

CHROM. 9448

## PREPARATION AND APPLICATION OF SURFACE-MODIFIED HIGH-RESOLUTION WALL-COATED OPEN TUBULAR COLUMNS

F. I. ONUSKA\* and M. E. COMBA

*Analytical Methods Research Section, Canada Centre for Inland Waters, P.O. Box 5050, 867 Lakeshore Road, Burlington, Ontario L7R 4A6 (Canada)*

---

### SUMMARY

Short wall-coated open tubular glass capillary columns were prepared from soft soda-lime and sodium borosilicate (Pyrex) glass. Whisker growth was affected by gaseous hydrogen fluoride at elevated temperatures. A substantial increase in total internal surface area was observed and documented by scanning electron microscopy. Examples of their application to mixtures of polychlorinated biphenyls, methyl esters of fatty acids, nonionic surfactants and polynuclear aromatic hydrocarbons are given.

---

### INTRODUCTION

Adaptation of glass capillary wall-coated open tubular columns (WCOT) for routine applications in gas chromatography (GC) is slowly becoming a realization. Many of the problems previously encountered with capillary column systems have been dissipated by the commercial availability of instrumentation especially designed for these purposes. The original limitations of low partition ratios, small sample capacities and column quality have been substantially altered with considerable effort devoted to improvements in coating procedures, surface preparation, and instrumentation<sup>1-20</sup>.

Propagation of whiskers on the inner surfaces of capillary walls has proven to be a significant advancement in the preparation of glass capillary columns. Tesařík and Novotný<sup>19</sup> successfully etched soft glass capillaries with hydrogen chloride, hydrogen fluoride, and 2-chloro-1,1,2-trifluoromethyl ethyl ether. The latter technique was extended by Schieke *et al.*<sup>21-24</sup> using more concentrated solutions which decompose at elevated temperatures to liberate hydrogen fluoride. During this process, formation of a carbon deposit was observed which can be very difficult and time consuming to remove<sup>22</sup>. Etching and surface modification techniques have also been described by Grob<sup>11</sup> and by Alexander and Rutten<sup>14</sup>.

Treatment of glass surfaces with gaseous hydrogen fluoride has not been extensively used, although its corrosive aspects are well documented<sup>19,25</sup>. This is basically due to the safety precautions associated with hydrogen fluoride which detract from its suitability. In view of this, a simplified procedure was developed for forming whisker-

---

\* Author to whom all correspondence should be addressed.

modified surfaces with gaseous hydrogen fluoride. Both Pyrex and soft glass were etched by this method to observe if any pronounced advantages in relation to other surface treatment techniques were obtained.

## EXPERIMENTAL

### *Preparation of glass columns*

Glass capillaries were prepared from soft soda-lime and sodium borosilicate (Pyrex) tubing according to the method outlined by Desty *et al.*<sup>26</sup> employing a Hewlett-Packard Model 1045 A drawing machine. A 40- and a 13-m column were drawn

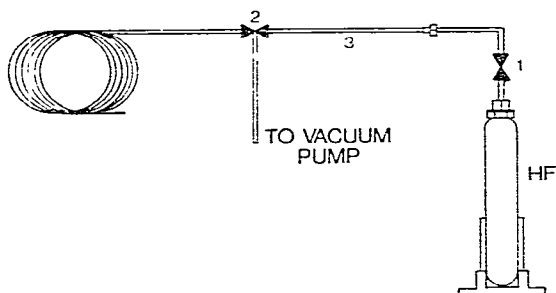


Fig. 1. Apparatus for hydrogen fluoride etching of glass capillary columns.

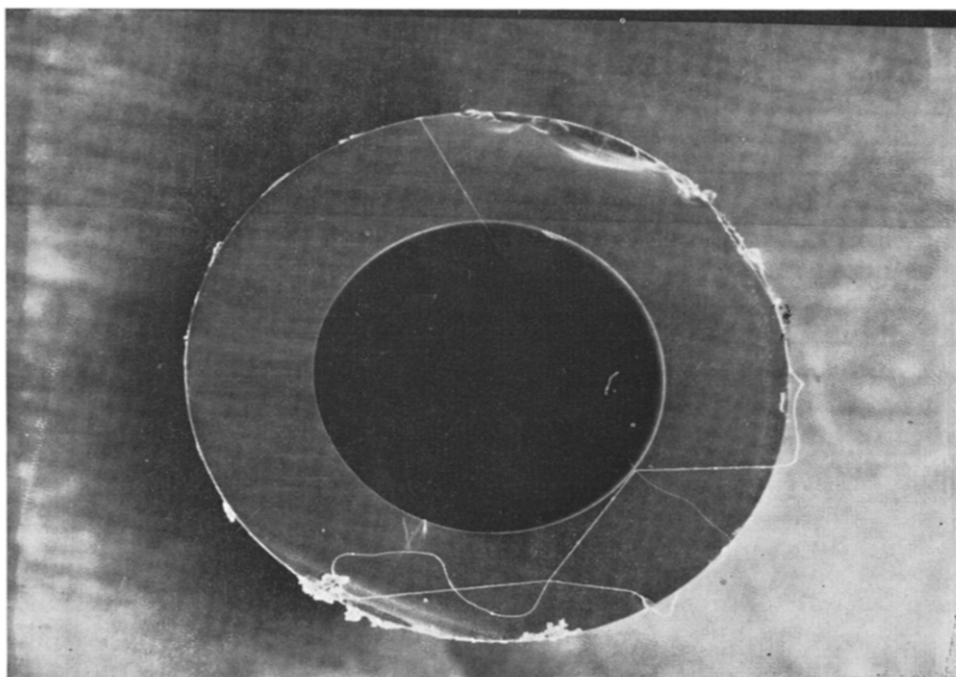


Fig. 2. Cross-section of column before treatment.

