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## SOME FACTORS AFFECTING THE PROPERTIES OF THIN FILMS OF CARBOWAX 20M INTENDED FOR DEACTIVATION OF GLASS CAPILLARY COLUMNS

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### SUMMARY

The adsorptivity of glass capillary columns has been suppressed by application of a thin non-extractable layer of Carbowax 20M to the glass surface. The properties of such polymer surfaces were found to differ greatly with the etching technique, the type of glass and the procedure of Carbowax application. Further, the temperature stability of columns deactivated by coating with SP-2100 was greatly affected by the deactivation procedure. Columns prepared from etched Pyrex glass showed the highest stability, and such columns have been used regularly for the separation of polycyclic aromatic hydrocarbons at temperatures up to 300°.

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### INTRODUCTION

Glass capillary columns are to an increasing extent being used in gas chromatographic separations; compared with packed columns, they offer higher efficiency and the possibility of shorter analysis time. However, although glass is a fairly inert material, it can cause severe adsorption problems with many polar compounds, resulting in tailing or the complete disappearance of chromatographic fractions<sup>1,2</sup>. Deactivation of the glass surface is therefore a pre-requisite for the separation of polar compounds.

Several methods have been proposed for deactivation. One is to cover the surface with some non-adsorbing material such as fumed silica (see ref. 3) or by silanization with long-chain siloxanes<sup>4</sup>. Further, active components in the glass surface may be removed by selectively etching<sup>5</sup>. Another approach is to saturate the active sites with some polar compound, e.g., a surface-active agent<sup>6</sup> or a polar stationary phase. As has been pointed out<sup>7,8</sup>, polar stationary phases have certain drawbacks when used in capillary columns, and such columns prepared in our laboratory show lower efficiencies than non-polar ones. Moreover, their long-term stability is limited (possibly due to penetration of water) and they are generally less thermostable, which is a dis-

advantage, as higher temperatures are required to elute polar compounds from such columns. When separating samples containing heat-sensitive compounds, it is of paramount importance to use the lowest possible temperatures for analysis. In most cases, we thus prefer the use of non-polar capillary columns.

A most effective and thermostable means of deactivation was described by Aue *et al.*<sup>9</sup>. Chromosorb W was coated with Carbowax 20M, after which the coated material was heat treated at 280° and then exhaustively extracted. After this treatment, the support remained coated with a residue of a thin non-extractable film of polymer (the film thickness was estimated to be less than 15 Å). It may be assumed that the heat treatment allowed a significant part of the long Carbowax 20M molecule physically to rearrange on the surface of the support, thus resulting in a large number of Van der Waals and/or hydrogen bonds between the adsorbent surface and the polymer<sup>10</sup>. Water is known to have a detrimental influence on the adherence of organic liquids to glass and silica surfaces<sup>11,12</sup>, and a further factor contributing to the formation of a firmly adherent film might be the displacement of water by Carbowax at the high temperature used in deactivation. It is generally known that the chemical properties of a thin film are strongly influenced by forces in the support surface, *e.g.*, in a thin layer of octadecanol coated on diatomite, the hydroxyl groups are orientated towards the support surface and the film surface thus exhibits a non-polar character<sup>13</sup>, (*cf.* autophobic liquids<sup>14</sup>). Further, the melting points might be shifted to higher temperatures, and, with very strongly adsorbed films, no melting has been observed<sup>15-17</sup>.

Cronin<sup>18</sup> applied a non-extractable Carbowax film to glass capillaries, and these surfaces were found to be suitable for further coating with Carbowax. Our intention was, however, in the first place to prepare non-polar glass capillary columns; we thus coated the thin polymer layer with such non-polar phases as SP-2100 or OV-101<sup>7</sup>. The utility of such columns has been demonstrated in the analysis of tobacco smoke<sup>7,19,20</sup>.

We have found that the deactivating properties of a thin film of Carbowax are, to a great extent, dependent on the procedure of application and on the nature of the glass tubing. The effects of such factors on the degree of deactivation and temperature stability of the column are demonstrated in this paper.

