

CHROM. 15,007

CAPILLARY GAS CHROMATOGRAPHY OF AZAARENES

I. PREPARATION OF COLUMNS

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(Received May 3rd, 1982)

SUMMARY

Reproducible methods for the preparation of non-polar, medium-polar and polar capillary columns with suitable wall surface deactivation for the analysis of nitrogen bases are described. Parameters affecting deactivation, efficiency and thermal stability are discussed.

INTRODUCTION

The gas chromatographic analysis of azaarenes, which are nitrogen-containing polycyclic aromatic hydrocarbons (NPAHs), is of widespread interest as these compounds occur in complex mixtures such as tobacco smoke¹, air particulate matter^{2,3}, automobile exhaust⁴, solvent-refined coal⁵, petroleum and recent sediments^{6,7}. The number of possible NPAH isomers increases drastically with increasing number of condensed aromatic rings, much faster than with neutral PAHs⁸. Further, in many mixtures of interest NPAHs occur together with their alkyl-substituted derivatives, which can also exhibit a very large number of isomers.

For these reasons and because of the polarity and low volatility of azaarenes, their gas chromatographic analysis requires capillary columns having four basic qualities: thermal stability, good deactivation level and high efficiency and selectivity. These characteristics are rarely found together in a single column. For instance, very important progress was made recently in the preparation of non-polar columns with deactivation by means of persilylation^{9,10}, but these stationary phases usually lack the necessary selectivity. Numerous methods for the preparation of columns coated with medium-polar or polar phases have been described during the last decade, but most of them have serious drawbacks, giving either irreproducible results or leading to columns that do not exhibit all four of the above qualities.

This situation and our preliminary results obtained in the investigation of petroleum nitrogen bases prompted us to undertake a systematic study of some factors that affect the preparation of columns in order to develop a method with which stationary phases of any polarity could be reproducibly coated.

Despite their wide range of applications, two of the most widespread methods for the preparation of capillary columns (*viz.*, HCl etching of soda-lime glass^{11,12} and barium carbonate treatment^{13,14}) in our hands did not give columns that were very suitable for the coating of very polar liquid stationary phases such as cyano-silicones. Thus, by analogy with the procedure developed for the barium carbonate treatment, we tried to develop a procedure for each class of stationary phase: non-polar, medium-polar and polar.

The procedures described under Experimental are the result of long optimization studies on physico-chemical modifications of the column wall (increase of the inner surface area by treatment with hydrofluoric acid if required and deactivation) in order to generate surfaces showing the best compatibility with a given type of stationary phase. Fused silica, which should provide a highly inert support for non-polar phases, was also evaluated during this study. These experiments involved the preparation and testing of about 100 columns. Columns were evaluated from the results obtained for the standardized test proposed by Grob *et al.*¹⁵ and for a specially designed test including the separation of isomeric and homologous azaarenes (*cf.*, Table I).

EXPERIMENTAL

Glass capillaries (0.2–0.3 mm I.D. and 0.9 mm O.D.) were drawn from Pyrex glass tubes (2.5 mm I.D. and 8 mm O.D., Sovirel, France) with a home-made apparatus. Great care was taken to avoid strong temperature variations during drawing through the use of a drawing furnace having inlet and outlet holes of minimum size and with control of the heating currents of the drawing and coiling furnaces. The quality of the drawn capillaries was checked by measuring the inner diameter of the capillary tubing every metre by means of a microscope. The results showed an average variation of $\pm 2\%$ along a tube length of 50 m, which is of the same order of magnitude as the fluctuations of the inner diameter of the starting glass tube over a length of 1.5 m.

Solvents (pro analysi grade, Merck, Darmstadt, G.F.R.) were glass-distilled before use. Silylating agents were obtained from Fluka (Buchs, Switzerland) and Petrarch Systems (Bristol, PA, U.S.A.).

Leaching

Leaching was carried out on all drawn glass tubes (maximum length 70 m) by filling under pressure with 20% hydrochloric acid; 5% of the volume was left empty at each end of the tube before sealing under vacuum and heating at 180°C for 15 h. After cooling, the tube was emptied and rinsed with distilled water (2 × 1 ml) and methanol (2 × 1 ml), then dried by heating at 250°C and applying the vacuum of a water pump at both ends of the column for 1 h. After discarding the two end parts (2 × 5% of the length), the tubing was cut into pieces of the desired lengths and all end sections were straightened. The columns were then immediately submitted to a deactivation step.

