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WHISKER-WALLED OPEN TUBULAR GLASS COLUMNS FOR GAS CHROMATOGRAPHY

TECHNIQUES FOR INDUCING WHISKER GROWTH

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SUMMARY

A method is described for growing silica whiskers on the inner surfaces of glass open tubular columns for gas chromatography. Whisker growth is effected in the vapour phase by introducing a fluoro-ether into the open tubular column, which is then sealed and heated for a certain time. The effect of various parameters on whisker growth is described. The whiskers show considerable promise as a substrate whereby the performance of open tubular columns may be improved.

INTRODUCTION

Open tubular columns, in which the liquid phase is deposited as a thin film on the essentially smooth inner surface of the tube [wall-coated open tubular columns (WCOT)], were introduced into gas chromatography in 1958[1,2] and were developed to a high degree, particularly by Dijkstra and De Goey[3], Condon[4], Desty[5–7], Kaiser and Struppe[8], Lipsky *et al.*[9,10], Lovelock[11], Scott[12] and Zlatkis and co-workers[13,14].

A major shortcoming of such columns, however, is their relatively high phase ratio, β (150–500), which decreases the potential number of effective theoretical plates. Another disadvantage is that WCOT columns can handle only small amounts of sample[15], which detracts from their analytical usefulness. Attempts to improve both of these aspects have been concerned with developing a means of increasing the surface area of the inner wall of the column is such a way that larger amounts of the stationary phase can be introduced and at the same time spread as a thin film on the surface, so that the plate height is not significantly increased. In this regard, mention can be made of etching[16] and deposition of sodium chloride[16–18]. Both of these col-

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umns can be described as wall-treated open tubular (WTOT) columns. Modifications involving the deposition of carbon black[19], diatomaceous earth[20–22] and microparticulate silica[23–27] are termed porous-layer open tubular (PLOT) columns and, more specifically, support-coated open tubular (SCOT) columns. The extent to which these modifications have improved the performance of open tubular columns is described in the references cited above. A new modification, which shows considerable promise, has been developed in our laboratories[28] and leads to the formation, in glass columns, of a relatively uniform layer of silica whiskers that have a villi-like appearance. The high surface area, openness of the structure and the fact that the surface consists of silica are factors which, in our opinion, provide an almost ideal substrate for the stationary phase. Details of the deactivation of the surfaces, coating techniques and the chromatographic performance of these columns will be reported elsewhere. This paper deals with the techniques that we have developed for forming the whisker surfaces.

EXPERIMENTAL

Open tubular columns were drawn to an I.D. of 0.25–0.35 mm and an O.D. of 0.9–1.1 mm on an apparatus similar to that developed by Desty *et al.*[29,30] and manufactured by Dr. Hupe Apparatebau. Pyrex glass (J. A. Jobling & Co., Staffs., Great Britain) was used and was thoroughly cleaned with an Extran solution (E. Merck, Darmstadt, G.F.R.), distilled water and ethanol before drawing. Columns of approximate length 10 m were used in these experiments, but much longer columns can be prepared successfully by the same means.

Whisker growth is effected in the vapour phase by introducing a fluoro-ether, *e.g.*, 2-chloro-1,1,2-trifluoroethyl methyl ether, which, after sealing the ends of the column, vaporizes at elevated temperatures and liberates hydrogen fluoride. The detailed mechanism by which the whiskers were formed is not relevant here. It suffices to say that the hydrogen fluoride probably reacts with the glass to form silicon tetrafluoride, which is converted into silicon dioxide, which in turn is deposited in the form of whiskers. More detailed descriptions can be found in standard works on the subject[31–33].

It has been found that it is essential to introduce the fluoro-ether into the column in such a way that it is spread uniformly over the entire length of the column. Unless this is done, the whisker growth is not evenly distributed throughout the column. Several techniques for this purpose have been studied and the one that gives the best results is as follows. One of the open ends of the columns is connected to a vacuum pump and the other to a short length of glass tubing of wider bore (*e.g.*, 5 mm I.D.) into which a silicone rubber septum is inserted. Heat-shrinkable PTFE is useful for making the connections. The system is evacuated to 10^{-4} mmHg by pumping and then the end of the column attached to the vacuum is sealed off by using a microflame. The required amount of fluoro-ether is injected through the septum and the end of the column connected to the septum is sealed off as described above.

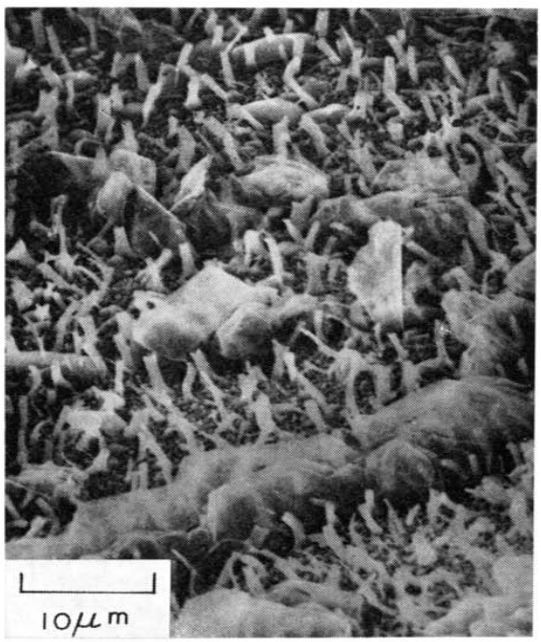
The sealed column is then placed in an oven that can attain temperatures of at least 500° and in which temperature gradients are small. This latter point is important as it has been found that temperature gradients cause uneven whisker growth. After heating for a suitable time, the column is removed from the oven, the ends are

opened and the column is immediately flushed with dry nitrogen at 200°. If this flushing is not carried out, whisker growth is imperfect and interspersed with crystal-like growths, as shown in Fig. 1.

