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## Carbon adsorbents in gas adsorption chromatography

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### ABSTRACT

The possibilities for the use of graphitized thermal carbon black (GTCB), especially in the separation of stereoisomers by gas chromatography, are surveyed. It is shown that the retention on GTCB, a monoatomic, highly homogeneous adsorbent, is defined mainly by the geometry of molecules. In spite of its great advantages, GTCB has two drawbacks: the carbon particles are not mechanically strong enough, and it has a very high adsorption potential, which leads to higher temperatures of separation in comparison with liquid stationary phases. These disadvantages can be removed by chemical and adsorption modifications. The influence of such modifications on adsorption and chromatographic properties has been systematically studied for carbon black and carbochrome.

In the case of adsorption modification, high-molecular-mass organic substances with various functional groups, and also polymers with flexible and rigid polymer links, were used as modifying agents. Of great interest are modifying agents with a flat structure of the molecules, such as phthalocyanines, etioporphyrins, crown ethers and their metallic complexes.

The use of chemical and adsorption modifications allows one to change the chemistry of the surface in a very wide range and to obtain selective adsorbents.

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### INTRODUCTION

Graphitized thermal carbon black (GTCB) is a monoatomic, highly homogeneous, non-specific adsorbent whose surface is formed by basal faces of graphite. Adsorption on such a surface depends mainly on the geometry of the molecules and their polarizability. The sequence of emergence of substances of different geometry and electron structure on such GTCBs differs greatly from those obtained on liquid stationary phases, where the separation of non-polar compounds depends on their boiling points. In the case of GTCB the order of elution is determined by the energy of non-specific dispersion forces. Saturated hydrocarbons are retained very strongly on GTCB, and their order of elution is determined by their boiling points and masses, but branched-chain compounds are retained to a lesser extent. The energy of dispersion interaction of branched molecules with the adsorbent is lower because of the greater distance of their links from a flat surface. In the series of unsaturated hydrocarbons, *cis*-isomers are retained less and *trans*-isomers are retained more strongly, in spite of their boiling points being lower [1,2]. Different isomers of hydrocarbons [3,4], dibutylbenzenes [5,6], isomers of dimethylcyclohexanes [7,8] and other isomers are well separated.

Similar effects occur with aromatic and cyclic hydrocarbons. The separation of methyl-substituted cyclohexanes is possible owing to the different number of links of the molecules that are in contact with the surface [2,7].

Cyclic and polycyclic compounds are of special interest. Such hydrocarbons can have many isomers, and can have sterane, triterpane, steroidal and alkaloidal structures. The separation of these hydrocarbons is difficult because of the similarity of their physico-chemical properties, but the difference in their structures effectuates their separation on GTCB [1,8-12] (Fig. 1).

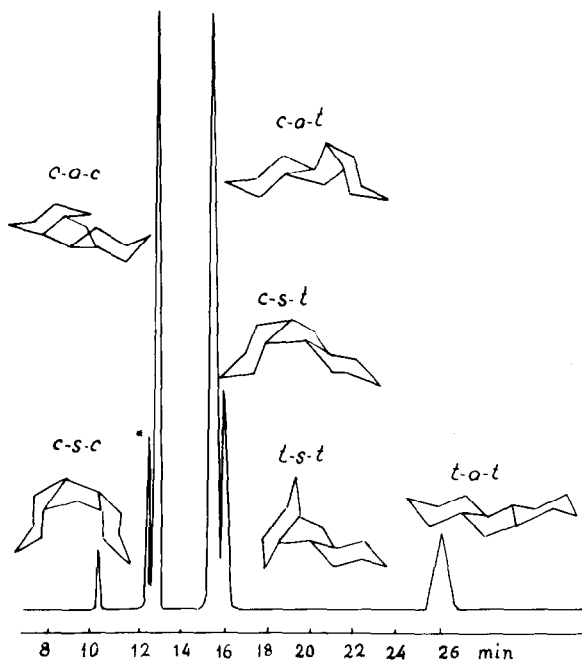


Fig. 1. Separation of perhydrofluorene isomers *cis-syn-cis* (c-s-c), *cis-anti-cis* (c-a-c), *cis-anti-trans* (c-a-t), *cis-syn-trans* (c-s-t), *trans-syn-trans* (t-s-t) and *trans-anti-trans* (t-a-t) on a capillary column with GTCB. Column, 4000 × 0.8 mm I.D., 250°C; hydrogen flow-rate, 8 cm<sup>3</sup>/min. Flame ionization detector.

