

Applications

All the fundamental tests performed to assess the quality of Meltfit connections showed an improved performance. Based on these findings, systems incorporating one or several Meltfit One connectors were applied for a large number of applications from the area of petrochemical, food, environmental, flavour and fragrance, and pharma-

ceutical analysis. An excellent performance was seen in all GC and GCxGC applications in these areas. Two relevant applications from food and mineral oil analysis are shown in Figure 4. The figure shows the comparison of the chromatograms obtained with 0 and 3 Meltfit connectors, the maximum number that will normally be used.

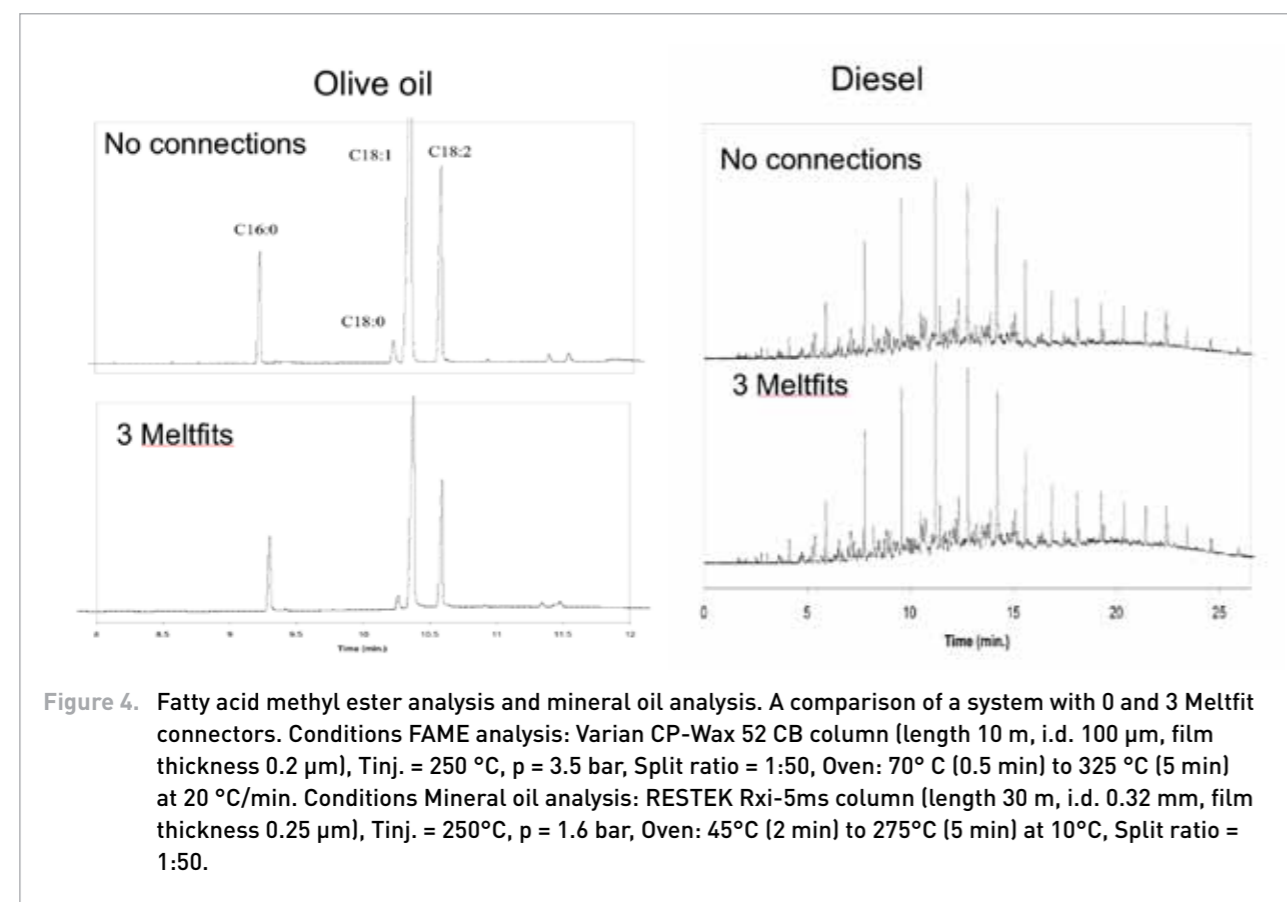


Figure 4. Fatty acid methyl ester analysis and mineral oil analysis. A comparison of a system with 0 and 3 Meltfit connectors. Conditions FAME analysis: Varian CP-Wax 52 CB column (length 10 m, i.d. 100 µm, film thickness 0.2 µm), $T_{inj.} = 250\text{ }^{\circ}\text{C}$, $p = 3.5\text{ bar}$, Split ratio = 1:50, Oven: $70\text{ }^{\circ}\text{C}$ (0.5 min) to $325\text{ }^{\circ}\text{C}$ (5 min) at $20\text{ }^{\circ}\text{C}/\text{min}$. Conditions Mineral oil analysis: RESTEK Rxi-5ms column (length 30 m, i.d. 0.32 mm, film thickness 0.25 µm), $T_{inj.} = 250\text{ }^{\circ}\text{C}$, $p = 1.6\text{ bar}$, Oven: $45\text{ }^{\circ}\text{C}$ (2 min) to $275\text{ }^{\circ}\text{C}$ (5 min) at $10\text{ }^{\circ}\text{C}$, Split ratio = 1:50.

Conclusions

There are many situations where capillary GC would benefit from coupling an additional column or a pre-column to the analytical separation column. Due to the experimental difficulties associated with the use of column connectors however, analysts have been reluctant to use coupled column systems. The new Meltfit One technology eliminates the drawbacks of the current column connectors available and will allow many more researchers to benefit from the advantages of coupled columns in GC.

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Application note 09NL.AN01.V2

Development and evaluation of an instant column connector for capillary gas chromatography

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Coupling capillary columns in gas chromatography (GC) is not an operation that is only relevant for the users of the most advanced capillary GC methods. Simple single-column separations can also benefit from a properly selected and installed pre-column. Pre-columns connected upstream of the main column can increase the life-time of the column, efficiently refocus the analyte bands to result in better separations and can be used for more rugged on-column injection in medium-bore columns. Additionally coupling devices can also be used for other applications such as connecting two columns when a higher resolving power is needed, to connect columns of different stationary phase chemistries for optimising selectivity or to mend a broken column. Finally, column connectors are also needed for the more advanced applications of GC such as heart-cut two-dimensional chromatography, comprehensive GCxGC or column back-flushing.

