Journal of Chromatography, 115 (1975) 373–381

CHROM. 8571

SURFACE-MODIFIED OPEN-TUBULAR COLUMNS FOR GAS CHROMATOGRAPHY
OBSERVATION AND ANALYSIS OF THE SURFACE USING SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY-DISPERSIVE X-RAY ANALYSIS

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(Received July 3rd, 1975)

SUMMARY

The inner surfaces of a variety of open-tubular columns, including wall-treated and support-coated types, have been studied by means of scanning electron microscopy and energy-dispersive X-ray analysis.

INTRODUCTION

Over the past few years, a number of attempts have been made to improve the performance of open-tubular columns (OTC) for gas chromatography by treating or modifying the inner surface of the column[1–32]. Although a visual image of such surfaces at a sufficiently high magnification to reveal structural details is undoubtedly useful for this purpose, few studies of this nature have been carried out[25,33,34].

We have previously described[35] an improved technique for viewing the inner surface of an OTC by using scanning electron microscopy (SEM). The essential feature of the technique is the use of osmium tetroxide to provide a conductive surface coating, thereby making it possible to view the inner surface directly through the open end of the column. This eliminates the need for cutting the column longitudinally so as to expose the inner surface[25,33,34], a process that often either damages the structure or introduces foreign matter on to the exposed surface. In this paper we give results that have been obtained by these means for observing the inner surfaces of columns treated in the variety of ways described in the literature.

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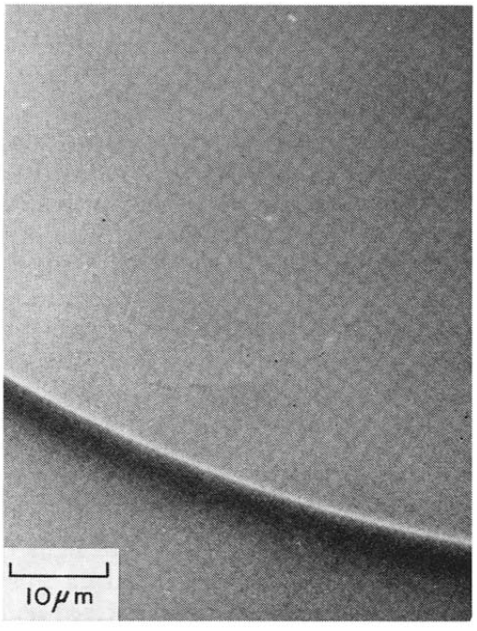


Fig. 1. Micrograph of the surface of an untreated borosilicate-glass OTC taken at an angle of 35° from the vertical axis.

EXPERIMENTAL AND RESULTS

Columns were drawn, using the method described by Desty and co-workers[36,37], to an inner diameter of 0.04–0.06 mm. Borosilicate (Pyrex, J. A. Jobling & Co.) and soda-glass tubing were used for this purpose. The glass was washed with a 10% solution of Extran (E. Merck, Darmstadt, G.F.R.) in distilled water, distilled water and ethanol, and dried with nitrogen. After treatment, as described below, a short length (5–8 mm) was cut and prepared for viewing as previously described[55]. A Jeol U3 scanning electron microscope and an attached EDAX energy-dispersive X-ray analyzer

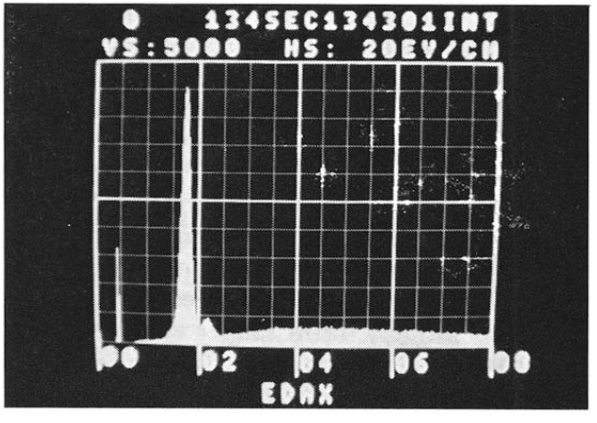


Fig. 2. Energy-dispersive X-ray analysis of the surface of an untreated borosilicate OTC. The X-ray spectrum in the range 0–8 keV is shown. The peaks are Si 1.74 keV and Au 2.12 keV. The presence of gold is due to the preparation of the sample for SEM analysis.

