

## Environmental analysis

# Determination of BTEX and volatile organic compounds (VOCs) in drinking water by GC-MS/MS coupled to static headspace and solid-phase microextraction sampling

## Authors

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## Keywords

Volatile organic compounds (VOCs), BTEX, drinking water, gas chromatography-mass spectrometry, GC-MS, triple quadrupole, TSQ 9000 mass spectrometer, ExtractaBrite ion source, static headspace, HS, solid-phase microextraction, SPME Arrow

## Goal

The aim of this application note is to report the analytical performance of static headspace (SHS) and solid-phase microextraction using Arrow technology (SPME Arrow) for the determination of benzene, toluene, ethylbenzene, and xylenes (BTEX) and chlorinated and brominated volatile organic compounds (VOCs) in drinking water using a Thermo Scientific™ TSQ™ 9000 triple quadrupole GC-MS/MS system.

## Introduction

Volatile organic compounds (VOCs) are characterized by a high vapor pressure and low water solubility and are typically used in industrial applications, petroleum fuels, hydraulic fluids, paint thinners, and dry-cleaning agents. Their presence in the environment is thus strongly dependent on human activities. VOCs easily evaporate into air at ambient temperature and dissolve in water leading to contamination of water resources.<sup>1</sup> This poses serious concerns for human health as many VOCs are known, or suspected, to be human carcinogens.<sup>1</sup> Regulatory authorities all over the world have established limits to control the amount of VOCs in drinking water, groundwater, or surface water (e.g., Safe Drinking Water Act (SDWA) in the USA or the European Directive 2008/105/EC),<sup>2,3</sup> therefore, public water service providers must ensure that distributed drinking water is in compliance with the maximum contaminant levels established for VOCs.<sup>4</sup>

Due to the high volatility of the compounds, analysis of VOCs is usually performed using gas chromatography coupled to static headspace sampling (SHS),<sup>5,6</sup> which offers the advantage of quick and minimal sample preparation combined with lower consumption of reagents and solvents. However, one of the main limitations of this sampling technique is the relatively low sensitivity, especially regarding the regulatory limits that have been established for certain VOCs, such as vinyl chloride.

Solid-phase microextraction (SPME)<sup>7</sup> has proven to be an effective alternative to SHS, combining extraction of VOCs and enrichment in a single step and consequently allowing lower detection limits to be achieved. It consists of a fiber coated with an organic solid phase that, when exposed to the sample, extracts and concentrates the analytes using selective absorptive/adsorptive processes, providing improved extraction efficiency and superior sensitivity. The fiber can be exposed in the vapor phase above the liquid or solid matrix (headspace-SPME) or directly immersed in the liquid sample (direct immersion-SPME) offering the flexibility to analyze several matrices with one single solution.

The advantages offered by SPME led to the adoption of this sampling technique in many official methods.<sup>8-10</sup> For example, the method specified by ISO 17943:2016<sup>11</sup> applies SPME for the determination of VOCs, including halogenated hydrocarbons, gasoline additives, volatile aromatic compounds, and highly odorous substances in drinking water, groundwater, surface water, and treated wastewater.

In this study, the performance of SHS and SPME sampling techniques were evaluated for the determination of chlorinated and brominated VOCs and BTEX in drinking water. The TSQ 9000 GC-MS/MS provided ease-of-use and operational flexibility in both single ion monitoring (SIM) acquisition mode for fast screening of samples and selected reaction monitoring (SRM) acquisition mode when higher selectivity was required to reduce interferences. Hydrogen was used as carrier gas for these experiments, providing good separation efficiency in shorter run times.

## Experimental

A TSQ 9000 triple quadrupole mass spectrometer featuring Thermo Scientific™ NeverVent™ technology was coupled to a Thermo Scientific™ TRACE™ 1310 gas chromatograph equipped with a Thermo Scientific™ iConnect Split/Splitless (SSL) injector. The Thermo Scientific™ ExtractaBrite™ ion source and the NeverVent option offered proven robustness and sensitivity to meet regulatory requirements, even allowing switching between EI and CI modes without breaking the MS vacuum. To confidently stay ahead to the toughest regulatory methods and business demands, the new Thermo Scientific™ TSQ 9610 GC-MS/MS coupled to the Thermo Scientific™ TRACE™ 1600 Series GC offers

the benefits of the ExtractaBrite ion source combined with the new Thermo Scientific™ XLXR™ detector for extended lifetime and dynamic range for similar and even better results.<sup>12</sup> A Thermo Scientific™ TriPlus™ RSH autosampler configured for SHS and SPME Arrow sampling was used to automate analyte extraction and transfer into the analytical system. To ensure the extraction of a wider number of analytes, a dual phase carbon WR/PDMS coated fiber (Thermo Scientific™ SPME Arrow fiber, Carbon Wide Range, P/N 36SA12B1) was selected and used for trace-level volatiles determination. Chromatographic separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-624SiIMS capillary column, 20 m × 0.18 mm × 1.0 μm (P/N 26059-4950). The TriPlus RSH autosampler allows overlap of independent chromatographic injections. Combined with a fast GC oven ramp, it ensures a short cycle time, enabling high sample throughput without compromising the chromatographic performance. For advanced automation, the new Thermo Scientific™ TriPlus™ RSH SMART autosampler provides an additional layer of reliability and confidence in the analytical results thanks to the automatic SMART syringes, fiber identification, and usage tracking capabilities for a smarter management of the consumables.<sup>13</sup>

Additional SHS and HS-SPME Arrow and GC-MS/MS parameters as well as a complete list of the target compounds are detailed in Appendixes 1 and 2, respectively.

