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SILVER ON LOW SURFACE AREA SILICA GEL AND ITS PERFORMANCE IN LIQUID CHROMATOGRAPHY

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SUMMARY

Silica gel was treated with water at various high temperatures, *i.e.*, hydrothermally, to reduce the surface area, in the presence of a silver salt. BET (Brunauer, Emmett and Teller) measurements were made to determine the effect of the salt on the surface area. The resulting silica gels were analyzed by atomic absorption for silver content. The materials were then evaluated by liquid chromatography with non-polar and weakly polar eluents for the separations of chloroaniline isomers. Silver, introduced by the present method, appears to affect the surface area and porosity of the silica gel. Some separations, mostly of drugs, were used to illustrate the performance of the silver-modified adsorbent.

INTRODUCTION

We have recently described the preparation and liquid chromatographic (LC) capability of silica gel hydrothermally loaded with cadmium¹. The references cited therein include reviews on charge transfer chromatography and some metal salt-impregnated adsorbents. Recent papers using silver salt modifiers may be added: Schomburg and Zegarski² used silver nitrate dissolved in the mobile phase to effect separation of olefins by reversed-phase LC; Aigner *et al.*³ demonstrated the LC separation of drugs on silver-impregnated silica gels; Warthen⁴ used silver-loaded cation-exchange resins, on a preparative scale, to remove impurities in insect attractants; and Wasik and Brown⁵ used glass beads coated with solid silver nitrate to analyze aromatic hydrocarbon mixture by gas chromatography (GC).

The present work extends the hydrothermal procedure of loading silica gel with metal salt to silver.

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EXPERIMENTAL

The loading of silica gel Davison 62 with silver by treating with water at high temperature was similar to a previously described method¹. Solutions of silver nitrate were used at hydrothermal temperatures (HT) of 250, 300 and 350°. The solution contained 10 g of silver nitrate per 30 ml of water for HT-300; and 15 g per 90 ml for HT-250 and HT-350. The solution was added to 20–30 g of silica gel, 325–400 mesh. A borosilicate glass insert containing the mixture was placed in a high-pressure bomb and was heated to the desired temperature. After 16 h at this temperature, the bomb was cooled to less than 100° and opened. The silica was washed on a sintered glass funnel with water until no silver chloride could be seen from the filtrate when dilute hydrochloric acid was added. The material was then washed with methanol followed by hexane and dried at 50° under vacuum. The support, resieved to 325–400 mesh, was slurry-packed using a balanced density solution of tetrabromoethane and carbon tetrachloride.

Blanks were silica gel hydrothermally treated in the absence of silver nitrate.

RESULTS AND DISCUSSION

Table I lists the results of the surface area measurements and atomic absorption analysis.

While in terms of the conventional per cent load, the three silver-modified silica gels have about the same load (0.3–0.4%), the silver content expressed per square meter is significantly different — this assumes that the silver is on the BET (Brunauer, Emmett and Teller) surface. The hydrothermal temperature does not seem to affect the amount of silver introduced in the silica gel. The surface area is influenced by the hydrothermal temperature and the presence of the silver nitrate.

Silica gels loaded with silver at HT-250, -300 and -350 were gray, off-white and light brown, respectively. Small portions of the materials were placed in a three-hole tubular furnace and, while flushing with air, were heated at 210° overnight. No change of color was observed in any of the material. This could indicate that silver is present in the form of oxide or even metal.

TABLE I
HYDROTHERMALLY LOADED SILICA GEL

<i>HT (°C)</i>	<i>Silver nitrate added</i>	<i>Surface area (m²/g)*</i>	<i>Amount of silver (ppm)**</i>	<i>mg silver/m²</i>
250	no	14.8 (Krypton)	4.3	
250	yes	38.9 (Argon)	3850	0.10
300	no		0.15	
300	yes	10.3 (Argon)	3380	0.33
350	no	1.64 (Krypton)	0.34	
350	yes	2.16 (Krypton)	3790	1.75

* Data from Micromeritics, Norcross, Ga., U.S.A.