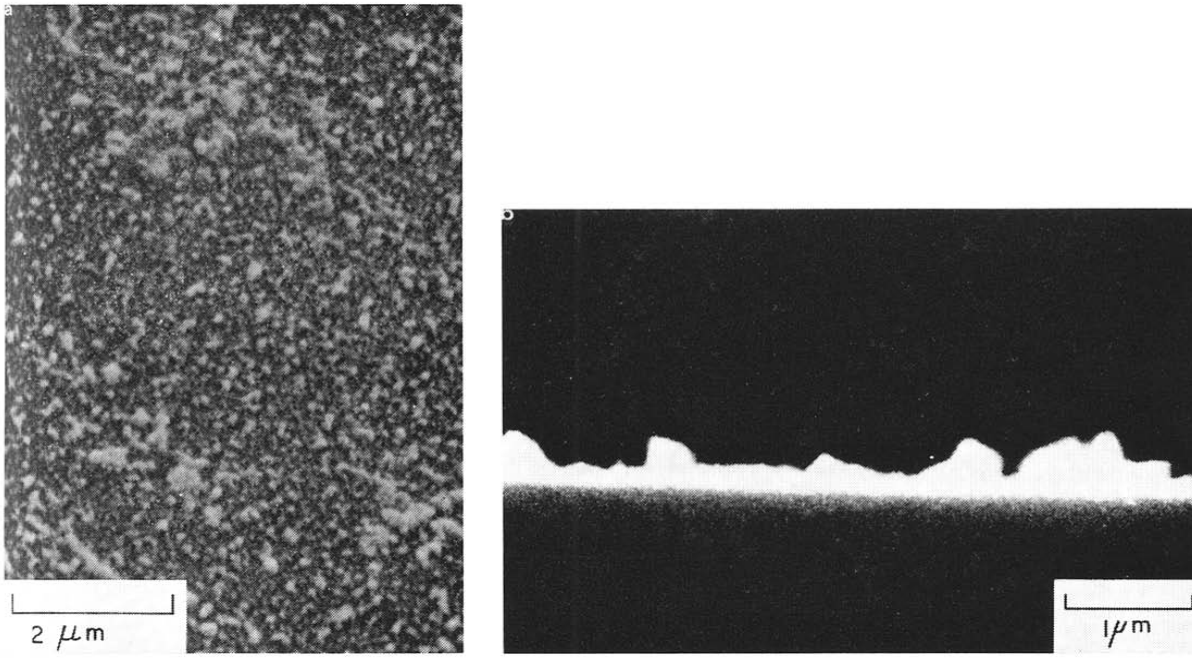
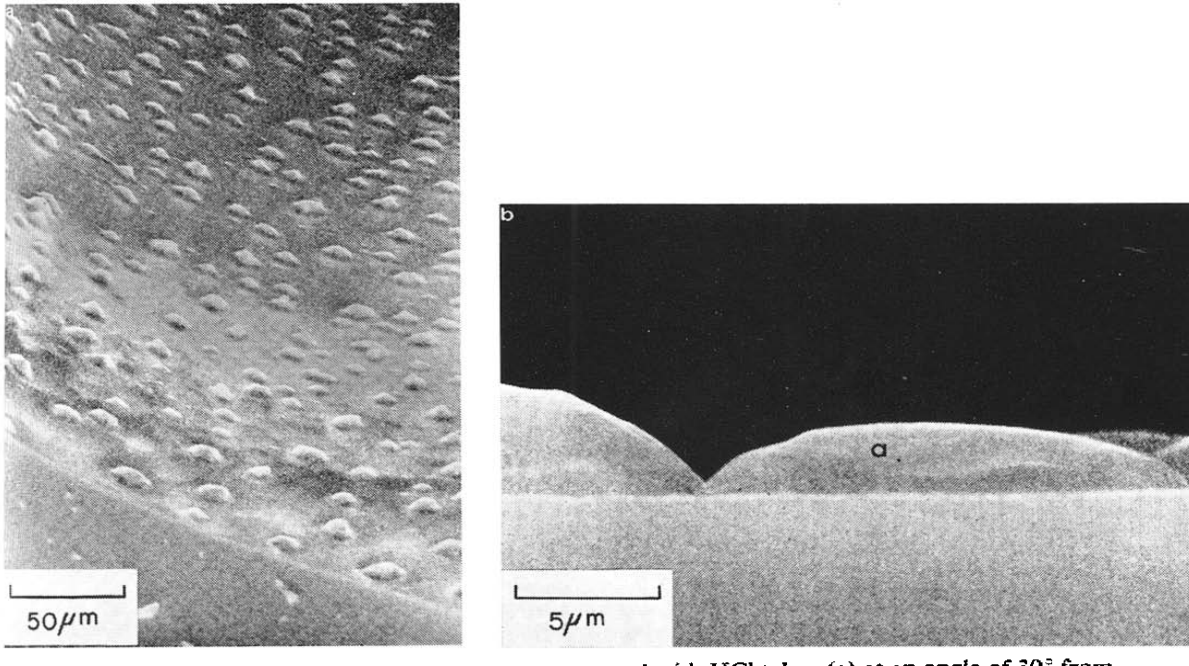


