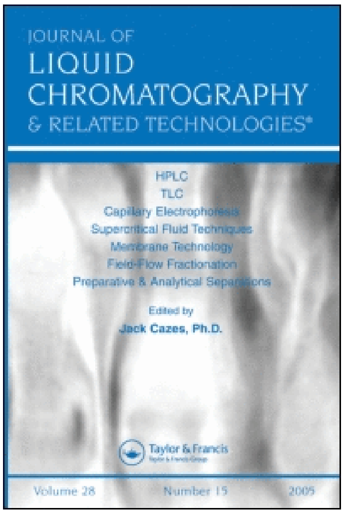

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Solute Retention in Column Liquid Chromatography. VIII. Preparation and Properties of Metal-Modified Silica

R. A. Djerki[a]; R. J. Laub[a]; S. K. Milonjič[a]
[a] Department of Chemistry San Diego, State University San Diego, California

To cite this Article Djerki, R. A. , Laub, R. J. and Milonjič, S. K.(1985) 'Solute Retention in Column Liquid Chromatography. VIII. Preparation and Properties of Metal-Modified Silica', Journal of Liquid Chromatography & Related Technologies, 8: 2, 281 — 298

To link to this Article: DOI: 10.1080/01483918508067078

URL: http://dx.doi.org/10.1080/01483918508067078

JOURNAL OF LIQUID CHROMATOGRAPHY, 8(2), 281-298 (1985)

SOLUTE RETENTION IN COLUMN LIQUID CHROMATOGRAPHY. VIII. PREPARATION AND PROPERTIES OF METAL-MODIFIED SILICA

R. A. Djerki, R. J. Laub*, and S. K. Milonjič
Department of Chemistry
San Diego State University
San Diego, California 92182

ABSTRACT

The method of preparation and chromatographic properties of a commercial silica lc packing, LiChrosorb SI 60, modified by surface incorporation of the cations H^+, Li^+, Cs^+ NH_4^+, Ag^+, Mg^{2+}, Co^{2+}, Cd^{2+}, and Al^{3+}, are reported. The total column porosity for all columns studied lay in the range 0.52-0.78, while the column resistance factor fell within 1060-1500. The Knox-Parcher column ratio was in all instances 14,100, while the packing density was 0.49 g cm^{-3}. The test solutes comprised N,N-dimethylaniline, N-methylaniline, o-chloroaniline, o-nitroaniline, 2,4-dimethylaniline, m-chloroaniline, and 4-chloroaniline, for which the elution order varied substantially depending upon the cation-form silica employed. Two Ag-form columns, each heat-treated at different temperatures, provided overall the best separations. There was found to be some correlation between metal-ligand complexation constants and retentions for species where data were available, but this was not the case for the base strengths of the solutes. The columns did not deteriorate to any great extent over at least 6 weeks' continued use, and are therefore said to hold potential advantage for selective separations.

---

*Author to whom correspondence may be addressed

0148-3919/85/0802-0281$3.50/0

INTRODUCTION

Interactions of solutes with stationary sorbents are governed in liquid chromatography very largely by the composition of the mobile phase, as described and discussed in preceding papers of this Series (1-7). Nevertheless, there is little doubt also that retentions are a function as well of the type and properties of the column packing. Moreover, the selectivity of a sorbent is in turn a function of particle geometry, specific surface area, porosity (along with pore shape and distribution of types of pores), as well as surface activity. However, and in contrast to solvent selectivity, there are comparatively few theoretical and experimental studies of sorbent selectivity, presumably because of practical difficulties associated with changing from one type of stationary phase to another (i.e., repacking the column) as opposed to the ease of altering the mobile phase. Coupled with this is the very powerful technique of in-situ generation of highly selective stationary phases by reversible sorption of one or another trace components of the mobile phase (8), as exemplified by the chiral separations achieved in the work of Hare and Gil-Av (9) and others (10,11).

Even so, there remain several means of altering the characteristics (hence selectivity) of commonly-utilized stationary sorbents that may well hold advantage over compositional variation of the mobile phase in column liquid chromatography. For example, the surface activity of a sorbent can be affected quite substantially by treatment at elevated temperature, as has been recognized in gas-solid chromatography (gsc) for many years. Generally, thermal "activation" results in shortened retention times, reduced peak asymmetry and, hence, improved separations. In addition, very many advances have of course been made in recent years in bonding chemically this or that specific reagent to silica, magnesia, and alumina surfaces. For example, we have shown elsewhere (12) that chemical attachment of an alkali metal ion (e.g., Li^+, Na^+, K^+, or Cs^+) to silica surfaces leads to a substantial change in surface activity, as reflected by very substantial changes in the retentions of a variety of classes of solutes when the modified materials are utilized as gsc stationary phases.

