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Methods for the immobilisation of hydroxyl-containing stationary liquid phases in capillary gas chromatography

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Abstract. The main results concerning the immobilisation of hydroxyl-containing stationary phases in capillary gas chromatography are surveyed and treated systematically. Attention is concentrated on the influence of the chemical reactions occurring during immobilisation and on the characteristics of the capillary column. It is noted that, together with the improvement of the methods for the immobilisation of known phases, the syntheses of new stationary liquid phases, the properties and the immobilisation conditions of which have been optimised taking into account the characteristics of the objects analysed, are promising. The bibliography includes 176 references.

I. Introduction

Capillary chromatographic methods are mainly employed in modern gas chromatography. This situation became possible as a consequence of the development of a fundamentally new technology for the preparation of open capillary columns with a stationary liquid phase immobilised within the capillary.

The idea of immobilising the stationary liquid phase on the inner surface of a capillary column appeared at the junction of the 1960s – 1970s [1,2] and acquired its present form a decade later as a consequence of the studies by K Grob and G Grob,[3–7] Blomberg *et al*.,[8] and Sandra *et al*.[9]

Immobilisation constitutes a method for the stabilisation of a film of a polymeric stationary phase as a result of its structuring (cross-linking) and (in certain cases) grafting to the walls of the capillary column. Immobilisation differs from the traditional methods for the stabilisation of a stationary phase employing different versions of the geometrical and/or chemical modification of the surface of the capillary column [10–17] by the fact that not only the walls of the column but also the stationary phase film are acted upon directly.

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As a result of the immobilisation, the macromolecules of the stationary phase lose their ability to migrate along the inner surface of the column and to form significant local thickened regions. At the same time, the stationary phase acquires a new important property — nonextractibility, which appreciably simplifies the use and regeneration of capillary columns. On comparing the properties of the phase before and after immobilisation, an increase in the reproducibility and stability of the chromatographic characteristics of the column and the expansion of the range of working temperatures were noted and the possibility of obtaining thick (up to 100 μm)[18,19] and multilayer films of the stationary phase was discovered.[20,21]

The evident practical advantages of capillary columns with immobilised stationary phases promoted very vigorous research in this field in recent years and led to the rapid practical application of the advances made. Effective methods have been developed to date for the immobilisation of nonpolar and moderately polar polysiloxanes (PS).[16,22–33] As a rule, the immobilisation of stationary phases of this class is accompanied by minimal changes in their chemical nature and chromatographic characteristics. The methods for the immobilisation of polar stationary phases are associated with considerable difficulties and are being improved.

The review gives a systematic account of experimental data on the immobilisation of hydroxyl-containing stationary phases. Compounds such as di- and poly-ols are of special interest in connection with their unique selectivity in the separation of polar and polarisable sorbates.[34–40] Poly(ethylene glycols (PEG) with a high molecular mass (not less then 2×10^4) comprising the commercial brands Carbowax, Superox, CP-WAX, DB-WAX, *etc*. are most often employed as hydroxyl-containing stationary phases in capillary gas chromatographic practice.[41–44] The chemical structure of the polymer macromolecules corresponds to the general formula $HO(CH_2CH_2O)_mH$.[45]

Together with organic hydroxyl-containing stationary phases, α,ω-dihydroxypolysiloxanes are considered in the review.

It is noteworthy that the studies on the method of preparation of capillary columns are within the sphere of commercial interests of the firms manufacturing chromatographic equipment. For this reason, many publications are concerned with advertising, which hinders the interpretation of the results. Although the questions which we have considered have been described to some extent in a series of reviews (see, for example, Refs 12, 28, 46, and 47), new experimental data, which need to be surveyed, have accumulated in recent years.

II. Radiation-induced initiation

The essential feature of the radiation-induced initiation of the immobilisation of stationary phases is that high-energy radiation is employed for the formation of the initial active centres.

The possibility of the immobilisation of a series of hydroxyl-containing stationary phases, such as Carbowax 20M, CP-WAX 51 ($M = 2 \times 10^4$), Superox 0.1 ($M = 1 \times 10^5$), and Superox 6 ($M = 6 \times 10^6$), under the influence of ^{60}Co γ-radiation [27, 41, 42, 46–51] and low-temperature argon plasma [52] has been investigated.

The efficiency of γ-quanta as initiators of the immobilisation of PEG is low. For example it has been possible to immobilise Carbowax 20M to the extent of 90% for an irradiation dose of 24 Mrad,[49, 51] whereas methylpolysiloxane is 80%–100% cross-linked already after the absorption of 2–10 Mrad.[28, 29, 50, 53–55] Such results may be regarded as evidence indicating the complexity of the radiation-chemical transformations in the PEG. However, this question has been scarcely investigated.[56–62] On the basis of the results obtained by capillary gas chromatographic, IR spectroscopic, and ^{13}C NMR methods, it is claimed in a brief communication [51] that hard radiation does not influence appreciably the chemical nature and the permeability of the PEG to diffusion. In our view, this conclusion requires additional confirmation.

Ideas according to which the mechanism of structure formation in polymers under the influence of radiation is of a radical character are most widespread,[58–60, 63, 64] but one cannot rule out [43, 60, 63] the possibility of the involvement of ions and radical-ions in cross-linking processes.

The effect of radiation on PEG depends not only on the overall dose absorbed but also on factors such as the average molecular mass of the polymeric stationary phase and the presence in the latter of impurities or specially introduced additives. Thus, for an irradiation dose of 10 Mrad, the degree of immobilisation of the Carbowax 20M and CP-WAX 51 fractions is 10%–14%,[48, 65] whilst that of the Superox 6 fraction is 25%.[65] If 5 mass%–10 mass% of cumenyl peroxide is added to CP-WAX 51 under these conditions, the degree of immobilisation of the stationary phase increases to 50%–52%. In the latter case, the polymer is subjected to direct and indirect action of the radiation, the latter consisting in the initiation of the homolysis of the peroxide.

Springston and Dezaro [52] used a low-temperature argon plasma as the initiator of the immobilisation of the PEG of the Superox 0.1 brand. The degree of immobilisation of the stationary phase did not exceed 12% and the capillary columns acquired in addition an adsorption activity.

III. Material initiation

The material initiation of the immobilisation of stationary phases is based on the use of individual compounds capable of decomposing into free radicals in a certain temperature range.

