

## Note

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### New approach to capillary columns for gas chromatography?

#### Condensation of hydroxyl-terminated stationary phases

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(Received August 2nd, 1985)

We should make it clear at the outset that the “approach” referred to in the title is new to individual column makers, although its development was started in 1978<sup>1</sup> since when it has received limited attention without influencing the common procedures for column preparation. Owing to the perfect secrecy surrounding commercially applied procedures, we cannot exclude the possibility (we even suspect) that the new approach has become of great importance in industrial column production.

Verzele *et al.*<sup>2</sup> presented a comprehensive survey of the background of the approach, which is characterized by various sidetracks for specific purposes that have meanwhile become less attractive. Advanced ideas including the approach among others have been discussed by Lipsky *et al.*<sup>3</sup>. Surprisingly, apart from a short complement by Sandra *et al.*<sup>4</sup>, the literature has been silent on the topic for almost 3 years.

Verzele *et al.*<sup>2</sup> described a surface pretreatment consisting of baking a thin deposit of a low-viscosity hydroxyl-terminated phenylmethylsilicone, which is followed by coating with a high-viscosity version of the same phase. Immobilization occurs by mere heat curing (150–250°C, repeatedly). The authors see the strong point of the procedure in the immobilized coating, with well-defined selectivity and polarity that are due to total absence of groups other than phenyl and methyl. As a mechanism of immobilization they assume the formation of very long chains, the terminal silanols of which can be capped by silylation. They also envisage additional cross-linking, if desirable. As an upper temperature limit, 280–300°C was indicated, which was subsequently<sup>4</sup> amended to 370°C.

#### EXPERIMENTAL

We have studied the following hydroxyl-terminated phases: OV-61 (33% phenyl); OV-17 (50% phenyl); OV-1701 (7% phenyl, 7% cyanopropyl); and an experimental phase with 17% cyanopropyl groups. All phases have been kindly provided, at our request, by Ohio Valley Specialty Chemicals.

DURAN glass was leached and dehydrated as usual<sup>5</sup>, but with a wide range of the experimental parameters. Persilylation for OV-61 and OV-1701 was carried out with diphenyltetramethyldisilazane (DPTMDS), for OV-17 with tetraphenyldi-

methylidisilazane (TPDMDS), and for the 17% cyano phase with the mixture of XF-1150 and DPTMDS, as recently reported<sup>6</sup>. All persilylations occurred at 400°C for 15 h.

For regular static coating, the phases were dissolved in pentane-methylene chloride (1:1, v/v), as described recently<sup>7</sup>. At the end of this procedure, the columns were mounted in a gas chromatograph with the exit connected to a flame ionization detector. At a gas flow-rate roughly three times the normal, and with strong attenuation, the columns were directly heated to 160–180°C, followed by temperature programming to 310°C at a rate determined by the column length (5°/min for 10 m, 2.5°/min for 20 m). During the entire heat treatment (40–100 min) a chromatogram was recorded. When the intense, and complex, elution came to a clear end, a first test was run. Further tests followed after prolonged baking.

#### THE IMMOBILIZATION PROCESS

Fig. 1 shows a chromatogram obtained during the first heat treatment of a freshly coated column. By the end of the treatment, immobilization was observed, so the chromatogram provides an indirect description of the immobilization process. For a given phase, the corresponding chromatogram is surprisingly typical and reproducible, in terms of the number, shape, and even minor details, such as the shoulders on the rear slope of the peaks. The peak areas correlate reasonably with the total mass of the stationary phase, which depends on the film thickness and the column length. It seems, therefore, that the thermal process produces a series of defined volatiles, which have not yet been checked mass spectrometrically. Typical for all phases is the step-wise sharp descent, which indicates complete elution of a volatile after chromatography under drastically overloaded conditions. Depending on the phase, the last volatile elutes between 280 and 310°C. Elution is also evidently influ-

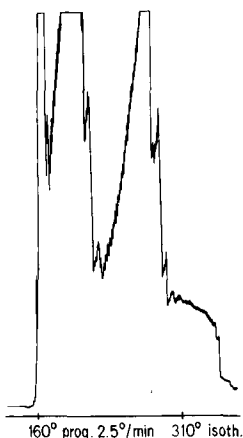


Fig. 1. Chromatogram recorded during the first conditioning of a column (20 m  $\times$  0.32 mm I.D.) fresh coated with 0.3  $\mu$ m OV-61-OH. Immediately after coating the column was connected to a stream of hydrogen at 1.0 bar, and heated directly to 160°C. Flame ionization detection Carlo Erba Model 4160; attenuation, 1024. The three major peaks with the shoulders on the rear slope are typical for OV-61-OH. Note the sharp descent of the baseline after *ca.* 15 min at 310°C isothermal, indicating the end of the gross condensation process.

enced by the column length and the filmthickness. A further influence related to some individual characteristics of the given column is discussed below. Normally, after 40–100 min, the recording suddenly returns to a clean baseline.

