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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Hurley, E. K. , Burke, M. F. , Heveran, J. E. and Rogers, L. B.(1967) 'Gas-Chromatographic Behavior of Pretreated Silica Gels', Separation Science and Technology, 2: 2, 275 — 282

To link to this Article: DOI: 10.1080/01496396708049931

URL: http://dx.doi.org/10.1080/01496396708049931

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SEPARATION SCIENCE, 2(2), 275–282 (1967)

Gas-Chromatographic Behavior of Pretreated Silica Gels*,†

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Summary

Silica gels were prepared by acid precipitation and dehydrated by refluxing in the presence of various aromatic solvents. The pretreatment was found to change the surface area and packing density of the gels. The chromatographic behavior of these gels toward organic adsorbates showed the treated gels to give better separations and resolution under time-normalized conditions. The columns were found to be thermally stable up to 200°C for long periods of time.

Silica gels have proved to be one of the widest used adsorbents in both gas-solid chromatography (GSC) and liquid-solid chromatography. They offer the advantages of wide ranges of surface areas, pore sizes, and surface activities. The role played by these factors in separation, however, has been and is still in question (*1,2*).

Superimposed on the above variables is the possibility of pretreating the silica surface to effect a given selectivity. Dickey's

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* Supported in part by the U.S. Atomic Energy Commission Contract AT(11-1)-1222.

† This article will be published later in a volume entitled *Separation Techniques: Proceedings of the Nineteenth Annual Summer Symposium on Analytical Chemistry.*

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original studies (3) on specific adsorbents using silica gels pretreated with methyl- and ethylorange have led to the postulation that a similar effect might be seen if the gel were pretreated with a less complex organic molecule. Vysotski et al. (*4*) reported a change in adsorption isotherms, pore size, and surface area when silica gels were pretreated with the vapors of various aromatic hydrocarbons. No work, however, has been reported on possible reasons for these changes or on the effect of such changes on the chromatographic behavior of such columns. The present study represents an attempt in that direction.

EXPERIMENTAL

Gels were prepared by mixing 35 ml of sodium silicate solution (Fisher, 40–42°, Be) with 165 ml of distilled water, acidifying with 100 ml of 4 *N* hydrochloric acid (Baker reagent grade) while stirring vigorously and allowing the gel to form overnight. The gel was then slurried with 300 ml of distilled water, allowed to settle, and the solution decanted. This washing procedure was repeated three times in an effort to remove most of the excess acid and sodium chloride.

The treatment consisted of refluxing the gels with each hydrocarbon. The water was removed from the refluxing mixture by means of a Barrett distilling receiver and was usually complete within 3 hr. The gel was then placed in a vacuum oven and heated at 125°C for several hours to remove the excess hydrocarbon. Gels treated with benzene, toluene, ethylbenzene, dephenylmethane, *o*-xylene, *m*-xylene, and a solution of naphthalene in benzene have been prepared in this manner.

The resulting brittle particles were ground in a mortar, sieved, and the 60/80 mesh fraction packed in 2-mm-I.D. × 50-cm stainless-steel columns. The packing of a precoiled column was done with the aid of a vibrator and suction from a water aspirator. All columns were conditioned at 200°C with nitrogen flowing for 24 hr before any measurements were made.

The chromatographs used in this study were an Aerograph Model 660 and an Aerograph Model 600 (Wilkens Instrument and Research Co., Walnut Creek, Calif.). Both instruments have flame-ionization detectors. The greater temperature stability of the column oven on the Model 660 was found necessary to obtain meaningful data. Although the long-term stability of the oven was only about ±0.2°C, by monitoring with an iron-constantan thermopile (three thermocouples) and a Leeds and Northrup potentiometer, the column temperature could easily be measured to the nearest 0.05°C during the relatively short time required to elute a sample.