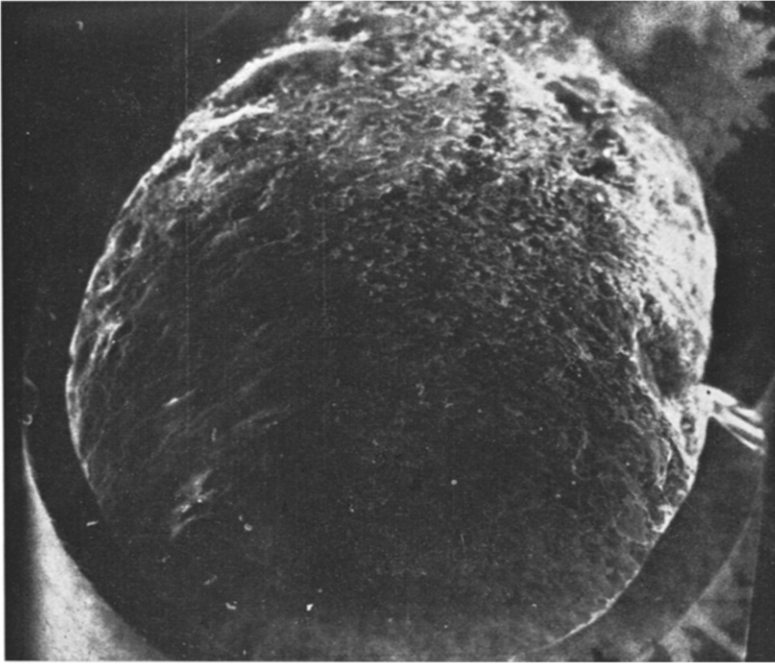


Fig. 3. Cross-section of etched soft glass capillary.

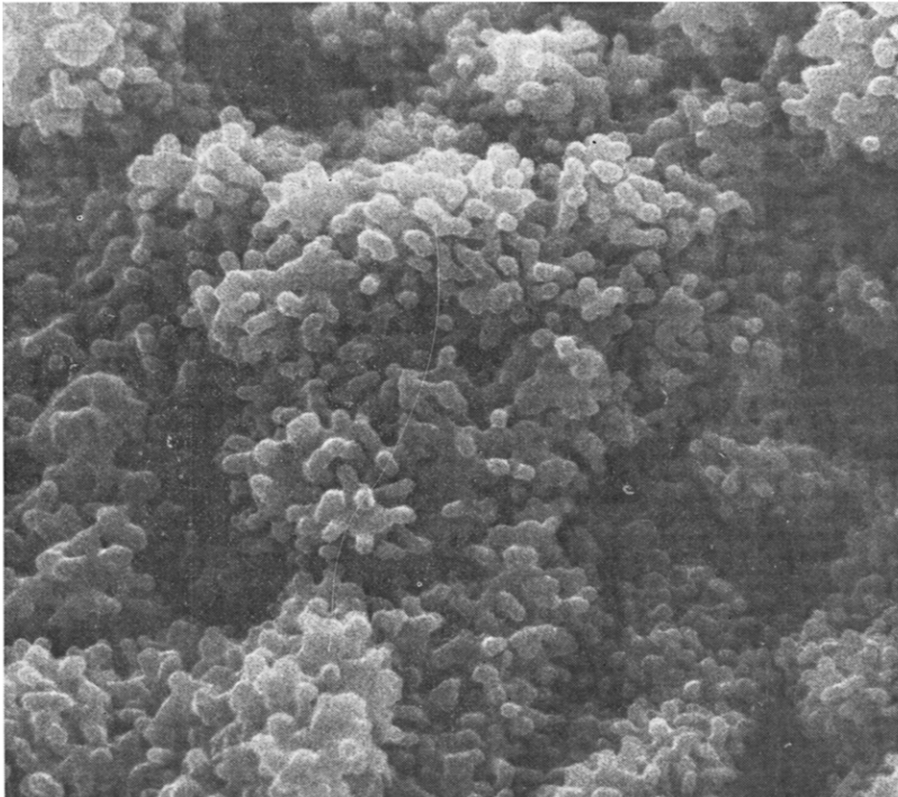


Fig. 4. Surface of etched soft glass capillary.

