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APPLICATION OF MOLYBDENUM AND TUNGSTEN SULPHIDES AS ADSORBENTS IN GAS CHROMATOGRAPHY

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SUMMARY

Gas chromatography was used for studying the adsorption of various organic compounds, including halogen-, oxygen-, sulphur- and nitrogen-containing ones, on molybdenum and tungsten sulphides. It is shown that the adsorption on MoS₂ and WS₂ is governed mainly by dispersion forces. Some practical application of these adsorbents in gas chromatography are exemplified.

INTRODUCTION

Graphitized thermal carbon black (GTCB), whose surface is formed by the basal faces of graphite, is the only non-polar homogeneous adsorbent with a planar surface which finds application in gas chromatography (GC)^{1,2}. Therefore, the preparation and study of non-specific and homogeneous adsorbents are of great importance.

The crystalline structure of molybdenum and tungsten sulphides is typically lamellar and resembles that of graphite³. It is characterized by strong, predominantly covalent, bonds between the metal atoms and those of the chalcogen. On the other hand, the bonds between sulphur layers are weak and originate mainly from intermolecular forces. In the absence of crystal imperfections and chemical admixtures, the surface of MoS₂ and WS₂ particles formed by basal planes is homogeneous and non-polar^{1,4,5}.

This paper describes a GC study of the adsorption of oxygen-, halogen-, sulphur- and nitrogen-containing compounds with various electronic structures on MoS₂ and WS₂. The data acquired are valuable in investigating the surface properties of metal sulphides and in solving some practical analytical problems.

EXPERIMENTAL

Samples of MoS₂ and WS₂ with specific surface areas of 2 and 3 m²/g, respectively, and a particle size of 0.16-0.2 mm were used as adsorbents at temperatures

up to 230°C. A TSVET-102 chromatograph equipped with a flame ionization detector was employed. The carrier gas was nitrogen of high purity, and the glass columns were 0.3–1.2 m × 1–4 mm I.D.

Retention volumes, $V_{A,1}$, differential molar changes in internal energy, $-\Delta\bar{U}_1$, and relative retention volumes, V_{rel} (with respect to *n*-alkanes), of various organic compounds were determined^{1,2}.

RESULTS AND DISCUSSION

Table I lists the retention volumes, $V_{A,1}$, and differential molar changes in internal energy, $-\Delta\bar{U}_1$, at a close-to-zero coverage on the surface of metal sulphides and GTCB².

The thermodynamic adsorption characteristics of individual compounds are similar on MoS₂ and WS₂ regardless of the different metal atoms contained in the adsorbents, *i.e.*, molybdenum and tungsten. This is an indirect proof that adsorption takes place mainly on the basal faces filled with sulphur atoms. The retention of *n*-alkanes on metal sulphides is stronger than that of mono-*n*-alkylbenzenes (ethylbenzene, *n*-propylbenzene) having the same number of carbon atoms, and the adsorption of di-*n*-butyl ether is weaker than that of *n*-nonane. Hence, neither the π -bonds of benzene derivatives nor a free electron pair on the oxygen atom of an ether have a pronounced effect on the adsorption on metal sulphides. Similar observations have been made for adsorption on non-specific adsorbents^{1,2,6-8}.

The values of $-\Delta\bar{U}_1$ for the individual compounds are similar on metal sulphides and GTCB. However, the values of $V_{A,1}$ on MoS₂ and WS₂ are much smaller than on GTCB (see Table I). Thus, the metal chalcogens have potential application in analytical GC.

Figs. 1 and 2 exemplify the application of metal sulphides and GTCB for the separation of a mixture of isomers differing in both geometrical structure and possible orientation at the surface. As seen in Fig. 1a, the retention of 1,2,4,5-tetramethyl-

TABLE I

VALUES OF $V_{A,1}$ (μm) AT 120°C, $-\Delta\bar{U}_1$ (kJ/mol) AND ΔI AT 120°C ON VARIOUS ADSORBENTS

