Achieving Higher Sensitivities Using GC-FID with the Agilent Multimode Inlet (MMI)

Application Note

All Industries

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Abstract

This application note discusses the effect that column installation length into the Multimode Inlet (MMI) has on the sensitivity of hydrocarbons using GC-FID. A hydrocarbon test mixture spanning a wide boiling point range was injected using the MMI in three different modes: hot split, hot splitless, and cold splitless. The sensitivity of each compound in the test mixture was determined at column installation lengths of 10 mm, 12 mm, 14 mm, and 16 mm for each injection mode. The optimum column installation depth was 12–14 mm for all modes.

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Introduction

The Agilent Multimode Inlet (MMI) is one of the most versatile inlets from Agilent. It can be used in hot split and splitless, cold split and splitless (with ramp rates up to 900 °C/min), pulsed split and splitless, solvent vent, and direct injection mode. It can also be cooled to subambient temperatures with cryogen (LN_2 or CO_2). Each of these modes have applications where their specific temperature or flow profiles provide optimal conditions for maximum transfer of analytes of interest from the inlet to the column [1,2].

In capillary GC systems, a critical part of the flow path is the interface between the inlet liner and the capillary column. Many different liner styles exist to maximize the amount of analyte that is transferred from the liner onto the head of the analytical column. If the column is not installed far enough into the liner, the vapor flowing out of the liner may not enter the column properly. This can result in poor peak shape, low analyte recovery, and high limits of detection (LOD). Conversely, if the column is installed too far into the liner, discrimination can happen in heavy analytes, and nonrepresentative sampling may occur. Thus, there is an optimum length for the column to be installed that will maximize analyte sensitivity over the widest boiling point range.

The column installation length refers to the length of column protruding past the ferrule into the liner when the inlet nut is installed. This distance depends on which inlet is used, as different inlets have different mechanical designs. Figure 1 shows an example of a column installation length of 10 mm past the ferrule within the brass inlet nut. The split/splitless (S/SL) inlet requires 4–6 mm. The volatiles inlet (VI) requires 6 mm. The recommendation for the MMI has been 10–12 mm. Liner design and flow patterns require that the column protrude several mm into the lower end of the liner.

In this experiment, four column installation lengths were tested: 10 mm, 12 mm, 14 mm, and 16 mm. Three different injection modes were tested at each installation length: hot split, hot splitless, and cold split. A test sample of 16 straight chain hydrocarbons ranging from *n*-C_{10} to *n*-C_{44} (b.p. 174 °C–545 °C) was chosen to test the inlet for thermal discrimination for both semivolatile and high boiling point compounds [3]. Calculating the sensitivity of each compound at each installation length for each injection mode will allow for the determination of the optimum installation length.

Experimental

The GC-FID system used was an Agilent 7890A GC with an Agilent 7693 ALS. Table 1 lists the instrumental parameters used in the study. The 16-component hydrocarbon test sample was purchased from LabCorp (see Table 2 for analyte concentrations). A 5 µL syringe injected 0.5 µL for all injections. Table 3 lists the inlet parameters used in each injection mode.

To install the column with a specified length, the inlet ferrule (0.4 mm id UltiMetal Plus FlexiFerrule, G3188-27501) was preswaged using the Agilent column installation preswaging tool (G3440-80227). Once the ferrule was snug (but not tight), the required length of column was carefully adjusted manually, and measured using a caliper. The ferrule was then tightened such that the column would not move, then installed into the inlet. Four lengths of column past the ferrule were tested: 10 mm, 12 mm, 14 mm, and 16 mm. At each length, four replicate injections were performed using three different injection modes: hot split (10:1 split ratio), hot splitless, and cold splitless. The hot splitless and cold splitless injections used a splitless liner (5190-2293). For the split injections, the liner was changed to the universal split liner (5190-2275). To reduce run to run time when using the cold splitless injections, the MMI was configured with LN_2 cryo using compressed air as the coolant [4].

