

GC/MS/MS Analysis of PAHs with Hydrogen Carrier Gas

Using the Agilent HydroInert source in a challenging soil matrix

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Abstract

The Agilent 8890 GC and 7000E triple quadrupole GC/MS system (GC/TQ) with a novel electron ionization (EI) source—the Agilent HydroInert source, which is optimized for hydrogen carrier gas—were used for the analysis of polycyclic aromatic hydrocarbons (PAHs). The optimized method using the HydroInert source provides excellent peak shape, sensitivity, and linearity of $R^2 \geq 0.999$, which was observed for all 27 analytes over their respective calibration ranges (0.1 to 1,000 pg for 26 analytes and 0.25 to 1,000 pg for one analyte). Method detection limits (MDLs) ranged from 0.03 to 0.16 pg with an average of 0.09 pg. The stability of calculated concentrations over 500 injections is presented, where, with routine maintenance and backflush, injection RSDs were <12% for all analytes. Further, the ability of the Agilent universal Ultra Inert (UI) mid-frit inlet liner to handle a complex matrix is demonstrated. By proper selection of instrument configuration and operating conditions, the system with hydrogen carrier gas can generate results comparable to or better than those with helium.

Introduction

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. Given the ubiquitous nature of this compound class, trace contamination is monitored in food products (i.e., edible oils, smoked meats, and seafood) and in the environment (i.e., air, water, and soil). 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 note focuses on the analysis of PAHs on a triple quadrupole GC/MS in multiple reaction monitoring (MRM) mode using hydrogen as the GC carrier gas. When adopting hydrogen for GC/MS analysis, there are several factors to consider. First, hydrogen is a reactive gas, and may potentially cause chemical reactions in the inlet, column, and sometimes the MS EI source, which can change analysis results. To address potential issues in the source of the MS, the Agilent HydroInert source was used. Additional information can be found in the Agilent technical overview of the HydroInert source.¹ Second, for GC/MS applications, hardware changes in the gas chromatograph and mass spectrometer may be required when

switching to hydrogen carrier gas. The Agilent Helium to Hydrogen Carrier Gas Conversion Guide² describes in detail the steps for conversion from helium to hydrogen carrier gas. Lastly, it is recommended that anyone working with flammable or explosive gases take a lab safety course covering proper gas handling and use. Further information on the safe use of hydrogen can be found in the Agilent Hydrogen Safety Manual³ and Hydrogen Safety for the Agilent 8890 GC System Guide.⁴

In addition to the challenges of hydrogen carrier, there are often matrix-related problems with the analysis of PAHs. For example, in food and soil analyses, high-boiling matrix contaminants that elute after the analytes can require extended bake-out times to prevent ghost peaks in subsequent runs, hence decreasing column lifetime. The highest boiling contaminants can deposit in the head of the column, requiring more frequent column trimming and adjustment of MRM and data analysis time windows from the resulting retention time shift. Thus, this application note uses mid-column backflush to address some of the matrix-related factors. Backflushing is a technique where the carrier gas flow is reversed after the last analyte has exited the column. After the MS data are collected, the oven is held at the final temperature in postrun mode, and the carrier gas flow through the first column is reversed. Any high-boiling contaminants that were in the column at the end of data collection are carried out of the head of the column and into the split vent trap by this reversed flow.

This application note presents an optimized MRM method for analyzing 27 PAHs 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 were diluted from the Agilent PAH analyzer calibration sample kit (part number G3440-85009) using isooctane. The kit contains a stock solution of 27 PAHs at 10 µg/mL and a stock solution of five internal standards (ISTDs) at 50 µg/mL. Twelve calibration levels were prepared: 0.1, 0.25, 0.5, 1, 2, 10, 20, 100, 200, 400, 750, and 1,000 ng/mL. Each level also contained 500 ng/mL of the ISTDs.

Instrumentation

The system used in this experiment (Figure 1) was configured to minimize the potential problems with hydrogen carrier gas and complex sample matrix in PAH analysis. The instrument operating parameters are listed in Table 1, and MRMs in Table 2. Table 3 contains a list of consumable items used for the current application. Important techniques to consider are outlined in Table 4.

