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SOME TECHNICAL ASPECTS OF THE PREPARATION OF A "RETENTION GAP" IN CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

The phenomena created by band broadening in space are eliminated by the use of a retention gap in the column inlet, *i.e.*, by keeping the first *ca.* 50–80 cm of the capillary column free of stationary phase. The extraction of the stationary phase from the retention gap zone is easy for polar coating. For non-polar silicone stationary phases, especially if immobilized, other methods have to be applied: (a) the phase may be burnt, (b) a deactivated, uncoated pre-column is connected to the column inlet or (c) the column is prepared with an inlet section free of stationary phase. Several methods for the preparation of a joint between a pre-column and the separating column are discussed. Glued joints are considered to be the most promising. It is proposed that commercial columns should be offered with an uncoated inlet section 3 m in length.

INTRODUCTION

In a previous paper[1] we described the phenomena of band broadening in space associated with splitless injections with a solvent effect or cold on-column sampling. It was shown that the cause of the band broadening in space was the large amount of condensed solvent flowing over a distance 10–60 cm from the injector further into the column. The sample components are spread over the whole length of the flooded column inlet. Such starting bands may cause peak broadening and peak distortion (even splitting). Peak distortion is pronounced if short columns, large sample volumes and medium to high polarity solvents are used.

Recently Knauss *et al.*[2,3] published work on the same subject. They came to different conclusions, which should be discussed briefly. They assumed that the band broadening in space is due to the fact that the sample is sprayed into the column in the form of micro-droplets. We agree that the droplets leaving the syringe needle fly surprisingly far until they touch the column wall: 5–10 cm, as can easily be observed with certain glass capillary columns. However, the dominating spreading mechanism rather resembles dynamic coating. It is a flow of liquid until its layer is reduced to a mechanically stable thickness. In addition to visual observation, this is supported by the facts that the length of the flooded zone is approximately proportional to the

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sample volume and that closely related phenomena exist in splitless injection with totally different introduction of the sample. We therefore do not agree that factors such as the size of the syringe needle and the injection rate have an influence on band broadening in space.

Knauss *et al.*[2,3] calculated an initial peak width on the basis of a (calculated) length of the flooded zone. As they did not realize the fundamental difference between band broadening in time[1] (observed, *e.g.*, as a result of the slow sample transfer of a splitless injection) and band broadening in space, they calculated the initial peak width in terms of seconds. Very small values were obtained, far too small to explain the peak broadening observed (and shown by the authors). In fact, the calculated values are correct only for non-retained peaks. The true broadening effect is the time indicated, multiplied by the capacity factor of the peak (which varies with retention).

The model proposed by Knauss *et al.* is too simple to allow a valid conclusion to be drawn. The recommendation to limit the sample volume to 2 μl is based on an erroneous calculation and on a very limited experimental background using a 25-m column. The same injection on to one of our standard columns of length 10–15 m would have produced intolerably distorted peaks. Further, their peaks might have looked worse if they had used other solvents.

In another paper[4] we proposed the concept of the "retention gap" to re-concentrate the band broadened in space. The gas chromatographic retention in the flooded zone is reduced to accelerate the migration of the spread sample components. These components become reconcentrated on the beginning of the regular film coating of the stationary phase. The two explanations given previously[4] are summarized in Fig. 1. By "retention gap" we do not mean a zone of "zero retention", but the retention in this section should be 10–100 times lower than in the remainder of the column to render peak distortion due to band broadening in space negligible.

The retention gap is achieved by using columns with an inlet section free of stationary phase or with at least 10–100 times less stationary phase than in the separating part of the column.

The length of the retention gap zone should be at least equal to the length of the flooded column inlet section. A length of 60–80 cm should be sufficient for all ordinary applications. A volume of 2 μl of solvent, if fully condensed, was found to flood 40–80 cm of the column inlet (for a capillary of 0.3 mm I.D.). As we found that an excessively long retention gap section does not reduce the separation efficiency of the column[4], it may be considered to prepare retention gaps of length 2–3 m to be able to cut off a dirty inlet section without being forced to make a new retention gap zone.