Adsorbate	MoS ₂		WS ₂		GTCB ²	
	$V_{A,1}$	$-\Delta\bar{U}_1$	$V_{A,1}$	$-\Delta\bar{U}_1$	$V_{A,1}$	$-\Delta\bar{U}_1$
<i>n</i> -Octane	2.5	52	2.5	49	24.6	49
<i>n</i> -Nonane	7.9	57	7.9	54	83.4	56
Ethylbenzene	2.1	49	2.1	46	15.2	48
<i>n</i> -Propylbenzene	5.9	54	5.9	50	46.2	53
Di- <i>n</i> -butyl ether	4.7	55	4.7	50	43.2	52
ΔI						
	MoS ₂		WS ₂		GTCB	
<i>n</i> -Propylbenzene	20		20		0	
Di- <i>n</i> -butyl ether	12		12		0	

cyclohexane stereoisomers on MoS₂ increases with increasing number of the equatorial substituents, *i.e.*, with the flattening of the molecules. Thus, a greater number of molecular links become capable of contacting the planar adsorbent surface. Fig. 1b shows that the elution sequence of isomers on MoS₂ is the same as that on GTCB^{1,9}. However, MoS₂ is preferred for the duration and temperature of the analysis are both reduced (see Table I).

The chromatograms of Fig. 2 were obtained for isomers of 5-vinylbicyclo[2.2.1]heptenes-2 on WS₂ and GTCB. Since *endo*-isomers are positioned farther from the planar surface than *exo*-isomers their separation on WS₂ can readily be accomplished in less time than on GTCB^{1,10}.

Retention index differences, ΔI , for *n*-propylbenzene and di-*n*-butyl ether on metal sulphides (Table I) were calculated by the Rohrschneider method proposed for characterizing stationary liquids in terms of their chromatographic polarities¹¹. GTCB was chosen as zero-polarity adsorbent because its surface is more homogeneous and non-polar than that of any other known adsorbent. The tabulated values of ΔI were calculated by the formula $\Delta I = I_X - I_{GTCB}$, where I_X and I_{GTCB} are the retention indices on metal sulphides and GTCB, respectively. These values indicate that in studying the adsorption of molecules capable of electrostatic interaction one should take into account a certain fraction of ionic bonding in MoS₂ and WS₂ crystals. This is the main difference between lamellar metal sulphides and GTCB. Nevertheless, the adsorption of low-polarity compounds on MoS₂ and WS₂ is significantly influenced by dispersion interaction with basal faces.

The adsorption of oxygen-, halogen- and nitrogen-containing compounds par-

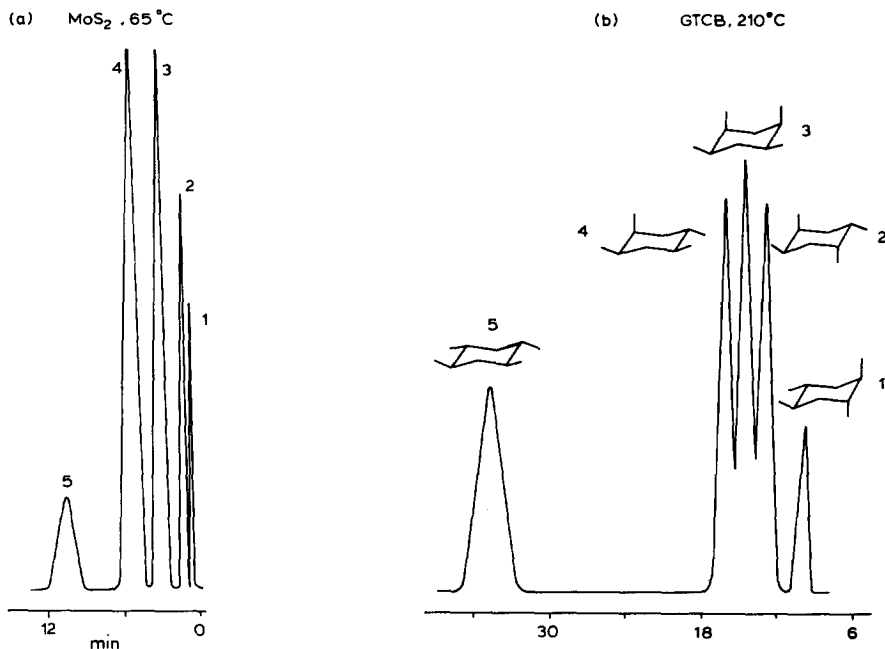


Fig. 1. Chromatograms of 1,2,4,5-tetramethylcyclohexane isomers on MoS₂ (a) and GTCB (b). Columns: a, 1 m × 2 mm I.D.; b, 2 m × 3 mm I.D.

