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SORBENTS FOR GAS CHROMATOGRAPHY WITH PHENYLQUINOXALENE AND SILOXAROPHENANTHRENE GROUPS*

K. I. SAKODYNSKII, L. D. GLAZUNOVA, I. P. YUDINA, L. I. PANINA and Yu. A. YUZHELEVSKY

Karпов Institute of Physical Chemistry, ul. Obukha 10, 107120 Moscow B-120 (U.S.S.R.)

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SUMMARY

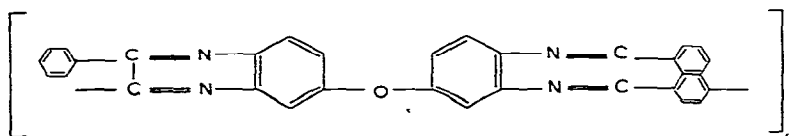
A polymer sorbent with phenylquinoxaline groups and a siloxane stationary phase with siloxarophenanthrene groups that possess high selectivity and thermal resistance are proposed.

INTRODUCTION

In recent years, a revived interest has been observed in the use of sorbents whose composition includes several different functional groups which can show various intermolecular interactions, and two new types are discussed in this paper.

POLYMER SORBENT WITH PHENYLQUINOXALENE GROUPS

A polymer sorbent based on polyphenylquinoxaline (PPQ) is proposed for use in gas chromatography. PPQ has the formula



The polymer in solution in *m*-cresol is synthesized using the technique described by Wrasidlo and Augl¹, and the polymer sorbent is obtained by spraying this polymer solution into a precipitating agent, such as acetone. This technique allows the sorbent to be obtained in the form of regular particles. The polymer based on PPQ is normally used for the formation of composite materials, films, etc.^{2,3}. It can be applied as a sorbent in gas chromatography owing to its structural properties, chemical features of the surface and high thermal stability.

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The sorbent has macroporous structural characteristics. The specific surface area measured by the nitrogen thermal desorption method at -196° is $50 \text{ m}^2/\text{g}$. The total pore volume determined by mercury porosimetry is $1.25 \text{ cm}^3/\text{g}$ and the average pore radius is 500 \AA . According to thermogravimetric analysis data, the upper temperature limit for the application of PPQ is 320° .

The characteristics of the sorbent were studied using a Unichrom 1100 chromatograph with $1 \text{ m} \times 3 \text{ mm}$ I.D. and a thermal conductivity detector. Helium was used as the carrier gas. Temperature programming was effected with a Packard gas chromatograph with $14 \times 3 \text{ mm}$ I.D. columns and a flame-ionization detector.

The influence of the gas chromatographic parameters on the main criteria of separation was studied. The HETP depended on the carrier gas flow-rate at temperatures in the range $100\text{--}150^{\circ}$; the optimal flow-rate was $20\text{--}40 \text{ ml/min}$, and the high efficiency was retained over a wide range of flow-rates ($20\text{--}60 \text{ ml/min}$). The HETP at 150° was $4\text{--}5 \text{ mm}$ for polar compounds of the acetonitrile type, and that for water was 3 mm .

The dependence of the HETP on the temperature was studied for alkanes, amines and alcohols, and minimal HETP values were achieved in the temperature range $200\text{--}250^{\circ}$.

The sorbent is multifunctional; it contains links and oxygen atoms, which makes its properties highly specific. The selective properties of PPQ determine the high values of the retention indices for polar substances (ethanol 621, *tert.*-butanol

TABLE I

RELATIVE RETENTION TIMES OF UNSATURATED, CYCLIC AND ISO-COMPOUNDS COMPARED TO USUAL COMPOSITION COMPOUNDS

Column temperature, 150° .

Substance	Boiling point ($^{\circ}\text{C}$)	Relative retention time (<i>n</i> -pentane = 1.0)
<i>n</i> -Pentane	36.1	1.0
Pentene-2	36.9	1.43
Pentadiene-1,3	44.1	1.54
Isopentane	27.9	0.62
<i>n</i> -Hexane	68.7	2.08
Hexene-1	63.5	2.30
Cyclohexane	81.4	3.03
Benzene	80.1	5.70
Methylcyclohexane	100.9	2.12
Toluene	110.6	11.8
<i>n</i> -Heptane	98.4	4.42
Heptene-3	95.7	5.46
<i>n</i> -Octane	124.6	9.0
Octene-2	121.2	12.6
Isooctane	99.2	0.82
<i>n</i> -Propanol	97.8	2.10
Isopropanol	82.4	1.33
<i>n</i> -Butanol	117.5	6.57
Isobutanol	107	4.45
<i>sec.</i> -Butanol	99.5	3.78
<i>tert.</i> -Butanol	82.8	1.94
Diethyl ester	35.6	1.1
Tetrahydrofuran	65	3.8

639, methyl ethyl ketone 732, nitromethane 761, acetonitrile 685, benzene 833, pyridine 939). The retention indices are similar to those for polar sorbents of the Porapak N and T type⁴.

