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## CAPILLARY COLUMNS WITH IMMOBILIZED STATIONARY PHASES

### II. PRACTICAL ADVANTAGES AND DETAILS OF PROCEDURE

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#### SUMMARY

Experimentally demonstrated advantages of stationary phase immobilization are considered, namely, prevention of thermal rearrangement, prevention of phase stripping, sharper peaks of solvent and major sample components, regeneration of columns by solvent washing, thick films produced from fluid phases, low bleeding rates, easy recoating and repeated coating to produce sandwich coatings. The cross-linking reaction which produces an immobilized stationary phase is strongly dependent on the structure of the stationary phase. OV-61 is representative of stationary phases having the maximum polarity allowing immobilization. The polarity limit will probably be shifted to higher values. Immobilization as a method of producing stable coatings on difficult to wet support surfaces is limited to support-stationary phase combinations providing nearly perfect wettability. The selection of a suitable peroxide for the cross-linking reaction is discussed. Based on arguments such as activity, cross-linking efficiency, influence of decomposition products, volatility, stability in solution, and safety of handling, a clear preference for a dialkyl peroxide, *e.g.*, dicumyl peroxide, is indicated. Appropriate peroxide concentrations are discussed, and detailed instructions for the immobilization procedure are given. Particular attention is paid to solvent washing of the immobilized stationary phase columns.

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#### INTRODUCTION

Immobilization of stationary phases seems to generate wide interest. Although some of this interest is justified, some is exaggerated and only practical experience will create a realistic picture of the nature and extent of the advantages offered by the technique. To increase the availability of experimental information, the results presented have supplemented those in our previous paper<sup>1</sup>.

#### MERITS OF IMMOBILIZATION

As stated previously<sup>1</sup>, immobilization is expected to offer two new possibilities: first, stabilization of the coating in cases where the wettability of a support surface for

a given liquid is not sufficient to ensure film stability, and second, non-extractability of the immobilized coating.

In our hands progress has proceeded primarily with the second aspect, advances with the first being slow. However, we consider that the modest results of the attempts to overcome the difficulties of insufficiently wettable, inert, thermostable surfaces by immobilization do not indicate an unrealistic expectation but rather the necessity for more fundamental work.

Below we list the advantages of the immobilization we have observed on our laboratory.

#### *Prevention of thermal rearrangement*

It is well known that the separation efficiency of freshly coated columns may decrease during the first conditioning, even when the support is sufficiently wettable for the given stationary phase. The decrease is most pronounced in the first few hours, then the efficiency tends to approach a plateau. As a rule, the decrease is smallest on smooth support surfaces and increases with increasing roughness. Further, it is also smallest with gum stationary phases<sup>2</sup> and increases with increasing fluid character of the phase.

The phenomenon is termed thermal rearrangement to account for its probable source. Prolonged heating may cause the stationary liquid to assume its most stable distribution which is, even under ideal wettability conditions, not necessarily identical with a coherent film of constant thickness. Deviation from ideal film symmetry is revealed by a reduction in separation efficiency.

Provided that this model explanation is correct, immobilization is expected to minimize thermal rearrangement as it is the final component in the sequence fluid film/gum film/immobilized film. The empirical verification of this hypothesis will require broad statistical comparisons. We are at present working primarily with gum stationary phases on smooth surfaces. As thermal rearrangement is very small anyway under these conditions, it is not easy to detect significant changes caused by immobilization. The differences will increase when the work expands to more polar stationary phases which are available as fluids and may require roughened surfaces. Our preliminary results with such stationary phases permit us to state that the concept of thermal rearrangement is correct and that immobilization plays the expected role.

#### *Prevention of phase stripping*

The danger of damaging a column by allowing an appreciable sample volume to be condensed in the column inlet section is well known. In the course of large-volume on-column or splitless injections, the danger can hardly be totally excluded, even with very careful planning and manipulation. Probably the most direct and clear-cut merit of immobilization is the complete avoidance of this danger. As far as physical film modification is concerned (simultaneous heavy contamination is a separate problem), immobilized coatings are positively resistant to any conceivable stress exerted by sampling.