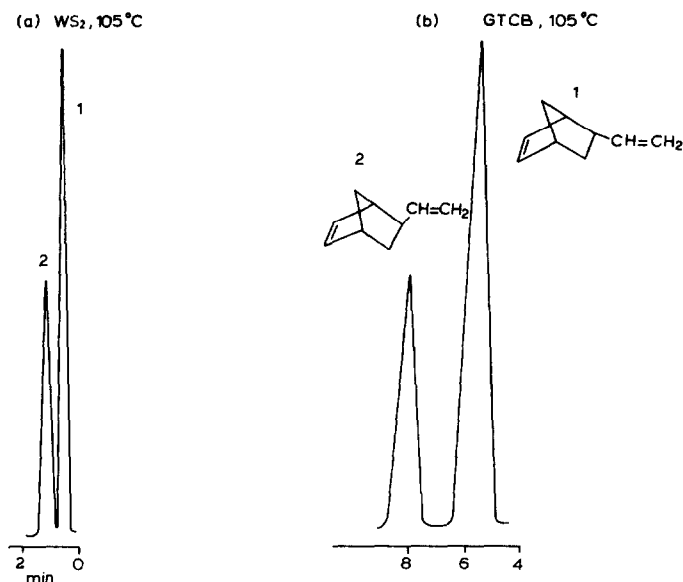


Fig. 2. Chromatograms of *endo*- (1) and *exo*- (2) -5-vinylbicyclo[2,2,1]heptenes-2 on WS_2 (a) and GTCB (b). Columns: a, $0.9 \text{ m} \times 4 \text{ mm}$ I.D.; b, $1.2 \text{ m} \times 2.5 \text{ mm}$ I.D.

ticularly susceptible to ions and dipoles at the adsorbent surface and to the geometrical and chemical inhomogeneity of the crystal faces was studied on metal sulphides^{1,2}. Compounds with active terminal groups gave asymmetrical peaks. This may be attributed both to the elution of faces having different indices, prismatic polar faces being included, and to cracks, microcavities, stages of growth and other surface flaws which enhance adsorption energy.

Table II shows that for molecules containing active groups the values of V_{rel} are much higher on MoS_2 and WS_2 than on GTCB¹². For example, V_{rel} for methyl ethyl ketone and 1-bromobutane on metal sulphides is 2-4 times that on GTCB. This

TABLE II

VALUES OF V_{rel} (WITH RESPECT TO *n*-HEPTANE) ON VARIOUS ADSORBENTS AT 60°C

T = Boiling point; μ = dipole moment; α = polarizability.

Adsorbate	T (°C)	μ (D)	α (\AA^3)	V_{rel}		
				MoS_2	WS_2	GTCB
Acetonitrile	81.6	3.94	4.15	0.2	0.1	
Ethanol	76.4	1.68	5.6	1.1	0.25	
Ethyl acetate	77.2	1.81	6.97	0.7	0.3	0.23
Methyl ethyl ketone	79.6	2.76	8.2	0.7	0.3	0.15
1,2-Dichloroethane	83.5	1.75		0.09	0.08	0.02
1-Bromobutane	101.6			0.42	0.34	0.13
Chlorobenzene	132	1.69	13.2	1.7	1.7	1.31