Table 1. Instrumental Parameters

Parameter	Value
GC	Agilent 7890A
Column	Agilent J&W HP-5ms Ultra Inert, 15 m × 0.25 mm, 0.25 µm (19091S-431UI)
Column flow	3 mL/min Helium
Ferrules	0.4 mm id UltiMetal Plus FlexiFerrule (G3188-27501)
MMI modes	Hot split, hot splitless, cold splitless
Inlet liners	5190-2275 for hot split injections (Universal Split/Splitless, taper, glass wool) 5190-2293 for hot and cold splitless injections (UI, splitless, single taper, glass wool)
Septum	Advanced Green (5183-4759)
Septum purge	3 mL/min
ALS	Agilent 7693
Syringe	5 µL tapered, FN23-26s/42/HP (G4513-80206)
Oven	40 °C hold 2 minutes, Ramp 20 °C/min to 325 °C, Hold 5 minutes
Detector	FID at 350 °C

Table 2. Analyte Concentrations

16 *n*-Alkanes in hexane	
200 ppm	C_{10}, C_{14}, C_{23}
100 ppm	C_{12}, C_{16}, C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{28}, C_{30}, C_{32}, C_{36}, C_{40}, C_{44}

Table 3. Multimode Inlet (MMI) Parameters

Parameter	Hot split 10:1	Hot splitless	Cold splitless
Initial temperature	350 °C	350 °C	50 °C
Initial time	–	-–	0.1 minute
Rate	–	–	900 °C/min
Final temperature	–	–	350 °C
Purge time	–	1 minute	1 minute
Purge flow	–	60 mL/min	60 mL/min
Injection volume	0.5 µL	0.5 µL	0.5 µL
Injection speed	Fast	Fast	Fast
Cryo	–	–	On (Air)

Results and Discussion

Figure 1 shows a caliper measuring 10 mm of column past the end of the ferrule. The MMI is unique in that it has a free-spinning nut that is screwed on over threads on the outside of the weldment (shown above caliper in Figure 1). The weldment is usually attached to the bottom of the heated zone of the MMI, but is shown here detached for clarity. The column nut screws into the free-spinning nut, and the ferrule seals at the bottom of the weldment to complete the flow path, as shown in Figure 2. At 10 mm, not enough column protrudes from the end of the weldment to actually enter the inlet liner sufficiently. Many split inlet liners (such as the 5190-2275) have a positioning bead on the bottom of the liner that lifts the liner up away from the sealing surface to allow more gas to pass through the split vent. However, at 10 mm the bead lifts the liner up enough that the column tip does not enter the liner.

Figure 3 shows a column nut with a 14 mm installation length coupled to the free-spinning nut placed adjacent to a splitless liner. At 14 mm, the column is positioned directly in the middle of the channel at the bottom of the liner. This column positioning is comparable to the length of column installed in a split/splitless inlet at the recommended 6 mm installation depth.

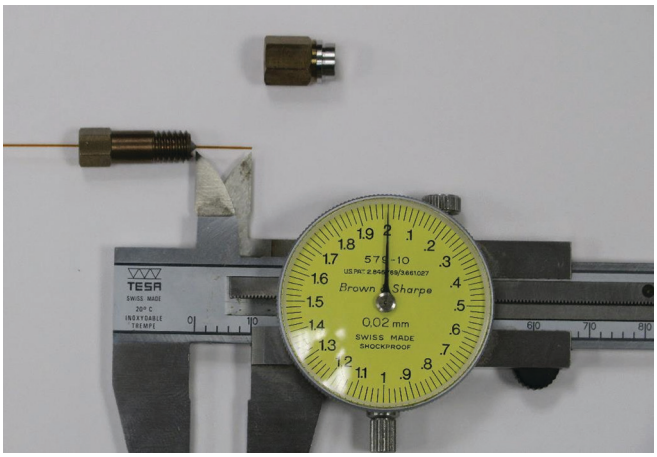

Figure 1. Column installation length of 10 mm past ferrule. A free-spinning nut attached to the weldment end (bright silver) is shown above the caliper.

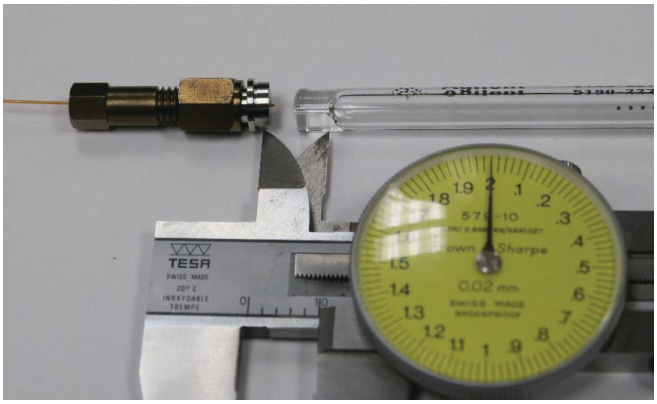

Figure 2. Column nut connected to free-spinning nut and weldment at an installation length of 10 mm with an Agilent liner (5190-2270) for scale. The column is not protruding enough past the weldment to enter the liner sufficiently.

