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Optimized Polycyclic Aromatic Hydrocarbons (PAHs) Analysis Using Triple Quadrupole GC/MS with Hydrogen Carrier

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Increased demand for using hydrogen carrier gas

PAHs are widely distributed as contaminants throughout the world. 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 air, water, and soil. This work focuses on gas chromatography triple quadrupole mass spectrometry (GC/TQ MS) analysis in Multiple Reaction Monitoring (MRM) mode using hydrogen as the GC carrier gas. While helium is, in general, the best carrier gas for GC/MS analysis, its reoccurring shortages have increased demand for methods that use hydrogen as the carrier gas.

Several aspects require consideration when converting to hydrogen for GC/MS analysis of PAHs:

- **Hydrogen gas:** Hydrogen with 99.9999% purity specification and low individual specs on water and oxygen was used as the carrier gas.
- **GC Column:** The original helium method uses a DB-EUPAH 30 m x 0.25 mm ID x 0.25 μm column, which cannot be used with hydrogen carrier, as either the flow will be too high, or the inlet pressure will be negative. Therefore, a DB-EUPAH 20 m x 0.18 mm ID x 0.14 μm column is used. This gives ~ 5 psig inlet pressure with 0.65 mL/min constant flow of H_2 . This column provides better separation of the PAHs while using the same oven program.
- **Injection and Inlet Liner:** Use pulsed splitless with Agilent Universal Low Pressure Drop Liner with glass wool (PN: 5190-2295) to optimize injection with the split/splitless inlet.
- **Collision Gas:** Use only nitrogen at 1.5 mL/min in collision cell.
- **Source Extractor Lens:** Install optional 9 mm Extractor lens (part number: G3870-20449).
- **System Conditioning:** Condition the system with the filaments on until the background falls to an acceptable level. Overnight usually works well.
- **Collision Energies:** Use the automated MRM Optimizer software in MassHunter Acquisition to determine the best collision energies for use with H_2 carrier.

System configuration

Figure 1 below shows the experimental setup used.

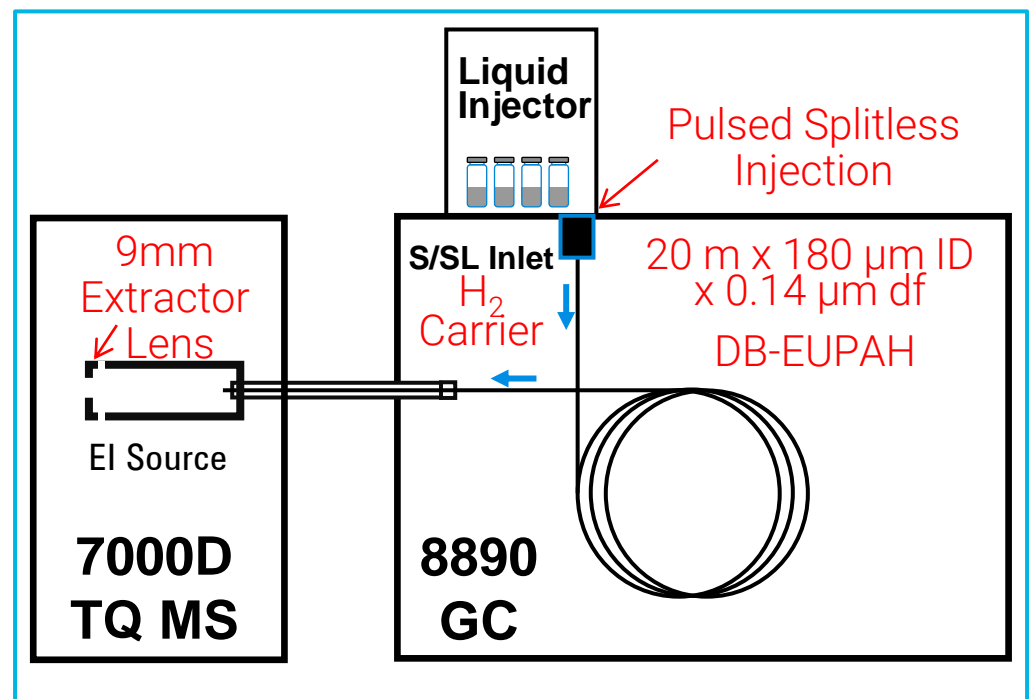


Figure 1. System configuration.