## Data acquisition, processing, and reporting

Data was acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. Integrated instrument control ensures full automation of the entire analytical workflow from sample incubation and extraction to data analysis, processing, customizable reporting, and storage in compliance with the United States Food and Drug Administration Title 21 Code of Federal Regulations Part 11 (Title 21 CFR Part 11).

## Standard and sample preparation

### Standard preparation

Volatile organic compounds standard mix (P/N 126253-01) and BTEX standard mix (P/N 120340-01) were purchased from o2si smart solutions. Tap water, previously tested negative for the presence of VOCs, was used as diluent.

The VOCs standard mix was diluted to obtain two sets of calibration solutions ranging from 0.5 to 20 μg/L (ppb) for VOCs assessments using SHS sampling and 0.1 to 2 μg/L for vinyl chloride determination using SPME Arrow extraction. BTEX were assessed using SHS sampling over a concentration range of 0.3 to 3.0 μg/L. Each calibration solution (10 mL) was transferred into 20 mL screw top headspace vials (P/N 6ASV20-1, with caps, P/N 6PMSC18-ST2) for analysis.

Drinking water samples, previously tested negative for VOCs, were spiked at the regulatory limits (VOCs and BTEX: 0.3 µg/L, vinyl chloride: 0.1 µg/L), and 10 mL aliquots were transferred into 20 mL screw top headspace vials before analysis.

Calibration solutions and spiked water samples were used to assess method linearity, sensitivity, recovery, and repeatability by using both SHS and SPME Arrow sampling techniques.

### Sample preparation for drinking water samples

Real water samples were provided by CAP Holding, a company that manages the Integrated Water Service in about 200 municipalities belonging to the Metropolitan City of Milan. Sample aliquots (10 mL) were transferred into 20 mL screw top headspace vials before analysis and used for method validation purposes by running typical sequences including calibration curves and QC spiked at the regulatory limits.

## Results and discussion

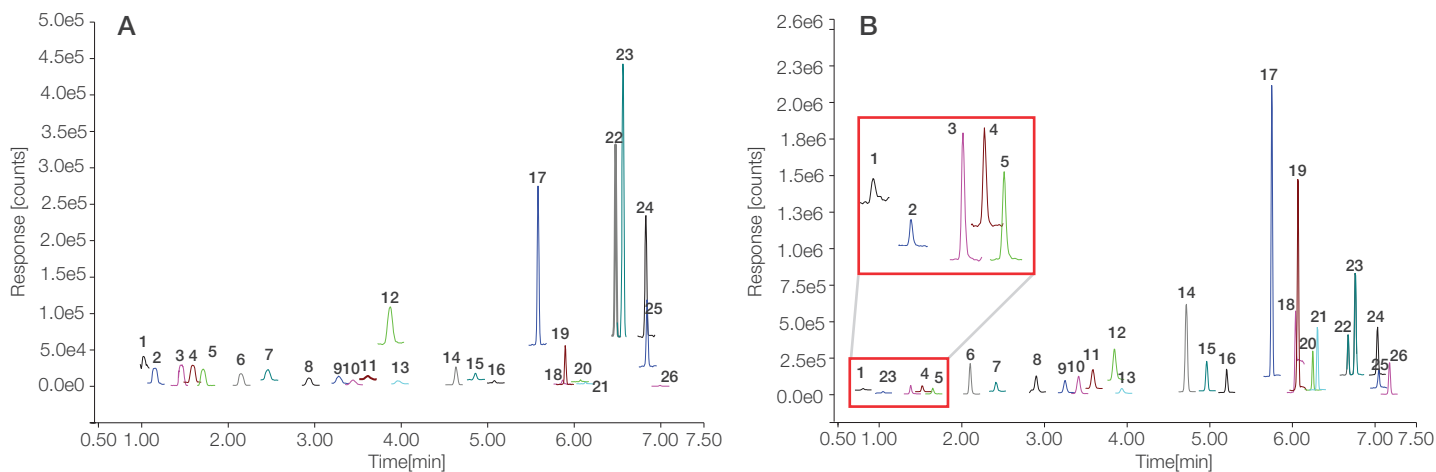
### Chromatography

The high thermal stability, low-bleed, and mid-polarity of the TraceGOLD TG-624SiIMS capillary column offered ideal chromatographic performance and helped to simplify method development. The use of the headspace sampling effectively removed the matrix, so that a clean sample was injected onto the GC, which helped in turn to reduce baseline noise. This allowed

for faster sample analysis, and operations were simplified by using a *t*-SIM acquisition mode. The SHS sampling technique provided adequate sensitivity to meet the regulatory limits set at 0.3 µg/L for the investigated VOCs and BTEX with the exception of vinyl chloride, for which the enrichment through the SPME Arrow technique was required to achieve the regulatory threshold set at 0.1 µg/L. As an example, the *t*-SIM acquisitions of VOCs and BTEX standards spiked at 0.3 µg/L (SHS extraction) and 0.1 µg/L (SPME Arrow) are shown in Figure 1.