## EXPERIMENTAL

Capillaries (20 m × 0.6 mm O.D. × 0.25 mm I.D.) were drawn on a vertically operated Shimadzu glass-drawing machine using Pyrex or AR-glass tubing (6 × 2 mm) that had been previously cleaned in chromic acid-sulphuric acid, carefully rinsed with water and acetone and then dried. Some capillaries were etched with gaseous hydrogen fluoride produced by thermal decomposition of chlorotrifluoroethyl methyl ether<sup>21</sup>. Etching with hydrochloric acid was effected according to published methods<sup>5,22</sup>. The capillaries were then coated dynamically (at 20 mm/sec) with a dry solution of 5% (w/v) of Carbowax 20M in freshly distilled dichloromethane; the solvent of the coating solution was evaporated, and the ends of the nitrogen-filled capillary were sealed in a micro-flame. After being heated for 24 h at 280°, the capillary was rinsed with 15 ml of dichloromethane (for some capillaries, the heat-treatment step was omitted). The capillaries were then further coated dynamically with Carbowax 20M or methylsilicone SP-2100 as stationary phase<sup>8</sup>.

The columns were tested on a laboratory-made gas chromatograph designed for precise thermostatic control and equipped with a Varian flame-ionisation detector. The capacity ratio,  $k$ , was measured for dodecane, 1-octanol and naphthalene at different temperatures. The test solution contained 0.1% of each substance in hexane, and the splitting ratio was adjusted to allow *ca.* 15 ng to enter the column. Dead retention time was measured by the injection of methane, and the carrier gas (nitrogen) flow-rate was 15 cm/sec. The analysis of polycyclic aromatic hydrocarbons was performed on a Carlo Erba 2350 gas chromatograph, with hydrogen as carrier gas.

## RESULTS AND DISCUSSION

For a glass capillary column coated with a relatively thick layer of Carbowax 20M, a drastic increase in retention is observed when the Carbowax melts (see Fig. 1). This phase consists of a mixture of compounds in the molecular weight range 15,000–20,000, so that melting occurs over a temperature interval; a hysteresis effect is also observed. For a capillary coated with a thin non-extractable layer of Carbowax 20M, a curve showing the variation in retention of 1-octanol with temperature exhibited a small inflection at the temperature at which thicker layers of Carbowax begin to melt (see Fig. 2). Retention is decreased as the layer melts, and this, together with the fact that the film is extremely thin, indicates that dissolution of the sample in the film is most unlikely. The sudden inflection in the retention curve might be caused by some rearrangement of the film, resulting in a different adsorption mechanism. A similar effect has been observed for relatively thick layers of chemically bonded Carbowax<sup>23</sup>.

Some degree of deactivation might be achieved when rinsing a capillary with a dilute Carbowax solution<sup>24–26</sup>. We found that capillaries so treated showed some residual activity towards alcohols; for instance, 1-octanol was not eluted from hydrogen fluoride-etched Pyrex or hydrochloric acid-etched AR-glass treated in this manner. Hydrogen fluoride-etched AR-glass has been shown to be more weakly active to

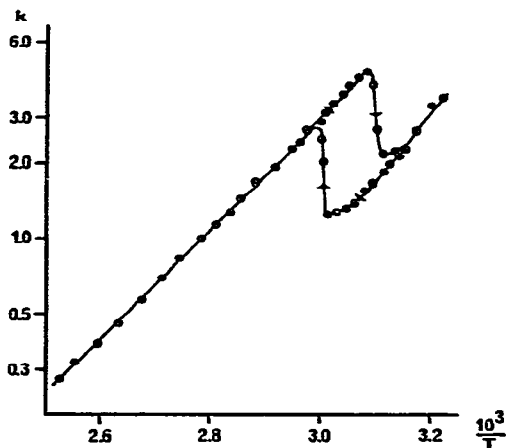


Fig. 1. Variation of  $\log k$  with  $1/T$  for a hydrogen fluoride-etched Pyrex-glass capillary coated with a thick layer of Carbowax 20M. Solute, dodecane.