Samples of adsorbates were prepared by injecting 5 μl of each liquid into a 1-liter septum-capped bottle which had been flushed with nitrogen. The benzene, toluene, and ethylbenzene were used alone and as a mixture. A Hamilton gas syringe was used to inject 15 μl of the gaseous sample into the column. Using an average liquid density of 0.85, the gas samples injected into the columns were calculated to be about 1×10^{-7} g of each adsorbate.

The nitrogen surface areas and pore sizes of the silica gels were measured using a flow apparatus similar to that of Nelsen and Eggertsen (5).

Heats of adsorption, ΔH_A, were calculated from retention data at three temperatures from 150 to 210°C. Each sample was injected three times at each temperature, thereby giving nine points for calculations. Both the order in which the temperatures were studied and the order in which individual samples were injected at a particular temperature were randomized so as to minimize systematic errors. The ΔH_A values were obtained from the slope of a plot of ln k vs. $1/T$ [here k is the capacity (or distribution) ratio and T the absolute temperature]. A least-squares procedure was performed using a computer program for regression analysis.

Two expressions are used for the calculation of resolution:

$$R = 2(t_{R_2} - t_{R_1})/(W_2 + W_1) \tag{1}$$

where t_R is the retention time, W the width of the base of a peak, and

$$R' = \frac{1}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k}{k+1}\right)N^{1/2} \tag{2}$$

where k is the capacity ratio, α the relative volatility, and N the number of theoretical plates. The following expression was used to calculate N:

$$N = 5.545\ (t_R/W_{1/2})^2 \tag{3}$$

where $W_{1/2}$ is the width at half-height. Equation (2) provides a more reproducible number than Eq. (1).

RESULTS AND DISCUSSION

Figure 1 contrasts a typical chromatogram of benzene, toluene, and ethylbenzene on a control gel with one from a column which had been pretreated with a saturated solution of naphthalene in benzene. In the first case, the adsorbates are well separated but are eluted as relatively broad peaks with long retention times, whereas in the second case the separation is not as great but the peaks are eluted sooner and in much narrower bands.

The data taken on the various columns are tabulated in Table 1. The relative volatility α, defined as the ratio of the capacity ratios for any two components, is used as a measure of the selectivity of a separation. Also the resolution R of the benzene and toluene peaks and the toluene and ethylbenzene peaks is shown. As can be seen in Table 1, the values of α and R decrease as the value of k decreases. The obvious conclusion is that resolution has been traded for time when the gels are compared at the same temperature.

However, another type of comparison was also undertaken to evaluate the chromatographic behavior of these columns. An attempt was made to hold constant the capacity ratio for ethylbenzene, k_3, by adjusting the temperature at which the mixture was

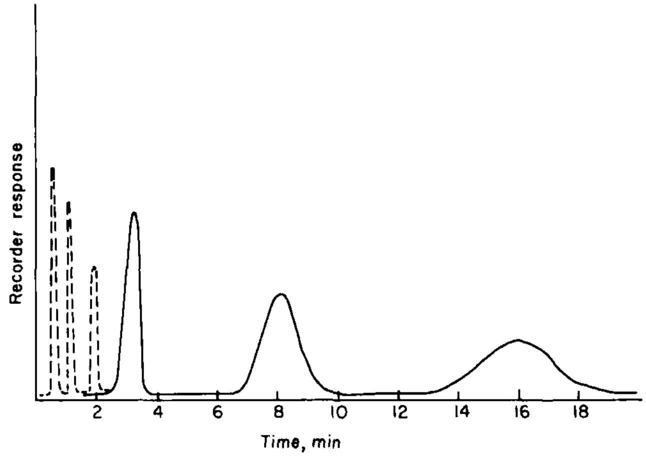

FIG. 1. Chromatograms of benzene, toluene, and ethylbenzene on control gel (solid line) and naphthalene gel (dashed line). Both columns at 183°C with carrier gas flow rate of 20 ml/min.