The advantage of separations on carbon black is that it makes it possible to determine the structure of the investigated compounds and makes their identification easier [13].

With oxygen-containing heterocyclics there is also a direct dependence of retention on the geometry of the molecules. However, we must take into consideration the lower polarizability of oxygen atoms in comparison with CH and CH<sub>2</sub> groups. In a mixture consisting of ethers such as tetrahydrofuran, dioxane, tetrahydropyran, 7-oxybicyclo [2.2.1] heptane and epoxycyclohexane, the order of elution of dioxane and tetrahydropyran is determined by the greater polarizability of the latter, and that of the last two compounds by their geometry. With bicyclic oxygen-containing compounds with one phenyl ring one observes the same sequence of emergence [14,15].

Oxygen diminishes the overall polarizability of the molecule whereas nitrogen increases it, leading to an increase in retention on GTCB. Hence with six-membered

rings, pyridine is retained more strongly than benzene, and pyridazine, containing two nitrogen atoms in the 1,2-position even more, which is connected with the increase in the polarizability of these molecules with increasing number of nitrogen atoms. However, on going from pyridine to pyrimidine, which has two nitrogen atoms in *meta*-positions, and pyridazine, which has two nitrogen atoms in *para*-positions, there is a distinct decrease in retention in comparison with pyridine. Three nitrogen atoms in the molecule of *s*-triazine lead again to a decrease in retention, which is even lower than that of cyclohexane. The same phenomenon is observed with bicyclic six-membered heterocyclics containing nitrogen atoms [16–18].

These examples show us that the great sensitivity of GTCB to the geometry of the molecules makes it a perfect adsorbent for analytical purposes when a mixture to be separated consists of isomers with similar physical properties but different geometric structures. However, in spite of the great advantages of GTCB over liquid stationary phases in the separation of isomers, it has two drawbacks: the carbon particles are not mechanically strong enough, which prevents prolonged usage of GTCB in chromatographic columns, and it has a very high adsorption potential, which leads to higher temperatures of separation in comparison with liquid stationary phases. These disadvantages can be removed by chemical and adsorption modifications.

The mechanical stability can be enhanced in two ways: by covering the surface with small amounts of polymers, which makes the mechanical stability 2–3 times higher, or by modification of the carbon by pyrocarbon. The latter method gives much better results. Depending on the conditions of pyrolysis, one can obtain adsorbents that are close in their adsorption and chromatographic properties to the surface of GTCB, but have much greater mechanical stability of the grains (see Table I).

The main parameters that determine the structure of pyrocarbon are the temperature, the hydrocarbon and its concentration. In the temperature range 900–1400°C and at very low concentrations of hydrocarbon a dense pyrocarbon film with a very homogeneous structure is deposited on the surface of carbon. The density of the pyrocarbon formed at temperatures of *ca.* 1000°C and low pressure of the

TABLE I  
MECHANICAL STABILITY OF CARBON BEFORE AND AFTER MODIFICATION

Adsorbent	Mechanical stability (% of crushed particles)	<i>s</i> (m <sup>2</sup> /g)
GTCB	62	6.0
GTCB + 0.1% polyamide	32	5.8
GTCB + 0.1% polyoxadiazole	20	6.7
Carbochrom A (GTCB + pyrocarbon)	4.0	5.5
Carbochrom B (Initial thermal carbon black + pyrocarbon)	1.4	6.0
Carbochrom C (Channel carbon + pyrocarbon)	0.4	70.0
Silochrom	6.0	80.0

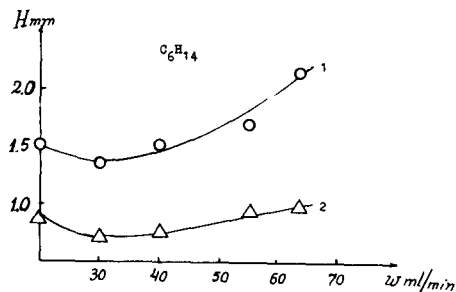


Fig. 2. Dependence of HETP on carrier gas flow-rate,  $w$ , for columns with (1) GTCB and (2) Carbochrome PAM-6.

hydrocarbon is fairly high ( $2\text{--}2.1\text{ g/cm}^3$ ) and approaches that of graphite ( $2.26\text{ g/cm}^3$ ) [19,20]. A high density of pyrocarbon provides a high mechanical stability of pyrocarbon coverages.