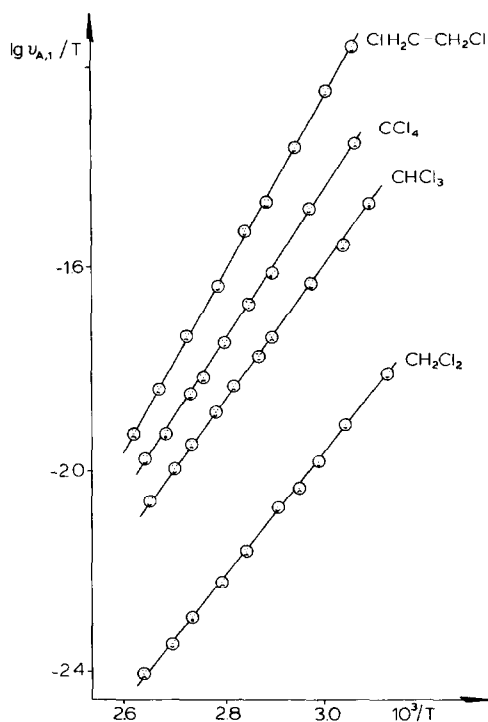
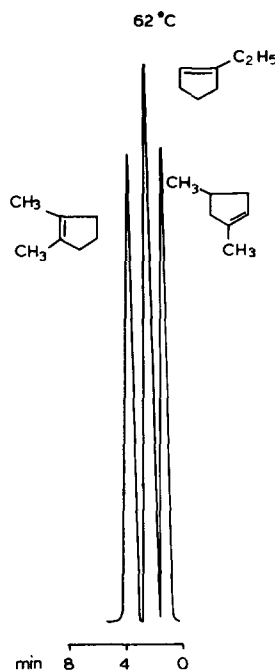


Fig. 3. Effect of reciprocal temperature on $\lg V_{A,1}/T$ for chlorine-containing compounds on MoS₂.

Fig. 4. Chromatogram of alkylcyclopentenes on MoS₂; column, 0.9 m \times 4 mm I.D.



may be due not only to the polarity of the adsorbents but also to the residual surface inhomogeneity of metal sulphides. At the same time, the adsorption of polar molecules is stronger on MoS₂ than on WS₂ due to a higher surface homogeneity of the latter.

It should be noted that, in the case of compounds with similar boiling points, the retention on metal sulphides increases with increasing polarizability and is little influenced by the dipole moments of the molecules. For example, ethanol and ethyl acetate are adsorbed more readily than acetonitrile in spite of the latter's higher dipole moment (Table II).

Although specific interaction accounts for a significant share of the intermolecular interaction between oxygen-, nitrogen- and halogen containing compounds and the metal sulphide surface, the data presented in Tables I and II show that the adsorption on MoS₂ and WS₂ is to a large extent determined by universal dispersion forces.

Low-boiling chlorine-containing compounds are widely used in various fields of chemistry so that a study of their adsorption on various adsorbents is of both practical and theoretical interest. Fig. 3 shows the effect of reciprocal temperature on $\lg V_{A,1}/T$ for some chlorine-containing compounds on MoS₂. An increase in the number of chlorine atoms in a molecule caused a non-uniform increase in the value of $V_{A,1}$ and $-\Delta\bar{U}_1$. Thus, a changeover from CH₂Cl₂ ($-\Delta\bar{U}_1 = 22$ kJ/mol) to CHCl₃ ($-\Delta\bar{U}_1 = 28$ kJ/mol) produced a 6 kJ/mol increase in the value of $-\Delta\bar{U}_1$,

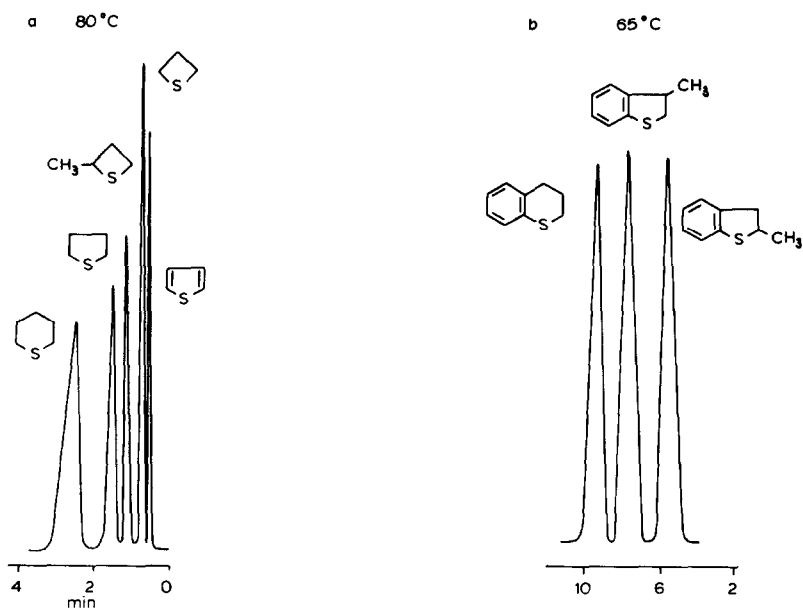


Fig. 5. Chromatogram of monocyclic (a) and bicyclic (b) sulphur-containing compounds on MoS_2 . Columns: a, $0.9 \text{ m} \times 4 \text{ mm}$ I.D.; b, $1 \text{ m} \times 1 \text{ mm}$ I.D.

