WIDE-POROSITY SILICAS FOR HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

The possibility of using wide-porosity micro-spherical silica gels (MS), obtained by hydrothermal modification, as packing materials for high-performance liquid chromatography (HPLC), has been studied. The systems obtained were applied in both normal-phase and reversed-phase HPLC. In the first, linear dependence of retention factor (k) on specific surface area was observed. In the second, this dependence is too far from linearity and can be explained by inaccessibility of part of the MS surface to molecules of modifier.

INTRODUCTION

Wide-porosity silica gels are mainly obtained by of two methods:
1. hydrothermal modification of the porous structure of medium-porosity silica gels
2. sol–gel technology on the basis of silica sols with large spherical particles.

The second method is rather complicated, because of the need to use silica sols with mono-disperse particles larger than 100 nm in diameter.

It is impossible to achieve silica skeleton harshness of the silica gels required for application in HPLC regimes during the preparation of wide-porosity silica gels on the basis of silica sols. This is especially important during the packing of columns when pressures reach 500–700 bar. A silica skeleton composed of large particles is usually characterized by a loose structure, owing to the small number of contacts between structure-forming particles. With increasing particle size the probability of formation of several siloxane bonds at the points of contact between particles decreases, which also causes structure loosening. It is necessary to note also that the obtaining silica sols with large particles is a rather complicated and laborious process. It is necessary to introduce armouring additives such as

"active silica" which increase the polydispersity of the system and reinforce their structure [1]. The silica gels obtained from this process usually have a loose structure, which restrict their range of usage. The first method is simpler and more reliable. By correct organization of the process wide-porosity silica gels with the required characteristics can be obtained. Apparently, the optimum combination of porous structure properties of the initial silica gels (including pore size distribution) and hydrothermal treatment conditions (temperature and duration of treatment, suspension pH) is necessary to obtain silica gels with sufficiently sharp pore-size distribution.

The principles of hydrothermal modification of the porous characteristics of silica, discovered by Mills and Hindin [2] in the first half of the last century, were developed somewhat later – during the nineteen-sixties and seventies. At the same time major theoretical advances explaining the mechanism of change of the porous characteristics under the action of hydrothermal treatment (HT) also occurred. Although the theories suggested could not always describe adequately the real picture of the changes in structure characteristics of the porous materials under HT, during that period much experience was accumulated in the field of preparation of wide-porosity systems, including silica gels [3–10].

It is possible to control properties such as pore diameter, pore-size distribution (PSD), and specific surface area by hydrothermal treatment. Although the main work on HT of silica gel was accomplished a rather long time ago, the method is still used to obtain wide-porosity silica gels [11–15].

Favourable conditions for processes performed in aqueous media are high pressure at temperatures near 200°C [16,17]. Solubility of the amorphous silica mainly depends on the sizes of the initial particles of the silica skeleton [1]. The rate of dissolution of the structure-forming silica particles of colloidal size is proportional to their specific surface areas. The curvature of the silica–water interface determines the solubility. Lower surface curvature results in higher local solubility. The solubility change for amorphous silica is linearly dependent on temperature. Maximum values are observed at 200°C.

EXPERIMENTAL

Experiments were conducted on mid-porosity silica gel of specific surface area, S_{sp}, 380 m^2 g^{-1}, total pore volume, V_p, 0.63 cm^3 g^{-1}, and average pore diameter, d_{av}, 7 nm. Hydrothermal treatment of the silica gel was

performed at 200 and 250°C and medium pH (8.0 and 9.0) for 2–20 h in a 500-mL autoclave; the mass ratio of solid to liquid phases, *S/L*, was 1:12 and the autoclave infilling level was 0.8. At the temperatures used for hydrothermal treatment large changes in the properties of water occur (ionic product, viscosity, etc.); these promote improvement of surface moisturizing and dissolution of silicon dioxide during hydrothermal treatment.

