

CHROM. 10,323

PREPARATION OF SURFACE-MODIFIED WIDE-BORE WALL-COATED OPEN-TUBULAR COLUMNS

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SUMMARY

A new procedure for modifying the inner surface of glass open-tubular capillary columns is presented. At elevated temperatures ammonium hydrogen difluoride dissociates to produce gaseous hydrogen fluoride which results in silica whisker formation. In comparison with similar procedures, greater uniformity and controlled whisker length can be achieved. The method can be applied to both wide-bore and analytical column preparation yielding high-performance capillary columns. Examples of wide-bore open-tubular columns prepared in this manner are given.

INTRODUCTION

Of the several techniques described for modifying inner glass surfaces of capillary columns, gaseous hydrogen fluoride has proven to be the most extensive roughening agent, by formation of silica whiskers. These whiskers represent filamentary crystals with properties close to near perfect structural form¹, exhibiting high mechanical strength and an increase in the glass surface area of up to 1000 fold. These characteristics and the ability to control the whisker growth rate can serve as a criterion for surface coverage of the stationary phase while providing an excellent means of obtaining high-performance capillary columns.

The methods presently employing gaseous hydrogen fluoride^{2,3}, however, have been limited by one or more of the following drawbacks of non-uniformity and safety considerations. It was our intent, therefore, to eliminate these drawbacks while retaining the desirable attributes in providing an alternative procedure for the preparation of wide-bore wall-coated open-tubular columns which would also be applicable to analytical column preparation. The advantages of wide-bore columns have been discussed in detail by Badings *et al.*⁴, Sandra *et al.*⁵ and Grob and Grob⁶, but their preparation has not employed surface modification.

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EXPERIMENTAL

Surface modification

Cleaned Pyrex glass tubes were drawn on a Hewlett-Packard glass drawing machine. The drawn capillaries (40 m \times 0.7 mm I.D.) were filled with concentrated hydrochloric acid, sealed and heated overnight at 80°. The columns were cooled and the acid removed by suction, followed by sequential washes with distilled water, acetone, diethyl ether and blown dry with nitrogen. The columns were filled with a 5% (w/v) saturated solution of ammonium hydrogen difluoride (BDH, Poole, Great Britain) in methanol and allowed to stand for 1 h. The solvent was then removed by a uniform nitrogen flow and continued until a milky film was observed. (A constant flow of nitrogen was critical for uniform coverage. For wide-bore columns a flow-rate of 2–3 cm/min is recommended. Wide-bore columns should be mounted vertically and connected to a buffer column at the exit end for best results.) The column ends were then sealed and placed in a heated muffle furnace at 450° for 3 h. After cooling, the columns were opened in a fume hood (ammonia gas) and washed with 20 ml of methanol, then blown dry with nitrogen. The uniformity of the whiskered surface should be directly visible.

Column preparation

Deactivation. Each column was deactivated by the procedure outlined by Grob and Grob⁷ employing two treatments of Carbowax 20M and Emulphor ON-870.

The column ends required extended deactivation if reshaped after surface modification. Extra care must be exercised if the ends need to be restraightened and a low heat flame should be used to avoid brittleness.

Coating. One column was dynamically coated, using a mercury plug method⁸ with 2% (v/v) SE-54 in chloroform. After gas chromatographic testing, the column was recoated again. The other column was coated statically with a 0.3% (w/v) solution of SE-52 in methylene chloride. Difficulties were encountered with wide-bore columns using static coating due to entrainment of air bubbles in the whiskers. This was overcome by continually pushing the coating solution back and forth until no bubbles were observed to form.

Testing. Each column was tested for adsorption characteristics and acidic-basic properties as previously described³ using the solutions proposed by Grob and Grob⁹.

Chromatography

A Carlo Erba Model 2301 gas chromatograph equipped with a splitless injector and FID detector was used.

Preparation of capillaries for scanning electron microscopy (SEM) analysis

Three-metre columns were treated with different concentrations of ammonium hydrogen difluoride at various temperatures and times. After chemical and thermal treatment 6-mm lengths were obtained at various points throughout the capillary and divided into two parts. One part was scored with a diamond pencil to 2–3 mm of length and fractured off while the remaining portion was fractured under pressure to obtain 1–3-mm chips of open capillary. Pieces of capillary and fractured chips are

shown in Figs. 1 and 2. The chips are mounted on separate specimen stubs by a conductive colloidal silver adhesive (Ernest F. Fallan, Schenectady, N.Y., U.S.A.) and allowed to dry completely at room temperature. Glass particles formed during fracturing and deposited into the lumen of the open capillaries are blown away with a stream of compressed air. The capillaries are mounted as closely as possible, perpendicular to the support stub, using a stereomicroscope; preferably only one capillary is mounted to the centre of the support, allowing for better orientation of the samples during SEM examination. The glass pieces are then coated with a conductive layer of aluminum employing a vacuum evaporator (Bendix CVC 14) under the following conditions. The support stubs with the intact capillaries are placed into the centre of a tilting variable-speed rotary table (Ladd Research Labs., Burlington, Vt., U.S.A.) operated in a horizontal plane while the support containing the open chips is located in one of the bores at the perimeter of the table.

