

Optimized PAH Analysis Using Triple Quadrupole GC/MS with Hydrogen Carrier

Authors

Anastasia A. Andrianova and
Bruce D. Quimby
Agilent Technologies, Inc.

Abstract

The Agilent 8890/7000D triple quadrupole GC/MS system with hydrogen carrier gas was used for the analysis of polycyclic aromatic hydrocarbons (PAHs). Optimized system performance with hydrogen carrier over an extended calibration range was achieved by carefully selecting instrument configuration and operating conditions. With the appropriate choice of column dimensions, liner, collision cell gas flow, collision energies, high-purity hydrogen, and an alternative drawout lens, excellent linearity across a calibration range of 0.1 to 1,000 pg was demonstrated.

Introduction

PAHs are a group of chemical compounds that are composed of at least two or more fused conjugated benzene rings with a pair of carbon atoms shared between rings in their molecules. Because PAHs originate from multiple sources, they are widely distributed as contaminants throughout the world. Given their ubiquitous nature, they are monitored as trace contaminants in many different food products ranging from seafood to edible oils to smoked meats. They are also monitored in the environment including in air, water, and soil. PAHs have been analyzed by multiple techniques including HPLC/UV, GC/FID, GC/MS, or GC/TQ.

This application note focuses on GC/TQ in multiple reaction monitoring (MRM) mode using hydrogen as the GC carrier gas. While helium is the best carrier gas for GC/MS analysis, its reoccurring shortages have increased demand for applications using hydrogen as the carrier gas. When adopting hydrogen for GC/MS analysis, there are several things to consider.

First, hydrogen is a reactive gas, and may potentially cause chemical reactions in the inlet, column, and sometimes the mass spectrometer electron ionization (EI) source that can change analysis results. It is important to ensure there are no chemical reaction problems between analytes and hydrogen gas at elevated temperatures in the GC/MS.

Second, 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 specs 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. It is also recommended that anyone working with flammable or explosive gases take a lab safety course covering proper gas handling and use.

Additionally, for GC/MS applications, hardware changes in the gas chromatograph and mass spectrometer are required when switching to hydrogen carrier gas.¹ This includes the inlet liner, column, vacuum pump, and EI drawout lens selection. Chromatographic conditions and injection solvent also need to be adjusted.

One of the advantages observed with hydrogen carrier gas is a reduced need for EI source cleaning. A similar improvement is observed when using Agilent JetClean technology, which uses a low continuous flow of hydrogen into the source during the analysis.²

PAHs are relatively durable compounds that do not exhibit high reactivity with hydrogen at the temperatures used in GC/MS analysis. Analysis of PAHs can therefore be performed with hydrogen carrier gas when using the optimized method and following the recommendations described in this application note. Other challenges with PAH analysis addressed in this work include peak tailing, often seen for late eluting analytes, and ISTD response inconsistency across the calibration range. With the optimized method, excellent linearity of $R^2 > 0.999$ was observed for 24 of 27 analytes over 0.1 to 1,000 pg calibration range, and $R^2 > 0.996$ for 26 analytes over the same range. For acenaphthylene, calibration was performed between 0.25 and 1,000 pg, with $R^2 = 0.9999$.

Experimental

The system used in this experiment was configured to minimize the potential problems with hydrogen carrier gas in PAH analysis. The important techniques used were:

- **Hydrogen gas:** In-house hydrogen with 99.9999% purity specification and low individual specs on water and oxygen was used as a carrier gas.
- **Pulsed splitless injection:** Used to maximize transfer of the PAHs, especially the heavy ones, into the column.
- **Column dimensions:** A DB-EUPAH column (20 m × 0.18 mm id, 0.14 μm) was used to maintain optimal gas flow and inlet pressure.
- **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 (Figure 1), which agreed with the user manual recommendation.
- **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.³ Interfering responses often require manual integration of quantifier or qualifier ions.

- Optimizer for GC/TQ:** The new optimizer software in Agilent MassHunter (MH) Acquisition 10 was used to determine the best collision energies for use with hydrogen carrier gas. With the *start with MRMs* workflow, the collision energies for the imported helium MRM transitions were optimized over two injections with no manual intervention. The re-optimized collision energies are shown in Table 1.

