

CHROM. 6539

Note

The gas chromatographic properties of a modified, wide-pore silica gel*

Silica gels have been used for gas chromatography (GC), with polar and unpolar carriers, since the early nineteenforties¹. Their main application today is in the analysis of gases; they play little role in the separation of higher, especially polar organics. There, diatomaceous supports are decidedly superior.

Yet silica gels command potential interest because they are inexpensive and easy to produce with a wide range of surface areas. Various processes of deactivation, *e.g.* silylation, hydrothermal treatment, coating with inorganics, polymers or polar molecules from the carrier gas stream, etc., have been employed to improve their performance with heavier organics². Improvements could be demonstrated but, as a whole, silica gels have remained inferior to diatomaceous supports in GC efficiency.

In this study, we decided to modify a low-priced silica gel — Davidson grade 62 (ref. 3), which has a low surface area of 3.40 m²/g, a large average pore diameter of 170 Å (ref. 4), a high pore volume of 1.15 cm³/g, and sells in the scientific retail trade for little more than a dollar per pound³. This material is not commonly used in GC, although it is capable of surprisingly good separation of hydrocarbons (Fig. 1, bottom trace).

Three simple deactivation processes were to be used — singly or in combination.

First, we wanted to reduce further the available surface area and widen the pores. This can be achieved by calcination, by treatment with salts or by treatment with water at high temperature. Neither process has been described in much experimental detail. We decided to use the last one, called "hydrothermal treatment" under experimental conditions (especially the state and amount of water) which may or may not have been identical to the procedures described in the literature⁵⁻⁹.

Second, we wanted to deactivate the silica gel surface¹⁰ by a non-extractable polymer layer; this is similar to a technique used to produce (nominally) monomolecular layers of Carbowax 20M on Chromosorb¹¹.

Third, we wanted to deactivate the silica gel surface by adding small amounts of a polar compound, in our case water, to the carrier gas. The use of polar mobile phases is well known and has been repeatedly applied (*e.g.* 12-23, compare ref. 24, 25).

Experimental

General preparation of the silica gel. Silica Gel Davidson 62 (Fisher Scientific Co., St. Louis, Mo.), 40-60 mesh, was washed in a Soxhlet (Kontos Model K-585100) with HCl at boiling point temperatures until no yellow hue could be detected in a fresh charge of conc. HCl, hot or cold, after several hours of extraction. The silica gel was then washed with distilled water to neutrality.

Hydrothermal treatment. A high-temperature bomb (Model 4740 with Pyrex

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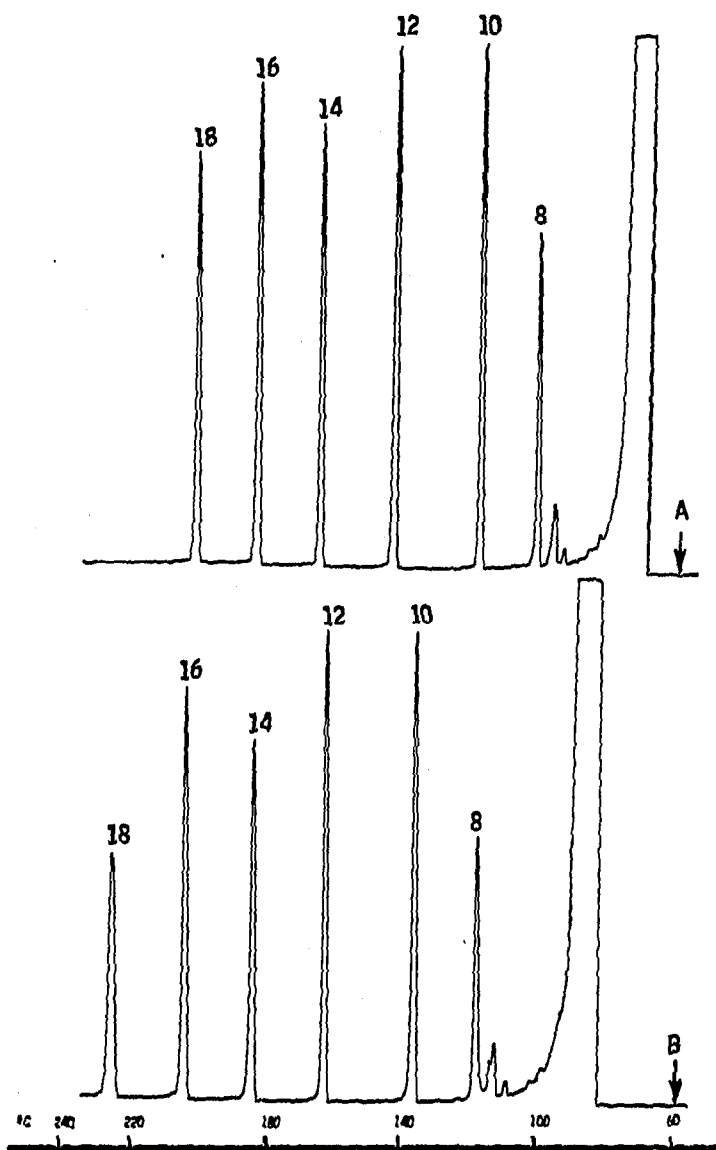


