Application Note

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Increased Reproducibility in the Analysis of EU and EPA PAHs with the Agilent J&W Select PAH GC Column and Agilent Intuvo 9000 GC

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Abstract

This Application Note demonstrates the use of the Agilent Select PAH GC column for the analysis of 25 polycyclic aromatic hydrocarbons (PAHs) using an Agilent 7890 GC and an Agilent Intuvo 9000 GC. The European Union (EU) and the US Environmental Protection Agency (EPA) require the analysis of a combined list of 24 PAHs. With the addition of triphenylene, a list of 25 difficult-to-separate isomers is created. The combination of the Select PAH GC column and use of selected ion monitoring (SIM) mode MS detection is needed to detect and separate these compounds. The Intuvo Guard Chip provides increased retention time stability, and increases injection-to-injection reproducibility.

Introduction

The analysis of PAHs required by the EU and the US EPA involves a combined list of 24 compounds. These analytes can be chromatographically challenging due to the existence of isomers. To optimize the separation of these 24 PAH compounds, the Select PAH GC column has been modified with an aromatic selector. Due to the heavy nature of the matrix, take care when preparing and injecting samples into the GC system. Even with sample preparation, frequent maintenance is needed to maintain peak shape, sensitivity, and overall performance.

The analysis of PAHs in salmon oil is an example of a type of analysis where overall performance of a system can be tested. The heavy matrix of the salmon oil and the low detection limits required by the EPA and EU are challenging aspects of the analysis. PAHs in salmon oil may have petrogenic or pyrogenic origins, and can contaminate seafood due to accumulation of petroleum constituents in water sources. Since levels of concern for PAHs can be as low as 1 ng/mL, a robust and efficient analysis method is required for accurate detection.

With a traditional GC, such as a 7890 GC, when sensitivity is lost, the first step to regain it is performing front-end maintenance. Following this maintenance, clipping roughly a meter from the front end of the column and replacing the septum, liner, and gold seal, sensitivity should return. However, retention times will shift a bit earlier. For sensitive methods that require SIM detection, a retention time shift could require that SIM windows are updated in the analytical method.

The Intuvo 9000 GC uses planar columns, direct heating, and metal microfluidic channels to separate compounds instead of traditional air bath ovens. At the inlet of an Intuvo 9000, the gold seal is exchanged with an easily replaceable Intuvo Guard Chip. The Guard Chip is a piece of metal microfluidic technology that functions as a gold seal and guard column, with an identical pathlength, enabling consistent retention times after replacement.

Experimental

Materials and methods

A 7890 GC equipped with a split/splitless inlet, an Intuvo 9000 GC equipped with a split/splitless inlet, an Agilent 5977B GC/MSD, and an Agilent 7693A automatic liquid sampler with Agilent MassHunter software was used for GC/MSD experiments.

7890 GC Conditions	
Column	Agilent J&W Select PAH, 30 m × 0.25 mm, 0.15 mm (p/n CP7462)
Carrier	Helium, constant flow, 1.2 mL/min
Oven	70 °C (0.7 minutes), Ramp 85 °C/min to 180 °C (0.0 minutes), Ramp 3 °C/min to 230 °C (7.0 minutes), Ramp 28 °C/min to 280 °C (10 minutes), Ramp 14 °C/min to 330 °C (3.0 minutes)
Inlet	Splitless mode, 300 °C
Inlet Line	Ultra Inert, splitless, single taper, glass wool (p/n 5190-2293)
GC/MSD	7890B GC equipped with 5977 GC/MSD
Sampler	7693 automatic liquid sampler

