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EFFECT OF HYDROTHERMAL TREATMENT IN THE PRESENCE OF SALTS ON THE CHROMATOGRAPHIC PROPERTIES OF SILICA GEL

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SUMMARY

The effects of hydrothermal treatment of silica gel in the presence of some inorganic salts on the chromatographic properties of the product have been studied. In addition to the specific surface area and the mean pore diameter, the selectivity and retention properties of the treated silica gel as well as some hydrodynamic properties are also changed. The extent of these changes depended both on the duration of the hydrothermal treatment and on the nature of the salt added. The treatment with phosphate ion solution produced a decrease in the specific pore volume and in the apparent specific weight of the silica gel skeleton, along with significant changes in its selectivity.

INTRODUCTION

The hydrothermal treatment of silica gel[1,2] usually results in the modification of its specific surface area and/or the mean pore diameter. It has been stated in various contexts that the chromatographic properties of silica gel[3–10] and/or other kinds of gel behaviour[11] depend on the so-called history of the particular gel, *e.g.*, the method of its production[10] and the influence of substances with which it comes into contact during routine application. It must therefore be assumed that the influence of inorganic salts, which can alter the rate of hydrothermal treatment, will also be manifested in the properties of the resulting product[12].

Sodium and potassium salts of hydrofluoric, carbonic, boric and orthophosphoric acids were chosen as the inorganic salts. After the hydrothermal treatment, sodium and/or potassium cations, which react with sufficiently acidic surface silanols by ion exchange[13], were washed out with dilute hydrochloric acid. The decrease in the specific surface area of the silica gel was regarded as a measure of the hydrothermal treatment of the starting irregular high-surface-area silica gel. The effects of the change in specific surface area or of the anion used for the hydrothermal treat-

ment on the following characteristics were measured: specific pore volume, mean pore diameter, apparent specific weight of the silica gel skeleton, retention and selectivity properties of the silica gel treated and the hydrodynamic characteristics of the bed. The validity of the selected measurements and tests was verified on several randomly chosen samples of commercial silica gels.

EXPERIMENTAL

Apparatus and materials

The starting material for hydrothermal treatment was a coarser fraction (d_p = 15 μm) of the commercial irregular silica gel Silasorb (Lachema, Brno, Czechoslovakia). A fraction with mean particle diameter 7.5 μm, selected from the same batch, was used as reference sample.

The silica gel was treated with a solution of fluoride, borate, carbonate or orthophosphate under atmospheric pressure at 373 K. The duration of hydrothermal treatment ranged from 20 to 60 min depending on the salt used and on the decrease in specific surface desired. The silica gel was then washed with water, until free from the anion of the salt used and then with diluted hydrochloric acid. Finally it was washed with distilled water until free from chloride.

The system of measurements and tests used for evaluation of the silica gel treated hydrothermally was verified on the initial Silasorb sample and on the following commercial silica gels selected at random: Nucleosil 100-10 (Macherey-Nagel, F.R.G.), Hypersil (Shandon Southern Products, U.K.), Separon SI-VSK (Laboratory Instruments, Prague, Czechoslovakia), LiChrospher Si 100 (E. Merck, F.R.G.) and LiChrosorb Si 60 (E. Merck).

The chromatographic apparatus was described previously[14] and the set-up used for the packing of unpolished stainless-steel columns, 200 × 6 mm, is shown in Fig. 1. The packing procedure, uniform for all silica gels listed in Tables I and V, was a variant of the high-pressure viscosity-filtration technique[15]. The suspension was prepared by stirring of silica gel (7 ml) ultrasonically in 1.5 volumes (10.5 ml) of cyclohexanol–methanol (95:5). After the apparatus had been assembled (Fig. 1), the column outlet (Fig. 2a) was plugged and both the column (9) and the connecting piece (8) were filled with chloroform. The freshly prepared suspension was introduced into the reservoir (7). Then the chloroform was let out of the column, the suspension was overlaid with 1–2 ml of suspending liquid and both the reservoir (7) and the reservoir head (6) were filled with the pressure liquid, a technical mixture of hydrocarbons free from polar impurities. The pressure reservoir (3) was pressurized to the packing pressure of 25 MPa and this pressure was then suddenly applied to the suspension reservoir and during packing was maintained within ±0.3 MPa. The bed was stabilized by washing with the pressure liquid at the maximum output of the pump (about 1.5 l/h) for 1 h. After washing the bed with 250 ml of methanol–denatured ethanol, the column inlet was adjusted for sampling by use of microsyringes[16] (Fig. 2a).