At this stage, the column has a brownish to blackish appearance due to the formation of a deposit of carbon on the inner surface. The deposit is removed by flushing the column with oxygen at approximately 450° for 6–12 h.

Whisker growth is affected by a variety of parameters, the most important of which, at this stage of our studies, appear to be the concentration of the fluoro-ether in the column, the temperature to which the column is heated and the duration of the heating. It has been established that at low fluoro-ether concentrations, such as used by Tesařík and Novotný[16], whisker formation does not take place, irrespective of the temperature employed. Under these circumstances, etching occurs, as shown in Fig. 2. At temperatures of 250° and below, whisker formation is absent, irrespective of the concentration of the ether, and etching similar to that shown in Fig. 2 occurs. All of the ether is not vaporized at high concentrations and the liquid that remains on the surface prevents access of hydrogen fluoride and little or no etching takes place. Accordingly, experiments were carried out at fluoro-ether concentrations of 2.5, 5.0 and 10.0%, temperatures of 250, 300, 350, 400 and 450° and heating times of 4, 10 and 24 h (concentration here is conveniently defined as the volume of liquid ether to the total column volume, expressed as a percentage).

In each of the above experiments, short lengths (5–8 mm) of the columns were prepared for viewing with a scanning electron microscope (SEM) as described



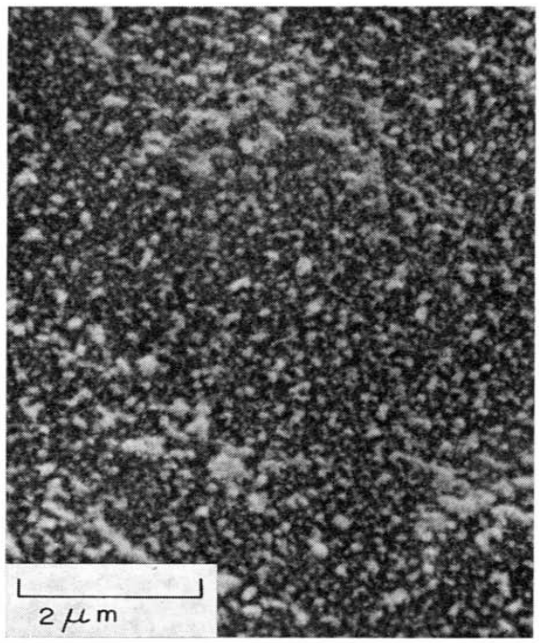


Fig. 1. Effect of inadequate cleaning on the formation of whiskers.

Fig. 2. Etching obtained with 2-chloro-1,1,2-trifluoroethyl methyl ether according to the method described by Tesařík and Novotný[16].

previously[34]. This technique enabled us to view the inner surface of the column through an open end at an angle of 40° and end-on. In all experiments, each column was sampled at five to seven points, evenly spaced over the entire column length, in order to determine the uniformity of the whisker growth throughout the column.

The chemical composition of the whiskers was studied *in situ* by using energy dispersive X-ray analysis and by X-ray powder diffraction of a pulverized sample of whiskers.

RESULTS AND DISCUSSION

Chemical composition of whiskers

It appears from discussions on whisker growth[35–37], the fact that an oxygen-containing ether was used as a source of hydrogen fluoride, and the particular conditions, particularly temperature, under which the experiment was performed, that the whiskers described here consist of silica. Point analysis by energy dispersive X-ray analysis shows the presence of silicon (Fig. 3); however, the technique is insensitive to elements with an atomic number of less than 10 and therefore cannot confirm the presence of oxygen.

The whiskers are soluble in a 40% solution of hydrogen fluoride at room temperature, which suggests that they consist of silica[38]. The X-ray powder diffraction pattern shows broad peaks that are characteristic of polycrystalline substances. From these data, we conclude that the whiskers consist of polycrystalline silica.

Uniformity of whisker growth

Whisker growth has been found to be completely uniform over the entire col-

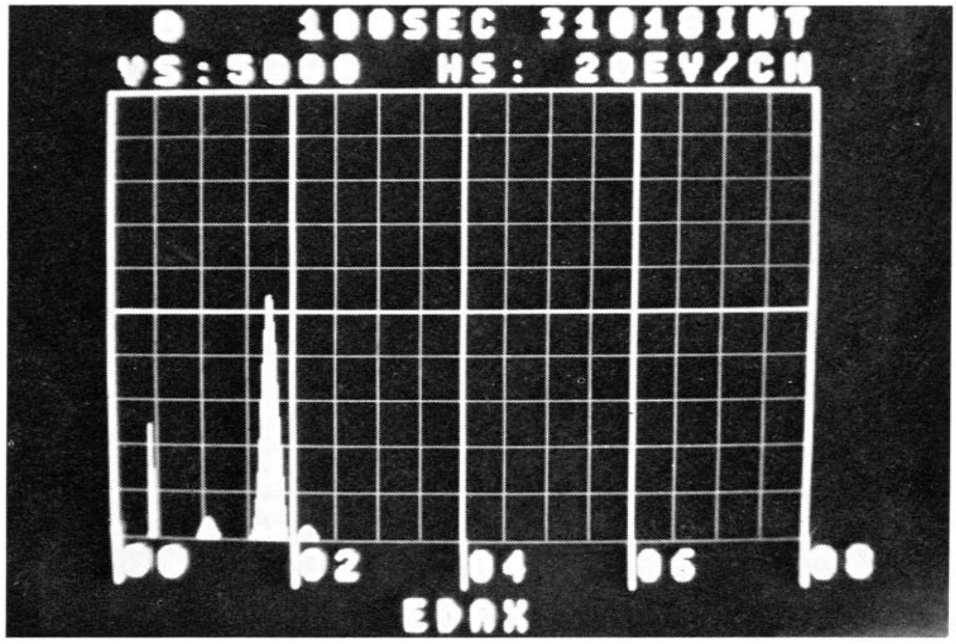


Fig. 3. Point analysis of a single whisker by energy dispersive X-ray analysis. The peak at 1.03 keV is due to sodium, at 1.74 keV to silicon and at 2.17 keV to gold. The energy scale represents 0–8 keV.

umn length, provided that temperature gradients are eliminated during the growth process and the fluoro-ether is uniformly distributed throughout the column.

