Proof of Long-Term, Leak-Free Performance for a Novel Self-tightening GC Column Nut

Application Note

Environmental

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Abstract

Specially designed self-tightening (ST) inlet and transfer-line column nuts maintain a leak-free seal over more than 300 injections using 85/15 Vespel/graphite (or polyimide/graphite) ferrules. In contrast, standard column nuts using the same type of ferrule require retightening within just a few injections. Another advantage of the ST column nuts is that ferrules are easily removed after use, rather than having to be dug out of a standard transfer-line nut.

Introduction

Vespel/graphite (or polyimide/graphite) ferrules have long been preferred for GC/MS analysis, primarily due to the cleanliness of the material. One drawback to using these ferrules has been their tendency to shrink, and then leak, with repeated heat cycling of the GC oven. [1] Users of these ferrules have learned to be cognizant of the material's shortcomings and subsequent need to retighten the ferrules as they shrink. In other words, the ferrules are a pain point users have learned to live with and continually work around.

This application note demonstrates leak-free performance of a self-tightening (ST) column nut design that continually maintains pressure on graphite/polyimide ferrules over hundreds of injections. An abbreviated or short mix of US-EPA 8270 compounds was chosen to test the performance of these fittings over hundreds of heat cycles, due to the range of low-to-high boiling components in the mix. [2] This process was repeated using an Agilent 7890A GC with an Agilent 5975C GC/MSD System and an Agilent 7890B GC with an Agilent 5977 Series GC/MSD System, where the heat-cycle performance of more traditional fittings versus those of the self-tightening nut were compared.

The design of ST fittings includes wings for finger-tight installation that, while improving ease-of-use, introduce additional mass relative to traditional fittings. The additional mass of the new column nut has the potential to introduce a cold spot into the flow path that could lead to deleterious chromatographic effects for compounds susceptible to cold-spot deposition. Polyaromatic hydrocarbons (PAHs) are notorious for demonstrating this effect and produce what appear as tailing peaks, resulting from dropping out of the gas phase onto cold surfaces or cold spots in the flow path. For this reason, PAHs were used to demonstrate the absence of cold spots.

Materials and Methods

The three Agilent GC/MS systems used to evaluate performance of the inlet and transfer line connectors were a 7890A GC with a 5975C Series GC/MSD System, a 7890B GC with a 5977 Series GC/MSD System and a 7890A GC with a 5975B Series GC/MSD System upgraded with a triple axis detector. Columns, inlets, tuning parameters, and instrument conditions were kept constant for the sake of comparison. On each instrument, only inlet and transfer-line connections were changed once a standard or self-tightening nut test was complete.

Semivolatiles standards were obtained from Ultra Scientific Kingstown, RI, USA, p/n CUS-3086 (semivolatile analytes at 2,000 µg/mL) and p/n US-108N (semivolatile internal standard mix at 4,000 µg/mL). A working standard solution with a nominal concentration of 8 µg/mL was prepared in Ultra-Resi-Analyzed grade methylene chloride (Avantor Performance Products, Center Valley, PA, USA) using manual syringes and Class A glassware.

PAH standards were obtained from Agilent Technologies, Inc. Santa Clara, CA, USA (p/n 8500-6035). A working standard at a nominal concentration of 5 µg/mL was prepared in iso-octane (Avantor Performance Products) using a manual syringe and Class A volumetric glassware.

Table 1. Chromatographic conditions for the Agilent 7890A GC with an Agilent 5975C GC/MSD System.

Column:	Agilent J&W DB-UI 8270D, 20 m × 0.18 mm, 0.36 µm (p/n 121-9723)
Oven:	32 °C, 0.8 min hold, to 320 °C at 25 °C/min, 4.8 min hold
Gas purifier:	Gas Clean GC/MS 1/8 inch kit (p/n CP17974)
Carrier:	Helium, 48.5 cm/s (1.2 mL/min), 32 °C, EPC - constant flow
Inlet:	Split/splitless with inert shell and top weldments (p/n G3452-60570 and G3452-60586)
Injector:	Agilent 7683B Automatic Liquid Sampler
Injection:	1.0 µL pulsed splitless 320 °C, 45 psi until 0.73 min, purge flow 60 mL/min on 0.75 min
Inlet liner:	Agilent Ultra Inert double taper, no wool (p/n 5190-3983)
Gold seal:	Agilent Ultra Inert Gold Seal (p/n 5190-6144)
Syringe:	Agilent Blue Line Autosampler Syringe, 10 µL (p/n G4513-80220)
Ferrule:	Inlet and transfer line (p/n 5181-3323)
Column nut:	Universal column nut, 1/16 inch hex, 2/pk (p/n 5181-8830)
MS nut:	MS interface column nut (p/n 05988-20066)
ST inlet:	Self-tightening inlet and detector column nut (p/n 5190-6194)
ST transfer:	Self-tightening MS interface column nut (p/n 5190-5233)
Detector:	MSD SCAN mode, 10 to 450 amu, 325 °C source temp, 180 °C quad temp, 320 °C transfer line

