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PROPERTIES AND USE OF THE SORBENT SPHERON SDA IN GAS CHROMATOGRAPHY

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SUMMARY

The properties of the recently developed macroporous sorbent Spheron SDA and its application in gas chromatography were studied. The measurements were carried out with low-molecular-weight polar and non-polar compounds and gaseous compounds. Compared with the existing commercial packings, Spheron SDA has a good separation efficiency for hydrocarbons up to C₁₀, alcohols, organic acids, glycols and other compounds, with comparatively short retention times. The sorbent is stable up to *ca.* 230°.

INTRODUCTION

When used in gas and liquid chromatography, macroporous organic sorbents do not separate solutes by a simple mechanism that could be characterized purely as an adsorption or partition process^{1,2}. Investigations of adsorption and desorption curves by the BET method revealed the existence of a measurable hysteresis, which seems to prove that part of sorbed polar or non-polar compounds is dissolved in the cross-linked polymeric structure³. The degree of hysteresis is a function of the sorbent-solute interaction and is roughly proportional to the adsorption energy.

At present, the gas chromatographic separation of low-molecular-weight compounds is carried out on commercial polymeric packings, such as Porapak (Waters Assoc., Milford, Mass., U.S.A.), Chromosorb (Johns-Manville, Denver, Colo., U.S.A.), PAR (Hewlett-Packard, Avondale, Pa., U.S.A.)² and Tenax (Applied Science Labs., State College, Pa., U.S.A.)⁴.

Macroporous organic copolymers obtained by the suspension copolymerization of vinyl monomers in an aqueous dispersion medium have a wide pore size distribution; their specific surface area is several hundreds square metres per gram. By choosing appropriate starting monomers, sorbents can be prepared with a wide range of polarity and a wide range of sorption properties⁵. In connection with the investi-

gation of relationships between chemical composition and physical structure carried out in our laboratory, we also examined the use of macroporous organic sorbents in reversed-phase liquid chromatography⁶. As densely cross-linked copolymers exhibit high thermal stability and a large specific surface area, their application in gas-solid chromatography can be envisaged. In the present work, the chromatographic behaviour of the copolymer Spheron SDA was studied.

EXPERIMENTAL

The sorbent Spheron SDA (Chemical Research Department, Laboratory Instruments Works, Prague, Czechoslovakia), is prepared by the suspension copolymerization of vinyl monomers of different polarity in the presence of organic solvents, which control its surface area and pore-size distribution⁷.

The chosen fraction of perfectly spherical particles was carefully extracted with benzene, ethanol and water and the specific surface area ($130 \text{ m}^2/\text{g}$) of the dry polymer was determined by the chromatographic desorption of nitrogen. The destruction of the copolymer was examined by thermogravimetry at a heating rate of $10^\circ \cdot \text{min}^{-1}$ with a DuPont 900 apparatus. In an inert nitrogen atmosphere, decomposition begins at 290° .

The sorbent, with a particle size range of $0.1\text{--}0.16 \text{ mm}$, *i.e.*, *ca.* 90–140 mesh, was packed into a glass column ($240 \text{ cm} \times 3 \text{ mm I.D.}$). By means of mechanical vibration, the sorbent was packed into the column until no change in packing volume could be observed.

All measurements were performed with a Chrom 41 chromatograph (Laboratory Instruments Works) provided with a flame-ionization (FID) and a thermal conductivity detector (TCD). Helium was used as the carrier gas at a standard flow-rate of $27.5 \text{ ml} \cdot \text{min}^{-1}$.

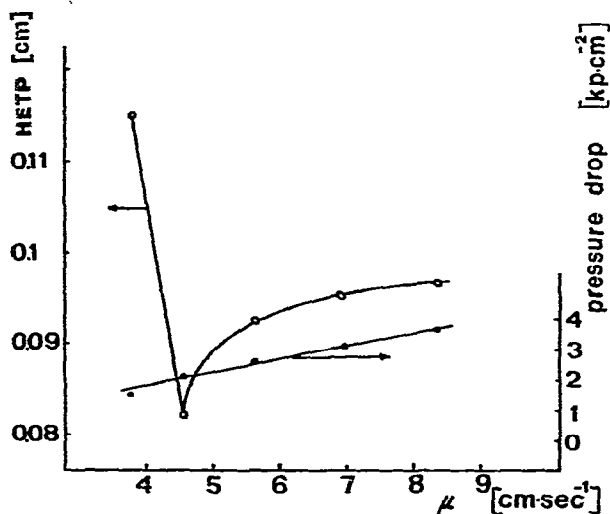


Fig. 1. Dependence of column efficiency and pressure drop on the linear flow-rate of the carrier gas. Spheron SDA, $100\text{--}160 \mu\text{m}$; helium as carrier gas; methyl ethyl ketone as standard; column temperature, 198° .