The specific properties of PPQ are manifested in the higher retention of alkenes compared with the corresponding alkanes and of aromatic compounds compared with the corresponding acyclic compounds (Table I), and in the good separation of molecules of groups B and D with similar boiling points (Table II). The retentions of pyridine, pentylamine and 1,2-diaminopropane relative to that of *n*-heptane are worth noting.

TABLE II

RELATIVE RETENTION TIMES OF GROUP B AND D SUBSTANCES WITH SIMILAR BOILING POINTS

Column temperature = 150°.

Substance	Boiling point (°C)	Relative retention time	
		<i>n</i> -Pentane = 1.0	<i>n</i> -Heptane = 1.0
<i>n</i> -Pentane	36.1	1.0	0.25
<i>n</i> -Heptane	98.4	3.9	1.0
Nitromethane	101	2.9	0.74
Pentanone-2	101.7	5.9	1.51
1,4-Dioxane	100.8	7.0	1.80
Propionitrile	96-97	3.2	0.82
Triethylamine	89.5	4.0	1.03
Pyridine	115.3	11.6	3.0
Acetaldehyde	102-104	6.5	1.67
Propionic acid	100.7	4.25	1.09
Water	100	0.50	0.13
Pentylamine	104	8.2	2.10
1,2-Diaminopropane	119	9.8	2.51

The lower retentions of iso-compounds and the higher retentions of cyclic compounds, in comparison with the corresponding compounds of the usual composition (Table I) are characteristic of polyphenylquinoxalene, which in this respect is similar to other polymer sorbents. Anomalous results are the very high retention of octane compared with that of isooctane (more than 6 times higher) and the blurring of the isooctane peak, the high retentions of benzene and toluene compared with that of methylcyclohexane and the high retention of *n*-heptane compared with that of methylcyclohexane.

It is also interesting to note the change in the order of retention of water, methanol and ethanol that occurs when the temperature of the column filled with PPQ is changed (Table III). At low temperatures water is the first to be eluted from the column. On increasing the temperatures the retention of water is increased to become comparable to that of C₁-C₂ alcohols, and at 200° its retention is more than twice that of C₁-C₂ alcohols.

The sorbent based on PPQ was used to separate mixtures of polar and aromatic compounds, simple and complex esters, alcohols, aldehydes, ketones,

TABLE III

DEPENDENCE OF CORRECTED RETENTION VOLUME (V_R) ON THE TEMPERATURE OF THE COLUMN

Substance	Temperature($^{\circ}C$)					
	60	80	100	132	150	200
Water	63.7	44.6	24.2	18.6	13.8	6.90
Methanol	139	66.6	32.2	14.2	11.7	2.0
Ethanol	369	174	68.2	23.6	16.0	2.60

amines, diamines, amides and mixtures containing ammonia. Examples of chromatograms are shown in Figs. 1-3.

The investigation showed that the sorbent based on PPQ is sufficiently heat resistant (320°) (determined both by thermogravimetry and gas chromatography at the minimum noise level of the detector) and specific and is obtained in the form of regular particles suitable for filling chromatographic columns. It can be used in the analysis of aqueous solutions and mixtures of polar compounds.

