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CHARACTERISTICS OF NON-POLAR GLASS SUPPORT-COATED OPEN-TUBULAR COLUMNS

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SUMMARY

The size and number of fine sodium chloride crystals deposited on the inside wall of the column were investigated with a scanning electron microscope. The number of crystals is related to the concentration of the sodium chloride solution, but their sizes are not greatly related to the concentration. It was found the adsorptivity of the column is small because the sodium chloride crystals are deposited on some of the active sites of the silanol groups and metal oxides. Also, it was shown that the thermal stability of such a column is superior to that of a wall-coated open-tubular column because of the adsorptive property of sodium chloride crystals on the glass wall.

INTRODUCTION

Recently, the materials and procedures used for the manufacture of glass capillary columns have been more frequently studied, and it has been found that polar liquid phases such as phenylsilicone polymer (OV-17) and polyethylene glycol 20M can be coated homogeneously on to the glass surface, with good thermal stability[1–6].

The glass is pre-treated by etching with acids[7–10], coating with fine particles of silica[5,11–13], depositing sodium chloride (NaCl) crystals on soft glass by etching with dry hydrogen chloride[4,10,14], depositing NaCl crystals by coating with NaCl solution, and other procedures.

A liquid phase of a methylsilicone polymer such as OV-101 and SF 96 has been spread homogeneously on the glass surface as a result of their low surface tension and chemical structure[15], and these polymers could therefore be coated on the glass wall with a high coating efficiency.

If the glass surface is not pre-treated, the film of liquid phase is not uniform and the coating efficiency is about 50%[16]. We have previously considered the simple pre-treatment of the surface and depositing fine NaCl crystals on the inside wall, to,

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give a suitable geometrical modification of the surface, and then coating the liquid phase on the surface of the NaCl[17]. This procedure results in the glass support-coated open-tubular (G-SCOT) column. It has an excellent performance, with a coating efficiency of about 90%, more than 3,500 theoretical plates per metre, and gives three or four times the theoretical plate performance of the wall-coated open-tubular (WCOT) column because of the increased amount of liquid phase and the regular distribution of the liquid phase along the entire column length. The adsorptivity towards polar solutes is smaller than that of the WCOT column, as shown in our previous paper[17]. Hence, it can be assumed that some part of the glass surface was covered with crystals.

In this work, the characteristics of the inside surface of the G-SCOT column were observed by using a scanning electron microscope (SEM), and the conditions of the deposited crystals and the coated liquid phase were investigated by studying the micrographs. Also, the influence of the concentration of NaCl solution was investigated, because this concentration will affect the numbers and sizes of crystals deposited.

It is known that a polar solute gives chromatograms that show tailing or adsorption when used for a long period or at high temperatures, owing to the increased adsorptivity of the column. The main reasons for this effect seem to be the influence of involatile compounds that are injected together with the sample, and adsorption on silanol groups and metal oxides that reappear on the support materials on the glass surface. The latter effect may be due to loss of the liquid phase as a result of vaporization of the liquid phase and the injected solutes or solvent. The G-SCOT column was therefore tested at high temperatures and the effect of time on its characteristics under these conditions was observed. As the G-SCOT column contains NaCl support material, which is hydrophilic in nature, its tolerance to water was also studied.

EXPERIMENTAL

The G-SCOT column was prepared as follows[17]: a 20-m glass capillary column (0.28 mm I.D.) was coated with NaCl solution by the dynamic coating method and dried while purging with dry nitrogen until an opaque layer was observed along the entire column length. The column was dried at 200 °C for 2 h while passing dry nitrogen through it in order to eliminate the adsorbed and absorbed water. This NaCl column was then coated with the surface-active agent benzyltriphenylphosphonium chloride (BTPPC), and next with liquid phase by the dynamic coating method as follows. The concentration of NaCl was 1, 5 and 10% (w/v) in distilled water–methanol (1:1, v/v). A 1-ml volume of this NaCl solution was introduced by suction into the column, which was coated under a nitrogen pressure of 6 kg/cm^2 and dried at the same pressure, then coated with liquid phase.

The WCOT column was prepared by the dynamic coating method[17].

A Hitachi Model HSM-2 scanning electron microscope (SEM) was used to investigate the inside wall of the above columns. A section of the column to be studied was obtained by breaking it with a bench-vice and then a layer of carbon and a layer of gold were evaporated on to the sections under vacuum.

The columns were tested in Hewlett-Packard Model 5711A gas chromatograph and a Hitachi Model 023 gas chromatograph. Helium was used as the carrier gas and bis(trimethylsilyl)acetamide diluted with acetonitrile (TMS–BA) as a silanization agent.

RESULTS AND DISCUSSION

Surface condition of the G-SCOT column

The characteristics of the G-SCOT column are discussed on the basis of both the micrographs obtained with the SEM, showing the surface condition on the inside wall, and the chromatograms of mixed polar samples. Our previous work[17] suggested that the size of the deposited NaCl crystals is about 5 μm or smaller and the surface activity of NaCl-modified glass capillary column is lower than that of the untreated column, because the crystals cover the active centres such as metal oxides and silanol groups on the glass surface.