The basic component of the mobile phases was n-hexane (Soyuzkhimexport, U.S.S.R.), to which ethanol (UV-grade) was added at concentrations of 0.7 or 0.05% (v/v). For measurement of the streaming current responses from the sorbent beds[17], butanol p.a. was employed instead of ethanol (both from Lachema) at a concentra-
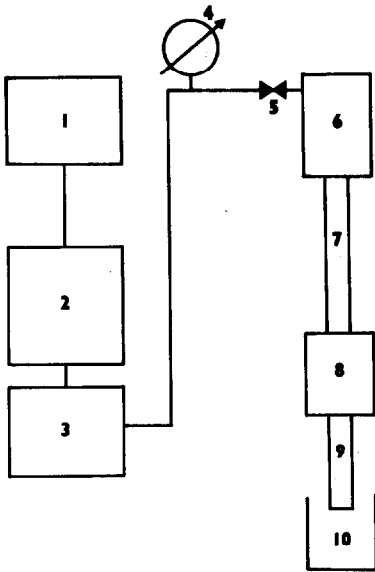
Fig. 1. Diagram of the packing apparatus. 1 = Low-pressure reservoir of pressure liquids; 2 = dual-head membrane pump, Orlita type; 3 = high-pressure reservoir of pressure liquid (volume 2 l); 4 = measurement of pressure; 5 = high-pressure valve; 6 = head of suspension reservoir; 7 = suspension reservoir (500 × 6 mm); 8 = connecting piece; 9 = packed column; 10 = waste.
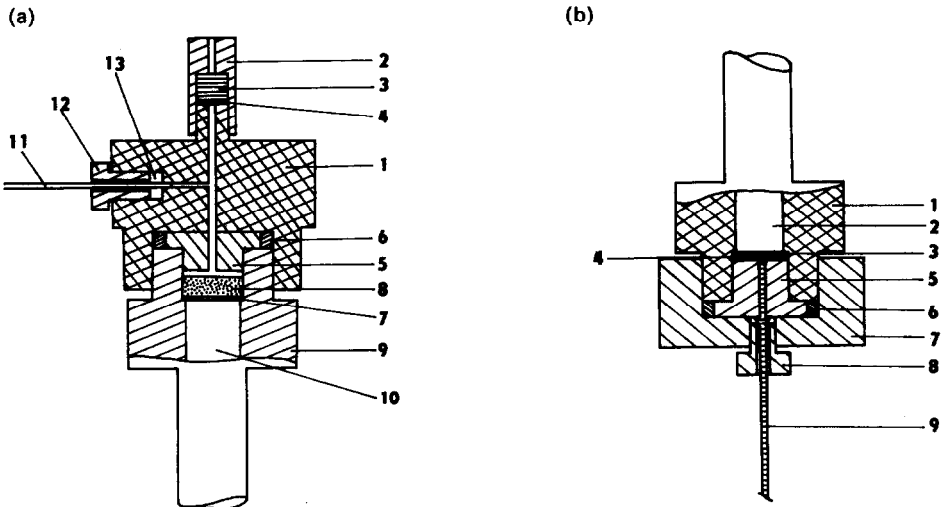

Fig. 2. Detail of the inlet (a) and outlet (b) of the column. (a) 1 = Injector body; 2 = needle guide; 3 = soft silicone rubber; 4 = hard hydrocarbon-resistant rubber; 5 = PTFE inlet seal; 6 = supporting ring; 7 = filter-paper; 8 = glass beds; 9 = column; 10 = silica gel bed; 11 = inlet capillary; 12 = screw; 13 = PTFE seal. (b) 1 = Column; 2 = silica gel bed; 3 = filter-paper; 4 = stainless-steel cloth; 5 = PTFE outlet seal; 6 = supporting ring; 7 = nut; 8 = screw; 9 = outlet capillary.

tion of 5% (v/v). Before use, the hexane was cleaned and dried by passing through an alumina bed. The alumina was activated for 8 h at 623 K. The alcohols were added to the mobile phase without drying. The dead volumes were measured using n-octane p.a. (Loba-Chemie, Austria) as a solute. The streaming current responses were generated by butanol injections. Nitrobenzene (NB), m-dinitrobenzene (DNB) and 2,4,6-trinitrotoluene (TNT) dissolved in the mobile phase with the addition of benzene (B) were used for the evaluation of column efficiency. Two other model mixtures were employed for the retention and selectivity evaluation. The mixture of oxygen-containing compounds consisted of anisole (AN), acetophenone (AP), o-hydroxyacetophenone (HAP), dimethyl phthalate (DMP) and 3-nitroacetophenone (NAP). The mixture of nitrogen-containing compounds was made up of diphenylamine (DPA), 2-bromopyridine (BP) and carbazole (CB). These model mixtures were dissolved in the mobile phase with the addition of ethanol. The samples were injected into the mobile phase stream with syringes.

The specific surface areas of the adsorbents were measured by the dynamic method of nitrogen heat desorption[18] using alumina as the standard ($S = 203$ m²/g). The specific pore volumes, mean pore diameters, apparent specific weights of the silica gel skeleton, exclusion bed volumes and mobile phase volumes inside the sorbent particles were calculated from the retention volumes of the streaming current responses generated by butanol injections[14].

Measurement procedure and evaluation of results

Each column was weighed prior to packing. After packing, the column was equilibrated with a mobile phase containing 0.7% of ethanol. Its dead volume, the dependence of its efficiency on the mobile phase flow-rate and the retention data for all model solutes were then measured. Finally the column was washed with 250 ml of dried, freshly distilled acetone and equilibrated with a mobile phase containing 0.05% of ethanol. The course of equilibration was always monitored by injecting the nitro derivatives used for measuring the column efficiency. The column dead volume and the retention characteristics were again measured. After washing the column with hexane–butanol (95:5), the exclusion column volume and the elution volume of the butanol vacant response[14] were measured using the streaming current detection. The column was then dried in a nitrogen stream at 160–190°C and weighed.

