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PREPARATION OF WALL-COATED GLASS CAPILLARY COLUMNS AFTER SURFACE ROUGHENING BY MEANS OF AMORPHOUS SILICA

II. FACTORS AFFECTING THE PERFORMANCE OF THE COLUMNS IN GAS CHROMATOGRAPHIC ANALYSES

H. T. BADINGS*, J. J. G. VAN DER POL and J. G. WASSINK

Netherlands Institute for Dairy Research (NIZO), P.O. Box 20, 6710 BA Ede (The Netherlands)

SUMMARY

The preparation of wall-coated open tubular glass columns by means of surface roughening with silicon tetrachloride is described. The conditions for deactivation of the surface and coating with different stationary phases have been investigated. The performance of a number of columns prepared by this method is discussed.

INTRODUCTION

Grob¹ and Verzele² have recently reviewed the preparation of glass capillary columns for gas chromatography (GC), the present "state of the art" and the difficulties which have to be solved to optimize column performance.

A basic problem in the preparation of such columns continues to be the formation on the glass surface of a thin and homogeneous film of the stationary phase, which must remain stable at the high temperatures of GC analysis. With most (polar) liquid phases this can be achieved only after the glass surface has been modified, either chemically (production of an interjacent layer or addition of surface-active compounds) or physically (roughening of the surface).

Methods of surface roughening are now preferred. Tesařík and Novotný³ proposed etching by pyrolysis of 2-chloro-1,1,2-trifluoroethyl methyl ether. Pretorius and co-workers^{4,5} demonstrated that use of the same ether at higher temperatures produces silica whisker surfaces. This technique was further extended by Verzele and co-workers^{6,7}, who showed that almost any stationary phase could be made to adhere to these whisker surfaces, but that deactivation was very difficult. Another technique that has found wide application is the etching of soda glass with gaseous HCl^{8,9}, which results in the formation of (sub)micron sodium chloride particles. Grob, in his earlier work^{10,11}, used carbonization by pyrolysis of methylene chloride vapour¹². In later work, Grob and co-workers^{13–15} made a detailed study of the deposition of barium carbonate particles on glass by reaction of barium hydroxide with gaseous CO₂.

Some other roughening techniques that have recently been reported are:

treatment of soda glass surfaces with HCl and HF at 450°C¹⁶; reaction with HF¹⁷; treatment with potassium hydrogen fluoride solution¹⁸ which probably produces a rough layer of potassium hexafluorosilicate; deposition of dendritic sodium chloride from aqueous solution¹⁹; deposition of sodium chloride particles from a sol²⁰ and surface roughening by means of amorphous silica²¹.

A second problem is the activity of the column surface. Although some of the roughening procedures may reduce the activity of the glass surface, in many cases a significant increase of the surface activity results. This may lead to loss of sample constituents and reduced separation due to tailing of peaks. Constituents of the column surface may also cause degradation of the liquid phase, as was demonstrated recently by Venema *et al.*²² for a number of polysiloxanes. Several deactivation procedures have been developed, such as leaching, addition of surface-active compounds and bonding of compounds to the surface (silanes, polyethylene glycol, aminol derivatives, etc.). Reviews of these procedures have been presented elsewhere^{1,2,21,23}. In this respect, the results of some recent studies on vapour phase deactivation by means of polyethylene glycol 20M (PEG 20M)^{24,25}, or silanes²⁶ deserve special attention.

With the object of developing a method of surface roughening by means of amorphous silica, we previously made a number of experiments in which a plug of dilute water glass was made to pass through the capillary followed by a flow of gaseous hydrochloric acid²¹. In this way a thin film of water glass is left on the glass surface, which, being in contact with the HCl gas, produces a fine granular deposit of amorphous silica. This method was found to be relatively simple and rapid. Also, the roughened surface was not modified or removed upon introduction of samples containing water, acids, etc., and could be fully deactivated. Roughening of the surface without the introduction of "foreign constituents" which may influence the stability of the liquid phase or components of the sample, was also considered an advantage. Further experiments showed that the conditions for preparation of a suitable deposit of fine amorphous silica were critical. Although columns of satisfactory quality could usually be prepared by the water glass-HCl method, occasionally a thick layer of silica with cracks was found instead of the expected deposit. An example is given in Fig. 1. It is clear that such a thick layer may have certain disadvantages: deactivation is difficult, the stationary phase may accumulate in the cracks and other parts of the surface may be too smooth to hold the liquid film properly.