We recommended many years ago removing the stationary phase from the column inlet, although for other reasons than for the retention gap. First, condensed solvent may dissolve some stationary phase, carry it further into the column and pile it up there (phase stripping). Second, non-volatile by-products of the sample (including proteins, sugars and salts) cause trouble as a result of physical or chemical damage to the film of stationary phase or by creating spots with an extra retention. The non-volatile by-products penetrate into the column with the flooding solvent. Thus the elimination of the stationary phase from the flooded inlet section greatly reduces the problems caused by these by-products.

In this paper we report some experiences with the several methods to create a

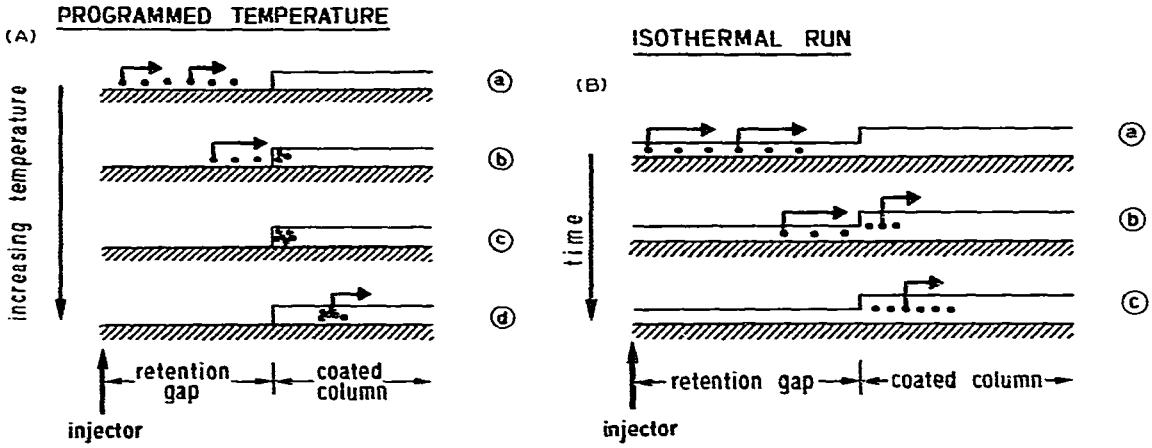

Fig. 1. The reconcentration mechanism of the retention gap. Summary of the two explanations given previously[4], both of which are simplified and account for one aspect of the phenomenon each. (A) Reconcentration in a temperature-programmed run. (a) The sample is spread out in the retention gap section. (b) At a certain column temperature a sample component is enabled to migrate in the section of low retention. However, the material is unable to migrate in the regularly coated column. (c) The component is blocked at the beginning of the regular coating. (d) At an increased temperature the reconcentrated band of the compound begins chromatography. (B) A hypothetical isothermal run; reconcentration by an insufficient retention gap with still half of the film thickness of the stationary phase (or half of the retention) compared with the regularly coated part of the column. Accordingly a component migrates through the retention gap zone at double the speed in the normally coated column. Assume that the first molecules of the band of, *e.g.*, 50 cm width have reached the beginning of the regular coating. The last molecules are 50 cm back. Where are the first molecules at the moment when the last molecules have reached the beginning of the regular coating situation (c)? As the forward molecules migrated at only half the speed of the rear molecules, they advanced only 25 cm. Hence the band width is reduced to half. An effective retention gap, however, should reduce the band width by a factor of 10 or 100 (depending on the conditions). Thus the film thickness of the stationary phase needs to be reduced accordingly.

retention gap. We did not find a universal method that is preferable to all others. At present, we use five techniques and choose between them according to convenience, the type of column used and the temperature range required in a particular application. Three fundamentally different approaches are discussed: (a) elimination of the stationary phase from the column inlet; (b) the use of disposable, empty pre-columns and (c) the preparation of columns with an uncoated inlet section.

ELIMINATION OF THE STATIONARY PHASE

Extraction with solvents

Some stationary phases are easily extracted from the column inlet with an appropriate solvent. Polyglycol phases such as the Carbowaxes, Pluronics and Ucons may be washed out with dichloromethane to a sufficient extent to create a retention gap. The remaining material of the stationary phase serves to deactivate the support surface in the retention gap zone.