The technique for coating carbon particles with a layer of pyrocarbon was described previously [21]. Pyrolysis of benzene over the heated surface of the carbon black grains under chosen conditions made it possible to obtain mechanically stable adsorbents from GTCB carbochrome A, from initial thermal carbon black carbochrome B and from initial channel carbon black carbochrome C [22].

A high mechanical stability of carbochrome grains provides a high efficiency of separation in comparison with GTCB. This can be seen from Fig. 2, where the dependence of the HETP on the carrier gas velocity for two samples, the initial carbon and carbochrome, is given. The surface of carbochrome is less homogeneous than that of GTCB, which can be seen from the adsorption isotherm of krypton at low temperature (Fig. 3). The adsorption isotherm on GTCB has a substantial vertical

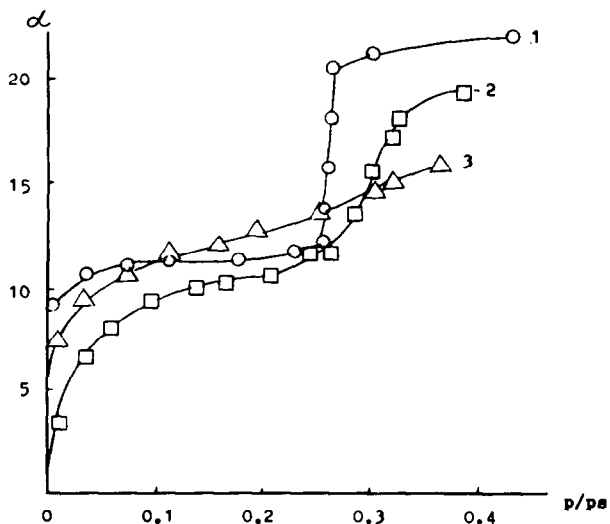


Fig. 3. Adsorption isotherms of Kr at  $-195^\circ\text{C}$  on (1) GTCB, (2) Carbochrom A and (3) thermal carbon black.

part, showing the energetic homogeneity of the surface. On the adsorption isotherm of krypton on carbochrome this stage is not so pronounced, and is absent on the adsorption isotherm on the non-graphitized carbon black.

To obtain specific adsorbents of GTCB and carbochrome it is possible to modify them by grafting different functional groups to the surface of the adsorbents by chemical reactions. However, the methods of chemical modification are very time consuming and it is not always possible to obtain a homogeneous surface.

The chemical modification is carried out by oxidation and amination reactions and some others. By oxidation of carbon blacks it is possible to graft to the surface different oxygen-containing groups. The intensity and velocity of oxidation depend on the extent of homogeneity of the structure. The greater the homogeneity of the structure, the more difficult is the process of oxidation [23]. The atoms of carbon placed at the corners and faces of crystallites in locations with high energetic potential are oxidized first. The oxidation process can be brought about by any oxidizing agents in a gaseous or liquid medium [23–25]. To obtain adsorbents for gas chromatography it is important to oxidize only the surface, without creating porosity. Oxidation by different agents in liquid medium at room temperature allows this. GTCB and carbochrome obtained from thermal carbon black TG-10 with a specific surface area of  $6 \text{ m}^2/\text{g}$  were oxidized with a mixture of concentrated sulphuric and nitric acids at room temperature. Hydroxyl, carbonyl and carboxyl groups were formed on the surface. The surface of carbochrome was oxidized more strongly, which is connected with its being less homogeneous.

As can be seen from Table II, the retention volumes and heats of adsorption of normal hydrocarbons on initial and oxidized carbochrome are similar. For molecules with active groups that interact with the functional groups of the surface these retention characteristics on oxidized carbon black increased markedly.

The grafting of amino groups to the surface of GTCB and carbochrome was done by the reaction of hydroxylamine with carbonyl groups, formed by the oxidation of the carbon black. The next step was the hydrogenation of the oxime obtained to an amino group. The carboxyl and hydroxyl groups of the surface were also reduced.