The material initiators of the immobilisation of PEG employed are usually cumenyl peroxide and, more rarely, benzoyl peroxide and aliphatic azo-compounds.

Compared with the nonpolar polysiloxanes, PEG exhibits an appreciably smaller (at least by a factor of 10) capacity for immobilisation under the influence of organic peroxides and azo-compounds, the process being extremely sensitive to experimental conditions. For example, Etler and Vigh [65] investigated the immobilisation of the PEG of the brand CP-WAX 51, initiated by cumenyl peroxide, on the walls of glass capillaries modified by $BaCO_3$ crystals. For a ratio of the masses of the stationary phase and cumenyl peroxide of 10:1 and a process temperature of 160–180 °C, the degree of immobilisation of the phase did not exceed 19%. Russo *et al.*[66] used graphitised lamp black as the modifying agent for the inner surface of the capillaries. For the same content of the initiator at 150 °C, it was possible to immobilise PEG 20M ($M = 2 \times 10^4$) to the extent of 75%. According to the authors, this entailed grafting the stationary phase to the layer of carbon black adsorbed on the glass. If account is taken of the chemical properties of the surface of the graphitised thermal black [36, 67] and the inefficiency of the immobilisation of the relatively low-molecular PEG (for example PEG-600 and PEG-1500), it appears unlikely that grafting was the dominant process in the immobilisation of this phase. The degree of immobilisation of the higher-molecular PEG of the brand Superox 4 ($M = 4 \times 10^6$) on the surfaces of capillaries deactivated by tetramethyldiphenyl disilazene (when grafting is impossible in principle) was only 45% under similar conditions.[68]

Glass capillaries with an active (not deactivated) surface have been used in certain experiments.[69, 70] Thus Yakabe *et al.*[69] achieved 80% immobilisation of the PEG-20M fraction in the presence of 15% of cumenyl peroxide at a process temperature of 160 °C. Bystricky [70] required 20%–40% of this initiator in order to achieve the 65%–97% immobilisation of Carbowax 20M at 150 °C.

It is difficult to explain the experimental results obtained in the above studies.[69, 71] According to Yakabe *et al.*,[69] when the cumenyl peroxide content is 2%–3% the degree of immobilisation of PEG 20M on glass is 60% whilst according to Buijten *et al.*[71] the degree of immobilisation on PEG of the brand CP™-WAX 40M ($M = 4 \times 10^4$) on quartz deactivated by PEG 20M is only 3%.[71]

Thus it is evident that the immobilisation of PEG under the influence of cumenyl peroxide is affected also by uncontrollable objective and subjective factors. For example PEG 20M specimens of different origin can differ in the degree of polydispersity and in the amount and nature of the admixture of the polymerisation catalyst.[72]

According to the results of the studies examined above, the use of higher concentrations of cumenyl peroxide does ultimately lead to the desired result namely the immobilisation of PEG, but according to the view of the majority of the investigators it impairs the efficiency [66, 69, 73] and the adsorption inertness [66, 71, 73–75] of the capillary columns. Furthermore, immobilisation under the influence of this initiator alters the polarity of the PEG [69, 71, 73, 75, 76] and imparts acid properties to the stationary phase.[68, 69, 73, 77, 78] Martinez de la Gandara *et al.*[73] concluded that the classical immobilisation method in which the initiator is introduced into the solution of the phase before depositing it onto the walls of the capillary is partly a source of such problems. The authors developed a two-stage method providing for the deposition of cumenyl peroxide as a separate layer onto a film of the stationary phase. However, this technical procedure did not afford appreciable advantages: an adequate degree of immobilisation (80%–90%) of Carbowax 20M was attained after the addition of 20% of the peroxide, but the immobilised phase manifested acid properties as before. Blomberg and Markides [79] also used a two-stage method but noted a low reproducibility of the results.

It was noted above that PEG is immobilised under the influence of organic peroxides appreciably less effectively than polysiloxanes. We shall consider in greater detail the causes of this phenomenon. Blum [80] believes that, in the immobilisation of PEG, an appreciable proportion of the peroxide is consumed on the side reaction involving the oxidation of the terminal hydroxy groups. There is no doubt that this process does occur. However, the number of OH groups in high-molecular PEG is small. For example, the proportion is $\sim$ 0.17% in Carbowax 20M.[81] Furthermore it is known [43, 82] that alkyl peroxides are capable of inducing not only the polymerisation but also the depolymerisation of PEG. In addition, the radicals arising in the thermolysis of the peroxide are capable of being incorporated in the chemical structure of the polymer,[23, 29, 83] which undoubtedly influences the immobilisation process. Finally, the macroradicals formed from the PEG and responsible for this cross-linking are capable of decomposing with dissociation of the polymer chain.[84–86] Bearing

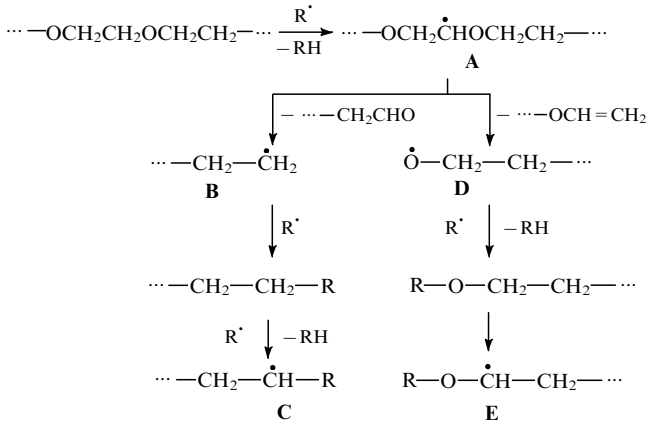
this in mind, one can assume that the immobilisation of PEG under the influence of cumenyl peroxide includes the following stages:

(1) Initiation of the free-radical reaction

$$[PhC(Me)_2O]_2 \xrightarrow{\Delta} 2PhC(Me)_2\dot{O} \xrightarrow{\Delta} PhC(O)Me + 2\dot{M}e;$$

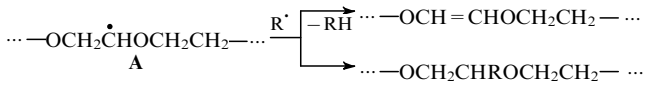
(2) The formation of the macroradicals **A** – **E** and others as a result of the occurrence of various reactions, for example S_N2 substitution reactions (abstraction of hydrogen), addition reactions, and β-cleavage (Scheme 1):

Scheme 1



$R^{\bullet}$ is any free radical present in the system: methyl, cumenyloxyl, a macroradical.