#### *Behaviour under overloading*

Heavy overloading causing large amounts of sample to be dissolved in the

stationary phase is related to but different from the phenomenon discussed in the previous section as long as the influence on the stationary phase is reversible and no dislocation of coating material occurs.

A valuable, though hardly expected, influence of immobilization on overloading was first observed by Blum<sup>3</sup>. The influence has nothing to do with the overloading mechanism causing broadened, in most instances leading, peaks. A large amount of dissolved sample material seems to cause a transient structural modification, possibly swelling, of the stationary phase. It seems that the original structure of the stationary phase may be restored only with some delay. This delay results in tailing, which occurs on all columns, including those from which substances of virtually all classes elute without tailing as long as overloading is avoided. The phenomenon is commonly known from the difficulty of detecting (and, particularly, quantifying) minor sample components eluted soon after a major component (see Fig. 1). The tailing effect is greater for the solvent peak (which may, however, also be caused by unsatisfactory equipment or manipulation).

It seems that an immobilized coating is structurally less influenced by a large amount of solute. Elution is less delayed, resulting in a rapid return to an undisturbed baseline.

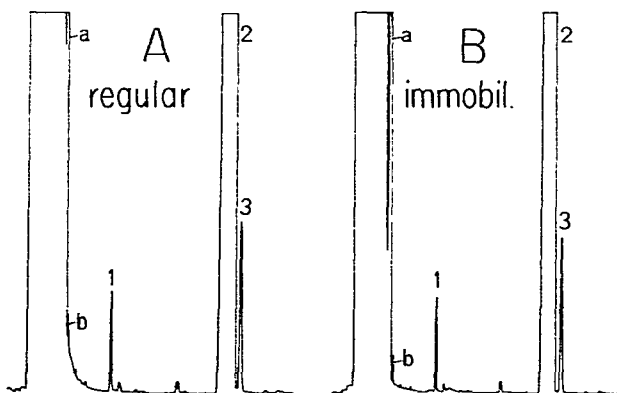


Fig. 1. Difference in resolution following bands with high solute concentration. Columns A and B are identical (16 m  $\times$  0.32 mm I.D., persilanized, 1.8- $\mu$ m OV-1) except that A is not cross-linked and B is immobilized with 0.4% DCUP at 160–180°C. 1 = Toluene; 2 = ethylbenzene; 3 = *p*-xylene; 2 and 3 are present in a ratio of 500:1. Solvent: *n*-hexane (with impurities a, b). Column temperature, 40°C; 2.0  $\mu$ l injected, splitless, 30 sec; carrier gas, hydrogen; standard flow-rate (0.5 m/sec). Compared with B, the stationary phase in A shows delayed recovery from heavy loading with solute. The effect is best seen at the rear end of the solvent band (peak shape, positions of a and b), and less clearly by the ethylbenzene-*p*-xylene resolution (2; 3). The poorer resolution by A seems to be caused by a generally broadened peak 2.

### Solvent washing

Large-volume injections often cause damage to the column, which has nothing to do with phase stripping or overloading. The typical symptom is an unchanged separation efficiency and increased adsorptive activity which may affect only certain sample components. In a very general (probably oversimplified) way, we attribute the damage to low-volatility or non-volatile sample components contaminating the coating. In certain instances a sample clean-up may prevent the phenomenon. In other

instances the only remedy is to break away a length of the column inlet. The lifetime of routinely used columns is often limited by an excessively reduced column length resulting from periodically repeated "therapy".

Fig. 2 shows an example of real "therapy" that can be given to columns with immobilized coatings. The damage, resulting in increased adsorption activity from an unknown cause, could not be repaired by discarding an inlet section of reasonable length (1.5 m). In contrast, a rapid (2 h) wash totally restored the original column quality.