Fig. 3. Micrograph of the surface of a glass OTC treated with 2-chloro-1,1,2-trifluoroethyl methyl ether taken (a) at an angle of 40° from the vertical axis and (b) end-on.



ig. 4. Micrograph of the surface of a glass OTC treated with HCl taken (a) at an angle of 30° from ie vertical axis and (b) end-on.

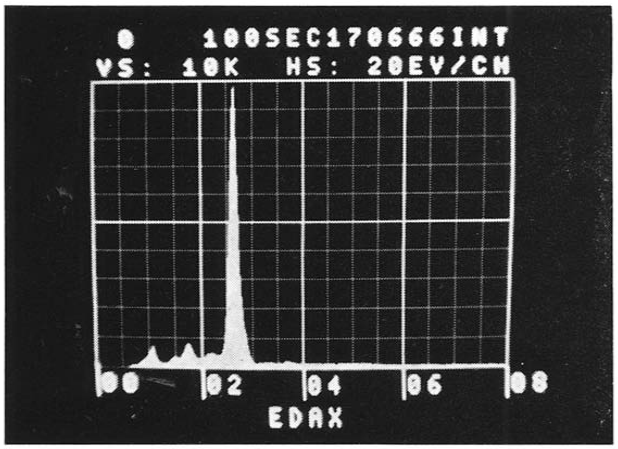


Fig. 5. X-ray analysis of point (a) on the protuberance in Fig. 4b. The X-ray spectrum in the range 0–8 keV is Si 1.74, Au 2.12 and Cl 2.62 keV. The small silicon peak arises from the glass background.