The packed column was first conditioned at 80° for 4 h with a flow-rate of helium carrier gas of *ca.* 30 ml·min⁻¹; the temperature was then increased at the rate of 1°·min⁻¹ to 150°. The temperature was maintained at 150° for 4 h, then increased to 205°, at which temperature the column was maintained for 8 h. After cooling, additional sorbent was added in order to complete the volume. Before the measurements were made, the column was heated to 198° and maintained at this temperature for a further 4 h.

RESULTS AND DISCUSSION

The dependence of the height equivalent to a theoretical plate (HETP) on the flow-rate of the carrier gas was studied at 198°. The optimal efficiency of the glass column was attained at a flow-rate of helium of 27.5 ml·min⁻¹ (Fig. 1). The Van

TABLE I

RELATIVE RETENTION TIMES (t_R) WITH RESPECT TO *n*-HEXANE OF SOME STANDARD COMPOUNDS ON THE SORBENT SPHERON SDA

Retention time of *n*-hexane = 2.6 min.

Conditions	Compound	t_R	Compound	t_R	
FID, column temperature 198°, injection temperature 210°	<i>n</i> -Pentane	0.72	Tetrachloro- methane	1.63	
	Cyclopentane	1.0	Monochloro- benzene	5.47	
	Methylcyclopentane	1.25	Formic acid	1.42	
	<i>n</i> -Hexane	1.0	Acetic acid	1.57	
	Cyclohexane	1.5	Propionic acid	2.52	
	Methylcyclohexane	2.02	Isobutyric acid	3.36	
	Benzene	1.89	<i>n</i> -Butyric acid	4.0	
	Toluene	3.05	Isovaleric acid	5.47	
	<i>n</i> -Heptane	1.5	<i>n</i> -Valeric acid	6.73	
	Isooctane	1.7	Methylamine	0.42	
	<i>n</i> -Octane	2.37	<i>n</i> -Butylamine	1.52	
	Acetone	0.84	Methanol	0.61	
	Ethyl formate	1.0	Ethanol	0.78	
	Ethyl acetate	1.15	Isopropanol	0.86	
	Methyl ethyl ketone	1.31	<i>n</i> -Propanol	1.11	
	Dichloromethane	1.05	Isobutanol	1.51	
	Chloroform	1.57	<i>n</i> -Butanol	1.75	
	FID, column temperature 230°, sample valve temperature 300°	Ethylene glycol dimethyl ether	1.43	Caproic acid	5.54
		Ethylene glycol monoethyl ether	2.18	Caprylic acid	12.05
		Ethylene glycol	2.93	Lactic acid	6.99
1,2-Propanediol		3.18	Benzyl alcohol	10.81	
1,3-Butanediol		5.31			
1,4-Butanediol		8.90			
TCD, column temperature 140°, Katharometer 200°, sample valve 190°, 80 mA	Diethylene glycol	8.90			
	Ammonia	0.28	Methanol	0.6	
	Water	0.47	<i>n</i> -Hexane	1.0	
	Formaldehyde	0.37			

