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Consumable Workflow Ordering Guide

Analysis of Benzene and its Derivatives (BTEX) in Water by Gas Chromatography

Benzene and its derivatives, toluene, ethylbenzene, and xylene isomers, are constituents of mineral oil products used in many industrial processes as solvents and the major water-soluble constituents of petroleum derivatives. They are usually found in soils and ground water samples near petroleum production and storage sites, by leaks from old underground storage fuel tanks and piping. These pollutants pose problems when they leach into groundwater used for drinking purposes and when old petrol stations and fuel depots are redeveloped. This is a hazard to the environment and to public health, and is the reason why environmental agencies regard these compounds as priority pollutants.

The US Environmental Protection Agency (EPA) has set the maximum permissible level of benzene in drinking water at 5 ppb. In general, benzene and its derivatives are a suitable mix for monitoring the quality of potable water from main intakes of water (surface or underground) and several agencies have established analytical methods for analyzing them.

In the US, most volatile organic compounds (VOC) methods can be used for the analysis of BTEX. These methods include EPA 524.2 and EPA 8260.[1]

The ISO method 17943-2016 for determination of volatile organic compounds in water is also popular in the European Union and is applicable for the analysis of BTEX compounds.[2]

In China, there is a specific method for benzene and its derivatives, method HJ 1067-2019,[3] but several other exist that address VOCs in water or BTEX as subset of VOCs, this includes HJ 686-2014, GB 11890-1089, HJ 810-2016 and HJ 639-2012.

To limit the effects of BTEX on the environment, it is necessary to develop accurate, sensitive, and reliable analytical methods to detect their presence. The samples are often composed of many other contaminants, which can interfere with the analysis and contaminate the gas chromatographic system. Static headspace is one of the most popular techniques for analyzing VOCs in a variety of matrices, as it eliminates tedious sample preparation steps and prevents contamination problems. HJ-1067-2019 uses static headspace analysis for analyzing BTEX in surface water, ground water and domestic sewage.[3] The Agilent 8890 GC coupled with the 8697 head-space sampler can easily achieve the performance specification for the compounds detailed in HJ 1067-2019.[4]

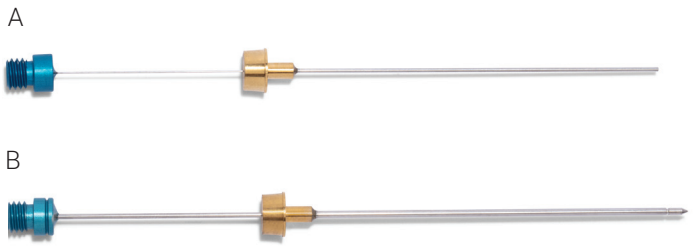

Figure 1. (A) CAR-WR/PDMS 95 µm SPME fiber (p/n 5191-5875)[8] (B) 120 µm CAR WR/PDMS Arrow (p/n 5191-5859).[6]

While static headspace sample preparation leaves a proportion of the analytes in the original matrix, the use of dynamic headspace (purge-and-trap) strips all the volatile components from the sample, leaving non-volatile contaminates behind in the matrix.[5] The US EPA methods for VOC analysis utilizes the purge-and-trap technique. While sensitivity is generally improved by the purge-and-trap technique, it is more prone to hardware complications such as salt build-up, blockage and corrosion of the sample pathway valves, lines, needles and sparge vessels.

To determine traces of BTEX in water, it is key to guard against the loss of these volatile analytes during sample storage and transportation. The ISO 17943-2016 method, which is common in the EU, recommends solid phase microextraction (SPME), which combines extraction and concentration in a single step making it a fast and efficient method for measuring trace-level BTEX in water samples.[6-8]

Agilent provide complete, reliable, and economical solutions for the analysis of benzene and its derivatives in water following any of the above techniques. The total inert flow path from headspace to detector provides reliable inertness that results in excellent peak shape, resolution, and great repeatability.

Best practices

1. To avoid loss of volatile molecules, it is best to perform the analysis as quickly as possible (preferably within a temperature-regulated laboratory) after sample collection.
2. During sampling, all air bubbles must be eliminated from the vial.
3. If analysis is to be performed after 14 days of sample collection, preserve the samples by adding one drop of HCl 1:1 (not necessary if the analysis is performed within 14 days).
4. To lower the detection limit when using headspace, increase the injection volume. The addition of NaCl increases the SPME extraction efficiency. This is due to the decrease of the partition coefficient between the liquid and gas phases, allowing more analytes to readily partition into the headspace.