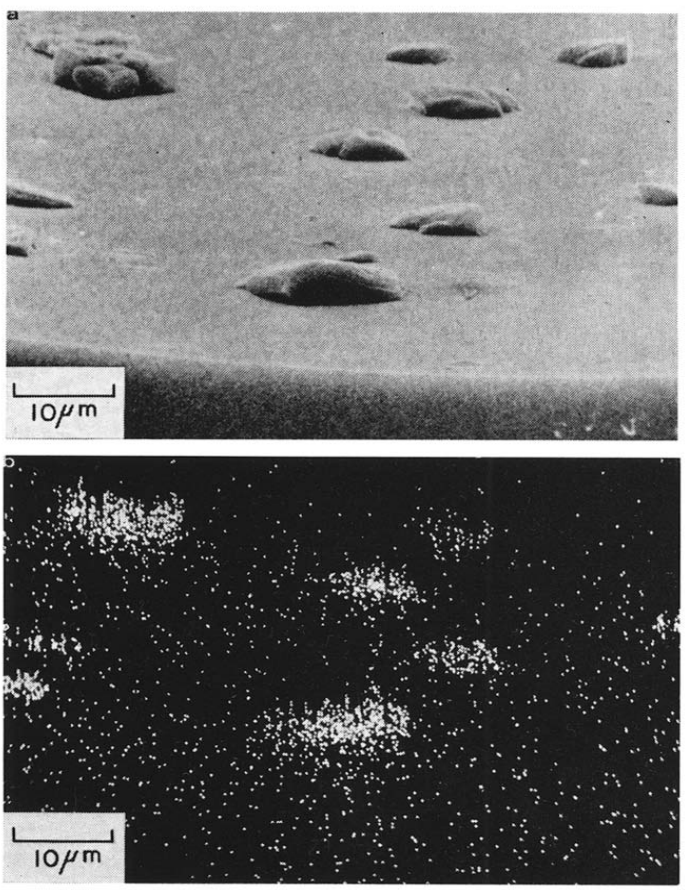


Fig. 6. a Surface structure of an OTC treated with HC . b Chlorine antigen mapping of the salt surface.

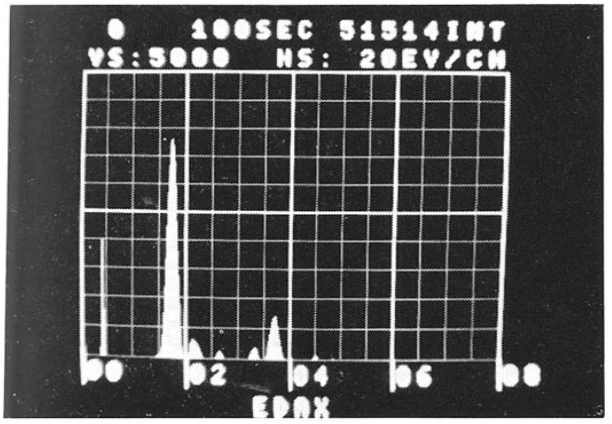


Fig. 7. Energy-dispersive X-ray analysis of the surface of an untreated soda-glass OTC. The X-ray spectrum in the range 0–8 keV is shown. The peaks are Si 1.74 keV, Au 2.12 keV, Cl 2.62 keV, K 3.31 keV, Ca 3.69 keV and Ba 4.47 keV.

