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## Note

# Miniature connector with a low dead volume for fused-silica capillary columns

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In practical capillary chromatography, there are many applications where low dead volume joints are required, *e.g.* when a pre-column is connected to the main column as a retention gap[1], when columns are connected in series, for gas chromatography–mass spectrometry connections, exit splitters etc. Also in more complex systems like multidimensional or preparative capillary gas chromatography (GC ), the use of simple and rapid butt connections to various flow systems equipped with fixed fused-silica tubing is very attractive.

Several constructions for connecting capillary columns have been proposed. Neuner-Jehle *et al.*[2] used a short length of platinum–iridium capillary tubing, which was inserted and melted onto a glass capillary column. This produces a tight coupling with no dead volume, but several workers have reported degradation of compounds on platinum surfaces[3,4]. Moreover, the concept cannot be applied to fused silica.

A common way of connecting capillary columns is by the use of shrinking PTFE. This is a simple operation, but the method has several deficiencies[5]. Oxygen can diffuse through PTFE into the column and damage the stationary phase. Shrinking PTFE connections can only be used over a limited temperature range, and for small-diameter fused-silica columns, we experienced increased problems with alignment and dead volume.

A number of workers have suggested the use of glued connections. Pretorius[6] reported the use of silver chloride as a cement, and this was used by Later *et al.*[7] and Goebel and Stan[8] for the construction of an effluent splitter. The first authors reinforced the joint with several coatings of polyimide. Sandra *et al.*[9] described a method where only polyimide prepolymer glue was employed, and additionally reported the use of a short length of thick-walled polyimide tubing as an alignment guide for fused-silica columns[10]. Grob Jr. *et al.*[11] used silicone rubber glue, protected by an outer glass capillary, and suggested several other configurations for glued joints. In this paper, aspects of various couplings are comprehensively described.

Although glued joints with a low dead volume can be constructed, these have the disadvantage that rapid connections cannot be made. The column often needs to be taken out of the oven, and some constructions are not suitable for columns with very small diameters.

Various threaded metal connectors with compression fittings are commercially available, but these are heavy constructions and were found to have unacceptable

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dead volumes[11]. Some of the more recent products (*e.g.* Supelco, Vici) show considerable improvement in this respect, but are still comparatively heavy and are not readily adaptable in a number of critical situations. Recently, Schomburg *et al.*[12] described a low dead volume connector, but no evaluation data have yet been reported.

The situation prompted us to develop an ultra-lightweight low dead volume coupling device for rapid column connections and exchanges. An exchangeable glass capillary liner allows the connector to be adapted to different column diameters and with a very low tolerance, thus avoiding excessive dead volume. The connector is particularly suitable for columns with a small diameter. The constructional details and an evaluation of this device are presented here.

## CONSTRUCTION OF THE CONNECTOR

A detailed drawing of the connector and its individual parts is shown in Fig. 1. The compression body of the connector consists of two threaded parts of cylindrical Dural (B and C). A slit was cut in the axial direction to facilitate the mounting and removal of these parts. The fused-silica columns are aligned inside a short piece (5 mm) of glass capillary tubing (D). This tubing was drawn from precision-bore preform (Schott & Gen., F.R.G.) on a glass-drawing machine, to have an outer diameter of 1 ± 0.05 mm. A close match (0.003–0.005 mm) of the inner diameter to the outer diameter of any fused-silica column can be obtained, since the preform material is available with all relevant inner/outer diameter ratios.