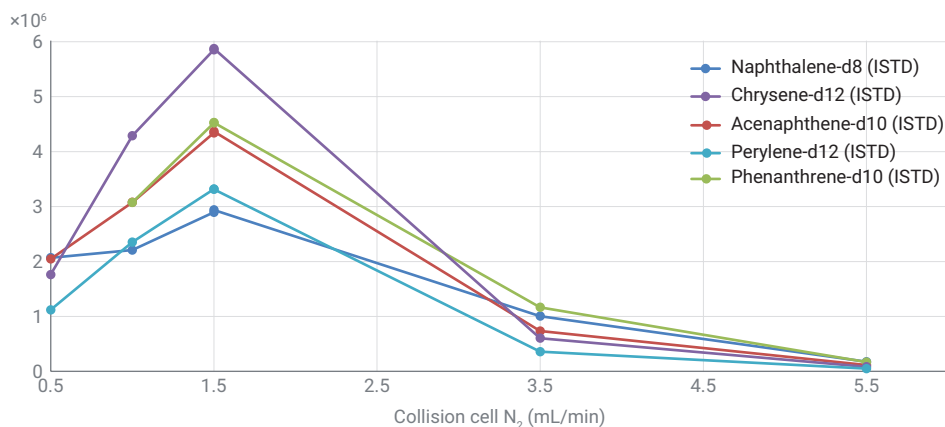


Figure 1. Absolute ISTD area response plotted versus collision cell nitrogen flow.

Table 1. MRM transitions used for quantifier and qualifiers with collision energies optimized for hydrogen carrier gas.

Name	RT	Quantifier	Collision Energy, Helium Carrier	Collision Energy, Hydrogen Carrier	Qualifier	Collision Energy, Helium Carrier	Collision Energy, Hydrogen Carrier
Napthalene-d8 (ISTD)	4.5768	136.0 → 136.0	19	25			
Napthalene	4.599	128.0 → 102.0	22	20	128.0 → 127.0	20	20
1-methylnapthalene	5.1946	142.0 → 115.0	30	35	142.0 → 141.0	30	20
2-methylnapthalene	5.3493	142.0 → 115.0	30	30	142.0 → 141.0	30	20
Biphenyl	5.7227	154.0 → 152.0	25	30	154.0 → 153.0	25	20
2,6-dimethylnapthalene	5.7501	156.0 → 115.0	30	35	156.0 → 141.0	30	20
Acenaphthylene	6.2923	152.0 → 151.0	40	20	152.0 → 150.0	40	35
Acenaphthene-d10 (ISTD)	6.3823	162.0 → 160.0	19	30			
Acenaphthene	6.4221	154.0 → 152.0	40	35	153.0 → 152.0	40	40
2,3,5-trimethylnapthalene	6.6007	170.0 → 155.0	25	20	170.0 → 153.0	25	30
Fluorene	6.933	166.0 → 165.0	30	25	166.0 → 163.0	34	50
Dibenzothiophene	8.1912	184.0 → 139.0	40	40	184.0 → 152.0	40	25
Phenanthrene-d10 (ISTD)	8.3459	188.0 → 188.0	19	25			
Phenanthrene	8.3881	178.0 → 176.0	34	35	178.0 → 152.0	30	30
Anthracene	8.4356	178.0 → 152.0	30	25	178.0 → 176.0	34	35
1-methylphenanthrene	9.4398	192.0 → 191.0	25	20	192.0 → 165.0	30	40
Fluoranthene	10.8	202.0 → 200.0	50	40	202.0 → 201.0	50	25
Pyrene	11.474	202.0 → 200.0	50	40	202.0 → 201.0	30	30
Benzo(a)anthracene	14.657	228.0 → 226.0	38	35	228.0 → 224.0	38	55
Chrysene-d12 (ISTD)	14.809	240.0 → 236.0	25	40	118.0 → 116.0	25	20
Chrysene	14.892	228.0 → 226.0	38	35	228.0 → 224.0	38	55
Benzo(b)fluoranthrene	17.738	252.0 → 250.0	42	40	250.0 → 248.0	40	40
Benzo(k)fluoranthrene	17.803	252.0 → 250.0	42	40	250.0 → 248.0	40	40
Benzo(j)fluoranthrene	17.886	252.0 → 250.0	42	40	250.0 → 248.0	40	45
Benzo(e)pyrene	18.696	252.0 → 250.0	40	40	250.0 → 248.0	40	45
Benzo(a)pyrene	18.833	252.0 → 250.0	40	40	250.0 → 248.0	40	40
Perylene-d12 (ISTD)	19.084	264.0 → 260.0	40	45	264.0 → 236.0	25	35
Perylene	19.156	252.0 → 250.0	40	40	250.0 → 248.0	40	45
Dibenz(a,c)anthracene	21.45	278.0 → 276.0	38	40	276.0 → 274.0	38	40
Indeno(1,2,3,-cd)pyrene	21.501	276.0 → 274.0	42	42	138.0 → 124.0	42	42
Dibenz(a,h)anthracene	21.536	278.0 → 276.0	42	42	278.0 → 272.0	60	60
Benzo(g,h,i)perylene	22.258	276.0 → 274.0	42	42	274.0 → 272.0	45	45

