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WHISKER-WALLED OPEN-TUBULAR GLASS COLUMNS IN GAS CHROMATOGRAPHY

I. DEACTIVATION

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SUMMARY

A number of techniques for deactivating the surface of whisker-walled open-tubular glass columns have been investigated. Silanization and treatment with surface-active agents were the most successful techniques.

INTRODUCTION

Techniques for growing silica whiskers on the inner surface of glass open-tubular columns have been described previously^{1,2}. The internal surface area can be increased considerably by these means and, when coated with stationary phase, acceptable values of the phase ratio, β , can be obtained^{1,3}.

The method of growing whiskers results in a highly active surface, which leads to excessive tailing of the eluted peaks, particularly when a non-polar stationary phase is used. Deactivation of the surface of the whiskers is therefore necessary before coating with the stationary phase if the potential performance of the column is to be realized. We report here an investigation that was carried out to assess various methods for the deactivation of the surface.

EXPERIMENTAL

Glass columns 10–15 m long and of I.D. *ca.* 0.03 cm were drawn and the inner surface was modified by growing silica whiskers as described previously². After deactivation by the methods outlined below, the columns were connected with heat-shrinkable PTFE tubing (Raychem, Olifantsfontein, South Africa) to a variable splitter⁴ in a Varian Aerograph Model VA 1800 gas chromatograph. The column outlet was connected in a similar manner to a flame-ionization detector, which was modified to allow the introduction of make-up carrier gas⁴. The splitter was constructed from glass-lined stainless-steel tubing (Scientific Glass Engineering, Mel-

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bourne, Australia), the inner surface of which was deactivated by silanization as described below. This procedure ensured that any tailing that was observed originated in the column and not in the inlet. The column was operated at 200° using nitrogen as the carrier gas.

The methods used to deactivate the surface of the whiskers were silanization, sorption of surface-active agents, surface carbonization and application of a non-extractable polymer layer.

Silanization

Three different methods of silanization were used. Firstly, a plug of dimethyl-dichlorosilane in toluene (5%, v/v) was propelled through the column using dry nitrogen as described by German and Horning⁵ and Pierce⁶, then washed with toluene and methanol and finally dried in a stream of dry nitrogen at 200°. The second method, which has been described by Novotný and Tešarik⁷, entailed bubbling nitrogen through a mixture of hexamethyldisilazane and trimethylchlorosilane (5:1) at 25° and filling the column with the resulting vapour at the same temperature. The column ends were then sealed and the column was heated at 200° for 48 h. The third method was similar to that of Novotný and Tešarik except that the silanization vapour mixture was passed continuously through the column at 200° for 24 h. In each of the procedures the column was finally cleaned by flushing it with dry nitrogen at 200° for 6–12 h.

Sorption of surface-active agents

This technique has been discussed by Novotný and Zlatkis⁸. A plug of a 0.2–1.0% (w/v) of the surface-active agent in a suitable solvent is propelled through the column using dry nitrogen. The excess of surfactant is washed out with solvent, which is then flushed using dry nitrogen at 200°. Benzyltriphenylphosphonium chloride was chosen as the surface-active agent because of its ready availability and good thermal stability⁹.

Surface carbonization

Three methods were used. The first has been described by Grob^{10,11}. Nitrogen was bubbled through pure dichloromethane at 20° and the vapour used to fill the column at a slightly higher temperature. After sealing its ends, the column was heated at 550° for 30–45 min and then flushed with dry nitrogen. In the second method, which has been briefly referred to by Grob^{10,11}, pure acetylene was passed through the column, its ends were sealed and the acetylene was pyrolyzed at 550° for 30–45 min. The column was then flushed with dry nitrogen. In the third method, one end of the column was connected to a high-vacuum pump and the other end to a septum through which pure *n*-hexane was injected until approximately 10% of the column volume was filled with liquid *n*-hexane. The ends of the column were sealed and the column was heated at 550° for 30–45 min, the column subsequently being flushed with dry nitrogen.

Application of a non-extractable polymer layer

This method was evolved by Aue *et al.*¹² and applied to open-tubular columns by Cronin¹³. The column was filled with a 2% (w/v) solution of Carbowax 20M in di-

chloromethane and allowed to stand for 3–6 h, then the solution was flushed out using dry nitrogen at 250° for 24 h. The column ends were closed and the column was heated at 280° for 24 h. The column was then opened, flushed with dichloromethane and methanol and dried with nitrogen at 200°.