The reduced height equivalent to a theoretical plate, h, and the reduced linear velocity of the mobile phase, v, were calculated in the usual way. The retention time of the non-retained mobile phase component[19], measured by injection of n-octane[14], was considered as the dead retention time. The diffusion coefficients of solutes in the mobile phase, D_m, were determined from the Wilke–Chang equation[20]. The capacity factors were calculated from the retention times at the peaks and then normalized to 1000 m² of the sorbing surface. During normalization, the measured capacity factors were multiplied by the correction factor $10^3/S_t$, where S_t is the total surface area of the silica gel in the column. The values of S_t are given in Tables IV and VIII.

The volume of liquid phase in the interparticle space of the silica gel bed (exclusion volume) is equal to the elution volume of the exclusion streaming current response, V_E[14,21]. The volume of the liquid in the pores of the silica gel bed, V_I, is equal to the difference between the elution volumes of the butanol vacant response[14],

V_V, and of the exclusion streaming current response[14]:

$$V_I = V_V - V_E \tag{1}$$

For the specific pore volume, V_p, the following relationship holds:

$$V_p = \frac{1}{G}(V_V - V_E) \tag{2}$$

The weight of the silica gel in the column, G, was determined from the weight of the empty column and the weight of the packed column after evaporation of the hexane–butanol mobile phase. The mean pore diameter, D, was calculated from[22]

$$D = \frac{4 V_p}{S} \cdot 10^{-3} \tag{3}$$

using the measured specific surface areas, S. After substituting V_p (cm^3/g) and S (m^2/g) in eqn. 3, the mean pore diameter is obtained in nm[23]. The apparent specific weight of the silica gel skeleton, ρ, was calculated from the relationship[14]

$$\rho = \frac{G}{V_0 - V_V} \tag{4}$$

where V_0 is the volume of the empty column. Columns with $V_0 = 5.65$ ml were used.

Choice of tests

For the measurements, columns of 200 mm in length and of 6 mm in diameter were chosen. Larger columns are convenient for measuring the elution volumes of streaming current responses, from which some characteristics of hydrothermally treated silica gels were calculated. Furthermore, when measuring the efficiency of such columns, the apparatus band broadening is less important. The contribution to band broadening caused by dispersions in the connections and the detector cell of the Variscan spectrophotometer (Fig. 3) was measured by the method described[24]. Its extrapolated value, used for the correction of variances read from the chromatograms, was $140 \cdot 10^{-6}$ cm^6. The correction was negligible for packings with $d_p = 10$ μm. In the case of finer grain sizes it was significant only at mobile phase velocities close to the optimum.

The test mixtures were chosen so as to obtain symmetrical peaks in the measurements involving the mobile phase containing 0.7% of ethanol. Solutes with small molecules were preferred in order to avoid any distortion of the retention measurement by steric exclusion effects[14,25].

A mixture of nitroderivatives was chosen for measuring the efficiency. All its components have groups of equal polarity which interact with the stationary phase primarily by dipole interaction[26,27]. Their peaks can therefore be expected to be symmetrical on all samples of silica gels, even with a lower content of ethanol in the mobile phase. The oxygen-containing solutes were used to compare the differences in selective interaction attributed to surface silanols. Therefore, they were chosen so
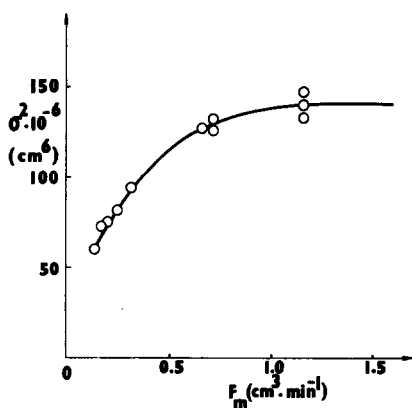
Fig. 3. Flow dependence of the band broadening caused by the Variscan spectrophotometer.

as to contain various oxyen functional groups and their combinations. The nitrogen-containing compounds were used chiefly for evaluation of the differences in the acidity of the surfaces[28,29].

The loss in column efficiency at linear mobile phase velocities exceeding the optimum value is reflected in the magnitude of the C term in the Van Deemter equation. In view of the considerable internal diameter of the columns used (6 mm), however, it was not possible to measure the flow dependence of the column efficiency over a sufficiently wide range of linear mobile phase velocities, necessary for an accurate determination of this constant. Therefore another criterion was chosen to express the loss in column efficiency: the increase in the reduced height equivalent to a theoretical plate, Δh, induced by an increase in the reduced mobile phase velocity, v, to three times that of the reduced optimum velocity of the mobile phase, v_{opt}. This criterion is sufficient for a mutual comparison of the packings, and, moreover, clearly illustrates the changes in column efficiency in the range of flow-rates of most practical interest.

The specific surface areas of the silica gels, and in the case of commercial preparations also their weights in the bed, exhibited significant differences (Tables I, IV and V). A direct comparison of the measured capacity factors would give a distorted picture of the sorption properties of the surfaces of the silica gels studied. Therefore, the measured capacity factors were normalized to an equal area of the sorbent surface, 1000 m².

