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GLASS CAPILLARY ADSORPTION COLUMNS FOR GAS CHROMATOGRAPHY

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SUMMARY

Adsorption columns for the separation of hydrocarbons have been prepared by coating glass capillary tubing with hydrophobic silica applied from organic solvents. Commercially available hydrophobic silicas, as well as some prepared in our laboratory, have been utilized. These columns provided sharp, symmetrical peaks for light hydrocarbons.

INTRODUCTION

Capillary adsorption columns coated with silica sols were described in 1963¹. The first columns were prepared with commercially available aqueous silica sols or with silica dispersions mixed in our laboratory. Capillaries prepared from Delrin, nylon, copper, or stainless-steel tubing were evaluated for the separation of hydrocarbon mixtures. Sharp, symmetrical peaks were obtained for saturated hydrocarbons. However, aromatic hydrocarbons had a tendency to "tail" and to show variable retention times on some of these columns. It is very difficult to separate and measure the adsorptive effects of the column tubing from that of the colloidal adsorbent coating. Further, the degree of adsorption depended on the water content of the adsorbent and/or the carrier gas as well as the size of the sample. These are all characteristics of separations by gas-solid chromatography with hydrophilic adsorbents.

Later, a commercially available hydrophobic silica², which could readily be dispersed in light hydrocarbon solvents, was tested as a coating for Delrin and stainless-steel capillary columns. Better results, in terms of efficiency and separation, were obtained with these columns than with the hydrophilic silica columns. Also, the problems caused by variable water content of the coating and the carrier gas were avoided. However, we still could not quantitatively separate the adsorptive effects of the steel column surface from those of the silica. The use of colloidal hydrophobic silica as an "addition agent", to help in the coating of capillaries with elastomers, or other viscous materials, was also proposed.

Recent work³ here has indicated that soft-glass columns provide more rapid elution of hydrocarbons than stainless-steel columns when non-polar liquid phases are utilized. Therefore, it appeared worthwhile to investigate the separation of hydro-

carbons with glass columns coated with adsorbents. It was expected that the glass columns would be more "inert" than stainless steel and that they could be used at sub-ambient as well as at elevated temperatures. This paper presents results for hydrocarbon separations obtained using glass columns coated with some typical hydrophobic silicas.

EXPERIMENTAL

A GDM-1 glass-drawing machine (Shimadzu) was used to draw the glass capillaries (Kimble R-6 soda-lime glass).

A Sigma 3 gas chromatograph (Perkin-Elmer), equipped with a hydrogen flame-ionization detector, was utilized. Columns were connected with heat-shrinkable 30 gauge PTFE.

A Model 3385A chromatographic automation system (Hewlett-Packard) was employed to provide retention time and peak area data.

Reagents

Solvent used for column coating was heptane from Burdick & Jackson Labs. (Muskegon, Mich., U.S.A.). The hydrocarbons used to prepare standard blends were high-purity reagents from Phillips Petroleum (Bartlesville, Okla., U.S.A.) or the American Petroleum Institute.

Igepal CO-430 was obtained as a sample from GAF Corp. (Charlotte, N.C., U.S.A.). Anhydrous sodium sulfate was procured from Matheson, Coleman & Bell (East Rutherford, N.J., U.S.A.). *p*-Toluenesulfonic acid monohydrate was obtained from Aldrich (Milwaukee, Wisc., U.S.A.). Methanol and xylene were Baker analyzed reagent grade.

CD-100, a colloidal hydrophobic silica, was a sample from Nalco (Houston, Texas, U.S.A.). This material is no longer available. Syloids, micron-sized amorphous silicas, were samples from W. R. Grace (Baltimore, Md., U.S.A.).

RESULTS

All experiments were performed with 300 ft. \times 0.02 in. I.D. columns prepared here from Kimble R-6 soda-lime glass. Hydrogen carrier gas, at 5 p.s.i., was used in all tests.

In order to compare results with those of our previous work, with a colloidal adsorbent, a glass column was coated with a 5% suspension of CD-100 in heptane. The results obtained are shown in Figs. 1, 2 and 3.