Figs. 1 and 2 show the micrographs of the inside wall treated with 1, 5 and 10% NaCl solution. The columns in Fig. 1a and 1b were dried simply by passing nitrogen through them without heating, so the shape of the crystals was not distinct. The angular shapes as in Fig. 1c were obtained by heating at 200 °C while passing nitrogen through the column (the micrograph is not shown here). Fig. 1c is a micrograph of the column coated with 10% NaCl solution and dried for 2 h at 200 °C while passing nitrogen through it, and the layer of NaCl crystals deposited on the glass can be seen to be uniform.

Fig. 2 are magnified micrographs of columns illustrated in Fig. 1. The largest size of the crystals is about 1 μm, but the numbers of crystals present in each micrograph are very different, depending on the concentration of NaCl solution used. Fig. 2a shows only a small number of crystals and the colouring of this column, prepared with 1% NaCl solution, was only slightly opaque, while the degree of colouring of that prepared with 5% NaCl solution was the same as that prepared

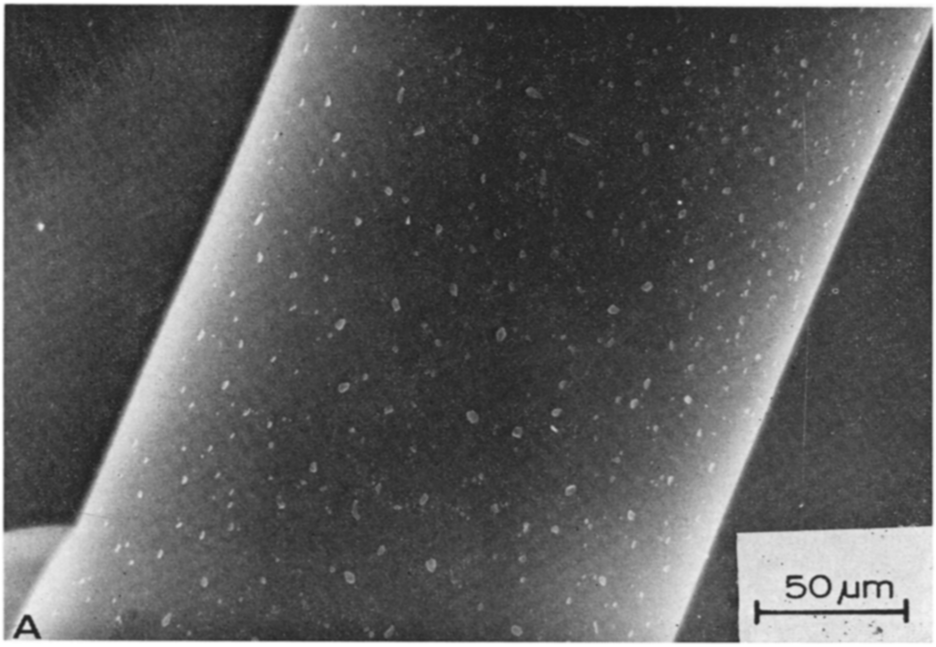

Fig. 1.