- 9 mm Extractor lens:** The standard 3 mm extractor (drawout) lens provided with the 7000D GC/TQ is a good choice for general analysis with helium carrier gas. However, the optional 9 mm lens is recommended when using hydrogen as a carrier gas in GC/MS analysis. Additionally, with the propensity of PAHs to deposit on surfaces, it has been found that the 9 mm lens provides better calibration linearity, ISTD response consistency, precision of response, and peak shape.^{4,5}

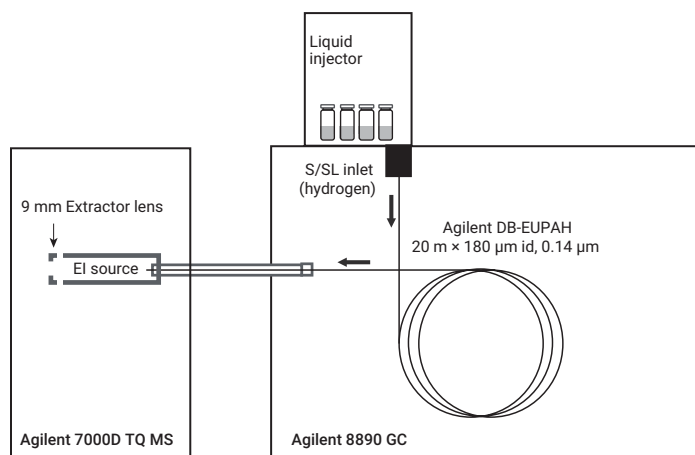


Figure 2. The Agilent 8890/7000D GC/TQ system configuration.

Figure 2 shows the system configuration used for the experimental work.

The instrument operating parameters are listed in Tables 1 and 2. Instrument temperatures must be kept high enough to prevent deposition of the highest boiling PAHs onto flow path components. The inlet and MSD transfer line are maintained at 320 °C. The MS source should be a minimum of 320 °C.

PAH calibration standards were diluted from the Agilent PAH Analyzer calibration kit (part number G3440-85009) using isoctane. The kit contains a stock solution of 27 PAHs at 10 µg/mL and a stock solution of five 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 pg/µL. Each level also contained 500 pg/µL of the ISTDs. See Table 1 and Figure 2 for compound identifications.

When using hydrogen as a carrier gas, laboratory safety considerations must be observed. The Agilent 8890 Gas Chromatograph Safety Manual and the operation manual for the instrument contain hydrogen safety instructions. It is also recommended that anyone working with flammable or explosive gases take a lab safety course covering proper gas handling and use.

Table 2. Gas chromatograph and mass spectrometer conditions for PAH analysis.

