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Analysis of PAHs Using Hydrogen Carrier Gas and the Hydrogen-Optimized Source with GC/MS and GC/MS/MS in Challenging Soil Matrix

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemical compounds that are composed of two or more fused conjugated benzene rings with a pair of carbon atoms shared between rings in their molecules. Further, PAHs originate from multiple sources and are widely distributed as contaminants throughout the world. The most common way to detect PAHs is with GC/MS on the single or triple quadrupole instrument. Helium is the preferred carrier gas for GC/MS analysis; however, its reoccurring shortages and mounting costs have increased demand for applications using hydrogen as the carrier gas. This application focuses on the analysis of 27 PAHs on a triple quadrupole GC/MS in multiple reaction monitoring (MRM) mode using hydrogen carrier gas, the HydroInert source, and mid-column backflush to address heavy matrix. A liquid-extracted soil sample was used as a worst-case scenario to test the Ultra Inert mid-frit inlet liner and the method for PAH analysis. Liner, column, and system robustness were demonstrated by 500 repeat injections of extracted soil sample.

Experimental

Chemicals and reagents

PAH calibration standards (part number G3440-85009) were diluted using isooctane. Twelve calibration levels were prepared: 0.1, 0.25, 0.5, 1, 2, 10, 20, 100, 200, 400, 750, and 1000 ng/mL. Each level also contained 500 ng/mL of the ISTDs.

Matrix sample preparation

Commercial topsoil (Weaver Mulch, Coatesville, PA, U.S.) was dried at 120 °C overnight. A 5 g sample of the dried soil was extracted with 30 mL dichloromethane/acetone (1:1 v/v) with agitation overnight. The extract was filtered, and the filtrate was reduced 7.5 fold in volume by evaporation. The resulting extract was spiked with 100 ppb of the 27 PAH analytes and 500 ppb of the five ISTD compounds.

Robustness testing

Calculated concentration stability was tested over 500 replicate injections using spiked soil extract. After every 100 injections, the liner and septa were replaced. After every 300 injections, the split/splitless inlet gold seal was replaced.
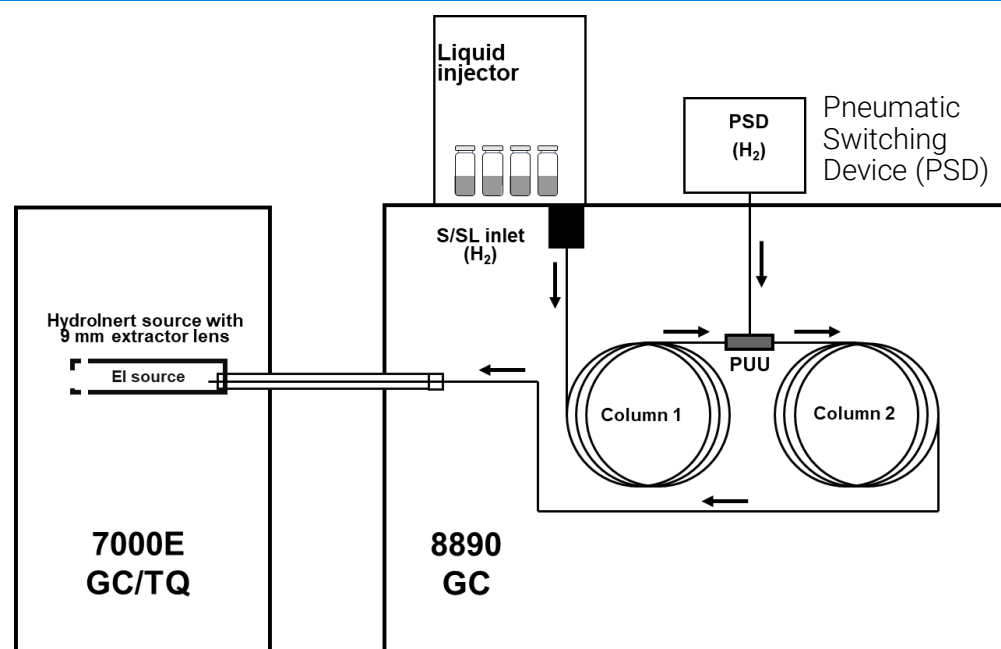
Instrumentation

Fig.1 GC/MS/MS configuration.