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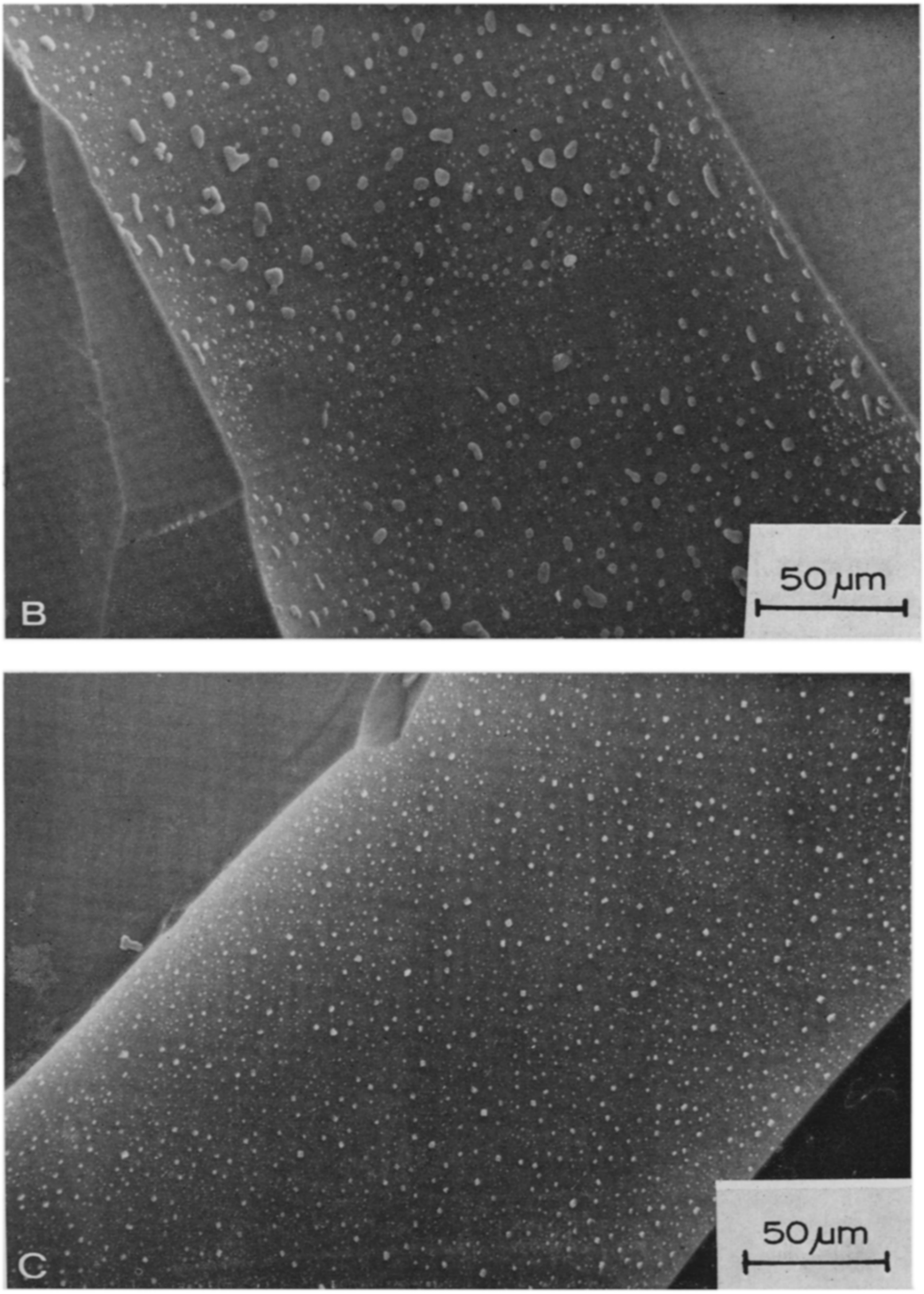

Fig. 1. Micrographs of modified inside wall (coated only with sodium chloride crystals). Concentration of NaCl solution used: (a) 1%; (b) 5%; (c) 10%.