Table 2. Chromatographic conditions for the Agilent 7890B GC with an Agilent 5977 Series GC/MSD System.

Column:	Agilent J&W DB-UI 8270D, 20 m × 0.18 mm, 0.36 µm (p/n 121-9723)
Oven:	32 °C, 0.8 min hold, to 320 °C at 25 °C/min, 4.8 min hold
Gas purifier:	Gas Clean GC/MS 1/8 inch kit (p/n CP17974)
Carrier:	Helium, 48.5 cm/s (1.2 mL/min), 32 °C, EPC - constant flow
Inlet:	Split/splitless with inert shell and top weldments (p/n G3452-60570 and G3452-60586)
Injector:	Agilent 7683B Automatic Liquid Sampler
Injection:	1.0 µL pulsed splitless 320 °C, 45 psi until 0.73 min, purge flow 60 mL/min on 0.75 min
Inlet liner:	Agilent Ultra Inert double taper, no wool (p/n 5190-3983)
Gold seal:	Agilent Ultra Inert Gold Seal (p/n 5190-6144 UI)
Syringe:	Agilent Blue Line Autosampler Syringe, 10 µL (p/n G4513-80220)
Ferrule:	Inlet and transfer line (p/n 5181-3323)
Column nut:	Universal column nut, 1/16 inch hex, 2/pk (p/n 5181-8830) for inlet
MS nut:	MS interface column nut (p/n 05988-20066)
ST nut:	Self-tightening inlet and detector column nut (p/n 5190-6194)
ST nut:	Self-tightening MS interface column nut (p/n 5190-5233)
Detector:	MSD SCAN mode, 10 to 450 amu, 325 °C source temp, 180 °C quad temp, 320 °C transfer line

Table 3. Chromatographic conditions for the Agilent 7890A GC with an Agilent 5975B Series GC/MSD System - PAH analysis.