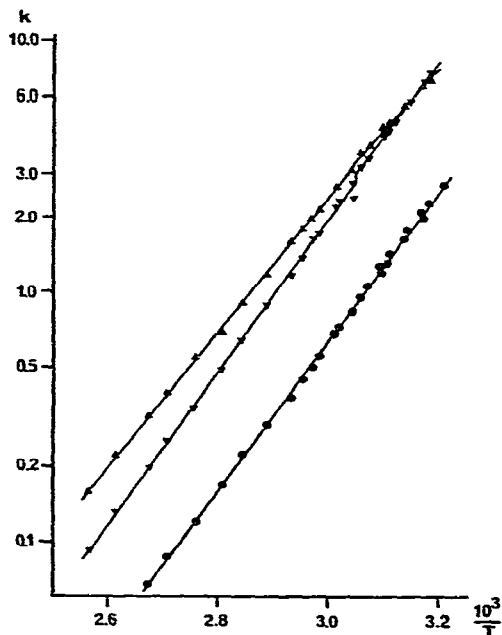


Fig. 2. Variation of  $\log k$  with  $1/T$  for a hydrogen fluoride-etched Pyrex-glass capillary coated with a thin non-extractable layer of Carbowax 20M. Solutes, naphthalene ( $\blacktriangle$ ), octanol ( $\blacktriangledown$ ), and dodecane ( $\bullet$ ).

alcohols<sup>7</sup>, and 1-octanol was eluted from such capillaries rinsed with Carbowax solution, appearing as a peak with severe tailing. Repeated treatment with Carbowax has been suggested as a method of improving deactivation<sup>27</sup>. For AR-glass capillaries repeated rinsing with Carbowax solution led to increased retention of naphthalene and dodecane and decreased retention of octanol (see column 11 of Table I). This might be interpreted as a result of an increased degree of surface coverage, *i.e.*, masking of active sites in the glass surface, affecting the octanol. Further, as a pure layer of Carbowax 20M retains naphthalene strongly, (column 6 of Table I), the increased retention of naphthalene might be explained as the result of an increasing amount of Carbowax attached to the glass after repeated rinsing.

Capillaries on which the Carbowax had been heat-treated were found to be more adequately deactivated, the test compounds giving symmetrical chromatographic peaks upon elution. The properties of such capillaries were unchanged when the deactivation procedure was repeated. Heat treatment of Carbowax capillaries led to increased retention of naphthalene (see Table I). This might be explained by the fact that, in the surface of a film of high-molecular-weight polyethylene glycol, the molecules are entangled and randomly orientated; in such a surface, the concentration of ether and terminal hydroxyl groups of Carbowax 20M capable of specific interaction with, *e.g.*, naphthalene, is considered to be lower than in a film of more regularly orientated molecules<sup>28</sup>. It can be assumed that heat treatment of a Carbowax 20M film will facilitate physical rearrangement of the molecules on the surface, resulting in an increase in the number of available polar functional groups. Additional factors

TABLE I  
CHARACTERISTICS OF SOME TYPICAL 20-m GLASS CAPILLARY COLUMNS

Column No.	Glass type	Etching	Carbowax deactivation			Capacity ratio					
			Coating	Heating	Rinsing	at 45°		at 65°			
						C <sub>11</sub>	Naphthalene	Octanol	C <sub>12</sub>	Naphthalene	Octanol
1	Pyrex	—	—	—	—	≈2.9	≈1.5	—	≈0.9	≈0.9	—
2	Pyrex	HF	—	—	—	≈1.5	≈0.8	—	≈0.4	≈0.3	—
3	AR	—	—	—	—	≈4.6	≈11.0	—	≈1.6	≈5.5	—
4	AR	HF	—	—	—	≈3.0	≈2.1	—	≈0.8	≈0.9	—
5	Pyrex	—	+	+	+	2.1	5.2	6.3	0.6	1.5	1.5
6	Pyrex	HF	+	+	+	1.9	5.7	5.6	0.6	1.8	1.5
7	Pyrex	HF	+	—	+	1.9	2.4	—	0.5	0.7	—
8	Pyrex	HF	+	+	+*	2.1	16.7	11.3	0.7	1.0	1.3
9	AR	—	+	+	+	2.4	3.0	5.2	0.6	1.0	1.5
10	AR	HF	+	+	+	2.0	3.4	5.6	0.5	0.4	2.2
11	AR	HF	+	—	+	1.8	1.5	6.6	0.5	0.6	1.5
12	AR	HCl	+	—	+	2.0	2.0	6.0	0.5	1.5	1.6
13	AR	HCl	+	—	+	2.6	2.0	6.2	0.6	0.6	—

\* Further coated with Carbowax.