(3) The recombination and disproportionation of macroradicals, which leads to the termination of the kinetic chain, for example with participation of the radical **A**:



If $R^{\bullet}$ is a macroradical, then recombination leads to the cross-linking of the macrochains and to a gradual development of immobilisation.

One cannot rule out the possibility of the occurrence also of other reactions, in particular those associated with the heterolytic decomposition of cumenyl peroxide and the presence of traces of O_2, H_2O, *etc.*

Thus the cause of the comparatively low efficiency of the immobilisation of PEG under the influence of peroxides is apparently that the macroradicals of many types (and especially of type **A**) undergo unimolecular β-decomposition (degradation of the polymer), leading, to a decrease in the degree of polymerisation of the PEG. This effect may be compensated by the high rate of generation of radicals obtained at a high initial peroxide concentration when the competition between radical – radical interactions (second order with respect to the radical) and the decomposition reaction (first order with respect to the radical) does not have an outcome in favour of the latter. There is also the possibility of other ways of solving the problem. For example, the radical immobilisation of PEG is facilitated by the introduction of vinyl groups [84] into the polymer structure or by employing special active additives (see below).

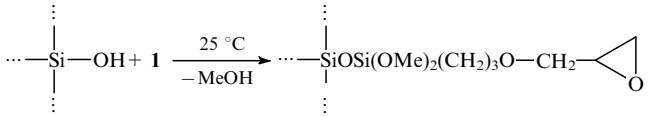
Comparison of the radiation-induced and chemical initiations of the immobilisation of hydroxyl-containing stationary phases has shown that the efficiency of both procedures is low, but the radiation method has experimental advantages: firstly, the heating of the capillary column before the immobilisation of the stationary phase is eliminated and, secondly, the process initiator (the source of radiation) is outside the column. Consequently the film of the stationary phase is acted upon not thermally and is not contaminated by the initiator decomposition products as in material initiation.

IV. Composite immobilisation

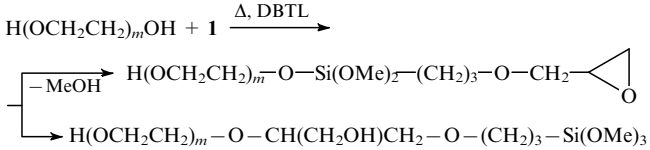
In order to increase the efficiency of the immobilisation of hydroxyl-containing stationary phases, cross-linking and cross-linking-grafting polyfunctional agents are frequently employed. The main function of the former is to form chemical cross-links between the macromolecules of the stationary phase; together with this feature, the latter are capable of grafting the phase to the walls of the column. Incidentally, when the inner surface of the column is modified appropriately, cross-linking agent can also induce the grafting of the phase to the wall of the column. At the same time, the cross-linking-grafting agent can itself act as a modifying agent, generating on the walls of the column an intermediate mono- or poly-molecular layer capable of interacting with the stationary phase. Since cross-linking and cross-linking-grafting agents usually constitute an appreciable proportion of the mass of the immobilised stationary phase, the immobilisation with their participation may be referred to as composite immobilisation. Polyfunctional alkoxy- and acetoxy-silanes are most widely employed as cross-linking-grafting agents: γ-glycidyloxypropyltrimethoxysilane **1**,[87–90] trimethoxyvinylsilane **2**,[87] triethoxymethylsilane **3**,[88,89] and tetraacetoxysilane **4**.[91]

Traitler *et al.*[87] were the first to suggest that alkoxysilanes (**1** or **2**) be used for the immobilisation of Carbowax 20M. A mixture of cumenyl peroxide and dibutyltin dilaurate (DBTL) served as the process initiator. The silane **1** makes it possible to obtain more thermally stable and adsorption-inert capillary columns. For a mass ratio of the stationary phase and compound **1** of 2 : 1, the degree of immobilisation of Carbowax 20M on the surface of borosilicate glass was 70% – 75%, which is lower by 10% – 25% than on quartz. According to the authors, this is a result of the catalytic action of the alkali and alkaline earth metals entering into the composition of the glass. Since a strong catalyst is present in sufficient amount (1.34% of DBTL) in the immobilised mixture, we suggest that other causes may also exist. It may be that the hydroxylated surface of the glass ensures more effective grafting of the stationary phase. On the basis of the ideas developed in a number of studies,[92–95] the immobilisation of PEG with participation of the silane **1** can be represented as follows:

(*1*) *Chemical modification of the column walls.*[92–94]



(*2*) *Chemical modification of the stationary phase.*[95]



(*3*) *Structure formation and grafting of the stationary phase to the column walls.* This stage is difficult to describe in the form of a scheme, since it is a complex set of inter-related and parallel homolytic and heterolytic reactions.

It follows from the schemes presented that the transesterification of the alkoxy groups of the silane by the silanol groups on the surface of the capillary columns and the aliphatic OH groups of the stationary phase makes an important contribution to the immobilisation of PEG in the presence of the silane **1**. In practice, certain stages of the immobilisation process coincide. Thus, a version of the combination of (*2*) + (*3*) stages has been developed,[87] whilst in other investigations [88–90] the (*1*) + (*2*) + (*3*)

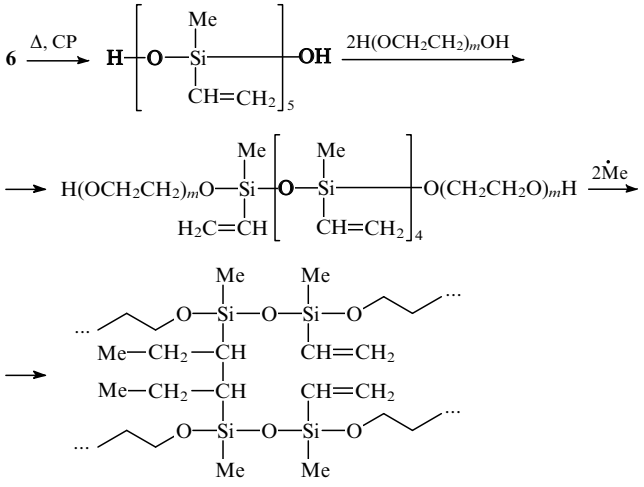
version was devised. It is noteworthy that, as a consequence of the high reactivity of alkoxysilanes, the structures of the immobilised stationary phase is extremely sensitive to the presence of impurities in the reaction medium. Thus at an elevated temperature traces of H_2O and O_2 induce the polymerisation of the silane **1** and also of the products of its interaction with glass and PEG. The polymerisation leads to the formation of siloxane polyethers.

