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CONNECTING CAPILLARIES BY FUSION

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SUMMARY

Connections between two fused-silica capillaries, two glass capillaries or a fused-silica and a glass capillary by fusing borosilicate glass to fused silica, based on the technique of Etzweiler, are described. Fused connections eliminate the major problem in using pre-columns, *viz.*, poor performance of the connection between the pre-column and the separation column. Contact between the sample and polymers, as used for tightening conventional connections (PTFE tubing, ferrules or glue), is ruled out, precluding distortion of the solvent peak or losses of solute material by adsorption on to or diffusion into the polymer.

INTRODUCTION

Coupling of capillaries has become an important technique, especially when using uncoated pre-columns (retention gaps). Such pre-columns are used (a) to reduce problems caused by non-volatile sample by-products in splitless and on-column injection[1,2], (b) to reconcentrate bands broadened in space, allowing injection of very large sample volumes[3,4] and (c) for automatic on-column injection into wide-bore pre-columns connected to separation columns with conventional inner diameters, allowing the use of larger syringe needles.

Several methods for coupling capillaries have been used but none of them is completely satisfactory. In fact, the connection was frequently the major limitation of techniques involving pre-columns. The methods of preparing connections proposed in this paper should substantially improve this situation.

The most important methods used at present for connecting capillary columns involve the use of shrinkable PTFE tubing or of butt connectors. PTFE connections can be made rapidly, but have several severe limitations: (a) thermal stability is limited to 210–240°C (depending, *e.g.*, on the gas pressure in the connection); at elevated temperature the capillary butts tend to slip apart; (b) above 160–180°C considerable amounts of solute material are lost by diffusion into and through the PTFE material[5]; (c) permeability of PTFE to oxygen causes deterioration of oxygen-sensitive stationary phases and solutes; (d) solvent peaks tend to be broadened and to form "humps" eluted after the major solvent peak on heating of the column, as shown by Etzweiler[6] and Pretorius *et al.*[7].

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Joints prepared using butt connectors are thermally stable and fully gas-tight, neither allowing carrier gas to diffuse out of nor air into the column. However, the use of butt connectors also has a number of drawbacks: (a) the preparation of connections with butt connectors is tedious because of frequent breakages, especially if glass capillaries are involved; (b) solvent peaks may be broadened and followed by "humps" as if PTFE connections are used (although to a reduced extent for most solvents); (c) losses of solute material have never been demonstrated (were such tests ever carried out?), but it is difficult to believe that only solvents are adsorbed by or retained in the ferrule material; (d) release of volatile material from the ferrule, producing "ghost" peaks, has been mentioned, especially for analyses involving specific detectors, but it does not appear to be a severe problem; (e) there is no possibility of direct control of the quality of a connection, with the effect that the performance of different connections varies considerably. For example, on one occasion a gap may remain between the capillary butts, and on another the sharp edges of a butt may scratch some material from the ferrule during its introduction, the removed material being deposited between or in the butts; (f) dead volumes around the capillary butts are not under control, a problem that becomes particularly severe after repeated drilling out of broken capillary pieces. Hence connection of capillaries by means of butt connectors is a valuable method, but there clearly remains room for improvement.

A third class of connections is based on tightening by glue. Several configurations are possible, using internal or external guiding tubes or inserting one capillary into the other[5]. However, the preparation of such connections is usually demanding. The quality of the result corresponds to that obtained with butt connectors, if the connection is well made. However, as visual control is practically excluded, it is difficult to achieve the result aimed for, *viz.*, that the glue fills the dead volume between the column and the guiding tubes or between the two capillary walls without entering the bore of the capillaries.

Whether using PTFE, polyimide or another ferrule material, the use of organic polymers for tightening connections between capillaries is irritating. At ambient temperature the polymers behave as solids. At elevated temperatures, however, they start to act as liquids, dissolving and retaining solute material analogous to stationary phases, whereby the "film thickness" is essentially infinite as molecules diffusing in the polymer do not find their way back into the stream of carrier gas. Broadening of the solvent peak and the formation of "humps" are due to solvent penetrating into the polymer, being released again with a considerable delay. The solvent swells the plastic material and enhances its tendency to pick up solute material. Finally, it can be seen by eye that the PTFE tubing around the capillary butts rapidly becomes brown and dirty. This dirt cannot consist of non-volatile sample by-products, as such dirt remains in the pre-column. It must consist of solute material, possibly belonging to the components of interest. These deposits of "dirt", presumably accumulating on all types of polymer surfaces, do not inspire confidence.