Accordingly, we report in this study an extension to liquid chromatography of our earlier work on the synthesis and properties of silica sorbents (here, LiChrosorb SI 60) obtained by chemical treatment with H^+, Li^+, Cs^+, NH_4^+, Ag^+, Mg^{2+}, Co^{2+}, Cd^{2+}, and Al^{3+}. We then illustrate the results in terms of the separation of some substituted aromatic amine test solutes and, in addition, test the feasibility of correlation of retentions with the "strength" (i.e., magnitude of the relevant equilibrium constant) of metal-ion/ligand interactions.

EXPERIMENTAL

Apparatus. Either of two chromatographs were employed in this work: a Model 5000 from Varian or a Waters Model 6000M. Sample introduction was via a Valco valve with a 10-μ external loop. The detector was a UV-100-II from Jasco set at 254 nm, while the recorder was from Linear. The quantitation of sorbed cations was carried out with a Perkin Elmer Model 403 atomic absorption spectrophotometer. The x-ray diffraction studies were performed with a Siemens Kristalloflex 4 diffractometer utilizing Cu $K\alpha$ radiation.

Materials and Supplies. The column tubes were obtained commercially (Jones Chromatography, Columbus, Ohio), and were 15 cm x 4.6 mm i.d. The packings were identical silicas and were obtained in batches either from E. Merck (Darmstadt, West Germany; LiChrosorb^{TM} SI 60, or from Jones Chromatography (LiChrosorb^{R} SI 60); each was modified chemically as indicated below. This form of silica consists of irregularly shaped particles of average diameter 10 μ, specific surface area of ca. 500 $m^2\ g^{-1}$, and average pore size of 6 nm. The remaining properties of this and other commercially-available silicas utilized in column liquid chromatography have been detailed by Unger (13), and by Ohmacht and Halasz (14).

The solvents, n-hexane, dichoromethane, and 2-propanol, were of "hplc" quality (Fisher Scientific). The composition of the mobile phase was maintained constant at 90.0:9.5:0.5% v/v n-hexane:dichloromethane:2-propanol. Each batch of mobile phase was degassed prior to chromatographic runs in an ultrasonic bath for approximately 20 min.

Table 1

Experimental Conditions for Chemisorption of Indicated Cations onto Silica

Electrolyte	C/mol dm^{-3}	Solution pH	Solution/Solid Ratio/(cm^3 g^{-1})	Sorbed Mass/ µmol g^{-1} SiO_x
HCl	0.01	2.2	100/3	-
LiCl	1.2	9.5	100/4	57
CsCl	1.1	9.5	100/4	200
NH_4Cl	0.9	9.5	100/4	52
$AgNO_3$[a]	0.5	6.0	100/3	14
$AgNO_3$[b]	0.5	6.0	100/3	16
$MgCl_2$	0.5	8.0	100/3	225
$CoCl_2$	0.0002	7.0	200/3	4
$CdCl_2$	0.0003	6.5	200/4	11
$AlCl_3$	0.0002	6.0	200/3	32

[a] Dried at 453K [b] Dried at 383K

The solutes, N,N-dimethylaniline (1), N-methylaniline (2), o-chloroaniline (3), o-nitroaniline (4), 2,4-dimethylaniline (5), m-chloroaniline (6), and 4-chloro-2-nitroaniline (7) were obtained from Chem Service and were analytical reagent-grade.

Methods and Procedures. Chemisorption of metal ions onto silica was carried out batchwise in aqueous solution (doubly-distilled water). The solution compositions and related experimental conditions are provided in Table 1. For the sake of comparison with starting materials, a sample of LiChrosorb was also treated with 10^{-2} mol dm^{-3} HCl, i.e., at pH 2, this value corresponding (12) to the pH (zero-point charge) of fully protonated silica (15).