Traitler's idea was developed further in Blum's investigations,[88,89] devoted to the immobilisation of a series of block copolymers of ethylene and propylene oxides (UCON 50HB 2000, 2800 and 5100, LB 550X, Pluronik P-94, as well as *N*,*N*,*N*′,*N*′-tetrasubstituted ethylenediamines (Sinperonik T/904, T/908). Blum abandoned the use of cumenyl peroxide and DBTL, because the role of the cumenyl peroxide-initiated radical processes in the immobilisation of PEG in the presence of alkoxysilanes is slight, while DBTL may impart an undesirable catalytic activity to the capillary column.

Alkoxy- and acetoxy-silanes and siloxanes have been used successfully also in the immobilisation of other hydroxyl-containing stationary phases, for example α,ω-dihydroxypolysiloxanes.[91,96–99]

Certain organic compounds containing more than one nonconjugated double bond have found an application as cross-linking agents for PEG and its analogues: 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane **5**,[100] 2,4,6,8,10-pentamethyl-2,4,6,8,10-pentavinylcyclopentasiloxane **6**,[71] 1,1,3,5,5-pentamethyl-1,3,5-trivinyltrisiloxane **7**,[100] and triallyl isocyanurate **8**.[69] The detailed mechanism of the cumenyl peroxide-initiated immobilisation of PEG with participation of the above compounds has not been established. The attempt to use NMR spectroscopy for this purpose was unsuccessful as a consequence of the low sensitivity of the method.[79]

Buijten *et al.*[71] proposed a method for the immobilisation of the PEG of the CP™-WAX 40M brand with the aid of methylvinylcyclopentasiloxane. They suggest that the process begins with the opening of the siloxane ring and its condensation with the PEG. The immobilisation proper of the phase is attained as a result of the cumenyl peroxide-initiated structure formation involving the siloxane fragments in the copolymer obtained. The following process mechanism has been put forward:



CP = cumenyl peroxide.

However, this route for the process is possible only in the presence of certain substances — acids, bases, and certain salts — capable of cleaving the siloxane linkage and of catalysing the polycondensation.[45] Organic peroxides induce structure formation in cyclosiloxanes without ring opening.[83,101] For this reason, in the presence of cumenyl peroxide the development of radical chain processes is most probable in the system under consideration, whereupon the polymerisation of methylvinylcyclopentasiloxane, its grafting to a PEG macromolecule, as well as structure formation in the PEG and in the copolymer formed take place simultaneously. The mechanism proposed by the authors can operate as a side process when the stationary liquid phase contains an appreciable amount of an admixture of a polymerisation catalyst or the inner surface of the capillary column is insufficiently deactivated.

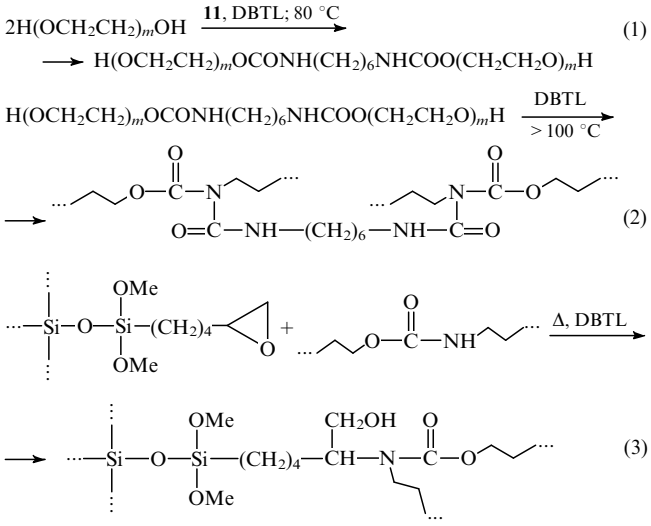
Siloxanes without vinyl groups also possess the properties of cross-linking agents but they are less reactive. Thus, when the cyclosiloxane **6** is replaced by octamethylcyclotetrasiloxane **9**, the degree of immobilisation of CP™-WAX 40M diminishes by a factor of 2.[71]

Schomburg *et al.*[102] immobilised Carbowax 20M using acryloylvaline-(*S*)-α-phenylethyl amide **10** containing one vinyl group. However, the latter is not a cross-linking agent. It is a chiral modifying agent which is grafted to the Carbowax 20M macromolecules in the course of the radical immobilisation. As a result, the immobilised phase acquires the property of enantioselectivity. In the study under consideration, the possibility of a deliberate alteration of the selectivity of the stationary phase in the course of immobilisation was first demonstrated. The structural fragments incorporating the immobilised phase are always chosen so that they resemble the sorbates being separated.[103,104]

Aliphatic and aromatic di- and poly-isocyanates constitute a special group of cross-linking agents: $OCN(CH_2)_6NCO$ **11**, $OCN(CH_2)_6N[CONH(CH_2)_6NCO]_2$ **12**, and $MeCH_2C[CH_2O–CONHC_6H_3(NCO)Me]_3$ **13**.