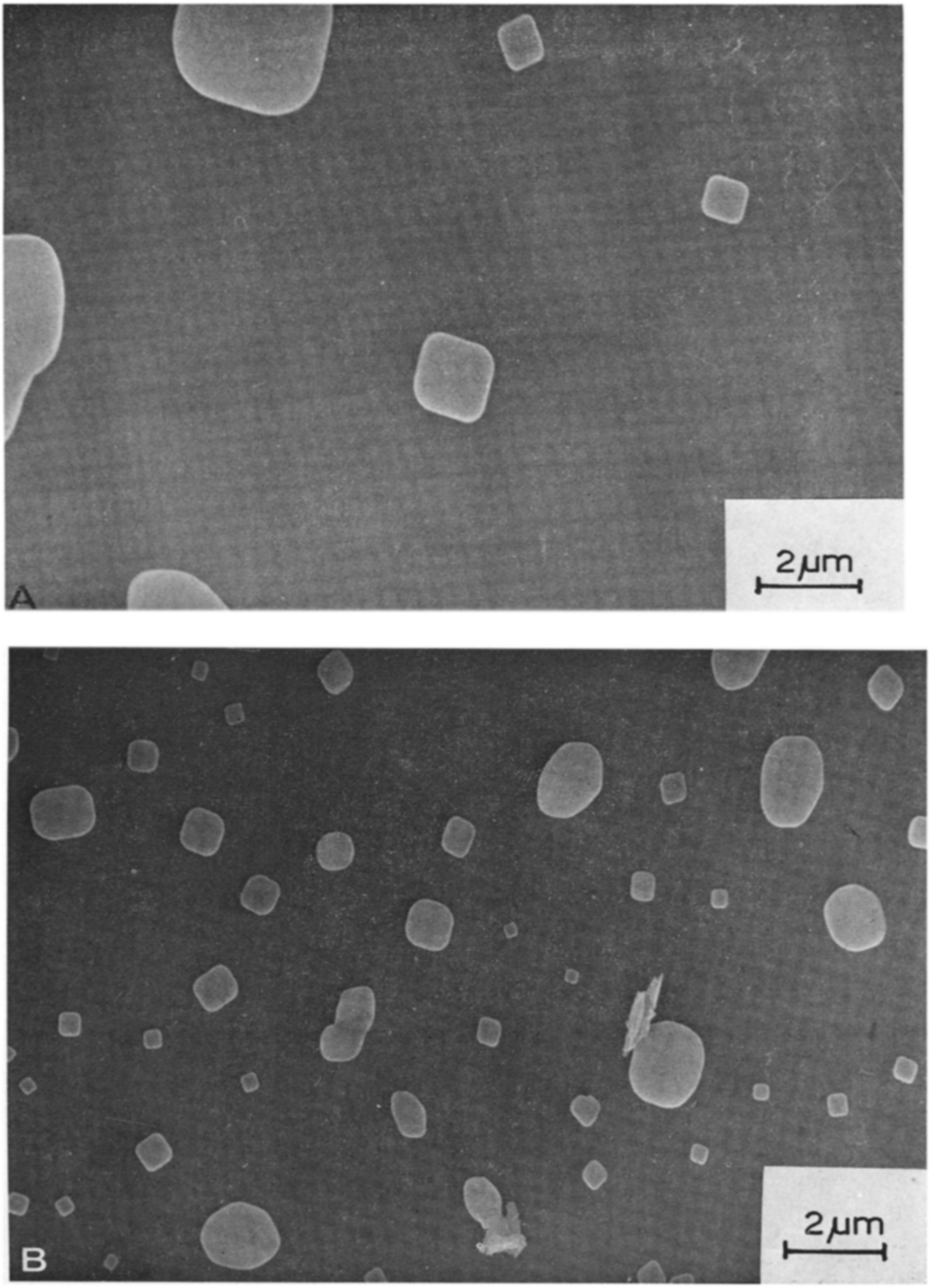

Fig. 2.

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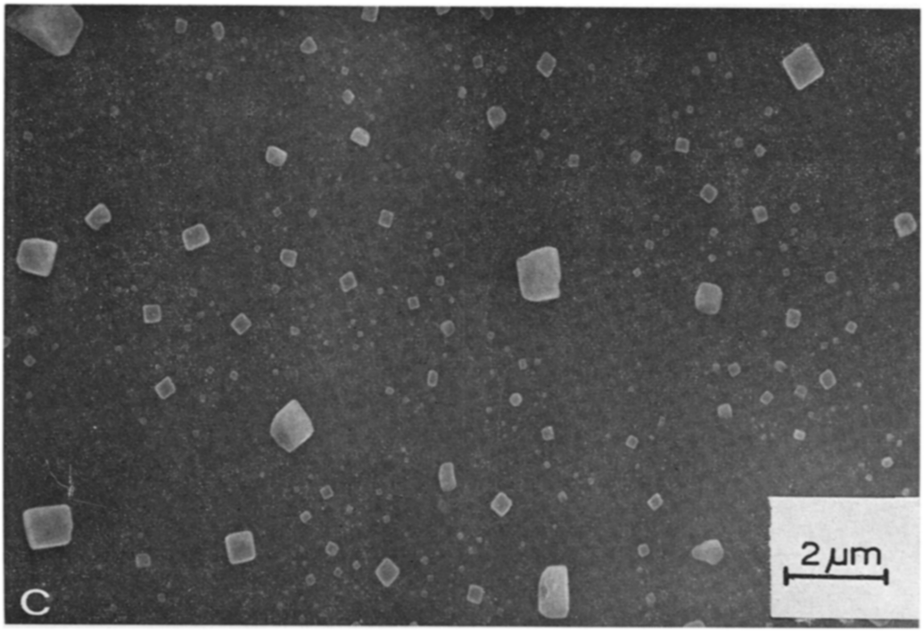

Fig. 2. Magnified micrographs of the columns shown in Fig. 1.

with 10% NaCl solution to the naked eye (Fig. 2a and 2b). The micrographs show that the ratio of number of crystals present is about 1:10:50 in the columns prepared with 1, 5 and 10% NaCl solution, respectively; this also indicates that the degree of coverage of the glass surface is affected by the concentration of NaCl solution used. This coverage is an important factor in coating such a modified surface with the liquid phase, and controls the roughness of the glass surface.

The crystals of the column prepared with 10% NaCl solution shown in Fig. 2c are about 0.1–1 μm in size and are not homogeneous, apparently because the solubility of NaCl is affected. In this work, the solvent was mixed with equivalent volumes of water and methanol, which decreases the solubility of NaCl. In the deposition process, after coating with the NaCl solution, nitrogen is passed through the column in order to make the crystals adhere to it, and the mixed solvent is gradually vapourized, the concentration of the NaCl solution reaching saturation immediately. As a result, a large number of very small crystals are deposited. Examination of Fig. 2c indicates that the number of crystals deposited is more than 500,000 per square millimetre of the inside wall, and the degree of coverage of the inside surface is about 20%. This 20% coverage is very effective when coating the liquid phase, because the critical surface tension (CST) of the modified surface (with about 1-μm crystals) will be more than 50 dyne/cm (ref. 16). If this is so, the polar liquid phases which have a high CST[3], such as diethylene glycol succinate (DEGS) (52.7 dyne/cm) and 1,2,3-tris-(2-cyanoethoxy)propane (TCEP) (49.2 dyne/cm), will spread freely on the glass wall, resulting in a small contact angle. Polar liquid phases such as PEG 20M, PEG 400, FFAP, OV-17, DEGS, diisodecyl phthalate and TCEP could be coated on such modified walls of glass capillary columns with high efficiency and thermal stability[6].