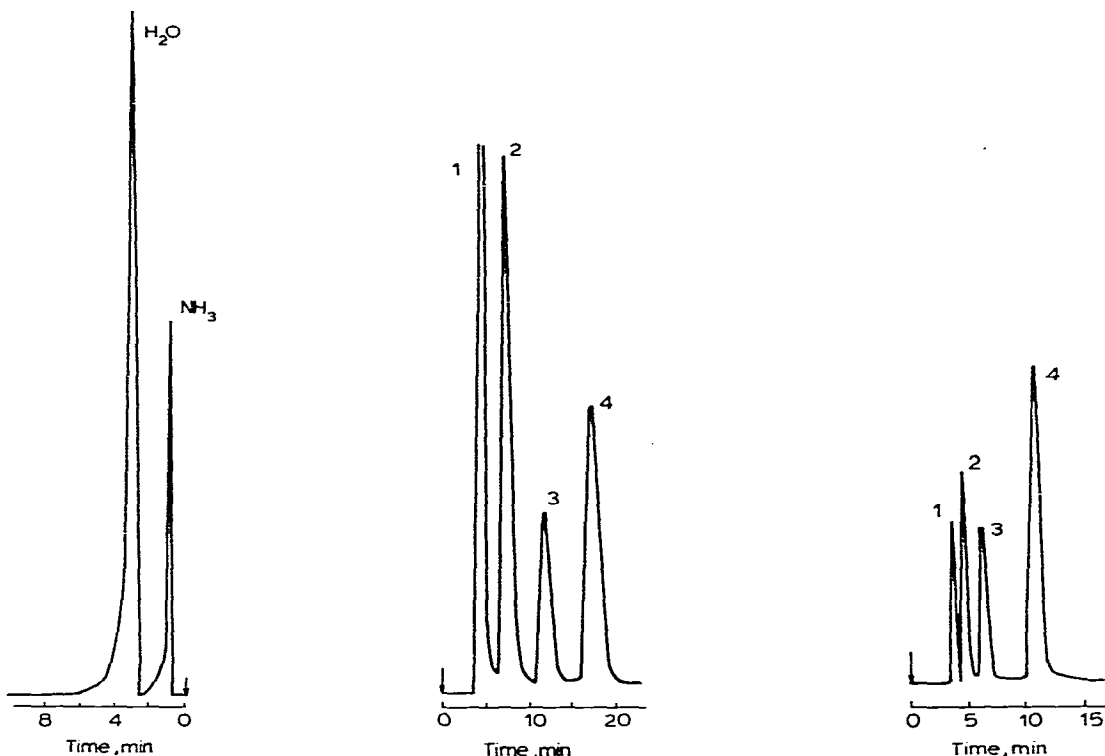


Fig. 1. Determination of ammonia in water using PPQ at 80° .

Fig. 2. Chromatogram of nitrile separation using PPQ. 1 = Acetonitrile; 2 = propionitrile; 3 = butyronitrile; 4 = valeronitrile. Column temperature programmed from 150° to 220° at $3^{\circ}/\text{min}$.

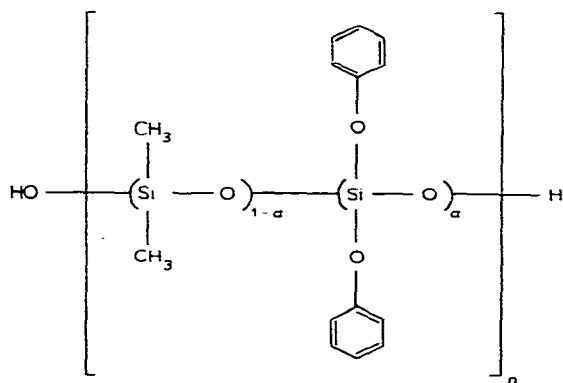
Fig. 3. Chromatogram of amine separation using PPQ. 1 = Diethylamine; 2 = butylamine; 3 = pentylamine; 4 = *o*-aminotoluene. Column temperature programmed from 150° to 200° at $3^{\circ}/\text{min}$.

STATIONARY PHASE WITH SILOXAROPHENANTHRENE GROUPS

In recent years, siloxane stationary phases have found wide application and have made it possible to achieve a higher temperature limit for gas-liquid chromatography. However, regulating the selectivity of high-temperature siloxane and carboranesiloxane phases is so far an unsolved problem.

A polydimethylsiloxane polymer with siloxarophenanthrene groups (SAPh) has been investigated as a stationary phase. This polymer is obtained by co-hydrolysis of corresponding diorganildichlorsilanes with subsequent condensation of the co-hydrolysis products (polycondensation of the monomer in the presence of a catalyst).

The general formula is



where $n = 50-5000$ and $a = 0.25$.

The stationary phase is a colourless, rubber-like polymer with a viscosity of about 1000 P. *n*-Hexane, chloroform, benzene, toluene and used as solvents. The maximum operating temperature when using a flame-ionization detector is 300°. The Rohrschneider constants (100°) are $x = 0.81$, $y = 1.51$, $z = 1.94$, $u = 2.73$ and $s = 2.38$.

The evaluation of the properties of the SAPh stationary phase was carried out using Aerograph and Perkin-Elmer Model 900 gas chromatographs with a thermal conductivity and a flame-ionization detector under isothermal and temperature-programmed conditions.