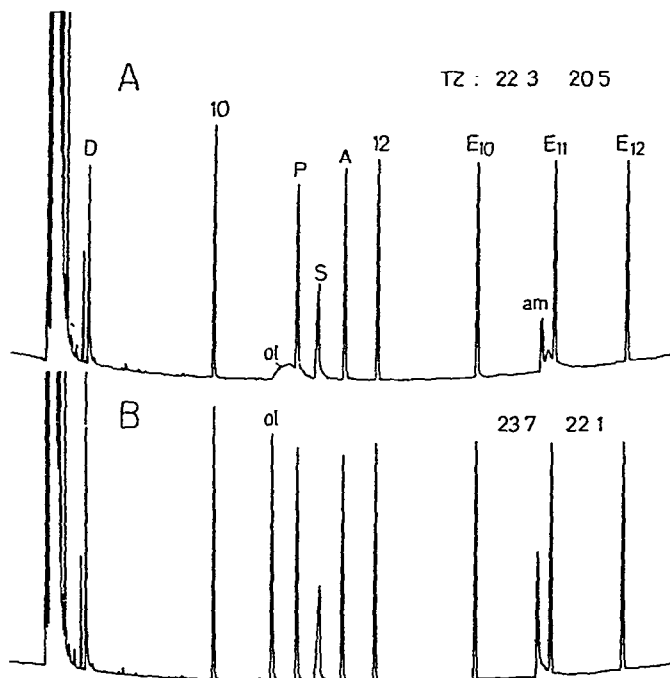


Fig. 2. Regeneration of a damaged column by washing. Column, 13 m  $\times$  0.32 mm I.D.; persilylated with HMDS; 0.3- $\mu$ m OV-1, cross-linked with 0.2% of DCUP at 160°C. Comprehensive, standardized quality test<sup>2</sup>. (A) Test after 3 weeks of continuous analysis of non-ionogenic detergents (free polyethoxylated nonylphenols) extracted from water<sup>5</sup>. Deteriorating results (poorer separation and quantification of detergents) necessitated a quality test, which showed severe adsorption of the slightly basic hydroxyl function (ol = 1-octanol), and weaker adsorption of more acidic hydroxyl groups (D = butanediol; P = dimethylphenol; S = ethylhexanoic acid). The basic substances (A = dimethylaniline, am = dicyclohexylamine) were even less affected. The alkanes (10 = decane; 12 = dodecane) and the esters (E<sub>10</sub>-E<sub>12</sub> = decanoic, undecanoic and dodecanoic acid methyl esters) were symmetrically eluted with nearly standard separation efficiency. The nature of damage was unknown; earlier experience had shown that discarding a 1-1.5 m long inlet section did not help, *i.e.*, the damage was not restricted to the inlet section. (B) The same test after washing the entire column with methylene chloride, methanol and *n*-pentane (for details, see text) for 1.5 h. The original quality was restored (note particularly ol), with a slightly increased separation efficiency. The elution temperature (film thickness) was not reduced. The detergents were again analysed with perfect results.

Although this example is not an isolated one, we are not yet able to discuss the range of applicability of the "therapy". We presume that damage may also be caused by insoluble contaminants. Rules concerning the application of solvent washing (in-

cluding solvent selection; see also the last section) have to be deduced from numerous long-term experiments.

#### *Thick films produced from liquid phases*

Gum stationary phases may be considered to be intermediates between fluids and immobilized films. Consequently, gums could be regarded as being dispensable, as immobilized coatings can be obtained directly from fluid phases. The preparation of immobilized coatings from fluid phases even offers a distinct advantage: much thicker films can be produced with fluid phases than with gum phases, owing to the much lower viscosity of solutions of fluid phases.

Our experiments have confirmed these expectations. However, practical realization is not necessarily easy. The period between the static deposition of the fluid film and the cross-linking reaction is a critical time during which the fluid phase may assume an irregular distribution or collapse. Preventing the trouble by adding a peroxide with a low decay temperature is feasible, but this creates the danger of premature cross-linking and consequent column plugging during static coating.

We have had complete success in preparing thick films from fluid phases after modifying three aspects of the procedure developed for gum stationary phases:

(1) Premature film breakage is delayed by adding some gum stationary phase. For example, a 3% coating solution (which can hardly be manipulated when prepared from a pure gum stationary phase) works perfectly when prepared from 2% OV-101 (fluid) and 1% OV-1 (gum).

(2) It is advantageous to use the less stable BP instead of DCUP (see *Selection of the peroxide*) for cross-linking.