The purpose of all the tests chosen was to express the differences in retention properties, selectivity properties and the geometrical characteristics of silica gels, as well as in the efficiency of their beds, caused by treatment of the silica gels with solutions of different salts, or with a single salt for various durations. It was therefore necessary to verify the effectiveness of the whole series of tests. Silica gels from different manufacturers, differing in shape and declared geometrical characteristics (specific surface area, specific pore volume, mean pore diameter), were chosen. Obviously, at least some of them must have been produced by different technological procedures.

The results which characterize the selected commercial silica gels and their beds are presented in Tables I–IV. As is seen, differences in the measured characteristics,

TABLE I

CHARACTERISTICS OF COMMERCIAL PACKINGS

sph = Spherical, irr = irregular.

Sorbent	Particle shape	d_p* (μm)	S (m^2/g)		V_p (cm^3/g)		D (nm)		ρ (g/cm^3)***
			cert.**	exptl.	cert.**	exptl.	cert.**	exptl.	
Nucleosil	sph	10	300	380	1.0	0.7	10	7.4	2.3
Hypersil	sph	5	200	200	–	0.7	10	14	2.4
Separon	sph	10	450	470	1.5	1.5	–	13	2.2
LiChrospher	sph	10	250	540	1.2	1.2	10	10	1.8
LiChrosorb	irr	10	550	590	–	0.7	6	4.8	1.8
			400		0.8		6		
Silasorb	irr	7.5	500	520	0.7–0.8	0.6	–	4.3	1.8

* Declared mean particle diameter.
** Declared values for Nucleosil, Hypersil and LiChrospher from ref. 31; for LiChrosorb the first values are from ref. 30, the second from ref. 10. Declared data for Separon and Silasorb are those given by the suppliers.
*** Apparent specific weight of the silica gel skeleton.

expected at least in some of the preparations, were found to occur between all the samples. The suitability of the technique used for measuring the geometrical characteristics of the silica gels had been demonstrated previously[14].

RESULTS

Properties of the silica gels

The influence of the duration of the hydrothermal treatment of the silica gel by an aqueous solution containing only one anion on the chromatographically important properties of the adsorbents and their beds was studied with a series of samples designated as Q15. The effect of the nature of the anion used in the hydro-

TABLE II

RELATIVE RETENTIONS ON COMMERCIAL SILICA GELS ELUTED BY HEXANE MODERATED WITH 0.7% ETHANOL

Figures in parentheses indicate capacity factors normalized to 1000 m^2 of the sorbent surface used as reference for the given group of solutes.

Sorbent	Nitro derivatives			Nitrogen-containing compounds			Oxygen-containing compounds				
	NB	TNT	DNB	DPA	BP	CB	AN	HAP	AP	DMP	NAP
Nucleosil	(0.27)	2.7	3.9	(0.32)	2.3	5.5	0.14	0.56	(0.44)	2.6	3.0
Hypersil	(0.45)	2.5	3.7	(0.48)	2.7	5.9	0.17	0.60	(0.75)	2.5	3.9
Separon	(0.40)	2.5	3.6	(0.44)	2.6	5.0	0.11	0.55	(0.62)	2.6	3.0
LiChrospher	(0.30)	2.7	4.4	(0.41)	2.4	5.8	0.12	0.54	(0.54)	2.7	3.2
LiChrosorb	(0.27)	2.6	4.8	(0.41)	2.8	5.9	0.10	0.53	(0.54)	2.6	3.8
Silasorb	(0.28)	2.8	4.8	(0.35)	2.7	4.1	0.098	0.54	(0.52)	2.7	3.0

TABLE III

RELATIVE RETENTIONS ON COMMERCIAL SILICA GELS ELUTED BY HEXANE MODERATED WITH 0.05% ETHANOL

Figures in parentheses indicate capacity factors normalized to 1000 m² of the sorbent surface used as reference for the given group of solutes.

Sorbent	Nitro derivatives			Nitrogen-containing compounds			Oxygen-containing compounds				
	NB	TNT	DNB	DPA	BP	CB	AN	HAP	AP	DMP	NAP
Nucleosil	(1.1)	8.8	7.8	(1.5)	5.7	3.7	0.082	0.43	(6.7)	3.5	>3.8
Hypersil	(1.9)	8.3	7.3	(2.2)	7.6	3.8	0.078	0.41	(8.6)	4.5	6.6
Separon	(1.7)	9.1	7.5	(2.2)	5.8	4.1	0.075	0.48	(9.6)	3.9	6.3
LiChrospher	(1.7)	13.0	9.7	(2.9)	4.5	2.5	0.085	0.40	(6.8)	2.6	6.5
LiChrosorb	(1.0)	8.6	8.2	(1.4)	5.6	4.4	0.074	0.39	(4.8)	4.2	>6.5
Silasorb	(1.0)	8.2	7.7	(1.4)	5.3	4.5	0.075	0.39	(4.5)	4.1	>7.9

TABLE IV

CHARACTERISTICS OF COMMERCIAL SILICA GEL BEDS

G = Weight of sorbent in the 200×6 mm bed; S_t = total sorbent surface in bed, $S_t = SG$; V_E = exclusion volume of bed; V_I = volume of mobile phase inside the particles of the packing; h_{opt} = reduced height equivalent to a theoretical plate measured at the optimum reduced linear velocity of the mobile phase, v_{opt}; Δh = increase in h caused by increasing v from v_{opt} to $3v_{opt}$.