It can easily be understood from the above micrographs that our method should increase the surface area of the inside wall.

Fig. 3 illustrates the inside wall of the column prepared with 10% NaCl solution and coated with OV-101 liquid phase. The fact that the wall could be coated almost perfectly with liquid film can be seen in Fig. 3a. This column was produced by modifying the surface by drying at 200 °C for 10 h while passing nitrogen through it, and the coating efficiency was about 90%. Fig. 3a shows the inside wall of a column that was insufficiently dried after depositing the NaCl crystals. It can be seen that the shape of the NaCl crystals is not distinct. This column had a poor performance, with a coating efficiency of only about 30%. When using this column, the chromatograms of polar solutes such as alcohols and amines showed tailed peaks (see peak 11 in Fig. 6c). This effect seems to be due to the influence of absorbed or adsorbed water remaining on the crystals or in gaps between the glass surface and the crystals.

Fig. 3c shows the inside wall of the column after washing three times with dichloromethane in order to remove liquid phase from the column shown in Fig. 3a. However, it can be seen that a very thin liquid film (about 0.01 μm) remains on the crystals, apparently owing to the influence of the surface-active agent (BTPPC) and the adsorption affinity of the crystals and the glass surface. Even if another liquid phase is coated on such a washed column, the influence of the film of the first liquid phase would still be apparent, although it will depend on the overall film thickness. The film thickness on the G-SCOT column was about 1 μm (compare Fig. 3a with 3c). This thick film is stable (see thermal stability of the column, Fig. 5) and thus a larger sample size can be used, the detection limits will be lower and the separation power will be increased. Novotný and Bartle also have reported the characteristics

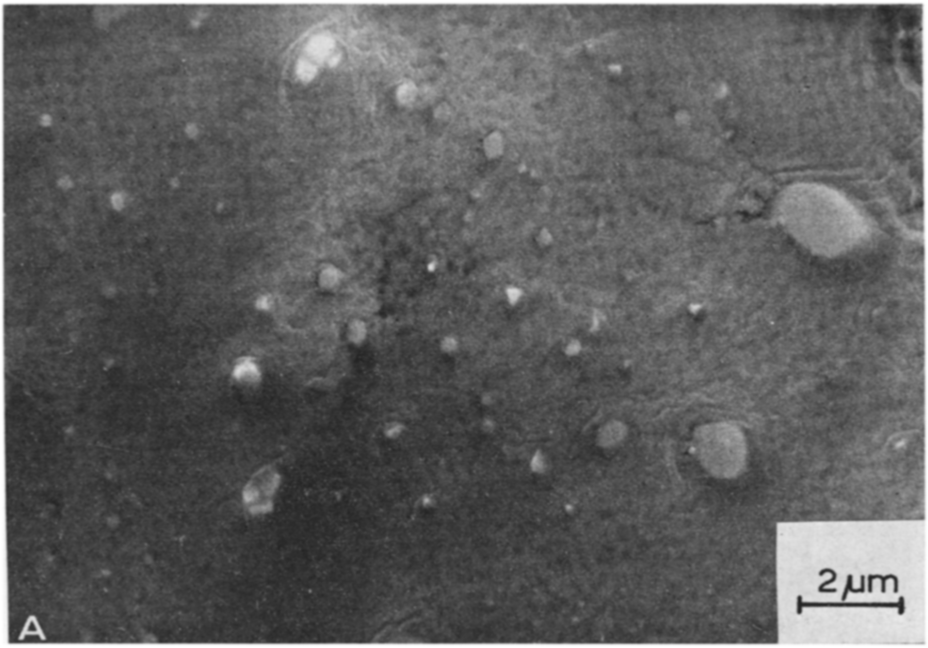

Fig. 3.

