Agilent CrossLab
From Insight to Outcome

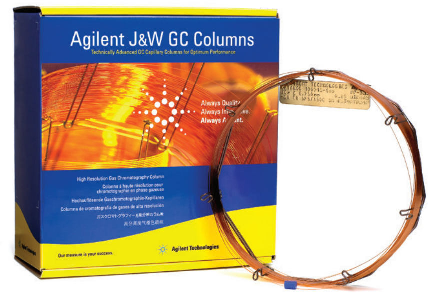
Polycyclic Aromatic Hydrocarbons Analysis in Environmental Samples

Using Single or Triple Quadrupole GC/MS with Helium or Hydrogen Carrier Gases

Consumables Workflow Ordering Guide

Agilent

Polycyclic Aromatic hydrocarbons (PAHs) are persistent, organic pollutants that result from various industrial activities in energy markets (coal, oil, gas), manufacturing (aluminum, rubber, cement, asphalt), power generation, and waste incineration. These contaminants are important to monitor as they are bioaccumulative and toxic even at low concentrations.



The US Environmental Protection Agency (EPA) regulates a series of 16 PAHs. Maximum contaminant levels (MCLs) exist for public water supplies to reduce adverse health effects from drinking contaminated municipal and industrial wastewaters.

EPA 625.1 and EPA 8270 C/D/E analyze PAHs as a subset of semivolatile analytes, while EPA 610 and EPA 8100 methods analyze for PAH only with greater accuracy, resolution and sensitivity. While PAHs have been analyzed by multiple techniques, GC/MS provides high selectivity and sensitivity for trace levels of PAHs in water, soil, and other complex matrices. Although helium is generally considered the best carrier gas for GC/MS analysis, its recurring shortages have increased demand for using hydrogen as the carrier gas.

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. The Agilent HydroInert source is a newly designed extractor source for GC/MSD that addresses these issues and improves performance with H_2 carrier gas in GC/MS.

Factors to consider when using hydrogen instead of helium as carrier gas

PAHs are relatively durable compounds and therefore can be analyzed with hydrogen carrier gas when using the optimized method and following the recommendations described in these application notes to avoid peak tailing.[1-3]

Table 1. Important factors to consider when using hydrogen carrier gas.

Consideration	Description
Hydrogen Gas	In-house hydrogen, with 99.9999% purity specification and low individual specifications on water and oxygen, is recommended 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. 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) are recommended to maintain optimal gas flow and inlet pressure in the backflush configuration.
8890 PSD Module and Midcolumn Backflushing	The Agilent 8890 GC pneumatics module is a pneumatic switching device (PSD), 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 required to sweep the connection. During backflushing, the make-up flow from the PSD needs to be raised to a much higher value, to sweep 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.[4] 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[5,6] 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 is 1.5 mL/min. This flow was also demonstrated to be optimal in previous work on PAHs with hydrogen carrier.[3]
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.

Separating PAH isomers

One of the challenges of analyzing PAHs is the chromatographic resolution of PAH isomers, as they have the same chemical structure. Mass spectrometers cannot distinguish these isomers due to their identical molecular weight.

Selecting the right GC column for PAHs depends on the goal of analysis. Table 2 shows how well the recommended columns can resolve the critical regulated environmental PAHs and impurities.

Table 2. Resolution of critical regulated PAHs and common impurity peaks by Agilent J&W GC columns.

Critical Regulated PAHs: EPA 610, EPA 8100, and EPA 8270D				
Analyte List	**Select PAH[*,7-9]**	**DB-EUPAH[*,10]**	**DB-5ms UI[*,10]**	**DB-UI8270D[*,11]**
Naphthalene	x	x	x	x
Acenaphthene	x	x	x	x
Acenaphthylene	x	x	x	x
Fluorene	x	x	x	x
Phenanthrene	x	x	x	x
Anthracene	x	x	x	x
Fluoranthene	x	x	x	x
Pyrene	x	x	x	x
Benz[a]anthracene	x	x	x	x
Cyclopenta[c,d]pyrene	x	x	x	x
Triphenylene (impurity)	x	Co-elute	Co-elute	Co-elute
Chrysene	x			
Benzo[b]fluoranthene	x	x	Co-elute	Co-elute
Benzo[j]fluoranthene	x	x		
Benzo[k]fluoranthene	x	x	x	x
Benzo[a]pyrene	x	x	x	x
Indeno[1,2,3-c,d]pyrene	x	x	x	x
Dibenzo[a,h]anthracene	x	x	x	x
Benzo[g,h,i]perylene	x	x	x	x
Total Analysis Time	**<15 min[7]**	**<24 min[10]**	**<18 min[10]**	**< 22 min[11]**
Max Operating Temp	**325 to 350 °C**	**320 to 340 °C**	**325 to 350 °C**	**325 to 350 °C**
Business Outcome	**Highest PAH specificity** **Productivity**	**Highest PAH specificity** **Economical**	**Versatility** **Productivity**	**Highest data integrity; best separation for all 8270 semi-volatile analytes including PAHs**
Selection Criteria	– Accurate quantification of all 16 EPA PAHs – Unique selectivity resolves all isomers – Only column separating chrysene from triphenylene, if present	**Best choice when resolving triphenylene: chrysene is not critical**	– Economical choice – Excellent for most EPA methods where fewer PAH isomers need to be reported	**Analyzing PAHs per EPA method 8270 C/D/E**

