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Short columns for gas chromatography packed with plasma-modified silica gels

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ABSTRACT

The development of contemporary gas chromatography is closely connected with improvements to packing materials and columns. New adsorbents obtained on the basis of treating silica gel with organic compounds in a high-frequency, low-temperature plasma give real possibilities in this direction. The influence of the time of exposure in the plasma on the gas chromatographic properties of packings such as selectivity, efficiency and retention was investigated. For this purpose modified silica gel of particle size 63–71 μm was used as a packing for short gas chromatographic columns (20 \times 0.2 cm I.D.). It was found that silica gels modified in plasma, with low degrees of coverage of their surface with polymer, have good selectivity and columns packed with them show high efficiency. The results confirm the opinion that the columns under consideration could be used successfully instead of the usual 1–2-m long packed columns.

INTRODUCTION

During the past 10 years the modification of supports, adsorbents and gas chromatographic (GC) packings by plasma polymerization has been demonstrated [1–9]. The method involves treatment with gases or organic vapours in a high-frequency, low-temperature plasma.

It has been found that a change in the chromatographic properties of the columns occurs in all instances. It is very difficult, however, to draw more general conclusions from the data published so far because of the different conditions used in the experiments. Only a limited number of organic compounds have been examined as modifiers of GC materials in plasma.

This paper describes investigations of the chromatographic properties of silica gels whose surfaces have been partially modified in plasma with different organic modifiers under comparable experimental conditions. It was examined whether samples obtained by plasma polymerization would be suitable as packings for short packed columns [10,11].

EXPERIMENTAL

Wide-pore silica gel (P.P.H. Polskie Odczynniki Chemiczne-Gliwice, Gliwice, Poland) of particle size 63–71 μm and with specific surface area 217 m^2/g and pore volume 0.902 cm^3/g was used as the material for modification in the plasma.

The silica gel was dried for about 6 h at 150°C and then impregnated with the corresponding liquid organic compound used as a monomer in the plasma polymerization. The air-dried samples were then treated in plasma with additionally introduced vapour of the corresponding compound. Thus efficient permeation of the modifier in the silica gel was ensured.

The apparatus and techniques used were described in previous papers [1,2,6,7,12]. A high-frequency generator (50 W, 13.5 MHz) was used to support a steady state in the plasma reactor. Traces of oxygen in the gases used in the treatment in the plasma discharge were removed on the line inlet catalytically.

The modified silica gel samples were extracted with *n*-hexane and isopropanol (10 h with each) in a Soxhlet apparatus. Finally they were conditioned in the columns until a stable baseline was obtained.

The measurements of the GC characteristics were carried out with a Hewlett-Packard Model 5890 gas chromatograph with a flame ionization detector and an HP 3396A integrator.

The glass columns (20 \times 0.2 cm I.D.) used had a with silanized internal surface. The pair benzene–cyclohexane was used as a test mixture to evaluate the change in the chromatographic properties of the columns. Benzene and cyclohexane have almost identical boiling points and their resolution provides a measure of the type and the strength of their interactions with the sorbent surface.

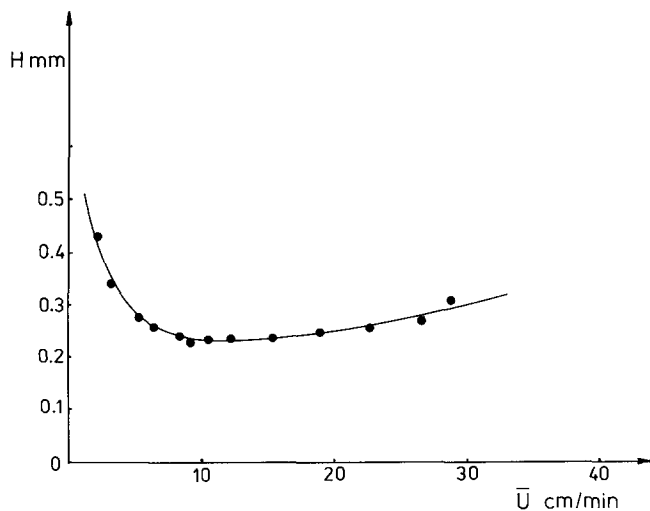


Fig. 1. Van Deemter curve for cyclohexane at 60°C. Column, 20 \times 0.2 cm I.D., packed with silica gel (63–71 μm), modified with cyclohexene in plasma, exposure time $\tau = 25$ s. \bar{U} = Linear velocity; H = plate height.

The measurements were carried out with nitrogen as carrier gas at a flow-rate of $15 \text{ cm}^3/\text{min}$. This value corresponds approximately to the minimum of the Van Deemter curve (Fig. 1).