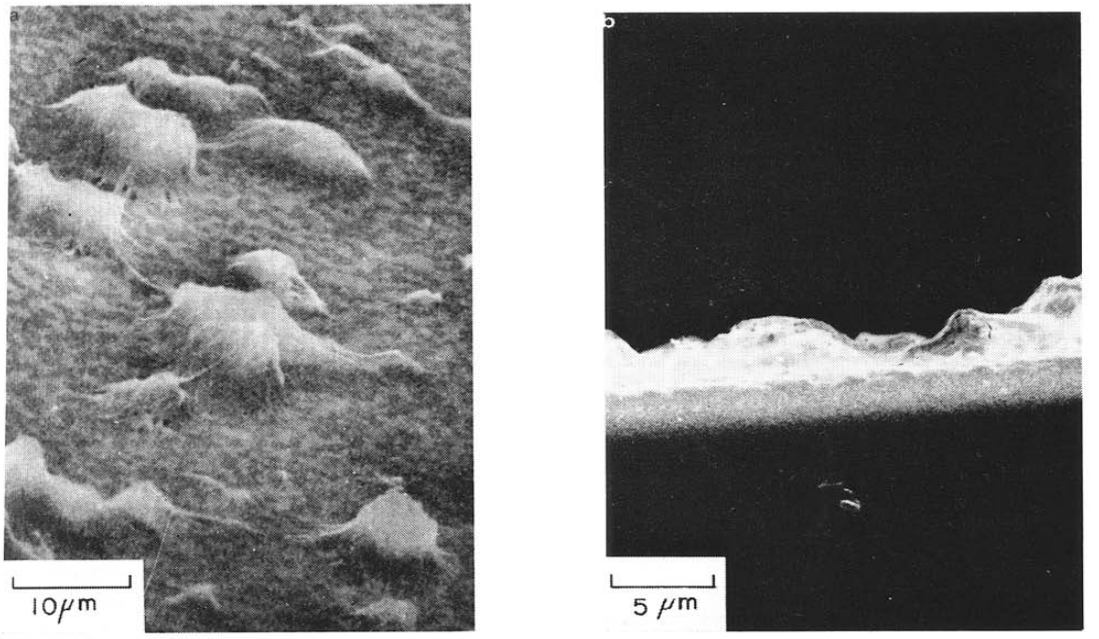


Fig. 8. Micrograph of the inner surface of a soda-glass OTC treated with ammonia taken (a) at an angle of 30° from the vertical axis and (b) end-on.

were used to study the surface and to determine its chemical composition. Micrographs of the surface were taken through the open end of the column at an angle of 30–35° from the longitudinal axis. The column was also viewed end-on.

Fig. 1 shows the surface of a freshly drawn, untreated borosilicate glass column at a magnification of about 2000 times. The surface is smooth with no visible structure. Even at high magnification (30 000 ×) no structure could be observed. This, incidentally, demonstrates that the method used for preparing the specimens for SEM viewing does not introduce any structural effects. For purposes of comparison (see below), the X-ray analysis of the surface is shown in Fig. 2.

The surface of a borosilicate glass column etched with 2-chloro-1,1,2-trifluoroethyl methyl ether according to the method of Tesařík and Novotný[8] is shown in Figs. 3a and 3b. The surface is finely textured with protuberances approx. 0.3 μm high. X-ray analysis of the finely textured surface is identical with that of the untreated surface (Fig. 2.)

Figs. 4a and 4b show the surface of a soda-glass column treated with hydrochloric acid as described by Tesařík and Novotný[8]. The surface protuberances are approx. 3 μm wide at the base. X-ray analysis of a protuberance (point a in Fig. 4b) is identical with that of a pure sodium chloride standard (Fig. 5). The surface structure of an OTC treated with HCl (Fig. 6a) and the element mapping for chlorine of the same surface (Fig. 6b) confirms this together with the results obtained by Alexander and Rutten[33,34]. The area between the sodium chloride crystals has the same composition as an untreated soda-glass surface (Fig. 7).

Soda-glass columns etched by the procedure of Mohnke and co-workers[1,2] using 17% ammonia solution are shown in Figs. 8a and 8b. Superficially, the surface resembles that obtained by hydrochloric acid etching, but the protuberances have the same composition as that of untreated soda-glass (*i.e.*, as shown in Fig. 7). In addition, the surface is more textured than that shown in Fig. 4 and appears to be porous to a depth of approx. 2 μm.

Figs. 9a and 9b show the inner surface of a borosilicate column on which whiskers have been grown[36,39]. The whiskers are cylindrical, approx. 1.5 μm in diameter and 20 μm long. An X-ray analysis of a whisker (point A in Fig. 9b) is shown in Fig. 10 and confirms the presence of silicon. We conclude from this and other evidence[39] that the whiskers consist of a microcrystalline silica.