TABLE 1

Capacity Ratios, Relative Volatilities, and Resolution for Benzene, Toluene, and Ethylbenzene at 183°C

Gel	T, °C	k_1	k_2	k_3	α_{12}	α_{13}	α_{23}	R_{12}	R_{23}
Control	183.3	19.60	48.20	97.40	2.45	4.97	2.02	3.43	2.87
Benzene	183.0	11.91	26.81	50.28	2.23	4.17	1.87	3.34	2.80
Toluene	182.8	6.11	13.42	24.61	2.20	4.02	1.83	3.43	2.77
Ethylbenzene	182.7	7.33	15.87	28.26	2.15	3.86	1.78	3.33	2.72
Diphenyl-methane[a]	182.7	6.83	13.80	23.50	2.07	3.44	1.70	3.06	2.53
o-Xylene	182.3	1.96	3.65	5.73	1.86	2.92	1.57	2.55	2.12
m-Xylene	182.3	1.62	2.98	4.59	1.83	2.83	1.54	2.17	1.89
Naphthalene	182.8	0.74	1.31	1.91	1.77	2.58	1.46	1.55	1.48

[a] Data questionable; gel was discolored, probably because of impurities or decomposition.

chromatographed. Here the separation and resolution obtained in a given time period increases in an order opposite to that seen at a constant temperature. Those results are shown in Tables 2 and 3. This behavior appears to be analogous to that reported by Karger and Cooke (6) for the effect of the amount of liquid phase on GLC columns under time-normalized conditions. That is, the resolu-

TABLE 2

Temperature, Capacity Ratios, and Relative Volatilities for Benzene, Toluene, and Ethylbenzene for Time-Normalized Conditions

Gel	T, °C	k_1	k_2	k_3	α_{12}	α_{13}	α_{23}
Control	210.8	12.18	23.93	40.37	1.95	3.41	1.74
Benzene	206.0	10.12	21.69	39.59	2.14	3.95	1.84
Toluene	169.8	8.81	20.82	39.42	2.36	4.51	1.90
Ethylbenzene	177.9	9.00	20.47	38.01	2.27	4.22	1.86
Diphenyl-methane[a]	167.6	10.07	21.86	39.53	2.16	3.92	1.81
o-Xylene	129.8	8.81	21.78	41.08	2.46	4.66	1.89
m-Xylene	125.6	8.87	19.95	37.69	2.24	4.22	1.89
Naphthalene	96.0	n7.67	19.57	38.05	2.58	5.00	1.94

[a] Data questionable; gel was discolored, probably because of impurities or decomposition.

TABLE 3

Number of Theoretical Plates and Resolution for Benzene, Toluene, and Ethylbenzene for Time-Normalized Conditions

Gel	N_1	N_2	N_3	R_{12}	R_{23}	R'_{12}	R'_{23}
Control	252	261	250	2.65	2.22	1.93	1.51
Benzene	290	277	280	1.19	1.36	2.12	1.86
Toluene	356	416	348	3.53	2.73	2.70	2.23
Ethylbenzene	441	452	419	3.60	2.89	2.80	2.34
Diphenylmethane	392	334	414	1.60	1.33	2.36	2.22
o-Xylene	456	421	428	4.00	2.61	2.79	2.96
m-Xylene	608	539	576	2.28	1.67	3.08	2.61
Naphthalene	858	751	747	5.52	4.08	3.93	4.26

tion and separation improved as the amount of liquid phase was decreased.

The decrease in column activity cannot be explained on the basis of a simple change in surface area. Table 4 shows that the surface areas of the various gels, measured by nitrogen adsorption, ranged between 730 and 148 m^2/g. A change in surface area by a factor of six is not sufficient to explain the change of approximately 20 in capacity ratios seen in Table 1. Therefore, not only was the surface area reduced, but also the number and/or energy of the sites per unit area.