** Samples not modified with silver nitrate were analyzed by flameless, otherwise by flame, atomic absorption.

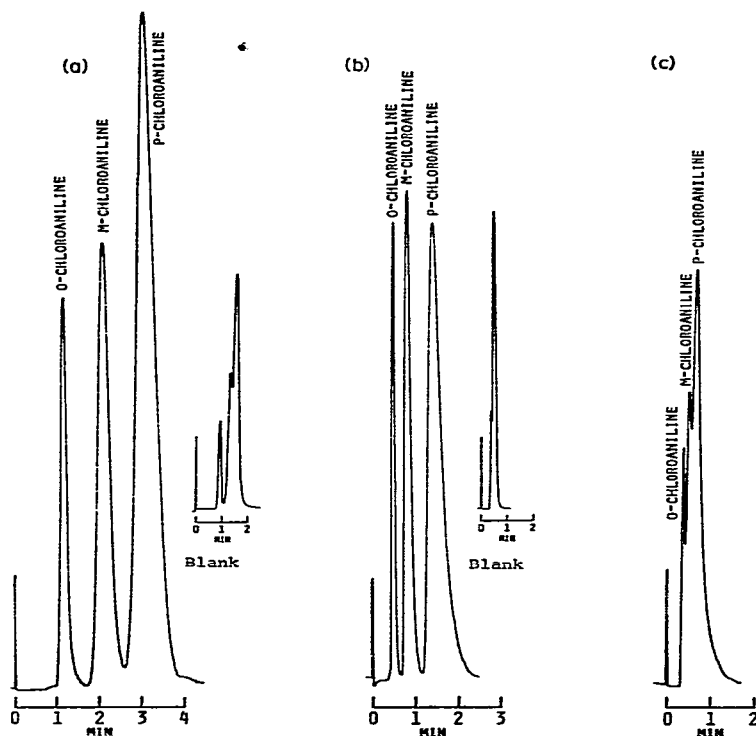


Fig. 1. Chromatograms of chloroanilines on silica gel hydrothermally loaded with silver nitrate. (a) Silver HT-250, 0.1% methanol in hexane; (b) silver HT-300, 0.2% methanol in hexane; (c) silver HT-350, 0.1% methanol in hexane. Column: 11 cm \times 4.5 mm I.D.; eluent flow-rate, 2 ml/min; 254-nm UV detector. Blank, run under identical LC conditions, refers to hydrothermally treated silica gel in the absence of silver nitrate.

Fig. 1 shows the chromatogram of the separation of the chloroanilines using methanol in hexane as the mobile phase. While silver HT-350 did not yield desirable separation, good separations were obtained with silver HT-250 and silver HT-300. This separation deteriorates with slight increases of methanol in the binary solvent. Fig. 2 shows the chromatogram obtained with acetonitrile in hexane as the eluent. It is apparent that methanol and acetonitrile in hexane gave identical chromatograms. In separate testings, none of the silver columns showed baseline separations of the more basic picolines. In this context, hydrothermally introduced silver affects the surface area but does not appear to act as electron pair acceptor.

The degree of surface activity of the columns is better seen by the elimination of the polar component of the mobile phase. Fig. 3 shows the chromatogram obtained with hexane as the eluent. Silver HT-250 retained chloroanilines more than silver HT-300 which, in turn, retained more than silver HT-350. The blanks follow the same order but at a lesser degree of retention. It is obvious that silver columns are more active than their corresponding blanks. This may be due to higher specific surface area of the former which is rich in active sites, either by the presence of the silanol groups or silver oxide. Note, however, that the chloroanilines were retained longer on the column packed with silver HT-250 ($100 \mu\text{g silver/m}^2$) than on silver HT-350 ($1750 \mu\text{g silver/m}^2$).