The sorbent was prepared by coating the stationary phase from solution in amounts of 10-20% (w/w) on to Chromaton N AW using the conventional method. The column was 2 m × 2 mm I.D. A study of the main properties revealed that the stationary phase possesses a high selectivity which is retained at relatively high temperatures. Hydrocarbons are weakly soluble in SAPh and have small retention volumes, whereas alcohols and aromatic compounds are retained to a much greater extent. Fig. 4 shows the chromatogram of a number of compounds with boiling points of 243-255° which indicates the high specificity of the sorbent relative to aromatic compounds and alcohols. In some instances this specificity can be utilized for a radical analysis, in particular the separation of hydrocarbons from alkylsulphamides (Fig. 5).

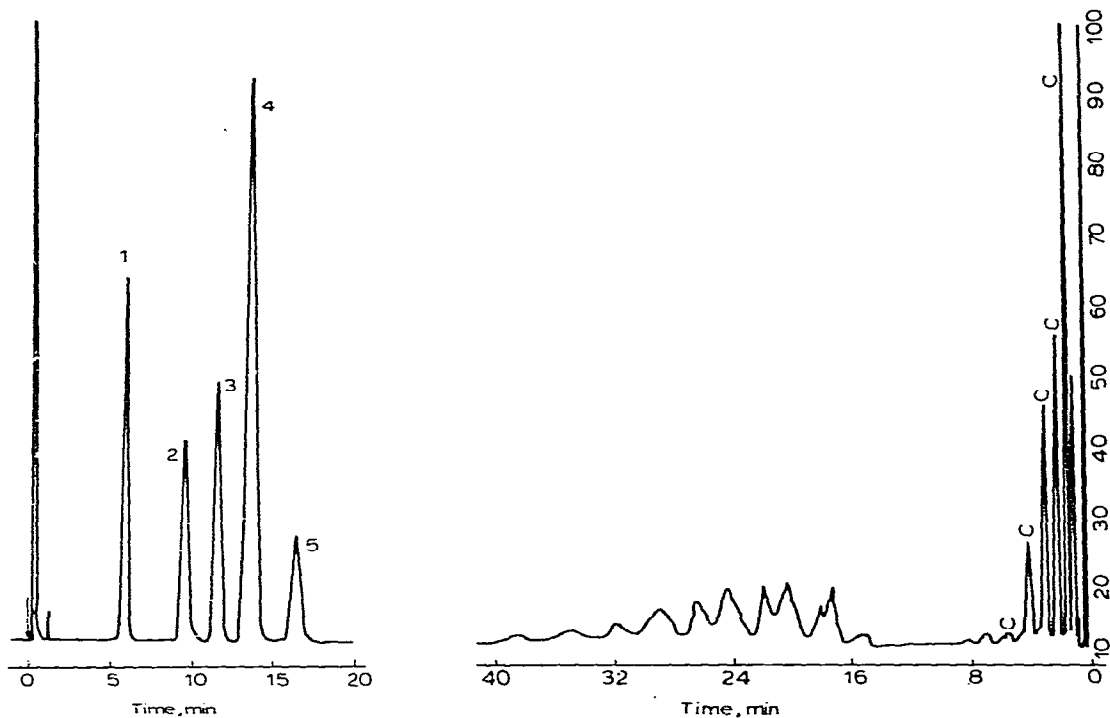


Fig. 4. Chromatogram of separation of a mixture of close boiling compounds. 1 = Tetradecane; 2 = *p*-anisidine; 3 = nitrochlorobenzene; 4 = dodecanol; 5 = biphenyl.

Fig. 5. Chromatogram of separation of C_{13} - C_{18} hydrocarbons from C_{12} - C_{18} alkylsulphamides.