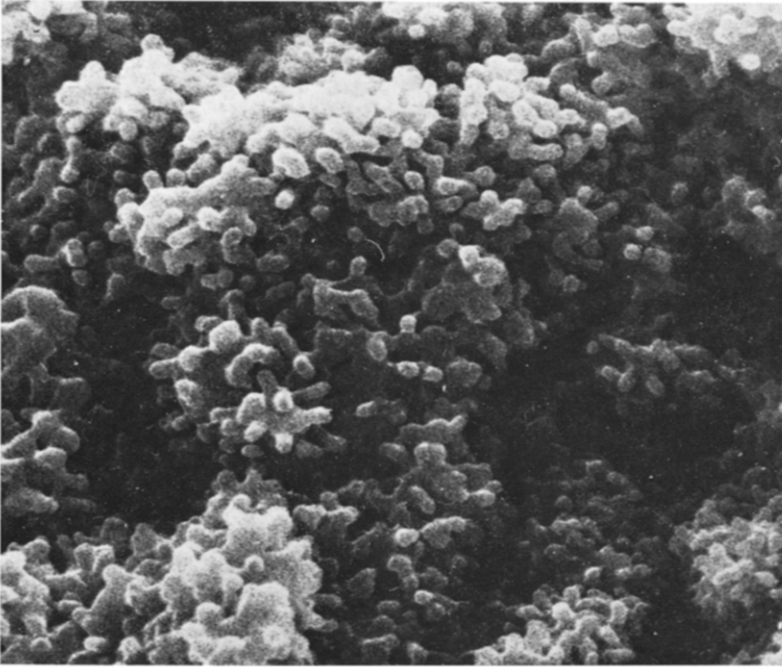


Fig. 5. Whisker formation on soft glass inner surface.

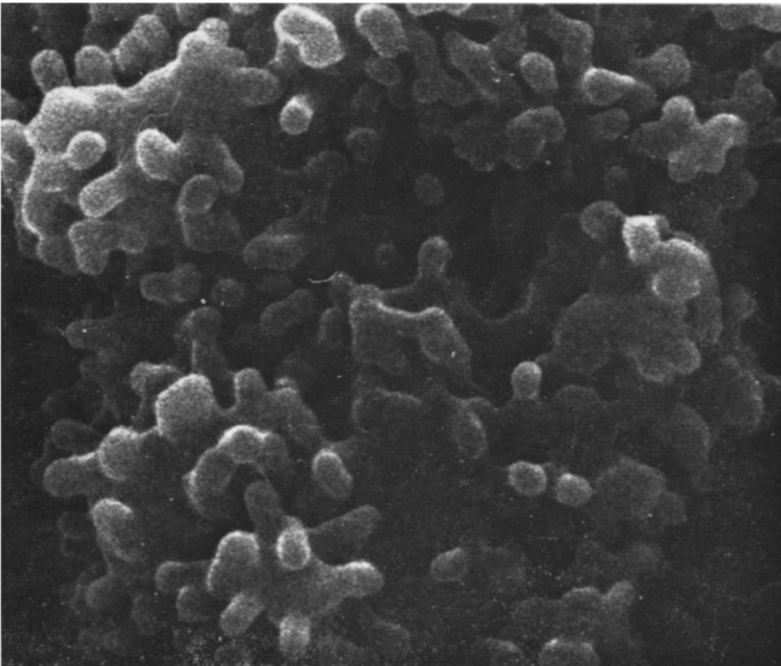


Fig. 6. Whisker formation on soft glass inner surface.

to 0.5 mm I.D. and 0.24 mm I.D. (tolerances of  $\pm 0.5\%$  of I.D. were acceptable), respectively.

#### *Surface modification*

Since the whisker growth is affected in the vapor phase, it is essential to introduce the hydrogen fluoride in a uniform manner over the entire length of the column. This may be accomplished by using the apparatus described in Fig. 1. The system must be located in a well-ventilated fume hood and operated using rubber gloves, apron, and aspirator mask. The column was sealed at one end with the open end being connected to the three-way switching valve using shrinkable PTFE tubing. The column was evacuated to a least  $10^{-1}$  mmHg using a small vacuum pump. Valve 2 was then switched to the hydrogen fluoride lecture bottle and hydrogen fluoride was released into the column by opening valve 1. The lecture bottle valve was closed and the column sealed off using a microflame torch. The seals on both ends of the column should be checked before removal by inserting each in a small beaker of water. The sealed column was then placed in a vented oven at ambient temperature. The oven was closed and the temperature raised to 400 for 12 h. After the hydrogen fluoride has

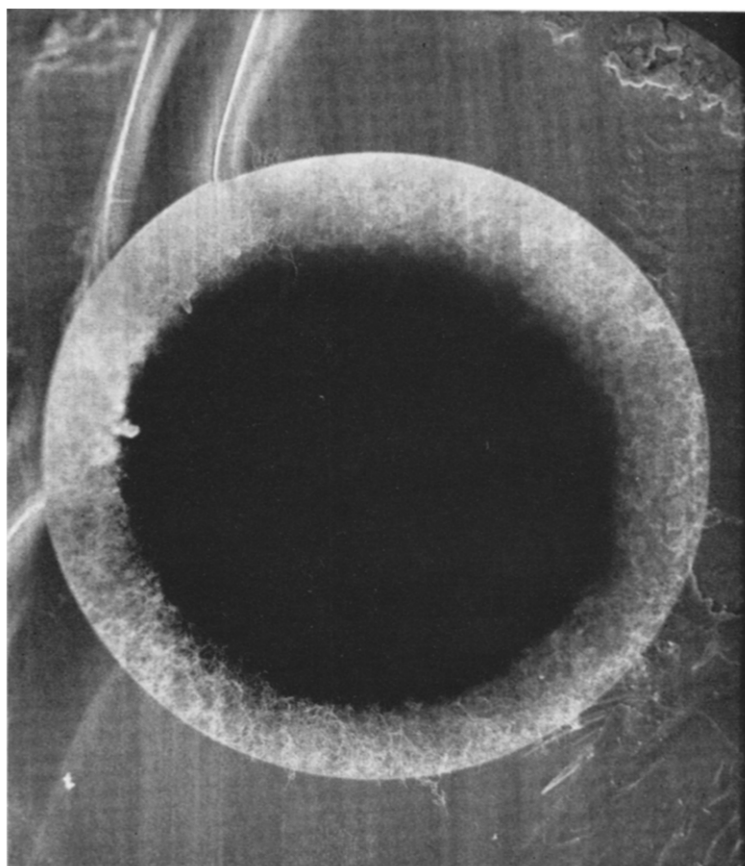


Fig. 7. Cross-section of etched Pyrex capillary.