(3) To produce an equivalent cross-linking effect, roughly three times more peroxide is required with OV-101 than with OV-1.

#### *Bleeding behaviour*

Immobilized coatings have reduced bleed rates. We assume that cross-linking prevents volatilization of fragments of the polymer chains produced by thermal or chemical breakdown.

In addition to this generally different bleeding behaviour, a substantially more important difference is associated with periodic solvent washings during long-term use. Thorough washing may eliminate both causes of bleeding, *viz.*, low-molecular-weight breakdown products of the stationary phase, and active, non-volatile substances (sample by-products, chemically altered stationary phase) which promote polymer breakdown. Accordingly, immobilized coatings offer an entirely new potential in the field of low-bleed capillary gas chromatography (GC), the practical utilization of which is far from being realized at present.

#### *Recoating; repeated coating*

The problem of recoating apolar silicone columns has a complex history. For many years very poor columns were obtained when expired silicone columns were washed and recoated. The effect was attributed to so-called autophobicity<sup>6</sup>. It was the success of Schomburg *et al.*<sup>7</sup>, who introduced a column preparation procedure based on the recoatability of a silicone-treated surface, that caused us to re-examine the situation. We found that recoating was practically impossible on the more active

support surfaces that we had used for many years. On persilylated surfaces it is feasible, but the quality of the recoated columns is frequently below the original quality.

A clear advantage of immobilization is that it allows the reliable production of high-quality columns on washed support surfaces, even those which have had previous silicone coatings. It seems that only the use of stationary phase immobilization conditions will permit the old "recoatibility problem" to be finally overcome.

A second (immobilized) coating may also be produced on a first layer which cannot be extracted because of cross-linking. This process results in an addition rather than in replacement. Consequently, it might be termed repeated coating instead of recoating. Our experience is not sufficient to discuss the potential of repeated coating. We state simply that the technique works easily and reliably. Its primary effect is, of course, an increased film thickness. Additional, more complex effects are observed when the stationary phase used for the second coating differs from the first one. We have produced such mixed phases (sandwich coatings) without difficulty. However, we have not yet investigated their practical applicability.

We repeat that all of the advantages of immobilization listed have been experimentally proved. Of course, this does not mean that the list is complete. An important advantage is expected in HPLC on capillary columns.

#### ROLE OF THE STATIONARY PHASE

The dependence of immobilization on the structure of the stationary phase is strong. However, this is not surprising in view of the established knowledge in the field of manufacturing silicone rubbers<sup>8</sup>. With adaption for the application to capillary GC, this knowledge may be summarized as follows.

The most frequent cross-linking reaction induced by peroxy radicals occurs between methyl groups of neighbouring silicone molecules. It is probable, though not proved, that it also occurs between methyl groups of the silicone and those of the persilylated support surface. This would then result in surface bonding rather than cross-linking.

The cross-linking between methyl groups is effectively hindered by phenyl side-groups of the polysiloxane chain and, less effectively, also by cyanoalkyl groups. In contrast, vinyl side-groups are even more reactive than methyl groups as points for cross-linking.

The practical importance of these rules may be demonstrated by describing the cross-linking behaviour of several common silicone stationary phases. The model substances for easy cross-linking are pure methyl polysiloxanes such as SE-30, OV-1 and OV-101. The ease of reaction is indicated by the small amount of peroxide [*e.g.*, 0.4% (w/w based on the stationary phase)] required to produce a non-extractable coating.

A 5% degree of phenyl substitution, as present in SE-52 and OV-73, hinders cross-linking to a surprising extent. Roughly three times more peroxide (1.0%) is required to assure a comparable cross-linking effect.

A 2% degree of vinyl substitution, combined with 5% of phenyl substitution, as in SE-54, requires a similar or even lower peroxide concentration compared with that needed for pure methyl silicones. This means that the high reactivity of vinyl

groups fully outweighs the hindering effect of the phenyl groups. It is conceivable that the high durability of SE-54 columns was caused by immobilization which automatically occurred during routine use, probably under the influence of peroxides present in the solvents injected. We know that some of our silicone columns, particularly the best of them, were non-extractable after prolonged use.