Recently, Etzweiler[8] reported the preparation of a column exit splitter by fusing two fused-silica capillaries into a glass capillary tube, which stimulated experiments on the connection of two capillaries by fusion. Our methods described below are based on the observation of Etzweiler that fused-silica and borosilicate glasses such as Pyrex and Duran can be fused together without creating excessive tension

owing to their different coefficients of expansion (the methods cannot be applied to soft glass!). The various types of connections exploit the fact that glass melts at much lower temperatures than fused silica, allowing the use of a fused-silica capillary to keep the bore open. Varying the same principles, it is possible to connect fused silica to fused silica, glass to glass or glass to fused silica.

Connections based on fusion between glass and fused silica are surprisingly easy to prepare, are very cheap and, most important, are nearly perfect in their gas chromatographic (GC) properties. Contact between the sample and plastic material is ruled out. For most types of connections described below, dead volumes are excluded; for the others the dead volume is small. The connection is transparent, allowing easy control by visual examination. Hence no time-consuming chromatographic experiments are necessary for assessing the quality of the connection. Distortion of the solvent peak disappeares (some chromatograms are shown in ref. 4) and losses of solute material in the organic polymers are ruled out.

EXPERIMENTAL

Burner

For fusing glass to fused silica, a small flame is required that is hot enough to melt the glass but not so hot that the fused-silica capillary collapses. Methane–air flames were not sufficiently hot, whereas butane–oxygen flames must be used with care as they tend to be too hot. A methane–oxygen flame, about 2 mm broad and 5 mm long, was found to be the most suitable. There are several suitable commercial microburners, usually sold for soldering metallic pieces. However, it is easy to construct such a burner in the laboratory.

The burner was constructed using a T-piece as shown in Fig. 1. The T-piece was connected to fuel gas (natural gas at low pressure from the tap) and to an oxygen

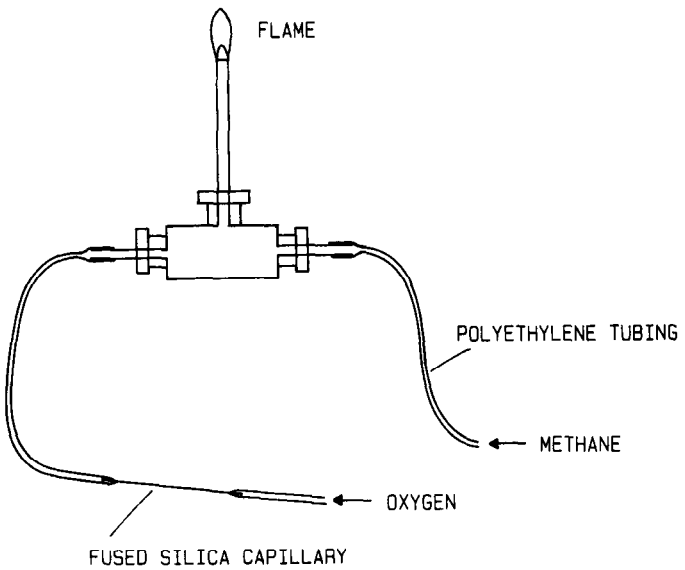

Fig. 1. Construction of the burner used for fusing glass to fused silica.

cylinder equipped with a pressure regulator. The third arm of the T-piece was fitted with the burner tube, consisting of an 8 cm × 0.5 mm I.D. stainless-steel tube. The flow-rates were adjusted by the resistances in the gas tubes (0.8 × 1.6 mm polyethylene tubes). The regulation of the oxygen supply by the pressure regulator was facilitated by the use of a restriction, consisting of a 50 cm × 0.32 mm I.D. fused-silica capillary fused into the polyethylene tube.

