

CHROM. 11,137

THE EFFECT OF LEACHED GLASS SURFACES ON THE QUALITY OF NON-POLAR FILMS OF A STATIONARY PHASE IN SURFACE-MODIFIED WALL-COATED OPEN TUBULAR COLUMNS

F. I. ONUSKA, B. K. AFGHAN and R. J. WILKINSON

Canada Centre for Inland Waters, P.O. Box 5050, Burlington, Ontario L7R 4A6 (Canada)

SUMMARY

Three different procedures for cleaning the inner wall of Pyrex glass tubes prior to the drawing of a capillary were studied. A new method of pre-treatment of the surface employing nitric acid-hydrofluoric acid is described, which shows a significant improvement in removing active sites giving a pitted surface similar to sintered glass.

As a result, lower activity of the inner wall is achieved and an excellent reproducibility in column uniformity is observed. The method can be applied to both analytical or wide-bore column preparation yielding almost an inactive surface.

INTRODUCTION

The past 25 years have been devoted to the development of techniques for the preparation of specific surfaces for glass open tubular columns. During the past five years, we have seen a significant growth in utilization of wall-coated open tubular (WCOT) columns. Their remarkable separation, efficiency and temperature stability is directly dependent upon formation of homogeneous layers on the inner wall of the capillary. A suitable preparation is required for the removal of the catalytic activity of the inner surface which can contribute to the decomposition of a solute, sensitive to high temperature or a particular active site. An inactive glass surface has not been prepared yet, but this goal may be achieved in the near future.

It is well known that the modification of solid support particles based on silica gel or various diatomaceous earth particles has been successfully studied by many surface chemists such as Kiselev and Yashin¹, Kiselev², Adam³, Adamson⁴, and Hair⁵. There are not many in depth studies performed on glass capillaries⁶⁻⁹. In some cases investigations were based on the assumption that the surface of the glass wall could be altered in the same manner as the surface of silica or aluminosilica solid supports.

Although glass is one of the most commonly used and cheapest materials, its surface interactions are of interest and importance to the analytical chemists. Our knowledge of glass surfaces is limited due to a lack of understanding of some of

the molecular interactions that may occur on such surfaces. In general, glass has an isotropic composition. It consists of many ingredients mixed together, such as silica, silicone dioxide, alkali oxides, borates and then prepared by a melting process. Hair⁵ states that during the cooling process exposure to oils, greases and variations in humidity may alter the surface composition. Thus, the starting material, a glass tube, cannot be properly defined. It is evident from this short content that there is a significant difference in composition between a glass surface of a capillary wall and that of silica gel or Chromosorb. The relatively high drawing temperature, approximately 800°, for Pyrex glass decreases the amount of free silanol groups on the surface of the capillary column, thus the total number of free hydroxyl groups is far less than expected five hydroxyl groups per 100 Å² on silicaceous surfaces in micro- and macroporous silica gel¹⁰.

The early work in capillary column technology of Grob¹¹ has been achieved by extensive laboratory experimental work. Tremendous effort and experimentation has brought significant evidence that inertness of the inner surface of the glass capillary must be accomplished by means of deactivation step, or suitable removal of active sites.

We report here an investigation that was carried out to assess the effect of leaching the inner wall of a glass tube for further deposition of a non-polar thin-film stationary phase.

EXPERIMENTAL

Surface preparation

Pyrex glass tubes (122 cm × 0.25 cm I.D.) were treated employing three different cleaning procedures. The first set of five tubes were rinsed with acetone and diethyl ether and blown dry with nitrogen for 30 min. Each tube was immediately used for drawing a glass capillary. The second set of Pyrex glass tubes were filled with a chromic acid-sulphuric acid mixture. The inner wall was leached at ambient temperature for 48 h. Afterwards, they were washed with deionized water and blown dry with nitrogen prior to drawing¹².