Effect of various parameters on whisker growth

Whisker growth, in terms of the length of the whiskers and the surface density, increases with the duration of the growth period within the range of concentrations of the fluoro-ether and the temperatures considered. Under the prevailing circumstances, whisker growth appears to be complete after 24 h, and this time has therefore been accepted as the best value. The results discussed below refer to this figure.

At temperatures between 300 and 350° and an ether concentration of 2.5%, whiskers are short and sparse (Fig. 4a and b). The whiskers are evenly distributed over the inner circumference of the column (Fig. 5). At an ether concentration of 10% and the same temperature range, the whiskers are longer, thicker and denser (Fig. 6). At high magnification, the whisker surface shows no detail and appears to be smooth (Fig. 7). The surface of the tube between the whiskers shows some etching (Fig. 8) and this structure remains essentially the same at the higher temperatures discussed below.

Whiskers obtained at 400° at low (2.5%) and high (10%) concentrations of the fluoro-ether are shown in Figs. 9 and 10. The main effect of increassing the temperature from 300 to 400° is an increase in whisker length, thickness and density at comparable concentrations of the ether. At the higher concentration (10%), whisker growth on the inner circumference is less even than at the lower temperature (Fig. 11). At high

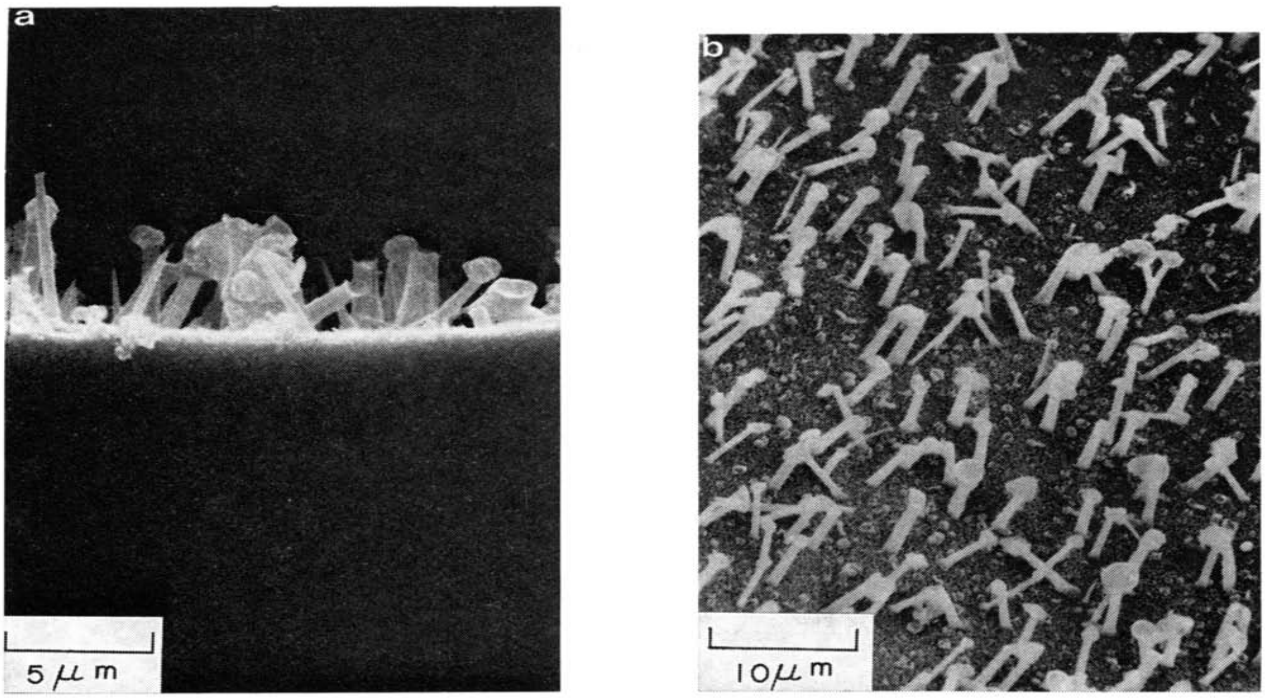


Fig. 4. Whiskers formed at 300–350° and 2.5% fluoro-ether concentration. (a) Viewed end-on; (b) viewed at an angle of 40° from the vertical axis.

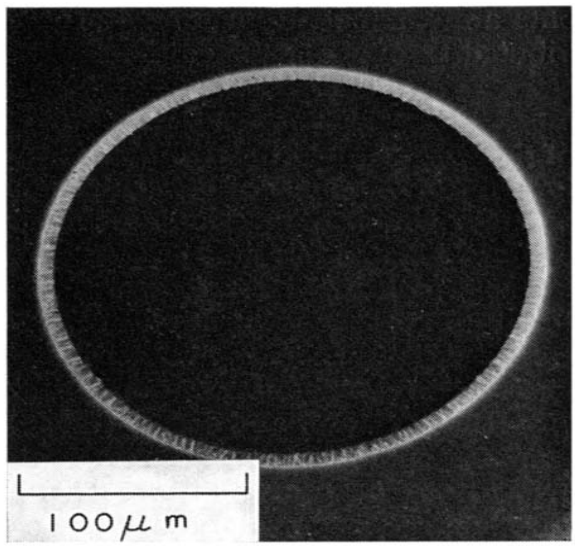


Fig. 5. Cross-section of a column prepared under the same conditions as in Fig. 4.

magnification, whiskers grown under these circumstances are seen to have a rougher surface than those grown at lower temperatures (Fig. 12).