The method for the immobilisation of PEG, its analogues, and acid derivatives (Carbowax 20M, Castorwax DD-026, Carbowax 20M-TPA, OV-351, FFAP) under consideration was developed further in the studies of Horka and coworkers.[105–111]

The immobilisation of hydroxyl-containing stationary phase with participation of isocyanates proceeds in the following manner.[45,47,112,113] In the presence of the DBTL catalyst or 1,4-diazabicyclo[2,2,2]octane (DABCO), the CO group of the isocyanate reacts with the OH groups of the phase with formation of urethane groups [process (1)]. The latter are extremely reactive and interact with the excess isocyanate and the silane **1** — the agent modifying the inner surface of the capillary column. Allophanate fragments, cross-linking the copolymer [process (2)] arise under these conditions. and the copolymer is also grafted to the walls of the capillary column [process (3)]:



According to the data of Horka and coworkers,[47,105,106] the immobilisation of PEG with participation of the isocyanates **11**–**13** makes it possible to obtain stationary phases which are thermally stable up to 305–320 °C. However, these data are inconsistent with the known facts. Thus it has been established[43,114] that above 200 °C the urethane fragments dissociate *via* a depolymerisation mechanism. There is a possibility of the dissociation of bonds with formation of an olefin and a primary amine.[63] The thermal degradation of the allophanate groups

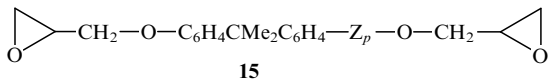
begins already at 120 °C. In the range 300–320 °C, PEG decomposes at an appreciable rate.[43] Evidently, in characterising the thermal stability of the stationary phase, it is insufficient to determine the maximum working temperature on attainment of which the properties of the phase are still not significantly impaired. One should also have an idea about the 'lifetime' of the column (or the magnitude of the background flow) at this temperature and about the chemical inertness of the phase in the region of high temperatures.

The immobilisation of acid derivatives of PEG by the method of Horka and coworker[105–111] is distinguished by the fact that, together with the isocyanate, 3,5-dinitrosalicylic acid (3,5-DNSA) is introduced into the reaction mixture. Apparently the acid is necessary to compensate for the loss of carboxy groups and hence of the specific properties of the phase in the course of immobilisation. Furthermore, if one considers the possible interactions in the PEG–isocyanate–3,5-DNSA system, it becomes evident that the carboxy group is retained only by the part of the acid which does not enter into the structure of the stationary phase. This conclusion is confirmed by data concerning the loss of acid properties after the extraction of the phase by a series of organic solvents.[47]

There have been few studies devoted to the immobilisation of relatively low-molecular PEG ($M < 10^4$). This is evidently associated with the limited stability of films of such stationary phases on the surfaces of glass and quartz and with the narrow range of working temperatures.[37] However, low-molecular PEG is characterised by a high functional selectivity.[36, 37] Thus, on passing from PEG 20M to PEG 600, the McReynolds constants (indices) $y-z$ increase by 60–95 units. In capillary gas chromatography, the requirement for phases with a high functional selectivity has not so far been satisfied,[115–122] so that the development of methods for the immobilisation of low-molecular glycols appears of very great current interest.

A novel method for the immobilisation of PEG 2500 and PEG 10 000 has been proposed by Sandra *et al.*[72] The composition comprising PEG and 3-triethoxysilylpropyl isocyanate **14** is immobilised on the walls of a quartz capillary by treatment with water, which is injected in pulses into the flow of carrier gas. The development of the process begins with the hydrolysis of the isocyanate **14**, whereupon a siloxane polyisocyanate is formed[123] and its action is subsequently similar to that of the organic isocyanates examined above.

The method of the immobilisation of low-molecular PEG 400 proposed by Mukhina and coworkers[124, 125] is based on the interaction with the bisphenol A epoxide resin (BE):



15

$Z = OCH_2CH(OH)CH_2OC_6H_4CMe_2C_6H_4$, $p = 0-3$.

According to the ideas developed in a number of investigation,[95, 126–130] the stationary phase is in this case immobilised in the following manner. Under the influence of the catalyst (triethylamine), the hydroxy groups of the PEG react with the epoxide groups of BE, which results in the formation of a linear copolymer.

$$HO(CH_2CH_2O)_mH + \mathbf{15} \xrightarrow{Et_3N;\ 200\ ^\circ C} AC_6H_4CMe_2C_6H_4Z_pA$$

$A = OCH_2CH(OH)CH_2(OCH_2CH_2)_mOH$.

In the presence of an excess of BE (for the molar ratio PEG : BE < 1), structure formation involving secondary OH groups takes place in the copolymer. There is a possibility of grafting the phase to the surface of glass *via* the both epoxide[131] and hydroxy groups.[132] Out of the multiplicity of compounds capable of accelerating the interaction of PEG 400 and BE, the authors gave preference to triethylamine taking into account not only its activity as a catalyst but also its possible influence on the chemical inertness as well as the catalytic and adsorption properties of the stationary phase. As a cross-linking agent, the BE resin also has a series of advantages: firstly, it exhibits a satisfactory adhesion to the surface of glass and quartz, which stabilises the stationary phase film on the walls of the capillary column; secondly, the BE macromolecules contain no functional groups other than the terminal epoxide and aliphatic OH groups and the resin is a polyether like PEG, *i.e.* the characteristics of their thermal and chemical stabilities are comparable;[133] thirdly, the loss of hydroxy groups by the PEG on interaction with BE is compensated by the formation of new OH groups.

Thus the use of the agents **1–15** generally promotes an increase in the efficiency of the immobilisation of hydroxyl-containing stationary phases (Table 1). However the problem of increasing the quality of the immobilised phase remains. Thus the copolymer of the PEG of the Superox 4^{TM} brand and the siloxane **7** has basic and acid adsorption centres;[75] the PEG of the brand CP^{TM}-WAX 40M, immobilised with the aid of the siloxane **6**, exhibits weak acid properties;[71] Carbowax 20M, immobilised in the presence of the isocyanates **11–13**, is distimetly.[42] Triallyl isocyanurate, used in an amount of 10% relative to the mass of PEG 20M, induces an asymmetry in the chromatographic peaks of all of Grob's test sorbates.[69] This is probably a consequence of the high functionality of the agents employed.

Regardless of the way in which it is carried out, immobilisation disturbs the molecular order in PEG,[134, 135] which lowers the degree of crystallinity and the melting point of the stationary phase. This effect is less pronounced in the radiation-induced immobilisation of PEG and is most marked for composite immobilisation. Fernandez-Sanchez *et al.*[134] established that at 40 °C the degree of crystallinity of PEG of the Superox 20M brand is 83%–86%, while after immobilisation by means of cumenyl peroxide using Bystricky's method[70] it is 47%–53%. On the other hand, the fraction of the crystalline phase of the polymer immobilised with participation of the silane **1** by the method of Traitler *et al.*[87] is only 24%–31%. The minimum working temperature of the immobilised high-molecular PEG is reduced in most cases by 20–30 °C.[49, 51, 65, 70, 71, 77, 134–137] This effect is well illustrated by the temperature dependence of the retention of the sorbate on a column containing PEG 20M before and after immobilisation (Fig. 1). However, the use of large amounts of reagents leads to the opposite result — an increase in the lower limit of the working temperatures owing to the high density of structure formation in the stationary phase.[87, 107, 110]

It is noteworthy that composite immobilisation leads in most cases to the formation of new phases which may be characterised as statistical copolymers of the initial phases and the cross-linking agents.