Fig. 1. Separation of even-numbered *n*-alkanes (octane through octadecane) on bare silica gels. Both columns: Silica Gel 62, 40-60 mesh, acid washed; in 120 cm \times 4 mm I.D. Pyrex U-tube, nitrogen flow-rate 80 ml/min, 6 °/min temperature program, FID. (A) Silica Gel 62 hydrothermally treated at 280° overnight and acid washed; (B) untreated silica gel. The *n*-alkanes are represented by their number of carbon atoms.

insert tube, Parr Instrument Co., Moline, Ill.) was filled with a slurry of acid-washed silica gel and distilled water such that their levels were at approximately 2/3 and 3/4 of the tube, respectively. The closed bomb was lowered into a muffle furnace at 280°, left overnight, and removed after the furnace had been allowed to cool down in the morning. The silica gel was then again acid-washed as before to remove any traces of metal originating from the steel bomb, its nickel gasket, or copper lubricant.

Coating with Carbowax 20M. Dry silica gel was coated with 6% Carbowax 20M, heat-treated under nitrogen overnight at 260°, and exhaustively extracted with methanol; this is similar to the procedure described for Chromosorbs¹¹.

Addition of water to the carrier gas. The carrier gas line of a Microtek-220 gas chromatograph was cut between flow-control module and injection port, and the nitrogen made to bubble through distilled water contained in a stainless-steel trap.

Results and discussion

The hydrothermal treatment reduced the surface area of silica gel considerably (to 141 m²/g, Micromeritics Instrument Corp., Norcross, Ga.). The non-extractable coating of Carbowax 20M on this support had a nominal thickness of 2 Å (carbon 1.52%, Peninsular Chemical Research).

Acid-washed Silica Gel 62, without the benefit of further modifications, gave good chromatograms of *n*-hydrocarbons (Fig. 1). It failed to pass any alcohols, however, at 140° (Fig. 2, trace A). This separation must be obtained by either hydrother-

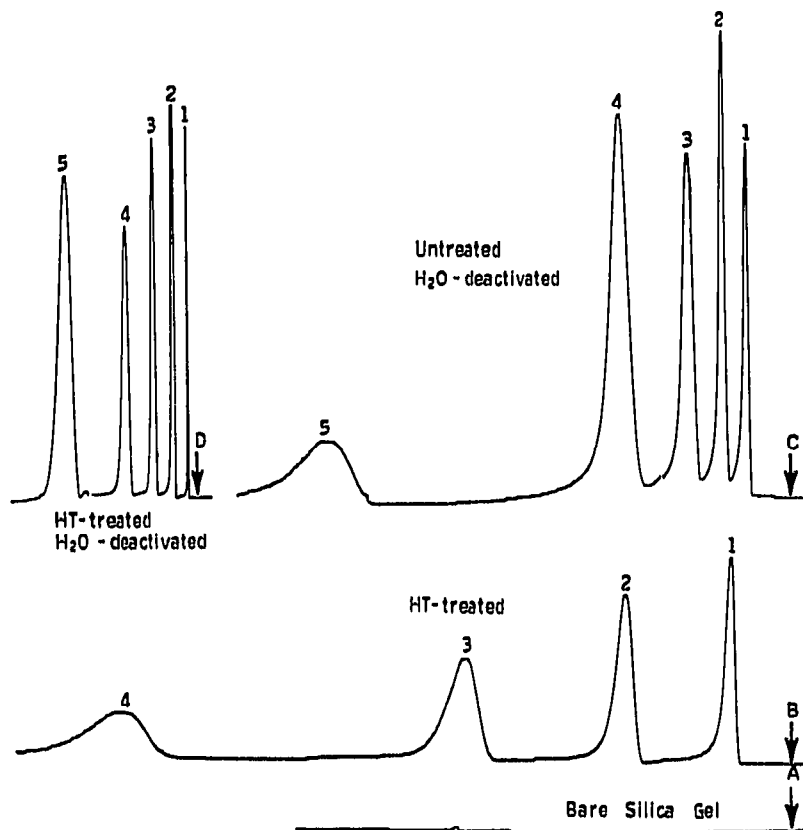


Fig. 2. Separation of *n*-alkanol standards (methanol through pentanol) on bare silica gels. All columns: Silica Gel 62, 40–60 mesh, acid washed; in 120 cm × 4 mm I.D. Pyrex U-tube at 140°, nitrogen flow-rate 80 ml/min, FID. (A) Bare silica gel; (B) Silica Gel 62 hydrothermally treated at 280° overnight and acid washed; (C) carrier gas saturated with water at ambient temperature; (D) water-deactivated and hydrothermally treated silica gel.

mal treatment (Fig. 2, trace C), or coating with Carbowax 20M (Fig. 3, trace D), or the presence of water in the carrier gas (Fig. 2, trace B). Other traces show various combinations of the three treatments, all tested under the same chromatographic conditions.

