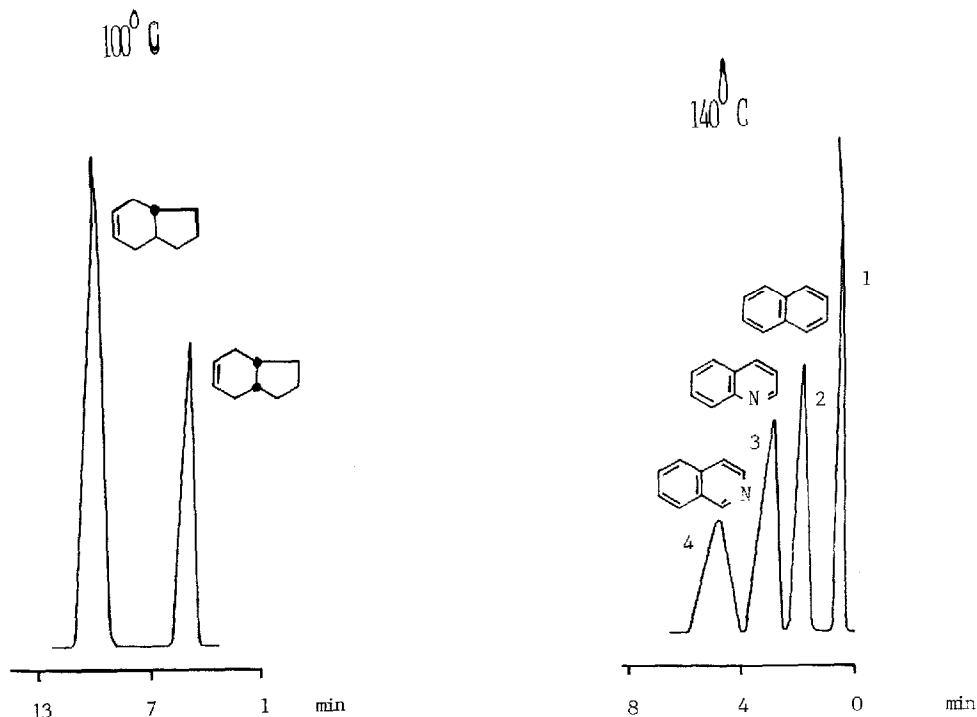


Fig. 2. Chromatogram of bicyclic hydrocarbons on sample III (Table I). Peaks: right, *cis*-bicyclononene; left, *trans*-bicyclononene. Column: 70 cm \times 0.2 cm.

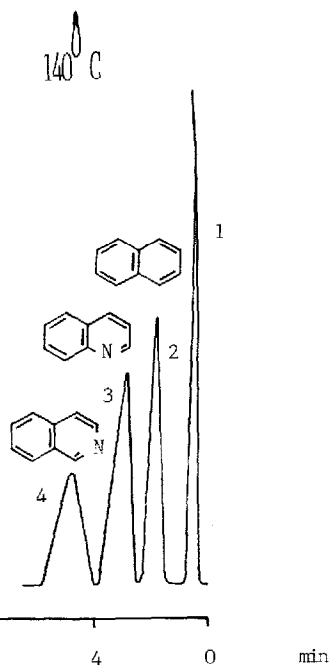


Fig. 3. Chromatogram of *n*-decane and aromatic compounds on sample III (Table I). Peaks: 1 = *n*-decane; 2 = naphthalene; 3 = quinoline; 4 = isoquinoline. Column: 80 cm \times 0.2 cm.