Equilibrations were performed in plastic bottles with a magnetic stirrer for 4 hr, after which the solid phase was separated by filtration and washed with doubly-distilled water until no further reaction with silver ion was observed. The materials were then dried in an air oven at 453K for 12 hr in order to remove physisorbed water, i.e., activate the sorbents, since the adsorption of water, even in trace amounts, lowers the surface activity. (Thermal treatment above 473K causes condensation of surface hydroxyl groups which in turn results also in the deactivation of silica.)

Each sorbent was slurry-packed into a well-washed column fitted with a 2-μ porous stainless-steel frit. Thus, 2.5 g of packing material and 11 cm^3 of CCl_4 were placed in an ultrasonic bath for a few minutes in order to destroy particle agglomeration. The slurry was then transferred by syringe into a precolumn (25 cm x 7 mm i.d.) joined to the column top. A pressure of 12,500-15,000 psig was then applied to displace the slurry into the column, following which 100 cm^3 of methanol was eluted through the system. Each column required approximately 10 min for completion. Upon connection to the liquid chromatograph, each column was conditioned by eluting about 20 cm^3 of 2-propanol; the mobile phase containing hexane:dichloromethane:2-propanol was then passed through the column until equilibration was achieved, as judged by the constancy of retention times (approximately 60 min at a flow rate of 1 cm^3 min^{-1}). The packing density for all columns was 0.49 g cm^3.

In order to measure accurately the retention volume of each solute, the outlet from the detector was connected directly to a 5-cm^3 graduated buret and the flow checked every 15-20 min. All solutes were dissolved in the mobile phase.

RESULTS AND DISCUSSION

Data Reduction. Retention volumes V_R, capacity factors k', and relative separations (values of alpha) $\alpha_{i/j}$ were calculated in the usual way via eqns. 1-4:

$$V_R = t_R F \qquad (1)$$

$$V_A = t_A F \qquad (2)$$

$$k' = \frac{V_R - V_A}{V_A} \qquad (3)$$

$$\alpha_{i/j} = \frac{k'_{(i)}}{k'_{(j)}} \tag{4}$$

Dead volumes V_A were determined by measuring the retentions of the homologous series members: benzene, naphthalene, and anthracene (5).

The total column porosity ϵ_{tot} was calculated from the relation:

$$\epsilon_{tot} = 21.22 \frac{t_A F}{(d_c)^2 L} \tag{5}$$

where d_c (mm) is the column diameter and L (mm) is the column length.

The column resistance factor (or flow resistance parameter) ϕ was also determined:

$$\phi = 100 \frac{\Delta p \; t_A \; (d_p)^2}{\eta L^2} \tag{6}$$

where Δp (bar) is the pressure drop across the column, d_p (μ) is the mean particle diameter, and η (cP) is the viscosity of the mobile phase, with t_A and L expressed in sec and mm, respectively. In this work, $\eta = 0.318$ cP.

The Knox-Parcher ratio I, calculated from the relation:

$$I = 10^3 \frac{(d_c)^2}{L \; d_p} \tag{7}$$

was 14,100 for all columns investigated in this work. In addition, the mean linear velocity of the mobile phase, calculated as $\bar{u} = L/t_A$, varied only over the range 1.1-1.2 mm sec^{-1} from one column to the next.

Column Characteristics. The influence of chemisorption of the cations of Table 1 is illustrated in Table 2 in terms of retentions of the test solutes, and ϕ and ϵ_{tot}.

We note, first, that the column resistance factor ϕ lies in the range 1060-1500 for all columns. Values of ϕ of between 500 and 1000 are usually cited for well packed systems while, when slurry packing is used, these lim-

TABLE 2

Column Characteristics

Solute No.	Untreated LiChrosorb SI 60		Acid-Form		Li-Form	
	V_R/cm^3	k'	V_R/cm^3	k'	V_R/cm^3	k'
1	2.38	0.25	2.51	0.25	2.27	0.18
2	3.60	0.89	3.65	0.82	3.35	0.74
3	3.78	0.99	3.58	0.78	3.48	0.81
4	7.28	2.83	6.84	2.40	6.85	2.57
5	7.96	3.19	8.71	3.33	7.32	2.81
6	9.05	3.76	9.14	3.55	7.68	3.00
7	11.2	4.90	10.9	4.42	10.1	4.26
ϕ	1501		1193		1127	
ϵ_{tot}	0.76		0.76		0.53	
$\alpha_{3/2}$	1.11		0.95		1.09	
$\alpha_{6/5}$	1.18		1.07		1.07	