The extraction was carried out similarly to the method described earlier[5]. A 100–500-μl syringe was connected to the column inlet by means of (elastic) polyethylene tubing or, if not available, by adjusting tubing of shrinkable PTFE. Some pressure

(about 0.3 atm of, *e.g.*, air) was applied from the other side of the column to ensure that no liquid may be sucked further into the column, *e.g.*, by a draught of air which cools the column and causes the gases inside the column to contract. A volume of solvent (*e.g.*, 70 μl) was then pushed rapidly into the column. This volume should be estimated previously according to the diameter of the column and the length of the capillary to be washed. It was intended to pass the solvent quickly over the film of stationary phase such that the front of the solvent plug did not have sufficient time to dissolve a substantial proportion of the phase. A slow introduction of the solvent would have allowed total dissolution of the stationary phase in the first few millimetres of the solvent plug. The front of the plug would have become extremely viscous, and when the plug was pulled back out of the column, a thick deposit of diluted stationary phase would have been left at the return point. The extract of the column inlet was discarded and a slightly higher volume of fresh solvent was injected (*e.g.*, 75 μl). This was followed by a third wash with, *e.g.*, 80 μl of solvent. The increased amount of solvent permitted the removal of a possible deposit of stationary phase at the return point of the solvent. The syringe was removed and the gas which provided the pressure from the other end of the column was allowed to sweep away most of the remaining solvent in the washed column inlet (10–30 sec). This procedure is easy to carry out with glass capillaries, as it may be followed visually.

Unfortunately, the extraction of common non-polar silicone stationary phases such as OV-1, -101, -73 and SE-52 and -54 causes problems. These stationary phases were sufficiently extractable before the column had been heated above about 250°C for some time. However, after a short period of use at elevated temperatures, a layer of stationary phase with a thickness of 0.02–0.08 μm became non-extractable. Thus only relatively thick-filmed columns (films exceeding about 0.4 μm thickness) could be extracted to an extent that created a sufficient retention gap. Columns with thin films, as used for triglycerides or thermolabile compounds (0.05–0.1 μm), were scarcely extractable after some use (which was in fact our starting point for the development of immobilized films of stationary phases[6]). It is obvious that the immobilized and the bonded silicone stationary phases are completely non-extractable.

Burning the stationary phase

When extraction of the stationary phase is impossible, it is worth considering burning the stationary phase in the retention gap zone. Obviously this method is restricted to columns without an organic outer coating. The inlet section of the glass capillary was heated with a small flame while air was passed through the column from the other end. To ensure complete burning it was convenient to heat the glass until it deformed. Thus a length of about 40–60 cm of the column was more or less straightened. The heating was started at the end of the column and about one and a half coils were wound off. Then the same section was flamed again in the reverse direction to ensure that partially burnt materials were eliminated. Finally, the heated section was wound up again to allow the installation of the column in the gas chromatograph.

Burning the stationary phase also means burning the organic deactivation of the support surface. Carbowax-deactivated columns tend to show extremely high activity after flaming, and should be re-deactivated by washing the surface with a solution containing about 0.1% of a Carbowax (*e.g.*, Carbowax 1000) in dichloro-

methane (carried out with a syringe connected to the column inlet by plastic tubing; the column is kept under pressure by about 0.3 atm of air from the other end). Leached and persilylated surfaces are far less active after burning the organic materials. Bare, not re-deactivated retention gap sections of such columns did not cause problems for most applications (including the analysis of polyaromatic hydrocarbons, free sterols and triglycerides). Carbowax deactivations of these surfaces were found to be of little help as they did not re-establish the full inertness of the column and caused increased bleeding of the column during a number of analyses.

Oxidation of the stationary phase allows an easy and rapid introduction of a retention gap for non-extractable stationary phases. The upper temperature limit of the column is not reduced. However, a highly inert column loses some of its inertness concerning chemical activity and adsorption, which, for our applications, was a hindrance with only a few exceptional samples.

PRE-COLUMNS

It appears attractive to use deactivated (*e.g.*, persilylated) but uncoated pre-columns to create a retention gap. Such pre-columns could be disposable and exchanged whenever they become contaminated with by-products of the sample. Thus they could represent a solution to the problems caused by the injection of dirty samples. As these pre-columns may consist of fused silica, they may allow easy installation of glass capillaries without the necessity for end straightening. Furthermore, pre-columns allow the use of narrow-bore capillaries for cold on-column injections if a pre-column with a sufficiently large inner diameter is chosen. This is particularly attractive because the low flow-rate through narrow bore columns does not allow regular splitless injection[7].