been consumed the column has a translucent appearance. The column was then removed and flushed with helium for 80 min. The whisker growth was checked by breaking short lengths (10 mm) from both ends of the column. An AMR Model 1000 scanning electron microscope (SEM) with an EDAX attachment for X-ray electron dispersive analysis was used. Small portions of each length were taken and mounted vertically in a capillary holder. The etched surface was then treated with protamine sulfate and gold to eliminate charging effects.

### *Coating*

Each column was tailored to a form suitable for connection to the gas chromatograph prior to coating. A liquid phase of 20% OV-17 (methyl phenyl silicone) in  $\text{CH}_2\text{Cl}_2$  was then applied to the Pyrex column using a mercury plug method<sup>17</sup>. The column was filled with the coating solution by suction, followed by a 5-cm mercury plug. The vacuum was removed and the capillary plug was pushed through the capillary at a constant velocity (80 cm/min). The end of the capillary column was connected to a buffer column (10 m of shrinkable PTFE) to ensure a constant linear flow through

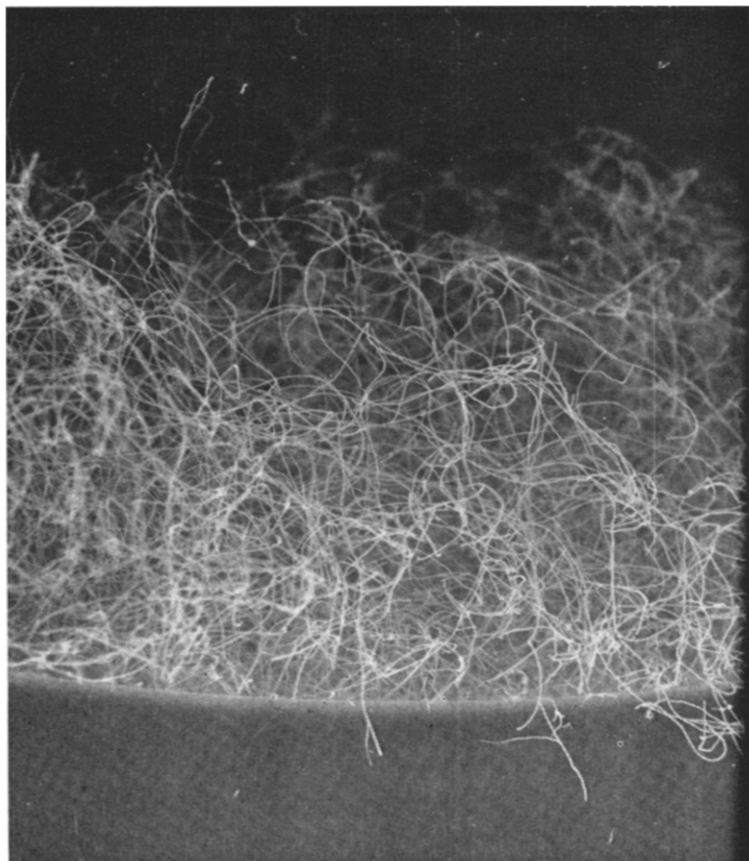


Fig. 8. End-view of whiskers formed on Pyrex capillary column.

the last part of the column. The quality of the column can be greatly reduced if degassed solvents are not used. Due to the enlarged surface area, air bubbles can be adsorbed on the surface and later may be entrained in the liquid phase. Excessive solvent was removed by passing helium through the column for approximately 80 min.

The soft (soda-lime) glass capillary was coated with a 4% solution of OV-3 in  $\text{CH}_2\text{Cl}_2$  using a dynamic coating procedure<sup>17</sup> with a Shimadzu Model MC T-1A treating stand.

#### *Gas chromatography*

A Carlo Erba Model 2300 gas chromatograph equipped with a flame ionization detector was used. The instrument incorporates a splitless injector with a modified insert<sup>27</sup>. A pre-column containing an ultra-thin layer of non-extractable Apiezon L on a diatomaceous support, prepared according to Aue and Younker<sup>28</sup> was located directly in the injector to increase the sample capacity. The glass insert and column ends were deactivated with a low concentration of Carbowax 20M (20 mg/ml) prior to use. The column was conditioned at a slow programming rate overnight (60–260°).

