

# Development of a Simple Vent-free Interface for Capillary Gas Chromatography–Mass Spectrometry

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A novel and simple interface for capillary gas chromatography–mass spectrometry (GC-MS) was developed using a piece of deactivated stainless-steel tubing. This interface eliminated the need to vent the MS ion source when changing columns. Various chromatographic performance indicators, such as inertness, and thermal and chemical stability, were confirmed to be unaffected by using this interface at an elevated temperature of around 300°C. The new interface should facilitate the characterization of polymeric materials using analytical pyrolysis techniques in which frequent switching is required in the measuring mode, such as evolved gas analysis-MS and flash pyrolysis-GC-MS.

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## Introduction

Most gas chromatography–mass spectrometry (GC-MS) systems employ a direct connection between the separation column and the MS ion source by extending the end of the separation column to a point near the ion source through a heated sleeve. The obvious advantages of the “direct” connection are inertness and the elimination of dead volume; however, there are a few major disadvantages which often outweigh the benefits of the direct connection. First of all, when the separation column is exchanged, the mass spectrometer must be vented and the ion source cover removed so that the column end can be properly positioned. Venting MS, installing a different column and re-establishing equilibrium often require more than 3 h. Even more exasperating is the fact that it may be necessary to re-tune the mass spectrometer, which often results in a sensitivity shift and spectrum pattern changes. Therefore, a new convenient connection approach without the need of venting MS has been needed.

This “vent-free” connection should be especially effective for analytical pyrolysis techniques for polymer characterization. In the pyrolysis-GC-MS (Py-GC-MS) measurements of polymeric samples, a wide variety of pyrolyzates differing in both volatility and polarity are often generated. Different sample types, therefore, often require not only different separation columns for Py-GC-MS measurements but also another sampling technique such as evolved gas analysis (EGA)-MS.<sup>1-3</sup> Frequent venting of MS to switch between EGA and Py-GC measurements, however, should cause considerable inefficiencies in the everyday productivity of the laboratory. On the contrary, once the vent-free GC-MS interface is installed, it is a simple matter to change columns or to switch from a column to an EGA tube.

Moreover, possible leaks might occur at ferrules to seal the

separation column in the GC-MS interface during the cycles in the temperature control. The ferrule material is typically Vespel, which is made of polyimide (PI) impregnated with 10 - 15% of graphite carbon that extends the maximum operating temperature to 280°C; however, above 280°C in a GC oven, PI gradually decomposes;<sup>4</sup> consequently, the ferrule shrinks and the seal begins to leak. When the GC oven temperature is cycled above 280°C, it is necessary to re-tighten the nut which compensates for the shrinkage of the ferrule. The reoccurring leak will often preclude the use of auto samplers because re-tightening will not be allowed during continuous GC analysis of each sample.

So far, several types of interfaces, which do not require one to vent MS, have been reported.<sup>5,6</sup> Most of them include a short length piece of narrow bore transfer tubing with a restricting function to provide a natural pressure drop between the end of the column and the ion source. This connection enables us to isolate the column from the vacuum effectively. The tubing is generally made of a fused silica (FS) capillary to secure the inertness for the smooth transfer of polar analytes without undesired adsorption and/or decomposition. The FS interface, however, needs to seal with Vespel ferrules for connection with a separation column, which might cause leaking as the GC oven cycles. In addition, PI clad on the outside of FS tubing could also thermally degrade above 280°C, which might result in severe damage of GC-MS vacuum system by the unexpected breakage of the FS tubing during analysis.

In this work, therefore, a simple and durable vent-free GC-MS interface was newly designed, with which the source vacuum is maintained during the change of a separation column (or an EGA tube). In order to eliminate the issues of the PI thermal degradation, we composed the interface of all metal ferrules and tubing, instead of Vespel and FS materials. The inertness of the transfer line was achieved by the deactivation of the inner surface of the interface tubing, which was basically the same procedure as that used to obtain deactivated stainless-steel capillary separation columns for GC.<sup>4</sup> The performance of the vent-free interface was evaluated through the measurements of