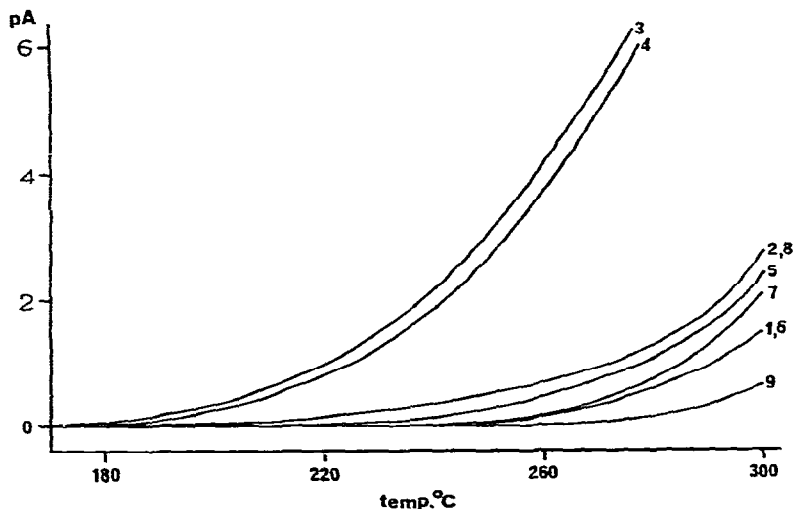


Fig. 3. Relative bleeding rates of 20-m glass capillary columns under a temperature programme of  $5^{\circ}/\text{min}$ . Column types: 1, AR-glass + Carbowax; 2, etched AR-glass + Carbowax; 3, AR-glass + Carbowax + SP-2100; 4, etched AR-glass + Carbowax + SP-2100; 5, Pyrex glass + Carbowax; 6, etched Pyrex glass + Carbowax; 7, Pyrex glass + Carbowax + SP-2100; 8, etched Pyrex glass + Carbowax - SP-2100; 9, Pyrex glass + SP-2100.

contributing to the increased retention of naphthalene could be increased film thickness and surface coverage.

Further, retention of naphthalene was higher for thin Carbowax layers applied to Pyrex glass than to AR-glass, whereas non-treated AR-glass was more active towards naphthalene than Pyrex (see columns 1 and 3 of Table I). It may be that application of Carbowax as a thin film to the more active AR-glass surface saturates many of the ether and hydroxyl groups of the Carbowax, thus leaving a surface having properties different from those of a corresponding film on Pyrex glass.

In order to improve the wetting of the glass wall with Carbowax, the glass was slightly etched with hydrogen fluoride. However, when intending to prepare deactivated non-polar glass capillary columns, such treatment might induce undesirable effects, such as increased activity and roughness<sup>29</sup>. Mild etching with hydrogen fluoride might, on the other hand, be considered as a method for thoroughly cleaning the glass surface, and our results indicate that the retention of naphthalene is lower on a glass surface treated in this manner than on non-etched glass (see columns 1-4 of Table I). Decreased activity after etching with hydrogen fluoride was also observed by Schomburg *et al.*<sup>30</sup>. When coating non-etched glass capillaries with Carbowax, some indications of poor wetting were observed, *e.g.*, "lenses" of thicker Carbowax film in the capillary. However, after heat-treatment and extraction, the degree of deactivation was acceptable, even for these columns. The spreading of Carbowax might, in this instance, have proceeded to some extent in the gas phase (a process similar to that described by Ives and Giuffrida<sup>31</sup>). With Pyrex glass, etching had a favourable effect on deactivation, but etching of AR-glass resulted in slightly impaired deactivation. This result might be expected, as etching with hydrogen fluoride has a more pronounc-