*x = complete baseline separation

Molecular weight discrimination

Another challenge with PAH analysis is molecular weight discrimination. This can occur if:

a. The injection port temperature is set too low (<300 °C) and there is incomplete sample vaporization in the inlet, or

b. The splitless injection hold time is not optimized to effectively transfer all the sample onto the head of the analytical column, or

c. The wrong inlet liner is chosen. Chromatographically, this will be observed as a lower response of the higher molecular weight PAHs.

Recommendations to overcome molecular weight discrimination and other best practices for optimizing PAH analysis by GC/MS or GC/MS/MS: [4,12]

- Injection volume: 1 to 2 µL
- Inlet, MS source and transfer line temperature: 320 °C. Temperatures below 300 °C will result in PAH tailing. Keep heated zones well insulated and hot to reduce the potential for system cold spots and resultant signal loss.
- Purge time activation: 45 to 90 seconds splitless
- 4 mm splitless liner with mid-frit (or glass wool). The frit (or wool) 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. Glass-fritted liners are superior alternatives to glass wool as they eliminate the risk of wool breakage or liner movement.
- Pulsed Splitless injection at 20 to 50 psi for 0.9 min to transfer high boiling PAHs onto the column. "Cold trapping" on the liquid phase is often applied for higher molecular, higher boiling analytes such as PAHs for splitless/PTV/MMI type of injections. An initial oven temperature of 75 °C usually provides good quality peak shapes for many sample solvents.
- Use a 0.15/0.18 mm i.d. high efficiency GC column for faster analysis time with no loss in resolution.
- Minimize inlet (and system) dwell time by operating at higher column flows without compromising MS detector sensitivity. Perform the analysis in constant flow mode.
  0.15 mm: 1.2 mL/min He
  0.18 and 0.25 mm: 1.2 to 1.4 mL/min He
  Note: Although 0.18 mm and 0.25 mm i.d. GC columns can handle higher flow rates, this will lead to decreased MS sensitivity. Exceeding 1.5 mL/min is not recommended for the HES source.
- Use retention gaps and/or backflushing to eliminate sample carry over, reduce maintenance and cut the analysis cycle times.
- Use Agilent JetClean to substantially reduce the need for manual source cleaning, especially with high-matrix samples. Continuous cleaning of the source with hydrogen (0.33 mL/min) has been demonstrated to significantly improve calibration linearity and precision of response over time for PAH analysis.
- A 9 mm extractor lens minimizes the surfaces available for deposition of the PAHs and is the default lens included with the HydroInert source which is optimized for use with hydrogen. This is the best choice for PAH analysis, as it provides the best calibration linearity, precision of response, and peak shape.
- Allow PAH standards to come to room temperature before diluting or prepping calibration mixtures since heavier molecular weight PAHs can fall out of solution during refrigerated storage.

The most common sample preparation for the EPA methods involves liquid-liquid extraction using methylene chloride. For larger numbers of samples, solid phase microextraction (SPME) with automation results in less sample manipulation, decreases solvent consumption and reduces analysis time per sample.[13-14] Agilent SPME Arrows, available on the PAL3 series RSI and RTC systems, have higher mechanical robustness and larger surface area capacity than their fiber counterparts. This design increases trace level sensitivity, shortens extraction time, and increases throughput. Both SPME fibers and arrows can be used for manual sampling.