Preparation of non-polar columns

To carry out silylation, a portion of the silanizing agent was sucked into the

column with a water pump and forced through it at a constant rate (1–2 cm/sec). The best results were obtained with the mixture hexamethyldisilazane (HMDS)–diphenyltetramethyldisilazane (DPTMDS)–*n*-pentane (1:2:1, v/v/v).

After the silanizing agent had been forced out of the tube, a vacuum was applied to both ends for 5 min, prior to sealing. After heating at 400°C for 15 h and cooling, the column was rinsed with pentane (two column volumes). Static coating was applied, using a sodium silicate seal; stationary phases were dissolved in either dichloromethane or pentane.

Fused-silica columns from various commercial sources (SGE, Milton Keynes, Great Britain, Phase Separations, Queensferry, Great Britain and Quartz et Silice, Paris, France) were rinsed first with pentane, then silylated at 310°C for 20 h and statically coated.

Preparation of medium-polar columns

Prior to hydrochloric acid leaching, the inner surface of the tube was roughened by hydrofluoric acid treatment, using a freshly prepared solution of ammonium hydrogen difluoride (NH_4HF_2 , 1%, w/v, in methanol). Each portion of the inner wall surface of a column must be in contact with the solution for the same period of time. Hence the same speed (4–5 cm/sec) was used for filling and emptying the column, and the time during which the column was allowed to stay was adjusted as a function of column length (10 min for a 25-m tube, whereas for a 50-m tube the column was filled and immediately emptied). After drying under a stream of nitrogen until it became opaque, the column was sealed with a flame, heated at 400°C for 4–5 h and then submitted to leaching.

Deactivation was achieved by silylation carried out as described for the non-polar columns. Static and dynamic coating using a mercury plug¹⁶ were used equally.

Preparation of polar columns

The same hydrofluoric acid treatment was applied first, except that a longer contact time was used (20 min for a 25-m column and 10 min for a 50-m column). Leaching was carried out as for the non-polar columns.

Instead of deactivating the column wall surface using the silanization treatment, a portion of a polyglycol solution (20% Carbowax 1000 in dichloromethane) was forced at a constant rate (2 cm/sec) through the column, which was emptied in the same way. After drying under argon, the column was sealed with a flame and heated at 280°C for 15 h. After cooling, the column was rinsed with 5 ml of dichloromethane and coated dynamically with the stationary phase.

Equipment

Several gas chromatographs were used during this work: Carlo Erba Models 4160 and 2151 and a Perkin-Elmer Model Sigma 3. The carrier gas was hydrogen, which allows lower pressure drops and faster analysis than helium.

RESULTS AND DISCUSSION

The chemical inertness and the thermal stability exhibited by persilylated glass capillary columns¹⁰ induced us to try to extend this deactivation procedure to all

types of stationary phases. A smooth persilylated glass surface, however, can only be wetted by non-polar phases, and a drastic decrease in efficiency is observed when the polarity of stationary phases exceeds that of SE-52 (5% phenyl groups for a methylsilicone); the surface tension of the liquid phase is too large and the surface energy of the silylated glass is too low.

A first type of solution consists in chemical modification of the surface, using silanizing agents that can generate a surface compatible with the stationary phase. We have applied this approach, which has been used previously by several workers^{10,17-19}, to the coating of phenylmethylsilicones (medium-polar stationary phases) after reacting the silanol groups of the glass surface with phenyl-substituted di-silazanes.

In a second approach, the surface of the inner walls of the columns is increased by controlled treatment with hydrofluoric acid, prior to the deactivation step²⁰. This procedure has been used for medium-polar and highly polar phases.

In all instances, we have tried to demonstrate the influence of the particular treatment applied to a column by comparing its performances with those of the persilylated non-polar columns which can be prepared with a high degree of reproducibility. Two basic characteristics were considered for this purpose: coating efficiency and deactivation level with regard to azaarenes. Thus, a certain number of parameters were kept constant (column length, 25 m; I.D., 0.3 mm; and film thickness, 0.15 μm). Nevertheless, the influence of column length and film thickness were also evaluated, particularly for the preparation of polar columns.

Evaluation of columns

A fairly complete evaluation of the quality of a column can be obtained by the test designed by Grob *et al.*¹⁵, as it combines qualitative and quantitative aspects with regard to the inertness of the column walls. An example is given in Fig. 1. A 100% and tail-free elution of 2,6-dimethylaniline is necessary for the analysis of azaarenes. Dicyclohexylamine, often fully adsorbed on non-polar coatings, is a very sensitive indicator of column acidity.

