Agilent CrossLab
From Insight to Outcome

Polycyclic Aromatic Hydrocarbons Analysis in Environmental Samples

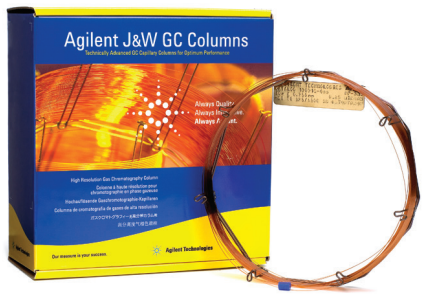
Using single quadrupole GC/MS and triple quadrupole GC/MS/MS:
Consumables workflow ordering guide

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 to humans and wildlife even at low concentrations (*1, 2*).

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.

Since PAHs are a subset of the semivolatile analytes, most contract testing laboratories utilize the standardized EPA 625.1 method for waste water samples. Surface water, ground water, and soil/solid samples are analyzed using the EPA 8270 C/D/E method, instead of PAH-only methods (EPA 610 and EPA 8100). This approach enables labs to use existing methods and system setup, eliminating the need for time-consuming reconfigurations or instruments dedicated for PAH testing. Other industrial, academic or research labs, on the other hand, may choose to test for the target PAHs utilizing PAH-specific (EPA 610 and EPA 8100) methods for greater accuracy, resolution, and sensitivity.



Agilent J&W GC columns

References

1. M. K. Hill, *Understanding Environmental Pollution*, Cambridge University Press, 3rd edition, 2010.
2. Polycyclic Aromatic Hydrocarbons (PAHs) Fact Sheet, CDC Environmental health, viewed May 2020, https://www.epa.gov/sites/production/files/2014-03/documents/pahs_factsheet_cdc_2013.pdf

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 1 shows how well the recommended columns can resolve the critical regulated environmental PAHs and impurities.

Table 1. 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***	**DB-EUPAH***	**DB-5ms UI***	**DB-UI8270D***
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[1]**	**<24 min[3]**	**<18 min[3]**	**< 22 min[5]**
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.

Recommended injection parameter ranges to overcome molecular weight discrimination:

- Injection volume: 1 to 2 µL
- Inlet temperature: 300 to 320 °C
- MS source and transfer line temperature: 320 °C
- Purge time activation: 45 to 90 seconds splitless
- 4 mm splitless liner with glass wool or fritted liners
- Pulsed Splitless 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.
- Minimize inlet (and system) dwell time by operating at higher column flows without compromising MS detector sensitivity:
  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.

Best practices for optimizing single and triple quadrupole GC/MS systems (GC/SQ and GC/TQ) for PAH analysis

Use retention gaps and/or backflushing to eliminate sample carry over, reduce maintenance and cut the analysis cycle times.

- Perform the analysis in constant flow mode
- Keep heated zones well insulated and hot to reduce the potential for system cold spots and resultant signal loss
- Keep MS transfer line and ion source at temperatures above 300 °C. Too low temperatures will result in PAH tailing
- Use a 0.15/0.18 mm i. d. High Efficiency GC columns for faster analysis time with no loss in resolution
- 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
- 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
- Use a 9 mm extractor lens to minimize the surfaces available for deposition of the PAHs.

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. 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.

Application notes

Method setup parameters and workflow details can be found in the following Agilent application notes:

1. Fast Separation of 16 US EPA 610 Regulated PAHs on Agilent J&W Select PAH GC Columns
2. Separation of 54 PAHs on an Agilent J&W Select PAH GC Column
3. PAH Analysis with High Efficiency GC Columns: Column Selection and Best Practices
4. 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
5. Semivolatile Analysis with Specially Designed Agilent J&W DB-UI8270D Columns
6. Analysis of Low-level PAHs in Drinking water with an Agilent PAL3 equipped with SPME ARROW
7. Examination of Lower Molecular Weight PAHs in Drinking Water Using Agilent PDMS SPME Fibers
8. Optimized GC/MS Analysis for PAHs in Challenging Matrices using the 5977 Series GC/MSD with JetClean and midcolumn backflush
9. 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

Recommended products for PAH analysis of environmental samples

The table, following, lists the products needed for the PAH analysis of environmental samples. Click the 'MyLists' link in each table heading to add all those items to your My Favorites list on the Agilent online store*. You can then enter the quantities for the products you need. The list will remain under My Favorites for you to use for future orders.