The third set of glass tubes were filled with 10% hydrofluoric acid in deionized water and allowed to stand 48 h at ambient temperature. They were then filled with conc. nitric acid and allowed to stand 1 h at ambient temperature. The tubes were then rinsed with 10% hydrofluoric acid followed by deionized water till neutral. The tubes were then dried using nitrogen and a heat gun. Immediately after drying a capillary column was drawn.

Glass capillaries 20 m long and of I.D. ca. 0.025 cm were drawn and further treatment of the inner wall was applied as follows. The first capillary of each set was thoroughly washed with methanol, acetone and diethyl ether and coated dynamically with a 2% solution of Carbowax 20M in chloroform.

The remaining twelve capillary columns were filled with a 0.5% solution of ammonium hydrogen difluoride in methanol, left to stand 1 h at ambient temperature and then were blown dry and sealed under nitrogen. The sealed columns were placed in a muffle oven at ambient temperature. The oven was closed and the temperature raised to 450° for 3 h. The columns were then removed and flushed a short period of time with helium. All exhibited a translucent appearance.

The second capillary column of each set was washed with 10 ml of distilled water and the filled capillaries were kept in an oven at 100° overnight. Afterwards, they were washed with methanol, acetone and diethyl ether and coated with Carbowax 20M similar to the first set of capillaries.

The third set of glass capillaries were filled with 12 *N* HCl, put to the oven and kept at 100° overnight. They were treated in the same way as the second set. The fourth set of capillaries were filled with 1% HF solution and the whole procedure was repeated as in the previous cases. The fifth set of columns were filled with 0.5% NaOH solution and the treatment was performed as in the previous three sets.

Deactivation

A 2% solution of Carbowax 20M in chloroform was passed through the glass capillary at the normal coating speed of 10 cm/sec employing a Hg-plug method. The columns were then purged with nitrogen for 1 h, after which they were mounted in the inlet of the gas chromatographic oven.

The capillary was flushed with helium at 120° for 5 min, then the flow was reduced almost to zero and the oven temperature was increased to 260° for 50 min. The flow-rate of the carrier gas was increased to 0.3 kg/cm² and the temperature was raised to 280° for 30 min. The cooling step was performed at an increased flow of carrier gas (0.5 kg/cm²) and each column was tested immediately, employing a polarity mixture as described earlier¹³. The results are summarized in Table I.

Some of the results are illustrated in Figs. 1-3.

TABLE I

TAILING FACTORS DETERMINED FOR THE TEST MIXTURE AFTER DEACTIVATION*
DMA = 2,6-dimethylaniline, DMP = 2,6-dimethylphenol. NP = No peak observed.

Compound	Column No.														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
2-Nonanone	92	93	98	99	95	93	91	99	100	91	97	98	99	100	96
1-Octanol	86	NP	96	97	NP	91	NP	97	98	NP	92	NP	99	100	32
Dodecane	97	95	97	97	96	97	95	100	100	89	98	95	100	100	89
Pentadecane	96	91	96	97	92	96	95	100	99	90	98	92	100	100	82
Naphthalene	92	81	96	98	91	97	91	98	99	92	99	94	100	99	89
DMA	93	91	96	98	90	95	94	97	98	82	97	93	99	99	85
DMP	91	72	96	97	35	95	92	97	98	45	98	93	98	99	52

* Isothermal at 90°.

Coating

All columns were coated with a 3% solution of SP-2100 silicone oil in chloroform. Approximately 8-10 loops were filled with the solution and a short plug of mercury was sucked into the capillary. A coating velocity of 3.5 cm/sec was maintained by means of a constant nitrogen flow adjusted with a two-stage regulator. Each column was tested at an optimum flow-rate for fluorene and the chromatographic performance was calculated as shown in Tables II-IV.