Agilent 8890 GC with Fast Oven, Autoinjector, and Tray	
Inlet	EPC split/splitless
Mode	Pulsed splitless
Injection Pulse Pressure	40 psi until 0.75 min
Purge Flow To Split Vent	50 mL/min at 0.70 min
Septum Purge Flow Mode	Standard, 3mL/min
Injection Volume	1.0 µL
Inlet Temperature	320 °C
Carrier Gas	Hydrogen
Inlet Liner	Agilent universal low pressure drop, with glass wool (p/n 5190-2295)
Oven	Hold 60 °C for 1 min; 25 °C/min to 200 °C; 8 °C/min to 335 °C; Hold for 6.325 min
Total Run Time	29 min
Post Run Time	0
Equilibration Time	0.5 min
Column	Agilent DB-EUPAH, 20 m x 0.18 mm, 0.14 µm (p/n 121-9627)
Control Mode	Constant flow
Flow	0.648 mL/min
Initial Inlet Pressure	4.8463 psig
Inlet Connection	Split/splitless
Agilent 7000D TQ MS	
Source	Inert extractor
Drawout Lens	9 mm
Tune File	atunes.eiex.tune.xml
Mode	MRM
Collision Gas	Nitrogen, 1.5 mL/min
Solvent Delay	3.5 min
EM Voltage Gain Mode	10
Quad Temperature	150 °C
Source Temperature	325 °C
Transfer line Temperature	320 °C

Results and discussion

Figure 3 shows the MRM TIC of the 100 pg/μL PAH calibration standard with the ISTDs present at 500 pg/μL. The chromatograms show the high chromatographic resolution achieved with hydrogen under the analysis

conditions. Peak tailing is commonly seen on the later eluting analytes, which would require manual integration and prolonged data review. With the instrument parameters and analysis conditions chosen here, the peak shapes for all PAHs, even the latest eluting ones, are very good.

