

CHROM. 8599

DEACTIVATION OF GLASS CAPILLARY COLUMNS FOR GAS CHROMATOGRAPHY

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(Received June 11th, 1975)

SUMMARY

The adsorption of some polar volatile compounds on glass capillary columns has been investigated. In general, silanization and etching with hydrogen fluoride or chloride reduces the column activity only slightly. Coating of such capillaries with some polar phases deactivates AR-glass but not Pyrex. As initially described by Aue for packed columns, a thin layer of non-extractable Carbowax 20M provides a well deactivated surface for further coating with polar or non-polar stationary phases. Such deactivated non-polar capillary columns are valuable for the separation of samples, e.g., tobacco smoke, containing both polar and non-polar compounds.

INTRODUCTION

Because of its inert nature, glass is a suitable material for columns used in gas chromatography (GC) and columns of high efficiency can be prepared¹. For polar compounds, however, the surface of glass exhibits an undesirable activity. This is caused to a great extent by boron, potassium and hydroxyl groups^{2,3}. The activity of the glass surface leads to tailing of chromatographic peaks and sometimes to total adsorption of polar compounds⁴⁻⁹. Several methods for the deactivation of glass have been investigated, e.g., silanization, etching with hydrogen fluoride, addition of surface-active agents to the stationary phase or utilization of some polar stationary phases. The composition of the glass is an important factor influencing the results achieved². Aue *et al.*⁹ coated Chromosorb W with Carbowax 20M, after which the material was heat-treated at 280° and then exhaustively extracted. After this treatment the support was still coated with a thin non-extractable film of polymer. This support was found to be a well deactivated chromatographic packing suitable for further coating with stationary phase¹⁰.

Some methods for the deactivation of glass capillaries have been tested and compared in this investigation. Heat treatment with Carbowax 20M has been found to give the best result. The deactivated surface thus obtained can be coated with polar or non-polar stationary phases to give inert and stable columns.

TABLE I
PERCENTAGE COMPOSITION OF PYREX AND AR-GLASS

| Component | Composition (%) | |
|--------------------|-----------------|----------|
| | Pyrex 7740 | AR-glass |
| Silicon dioxide | 80.3 | 69.5 |
| Boron trioxide | 12.2 | 1.4 |
| Aluminium oxide | 2.8 | 4.2 |
| Sodium monoxide | 4.0 | 10.8 |
| Potassium monoxide | 0.4 | 5.3 |
| Calcium monoxide | 0.3 | 7.8 |

EXPERIMENTAL

Capillaries (20 m \times 0.6 mm \times 0.25 mm) were drawn on a vertically operated Shimadzu glass-drawing machine using glass tubing (6 \times 2 mm) which had been previously cleaned in chromic acid-sulphuric acid, carefully rinsed with water and acetone and dried. Pyrex and AR-glass were used, the compositions of which are shown in Table I¹¹. The capillaries were treated in various ways before coating. Silanization was carried out in the gas phase with hexamethyldisilazane-chlorotrimethylsilane (5:1)¹². Some capillaries were etched with gaseous HF produced by the thermal decomposition of chlorotrifluoroethyl methyl ether¹³. Etching with HCl was performed according to Alexander *et al.*¹⁴, and the effect of rinsing with dry acetone after the etching¹⁵ was also examined.

The procedure of Cronin¹⁶ for the preparation of a non-extractable layer of Carbowax 20M in a glass capillary was slightly modified. The capillaries were etched with gaseous HF¹³ to improve the wettability, and then coated dynamically at a rate of 20 mm/sec with a solution of 5% (w/v) Carbowax 20M in freshly distilled dichloromethane. The solvent of the coating solution was then evaporated slowly¹⁷; this seemed to be necessary when coating with Carbowax 20M at room temperature since a fast evaporation rate led to the formation of lenses of Carbowax in the column, *i.e.*, an uneven phase layer. The ends of the nitrogen-filled capillary were sealed in a flame, and the capillary was placed in an oven at 280° for 24 h. The capillary was allowed to cool to room temperature and then the extractable part of the polymer film was removed by rinsing the capillary successively with 15 ml of dichloromethane and 15 ml of methanol. The capillaries were then coated dynamically at a rate of 20 mm/sec. The methyl silicones SF-96, SP-2100 and OV-101 were dissolved in toluene, the fluoroalkyl silicone SP-2401 in ethyl acetate, the cyanoalkyl silicone XF-1150 in acetone and the polyethylene glycol Carbowax 20M in dichloromethane. Freshly distilled solvents were used, and the concentrations of the solutions were 10% (v/v) for the silicones and 5% (w/v) for Carbowax 20M.