With increasing phenyl concentration, cross-linking becomes rapidly difficult or unfeasible. As reported previously<sup>1</sup>, the limit may be represented by OV-61 (33% phenyl). Fig. 3 gives a visual indication of the situation. A 0.2- $\mu\text{m}$  film of OV-61, containing 4% of peroxide (*i.e.*, 20 times the amount for OV-1), was deposited and heated to induce cross-linking. Washing with methylene chloride reduced the film thickness to 0.07  $\mu\text{m}$ . Substantial, but only partial, cross-linking had taken place. While it remains an open question whether or not OV-61 should be termed suitable for immobilization, all stationary phases with lower phenyl contents than OV-61 can be reasonably immobilized.

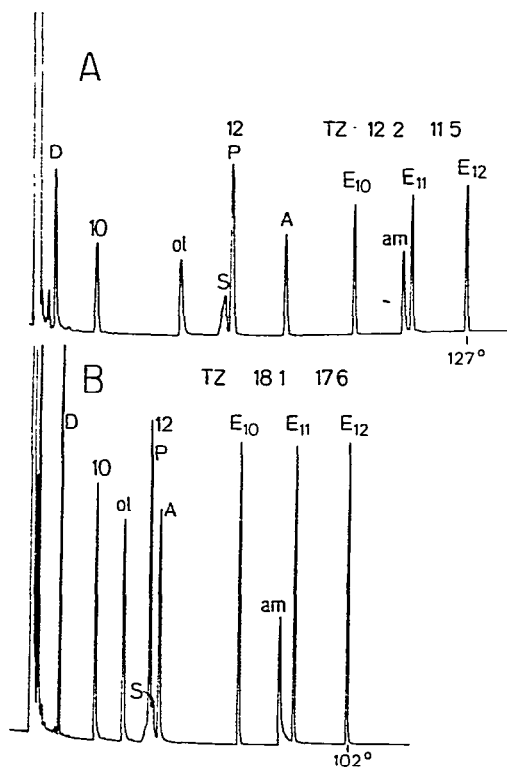


Fig. 3. Limit of immobilization. Column, 15 m  $\times$  0.32 mm I.D.; persilylated with pure DPTMDS<sup>o</sup>; 0.2- $\mu\text{m}$  OV-61 containing 4% of DCUP. Comprehensive quality tests; for substances see Fig. 2. (A) Test run immediately after immobilization at 160–180°C. Reasonably symmetrical, but intensely broadened peaks, the early peaks more affected than the later ones; typical result from irregularly distributed stationary phase. Standard separation efficiency should be about  $TZ = 26\text{--}28$ . (B) Test after washing with methylene chloride. The elution temperature of  $E_{12}$  was reduced by 25°C, indicating a 65% loss of stationary phase, *i.e.*, about 35% of the stationary phase is immobilized. The striking increase in separation efficiency demonstrates that the immobilized part of the stationary phase covers the support with a reasonably even distribution, whereas the extractable part formed the bulk of the irregularly distributed material.

Phases with higher phenyl contents, *e.g.*, OV-17, are clearly unsuitable for immobilization. Treatment with 5% peroxide did not result in a significant non-extractable layer. OV-225 differs from OV-17 by having half the phenyl groups replaced with cyanoethyl groups. This change is expected to facilitate cross-linking. Nevertheless, OV-225 can hardly be immobilized by reaction with peroxide.

Introducing vinyl groups into more polar silicones should make their immobilization feasible. It may be challenging work to extend the polarity limit of stationary phases amenable to cross-linking.

#### WETTABILITY VERSUS IMMOBILIZATION

We have looked for experimental evidence to demonstrate the stabilization by cross-linking of a film which is unstable on a given support surface. For this purpose, OV-61 was intentionally deposited on a phenyl dimethyl persilylated surface<sup>9</sup> (Fig. 3) which is not wettable by OV-61. The wettability gap in this surface-stationary phase combination is relatively small, as shown by the fact that the same surface is, at least temporarily, wettable with OV-7. The answer to the question of whether or not this small gap can be bridged by immobilization was not simple.