Isomeric and homologous reference azaarenes were chosen as constituents of a test mixture because their separation can only be achieved on columns that are sufficiently inert and also possess good selectivity and efficiency. The structures of these di- and tricyclic aromatic nitrogen bases are given in Table I. Typically the same temperature programming rate used for the analysis of the Grob test mixture was applied to the separation of this series of compounds.

Coating efficiencies (CE) were used for the evaluation of the quality of the film of phase. CE is defined as the ratio of the theoretical to the experimental plate height under optimum conditions^{22,23}:

$$\text{CE} = \left(\frac{H_{\text{theor.}}}{H_{\text{exp.}}} \right)_{\text{min}} = \frac{r \left(\frac{11k^2 + 6k + 1}{3(1 + k)^2} \right)^{1/2}}{H_{\text{exp. min}}}$$

where H = plate height, r = column radius and k = capacity ratio of a solute, assuming in the calculation of the theoretical plate height that the resistance to mass transfer in the liquid phase is negligible, an ideal situation.

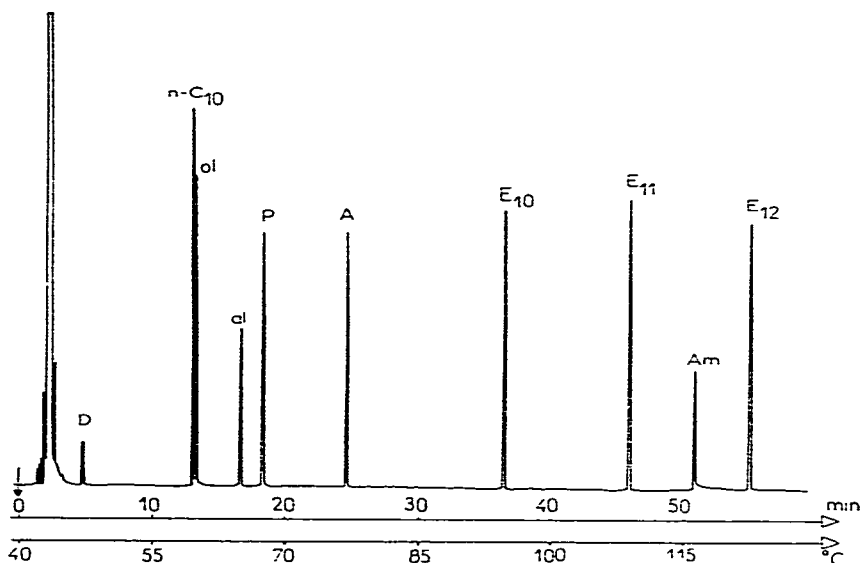


Fig. 1. Separation of a test mixture according to Grob *et al.*¹⁵ on a non-polar stationary phase (ethylene-propylene copolymer²¹). Column length, 34 m; I.D., 0.3 mm; film thickness, 0.22 μm . Peak identification: ol = *n*-octanol; al = nonanal; P = 2,6-dimethylphenol; A = 2,6-dimethylaniline; E₁₀-E₁₂ are methyl esters with 10-12 carbon atoms, respectively; Am = dicyclohexylamine.

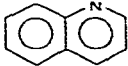
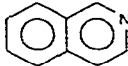
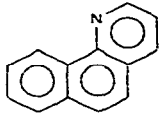
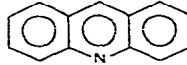
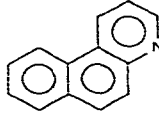
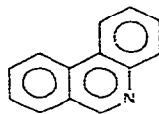
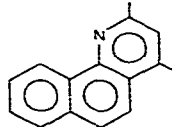
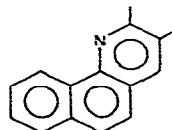
This equation, although it fails to describe correctly some practical situations, giving values higher than 100% for non-polar stationary phases coated on smooth surfaces and too small values for roughened surfaces on which the phase is not evenly distributed²⁴, allows a reasonable comparison between columns. As a rough empirical rule, even coatings, resulting in efficient columns, are found for columns with CE values higher than 70%.