The advantages of the pre-column justify some detailed investigations into the problematic part of this configuration, *i.e.*, the connection of the pre-column to the analytical column. We were not able to find a generally applicable method without drawbacks. We therefore prefer to report our experiences with different techniques.

Shrinkable PTFE tubing

The use of shrinkable PTFE tubing for column connection purposes is well established. PTFE couplings may also be used for fused silica columns, provided the diameter of the tubing is sufficiently small when shrunk. Shrinkable PTFE connections are very popular as they are cheap and rapidly made. However, their limitations need to be considered.

PTFE loses its mechanical stability above about 240°C. The connection may be deformed if there is strain on the coils and the two butts are pushed apart by the carrier gas pressure (which is relatively high as the connection is in the columns inlet). The connection may be reinforced by a second or even a third PTFE tube slipped over the lower, shrunk one. A 1.5–2.5 cm long glass or metal tube pushed over the connection and fixed with glue is preferable.

PTFE tubing is known to allow air (oxygen) to diffuse into the column. This is a serious problem for columns coated with oxygen-sensitive stationary phases such as the polyglycols. The columns show increased bleeding and deteriorate unusually rapidly. However, columns with non-polar silicone phases coated on to persilylated

supports were found to support even air as the carrier gas up to about 280°C without any noticeable deterioration[8], thus allowing higher temperatures than the PTFE connection.

The most serious drawback of connections with shrinkable PTFE tubing is their tendency to cause discrimination, *i.e.*, to retain preferentially high-boiling materials. This discrimination was often found to be unstable, thus contributing to high standard deviations. Poorly made connections with an excessive distance between the two butts of the columns nearly completely eliminated the peaks eluting at elevated column temperature (especially if the PTFE surface in the critical area was contaminated). However, even well made connections showed some discrimination, which typically increased during the use of the column.

The two ends of well linked columns are some fractions of a millimetre apart. This distance is in the range of the height equivalent to a theoretical plate (HETP) and similar to the average length of the path of a molecule between two contacts with the stationary phase. It is likely that a certain amount of a sample component "falls" between the two butts of the columns. This material is retarded and may not elute together with the normal peak. Either it returns slowly into the bore of the column (without the formation of a peak) or it is lost inside the PTFE tubing.

Driessen and Lugtenberg[9] have shown such losses by means of the chromatography of a fluorescent sample component. Part of the substance left the bore of the column through the gap between the two columns and diffused through the shrunk PTFE tubing. It spread over most of the plastic and the chance of it returning into the column was negligible. Thus the connection was not tight, either for the oxygen entering the column or for the sample leaving the column.

The chromatogram obtained from a column with a plastic connection represents only the material that "jumped" over the gap. The proportion of the material lost through the joint depends on the type of compounds and the chromatographic conditions. Hence, losses are not linear.

Connections with shrinkable PTFE tubing are useful for qualitative analyses as they are easy to prepare. For quantitative analyses they sometimes seem to allow reasonable results. However, they are not reliable.

Screwed joints

Screwed joints allow the most convenient exchange of pre-columns. Connections are rapidly made and do not require the column to be taken out of the oven. There are many screwed joints available on the market. Most of them consist of a piece of metal with a hole adjusted to the outer diameter of the columns to be joined. The columns are tightened by screws and fittings from each side.

Our experience with screwed joints was disappointing. The joints tend to be heavy and require a special suspension. Glass capillaries need to be straightened for the short section to fit into the joint, which is a considerable drawback if the necessary attention that has to be paid to the activity of these heated sections is considered. Finally, the problem of the dead volume cannot be considered to have been solved. Solvent peaks are strongly broadened by trace amounts of solvent diffusing into these volumes and returning with a delay. The bore of the screwed joint is not well enough adjusted to the outer diameter of the column. Connections of two columns with different outer diameters (*e.g.*, a glass capillary column to a fused-silica pre-column) are impossible.