Sorbent	G (g)	S_t (m²)	V_E (ml)	V_I (ml)	Benzene			m-Dinitrobenzene		
					v_{opt}	h_{opt}	Δh	v_{opt}	h_{opt}	Δh
Nucleosil	3.16	1191	2.11	2.15	5.5	2.0	3.1	4.7	4.1	1.5
Hypersil	3.22	631	2.19	2.11	2.3	2.1	2.2	4.5	3.8	3.2
Separon	1.97	916	2.07	2.88	5.0	2.0	3.5	5.0	2.4	2.6
LiChrospher	2.03	1089	2.13	2.38	4.5	1.8	4.7	5.0	2.2	2.4
LiChrosorb	2.74	1622	2.33	1.88	5.2	2.5	1.4	4.3	3.1	1.8
Silasorb	3.02	1570	2.26	1.70	4.0	2.0	1.3	7.5	3.3	1.8

TABLE V

CHARACTERISTICS OF HYDROTHERMALLY TREATED SILICA GELS

S = Specific surface area; V_p = specific pore volume; D = mean pore diameter; ρ = apparent specific weight of the silica gel skeleton.

Sorbent	Modifying ion	S (m²/g)	V_p (cm³/g)	D (nm)	ρ (g/cm³)
Silasorb	—	520	0.6	4.3	1.8
Q15-2AW	F^-	450	0.6	5.4	2.0
Q15-6AW	F^-	290	0.6	8.3	1.9
Q15-10AW	F^-	190	0.6	13	2.0
P129-3AW	F^-	290	0.6	8.3	2.0
P129-5AW	$H_2BO_3^-$	290	0.6	8.3	2.0
P129-7AW	CO_3^{2-}	290	0.6	8.3	1.9
P129-8AW	PO_4^{3-}	290	0.5	8.3	1.6

thermal treatment was investigated in the sample series P129. When treating the silica gels with different anions, the duration of treatment was chosen so as to attain approximately the same value of the specific surface area.

It follows from Table V that during the hydrothermal modification of the specific surface area of irregular silica gel in aqueous solutions of inorganic salts, the specific pore volume varied only when phosphate was used for the modification. The increase in the apparent specific weight of the silica gel skeleton, ρ, following the hydrothermal treatment with fluoride, carbonate and borate solutions can most readily be explained by the extinction of micropores inaccessible to the molecules of the mobile phase[31]. When measuring the quantity ρ using the method described[14], their volume is included in the volume of the bed occupied by the silica gel skeleton and the calculated apparent specific weight, ρ, must therefore, be lower than the real one. The cause of the decrease ρ in the case of the silica gel treated with the aqueous solution of phosphate buffer, pH $\approx$ 7, cannot be stated unambiguously on the basis of the tests performed. However, in view of the differences in retention properties of the silica gel washed with hydrochloric acid and of the same sample washed additionally with phosphate buffer, as described[11], and on the basis of some other yet unpublished findings, we assume that a chemical reaction takes place between the phosphate ions and the surface of the silica gel. This is in accord with the formation of a highly stable complex of phosphoric acid with surface silanol groups[32]. When other strong inorganic acids are added, the complex is produced even at room temperature[32]. At higher temperatures the silica gel dissolves in excess of orthophosphoric acid, even without adding another acid[33]. Depending on the reaction conditions, silicon phosphates or pyrophosphates of different compositions are produced.

The differences found in both the absolute and relative retentions are distinctly smaller in the mobile phase containing 0.7% ethanol than in the mobile phase containing lower alcohol concentrations (Tables VI, VII). Similar behaviour was found on the commercial silica gels (Tables II, III). If the alcohol content in the mobile phase is reduced from 0.7 to 0.05%, but the silica gel bed is not dried with acetone, then the absolute as well as the relative retentions of the solutes remain almost un-

TABLE VI

RELATIVE RETENTIONS ON HYDROTHERMALLY TREATED SILASORBS ELUTED BY HEXANE MODERATED WITH 0.7% ETHANOL

Figures in parentheses indicate capacity factors normalized to 1000 m^2 of the sorbent surface used as reference for the given group of solutes.

Sorbent	Nitro derivatives			Nitrogen-containing compounds			Oxygen-containing compounds				
	NB	TNT	DNB	DPA	BP	CB	AN	HAP	AP	DMP	NAP
Silasorb	(0.28)	2.8	4.8	(0.35)	2.7	4.1	0.098	0.54	(0.52)	2.7	3.0
Q15-2AW	(0.37)	2.4	3.4	(0.40)	2.9	4.2	0.14	0.57	(0.56)	2.6	3.0
Q15-6AW	(0.43)	2.4	3.3	(0.50)	2.4	4.0	0.12	0.56	(0.62)	2.6	3.0
Q15-10AW	(0.42)	2.7	5.0	(0.56)	2.5	5.9	0.20	0.59	(0.82)	2.4	3.2
P129-3AW	(0.39)	2.7	5.7	(0.50)	2.8	6.1	0.12	0.54	(0.68)	2.6	3.8
P129-5AW	(0.40)	2.7	5.5	(0.53)	3.2	6.0	0.13	0.51	(0.70)	2.5	3.8
P129-7AW	(0.40)	2.7	5.4	(0.54)	2.7	6.0	0.11	0.54	(0.70)	2.6	3.7
P129-8AW	(0.43)	2.6	5.4	(0.60)	2.8	6.2	0.15	0.57	(0.79)	2.5	3.8

TABLE VII

RELATIVE RETENTIONS ON HYDROTHERMALLY TREATED SILASORBS ELUTED BY HEXANE MODERATED WITH 0.05% ETHANOL

Figures in parentheses indicate capacity factors normalized to 1000 m² of the sorbent surface used as reference for the given group of solutes.