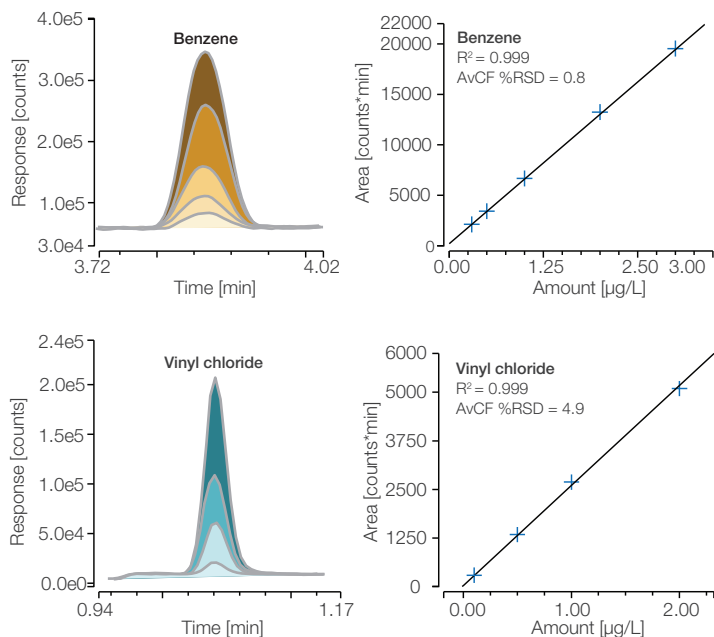
### Linearity and method detection limit (MDL)

Calibration curves ranging from 0.50 to 20 µg/L for VOCs and from 0.3 to 3.0 for BTEX were used to assess method linearity and detection limits using SHS extraction. Linearity for HS-SPME extraction was evaluated by injecting four VOC calibration standards ranging from 0.10 to 2.0 µg/L. External calibration curves were plotted using a linear fit and acceptance criteria for linearity were: (i) coefficient of determination ( $R^2$ ) > 0.990, (ii) average calibration factor %RSD (AvCF %RSD) < 20%, and (iii) concentration tolerance of 25% at the lowest calibration point. All three acceptance criteria were met for both SHS and HS-SPME sampling techniques, with average  $R^2$  of 0.999 and 0.996, respectively, AvCF %RSD < 9%, and concentration deviations within 25% of the expected values at the lowest calibration point, as reported in Appendix 3. Examples of calibration curves for benzene (SHS sampling) and vinyl chloride (HS-SPME sampling) are reported in Figure 2.



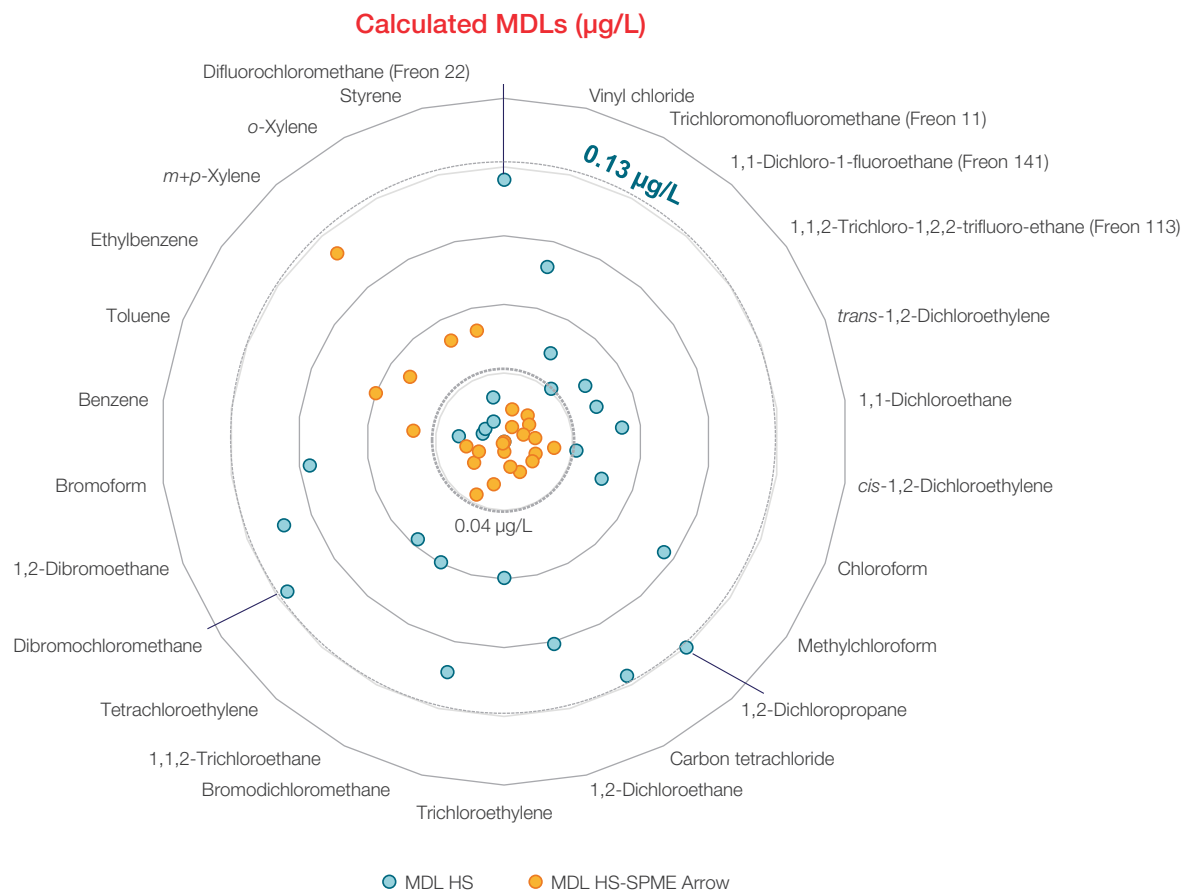
1=1,1-Difluoroethane (Freon 22), 2=Vinyl chloride, 3=1,1,1-Trichloroethane (Freon 113), 4=1,1,1-Trichloro-2,2,2-trifluoroethane (Freon 113), 5=1,1,1-Trichloro-2,2,2-trifluoroethane (Freon 113), 6=*trans*-1,2-Dichloroethane, 7=1,1-Dichloroethane, 8=*cis*-1,2-Dichloroethane, 9=Chloroform, 10=Methyl-Chloroform, 11=Carbon tetrachloride, 12=Benzene, 13=1,2-Dichloroethane, 14=Trichloroethylene, 15=1,2-Dichloropropane, 16=Bromodichloromethane, 17=Toluene, 18=1,1,2-Trichloroethane, 19=Tetrachloroethylene, 20=Dibromochloromethane, 21=1,2-Dibromoethane, 22=Ethylbenzene, 23=*m,p*-Xylene, 24=*o*-Xylene, 25=Styrene, 26=Bromoform