The smallest and lightest screwed joint is made with a single fitting, inside which the two columns are joined. The fitting is squeezed on to the columns by two cases screwed on to each other[10]. This connection has several advantages: it does not require a special suspension system, the columns do not need to be straightened as the column sections inside the fitting may be kept very short and there is almost no dead volume as there is no space between the outside of the column ends and the fitting. However, there remains the problem of finding an appropriate material for the fitting. Plastic materials such as Kalrez (a high-temperature PTFE material from DuPont) showed similar effects to shrinkable PTFE. Hard materials are difficult to tighten. The fitting should probably be made of metal with thin walls.

The relatively high thermal mass of metallic joints requires more time to warm up than the column. Thus the temperature of the columns located inside the joint lags behind the temperature of the remainder of the column. Such temperature differences are particularly large if the analytical procedure involves a rapid heating step, *e.g.*, because the injection has to be carried out at a lower temperature than the analyses, as is common for cold on-column injections and splitless sampling with a cold trapping effect. Under such conditions the difference in the temperatures inside the joint and in the oven easily exceeds 30°C. However, even during normal temperature programming the temperature differences are notable. Table I gives some results for temperature programming rates of 2 and 10°C/min using two joints with different characteristics: (a) a home-made screwed joint consisting of a Kalrez fitting and two thin-walled aluminium cases (1 g) and (b) a relatively light (7.5 g) commercial screwed fitting containing a central metal piece and two screws (Miconn Antech, Bad Dürkheim, G.F.R.). The temperature inside the joint was determined by means of a thermocouple.

TABLE I

DIFFERENCES IN TEMPERATURE INSIDE A SCREWED JOINT AND THE GC OVEN DURING TEMPERATURE PROGRAMMING

Programming rate (°C/min)	*Temperature difference (°C)*	
	Miconn (two fittings)	*Low-mass joint (one fitting)*
2	5	4
10	16	8

Although the temperature differences in Table I are considerable, we were not able to detect detrimental effects caused by them, even if the column ends inside the joint were coated with stationary phase. The retention of the peaks may have increased slightly although in a reproducible manner. There was no significant decrease in separation efficiency and we never observed distorted or split peaks. This result is in agreement with the explanation used for the discrimination due to PTFE connections: as the cold spot due to the metallic joints is many-fold longer than the average path of a solute molecule between two contacts with the stationary phase, all molecules experience the same extra retention.

Dosch[11] proposed to align the two columns inside the screwed joint by a short piece of platinum–iridium capillary.

Joints with metal capillaries

The ends of the two capillaries to be joined are slipped on to a short piece of platinum–iridium capillary and melted on to it using a flame[12]. This connection is free of dead volumes and plastic materials. It is rapidly made and is both thermally and mechanically stable. However, it can be used only for glass capillaries and its application is limited by the activity of the metal surface. There is no concensus on the activity of platinum–iridium surfaces, probably primarily because these surfaces readily change their properties depending on the materials with which they come into contact[13–15].

It would be attractive to replace the platinum–iridium tubing with a more inert material, *e.g.*, fused silica (after burning off its plastic coating). However, we were not able to melt the two butts of the glass capillaries together without fixing them on to the fused silica. The different contraction properties of fused silica and glass cause the joint to crack. The idea of Müller and Walther[16] of melting two glass capillaries together on to a platinum–iridium capillary and of etching away the metal with aqua regia to obtain an all-glass joint is probably not applicable to our purpose.

Glued joints

Mechanically reinforced connections may be tightened by glue. This appears to be a promising method for all types of joints, either glass to glass or fused silica to fused silica or to glass.

Mitchum *et al.*[17] connected fused-silica capillary columns to a moving needle injector using Silicoset 151 (ICI, Organics Division, Stevenston, Ayrshire, Great Britain) as a sealant. They reported good stability of the connection over several months at oven temperatures up to 250°C. Later *et al.*[18] prepared effluent splitters sealing fused-silica capillary ends into a glass sleeve with silver chloride[19]. The splitter was protected and strengthened with a coating of polyimide. It was pointed out that several thin layers of the pre-polymer [Pedigree No. 1840 Imide wire enamel, P. D. George Co., St. Louis, MI, U.S.A., diluted 1:4 with N-methyl-2-pyrrolidone–toluene (4:1)] have to be deposited on the joint and baked at 400°C. Sandra *et al.*[20] used polyimide (PI 2550, DuPont, Wilmington, DE, U.S.A., undiluted) without silver chloride cement to join columns.