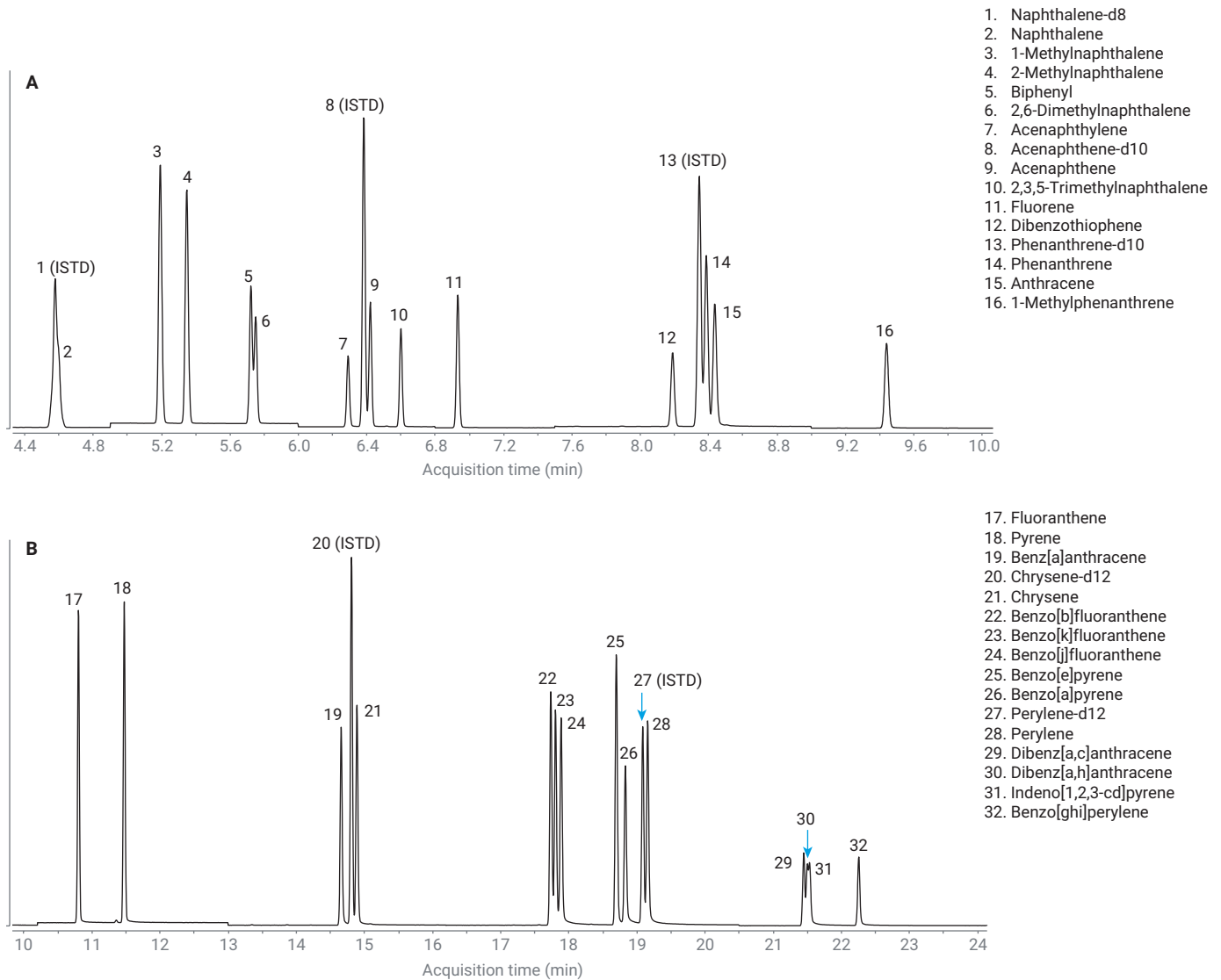


Figure 3. The MRM TIC of the 100 pg/μL calibration standard with 500 pg/μL ISTDs.

With the DB-EUPAH GC column and oven temperature program ramp described in the experimental section, near baseline separation was achieved for benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(j)fluoranthene, shown in Figure 4. The resolution was maintained throughout the calibration range and the MRM chromatograms for the quantifier and qualifier ions are shown for 0.1 pg/ μ L (lowest calibration standard), 1 pg/ μ L, and 100 pg/ μ L. Total analysis time was 29 minutes, with the latest target analyte eluting before 23 minutes. A faster oven temperature ramp will shorten run time and can be used if extra resolution is not needed.