Instrument Parameters

Inlet	EPC Split/splitless
Mode	Pulsed Splitless, 40 psi until 0.75 min
Purge Flow to Split Vent	50 mL/min at 0.70 min
Injection Volume	1.0 μL
Inlet temp	320°C
Carrier Gas	Hydrogen
Inlet Liner	Agilent Universal Low Pressure Drop, with glass wool
Inlet Liner Part number	5190-2295
Oven Ramp	60°C (1min), 25°C/min to 200°C, 8°C/min to 335°C, 6.33 min.
Column	DB-EUPAH, 20 m x 0.18 mm ID x 0.14 μm df
Column part number	121-9627
Column flow	0.648 mL/min (constant flow mode)
Initial Inlet Pressure	4.85 psig
TQ MS	7000D w/ Inert Extractor Source and 9mm XTR lens
Tune	Extraction Autotune
Collision Gas	Nitrogen, 1.5 mL/min.
Solvent Delay	3.5 min.
MS Temperatures	Source 325°C, Quad 150°C, Transfer line 320°C

Note the use of high temperatures for the inlet, transfer line and MS source are key to obtaining best results.

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

The table below lists the acquisition parameters for the hydrogen carrier method. The collision energies for use with hydrogen were determined automatically with the Optimizer for GC/TQ software.

Time Segment	Start Time	Compound Name	Transition	Dwell (ms)	Collision Energy	Gain
1	3.5	Naphthalene-d8	136 → 136	30	25	10
1		Naphthalene	128 → 127	30	20	10
1		Naphthalene	128 → 102	30	20	10
2	4.9	2,6-dimethylnaphthalene	156 → 115	20	35	10
2		2,6-dimethylnaphthalene	156 → 141	20	20	10
2		Biphenyl	154 → 152	20	30	10
2		Biphenyl	154 → 153	20	20	10
2		1-methylnaphthalene	142 → 115	20	35	10
2		2-methylnaphthalene	142 → 115	20	30	10
2		1-methylnaphthalene	142 → 141	20	20	10
2		2-methylnaphthalene	142 → 141	20	20	10
3	6	2,3,5-trimethylnaphthalene	170 → 153	20	30	10
3		2,3,5-trimethylnaphthalene	170 → 155	20	20	10
3		Acenaphthene-d10	162 → 160	20	30	10
3		Acenaphthene	154 → 152	20	35	10
3		Acenaphthene	153 → 152	20	40	10
3		Acenaphthylene	152 → 150	20	35	10
3		Acenaphthylene	152 → 151	20	20	10
4	6.8	Fluorene	166 → 163	40	50	10
4		Fluorene	166 → 165	40	25	10
5	7.5	1-methylphenanthrene	192 → 165	20	40	10
5		1-methylphenanthrene	192 → 191	20	20	10
5		Phenanthrene-d10	188 → 188	20	25	10
5		Dibenzothiophene	184 → 139	20	40	10
5		Dibenzothiophene	184 → 152	20	25	10
5		Anthracene	178 → 176	20	35	10
5		Phenanthrene	178 → 176	20	35	10
5		Phenanthrene	178 → 152	20	30	10
5		Anthracene	178 → 152	20	25	10
6	9	1-methylphenanthrene	192 → 165	20	40	10
6		1-methylphenanthrene	192 → 191	20	20	10

Time Segment	Start Time	Compound Name	Transition	Dwell (ms)	Collision Energy	Gain
7	10.2	Fluoranthene	202 → 200	40	40	10
7		Pyrene	202 → 200	40	40	10
7		Pyrene	202 → 201	40	30	10
7		Fluoranthene	202 → 201	40	25	10
7		1-methylphenanthrene	192 → 165	40	40	10
7		1-methylphenanthrene	192 → 191	40	20	10
8	13	Chrysene-d12	240 → 236	40	40	10
8		Chrysene	228 → 224	40	55	10
8		Benzo(a)anthracene	228 → 224	40	55	10
8		Chrysene	228 → 226	40	35	10
8		Benzo(a)anthracene	228 → 226	40	35	10
8		Chrysene-d12	118 → 116	40	20	10
9	16.2	Benzo(b)fluoranthene	252 → 250	40	40	10
9		Benzo(j)fluoranthene	252 → 250	40	40	10
9		Benzo(k)fluoranthene	252 → 250	40	40	10
9		Benzo(j)fluoranthene	250 → 248	40	45	10
9		Benzo(b)fluoranthene	250 → 248	40	40	10
9		Benzo(k)fluoranthene	250 → 248	40	40	10
10	18.3	Perylene-d12	264 → 260	40	45	10
10		Perylene-d12	264 → 236	40	35	10
10		Perylene	252 → 250	40	40	10
10		Benzo(e)pyrene	252 → 250	40	40	10
10		Benzo(a)pyrene	252 → 250	40	40	10
10		Perylene	250 → 248	40	45	10
10		Benzo(e)pyrene	250 → 248	40	45	10
10		Benzo(a)pyrene	250 → 248	40	40	10
11	20.5	Dibenz(a,h)anthracene	278 → 272	40	60	10
11		Dibenz(a,c)anthracene	278 → 276	40	40	10
11		Dibenz(a,c)anthracene	277 → 275	40	40	10
11		Indeno(1,2,3-cd)pyrene	276 → 274	40	42	10
11		Benzo(g,h,i)perylene	274 → 272	40	45	10
11		Indeno(1,2,3-cd)pyrene	138 → 124	40	42	10

