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GAS CHROMATOGRAPHIC ANALYSIS OF ORGANIC COMPOUNDS ON NON-POLAR ADSORBENTS

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SUMMARY

The applicability of new non-polar adsorbents in gas chromatography has been investigated. Molybdenum and tungsten sulphides are characterized by a lamellar structure, which resembles the structure of graphite, and hence are expected to show chromatographic properties similar to those of graphitized thermal carbon black (GTCB). This assumption was verified chromatographically by comparing the properties of argon plasma-treated thermal carbon black (TCB) with the properties of MoS_2 and WS_2 and $MoSe_2$. The adsorption characteristics (relative retentions, heats of differential adsorption) were determined at low levels of adsorbent surface coating with reference compounds.

The results indicate that the treatment of TCB in a hydrogen-containing plasma (oxygen-free flow) results in lower retentions. The retention of *n*-alkanes by MoS_2 and WS_2 is higher than that of monoalkylbenzenes with the same number of carbon atoms. Di-*n*-butyl ether is adsorbed by MoS_2 and WS_2 more weakly than *n*-nonane, which indicates a homogenous sorbent surface. The adsorption of di-*n*-butyl ether on $MoSe_2$ is stronger than that of *n*-nonane, which indicates an non-homogeneous adsorbent surface.

The results made it possible to derive several practically applicable conclusions. MoS_2 and WS_2, for instance, can be used for analytical purposes at lower temperatures than thermal carbon black. The adsorbents under consideration are suitable for the separation of structural and geometrical isomers.

INTRODUCTION

The application of new adsorbents with different chemical natures can extend the possibilities of gas–solid chromatography (GSC). Non-polar adsorbents are promising for use in GSC as they can be used for the analysis of many classes of organic compounds and are especially selective for the separation of mixtures containing structural and geometrical isomers with similar physical and chemical properties[1,2].

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It was found in earlier studies[3–5] that modification of the surface of non-graphitized carbon black of different types results in the preparation of basically homogeneous non-specific adsorbents. The investigation of the adsorption properties of metal sulphides with a lamellar structure, similar to the structure of graphite, revealed that by synthesis of MoS_2 and WS_2 on an inert diatomic support it is possible to produce non-specific adsorbents[6].

This study is related to the above-mentioned considerations and deals with investigations of the surface properties of thermal carbon black (TCB) type TG-10, which was modified by various agents in a high-frequency plasma[7,8], and MoS_2, WS_2 and $MoSe_2$, which were produced synthetically by the method described in ref. 6, in view of their application as non-polar adsorbents in analytical GSC.

The adsorption characteristics [relative retention volumes (with respect to n-alkane), V_{rel}, and differential heats of adsorption] of *n*-alkanes, alkylbenzenes and oxygen-, halogen- and nitrogen-containing substances were determined by gas chromatographic methods at low levels of surface coating.

EXPERIMENTAL

The experiments were carried out using a Tsvet 102 chromatograph with a flame ionization detector. Helium and high-purity nitrogen were used as carrier gases. Glass columns with lengths from 0.3 to 1 m and inner diameters from 1.5 to 2.5 mm were applied.

Thermal non-graphitized carbon blacks have a non-homogeneous surface, which makes them unsuitable for GSC owing to broadening of the chromatographic peaks and the long retention times of the components of the mixture being separated.

The packing material, thermal carbon black type TG-10, with a specific surface area of 8 m^2/m, was pre-treated in a high-frequency, low-temperature plasma in argon (PAr) and hydrogen (PH_2) atmospheres.

RESULTS AND DISCUSSION

The relative retention volumes (with respect to *n*-hexane) of a number of adsorbates are given in Table I. The values of V_{rel} were measured at 273 K on samples of TCB.

The treatment of TG-10 in a high-frequency, low-temperature plasma in a hydrogen (oxygen-free) atmosphere results in a considerable decrease in the retention of oxygen-containing compounds, which react most vigorously to the chemical and geometrical irregularities of the adsorbent surface. This is accompanied by decreased V_{rel} of hydrocarbons and increased symmetry of the chromatographic peaks. Therefore, the most homogeneous and non-polar is the adsorbent produced by modifying TG-10 in a hydrogen plasma.

Samples of MoS_2, WS_2 and $MoSe_2$, prepared synthetically[6], were also investigated. Table II gives the values of V_{rel} (with respect to *n*-nonane) for some of the compounds on all sulphide and selenide adsorbents under study.