RESULTS AND DISCUSSION

Time of exposure

The silica gel used as the material for modification in the plasma was found to be suitable because of its high specific surface but wide pore surface. Working with short columns thus gives the possibility of obtaining normal retention [13].

The influence of the time of exposure in the plasma on the chromatographic properties was studied at 25, 50, 75 and 100 s with cyclohexene as modifier.

The most important characteristics of columns prepared with the modified silica gels showed decreasing or constant values, depending on the time of exposure (Figs. 2 and 3). The results also show that the modification is more intense in the first few seconds of the treatment. Further increases in the time of exposure lead asymptotically to a constant value of the measured quantity.

The decrease in the benzene retention volumes, capacity factor and relative retention is probably due to the decrease in the contribution of the specific interaction to the total interactions with the sorbent surface through the modification.

Elemental analysis of the modified samples showed that the carbon content varied from 0.58 to 1.82%.

The height equivalent to a theoretical plate (HETP) fluctuates around a mean value. Obviously the technique of column filling has an influence. It can be accepted, however, that the HETP does not depend on the time of exposure. The mean HETP for benzene is 0.291 mm, which corresponds to *ca.* 3400–3500 plates per metre.

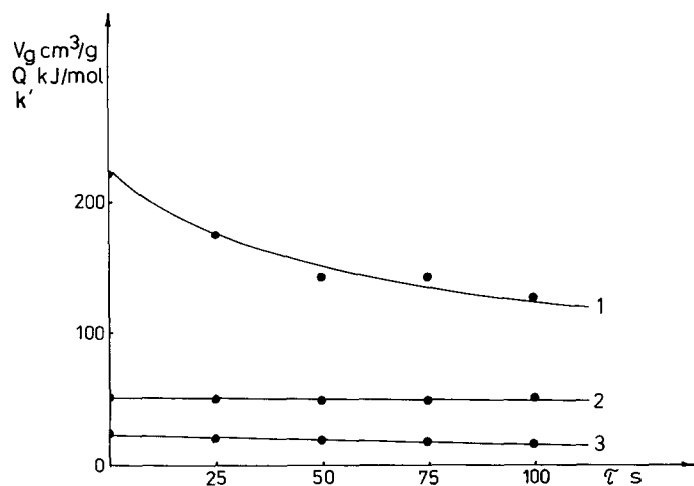


Fig. 2. Plot of (1) specific volumes (V_g), (2) differential heats of adsorption (Q) and (3) capacity factor (k') of benzene vs. time of exposure. Column, $20 \times 0.2 \text{ cm}$ I.D., packed with silica gel ($63\text{--}71 \mu\text{m}$), modified with cyclohexene in plasma. Column temperature, 90°C

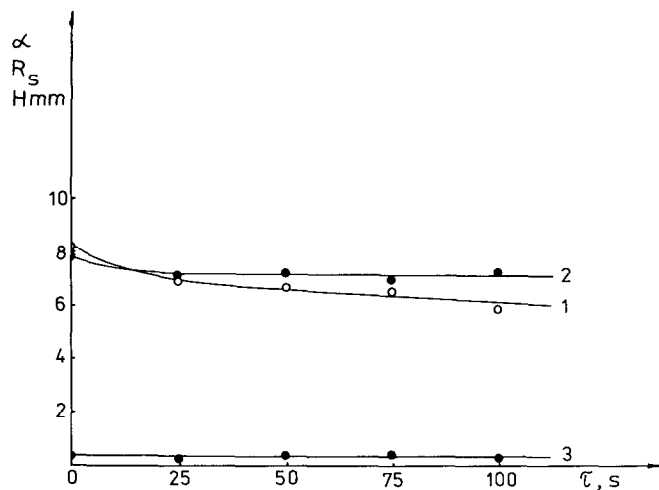


Fig. 3. Dependence of (1) relative retention (α) and (2) resolution (R_s) of benzene-cyclohexane and (3) height of a theoretical plate (H) of benzene on the time of exposure of silica gel (63–71 μm) in plasma. Modifier, cyclohexene; column temperature, 90°C.