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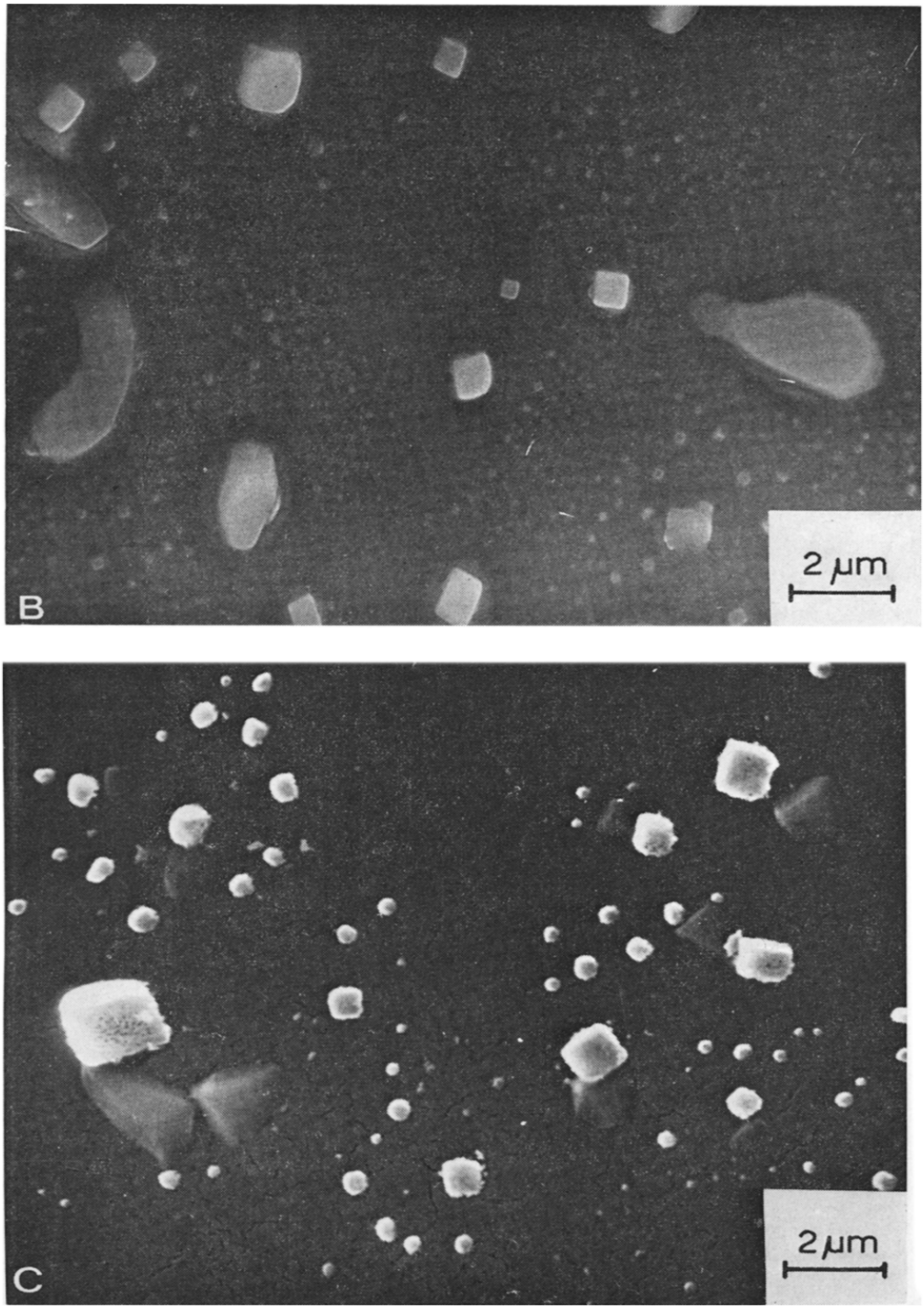

Fig. 3. Micrographs of the inside wall of the coated column. (a) G-SCOT column coated with OV-101 on 10% NaCl column (coating efficiency about 90%); (b) same as (a) but inadequately dried column (coating efficiency about 30%); (c) condition of the surface following removal of the liquid phase from the column shown in (a) with solvent.

of a column with a thick film (about 1.7 μm), using a soft glass column with NaCl deposited by etching with dry hydrogen chloride[14].

In this work, the glass was a borosilicate glass (boron oxide content about 12%), with a very high affinity for polar solutes[18]. As can be seen in the micrographs, part of the glass surface is covered with NaCl crystals. Fig. 4 shows chromatograms of an alkanol mixture on untreated and treated columns. *n*-Octane was used to check the presence of dead volumes between the column and the detector and gave a symmetrical peak shape, but that of the alkanols differed in the two chromatograms. Consequently, it is assumed that the activity of silanol groups and metal oxides on the glass surface is decreased. However, in the analysis of a large sample such as hydrocarbons in air using the concentration technique at a low temperature[19], some liquid phase and NaCl crystals at the head of the column were stripped off by the moisture.