The observations of the $MoSe_2$ surface revealed that *n*-alkanes are adsorbed more strongly than mono-*n*-alkylbenzenes with the same number of carbon atoms in the molecule and that the V_{rel} of di-*n*-butyl ether is higher than that of *n*-nonane.

TABLE I

VALUES OF V_{rel} (WITH RESPECT TO *n*-HEXANE) AT 273 K

Adsorbate	*Untreated TG-10*	*Plasma-treated TG-10*	
		Argon (PAr)	*Hydrogen (PH_2)*
n-Heptane	4.55	3.88	4.17
Benzene	0.69	0.63	0.61
Toluene	4.17	3.12	3.42
n-Propanol	0.29	0.38	0.25
n-Butanol	0.93	1.21	0.84
Diisopropyl ether	0.99	1.01	0.97
Acetone	0.17	–	0.13
Acetonitrile	0.07	0.09	0.06

The non-homogeneous surface structure of $MoSe_2$ can be explained by the presence of oxygen on its surface and by the fact that a considerable number of the crystals are formed by lateral planes, incorporating both metallic and non-metallic atoms.

n-Alkanes are adsorbed on molybdenum and tungsten sulphides more strongly than the respective mono-*n*-alkylbenzenes (ethylbenzene, *n*-propylbenzene), and di-*n*-butyl ether is retained more weakly than *n*-nonane. Therefore, the presence of π-bonds in the substituted benzenes, the free electron pair and the dipole moments which are inherent to the ether molecules do not contribute noticeably to the adsorption of metal sulphides.

It is possible on the basis of the adsorption characteristics to draw the conclusion that hydrogen-treated TG-10 and the sulphides of molybdenum and tungsten possess homogeneous non-polar surfaces.

The differential heats of adsorption, q_1, of benzene and *n*-hexane were determined for TG-10-based samples with high homogeneity (Table III) and for MoS_2 and WS_2.

The molecules of *n*-hexane and benzene are similar in geometry and dimensions. As the value of q_1 for hexane is higher than that for benzene, it is possible to conclude that adsorption depends primarily on the smaller number of hydrogen

TABLE II

VALUES OF V_{rel} (WITH RESPECT TO *n*-NONANE) AT 393 K

Adsorbate	*Adsorbent*		
	$MoSe_2$	*WS_2*	*MoS_2*
n-Octane	0.31	0.31	0.31
Ethylbenzene	0.34	0.27	0.27
n-Nonane	1.00	1.00	1.00
n-Propylbenzene	0.94	0.75	0.75
Di-*n*-butyl ether	1.20	0.60	0.64
n-Butanol	–	0.30	0.60
Bromobenzene	–	0.36	0.33
Nitrobenzene	–	1.20	1.30

TABLE III

VALUES OF q_1 (kJ/mol)

Adsorbate	MoS_2	WS_2	*TG-10*		*GTCB*[1]
			Untreated	*Hydrogen-treated*	
n-Hexane	42	40	47	40	38
Benzene	39	37	40	38	36

atoms in the benzene molecule and not on the presence of π-bonds in the ring.

Similar results were also observed in the adsorption of hydrocarbons on graphitized TCB (GTCB) with a homogeneous flat non-polar surface (Table III)[1,2]. Therefore, hydrogen plasma-treated TCB adsorbents and also MoS_2 and WS_2 can be classified as adsorbents of the first type with non-polar properties (according to the classification of Kiselev and Yashin)[2].

The retention values, $V_{A,1}$ (equal to the Henry constants at adsorption equilibrium), of *n*-alkanes on the adsorbents under study and on GTCB were compared. As shown in Fig. 1, the values of $V_{A,1}$ for GTCB and TG-10 treated in a high-frequency, low-temperature plasma and hydrogen are nearly identical, and therefore can be considered to be also similar with respect to the nature of their surfaces. The values of $V_{A,1}$ for metal sulphides and identical adsorbates, as in the former instance, are considerably lower in comparison with GTCB. This means that MoS_2 and WS_2 can be used in analytical GSC at considerably lower temperatures than carbon blacks.