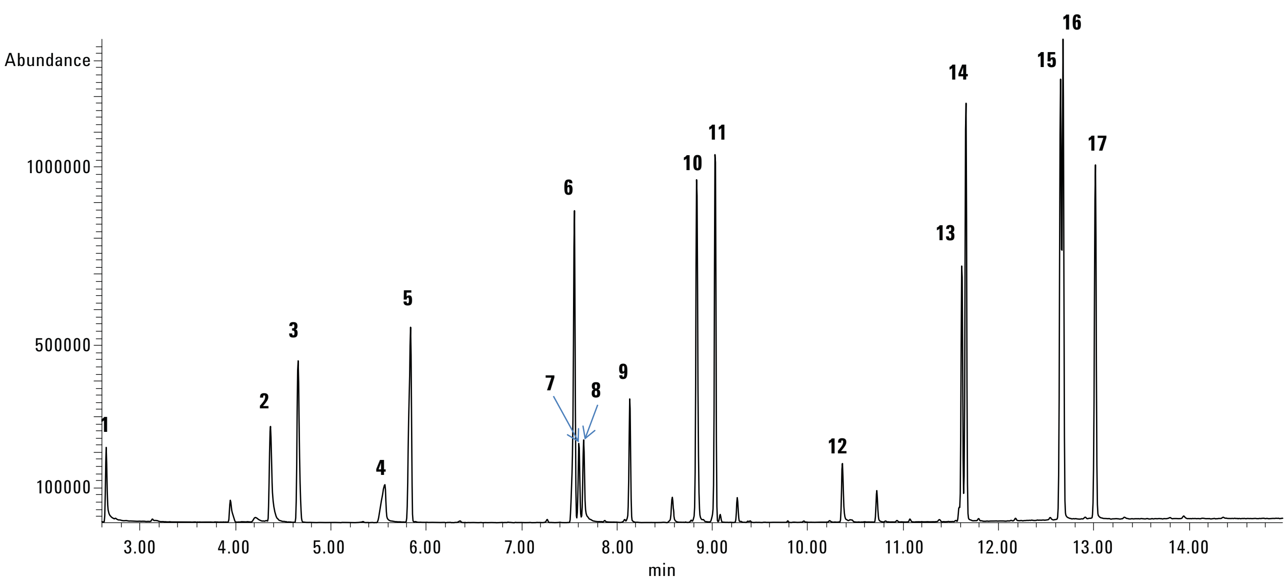
Column:	Agilent J&W DB-UI 8270 D, 20 m x 0.18 mm, 0.36 µm (p/n 121-9723UI)
Oven:	40 °C, 1.0 min, to 100 °C at 12 °C/min, to 210 °C at 20 °C/min, 1.3 min hold, to 310 °C at 15 °C/min, 5.3 min hold
Gas purifier:	Gas Clean GC/MS 1/8 inch kit (p/n CP17974)
Carrier:	Helium, 48.5 cm/s (1.2 mL/min), 40 °C, constant flow
Inlet:	MMI pulsed splitless, 45 psi, 0.73 min, 0.1 µL at 320 °C, total flow 64.2 mL/min, 3 mL/min switched septum purge, gas saver off, 60 mL/min purge flow after 0.75 min
Sample:	EPA 16 PAH mix, 5 µg/mL
Inlet liner:	Agilent Ultra Inert double taper, no wool (p/n 5190-3983)
Gold seal:	Agilent Ultra Inert Gold Seal (p/n 5190-6144)
Syringe:	Agilent Blue Line Autosampler Syringe, 10 µL (p/n G4513-80220)
Ferrule:	Inlet and transfer line (p/n 5181-3323)
Column nut:	Universal column nut, 1/16 inch hex, 2/pk (p/n 5181-8830) for inlet
MS nut:	MS interface column nut (p/n 05988-20066)
ST nut:	Self-tightening inlet and detector column nut (p/n 5190-6194)
ST nut:	Self-tightening MS interface column nut (p/n 5190-5233)
MSD:	MSD SCAN mode, 10 to 450 amu, 325 °C source temp, 180 °C quad temp, 320 °C transfer line

Additional supplies

Vials:	Amber silanized screw top vials, 100/pk (p/n 5183-0716)
Vial caps:	Green screw caps (p/n 5185-5861 500 pk)
Vial inserts:	Glass/polymer feet, 250 µL (p/n 5181-8872)
Septum:	Advanced Green (p/n 5183-4759)
Inlet ferrules:	UltiMetal Plus Flexible Metal ferrules, 10/pk (p/n G3188-27501)
Magnifier:	20x Magnifier loop (p/n 430-1020)
PAH standard:	PAH mixture, 500 µg/mL (p/n 8500-6035)
Syringes:	Replaceable needle, PTFE plunger, 1 mL (p/n 5190-1539), 0.5 mL (p/n 5190-1525)

Results and Discussion

Figure 1 shows a typical total ion chromatogram (TIC) for the nominal 8 µg/mL semivolatile short mix plus internal standard solution used throughout the repetitive heat-cycle testing of the self-adjusting fittings. N-nitrosodimethylamine, the first analyte to elute, represents a low boiler in the semivolatile sample set while benzo[b] fluoranthene and benzo[k]fluoranthene represent higher boilers, including PAHs found in the sample set.



Key

1. N-nitrosodimethylamine
2. Aniline
3. 1,4 Dichlorobenzene D-4
4. Benzoic acid
5. Naphthalene-D8
6. Acenaphthene-D10
7. 2,4-Dinitrophenol
8. 4-Nitrophenol
9. 4,6 Dinitrotoluene
10. Pentachlorophenol
11. Phenanthrene-D10
12. Benzidine
13. 3,3' Dichlorobenzidine
14. Chrysene D-12
15. Benzo[b]fluoranthene
16. Benzo[k]fluoranthene
17. Perylene D-12

Figure 1. Example total ion chromatogram of a semi volatile short mix, 8 ng on-column. Conditions in Table 1.

The TIC in Figure 2A depicts the semivolatile short mix and the start of an evaluation of a standard fitting set with 85/15 polyimide/graphite ferrules installed in the inlet and at the transfer line to the mass spectrometer. The TIC in Figure 2B depicts the same system after 25 heat cycles. The baseline rise early in the lower trace is due to air infiltration from ferrule shrinkage, particularly at lower temperature after high temperature exposure. Clearly, the integration or quantification, or both, of early analytes in this injection are suspect. The extent of the leak required that the Y-axis in the lower trace be expanded three-fold to view the signal from the start of the injection.