In the present paper an alternative method of surface roughening with amorphous silica produced from silicon tetrachloride is described. The surface deposit is finer and more granular than that obtained by the water glass-HCl method. Experimental details are given of the roughening procedure, the deactivation and the preparation of a number of columns with different stationary phases.

EXPERIMENTAL

Drawing of glass capillary columns and pretreatment

Soda glass tubing (Ruhr AR, Schott, Mainz, G.F.R.) of suitable size was drawn in to capillaries of 0.25–0.30 mm I.D. on a Shimadzu glass drawing machine, Type GDM-1 (Shimadzu, Tokyo, Japan). The capillaries were rinsed with dichloromethane and air-dried. In a few cases the capillaries were also treated with a 1% HF solution, and leached with a 20% HCl solution, as described earlier²¹.

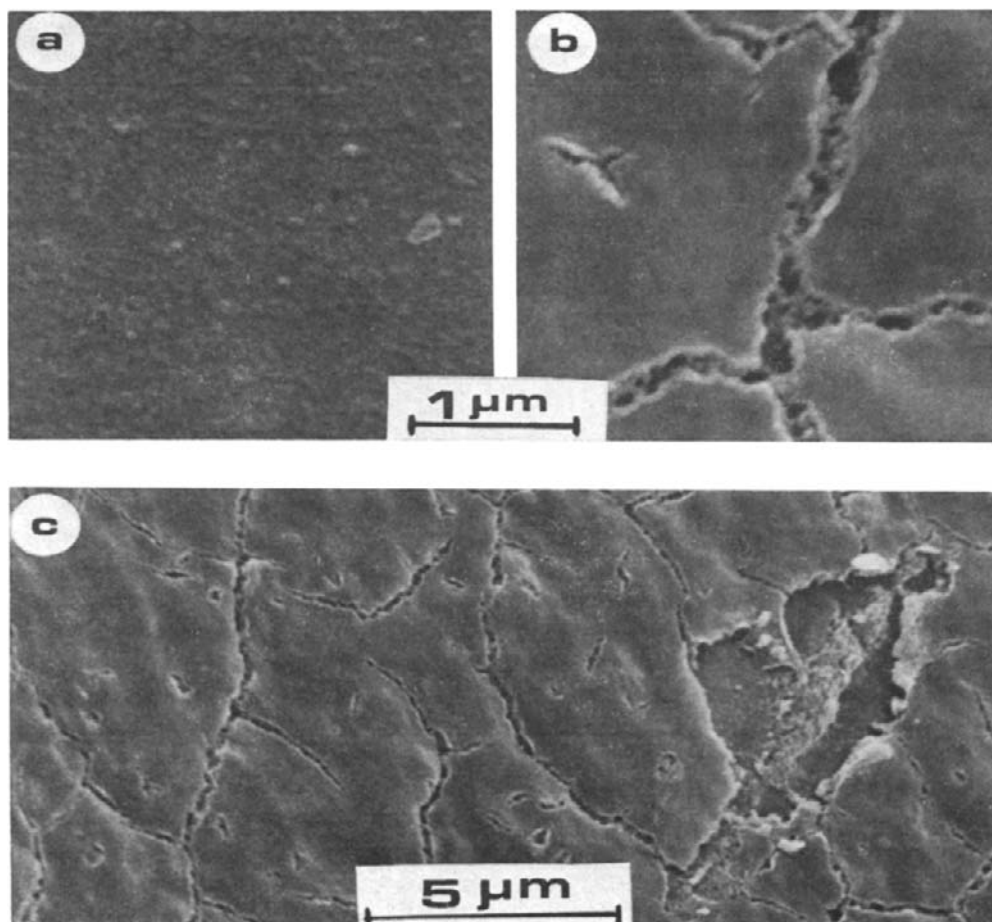


Fig. 1. Some examples of the inner surface of glass capillaries, after surface roughening with silica by the water glass-HCl method. Scanning electron micrographs: a, correctly roughened surface; b, irregular, thick silica surface layer with cracks; c, same layer as b but at smaller magnification: note the thick deposit with cracks and local interruptions.