and a further change to CCl_4 ($-\Delta\bar{U}_1 = 30 \text{ kJ/mol}$) increased this value by 2 kJ/mol only. The explanation is that a CCl_4 molecule contacts the adsorbent surface only with three chlorine atoms while the fourth atom is raised above the surface and contributes little to the energy of interaction. Similar relationships were obtained for the adsorption of chlorine-containing compounds on GTCB .

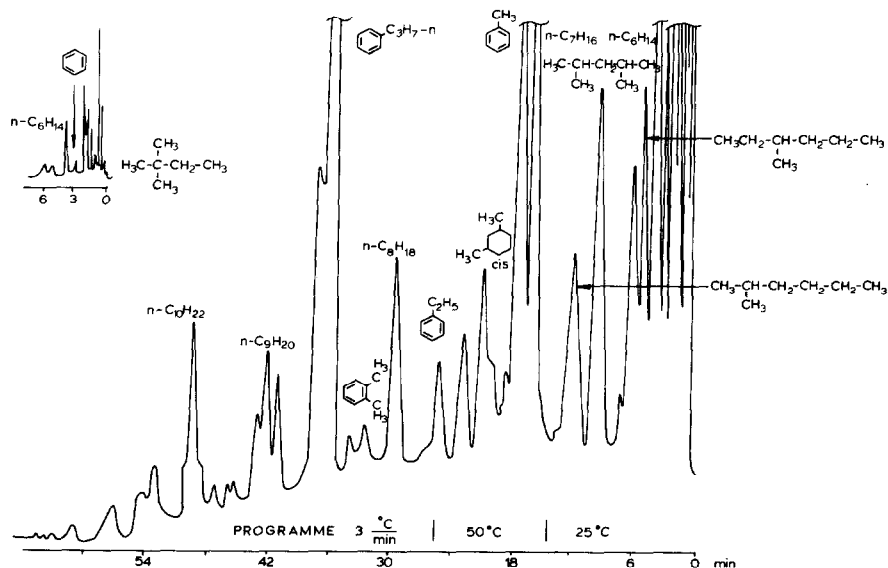


Fig. 6. Chromatogram of grade A-72 petrol on WS_2 . Column: $1 \text{ m} \times 3 \text{ mm}$ I.D.

Figs. 4-6 provide examples of the use of metal sulphides as adsorbents in GC. The separation of dimethyl- and ethyl-substituted cyclopentene on MoS₂ poses no problems and takes 4 min, because adsorption on the metal sulphide surface is highly susceptible to the geometrical structure of compounds.

The elution sequence of cyclic sulphur-containing compounds on a column packed with MoS₂ is determined by the geometrical and electronic structures of the molecule. Thus, thiocyclobutane is eluted after thiophene, apparently due to a more pronounced delocalization of valence electrons in the latter. Isomeric 1-methylthiocyclobutane and thiophene produce different peaks possibly due to a difference between the amount of strain in four- and five-membered rings; thiocyclohexane (Fig. 5a) has the strongest retention.

Molybdenum sulphide enables an almost complete separation of isomers of methylthioindene and thiotetrahydronaphthalene even when the bicyclic sulphur-containing compounds have only slightly different structures (Fig. 5b).

Grade A-72 petrol was separated on a WS₂-packed column under temperature-programmed conditions within the range of room temperature to 150°C without preliminary fractionation. A total of 40 components were separated with an efficiency of only 1000 theoretical plates (Fig. 6).

The present separations of structural and steric isomers on molybdenum and tungsten sulphides have shown that the two adsorbents are suitable for analyzing a wide range of organic compounds which have practical significance.

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