Effect of modifier

The influence of the type of modifier on the chromatographic properties of the sorbents is shown in Table I. Fifteen organic compounds from different series were used as modifiers and identical experimental conditions were used for each. The

TABLE I

CHROMATOGRAPHIC CHARACTERISTICS OF SILICA GELS MODIFIED IN PLASMA ($\tau = 25$ s) FOR CYCLOHEXANE AND BENZENE AT 90°C

Modifier	Cyclohexane			Benzene			Benzene-cyclohexane	
	V_g (cm^3/g)	k'	H (mm)	V_g (cm^3/g)	k'	H (mm)	α	R_s
—	26.7	3.2	0.34	219.5	26.3	0.30	8.2	8.0
1-Hexene	23.0	2.8	0.33	161.2	19.9	0.25	7.1	8.2
Cyclohexene	25.4	2.9	—	174.5	19.6	0.25	6.9	6.9
Benzene	26.5	3.4	0.29	206.6	25.9	0.26	7.8	8.4
Ethylbenzene	23.0	2.9	0.32	173.9	21.7	0.29	7.6	7.7
Styrene	24.2	3.1	0.33	175.7	22.3	0.28	7.2	7.8
Methylene chloride	27.7	3.5	0.33	222.7	28.5	0.36	8.2	7.4
Chloroform	25.8	3.0	0.38	208.7	24.3	0.33	8.1	7.4
Carbon tetrachloride	26.3	3.1	0.39	214.4	25.5	0.36	8.0	7.6
1-Propanol	25.3	2.8	0.28	193.9	22.1	0.24	7.8	8.7
1-Butanol	24.7	2.8	0.31	186.3	21.2	0.31	7.5	7.6
Allyl alcohol	23.3	2.9	0.29	154.7	19.0	0.23	6.6	8.4
Acrolein	22.1	2.8	0.39	129.4	16.3	0.33	5.9	8.4
<i>n</i> -Propylamine	23.1	2.8	0.38	121.1	14.7	0.27	5.2	6.9
Di- <i>n</i> -propylamine	27.0	3.0	0.33	162.9	18.4	0.26	6.1	7.6
Pyridine	22.7	2.7	0.41	138.2	16.5	0.32	6.1	6.7

TABLE II

DIFFERENTIAL HEATS OF ADSORPTION OF CYCLOHEXANE AND BENZENE ON SILICA GELS MODIFIED IN PLASMA

Modifier	Q (kJ/mol)		Modifier	Q (kJ/mol)	
	Cyclohexane	Benzene		Cyclohexane	Benzene
No modification	38	50	Carbon tetrachloride	40	59
1-Hexene	38	51	1-Propanol	38	51
Cyclohexene	38	50	1-Butanol	39	50
Benzene	37	52	Allyl alcohol	37	50
Ethylbenzene	38	50	Acrolein	35	47
Styrene	36	48	<i>n</i> -Propylamine	36	48
Methylene chloride	39	53	Di- <i>n</i> -propylamine	37	48
Chloroform	40	51	Pyridine	31	46

reproducibility of the specific retention volumes is $0.8 \text{ cm}^3/\text{g}$ and of the heats of adsorption 1 kJ/mol . The monomer purity was not found to have an observable influence.

It can be seen that cyclohexane, ethylbenzene and styrene have almost equal effects as modifiers. It is interesting that in plasma ethylbenzene and the typical monomer styrene behave in an identical manner. Benzene is a poor modifier than ethylbenzene and styrene, but some weak modification of the silica gel surface and a corresponding change in the chromatographic properties occur.

The chloro derivatives of methane do not show a substantial change in the



Fig. 4. Separation on a column, $20 \times 0.2 \text{ cm}$ I.D., packed with silica gel, modified with pyridine in plasma, $\tau = 25 \text{ s}$, $d_p = 63\text{--}71 \mu\text{m}$, temperature 90°C . Peaks: 1 = Cyclohexane (b.p. 80.7°C); 2 = benzene (b.p. 80.1°C).

Fig. 5. Separation on column, $20 \times 0.2 \text{ cm}$ I.D., packed with silica gel ($63\text{--}71 \mu\text{m}$), modified with pyridine in plasma, $\tau = 25 \text{ s}$, at 150°C . Peaks: 1 = Solvent; 2 = methyl acetate (b.p. 56.9°C ; $\mu = 1.72 \text{ D}$); 3 = acetone (b.p. 56.2°C , $\mu = 2.85 \text{ D}$).



Fig. 6. Separation on a column, 20×0.2 cm I.D., packed with silica gel ($63\text{--}71 \mu\text{m}$), modified with pyridine in plasma, $\tau = 25$ s, at 150°C . Peaks: 1 = Cyclohexane (b.p. 80.7°C ; $\mu = 0$ D); 2 = ethanol (b.p. 78.4°C ; $\mu = 1.68$ D); 3 = ethyl acetate (b.p. 77.2°C ; $\mu = 1.81$ D).

retention of the adsorbates compared with the unmodified silica gel. The differential heats of adsorption however, are higher (Table II).

The action of alcohols used as modifiers is stronger than in previous instances. On the basis of the two alcohols investigated it could be considered that a linear decrease in retention volume occurs, depending on the number of carbon atoms. If a double bond is present in the chain of the alcohol (allyl alcohol) the modifying effect is better than it is for the saturated compound with the same number of carbon atoms.