Porosity characteristics were determined by mercury porosimetry (Pore-Sizer-9300 porosimeter). Chromatographic investigations were performed with a Gilson HPLC chromatograph with UV-detector. Normal and reversed-phase HPLC were both performed with 150 mm × 4.6 mm columns.

Modification of the systems with C_{18} groups was achieved by means of a technique described elsewhere [18].

RESULTS AND DISCUSSION

The porosity characteristics of silica gels obtained by hydrothermal treatment of the initial silica gel are listed in Table I; their porograms (integral curves of pore distribution by size) are shown in Fig. 1.

Table I

Porosity characteristics of the silica gels obtained by hydrothermal treatment

Samples	HT conditions			Porosity characteristics		
	τ (h)	T (°C)	pH	S_{sp} (m^2 g^{-1})	V_p (cm^3 g^{-1})	d_{av} (nm)
Initial	–	–	–	350	0.63	7.2
No. 1	2	200	8.0	180	0.63	14
No. 2	8	200	8.0	85	0.64	30.1
No. 3	20	200	8.0	50	0.64	51.2

It follows from the Fig. 1 that when MS are obtained by HT, widening of the PSD curves are observed, with increasing average pore diameters. It is also apparent that residual regions with comparatively smaller pores still remain in wide-porosity samples.

Chromatograms obtained from a mixture of benzene, nitrobenzene, *m*-dinitrobenzene, and *o*-dinitrobenzene by normal-phase HPLC on columns packed with the treated silica are presented in Figs 2–5. The columns were 150 mm × 4.6 mm, the mobile phase was hexane containing 5% propanol, the flow rate was 1.0 mL min^{-1}, and UV detection was performed at 254 nm.
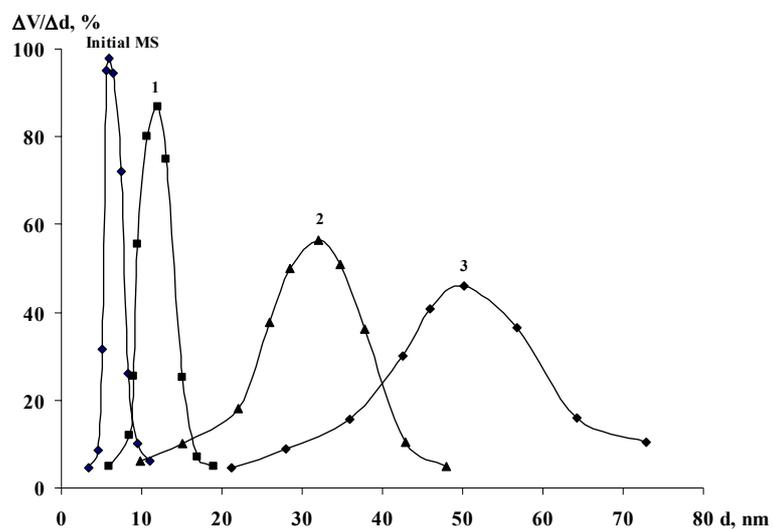
Fig. 1

Pore-size distribution for MS obtained by HT. The numbers on the curves correspond to the sample numbers in Table I
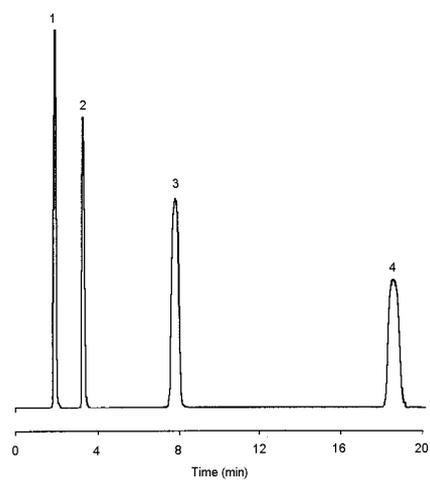