Figure 1. *t*-SIM acquisition for tap water samples spiked with VOCs and BTEX. (A) at 0.3 µg/L, SHS sampling; (B) at 0.1 µg/L, SPME Arrow sampling.



**Figure 2. Examples of calibration curves for benzene (SHS sampling, 0.3–3.0 µg/L) and vinyl chloride (HS-SPME sampling, 0.1–2.0 µg/L). R<sup>2</sup> and AvCF %RSD are annotated.**

To evaluate the method detection limits, tap water samples (n=10) were spiked with BTEX at 0.3 µg/L and VOCs at 0.5 µg/L for SHS sampling, and BTEX at 0.1 µg/L and VOCs at 1.0 µg/L for HS-SPME sampling. MDLs were then calculated considering the one-tailed Student's *t*-test values for the corresponding n-1 degrees of freedom at 99% confidence and multiplying them for the standard deviation of the replicated analysis. Calculated MDLs resulted in the range of 0.01–0.13 µg/L as reported in Figure 3 and Appendix 3, with recoveries between 60 and 130%. HS-SPME Arrow sampling was confirmed to be the required solution when lower limits of detection need to be achieved. Remarkably lower extraction efficiency was observed for difluorochloromethane as a result of the low affinity for the coating phase, thus resulting in poor linearity R<sup>2</sup> < 0.95 and MDL > 20 µg/L. In a similar way, the lower affinity of toluene and xylenes for the carbon WR/PDMS coating phase compared to the DVB/Carbon WR/PDMS (divinylbenzene/carbon WR/PDMS) can explain the higher MDLs for the high boiling BTEX compared to the SHS sampling.<sup>14</sup>