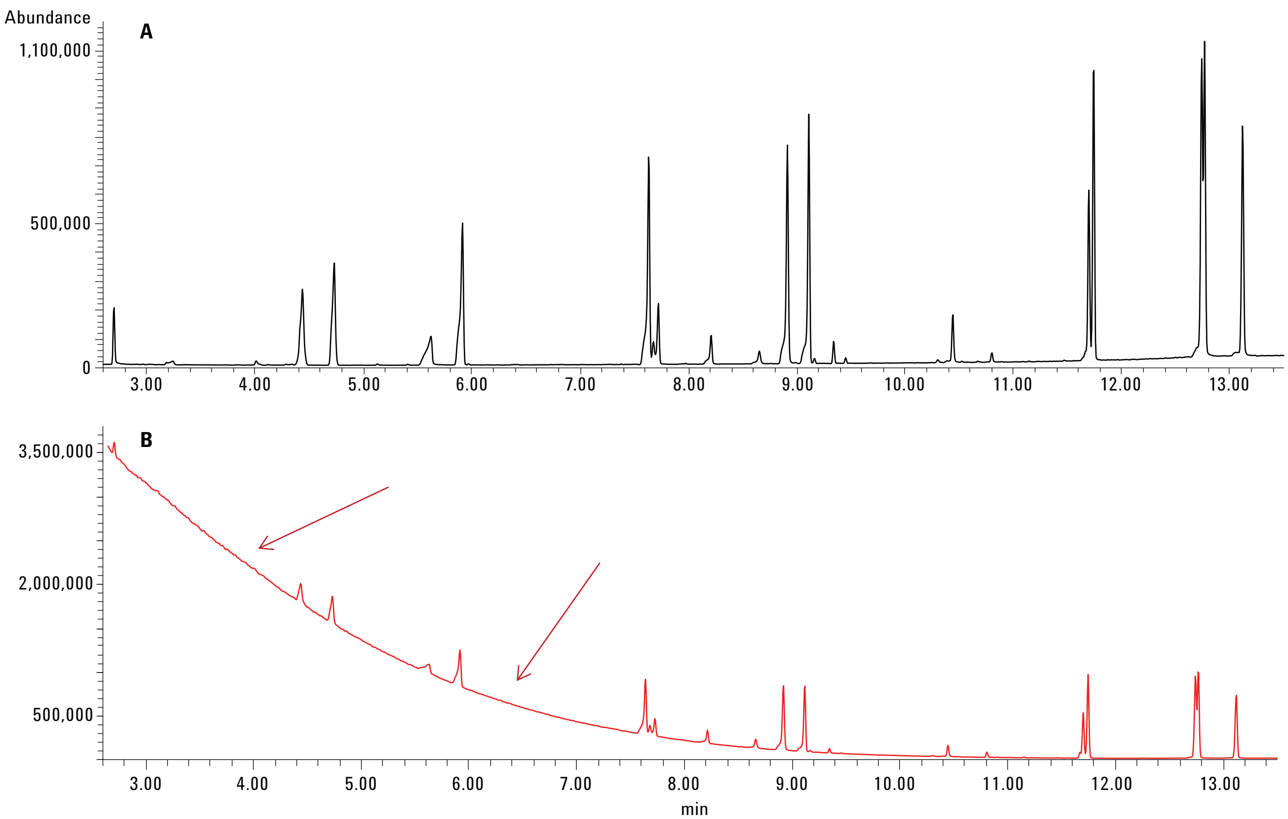


Figure 2. Total ion chromatograms (TICs) of a semivolatile short mix on installation (A) and after 25 injections (B) using standard fittings with 85/15 polyimide/graphite ferrules. The extent of the air leak, shown by the arrows, required a three-fold expansion of the bottom trace Y-axis to show the signal from the start of the injection. Conditions in Table 1.

Figure 3 continues the evaluation of standard fittings just after retightening of the transfer-line fitting and then 25 injections later. Even after retightening, the ferrule at the transfer line continued to shrink and not seal properly at the low end of the temperature ramp on repeated exposure to oven temperature cycling.