The columns were tested on a home-built gas chromatograph equipped with a Varian flame-ionization detector (FID). The capacity ratio and number of theoretical plates were determined for benzene at 38° with a carrier gas (nitrogen) flow-rate of 15 cm/sec. Dead retention time was measured by the injection of methane. The capacity ratio denoted the film thickness, and the number of theoretical plates indicated the column efficiency when comparing columns used in this investigation. The

columns were tested for acidity, polarity and adsorption according to Grob and Grob¹⁸. The acidity was indicated by the relative peak areas of 2,6-dimethylaniline and 2,6-dimethylphenol. The polarity was demonstrated by the retention values of 5-nonanone, 1-octanol and naphthalene (polarity mixture) relative to those of the *n*-alkanes C₁₀-C₁₆ (Kováts index). The adsorption was denoted by the peak symmetry of the polar substances tested and of the relative peak heights. The solutions tested contained 0.1% of the substances in hexane and 1- μ l amounts were injected with a splitting ratio of 1:60, *i.e.*, *ca.* 15 ng were allowed to enter the column, the temperature of which was 114°.

RESULTS AND DISCUSSION

Comparison of Pyrex and AR-glass

The acidity is an important property of a column. It affects the elution of typical acidic or basic compounds and also many so-called neutral substances, *e.g.*, slightly basic columns are preferred for alcohols and slightly acidic for most ketones^{6,18}. AR-glass columns coated directly with SF-96 were slightly basic, but silanization or etching with HF prior to coating gave neutral columns. This may increase the column stability, since it is possible that the silicones and polyglycols are sensitive to a basic environment^{7,18}. It was not possible to determine the acidity of the Pyrex columns because of strong adsorption of 2,6-dimethylaniline. These columns also adsorbed 1-octanol and no peak was obtained with this compound. The alcohol was eluted as a peak on AR-glass, but it showed severe tailing (Figs. 1A and 1B). The ketone 5-nonanone gave symmetrical peaks in both cases.

The adsorption properties of Pyrex were also evident when attempting to deactivate the capillaries with polar stationary phases. Pyrex capillaries which had been etched with HF and coated with fluoroalkyl silicone SP-2401 or with cyanoalkyl silicone XF-1150 gave no alcohol peak. For columns coated with the polar phase

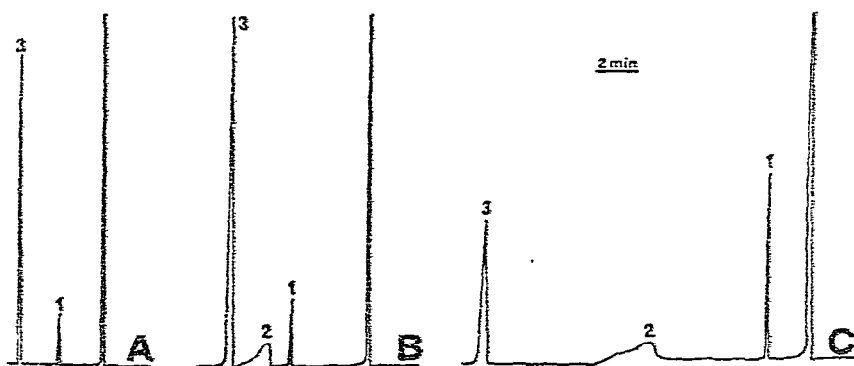


Fig. 1. Gas chromatograms (FID) of a polar mixture on different 20-m capillary columns: A = silanized Pyrex coated with SF-96; B = silanized AR-glass coated with SF-96 and C = Pyrex etched with HF and coated with Carbowax 20M. Temperature, 114°. Carrier gas (nitrogen) flow-rate, 15 cm/sec. Peaks: 1 = 5-nonanone (sample size, *ca.* 15 ng); 2 = 1-octanol (*ca.* 15 ng) and 3 = naphthalene (*ca.* 30 ng).