For sealing the glass tubing to the fused-silica columns, several types of fitting can be employed, but our preference is for a miniaturised version of a commercially

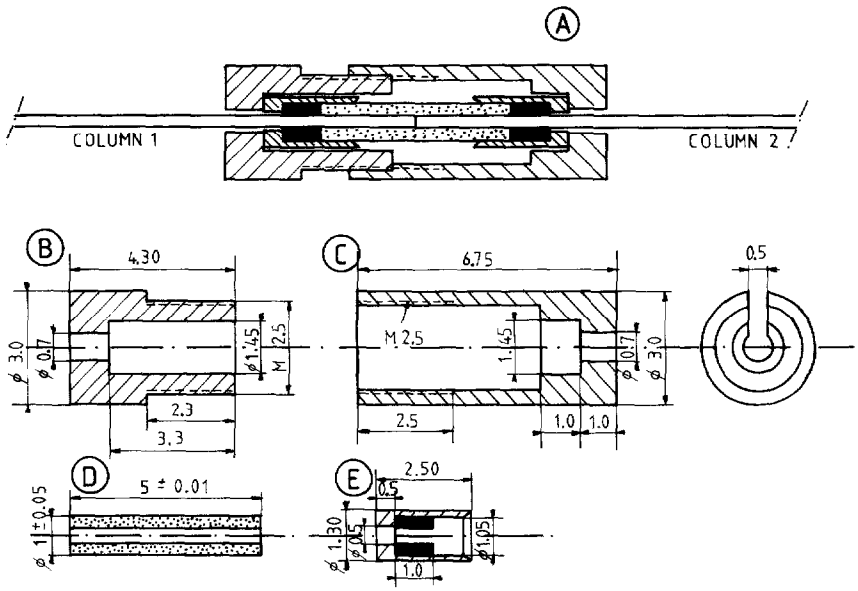


Fig. 1. Constructional details of the low-mass connector. A = Assembled construction; B and C = Dural body; D = glass liner; E = stainless-steel cup with compressed graphite foil.

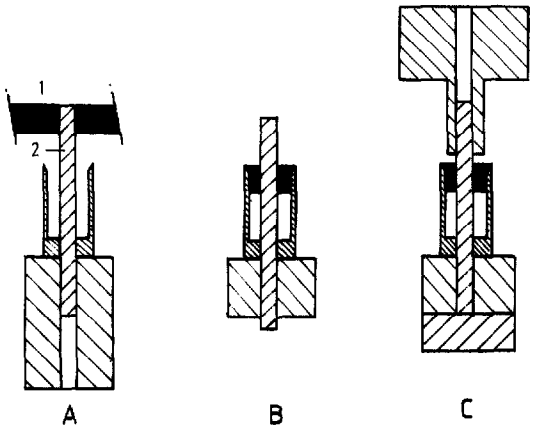


Fig. 2. Procedure for filling the stainless-steel cup with graphite. 1 = Graphite foil; 2 = central aligning rod (the smooth piece of a broken drill can be used).

available flat graphite ferrule (Gerstel, F.R.G.). The ferrule was made in the following way: A cylindrical piece of graphite foil (Le Carbone, France) was punched out with a sharp-edged stainless-steel cup (D). Before this, a small hole (0.5 mm diameter) was drilled in the graphite foil to act as a central aligning guide. The piece of foil was subsequently compressed. The procedure and the necessary tools are depicted in Fig. 2. The glass capillary inserts were flat-end ground to size.

Before the joint is made, the column ends should be carefully trimmed[13] to obtain the closest possible butt connection. The connection can be optically inspected (pocket microscope) before the slitted metal parts are mounted. Compression of the fittings is done without the use of any tools. Finger force is sufficient to obtain a tight seal, because of the small size of the fitting.

## RESULTS AND DISCUSSION

Any dismountable coupling system is bound to have a certain dead volume. This volume should be minimized to such an extent that, even when several couplings are used in series, there is no tailing and loss of column efficiency. Therefore the present construction has a very short aligning tube with a minimal clearance (3–5 $\mu$m) between the column wall and the inner wall of the tube. The gap between the butt of the two square-cut fused-silica columns was measured with a microscope and found to be *ca.* 0.05 mm. Thus, a coupling with an unrestricted flow path and a total dead space of *ca.* 10–20 nl is obtained. This should be satisfactory even for demanding applications such as rapid gas chromatography with narrow-bore columns, where extra-column contributions to band broadening are particularly critical[14]. This was experimentally verified with a 0.1 mm I.D. capillary column. The column was cut in two parts which were reconnected with the described coupling device. No difference in tailing could be detected when chromatograms were compared with the results obtained with the intact column (Fig. 3), not even on the solvent peak, which is a very sensitive marker for dead volumes. The preservation of the resolution is indicated by Fig. 4, which shows part of a complex chromatogram: identical chromato-