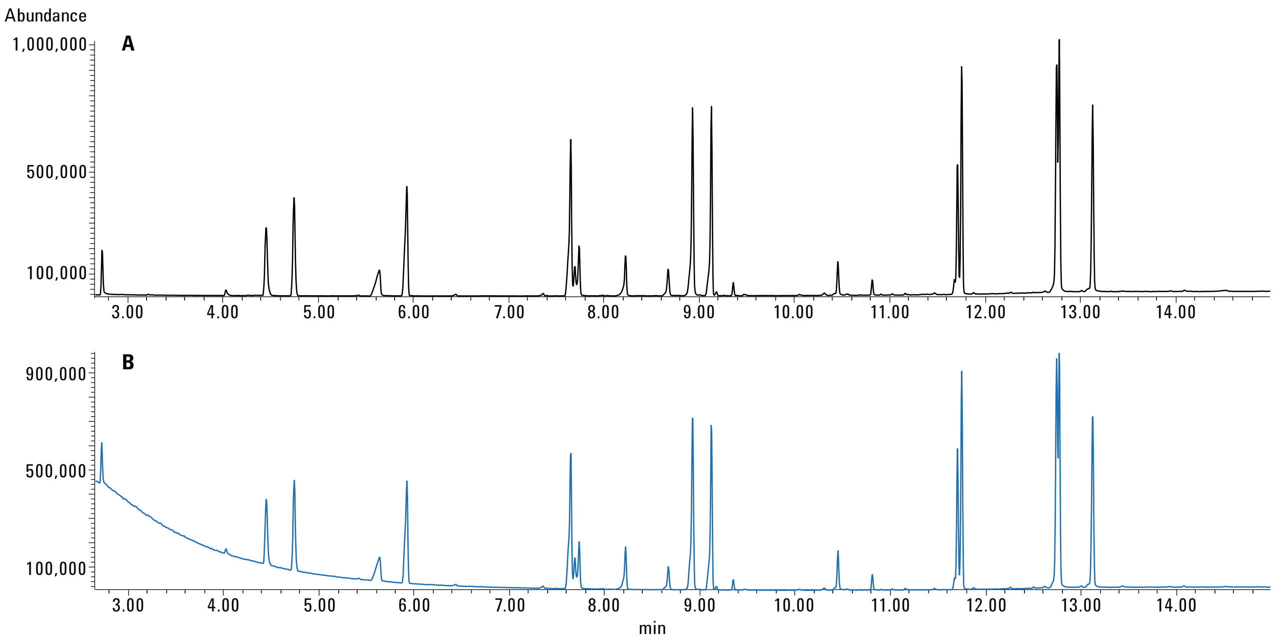


Figure 3. Total ion chromatograms of a semivolatile short mix immediately after ferrule retightening (A) and after 25 subsequent injections using standard fittings (B) with 85/15 polyimide/graphite ferrules. Conditions in Table 1.

Figure 4 shows TIC traces before and after 300-plus injections using the self-tightening fittings, with no evidence of air infiltration. An air and water check after more than 300 injections confirmed that there was no air infiltration, with nitrogen *m/z* 28 less than one percent of the 69 peak. No retightening of the ferrules was necessary to achieve this result with standard 85/15 polyimide/graphite ferrules installed in the self-tightening column nut.

When the ST column nut and ferrule were dismantled after 300-plus injections, the ferrules were easily removed from the column tubing and fitting. With standard column nuts, the polyimide/graphite ferrules stuck in the transfer-line nut, requiring a dental tool to remove the ferrule from the nut. The ease of ferrule removal from the ST transfer-line fitting makes fitting reuse a much simpler process.