TABLE II

RETENTION VOLUMES,  $V_A$ , AT  $100^\circ\text{C}$  AND HEATS OF ADSORPTION,  $q_v$ , OF INITIAL AND OXIDIZED CARBOCHROM

Adsorbate	$V_A$ at $100^\circ\text{C}$ ( $\text{ml}/\text{m}^2$ )		$q_v$ (kcal/mol)	
	Initial	Oxidized	Initial	Oxidized
$n\text{-C}_5\text{H}_{12}$	0.74	0.7	8.7	8.9
$n\text{-C}_6\text{H}_{14}$	3.1	3.5	10.6	10.4
$n\text{-C}_7\text{H}_{16}$	12.0	15.4	12.5	11.9
$\text{C}_6\text{H}_6$	1.7	4.9	9.8	—
$\text{CH}_3\text{CN}$	0.1	1.2	7.6	15.0
$\text{CH}_3\text{NO}_2$	0.12	1.4	7.9	8.5
$\text{CH}_3\text{COOC}_2\text{H}_5$	1.02	5.7	10.1	11.6
$(\text{C}_2\text{H}_5)_2\text{O}$	0.46	5.0	8.7	14.3
$(\text{CH}_3)_2\text{CO}$	0.29	4.1	8.6	13.2
$\text{CH}_3\text{OH}$	0.06	7.0	5.8	8.6

Such grafting of amino groups led to a high adsorption capacity and an increase in the retention volumes of *n*-alkanols, phenols and especially lower fatty acids (Table III). Oxidized and aminated carbochromes and GTCB can be used as adsorbents for gas chromatography. The surface of the adsorbents obtained remains homogeneous. Oxidized carbon blacks are selective towards the separation of unsaturated hydrocarbons.

TABLE III  
SPECIFIC RETENTION VOLUMES OF ADSORBATES ON INITIAL AND AMINATED CARBOCHROM

Adsorbate	$V_A$ (ml/g)	
	Initial	Aminated
<i>n</i> -Hexane	3.78	3.71
Phenol	10.9	16.2
<i>n</i> -Hexanol	20.4	29.2
Acetic acid	0.96	14.0

#### ADSORPTION MODIFICATION OF CARBON BLACKS AND CARBOCHROMES

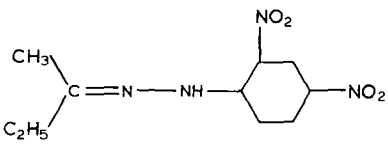
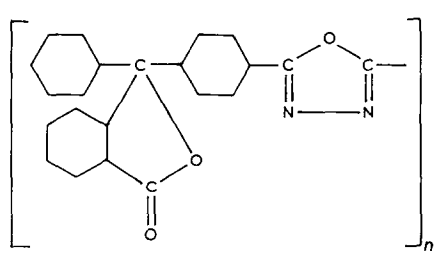
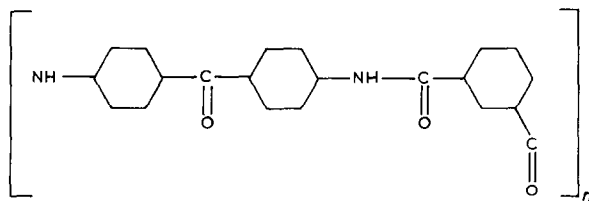
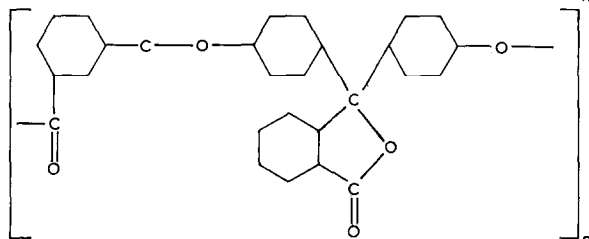
Adsorption modification of GTCB and carbochromes has been widely used to obtain adsorbents with a changed surface chemistry. This can be done when the modifying substances are deposited in amounts not exceeding a dense monolayer. These substances are usually high boiling or polymeric, and they are firmly retained on the GTCB surface, changing its chemical nature and, in many instances, reducing the interaction energy, without markedly changing the surface geometry. In this way it is possible to obtain adsorbents of different types, according to the classification of Kiselev, which are selective towards different classes of organic compounds.

The adsorption modification of carbon blacks by high-molecular-weight substances leads to a decrease in the energy of the interaction between the molecule and the GTCB, owing to the decrease in the concentration of force centres on the surface. This permits gas chromatographic separations of investigated substances at lower temperatures and in a shorter time. In addition, such modification increases the mechanical stability of carbon [26,27]. The most promising approach is modification with small amounts of modification agents not exceeding a monolayer [28]. In this case the molecules of modifying agents are in a strong adsorption field on the carbon surface and are held very strongly. They have a low volatility from the surface of the adsorbent, much lower than that from the bulk phase.