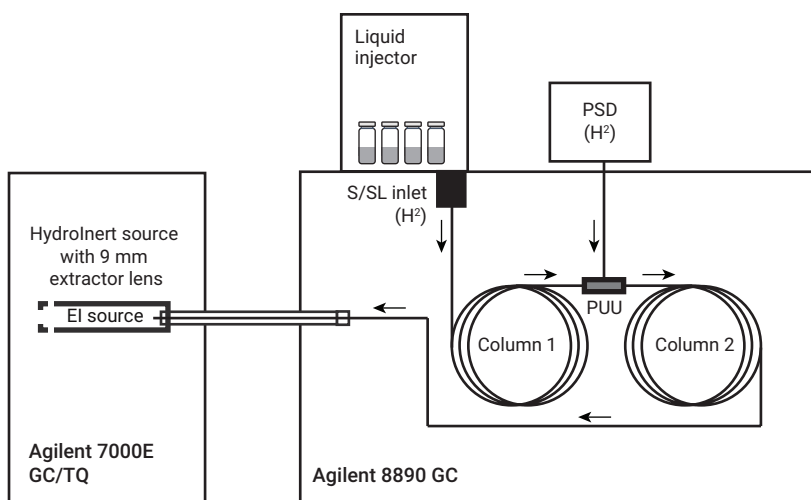


Figure 1. System configuration.

Table 1. GC and MS conditions for PAH analysis.

Agilent 8890 GC with Fast Oven, Auto Injector, and Tray	
Injection Volume	1.0 μ L
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 $^{\circ}$ C
Oven	Initial: 60 $^{\circ}$ C (1 min hold) Ramp 1: 25 $^{\circ}$ C/min to 200 $^{\circ}$ C Ramp 2: 10 $^{\circ}$ C/min to 335 (4.4 min hold)
Column 1	Agilent J&W DB-EUPAH, 20 m \times 0.18 mm, 0.14 μ m
Control Mode	Constant flow, 0.9 mL/min
Inlet Connection	Split/Splitless
Outlet Connection	PSD (PUU)
Postrun Flow (Backflushing)	-5.274 mL/min
Column 2	Agilent J&W DB-EUPAH, 20 m \times 0.18 mm, 0.14 μ m
Control Mode	Constant flow, 1.1 mL/min
PSD Purge Flow	3 mL/min
Inlet Connection	PSD (PUU)
Outlet Connection	Agilent 7000E GC/TQ
Postrun 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 $^{\circ}$ C
Source Temperature	325 $^{\circ}$ C
Quadrupole Temperature	150 $^{\circ}$ 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 2. MRM transitions used for quantifiers and qualifiers, with hydrogen carrier optimized collision energy.