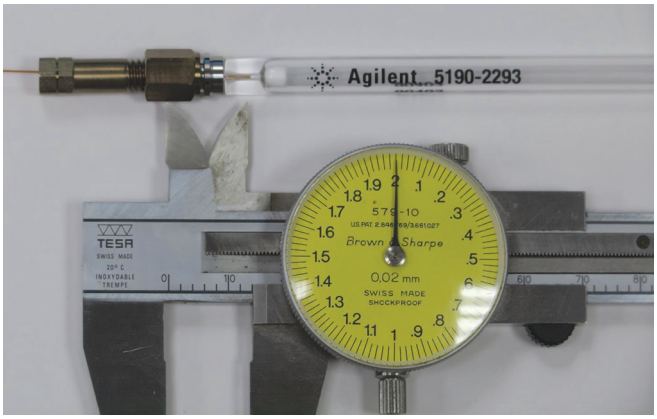

Figure 3. Column nut connected to free-spinning nut and weldment at an installation length of 14 mm with an Agilent liner (5190-2293). The column is positioned ideally in the center of the liner taper.

Figure 4 shows an overlay of four replicate chromatograms of the $C_{10–44}$ mixture using the hot splitless mode at 14 mm installation length. For brevity, only one set of chromatograms is shown. The sensitivity of each analyte is calculated by dividing the area of the peak (measured in milliamp seconds, mA.sec) by the mass of carbon injected (in grams). The sensitivity (mA.sec/g carbon) of each analyte is then normalized to the mean sensitivity of all of the hydrocarbons in the sample. Because the FID is a mass-sensitive detector, a drop in sensitivity can be attributed to a loss in the amount of sample actually being injected onto the column.

Figure 5 is a plot of the normalized sensitivity ratios for the $C_{10–44}$ sample versus column installation length for the hot split injections. The color of each line corresponds to the installation length (black = 10 mm, blue = 12 mm, green = 14 mm, and red = 16 mm). Each line shows a similar trend: a slight decrease in sensitivity towards the higher boiling point compounds. The heavier analytes, C_{40} and C_{44} show between 5 and 8 % loss in sensitivity. The 14 mm length has a slightly higher (2–3 %) sensitivity value than the other three lengths for C_{44}.

Figure 6 is a plot of the normalized sensitivity ratios for the $C_{10–44}$ sample versus column installation length for the hot splitless injections. It is clear that the 10 mm installation (black line) is losing a significant amount of the heavier analytes; C_{44} only has ~60 % recovery. At 10 mm, as shown in Figure 2, the column does not enter the liner sufficiently. The remaining lengths, 12 mm, 14 mm, and 16 mm, show good recovery of all the analytes.

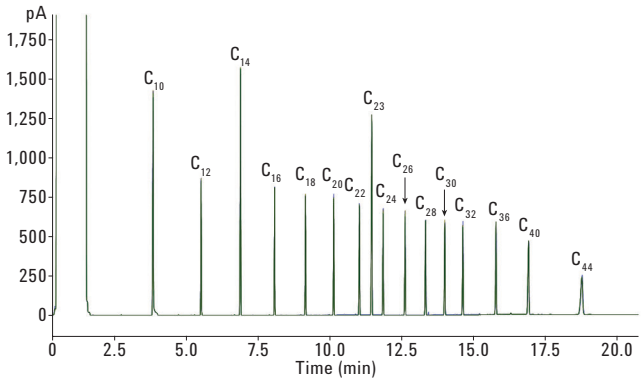

Figure 4. Overlay of four replicate chromatograms of the $C_{10–44}$ mixture in hot splitless mode at 14 mm install length.