Non-polar columns. Columns coated with non-polar stationary phases that are prepared according to the barium carbonate procedure^{13,14} usually possess the degree of deactivation required for the analysis of azaarenes⁶ but their thermal stability is limited to 260-280°C, which is significantly lower than the limit exhibited by columns deactivated by persilylation. Therefore, and also because the barium carbonate procedure is time consuming, wall deactivation by high-temperature silylation is clearly preferable. However, during our preliminary experiments, we were first unable to achieve the degree of chemical inertness demonstrated by columns prepared by the barium carbonate procedure. It became obvious that the various experimental parameters affecting the quality of leaching had to be optimized in order to permit proper deactivation of the glass surface in the absence of a barium carbonate layer.

The parameters investigated were the temperature and time of leaching, the length of tube treated and the conditions of rinsing and drying. The results for the first three points were similar to those of Grob *et al.*¹⁰, but we noticed some differences in column performance when using different batches of glass tubes. Thus, a general recommendation is to work as long as possible with the same batch of glass, *i.e.*, to buy it in large amounts. The rinsing step, effected after the hydrochloric acid treatment, may affect the acid-base activity of columns. Various combinations, in-

TABLE I

REFERENCE AZAARENES CONSTITUTING THE TEST MIXTURE USED FOR COLUMN EVALUATION

<i>Compound No.</i>	<i>Name</i>	<i>Structure</i>
1	Quinoline	
2	Isoquinoline	
3	Benzo[<i>h</i>]quinoline	
4	Acridine	
5	Benzo[<i>f</i>]quinoline	
6	Phenanthridine	
7	2,4-Dimethylbenzo[<i>h</i>]quinoline	
8	2,3-Dimethylbenzo[<i>h</i>]quinoline	

cluding the use of distilled water, 0.1–1 % hydrochloric acid and 0.1–1 % potassium hydroxide solution (1–5 column volumes), were tried without producing any significant or reproducible changes in the acid–base character of the glass surface. As outlined by several workers^{10,25,26}, the most important step in the preparation of a surface that can be properly silylated is dehydration, involving the removal of physically and chemically sorbed water and the production of an adequate concentration of silanol groups.

TABLE II

COMPARISON OF SILANIZING AGENTS USED FOR PERSILYLATION OF GLASS CAPILLARY COLUMNS COATED WITH NON-POLAR STATIONARY PHASES

<i>Deactivating solution</i>	<i>Proportions*</i>	<i>Temperature (°C)</i>	<i>Time (h)</i>	<i>Inertness towards hydrogen bonding</i>	<i>Inertness towards NPAH adsorption</i>	<i>Remarks</i>
HMDS-DPTMDS- <i>n</i> -pentane	1:0:1	400	12	+++	+++	
	1:1:2	390	10	++	+++	
	1:2:1	400	15	++++	++++	
	1:3:1	400	15	+++	+++	
TPDMDS-DPTMDS-diethyl ether	1 ml:1 g:5 ml	360	15	++	+++	
TPDMDS-diethyl ether	1.5 g:5 ml	400	15	+++	+++	<i>Cf.</i> , ref. 10
F ₃ F ₄ -dichloromethane**	2 g:5 ml	380	15	(+++)	(+++)	Irreproducible results.

* By volume except where specified otherwise.

** (3,3,3-Trifluoropropyl)methylsiloxane cyclics, *cf.* ref. 19.

Various combinations of silylating agents were tested in order to determine the degree of deactivation they provide. As shown in Table II, a mixture of HMDS, DPTMDS and pentane (1:2:1) was found to be most effective when used at 400°C. In general, the highest possible temperature should be used with a reaction time of not less than 12 h. Columns treated with tetraphenyldimethyldisilazane (TPDMDS) were found to be slightly active, the incompleteness of the deactivation being probably due to the large size of this reagent molecule.

TABLE III

COMPARISON OF COATING EFFICIENCIES AND THERMAL STABILITIES OBTAINED BY VARIOUS METHODS OF PREPARATION FOR NON-POLAR, MEDIUM POLAR AND POLAR STATIONARY PHASES

<i>Stationary phase</i>	<i>HF roughening</i>	<i>Deactivation</i>	<i>Mean value of coating efficiency</i>	<i>No. of columns</i>	<i>Limit of thermal stability (°C)</i>	<i>Remarks</i>
OV-1	-	HMDS-DPTMDS	105	10	280-300	
OV-73	-	HMDS-DPTMDS	110	10	280-300	
OV-73	+	HMDS-DPTMDS	75	3	280-300	
Dexsil 400	-	TPDMDS-DPTMDS	110	1	240	Film breaking after 2 days
SP-2250	-	TPDMDS-DPTMDS	70	2	260-270	Slightly active
OV-61	-	TPDMDS-DPTMDS	70	3	260-270	
OV-61	+	Polyglycol	85	5	250-260	
OV-61	+	HMDS-DPTMDS	90	3	280-290	
OV-225	+	HMDS-DPTMDS	75	2	260-270	
Pluronic L4	+	TPDMDS	55	2	220-230	
Pluronic L64	+	Polyglycol	75	3	230-240	
SP-2340	+	Polyglycol	85	5	270-280	