The coating produced under intense cross-linking conditions showed a separation efficiency of only 40% of the efficiency expected for a column of this geometry. This demonstrates that the lack of intermolecular attraction between the support and the stationary phase was great enough to cause the liquid film to break up before this could be prevented by cross-linking. Some similar experiments supported this conclusion. This leads to the empirical rule that (unfortunately) immobilization produces ideal coatings only with surface-stationary phase combinations that ensure full or almost full wettability without additional stabilization. "Almost full" wettability (without cross-linking) leads to columns that have the standard separations efficiency after mild conditioning but show continuously decreasing efficiency during prolonged use. Only in this particular instance is cross-linking able to replace full wettability.

However, Fig. 3 shows a surprising side effect. We found that the separation efficiency increased by 50% after washing; there is no obvious explanation for this. A decrease in film thickness from 0.2 to 0.07  $\mu\text{m}$  has a negligible effect; the 25°C lower elution temperature causes only an 8–10% higher efficiency. A possible explanation for the increase may be the following: for an unknown reason the immobilization reaction may have been preferentially effective between the support and the stationary phase. The washing then preferentially eliminated the irregular stationary phase accumulations caused by film breakage, whereas a more evenly distributed, and non-extractable, layer remained on the support surface. Of course, this tentative interpretation is a guideline for further experiments rather than a definitive conclusion.

#### IMMOBILIZATION PROCEDURE: FURTHER INFORMATION

##### *Selection of the peroxide*

Of a large number of available peroxides we tested four products with different decay temperatures. Table I lists the temperatures at which half the amount of peroxide was decomposed in 1 h. (Information supplied by ELFA-Oxychemie, Beethovenstrasse 48, 8002 Zürich, Switzerland.)



TABLE I  
DECAY TEMPERATURES OF DIFFERENT PEROXIDES

Product*	Abbreviation	Active oxygen (%)	Decay temperature (°C)
Bis(2,4-dichlorobenzoyl) peroxide	DCIBP	4.2	72
Dibenzoyl peroxide	BP	6.4	91
Dicumyl peroxide	DCUP	5.7	136
Di- <i>tert.</i> -butyl peroxide	DTBP	10.7	146

\* Available from ELFA-Oxychemie, Zürich, Switzerland.

Below we present the practical arguments contributing to the selection of a peroxide.

*Activity*. There may be the spontaneous idea that peroxides with low decay temperatures are more active and therefore more efficient cross-linking agents. In contrast, we have found the cross-linking efficiency to be surprisingly little dependent on decay temperature, while being roughly proportional to the content of "active oxygen", at least when apolar silicones are treated.

*Efficiency of difficult cross-linking*. Cross-linking of strongly hindered stationary phases such as OV-61 works slightly better with peroxides that have high decay temperatures. A possible explanation may be that increased molecular mobility counteracts the hindrance.

*Role of decomposition products*. As reported previously<sup>1</sup>, increased amounts of peroxide produce columns of increased activity. It seems reasonable to attribute this activity to the decomposition products of the peroxides. The explanation is supported by the fact that the dialkyl peroxides (DCUP and DTBP) cause less activity than diacyl peroxides (DCIBP and BP). The difference may be due to the breakdown products, which are alcohols and ketones from dialkyl peroxides and mainly benzoic acid derivatives from diacyl peroxides.

*Volatility*. For experimental convenience and in order to remove by-products, some gas flow through the column during the immobilization treatment, even at elevated temperature, should not be precluded (see below). Consequently, relatively volatile peroxides such as DTBP are less desirable.

*Stability of solution*. It is convenient to add the peroxide to the stationary phase as a 1–2% solution. Alkanes would be the ideal solvents for this purpose because of their minimal contribution to the peroxide decay. However, most peroxides require more polar solvents. Our preferred solvent is toluene. A 2% solution of BP in toluene stored in the dark at 4°C showed signs of alteration (colour, precipitation), whereas a correspondingly treated solution of DCUP was totally unchanged after 3 weeks.

*Safety of handling*. Peroxides are generally classified as hazardous chemicals. Although the handling of all listed peroxides is safe, provided some elementary precautions are observed, the increasing safety with increasing decay temperature may be of practical interest. For instance, the increased safety may, in certain countries, simplify the shipping conditions.