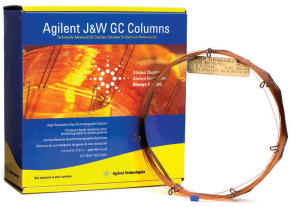
Item	Part Number
View MyList of EPA 8100 Standards	
1-Fluoronaphthalene	IST-180-1
2-Fluorobiphenyl	ATS-140-1
PAH standard (16 analytes; calibration standard)	PM-810-1
PAH mixture (16 analytes; QC reference standard)	PM-613A-1
View MyList of EPA 610 Standards	
PAH kit (17 ampoules)	PK-610
Matrix spike standard (6 analytes)	PM-025-1
PAH standard (2000 µg/mL)	US-106N-1
View MyList of 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

View Mylist of GC Inlet Supplies	
Inlet septa, Advanced green, nonstick, 11 mm, 50/pk	5183-4759
Inlet septa, Advanced green, nonstick, 11 mm, 100/pk	5183-4759-100
Ultra Inert Splitless, single taper, glass wool	5190-2293
Ultra Inert splitless single-taper liner with glass frits	5190-5112
Ultra Inert gold seal, with washer, 1/pk	5190-6144
Ultra Inert gold seal, with washer, 10/pk	5190-6145
Self-tightening column nut, collared, inlet	G3440-81011
Self-tightening column nut, collared, MSD	G3440-81013
Replacement collar for self tightening nut	G3440-81012
15%Graphite/85% Vespel ferrules, 0.4 mm i.d., 10/pk	5181-3323
5 µL ALS syringe, fixed needle, 23-26s/42/cone	5181-1273
5 µL ALS syringe, fixed needle, 23-26s/42/cone 6/pk	5181-8810
10 µL ALS syringe, fixed needle, 23-26s/42/cone	5181-1267
10 µL ALS syringe, fixed needle, 23-26s/42/cone 6/pk	5181-3360
20x magnifier loop	430-1020

If this is your first time using the Agilent online store, you will need to enter your email address for account verification. If you don't have a registered Agilent account, you will need to register for one. The "My List" feature is valid only in regions that are e-commerce enabled. All items can also be ordered through your regular sales and distributor channels. Not available in all countries. Please contact your local sales representative for availability.

View Mylist of GC column	
Agilent J&W DB-5ms UI 20 m x 0.18 mm, 0.18 µm	121-5522UI
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 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 DB-EUPAH, 20 m x 0.18 mm, 0.14 µm	121-9627
View Mylist of Intuvo GC columns	
Agilent J&W DB-5ms UI 20 m x 0.18 mm, 0.18 µm	121-5522UI-INT
Agilent J&W Select PAH, Intuvo GC column, 30 m x 0.25 mm, 0.15 µm	CP7462-INT
Agilent J&W Select PAH, 15 m x 0.15 mm, 0.10 µm	CP7461-INT
Agilent DB-UI8270D INT, 30 m x 0.25 mm, 0.25 µm	122-9732-INT
Agilent DB-UI8270D INT, 20 m x 0.18 mm, 0.36 µm	121-9723-INT
Agilent J&W DB-EUPAH, Intuvo GC column 20 m x 0.18 mm, 0.14 µm	121-9627-INT
View Mylist of Intuvo Supplies	
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
View Mylist of MS Supplies	
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
View Mylist of Gas filters	
Gas Clean carrier gas Kit for 7890	CP17988
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
View Mylist of Vials and caps	
2 mL screw top amber, write-on spot, deactivated, certified, 100 pc	5183-2072
Screw caps, blue, certified, PTFE/silicone/PTFE septa	5182-0723
100 µL vial insert, glass with polymer feet	5181-8872



View Mylist of Automated Sample Preparation supplies	
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
View Mylist of CTC/CombiPAL and SPME headspace supplies	
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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