The heats of adsorption for several adsorbates are given in Table

TABLE 4

Surface Areas, Packing Densities, and Average Pore Diameter of Column Packing

Gel	A_s, m^2/g	*d*, g/cc	Diam., Å
Control	730	0.52	20
Benzene	424	0.46	—
Toluene	381	0.30	—
Ethylbenzene	400	0.32	—
Diphenylmethane	—	0.39	—
o-Xylene	227	0.29	—
m-Xylene	200	0.25	—
Naphthalene	148	0.22	90

TABLE 5

Enthalpy of Adsorption of Representative Adsorbates on Pretreated Silica Gel

Column	Hexane	Cyclohexane	Benzene	Toluene	Ethylbenzene
Control	7.6 ± 0.3	7.3 ± 0.0	10.0 ± 0.1	11.7 ± 0.0	13.1 ± 0.1
Toluene	8.3 ± 0.3	8.2 ± 0.2	11.1 ± 0.4	13.1 ± 0.5	14.9 ± 0.4
Ethylbenzene	8.4 ± 0.8	8.0 ± 0.4	10.8 ± 0.8	12.7 ± 0.9	13.8 ± 1.0
o-Xylene	6.0 ± 0.7	5.3 ± 1.0	7.6 ± 0.6	8.8 ± 1.1	9.9 ± 1.2
Benzene			10.3 ± 1.2	12.4 ± 1.4	13.7 ± 1.3
Naphthalene			7.5 ± 0.7	8.8 ± 0.4	9.7 ± 0.2

5. These values are seen to decrease in a manner similar to that noted by Kiselev et al. (7) when silica gels were dehydrated. Since the temperatures at which the pretreatments were carried out were probably not great enough to cause extensive dehydroxylation, it must be assumed that organic material was retained on the surface and blocked access to some of the active sites. That view is supported by the observation that although the columns proved to be stable over extended periods of time (several months) at a temperature of 200°C, upon heating to temperatures in excess of 250°C they became extremely active. However, the column could then be deactivated again by injection of liquid samples of the organic solvent used for the pretreatment. Byrne (8), using a technique which confined combustion and gas chromatography, furnished data which indicated a significantly larger amount of hydrocarbon to be present on the pretreated gels. No quantitative conclusions could be drawn about which pretreatment gave the most hydrocarbon on the surface.

These results were compared to those obtained on a commercially available silica gel, Davison #58, which has a surface area 300 m^2/g and a packing density close to those of the gel treated with *o*-xylene. The Davison gel was found to become extremely active after being dried at 200°C for 24 hr. It then behaved very similar to a control gel.

Also shown in Table 4 are the packing densities of the various gels along with the average pore diameters for the control and napthalene gels. The packing density decreased in the same order as the surface area, which implies that the average pore diameter is increasing from the control to the napthalene gel. The fact that separation increased with decreasing pore size would seem to support the argument, put forth by Snyder (*1*), that the number of active sites available rather than the pore size affects the separations.

Several oxygenated compounds were chromatographed on both control and napthalene columns to explore the relative inertness of the latter. The fact that acetone and diethyl ether eluted rapidly from the treated gel with only a small degree of tailing is taken to signify a relatively inert surface.

The pretreatments appear to follow the boiling-point order of the organic solvents used for the dehydration. The pretreatment was shown to be independent of the length of time of refluxing. A benzene gel was refluxed for 72 hr and was found to have the same packing density and chromatographic behavior as one prepared under the normal conditions of about 3 hr for removal of water.

While the exact nature of the interaction of the organic solvents with the silica gels is not clear, the fact that such pretreatment can serve to produce a wide range of chromatographic columns is of great interest. It is hoped that further studies now in progress, which involve other organic adsorbates, will provide a more complete picture.

Acknowledgments

The authors would like to thank J. A. Barnes for constructing the integrator used in this work and A. K. Moreland, who built the surface-area and pore-volume apparatus.

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Received by editor December 30, 1966
Submitted for publication January 30, 1967