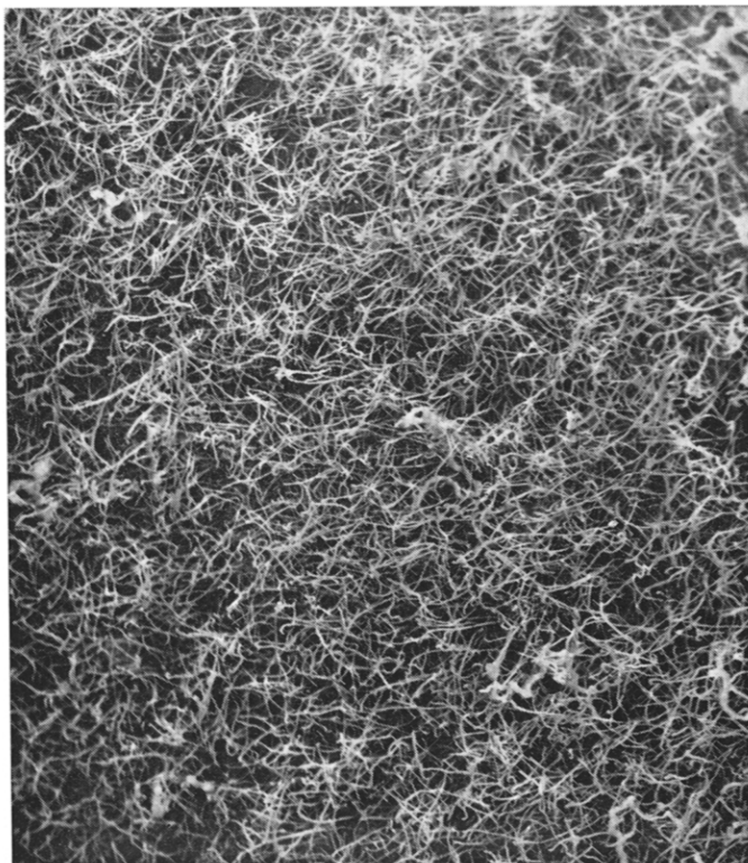


Fig. 9. Surface of etched Pyrex capillary.

Film homogeneity and column quality were evaluated using a polar mixture containing Reynolds mixture. Column inertness was checked according to Grob<sup>11</sup> using a mixture of *n*-undecane, dibutyl ketone, 2-*trans*-2-ethyl- and 2-*cis*-2-ethylcyclohexanol, and 2,6-dimethylaniline.

## RESULTS AND DISCUSSION

In comparison to untreated surfaces (Fig. 2), ideal support media for the retention of the stationary phase were achieved by hydrogen fluoride etching. Whisker formations on the soft (soda-lime) glass were 2–3  $\mu\text{m}$  in length, coral-like in nature, and relatively uniform, as shown in Figs. 3–6. Pyrex yielded finer whiskers, 3–5  $\mu\text{m}$  in length, under the same conditions. Fairly dense, uniform silica fibres were observed (Figs. 7–10) resembling glass wool.

The prepared columns as described in Table I were applied to a number of complex mixtures. Figs. 11 and 12 show the separation of various distillation cuts of Aroclors, using the OV-17 capillary column. Although it is difficult to compare two

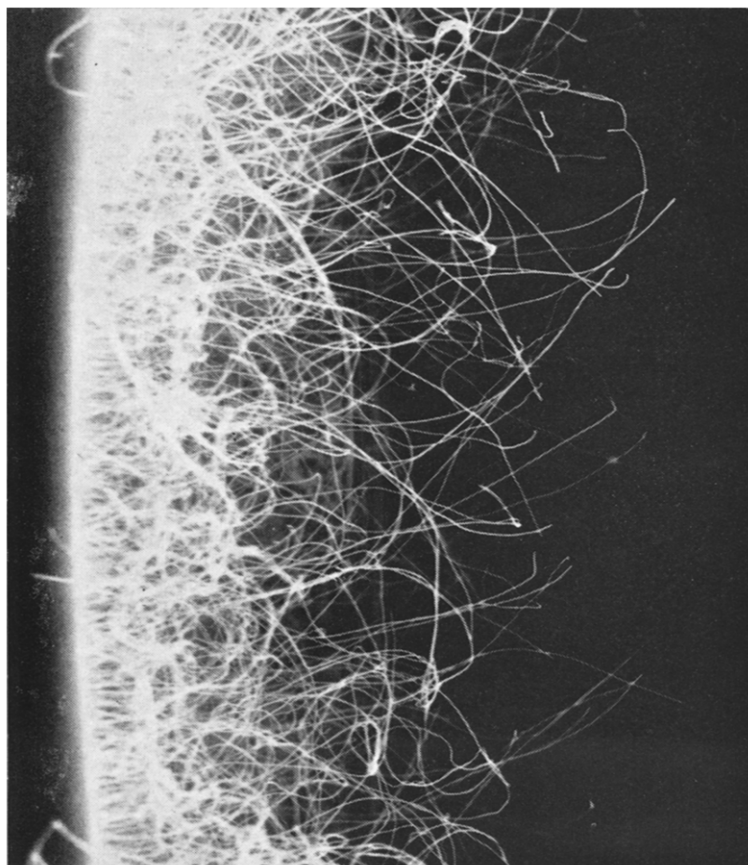


Fig. 10. End-view of etched Pyrex capillary.



TABLE I  
PHYSICAL PARAMETERS OF WCOT COLUMNS

<i>Parameter</i>	<i>Unit</i>	<i>Column 1</i>	<i>Column 2</i>
Stationary phase	—	OV-17	OV-3
Flow-rate* (helium)	ml/min	4	1.4
Length	m	38	12
Internal diameter	mm	0.50	0.24
Total volume	ml	7.46	0.54
Number of theoretical plates** ( <i>N</i> )	—	228,000	96,500
Number of theoretical plates per metre ( <i>N/m</i> )	—	6000	8041
Height equivalent to a theoretical plate (HETP)	mm	0.166	0.125
Partition ratio ( <i>k</i> )***	—	18	19
Separation number ( <i>TZ</i> )	—	47	31

\* Dial setting of 0.7–0.8 atm (at ambient temperature).