Fig. 1 demonstrates the separation of a 13-component hydrocarbon blend at 75°F. The C₆-C₇ resolution was 22, and the ratio (retention time for cyclohexane/retention time for 2,4-dimethylpentane) (t_N/t_P) was 0.98. Benzene was not resolved in this chromatogram; therefore, the ratio (retention time for benzene/retention time for 2,4-dimethylpentane) (t_A/t_P) was not determined.

Better results were obtained with this column at 32°F. Fig. 2 depicts the separation of the 13-component mixture. All components were resolved; the C₆-C₇ resolution was 42, and t_N/t_P and t_A/t_P were each 0.94. During work with CD-100, we noted a strong odor which indicated that, perhaps, free alcohol was present. To test

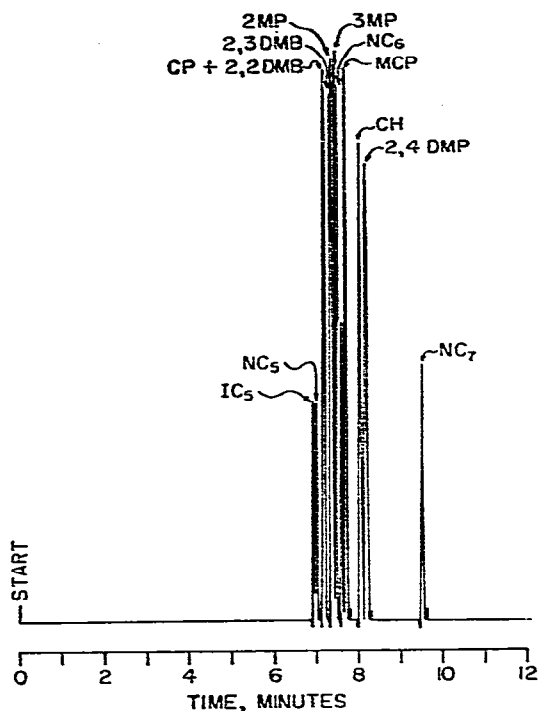


Fig. 1. Separation of light hydrocarbons. Column, 300 ft. \times 0.02 in. I.D. glass coated with 5% CD-100; temperature, 75°F; pressure, 5 p.s.i. hydrogen.

this possibility, we conditioned the column, used in Figs. 1 and 2, for 16 h at 100°C.

The results for the separation of the 13-component mixture at 72°F, on the conditioned column, is shown as Fig. 3. It should be noted that the retention times have increased relative to those of the original column (Fig. 1). Benzene and even normal heptane are "tailing". These results are probably due to the removal of the excess alcohol by the conditioning process. Thus, we conclude that in the original column the excess alcohol was functioning as a modifier of the solid and was helping to provide symmetrical peaks. The C_6 - C_7 resolution was 27, t_N/t_P was 0.88 and t_A/t_P was 1.18. Although benzene was not resolved with the column used in Fig. 1, the t_A/t_P value for Fig. 1 was lower than that obtained, in Fig. 3, after conditioning.

As CD-100 is no longer available from Nalco, we directed our attention to the preparation of other hydrophobic silicas from commercially available hydrophilic silicas. A synthesis of such a silica, prepared from Syloid-244 and Igepal CO-430, is described below.

The reaction product obtained appears to result from both an esterification⁴ and the strong adsorption of the Igepal on the silica surface similar to that described by Aue and Younker⁵ for Carbowax on a siliceous support.

Synthesis

In a typical procedure, a 1000-ml round-bottom flask was charged with 25 g of Syloid-244 (4- μ m silica), 25 g of Igepal CO-430 and 500 ml of xylene. A 2-g portion

