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APPLICATION OF SILANE-COUPLING AGENTS FOR MEDIUM-POLARITY CAPILLARY COLUMNS

H. TRAITLER* and L. KOLAROVIC

Nestlé Research Department, P.O. Box 88, CH-1814 La Tour-de-Peilz (Switzerland)

and

A. SORIO

Union Carbide Europe, Versoix/Geneva (Switzerland)

SUMMARY

Silane-coupling agents (SCA) were applied for deactivation and increasing the wettability in both glass and fused-silica capillary columns prior to coating with medium-polarity stationary phases, such as Carbowax 20M or Superox. γ -Glycidoxypropyltrimethoxysilane induced a satisfactory surface deactivation, offering the possibility of preparing highly efficient columns in a one-stage (fused-silica) or two-stage (glass) process. Further laboratory experiments indicated the potential of SCA for generating the effect of phase immobilization via a radical-induced grafting and cross-linking mechanism. Immobilized-phase (IP) Carbowax 20M capillaries, operating in the range 80–280°C, started to destabilize only above 305°C. A gas chromatographic (GC) evaluation of the IP columns before and after methanol flushing demonstrated different polarity behaviour. The IP columns are suitable for GC analyses of broad-range mixtures [C₆–C₃₀] of fatty acid methyl esters including *cis-trans* isomers.

INTRODUCTION

The preparation of capillary columns is generally associated with three possible mechanisms: the first concerns stabilization of the parent coating on unwettable column surfaces (*bonding*), the second involves *grafting* of silane monomers on the chain of the parent polymer, and the third *cross-linking* of the silane units grafted on the parent polymer matrix.

A recent publication¹, referring to previously published data on the capacity of silane-coupling agents (SCA) to bond organic polymers to inorganic materials, described a preparation of both glass and fused-silica capillaries, coated with medium-polarity phases. Acid-leached and dried Pyrex glass columns or, alternatively, fused-silica columns were first flushed with a solution containing 5% (w/v) γ -glycidoxypropyltrimethoxysilane (GPTMS) (Union Carbide, New York, NY, U.S.A.) in methanol and then loaded by suction with the coating solution. This work demonstrated the possibility of inducing both wettability and deactivation of capillaries by SCA, whereas the bonding mechanism remained unconfirmed in terms of practical experiments or plausible theories.

Previously published results²⁻⁴ demonstrated the possibility of phase immobilization by reacting vinyl, methyl or cyanoalkyl side groups *in situ* with peroxides. Apolar or very low polarity stationary phases produced non-extractable films, suitable for regeneration by certain organic solvents and, also, resistant towards the phase stripping effect induced by on-column injections (OCI). The extent of phase immobilization, suppressing the risk of thermal rearrangement in the polymer matrix, correlated positively with low bleeding rates of immobilized-phase (IP) capillaries. These results were causally associated with the cross-linking mechanism, as the effect of chemical bonding to the glass surface remained unconfirmed, as in the above instance.

This paper describes the preparation of medium-polarity IP capillary columns, taking into account the possibility of combining the action of immobilization agents or their mechanisms. Fused-silica or, alternatively, acid-leached glass capillaries, after treatment with GPTMS, were coated with a mixture containing Carbowax 20M, GPTMS, dicumyl peroxide (DCUP) and dibutyltin dilaurate (DBTDL) as a cocatalyst. The resulting film, after it was flushed with methanol, was more resistant to higher temperatures than the parent polymer without any decrease in separation efficiency.

EXPERIMENTAL

Fused-silica (25 m × 0.32 mm I.D.) or acid-leached glass (25 m × 0.30 mm I.D.; Duran) capillary columns were loaded by suction with a deactivation solution containing 5 % (w/v) of GPTMS in methanol¹, as already described. The coating solution, prepared by dissolving 1000 mg of Carbowax 20M (Applied Science Labs., State College, PA, U.S.A.), 500 mg GPTMS, 15 mg of DCUP (Merck, Darmstadt, G.F.R.) and 13.5 mg of DBTDL (Fluka, Buchs, Switzerland) in 100 ml of dichloromethane, was diluted from the initial 15.285 to 2.55 mg ml⁻¹, passed through a dichloromethane-pretreated, fluted filter-paper and then loaded by suction into the capillary column. After static coating at 50°C, the column was conditioned cyclically overnight, from 80 to 240°C at a rate 2°C min⁻¹, and then evaluated by the Grobtest. After flushing with 5 ml of methanol, the column was further conditioned up to 290°C by increasing the range of the previous temperature cycle in 10°C increments. A 290°C isotherm was maintained several times until the bleeding rate became stabilized. After a second Grobtest evaluation, the column was ready for routine work.