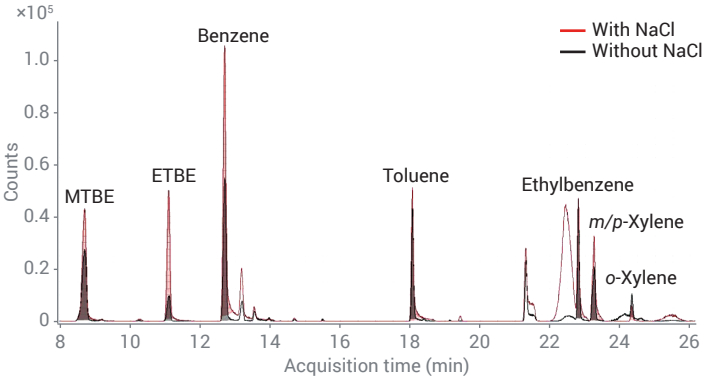

Figure 2. Chromatogram of 0.8 ppb BTEX standard analyzed by a 120 µm CAR WR/PDMS SPME Arrow with NaCl (red trace) and without NaCl (black trace).[8]

5. Benzene, toluene and ethyl benzene exhibit outgassing with most purge-and-trap traps. A Carbopak B/Carbopak C is most suitable to trap BTEX efficiently.
6. The extraction by SPME is influenced by several factors:
   - Agitation
   - Temperature
   - The amount of sample
   - The size of the headspace vial
   - The ratio of the headspace to the aqueous phase, and
   - The position of the coated fiber in the HS

While the ISO 17943:2016 method recommends 75–85 µm SPME film thickness, for the analysis of BTEX in water the CAR-WR/PDMS 95 µm is recommended due to its selectivity for gases and low molecular weight compounds (30–225 g/mol). The CAR-WR/PDMS 95 µm SPME fiber maintained a linearity (R^2) of > 0.99, and a calibration accuracy between 98.8 to 100.9% over the calibration range for each target analyte. The MDL and LOQ for all compounds were < 0.80 and < 2.39 ppb respectively.[6]

Table 1. SPME headspace parameters.[6]

Parameter	Value
Script Name	ARROW-STD-V2.0
Tool	SPME 1
SPME Fiber Phase	CAR-WR/PDMS 95 µm (Figure 1)
Incubation Time	5 minutes
Stirrer	Heatex Stirrer 1
Heatex Stirrer Speed (Agitation)	1,000 rpm
Heatex Stirrer Temperature (Extraction Temperature)	40 °C
Agitator	None
Sample Extract Time	24 minutes
Extraction Temperature	40 °C
Sample Vial Penetration Depth	40 mm
Sample Vial Penetration Speed	20 mm/s
Inlet Penetration Depth	40 mm
Inlet Penetration Speed	100 mm/s
Injection Signal Mode	Before fiber expose
Sample Desorption Time	4 minutes
Conditioning Port	SPMEArrowCond 1
Predesorption Conditioning Time	5 minutes (analytical run)/ 60 minutes (precondition)
Fiber Conditioning Station Temperature	297 °C
Postdesorption Conditioning Time	0 minutes
GC Cycle Time	5 minutes (set for sequence overlap)

GC column selection criteria

The Agilent J&W HP-INNOWAX GC column, a polyethylene glycol (PEG) stationary phase featuring high polarity and upper temperature limits, is ideal for full separation of o/m xylenes in hydrocarbon processing industry (HPI) applications. These columns have extended inertness lifetime and withstand repeated temperature cycling to the upper temperature limits of the column. Although resolution of the o/m xylenes is not critical for purposes of determining BTEX contaminants in water, the HJ 1067-2019 method recommends the use of a PEG column for BTEX separation on a GC/FID system. A 6% cyanopropyl-phenyl 94% dimethylpolysiloxane (PDMS) column, such as Agilent J&W DB-624, is recommended as a confirmation column to exclude false positive or false negative results.