Surface roughening

In order to be able to humidify the glass capillary in a reproducible way, it was first dried for 2 h at 180°C with a flow of dry nitrogen (2 ml/min), cooled to room temperature and flushed with humid air (relative humidity 100%) for 4 h at a rate of 2 ml/min.

After humidification, the capillary was connected to a flow of dry nitrogen containing silicon tetrachloride vapour, as shown in Fig. 2. A glass tube (10 cm × 5 mm I.D.) was bent through an angle of *ca.* 120°. One end was drawn out to a capillary of 0.8 mm I.D. and 1.2 mm O.D., in order to facilitate its connection with a glass capillary by means of silicone tubing. A few millilitres of silicon tetrachloride were transferred to the glass tube, and a flow of dry nitrogen (1–2 ml/min) was passed through the liquid and into the capillary for 1 h. Then the position of the capillary was reversed by connecting its open end to the vapour inlet, after which the treatment

with silicon tetrachloride was continued for another hour. Subsequently the capillary was closed by melting the ends, and heated at 450°C for 30 min. For the removal of contaminants from the roughened surface, the capillary was leached with 18% hydrochloric acid solution (1 ml/h) for 2 h at 90°C, cooled, rinsed with water and acetone and dried with a flow of nitrogen at 120°C. Finally, the capillary was dried at 300°C for 12 h with a flow of dry nitrogen gas (1–2 ml/min).

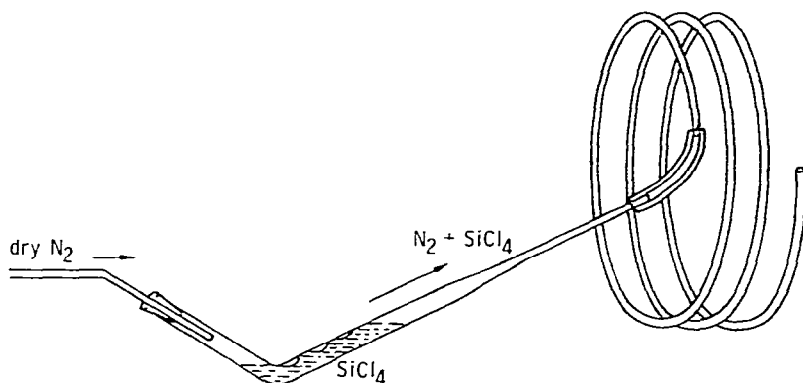


Fig. 2. Set-up for the treatment of a glass capillary with silicon tetrachloride vapour. For further details, see text.

Deactivation

For the deactivation of the roughened capillaries two methods were used: gas phase deactivation with polyethylene glycol 20M according to Franken *et al.*²⁴ and De Nijs *et al.*²⁵, or dynamic vapour phase silylation as we described recently²⁶. The efficiency of the deactivation was determined by testing the uncoated column with a mixture containing *n*-alkanes, *n*-alkanols, 2,6-dimethylphenol and 2,6-dimethylaniline as outlined previously^{21,26}.

Electron microscopy

Scanning electron micrographs were taken from the inner surface of the capillaries after these had been broken and then covered by a thin layer of gold by a sputtering technique. A Jeol JSM-U3 scanning electron microscope of the Technical and Physical Engineering Research Service at Wageningen (The Netherlands) was used.

Coating of capillaries

The capillaries were coated by the static method of Bouche and Verzele²⁷, as outlined by Rutten and Rijks²⁸. Usually the thickness of the liquid film was 0.1–0.2 μm .

Gas chromatography

GC analyses were made on a Varian gas chromatograph, Type 3700, equipped with a Grob-type injector splitter and a flame ionization detector. An all-glass system was made by inserting the straightened column ends into the injector vaporizer and the FID-tip respectively. Experimental condition: for running test chromatograms with the prepared capillary columns were: carrier gas flow 1.5–2 ml/min; injector splitting ratio 1:100; temperature of injector 200°C; detector temperature 220°C; oven

temperature isothermal at 120°C (for determination of plate number, separation number and coating efficiency) or programmed from 100°C to 140 or 150°C at a rate of 3°C/min (for the test chromatograms in Fig. 5).

RESULTS

Surface roughening

The scanning electron micrographs taken from the inner surface of the glass capillaries after the SiCl_4 treatment showed a fine granular deposit of silica. An example of such a deposit is shown in Fig. 3b. Leaching of the capillary with a 20% hydrochloric acid solution at 160°C for 15 h changed the surface in such a way that treatment with SiCl_4 did not produce the desired roughened silica surface. This effect is shown in Fig. 3a. For this reason the capillary was not leached prior to the roughening procedure, but after it. In this stage of column preparation the leaching step does not influence the surface roughening significantly.