Glass connection tubes

Glass tubes of suitable inner diameters were drawn on a glass-drawing machine (Carlo Erba, Milan, Italy). For connecting fused-silica capillaries of different diameters, two glass tubes with adjusted inner diameters were fused together on a pencil-lead. Straight glass tubes for connecting fused-silica capillaries with identical outer diameters and also the composed glass tubes are available from H. Habich (Zürich, Switzerland) and Carlo Erba.

Widening of glass capillaries

In order to allow the introduction of fused-silica capillaries into glass capillaries, the latter were widened for a length of 5–8 mm, using a pencil-lead of suitable diameter and a small bunsen burner or the burner described above. The 0.5 or 0.7 mm O.D. pencil-leads (for refillable pencils) were kept in a pin vice (Supelco or tool shops). The pencil-lead was first heated in the flame to burn off combustible material, then the tip was sharpened to a point using emery cloth. If necessary, the diameter of the pencil-lead can be reduced by turning it between two pieces of emery cloth.

To widen the capillary butt, the pencil-lead was heated just behind its tip and pushed into the glass capillary bore (Fig. 2). The flame followed the tip of the pencil-lead. Heating ahead of the tip caused the glass capillary to be distorted. Widening of the capillary was easy for a length of about 10 mm. For widening longer capillary sections it is necessary to use a broader flame, keeping the glass soft over the whole length of the widened section.

Turning of the pencil-lead during its introduction into the glass capillary butt was abandoned because of deposition of abrasion material on the glass wall. For the same reason the flame should be not hotter than necessary. However, deposits of

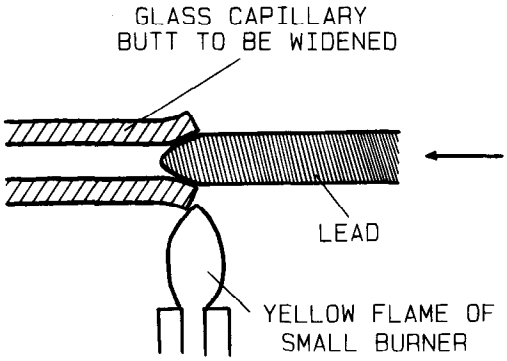

Fig. 2. Widening of glass capillary butts by means of a heated pencil-lead kept in a pin vice. The small flame is applied just behind the tip of the pencil-lead. Excessively hot flames cause deposition of material from the pencil-lead on the glass wall.

small amounts of black material stemming from the pencil-lead have never caused any problems.

If the glass capillary is coated with stationary phase, the latter should be removed from the section to be heated in order to rule out rupture of the film in the column section neighbouring the connection or carbonization of the stationary phase, forming highly active sites outside the connection and hindering fusion within the connection. Pressurized air (0.3–0.5 atm) is applied to the other end of the column and the first 2–3 cm of the capillary are heated in a small flame.

Glues

The described connections can be used without reinforcement by glue if the inner diameter of the connection glass tube accurately fits the outer diameter of the fused-silica capillary. However, a drop of glue applied to the point where the fused-silica capillary enters the connection glass tube further reduces the risk of breakage inside the connection, at the cost of very small effort. One type of connection (see Fig. 7) relies on glue.

Polyimide is a highly thermostable polymer that can serve as a glue. Its hardness is ideal for keeping the fused-silica capillary from moving or vibrating within the connection. However, the application of polyimide glue is demanding owing to the formation of gas during the hardening (polymerization) process; the gas forms bubbles, creating a foam instead of a hard material. Formation of bubbles can be avoided by application of thin films of the polyimide pre-polymer and by very slow heating (temperature programme 0.5–1°C/min from 100 to 200°C). The application of thin films of glue requires the use of a liquid pre-polymer containing a solvent (available from Alltech, Eke, Belgium). Depending on the application, several layers of the glue must be applied[9], rendering the method time consuming.

The application of a solvent-free polyimide pre-polymer (SGE, Victoria, Australia) is more rapid, but also is more difficult. A small piece of the relatively hard material is warmed on a small spatula over a flame. First the material melts, starting to polymerize when heated to higher temperatures (visible by the formation of bubbles). Shortly before the material becomes definitely hard, it is applied to the connection. It immediately solidifies on cooling, rendering the connection mechanically stable, which is an important advantage for the transfer of the column into the GC oven. The polyimide may become soft again in the GC oven on increasing the oven temperature (depending on how far polymerization was completed before application of the glue to the connection). Therefore, there must be no strain on the connection until polymerization is completed. It cannot be avoided that the resulting polyimide material is porous. However, as gas tightness is not relevant, this is not an important drawback.