Table 2. Agilent 8890-8697 headspace GC instrument setting for BTEX analysis using method HJ 1067-2019.[4]

Parameter	Value
Agilent 8697 Headspace Sampler	
Loop Size	1 mL
Pressurization Gas	Nitrogen
Oven Temperature	80 °C
Loop Temperature	80 °C
Transfer Line Temperature	100 °C
Vial Equilibration Time	40 min
Injection Duration	0.5 min
Vial Size	20 mL
Fill Pressure	15 psi
Loop Fill Mode	Default
Vial Shaking	Level 8
Agilent 8890 GC	
Inlet	Split/splitless 200 °C, split ratio 10:1 Liner: Straight, deactivated, 2 mm id (p/n 5181-8818)
Column	Agilent J&W HP-INNOWax, 30 m × 0.32 mm, 0.5 µm (p/n 19091N-213I)
Carrier	Nitrogen, 2 mL/min, constant flow
Oven	40 °C (5 min), then 5 °C/min to 80 °C (5 min), then 30 °C/min to 200 °C (5 min)
FID	250 °C, hydrogen: 30 mL/min, air: 300 mL/min

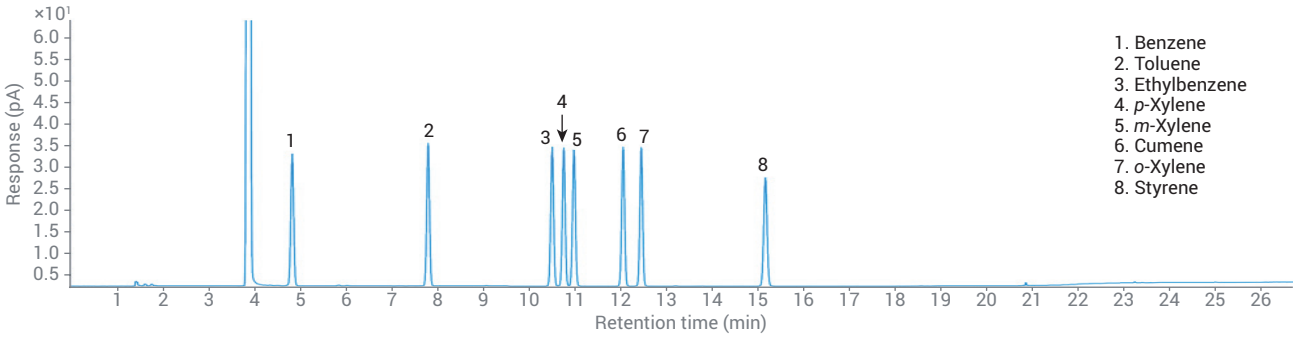

Figure 3. Chromatogram of the eight target compounds at a concentration of 200 µg/L.[4]

The ISO 17943:2016 method recommends:

- Specific VOC-type GC column with a diphenyl-/dimethylpolysiloxane (PDMS) phase. Agilent J&W CP-Sil 5 CB is a general purpose, non-polar column containing a 100% PDMS phase. Due to extensive crosslinking, CP-Sil 5 CB is highly inert and ideal for large solvent injections and when separation of the xylene isomers is not required.
- 5% Phenyl 95% PDMS, like the Agilent J&W DB-5ms UI (122-5532UI). Like other low-polar phases, this GC column can be used when separation of m/p-xylene is not required.
- Mid-polar phases, including 6% cyanopropyl-phenyl, 94% PDMS, like DB-624 UI (122-1334UI). These columns can separate xylene isomers and are designed for the analysis of volatile organic compounds (VOC) by GC/MS. While longer (60 m) and thicker (>1 µm) stationary phases are recommended for the larger suite of VOCs, this is not necessary for BTEX analysis.

For a list of columns and supplies for VOC analysis using EPA 8260 B/C/D, EPA 524.2 and EPA 624.1 methods, see the Volatile Organic Compounds in Water – Workflow Consumables Ordering Guide (5994-0345EN).