References

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3. Optimized PAH Analysis Using Triple Quadrupole GC/MS with Hydrogen Carrier, 5994-2192EN
4. Optimized GC/MS/MS Analysis for PAHs in Challenging Matrices Using the Agilent 8890/7000D Triple Quadrupole GC/MS with Jet Clean and Midcolumn Backflush, 5994-0498EN
5. Anderson, K. A. *et al.* Modified Ion Source Triple Quadrupole Mass Spectrometer Gas Chromatograph for Polycyclic Aromatic Hydrocarbons. *J. Chromatog*. A **2015**, *1419*, 89–98. DOI: 10.1016/j.chroma.2015.09.054
6. Quimby, B. D. *et al.* In-Situ Conditioning in Mass Spectrometer Systems. US 8,378,293, **2013**.
7. Fast Separation of 16 US EPA 610 Regulated PAHs on Agilent J&W Select PAH GC Columns, SI-02263
8. Separation of 54 PAHs on an Agilent J&W Select PAH GC Column, SI-02232
9. Increased Reproducibility in the Analysis of EU and EPA PAHs with the Agilent J&W Select PAH GC Column and Agilent Intuvo 9000 GC system, 5994-0877EN
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11. Semivolatile Analysis with Specially Designed Agilent J&W DB-UI8270D Columns, 5991-0250EN
12. Optimized GC/MS Analysis for PAHs in Challenging Matrices Using the 5977 Series GC/MSD with JetClean and Midcolumn Backflush, 5994-0499EN
13. Analysis of Low-level PAHs in Drinking Water with an Agilent PAL3 Equipped with SPME ARROW, 5994-0590EN
14. Examination of Lower Molecular Weight PAHs in Drinking Water Using Agilent PDMS SPME Fibers, 5994-1301EN

Easy selection and ordering information

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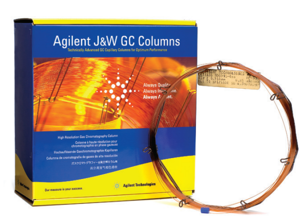
MyList of PAH standards

Description	Part No.
Agilent PAH analyzer Calibration Sample Kit	G3440-85009
EPA 8100 Standards	
PAH standard (16 analytes; calibration standard)	PM-810-1
PAH mixture (16 analytes; QC reference standard)	PM-613A-1
EPA 610 Standards	
PAH kit (17 ampules)	PK-610
PAH standard (2000 µg/mL)	US-106N-1
Matrix spike standard (6 analytes)	PM-025-1
EPA 8270 C/D/E Standards	
EPA Method 8270 C/D calibration standard kit	US-121K
Semi-volatiles internal standard	US-108N-1
Base, neutrals surrogate standard	ISM-280N-1
Acids surrogate standard	ISM-290N-1
Semi-volatile surrogate standard	ISM-333X

Please go to www.agilent.com/chem/standards for additional volume and concentration standard options.

MyList of GC columns

Description	Part No.
Agilent J&W DB-EUPAH, 20 m x 0.18 mm, 0.14 µm (Qty: 2 recommended when using hydrogen carrier gas)	121-9627
Agilent DB-UI8270D, 30 m x 0.25 mm, 0.25 µm	122-9732
Agilent DB-UI8270D, 20 m x 0.18 mm, 0.36 µm	121-9723
Agilent J&W Select PAH, 30 m x 0.25 mm, 0.15 µm	CP7462
Agilent J&W Select PAH, 15 m x 0.15 mm, 0.10 µm	CP7461
Agilent J&W DB-5ms UI 20 m x 0.18 mm, 0.18 µm	121-5522UI



MyList of HydroInert source for transitioning to H_2 carrier gas

Description	Part No
HydroInert Complete Source Assembly for 5977	G7078-67930
HydroInert Complete Source Assembly for 7000 TQ	G7006-67930
HydroInert GC/MSD Upgrade. Contains parts needed to upgrade an existing 5977A/B/C Inert Plus Source	5505-0083
HydroInert GC/TQ Upgrade. Contains parts needed to upgrade an existing 7000C/D/E Inert Plus Source	5505-0084
Install Kit for GCs, Stainless Steel. Contains 1/8" stainless steel tubing, fittings, Big Universal Trap with stainless steel fittings, and tool kit	19199S

MyList of GC supplies

Description	Part No.
Inlet liner, universal, Ultra Inert, mid-frit, 870 µL, 4 mm, 1/pk (recommended)	5190-5105
Inlet septa, Advanced Green, nonstick, 11 mm, 50/pk	5183-4759
GC inlet seal, gold plated with washer, Ultra Inert, 1/pk	5190-6144
Purged Ultimate Union Assembly	G3186-80580
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
Blue Line autosampler syringe, 10 µL, fixed needle	G4513-80220
Ferrule, 0.4 mm id, 15% graphite/85% Vespel, 0.1 to 0.25 mm column, 10/pk	5181-3323
Self-tightening column nut, collared, inlet	G3440-81011
Self-tightening column nut, collared, MSD	G3440-81013