Solute No.	NH_4-Form		Cs-Form		Ag-Form[a]	
	V_R/cm^3	k'	V_R/cm^3	k'	V_R/cm^3	k'
1	2.26	0.22	2.59	0.30	2.32	0.18
2	3.60	0.78	3.90	0.95	3.61	0.84
3	3.73	0.85	3.87	0.94	4.01	1.04
4	7.16	2.54	9.87	3.94	7.17	2.66
5	7.81	2.87	8.64	3.32	12.5	5.36
6	8.15	3.03	8.39	3.20	10.1	4.17
7	10.7	4.28	14.2	6.09	10.7	4.46
ϕ	1168		1474		1481	
ϵ_{tot}	0.55		0.80		0.75	
$\alpha_{3/2}$	1.09		0.99		1.11	
$\alpha_{6/5}$	1.06		0.96		0.78	

[a] Dried at 453K

TABLE 2 (Continued)

Solute No.	Ag-Form[b]		Mg-Form		Co-Form	
	V_R/cm^3	k'	V_R/cm^3	k'	V_R/cm^3	k'
1	2.37	0.23	1.99	0.06	2.20	0.15
2	4.14	1.16	2.72	0.45	3.23	0.69
3	4.59	1.39	3.08	0.65	3.49	0.83
4	6.87	2.58	6.24	2.34	6.84	2.58
5	27.2	13.2	5.13	1.74	6.65	2.48
6	15.8	7.23	6.25	2.34	7.60	2.98
7	10.4	4.42	9.15	3.89	10.2	4.36
ϕ	1111		1060		1440	
ϵ_{tot}	0.63		0.74		0.76	
$\alpha_{3/2}$	1.20		1.44		1.20	
$\alpha_{6/5}$	0.55		1.34		1.20	

[b] Dried at 383K

Solute No.	Cd-Form		Al-Form	
	V_R/cm^3	k'	V_R/cm^3	k'
1	2.36	0.19	2.52	0.28
2	3.56	0.80	3.86	0.97
3	3.74	0.89	3.83	0.95
4	6.86	2.46	7.35	2.75
5	8.33	3.21	9.06	3.62
6	9.26	3.68	9.73	3.96
7	10.6	4.35	11.6	4.90
ϕ	1122		1481	
ϵ_{tot}	0.78		0.77	
$\alpha_{3/2}$	1.11		0.98	
$\alpha_{6/5}$	1.18		1.09	

its are reduced by between a half and two-thirds (16,17). However, ϕ depends also on particle shape, size distribution, porosity, and pore structure. Thus, Unger (13) has argued that, for porous particles, ϕ is expected to be larger as a result of the increase in total packing porosity. In a comparative study of column resistance factors for spherical versus angular silicas, Unger, et al. (17) also found that the resistance factor for all granular silica supports (d_p = 2.8-10.9 μ) was greater by roughly a factor of two over spherical particles, and was 1175-1875 which is in good agreement with our results.

Values of the total column porosity ϵ_{tot} for the columns studied here fell within the range 0.52-0.78, in accordance with the findings of others for similar packing materials (16,17).

Chromatograms of the Test Solutes. A chromatogram of the test compounds with untreated silica is shown in Figure 1: solutes 2 and 3 are unresolved, as are 4 and 5. With the acid-treated form of silica, Figure 2, solutes 2 and 3 are still unresolved, while 4 is well separated from 5. However, 5 now overlaps nearly completely with 6.

Examples of separations of the anilines with silicas contacted with metal cations are provided in Figures 3-11, where there are substantial changes in the solute elution order. For example, full separation of the pairs 2 and 3, and 4 and 5 are found with the Ag-form columns, Figures 3 and 4, despite low capacity factors of the former two compounds. However, only partial separation of these solutes could be achieved with columns containing the Mg- and Co-form supports, Figures 5 and 6.

Complete separation of solutes 4 and 5 was found with the Cd-form packing, Figure 7, while these two solutes are only partially resolved with the Li-, NH_4- , and Cs-form columns, Figures 8-10. Separation of solutes 4 and 5 with, however, incomplete resolution of solutes 5 and 6, was obtained with the Al-form column, Figure 11.