Analyte	Retention Time (minutes)	Quantifier	Collision Energy	Qualifier	Collision Energy
Naphthalene-d ₈ (ISTD)	5.902	136.0 → 136.0	5	136.0 → 108.0	15
Naphthalene	5.922	128.0 → 102.0	20	128.0 → 127.0	20
1-Methylnaphthalene	6.514	142.0 → 115.0	35	142.0 → 141.0	20
2-Methylnaphthalene	6.675	142.0 → 115.0	30	142.0 → 141.0	20
Biphenyl	7.049	154.0 → 152.0	30	154.0 → 153.0	20
2,6-Dimethylnaphthalene	7.081	156.0 → 115.0	35	156.0 → 141.0	20
Acenaphthylene	7.738	152.0 → 151.0	20	152.0 → 150.0	35
Acenaphthene-d ₁₀ (ISTD)	7.841	162.0 → 160.0	15	164.0 → 162.0	15
Acenaphthene	7.889	154.0 → 152.0	35	153.0 → 152.0	40
2,3,5-Trimethylnaphthalene	8.085	170.0 → 155.0	20	170.0 → 153.0	30
Fluorene	8.539	166.0 → 165.0	25	166.0 → 163.0	25
Dibenzothiophene	10.1	184.0 → 139.0	40	184.0 → 152.0	25
Phenanthrene-d ₁₀ (ISTD)	10.265	188.0 → 188.0	5	188.0 → 184.0	25
Phenanthrene	10.313	178.0 → 176.0	35	178.0 → 152.0	30
Anthracene	10.367	178.0 → 152.0	25	178.0 → 156.0	35
1-Methylphenanthrene	11.452	192.0 → 191.0	20	192.0 → 165.0	40
Fluoranthene	12.842	202.0 → 200.0	40	202.0 → 201.0	25
Pyrene	13.51	202.0 → 200.0	40	202.0 → 201.0	30
Benz[a]anthracene	16.327	228.0 → 226.0	35	228.0 → 224.0	55
Chrysene-d ₁₂ (ISTD)	16.46	240.0 → 236.0	35	240.0 → 240.0	5
Chrysene	16.531	228.0 → 226.0	35	228.0 → 224.0	55
Benzo[b]fluoranthene	18.953	252.0 → 250.0	40	250.0 → 248.0	40
Benzo[k]fluoranthene	19.003	252.0 → 250.0	40	250.0 → 248.0	40
Benzo[j]fluoranthene	19.087	252.0 → 250.0	40	250.0 → 248.0	45
Benzo[e]pyrene	19.793	252.0 → 250.0	40	250.0 → 248.0	45
Benzo[a]pyrene	19.903	252.0 → 250.0	40	250.0 → 248.0	40
Perylene-d ₁₂ (ISTD)	20.115	264.0 → 260.0	35	264.0 → 236.0	35
Perylene	20.177	252.0 → 250.0	40	250.0 → 248.0	45
Dibenz[a,c]anthracene	22.386	278.0 → 276.0	42	276.0 → 274.0	40
Dibenz[a,h]anthracene	22.488	278.0 → 276.0	40	276.0 → 274.0	40
Indeno[1,2,3-cd]pyrene	22.526	276.0 → 274.0	42	138.0 → 124.0	42
Benzo[ghi]perylene	23.562	276.0 → 274.0	42	274.0 → 272.0	45

Table 3. Agilent consumables and part numbers used in the method for PAH analysis.

Consumable	Description	Part Number
Injector Syringe	Blue Line autosampler syringe, 10 µL, fixed needle	G4513-80220
Inlet Septum	Advanced Green septum, nonstick, 11 mm	5183-4759
Inlet Liner	Universal Ultra Inert mid-frit inlet liner	5190-5105
Gold Seal	GC inlet seal, gold plated with washer, Ultra Inert	5190-6144
Column	DB-EUPAH, 20 m × 0.18 mm, 0.14 µm (quantity: 2)	121-9627
Backflush Union	Purged Ultimate union assy	G3186-80580
Backflush Ferrules	CFT Ferrule Flex Gold flexible metal ferrule, gold plated, 0.4 mm id, for 0.1 to 0.25 mm id fused silica tubing	G2855-28501
Steel Tubing	Install kit for GCs, stainless steel	19199S
GC/MS Source	HydroInert complete source assembly for 7000 GC/TQ	G7006-67930

Table 4. Important techniques to consider in this study.

Consideration	Description
Hydrogen Gas	In-house hydrogen, with 99.9999% purity specification and low individual specifications on water and oxygen, was used as a carrier gas. It is essential to use a reliable source of clean hydrogen gas. For long-term use, generators with a >99.9999% specification and low individual specifications on water and oxygen are recommended. Moisture filters are recommended for use with hydrogen generators. For short-term use, cylinders with chromatographic or research-grade hydrogen are acceptable.
Pulsed Splitless Injection	Used to maximize transfer of the PAHs, especially the heavy ones, from the GC inlet into the column.
Inlet Liner	The Agilent universal UI mid-frit inlet liner was found to give good peak shape, inertness, and longevity with the soil extracts described later. The frit transfers heat to the PAHs and blocks the line of sight to the inlet base. If the PAHs condense on the inlet base, they are difficult to vaporize and sweep back into the column.
Column Dimensions	Two Agilent J&W DB-EUPAH columns (20 m × 0.18 mm id, 0.14 μm) were used to maintain optimal gas flow and inlet pressure in the backflush configuration.
8890 PSD Module and Midcolumn Backflushing	The pneumatic switching device (PSD) is an Agilent 8890 GC pneumatics module optimized for backflushing applications and provides for seamless pulsed injections. The capability to reverse the flow is provided by the Agilent purged Ultimate union (PUU). The PUU is a tee, inserted, in this case, between two identical 20 m columns. During the analysis, a small make-up flow of carrier gas from the 8890 PSD module is used to sweep the connection. During backflushing, the make-up flow from the PSD is raised to a much higher value, sweeping high-boiling contaminants backward out of the first of column and forward from the second.
HydroInert EI Source	The Agilent HydroInert source is a substitute for the extractor source when hydrogen carrier is used. It is constructed with materials that greatly reduce undesirable reactions in the source to maintain spectral fidelity when used with hydrogen. As commonly known, PAHs present unique challenges regarding the MS EI source, even with helium as the carrier gas. ⁵ With hydrogen carrier gas, the performance of PAHs is improved, especially with the HydroInert source. The 9 mm extractor lens is the default included with the HydroInert source and the best choice for PAH analysis ^{6,7} as it provides the best calibration linearity, precision of response, and peak shape.
Collision Gas	Only nitrogen should be used as collision gas in GC/TQ when hydrogen is the carrier gas. The collision cell helium inlet fitting must be capped. The optimal nitrogen gas flow was shown to be 1.5 mL/min, which agreed with the user manual recommendation. This flow was also demonstrated to be optimal in previous work on PAHs in hydrogen carrier. ⁸
MS/MS	The added selectivity of MRM mode in GC/TQ simplifies the data review of high-matrix samples relative to GC/MS by reducing or eliminating interfering responses from the matrix. Interfering responses often require manual integration of quantifier or qualifier ions.