Intuvo 9000 GC Conditions	
Column	Agilent J&W Select PAH Intuvo GC column module, 30 m × 0.25 mm, 0.15 mm (p/n CP7462-INT)
Carrier	Helium, constant flow, 1.2 mL/min
Oven	70 °C (0.7 minutes), Ramp 85 °C/min to 180 °C (0.0 minutes), Ramp 3 °C/min to 230 °C (7.0 minutes), Ramp 28 °C/min to 280 °C (10 minutes), Ramp 14 °C/min to 330 °C (3.0 minutes),
Inlet	Splitless mode, 300 °C
Inlet Liner	Ultra Inert, splitless, single taper, glass wool (p/n 5190-2293)
Guard Chip	Guard Chip, Intuvo split/splitless (p/n G4587-60565), 300 °C isothermal
Main Bus	300 °C
GC/MSD	Intuvo 9000 GC equipped with a 5977 GC/MSD
Sampler	7693 automatic liquid sampler

Sample preparation

GC EU PAH standard (p/n 5190-0487), US-EPA mixture (p/n 8500-6035), and triphenylene (Sigma-Aldrich) were diluted separately to a concentration of 20 mg/mL using class A glassware and pipettes. These solutions were then mixed together to a final concentration of 1 to 2 mg/mL of all 24 regulated PAHs and triphenylene.

A commercially available salmon oil was prepared at a 1:10 dilution in dichloromethane (DCM) (Sigma-Aldrich), and analyzed on a 7890 GC and an Intuvo 9000 GC using a Select PAH GC column. Standards of PAH compounds, at concentrations ranging from 1 to 1,000 ng/mL, were injected every 50 injections of salmon oil. Column maintenance was performed to maintain sensitivity.

Flowpath Supplies	
Vials	2 mL, screw top, amber, write-on spot, certified, (p/n 5182-0716, 100/pk)
Vial Caps	9 mm blue screw cap, PTFE/RS (p/n 5185-5820, 500/pk)
Septum	Bleed and temperature optimized (BTO), 11 mm septa (p/n 5183-4757, 50/pk)
Gold Seal (7980)	Ultra Inert gold seals (p/n 5190-6145, 10/pk)
Guard Chip	Guard Chip, Intuvo split/splitless (p/n G4587-60565)
Flow Chips	Intuvo inlet chip (p/n G4581-60031) Flow Chip, Intuvo, D2-MS (p/n G4581-60033) Flow Chip, Intuvo, swaged HES MS tail (p/n G4590-60109)
Inlet/MSD (7890)	85:15 Vespel: graphite ferrules (p/n 5062-3508, 10/pk)
Inlet/MSD (Intuvo)	Polyimide Intuvo gasket (p/n 5190-9072)

MSD SIM parameters

Peak	Component	CAS	SIM Group	*m/z*	Q1	Q2	EU 15+1	EPA
1	Naphthalene	91-20-3	1	128				X
2	Acenaphthylene	208-96-8	1	152				X
3	Acenaphthene	83-32-9	1	154	128	152		X
4	Flourene	86-73-7	1	166				X
5	Phenanthrene	85-01-8	2	178	76			X
6	Anthracene	120-12-7	2	178	76			X
7	Flouranthene	206-44-0	3	202	101			X
8	Pyrene	129-00-0	3	202	101			X
9	Benzo(c)fluorene	205-12-9	3	216			X	
10	Benz(a)anthracene	56-55-3	4	228	226	113	X	X
11	Cyclopenta(c,d)pyrene	27208-37-3	4	226	113		X	
12	Tripheylene	217-59-4	4	228	226	113		
13	Chrysene	218-01-9	4	228	226	113	X	X
14	5-Methylchrysene	3697-24-3	4	242	226		X	
15	Benzo(b)fluoranthene	205-99-2	5	252			X	X
16	Benzo(k)fluoranthene	207-08-9	5	252			X	X
17	Benzo(j)fluoranthene	205-82-3	5	252			X	
18	Benzo(a)pyrene	50-32-8	5	252			X	X
19	Indeno(1,2,3-cd)pyrene	193-39-5	6	276	138		X	X
20	Dibenz(a,h)anthracene	53-70-3	6	278	139		X	X
21	Benxo(g,h,i)perylene	191-24-2	6	276	138		X	X
22	Dibenzo(a,l)pyrene	191-30-0	7	302			X	
23	Dibenzo(a,e)pyrene	192-65-4	7	302			X	
24	Dibenzo(a,i)pyrene	189-55-9	7	302			X	
25	Dibenzo(a,h)pyrene	189-64-0	7	302			X	

Results and discussion

While the separation of 25 PAH compounds can be challenging, Figure 1 demonstrates that resolution of isomers is possible with the Select PAH GC column and mass spectral acquisition in SIM mode. High fat matrices such as salmon oil can be problematic if not prepared properly. Even a traditional dilution in a solvent such as DCM can still lead to matrix accumulation in the flowpath.