Whisker growth obtained at 450° at low and high ether concentrations is shown in Figs. 13 and 14. At the low concentration, whiskers are thin and sparse, whereas at high concentration the whiskers are less uniform than those obtained at the lower temperatures.

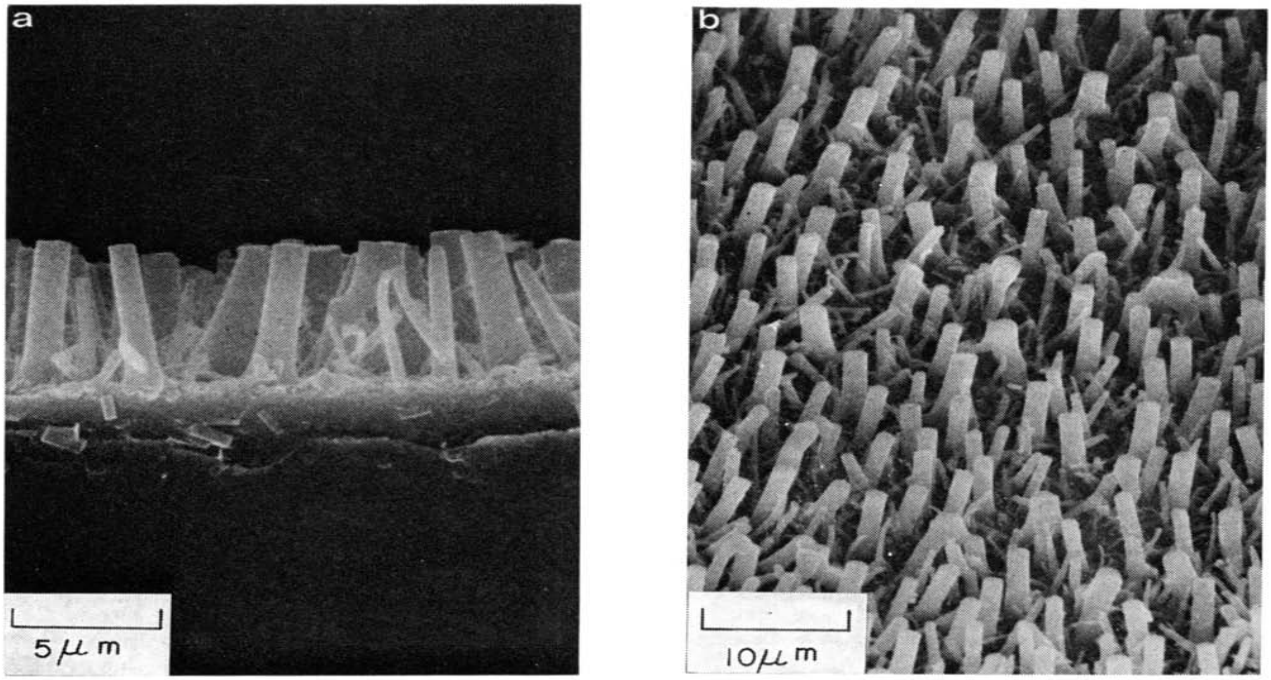
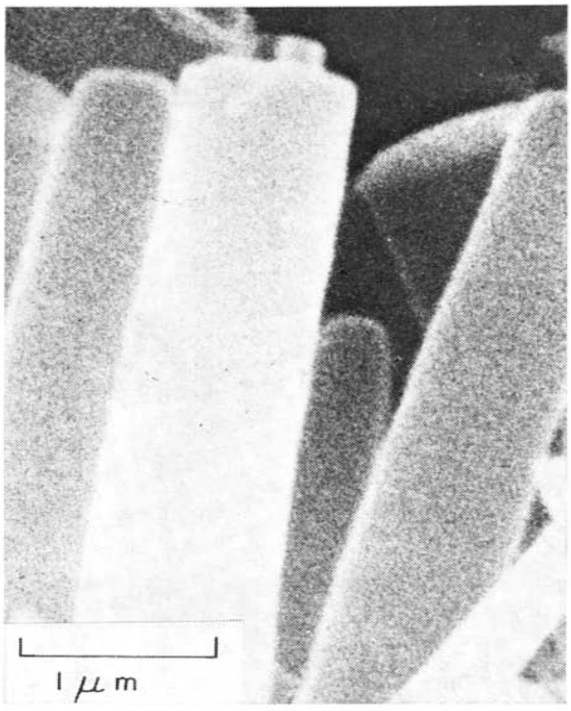


Fig. 6. Whiskers formed at 300–350° and 10% fluoro-ether concentration. (a) Viewed end-on; (b) viewed at an angle of 40° from the vertical axis.