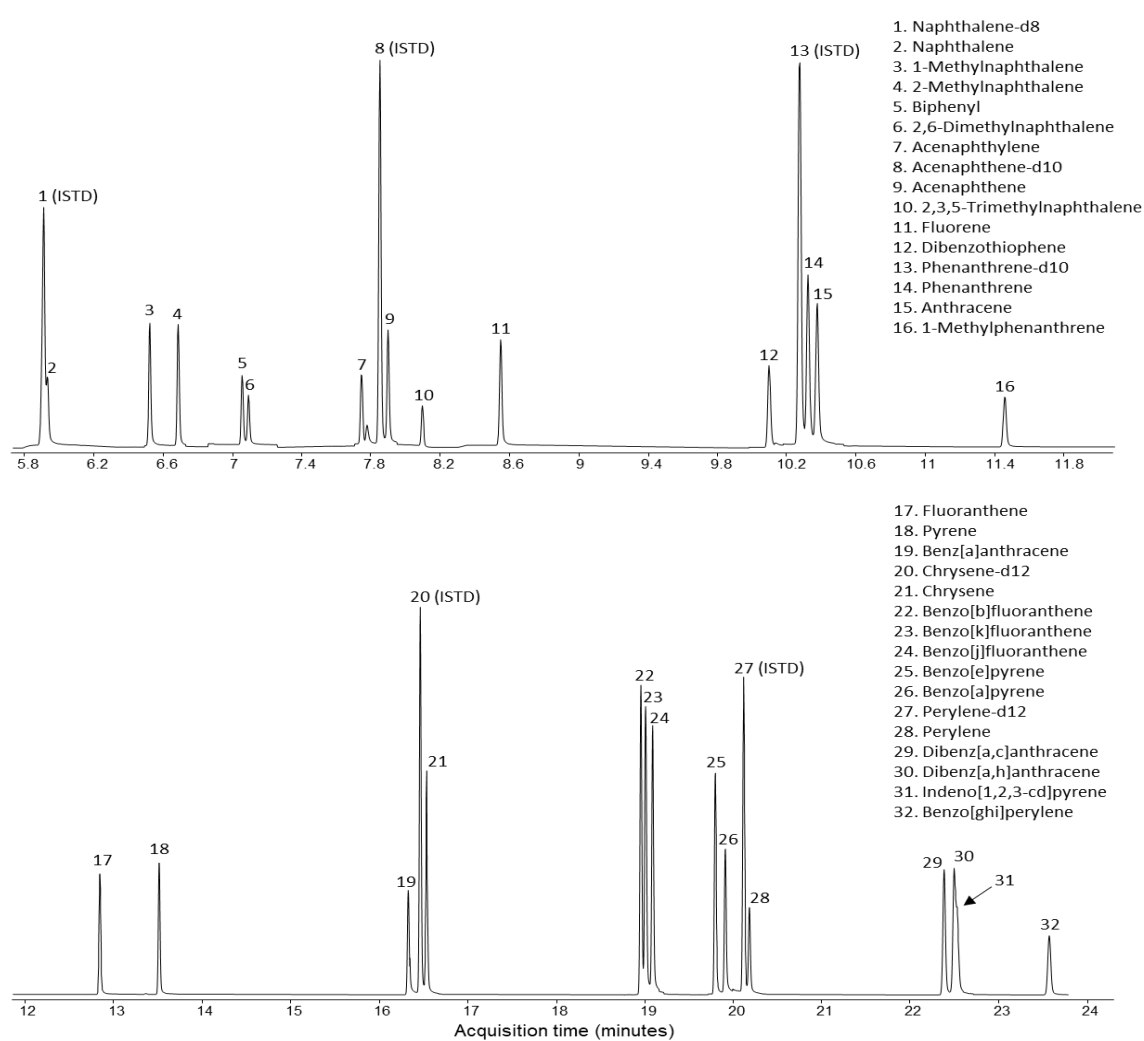| Agilent 8890 GC with Fast Oven, Auto Injector, and Tray	
Injection Volume	1.0 µL
Inlet	EPC split/splitless
Mode	Pulsed splitless
Injection Pulse Pressure	40 psi until 0.7 min
Purge Flow to Split Vent	50 mL/min at 0.75 min
Septum Purge Flow Mode	Standard, 3 mL/min
Inlet Temperature	320 °C
Oven	Initial: 60 °C (1 min hold) Ramp 1: 25 °C/min to 200 °C Ramp 2: 10 °C/min to 335 (4.4 min hold)
Column 1	Agilent J&W DB-EUPAH, 20 m x 0.18 mm, 0.14 µm
Control Mode	Constant flow, 0.9 mL/min
Inlet Connection	Split/Splitless Inlet
Outlet Connection	Purged Ultimate Union (PUU)
Post-run Flow (Backflushing)	−5.274 mL/min
Column 2	Agilent J&W DB-EUPAH, 20 m x 0.18 mm, 0.14 µm
Control Mode	Constant flow, 1.1 mL/min
PSD Purge Flow	3 mL/min
Inlet Connection	Purged Ultimate Union (PUU)
Outlet Connection	Agilent 7000E GC/TQ
Post run Flow (Backflushing)	5.443 mL/min
Agilent 8890 GC Backflush Parameters	
Inlet Pressure (Backflushing)	2 psi
Backflush Pressure	80 psi
Void Volumes	7.2
Backflush Time	1.5 min
Agilent 7000E GC/TQ	
Source	Agilent HydroInert source
Drawout Lens	9 mm
Transferline Temperature	320 °C
Source Temperature	325 °C
Quadrupole Temperature	150 °C
Mode	Dynamic MRM
EM Voltage Gain	10
Solvent Delay	5.5 min
Collision Gas	Nitrogen (only), 1.5 mL/min
Automatically Subtract Baseline	Yes
Advanced SIM/MRM Thresholding	Yes
Tune File	atunes.eiex.jtune.xml