Complexation with Silver-Form Silica. Solute 5 (2,4-dimethylaniline) was strongly retained on both of the Ag-form columns. In fact, these columns exhibited the best separations of all of the solutes, which we attribute to $n-\pi^*$ complexation with Ag. However, there is a paucity of data regarding the relevant stability constants. Those available (18) for Ag^+ with N-methylaniline, o-chloroaniline, o-nitroaniline, and m-chloroan-

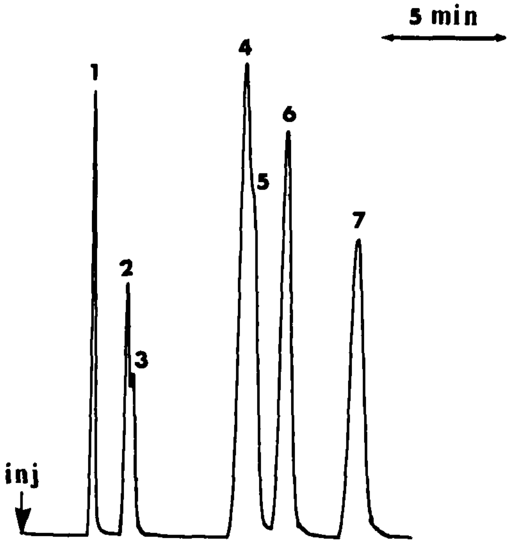

FIGURE 1. Chromatogram of the test solutes N,N-dimethylaniline (1), N-methylaniline (2), o-chloroaniline (3), o-nitroaniline (4), 2,4-dimethylaniline (5), m-chloroaniline (6), and 4-chloro-2-nitroaniline (7) with LiChrosorb SI 60 10 u silica. Column: 15 cm x 4.6 mm i.d.; mobile phase: 90.0:9.5:0.5% v/v n-hexane:dichloromethane:2-propanol; flow rate: 0.86 cm^3 min^{-1}.

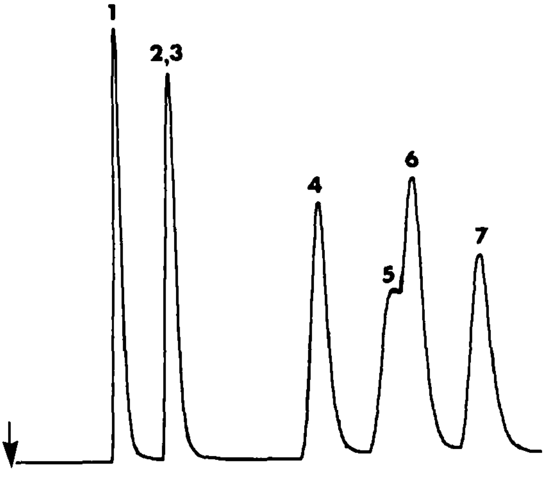

FIGURE 2. As in Figure 1; flow rate: 0.65 cm^3 min^{-1}; acid-form silica (cf. Text).

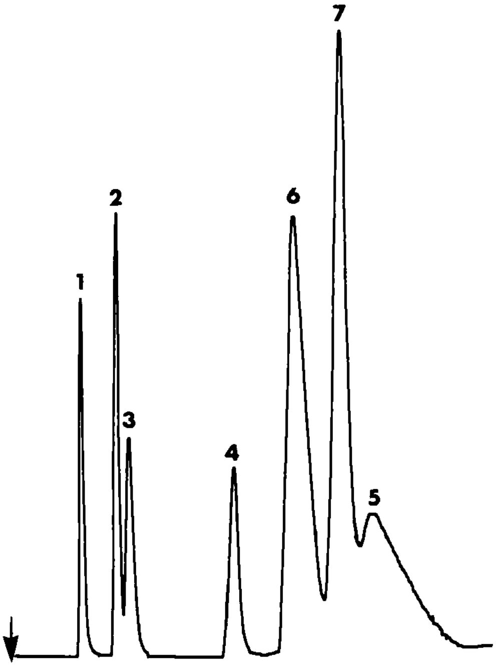

FIGURE 3. As in Figure 1; flow rate: 0.87 cm^3 min^{-1}; silver-form silica heat-treated at 453K (cf. Text).