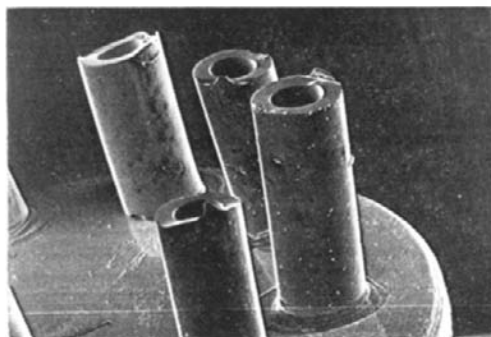


Fig. 1. Mounted pieces of intact capillaries for SEM analysis.

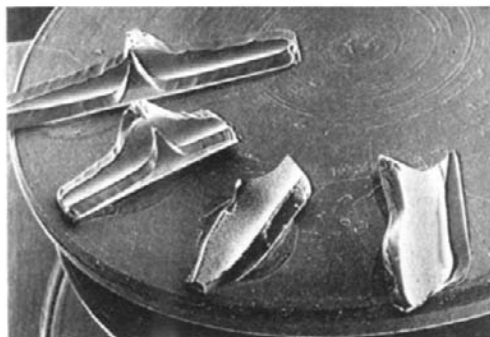


Fig. 2. Mounted chips of fractured capillaries for SEM analysis.

The whole assembly is then placed on the baffle plate of the coating unit, with the two evaporative sources and the rotary table, respectively, adjusted one to the other as shown in Fig. 3. The evaporation unit is evacuated to $1.33 \cdot 10^{-3}$ P ($1 \cdot 10^{-5}$ torr) and carbon is deposited on the specimens to a thickness of 10 nm while the rotary table turns at 100 rpm. The pressure is then raised to $6.66 \cdot 10^{-1}$ P ($5 \cdot 10^{-3}$ torr) and maintained at this level while 2.5 mg of aluminum wire (Ernest F. Fallan) is slowly evaporated from a tungsten coil to a thickness of 20 nm. Duration of evaporation should be at least 60 sec while maintaining a rotation of 100 rpm. If the samples cannot be examined immediately, they should be stored under vacuum.

The analysis was performed employing an AMR, Model 1000 scanning electron microscope, operated at 20 kV and $150 \mu\text{A}$ emission current at a working distance of 12 mm. The support was tilted at 40° towards the incident beam for examination of the open chips while the intact capillaries were adjusted to the horizontal plane, parallel to the electron beam. This method produces consistent results having good contrast and artifact free images.

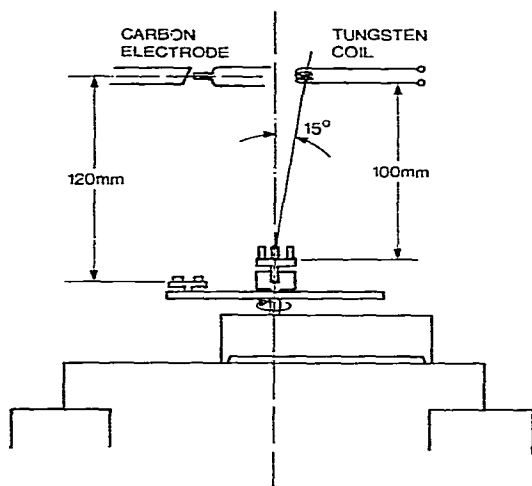


Fig. 3. Assembly for SEM analyses.

DISCUSSION

Ammonium hydrogen difluoride decomposes at elevated temperatures to form gaseous hydrogen fluoride and ammonia. This mechanism was found to be a suitable alternative to present procedures employing gaseous hydrogen fluoride, while substantially improving many of the previously described drawbacks and safety aspects. By determining the optimum factors influencing crystal growth, uniform coverage and controlled whisker growth was obtained.