In order to ensure reproducibility of the chromatographic column, it is necessary to establish the thermal stability of the adsorbent. For both carbon black and

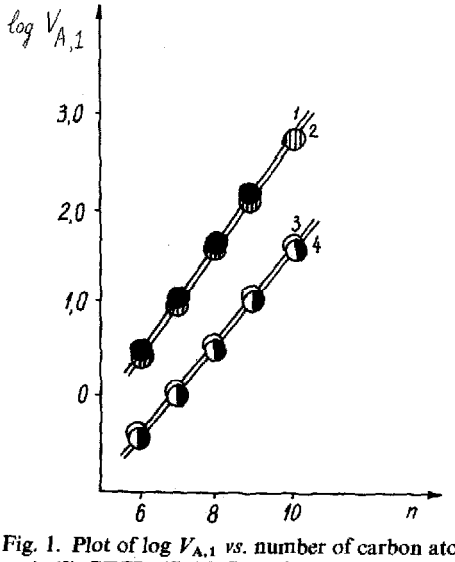

Fig. 1. Plot of log $V_{A,1}$ *vs.* number of carbon atoms in *n*-alkanes on (1) TG-10 (plasma treated in hydrogen), (2) GTCB, (3) MoS_2 and (4) WS_2. Temperature, 393 K.

metal sulphides the lower temperatures are unlimited, which is a major advantage in comparison with the liquid stationary phases used in gas–liquid chromatography.

The upper temperature limits for MoS_2, WS_2 and TG-10 (PH_2) were established by heating samples of these substances in nitrogen, helium and hydrogen (oxygen-free) atmospheres for 10 h at temperatures from 293 K to 573 K and at 623 K. Fig. 2 shows the results of the chromatographic measurements. It is apparent that synthetic MoS_2 and WS_2 preserve their surface properties when heated in a high-purity nitrogen stream at temperatures up to 473 K. At temperatures above 473 K the surface irregularities of the metal sulphide crystal begin to increase. Similar results were obtained after heating the samples in helium or hydrogen flows.

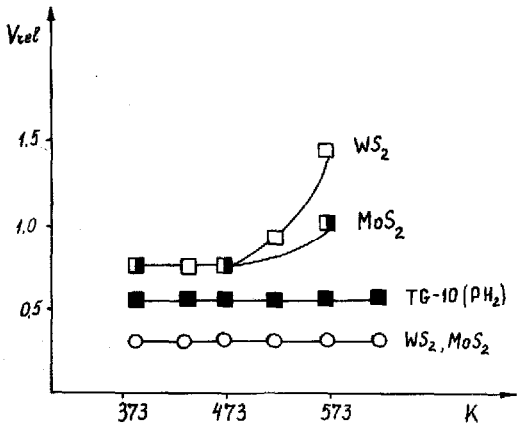

Fig. 2. Dependence of $V_{rel} = V_g/V_g(n\text{-}C_9H_{20})$ on the temperature of preliminary treatment of adsorbents in nitrogen. Temperature of analysis, 393 K.

The changes in the surface properties of metal sulphides that occur after heating in a gas stream can be explained by irreversible surface structural changes, the appearance of free position, cracks, microcavities and other imperfections with increased adsorption energy both on the external basal planes and on the lateral edges of the crystals.

No changes in the samples were established by differential thermal analysis and differential thermogravimetric methods or by X-ray analysis after the samples were heated to 673 K in a nitrogen stream. Therefore, the changes in the surface properties of metal sulphides after heating to 573 K can be observed by gas chromatographic means only.

In contrast to metal sulphide adsorbents, the packing material prepared by treatment of TG-10 in a hydrogen atmosphere is temperature resistant within the temperature range considered.

The non-polar adsorbents under discussion were used to separate mixtures of various classes of organic compounds. The chromatograms of mixtures of saturated and unsaturated hydrocarbons, containing primary, secondary and tertiary carbon atoms in their molecules, indicate that the first to appear from the TG-10 (PH_2) and WS_2 columns are the most branched molecules, lying on a flat surface, with the

smallest number of CH_2 groups (Fig. 3a and b). The geometric structure of the adsorbates also influences the separation of *cis*- and *trans*-alkene isomers. *cis*-2-Heptane, for instance, is retained more weakly than the corresponding *trans*-isomer, although the boiling point of the latter is lower (Fig. 3b).