The method of preparation described under Experimental has been found to be very reproducible, yielding columns with coating efficiencies between 100 and 110% (Table III). Most columns were found to be neutral, but some had a slightly basic character; this could not be prevented from happening from time to time in spite of careful control of all of the investigated parameters. The recent work by Grob and Grob²⁷ on immobilized vinylsilicone stationary phases seems promising for obtaining control of the basicity of a glass surface. Nevertheless, azaarenes which are more or less strongly basic can be studied on persilylated non-polar columns, some of the most basic compounds of this series (quinoline and isoquinoline) being eluted without adsorption (Fig. 2). Such columns are very useful for the analysis of high-molecular-weight azaarenes, because they compensate for their lack of selectivity, demonstrated by the incomplete separation of benzoquinoline isomers, by high thermal stability, allowing routine temperature programming up to 300°C. The separation of nitrogen bases having up to seven fused aromatic rings is an illustration of this feature (Fig. 3).

Medium-polar columns. Two basic approaches have been used: on the smooth surface obtained after hydrochloric acid leaching, deactivation by silanizing agents using various amounts of different phenyl-substituted silicon derivatives; and on the roughened surface obtained after hydrofluoric acid treatment followed by hydrochloric acid leaching, deactivation by either silylation or high-temperature degradation of various stationary phases.

The first approach, designed for methylphenylsilicones as stationary phases, generated inert surfaces that could be coated by several phases having polarities lower than or equal to that of SP-2250 (50% phenyl groups) when a mixture of TPDMS and DPTMDS was used. However, values observed for the coating efficiencies and

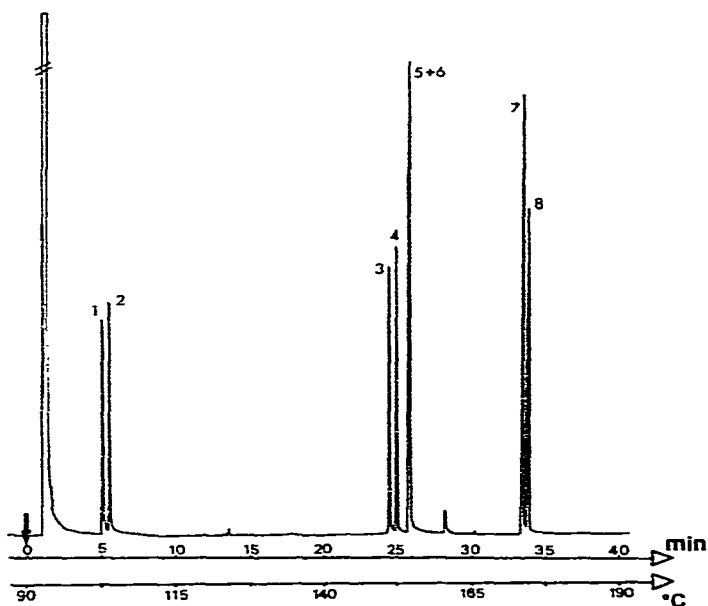


Fig. 2. Separation of reference azaarenes on a non-polar stationary phase (OV-1; *cf.*, Table III). Column length, 25 m; I.D., 0.3 mm; film thickness, 0.15 μm . For peak identification, see Table I.