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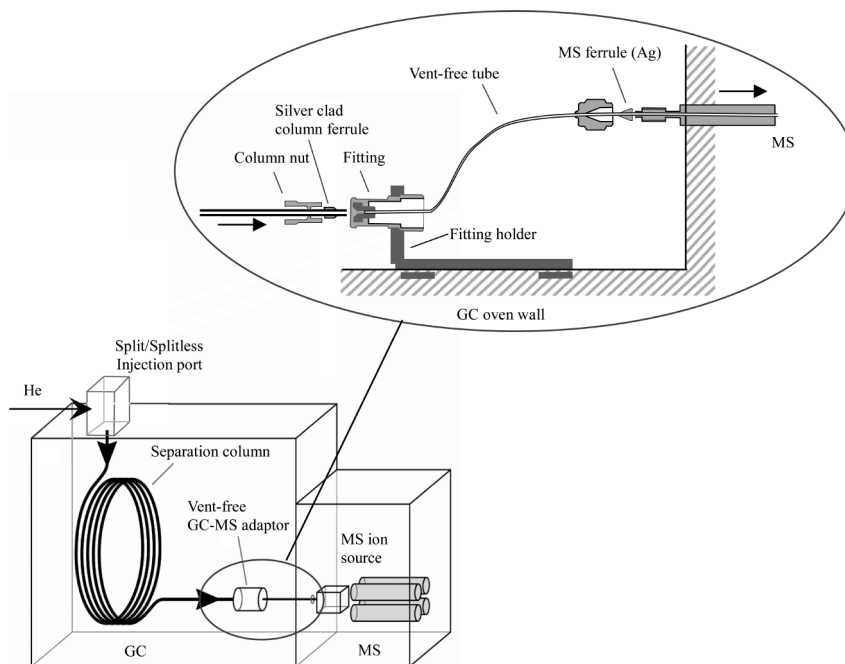


Fig. 1 Schematic diagram of the vent-free GC-MS interface.

test sample mixtures in terms of its inertness together with chemical and thermal stabilities.

## Experimental

### *Design of the vent-free GC-MS interface and its column connection*

Figure 1 illustrates the flow diagram of the GC-MS system using the newly designed vent-free interface. A metal capillary tube having a large flow resistance was used to connect between the fitting that connects the column outlet and the MS ion source. In order to assure the inertness, thermal and chemical stability and mechanical strength, we used a thick-wall deactivated stainless capillary tube<sup>4</sup> (0.15 mm i.d., 0.47 mm o.d., 55 cm length; Ultra ALLOY®; Frontier Laboratories) as this vent-free tube. Installation of the vent-free tube is straightforward. One end is positioned in the ion source, similarly to a direct capillary column connection, it is sealed using a silver (Ag) ferrule (Frontier Laboratories), while the other end is welded to the fitting. By using the silver ferrule, a metal capillary column can be sealed up to 400°C, and an ordinary fused silica capillary also up to its upper usable temperature around 320°C.

In the direct connection between the column and the ion source, the connecting position of the end of the GC separation column is normally at the side of MS interface in the GC oven. This arrangement often leads to difficulty in switching columns due to the narrow space between the outlet of the GC injection port and the inlet connection port of MS interface. Meanwhile, in the proposed vent-free connection, the fitting can be placed in any convenient position in the GC oven. The fitting was welded to the fitting folder, and the folder was secured to the bottom wall of the GC oven by inserting the tongue into the fold of the bottom plate. A specially designed column ferrule whose seal surface was clad with silver was developed and was used at the fitting that connects the column outlet to the interface. The use

of this ferrule allowed leak-free switching of columns up to several dozen times.

### *Test sample mixture and its measurements*

Three standard mixtures were prepared with 500, 25 or 0.1 ppm each of undecane, 4-chlorophenol, 1-decylamine, tridecane, methylcaprate, tetradecane, 1-dodecanol, acenaphthylene and pentadecane in hexane solution. The GC-MS measurements were performed with an Agilent 6890 GC equipped with a split/splitless injection port and 5973 MS, using a diffusion pump system with relatively low venting ability (90 L/s). The standard sample solution (1 µL) was injected at 250°C with split ratio of 1/50. The separation column was a stainless-steel capillary coated with polydimethylsiloxane (Ultra ALLOY-1 (MS/HT): 30 m length, 0.25 mm inner diameter with 1.0 µm of the film thickness, Frontier Laboratories) and the flow rate of the carrier gas was 1 ml/min. The GC oven temperature was programmed from 70°C (held for 2 min) to 300°C at a rate of 20°C/min and the GC-MS interface temperature was kept at 280°C. Ionization was carried out by electron ionization mode and the scanning range was from  $m/z$  29 to 400 at a rate of about 5 scans/s.