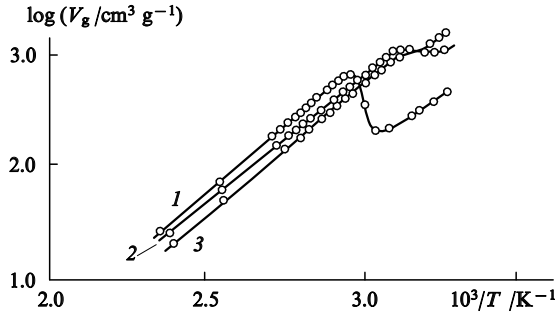


Figure 1. Temperature dependence of the retention of l-butanol on capillary columns containing PEG 20M before (*1*) and after immobilisation by treatment with cumenyl peroxide (*2*) or a mixture of cumenyl peroxide with γ-glycidyloxypropyltrimethoxysilane (*3*).[134]

Table 1. Immobilisation of PEG and its analogues.

Column material	Column modifying agent	Initiator or catalyst		Cross-linking agent		Immobilisation conditions			Z (%)	SP working temperature range /°C	Ref.
		I	*II*	*III*	*IV*	regime	T /°C	τ /h			
Stationary phase — CP-WAX 51											
B-glass	$BaCO_3$	γ-^{60}Co	(10)	–	–	st	25	–	10	> 40	65
	$BaCO_3$	γ-^{60}Co, CP	(10), 5 – 10	–	–	"	25	–	50 – 65	> 40	65
	$BaCO_3$	CP	10	–	–	"	180	2	19	–	65
Stationary phase — CP™-WAX 40M											
Quartz	PEG	CP	2	–	–	dn	200	1	3	–	71
Na-glass, quartz	PEG	CP	2	**9**	4	dn	200	1	40	30 – 300	71
	–	–	–	ethylene oxide	–	st	280	3	67	30 – 260	71
	PEG	CP	20	**2**	4	st	200	1	80 – 90	30 – 300	71
Stationary phase — Superox 01											
Quartz	–	plasma Ar	–	–	–	st	25	–	12	–	52
Stationary phase — Superox 4											
Glass	DPS	CP	5	–	–	st	180	1	32	< 280	68
	DPS	CP	10	–	–	"	180	1	45	< 280	68
	DPS	Irganox	10, 10	–	–	"	180	1	100	–	68
	DPS	AtO	10	–	–	"	180	1	0	–	68
Stationary phase — Superox 4™											
Pyrex,	PEG	CP	3	**7**	10	st, dn	180	3	30	–	75
quartz	PEG	CP	3	**7**	50	"	180	3	90	–	75
Stationary phase — Superox 6											
B-glass	$BaCO_3$	γ-^{60}Co	(10)	–	–	st	25	–	25	> 40	65
Stationary phase — Carbowax 20M											
Quartz	–	γ-^{60}Co	(24)	–	–	–	25	–	90	30 – 280	49, 51
	1	CP, DBTL	1.50, 1.35	**1**	50	dn	240	24	50 – 60	80 – 280	87
B-glass,	SE-54	γ-^{60}Co	(2)	–	–	st	25	–	3	–	48
Na-glass	SE-54	γ-^{60}Co	(10)	–	–	"	25	–	14	–	48
	–	CP	20	–	–	dn	150	2	65	< 260	70
	–	CP	40	–	–	"	150	2	97	< 260	70
Pyrex	**1**	CP, DBTL	1.50, 1.35	**1**	50	"	240	24	70 – 75	80 – 280	87
	PEG	CP	20	–	–	st	130	1	80 – 90	–	73
Stationary phase — Carbowax 20M											
Simax	**1**	DBTL	1	**11**	17	st	145	6	87	60 – 305	105, 106
	1	DBTL	1	**11**	25	"	145	6	98	60 – 305	105, 106
	1	DABCO	1	**12**	15	"	145	6	97	60 – 310	107
	1	DABCO	1	**13**	20	"	145	6	97	60 – 320	107
Na-glass, quartz	PEG	CP	40	**10**	100	"	200	–	–	–	102
Stationary phase — Carbowax 20M-TPA (FFAP, OV-351)											
Simax	**1**	DABCO	1	**13**, 3,5-DNSA	20 10	st	145	5	97 – 100	60 – 220	109
Stationary phase — Carbowax 20™											
Pyrex	PEG	CP	3	**7**	50	st, dn	180	3	50	–	75
Stationary phase — Castrowax DD-026											
Simax	**1**	DABCO	0.1	**13**	55	st	145	5	96	80 – 225	110

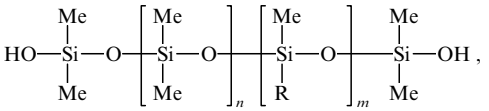
Table 1 (continued).

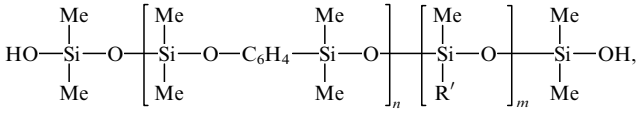
Column material	Column modifying agent	Initiator or catalyst		Cross-linking agent		Immobilisation conditions			*Z* (%)	SP working temperature range /°C	Ref.
		I	*II*	*III*	*IV*	regime	*T* /°C	τ /h			
Stationary phase — PEG 20M											
B-glass	GTB	CP	5	–	–	st	150	1	75	–	66
	GTB	CP	30	–	–	"	150	1	80	–	66
	–	BP	10	–	–	"	200	1	90	40 – 280	77
Quartz	–	CP	3	**3**	5	st	160	1	80	–	69
	–	CP	5	**3**	5	"	160	1	85	–	69
	–	CP	–	–	–	st	160 – 200	4 – 6	40 – 84	< 300	100
Glass	NaCl	BF_3	–	**1**	–	st	150	4	–	–	90
Pyrex	–	CP	3	–	–	dn	160	1	50	–	69
	–	CP	15	–	–	dn	160	1	80	–	69
Stationary phase — PEG 2500, PEG-NM 10 000											
Quartz	PEG	H_2O	–	**14**	–	dn	150	0.25	–	–	72
Stationary phase — PEG 400											
Pyrex	–	$(C_2H_5)_3N$	–	**15**	100	st	200	2	55 – 61	30 – 280	124, 125
Stationary phase — acrylic aster of PEG 20M											
Glass	NaCl	AIBN	0.1 – 1	–	–	st	100	2	–	–	84
Stationary phase — diethyleneglycol adipate											
Pyrex	PEG	CP	20	–	–	st	130	1	60	–	73
Stationary phase — UCON (50HB-2000, 2800, 5100, LB550X)											
Glass	**3**	CF_3COOH	0.5	**3**	7	st	200	2	50	20 – 250	88
Stationary phase — Pluronik P-94											
Glass	**1**	CCl_3COOH	4	**1**	–	st	200	2	20	20 – 250	88
Stationary phase — Sinperonik T/904, T/908											
Glass	**1**	Irganox	0.8	**1**	8	st	200	2	90 – 100	< 280	89