Since the resulting rate of growth and steepness in growth of a crystal is directly related to concentration and a function of supersaturation in the vapour phase, it seemed reasonable that the maximum concentration achievable would produce optimum crystal growth. This was found to hold true as shown in Fig. 4 where the maximum concentration (5% w/v, saturated) gave the longest whiskers. Under optimum conditions of temperature and time, whisker growths of $4\ \mu\text{m}$ were consistently observed.

The crystal shape and conditions of growth were mainly dependent on temperature. The structure of a near perfect crystal remains practically flat until a transi-

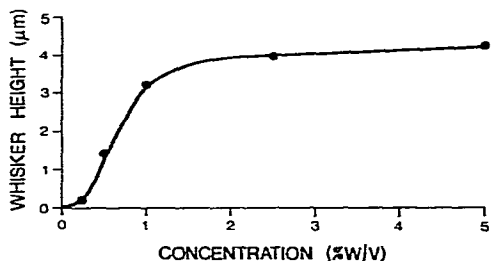


Fig. 4. Concentration vs. whisker height. Temperature, 450° ; time, 3 h.

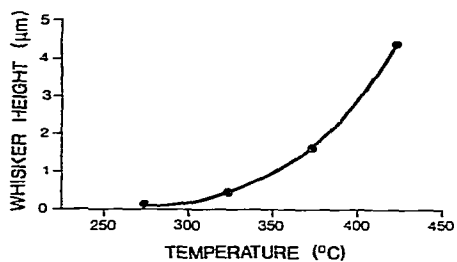


Fig. 5. Temperature vs. whisker height. Concentration, 5% (w/v); time, 3 h.

tion temperature is reached, at which point the roughness of the surface increases rapidly (surface melting). At this time, the propagation rate of whiskers accelerates, forming needle-like crystals with greater density. This can be observed in Fig. 5, where the longest crystal growth is found to occur at 450 °C. Figs. 6 and 7 show the differences achieved in the density of crystal growth at temperatures of 400° and 450°, respectively, for optimum conditions of time and concentration. Temperatures higher than 450° produced whiskers with rounded terminations and diaxial growths.

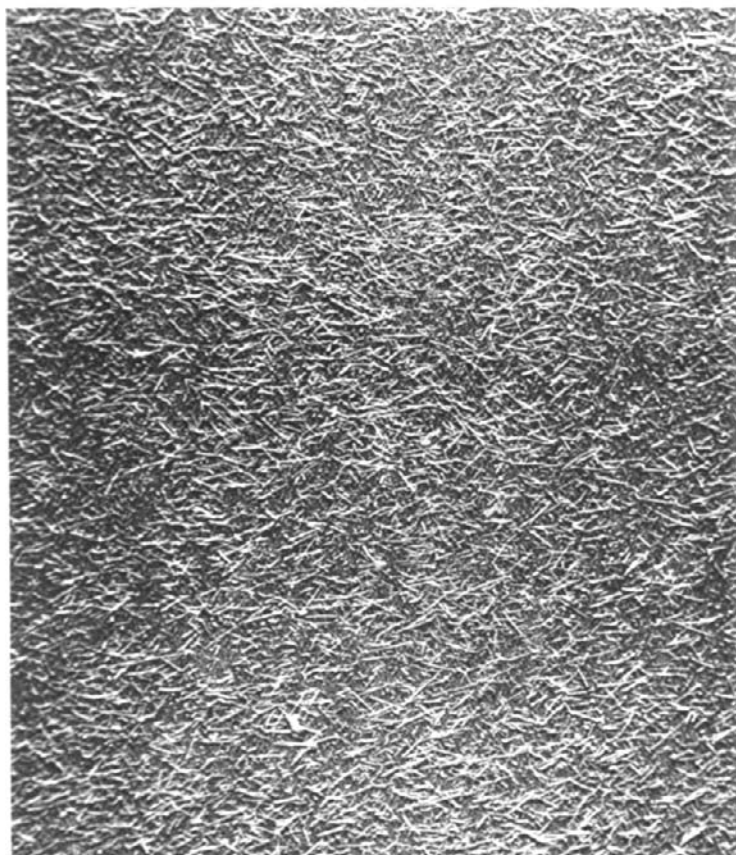


Fig. 6. Whisker density. Temperature, 400 °C; concentration, 5% (w/v); time, 3 h.