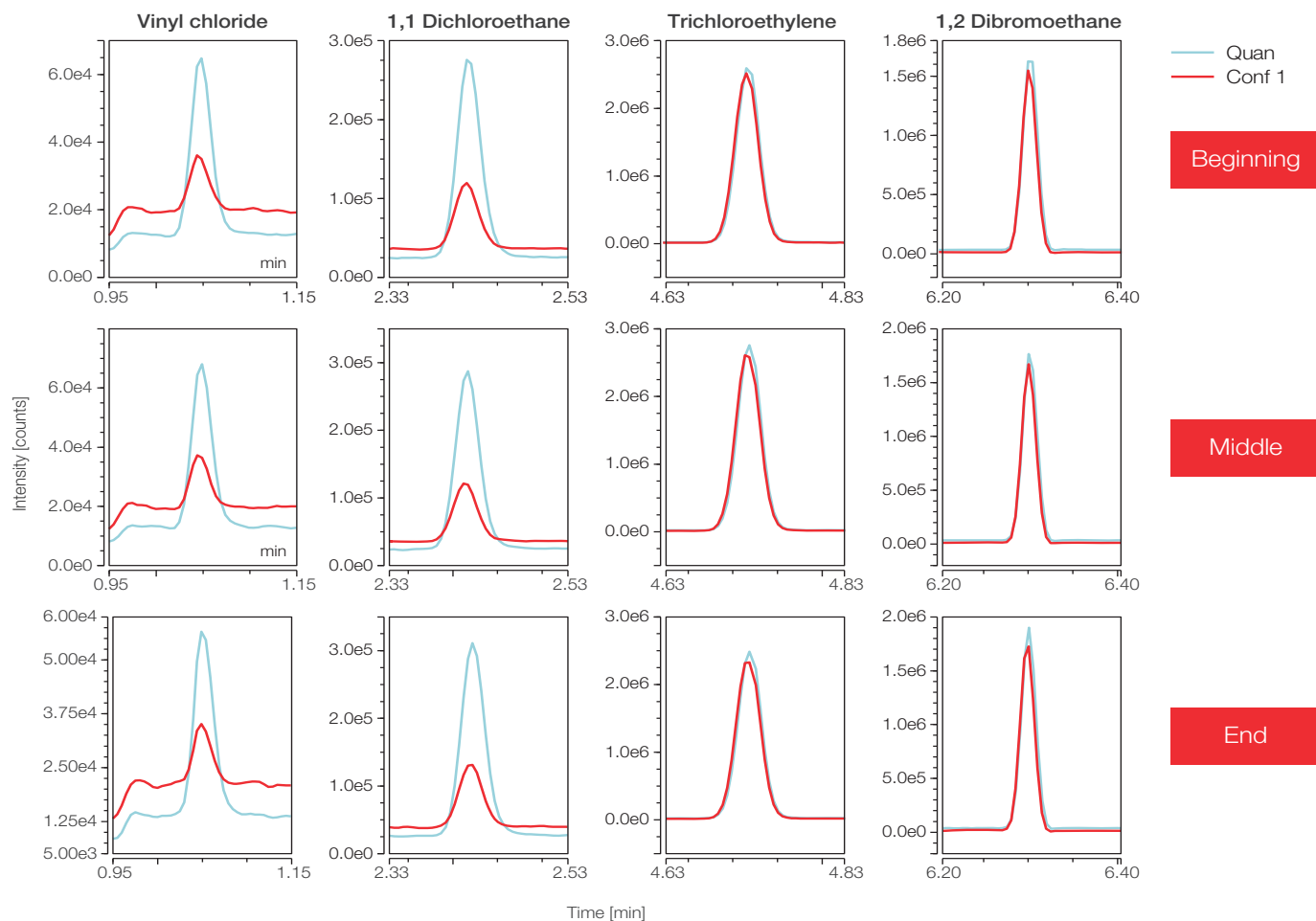


**Figure 3. Calculated MDLs for VOCs using both SHS and HS-SPME Arrow sampling. Overall HS-SPME Arrow sampling was confirmed to be the required solution to achieve lower limits of detection.**

## Method validation for everyday analysis

Method performance for everyday analysis was evaluated for both sampling techniques by running two sequences including calibration curves, spiked tap water samples, QCs, and real water samples for a period of approximately 48 hours (n=129 samples in total). An empty vial was run every 10 samples to monitor the carryover. To evaluate system stability over time, a calibration curve and a QC spiked at 0.5 µg/L were run at the beginning, middle, and end of the sequence. Overall retention time was

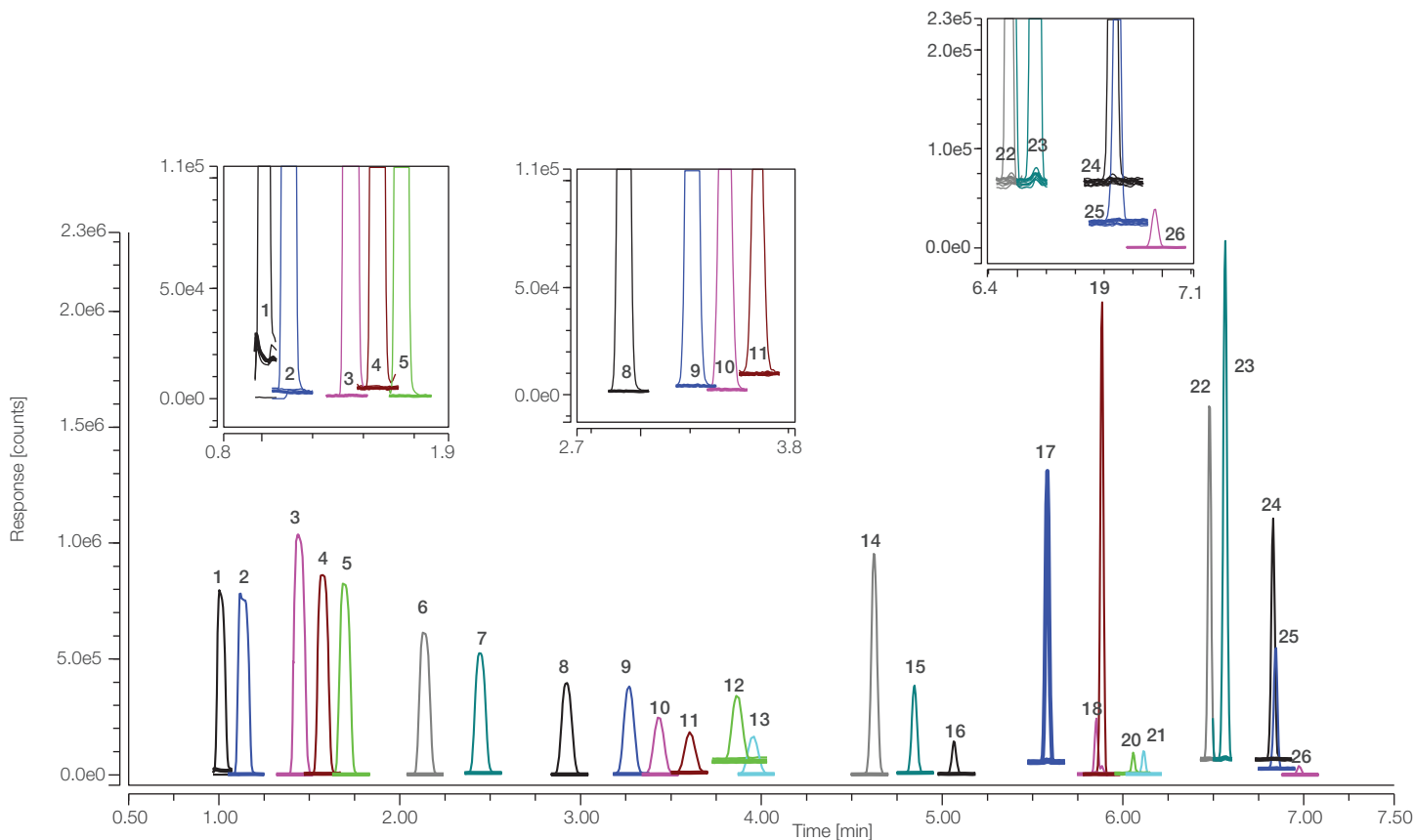
stable with a standard deviation of less than 0.04 minutes. Absolute peak area %RSDs, calculated concentrations, and ion ratios were well within ±15% of the expected values, and examples are reported in Figure 4 for HS-SPME Arrow sampling. Carryover could not be detected (less than 0.01%) for both sampling techniques when running an injection from an empty vial. As an example, the XICs for empty vials run every n=10 samples over an 80-sample sequence with SHS sampling are shown in Figure 5.