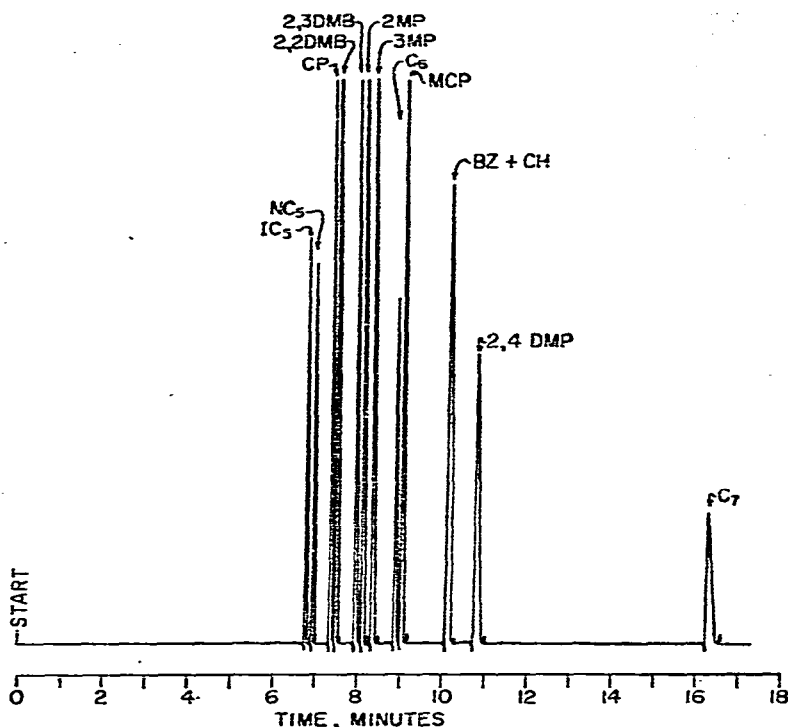


Fig. 2. Separation of light hydrocarbons. Column, 300 ft. \times 0.02 in. I.D. glass coated with 5% CD-100; temperature, 32°F; pressure, 5 p.s.i. hydrogen.

of *p*-toluenesulfonic acid monohydrate was added as catalyst. The flask was attached to a Soxhlet extraction apparatus and stirred magnetically at reflux for 48 h. The extraction thimble was filled with anhydrous sodium sulfate to remove water.

After cooling to room temperature, the reaction mixture was diluted with 300 ml of methanol and filtered. The filter cake was washed with methanol, the silica was filtered, washed again with methanol and dried on the suction filter. The white hydrophobic product was further dried in an oven for 1 h at 90°C. Loss on ignition indicated an organic content of approximately 23%.

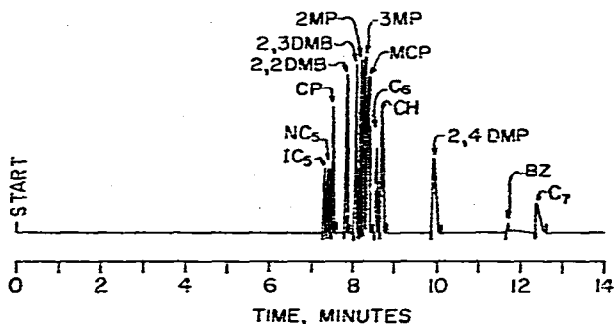


Fig. 3. Separation of light hydrocarbon standard on CD-100 column after conditioning for 16 h at 100°C. Conditions as in Fig. 1.

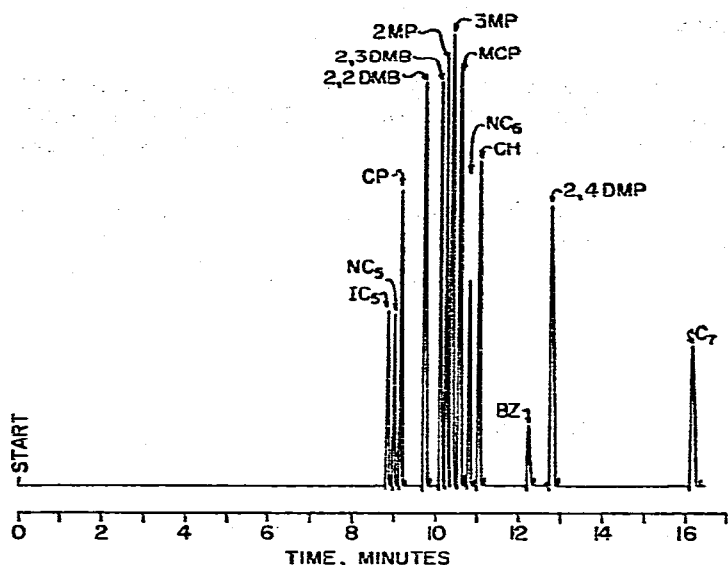


Fig. 4. Analysis of 13-component hydrocarbon mixture. Column: 300 ft. \times 0.02 in. I.D. glass coated with 5% Syloid 244-Igepal CO-430 reaction product; temperature, 77°F; pressure, 5 p.s.i. hydrogen.

