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PREPARATION OF GLASS CAPILLARY COLUMNS FOR LIQUID CHROMATOGRAPHY*

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SUMMARY

Procedures were tested for the preparation of capillary columns for liquid–solid and liquid–liquid systems. A layer of silica gel of thickness 0.3–50 μm is formed by the reaction between a solution of ammonia and tetramethylammonium hydroxide, which even permits coating with a liquid stationary phase.

INTRODUCTION

Utilization of theoretical knowledge and practical experience of gas chromatography in high-performance liquid chromatography led to experimental verification of the assumption that capillary columns[1–7] could be applied in liquid chromatography. Considering the similarity between gas and liquid chromatography, if a diameter of about 200–300 μm were the optimal compromise for a capillary column in the gas chromatography, the corresponding diameter in liquid chromatography would be 20–30 μm.

Both liquid–solid and liquid–liquid systems can be prepared in the form of capillary columns, either as SCOT or PLOT columns with a thin layer of adsorbent or as WCOT columns for liquid–liquid systems.

As silica gel is very useful as a stationary phase or a matrix carrying chemically bonded phases, only this alternative was considered here.

When preparing capillary columns proper, glass was preferred to metal because (a) glass capillaries can easily be drawn in laboratory equipment to the required dimensions; (b) glass is hard enough (capillaries with diameters of 60 and 800 μm were subjected to the pressures up to 120 MPa without any damage)[8]; (c) glass is transparent and the process of preparation can be checked visually; (d) glass is a solicate material and can be used as a raw material for the preparation of silica gel layers by using a suitable procedure.

It is necessary that an optimal and constant thickness of the adsorbent layer is obtained and for the mechanical strength of the layer on the capillary wall to be adequate at high flow-rates of the mobile phase.

* Note by the Editor: Similar work using sodium hydroxide solutions was subsequently presented by Ishii *et al.* at the *4th International Symposium on Column Liquid Chromatography, Boston, Mass., May 7–10, 1979* (D. Ishii, T. Tsuda and T. Takeuchi, *J. Chromatogr.*, 185 (1979) 73).

EXPERIMENTAL

Preparation of capillaries

Glass capillaries were drawn in an arrangement described by Desty *et al.*[9] from tubes of both soft and Pyrex glass. In order to verify the possibilities of preparing capillary columns by means of various techniques, 25–80 m long capillaries with diameters of 30–200 μm were prepared.

Reagents

Solutions of ammonia in distilled water of concentration 8–16% and solutions of tetramethylammonium hydroxide in methanol of concentration 2.5–20% were prepared.

Operating procedures

(1) The capillary was filled to 90% of its length with the solution of the reagent, both ends were sealed and the column was maintained at 150–170° for 2–24 h. After cooling the solution was forced out with nitrogen and, under a continuous flow of nitrogen, the capillary was heated at 150–350° for 10–120 min.