\*\* Calculated for fluorene at 140°.

\*\*\* Calculated for fluorene.

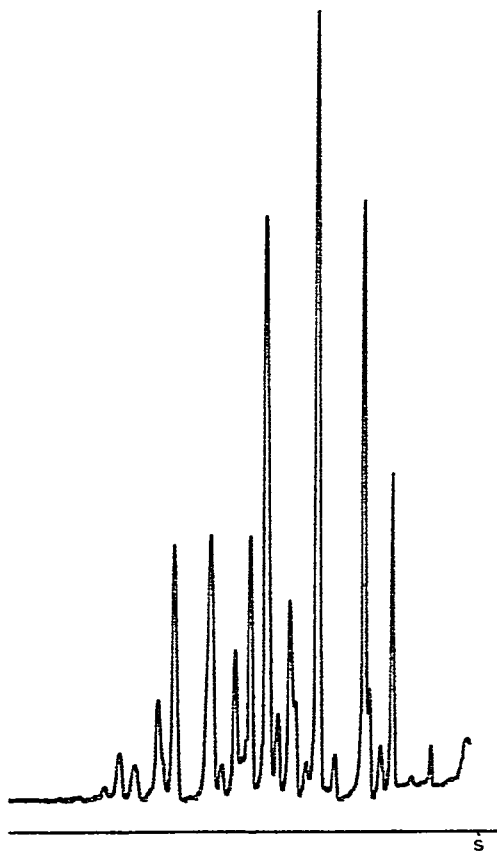


Fig. 11. Gas chromatogram of Aroclor 1016 on OV-17. Temperature programmed from 140–190° at 4°/min; 3 min hold. For other column conditions, see Table I.

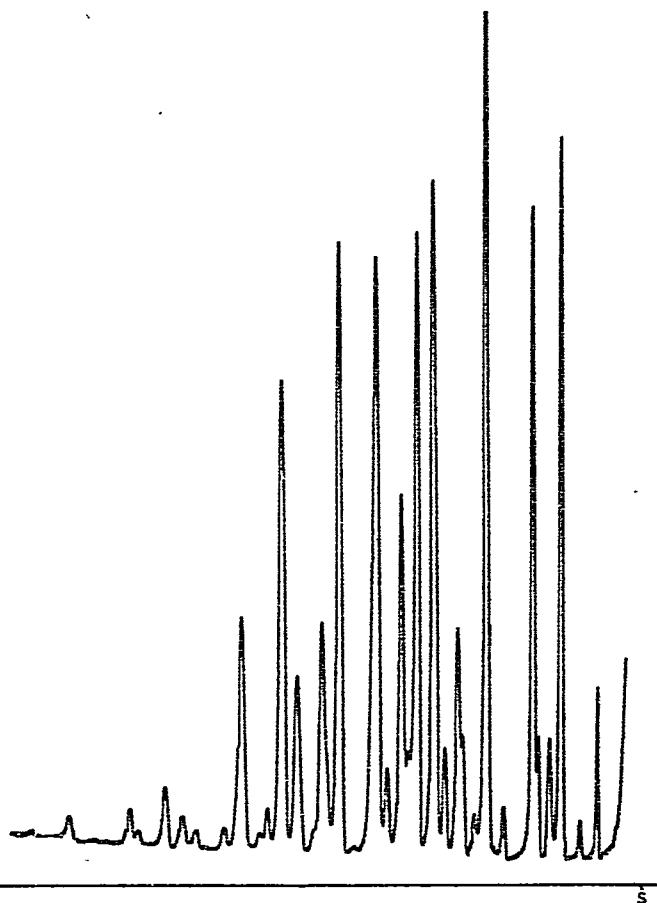


Fig. 12. Gas chromatogram of Aroclor 1242 on OV-17. Temperature programmed from 140–190° at 4°/min; 3 min hold. For other column conditions, see Table I.

different columns, the separation achieved on Aroclor 1016 was similar to that obtained by Schomburg *et al.*<sup>13</sup> on a 120-m Dexsil 300 column.

The separation of methyl esters of fatty acids using the same column is shown in Fig. 13. Although OV-17 is not a specific phase to effect proper separation, it is evident that reasonable results can be obtained for  $C_8$ – $C_{22}$  esters using temperature programming, with reproducible retention data, symmetrical peaks, and short analysis time. Excellent separation was also achieved on a nonionic detergent formulation (Fig. 14) containing various amounts of ethoxy groups on a  $C_{14}$  alkoxy moiety.

The column prepared from soft glass and coated with OV-3 gave equivalent separation on a mixture of polynuclear aromatic hydrocarbons (Fig. 15), as previously experienced with a SE-52 column prepared by a static coating method.