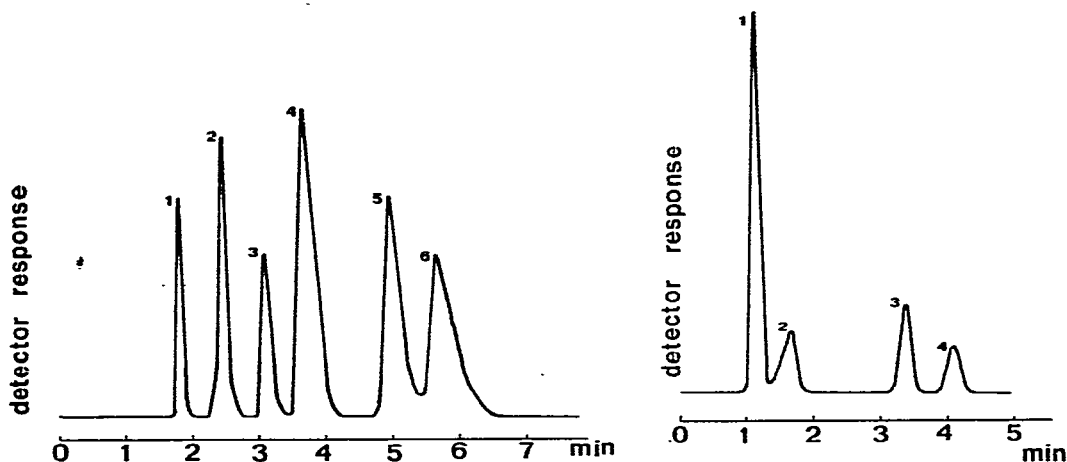


Fig. 2. Separation of a mixture of hydrocarbons on a Spheron SDA column. Flow-rate of helium carrier gas, $27.5 \text{ ml} \cdot \text{min}^{-1}$; column temperature, 198° ; amount of mixture injected, $1 \mu\text{l}$; sample valve temperature, 210° ; flame-ionization detection. Peaks: 1 = *n*-pentane; 2 = *n*-hexane; 3 = cyclopentane; 4 = *n*-heptane; 5 = methylcyclohexane; 6 = *n*-octane.

Fig. 3. Separation of a mixture of nitrogen and its oxides on a Spheron SDA column. Flow-rate of helium carrier gas, $27.5 \text{ ml} \cdot \text{min}^{-1}$; column temperature, 34° ; katharometer temperature, 50° ; amount injected, $1 \mu\text{l}$. Peaks: 1 = nitrogen; 2 = nitric oxide; 3 = nitrogen dioxide; 4 = nitrous oxide.

Deemter curve indicates that even at higher flow-rates of the carrier gas the column does not lose much of its efficiency. The dependence of the pressure drop on the linear velocity of the carrier gas, shown in Fig. 1, is linear in the range studied. For the optimal flow-rate of the carrier gas, the HETP for methyl ketone is 0.82 mm.

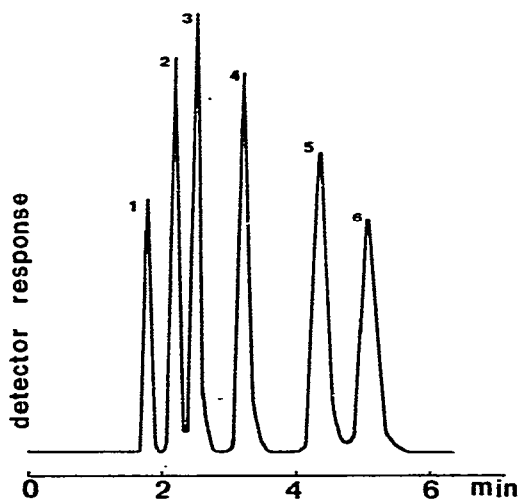


Fig. 4. Separation of a mixture of alkanols on a Spheron SDA column. Flow-rate of helium carrier gas, $27.5 \text{ ml} \cdot \text{min}^{-1}$; column temperature, 198° ; injection temperature, 210° ; amount injected, $1 \mu\text{l}$; flame-ionization detection. Peaks: 1 = methanol; 2 = ethanol; 3 = isopropanol; 4 = *n*-propanol; 5 = isobutanol; 6 = *n*-butanol.

The sorbent was tested by using various chromatographically pure polar and non-polar compounds. The relative retention times are summarized in Tables I and II. Spheron SDA was found to exhibit very good separation properties towards liquid hydrocarbons (Fig. 2) and low-boiling and gaseous hydrocarbon mixtures (Table II). A satisfactory separation of a mixture of nitrogen and nitrogen oxides was achieved at 34° (Fig. 3). By increasing the column length to 300 cm, nitrogen could be clearly separated from nitric oxide.

Spheron SDA also yielded good results in the separation of highly polar compounds. At 50°, the mixture ammonia–water can be separated, ammonia being eluted from the column first. In this way low ammonia concentrations in water can be determined chromatographically, as the tailing of water does not interfere with the analysis. Similarly, formaldehyde is eluted first in the mixture formaldehyde–methanol–water.

Some alkanols were separated successfully at 198° on Spheron SDA, in a similar manner to their separation on Chromosorb-type sorbents (Fig. 4). The order of elution of the alkanols is typical of organic sorbents; water behaves as an unalkylated hydroxy derivative and is characterized by the shortest retention time. Fatty acids are also separated according to increasing molecular weight of the alkyl group (Fig. 5). A chromatogram of the mixture acetone–ethyl acetate–methyl ethyl ketone–tetrachloromethane–monochlorobenzene is shown in Fig. 6.