RESULTS

The success of a particular method of deactivation was determined by injecting into each of the deactivated columns a series of compounds containing different functional groups that could be expected to be encountered in a wide variety of practical separations. Samples of 0.2–0.5 μ l of the liquid solutes were injected, and also 20–50- μ l samples of methane gas. These compounds and their associated functional groups are listed in Table I. The tailing factor of each peak:

$$\text{TF} (\%) = \frac{a}{b} \times 100\%$$

where a and b were measured at 10% of the peak height, as shown in Fig. 1¹⁴. The values that were obtained for the different deactivated surfaces are given in Table II.

As it would be unrealistic to expect that a support surface could be produced that is completely unreactive to all solutes, *i.e.*, TF = 100%, the results obtained

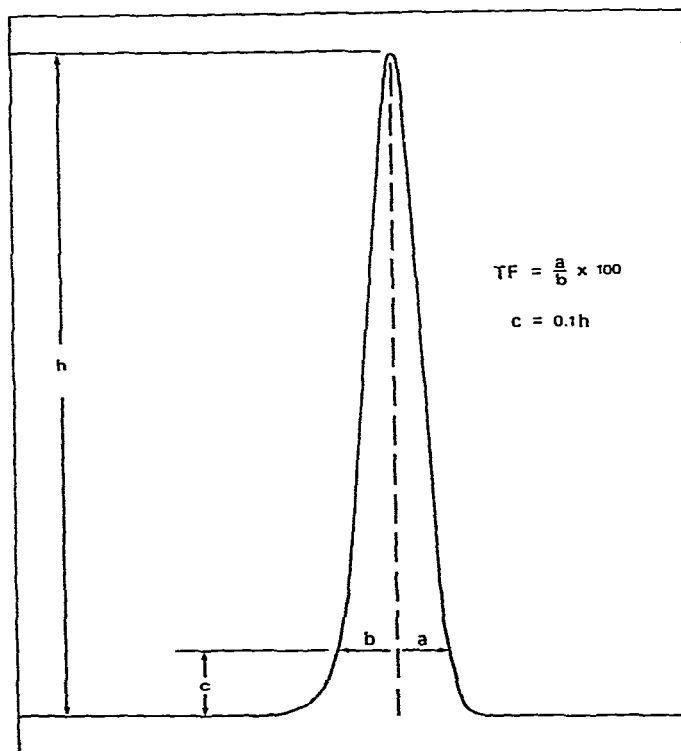


Fig. 1. Definition of the tailing factor, TF (%).

TABLE I

COMPOUNDS USED IN THE STUDY OF THE EFFICIENCY OF DEACTIVATION

| Functional group | Solute |
|------------------|----------------------------|
| Aliphatic | Methane, <i>n</i> -heptane |
| Aromatic | Benzene |
| Ether | Diethyl ether |
| Ketone | Methyl isobutyl ketone |
| Alcohol | Methanol, cyclohexanol |
| Amine | Dimethylaniline, pyridine |

were compared with those pertaining to a support surface that is generally considered to be the best attainable in practice, *i.e.*, Chromosorb W HP (Johns-Manville, Denver, Colo., U.S.A.)¹⁵. The tailing factors obtained by injecting the solutes listed in Table I onto this surface are therefore included in Table II for comparison purposes.