Note. The following designations have been adopted: *I* — initiator or catalyst: *II* — concentration of initiator or catalyst (mass %) [the irradiation dose (Mrad) is indicated in brackets]; *III* — cross-linking or cross-linking-grafting agent: *IV* — concentration of cross-linking or cross-linking – grafting agent (mass %); SP — stationary phase; st — static immobilisation regime (in a sealed column); dn — dynamic immobilisation regime (in a stream of carrier gas); *Z* — immobilisation efficiency equal to the ratio of the capacity factors of the capillary columns before (*K*) and after (*K′*) extraction of the immobilised stationary phase: $Z = (K/K')100$; DPS — diphenyltetramethyldisilazane; Irganox — pentaerythritol tetrakis-3,5-di-*tert*-butylphenyl-β-4-hydroxypropionate; GTB — graphitised thermal black; BP — benzoyl peroxide; AIBN — azobisisobutyronitrile; 3,5-DNSA — 3,5-dinitrosalicylic acid; AtO — azo-*tert*-octane; SE-54 — methylsiloxane containing 5% of phenylpolysiloxane units. Cross-linking and cross-linking – grafting agents: **1** – **15** — see text. The isocyanates **12** and **13** tend to undergo oligomerisation; the corresponding oligomers are known under the commercial names Desmodur N75 (the number of functional groups is 5 – 6) and Desmodur L75 (the number of functional groups is 6 – 7). The main properties of the stationary phases of the commercial brands indicated are quoted in chromatographic handbooks and Company Catalogues.

V. Thermal immobilisation

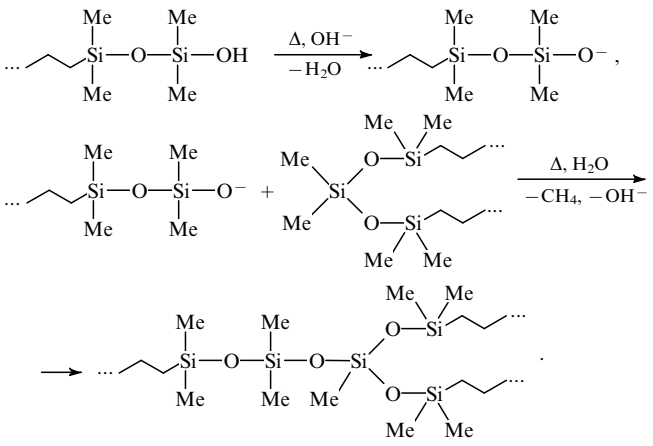
In the majority of methods for the immobilisation of the stationary phase, use is made of the activating effect of thermal energy. Furthermore, in the case of polymeric stationary phases with a specific structure, the thermal energy can function as the principal initiator of the immobilisation process. This was illustrated for the first time in relation to the immobilisation of α,ω-dihydroxypolysiloxanes [97, 99, 138 – 140] and α,ω-dihydroxysilarenes.[141, 142]





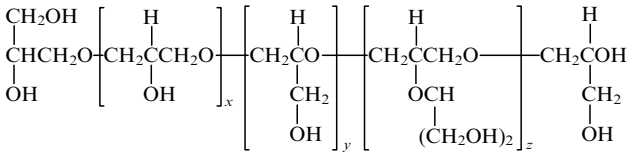
R = Me, Ph, $(CH_2)_3CN$, $(CH_2)_3CF_3$; R′ = Me, Ph.

On the basis of the analysis of the volatile products formed on thermal immobilisation of α,ω-dihydroxypolysiloxanes, Welsch and Teichmann [143] proposed the following process mechanism. Under the influence of temperature and catalytically active impurities (traces of O_2, H_2O and the basic catalyst for the polymerisation of the stationary phases), present in the column, siloxide ions are formed and attack the Si – C bond of the polymer and/or the silanised surface of the column. The corresponding hydrocarbon is then evolved and the cross-linking and grafting of the stationary phase take place.



Polycondensation *via* silanol groups makes an appreciably smaller contribution to the immobilisation of α,ω-dihydroxypolysiloxanes than was postulated initially.[138, 139, 144–149] The application of the thermal method for the immobilisation of polysiloxanes improves significantly the inertness and thermal stability of the capillary column. As a consequence of this, the possibilities of capillary gas chromatography for high-temperature analysis have expanded. Using thermally immobilised α,ω-dihydroxypolysiloxanes, Blum and coworkers[98, 150, 151] developed methods for the direct gas-chromatographic determination of petroleum porphyrin bases, their metal complexes, and other organic compounds with molecular masses up to 1196 (the traditional applications of gas chromatography involve compounds with molecular masses up to 500).[152] However, on increase in the content of functional groups, the capacity of α,ω-dihydroxypolysiloxanes for immobilisation under the influence of temperature diminishes. Thus the degree of thermal immobilisation of α,ω-dihydroxypolysiloxane containing 60% of cyanopropyl groups does not exceed 40%.[140] For this reason, the polar α,ω-dihydroxypolysiloxanes are usually immobilised with the aid of cross-linking-grafting agents.[91, 98, 99]

The thermal method has been used by ourselves in the immobilisation of a hydroxyl-containing stationary phase with a polyglycidol (PG) structure.[153, 154]



It was proposed to use the capacity of polyalcohols for structure formation on heating as a result of dehydration.[155] Evidently the main condition governing the application of this approach in chromatography is an optimum hydroxyl functionality of the initial polymer, ensuring not only its capacity for structure formation but also the permeability of the structured polymer film to sorbate molecules over a sufficiently wide temperature range. The range of working temperatures of the PG-based thermally immobilised phase (PG^{TM}) is from 80 to 300 °C. The chromatographic characteristics of PG change only slightly in the thermal immobilisation process. This makes it possible to postulate that the chemical nature of the bulk of the stationary phase, accessible to sorbate molecules, also hardly changes, *i.e.* an appreciable proportion of the OH groups are retained, although the phases are in fact immobilised *via* these groups. The PG^{TM}-based thermally immobilised phase is characterised by a high resistance to the action of organic solvents and water even at an elevated temperature.