A column temperature of *ca.* 200° was too low for the separation of diols and

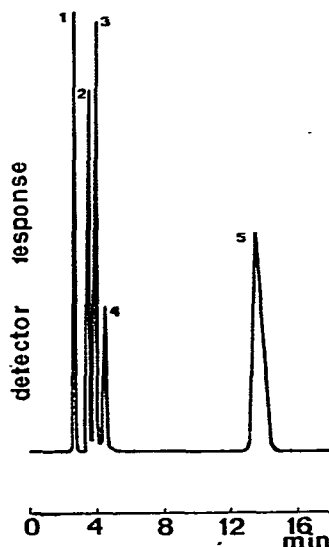
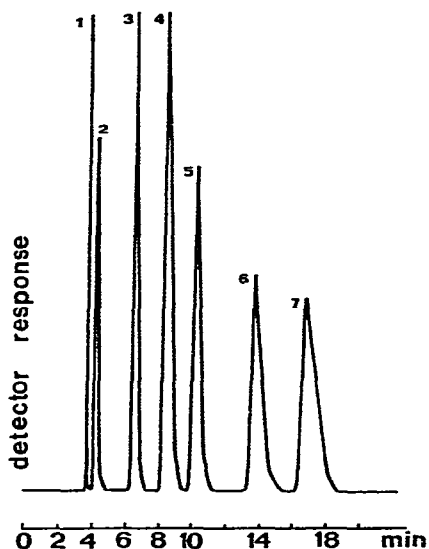


Fig. 5. Separation of a mixture of organic acids on a Spheron SDA column. Flow-rate of helium carrier gas, 27.5 ml·min⁻¹; column temperature, 198°; sample valve temperature, 210°; amount injected, 1 μ l; flame-ionization detection. Peaks: 1 = formic acid; 2 = acetic acid; 3 = propionic acid; 4 = isobutyric acid; 5 = *n*-butyric acid; 6 = isovaleric acid; 7 = *n*-valeric acid.

Fig. 6. Separation of a mixture of compounds on a Spheron SDA column. Flow-rate of helium carrier gas, 27.5 ml·min⁻¹; column temperature, 198°; sample valve temperature, 210°; amount injected, 1 μ l; flame-ionization detection. Peaks: 1 = acetone; 2 = ethyl acetate; 3 = methyl ethyl ketone; 4 = tetrachloromethane; 5 = monochlorobenzene.

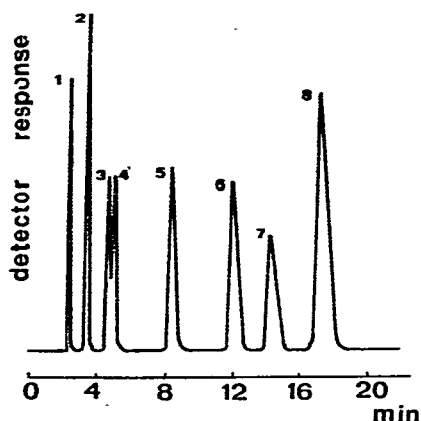


Fig. 7. Separation of a mixture of glycols, their ethers and benzyl alcohol on a Spheron SDA column. Flow-rate of helium carrier gas, $27.5 \text{ ml} \cdot \text{min}^{-1}$; column temperature, 230° ; sample valve temperature, 300° ; amount injected, $1 \mu\text{l}$; flame-ionization detection. Peaks: 1 = ethylene glycol dimethyl ether; 2 = ethylene glycol monoethyl ether; 3 = ethylene glycol; 4 = 1,2-propanediol; 5 = 1,3-butanediol; 6 = 1,4-butanediol; 7 = diethylene glycol; 8 = benzyl alcohol.

benzyl alcohol. The column was therefore heated to 230° by using temperature programming and conditioned for 8 h at a flow-rate of helium of $27 \text{ ml} \cdot \text{min}^{-1}$, then a mixture of diols, their ethers and benzyl alcohol was injected onto the column at 230° . Their separation is illustrated in Fig. 7, which indicates a very good resolution of the individual components within a comparatively short period.

The separations illustrated here confirm the possibilities for the application of the macroporous sorbent Spheron SDA in the gas chromatographic separation of polar and non-polar compounds at temperatures up to 230° . Repeated analyses showed a high reproducibility of the retention data and a high separation efficiency.

TABLE II

RELATIVE RETENTION TIMES (t_R) OF COMPOUNDS ON THE SORBENT SPHERON SDA

Conditions	Reference compound	Compound	t_R	Compound	t_R
TCD, column temperature 35° , katharometer 50° , 120 mA	Nitrogen (1.1 min)	Nitrogen	1.0	Nitric oxide	1.50
		Air	1.0	Nitric dioxide	3.04
		Carbon monoxide	1.0	Nitric monoxide	3.72
		Carbon dioxide	3.18		
TCD, column temperature 50° , katharometer 150° , 80 mA	Methane (1.15 min)	Nitrogen	0.72	Ethylene	2.15
		Methane	1.0	Ethane	2.60
		Carbon dioxide	1.72	Acetylene	3.05

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