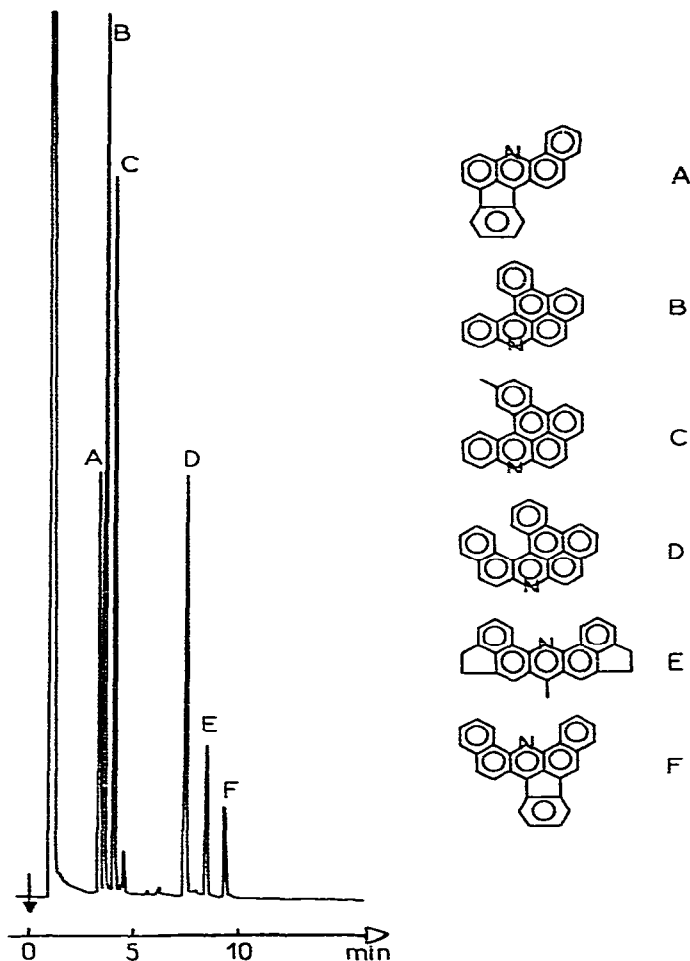


Fig. 3. Separation of high-molecular-weight reference azaarenes. Stationary phase, SE-52; column length, 30 m; I.D., 0.3 mm; film thickness, 0.15 μm ; temperature, 280°C.

the thermal stability were disappointing if compared with those obtained with the non-polar stationary phases (Table III). This fact was not too surprising, however, and also because gum phases usually give better results than fluid ones, but it was obvious that the surfaces obtained with this procedure were not ideally wetted by medium-polar phases. Hence we conclude that this particular approach should be restricted to stationary phases having a polarity lower than that of OV-61 (33% phenyl groups).

In a second approach, we applied a hydrofluoric acid treatment using a procedure similar to that described by Onuska *et al.*²⁰. Three points require special attention in this method: the regularity and the intensity of the attack and the production of a well deactivated surface. The roughening intensity can be varied by changing the contact time of the ammonium hydrogen difluoride solution with the glass surface; of course, when adjusting the contact time, the column length and the time necessary for filling and emptying must be taken into account.

Deactivation was carried out after hydrochloric acid leaching, by means of various methods including polyglycol deactivation^{13,28,29}, stationary phase degradation³⁰ and persilylation. Treatment with Carbowax 1000 at 280°C is as effective as persilylation as a deactivation method, but with the drawback of a lower thermal stability (around 250°C, as shown in Table III). The degradation of stationary phases other than polyglycols is also efficient and this treatment has often been applied to the recycling of columns, before recoating with a new stationary phase. Deactivation levels achieved with hydrofluoric acid-treated and non-roughened surfaces are comparable, which again demonstrates the high efficiency of persilylation. Values of coating efficiencies obtained by the second method (hydrofluoric acid treatment, hydrochloric acid leaching, persilylation) were found to be reproducible, significantly higher than in the absence of roughening for the same stationary phase, but also lower than values obtained for non-polar gum phases on a smooth surface (Table III).

The increase in the polarity of stationary phases obtained by increasing the amount of phenyl substituents in silicone polymers results in an improved separation of isomeric reference azaarenes (Fig. 4), but as for non-polar methylsilicones the elution sequence follows the number of carbon atoms in the skeleton. This aspect of stationary phase selection will be discussed in a forthcoming paper.