#### POLARITY

The idea that the absence of groups other than methyl or phenyl should ensure a defined polarity works in a less straightforward way than expected. As Fig. 2 shows, the polarity slowly drops during conditioning. A slight decrease may even be observed after several days of continuous heating above 300°C. It seems logical to attribute the change to a gradual loss of terminal silanols, which may no longer play a role in immobilization but still influence the polarity.

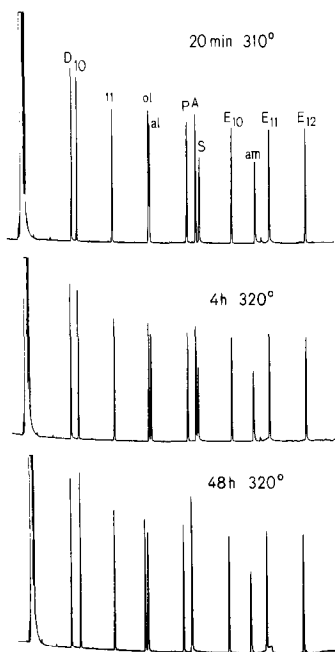


Fig. 2. Decreasing polarity owing to loss of terminal hydroxyl groups. Column, 15 m  $\times$  0.32 mm I.D., persilylated with DPTMDS, coated with 0.25  $\mu$ m OV-1701-OH. First test immediately after the condensation reaction, further tests after prolonged conditioning. Peaks: D = 2,3-butanediol; 10,11 = *n*-alkanes; ol = 1-octanol; al = nonanal; P = 2,6-dimethylphenol; A = 2,6-dimethylaniline; S = 2-ethylhexanoic acid; am = dicyclohexylamine; E<sub>10</sub>–E<sub>12</sub> = fatty acid methyl esters. Injection at 25°C, programme 2.5°/min from 40°C. Note the increasing distance of D from 10, and of ol from al, as well as the merging of S with A. Note also the slight loss of inertness at 320°C. Less balanced columns may show far stronger polarity drift. (An unknown impurity influences the baseline of E<sub>11</sub>.)

Here, we think the following observation to be of importance. As a typical feature of glass, the density of hydroxyls on the silica surface can be varied over a wide range by varying the intensity of leaching (130–185°C, 5–20 h) and of dehydration (150–450°C, 1–4 h), as well as by varying the persilylation conditions. The observation is that the polarity decreases more rapidly on a strongly hydroxylated sur-

face. This, together with further observations (see next paragraph), causes us to suspect that the condensation reaction between silanols on chain-ends and on the surface is faster than the reaction between chain ends. Thus, immobilization may be based primarily on surface bonding, rather than on a big increase of chain length (the latter may occur as well, but with an effect more on the polarity than on immobilization). This interpretation is further supported by the fact that heating the pure phase (to the same temperature, for the same time) is a far less efficient way of producing an insoluble (immobilized) material than heating the phase on the silica surface.

Verzele *et al.*<sup>2</sup> mentioned in passing the possibility of silylating the condensed coating. We confirm, and emphasize, this information. Except for apolar phases, the silylation of silicone coatings generally produces no effect, or even a negative one. In contrast, coatings based on hydroxyl-terminated phases are well suited to silylating. A slow injection, without splitting, of 20–50  $\mu$ l of hexamethyldisilazane onto a column at 140°C is rather effective. Residual silanols are eliminated, with a corresponding reduction of polarity. Important column-to-column differences in the efficiency of silylation are observed, probably owing to different degrees of silanol consumption by the bonding process.

If reproducibility of the polarity is the major purpose, thorough silylation should be included as the last step of column preparation.

#### INERTNESS

Coatings obtained from hydroxyl-terminated phases are generally more inert than traditional ones. We attribute this to the elimination of residual surface silanols (not eliminated by persilylation) by the condensation reaction with the phase.