Table 1. Experimental parameters.

1. Naphthalene-d8
2. Naphthalene
3. 1-Methylnaphthalene
4. 2-Methylnaphthalene
5. Biphenyl
6. 2,6-Dimethylnaphthalene
7. Acenaphthylene
8. Acenaphthene-d10
9. Acenaphthene
10. 2,3,5-Trimethylnaphthalene
11. Fluorene
12. Dibenzothiophene
13. Phenanthrene-d10
14. Phenanthrene
15. Anthracene
16. 1-Methylphenanthrene

17. Fluoranthene
18. Pyrene
19. Benz[a]anthracene
20. Chrysene-d12
21. Chrysene
22. Benzo[b]fluoranthene
23. Benzo[k]fluoranthene
24. Benzo[j]fluoranthene
25. Benzo[e]pyrene
26. Benzo[a]pyrene
27. Perylene-d12
28. Perylene
29. Dibenz[a,c]anthracene
30. Dibenz[a,h]anthracene
31. Indeno[1,2,3-cd]pyrene
32. Benzo[ghi]perylene

Fig 2. MRM TIC of 27 PAHs at 100 pg/µL and 5 ISTDs at 500 pg/µL.

Analyte	Linear Range (pg)	Correlation Coefficient (R^2)	MDL(pg)
Naphthalene	0.1−1000	0.9999	0.07
1-Methylnaphthalene	0.1−1000	0.9995	0.09
2-Methylnaphthalene	0.1−1000	0.9995	0.06
Biphenyl	0.1−1000	0.9994	0.16
2,6-Dimethylnaphthalene	0.1−1000	0.9994	0.10
Acenaphthylene	0.25−1000	0.9996	0.15
Acenaphthene	0.1−1000	0.9996	0.13
2,3,5-Trimethylnaphthalene	0.1−1000	0.9994	0.10
Fluorene	0.1−1000	0.9996	0.05
Dibenzothiophene	0.1−1000	0.9995	0.10
Phenanthrene	0.1−1000	0.9997	0.09
Anthracene	0.1−1000	0.9996	0.15
1-Methylphenanthrene	0.1−1000	0.9996	0.08
Fluoranthene	0.1−1000	0.9995	0.03
Pyrene	0.1−1000	0.9998	0.08
Benz[a]anthracene	0.1−1000	0.9995	0.13
Chrysene	0.1−1000	0.9996	0.11
Benzo[b]fluoranthene	0.1−1000	0.9995	0.06
Benzo[k]fluoranthene	0.1−1000	0.9999	0.09
Benzo[j]fluoranthene	0.1−1000	0.9999	0.12
Benzo[e]pyrene	0.1−1000	0.9997	0.07
Benzo[a]pyrene	0.1−1000	0.9998	0.11
Perylene	0.1−1000	0.9996	0.11
Dibenz[a,c]anthracene	0.1−1000	0.9997	0.05
Dibenz[a,h]anthracene	0.1−1000	0.9994	0.09
Indeno[1,2,3-cd]pyrene	0.1−1000	0.9996	0.08
Benzo[ghi]perylene	0.1−1000	0.9997	0.06

Table 2. 12-level MRM ISTD calibration curve with a range of 0.1 to 1000 pg. MDLs were defined as MDL = t (n − 1,0.99) x SD, where t (n − 1,0.99) is the one-sided Student's t-statistic at the 99% confidence limit for n − 1 degrees of freedom, (2.998 for n = 8), and SD is the standard deviation of replicate solvent samples spiked at 0.25 pg.