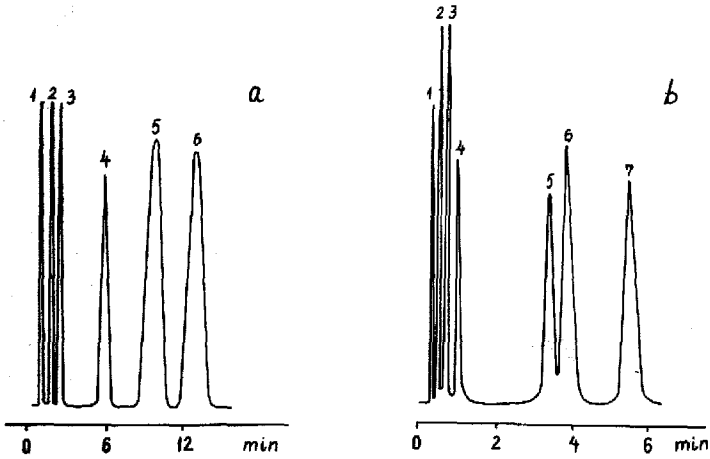

Fig. 3. Chromatogram of mixtures of hydrocarbons with different structures. (a) TG-10 (plasma treated in hydrogen). Peaks: 1 = *n*-pentane; 2 = 3-methylpentane; 3 = *n*-hexane; 4 = 2,2-dimethylhexane; 5 = 4-methylheptane; 6 = *n*-octane. Column, 70 × 0.15 cm I.D.; 363 K. (b) WS_2. Peaks: 1 = Neohexane; 2 = 2,3-dimethylbutane; 3 = 2-methylpentane; 4 = *n*-hexane; 5 = *cis*-heptene-2; 6 = *trans*-heptene-2; 7 = *n*-heptane. Column, 80 × 0.15 cm I.D.; 293 K.

The adsorption of halogen- and oxygen-containing substances on MoS_2 and WS_2 is most strongly influenced by the steric arrangement of the molecules on their surface and their polarizability. 2-Methyl-2-chloropropane, for instance, is retained more weakly than the flatter 2-methyl-3-chloropropane, and 2-methyl-3-chloropropane is eluted earlier than 1-chlorobutane, as all links within the last isomer are in contact with the adsorbent surface (Fig. 4a). The sensitivity of the retention time of MoS_2 to the molecular geometry made it possible to separate some isomers of pentyl alcohol (Fig. 4b).

The chromatograms of the products separated by hydration of naphthalene are shown in Fig. 5. For both TG-10 (PH_2) and MoS_2 packing materials, the *cis* isomer of decalin is eluted first; it is characterized by a less planar structure of the two isomers. The molecule of tetralin, with its more planar structure, is retained more strongly than decalin. The time and temperature of the analysis on MoS_2 are lower than on carbon black.

The high sensitivity of the retention parameters to the molecular structure in adsorption on non-polar adsorbents facilitated their application to the separation of isomeric polycyclic saturated hydrocarbons. Fig. 6 shows chromatograms of the complete separation of isomers such as adamantane and *endo*- and *exo*-trimethylenenorbornane (TMNB) on primary TG-10 and on TG-10 (PH_2). Adamantane, with a more compact structure of the molecule, is retained the weakest and is eluted first, followed by *endo*-TMNB, which has a larger number of contacts with the surface.

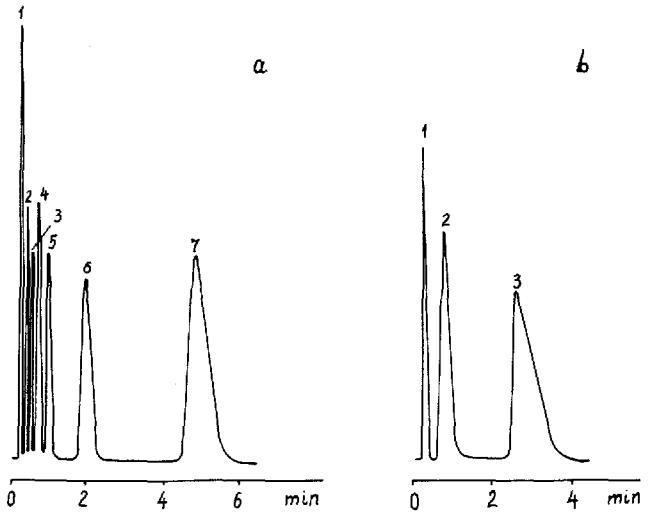

Fig. 4. Analysis of halogen- and oxygen-containing compounds. (a) WS_2 (293 K). Peaks: 1 = 2-methyl-2-chloropropane; 2 = 2-methyl-3-chloropropane; 3 = 1-chlorobutane; 4 = 2-methyl-3-bromopropane; 5 = 1-bromobutane; 6 = 1-chloro-3-bromopropane; 7 = 1,3-dibromopropane. Column, 80 × 0.15 cm I.D. (b) MoS_2 (393 K). Peaks: 1 = *tert.*-pentanol: *sec.*-pentanol(2); 3 = *n*-pentanol. Column, 100 × 0.2 cm I.D.