As modifying agents substances with different structures and natures have been used, as can be seen from Table IV.

The investigation of the adsorption properties of graphitized carbon blacks modified by different amounts of modifying agents shows that more significant changes in retention volumes occur in the region of very low surface coverage by the molecules of the modifier until the formation of a monolayer. At surface coverages

TABLE IV  
MODIFYING SUBSTANCES

Modifier	Structure
Apiezon L	Mixture of high-molecular-mass hydrocarbons
2,4-Dinitrophenylhydrazone of methyl ethyl ketone (2,4-DNPH MEK)	
PEG	$\text{OH}-\text{CH}_2-\left[\text{CH}_2-\text{O}-\text{CH}_2\right]_n-\text{CH}_2\text{OH}$
Poly-1,3,4-oxadiazole (PODA) ( $M_r = 60\ 000$ )	
Polyamide (PAM) ( $M_r = 55\ 000$ )	
Polyarylate $\Phi$ -I ( $M_r = 30\ 000$ )	

exceeding a monolayer the retention volumes of all substances change only slightly. In this case we have the version of gas-liquid chromatography. The inflection point on the curve of the dependence of retention volumes on the amount of modifier applied to GTCB corresponds to the monolayer (Fig. 4). The monolayer capacity can also be estimated from the adsorption isotherm from a solution of the modifying agent on the adsorbent support and also calculated from the Van der Waals dimensions of molecules with a flat orientation on the surface.

The comparison of these methods allows one to draw conclusions about the

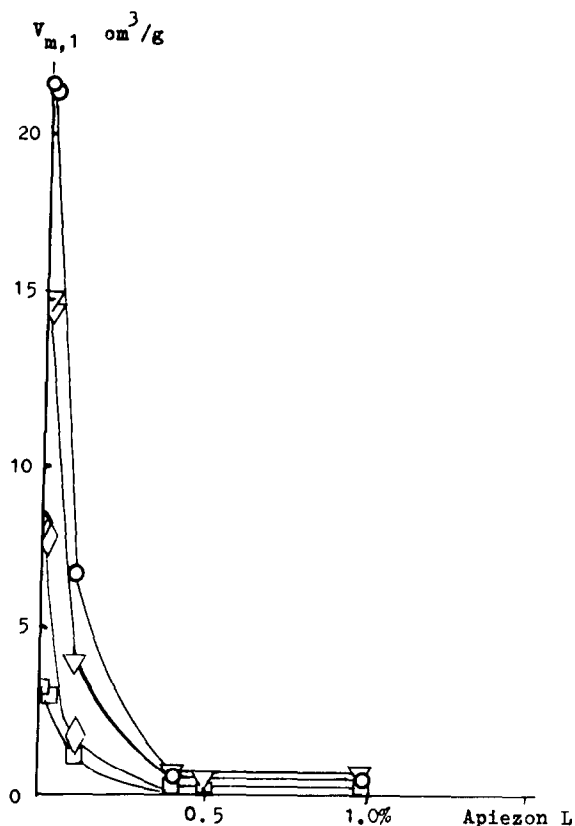


Fig. 4. Dependence of retention volumes of ( $\circ$ ) *n*-hexane, ( $\Delta$ ) benzene, ( $\square$ ) diethyl ether and ( $\diamond$ ) *n*-butanol on the amount of Apiezon L on GTCB.

orientation of the molecules of the modifier on the surface and their packing and to explain the specificity of modified adsorbents [28]. With modification by poly(ethyleneglycol) having a molecular mass ( $M_r$ ) of 300 (PEG-300) the values of the monolayer capacity,  $\alpha_m$ , obtained by these methods are in good agreement. The values of the monolayer capacity for modification with PEG-15000 obtained from the experimental data are double those calculated from the Van der Waals dimensions of the molecules (Table V). The molecules of polymers with a high molecular mass do not straighten completely at the surface of carbon black, and are adsorbed like globules. It is especially characteristic for rigid-chain polymers, such as polyarylate  $\Phi$ -1, poly-1,3,4-oxadiazole ( $M_r = 60\,000$ ) and polyamide ( $M_r = 55\,000$ ), used for the modification of acetylene carbon black.