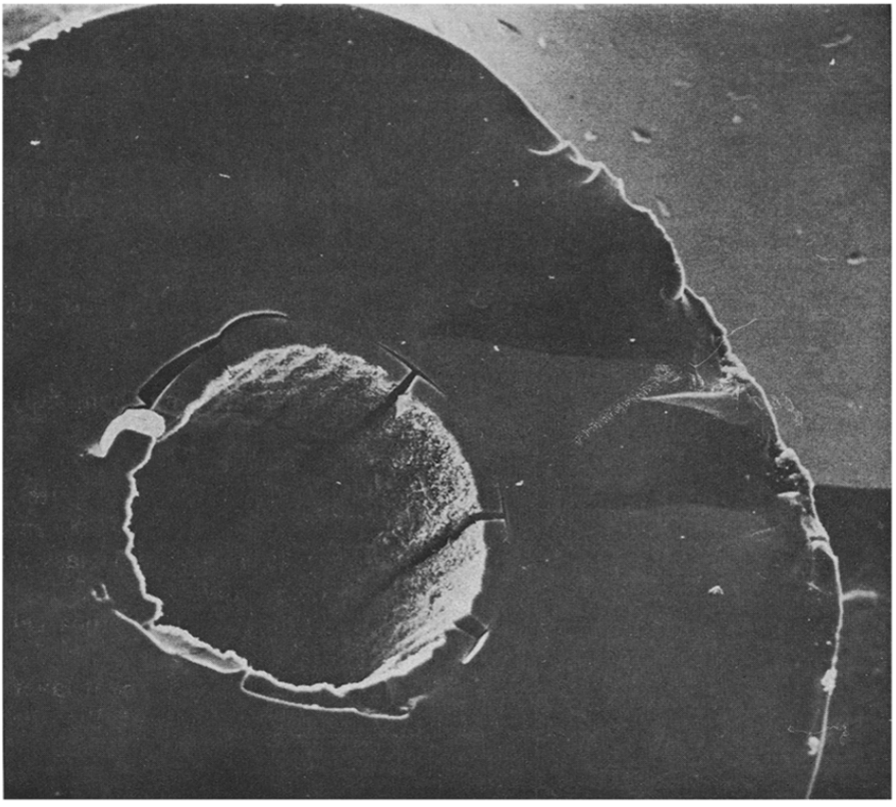

Fig. 1. Section through the capillary column with the silica gel layer prepared by the action of ammonia solution.

(2) The capillary was filled to a length of 1 m with the solution of the reagent and this column of reagent was forced through the whole capillary. The excess of the solution was forced out and the capillary was heated at 150–170° for 2 h. The temperature was then increased to 350°.

RESULTS AND DISCUSSION

With both procedures the reagent used reacts with the silicate component of the glass wall, and either the ammonium or tetramethylammonium salt of silicic acid is formed. The salts are deposited firstly on the wall of the capillary where they were created, but are subsequently partly transferred into the solution with which they are later forced out of the capillary when the excess of reagent is removed.

Ammonium and tetramethylammonium salts of silicic acid decompose on heating and, after volatile components (ammonia, trimethylamine etc.) have been removed, silica gel remains on the wall of the capillary.

The preparation of silica gel layer according to Mohnke and Saffert[10] with either ammonia solution or tetramethylammonium hydroxide solution is suitable only for capillaries with diameters of 100 μm or greater. Capillary columns were