In Figure 2, a standard of 50 ng/mL was injected before and after 50 injections of salmon oil diluted 1:10 in DCM.

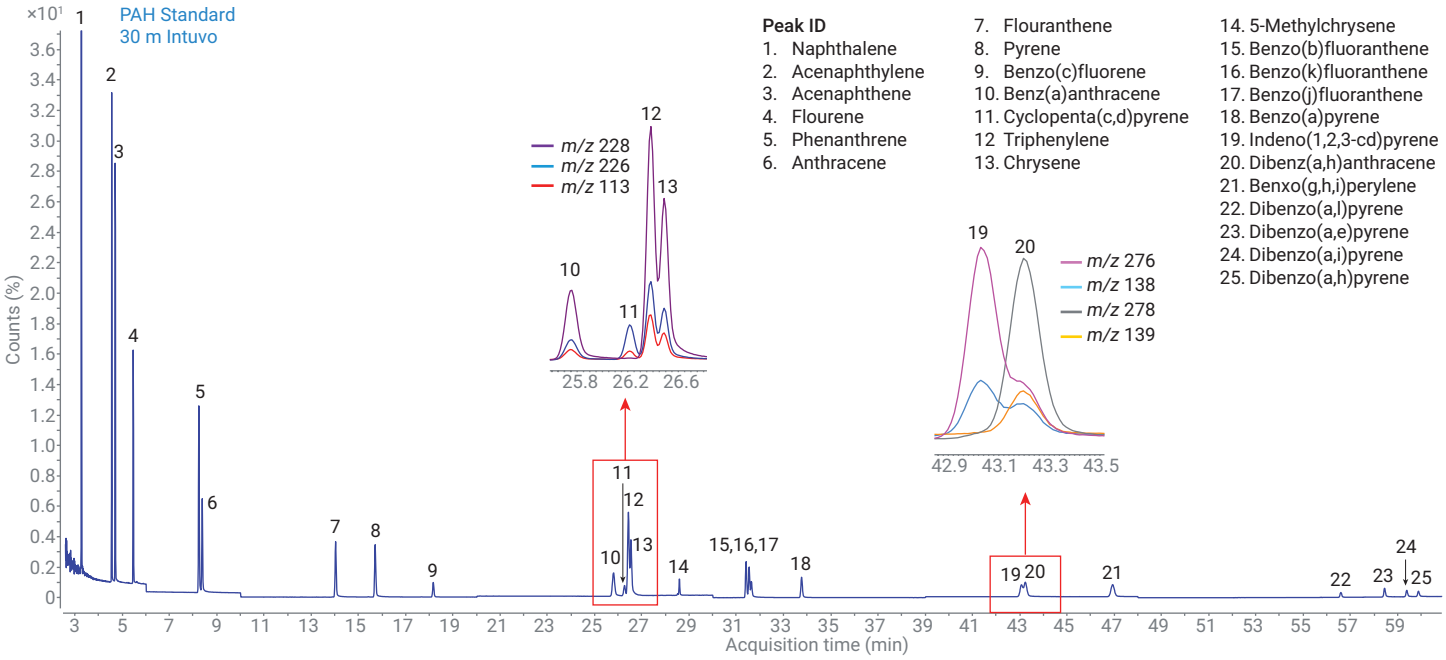

Figure 1. A 50 ng/mL standard of 25 PAH compounds analyzed on a 7890 GC with a Select PAH GC column.