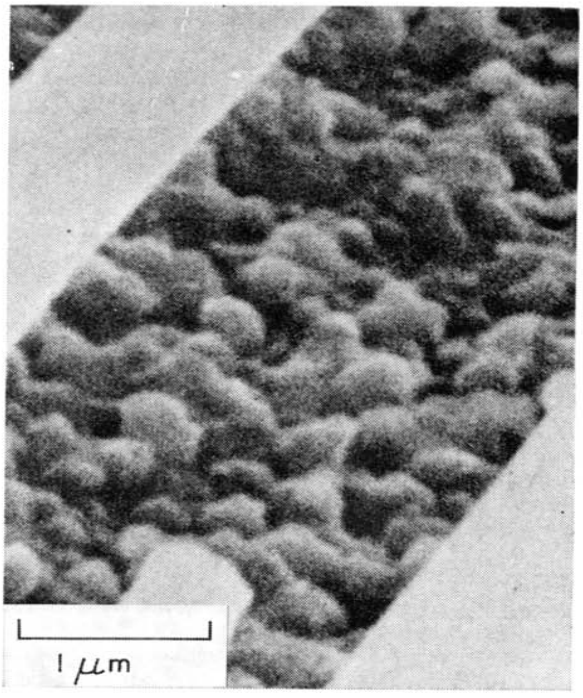
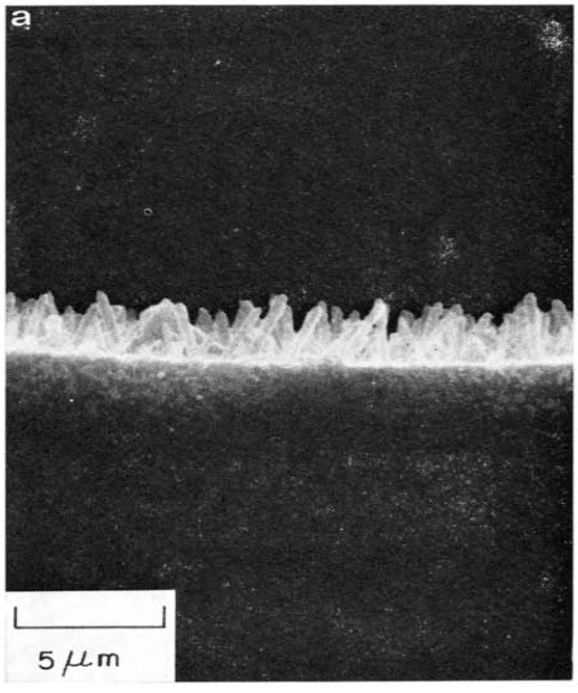


Fig. 7. Surfaces of single whiskers grown under the same conditions as in Fig. 4.
Fig. 8. Surface between whiskers.



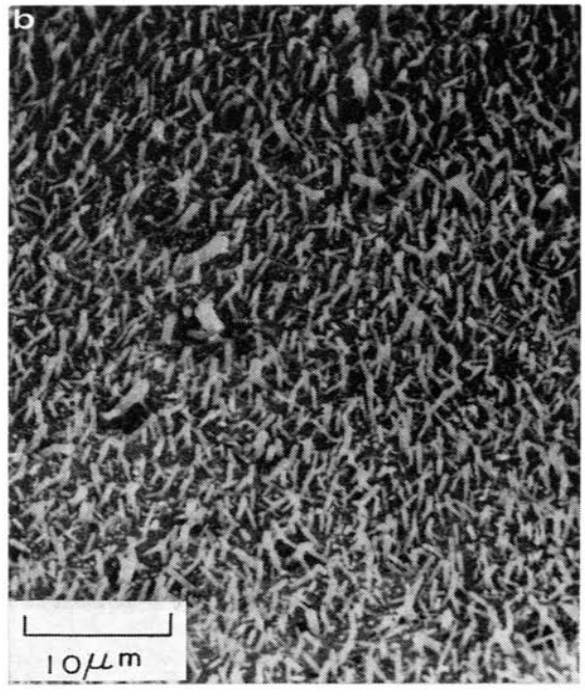


Fig. 9. Whiskers formed at 400° and 2.5% fluoro-ether concentration. (a) Viewed end-on; (b) viewed at an angle of 40° from the vertical axis.