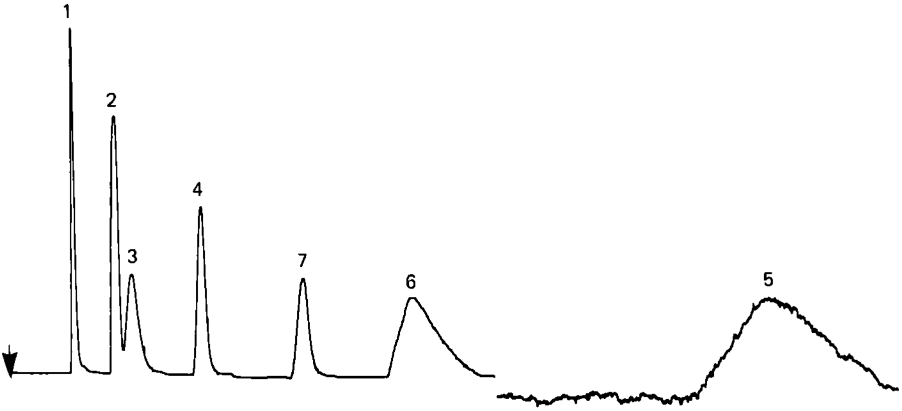

FIGURE 4. As in Figure 1; flow rate: 0.61 cm^3 min^{-1}; silver-form silica heat-treated at 383K (cf. Text).

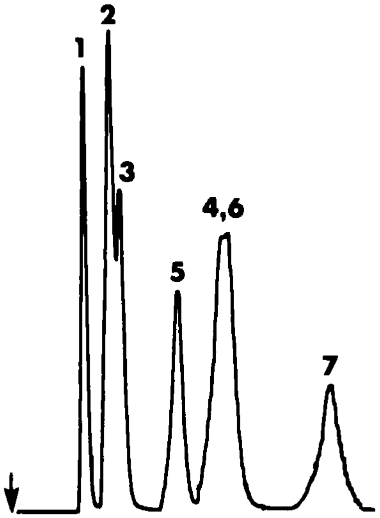

FIGURE 5. As in Figure 1; flow rate: 0.89 cm^3 min^{-1}; magnesium-form silica (cf. Text).

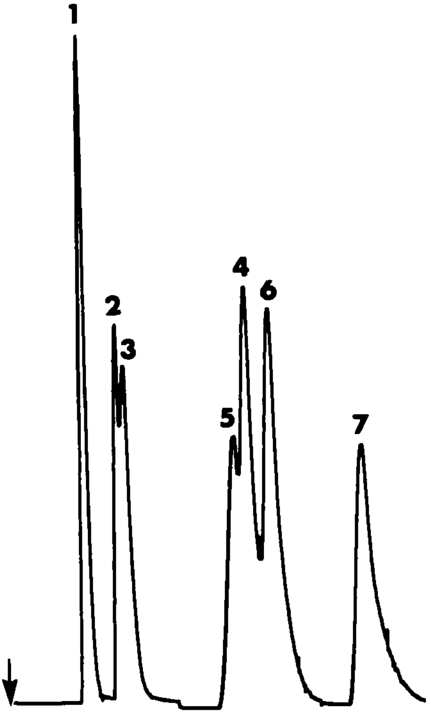

FIGURE 6. As in Figure 1; flow rate: 0.90 cm^3 min^{-1}; cobalt-form silica (cf. Text).

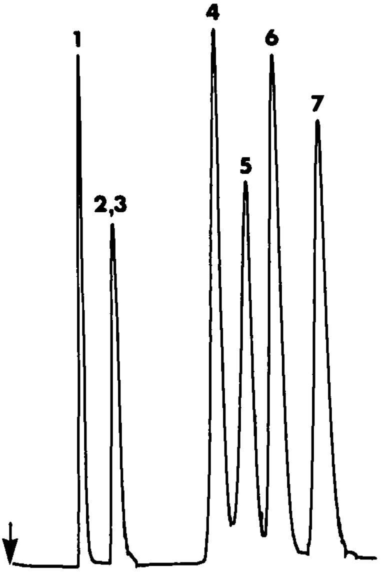

FIGURE 7. As in Figure 1; flow rate: 0.89 cm^3 min^{-1}; cadmium-form silica (cf. Text).