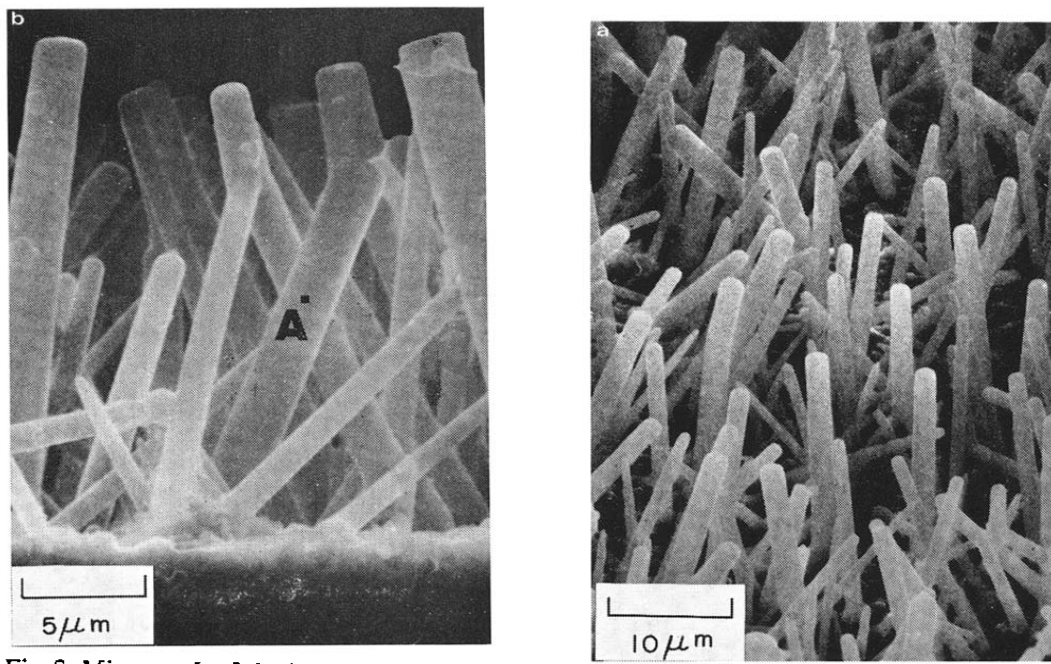


Fig. 9. Micrograph of the inner surface of a whisker-walled glass OTC taken (a) at an angle of 35° from the vertical axis and (b) end-on.

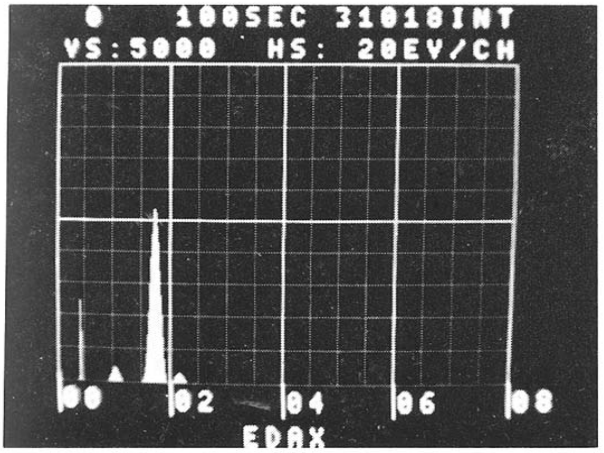


Fig. 10. Energy-dispersive X-ray analysis of a single whisker (point A in Fig. 9b). The X-ray spectrum in the range 0–8 keV is shown. The peaks are Na 1.04 keV, Si 1.74 keV and Au 2.12 keV.

Two types of support-coated open-tubular (SCOT) columns were included in this study. Fig. 11 shows the inner surface of a glass column coated with a layer of silanized microparticulate silica in an aerogel form (Silanox 101, Cabot, Boston, Mass., U.S.A.). The technique used for preparing these columns has been described by German and co-workers[20,21], Bertsch *et al.*[22] and Nikelly and Blumer[16–19]. The porous layer is not uniformly thick, but the average thickness is approx. 6 μm. A degree of particle agglomeration is evident, but individual particles could not be observed even at high magnification (50,000×). This is not surprising as the particles are stated to be 70 Å in diameter (Cabot Corp.).

Figs. 12(a) and 12(b) show a commercial SCOT stainless-steel column, I.D.