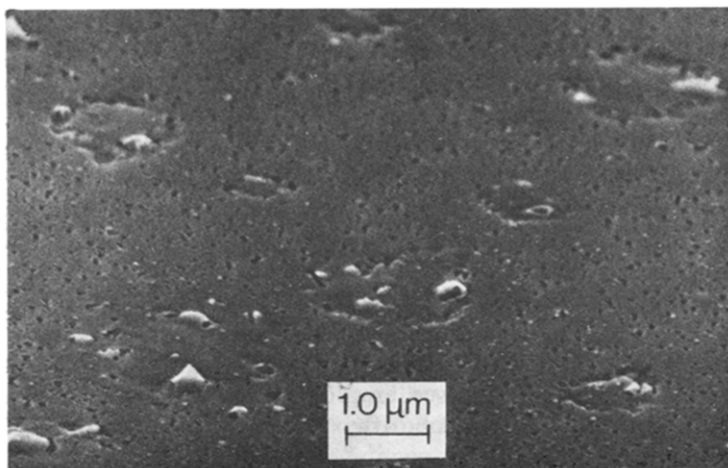


Fig. 1. Sintered surface of HNO_3 -HF capillary.

RESULTS AND DISCUSSION

It is evident from the data presented in Tables II-IV that the pre-treatment process has played a very important role during column preparation. Data from Table I indicate that columns 1, 6 and 11 which were washed before the drawing step with different solutions exhibit different activities to the testing solution. Column 1

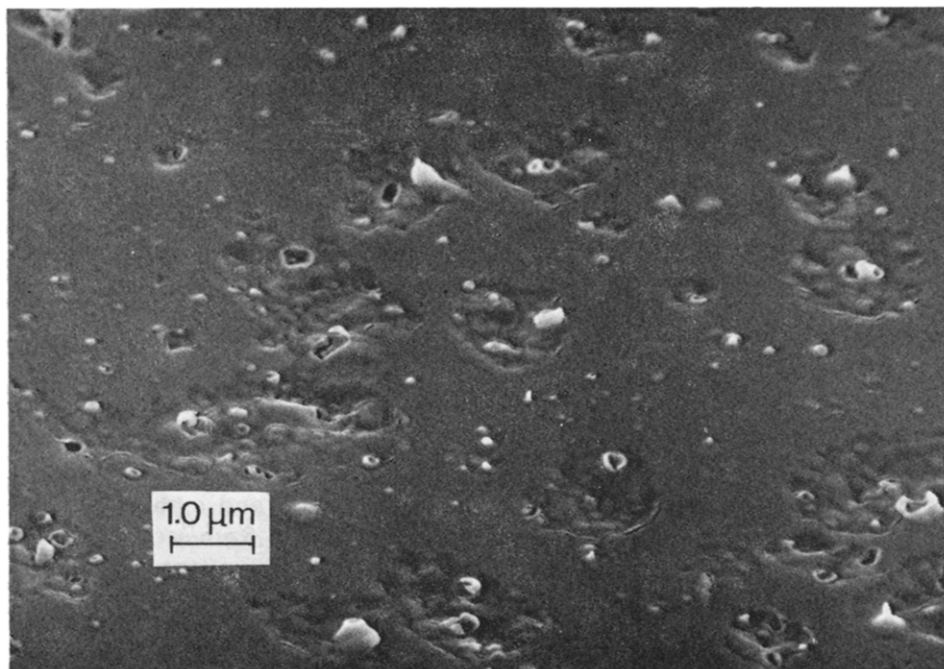


Fig. 2. Sintered surface of HNO_3 -HF capillary treated with 0.5% NH_4F_2 and washed with 1% HF.

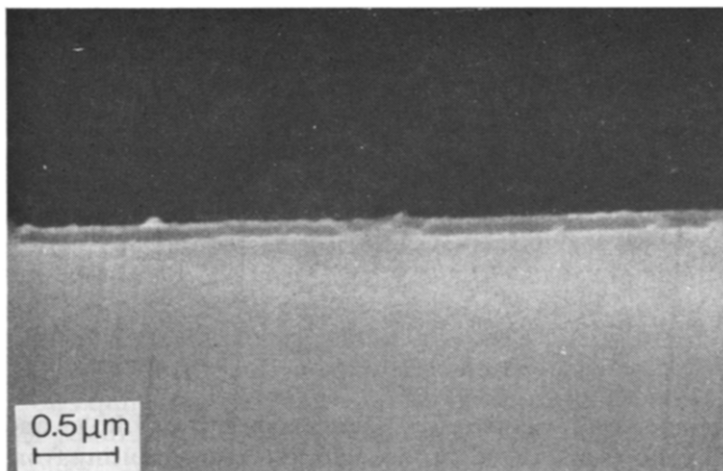


Fig. 3. The same capillary after coating with SP-2100.