Douglas and Hall[21] joined two capillaries of the same outer diameter inside a third glass capillary (Fig. 2a). The arrangement was tightened with a drop of glue on each side of the covering tube. The critical point of this system is the dead volume. The inner diameter of the covering tube needs to be carefully adjusted to the outer diameter of the two columns to be joined. This was achieved by drawing glass tubing on a glass drawing machine according to the adjusted ratio. If the two butts of the columns were well cut and the covering tube was tight on the capillaries, we only found very little broadening of the solvent peak (the most sensitive marker of a dead volume). Douglas and Hall[21] used the Silicoset 151 (Fleming Services, Royston, Great Britain), a single-component silicone glue containing acetic acid. We preferred to use a guiding tube inside the two columns to be connected. We inserted 3–5 mm of fused-silica capillary tubing into each butt, put some glue on the joint and pushed a

glass tube about 30 mm long over the glue (Fig. 2b). We usually linked a glass capillary column with a fused-silica pre-column. To avoid dead volumes, the inserted piece of fused-silica tubing should fit tightly into the columns. This also means that the two columns should have very similar inner diameter ($\pm$0.01–0.02 mm). Any excessive length of the inserted capillary may broaden the solvent peak, especially if its outer diameter makes it difficult to fit into the columns. In fact the inserted capillary tubing may be short because it only serves to keep the two columns in the correct position and to prevent the glue from penetrating into the bore of the column.

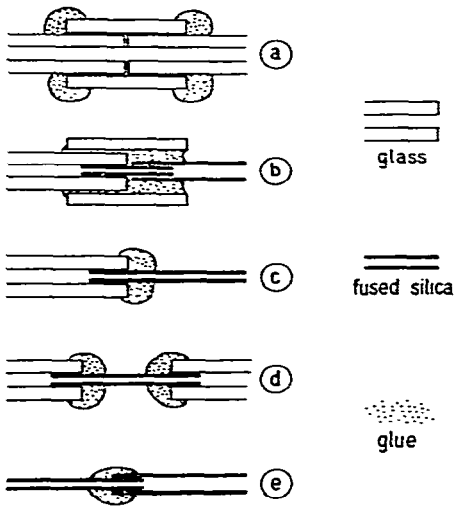

Fig. 2. Joints tightened by glue. (a) Two glass or two fused-silica columns joined inside a covering tube. A drop of glue tightens the columns against the covering tube. (b) Two columns (*e.g.*, a glass capillary and a fused-silica pre-column) joined on a short piece of inserted fused silica. A glass tube protects the joint mechanically and keeps air from the critical part of the joint. (c) A fused-silica pre-column inserted in the analytical column (glass or fused silica). The protecting glass tube is not shown. (d) Connection of two glass capillaries. To reduce the risk of breakage, a few centimetres of fused-silica tubing are left between the butts of the glass columns. (e) A pre-column pushed over a narrow-bore fused-silica column. This arrangement allows cold on-column sampling whereas splitless sampling is excluded because of an insufficient carrier gas flow-rate.

We did not find that the polyimide coating of the inserted fused silica capillary disturbs the chromatography. A mixture of C_{10}–C_{44} alkanes did not show any discrimination due to losses of heavier components in the plastic coating. The polyimide coating did not produce "ghost peaks" on the flame-ionization detector. Finally, solvents including dimethylformamide did not show increased tailing.

We used a two-component silicone rubber (C. Roth, Karlsruhe, G.F.R.), presumably a silicone hardened by a peroxide, as a glue. This glue was put on the joint and covered with a glass capillary tube. Another drop of glue was put on each side of this glass tube, then the persilylated and non-polar, hence oxygen-resistant, columns were heated at 120°C for 30 min without applying pressure. Oxygen-sensitive columns were installed in a GC and rinsed backwards, *i.e.*, with a (low) flow of carrier gas fed into the outlet of the column in order to minimize the pressure on the freshly made connection. After this heat treatment the rubber was polymerized to an extent that

allowed the column to be installed normally and to be programmed with a normal flow-rate of carrier gas from 100°C to at least 250°C at, *e.g.*, 5°C/min.