GC/MS methodology

Figure 2 shows the MRM total ion chromatogram (TIC) of the 100 pg/µL calibration standard with 500 pg/µL ISTDs. Using these parameters, the peak shapes for PAHs—especially the latest ones—are excellent. In general, the HydroInert source provided the best peak shapes for PAHs when using hydrogen carrier gas.

Table 2 shows the calibration results of the system with 12 calibration levels from 0.1 to 1000 pg. All analytes show excellent linearity across the entire range. Using the HydroInert source also resulted in excellent signal-to-noise ratios, allowing the calibration range to be extended to subpicogram levels. Of the 27 analytes, 26 had sufficient signal for calibration from 0.1 to 1000 pg. One was calibrated from 0.25 to 1000 pg.

One of the problems encountered when using helium carrier gas and the standard 3 mm EI source extractor lens for the analysis of PAHs is the response of ISTDs climbed with increasing concentration of the analytes. This effect can cause the response of perylene-d12 to increase by as much as 60% over the calibration range and cause significant errors in quantitation. Figure 3 shows the ISTD response stability over the calibration range with the current method. As demonstrated in Figure 3, the use of hydrogen carrier gas with the HydroInert source and a 9 mm extractor lens also eliminates the creeping ISTD response problem. The %RSD for the raw area responses across the calibration range are all 6.4% or less. This is important for achieving the excellent calibration linearity shown in Table 2.

Napthalene-d8 (6.24%)
Acenaphthene-d10 (6.23%)
Phenanthrene-d10 p(5.86%)
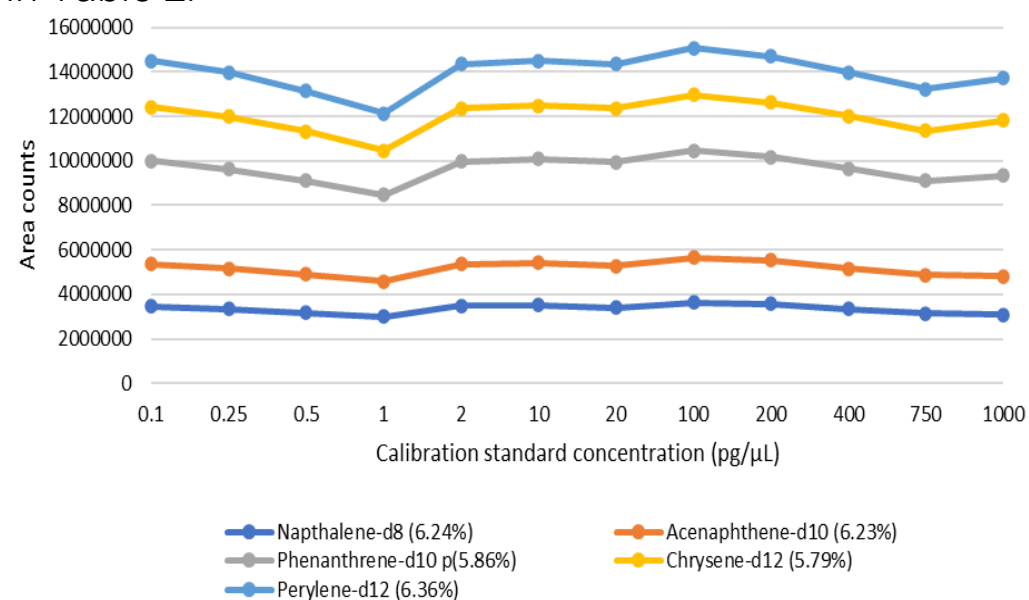Chrysene-d12 (5.79%)
Perylene-d12 (6.36%)