The study of inertness has confirmed a basic idea we have gradually built up over years from scattered observations. The idea is that silanols in the phase increase the polarity without influencing inertness. In contrast, silanols on the surface (besides also affecting the polarity) first of all reduce inertness. Consequently, inertness should not be correlated with the incidence of silanol groups on the column as a whole, but specifically with the silanol groups on the surface of the support.

From a large number of columns produced with widely varying parameters, we deduce an essential role of the balance between residual surface silanols (surviving persilylation) and phase silanols (resulting from the molecular weight of the phase, and film thickness). Columns reaching the balance show perfect inertness and easy conditioning (condensation). Excess phase silanols cause top inertness, but slow immobilization accompanied with a strong and long-lasting polarity drift. Excess surface silanols result in rapid immobilization and quick attainment of the final polarity. However, inertness is modest and never attains the desired level, although it considerably improves during conditioning. Also, it cannot be influenced significantly by silylation.

#### FILM STABILITY

Here, we face the main general limitation of our coating technique. The immobilized film is absolutely stable. However, we have to deposit it, at least for a short period, non-immobilized. This means that, for this period, stabilization has to be

based on the well-known physical interactions between the phase and the surface that create wetting. In other words, to make the film survive for one critical hour (before it will be stable for years), we have to invest a wealth of perspicacity and care without contributing to the final quality of the product. In fact, our efforts may even limit the final quality. And, as a matter of most regrettable fact, we are unable to make quite a number of columns because we are unable to master the problem of first-hour film stability.

To a certain extent, critical, or even missing, wettability can be replaced by increased phase viscosity (gum phases<sup>8</sup>), but this is not a general way out of the difficulty. The more polar phases (containing more than 50% of cyano groups) in particular are hardly amenable to a gum state, although being able to use them as gums would be especially beneficial. Thus, finding a principle to circumvent wettability as a basis of the first-hour film stability would be a real breakthrough.

Wettability requirements also reduce our freedom to vary the persilylation conditions. Of course, this restriction hinders the free selection of the density of surface silanols. This is a major reason why we are unable to present the above-mentioned balance concept in a more quantitative way.

#### BLEEDING AND THERMOSTABILITY

A most impressive feature of the new columns is the bleeding, which drops sharply to a very low level after the first condensation (immobilization) reaction and reaches the final level in a few hours, provided that balance has been attached. Bleeding is clearly related to the polarity drift. It may drop during conditioning at 310–330°C for 24–48 h, when polarity also further drops during the treatment.

Bleeding is a reasonable indicator of thermostability. It is difficult, however, to deduce absolute temperature limits from absolute bleed-rates. In most cases, relative indications are more informative. Good coatings based on hydroxyl-terminated phases reach a comparable bleeding behaviour at temperatures 60–80°C higher than conventional coatings, *e.g.* hydroxyl-terminated OV-1701 bleeds as much at 330°C as the conventional phase (vinylated, immobilized) at 250°C.

Our primary purpose of studying both phenyl and cyano phases, was to learn whether the new approach is equally applicable to both types (the earlier work was limited to phenyl phases). Fortunately, we found no dependence on the type of substitution. We agree with the statement of the first authors<sup>4</sup> on that phenyl-containing hydroxyl-terminated coatings reach a critical bleed-rate at 360–380°C. We found the corresponding value for cyano phases to be 330–350°C.

However, we are frequently more interested in knowing at what maximum temperature the inertness is affected within 24 h. Obviously, this temperature limit is below the one based on bleeding. It is here where we find a particularly strong point of the new approach. The difference between the temperatures at which comparable losses of inertness occur is as much as 80–100°C. Hydroxyl-terminated OV-1701 keeps its full inertness during 24 h at 320°C, compared with 220°C for the conventional coating.

## CONCLUSIONS

In our view, coatings based on hydroxyl-terminated phases represent an important progress, possibly even a revolution, in column technology. The specific strong points of more defined polarity, and ease of immobilization, are of secondary importance in our experience. The primary advantages are increased thermostability and increased inertness. The final weight of the progress will greatly depend on further advances in film stabilization, which would permit application to more polar phases. An important gap in our evaluation of the new approach is our lack of experience with apolar phases. Some additional information is in preparation<sup>9</sup>.

## ACKNOWLEDGEMENT

Basic parts of this work have been done in collaboration with W. Blum. He was the first to see the role of condensation between phase and surface silanols.

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