In order to test the extent of phase immobilization, a fused-silica column was subjected to an additional methanol flushing, after which the phase behaviour was evaluated as already indicated.

RESULTS AND DISCUSSION

Experimental assessment of stoichiometric ratios for the components of copolymerization was performed by the reaction of complete phase mixtures (Fig. 1) under reflux and a subsequent gravimetric evaluation of the dichloromethane-insoluble copolymer. A major part of the work was carried out with Carbowax 20M, DCUP, DBTDL and vinylsilane (Union Carbide, New York, NY, U.S.A.). The latter was later replaced with GPTMS, whereby thermal stability of the resulting copolymer increased by 30°C when tested under GC conditions.

As shown in Fig. 1, the degree of copolymerization was modulated by the concen-

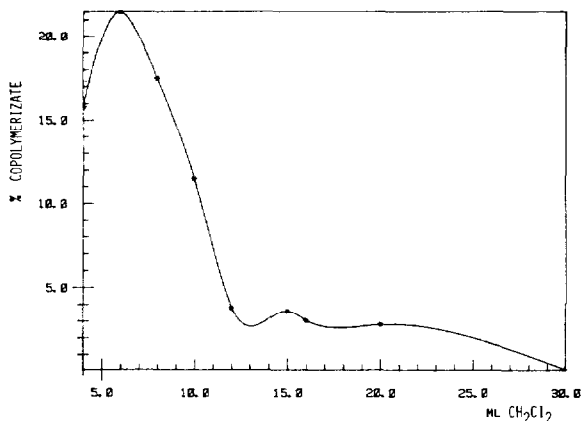


Fig. 1. Different levels of the dichloromethane-insoluble copolymer, obtained after a 2-h reaction of a mixture of 100 mg of Carbowax 20M, 500 mg of vinylsilane, 15 mg of DCUP and 13.5 mg of DBTDL at various concentrations under reflux.

tration of experimental mixtures. As the effect of temperature upon copolymerization was almost suppressed in this experiment, the maximum level of dichloromethane-insoluble materials reflected predominantly the influence of other parameters, such as humidity, viscosity, concentration or stoichiometric ratio of the reactants.

These experimental data, essential for assessment of the stoichiometric formulae, were not relevant to the problem of the determination of real filmthicknesses in IP capillaries. Particularly after methanol flushing this parameter remained unknown, as

TABLE I

RETENTION TIME DIFFERENCES Δt_R of GROB-TEST MIXTURE, AS RECORDED BEFORE AND AFTER METHANOL FLUSHING

Injection temperature: 70°C. Rate: 1.7°C min⁻¹.

Peak No.	Compound	Δt_R (%)	IP fused-silica column	
			1st flushing	2nd flushing
1	Decane	3.05	20.51	3.45
2	Undecane	4.00	29.73	3.57
3	Nonanal	15.13	*	17.13
4	1-Octanol	**	20.15	27.59
5	2,3-Butanediol	16.01	37.35	20.3
6	Methyl decanoate	13.98	32.87	13.83
7	Dicyclohexylamine	**	33.01	7.68
8	Methyl undecanoate	**	28.32	12.12
9	Methyl dodecanoate	10.27	27.34	17.18
10	2,6-Dimethylaniline	12.32	26.31	10.59
11	2,6-Dimethylphenol	11.54	31.33	16.73
12	2-Ethylhexanoic acid	***	***	***

* Adsorbed by the unflushed film.

** Not included in this mixture.

*** Tailing peak.

the IP column, operating only at temperatures higher than 70–75°C, could obviously not be tested at oven-temperatures to fulfill this Grobtest criterion (usually <50°C). Consequently, both Carbowax 20M and IP Carbowax columns were evaluated by comparing the retention time differences of fatty acid methyl esters (FAMES) in order to determine which concentration of the IP mixtures correlated best with the performance of Carbowax 20M (filmthickness 0.15 μm). This procedure demonstrated that the most probable concentration ratio between the IP mixture and Carbowax 20M was 1.38:1. Consequently, a previously published equation⁴ for calculating the concentration of coating solutions was modified for fused-silica columns as follows:

$$\text{mg IP mixture/ml} = 1.38 \cdot 4 \cdot \frac{\text{desired film thickness } (\mu\text{m})}{\text{column I.D. (mm)}}$$

This empirical evaluation suggested that from 70 up to 75 % of the immobilized phase remained in the column after methanol flushing. This finding, when associated with results of the reflux procedure (Fig. 1) also emphasized the importance of elevated temperatures, apart from other parameters, on the extent of copolymerization or phase immobilization.