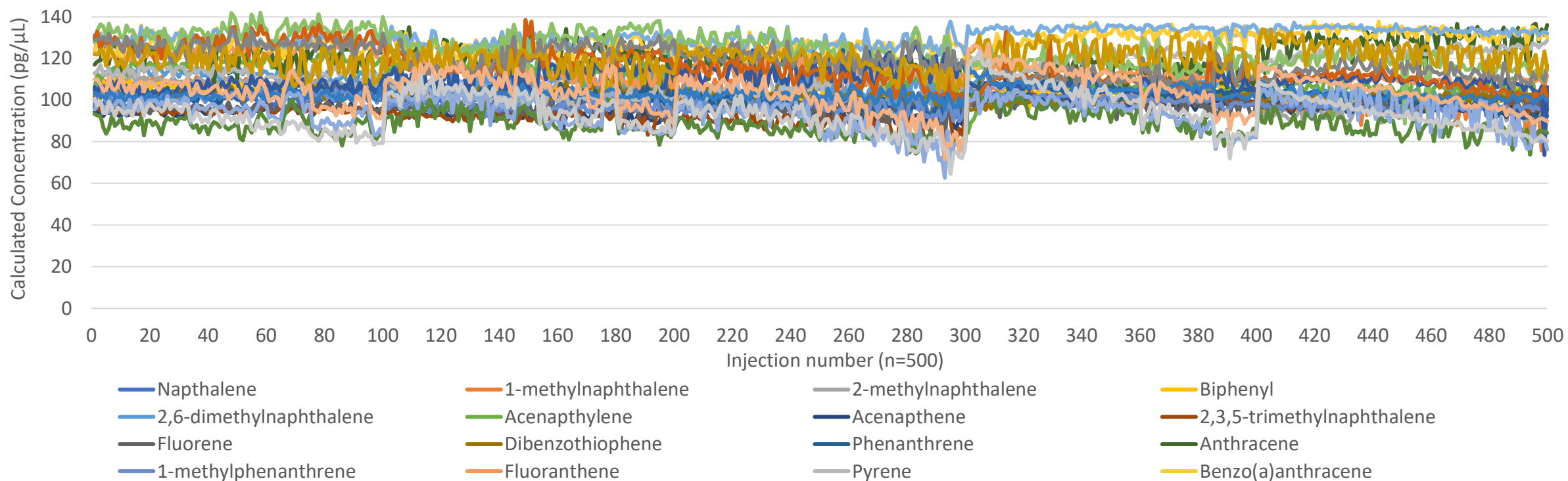Fig 3. ISTD response over calibration range.

Fig 4. Stability of calculated concentrations over 500 injections of soil matrix spiked with 100 pg PAH standard and 500 pg of ISTD

Method Robustness in Complex Matrix

The stability of calculated concentration over 500 injections is presented in Figure 4. For 23 of 27 analytes, the response is stable, where the RSDs for each set of 100 injections are under 5%. However, the calculated concentrations start to decline for dibenz[a,c]anthracene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene around injection 70 (in a sequence of 100) and RSDs are slightly higher than 5% for each set of 100 injections. Over all 500 injections, with routine maintenance and backflush, injection RSDs were < 12% for all analytes. This demonstrates excellent quantitation stability while continuously challenging the system with a complex soil extract. After each set of 100 injections, the liner and septa were replaced, which resulted in the concentration for dibenz[a,c]anthracene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene to recover back to starting concentrations. The UI mid-frit liner performed well at trapping complex matrix. The observation of a decline in concentration at approximately injection 70 for the four late-eluting compounds demonstrates that the liner was becoming saturated with matrix. As the liner saturates, the transfer of late-eluting compounds becomes inhibited.

Conclusions

The triple quadrupole GC/MS method for analyzing PAHs using hydrogen carrier gas, the Agilent HydroInert source, and backflush described here demonstrated several improvements over previous hydrogen and helium methods:

- Excellent chromatographic peak shape with little or no tailing
- MDL and linearity comparable to or better than obtained with helium
- Better chromatographic resolution with a shorter run time
- ISTD response stability across four orders of calibration
- Excellent linearity over 0.1 to 1,000 pg for 26 out of 27 analytes
- Average MDL of 0.09 pg for 27 analytes
- Reliable and accurate quantitation over 500 injections of a challenging soil extract with routine maintenance
- Excellent performance of the Agilent universal Ultra Inert mid-frit inlet liner when analyzing challenging soil matrix

For those laboratories looking to change their PAH analysis to the more sustainable hydrogen carrier gas, the HydroInert source with the 9 mm extractor lens enables the transition with equivalent or better performance.

References

1. Haddad, S.P., Quimby, B.D., Andrianova, A.A. GC/MS/MS Analysis of PAHs with Hydrogen Carrier Gas Using the Novel Agilent HydroInert Source in a Challenging Soil Matrix, *Agilent Technologies application note*, publication number 5994-5776EN, 2023

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