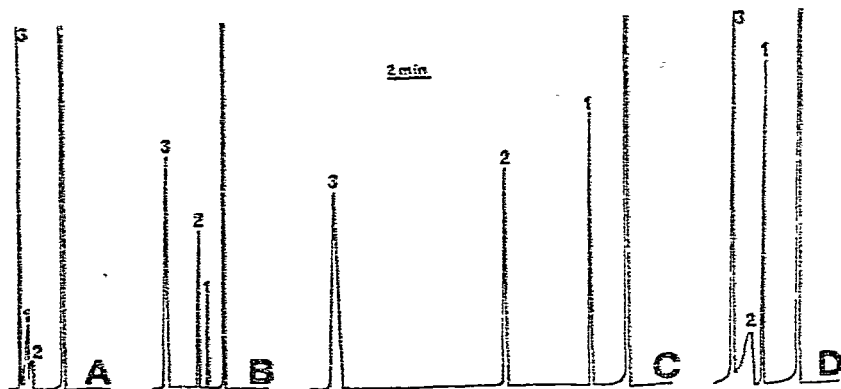


Fig. 2. Gas chromatograms (FID) of a polar mixture on different 20-m capillary columns: A = AR-glass etched with HF and coated with SP-2401; B = AR-glass etched with HF and coated with XF-1150; C = AR-glass etched with HF and coated with Carbowax 20M and D = Pyrex treated with Na_2O and coated with SF-96. Peak numbers and conditions as in Fig. 1.

Carbowax 20M, a peak was obtained although it showed tailing (Fig. 1C). AR-Glass which had been etched with HF could be deactivated with SP-2401 to give a slightly tailing alcohol peak; XF-1150 and Carbowax 20M gave perfect deactivation (Figs. 2A-2C).

Deactivation of the silanol groups by means of silanization had no effect on peak shape for alcohols, thus other active centres must be present on the glass surface^{8,19}. The higher activity of Pyrex might be attributed to the higher content of boron^{20,21} which forms Lewis-acid sites on the surface³ and is considered to exhibit a catalytic activity⁸. Many types of glass are not homogeneous, but consist of different phases which are in equilibrium with each other^{21,22}. Heating of certain borosilicate glasses to between 550 and 700° results in a phase separation^{21,22}, and the concentration of boron on the inner surface of the Pyrex capillaries might be higher than in the bulk of the glass. This condition is perhaps affected by the glass-drawing procedure, e.g., long or short heating zones and vertical or horizontal mode of operation. In AR-glass the activity might be due in part to calcium which forms Lewis-acid sites². Since the adsorption of alcohols is to some extent due to boron, a Pyrex surface enriched with sodium monoxide should show less activity. For the preparation of such capillaries an even layer of Na_2O was applied to the inner surface of Pyrex glass tubing, and when the capillaries were drawn the Na_2O became associated with the glass. Such capillaries were basic, and showed an activity similar to that of AR-glass (Fig. 2D, Table II).