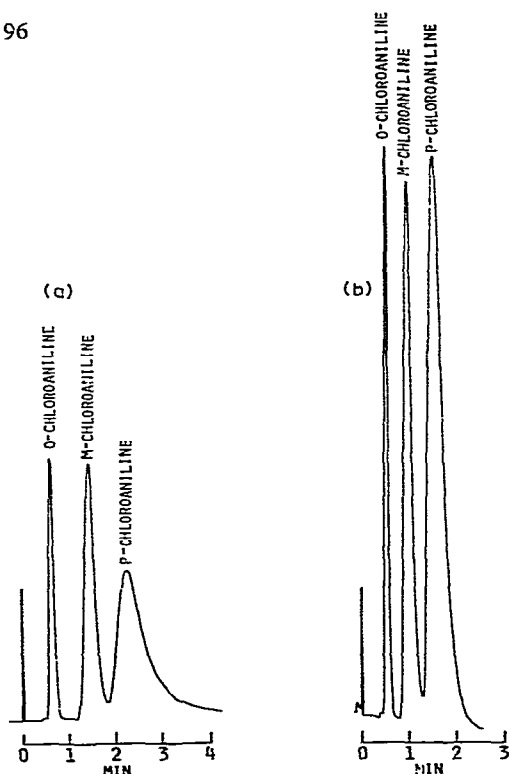


Fig. 2. Same as Fig. 1. (a) Silver HT-250, 0.2% acetonitrile in hexane; (b) silver HT-300, 0.1% acetonitrile in hexane. Eluent flow rate, 4 ml/min. Attenuation: (a) $\times 0.1$; (b) $\times 0.05$.

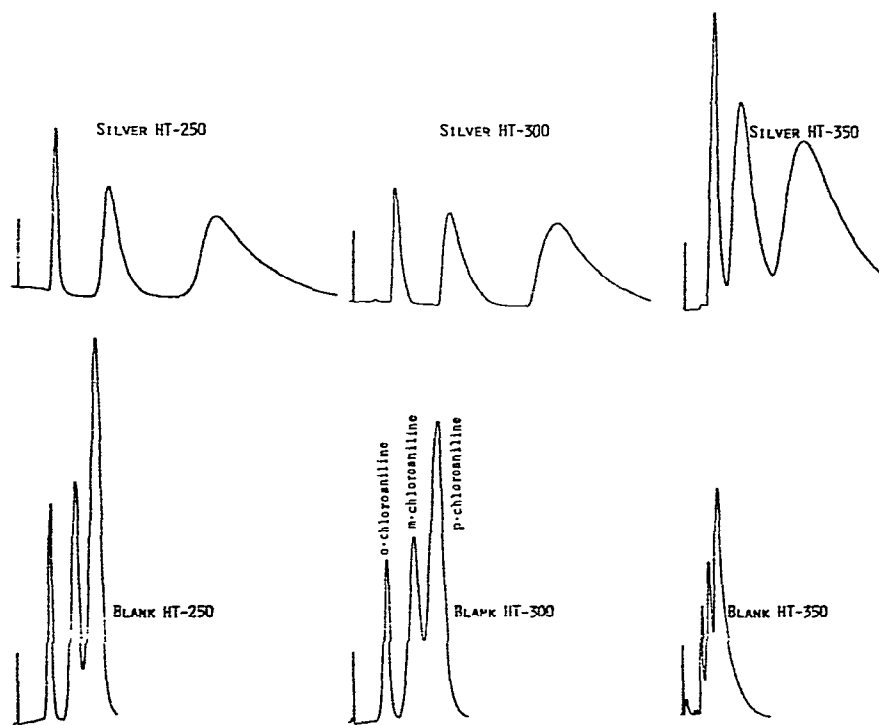


Fig. 3. Comparison of the separation of chloroaniline isomers on silver loaded silica gel using hexane at 2 ml/min as mobile phase. All other LC conditions the same as on Fig. 1.