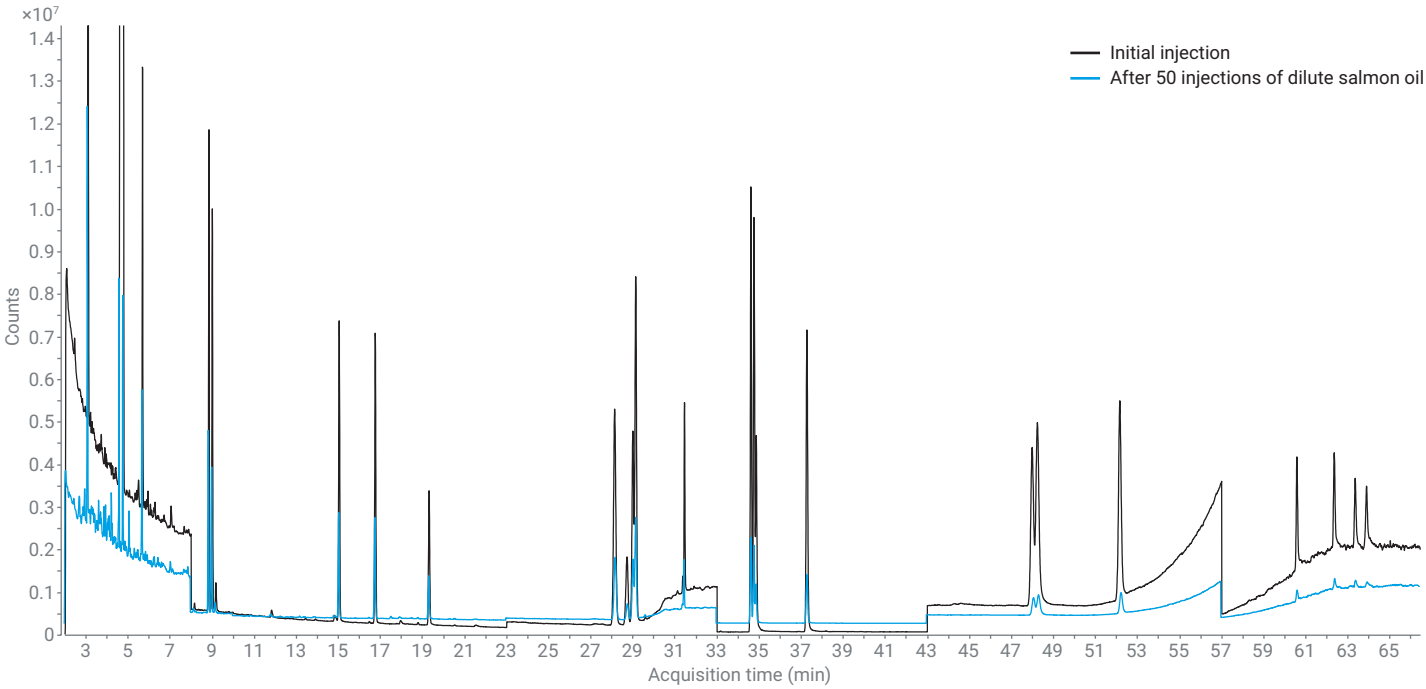

Figure 2. A standard of 50 ng/mL before and after 50 injections of dilute salmon oil analyzed on a 7890 GC.

After the 50 injections of dilute salmon oil, a dramatic loss in sensitivity was observed, as well as buildup in the inlet liner, gold seal, and septum, as shown in Figure 3.

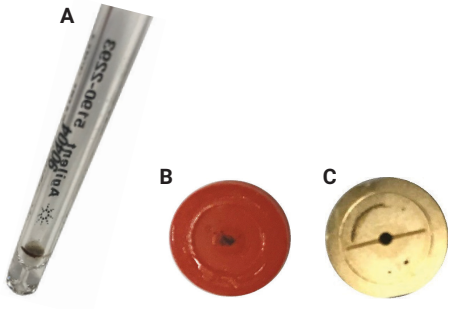

Figure 3. Liner (A), septum (B), and gold seal (C) after 50 injections of diluted salmon oil.