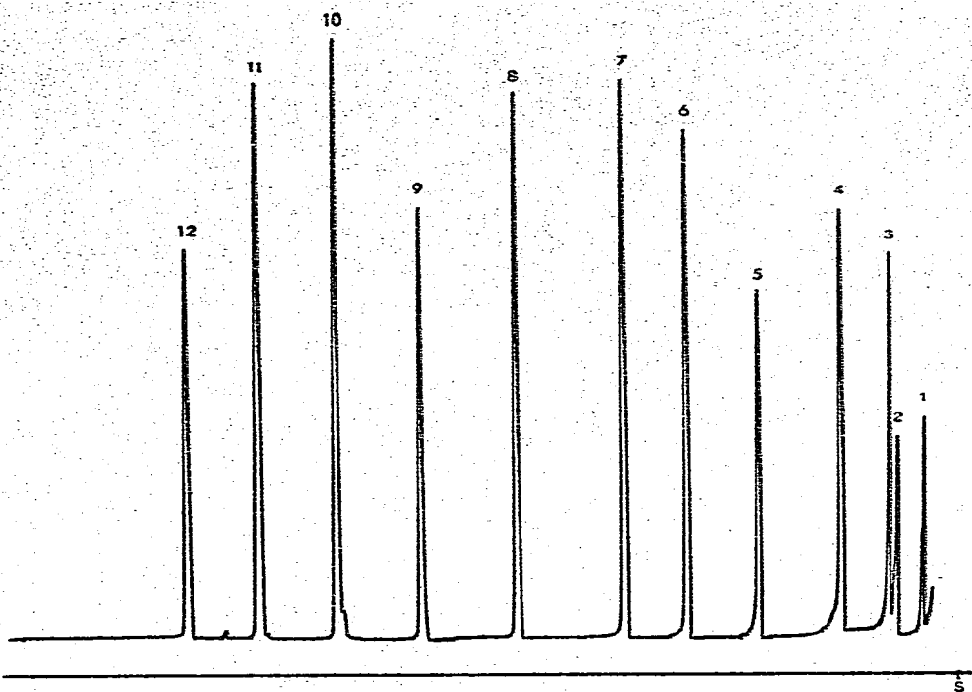


Fig. 13. Gas chromatogram of fatty acid methyl esters on OV-17. Temperature programmed from 70-210° at 4°/min; 3 min hold. For other column conditions, see Table I. 1 = Hexanoic; 2 = heptanoic; 3 = octanoic; 4 = nonanoic; 5 = decanoic; 6 = hendecanoic; 7 = dodecanoic; 8 = tetradecanoic; 9 = hexadecanoic; 10 = octadecanoic; 11 = eicosanoic; 12 = docosanoic acids.

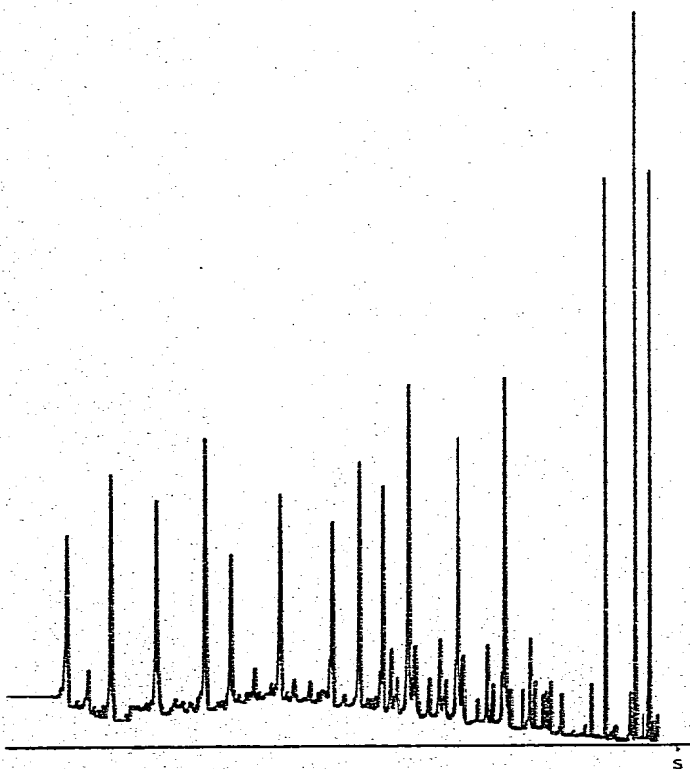


Fig. 14. Gas chromatogram of nonionic surfactant on OV-17. Temperature programmed from 90-250° at 4°/min; 3 min hold. For other column conditions, see Table I.