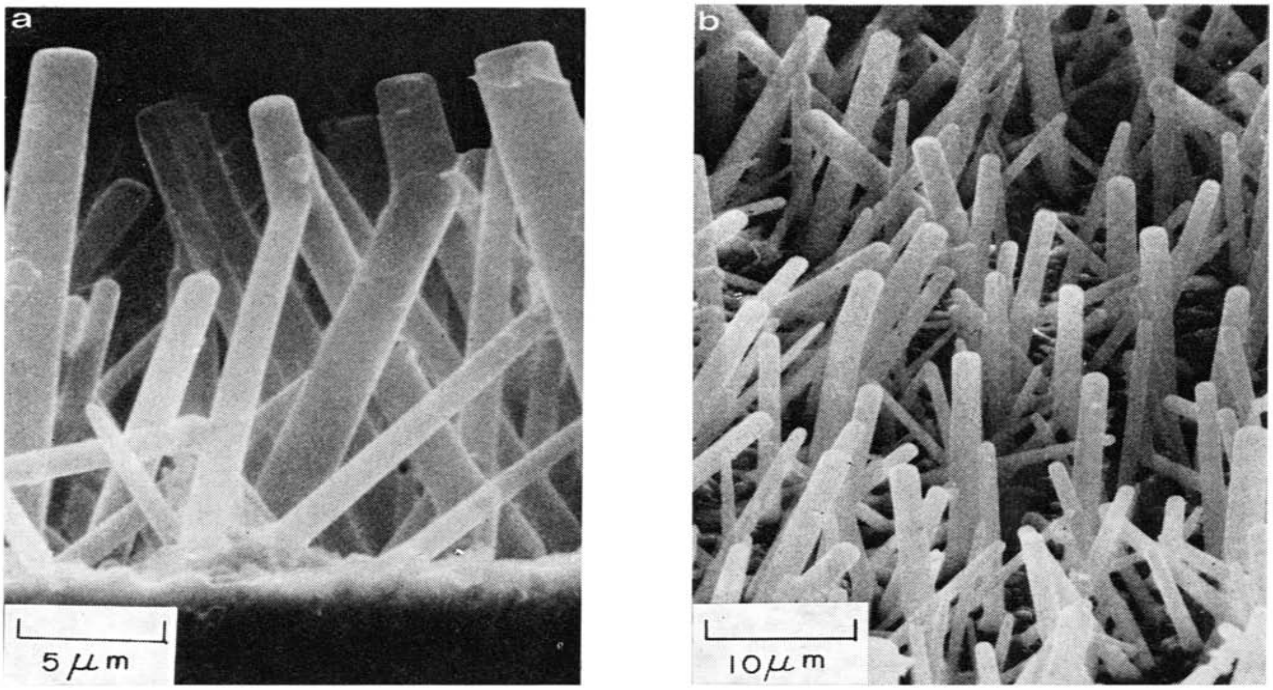


Fig. 10. Whiskers formed at 400° and 10% fluoro-ether concentration. (a) Viewed end-on; (b) viewed at an angle of 40° from the vertical axis.

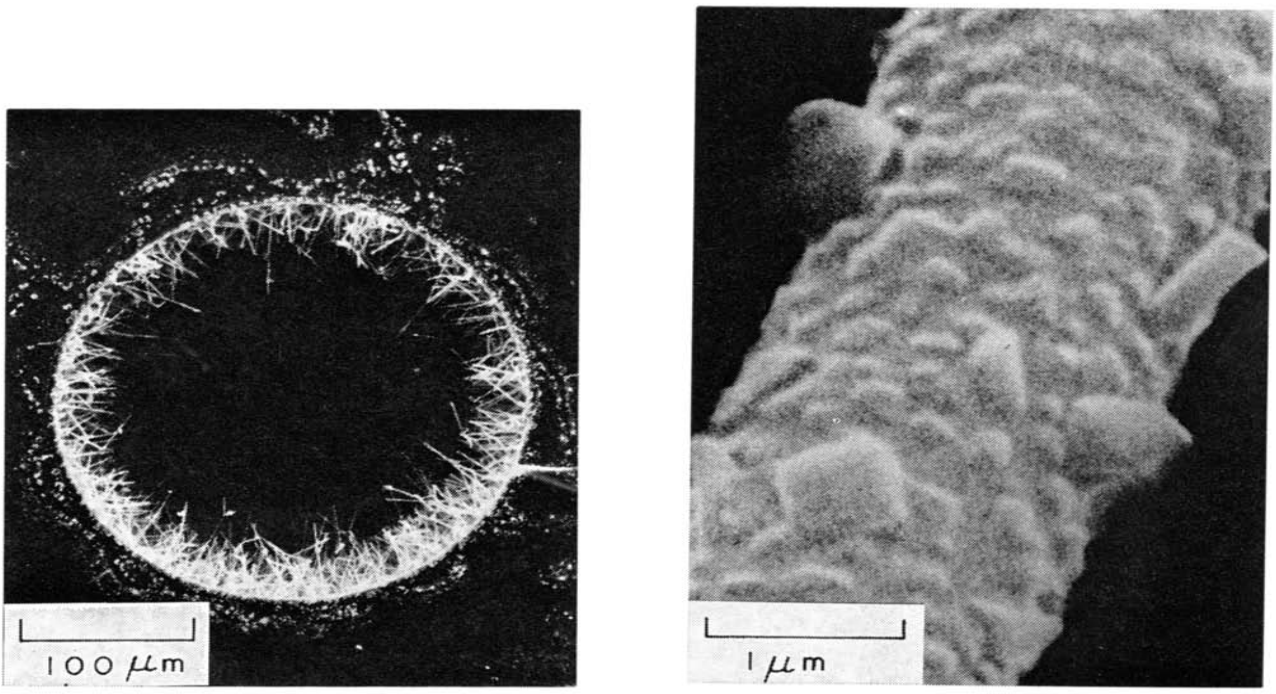


Fig. 11. Cross-section of a column prepared under the same conditions as in Fig. 10.
Fig. 12. Surface of a single whisker grown under the same conditions as in Fig. 10.