MyList of MS supplies

Description	Part No
EI filament (for 7000A/B/C/D, 5977B Inert Plus, 5977A extractor, inert or stainless steel and 5975 systems)	G7005-60061
HES Filament for 7010 Triple Quadrupole GC/MS	G7002-60001
Drawout plate, 9 mm, inert source	G3440-20022
Drawout plate, 9 mm, extractor source*	G3870-20449

**G3870-20449 includes a 3 mm drawout plate. For PAH applications replace with the 9 mm drawout plate P/N G3440-20022.*

MyList of Gas Clean filters

Description	Part No
Gas Clean Carrier Gas Kit for 8890 and 8860	CP179880
Gas Clean Carrier Gas purifier replacement cartridge	CP17973
Gas Clean Filter Kit for Intuvo	CP17995

MyList of sample containment supplies

Description	Part No
A-Line screw top vial, 2 mL, amber, write-on spot, 100/pk. Vial size: 12 x 32 mm (12 mm cap)	5190-9590
Cap, screw, blue, PTFE/red silicone septa, 100/pk. Cap size: 12 mm	5182-0717

MyList of Intuvo GC columns

Description	Part No
Agilent J&W DB-EUPAH Intuvo, 20 m x 0.18 mm, 0.14 µm	121-9627-INT
Agilent DB-UI8270D Intuvo, 30 m x 0.25 mm, 0.25 µm	122-9732-INT
Agilent DB-UI8270D Intuvo, 20 m x 0.18 mm, 0.36 µm	121-9723-INT
Agilent J&W Select PAH Intuvo, 30 m x 0.25 mm, 0.15 µm	CP7462-INT
Agilent J&W Select PAH Intuvo, 15 m x 0.15 mm, 0.10 µm	CP7461-INT
Agilent J&W DB-5ms UI Intuvo, 20 m x 0.18 mm, 0.18 µm	121-5522UI-INT

MyList of Intuvo GC supplies

Description	Part No
Guard Chip, Intuvo Split/Splitless	G4587-60565
Intuvo inlet chip	G4581-60031
Flow Chip, Intuvo, D2-MS	G4581-60033
Flow Chip, Intuvo, swaged HES MS tail	G4590-60109
Inlet/MSD (Intuvo) Polyimide gasket	5190-9072

MyList of automated sample preparation supplies

Description	Part No
Agilent SPME Arrow PDMS 100 µm, 1.1 mm	5191-5862
Agilent SPME Arrow PDMS 100 µm, 1.5 mm	5191-5866
SPME Fiber PDMS 7 µm	5191-5870
SPME Fiber PDMS 30 µm	5191-5871
SPME Fiber PDMS 100 µm	5191-5872
Manual injection kit for SPME fiber and SPME Arrow	5191-5877
Merlin Microseal SPME replacement Microseal	392609902
PAL3 Alignment Ring (for manual injection)	G7371-67001

MyList of CTC/CombiPAL and SPME headspace supplies

Description	Part No
Inlet liner Ultra Inert, splitless, straight, 2 mm id, for SPME Arrows	5190-6168
Inlet liner Ultra Inert, straight, 0.75 mm id, for SPME fiber	5190-4048
Sample loop, headspace, 1.00 mL, inert	G4556-80106
Sample probe, deactivated, for Agilent 7697A headspace sampler	G4556-63825
Headspace syringe CTC/CombiPAL, 1.0 mL	G6500-80107
Headspace syringe CTC/CombiPAL, 2.5 mL	G6500-80109
Headspace syringe CTC/CombiPAL, 5.0 mL	G6500-80111
Fused silica tubing, deactivated, 5 m, 0.32 mm, 0.43 mm od	160-2325-5
Ferrule, polyimide, graphite 1/32 inch, 5/pk	0100-2595
Fitting, internal reducer, 1/16 to 1/32 inch	0100-2594
Headspace crimp top vials; clear, 10 mL, 23 x 46 mm, 20 mm cap, 100/pk	5182-0838
Headspace crimp top vials; clear, 20 mL, 23 x 75 mm, 20 mm cap, 100/pk	5182-0837
Headspace crimp top vials, amber, 10 mL, 23 x 46 mm, 20 mm cap, 100/pk	5190-2287
Headspace crimp top vials, amber, 20 mL, 23 x 75 mm, 20 mm cap, 100/pk	5067-0226
Headspace crimp cap, aluminum, PTFE/silicone septa, 20 mm, 100/pk	5183-4477

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