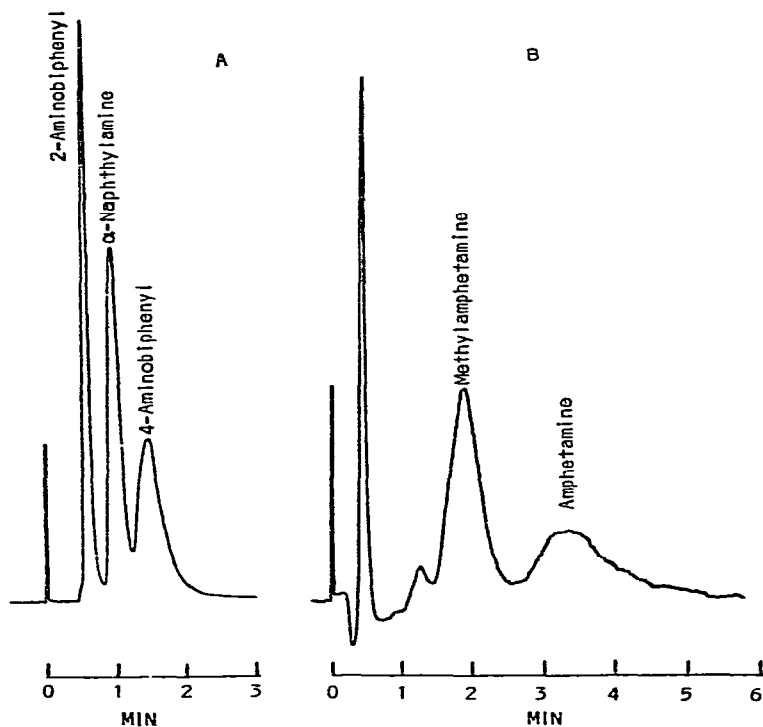


Fig. 4. Separations on silica gel hydrothermally treated at 300° in the presence of silver nitrate; Column: 11 cm × 4.5 mm I.D.; A, 0.5% acetonitrile in hexane; B, chloroform-methanol-hexane-diethylamine (54:1:45:0.01); both at 4 ml/min; 254-nm UV detector.

It appears that if silver, as silver oxide, exerts some effect, it is to a lesser extent than the silanols. On the chromatographic testing shown on Fig. 3, the LC pressures of the silver-loaded columns were 200, 200 and 175 p.s.i. for HT-250, -300 and -350, respectively. However, the blanks were 300 (HT-250), 250 (HT-300) and 200 p.s.i. (HT-350).

The silver HT-300 column was further tested. Fig. 4A shows the separation of the carcinogenic 4-aminobiphenyl from the 2-amino isomer and α -naphthylamine. Fig. 4B shows the separation of amphetamine from methylamphetamine using chloroform-methanol-hexane-diethylamine (54:1:45:0.01).

As is known, superior chromatographic efficiency is obtained by using small size particles, usually in the range of 5–10 μ m. However, the goal of the present study is to introduce silver to the silica. Therefore to reduce cost, all the experiments were done on ground silica gel corresponding to 38–45- μ m particles.

The LC conditions and solvent composition were adjusted to evaluate the elution of drugs of diversified chemical structures. Fig. 5a shows the separation of caffeine (0.2 μ g), thebaine (1 μ g), LSD (2.5 μ g), procaine (5 μ g) and morphine (4 μ g) using gradient elution from A to 60% B, where A = chloroform-hexane (1:1) and B = chloroform-methanol-diethylamine (90:10:0.1). As indicated by the dashed line on Fig. 5a, the sequence of gradient is: linear from A to 20% B in 4 min, step-up to 45% B, then gradient to 60% B in 6 min. A similar mixture (of slightly different concentra-