Peak name	RT (min)			Absolute peak area (counts * min)			Amount (µg/L)			Ion ratio (%)			
	Beginning	Middle	End	Beginning	Middle	End	Beginning	Middle	End	Expected	Beginning	Middle	End
Vinyl chloride	1.05	1.05	1.05	1339	1536	1127	0.50	0.58	0.42	34.04	29.44	28.48	28.86
1,1 Dichloroethane	2.42	2.42	2.42	8196	8445	8646	0.55	0.57	0.59	32.26	32.93	33.68	34.96
Trichloroethylene	4.72	4.72	4.72	83032	87967	78875	0.52	0.55	0.49	99.47	99.32	98.95	98.90
1,2 Dibromoethane	6.30	6.30	6.30	33127	34863	36912	0.51	0.54	0.58	93.22	92.07	93.91	93.08

Figure 4. Examples of XICs for qualifier and quantifier ions for calibration standard and QC samples spiked at 0.5 µg/L run at the beginning, middle, and end of a typical sequence (HS-SPME Arrow sampling). Retention times were stable across the entire sequence with absolute peak area %RSDs, calculated concentrations, and ion ratios (expected and measured) within 15% of the expected values.





1=1,1-Difluoroethane (Freon 22), 2=Vinyl chloride, 3=Trichloroethene (Freon 11), 4=1,1-Dichloro-1-fluoroethane (Freon 141), 5=1,1,1-Trichloro-2,2,2-trifluoroethane (Freon 113), 6=*trans*-1,2-Dichloroethene, 7=1,1-Dichloroethane, 8=*cis*-1,2-Dichloroethene, 9=Chloroform, 10=Methyl-Chloroform, 11=Carbon tetrachloride, 12=Benzene, 13=1,2-Dichloroethane, 14=Trichloroethylene, 15=1,2-Dichloropropane, 16=Bromodichloromethane, 17=Toluene, 18=1,1,2-Trichloroethane, 19=Tetrachloroethylene, 20=Dibromochloromethane, 21=1,2-Dibromoethane, 22=Ethylbenzene, 23=*m,p*-Xylene, 24=*o*-Xylene, 25=Styrene, 26=Bromoform

**Figure 5. Overlaid XICs for empty vials (n=8) run every n=10 samples and a VOCs/BTEX standard at 0.3 µg/L.** Carryover was assessed by running an 80-sample sequence (SHS sampling) including calibration curves, spiked tap water samples, and real water samples. Empty vials were run every n=10 samples to monitor the carryover. The insets show zoomed details of the overlaid XICs for empty vials and standard solutions.

## Conclusions

The TSQ 9000 triple quadrupole GC-MS/MS system in combination with the TriPlus RSH autosampler configured for SHS and HS-SPME Arrow sampling allows for robust and reliable routine analysis of BTEX and VOCs in drinking water in compliance with the regulatory limits of quantitation, making this configuration ideal for analytical testing laboratories requiring fast and high-throughput testing.

- SHS and HS-SPME sampling significantly reduce the efforts required for sample preparation step and ensure fully automated sample extraction and pre-concentration in a single step.
- SHS sampling provided adequate sensitivity to meet the regulatory limits set at 0.3 µg/L for the investigated VOCs and BTEX, with the exception of vinyl chloride. For this compound, the SPME Arrow technique was used to reach the regulatory limits set at 0.1 µg/L.
- Acceptance criteria for linearity of the method were met for both SHS and HS-SPME sampling techniques with average  $R^2$  values of 0.999 and 0.996, respectively. AvCF %RSD was found to be <9% and concentration deviations were found within 25% of the expected values at the lowest calibration point.
- Calculated MDLs resulted in the range of 0.01–0.13 µg/L with recovery between 60 and 130%. HS-SPME Arrow sampling is required to reach lower limits of detection compared to the SHS sampling technique, especially for critical VOCs such as vinyl chloride.
- System stability evaluation over time demonstrated stable retention times, as well as absolute peak area (RSD <11 %), calculated concentrations, and ion ratios within 15% the expected values.
- Less than 0.01% carryover could be detected for both sampling technique when bracketing samples with empty vials across 48-hour sequences.