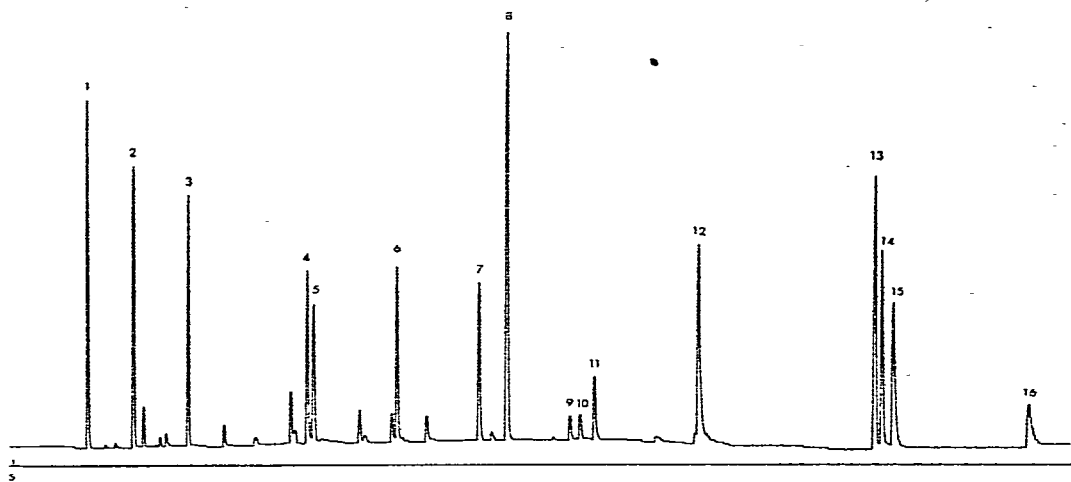


Fig. 15. Gas chromatogram of polynuclear aromatic hydrocarbons on OV-3. Temperature programmed from 60–230° at 2°/min; 3 min hold. For other column conditions, see Table I. 1 = Biphenyl; 2 = acenaphthene; 3 = fluorene; 4 = phenanthrene; 5 = anthracene; 6 = 9-methylphenanthrene; 7 = fluoranthrene; 8 = pyrene; 9 = benzo[*a*]fluorene; 10 = benzo[*b*]fluorene; 11 = 1-methylpyrene; 12 = triphenylene; 13 = benzo[*e*]pyrene; 14 = benzo[*a*]pyrene; 15 = perylene; 16 = dibenz[*a,c*]anthracene.

## CONCLUSIONS

Surface modification of glass capillaries substantially contributes to the technology of column preparation and provides an excellent substrate for coating. It would be unreasonable to believe that only one general procedure can provide suitable results. We are confident, however, that etching with hydrogen fluoride will produce reliable columns and is competitive with other treatments.

## ACKNOWLEDGEMENTS

We would like to thank Mr. T. Bistricki, AMRS, Canada Centre for Inland Waters, for developing the SEM technique and Dr. M. Novotný, Indiana University, Bloomington, Ind., for his friendly assistance.

## REFERENCES

- 1 M. J. E. Golay, in U. J. Coates, H. J. Noebels and I. S. Fagerson (Editors), *Gas Chromatography*, Academic Press, New York, 1958, pp. 1–13.
- 2 M. J. E. Golay, in D. H. Desty (Editor), *Gas Chromatography 1958*, Butterworths, London, 1958, pp. 36–55.
- 3 L. S. Ettre, *Instr. News*, 13, No. 1 (1961) 1.
- 4 A. Zlatkis and J. Q. Walker, *J. Gas Chromatogr.*, 1 (5) (1963) 9.
- 5 K. Tesařík, K. Hana and M. Janiček, *Chem. Listy*, 55 (1961) 1467.
- 6 M. Novotný and A. Zlatkis, *Chromatogr. Rev.*, 14 (1971) 1.
- 7 K. Grob, *J. Gas Chromatogr.*, 3 (1965) 52.
- 8 A. V. Kiselev, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 3.
- 9 J. Merle d'Aubigne, C. Landault and G. Guicchon, *Chromatographia*, 4 (1971) 309.
- 10 M. Novotný, *Chromatographia*, 2 (1969) 350.
- 11 K. Grob, *Helv. Chim. Acta*, 51 (1968) 718.

- 12 K. Grob and G. Grob, *J. Chromatogr. Sci.*, 7 (1969) 584.
- 13 G. Schomburg, H. Husmann and F. Weeke, *J. Chromatogr.*, 99 (1974) 63.
- 14 G. Alexander and G. A. F. M. Rutten, *J. Chromatogr.*, 99 (1974) 81.
- 15 K. Grob, *Chromatographia*, 8 (1975) 423.
- 16 G. C. Geretti, A. Liberti and G. Nota, *Chromatographia*, 8 (1975) 486.
- 17 G. Schomburg and H. Husmann, *Chromatographia*, 8 (1975) 517.
- 18 J. Roeraade, *Chromatographia*, 8 (1975) 511.
- 19 K. Tesařík and M. Novotný, in H. S. Struppe (Editor), *Gas Chromatographia 1968*, Akademie-Verlag, Berlin, 1968, p. 575.
- 20 M. Novotný and K. Tesařík, *Chromatographia*, 1 (1968) 332.
- 21 J. D. Schieke, N. R. Comins and V. Pretorius, *Chromatographia*, 8 (1975) 354.
- 22 J. D. Schieke, N. R. Comins and V. Pretorius, *J. Chromatogr.*, 112 (1975) 97.
- 23 J. D. Schieke, N. R. Comins and V. Pretorius, *J. Chromatogr.*, 114 (1975) 190.
- 24 J. D. Schieke, N. R. Comins and V. Pretorius, *J. Chromatogr.*, 115 (1975) 373.
- 25 A. V. Kiselev and Ya. I. Yashin, *Gazo-adsorbcionnaya Chromatografiya (Gas Adsorption Chromatography)*, Nauka, Moscow, 1967, p. 233.
- 26 D. H. Desty, J. N. Haresnape and B. H. Whyman, *Anal. Chem.*, 32 (1960) 302.
- 27 F. I. Onuska, M. E. Comba, M. Novotný and M. Lee, *Anal. Lett.*, (1976).
- 28 W. A. Aue and D. R. Younker, *J. Chromatogr.*, 88 (1974) 7.