The problems caused by the formation of gas during hardening of polyimide glues are eliminated when using silicone rubber as the glue. This two-component glue (Roth, Mannheim, F.R.G.) hardens either on standing for several hours or by heating at 100–120°C for a few minutes. Rapid heating, *e.g.*, using a heat gun, is possible. Silicone rubber is slightly less thermally stable than polyimide; it becomes brittle above 300°C. However, if gas tightness is not critical, prolonged use at up to 340°C was found to be possible.

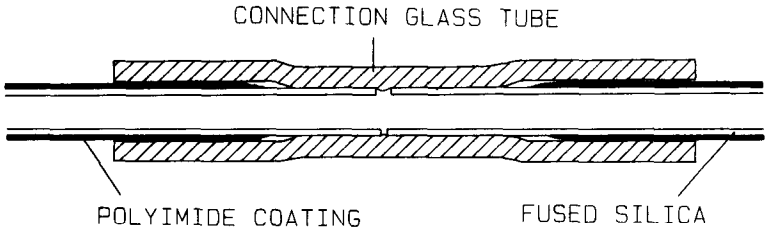

Fig. 3. Connection between two fused-silica capillaries of identical diameter in a glass tube (Duran or Pyrex) about 4 cm long. Perfect perpendicular cutting of the butts is not essential. The critical point concerning mechanical stability is the bare fused-silica capillary section at the edges of the fused zone. The glass tube cannot be fused to the fused silica up to the beginning of the polyimide coating because the formation of pyrolysis gases causes deformation of the glass tube. The guiding glass tube prevents breakage of the bare fused silica. Stability of the connection can be enhanced by applying a drop of glue to the point where the fused-silica capillaries enter the glass tube.

Types of Connections

Fused silica to fused silica of identical diameters. A typical application of this connection is to join a 0.32 mm I.D. fused-silica separation column with a retention gap of identical diameter.

The joint is formed in a glass tube about 40 mm long and with an inner diameter fitting the outer diameter of the fused-silica capillaries (including polyimide coating) (Fig. 3). The polyimide is burnt off the two capillary butts for a length of about 5–7 mm and the black residues are removed. Air should pass through coated columns to ensure complete burning of the stationary phase. The two butts are then pushed into the glass tube. The joint is deposited on a piece of charcoal (commonly used in blowpipe analysis), keeping the remainder of the two capillaries in a position that minimizes mechanical tension on the joint. With a small flame the glass tube is fused on to the bare fused silica, heating for about 5–10 sec.

Tightness of such connections is no problem (check in a water-bath). The critical point is breakage of the bare fused silica just behind the fused zone, caused by motion. Breakage is practically ruled out if the glass connection tube retains the fused silica firmly. In case of some motion of the fused silica in the glass tube (the outer diameter of fused silica capillaries is not strictly constant) or just for safety, a drop of glue is deposited at each of the two ends of the glass tube.

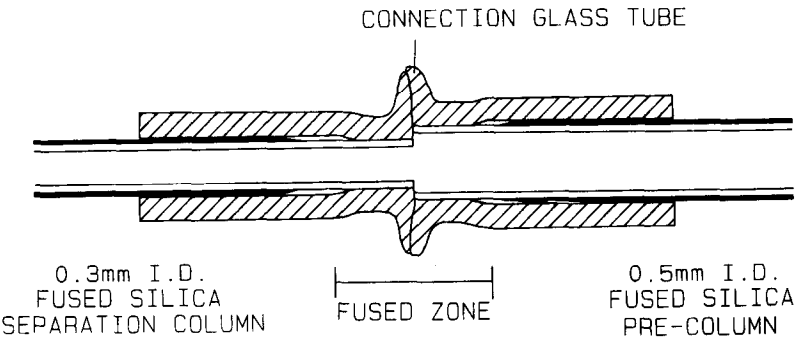

Fig. 4. Connection of fused-silica capillaries of different diameters. In order to keep the capillary ends firmly inside the connection, two glass tubes with inner diameters adjusted to the two fused-silica capillaries are used, fused together before forming the connection.