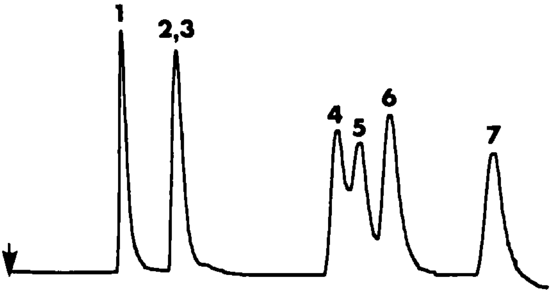

FIGURE 8. As in Figure 1; flow rate: 0.60 cm^3 min^{-1}; lithium-form silica (cf. Text).

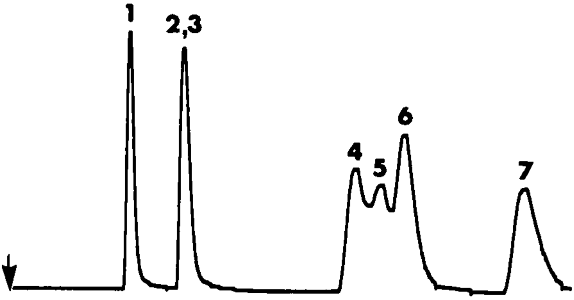

FIGURE 9. As in Figure 1; flow rate: 0.60 cm^3 min^{-1}; ammonium-form silica (cf. Text).

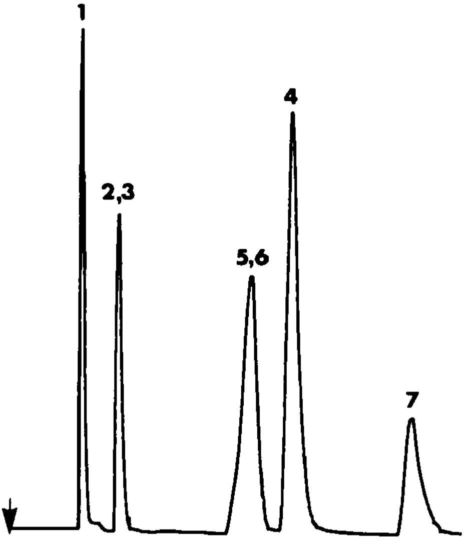

FIGURE 10. As in Figure 1; flow rate: 0.92 cm^3 min^{-1}; cesium-form silica (cf. Text).

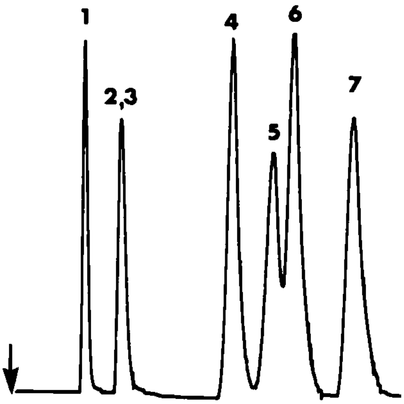

FIGURE 11. As in Figure 1; flow rate: 0.88 cm^3 min^{-1}; aluminum-form silica (cf. Text).

iline are: log K_1 = 1.00, log K_2 = 2.5, log K_2 = 1.90, and log K_2= 2.55, respectively, where K_1 is the stability constant of 1:1 complexes, and where K_2 indicates the stability constant of 1:2 (AgL_2) complexes. Accordingly, of these solutes, m-chloroaniline would be expected to be the strongest retained with the Ag-form columns, as borne out by our observations as well as those of others (19-24). However, there was no correlation of retentions with base strength of the amines, which indicates that the elution order is more than likely the result of a combination of non-specific adsorption, specific intermolecular complexation, and steric effects (25,26).

Differences in solute capacity factors with the two Ag-form columns are probably due to different surface activities, since the packings were heated to different temperatures. In fact, that taken to 453K appeared brown to black, while the material heated only to 383K was yellow to brown in color. Aigner, et al. (22) have also shown that silver silicates decompose under the influence of heat and/or light to silver oxide, thence to elemental silver. Unfortunately, the sensitivity of the x-ray diffraction instrument precluded detection of species other than amorphous silica. This matter appears to us to merit further study by spectroscopic techniques, since the separations with the two forms of argentation columns clearly are substantially different.

Other Metal-Form Silicas. In contrast to the above, modification of LiChrosorb SI 60 with Co^{2+}, Cd^{2+}, and Al^{3+} did not lead to noticable changes in retentions. We believe at this time that the explanation lies with insufficient amounts of ions actually sorbed onto the surface, as indicated by the data provided in Table 1. Moreover, the sorption reactions were, in these cases, carried out under conditions such that there was no hydrolysis of the ions. Sorption of greater amounts of these species would require higher pH and electrolyte concentration, which may then result in the production, thence sorption, of different hydrolytic products.