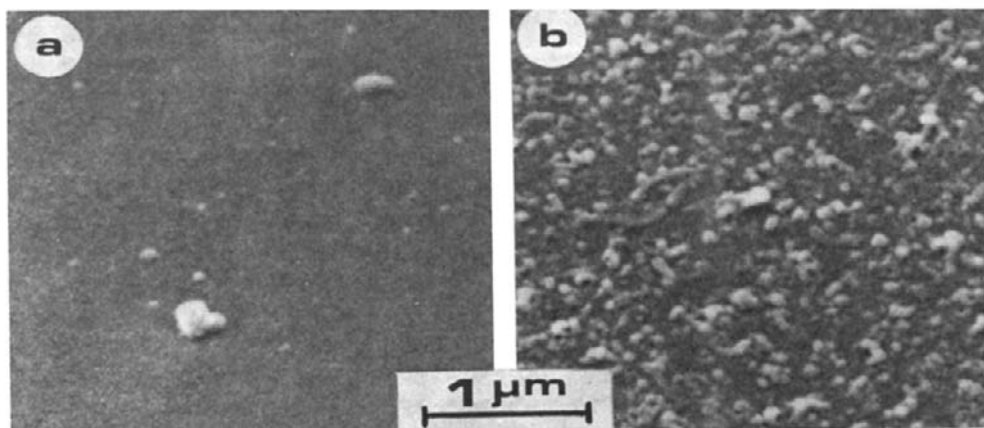


Fig. 3. Scanning electron micrographs of the inner surface of glass capillaries, after surface roughening with silica produced from silicon tetrachloride: a, inadequate roughening as a result of leaching prior to SiCl_4 treatment; b, correctly roughened surface, leaching pre-treatment being omitted.

Another important parameter was the humidity of the glass surface. If the capillary had a dry surface, the SiCl_4 treatment resulted in a poorly roughened surface. Conversely, a very moist glass surface resulted in accumulation of amorphous silica. A variety of conditions for pre-drying of the glass and for subsequent humidification were investigated. Some of the results are given in Fig. 4. Pre-drying at a relatively low temperature (110°C) gave irreproducible results, and humidification with air having a reduced humidity (r.h. 40%) resulted in limited roughening. Good results were obtained when pre-drying was carried out at 180°C for 2 h, followed by humidification with air of relative humidity 100% for 4 h at room temperature.

A few experiments were made in which the whole SiCl_4 surface-roughening procedure was carried out twice, consecutively. The treatment appeared to yield a rougher surface and may be beneficial to the application of thicker liquid films, but we did not study it in more detail.