Chromatographic performance

The use of the 20 m x 0.18 mm ID column with hydrogen carrier gas provided increased chromatographic resolution compared to the 30 m x 0.250 mm column with helium carrier when using the same oven ramp. This results in the improved resolution of benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[j]fluoranthene and the other late eluting PAHs, as seen in Fig. 2.

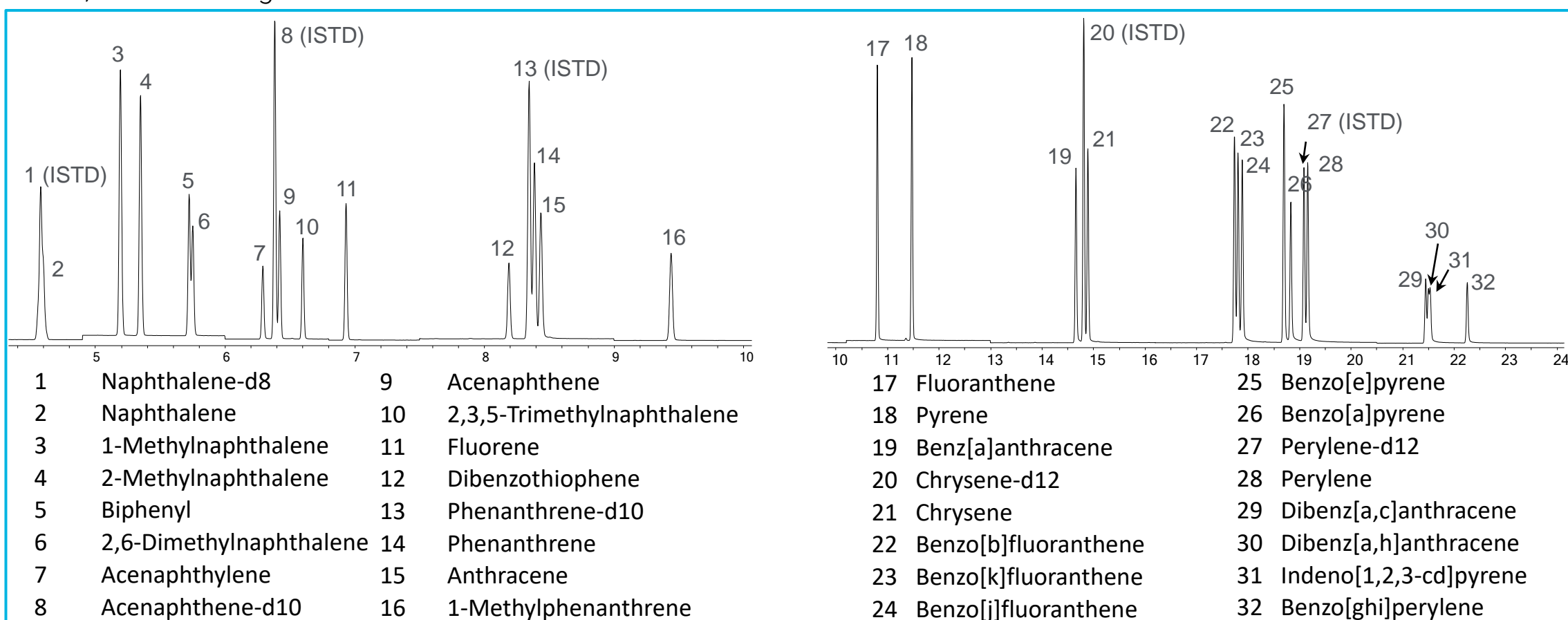


Figure 2. MRM TIC of the 100 pg/μL calibration standard with 500 pg/μL ISTDs.