Matrix sample preparation

A sample of commercial topsoil (Weaver Mulch, Coatesville, PA, U.S.) was chosen to perform a response stability and robustness test. Extraction is described briefly. Topsoil 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 soil extract spiked with PAHs at 100 ppb. For this test, the MS was tuned at the beginning of the test only with no need to retune it throughout the robustness testing experiment.

After every 100 injections, the liner and septa were replaced and the EM gain was updated. After every 300 injections, the split/splitless inlet gold seal was replaced. The column was not trimmed or replaced throughout the entire 500 injections. This test was designed to demonstrate the robustness of the system over continuous injections of an intentionally challenging matrix.

Results and discussion

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, and are comparable to previous hydrogen work.⁸ In general, the HydroInert source provided the best peak shapes for PAHs when using hydrogen carrier gas. The

chromatographic resolution obtained with the current setup is also better than that obtained with helium.⁵ Due to the combination of hydrogen carrier and a smaller diameter column, the run time with the current method is 24 versus 26 minutes used in the helium method. The run time of the current method could have been reduced further and still maintained similar resolution. However, the current method conditions were chosen to achieve the best resolution of dibenz[a,c]anthracene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene, because a more aggressive temperature ramp in the latter half of the method can reduce the resolution of this challenging cluster.

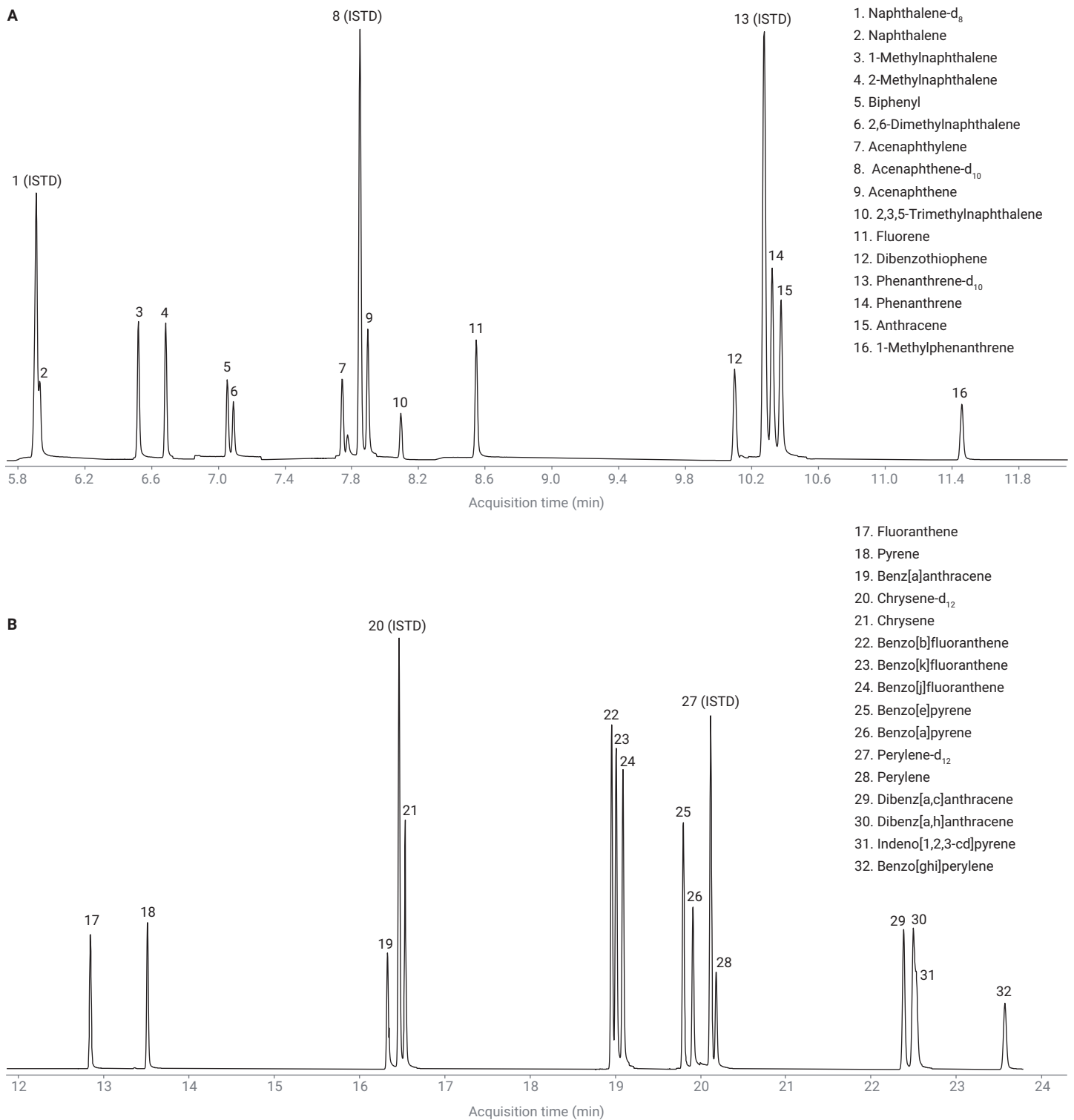


Figure 2. MRM TIC of 27 PAHs at 100 pg/ μ L and five ISTDs at 500 pg/ μ L.

Table 5 shows the calibration results of the system with 12 calibration levels from 0.1 to 1,000 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 1,000 pg. One was calibrated from 0.25 to 1,000 pg. The calibration ranges and signal-to-noise observations demonstrated high sensitivity at the lowest calibration level, similar to previous PAH work performed with hydrogen.⁸

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 that 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. This problem has been addressed previously using the Agilent JetClean self-cleaning ion source and a 9 mm extractor lens.^{3,4} With JetClean, helium is used as the carrier gas, but hydrogen is continuously added to the source at a flow typically in the range of 0.16 to 0.33 mL/min. This approach reduces the creeping ISTD effect and results in excellent calibration linearity and 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 5.

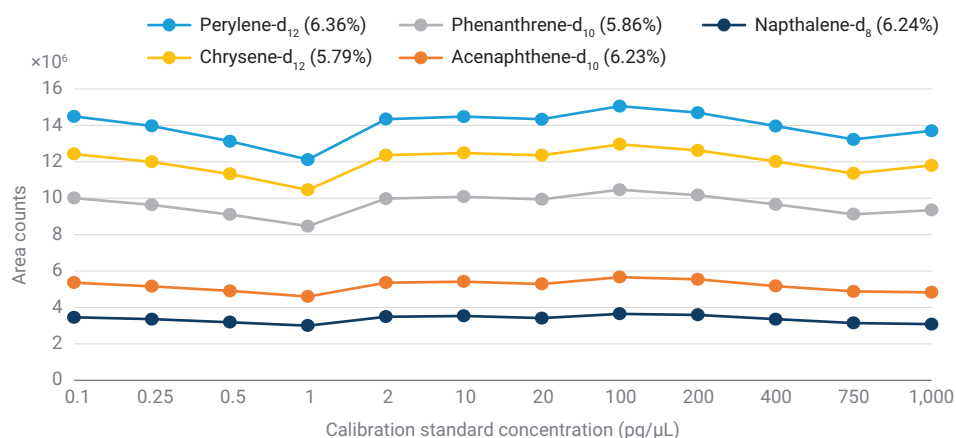


Figure 3. ISTD response over the calibration range.