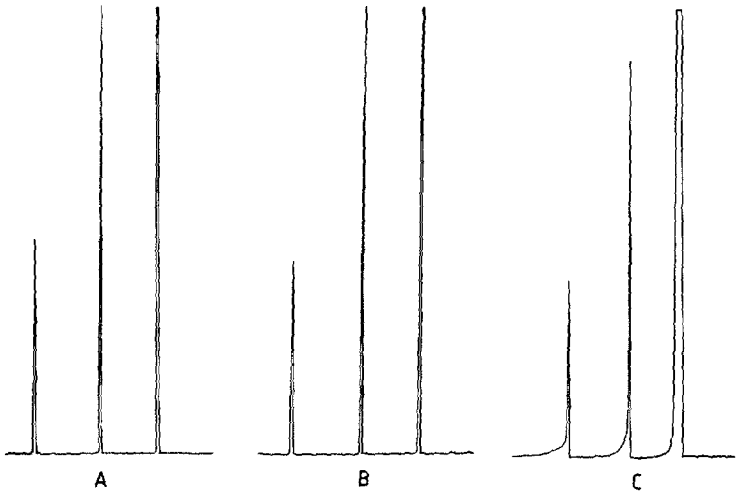


Fig. 3. Evaluation of the coupling device with a narrow bore column. (A) Intact column; (B) the column has been cut into two parts which were reconnected with the low-mass coupling device; (C) the same column parts as in B, but reconnected with a commercially available "zero-dead-volume" connector (Vici).

grams were obtained with the intact column and the spliced and reconnected column.

Experiments with wider bore columns showed similar results. A 0.3 mm I.D. fused-silica column was divided into eight pieces which were reconnected with the coupling devices. No loss of resolution or peak tailing was observed, although solvent tailing increased slightly.

Some connectors that have recently become commercially available were also tested and were found to give acceptable results, although not as good as the device

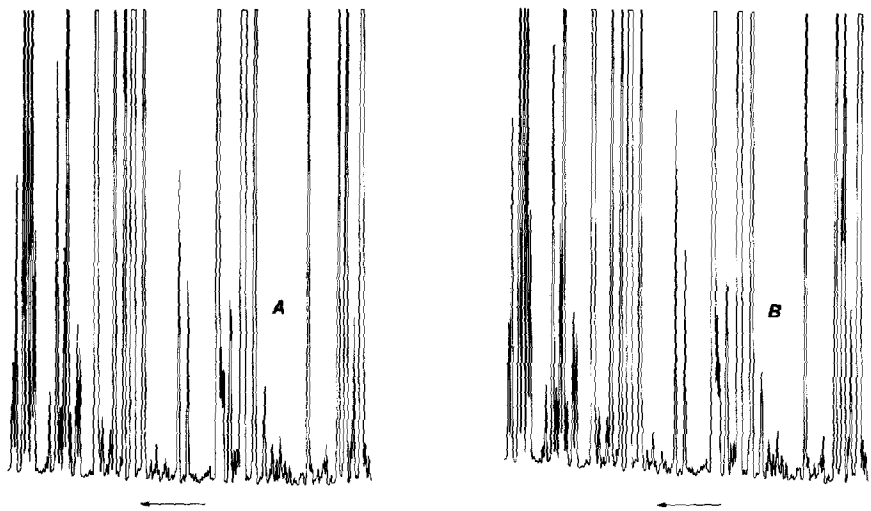


Fig. 4. Part of a chromatogram of gasoline. The same column was employed as in Fig. 3. (A) Intact column; (B) the column was cut into two parts, which were reconnected with the low-mass coupling device. (Identical GC conditions for A and B.)