Polar columns. A roughened surface is a fundamental requirement for even coating of polar stationary phases. The same hydrofluoric acid treatment, but with an increased intensity of attack, was used, followed by hydrochloric acid leaching. Persilylation of such surfaces still yielded fairly inert columns, as demonstrated by tests run with non-polar stationary phases, that is, with stationary phases that do not have shielding effects on the active sites. However, all coatings of polar stationary phases rapidly separated into visible droplets, whether at room temperature or after brief

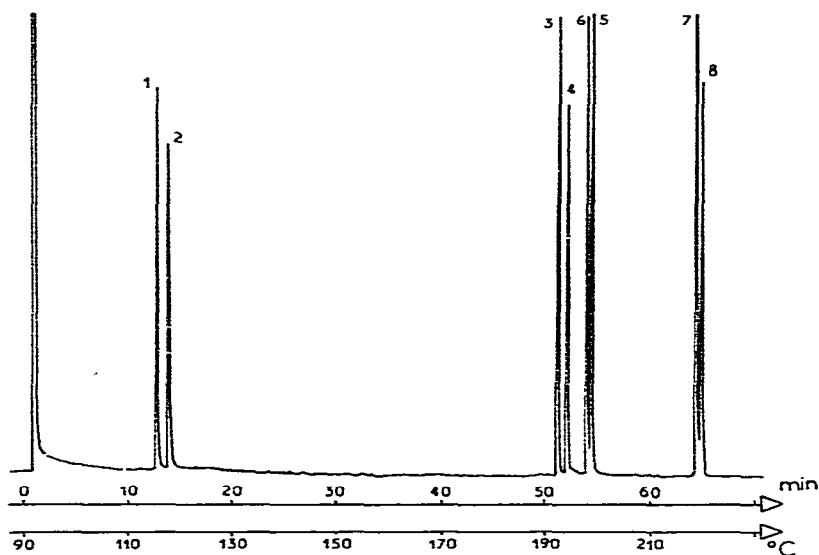


Fig. 4. Separation of reference azaarenes on a medium-polar stationary phase (OV-61; cf., Table III). Column length, 40 m; I.D., 0.3 mm; film thickness, 0.21 μm . For peak identification, see Table I.

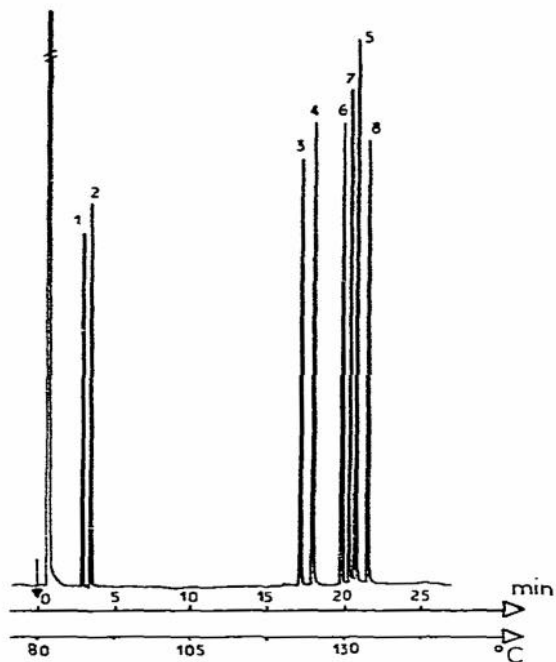


Fig. 5. Separation of reference azaarenes on a polar stationary phase (SP-2340; *cf.*, Table III). Column length, 20 m; I.D., 0.3 mm; film thickness, 0.15 μm . For peak identification, see Table I.

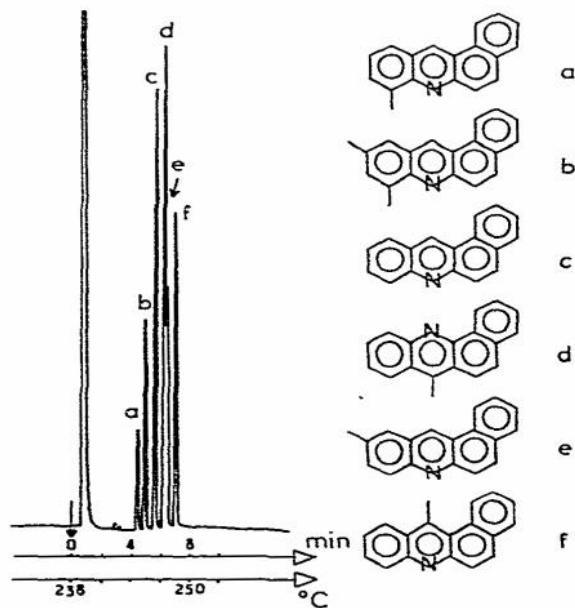


Fig. 6. Separation of benzacridines on SP-2340. Column characteristics as in Fig. 4.

heating. Thus, polyglycol deactivation, with which this last phenomenon does not occur, seemed to be the most useful method. Results in terms of efficiency and deactivation were good, as shown in Table III. As for medium-polar columns, thermal stability is limited around 250–260°C in routine use, but some columns coated with SP-2340 (75% cyanopropyl, methylsilicone) could be programmed up to 280°C without observing too high bleeding rates.