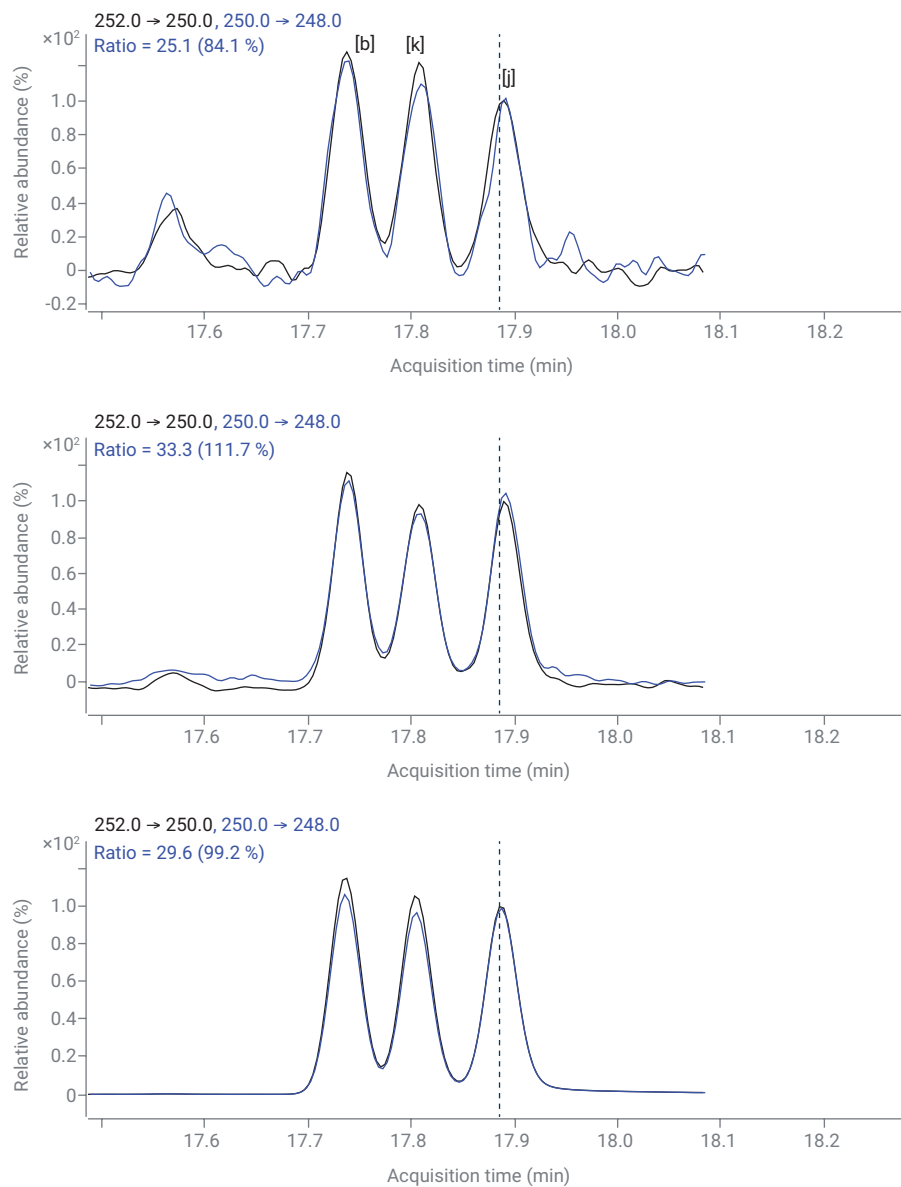


Figure 4. Response at quantifier and qualifier MRM transitions for benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(j)fluoranthene at 0.1 pg (the lowest calibration level), 1 pg, and 100 pg.

The use of hydrogen carrier gas typically results in a slightly reduced signal-to-noise ratio (S/N), so it is important to check the lowest desired calibration level. Table 3 shows the S/N of the quantifier ion for the target PAH analytes at 0.1 pg. For 26 out of 27 targets, S/N >3 was observed at 0.1 pg. For acenaphthylene, the lowest limit of calibration was increased to 0.25 pg to achieve S/N >3.

Excellent linearity with $R^2 > 0.999$ was observed for 24 out of 27 analytes over the calibration range 0.1 to 1,000 pg and $R^2 > 0.996$ for 26 analytes over the same range. For acenaphthylene, calibration was performed between 0.25 and 1,000 pg, with $R^2 = 0.9999$. Quantitation accuracy was maintained throughout

the calibration range. As an example, accuracy at 100 pg is shown in Table 3. It is within $\pm 4\%$ for 26 out of 27 targets, and dibenz(a,h)anthracene was quantified within $\pm 9\%$ of its target concentration.

Table 3. R^2 values of 12-level ISTD calibration 0.1 to 1,000 pg MRM, S/N at the lowest calibration level of 0.1 pg, and quantitation accuracy at 100 pg.