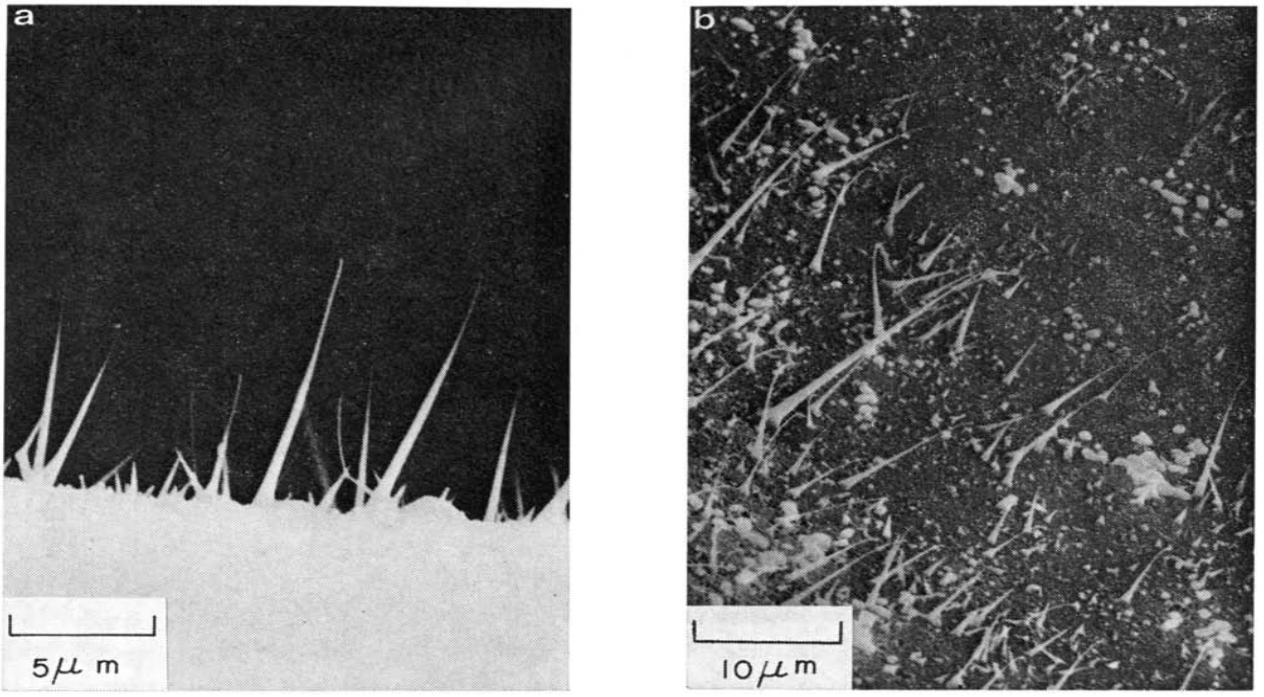


Fig. 13. Whiskers formed at 450° and at 2.5% fluoro-ether concentration. (a) Viewed end-on; (b) viewed at an angle of 40° from the vertical axis.

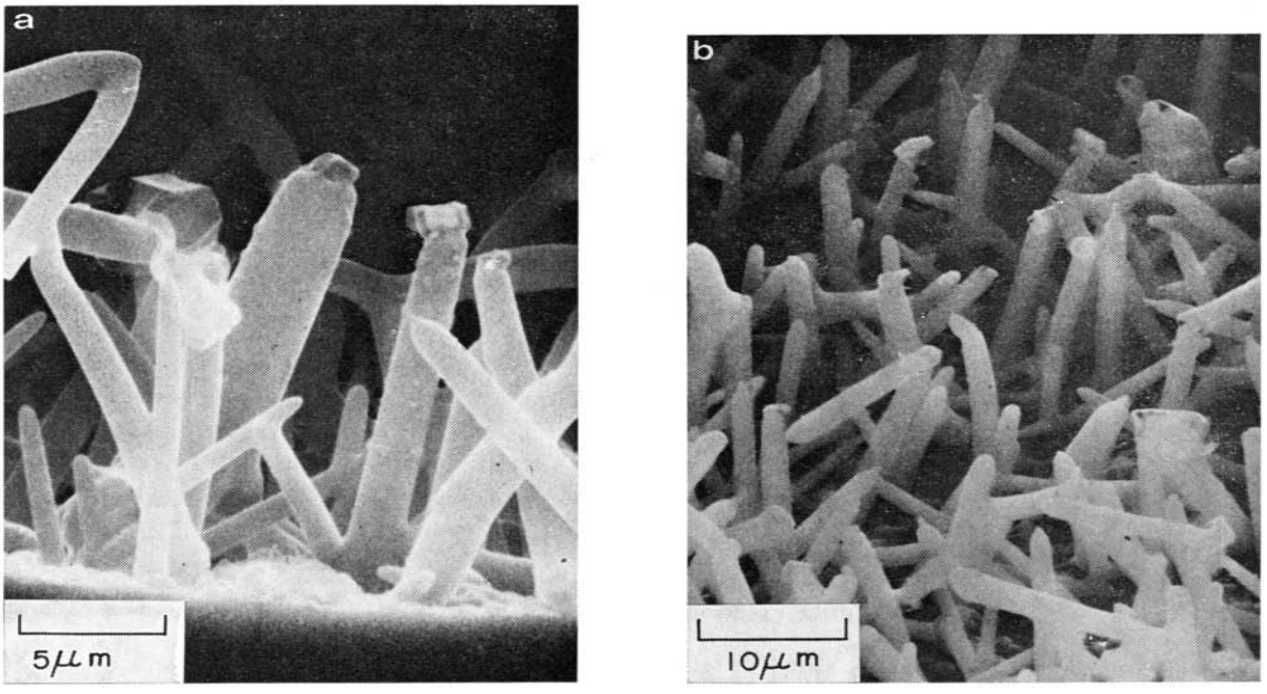


Fig. 14. Whiskers formed at 450° and at 10% fluoro-ether concentration. (a) Viewed end-on; (b) viewed at an angle of 40° from the vertical axis.

From these studies, it appears that a temperature of approximately 400° yields the best results. Whisker length and density can be controlled at this temperature by varying the concentration of the ether in the range 2.5–10%. In general, we have found whiskers to be cylindrical. In exceptional instances, whiskers are formed with a knob-like top, as shown in Fig. 15. The reason for this is unknown.

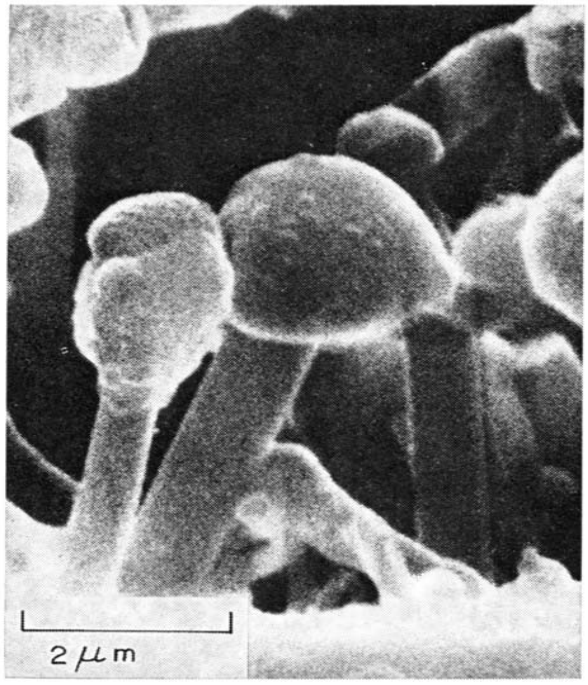


Fig. 15. Whiskers with a knob-like top.