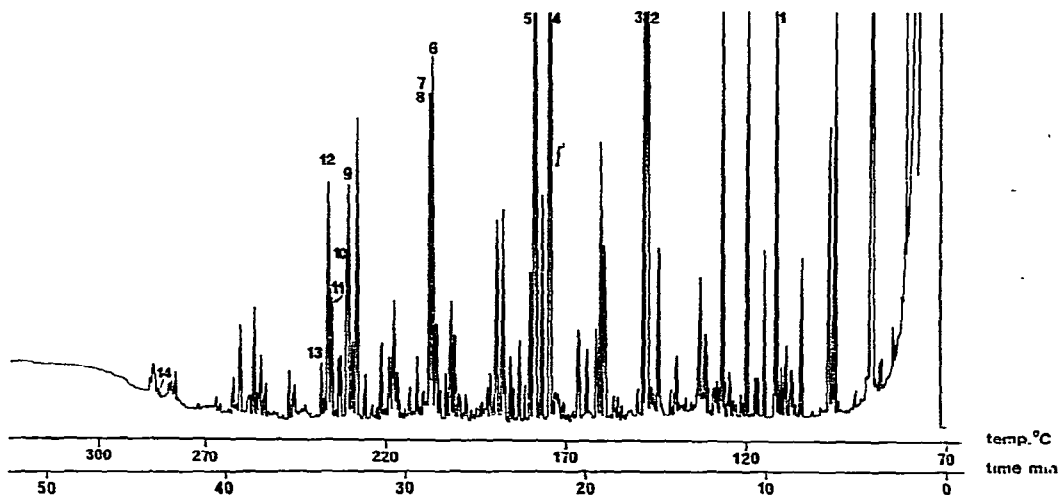


Fig. 4. Gas chromatogram (flame ionisation detector) of a tar sample containing polycyclic aromatic hydrocarbons. Pyrex-glass capillary column (16 m × 0.20 mm I.D.), treated with Carbowax 20M and coated with SP-2100. Initial temperature on injection, 70°; after 1 min programmed to 300° at 5°/min, then isothermal for 4 min. Carrier gas (hydrogen) velocity at 70°, 73 cm/sec. Inlet splitter opened 1 min after injection. Peaks: 1, acenaphthylene; 2, phenanthrene; 3, anthracene; 4, fluoranthene; 5, pyrene; 6, benz [a] anthracene; 7, chrysene; 8, triphenylene; 9, benzo [b] fluoranthene; 10, benzo [k] fluoranthene; 11, benzo [e] pyrene; 12, benzo [a] pyrene; 13, perylene; 14, coronene.

ed effect on AR-glass; further, etching of AR-glass with hydrochloric acid makes it more difficult to achieve a satisfactory degree of deactivation.

The influence of the support on the thermal properties of capillaries deactivated with a thin layer of non-extractable Carbowax was investigated (see Fig. 3). For capillaries coated with a thin Carbowax film only, thermal stabilities were similar for differently treated columns. When coated further with methylsilicone SP-2100, the AR-glass capillaries showed drastically increased bleeding, while a corresponding Pyrex-glass column showed bleeding rates of the same order as those of the capillaries coated with thin Carbowax layers only (see Fig. 3). It is possible that the active AR-glass surface saturates most of the functional groups of the Carbowax, yielding a rather inactive surface, to which adherence of the silicone is inferior. Obviously, ideal deactivation should leave a surface having an activity so adjusted as to be saturated after being coated with stationary phase.