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## Appendix 1

**Table A1. HS, HS-SPME Arrow, and GC-MS/MS experimental conditions for the analysis of VOCs**

TriPlus RSH - HS Autosampler parameters	
Injection type	HS
Syringe volume (mL) and type	2.5, HT gas-tight syringe (P/N 365Q2131)
Sample draw (mL)	1
Sampling depth mode	Standard
Agitator temperature (°C)	80
Incubation time (min)	25
Agitation speed (rpm)	250
Syringe temperature (°C)	90
Fill strokes volume (mL)	1.5
Fill strokes counts	3
Filling delay (s)	1
Pre-injection syringe flush	Enabled
Post-injection syringe flush (s)	120
Filling speed (mL/min)	30
Injection speed (mL/min)	30
Injection depth (mm)	45
Penetration speed (mm/s)	25
Pre-injection delay (s)	1
Post-injection delay (s)	3

iC-SSL parameters	
Injection temperature (°C)	230
Liner	SPME Arrow Liner Straight, 1.7 mm i.d. (P/N 453A0415)
Inlet module and mode	SSL, split
Split flow (mL/min)	10
Split ratio	20:1
Septum purge flow (mL/min)	5, constant
Carrier gas, flow (mL/min)	H <sub>2</sub> , 0.5

TRACE 1310 GC parameters	
<b>Oven temperature program</b>	
Temperature (°C)	50
Hold time (min)	4
Rate (°C/min)	40
Temperature 2 (°C)	130
Hold time (min)	2
GC run time (min)	8
<b>Column</b>	
TraceGOLD TG-624 SiIMS	20 m, 0.18 mm, 1.0 µm (P/N 26059-4950)

Appendix 1 (continued)

Table A1. HS, HS-SPME, and GC-MS/MS experimental conditions for the analysis of VOCs

TSQ 9610 Mass Spectrometer parameters	
Transfer line temperature (°C)	280
Ion source type and temperature (°C)	ExtractaBrite, 300
Ionization type	EI
Emission current (µA)	50
Electron energy (eV)	70
Acquisition mode	timed-SIM ( <i>t</i> -SIM)
Tuning parameters	EI SmartTune

TriPus RSH - SPME Arrow Autosampler parameters	
Injection type	SPME Arrow
Fiber type	Carbon WR/PDMS (P/N 36SA12B1)
Incubation / extraction temperature (°C)	40
Incubation time (min)	20
Agitation speed (rpm)	500
Extraction speed (rpm)	1000
Needle speed in vial (mm/s)	20
Needle depth in vial mode and depth (mm)	Custom, 20
Injection depth (mm)	70
Penetration speed (mm/s)	60
Desorption time (min)	1
Conditioning temperature (°C)	270
Pre-desorption conditioning time (min)	1
Post-desorption conditioning time (min)	3

iC-SSL parameters	
Injection temperature (°C)	270
Liner	SPME Arrow Liner Straight, 1.7 mm i.d. (P/N 453A0415)
Inlet module and mode	SSL, split
Split flow (mL/min)	5
Split ratio	10:1
Septum purge flow (mL/min)	Off
Carrier gas, flow (mL/min)	H <sub>2</sub> , 0.5

TRACE 1310 GC parameters	
Oven temperature program	
Temperature (°C)	35
Hold time (min)	0.1
Rate (°C/min)	50
Temperature 2 (°C)	125
Hold time (min)	4
Rate (°C/min)	40
Temperature 2 (°C)	130
Hold time (min)	2
GC run time (min)	9



## Appendix 2

Table A2. List of target VOCs, retention times (RT, min), and SIM ions (*m/z*)

Compound	RT (min) - HS	RT (min) - SPME	Quantifier ion ( <i>m/z</i> )	Qualifier ion ( <i>m/z</i> )
Difluorochloromethane (Freon 22)	1.00	0.81	51	67
Vinyl chloride	1.14	1.05	62	64
Trichloromonofluoromethane (Freon 11)	1.45	1.39	101	103
1,1-Dichloro-1-fluoroethane (Freon 141)	1.57	1.53	81	83
1,1,2-Trichloro-1,2,2-trifluoro-ethane (Freon 113)	1.70	1.66	101	151
<i>trans</i> -1,2-Dichloroethylene	2.13	2.11	61	96
1,1-Dichloroethane	2.45	2.42	63	65
<i>cis</i> -1,2-Dichloroethylene	2.92	2.91	61	96
Chloroform	3.26	3.26	83	85
Methylchloroform	3.43	3.42	97	99
Carbon tetrachloride	3.60	3.60	117	119
Benzene	3.88	3.85	78	77
1,2-Dichloroethane	3.94	3.95	62	64
Trichloroethylene	4.62	4.72	130	132
1,2-Dichloropropane	4.84	4.97	63	62
Bromodichloromethane	5.06	5.21	83	85
Toluene	5.58	5.75	91	92
1,1,2-Trichloroethane	5.85	6.04	97	83
Tetrachloroethylene	5.88	6.07	166	164
Dibromochloromethane	6.06	6.24	129	127
1,2-Dibromoethane	6.11	6.31	107	109
Ethylbenzene	6.48	6.67	91	106
<i>m+p</i> -Xylene	6.57	6.76	91	106
<i>o</i> -Xylene	6.84	7.03	91	106
Styrene	6.83	7.04	104	103
Bromoform	6.98	7.18	173	171