Table 5. Results of a 12-level MRM ISTD calibration curve with a range of 0.1 to 1,000 pg. All calibration curves were linear, ignoring the origin, and weighted 1/x. MDLs were defined as $MDL = t(n - 1, 0.99) \times SD$, 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.

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

Method robustness in complex matrix

The soil extract used for the robustness test was deliberately chosen to have a high matrix content to challenge the system. Figure 4 shows the scan TIC of the spiked extract and the MRM TIC for comparison. As shown, the soil extract had a high level of matrix. When using MRM on the 7000E GC/TQ, the background is greatly reduced, allowing for low-level quantitation of PAHs using the current method.

Also, note that for soils with this level of organic content, further sample cleanup should be considered for routine analysis. The sample preparation used here was for test purposes only to deliberately challenge the system. Also, the extraction solvent (1:1 v/v dichloromethane/acetone) is not recommended for routine analysis with hydrogen carrier gas. Halogenated solvents like dichloromethane may react with hydrogen in the hot injection port and form low levels of HCl, which can degrade the liner and column head over time.

The stability of calculated concentration over 500 injections is presented in Figure 5. For 23 of 27 analytes, the response is stable, as shown in Table 6, 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.

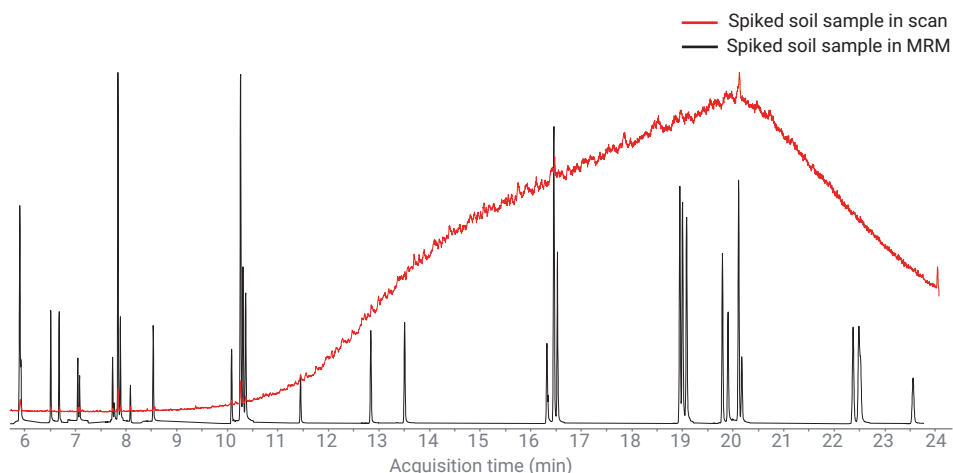


Figure 4. Spiked soil sample comparison of scan TIC and MRM TIC. The MRM trace is scaled up by an order of magnitude for visibility.