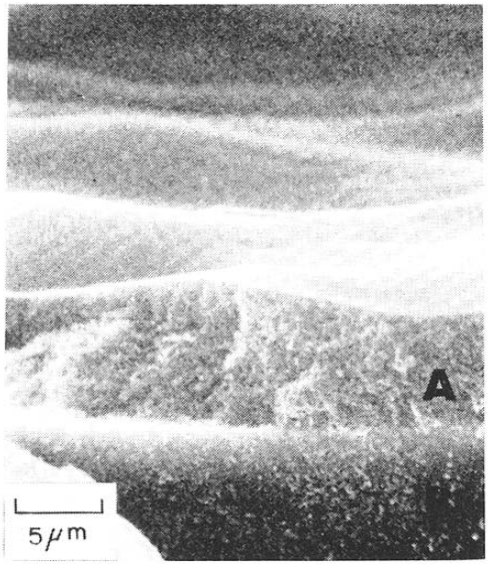


Fig. 11. Glass OTC coated with Silanox 101 (A, Silanox layer; B, column end).

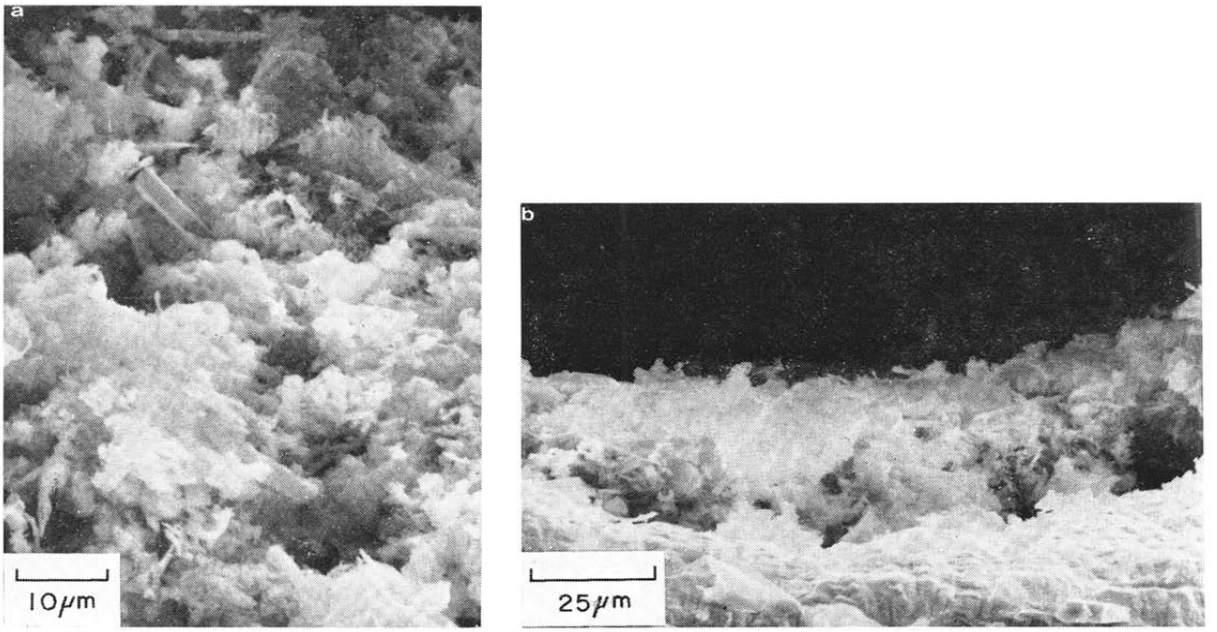


Fig. 12. Micrograph of a commercial SCOT column taken (a) at an angle of 35° from the vertical axis and (b) end-on.

0.05 cm, coated with diatomaceous earth[23–25]. The thickness of the layer is fairly constant at approximately 30 μm, but the surface is extensively pitted.

CONCLUSION

SEM is a useful technique for studying various methods of treating the inner surface of OTCs. Details of both the physical and chemical nature of the surfaces so formed are readily obtained and the technique also enables the uniformity of the treated surface to be determined.

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