## Results and Discussion

### *Inertness*

Regardless of how easy it is to change columns using the vent-free GC-MS interface, it is essential that the inner surface be inert and stable. Figure 2 demonstrates the inertness of the connection using the vent-free GC-MS interface (B) compared with that of the direct connection of the separation column into the MS ion source (A) through the measurements of a standard mixture of polar compounds. The top total ion chromatogram (TIC) (A) shows the results of the direct connection and the bottom chromatograms (B) show those of the vent-free GC-MS interface using deactivated and non-deactivated tubing.

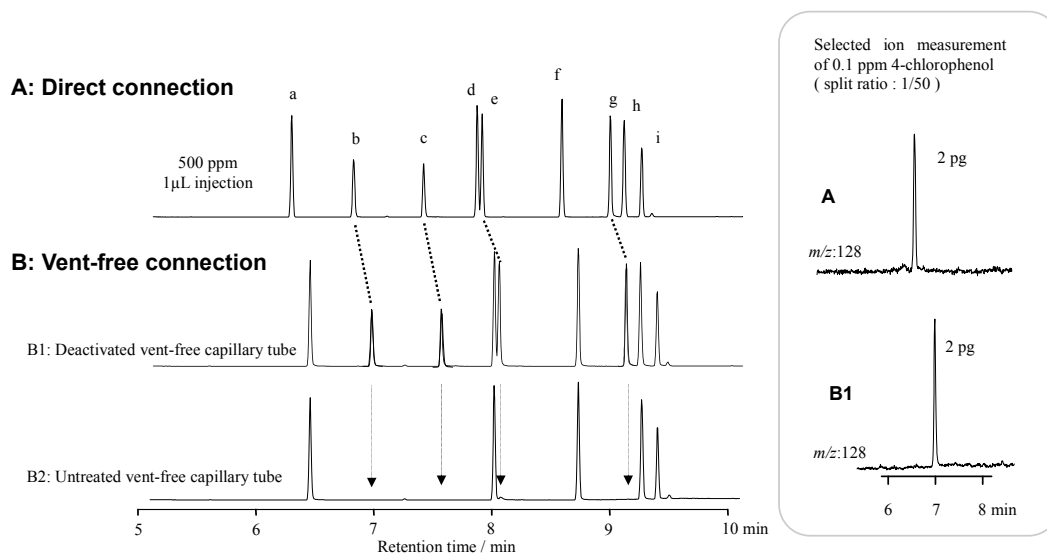


Fig. 2 Comparison of chromatograms of standard sample mixture using conventional direct (A) and vent-free connections (B). Left chromatograms, observed in TIC by injection of 1  $\mu\text{L}$  of standard sample mixture with 500 ppm for each component. Right box, a partial selected ion chromatograms at  $m/z$  128 for 0.1 ppm of 4-chlorophenol (2 pg) on column using single ion monitoring of  $m/z$  128 with direct and deactivated vent-free connections. (a)  $n\text{-C}_{11}\text{H}_{24}$ , (b) 4-chlorophenol, (c) 1-decylamine, (d)  $n\text{-C}_{13}\text{H}_{28}$ , (e) methylcaprate, (f)  $n\text{-C}_{14}\text{H}_{30}$ , (g) 1-dodecanol, (h) acenaphthylene, (i)  $n\text{-C}_{15}\text{H}_{32}$ .

Note that both the peak responses and the peak shapes for an acidic compound, 4-chlorophenol (b) and a basic compound, 1-decylamine (c) are almost the same using either a direct connection (A) or the deactivated vent-free GC-MS interface (B1), not only for the ordinary amounts of the compounds (500 ppm) in TIC (left chromatograms) but also at extremely low levels of 4-chlorophenol (0.1 ppm; *ca.* 2 pg on column) using selected ion monitoring detection ( $m/z$ : 128) in the right box. It is clear that the inertness of the deactivated vent-free tube is comparable to that obtained with a conventional direct connection. However, the use of a piece of non-deactivated tubing (B2) results in the strong adsorption of polar materials such as phenols, amines, esters and alcohols onto the inner surface of the tube.

#### Ion source pressure stability

As shown in Fig. 2, the chromatograms for the vent-free connection show slightly longer retention times than those for the direct connection. This result should be attributed to the pressure drop across the vent-free interface. To obtain comparable retention for the vent-free connection to that for the direct connection, it was experimentally confirmed that one needs to apply *ca.* 20 kPa more inlet pressure to the vent-free connection. This pressure increment (20 kPa) corresponds to a virtual 10 m in length of the separation column used (0.25 mm i.d.). The existence of this virtual column should guarantee the reliable disconnection of the column from the interface with keeping the vacuum level in the ion source.