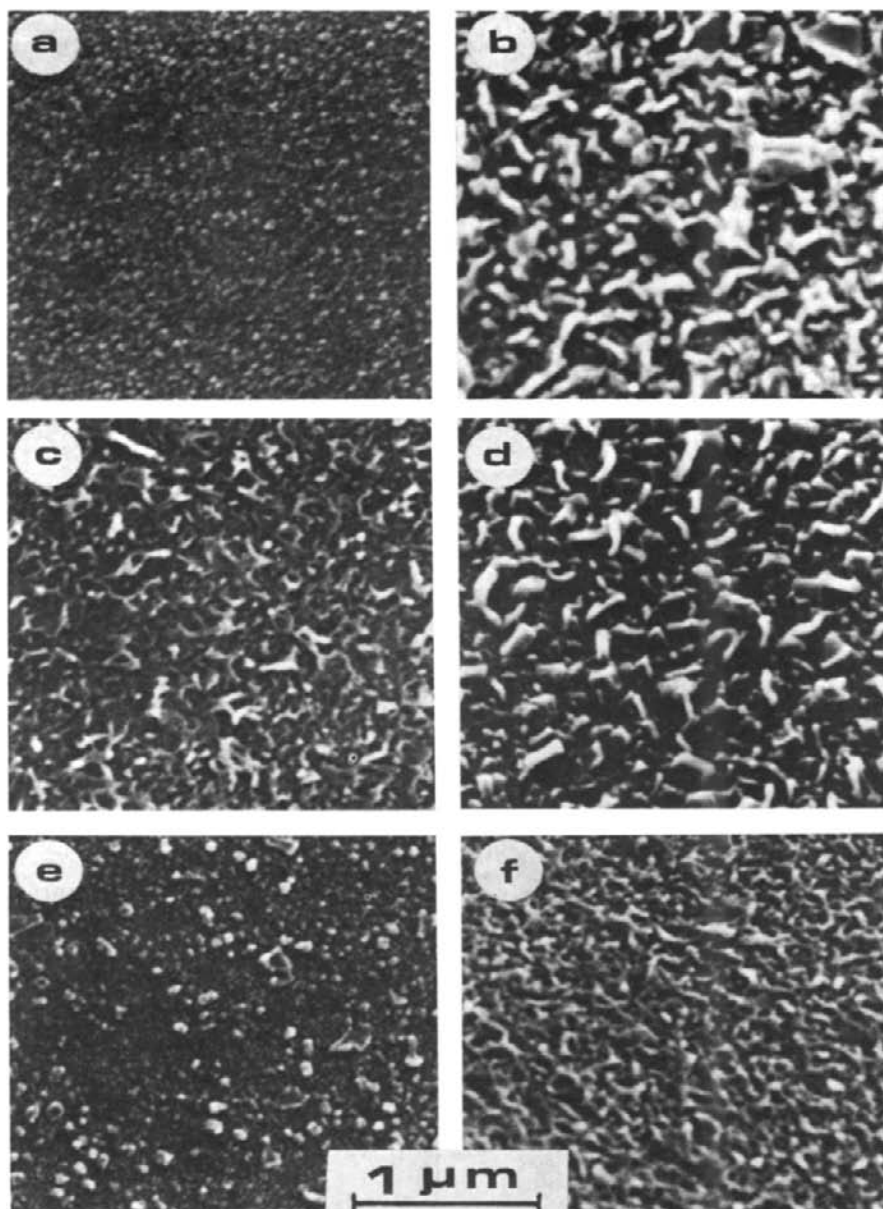


Fig. 4. Effect of pre-drying (p.d.) and humidification (relative humidity, r.h.) of the glass capillaries on the formation of a silica surface layer by the SiCl_4 method. Conditions: a, p.d. 110°C , r.h. 0%; b, p.d. 110°C , r.h. 100%; c, p.d. 180°C , r.h. 40%; d, p.d. 180°C , r.h. 100%; e, p.d. 280°C , r.h. 60%; f, p.d. 280°C , r.h. 100%.

Deactivation

Gas phase treatment with polyethylene glycol or dynamic vapour phase silylation yielded well deactivated surfaces on which *n*-alkanols, dimethylphenol and di-

methylaniline did not show significant tailing. If the roughened surface had been dried for 12 h at 300°C prior to the vapour phase treatment, improved deactivation resulted.

Performance of prepared capillary columns

Several columns were prepared, according to the present method, with different types of stationary phase. Some of the results obtained are given in Table I. Capillary columns coated with non-polar stationary phases were deactivated by dynamic vapour phase silylation, those coated with medium-polar stationary phases by a gas phase treatment with polyethylene glycol 20M. Although the latter procedure may not be necessary for coating with polar phases, it was used because it improved the prepared columns.

TABLE I

PREPARATION AND PERFORMANCE OF CAPILLARY COLUMNS

Liquid film thickness, $d_f = 0.2 \mu\text{m}$; for Silar-10, $d_f = 0.3 \mu\text{m}$.

Liquid phase	Capillary*		Deactivation	Performance**				
	l (m)	rn		Compound k	N/m	S_n	Coating efficiency	
OV-101	10	d	Silylation	C17/16	28.2	3600	24	88
OV-101	10	s	Silylation	C17/16	26.7	3350	22	81
PEG 20M	20	s	PEG 20M	O12/11	18.0	3300	30	80
OV-225	18	s	PEG 20M	O12/11	12.7	3300	27	77
Silar-10	19	s	PEG 20M	F16/15	19.7	2600	21	62

* 0.26 mm I.D.; rn = roughening with SiCl_4 ; s = single, d = double.

** Temperature 120°C. C = Alkane; O = 1-alkanol; F = fatty acid methyl ester. k = capacity ratio for first compound. N/m = theoretical plates/metre; S_n = separation number.