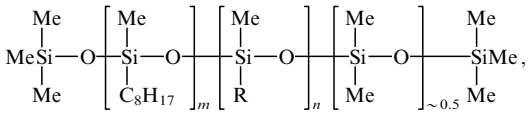
The resistance of immobilised polar phases to the action of solvents is known[7, 24, 28, 29] to be determined to a large extent by the presence of chemical bonds between the stationary phase and the walls of the capillary column. However, in the case under consideration the multicentre sorption of the hydroxyl-containing PG^{TM} macromolecules on the dehydrated surface of the glass column is apparently of decisive importance. Among the disadvantages of PG^{TM} one should note the low permeability of this phase to diffusion, which is largely caused by the low segmental mobility of the polymer macromolecules owing to the high density of the hydrogen bonds. When PG^{TM} is used under the conditions of steam chromatography, water loosens the supermolecular structure of the stationary phase films and hence the HETP is reduced by a factor of 2.8, while the minimum working temperature falls by 40–45 °C. On the other hand, the functional selectivity of PG^{TM} increases by only 5%. It is of interest that the corresponding characteristics of PEG 20M under analogous conditions vary in a different way: the selectivity of the phase changes most appreciably (it increases on average by 20%), whereas the efficiency of the separation increases only by a factor of 1.1. By virtue of the high content of the reactive OH groups and the resistance to the action of solvents, PG^{TM} may be used as a matrix for the preparation of new polar immobilised stationary phases *via* their chemical modification *in situ*.[156]

Thus the thermal method for the immobilisation of hydroxyl-containing stationary phases makes it possible to obtain the most inert and thermally stable capillary columns and also leads to new possibilities in the synthesis of polar immobilised phases.

VI. Design of hydroxyl-containing stationary phases to be immobilised

Until recently polymeric materials obtained for other purposes have been used as the stationary phases in capillary gas chromatography.[36, 37] However, it was found that the properties of many stationary phases do not meet the necessary set of requirements most fully formulated by Blomberg.[39] According to these requirements, the stationary phases must possess a definite type of selectivity, chemical inertness, thermal stability, reproducibility of properties, an adequate diffusional permeability, and the capacity for immobilisation *in situ*. The experimental data accumulated towards the middle of the 1980s made it possible to proceed to the deliberate synthesis of phases specially designed for capillary gas chromatography.[115, 116, 120, 157–160] Computer modelling has been used in recent years to determine the composition, structure, and immobilisation conditions for new phases employed in the analysis of specific objects.[23, 120, 161–164] For example, the stationary phase DB-Dioxin, described by Lautamo *et al.*[162] and Jennings and Nikelly,[163] represents the application of a computer model of a selective stationary phase for the separation of a series of isomers of polychlorinated dibenzo-*p*-dioxins and dibenzofurans.

The search for phases comparable to PEG in their selectivity but having a wider range of working temperatures and more readily immobilised, is being prosecuted. For this purpose, studies are made on block copolymers of dimethylpolysiloxane and PEG[165] and on copolymers of ethylene glycol and siloxane (brand OV-330 phase).[71] However, polysiloxanes of grafted oligo(ethylene oxide) fragments (PS-OEO) exhibited the best chromatographic characteristics.[166–169]



R = $(CH_2)_3C_6H_4O(CH_2)_2(OCH_2CH_2)_{2-3}OMe$,
$m = 0.02-0.05$, $n = 0.45-0.48$.

The composition and structure of the copolymer were optimised taking into account the requirements, listed above, which must be met by the phases: thermal stability, satisfactory adhesion to glass and quartz, and excellent permeability to diffusion are characteristic of the polysiloxane; oligo(ethylene oxide) ensures the required type of selectivity, while the octyl substituent simplifies

the immobilisation by treatment with radical process initiators. This type of 'brush' structure, which successfully combines the advantages of the siloxane skeleton and functional-selective substituents, is characteristic of the majority of new generation stationary phases.[170–175] Certain characteristics of such phases are presented in Table 2.

Table 2. The capacity factor (k'), the retention index (I), the number of effective theoretical plates (N), and the range of working temperatures of a quartz capillary column (20 m × 200 μm) with different stationary phases.[168]

Stationary phase	Dodecanol		Biphenyl		N /tp m^{-1}	Range of working temperatures /°C
	k'	I	k'	I		
PS–OEO	16.0	1800	15.2	1920	5700	20–280
Carbowax 20M	15.4	1756	15.5	1925	5400	60–220
Bondable PEG	17.1	1985	14.2	1740	5600	40–260

It must be emphasised that the advances in the practical realisation of the possibilities of capillary gas chromatography are determined to a large extent by the high quality and diversity of the properties of the capillary columns. The synthesis of new stationary phases, the composition and structural parameters of which have been optimised taking into account the general requirements and characteristics of the objects to be analysed, is therefore one of the principal aspects of the development of capillary gas chromatography.

VII. Conclusion

Hydroxyl-containing stationary liquid phases are nowadays the commonest selective phases in capillary gas chromatography. The polarity of such phases varies within fairly wide limits. The methods for the preparation of immobilised phases examined in the present review make it possible to create the optimal stationary phase of this type for the given variety of separation.

The further development of the methods for the preparation of hydroxyl-containing stationary phases should in our view take place in the following principal directions (1) preparation of hydroxyl-containing chiral phases; (2) increase in the thermal stability of the hydroxyl-containing phases; (3) deliberate alteration of the properties of the hydroxyl-containing phases by dissolving organic and inorganic solvents in them.

In conclusion we may note that the immobilised phases are of interest also for employment in packed columns.[176]

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