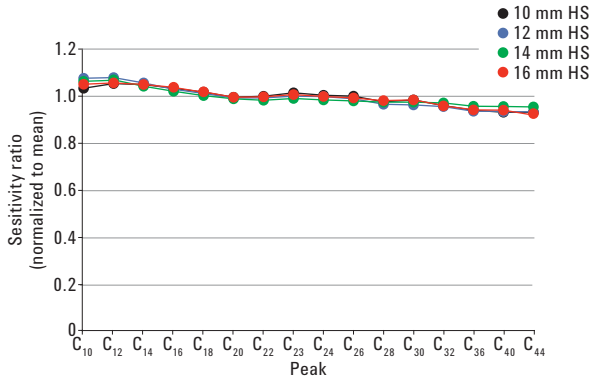

Figure 5. Plot of the normalized sensitivity ratios of the $C_{10–44}$ sample for each column installation length in the hot split mode (10:1 split ratio).

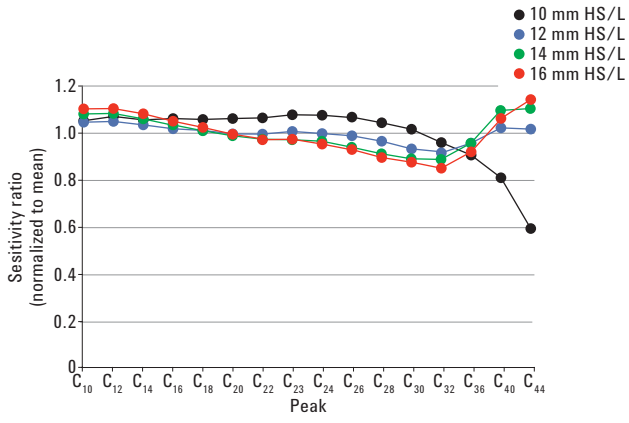

Figure 6. Plot of the normalized sensitivity ratios of the $C_{10–44}$ sample for each column installation length in the hot splitless mode.

Figure 7 is a plot of the normalized sensitivity ratios for the $C_{10–44}$ sample versus column installation length for the cold splitless injections. With the cold splitless injection, the MMI starts at 50 °C, ramps at 900 °C/min to 350 °C, then holds for the remainder of the run. This injection mode appears to perform the best out of the three. The sensitivity ratio is nearly constant across the range of compounds in the mixture. The 10 mm line (black) again shows loss in sensitivity of the heavier compounds, where 12 mm, 14 mm, and 16 mm show good recovery of all analytes.

Conclusion

The data show that a column installation length range of 12–14 mm past the end of the ferrule is the optimal distance the column should protrude in the MMI. At shorter lengths, the column does not enter the liner sufficiently, and discrimination of heavier analytes (C_{40} and C_{44}) occurs. Column installation lengths greater than 14 mm risk entering the liner too far, and can disturb the glass wool at the bottom of certain liners. While the data show results for hydrocarbons, the column installation length should be applicable to users of the MMI in other fields as well.

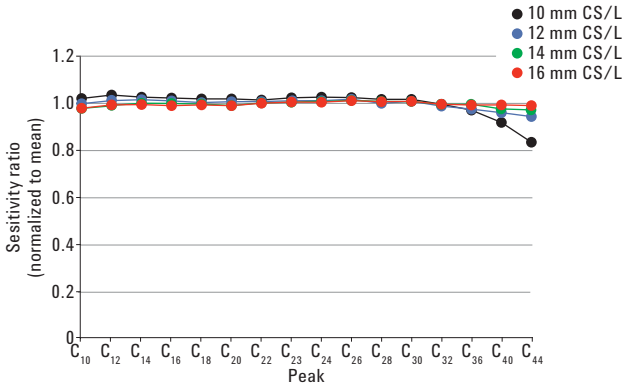

Figure 7. Plot of the normalized sensitivity ratios of the $C_{10–44}$ sample for each column installation length in cold splitless mode. The MMI heated at 900 °C/min to transfer the analytes to the column.

References

1. Agilent Multimode Inlet for Gas Chromatography, *Agilent Technologies Technical Note*, publication 5990-3954EN (**2009**).
2. Bill Wilson, Chin-Kai Meng, Achieving Lower Detection Limits Easily with the Agilent Multimode Inlet (MMI), *Agilent Technologies Application Note*, publication number 5990-4169EN (**2009**).
3. ASTM D6352 "Boiling range distribution of petroleum distillates in boiling range from 174 °C to 700 °C by gas chromatography".
4. Restrictor for Air Cooling the LN_2 Version of the MMI, Agilent Technologies Installation Guide, publication number G3510-97000 (**2012**).

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