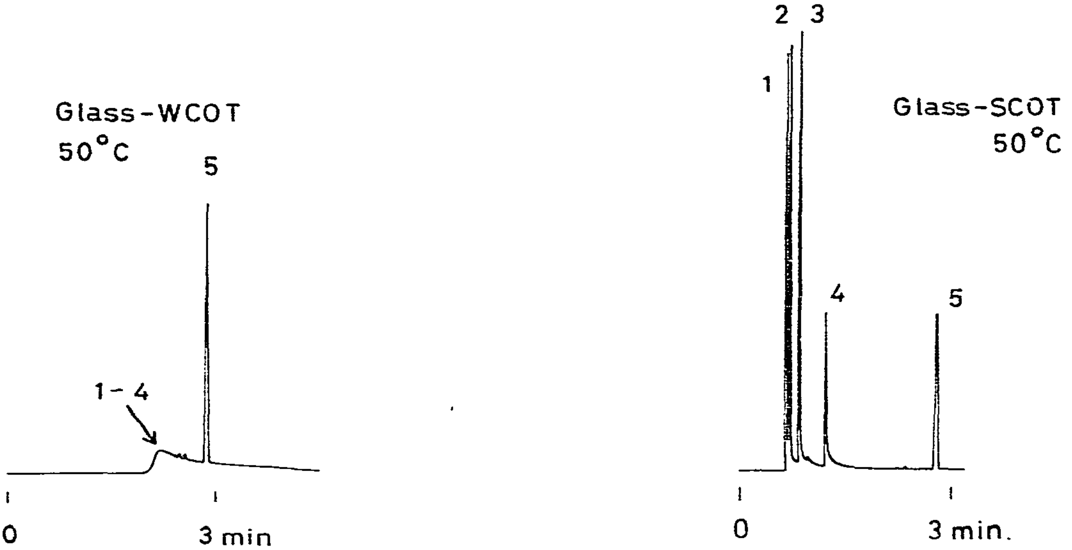

Fig. 4. Chromatograms of alkanols and *n*-octane using the WCOT and G-SCOT columns (OV-101, 20 m × 0.3 mm I.D.; carrier gas, helium at 1.6 ml/min). Peaks: 1, methanol; 2, ethanol; 3, *n*-propanol; 4, *n*-butanol; 5, *n*-octane. Sample injected: 0.5 μl. FID: $9\cdot10^{-10}$ A f.s.d.

Thermal stability of the column

It is necessary for a column to have a high efficiency and good stable layers of liquid phase, the former requirement meaning a uniform thickness and a smooth film of liquid phase on the inner wall over the entire column length. It is obviously insignificant that the condition of the liquid phase changes owing to irregular layers, waves and droplets after a few days' use at or below the recommended temperature (*e.g.*, the OV-17 column at 150 °C). As mentioned above, the columns gradually deteriorate and consequently an increased adsorptivity and a decreased column separating power may result.

Fig. 5 illustrates the thermal stability in the G-SCOT and the WCOT columns over a 300-h period in terms of the variation of the number of theoretical plates (*n*) and the capacity ratio (*k*) with heating time[20]. The variation in performance of the G-SCOT column was very small, presumably owing to the influence of the adsorptivity and absorptivity of the NaCl crystals.

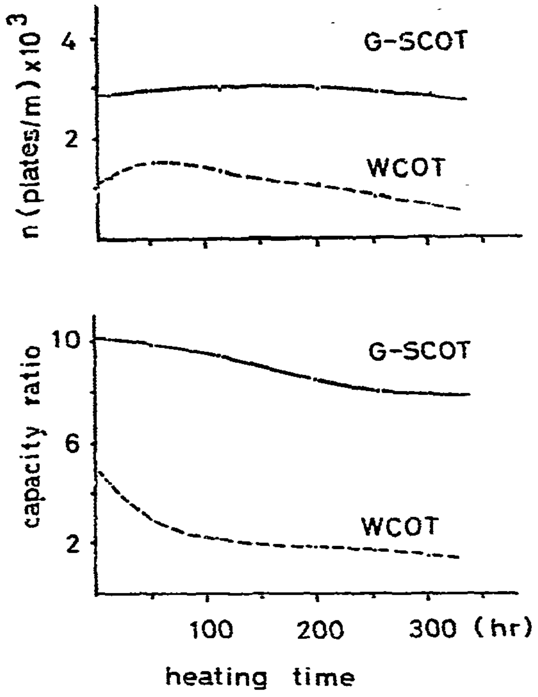

Fig. 5. Change of capacity ratio (*k*) and number of theoretical plates per metre (*n*) with heating time at 300°C. OV-101 column, 20 m × 0.28 mm I.D., at 110°C; carrier gas, helium at 1.5 ml/min. Sample: *n*-tridecane.

Fig. 6 illustrates the chromatograms obtained in studies of a mixed perfume. Fig. 6a shows the analysis of the mixed perfume using a newly produced column. After injecting $2.5 \cdot 10^{-2}$ μl of water and $1.25 \cdot 10^{-2}$ μl of the mixed perfume alternately 20 times into the column, the chromatogram of alcohols such as peak 11 in Fig. 6c showed tailing, but no variation in the condition of the coating along the inside wall of the entire column length could be observed with the naked eye. On the injection of water, the chromatogram shown in Fig. 6b was obtained, but this chromatogram is considered to be that of the mixed perfume that remained in the injection port and dissolved oxygen in the water.