Fused silica to fused silica of different diameters. Fused-silica capillaries of different diameters are coupled, *e.g.*, for automatic on-column injection, involving a 0.50 or 0.53 mm I.D. pre-column and a separation column of 0.32 mm I.D., or for connection of a 0.32 mm I.D. pre-column to a narrower bore separation column, allowing manual on-column injection into narrow-bore separation columns (inner diameters down to 0.13–0.20 mm, depending on the carrier gas flow-rate).

The basic technique for connecting fused-silica capillaries of different diameters is the same as described above. However, instead of using a straight glass tube, a connection glass tube composed of two tubes with inner diameters fitting to the two fused-silica capillaries is applied. The two butts (free of polyimide coating for the first 5–7 mm) are pushed into the connection tube. The large-bore capillary is automatically stopped at the point where the glass tubes are fused together. The separation column is positioned by eye; it should not enter the large bore capillary, in order to avoid dead volumes. A small gap between the capillary butts is not critical. The final connection (without application of glue) is shown in Fig. 4.

During heating, the connection glass tube loses its mechanical stability, keeping the capillary butts concentrically; if there is strain on the butts, the glass tube is deformed. This problem is overcome by using a piece of charcoal with the route of the fused-silica capillaries and the position of the connection engraved into the surface, as shown in Fig. 5, prepared with a knife and/or file. It is 1–1.5 mm deep for the capillaries and wider and deeper (2–3 mm) for the connection glass tube. The capillaries are kept in this channel with two fingers of one hand and the other hand holds the burner.

Charcoal helps in heating the connection from the side that the flame cannot approach directly. It glows underneath the glass tube and eventually burns away in this area, thus requireing replacement of the channel (and finally of the piece of charcoal) after the preparation of several dozen connections.

The connection must be well heated. Fusion at minimal temperatures results in high tensions and relatively frequent breakage of the bare fused silica at the edge of the fused zone. Occasionally the fused silica even breaks within the fused zone. Relatively slow cooling of the fused zone appears to be helpful in reducing tensions. When using charcoal, the connection should remain in position for another 5–10 sec, being warmed by the charcoal.

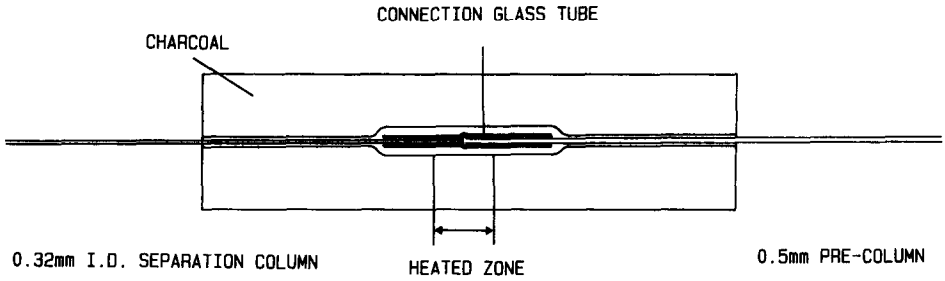

Fig. 5. Keeping the capillary butts concentrically in place during fusion of the connection glass tube on to the fused-silica butts. A channel is engraved in a piece of charcoal (about 12 × 4 cm; thicknes 2 cm) commonly used for blowpipe analyses. This channel prevents strain on the capillary end pieces being effective on the glass tube during connection. Although shown for the connection of a wide-bore precolumn to a separation column of standard inner diameter, the device is also useful for connecting capillaries of equal diameters.