The only aldehyde studied (acrolein) has the strongest modifying action among the compounds under investigated. Amines and pyridine also have considerable modifying effects. It is interesting that only the sample modified with pyridine in plasma is completely hydrophobic. A qualitative test showed that it has no wettability: all particles of the sample floated, whereas the other samples sank to the bottom in water.

The results show that the modified silica gel can interact with the analysed compounds specifically. Specific interactions arise with both non-polar (Fig. 4) and polar compounds (Figs. 5 and 6). The nature of the modified surface is obviously moderately polar. Hence, if the analysed compounds have close boiling points their separation depends on the difference in their dipole moments (Fig. 5). It can be assumed also that the modification removes interactions such as hydrogen bonding with silanol groups. For instance, ethanol is separated and leaves the column before ethyl acetate, in accordance with its lower polarity (Fig. 6).

If the difference in the boiling points of the separated compounds is large, the difference in the dipole moments cannot change the order of retention. Thus, under the experimental conditions for the chromatograms in Figs. 5 and 6, the retention time of acetone is 5.7 min whereas that of ethyl acetate is 7.8 min.

An example of a separation according to the boiling points only is shown in Fig. 7 and an analysis of a more complicated mixture of hydrocarbons in Fig. 8.

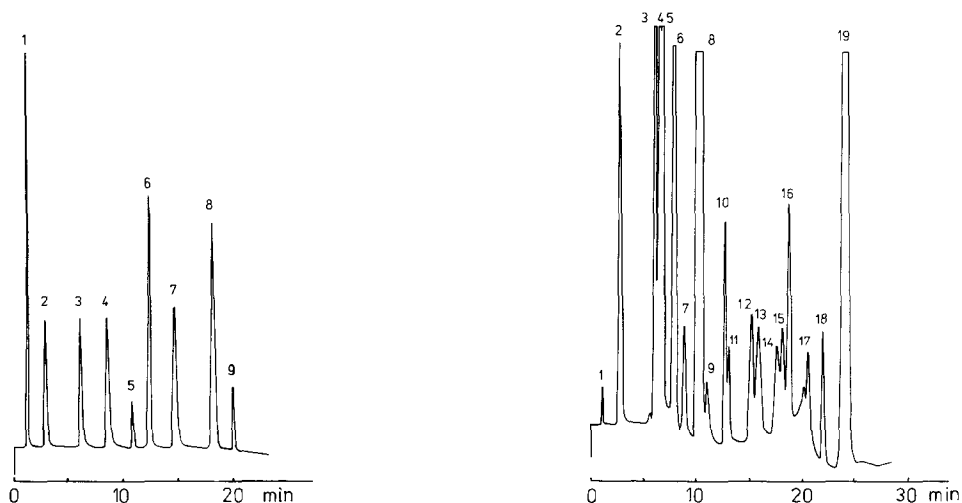


Fig. 7. Analysis of *n*-alkanes (C_5-C_{13}). Peaks: 1 = *n*-pentane; 2 = *n*-hexane; 3 = *n*-heptane; 4 = *n*-octane; 5 = *n*-nonane; 6 = *n*-decane; 7 = *n*-undecane; 8 = *n*-dodecane; 9 = *n*-tridecane. Column, 20×0.2 cm I.D., packed with silica gel ($63-71 \mu m$), modified with cyclohexene in plasma, $\tau = 25$ s. Temperature, programmed from 50 to $150^\circ C$ at $10^\circ C/min$.

Fig. 8. Separation of hydrocarbons. Peaks: 1 = *n*-pentane; 2 = cyclohexane; 3 = *n*-heptane; 4 = 1-hexene; 5 = isooctane; 6 = cyclohexene; 7 = *n*-octane; 8 = benzene; 9 = *n*-nonane; 10 = *n*-decane; 11 = toluene; 12 = *n*-undecane; 13 = ethylbenzene; 14 = *m*- + *p*-xylene; 15 = *o*-xylene; 16 = *n*-dodecane; 17 = *n*-tridecane; 18 = naphthalene; 19 = methylnaphthalene. Column, 20×0.2 cm I.D., packed with silica gel ($63-71 \mu m$), modified in plasma with cyclohexene, $\tau = 25$ s. Temperature, programmed from 50 to $150^\circ C$ at $10^\circ C/min$.

CONCLUSIONS

By using the method of plasma modification with organic vapours it is possible to achieve a small change in the GC properties of silica gel with a decrease in its too strong interactions with analysed compounds. The extent of the change depends on the time of exposure. By changing the modifier the additional effect of forming the properties of the sorbent could be achieved. The sorbents so obtained are very suitable as packings for short packed columns.

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