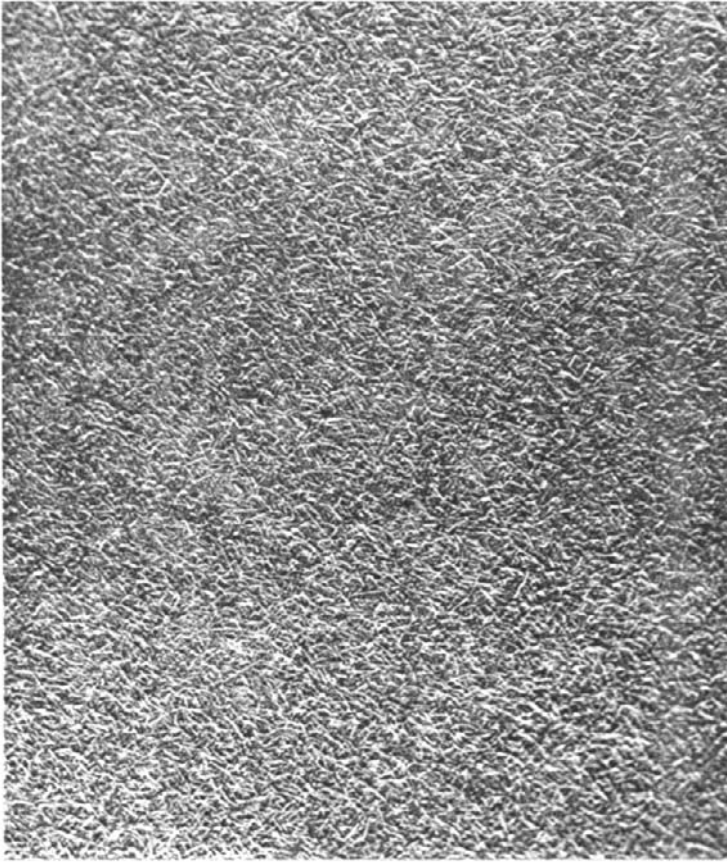


Fig. 7. Whisker density. Temperature, 450° ; concentration, 5% (w/v); time, 3 h.

Growth rate and crystal shape were also found to be an important factor of time. Since a vapour-liquid-solid mechanism is probably employed in whisker growth, the equilibrium conditions influencing the type of growth is complex. Using the previously determined conditions, one-dimensional whisker leaders were observed even after exposure to heat for only 30 min, with maximum whisker growth and symmetry occurring after 3 h as shown in Fig. 8. Continued heating beyond this

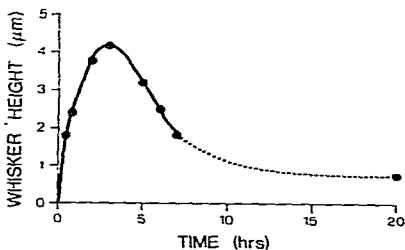


Fig. 8. Time vs. whisker height. Concentration, 5% (w/v); temperature, 450° .

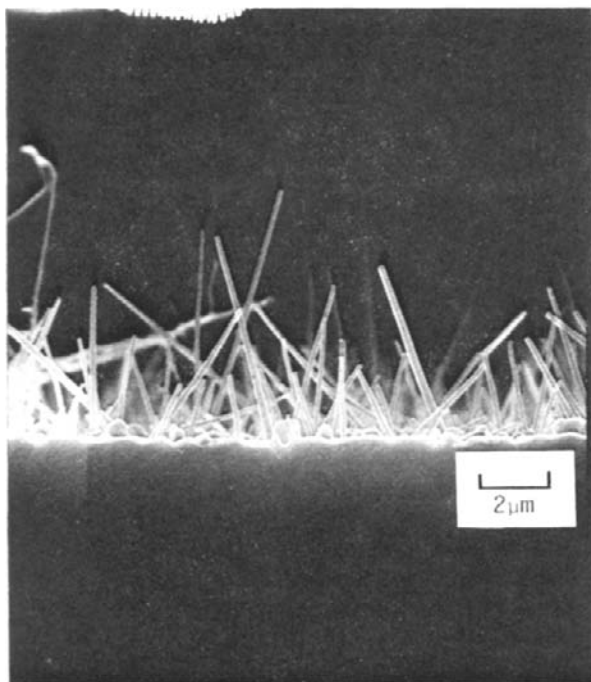


Fig. 9. Optimum whisker symmetry and height: concentration, 5% (w/v); temperature, 450°; time, 3 h.