Sorbent	Nitro derivatives			Nitrogen-containing compounds			Oxygen-containing compounds				
	NB	TNT	DNB	DPA	BP	CB	AN	HAP	AP	DMP	NAP
Silasorb	(1.0)	8.2	7.7	(1.4)	5.3	4.5	0.075	0.39	(4.5)	4.1	7.9
Q15-2AW	(1.1)	8.6	7.9	(0.88)	5.4	4.4	0.076	0.39	(5.7)	3.9	6.3
Q15-6AW	(1.3)	9.2	8.3	(1.9)	5.1	4.3	0.079	0.38	(5.6)	4.0	6.5
Q15-10AW	(1.2)	11.0	9.9	(2.2)	5.0	4.5	0.084	0.40	(6.8)	4.0	6.2
P129-3AW	(1.3)	8.2	8.2	(2.0)	5.3	4.7	0.093	0.40	(5.8)	4.0	6.2
P129-5AW	(1.3)	8.2	7.8	(2.5)	3.1	3.1	0.094	0.45	(7.0)	3.5	6.0
P129-7AW	(1.3)	8.5	7.8	(2.1)	4.2	5.4	0.062	0.38	(5.9)	4.0	4.7
P129-8AW	(1.2)	7.3	7.2	(1.6)	5.0	4.2	0.096	0.41	(4.1)	1.9	2.7

changed. This is accounted for by the deactivation of the silica gel surface by water adsorbed from the mobile phase containing 0.7% ethanol. Polar acetone, which has an unlimited ability to dissolve water, causes a very rapid drying of the column. In the mobile phase containing 0.05% ethanol, high retentions are established after washing the column with about fifty times the dead volume and remain constant during the whole measurement.

Properties of the beds

For the silica gel with a declared mean particle size of 15 μm, the hydrothermal treatment under different conditions did not produce any measurable differences in the volume of mobile phase in the interparticle space. Likewise, there was hardly any change in the volume of liquid phase inside the sorbent particles. Only on application of the neutral phosphate buffer was it reduced by 0.4 ml compared with the other beds, although the amount of sorbent in the column was diminished by only 0.1–0.2 g. This decrease in V_1 was manifested also in a smaller specific pore volume of the resulting product (Table V). The surface reaction of phosphate ions with the silica gel, considered earlier in connection with the decrease in the apparent specific weight of the skeleton of this sample, might again be responsible for the above behaviour.

The small differences in the volume of liquid phase in the interparticle space of the beds of hydrothermally treated samples, as well as the high reproducibility of the amounts of differently treated silica gels in the bed with dimensions of 200 × 6 mm are, among other things, determined by an effectiveness and reproducibility of the column-packing technique. Nevertheless, the h values at the minimum of Van Deemter's curve are surprisingly low. The mean particle diameter was not determined after the hydrothermal treatment. Therefore, we cannot say whether the observed high bed efficiencies are produced by a relatively narrow distribution of the particles of the coarser silica gel, or by a change in the mean particle diameter due to the hydrothermal treatment. In the treated samples, $h_{opt} \approx 2$ for $d_p = 12.5$ μm. Even in that case, however, the Δh values measured would remain lower than for the starting silica gel (Table VIII).

TABLE VIII

CHARACTERISTICS OF BEDS OF THE HYDROTHERMALLY TREATED SILASORBS

Details as in Table IV.

Sorbent	G (g)	S_t (m²)	V_E (ml)	V_I (ml)	Benzene			m-Dinitrobenzene		
					v_{opt}	h_{opt}	Δh	v_{opt}	h_{opt}	Δh
Silasorb	3.02	1570	2.26	1.70	4.0	2.0	1.3	7.5	3.3	1.8
Q15-2AW	2.79	1250	2.73	1.50	7.0	1.7	0.9	6.5	2.0	1.2
Q15-6AW	2.72	792	2.68	1.57	4.7	1.4	0.8	4.5	1.6	1.2
Q15-10AW	2.70	510	2.67	1.63	6.3	1.7	0.9	3.5	2.0	0.8
P129-3AW	2.69	769	2.65	1.67	4.8	1.6	0.4	6.0	2.4	1.2
P129-5AW	2.70	791	2.79	1.50	5.0	1.6	0.8	6.2	2.4	1.6
P129-7AW	2.68	766	2.67	1.59	5.5	1.8	0.5	7.0	2.7	1.6
P129-8AW	2.59	761	2.72	1.26	5.5	1.4	1.2	5.1	2.0	1.6

The measurements of efficiency indicate that the hydrodynamic properties of the column as characterized by h_{opt} and Δh (and/or their sum) were improved upon hydrothermal treatment of irregular silica gel. The lower the specific surface area of the sorbent after the treatment with fluoride solution, the better were the properties of its bed in terms of the magnitude of Δh. When the specific surface area was normalized, fluoride ions were the most effective in decreasing Δh. The rather poor quality of the initial preparation cannot be regarded as causing a smaller decrease in the efficiency of the hydrothermally treated silica gel beds. As regards the maximum possible bed efficiency, h_{opt}, and the loss in bed efficiency, Δh, the Silasorb used was equivalent to the LiChrosorb sample, and both these irregular silica gels were at least comparable with the spherical silica gels (Fig. 4, Table IV).