This synthetic product was coated onto another glass column and some results obtained are shown in Figs. 4 and 5. The results obtained at 77°F, for the 13-component Fig. 4 mix, showed a C_5 - C_7 resolution of 37, a t_N/t_P of 0.87 and a t_A/t_P of 0.96. Fig. 5 shows the separation of a typical East Texas distillate fraction³ obtained with this column at 79°F. Further work will be required to identify the components of this distillate. However, these results were suitable for our analytical purposes.

This column was conditioned at 250°C for several hours. Upon cooling to room temperature, results similar to those shown in Figs. 4 and 5 were obtained.

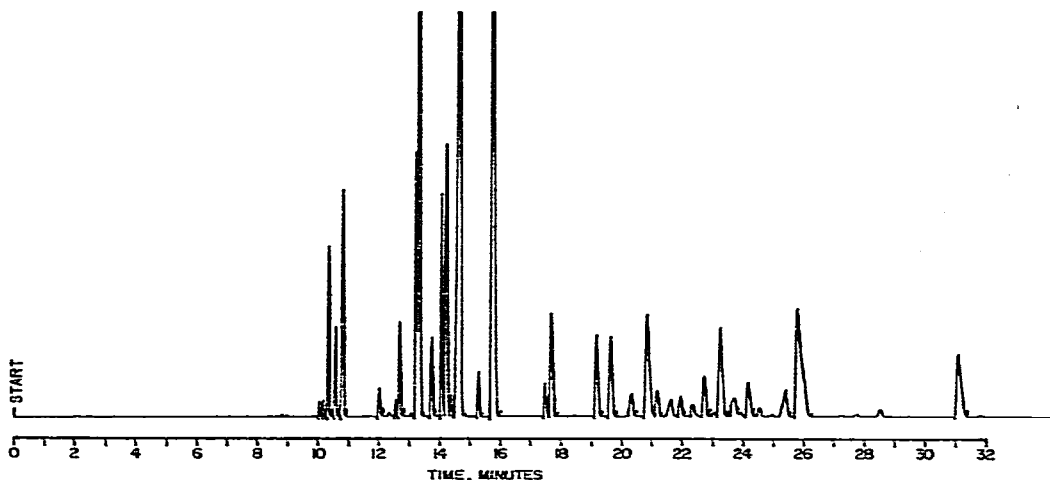


Fig. 5. Analysis of East Texas distillate fraction. Column: 300 ft. \times 0.02 in. I.D. glass coated with 5% Syloid 244-Igepal CO-430 reaction product; temperature, 79°F; pressure, 5 p.s.i. hydrogen.

DISCUSSION AND CONCLUSIONS

The results obtained indicate that chemically modified silicas, prepared as described, can be readily coated onto glass capillary columns. These columns, which are stable to at least 200°C, provide useful and efficient separations of light hydrocarbons.

Further, other stationary phases, such as silicones, can be coated onto glass columns by addition to these silicas, in a solvent such as heptane. We are currently engaged in studies of the preparation of glass columns coated with hydrophobic silica-silicone mixtures.

REFERENCES

- 1 R. D. Schwartz, D. J. Brasseaux and G. R. Shoemake, *Anal. Chem.*, 35 (1963) 496.
- 2 R. D. Schwartz, D. J. Brasseaux and R. G. Mathews, *Anal. Chem.*, 38 (1966) 303.
- 3 R. G. Mathews, J. Torres and R. D. Schwartz, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 139.
- 4 R. K. Iler, *The Colloid Chemistry of Silica and Silicates*, Cornell University Press, Ithaca, New York, 1955, p. 170.
- 5 W. A. Aue and D. R. Younker, *J. Chromatogr.*, 88 (1974) 7.