Fig. 5 shows the dependences of the retention volumes of different adsorbates on the amount of these polymers applied to the surface of acetylene carbon black. The retention volumes of normal hydrocarbons decrease with increase in the amount of polyoxadiazole and polyarylate. This is related to the relaxation of the dispersion potential because one part of the surface is covered with polymers. The retention



TABLE V

CAPACITY VALUES OF DENSE MONOLAYERS OF PEG ON THE SURFACE OF GRAPHITIZED CHANNEL CARBON BLACK ( $\alpha_m$ , mg/m<sup>2</sup>)

Modifying agent	Calculated from Van der Waals dimensions of macromolecules	Determined by means of adsorption isotherms from solution	Determined from gas chromatographic data
PEG-300	0.44	0.43	0.42
PEG-3000	0.44	0.60	0.57
PEG-15000	0.44	0.74	0.73

volumes of benzene and diethyl ether also decrease but to a lesser extent. This is related to the fact that two concurrent phenomena are in operation: the lowering of the dispersion potential and the appearance of specific interactions with the functional groups of the polymers. With low-molecular-mass alcohols, nitromethane and acetonitrile, the retention volumes increase with increasing amount of polymer on the carbon surface. However, on these curves we do not observe a distinct bending for all adsorbates with the same coverage of carbon by the modifying agents. It is seen that even at 0.9 mg/m<sup>2</sup> of polymer on the surface of carbon a dense monolayer is not obtained. Such a character of the dependence of retention volumes for all the investigated adsorbates is observed only when 2% of polyoxadiazole covers the

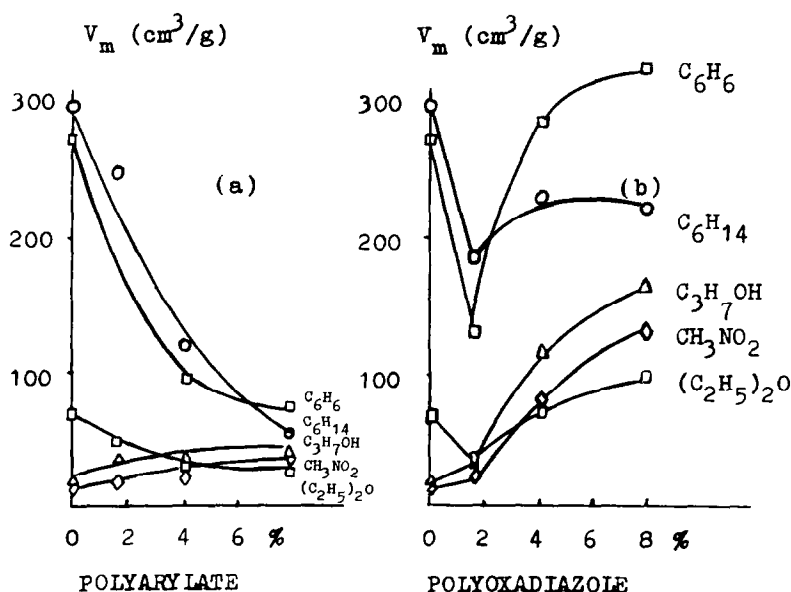


Fig. 5. Dependence of retention volumes of different adsorbates on the amount of polymers applied to the surface of acetylene carbon black: (a) polyarylate  $\phi$ -1 and (b) polyoxadiazole at 100°C.

surface. After this, a sharp increase in retention volumes takes place both for substances which are able to undergo specific interactions with the molecules of polyoxadiazole and also for hydrocarbons as well. This shows that at such a concentration of the polymer supermolecular structures are formed where the adsorbed molecules penetrate as if into pores.

In Table VI adsorption properties of acetylene carbon modified with equal amounts of these polymers are compared, and also for polymers with a flexible chain and high-molecular-mass organic substances. As can be seen, the retention volumes decrease considerably on samples of carbon modified with flat molecules of high-molecular-mass organic substances [26] and flexible polymers [28].

TABLE VI  
SPECIFIC RETENTION VOLUMES OF SOME ADSORBATES ON INITIAL AND MODIFIED ACETYLENE CARBON

Adsorbent	$V_m$ (cm <sup>3</sup> /g)				
	C <sub>5</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>14</sub>	C <sub>6</sub> H <sub>6</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	C <sub>3</sub> H <sub>7</sub> OH
Initial acetylene carbon	82.0	301.0	267.4	66.3	20.2
Carbon + Apiezon	6.0	15.2	14.1	5.0	5.7
Carbon + 2,4-DNPH MEK	5.1	13.5	14.1	5.1	7.6
Carbon + PEG 15000	2.5	5.6	9.2	2.8	8.1
Carbon + $\phi$ -I 30000	37.2	121.5	95.0	30.1	31.6
Carbon + PODA 60000	94.0	—	—	73.3	117.9
Carbon + PAM	38.5	132.7	103.8	—	71.1

By modification of carbon black with polymers with a rigid structure of the polymer chain,  $V_m$  is not decreased significantly even for *n*-alkanes. This shows that these polymers do not straighten out on the surface of carbon black, but form globular structures. The penetration of molecules into these globules leads to an increase in heats of adsorption.