Column Life of Cation-Contacted Silicas. In order to investigate whether, and to what extent, cation desorption occurred during the normal course of column operation, several columns were unpacked and examined by AAS following continual use for ca. 6 weeks' time. The results showed decreases of metal content of 5%, 14%, and 6%, respectively, for the Cs-form, Ag-form (453K), and Ag-form (383K) columns. Although these amounts certainly are not large, it is evident that some loss does in fact take place over the course of time. Even so, these levels are considerably less than are found to occur with other batch- or in-situ impregnation techniques. The higher loss for the 453K-treated Ag-form silica, in comparison with that treated at 383K, is due most likely to decomposition of silver silicates as noted above.

The effects on retentions of the quantity of sorbed ions as well as modification procedures carried out in-situ are currently under further study, the results of which we hope soon to report.

ACKNOWLEDGMENT

We gratefully acknowledge support of this work provided by the Department of Energy.

REFERENCES

1. Hsu, A.-J., Laub, R. J., and Madden, S. J., **J. Liq. Chromatogr., 7,** 599, 1984.

2. Hsu, A.-J., Laub, R. J., and Madden, S. J., **J. Liq. Chromatogr., 7,** 615, 1984.

3. Laub, R. J., **J. Liq. Chromatogr., 7**, 647, 1984.

4. Laub, R. J., and Madden, S. J., **J. Liq. Chromatogr., 7**, 1984, submitted for review.

5. Laub, R. J., and Madden, S. J., **J. Liq. Chromatogr., 7**, 1984, submitted for review.

6. Laub, R. J., and Madden, S. J., **J. Liq. Chromatogr., 7**, 1984, submitted for review.

7. Laub, R. J., and Madden, S. J., **J. Liq. Chromatogr., 7**, 1984, submitted for review.

8. Scott, R. P. W., and Kucera, P., **J. Chromatogr., 112**, 425, 1975.

9. Hare, P. E., and Gil-Av, E., **Science, 204**, 1226, 1979.

10. Vonach, B., and Schomburg, G., **J. Chromatogr., 149**, 417, 1978.

11. Cooke, N. H. C., Viavattene, R. L., Ersteen, R., Wong, W. S., Davis, G., and Karger, B. L., **J. Chromatogr., 149**, 391, 1978.

12. Kopečni, M. M., Laub, R. J., and Milonjič, S. K., **Anal. Chem., 52**, 1032, 1982.

13. Unger, K. K., **Porous Silica**, Elsevier, Amsterdam, 1979.

14. Ohmacht, R., and Halasz, I., **Chromatographia, 14**, 155, 1981.

15. Parks, G. A., **Chem. Rev., 65**, 177, 1965.

16. Bristow, P. A., and Knox, J. H., **Chromatographia, 10**, 279, 1977.

17. Unger, K. K., Messer, W., and Krebs, K. F., **J. Chromatogr., 149**, 1, 1978.

18. Sillen, L. G., and Martell, A. E., **Stability Constants of Metal-Ion Complexes**, Special Publication No. 17, The Chemical Society, London, 1964.

19. Mikeš, F., Schurig, V., and Gil-Av, E., **J. Chromatogr., 83**, 91, 1973.

20. Vivilecchia, R., Thiebaud, M., and Frei, R. W., **J. Chromatogr. Sci., 10**, 411, 1972.

21. Kunzru, D., and Frei, R. W., **J. Chromatogr. Sci., 12**, 191, 1974.

22. Aigner, R., Spitzy, H., and Frei, R. W., **Anal. Chem., 48**, 2, 1976.

23. Heath, R. R., Tumlinson, J. H., Doolittle, R. E., and Proveaux, A. T., **J. Chromatogr. Sci., 13**, 380, 1975.

24. Heath, R. R., Tumlinson, J. H., Doolittle, R. E., and Proveaux, A. T., **J. Chromatogr. Sci., 15**, 10, 1977.

25. Laub, R. J., Ramamurthy, V., and Pecsok, R. L., **Anal. Chem., 46**, 1659, 1974.

26. Laub, R. J., and Purnell, J. H., **J. Chem. Soc. Perkin Trans. II**, 895, 1978.