There are many more GC applications that could benefit from the use of good column connectors. Many GC users are reluctant to use column connectors because in practice they are not always reliable. Indeed a poor column connector can destroy much more than a good connector could deliver! Moreover, coupling capillary columns has never been an easy task. All connectors available to date have suffered from clear disadvantages. The very popular glass press-fit connectors are easy to install, cheap and can be used with a wide range of column diameters. Unfortunately they are prone to leaking especially in temperature programmed operation or at high temperatures.

Metal connectors with ferrules have a significantly reduced risk of leakage, but are much more expensive and need to be closely adapted to the size of the column. They can also induce metal-catalysed degradation and

are difficult to install. As a result of all these problems many users have avoided the use of connectors whenever possible. Only if their use cannot be avoided have connectors been used. The decision to use either, press-fit or metal is a compromise of many factors including:

- Purchase price
- Cost of ownership
- Leak tightness
- Risk of down time
- Dead volume
- Inertness or adsorption
- Extra column band broadening
- Thermal degradation
- Size
- Mechanical stability

Recently the company NLISIS has introduced a novel instant column connector, the Meltfit One connector. The Meltfit One connector combines the excellent properties of glass connectors with the leak-tightness and mechanical stability of metal connectors. In principle the Meltfit technology uses heat and gas-pressure to shrink a glass tube around the column. According to the founders of the company the idea was born in a brainstorm session where people from the packed-column years of GC jealously reflected on the early days when packed columns were connected using heat-shrinkable Teflon tubing. A low melting glass was used to replace the Teflon and the Meltfit technology was born. The principle of the Meltfit technique is shown in Figure 1.



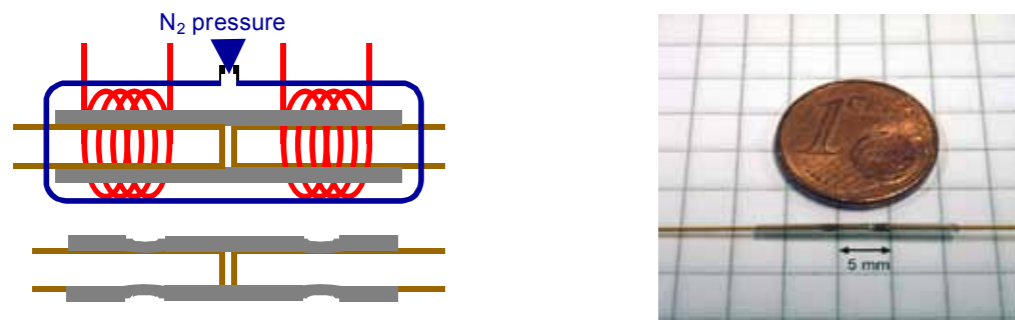


Figure 1. Principle of the Meltfit device. Columns are inserted into a small glass tube made of low-melting proprietary glass (softening temperature 380 °C). After heating, a small gas pressure (typically between 1 and 2 bar) is applied. The softened glass then closes tightly around the connector. The insert shows a schematic drawing of a connection and a photograph of a real connector.