TABLE I

TEMPERATURE DIFFERENCES BETWEEN THE INSIDE OF SOME COUPLING DEVICES AND THE GC OVEN DURING TEMPERATURE PROGRAMMING

| | *Temperature difference (°C)* | |
|---|---|---|
| | *At 10°C/min* | *At 30°C/min* |
| SGE | 8 | 22 |
| Vici zero-dead-volume union | 5 | 14 |
| Polyimide cylinder (3 mm O.D.) | – | 2 |
| Present construction | – | 1 |

described here. They failed, however, with narrow bore columns (Fig. 3C). This is understandable, because these devices rely on fixed holes that do not have the same degree of fit as the individually matched glass capillary liners.

Polyimide liners, which are used in some constructions, can be drilled to close tolerance, but this becomes difficult for hole sizes less than 0.2 mm. When a close tolerance polyimide liner is mounted, there is a risk that the sharp edge of the fused-silica column will scrape some of the polyimide from the inner walls of the liner, which contaminates the flow path. Moreover, polyimide constructions under compression deform at high temperatures and have a tendency to stick to the fused-silica tubing.

Another feature of our connection device is the total weight of only 100 mg. This is 30–50 times less than commercially available "light weight" metal connectors. The heat capacity of such devices is great enough to cause their temperature to lag considerably behind that of the column during temperature programming[11].

We evaluated this effect at different programming rates, and Table I shows the results obtained with various connectors. Our coupling device nearly follows the oven temperature, even at high programming rates, whereas the other metal connectors lag considerably behind in temperature. It can be assumed[11] that this would delay the elution of the solutes. This is particularly undesirable in time-optimised GC with narrow bore capillaries, where very high temperature programme rates are used[14].

An experiment was carried out to quantify the effect. For this purpose, our connector was fitted into a cylindrical piece of stainless steel (weight 5.3 g), which gave a thermal mass similar to that of the conventional devices. The connector was then used with the 0.1 mm I.D. methylpolysiloxane column as described for the previous experiment. A gasoline sample was chromatographed and eluted at 30°C/min. Surprisingly, we could not detect statistically significant differences in retention, when we compared with the peaks in the chromatograms, where the extra stainless-steel piece was removed. This is probably due to the short residence time of the carrier gas in the connector (only *ca.* 50 msec for a gas velocity of 30 cm/sec). Thus, the hot carrier gas is not appreciably cooled. This effect may be important to realize when designing cold trapping devices.

The coupling device can also be used for connecting fused-silica capillary columns of different diameters. In this case, a glass capillary sleeve (length 2.5 mm) is slipped over the end of the column with the smallest diameter. The sleeve must fit tightly on the column and be of the same outer diameter as the fused-silica column

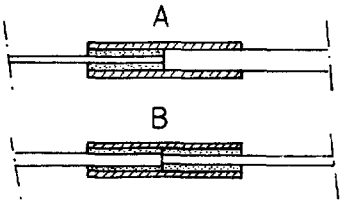


Fig. 5. Butt-connection of columns with different outer diameters. For further explanation, see the text.

with the largest diameter (Fig. 5A). If the difference in column diameter is small, both ends should be fitted with a glass sleeve (Fig. 5B), otherwise very thin glass sleeves have to be used, which are too fragile to be handled. The disadvantage of this solution is that more dead space is created between the concentrically arranged capillaries. Also, handling of the small thin-walled sleeves requires a certain skill. A better solution would be to have glass capillary liners in one piece. We are presently developing such inserts.

The very small dead volume of the coupling device allows the column to be rapidly connected to pieces of fused-silica tubing, which have been pre-mounted to the injector and the detector. This is of particular advantage when exact positioning of the column ends is necessary, *e.g.* for direct connections to the ion source of a mass spectrometer. Accurate positioning of the entrance and the exit of the column also becomes important when columns with a very small inner diameter are employed. The use of the precision glass capillary inserts permits a butt connection of capillaries with an outer diameter well below 0.1 mm. This, together with the low mass and the small dimensions, makes the construction described here ideally suited to applications in future miniaturised GC systems. The connector should also be suitable for critical joints in microbore liquid chromatography systems.

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