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Note

Deactivation of whisker-walled open tubular columns with octamethylcyclotetrasiloxane

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The increasing awareness of the glass surface chemistry of open tubular columns has led to improvements in deactivation methods involving acid leaching techniques followed by silanization. Reports[1,2] have indicated that acid leaching removes metal ions from the glass surface, an observation that was confirmed by Auger spectroscopy[3]. Back-migration of the metal ions from the bulk glass to the surface was observed at high temperature[4,5] and a leaching depth of 5–8 μm was suggested to prevent this phenomenon[5]. Various silanization methods at moderate temperatures were investigated for deactivation of the glass surface[6–11], however, silanization only succeeded as a viable deactivation technique when high temperatures (300–400°C) were used[12,13]. Subsequent studies which incorporated these modifications, as well as new silanization reagents[4,14–16], demonstrated marked improvement in deactivation. With the advent of the fused silica column, Stark *et al.*[17] demonstrated that octamethylcyclotetrasiloxane provided thermostability to 350°C for coating apolar liquid phases on such a surface. This report describes a method to deactivate whisker-walled open tubular columns with this reagent.

EXPERIMENTAL

The whisker-walled open tubular columns were prepared as reported elsewhere[18]. Octamethylcyclotetrasiloxane (OMCTS) was purchased from Ohio Valley Specialty Chemical (Marietta, OH, U.S.A.). Concentrated hydrochloric acid was purchased from Fisher Scientific (King of Prussia, PA, U.S.A.), and a 20% solution was prepared in Milli-Q® filtered distilled water.

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RESULTS AND DISCUSSION

The persilylation method of the Grobs[13,14], employing hexamethyldisilazane (HMDS), was studied for the deactivation of whisker-walled capillaries. However, the resulting columns, although reasonably good when evaluated with a polarity test mixture, deteriorated rather quickly ($\approx$2 weeks), indicating loss of deactivation, even when the columns were sealed under nitrogen. With whisker glass capillary columns, a prohibitive amount of ammonia was liberated as a by-product of the HMDS reaction in comparison to a 30% column volume produced with smooth glass capillary columns. This observation was thought to result from the increased surface area (*ca* 10 times) of the whisker-walled column reacting with more HMDS than observed with a smooth-walled column of similar dimension. This excess ammonia was postulated to cause the poor deactivation stability since, as mentioned by Grob[14], excess ammonia continually exposes more of the silica glass structure.

The Grob technique[13,14] of acid leaching and dehydration combined with the octamethylcyclotetrasiloxane reagent introduced by Stark *et al*[17] for deactivating fused silica capillary columns produced well deactivated whisker glass capillary columns.

The whisker-walled glass capillary was leached with acid according to the following procedure: both ends of the capillary were straightened to approximately 30 cm in a Bunsen burner flame. The column was filled to a volume of *ca* 92% capacity with a 20% hydrochloric acid solution using dry nitrogen. The ends of the capillary were microtorch sealed and the column placed in a beaker in a vacuum oven where the temperature was gradually raised to 180°C and the oven evacuated to 60 Torr. After 16 h, the acid solution was washed out of the capillary with one column volume of water followed by a one-column volume water wash in the opposite direction. The capillary was positioned in the gas chromatograph with the straight ends protruding outside above the oven. The capillary surface, regardless of column length, was dehydrated at 150°C for 20 min with the column ends open to the atmosphere. Vacuum (120 Torr) was then applied to both ends of the capillary through a glass T-piece connected to a water aspirator for a time dictated by the column length as described by Grob[14]. As soon as the oven temperature was lowered, both ends of the capillary were immediately sealed under vacuum. One end of the cooled dehydrated capillary was broken and immediately immersed in octamethylcyclotetrasiloxane. After a sufficient amount of this solution was drawn into the column, this end of the column was attached to an SGE glass septum connection and dynamically coated at a velocity of 2 cm/sec with pressure regulated dry nitrogen. Immediately after coating, both ends of the capillary were attached to vacuum (120 Torr) for a specified time[14]. The ends were microtorch sealed and the column was placed in the gas chromatograph. The oven temperature was programmed from 250°C to 400°C at 10°/min and held at 400°C for 12 h. One end of the column was broken under toluene and sequentially washed once in each direction with one-third column volume of toluene, methanol and diethyl ether. Dry nitrogen was employed to push the solvent through the column. The dry column was subsequently connected to the injection port of a gas chromatograph and subjected to temperature program treatment from 40°C to 250°C at 6°/min with a final hold of 1 h at 250°C. A helium carrier gas pressure of 10 p.s.i. was maintained during this period. At this point, the deactivated