Finally, *exo*-TMNB, which has the most planar structure, is eluted. The chromatographic peaks of primary TG-10 are asymmetrically distributed and also the analysis time is considerably longer in comparison with the adsorbent that was pre-treated in a plasma.

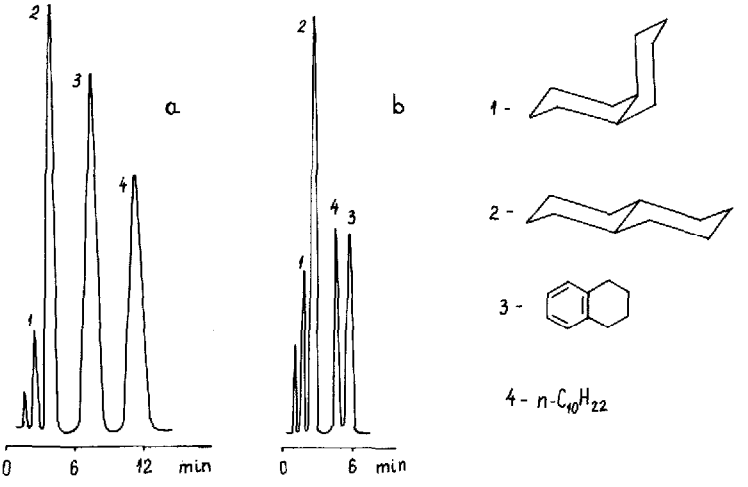

Fig. 5. Separation of *cis*-decalin (1), *trans*-decalin (2), tetralin (3) and *n*-decane (4) on (a) a TG-10 (plasma treated in hydrogen) column, 433 K (70 × 0.22 cm I.D.) and (b) an MoS_2 column, 403 K (100 × 0.23 cm I.D.).

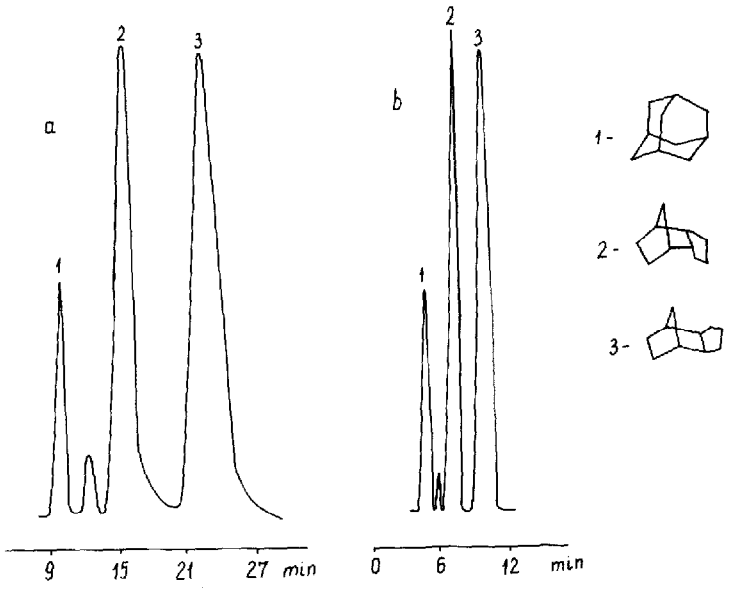

Fig. 6. Chromatogram of adamantane (1), *endo*-trimethylenenorbornane (2) and *exo*-trimethylenenorbornane (3) on (a) TG-10 and (b) TG-10 (plasma treated in hydrogen). Column, 70 × 0.22 cm I.D.; 393 K.

CONCLUSION

The surface properties of thermal carbon black, which was modified in a high-frequency, low-temperature plasma, and the surface properties of metal sulphides, prepared synthetically[6], were investigated. It was found that the most homogeneous non-polar adsorbents show high selectivity for the separation of mixtures of molecules with various structures, including steric isomers of polycyclic saturated hydrocarbons.

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