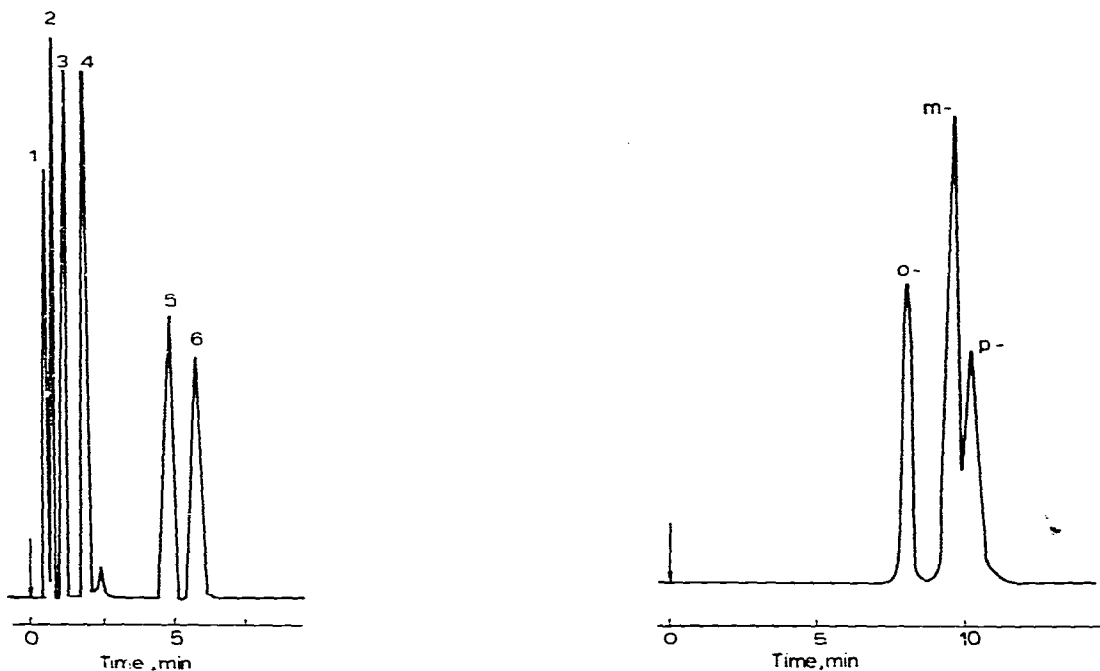


Fig. 6. Chromatogram of separation of a complex mixture of cyclic and aromatic compounds. 1 = Cyclohexane; 2 = benzene; 3 = toluene; 4 = cyclohexylamine; 5 = phenol; 6 = aniline.

Fig. 7. Chromatogram of separation of a mixture of isomers of *N,N'*-diethylamidetoluene acid.

The rather difficult problem of separating aniline and phenol is easily solved by using this sorbent and the peaks obtained have excellent symmetry (Fig. 6).

An important feature of the proposed stationary phase is its high selectivity during the separation of isomers of high-boiling compounds. Fig. 7 shows separation of a mixture of isomers of *N,N'*-diethylamidetoluene acid. It is possible to separate anisidine isomers in the form of free bases without converting them into trifluoroacetamides (Fig. 8). The high selectivity is shown in the separation of complex mixture of dinitrotoluene isomers (Fig. 9).

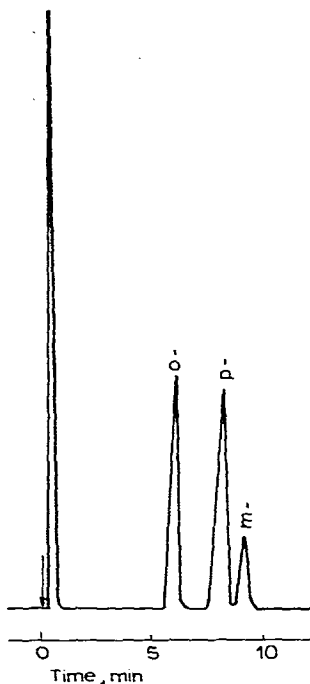


Fig. 8. Chromatogram of separation of anisidine isomers.

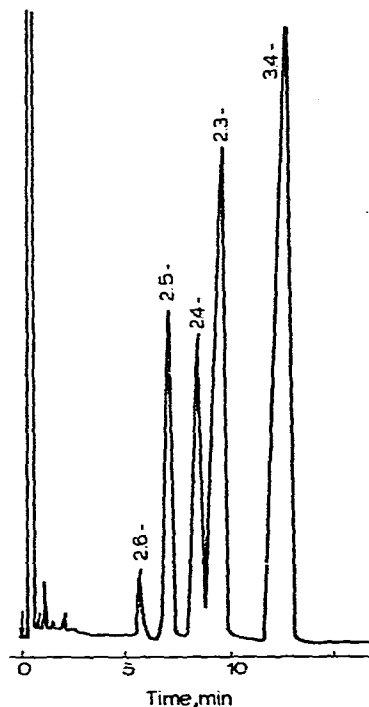


Fig. 9. Chromatogram of separation of a mixture of dinitrotoluene isomers.

The above examples illustrate the high selectivity of the SAPH stationary phase at high temperatures. A particular feature is its high selectivity relative to aromatic nitrogen-containing compounds.

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