Open Split Connection of Glass Capillary Columns to Mass Spectrometers

D. Henneberg / U. Henrichs / G. Schomburg

Max-Planck-Institut für Kohlenforschung, D-433 Mühlheim a. d. Ruhr, Kaiser-Wilhelm-Platz 1, Federal Republic of Germany

Summary

An open split-type connection is described with a platinum capillary as the inlet line to the mass spectrometer. This connection device is suited to various types of columns, but especially for glass capillaries. Advantages of the open split are (i) a rather high yield, (ii) high flexibility with regard to column parameters, and (iii) optimal reliability, because the open split requires no vacuum-tight seal of the column to the spectrometer and no special geometry of the column end. An additional feature is the possibility of suppressing very large (solvent) peaks.

Introduction

The various ways of connecting gas chromatographic columns to mass spectrometers can be classified into three types: (i) direct connection, (ii) open split connection, and (iii) separator split.

In a direct connection the end of the columns is joined to the mass spectrometer by a vacuum seal.

In an open split connection the inlet line to the mass spectrometer is a flow resistance — normally a capillary — which restricts the flow of carrier gas into the mass spectrometer. The effluent is divided into a constant part, taken from the mass spectrometer and an excess part, which is vented to atmosphere.

Separator splits are connections of columns to a mass spectrometer with any one of the many different types of separator. A separator in principle is a splitting device the split ratio of which depends upon molecular weight. Seen from the mass spectrometer the yield is high for big molecules and very low for the small carrier gas molecules.

During the first years of application of GC/MS techniques, the open split was used to connect packed columns [1, 2] and also capillary columns [3, 4]. At that time the main drawback of this type of connection was the considerable loss of substance and the old constructions were prone to clogging and required careful adjustment.

For this reason the other two types of connection, directly and via separator, were used exclusively in later years. Since at that time the maximum allowable flow into mass spectrometers was limited to about 1 cm$^3$ min$^{-1}$ helium, only capillary columns could be used in direct connection. Such a connection was first described by de Brauw in 1964 [5]. We ourselves used it also from 1965 to 1970. The great advantage of this type of connection is the 100% yield and the lack of dead volumes which reduce the separating power of high resolution columns.

Separators have been used mainly for packed columns. For capillary columns only certain types of separators are suitable, provided that care is taken to avoid dead volumes. Examples are the jet separator [6] and the variable split separator [7]. The main drawback of separators is that they need maintenance, cleaning, and, possibly, conditioning. Furthermore, separators are more (jet separator) or less (variable split separator) inflexible to choice of different types of columns or optimal separation parameters.

Both types of connection suffer from the drawback that the end of the columns is at an undefined pressure — lower than atmospheric. One consequence of this is that the separating power of the columns is lowered. Another consequence is, that the direct comparison of chromatograms measured in or outside a GC/MS combination is complicated. It is impossible directly to adopt parameters which had been optimized independently from the GC/MS combination. Finally, the exact measurement of carrier gas flow rates in a GC/MS combination is technically very difficult, but needed, for instance, to determine sample loads.

Because of the drawbacks of the direct as well as the separator connection, we have been using the open split again since 1973. An important prerequisite is the use of platinum capillaries as the inlet line and restriction to the mass spectrometer. Neuner-Jehle and co-workers in a publication on direct connection described that great advantage of the use of platinum capillaries [8]: connections can be made readily to metal by soldering and to glass by fusing. These connections are reliable and vacuum-tight up to high temperatures and they remain tight after use at various temperatures. The surface properties are equivalent to those of glass with respect to tailing or decomposition.

The yield of an open split is defined by the ratio of flow into the MS and the eluate flow. This theoretical value was verified in practice for flow rates of 1.5 and 6.5 cm$^3$ min$^{-1}$. Furthermore, the yield is independent of the exact position of the end of the inlet capillary inside the teflon tubing. We use capillary columns in GC/MS almost
exclusively, the flow rates concerned being between 0.6 and 3 cm$^3$ min$^{-1}$ helium. Our mass spectrometer (CH4 - Varian-MAT) is capable of taking 1 to 1.5 cm$^3$ min$^{-1}$ helium. The resulting yields are between 30 and 100 %, values which are reached only by good separators in their optimal ranges.

**Instrumental**

Our construction of the open split consists of a capillary as the inlet line to the MS and the actual splitting device. Fig. 1 shows a schematic drawing and Fig. 2 a photograph of the splitting device with a glass capillary column connected. Obviously the device can be used for any other type of column with a small diameter. In the case of columns with greater diameters one either uses an adapter tube or simply inserts the platinum capillary several millimeters into the column.

**The Splitting Device**

After leaving the column, the effluent flows along the outer end of the spectrometer inlet capillary (see Fig. 1). On this way, the effluent is led into a narrowing tube, which consists of a piece of shrunken teflon tubing, put onto the end of the column. The shrinking is performed by using a small flame. After insertion of the spectrometer inlet capillary into the open end of the teflon tube, the actual splitting device is constituted: a constant amount of the effluent enters the mass spectrometer by the inlet capillary, the excess part is vented to atmosphere and avoids the entry of air to the splitting region.

If, however, the carrier gas flow is smaller than the flow through the inlet capillary, the open end of the teflon tube has to be flushed with helium. This is achieved by leading excess helium from the injection splitter into a mantling tube, which can be slid back to gain access to the teflon tube. Furthermore, this mantling tube is a mechanical protection for the free end of the very thin platinum capillary as long as no column is connected, or as a support for the end of the column after connection.

For special applications the splitting device can be completed by a second capillary (see Fig. 1). A large flow of helium — between 20 and 60 cm$^3$ min$^{-1}$ for instance — through this scavenging capillary dilutes the effluent and thus reduces the amount of substance entering the mass spectrometer. By this means the mass spectrometer can be protected from the main part of the solvent peak or from components of undesirably high concentrations. By precise “switching” of the scavenging flow [9], cuts in the chromatogram can be performed with an accuracy of a few tenths of a second.

**The Inlet Capillary**

We use as the inlet line a platinum capillary which is 90 cm long with about 0.15 mm I. D. and 0.3 mm O. D. Since tubing of this small diameter cannot be produced in the desired length, two pieces are joined by fusing in a 10 mm piece of glass capillary. Before assembling, the two pieces are heated to glowing in an oxygen stream (see in [8]) to clean the inner surface. To obtain the desired flow of 1.5 cm$^3$ min$^{-1}$ at 250°C we inserted as additional restriction 4 cm of platinum wire of 0.1 mm diameter.

The flow resistance of the inlet line can be varied very easily by insertion of a piece of wire. This can be useful in the case of mass spectrometers with high pumping capacity and inlet lines designed for high flow rates: when columns with lower flow rates are connected, the flow into the mass spectrometer can be reduced by such an additional restriction with a resulting lower pressure in the ion source and therefore higher quality of spectra.

To obtain the desired flow into the mass spectrometer, the temperature dependency of the flow resistance of the capillary has to be considered. Reducing the temperature from 250 to 100°C, for instance, doubles the flow. The flow is also doubled when hydrogen is flowing instead of helium.

On the mass spectrometer side the platinum capillary is soldered to a flange on the ion-source housing. This flange (“line-of-sight-inlet”, Varian MAT) carries a heated tube.