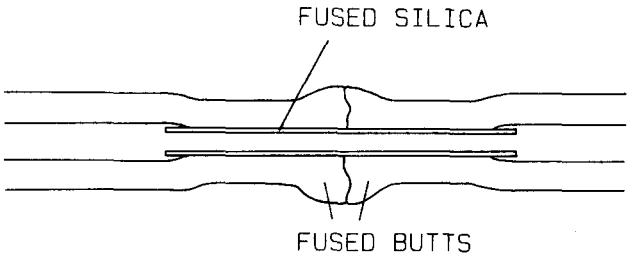

Fig. 6. Fusion of two glass capillaries on a 6–10 mm piece of a bare fused-silica capillary. The outer diameter of the latter is not critical; however, the use of a fused-silica tube of maximum diameter entering the glass capillary facilitates preparation of the connection. The combined butts are kept in the flame by hand, gently pressing the butts together to produce a small hump of collapsed glass. The critical moment during preparation of this kind of connection is avoidance of breakage of the fused-silica tube before the glass capillary butts are fused. Tightness and mechanical stability of this connection are never a problem.

Glass to glass. As shown in Fig. 6, glass capillaries are fused together on a piece of bare fused silica, preventing collapse of the tubing and keeping the capillary butts straight. The polyimide coating of a fused-silica capillary with an outer diameter fitting into the bore of the glass capillaries is burnt away. A piece 8 mm long is inserted half way into the bore of the first glass capillary, then the second capillary is brought into a position that ensures little tension on the composed butts, keeping the flame of the small burner near to position where the butts are placed together. The first capillary butt is kept at the very front, also keeping the fused-silica tube in position, and the butt of the second glass capillary is pushed over the fused-silica tube. This composition is highly fragile and should be moved into the flame only for a short distance.

The flame should first heat the position where the two glass capillaries meet. The glass is melted and the two butts are moved against each other using gentle pressure, forming a swelling of collapsed glass. Then the heated zone is broadened to collapse the glass on to the fused silica nearly up to the end of the latter, avoiding a noticeable dead volume between the walls of the fused silica and the glass capillary (a small dead volume is shown in Fig. 6). Pushing must be avoided at this stage because otherwise the glass capillary beyond the guiding fused-silica tube is deformed.

If glass capillaries with considerably different diameters are connected (*e.g.*, a 0.25–0.32 mm separation column and a 0.5 mm pre-column), it is preferable to widen the butt of the smaller bore column to accept a fused-silica tube of larger outer diameter. Widening of the butt with a 0.5 mm O.D. pencil-lead allows the use of a piece of a 0.32 mm I.D. fused-silica capillary. We prefer the use of fused-silica tubes with larger outer diameters because of the size of the dead volume created when the large-bore glass capillary is not shrunk down to the fused silica for the full length of the latter.

Glass to fused silica. In order to allow the fusion of fused-silica capillaries into glass separation columns, the butt of the glass capillary must be widened as described above. The 0.5 mm O.D. pencil-leads are appropriate for 0.32 mm I.D. fused-silica capillaries, whereas pencil-leads of 0.7 mm O.D. must be used to allow the introduction of 0.5 mm I.D. fused-silica capillaries into glass capillaries.

Tightness of the connection is achieved by fusing the widened butt of the glass capillary on to the bare surface of the introduced fused-silica column. Again the