The utility of Carbowax-deactivated Pyrex-glass capillary columns coated with methylsilicone SP-2100 is demonstrated in the analysis of a tar sample containing polycyclic aromatic hydrocarbons. Such a separation puts heavy demands on the chromatographic system. First, the sample may contain several components inclined to adsorption and decomposition, which necessitates use of a low-adsorbing chromatographic system, a short analysis time and the lowest possible temperature of analysis. Further, the samples contain numerous isomers of certain polycyclic aromatic hydrocarbons, some of which have very different tumour-promoting properties, e.g., benzo [a]pyrene and benzo [e]pyrene. For proper evaluation of the sample, such close isomers must be separated, i.e., efficient and/or selective columns are required. Our

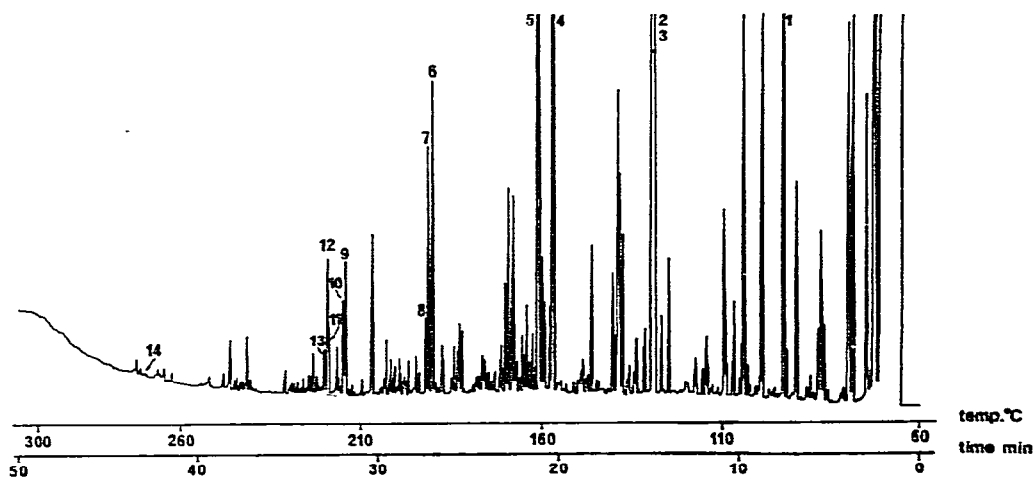


Fig. 5. Gas chromatogram of the same sample as in Fig. 4. Pyrex-glass capillary column (50 m  $\times$  0.20 mm I.D.) coated only with a thin layer of non-extractable Carbowax 20M. Initial temperature on injection, 60°, after 1 min programmed to 300° at 5°/min, then isothermal for 1 min. Other conditions, and peak numbers, as in Fig. 4.

system was developed for routine analysis of polycyclic aromatic hydrocarbons, and it was important to shorten the time of analysis as much as possible. We have attempted to fulfil these requirements by using relatively short, well-deactivated, thin-film, non-polar glass capillary columns and by using hydrogen as carrier gas, so permitting higher flow-rates. To decrease the analysis time, we use a relatively fast temperature programme, which results in higher elution temperatures for the low-vapour-pressure components<sup>32</sup>; the final column temperature is thus the result of a compromise. A typical chromatogram is shown in Fig. 4.

The separation of polycyclic aromatic hydrocarbons on polar columns is also of value. It is difficult to separate some of the polycyclic aromatic hydrocarbon isomers on a non-polar column, and further advantage is gained from the fact that separation on two columns of different polarities increases the certainty of the results. For this purpose, following methods already applied to packed columns<sup>10,33</sup>, we used a capillary coated only with a thin non-extractable layer of Carbowax 20M. Such a column shows poor efficiency. However, since the thin layer of stationary phase allows rapid elution of the sample components, it is possible to compensate for poor efficiency by using a longer column and still to obtain a relatively rapid analysis (see Fig. 5). This is indeed a practical approach, yet, as far as an analytical problem can be solved, it might be justified. By using a 50-m column, it was possible to separate some close isomers that were not resolved on the non-polar column, *e.g.*, the separation of benzo[*b*]fluoranthene from benzo[*k*]fluoranthene and of chrysene from triphenylene (see Figs. 4 and 5). The stability of such a capillary with regard to efficiency and polarity was remarkably good; no deterioration was observed after more than 200 analyses with rapid temperature programming up to 300°.



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