Name	RT	CF Limit Low (pg)	CF Limit High (pg)	CF R^2	S/N at 0.1 pg	Accuracy at 100 pg
Naphthalene-d8 (ISTD)	4.577					
Naphthalene	4.599	0.1	1000	0.9996	11.9	102
1-methylnaphthalene	5.195	0.1	1000	0.9996	11.0	104
2-methylnaphthalene	5.349	0.1	1000	0.9996	12.5	103
Biphenyl	5.723	0.1	1000	0.9996	15.1	103
2,6-dimethylnaphthalene	5.750	0.1	1000	0.9999	15.6	102
Acenaphthylene	6.292	0.25	1000	0.9999	1.1 (3.6 at 0.25 pg)	99
Acenaphthene-d10 (ISTD)	6.382					
Acenaphthene	6.422	0.1	1000	0.9996	57.3	103
2,3,5-trimethylnaphthalene	6.601	0.1	1000	0.9997	5.0	102
Fluorene	6.933	0.1	1000	0.9995	38.3	104
Dibenzothiophene	8.191	0.1	1000	0.9998	26.9	101
Phenanthrene-d10 (ISTD)	8.346					
Phenanthrene	8.388	0.1	1000	0.9997	31.9	103
Anthracene	8.436	0.1	1000	0.9999	6.7	99
1-methylphenanthrene	9.440	0.1	1000	0.9997	7.8	102
Fluoranthene	10.800	0.1	1000	0.9997	30.7	102
Pyrene	11.474	0.1	1000	0.9998	16.1	102
Benzo(a)anthracene	14.657	0.1	1000	0.9997	11.9	101
Chrysene-d12 (ISTD)	14.809					
Chrysene	14.892	0.1	1000	0.9999	18.1	99
Benzo(b)fluoranthene	17.738	0.1	1000	0.9997	18.1	102
Benzo(k)fluoranthene	17.803	0.1	1000	0.9999	8.0	101
Benzo(j)fluoranthene	17.886	0.1	1000	0.9961	13.7	98
Benzo(e)pyrene	18.696	0.1	1000	0.9997	26.5	103
Benzo(a)pyrene	18.833	0.1	1000	0.9998	3.2	97
Perylene-d12 (ISTD)	19.084					
Perylene	19.156	0.1	1000	0.9999	25.4	98
Dibenz(a,c)anthracene	21.450	0.1	1000	0.9998	3.3	97
Indeno(1,2,3,-cd)pyrene	21.501	0.1	1000	0.9994	7.6	97
Dibenz(a,h)anthracene	21.536	0.1	1000	0.9973	4.5	91
Benzo(g,h,i)perylene	22.258	0.1	1000	0.9999	6.3	99

Selected calibration curves for early- and late-eluting PAHs, including naphthalene, fluorene, indeno(1,2,3-cd)pyrene, and benzo(g,h,i)perylene are shown in Figure 5. The insets in Figure 5 show the magnified part of the calibration levels of 0.1 to 20 pg to demonstrate excellent accuracy even at low concentrations.

Another challenge to PAH analyses reported in previous literature⁵ is ISTD response inconsistency across the

calibration range, which can lead to problems with linearity of the method. Under these method conditions, ISTD response was consistent throughout the calibration range with RSDs not exceeding 8%. The RSDs for naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 over a 12-point calibration bracketed with two solvent blanks were 4.8%, 5.7%, 5.8%, 6.1%, and 7.5%, respectively. This was within $\pm 20\%$

typically specified by the regulatory methods with calibration standards.

Use of the Ultra Inert universal low pressure drop liner (4 mm, glass wool) with pulsed splitless injection contributed to the observed method sensitivity, precision, and consistency of the ISTD responses.