Such columns provided the required selectivity for the separation of isomeric azaarenes, as shown for instance when comparing Fig. 5 with Fig. 2. The higher limit of molecular weight or degree of aromaticity of solutes that can be analysed on polar columns is, of course, lower than for non-polar coatings, usually lying between four and five fused rings. Silicone stationary phases substituted by cyano groups are interesting because of their thermal stability and particular selectivity, as illustrated by the separation of tetraaromatic benzacridines on SP-2340 (Fig. 6). On such a stationary phase, the elution sequence of azaarenes is no longer mainly related to the number of carbon atoms in the skeleton, but to the steric hindrance around the nitrogen atom, with a high selectivity for different locations of this latter atom.

Fused-silica columns. Because of the intrinsic characteristics of fused silica, these columns can usually be coated only with non-polar stationary phases or polyglycols³¹. Leaching can be omitted because of the high purity of this material, which results in a significant gain in time during the preparation. Thus, fused silica deactivated by persilylation seemed to be an ideal support for non-polar stationary

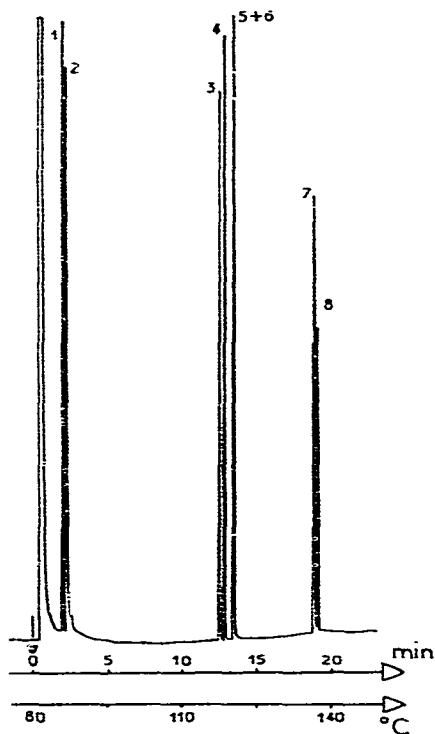


Fig. 7. Separation of reference azaarenes on a fused silica column coated with a non-polar phase (OV-1). Column length, 15 m; I.D., 0.32 mm; film thickness, 0.16 μm . For peak identification, see Table I.

phases. To our disappointment, we commonly observed that deactivation led to silica surfaces with irreproducible qualities. The results varied greatly with the commercial origin of this material, and also with the position along a single tube 100 m long. At the time when this study was discontinued, it was obvious that persilylated fused-silica columns were slightly more acidic than deactivated glass columns, as indicated by the tailing observed for the peaks of some basic compounds, both with the Grob test mixture and with reference azaarenes (e.g., isoquinoline, peak 2 in Fig. 7). These poor results were probably due to the poor quality of the outer coatings and to the fact that most of these coatings do not withstand temperatures higher than 300°C for any significant length of time, preventing us from carrying out the silanization reaction at 400°C, which reduces significantly its efficiency. Other problems are presumably related to the number of hydroxy groups present on the silica surface; this concentration can be properly adjusted, but only with a time-consuming treatment. All of these drawbacks render this material much less attractive in comparison with glass. As this material is still restricted to a very limited number of stationary phases, we prefer glass, as it is possible to prepare reproducibly tailor-made glass columns. Nevertheless, it must be emphasized that we did not carry out exhaustive tests on all commercially available fused-silica tubings and that improved outer coatings should soon appear on the market.

CONCLUSION

Reproducible results in terms of deactivation and efficiency could be obtained by using one of the three methods described under Experimental depending on the polarity of the stationary phase selected. The columns prepared in this way have been applied to the separation of azaarenes from petroleum; a discussion of the results will be presented in a forthcoming paper. Significant improvements are still necessary with medium-polar and polar columns in order to match the qualities exhibited by non-polar columns. The preparation of immobilized polar stationary phases^{32,33} and of highly thermostable stationary phases, preferably gums, may be the keys to the solution of this problem.

ACKNOWLEDGEMENTS

The authors thank Mr. G. Préau for having drawn several kilometres of capillary tubing over a number of years.

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