Fig. 2

Chromatogram obtained by use of a column packed with MS of average pore diameter 7.2 nm. 1. benzene, 2. nitrobenzene, 3. *m*-dinitrobenzene, 4. *o*-dinitrobenzene
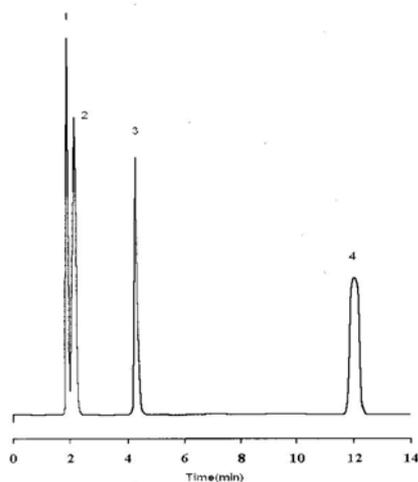
Fig. 3

Chromatogram obtained by use of a column packed with MS of average pore diameter 14.0 nm. 1. benzene, 2. nitrobenzene, 3. *m*-dinitrobenzene, 4. *o*-dinitrobenzene
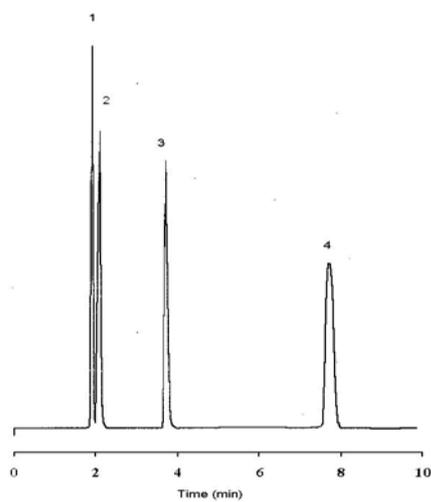

Fig. 4

Chromatogram obtained by use of a column packed with MS of average pore diameter 30.0 nm. 1. benzene, 2. nitrobenzene, 3. *m*-dinitrobenzene, 4. *o*-dinitrobenzene
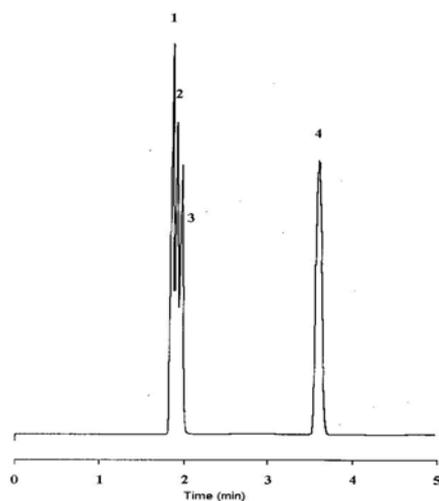
Fig. 5

Chromatogram obtained by use of a column packed with MS of average pore diameter 51.0 nm. 1. benzene, 2. nitrobenzene, 3. *m*-dinitrobenzene, 4. *o*-dinitrobenzene

The dependence of the retention factors of *o*-dinitrobenzene and *m*-dinitrobenzene on specific surface area in normal-phase HPLC is depicted in Fig. 6. The dependence is linear and correlation coefficients for both straight lines do not differ from unity.
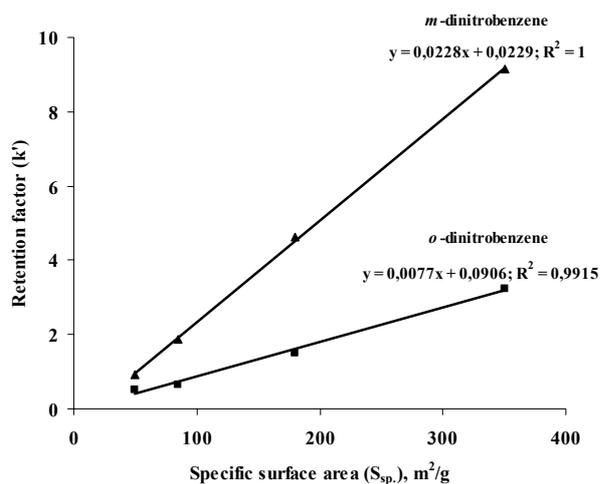

Fig. 6

Dependence on specific surface area of retention factor, *k*, for *o*-dinitrobenzene and *m*-dinitrobenzene in normal-phase HPLC

Chromatographic properties of columns packed with silica modified with C_{18} groups for use in RP HPLC are listed in Table II.