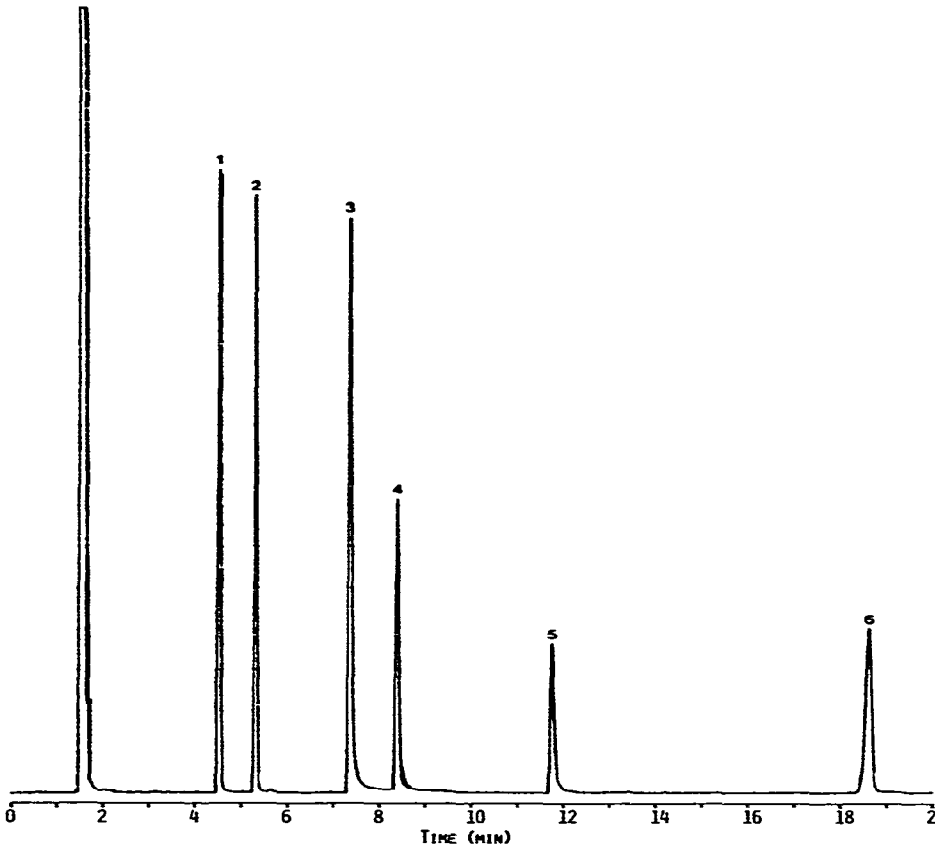

Fig 1 Chromatogram of a polarity test mixture on an octamethylcyclotetrasiloxane deactivated whisker-walled glass capillary column (25 m × 0 25 mm I D , d_f = 0 2 μm), static coated with SE-30 Linear velocity 28.5 cm/sec Λ = 3378 plates per m Helium carrier gas at 20 p s i k = 11 5 Temperatures detector, 245°C, injector, 250°C, column, 83°C Split ratio 100 1 Attenuation 32 × 1 Sample polarity test mixture in hexane Peaks 1 = 2-octanone, 2 = *n*-decane, 3 = 1-octanol, 4 = 2 6-dimethylphenol, 5 = 2,4-dimethylaniline, 6 = *n*-dodecane

column was sealed under nitrogen for storage or directly coated with a liquid phase

A 25 m × 0 25 mm I.D. whisker walled glass capillary column deactivated in this manner was static-coated with SE-30 at a film thickness of 0 2 μm A chromatogram (Fig 1) of a test mixture, which was separated on this column, illustrates the results obtained using this deactivation technique Whisker-walled capillaries deactivated with this procedure have provided thermal stable columns coated with OV-17 (≥270°C), OV-210 (250°C) and Carbowax 20M (220°C) Using this technique on an OV-210 coated column was found useful in the separation of biologically important prostaglandins[19]. The dramatic difference in this separation compared to that obtained with an SE-30 column resulted from the inherent variation in the selectivity offered by OV-210. This deactivation procedure allows the preparation of stable columns coated with moderately polar and polar liquid phases Such stable polar columns provide the increased selectivity necessary for difficult separations, as illustrated by the prostaglandin studies

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