Lower efficiency losses were also found for two laboratory samples of spherical silica gel, examined under other circumstances (Fig. 5). Noteworthy is the fact that
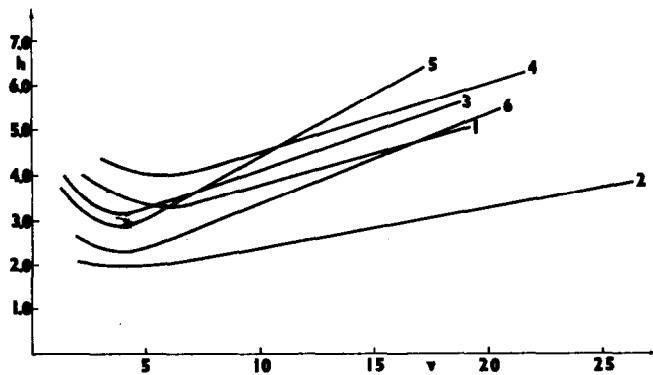

Fig. 4. Flow dependences of the bed efficiency of some commercial silica gels and Silasorb hydrothermally treated with fluoride solution. Solute = m-dinitrobenzene. Curves: 1, Silasorb before hydrothermal treatment; 2, Silasorb after hydrothermal treatment; 3, LiChrosorb; 4, Nucleosil; 5, Hypersil; 6, LiChrospher.
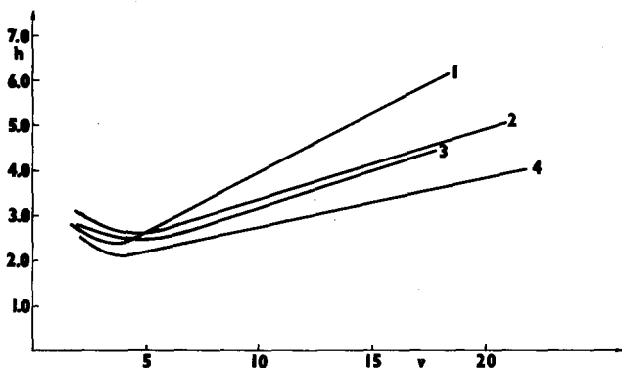
Fig. 5. Effect of hydrothermal treatment of laboratory samples of spherical gels on the bed efficiency. Solute = m-dinitrobenzene. Curves: 1, sample A before hydrothermal treatment (specific surface area, $S = 510$ m^2/g; specific pore volume, $V_P = 1.0$ cm^3/g; mean pore diameter, $D = 8.1$ nm); 2, sample A after hydrothermal treatment ($S = 280$ m^2/g, $V_P = 1.2$ cm^3/g, $D = 17$ nm); 3, sample B before hydrothermal treatment ($S = 300$ m^2/g, $V_P = 1.8$ cm^3/g, $D = 24$ nm); 4, sample B after hydrothermal treatment ($S = 250$ m^2/g, $V_P = 2.0$ cm^3/g, $D = 32$ nm).

after the treatment with the fluoride ion solution, Δh decreased even for a sample with an initial specific surface area of 300 m^2/g and a pore volume of 1.8 cm^3/g. According to the commonly used relationship 3, the mean pore diameter corresponding to these values is 24 nm.

DISCUSSION

At the moment no integrated set of generally recognized and accepted quantitative criteria is available for a comprehensive evaluation of silica gel as a chromatographic material. The limiting bed efficiency for a non-retained solute under ideal conditions, $h_{opt} \approx 2$ for v lying in the range 3–6, is the only quantitatively determined and generally accepted criterion. There are recommendations concerning the loss in bed efficiency with increasing linear velocity of the mobile phase, expressed by the magnitude of the C term in Van Deemter's equation (C of the order of 10^{-3})[34], of the mean pore diameter ($D \geqslant 6$ nm)[10] or of the specific pore volume (V_P not exceeding 1 cm^3/g for conventional silica gels)[35]. However, no criteria are available for the evaluation of the retention and selectivity properties of silica gels.

The set of measurements used in the present study was chosen so as to provide information, with minimum expenditure of time and effort, about those characteristics of silica gels or their beds which can be regarded, on the basis of theoretical studies, practical experience or traditional views, as chromatographically important. Chromatographic measurements were preferred. The numerical data summarized in this study are only one means of evaluating the occurrence and extent of changes caused by the hydrothermal treatment of silica gels with aqueous solutions of different salts. They are not meant to be instrumental in drawing conclusions concerning the suitability of the silica gels for practical uses or their quality.