The covering glass tube was taken from the tip of a Pasteur capillary pipette (WU, Mainz, G.F.R.) and was about 3 cm long. It may be useful for two purposes. First, it may reinforce the joint mechanically. As the fused-silica pre-column must be coiled, there is considerable strain on the joint. The two critical points for breakage are where the two columns meet and where the inserted fused silica tubing ends in the fused-silica pre-column. The covering glass tube should protect both of them. Second, the glass tube protects the silicone rubber from air. This is important at temperatures above 300°C to prevent the rubber from becoming hard and brittle.

Tests with 2 atm pressure showed that our glued joints started to leak when heated to 370–390°C for several hours. For routine use we heated columns with glued joints up to 340°C for instruments without a hydrogen sensor and up to 360°C if a hydrogen sensor was used to check for leakages and to eliminate the risk of oven explosions if hydrogen was used as the carrier gas (hydrogen sensor from Brechbühler, Schlieren, Switzerland).

We preferred the silicone rubber to the polyimide because of the simplicity of its handling. Silver chloride, proposed by Pretorius[19], is thermally stable, but we found it difficult to work with it and the joints tended to leak.

Fig. 2c–e show some other types of glued joints. The arrangement in Fig. 2c is simplest. The pre-column is chosen to fit into the analytical column, which eliminates the need for an inserted guiding tube. However, it forces one to use narrow-bore pre-columns, excludes the cold on-column injection technique and may cause problems for heavy solvent effects (plug formation).

Fig. 2d shows the connection of two glass columns (useful also if a column is broken or if two glass columns need to be joined to form a long column). We used a 5–8-cm long piece of fused-silica capillary to join such columns. This left a fairly long piece of flexible fused silica between the two rigid glass columns and reduced the risk of breakage.

The arrangement in Fig. 2e offers an interesting feature, *viz.*, the use of a narrow-bore analytical column (made of fused silica) and a wider pre-column (which may be of glass or of fused silica). This system allows one to work with split or cold on-column injection where the low flow-rate through the column precludes the splitless sampling technique.

The pre-column should be deactivated, *e.g.*, by persilylation[22], if adsorbing or labile sample components need to be chromatographed. Persilylated fused-silica capillary tubing of 0.32 mm I.D. is available from MEGA (Milan, Italy), through the agencies of Carlo Erba (Milan, Italy). A selection of narrow- and wide-bore fused-silica tubing to prepare joints is available from SGE (North Melbourne, Australia).

We preferred the glued joints to the other possibilities for connecting pre-columns to the analytical column. Glued joints were thermally stable, did not show effects of dead volumes if properly made and did not produce ghost peaks or increased bleeding. We did not detect any discrimination effects with such joints. However, there remained the drawback of all types of connections needed if pre-columns are used to form the retention gap, *i.e.*, the fact that an additional critical point requires attention during preparation and use.

COLUMNS PREPARED WITH AN UNCOATED INLET

At least for non-polar silicone stationary phases, the extraction of the stationary phase from the retention gap section is difficult or impossible. The use of pre-columns may be useful for certain aspects, but in general it is more attractive in theory than in practice. The replacement of a dirty pre-column appears to be an advantage, as it does not necessitate shortening of the analytical column. However, this argument should not be overstressed, especially if the column is home-made. The simplest and most generally applicable solution to the problem is the preparation of columns with deactivated but uncoated inlet sections. As under most conditions the retention gap does not broaden peaks[4], we propose leaving the first 3 m of the column uncoated. This allows one to eliminate a dirty inlet section at least five times until there is no retention gap left. There should be a mark to indicate the beginning of the stationary phase.

The production of columns with uncoated inlet sections does not create problems. Virtually all non-polar silicone stationary phases require a static coating. After the column has been filled with the solution of the stationary phase, pressure is applied to push the liquid out of the first 3 m of the column; only then is the other end section closed. A mark is made on the column at the rear meniscus of the liquid and the solvent is started to be pumped off. If the column is coated dynamically, the stationary phase is extracted from the inlet section before conditioning of the column is started. At this moment the stationary phase is still easily extractable even if the coating is immobilized afterwards. The retention gap zone is automatically deactivated together with the analytical part of the column.

It is proposed that commercial columns should include a retention gap. A 15-m column should be elongated by 3 m of retention gap. Such columns are available from MEGA.

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