A few examples of separations obtained with the prepared capillary columns are given in Fig. 5.

DISCUSSION

Amorphous silica is produced as a result of reaction of silicon tetrachloride with water. Reproducible results were obtained under the experimental conditions described: a very fine and thin granular deposit of amorphous silica formed on the inner surface of the glass capillary. The roughened surface could be deactivated fairly easily by means of a vapour phase treatment with PEG 20M or with silyl-8. It should be noted that the present method gives a rough silica layer having a thickness of only a few tenths of a micrometre. This is much thinner than the layers produced by other methods, such as NaCl formation by etching with gaseous HCl, silica whisker formation, etc. Nevertheless, the present thin layer of amorphous silica is capable of holding a $\leq 0.3\text{-}\mu\text{m}$ thick quasi film of the liquid phase. Thicker films have not been tested, but they may be produced with appropriate liquid phases.

For the sake of completeness two other methods should be mentioned here, in which silica or siliceous material is used for the preparation of capillary columns. Schulte²⁹ made columns by coating capillaries after deposition of colloidal silicic acid.

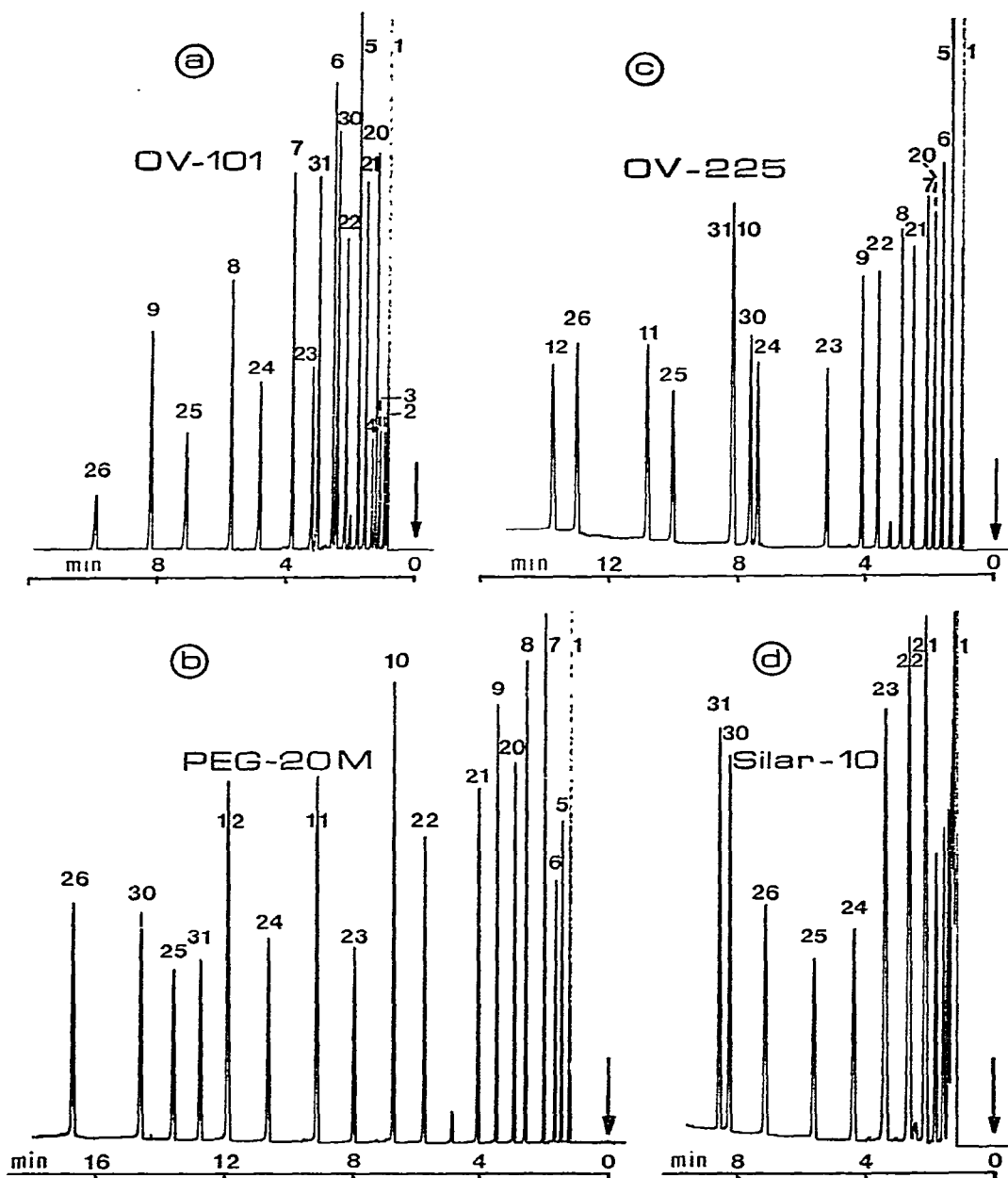


Fig. 5. Separation of a test mixture on a number of capillary columns roughened by the SiCl_4 method, each coated with a different liquid phase. a, 19 m \times 0.26 mm I.D. column, 0.2- μm OV-101; b, 20 m \times 0.26 mm I.D. column, 0.2- μm PEG 20M; c, 18 m \times 0.26 mm I.D. column, 0.2- μm OV-225; d, 19 m \times 0.26 mm I.D. column, 0.2- μm Silar-10. *n*-Alkanes: 1 = C_5 ; 2 = C_7 ; 3 = C_8 ; 4 = C_9 ; 5 = C_{10} ; 6 = C_{11} ; 7 = C_{12} ; 8 = C_{13} ; 9 = C_{14} ; 10 = C_{16} ; 11 = C_{17} ; 12 = C_{18} ; 1-Alkanols: 20 = O_6 ; 21 = O_7 ; 22 = O_8 ; 23 = O_9 ; 24 = O_{10} ; 25 = O_{11} ; 26 = O_{12} . Other peaks: 30 = 2,6-dimethylphenol; 31 = 2,6-dimethylaniline.