The method of measuring efficiency applied is based on that proposed by Bristow and Knox[34]. The results (Table VIII) show that the hydrothermal treatment of

Silasorb with salt solutions always improved the attainable bed efficiency for the sorbed solutes. The extent of improvement depended on the particular salt anion. Silica gel can thus be treated even after sieving. Of note are the decrease in Δh caused by the hydrothermal treatment and the dependence of the magnitude of this decrease on the particular salt anion. Although the decrease in Δh was found also with two laboratory samples of spherical silica gel (Fig. 5), a closer examination of the effect of the hydrothermal treatment on the magnitude of the C term in Van Deemter's equation is necessary before the hydrothermal treatment in the presence of salts may be declared as a process suited to improve the migration of the solutes inside the sorbent particles.

The data in Tables V and VIII seemingly imply that the decrease in Δh occurring with the beds of silica gels whose specific surface area was diminished by treatment in the fluoride solution is caused by an increase in the mean pore diameter. However, it is evident from the data summarized in Tables I and IV, as well as from the decrease in Δh for the spherical laboratory preparation initially having $D = 24$ nm (Fig. 5), that there is no straightforward relationship between D and Δh. Also, a greater mean pore diameter by itself is no guarantee of better hydrodynamic properties of the bed at higher linear velocities of the mobile phase. The measurements obtained show that it is possible, at the same reduced mobile phase velocities, that two silica gels having the same particle shape and the same mean pore diameter differ in the magnitude of Δh, or that the bed of material having smaller D is distinctly more effective. Mere differences in the magnitudes of the mean pore diameter cannot explain why both the irregular silica gels, LiChrosorb and Silasorb, exhibited a lower Δh than did some spherical silica gels. At the same time, the mean pore diameter found for the two irregular types of silica gel was below the 6-nm limit considered to be essential for high bed efficiency[10]. None of these facts can be satisfactorily explained only on the basis of the measurements taken and existing knowledge. It is obvious, however, that a modification of the surface, associated with the hydrothermal treatment in aqueous solutions of the salts, improves the conditions for solute migration inside the particles of the sorbent. The effects of the different anions might be connected with the mechanism of this modification, or with irreversible interactions of the anions present in the solution with the surface of the silica gel. The differences in selectivity properties of the silica gels treated with solutions of salts containing diverse anions seem to be in accord with the latter possibility.

As is seen, qualitative judgements concerning the conditions of solute transport in the particles of different silica gels, in the range of D values usually exhibited by chromatographic silica gels, also cannot be made from the magnitudes of the mean pore diameter (at least from the values obtained by the procedure[22,23] used in the present work).

It is commonly accepted that the structure of the silica gel surface changes during modification. Hence, upon hydrothermal treatment involving a certain salt solution, the relative retentions of the solutes would also be expected to vary to some extent with the decreasing specific surface area. However, there are surprising differences in retentions, and especially in relative retentions, the decrease in the specific surface being the same upon treatment with solutions of different salts (series P129). The relatively small differences between the samples treated with fluoride, carbonate or borate solutions might perhaps be explained as being due to differences in the

rates of decrease of the silica gel specific surface area in the solutions of these salts. However, the substantially more marked differences found with the sample treated with the phosphate medium cannot be so explained. As with specific pore volume and specific skeleton weight, the retention also suggests that, during the hydrothermal treatment, phosphate ions react with silica gel. This is in agreement with some previous measurements[11].

The duration of hydrothermal treatment of the tested samples varied in the order of tens of minutes. The kinetics of the reaction of phosphate ion with the silica gel is unknown. However, the reaction of silica gel with phosphate ions may take place also at room temperature, and is expected[32] to increase in rate with increasing mobile phase acidity. Taking into consideration the proposed mechanism of degradation of silica gel in a phosphoric acid medium[32], it is probable that the phosphoric acid buffers not only alter, through their chemical action, the selectivity of the silica gel, but also unfavourable affect the lifetime of the chemically bound stationary phases.

As a whole, the measurements demonstrate that the hydrothermal treatment with salt solutions exerts a considerable influence on all the chromatographically important properties of silica gel. The extent of this influence depends not only on the decrease in the specific surface area, but also on the anion of the salt added.

The hydrothermal treatment invariably has a positive influence on the transport of solutes in the sorbent particles. As for the mobile phase linear velocities, of practical importance, the dependence of the bed efficiency on the linear velocity decreases. In this respect, fluoride appeared to be the most effective among the anions tested. The effect on the bed efficiency at the optimum mobile phase velocity probably depends on the mean pore diameter of the silica gel before the treatment. With the irregular Silasorb which possesses a small mean pore diameter ($D = 4.3$ nm), the bed efficiency was improved in all cases tested, but remained unchanged in the case of spherical gels having the initial D values greater than 10 nm.

The practical impact and importance of the changes in selectivity properties induced by the hydrothermal treatment cannot generally be evaluated on the basis of the present measurements. It is evident, however, that the interaction of silica gel with salt solutes during its production, especially at elevated temperatures, is one of the factors responsible for the familiar differences in selectivity properties of commercial silica gels. Further changes in the retention and selectivity properties may take place if aqueous or aqueous–organic solutions of salts are used as mobile phases.

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