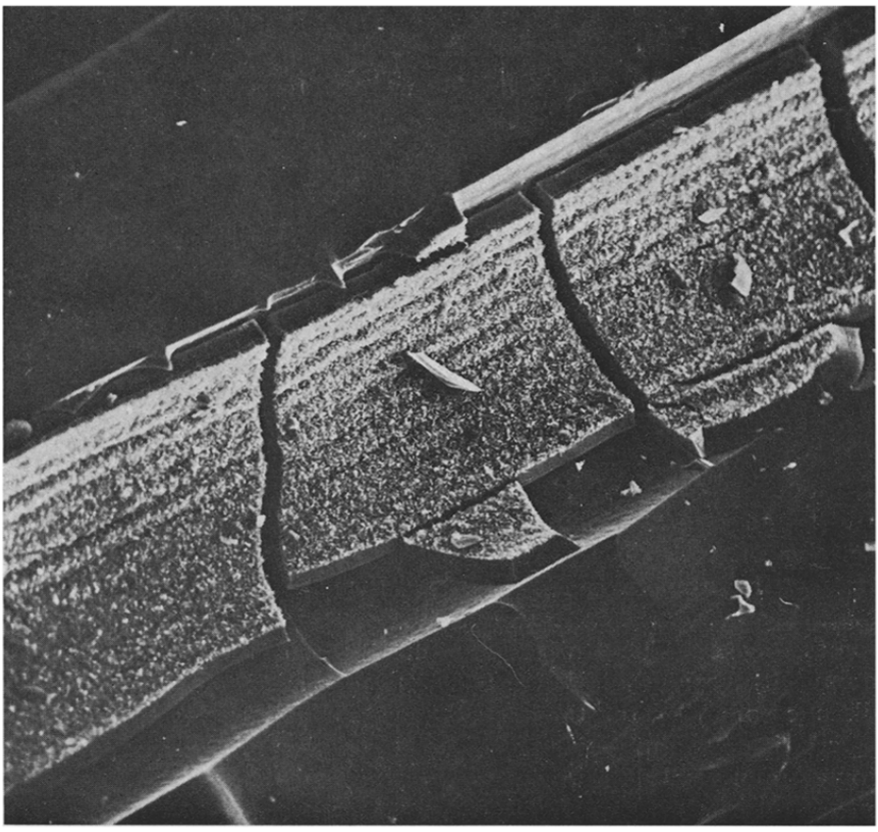

Fig. 2. Micrograph of the column in Fig. 1 in a longitudinal section.

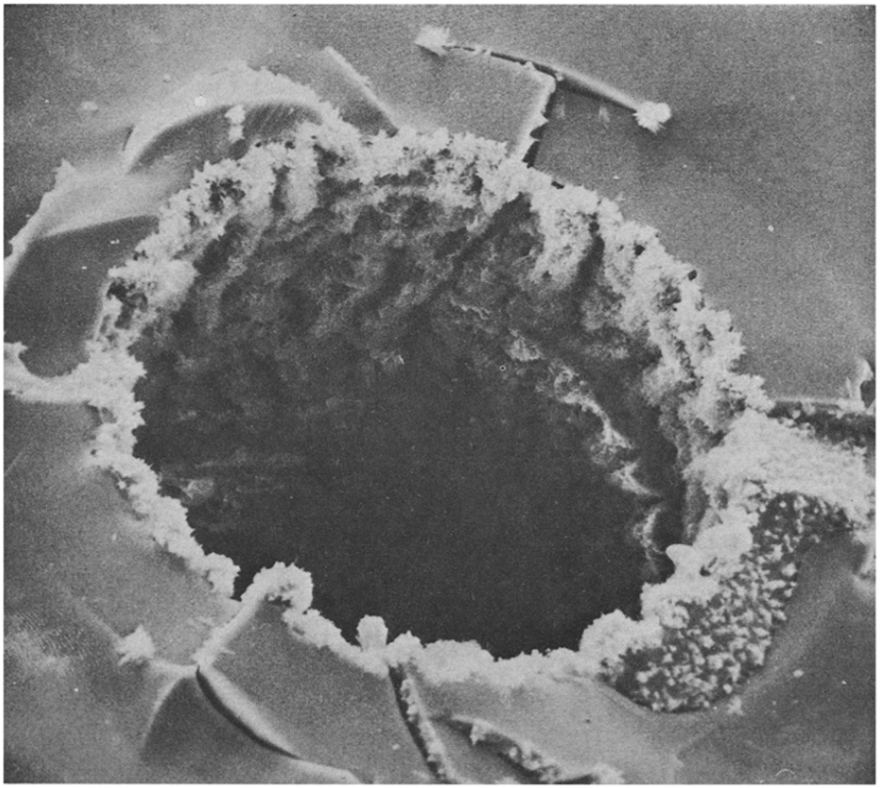

Fig. 3. Section through the capillary column with the silica gel layer prepared by the action of tetramethylammonium hydroxide solution.

prepared with layers 0.3–50 μm thick. The appearance of the layer can be seen in Figs. 1–4.

Silica gel prepared by the action of ammonia solution consists of particles of approximately equal sizes but, being activated, thicker layers break and cracks are created. An adsorbent prepared by the action of quaternary tetramethylammonium bases has a layer without cracks, like coarse cloth.

Applying the procedure according to Mohnke and Saffert[10], the optimal concentrations of both ammonia solution and tetramethylammonium hydroxide solution were chosen. It was found with ammonia solution that a concentration of 16% led to very rapid formation of thick silica gel layers so that an optimal layer might be obtained fortuitously rather than as a rule. It often happens that the solution of silicate that originates is so viscous that it cannot be removed from the capillary and the capillary becomes blocked. The same also applies at higher concentrations of tetramethylammonium hydroxide solution (10–20%). On decreasing the concentrations of the alkaline solutions, the time of action was increased but the reproducibility of the layer thickness improved. The optimal concentrations were found to be about 8–9% for ammonia solution and about 3–4% for tetramethylammonium hydroxide solution.