Cramers *et al.*³⁰ produced capillary columns by deposition of cab-o-sil on the inner surface, followed by dynamic coating with the liquid phase. The porous layer of siliceous material and the liquid phase were found to produce a stabilized phase.

It should be noted that these two methods produce columns which are more or less of the *porous-layer* type and have a relatively thick surface layer. The present paper describes a method for making wall-coated open tubular columns. Capillary columns prepared according to this method showed a satisfactory stability for the injection of aqueous samples. Apparently the silica surface layer is not affected by water. In contrast, columns with NaCl surface layers (produced by HCl etching of soda glass) are affected by water, as illustrated in Fig. 6. Injection of water into these columns causes solubilization and recrystallization of the NaCl particles.

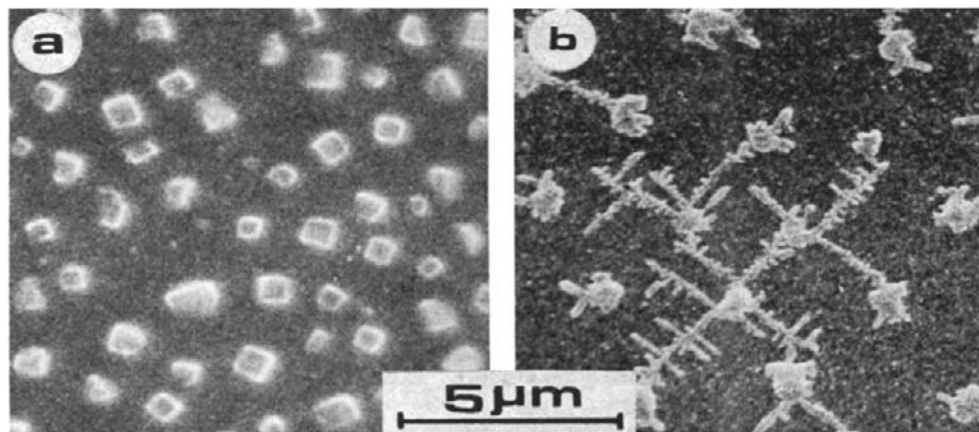


Fig. 6. Effect of analysis of aqueous samples on a capillary column produced by HCl-“etching” of soda glass. Stationary phase PEG 20M. Note the change in the deposit of the NaCl particles before (a) and after (b) injection of aqueous samples.

In conclusion from preliminary results, the present method of surface roughening looks promising for the roughening of fused silica capillaries. It may also be of practical value in the preparation of columns for capillary liquid chromatography.

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