Table II

Chromatographic properties of columns packed with C_{18}-silica

Co-lumn	Car-bon load (%)	Retention time (min)				Retention factor, k'		S_{sp} $(m^2\,g^{-1})$	Number of C_{18} groups per 1 nm^2	Calculated S_{sp} $(m^2\,g^{-1})$	Fraction of surface accessible to modifier
		Ura-cil	Phe-nol	Ben-zene	To-luene	Ben-zene	To-luene				
1	16	1.49	3.33	6.81	9.66	3.57	5.48	350	1.15	268	0.81
2	10	1.55	2.38	4.92	6.90	2.17	3.45	180	1.39	167	0.93
3	5	1.58	2.07	3.40	4.04	1.15	1.56	85	1.48	84	0.98
4	3	1.59	1.84	2.56	2.90	0.61	0.82	50	1.50	50	1.00

Chromatograms obtained from a mixture of uracil, phenol, benzene, and toluene by reversed-phase chromatography are presented in Figs. 7–10. The columns were 150 mm × 4.6 mm, the mobile phase was acetonitrile–water, 1:1, the flow rate was 1.0 mL min^{-1}, and UV detection was performed at 254 nm.
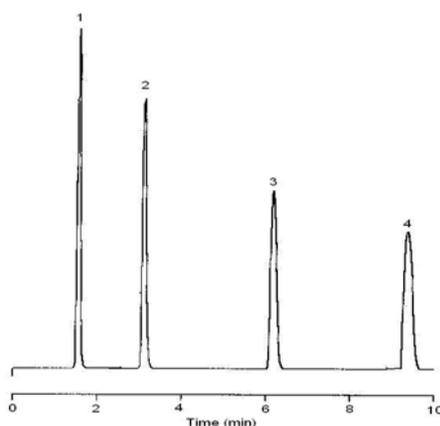

Fig. 7

Chromatogram obtained under reversed-phase conditions by use of a column packed with MS of average pore diameter 7.2 nm. 1. uracil, 2. phenol, 3. benzene, 4. toluene
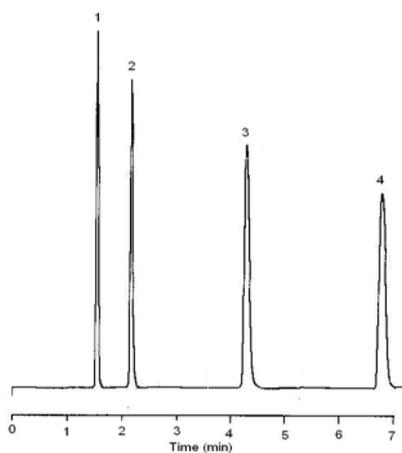
Fig. 8

Chromatogram obtained under reversed-phase conditions by use of a column packed with MS of average pore diameter 14.0 nm. 1. uracil, 2. phenol, 3. benzene, 4. toluene
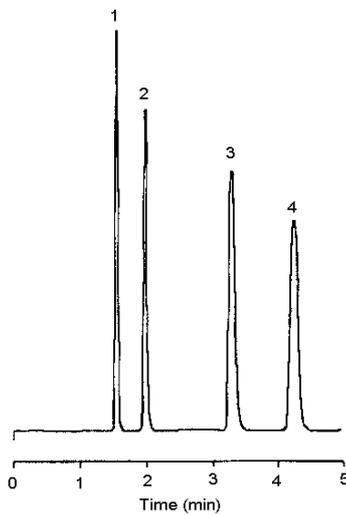