A method was applied on an Intuvo 9000 GC identical to that used on the 7890 GC, except for the Guard Chip, which was not present on the 7890 GC. The Intuvo 9000 uses a planer column design, and click and run connections.

The same standard containing 25 PAH analytes at 100 ng/mL was analyzed on the Select PAH GC column designed for a 7890 GC with a traditional 7 in. cage, and a Select PAH GC column designed for the Intuvo 9000 with planar column design. The same temperature program, pressure settings, column phase, and column dimensions were used on the Intuvo 9000 as with the 7890 GC. Figure 4 demonstrates that, under identical conditions, the two chromatograms are almost indistinguishable concerning time and peak height.

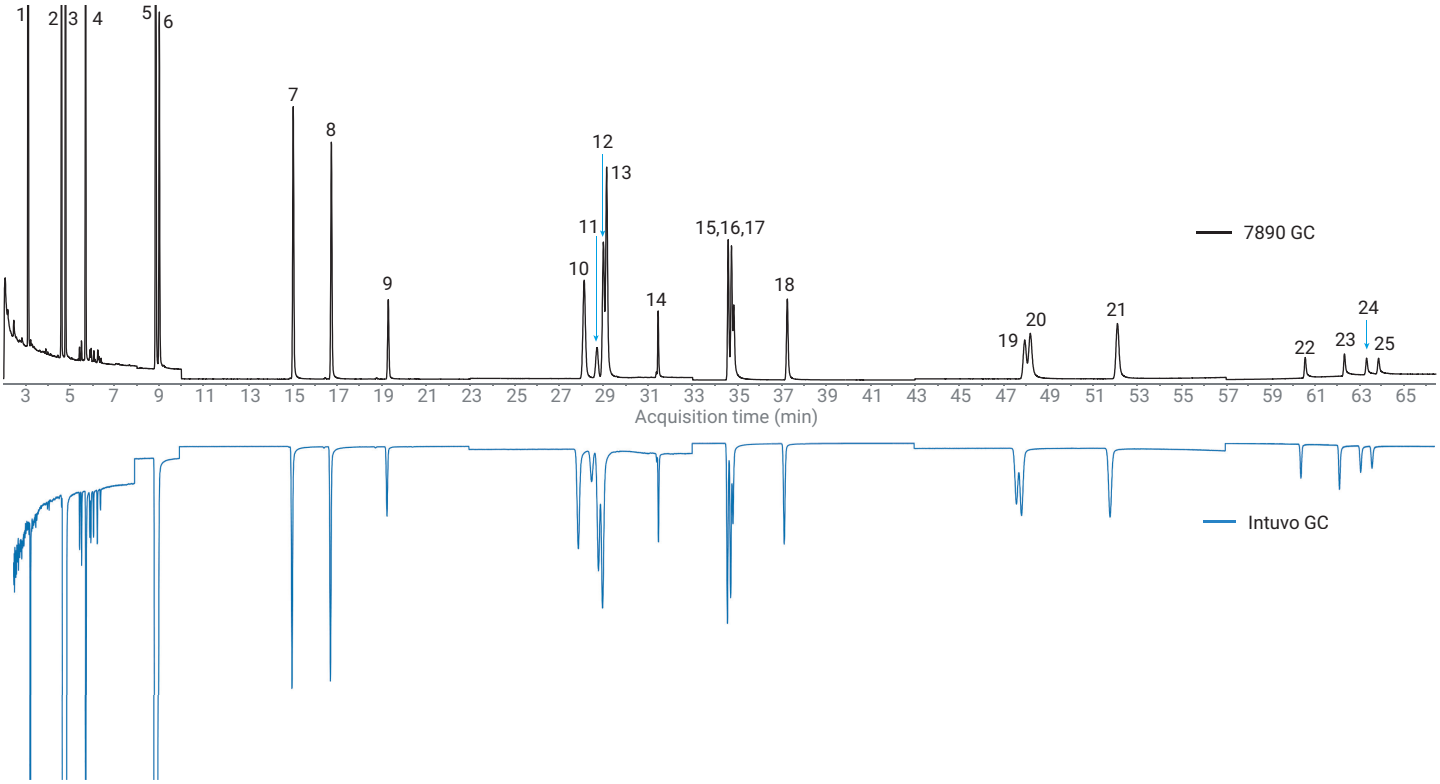

Figure 4. A 100 ng/mL standard of 25 PAH compounds analyzed with a 7890 GC and an Intuvo 9000 GC.