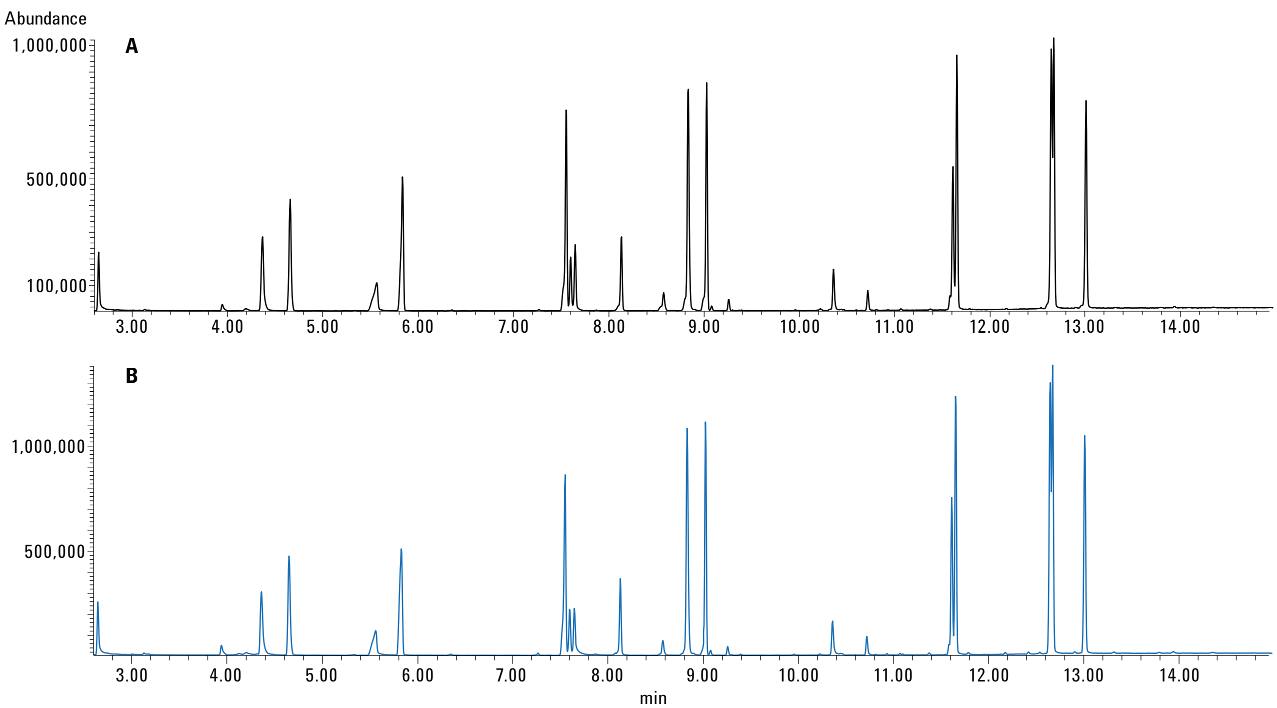


Figure 4. Total ion chromatograms of a semivolatile short mix on installation (A) and after (B) 300-plus injections using self-tightening column nut fittings with 85/15 polyimide/graphite ferrules. Conditions in Table 1.

The TIC traces in Figure 5 show leak-free performance after 400 injections using the self-adjusting ferrules without the need to retighten the fittings. These results were generated on a second instrument, a 7890B GC with a 5977 Series GC/MSD System. As a precaution, a new septum was installed after 200-plus injections to make sure a mechanical leak from piecing the septum more than several hundred times did not skew the evaluation of the fittings. Once again, an air and water check, after 400 injections this time, gave no indication of an air leak.