The formation of the silica gel layer forming the wall of the capillary is a

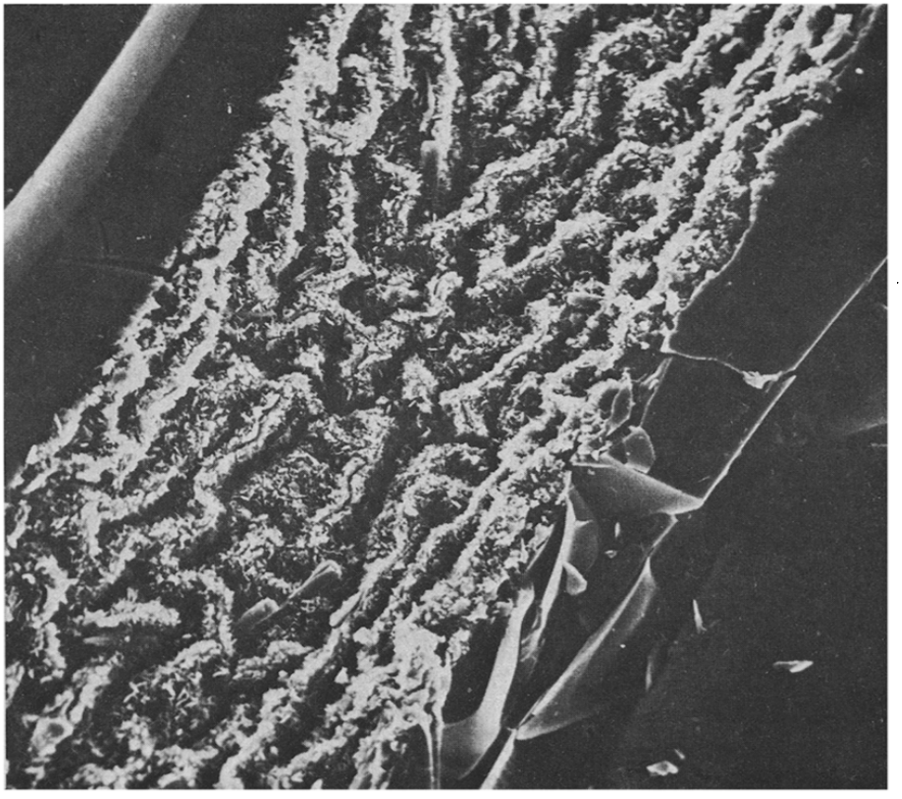

Fig. 4. Micrograph of the column in Fig. 3 in a longitudinal section.

natural consequence of the technique used. After etching and activation, it can be seen from the capillary section that the thickness of the original wall of the capillary was reduced by the creation of a porous layer and that the original inside diameter was further increased by removal of the solution from the capillary. This effect naturally becomes greater with increasing thickness of the silica gel layer.

The optimal solution of the problems associated with the preparation of capillary columns with silica gel layers consists in the use of the second procedure, in which a thin layer of the tetramethylammonium hydroxide solution is deposited. The amount of substance participating in the reaction and hence also the thickness of the silica gel layer can be controlled by adjusting the concentration of the solution. Depending on the concentration (5–20%), layers of thickness $7 \cdot 10^{-2}$–$3 \cdot 10^{-1}$ μm can be prepared, which would satisfy the demands of subsequent coating with a suitable stationary phase or the fixation of chemically bonded organic substances.

The use of tetramethylammonium hydroxide solution appears to be a universal procedure for the preparation of porous silica gel layers in glass columns with the smallest diameters irrespective of the composition of the glass. This procedure, and also the utilization of the pyrolysis of fluorinated ethers[11] or of a solution of ammonium bifluoride according to Onuska *et al.*[12], is also suitable for modifying the surfaces of glass capillaries for gas chromatography.

A study of the properties of capillary columns prepared in this way will be described elsewhere[13].

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