shows the highest activity expressed by the tailing factor values. Column 6, cleaned before drawing with acidic dichromate indicates an improvement, especially for 1-octanol and naphthalene peaks, however, the HF-HNO₃-treated column 11 produced the most symmetrical peaks from that set. Column 1 has a very smooth inner wall,

TABLE II

CHROMATOGRAPHIC PERFORMANCE OF ACETONE-DIETHYL ETHER-WASHED COLUMNS COATED WITH SP-2100 FOR FLUORENE AT 120°

d = Diameter; t_0 = gas hold-up time; t_R = retention time; W_b = peak width; k' = partition ratio; n = number of theoretical plates; H = height equivalent to a theoretical plate; $N_{eff.}$ = effective plate numbers; $H_{min.}$ = minimum of a height equivalent to a theoretical plate; UTE = coating efficiency.

Column No.	$d(mm)$	$t_0(sec)$	t_R	$W_b/2(sec)$	k'	N	H	$N_{eff.}$	$N_{eff./m}$	$H_{min.}$	UTE (%)
1	0.217	82	561	7.06	5.84	35012	0.511	25523	1276	0.1857	32.5
2	0.250	79	578	9.77	6.31	19407	0.972	14496	725	0.216	22.2
3	0.233	101	661	6.19	5.54	63230	0.316	45371	2269	0.196	62.0
4	0.250	176	1490	14.80	7.46	56200	0.355	43700	2185	0.219	61.5
5	0.250	82	622	11.67	6.58	15752	1.269	11870	593	0.216	17.1

TABLE III

CHROMATOGRAPHIC PERFORMANCE OF CHROMIC ACID-SULPHURIC ACID-WASHED COLUMNS COATED WITH SP-2100 FOR FLUORENE AT 120°

For explanation of symbols, see Table II.

Column No.	$d(mm)$	$t_0(sec)$	t_R	$W_b/2(sec)$	k'	N	H	$N_{eff.}$	$N_{eff./m}$	$H_{min.}$	UTE (%)
1	0.250	84	197	2.40	1.35	37360	0.535	12330	616	0.166	31.0
2	0.233	80	412	6.68	4.15	21093	0.948	13696	685	0.189	20.0
3	0.244	86	500	3.98	4.81	87513	0.229	59980	2999	0.204	89.1
4	0.240	83	579	4.60	5.98	87850	0.228	64481	3224	0.205	90.2
5	0.250	83	458	6.14	4.51	30852	0.648	20670	1034	0.212	32.7

TABLE IV

CHROMATOGRAPHIC PERFORMANCE OF NITRIC ACID-HYDROFLUORIC ACID-WASHED COLUMNS COATED WITH SP-2100 FOR FLUORENE AT 120°

For explanation of symbols, see Table II.

Column No.	$d(mm)$	$t_0(sec)$	t_R	$W_b/2(sec)$	k'	N	H	$N_{eff.}$	$N_{eff./m}$	$H_{min.}$	UTE (%)
1	0.267	89	378	4.44	3.25	40190	0.497	23502	1175	0.211	42.5
2	0.293	71	333	4.25	3.69	34041	0.588	21072	1054	0.237	40.3
3	0.280	76	420	3.37	4.53	86127	0.232	57794	2889	0.233	100.4
4	0.260	67	395	3.10	4.89	90027	0.222	62052	3102	0.218	98.2
5	0.260	63	494	6.39	6.84	33140	0.604	25225	1261	0.226	37.4

but column 6 shows that the inner wall was partially roughened with tiny holes and was slightly pitted. Column 11 shows a sintered surface with pit-holes resulting from significant leaching of the sodium and baron ions from the surface (Fig. 1), and thus had the lowest activity related to adsorption or chemisorption on the surface.