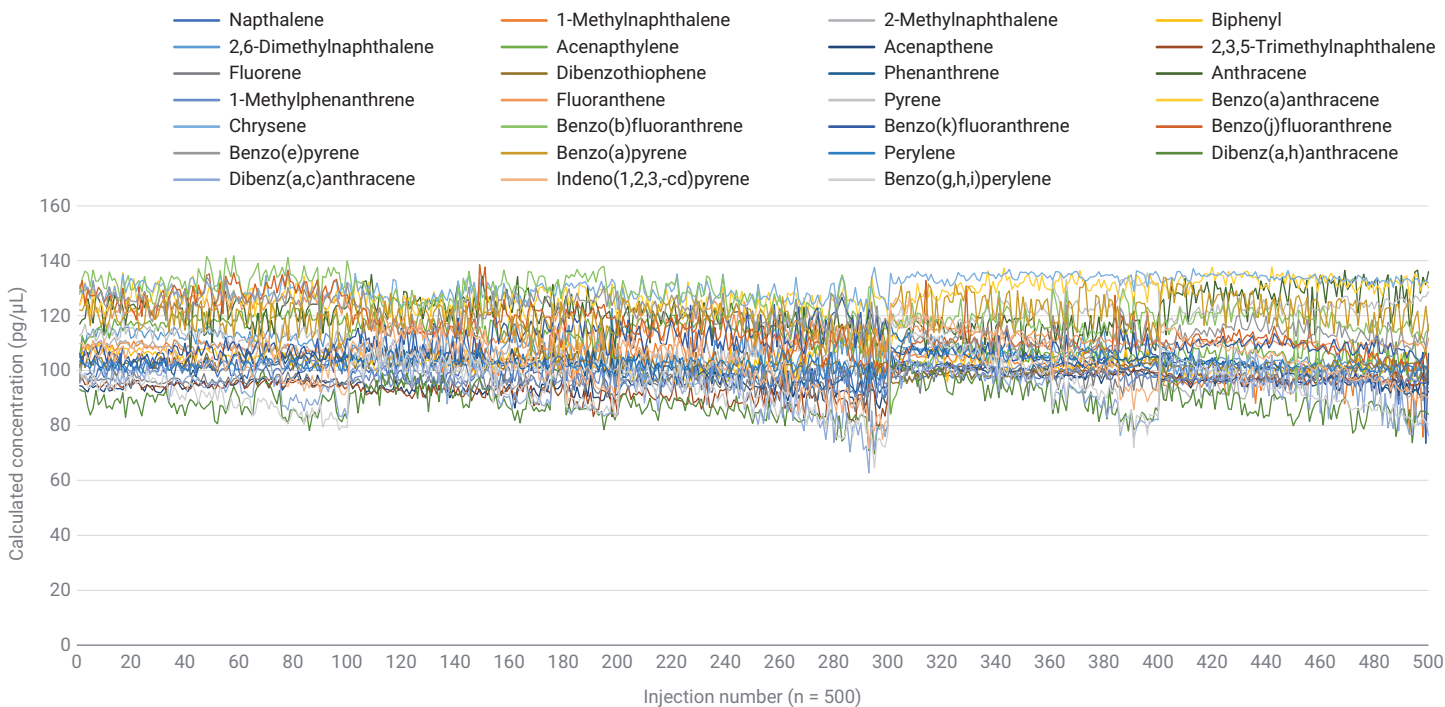


Figure 5. Stability of calculated concentrations over 500 injections of soil matrix spiked with 100 pg PAH standard and 500 pg of ISTD.

Table 6. Calculated concentration RSD% for every 100 injections and total 500 injections of extracted soil matrix spiked with 100 pg of PAH standard and 500 pg of ISTD standard.

Analyte	Injection RSD (%)					
	1 to 100	101 to 200	201 to 300	301 to 400	401 to 500	All (1 to 500)
Naphthalene	2.17	2.86	3.54	1.32	3.18	2.92
1-Methylnaphthalene	1.83	3.53	4.15	2.36	4.00	5.77
2-Methylnaphthalene	1.91	3.18	3.62	2.39	3.85	5.23
Biphenyl	1.94	2.74	4.86	2.30	2.56	3.55
2,6-Dimethylnaphthalene	1.97	4.08	4.56	2.28	1.87	4.50
Acenaphthylene	2.43	2.97	3.55	4.07	4.85	5.82
Acenaphthene	1.65	2.37	3.28	1.70	1.74	3.25
2,3,5-Trimethylnaphthalene	1.09	3.03	4.17	1.09	1.36	4.59
Fluorene	1.25	2.61	3.76	2.98	2.17	3.07
Dibenzothiophene	1.78	2.39	2.19	1.95	1.12	2.58
Phenanthrene	2.04	2.55	3.56	1.68	4.01	3.74
Anthracene	3.68	3.54	3.58	4.29	4.05	5.58
1-Methylphenanthrene	1.80	2.15	3.11	2.03	1.16	3.29
Fluoranthene	2.02	4.19	3.96	2.09	0.97	5.08
Pyrene	2.71	2.63	4.84	4.71	2.25	7.93
Benz[a]anthracene	2.82	2.92	2.93	3.81	1.91	3.71
Chrysene	1.96	2.41	2.59	1.14	1.00	2.86
Benzo[b]fluoranthene	2.97	3.74	4.22	3.48	4.40	6.07
Benzo[k]fluoranthene	2.29	4.24	4.67	2.90	3.78	4.68
Benzo[j]fluoranthene	3.29	4.16	4.89	4.89	3.75	7.44
Benzo[e]pyrene	2.52	4.32	3.33	3.67	2.79	5.75
Benzo[a]pyrene	4.53	4.62	4.60	4.44	4.46	4.92
Perylene	1.55	1.81	2.49	3.03	1.94	2.65
Dibenz[a,c]anthracene	4.61	5.89	4.86	6.91	5.08	6.36
Dibenz[a,h]anthracene	5.03	7.49	9.34	7.86	8.80	8.27
Indeno[1,2,3-cd]pyrene	5.26	7.23	9.31	8.99	6.86	8.38
Benzo[ghi]perylene	6.40	7.74	9.01	11.13	8.08	9.89