In our laboratory the Meltfit connectors were subjected to a series of critical tests. The test protocol included tests for leak tightness, inertness (both in terms of adsorption as well as with regard to surface catalysed degradation) and dead-volume.

Leak-tightness

Leak-tightness was tested both under elevated pressure conditions and under vacuum operation. Leak detection for operation at elevated pressures was done visually using leak-detection fluid. Tests were performed up to pressures of 20 bar using helium as the carrier gas. Even at this very high pressure no leaks were seen. Air ingress under vacuum conditions was evaluated using mass spectrometry (MS). Even in the most critical MS, the ToF analyser, no ingress of air was detected. The results of these experiments are shown in Figure 2. In MS it is standard practice to monitor the leak tightness by looking at the signals of nitrogen, oxygen and water. After the installation of a new column these are very high, but

they should decrease rapidly. A very good indicator for a fully leak-tight system is the level of water. For a good connection the water level should be above that of air and nitrogen.

Figure 2 shows a comparison of a standard press-fit connection and the new Meltfit technology. At vacuum conditions press-fit connectors will always show a small, but not very relevant, leakage.

The Meltfit connector demonstrates a much better performance. Air ingress is absent as indicated by the relative levels of water versus nitrogen and oxygen and the low absolute values of the last two components.

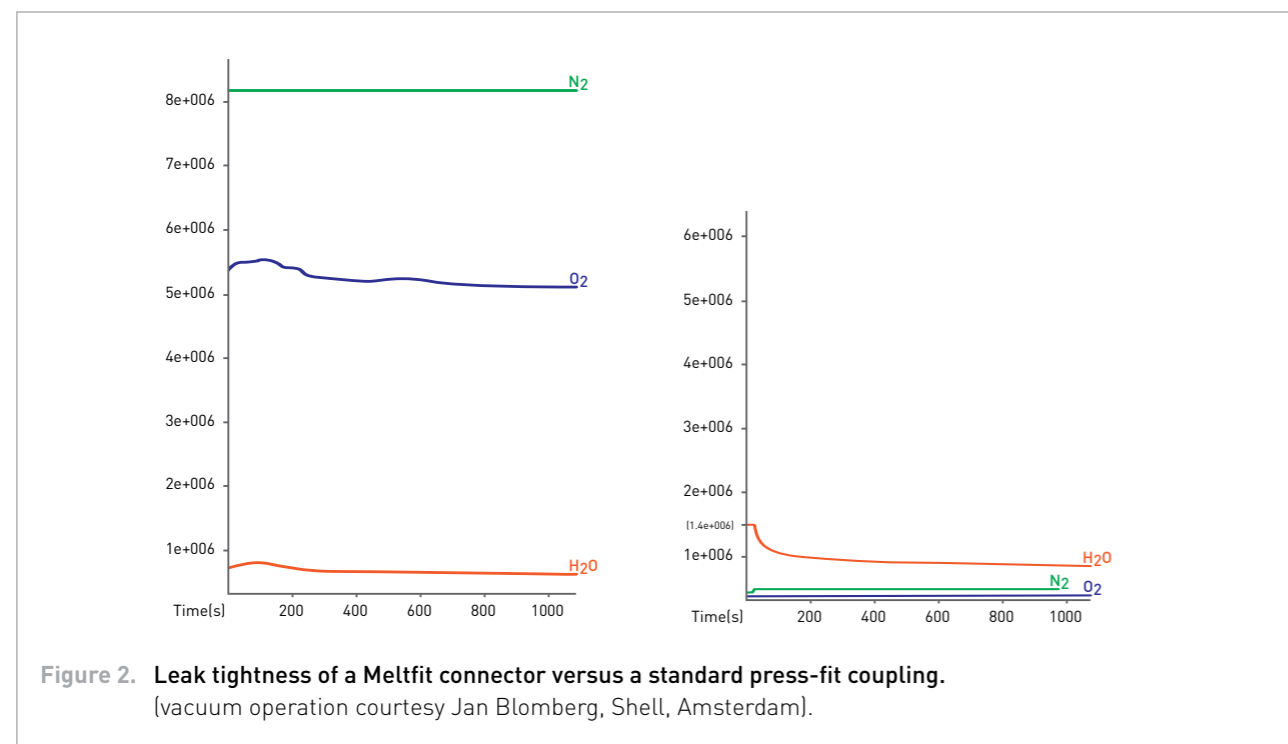


Figure 2. Leak tightness of a Meltfit connector versus a standard press-fit coupling. (vacuum operation courtesy Jan Blomberg, Shell, Amsterdam).