The experiment performed with the highly hydroxylated surface using water treatment provided information related to interactions of solute with free hydroxyl groups. As can be seen from the data in Table I, the hydroxylated surface of columns 2, 7 and 12 indicate that free hydroxyl groups on the surface interact with 1-octanol, naphthalene and partially with 2,6-dimethylaniline (DMA) and 2,6-dimethylphenol (DMP). It may be assumed that hydrogen bonding takes place through the interacting of the alcohol molecules and the free silanol groups on the surface of the capillary. Modification of the surface with Carbowax 20M does not eliminate this surface activity significantly. Partial improvement could be achieved with repeated coating by means of Carbowax 20M. The resulting film was stable and uniform after thermal pre-treatment at 280°. This experiment confirmed that the water washing must be avoided during the preparation step.

It has been shown that washing the inner wall of the capillaries containing whiskers by means of hydrochloric and hydrofluoric acid improves wettability of the capillaries. This may be attributed to the replacement of the free hydroxyl groups on the leached surfaces by chlorine or fluorine atoms and making the surface hydrophobic. This fact can be supported with the findings that liquid phase covers the inner wall evenly, as shown in the Fig. 3 taken by SEM. This result is in contradiction with the recently published work of Grob *et al.*¹⁴ claiming that the whiskers (vertical particles) "...are undesirable since their position and shape prevents them from becoming immersed in, or at least, covered by even thick liquid films".

It is evident that the surface containing whiskers can be evenly covered by the liquid phase but the film must be properly spread on the surface. The whiskers should not be immersed into the liquid phase but coated with the phase. It is also our experience that whisker growth must be regulated, in such a way that their length will not be criterion for the preparation of a suitable column but the film thickness of the liquid phase for a particular separation process. Thus, it must be considered before the column is prepared whether an analytical column with the maximum number of theoretical plates is desirable or a column which may withstand heavier loadings and wide changes of temperature during the run is required. In the first

case, where high performance is desired, whisker growth must be less than $0.8 \mu\text{m}$, however for the second type of WCOT columns, filamentary crystals up to $5 \mu\text{m}$ are acceptable. We assume that as a rule of thumb, the ratio between whisker length and coating thickness should be between 10:1 (depending also on the column diameter). The wettability of the coating liquid on the glass surface, probably results in a lowering of the surface tension of a polar substrate. If the solute molecules do adsorb at the solid-liquid interface, it is one of the results of wetting and not the cause. Thus, deposition of an unextractable layer of a suitable deactivating solute has a two-fold purpose. Firstly, it masks or interacts with remaining Lewis acid sites and secondly, the non-polar part of the molecule attracts a non-polar part of the non-polar liquid phase and thus probably mix well.

The last group of capillaries washed and heated with 0.5% solution of NaOH shows quite interesting results. As shown by Ahrland *et al.*¹⁵ the corresponding high pH results in the $\equiv\text{Si}-\text{OH}$ groups being transformed into $\equiv\text{Si}-\text{ONa}$ groups. We thought that this type of remaining silanol groups would react with the Carbowax free hydroxyl groups. It proved to be correct, but all columns exhibited a strong chemisorption and activity, probably caused by the formation of free NaOH molecules. The activity increased with time and column temperature.

CONCLUSION

The experimental data obtained so far, suggest the following summing-up may be made:

(1) Correlation based exclusively on the comparison of the tailing factor values for three different pre-treatments of the inner wall of the capillaries revealed that a nitric acid-hydrofluoric acid leached glass surface is superior to the acidified dichromate etching pre-treatment, or just much better than just simple washing of the glass tube with acetone-ether solvents.

(2) Both pre-treatments, after drawing the capillary, produce a capillary surface that is serrated so that the stationary phase can be more evenly distributed.

(3) The porous glass surface, treated with ammonium hydrogen difluoride exhibits an increased surface area and a decreased activity. It has been shown that an inactive glass surface can be prepared if potential Lewis acid sites are removed from the active glass surface.

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