References

1. SW-846 Test Method 8260D: Volatile Organic compounds by Gas Chromatography/Mass Spectrometry (GC-MS).
2. ISO 17943:2016: Water quality – Determination of volatile organic compounds in water – Method using headspace solid-phase micro-extraction (HS-SPME) following GC-MS.
3. HJ 1067-2019: Water quality – Determination of benzene and its analogs – Headspace/Gas Chromatography.
4. Determination of Benzene and its derivatives in water with the Agilent 8697 headspace sampler and 8890 GC system (5994-3074EN).
5. Volatile Organic Compounds in Water – Agilent GC/MS workflow consumables guide. (5994—0345EN).
6. Analysis of BTEX in water with a CAR-WR/PDMS 95 um SPME Fiber (5994-1104EN).
7. Analysis of BTEX in Natural water with SPME (SI-01251).
8. Determination of VOCs in Water by GC/MS after Headspace-Solid-Phase Microextraction (HS-SPME) (5994-1045EN).

Table 3. GC/FID/MS instrument settings for BTEX analysis using the Agilent J&W CP-Sil 5 CB GC column.[6]

Setting	Value
Inlet liner	Inlet liner, Ultra Inert, splitless, straight, 0.75 mm id (p/n 5190-4048)
Injection Mode/Temperature	Splitless/290 °C
Oven Program	30 °C (hold 4 minutes); 4 °C/min to 100 °C (hold 0 minutes)
Equilibration Time	0.5 minutes
Control Mode	Constant flow (3 mL/min; 1.4 mL/min into MSD)
Column	Agilent J&W CP-Sil 5 CB GC column, 30 m, 0.25 mm, 1.00 µm (p/n CP8770)
MSD Restrictor	Fused silica tubing, 1.7 m, 0.15 mm (p/n CP801505)
FID Restrictor	Fused silica tubing, 0.7 m, 0.25 mm (p/n CP802505)
Septum Purge Flow Mode	Standard at 3 mL/min
Purge Flow to Split Vent	15 mL/min at 0.75 minutes
GC/FID Parameters (Constant Makeup and Fuel Flow)	
Makeup Gas	He
Heater	300 °C
Air Flow	400 mL/min
H_2 Flow	40 mL/min
Make up flow	25 mL/min
Agilent 5977B GC/MS Conditions	
Transfer Line	260 °C
Acquisition Mode	Scan
Solvent Delay	4 minutes
Tune File	atune.u
Gain	1
MS Source Temperature	280 °C
MS Quad Temperature	150 °C

Easy selection and ordering information

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MyList of columns and supplies for HJ 1067-2019

Description	Part Number
Standards and Solvents	
B.E.T.X. standard, 1 mL, methanol, 2000 µg/mL	BTX-2000N
B.E.T.X. standard, 1 mL, methanol, 100 µg/mL	BTX-100-1
InfinityLab Ultrapure LC/MS water, 1 L	5191-4498
InfinityLab Ultrapure LC/MS methanol	5191-4497
GC Column and Column Connectors	
Agilent J&W HP-INNOWax, 30 m × 0.32 mm, 0.5 µm	19091N-213I
Agilent J&W DB-624 UI, 30 m × 0.25 mm, 1.4 µm (confirmation column)	122-1334UI
Column nut, collared, self-tightening, inlet/detector	G3440-81011
Ferrule, 0.4 mm id, 15% graphite/85%Vespel, 0.1 to 0.25 mm column, 10/pk	5181-3323
GC Inlet Supplies	
Liner: Straight, deactivated, 2 mm id, split/splitless	5181-8818
BTO inlet septa, 11 mm, 50/pk	5183-4757
BTO inlet septa, 11 mm, 100/pk	5183-4757-100
Ultra-Inert gold seal with washer, 10/pk	5190-6145
Ultra-Inert gold seal with washer, 50/pk	5190-6149
Headspace Supplies	
Sample probe, deactivated, for Agilent 7697A headspace sampler	G4556-63825

Description	Part Number
1 mL sample loop, inert	G4556-80106
Transfer Line Connections	
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, each	0100-2594
Headspace Vials and Caps	
Vial, screw top, headspace, amber, round bottom, 20 mL, 23 x 75 mm, 100/pk	5188-6537
Caps/septa, screw, headspace, 18 mm, silver, magnetic, PTFE/silicone septa, 100/pk.	8010-0139
Amber, crimp, flat bottom, 20 mm, 20 mL, 100/pk	5067-0226
Cap, crimp, PTFE/silicone, 20 mm, 100/pk	5183-4477
Crimper, manual for 20 mm caps	5040-4669
A-line e-crimper, electronic for 20 mm caps	5191-5615
Gas Clean System	
Gas Clean kit for 8890 and 8860; includes carrier gas filter, 1/8-inch connection unit with mounting bracket and Gas Clean senso	CP179880
Gas Clean carrier gas purifier replacement cartridge	CP17973
Gas Clean Carrier Gas Kit for 7890	CP17988