We can judge the homogeneity of the surface not only from the form of chromatographic peaks, but also from the form of the adsorption isotherms and the shape of the relationship between heats of adsorption and surface coverage. This is shown in Fig. 6.

Polysiloxane polymers, having a high flexibility of unbranched chains, solubility in almost all solvents and high thermal stability, have been used for adsorption modification of industrial acetylene carbon to obtain cheap adsorbents with properties similar to those of GTCB. Preadsorption of such polymers as dense monolayers or parts of a monolayer lowers the adsorption potential of carbon and increases the homogeneity of the surface and mechanical strength, which leads to a greater efficiency of gas chromatographic columns.

Di Corcia and co-workers [29–41] used different substances for modification of the surface of GTCB: squalene and glycerine [32], tetraethylenepentamine and polyethylenimine [29,34], a mixture of polyfluorophenyl and benzophenone [30]. Dexil

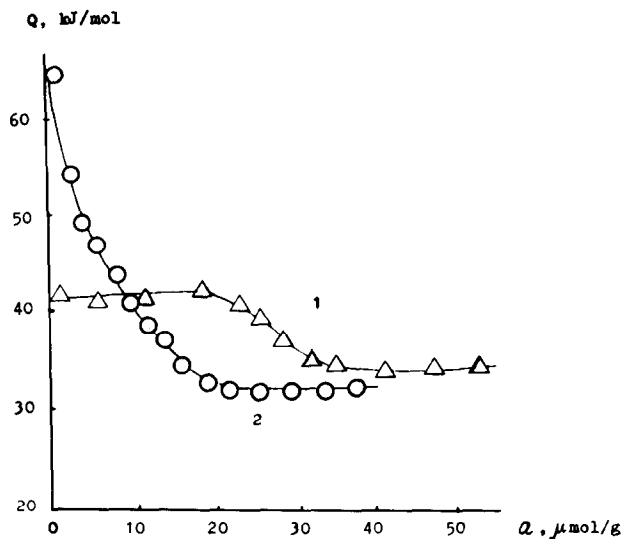


Fig. 6. Dependence of isosteric heats of adsorption of benzene on the amount adsorbed, (1) on GTCB, (2) on GTCB, modified by 0.1% PAM.

300 [31], poly(ethylene glycol) with addition of acids or alkali according to the acidity of the compounds being analysed [35–37], picric acid [38,39], 1,3,5-trinitrobenzene [40] and tetranitrofluorene [41]. They showed the great possibilities of modified GTCB in analytical applications. The use of these adsorbents allowed the determination of acids and amines in dilute aqueous solutions, and the separation of heterocyclic compounds, aliphatic saturated and unsaturated hydrocarbons, aromatic hydrocarbons and also aggressive gases. It was possible to use these adsorbents for the environmental analyses, of products of oil cracking and also any food products such as milk, tea aroma, citric oil and others [42].

Carbon blacks covered with thin layers of substances of low volatility, owing to the weakening of the molecular interactions, could be used for the separation of steroids and barbiturates [43]. Bruner *et al.* [44] successfully used particles of carbon modified with small amounts of liquid phases for mini-columns for gas chromatography and for semi-preparative separations of isotopic mixtures.

#### MODIFICATION WITH FLAT MOLECULES

The modification of the surface with flat molecules of crystals is of great interest. Crystalline substances were first used as stationary phases by Scott [45], who used benzophenone deposited on Chromosorb. Adsorption modification of GTCB with different organic substances was used by Guiochon and co-workers [46–52]. As modifying agents they used phthalocyanines and their metal complexes, which have great chemical and thermal stability. They showed that the selectivity of the adsorbents depends on the complex-forming metal. Thus, on copper phthalocyanine aromatic compounds are well separated, on nickel phthalocyanine amines and on zinc

phthalocyanine ethers and ketones. Phthalocyanine itself and phthalocyanines of heavy metals do not dissolve in any solvents, which is why Guiochon and co-workers used not adsorption from solution, but deposition, using soluble lithium phthalocyanine. The result was the formation of bulk crystals on the surface. The amount of these substances on the surface of GTCB exceeded significantly (more than 10-fold) the capacity of the monolayer.