To regain sensitivity, front-end maintenance was performed, including replacement of the inlet liner, gold seal, and septum, and clipping a meter off the column on the 7890 GC. On the Intuvo 9000, the Guard Chip, a piece of metal microfluidic technology with identical pathlength, was replaced. Figure 5A demonstrates the resulting retention time shift on analytes as a result of front-end maintenance on the 7890 GC, versus no retention time shifting when replacing the Guard Chip on the Intuvo 9000 GC (Figure 5B). The ability to maintain retention times increases the reproducibility of the analysis of PAH compounds in high fat matrices such as salmon oil.

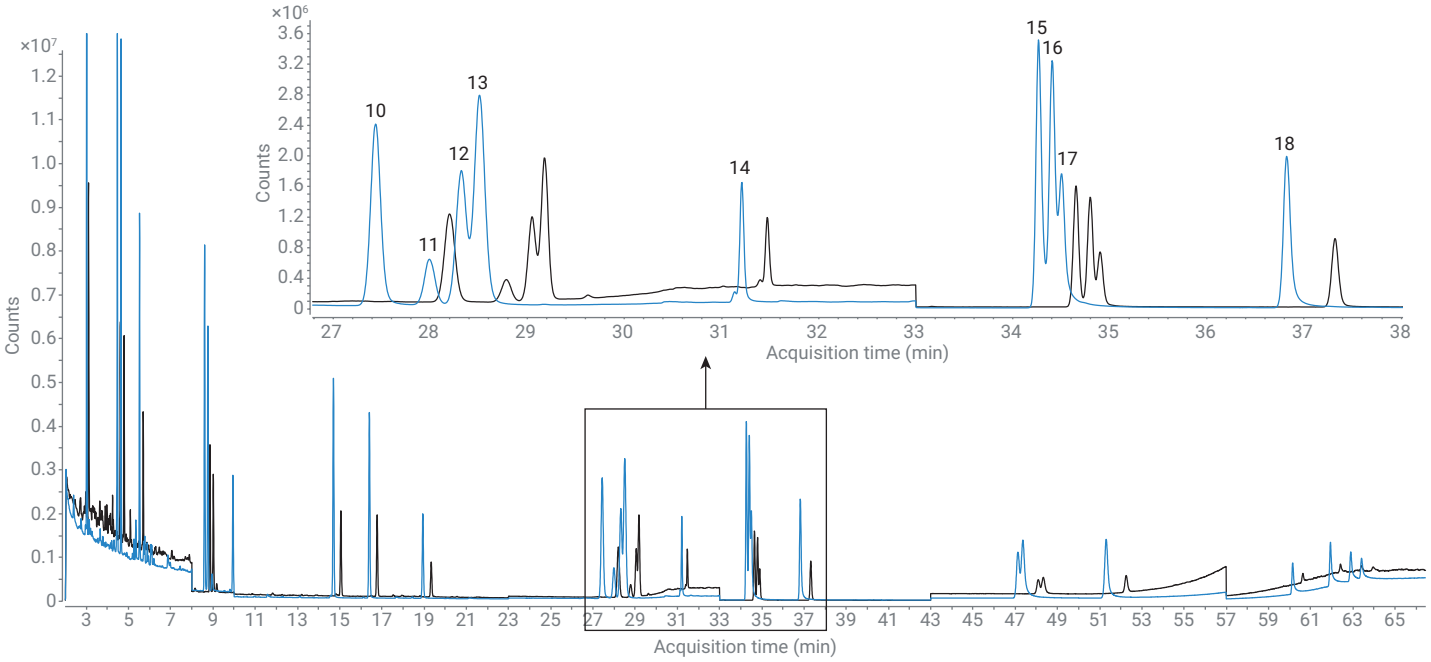

Figure 5A. A 50 ng/mL standard of 25 PAH compounds before and after front-end column maintenance on a 7890 GC.