Etching with HF had little effect on the column activity, but it produced a surface suitable for coating with the polar stationary phases used in this investigation. After etching, the columns were flushed with dry nitrogen at 180°. The issuing gas was acidic for Pyrex capillaries, indicating an excess of reagent, but was neutral for AR-glass capillaries. This was also the case for capillaries which had been etched with HCl, which is in accordance with the results of Alexander and Rutten²³ who found that HCl has little effect on Pyrex glass. Etching with HCl had no effect on the column activity for alcohols, and AR-glass columns coated with SF-96 were

TABLE II

CHARACTERISTICS OF SOME TYPICAL 20-m CAPILLARY COLUMNS

| Column number | Glass type | Stationary phase | Pre-treatment | Capacity ratio | HETP* (mm) | Kováts index | | Acid-base condition |
|---------------|------------|------------------|-------------------|----------------|------------|--------------|-------------|---------------------|
| | | | | | | 1-Octanol | 5-Nona-none | |
| 1 | AR | SF-96 | — | 0.56 | 0.364 | — | 1064 | basic |
| 2 | AR | SF-96 | HF etched | 0.59 | 0.268 | 1087 | 1056 | neutral |
| 3 | Pyrex | SF-96 | HF etched | 0.58 | 0.222 | — | 1056 | |
| 4 | AR | SP-2401 | HF etched | 0.20 | 0.444 | 1323 | 1338 | neutral |
| 5 | AR | XF-1150 | HF etched | 0.29 | 0.400 | 1500 | 1418 | neutral |
| 6 | Pyrex | Carbowax | HF etched | — | 0.400 | 1561 | 1323 | neutral |
| 7 | AR | Carbowax | HF etched | — | 0.302 | 1560 | 1320 | neutral |
| 8 | Pyrex | SF-96 | Na ₂ O | 0.47 | 0.500 | 1081 | 1062 | basic |
| 9 | Pyrex | SF-96 | HCl etched | 0.53 | 0.408 | — | 1043 | acidic |
| 10 | AR | SF-96 | Carbowax | 0.40 | 0.323 | 1061 | 1058 | neutral |
| 11 | Pyrex | SF-96 | Carbowax | 0.53 | 0.209 | 1064 | 1056 | neutral |
| 12 | Pyrex | — | Carbowax | — | 0.572 | 1310 | 1172 | neutral |
| 13 | AR | — | Carbowax | — | 0.500 | 1308 | 1170 | neutral |
| 14 | AR | Carbowax | Carbowax | — | 0.308 | 1468 | 1288 | neutral |
| 15 | Pyrex | Carbowax | Carbowax | — | 0.267 | 1466 | 1287 | neutral |
| 16 | Pyrex | SP-2100 | Carbowax | 0.17 | 0.143 | 1088 | 1064 | neutral |
| 17 | Pyrex | SP-2100 | Carbowax | 0.48 | 0.160 | 1060 | 1050 | neutral |
| 18 | AR | OV-101 | Carbowax | 0.47 | 0.166 | 1062 | 1054 | neutral |
| 19 | Pyrex | OV-101 | Carbowax | 0.53 | 0.154 | 1059 | 1053 | neutral |

* Height equivalent to a theoretical plate.

acidic. Rinsing the capillary with dry acetone¹⁵ before coating had no effect on the acidity.

The column efficiency is in general higher for the Pyrex columns; this might be explained by the fact that Pyrex is less affected by etching with HF than AR-glass, and thus possesses a smoother surface to which the stationary phase is applied.

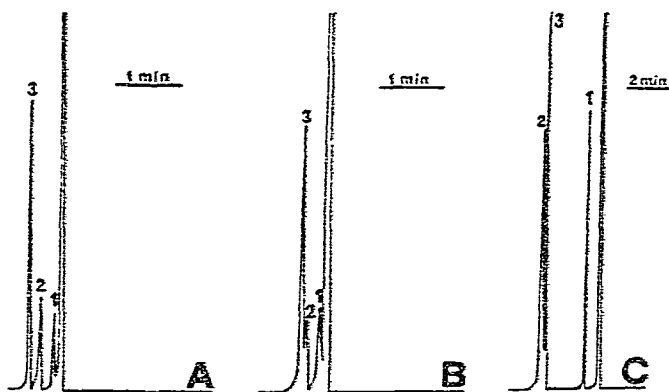


Fig. 3. Gas chromatograms (FID) of a polar mixture on different 20-m Carbowax-treated capillary columns: A = Pyrex, etched with HF, temperature 114°; B = AR-glass etched with HF, temperature 114° and C = the same column as in B, temperature 60°. Chart speeds: A and B, 30 mm/min; C, 10 mm/min. Peak numbers as in Fig. 1.