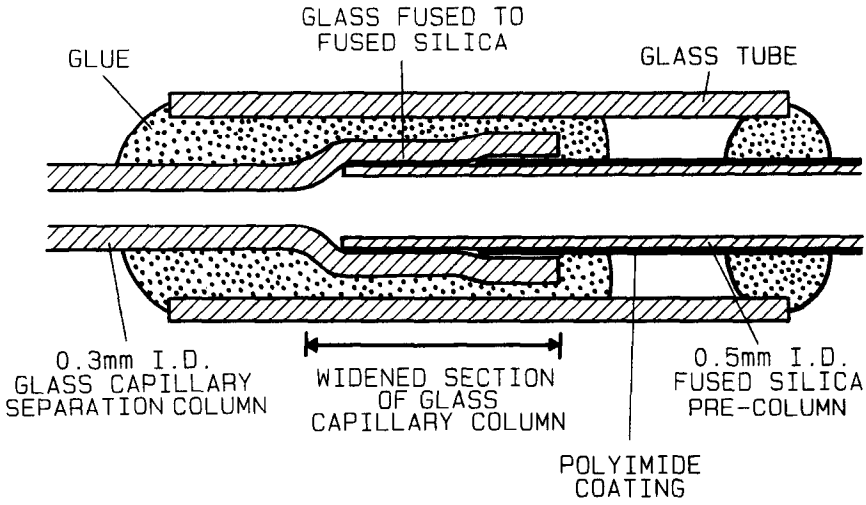

Fig. 7. Connection between a fused-silica and a glass capillary by introducing the fused-silica capillary into the widened butt of the glass capillary (possible even if the inner diameter of the fused-silica capillary far exceeds that of the glass capillary). Mechanical stabilization by glue (silicone rubber): the glue prevents movement of the fused-silica capillary in the glass capillary by fixation at the entrance of the glass capillary butt. The glass tube, about 30 mm long, slid over the connection protects the silicone glue from oxygen (and from becoming brittle), prevents the glue dropping from the connection and provides additional stabilization of the joint.

problem is mechanical stability: the butt of the glass capillary cannot be widened to an inner diameter that accurately fits the outer diameter of the polyimide-coated fused silica. The tendency of the fused silica to break at the edge of the fused zone is accordingly high whenever the arrangement is moved. There are two ways of mechanically stabilizing this type of connection, as indicated below.

Connection stabilized by glue. If the connection is stabilized using glue as shown in Fig. 7, the glass capillary is widened as far as feasible (about 10 mm) in order to introduce the fused silica a distance into the glass capillary such that a coated section of the fused-silica capillary also enters. Some glue (preferrably silicone rubber) is placed on the position where the fused silica enters the glass capillary. A glass tube, slipped over the fused-silica capillary before preparing the joint, is pushed over the glue. The inner diameter of the glass tube is not critical; it must be large enough to accept the (widened) glass capillary. Suitable glass tubes can be taken from the rear of the tips of Pasteur pipettes (the trumpet-like rear of the tip fits over the glass capillary butt). When slid over the connection, the glass tube takes some of the glue along, filling the space between the glass tube and the glass capillary. An additional drop of glue is deposited at the rear of the glass tube to prevent movement of the fused-silica capillary within the connection.

Connection stabilized with a reinforcing glass tube. A more rapid and safer method for mechanical stabilization of the fused-silica capillary involves use of a reinforcing glass tube (length *ca.* 25 mm) fused to the glass capillary. In fact, the glass capillary is elongated with a tube of accurate inner diameter to prevent movement of the fused-silica tube (as used for connecting two fused-silica capillaries) (Fig. 8).

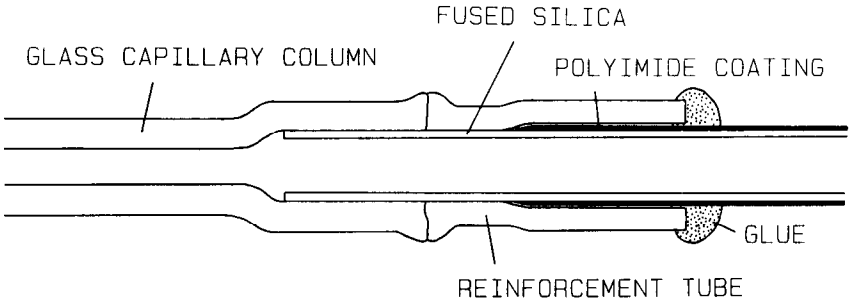

Fig. 8. Connection of a fused-silica capillary with a glass capillary, involving mechanical stabilization with a reinforcement glass tube with an inner diameter fitting to the polyimide-coated fused-silica capillary.

The polyimide coating of the fused silica capillary is removed for a length of 10–12 mm, then the reinforcement tube is slipped over the fused-silica butt. If the latter slips with some friction (*i.e.*, if it fits the fused-silica capillary well), its position must be adjusted before preparing the connection: the bare fused-silica butt should protrude from the reinforcement glass tube a distance 1–2 mm less than it can enter the widened glass capillary butt (the glass is crimped at the point where the reinforcement tube is fused with the glass capillary). The connection is held with two hands. First, the glass tube is fused to the glass capillary, pushing them together until the fused-silica tube penetrates up to the front of the widened section and a hump of collapsed glass is formed at the fusion point. Then the glass is fused down to the fused-silica tube on a wider section.

The resulting connection is mechanically stable under most circumstances but, as mentioned for the other connections, a drop of glue enhances security.

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