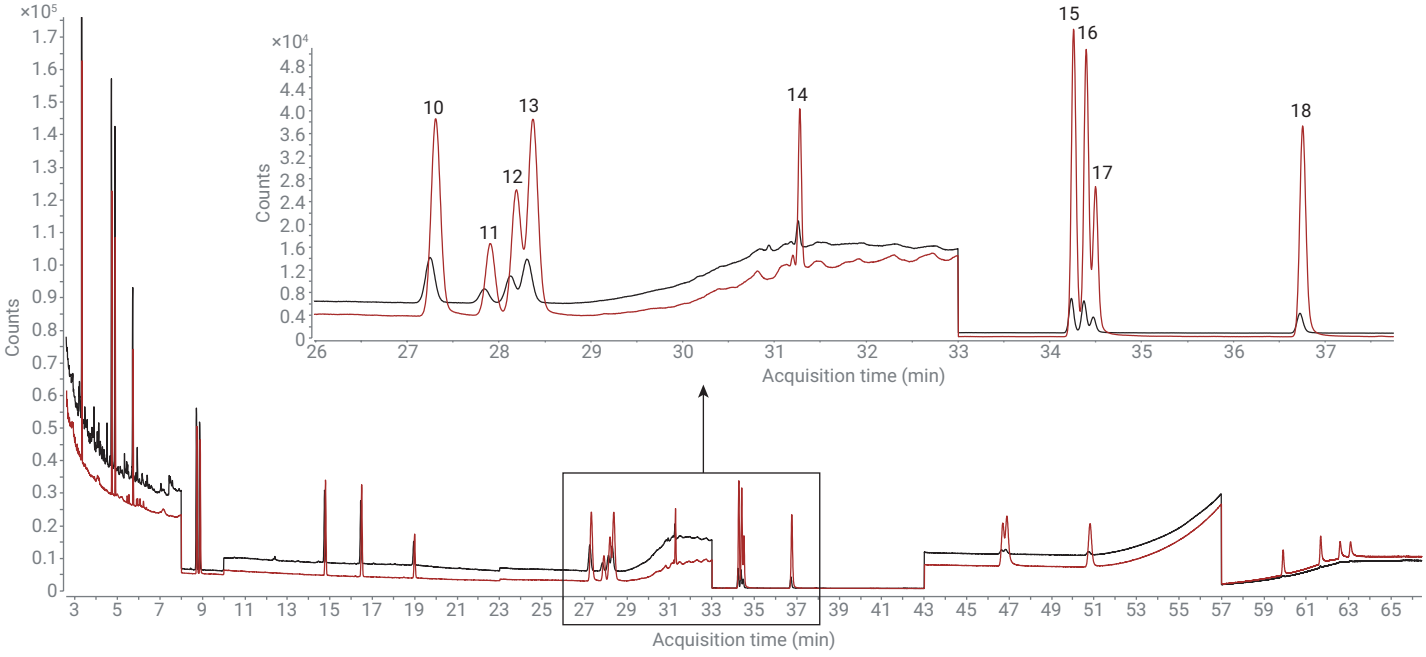

Figure 5B. A 50 ng/mL standard of 25 PAH compounds before and after front-end column maintenance on an Intuvo 9000 GC.

Conclusion

Good resolution of 25 PAH compounds is achievable with a Select PAH GC column on a traditional 7890 GC and an Intuvo 9000 GC. The replacement of a metal microfluidic Guard Chip on the Intuvo 9000 allows for consistent retention times after front-end maintenance.

References

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