Columns deactivated with Carbowax

The method of Aue *et al.*⁹ for deactivation of the chromatographic support Chromosorb W can also be applied to capillary columns, and it was used by Cronin¹⁶ in order to achieve a compatible surface for subsequent coating with Carbowax 20M. Schomburg *et al.*⁵ used Carbowax 20M for deactivation followed by coating with non-polar phases, but in this case the Carbowax was not heat-treated before extraction; these columns could not be used at temperatures above 200°.

Capillaries which were coated with Carbowax 20M, heat-treated and extracted had very thin films. In contrast to Carbowax-coated columns before heating and extraction, such Pyrex capillaries showed good deactivation (Figs. 1C and 3A). AR-glass capillaries with this thin polymer coating showed some activity towards 1-octanol; at a lower temperature (60°) 1-octanol gave a slightly tailing peak, eluted after naphthalene (Figs. 3B and 3C). Carbowax-treated AR-glass capillaries coated with stationary phase exhibited no activity, capillaries coated with SF-96 gave good alcohol peaks (Fig. 4A) and on Pyrex the alcohol showed slight tailing (Fig. 4B). However, symmetrical alcohol peaks were achieved on Carbowax-deactivated Pyrex capillaries when the GC-grade stationary phases OV-101 and SP-2100 were used (Fig. 4C). Furthermore, columns coated with these phases showed higher efficiencies, and they could be used up to 250°.

The polarity of Carbowax-deactivated capillary columns coated with SF-96 was essentially the same as for capillaries etched with HF and coated with this phase, as can be seen from the Kovát index in Table II; this was also found by Hastings and Aue¹⁰ for packed columns. However, when a thinner layer of stationary phase was applied as on column 16 (Table II) the column polarity increased. Polar columns could be prepared according to Cronin¹⁶ (Fig. 4D).

When analyzing unstable, usually polar, compounds it is essential to use as mild conditions as possible, e.g., low temperature. On polar phases high temperatures are required for the elution of such polar compounds, and a further drawback is that polar phases are in general the least thermally stable. Consequently, deactivation of

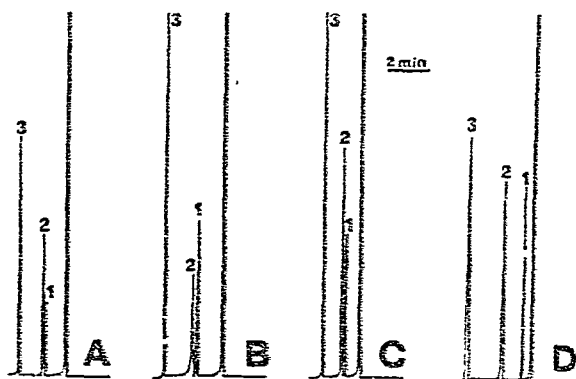


Fig. 4. Gas chromatograms (FID) of a polar mixture on different 20-m capillary columns: A = AR-glass etched with HF, treated with Carbowax and coated with SF-96; B = Pyrex etched with HF, treated with Carbowax and coated with SF-96; C = Pyrex etched with HF, treated with Carbowax and coated with Carbowax 20M. Peak numbers and conditions as in Fig. 1.