Kiselev and co-workers [26,53–55] used soluble modifying agents, *viz.*, sodium salts of the sulphonic acid of cobalt phthalocyanine,  $\text{CoPht}(\text{SO}_3\text{Na})$ , and of copper phthalocyanine,  $\text{CuPht}(\text{SO}_3\text{Na})_4$ , with different contents of sulphonate groups. Such a modification gave dense monolayers held by adsorption forces of carbon. The monolayer capacity was determined by the three methods described. In all instances values of 0.7–0.8 mg/m<sup>2</sup> were obtained. The retention volumes of *n*-alkanes on dense monolayers of sulphonic acids of copper and cobalt phthalocyanines are lower on carbochrome. However, the retentions of ethers, ketones and especially alcohols increase markedly on modified adsorbents owing to the specific molecular interaction of these molecules with the molecules of the modifier.

The specificity of the modified carbochrome is determined mainly by the presence of  $\text{NaSO}_3$  groups in the molecule, in which the positive charge is situated in the small Na cations and the negative is distributed in the anions  $\text{SO}_3$ . The complex-forming metal does not play any part [54]. The additional specific interaction with unsaturated and aromatic hydrocarbons by maintaining high enough values of the energy of non-specific interaction makes them especially selective for the separation of saturated, unsaturated, cyclic and aromatic hydrocarbons. GTCB modified with sodium salts of sulphonated cobalt phthalocyanine was used as a specific adsorbent in the gas chromatography of the products of the catalytic conversion of hydrocarbons [54].

The modifying agents used also include derivatives of porphyrins such as etioporphyrin and its complexes with Cu, Ni and VO [55–57]. Porphyrins are structural analogues of phthalocyanine. Just like phthalocyanines they have a planar structure and high thermal stability. They are readily soluble in organic solvents owing to their low crystal lattice energy. Adsorbents covered with a monolayer of porphyrin derivatives provide a lowering of heats of adsorption owing to the decrease in the concentration of force centres at the surface and the appearance of specific interactions with unsaturated, aromatic and oxygen-containing compounds.

The molecules of porphyrins and their derivatives have a complicated electronic structure and a complex contour system of conjugation. By formation of inter-complex compounds, the complex-forming metal influences all properties of such molecules [58]. Therefore, the adsorption properties of monolayers of etioporphyrin derivatives and phthalocyanines depend on the complex-forming metal. Most specific are nickel and vanadyl etioporphyrins. The lowering of the energy of adsorption by modification of carbon black and carbochrome by etioporphyrins allows one to achieve separations on modified adsorbents at lower temperatures than on initial carbon. Carbon black modified by etioporphyrin and its metal complexes retain a flat structure of the surface and therefore these adsorbents can be used for the separation of structural isomers.

A monolayer of etioporphyrin deposited on GTCB is selective to the separation of halogen derivatives of hydrocarbons. A high selectivity of GTCB modified with

vanadyl etioporphyrin (VOEP) to oxygen-containing compounds allows the separation of cyclohexanol and cyclohexanone. These substances have similar molecular masses, similar molecular structures and are retained to the same extent on GTCB at all temperatures and elute in one peak.

For the separation of alcohols, GTCB modified by etioporphyrin and copper etioporphyrin are more selective. The VOEPs are less selective [56].

The modification of GTCB by tetra-*p*-methoxyphenylporphyrin (H<sub>2</sub>TMPP) made it possible to separate all three isomers of xylene, which is impossible on GTCB. By modification of GTCB by crown ethers (*e.g.*, dibenzo-18-crown-6), as with modification by etioporphyrins, the dispersion energy is decreased and the selectivity to polar compounds increases [57–59]. GTCB and carbochrome modified with dibenzo-18-crown-6 are especially selective to the separation of substances with acceptor properties, particularly halogenated hydrocarbons. The lowering of retention volumes and the energy of dispersion interaction leads to faster analyses at lower temperatures. This is especially important in the analysis of thermally unstable compounds such as DDT and DDE [59].

The use of chemical and adsorption modification makes it possible to change the chemistry of the surface in a very wide range and to obtain selective adsorbents.

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