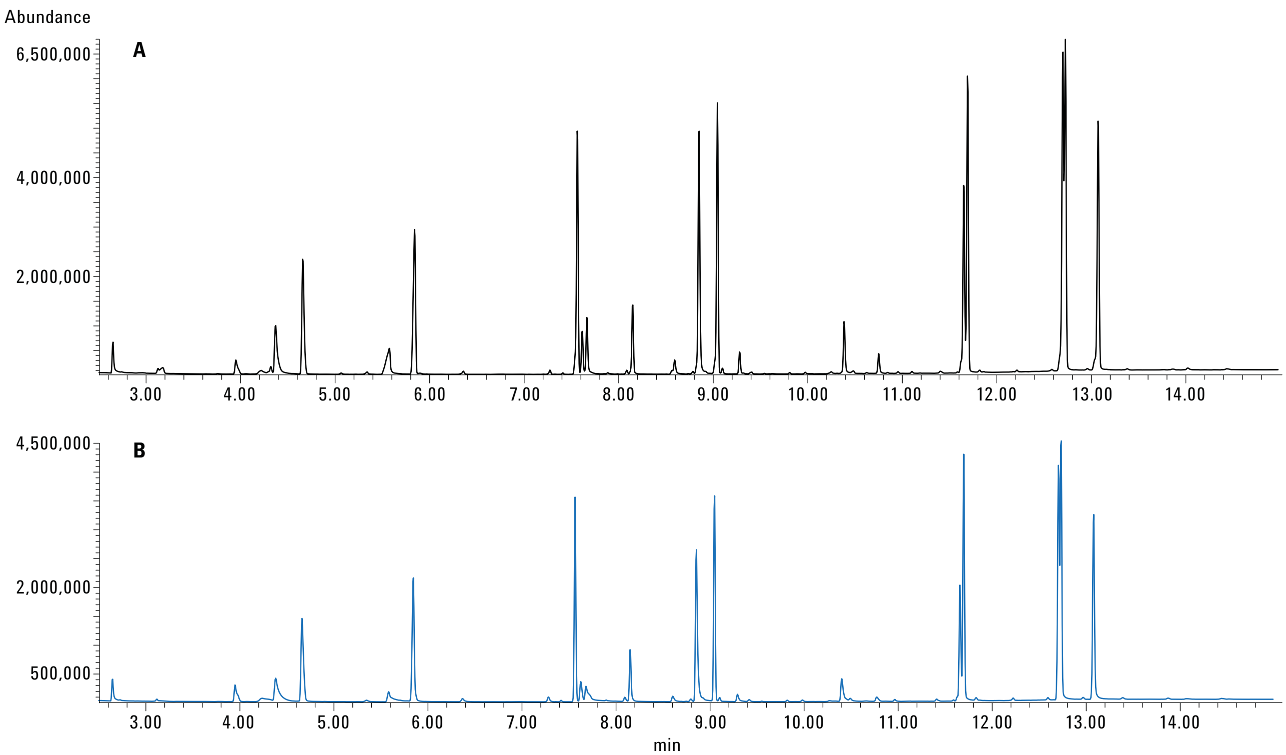
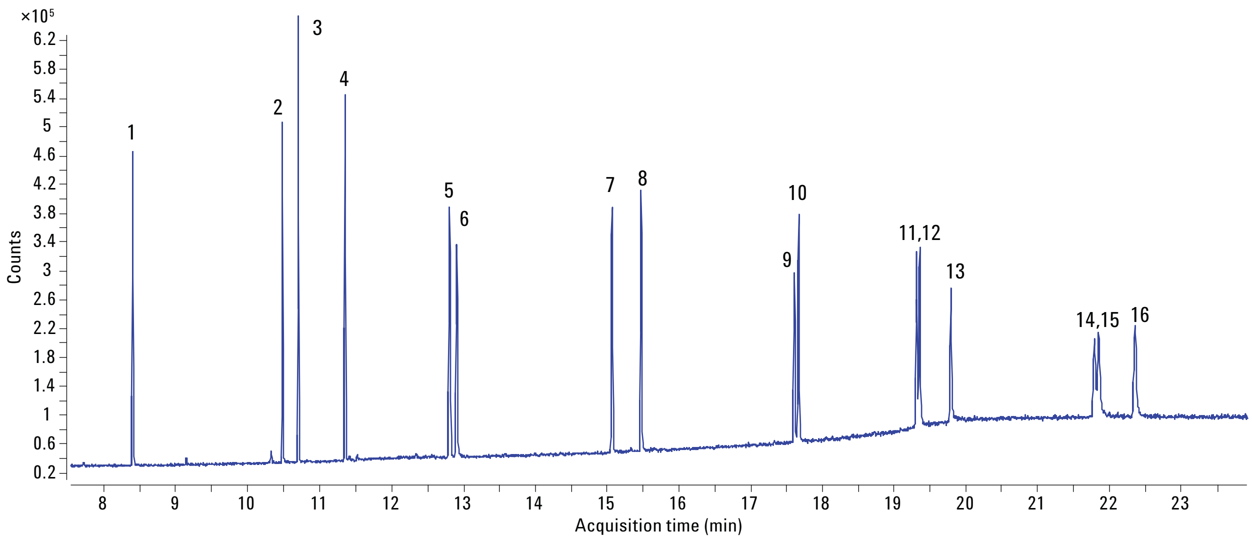


Figure 5. Total ion chromatograms of a semivolatile short mix on installation (A) and after (B) 400-plus injections using a self-tightening column nut with 85/15 polyimide/graphite ferrules. Conditions in Table 2.

The total ion chromatogram in Figure 6 is an example trace of the 16 US-EPA PAHs using the ST nut. This mix was used to demonstrate that the additional mass of the new fittings did not introduce a cold spot into the flow path that would lead to PAH peak tailing.



Key

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo[a]anthracene
10. Chrysene
11. Benzo[b]fluoranthene
12. Benzo[k]fluoranthene
13. Benzo[a]pyrene
14. Indeno[1,2,3 cd]pyrene
15. Di-benzo[a,h]anthracene
16. Benzo[g,h,i]perylene

Figure 6. Total ion chromatogram of 16 PAHs using a self-tightening column nut with 85/15 polyimide/graphite ferrules. Conditions in Table 3.