*Summarized comparison.* The combination of the listed arguments yields a clear preference for DCUP (high efficiency, inactive decomposition products, low volatility, relatively stable solution, relatively safe handling).

#### *Concentration of the peroxide*

We have insufficient experimental evidence to present consistent information about this essential aspect. We suspect that this information will be complex, as different types of application of the columns may require differently conducted immobilization reactions.

One reasonable argument (although probably not the only argument) for optimizing the peroxide concentration is to use the lowest amount of peroxide that just ensures an almost non-extractable coating (see Table II).

TABLE II

MINIMAL CONCENTRATIONS OF DCUP (WEIGHT PER UNIT WEIGHT OF STATIONARY PHASE) PRODUCING A 90–100% NON-EXTRACTABLE COATING

<i>Stationary phase</i>	<i>Solvent</i>	<i>Minimal concentration (% w/w)</i>
SE-54	<i>n</i> -Pentane	0.2
SE-30, OV-1	<i>n</i> -Pentane	0.4
SE-52, OV-73	<i>n</i> -Pentane	1.0
OV-3	Diethyl ether	4.0
OV-7	Diethyl ether	10.0

#### *Immobilization reaction*

As recommended previously<sup>1</sup>, the peroxide is added to the stationary phase solution immediately before static coating. It should be noted that with a critical combination of parameters favouring cross-linking (reactivity of stationary phase, activity and concentration of peroxide, influence of solvent, column temperature during pumping), plugging may occur due to premature cross-linking in solution.

We have tried to eliminate partial evaporation or dislocation of the peroxide by carrying out the immobilization in the closed column. After pumping, we flushed the column with nitrogen and closed it with PTFE caps or sealed it in a flame under vacuum. All of these trials yielded poorer results (reduced cross-linking effect and increased activity). It seems that a by-product (water?) of the reaction should be continuously eliminated.

We have simplified the previously recommended cross-linking procedure. For DCUP, the statically coated column is mounted in a gas chromatograph with the exit end disconnected, and is flushed for 5–10 min using twice the regular carrier gas flow-rate. The flow-rate is reduced to the minimum that can be reliably maintained (0.02–0.1 ml/min). The oven is immediately heated to 160°C and, after 1 h, is heated to 180°C. Depending on the equipment, the carrier gas flow-rate should be checked periodically. After 1 h at 180°C, still with a low carrier gas flow-rate, the flow-rate is increased to the normal level for at least 1–2 h. The temperature may be kept at 180°C

if a fresh test is of interest, or may be increased to any desired conditioning temperature. The column exit is then connected to the detector and a test is run.

We suspected that the column ought to be washed before more intense conditioning to prevent peroxide by-products from undergoing high-temperature reactions. However, we have no experimental evidence that supports this precaution. Thus, it remains up to the user to decide whether he wants to wash the column immediately, *e.g.*, to check the degree of immobilization, or whether he prefers to apply the first washing when extraction of a suspected contaminant becomes desirable.

During the entire treatment we use our regular carrier gas (hydrogen). Our initial thoughts that hydrogen might inactivate some peroxides have not been verified experimentally.

### *Solvent washing*

Contaminants, including non-immobilized polymer molecules, may be captured in the cross-linked network. To facilitate their elimination, we use a solvent that is known to cause swelling of the coating (methylene chloride). For a rapid, general-purpose washing we use the following procedure. Twice the column volume of methylene chloride is forced through the column at a rate of 2 cm/sec and is immediately followed by one volume each of methanol, methylene chloride, and *n*-pentane. *n*-Pentane serves to flush the more effectively retained methylene chloride.

If a contaminant of low solubility is suspected, a large-volume washing overnight is applied.

The selection of solvents to achieve specific cleaning effects may hold considerable potential. Again, our results so far do not permit a consistent discussion of this matter. An example may demonstrate that solvent selection is not just secondary work. An overnight washing of an OV-1 column with acetone produced a column with drastically increased bleeding. The bleeding decreased during conditioning for several days, but did not return to the low value which is typical for this type of column.

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