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, similar to previous studies.^{9,10} 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. Table 7 shows the RSDs for only the first 70 injections of each set of 100, and the RSD for the total set of injections that comprise of just the first 70 injections. RSDs for each

set of injections and total injections are improved when considering only the first 70 injections for dibenz[a,c]anthracene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene. Also, at 300 injections the gold seal was changed, which resulted in tighter RSDs for 17 of 27 PAHs (Table 6).

Table 7. Calculated concentration RSD% of the first 70 injections of every 100 injections and total injections (using only the first 70 from each set) of extracted soil matrix spiked with 100 pg of PAH standard and 500 pg of ISTD.

Analyte	Injection RSD (%)					
	1 to 70	101 to 170	201 to 270	301 to 370	401 to 470	All (1 to 500)
Naphthalene	2.19	2.56	3.00	1.18	2.91	2.70
1-Methylnaphthalene	1.87	2.80	4.19	2.17	2.38	5.22
2-Methylnaphthalene	1.82	2.90	3.38	2.14	3.89	5.31
Biphenyl	1.73	2.35	3.99	2.34	1.78	3.53
2,6-Dimethylnaphthalene	1.89	3.09	3.98	2.15	1.55	4.43
Acenaphthylene	2.48	2.63	2.22	4.72	4.92	5.73
Acenaphthene	1.50	2.05	2.30	1.83	1.29	2.97
2,3,5-Trimethylnaphthalene	1.11	2.03	3.21	1.17	1.16	4.11
Fluorene	1.23	1.95	2.75	2.52	1.76	2.55
Dibenzothiophene	1.77	2.37	2.26	1.45	1.11	2.70
Phenanthrene	2.13	2.42	3.40	1.40	2.58	3.08
Anthracene	3.88	3.24	3.26	4.55	3.77	5.42
1-Methylphenanthrene	1.82	2.00	2.57	1.47	1.12	3.13
Fluoranthene	1.94	3.25	3.74	1.73	0.93	4.59
Pyrene	2.49	2.56	3.43	3.59	2.25	7.48
Benzo[a]anthracene	2.89	2.80	2.70	4.25	1.91	3.88
Chrysene	1.95	2.43	2.28	1.10	0.87	2.93
Benzo[b]fluoranthene	2.99	3.53	3.41	3.00	4.76	5.53
Benzo[k]fluoranthene	2.36	4.31	4.13	2.34	1.69	3.85
Benzo[j]fluoranthene	3.27	4.44	3.64	4.85	2.07	6.52
Benzo[e]pyrene	2.55	4.45	2.94	3.01	2.37	5.45
Benzo[a]pyrene	3.96	4.09	2.72	4.19	4.16	4.25
Perylene	1.45	1.65	2.14	2.85	1.99	2.63
Dibenz[a,c]anthracene	4.10	5.00	3.43	4.52	4.48	5.64
Dibenz[a,h]anthracene	3.10	5.79	6.06	3.98	5.98	5.61
Indeno[1,2,3-cd]pyrene	3.24	4.26	5.51	5.34	4.49	5.82
Benzo[ghi]perylene	4.38	5.82	5.37	7.23	6.06	7.83

Conclusion

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 hydrogen⁸ and helium⁵ 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.

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