MyList of columns and supplies for ISO 17943-2016

Description	Part Number
Standards and Solvents	
B.E.T.X. standard, 1 mL, methanol, 2000 µg/mL	BTX-2000N
B.E.T.X. standard, 1 mL, methanol, 100 µg/mL	BTX-100-1
InfinityLab Ultrapure LC/MS water, 1 L	5191-4498
InfinityLab Ultrapure LC/MS methanol	5191-4497
GC Column and Column Connectors	
Agilent J&W DB-5ms Ultra Inert GC Column, 30 m, 0.25 mm, 0.25 µm (recommended)	122-5532UI
Agilent J&W DB-624 Ultra Inert GC Column, 30 m, 0.25 mm, 1.40 µm (resolves m/p xylene isomers)	122-1334UI
Agilent J&W CP-Sil 5 CB GC column, 30 m, 0.25 mm, 1.00 µm	CP8770
Column nut, collared, self-tightening, inlet/detector	G3440-81011
Column nut, collared, self-tightening, MSD	G3440-81013
Ferrule, 0.4 mm id, 15% graphite/85% Vespel, 0.1 to 0.25 mm column, 10/pk	5181-3323
Ultimate Plus deactivated fused silica tubing, 5 m, 0.15 mm (MSD restrictor)	CP801505
Ultimate Plus deactivated fused silica tubing, 5m, 0.25 mm (FID restrictor)	CP802505
GC Inlet Supplies	
Inlet liner, Ultra Inert, splitless, straight, 0.75 mm id, each	5190-4048
Inlet liner, Ultra Inert, splitless, straight, 0.75 mm id, 5/pk	5190-4056
BTO inlet septa, 11 mm, 50/pk	5183-4757
BTO inlet septa, 11 mm, 100/pk	5183-4757-100
Ultra Inert gold seal with washer, 10/pk	5190-6145
Ultra Inert gold seal with washer, 50/pk	5190-6149
Supplies for HS-SPME	
CAR-WR/PDMS 95 µm SPME fiber, 3/pk	5191-5875
Smart SPME fiber, carbon wide range/PDMS, 95/10, dark blue, 3/pk	5610-5875
SPME Arrow, carbon WR/PDMS (carbon wide range, polydimethylsiloxane), 1.10 mm, 120 µm, light blue, 3/pk	5191-5859

Description	Part Number
Smart SPME Arrow, carbon WR/PDMS (carbon wide range, polydimethylsiloxane), 1.10 mm, 120 µm, light blue, 3/pk	5610-5859
SPME fiber or arrow manual injection kit	5191-5877
PAL3 Alignment ring (Grey) f S/SL Inlet (for use with 5191-5877)	G7371-67001
Merlin Microseal 100 psi nut	5182-3445
Merlin Microseal general purpose (100 psi) replacement Microseal	5182-3444
Merlin Microseal SPME kit, for Varian/Bruker 1079 GCs, 23 gauge	392609901
Merlin Microseal SPME replacement Microseal, for Varian/Bruker 1079 GCs, 23-gauge	392609902
Merlin Microseal nut for use with SPME Arrows	5182-3446
Replacement Microseals for use with 1.1 mm Arrow SPME Probes	5182-3447
Replacement Microseals for use with 1.5 mm Arrow SPME Probes	5182-3448
Headspace Vials and Caps	
Vial, screw top, headspace, amber, round bottom, 20 mL, 23 x 75 mm, 100/pk	5188-6537
Caps/septa, screw, headspace, 18 mm, silver, magnetic, PTFE/silicone septa, 100/pk	8010-0139
MS Source Parts	
Filament, inert	G7005-60061
Draw-out plates 9 mm (recommended)	G3440-20022
Draw-out plates 6 mm, inert	G2589-20045
Gas Clean system	
Gas Clean kit for 8890 and 8860; includes carrier gas filter, 1/8-inch connection unit with mounting bracket and Gas Clean sensor	CP179880
Gas Clean carrier gas purifier replacement cartridge	CP17973
Gas Clean Carrier Gas Kit for 7890	CP17988

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