Generally, by opening the column fitting during column exchange, air flows into the ion source and hence the chamber pressure increases. In this experiment, its increment was from  $3.2 \times 10^{-5}$  to  $8.8 \times 10^{-4}$  torr even by using relatively less venting power of a diffusion pump system. This pressure increase does not cause an emergency shutdown of the vacuum operation system.

#### Chemical stability of vent-free tubing by passing air at high temperature

It is essential that the inner surface is not oxidized by the air passing through the tube while the fitting in the oven is "open". This occurs in the heated portion of the tubing when the columns are actually being changed. Two pairs plus one of chromatograms are presented in Fig. 3 to demonstrate the performance of the vent-free interface. The upper trace shows the analysis of a typical mixture of polar compounds at two concentrations using a newly installed interface. The middle pair shows the same analyses after the tube has been exposed to air at 280°C for 30 h. These results show that the inertness was changed very little at this condition. After the interface was further exposed at 350°C for 12 h in air flow, the peak shapes of 4-chlorophenol (b) and 1-decylamine (c) broadened and the peak height of 1-dodecanol (g) slightly decreased, which indicated a small loss of inertness under this conditions, as shown in the bottom chromatogram.

## Conclusions

The newly developed vent-free GC-MS interface is an inert, simple-to-install alternative to a direct column connection. The vent-free tube maintains its inertness even when exposed to air at elevated temperatures for an extended period of time. The vent-free tube itself is deactivated stainless-steel and will not break; the ferrules are metal (Ag) and will not leak even when used at temperatures in excess of 400°C. Most importantly, with a vent-free GC-MS interface it is a simple matter to change columns, requiring less than a few minutes.

## Acknowledgements

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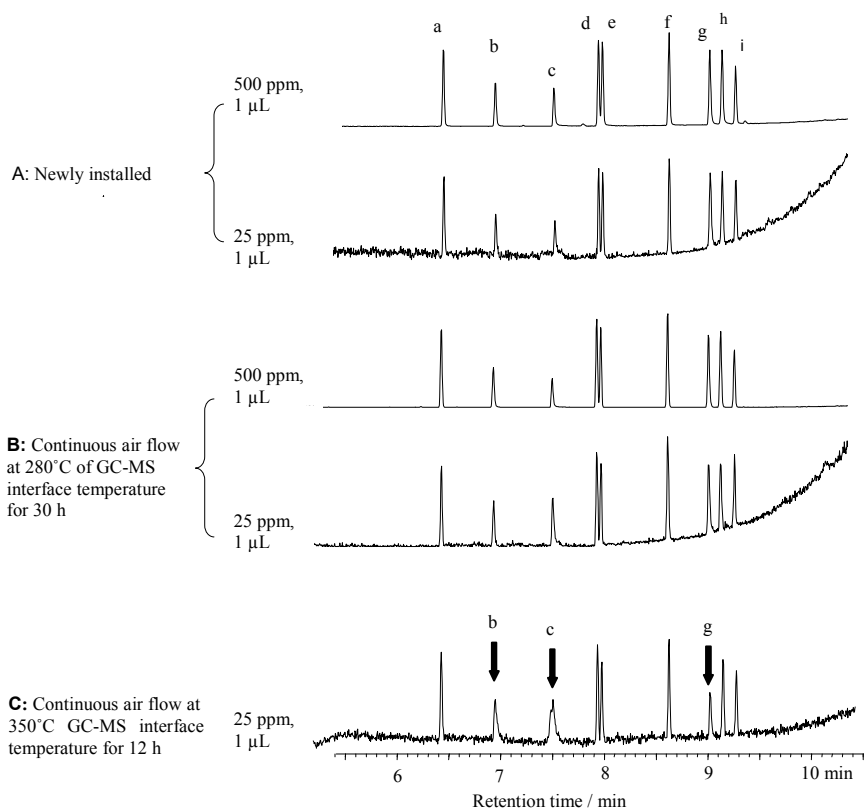


Fig. 3 TIC comparison in stability and inertness of the vent-free tube when exposed to air at elevated temperatures of 280 and 350°C for 30 and 12 h, respectively. The sample concentration was either 500 or 25 ppm for each component in the standard sample.

Shin Tsuge (Nagoya University) and Patrick W. Langvardt, Ph.D. of Dow Corning, Midland, USA on our proposed interface.

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