An attempt was also made to monitor a relative filmthickness reduction after

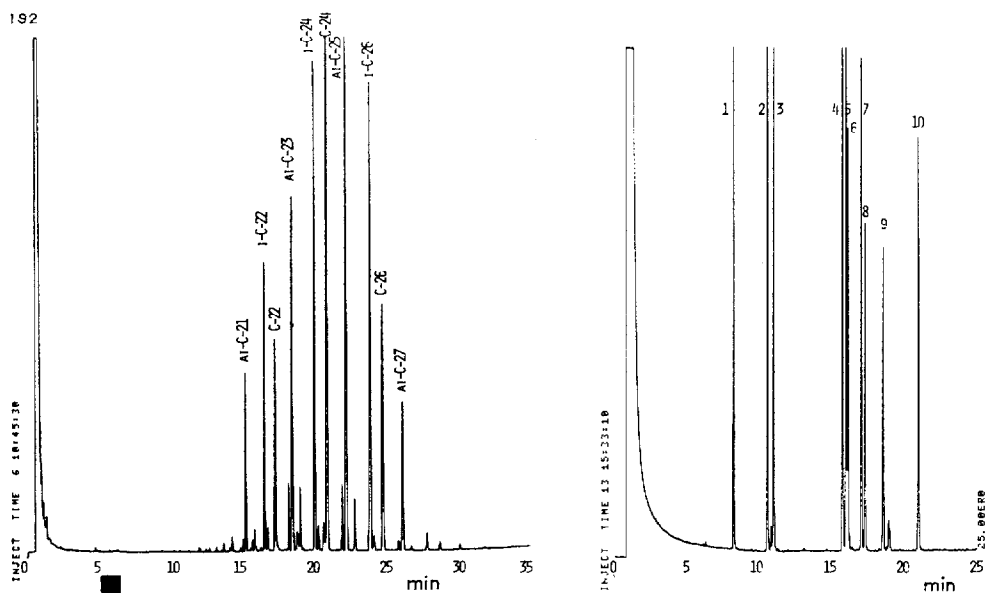


Fig. 2. GC separation of long-chain FAMES including iso (I) and *ante*-iso (AI) isomers after a second column flushing with methanol. Column: fused-silica, coated with IP Carbowax 20M. Aparatus: Carlo Erba Series 4160. Injection: cold on-column. Carrier: 0.81 kg cm⁻² H₂. Programme: 80°C, 2 min isothermal, 15°C, min⁻¹ to 135°C, 1 min isothermal, 10°C min⁻¹ to 185°C, 1 min isothermal, 3°C min⁻¹ to 250°C.

Fig. 3. GC separation of *cis*-*trans* isomers of FAMES, previously dissolved in methanol. Peaks (1) C-15:0; (2) C-16:0; (3) C-16:1; (4) C-18:0; (5) C-18:1 *cis*; (6) C-18:1 *trans*; (7) C-18:2 *cis, cis*; (8) C-18:2 *trans, trans*; (9) C-18:3; (10) C-20:0 Column: as in Fig. 2, but flushed only once. Programme: 120°C, 2 min isothermal, 3°C min⁻¹ to 185°C, 1 min isothermal, 5°C min⁻¹. Pre-set splitting ratio: 1:25. Carrier gas: 0.80 kg cm⁻² H₂.

methanol flushing. This was accomplished by analysing the polarity testmixture at the lowest possible temperature (70°C) in order to determine the retention time differences Δt_R for flushed and unflushed columns as percent values (Table I). IP glass columns responded to methanol flushing with lower Δt_R than their fused-silica equivalents, which only after a second treatment produced comparable values. Such a tendency suggests that certain residual metals (Na, Al, Ca) in the acid-leached borosilicate-glass capillaries were possibly implicated in a catalysis of the copolymerization, thus producing less extractable films. The amount of metals in fused-silica columns is almost insignificant (0.001 – 0.2 ppm) in comparison with the values found for untreated borosilicate columns (0.5 – 13 %).

The separation efficiency of IP Carbowax 20M capillaries is suitable for GC analyses of broad-range mixtures of FAMEs ($C_6 - C_{30}$), as the upper temperature limit is 280°C (Fig. 2). The column properties were indispensable in the case of fatty acid pyrolidides (FAPs), which are less volatile than FAMEs. Also *cis-trans* isomers of FAMEs were adequately resolved (Fig. 3). On the other hand, the IP Carbowax 20M column, operating only above 70°C, was found to be inefficient in analyses involving methyl butyrate.

Phase immobilization was more efficient in glass capillaries than in fused-silica columns (Table I). However, this tendency was insignificant in practical applications. Also, fused-silica columns offer two principal advantages, as they can be coated without acid leaching and their mechanical properties guarantee an increased resistance toward inept handling.

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