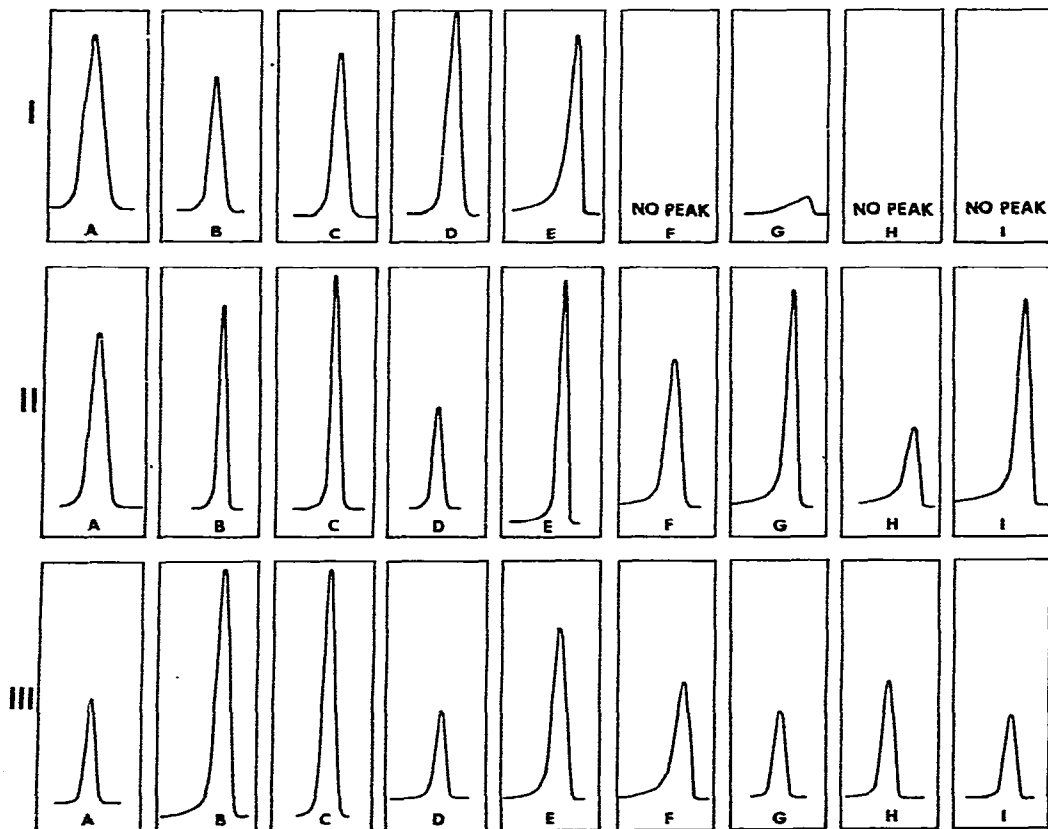


Fig. 2. Chromatograms of test solutes on various supports: I, untreated silica whiskers; II, continuous-flow silanization; III, Chromosorb W HP. Solutes: A, methane; B, *n*-hexane; C, benzene; D, diethyl ether; E, methyl isobutyl ketone; F, methanol; G, cyclohexanol; H, dimethylaniline; I, pyridine.

TABLE II
TAILING FACTORS DETERMINED FOR THE COMPOUNDS LISTED IN TABLE I ON VARIOUS SURFACES

| Solute | Tailing factor, <i>TF</i> (%), for different surfaces | | | | | | | | | |
|---------------------------|---|------------------------------------|------------------------------|---|-------------------------------------|--------------------------|----------------------------------|---|--------------------|--|
| | Whiskers and BTPPC | Whiskers and Carbowax 20M | Whiskers and acetylene | Whiskers and dichloro- methane | Whiskers and <i>n</i> -hexane | Whiskers and DMDCS | Whiskers and HMDS/ TMCS | Whiskers and HMDS/ TMCS (conitions) | Chromosorb W HP | |
| Methane | 96 | 94 | 95 | 80 | 98 | 99 | 64 | 92 | 90 | |
| <i>n</i> -Hexane | 80 | 74 | 70 | 14 | 85 | 68 | 69 | 98 | 78 | |
| Benzene | 78 | 70 | 65 | <5 | 60 | 63 | 78 | 100 | 72 | |
| Diethyl ether | 86 | 73 | 75 | <5 | 80 | NP* | 11 | 100 | 71 | |
| Methyl isobutyl ketone | 33 | 60 | 66 | <5 | 70 | 8 | <5 | 73 | 65 | |
| Methanol | NP* | 54 | NP* | NP* | 60 | NP* | 17 | 69 | 44 | |
| Cyclohexanol | 21 | 51 | 50 | NP* | 38 | NP* | NP* | 60 | 77 | |
| Dimethylaniline | NP* | 34 | NP* | NP* | 14 | NP* | NP* | 30 | 69 | |
| Pyridine | NP* | 22 | NP* | NP* | 10 | NP* | NP* | 40 | 63 | |

* NP = no peak observed.

DISCUSSION

The best deactivation of the whisker surface was obtained using the third silanization method. Only for compounds containing an amine group did this surface compare badly with Chromosorb W HP. This problem could possibly be overcome by treating the column with sodium or potassium hydroxide, as is often done in the chromatographic separation of amines^{16,17}.

The other deactivation techniques were less effective but, with the exception of the carbonization of dichloromethane and acetylene, may be acceptable for many applications.

Examples of the chromatograms obtained using the best silanization deactivation technique are shown in Fig. 2, together with those obtained on undeactivated whiskers and also on Chromosorb W HP.

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