Calibration results for linearity, accuracy, and signal-to-noise ratio

The use of hydrogen carrier gas typically results in a somewhat reduced signal-to-noise ratio (S/N), so it is important to check the lowest desired calibration level. The table below shows S/N of the quantifier ion for the target PAH analytes at 0.1 pg. For 26 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 of 27 analytes over the calibration range 0.1-1,000 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 $R^2 = 0.9999$. Good quantitation accuracy was maintained throughout the calibration range. As an example, accuracy at 100 pg is shown in the table below. It is within $\pm 4\%$ for 26 of 27 targets, and dibenz(a,h)anthracene was quantified within $\pm 9\%$ of its target concentration.

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, which was within $\pm 20\%$ typically specified by the regulatory methods with calibration standards.

Name	RT	ISTD	Calibration				0-1 ppb_PAHs	100 ppb_PAHs
			CF	CF Limit Low, ppb	CF Limit High, ppb	CF R2	S/N @ 0.1 ppb	Accuracy @ 100 ppb
Naphthalene-d8	4.577	ISTD						
Naphthalene	4.599		Linear	0.1	1000	0.9996	11.9	102
1-methylnaphthalene	5.195		Linear	0.1	1000	0.9996	11.0	104
2-methylnaphthalene	5.349		Linear	0.1	1000	0.9996	12.5	103
Biphenyl	5.723		Linear	0.1	1000	0.9996	15.1	103
2,6-dimethylnaphthalene	5.750		Linear	0.1	1000	0.9999	15.6	102
Acenaphthylene	6.292		Linear	0.25	1000	0.9999	1.1 (3.6 @ 0.25 ppb)	99
Acenaphthene-d10	6.382	ISTD						
Acenaphthene	6.422		Linear	0.1	1000	0.9996	57.3	103
2,3,5-trimethylnaphthalene	6.601		Linear	0.1	1000	0.9997	5.0	102
Fluorene	6.933		Linear	0.1	1000	0.9995	38.3	104
Dibenzothiophene	8.191		Linear	0.1	1000	0.9998	26.9	101
Phenanthrene-d10	8.346	ISTD						
Phenanthrene	8.388		Linear	0.1	1000	0.9997	31.9	103
Anthracene	8.436		Linear	0.1	1000	0.9999	6.7	99
1-methylphenanthrene	9.440		Linear	0.1	1000	0.9997	7.8	102
Fluoranthene	10.800		Linear	0.1	1000	0.9997	30.7	102
Pyrene	11.474		Linear	0.1	1000	0.9998	16.1	102
Benzo(a)anthracene	14.657		Linear	0.1	1000	0.9997	11.9	101
Chrysene-d12	14.809	ISTD						
Chrysene	14.892		Linear	0.1	1000	0.9999	18.1	99
Benzo(b)fluoranthene	17.738		Linear	0.1	1000	0.9997	18.1	102
Benzo(k)fluoranthene	17.803		Linear	0.1	1000	0.9999	8.0	101
Benzo(j)fluoranthene	17.886		Linear	0.1	1000	0.9961	13.7	98
Benzo(e)pyrene	18.696		Linear	0.1	1000	0.9997	26.5	103
Benzo(a)pyrene	18.833		Linear	0.1	1000	0.9998	3.2	97
Perylene-d12	19.084	ISTD						
Perylene	19.156		Linear	0.1	1000	0.9999	25.4	98
Dibenz(a,c)anthracene	21.450		Linear	0.1	1000	0.9998	3.3	97
Indeno(1,2,3,-cd)pyrene	21.501		Linear	0.1	1000	0.9994	7.6	97
Dibenz(a,h)anthracene	21.536		Linear	0.1	1000	0.9973	4.5	91
Benzo(g,h,i)perylene	22.258		Linear	0.1	1000	0.9999	6.3	99

Conclusions

The system described here enables successful analysis of PAHs over an extended calibration range of 0.1-1,000 pg. The method addresses many of the problems encountered utilizing hydrogen carrier gas and GC/MS PAH analysis. The use of 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.

References

A. Andrianova and B.D. Quimby, "Optimized PAH Analysis Using Triple Quadrupole GC/MS with Hydrogen Carrier", Agilent application note 5994-2192EN, 2020.

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