The tailed chromatogram as illustrated in Fig. 6c is due mainly to the silanol groups because, after the silanization agent (TMS–BA) had reacted with the reappeared silanol groups on the glass wall at 200 °C while passing the carrier gas through the column, the chromatogram was greatly improved and was similar to that shown

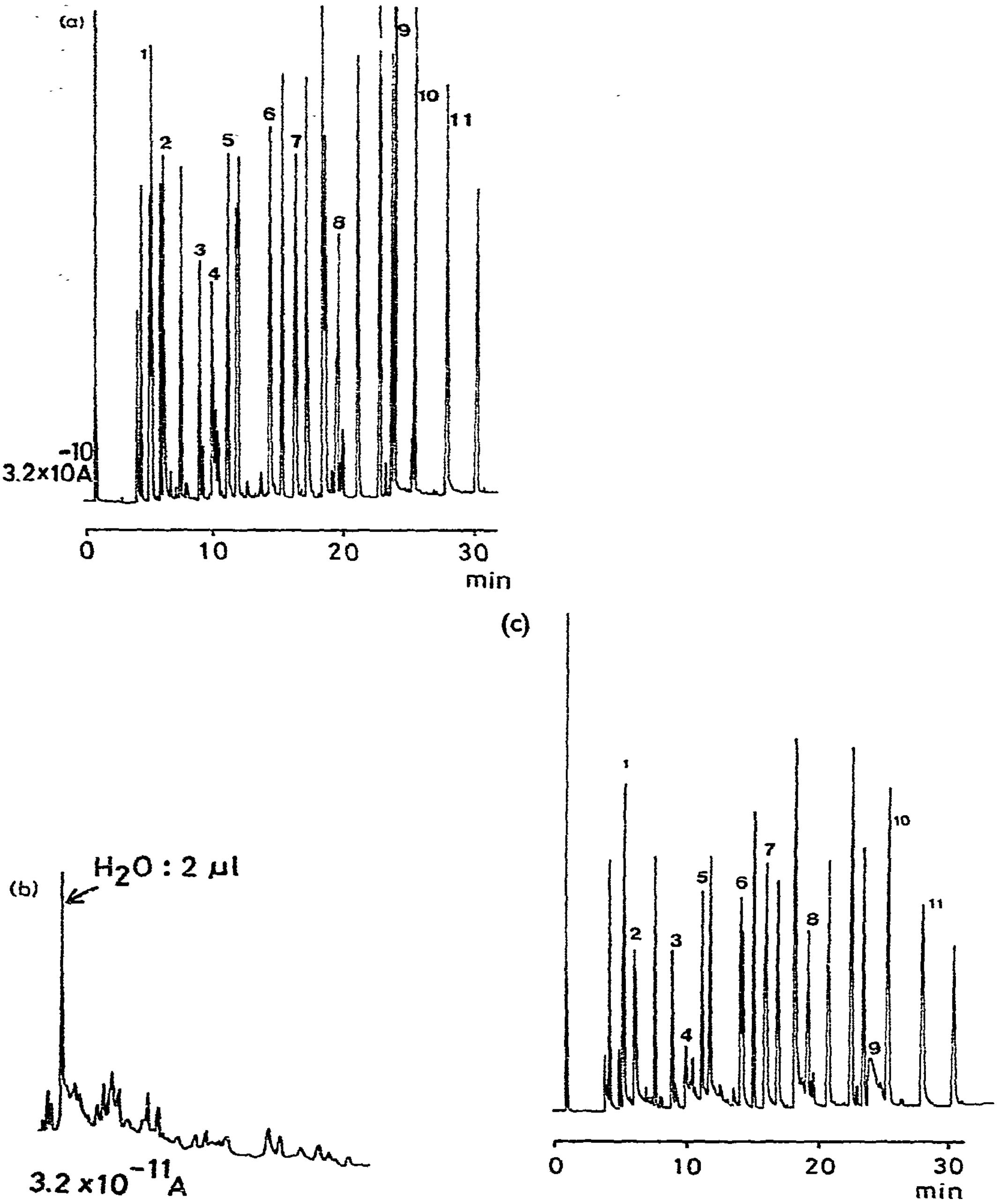

Fig. 6. Chromatograms obtained with a mixed perfume. (a) Analysis of mixed perfume on a non-polar G-SCOT column (OV-101, 20 m × 0.28 mm I.D.; carrier gas, helium at 1.8 ml/min; splitting ratio, 1:40; column temperature, 90–230°C at 5°C/min). Peaks: 1, limonene; 2, phenylethanol; 3, citronellol; 4, linalyl acetate; 5, eugenol; 6, coumarin; 7, methylionene; 8, linalool; 9, myristyl alcohol; 10, benzyl benzoate; 11, benzyl salicylate. (b) chromatogram of injected water at 200°C (isothermal); (c) chromatogram after 20 alternate injections of water and solutes [conditions as in (a)].

in Fig. 6a, and the column performance did not decrease substantially after the eighth analysis of the mixed perfume. In this silanization process, the injection port temperature was kept at about 200 °C in order to vaporize the silanization agent.

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