GC of lower aliphatic alcohols provides in our opinion a severe test for the degree of deactivation of the adsorbent surface. Each of the methods did well on its own — combining all three of them (Fig. 3, trace A) may have been a case of overkill (at least in this particular analysis), but was included to allow a visual comparison of effects accumulating under the same chromatographic conditions. Fig. 4 represents a more reasonable choice of parameters for the separations of the alcohols, *i.e.*, a temperature-programmed run without the benefit of water in the carrier gas.

Judging from the chromatographic improvement obtained by the use of these

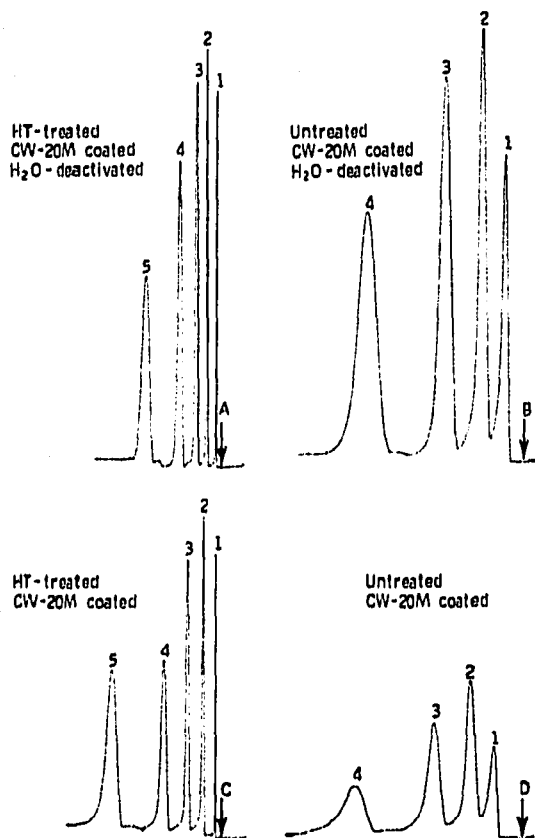


Fig. 3

Fig. 3. Separation of *n*-alkanol standards (methanol through pentanol) on Carbowax-coated silica gels. All columns: Silica Gel 62, 40–60 mesh, acid washed, coated with Carbowax 20 M, heat-treated and extracted; in 120 cm × 4 mm I.D. Pyrex U-tube at 140°, nitrogen flow-rate 80 ml/min, FID. (A) Silica Gel 62 hydrothermally treated at 280° overnight and acid washed (before coating with Carbowax), carrier gas saturated with water at ambient temperature; (B) water-deactivated silica gel; (C) hydrothermally treated silica gel; (D) untreated silica gel.

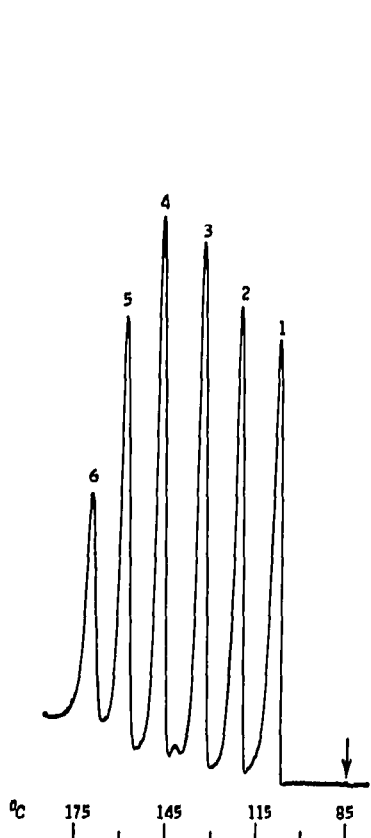


Fig. 4

Fig. 4. Separation of *n*-alkanols (methanol through hexanol). Column: Silica Gel 62, 40–60 mesh, acid washed, HT-280°, coated with Carbowax 20 M; in 150 cm × 2 mm I.D. Pyrex U-tube, nitrogen flow-rate 80 ml/min, temperature program 6°/min, FID.

three simple techniques, it would appear feasible to modify silica gels further (*e.g.* by further reduction of the surface area combined with the use of better monomolecular layers) to a point where they can be used in place of diatomaceous supports for many GC analyses. The coated materials should also provide interesting materials for liquid chromatography²⁰ and physicochemical studies.

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