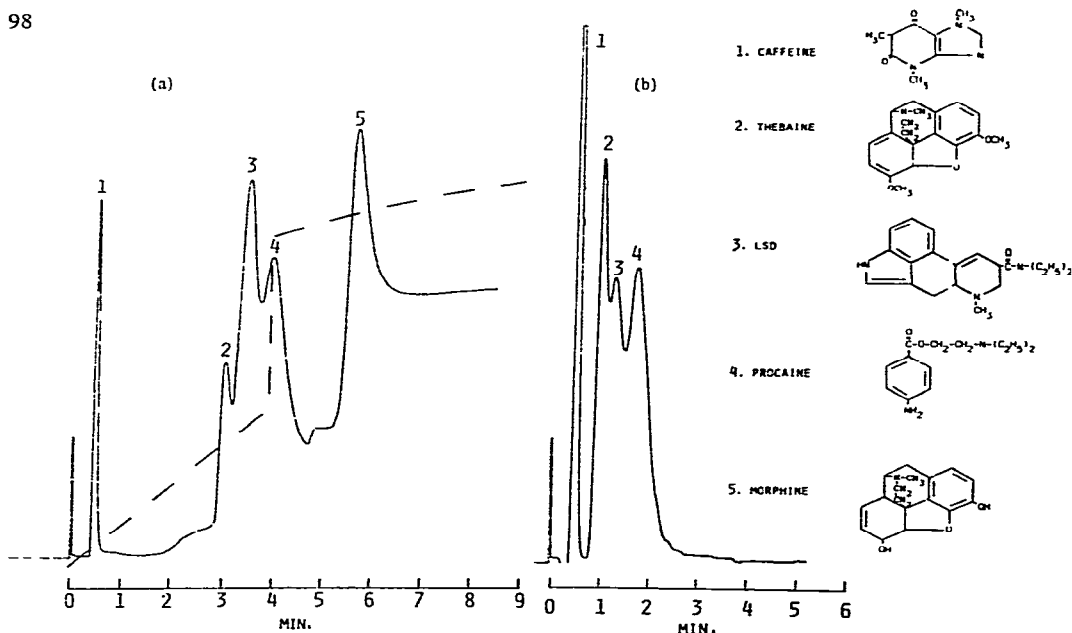


Fig. 5. Separation of selected drugs. Column: same as in Fig. 4. (a) Gradient elution, shown by the dashed line, from A to 60% B (see text); (b) isocratic elution (see text); Waters Assoc. Model 440 absorbance detector (254 nm); both at 4 ml/min.

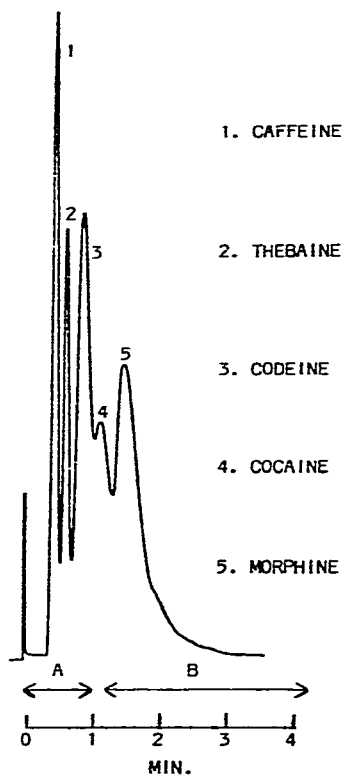


Fig. 6. Stepwise elution of a model drug mixture. Packing and column same as in Fig. 4. Solvent: chloroform-methanol-hexane-diethylamine; A = 66:4:30:0.04; B = 65:12:23:0.06; both at 4 ml/min; 254-nm UV detector.

tions) was run isocratically with chloroform–methanol–hexane–diethylamine (58:2:40:0.02). As shown on Fig. 5b, morphine is not eluted from the column. In this isocratic run, if the 0.02% diethylamine is eliminated from the mobile phase, all but caffeine were irreversibly adsorbed. In addition, butalbital and barbital (compounds with structural analogy to caffeine) were essentially unretained with chloroform–hexane (1:1).

A two-stepwise elution was also demonstrated with chloroform–methanol–hexane–diethylamine: Step A: 66:4:30:0.04; step B: 65:12:23:0.06. This is shown in Fig. 6. The retention volumes of the different drugs show strong interactions of these solutes with the adsorbent.

CONCLUSION

Silver can be incorporated into silica by a modification of hydrothermal treatment. Three such silicas with surface areas ranging from 2 to 40 m²/g and silver contents from 0.1 to 2 mg silver/m² have been prepared and their behaviour in liquid chromatography has been investigated. These phases appear to differ from comparable silica blanks mainly in surface activity rather than selectivity. They are suited for a variety of separations, including some drugs of current interest.

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