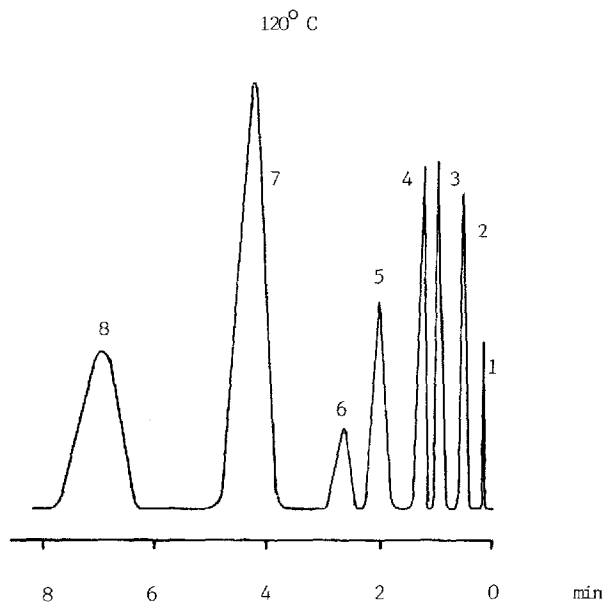


Fig. 4. Chromatogram of a mixture of organic solvents on pyrene-modified and plasma-treated silochrome (sample VI, Table I). Peaks: 1 = *n*-heptane; 2 = toluene; 3 = bromobenzene; 4 = acetonitrile; 5 = diethyl ether; 6 = acetone; 7 = ethyl acetate; 8 = nitrobenzene. Column: 60 cm \times 0.2 cm.

for molecules capable of forming hydrogen or donor-acceptor bonds (ethanol, nitrobenzene) with pyrene (the modifier). The longer retention of such compounds may be attributed to the additional specific interaction with the pyrene molecules available on the silochrome surface.

Thus, V_{rel} is largely dependent upon the type of adsorbent support.

Fig. 1 shows the separation of the isomers of adamantane, *endo*- and *exo*-trimethylenenorbornanes (TMNB) on unmodified TG-10 and TG-10 modified with a pyrene monolayer and then treated with HLP. Using sample III (Table I) for the separation of this mixture, it is possible to reduce the analysis time and use lower temperatures (the columns used in each case contained the same amount of adsorbent).

Owing to their different ring conjugations, the *cis*- and *trans*-isomers of bicyclononene and decalene are characterized by widely different geometric structures. The isomeric hydrocarbons with condensed rings can therefore be separated rapidly on TG-10 modified with pyrene and treated by HLP. Fig. 2 shows an example of the separation of the *cis*- and *trans*-forms of bicyclononene.

The retention of naphthalene and its nitrogen-containing analogues on sample III (Table I) depends on the dipole moment of these molecules and is different from that on graphitized thermal carbon black (GTCB)¹⁰. In contrast to GTCB, the treatment of pyrene-modified TG-10 with HLP to enhance the specific interaction with nitrogen-containing compounds allows its use for separation of isomeric quinoline and isoquinoline (Fig. 3).

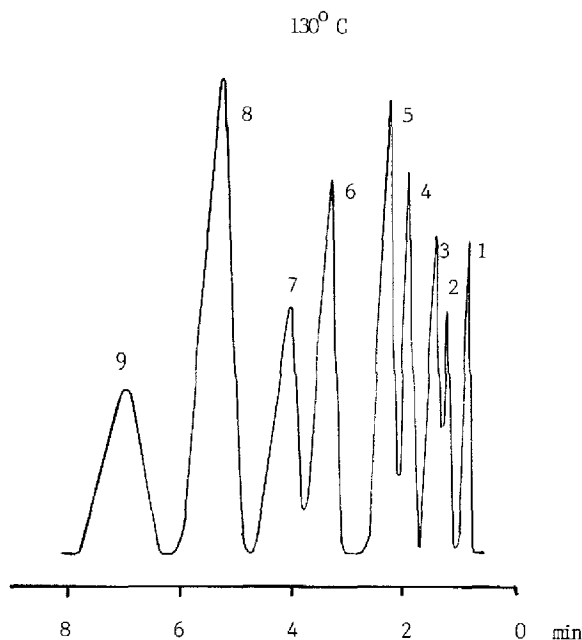


Fig. 5. Chromatogram of oxygen-containing compounds on sample VI (Table I). Peaks: 1 = diethyl ether; 2 = diisopropyl ether; 3 = di-*n*-propyl ether and ethyl acetate; 4 = methyl butyrate; 5 = *n*-propyl acetate; 6 = *sec.*-butyl acetate; 7 = di-*n*-butyl ether; 8 = *sec.*-butyl propionate; 9 = amyl acetate. Column: 100 cm \times 0.15 cm.

Fig. 4 gives an example of the separation of a mixture of organic solvents on silochrome modified with pyrene and treated by HLP (sample VI). The high efficiency of the separation of such pairs as acetone-*n*-heptane and toluene-nitrobenzene indicates that there is a strong electrostatic interaction between the adsorbate and adsorbent. The separation of a mixture of ethers and esters shown in Fig. 5 was obtained on silochrome modified with pyrene and treated by HLP.

From the specificity of the surface of silochrome samples modified by HLP and the good symmetry of the chromatographic peaks it may be concluded that the investigated adsorbents may be used in GC.

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