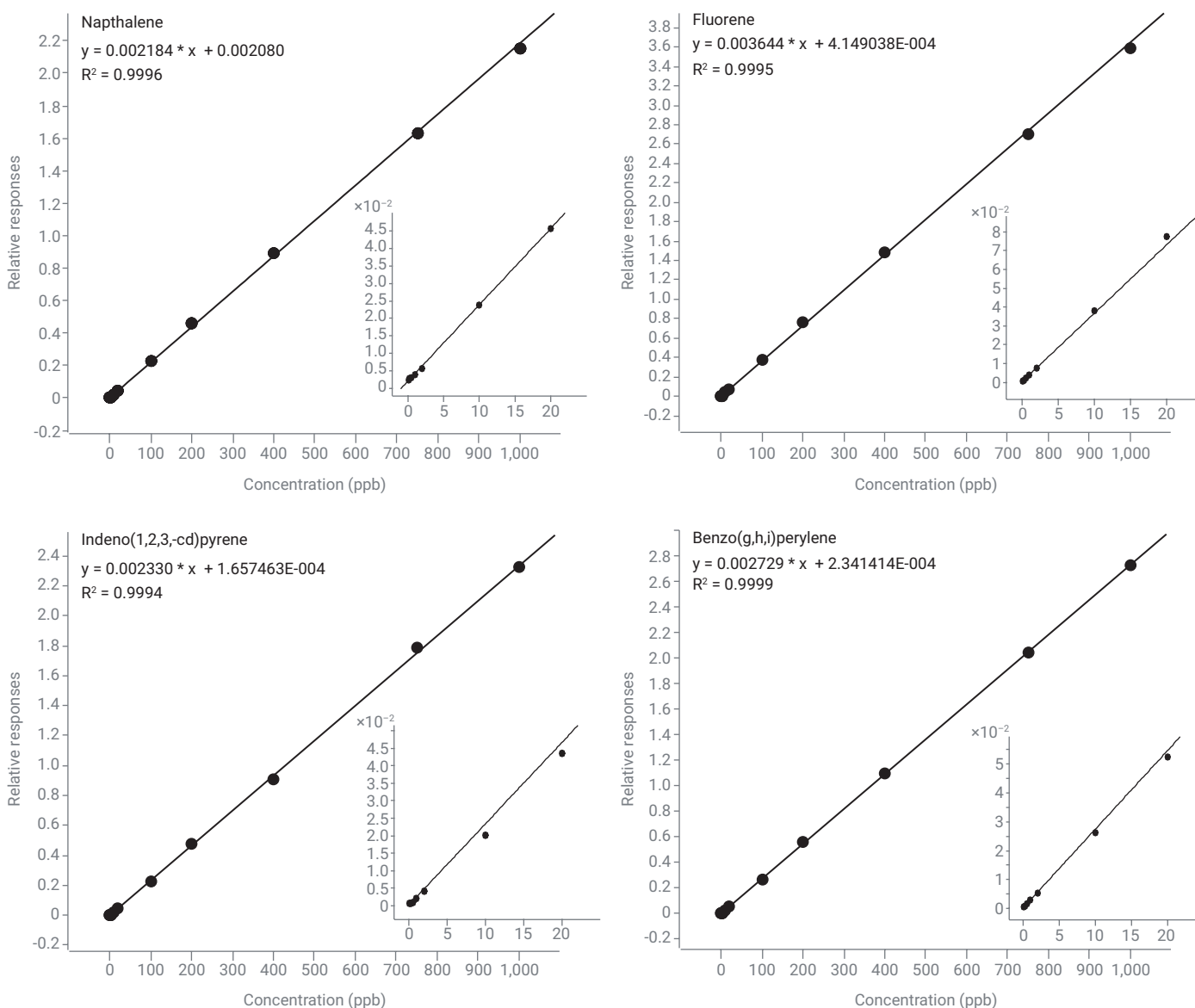


Figure 5. Selected calibration curves over the ranges of 0.1 to 1,000 pg and enlarged 0.1 to 20 pg for early- and late-eluting PAHs, including (a) naphthalene, (b) fluorene, (c) indeno(1,2,3-cd)pyrene, and (d) benzo(g,h,i)perylene.

Conclusion

The system described here enables successful analysis of PAHs over an extended calibration range of 0.1 to 1,000 pg. The method addresses many of the problems encountered using hydrogen carrier gas and GC/MS PAH analysis. Use of GC/TQ in MRM mode simplifies data review by providing much higher selectivity over spectral interferences from the matrix. Using the 9 mm extractor lens, higher zone temperatures, suitable column dimensions, and the appropriate liner results in substantial improvements in linearity, peak shape, and system robustness. Optimization of the collision energies with hydrogen carrier gas was greatly simplified using the MassHuter Optimizer for GC/TQ.

References

1. <https://www.agilent.com/en/promotions/this-is-how-you-gc>
2. Quimby, B. *et al.* In-Situ Conditioning in Mass Spectrometer Systems, US Patent 8,378,293, February 19, **2013**.
3. Andrianova, A.; Quimby, B. Optimized GC/MS/MS Analysis for PAHs in Challenging Matrices. *Agilent Technologies application note*, publication number 5994-0498EN, **2019**.
4. Szelewski, M.; Quimby, B. Optimized PAH Analysis Using the Agilent Self-Cleaning Ion Source and Enhanced PAH Analyzer. *Agilent Technologies application note*, publication number 5191-3003EN, **2013**.
5. Anderson, K. *et al.* Modified Ion Source Triple Quadrupole Mass Spectrometer Gas Chromatograph for Polycyclic Aromatic Hydrocarbons. *J. Chromatog. A* **2015**, 1419(6), 89–98.

www.agilent.com/chem

DE.4629861111

This information is subject to change without notice.

© Agilent Technologies, Inc. 2020
Printed in the USA, July 6, 2020
5994-2192EN