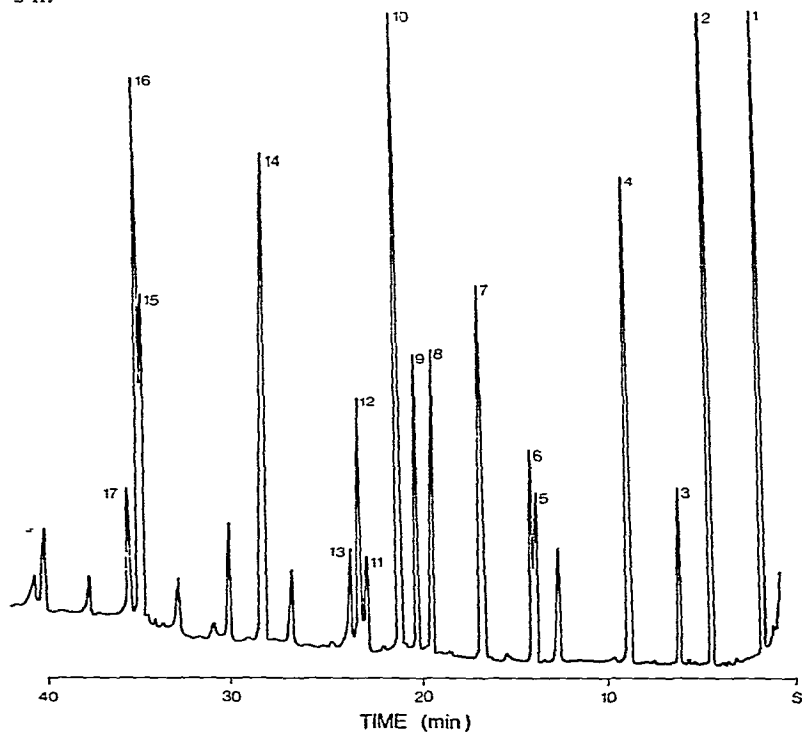


Fig. 10. Gas chromatogram of polycyclic aromatic hydrocarbons. 1 = Naphthalene; 2 = biphenyl; 3 = acenaphthene; 4 = fluorene; 5 = phenanthrene; 6 = anthracene; 7 = 2-methylphenanthrene; 8 = 9-methylanthracene; 9 = fluoranthene; 10 = pyrene; 11 = benzo[*a*]fluorene; 12 = benzo[*b*]fluorene; 13 = 1-methylpyrene; 14 = chrysene; 15 = benzo[*e*]pyrene; 16 = benzo[*a*]pyrene; 17 = perylene. Column: 40 m × 0.71 mm I.D., 0.3% SE-52; carrier gas (helium) flow-rate, 16 ml/min; split ratio, 10:1; temperature programming from 90° (hold 3 min) to 250° at 4°/min.

period resulted in globular terminations and shorter whisker lengths. It would appear that a severe equilibrium shift occurs at this point resulting in the crystal surfaces redissolving into the vapour phase.

Fig. 9 shows the whiskered column surface at optimum conditions.

Columns prepared and deactivated in this manner were found to be neutral, with no adverse adsorption properties for 20–40 ng injected. The wide-bore columns gave a slight peak-broadening effect at the base of the peaks, since the exit end of the column could not at this time be directly inserted into the flame jet.

Environmental applications of wide bore columns prepared by this procedure are shown in Figs. 10 and 11.

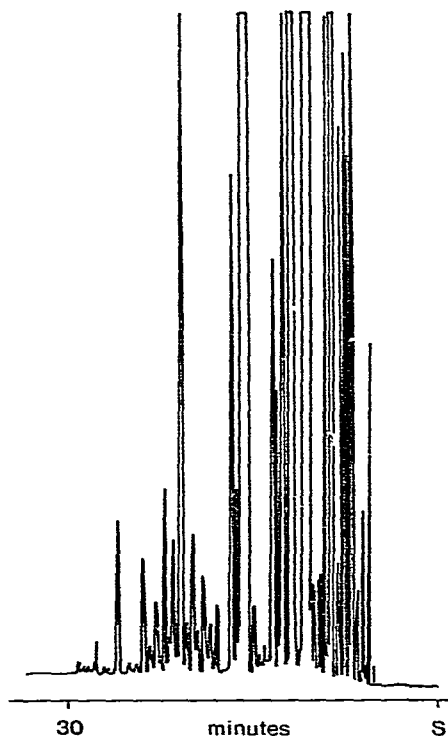


Fig. 11. Gas chromatogram of lavender oil on a 40 m \times 0.69 mm I.D. glass capillary column coated with SE-54. Temperature, isothermal at 60° for 3 min then programmed from 60 to 180° at 3°/min; carrier gas (helium) flow-rate, 11 ml/min.

Finally, it may be stated that the major requirement for preparing highly effective columns for multipurpose applications is uniformity and defined film thickness. Compromises on separation efficiency, sample capacity and column temperature for β -values between 50–90 the film thickness should be 0.7–1.5 μ m. It is important to realize that for very polar substances such as free phenols and amines thicker films will significantly reduce undesired adsorption which must be compensated for, by increased starting column temperatures.

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