Fig. 9

Chromatogram obtained under reversed-phase conditions by use of a column packed with MS of average pore diameter 30.0 nm. 1. uracil, 2. phenol, 3. benzene, 4. toluene
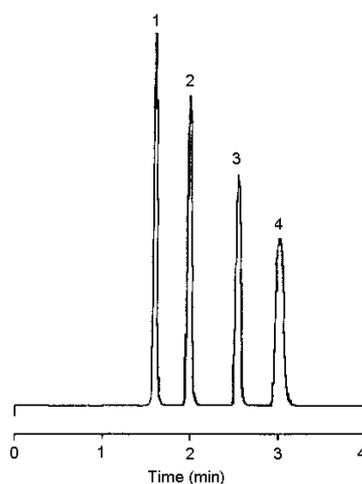
Fig. 10

Chromatogram obtained under reversed-phase conditions by use of a column packed with MS of average pore diameter 51.0 nm. 1. uracil, 2. phenol, 3. benzene, 4. toluene

Dependence of the retention factors of benzene and toluene on specific surface area in RP HPLC is depicted in Figs 7–10. The dependence is non-linear, probably because population of the surface by C_{18} groups is less than for micro-porous silica gel.
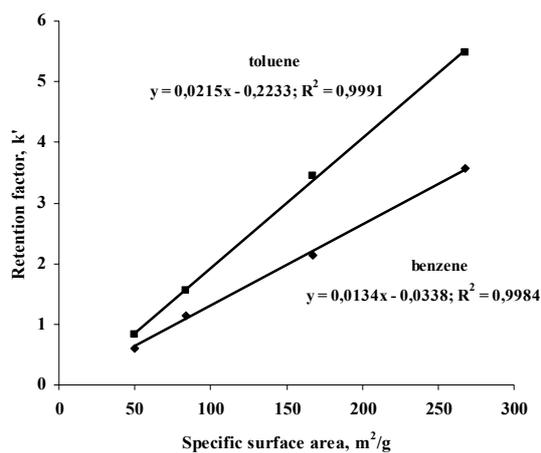

Fig. 11

Dependence of retention factors on calculated accessible specific surface area in reversed-phase chromatography

One can conclude from comparison of Figs 6 and 11 that the k values are dependent on specific surface area. Somewhat different dependence of k on S was observed for RP columns. The absence of linearity in RP HPLC is because the whole surface of the adsorbent is not accessible to modifier molecules and the accessible part is different for adsorbents with different values of the average pore diameter (Table II). Thus, for MS with 50 nm average pore diameter the whole surface is accessible for modification whereas for MS with 7.2 nm average pore diameter only 81% of the surface is accessible.

It follows from the Fig. 1 that the proportion of smaller pores decreases with increasing average pore diameter, i.e. the part of the surface not participating in the modification process becomes less and less. Berendsen and co-workers [19] revealed that pore size must be not less than 5.8 nm for complete modification by C_{18} groups. For modification of silica gel with 7.2 nm average pore diameter ($S_{sp} = 380$ m^2 g^{-1}) the proportion of smaller pores is much higher than for silica gel with larger pores (12–50 nm).

The dependence of the k on calculated amounts of surface accessible for modification is presented in the Fig. 11. The plot is linear and correlation coefficients either for benzene or for toluene are close to unity. Preparation of efficient reversed phases is possible only for silica with suitable surface accessibility.

CONCLUSION

The retention factors, k', for o-dinitrobenzene and m-dinitrobenzene in normal-phase HPLC on columns packed with MS of different specific surface area decreases linearly as the specific surface decreases. The retention factors, k', for benzene and toluene in RP HPLC on columns packed with the same MS but modified by C_{18} groups also decreases, but not linearly. The part of the surface accessible for modification with C_{18} groups increases with increasing average pore diameter of the MS.

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