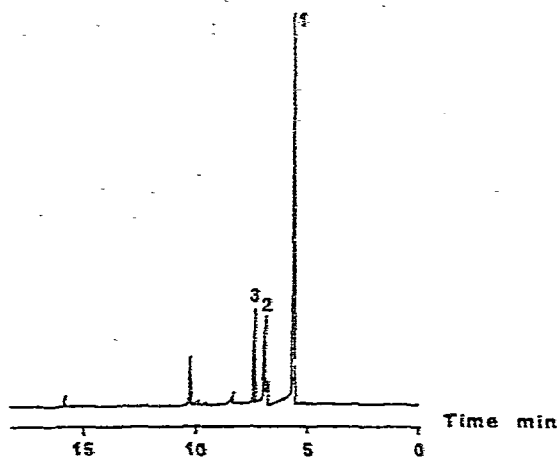


Fig. 5. Gas chromatogram (FID) of a fraction of the gas phase of tobacco smoke; splitting ratio, 1:80. Pyrex glass capillary column (20 m \times 0.25 mm I.D.) treated with Carbowax and coated with SF-96. Carrier gas, nitrogen. Initial temperature on injection, -70° ; programmed to -10° at $20^{\circ}/\text{min}$ and to 60° at $5^{\circ}/\text{min}$. Peaks: 1 = propionitrile; 2 = 2-butenal and 3 = 2,3-pentanedione.

glass capillary columns by means of applying a polar stationary phase sometimes involves undesirable effects on the analysis. Moreover, in this laboratory, polar columns have been found to possess lower efficiency than non-polar ones. Thus, at present, non-polar capillary columns are preferred in most cases, provided the support is carefully deactivated. Polar columns should be reserved for special separations, e.g., isomers differing only in the position of hydroxyl or other typical groups. In order to minimize adsorption and secondary reactions, the time the sample remains

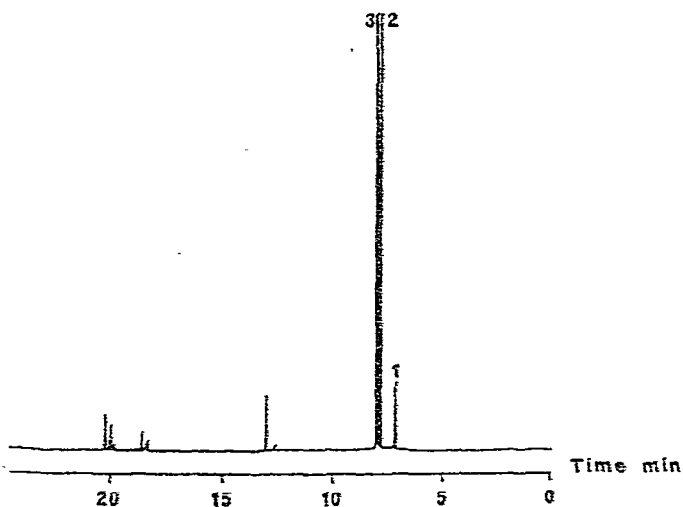


Fig. 6. Gas chromatogram (FID) of a fraction of the gas phase of tobacco smoke; splitting ratio, 1:100. Initial temperature on injection, -70° ; programmed to 0° at $20^{\circ}/\text{min}$ and to 105° at $5^{\circ}/\text{min}$. Other conditions as in Fig. 5. Peaks: 1 = 2-butanone. 2 = 3-methylbutanal and 3 = 2-methylbutanal.

in the column should be as short as possible, *i.e.*, the column length should be adjusted for the specific separation problem⁷.

The utility of Carbowax-deactivated capillary columns is demonstrated in the analysis of fractions of tobacco smoke (Figs. 5 and 6). Tobacco smoke is a complicated mixture of many components with different polarity²⁴. Thus, for a good separation a highly efficient deactivated column is required. In order to improve the analysis, the smoke was pre-separated on a packed polar column and fractions were withdrawn and re-injected on the capillary column according to the method described earlier⁴. The temperature programming and capillary column length were chosen to minimize the analysis time, thus avoiding excessive contact between the sample and column. Symmetrical peaks were achieved for propionitrile, 2-butenal and 2,3-pentanedione (Fig. 5) and for 2-butanone, 3-methylbutanal and 2-methylbutanal (Fig. 6).

ACKNOWLEDGEMENTS

This investigation was kindly supported by the Department of Analytical Chemistry. Thanks are due to Professor G. Widmark for helpful discussions, Mr. B. Lengsted for technical assistance and Mrs. B. Holm for reviewing the manuscript. The author is indebted to Dr. K. Grob for his stimulating seminar in Oslo on September 5th and 6th, 1974.

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