Stability of whiskers

The whiskers appeared to be intrinsically strong, as might be expected[31–33], and are firmly attached to the inner surface of the column. They are not dislodged or broken by either forcing a liquid through the column or by relatively rough handling.

CONCLUSION

Silica whiskers covering a wide range of lengths and densities can be grown to form a uniform layer in glass open tubular columns. Preliminary experiments have shown that they provide an excellent substrate for the stationary phase and that high performance and generally useful open tubular columns are be easily constructed by these means. These latter details will be published later.

REFERENCES

1 M. J. E. Golay, in V. J. Coates, H. J. Noebels and I. S. Fargerson (Editors), *Gas Chromatography*, Academic Press, New York, 1958, p. 1.
2 M. J. E. Golay, in D. H. Desty (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958, p. 36.

3 G. Dijkstra and J. de Goey, in D. H. Desty (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958, p. 56.
4 R. D. Condon, *Anal. Chem.*, 31 (1959) 1717.
5 D. H. Desty, in H. P. Angelé (Editor), *Gas Chromatographie 1958*, Akademie-Verlag, Berlin, 1959, p. 176.
6 D. H. Desty, *Nature (London)*, 183 (1959) 107.
7 D. H. Desty, *J. Inst. Petrol.*, 45 (1959) 287.
8 R. E. Kaiser and H. G. Struppe, in R. E. Kaiser and H. G. Struppe (Editors), *Gas Chromatographie 1959*, Akademie-Verlag, Berlin, 1959, p. 177.
9 S. R. Lipsky, R. A. Landowne and J. E. Lovelock, *Anal. Chem.*, 31 (1959) 852.
10 S. R. Lipsky, J. E. Lovelock and R. A. Landowne, *J. Amer. Chem. Soc.*, 81 (1959) 1010.
11 J. E. Lovelock, *Nature (London)*, 182 (1958) 1663.
12 R. P. W. Scott, *Nature (London)*, 183 (1959) 1753.
13 A. Zlatkis and H. R. Kaufman, *Nature (London)*, 184 (1959) 184.
14 A. Zlatkis and J. E. Lovelock, *Anal. Chem.*, 31 (1959) 620.
15 L. S. Ettre, *Open Tubular Columns in Gas Chromatography*, Plenum Press, New York, 1965.
16 K. Tesařík and M. Novotný, in H. G. Struppe (Editor), *Gas Chromatographie 1968*, Akademie-Verlag, Berlin, 1968, p. 575.
17 G. Alexander and G. A. F. M. Rutten, *Chromatographia*, 6 (1973) 231.
18 G. Alexander and G. A. F. M. Rutten, *J. Chromatogr.*, 99 (1974) 81.
19 G. Nota, G. C. Goretti, M. Armenante and G. Marino, *J. Chromatogr.*, 95 (1974) 229.
20 L. S. Ettre and J. E. Purcell, *Advan. Chromatogr.*, 10 (1974) 1.
21 J. G. Nikelly, *Anal. Chem.*, 44 (1972) 623.
22 J. G. Nikelly, *Anal. Chem.*, 44 (1972) 625.
23 M. Blumer, *Anal. Chem.*, 45 (1973) 980.
24 J. G. Nikelly and M. Blumer, *Amer. Lab.*, 6 (1974) 12.
25 A. L. German and E. C. Horning, *J. Chromatogr. Sci.*, 11 (1973) 76.
26 A. L. German, C. D. Pfaffenberger, J.-P. Thenot, M. G. Horning and E. C. Horning, *Anal. Chem.*, 45 (1973) 930.
27 W. Bertsch, F. S. Shunbo, R. C. Chang and A. Zlatkis, *Chromatographia*, 7 (1974) 128.
28 J. D. Schieke, N. R. Comins and V. Pretorius, *Chromatographia*, in press.
29 D. H. Desty, J. N. Haresnape and B. H. F. Whyman, *Anal. Chem.*, 32 (1960) 302.
30 D. H. Desty, J. N. Haresnape and B. H. F. Whyman (to British Petroleum Co.), *U.S. Pat.* 3,046,699 (1962) (British priority: April 9, 1959).
31 R. H. Doremus, B. W. Roberts and D. Turnbull (Editors), *Growth and Perfection of Crystals, Proc. Int. Conf. on Crystal Growth, Cooperstown, New York, August 27–29, 1958*, Wiley, New York, 1958.
32 I. Tarján and M. Mátrai, *Laboratory Manual on Crystal Growth*, Akademiai Kiadó, Budapest, 1972.
33 M. M. Faktor and I. Garrett, *Growth of Crystals from the Vapour*, Chapman & Hall, London, 1974.
34 J. D. Schieke, N. R. Comins and V. Pretorius, *J. Chromatogr.*, in press.
35 Y. Avigal and M. Schieber, *J. Cryst. Growth*, 9 (1971) 127.
36 Y. Avigal and M. Schieber, *J. Cryst. Growth*, 24/25 (1974) 188.
37 Y. Avigal and M. Schieber, *J. Cryst. Growth*, 26 (1974) 157.
38 R. C. Weast (Editor), *Handbook of Chemistry and Physics*, CRC Press, Cleveland, Ohio, 54th ed., 1973.