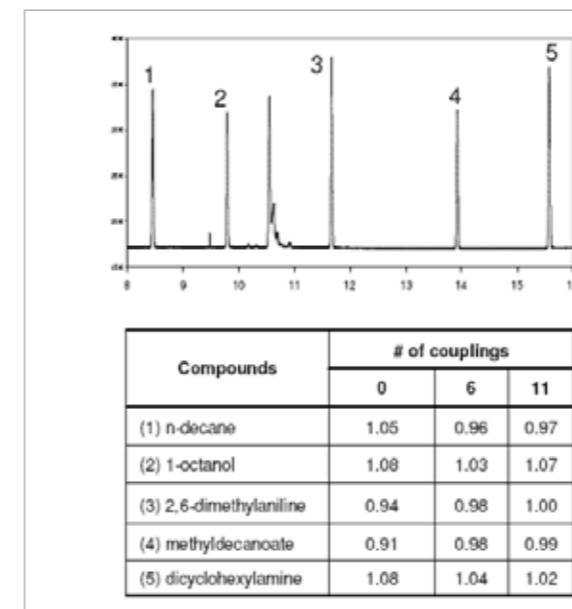
Dead volume

A key factor in the performance of couplings for capillary GC is the absence of any dead volume. This is because even the slightest dead volume will be detrimental for the separation power of the capillary column. Dead volumes are particularly critical for narrow-bore columns and compounds that have low retention factors, or more in general, for narrow peaks. Table 1 shows the results of dead-volume tests. The test conditions applied here were selected to be as critical as possible: the column used was a 10 meter 100 μ m inner diameter narrow-bore column; the test analyte was methane which on this column was unretained and will not be refocused by temperature or stationary phase effects. The number of connections made was 6 and 11 respectively. Even with 11 connections no significant peak-broadening was seen. Dead volume was also assessed by monitoring the peak shape of the solvent peak. Even a slight dead volume would immediately result in severe tailing of the solvent. In this case no evidence of any dead-volume was seen.

Table 1.

Dead volume of 6 and 11 Meltfit connections in a narrow-bore column (RESTEK RTX-5 column, length 10 m, i.d. 100 μ m, film thickness 0.4 μ m), $p = 3.5$ bar.

# of connections	Tailing factor at 10% of height	Peak width at 50% of height (sec)
0	1.06	0.21
6	1.07	0.23
11	1.08	0.23



Inertness:

Adsorption and thermal degradation

A serious problem with metal connectors is their poor inertness. Many compounds adsorb on the metal and unstable analytes are easily lost through (metal-catalysed) degradation reactions. Similar effects, although usually less pronounced, can also occur due to the presence of metal impurities in the column or stationary phase, or due to surface silanols on the wall of the fused-silica capillary. In the past, two very critical tests for adsorption and thermo-catalytic degradation in chromatographic columns have been developed by Grob and Donike, respectively. These tests, developed decades ago, are still used today for assessing the inertness of chromatographic systems.

The Grob adsorption test consists of a number of different acids and bases. Only on perfectly neutral surfaces is a good performance obtained for the test analytes. On poorly deactivated surfaces either the acids, the bases, or both, show tailing. The Donike test mixture, named after the famous sports doping investigator, uses unstable trimethylsilyl-esters of higher fatty acids to monitor chemical inertness of the chromatographic system. Even the slightest activity in the system results in losses of the unstable esters. Figure 3 shows the combined results of the Grob and Donike tests.

Figure 3. Results of the Grob and Donike test for multiple numbers of Meltfit connectors.

Grob test: RESTEK RTX-5 column, length 10 m, i.d. 100 μ m, film thickness 0.4 μ m, $p = 3.5$ bar.

Donike test: RESTEK Rxi-5ms column, length 30 m, i.d. 0.32 mm, film thickness 0.25 μ m. $p = 1.6$ bar. Amounts introduced onto the column: 5 ng/compound.