The trace in Figure 7A is a TIC of the 16 US-EPA PAHs using standard column nuts. The trace in Figure 7B is a TIC of the same solution on the same system, this time using the ST column nuts. No increase in tailing is observed that would be indicative of cold-spot formation. Peak shapes in Figure 7B are as sharp as or sharper than those in Figure 7A.

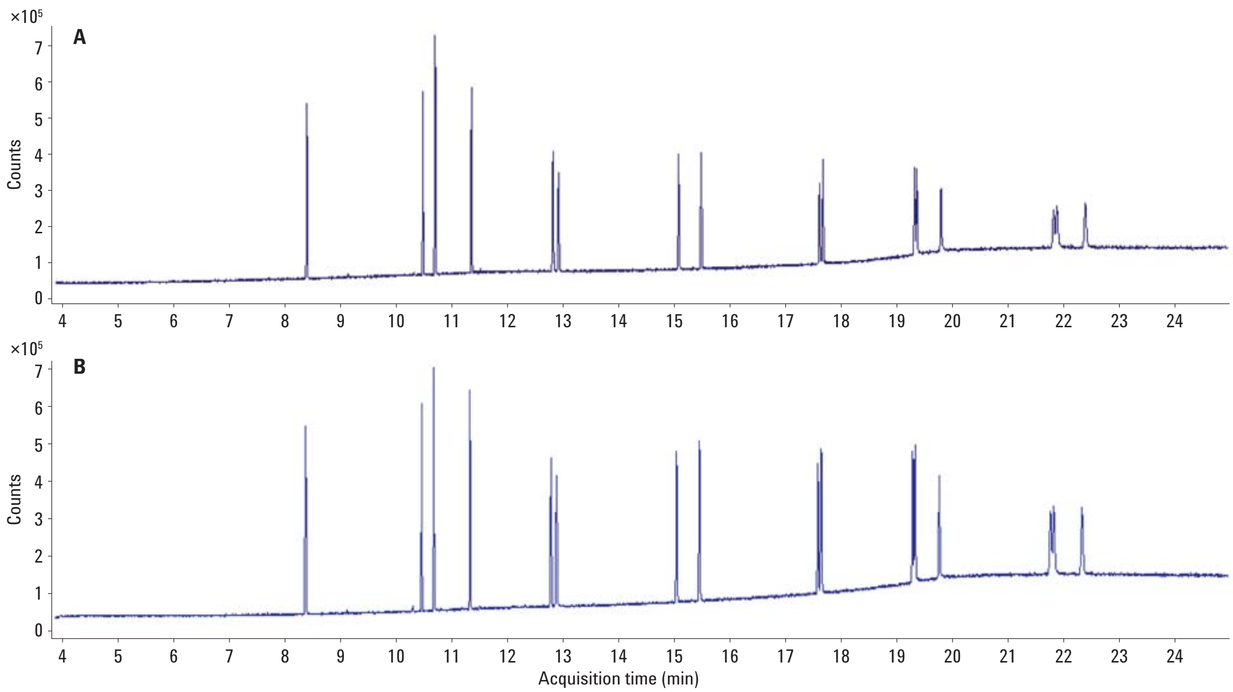


Figure 7. Total ion chromatograms of 16 PAHs comparing standard fittings (A) and self-tightening column nuts (B) with 85/15 polyimide/graphite ferrules. Note the absence of any cold-spot formation. Conditions in Table 3.

Conclusions

Self-tightening column nuts using 85/15 polyimide/graphite ferrules delivered a gas tight seal, with heat cycling between 32 °C and 320 °C, over 300-plus injections without user intervention to retighten the fitting at either the inlet or transfer line. In contrast, standard fittings with the same type of polyimide/graphite ferrules leaked, and required retightening at the transfer line after just a few heat cycles. These self-tightening nuts offer a major improvement in terms of ease-of-use by eliminating the need to retighten polyimide/graphite ferrules once and for all.

Another key feature of the self-tightening column nuts is that polyimide/graphite ferrules do not stick inside them. Columns can be easily changed and the fittings reused without the need to dig old ferrules out of the transfer-line nut.

References

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2. Anon. *Method 8270D*. United States Environmental Protection Agency, Washington, DC, USA (2007). http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8270d.pdf

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