### Appendix 3

Table A3. Calibration ranges, as well as R<sup>2</sup>, AvCF %RSD, calculated MDL (µg/L), recovery (%), and absolute peak area %RSD for VOCs and BTEX by using SHS sampling

Peak name	SHS sampling						
	Retention time (min)	Calibration range (µg/L)	Coefficient of determination (R <sup>2</sup> )	AvCF %RSD	Calculated MDL (µg/L)	Recovery (%)	Absolute peak area %RSD
Difluorochloromethane (Freon 22)	1.00	0.5–20	0.9989	3.4	0.12	88	10.8
Vinyl chloride	1.14	0.5–20	0.9998	3.5	0.09	110	5.3
Trichloromonofluoromethane (Freon 11)	1.45	0.5–20	0.9999	1.1	0.05	88	3.6
1,1-Dichloro-1-fluoroethane (Freon 141)	1.57	0.5–20	0.9999	1.1	0.04	90	2.8
1,1,2-Trichloro-1,2,2-trifluoro-ethane (Freon 113)	1.70	0.5–20	0.9998	1.3	0.05	95	3.6
<i>trans</i> -1,2-Dichloroethylene	2.13	0.5–20	0.9995	2.2	0.05	106	3.4
1,1-dichloroethane	2.45	0.5–20	1.0000	0.6	0.06	95	4.0
<i>cis</i> -1,2-dichloroethylene	2.92	0.5–20	0.9999	1.2	0.04	120	2.7
Chloroform	3.26	0.5–20	0.9999	1.1	0.06	118	3.6
Methylchloroform	3.43	0.5–20	0.9997	1.8	0.09	111	6.3
Carbon tetrachloride	3.60	0.5–20	0.9990	3.3	0.13	105	9.1
1,2-Dichloroethane	3.94	0.5–20	1.0000	0.6	0.10	108	6.7
Trichloroethylene	4.62	0.5–20	0.9995	5.2	0.07	108	4.6
1,2-Dichloropropane	4.84	0.5–20	0.9998	1.3	0.13	114	8.2
Bromodichloromethane	5.06	0.5–20	0.9999	1.0	0.11	123	8.2
1,1,2-Trichloroethane	5.85	0.5–20	0.9996	2.1	0.07	130	3.9
Tetrachloroethylene	5.88	0.5–20	0.9994	2.6	0.07	119	4.6
Dibromochloromethane	6.06	0.5–20	0.9994	2.4	0.13	107	9.7
1,2-dibromoethane	6.11	0.5–20	0.9997	1.9	0.11	117	8.6
Bromoform	6.98	0.5–20	0.9995	5.4	0.10	112	6.3
Benzene	3.88	0.3–3.0	0.9999	0.8	0.03	96	3.5
Toluene	5.58	0.3–3.0	0.9999	1.1	0.02	96	2.2
Ethylbenzene	6.48	0.3–3.0	1.0000	0.7	0.02	95	2.1
<i>m+p</i> -Xylene	6.57	0.3–3.0	0.9999	1.0	0.01	98	1.7
<i>o</i> -Xylene	6.84	0.3–3.0	0.9998	1.2	0.02	99	2.9
Styrene	6.83	0.3–3.0	0.9999	0.9	0.03	96	3.5

**Appendix 3** (continued)

**Table A3. Calibration ranges, as well as R<sup>2</sup>, AvCF %RSD, calculated MDL (µg/L), recovery (%), and absolute peak area %RSD for VOCs and BTEX by using HS-SPME Arrow sampling**

Peak name	HS-SPME sampling						
	Retention time (min)	Calibration range (µg/L)	Coefficient of determination (R <sup>2</sup> )	AvCF %RSD	Calculated MDL (µg/L)	Recovery (%)	Absolute peak area %RSD
Difluorochloromethane (Freon 22)	0.81	0.1–2.0	< 0.950	n.a.	> 20	n.a.	n.a.
Vinyl chloride	1.05	0.1–2.0	0.9994	4.9	0.02	93	8
Trichloromonofluoromethane (Freon 11)	1.39	0.1–2.0	0.9931	8.4	0.02	97	4.3
1,1-Dichloro-1-fluoroethane (Freon 141)	1.53	0.1–2.0	0.9948	7.3	0.03	97	6.2
1,1,2-Trichloro-1,2,2-trifluoro-ethane (Freon 113)	1.66	0.1–2.0	0.9943	7.8	0.02	106	6.1
<i>trans</i> -1,2-Dichloroethylene	2.11	0.1–2.0	0.9930	8.5	0.02	95	5.2
1,1-dichloroethane	2.42	0.1–2.0	0.9902	9.7	0.02	95	5.3
<i>cis</i> -1,2-dichloroethylene	2.91	0.1–2.0	0.9970	5.0	0.03	97	4.3
Chloroform	3.26	0.1–2.0	0.9950	11.6	0.02	93	5
Methylchloroform	3.42	0.1–2.0	0.9980	8.1	0.02	97	5.5
Carbon tetrachloride	3.60	0.1–2.0	0.9940	13.1	0.02	100	5.7
1,2-Dichloroethane	3.95	0.1–2.0	0.9930	13.3	0.02	85	4.7
Trichloroethylene	4.72	0.1–2.0	0.9958	6.7	0.02	87	4.1
1,2-Dichloropropane	4.97	0.1–2.0	0.9920	14.0	0.01	86	5.5
Bromodichloromethane	5.21	0.1–2.0	0.9930	13.0	0.03	84	6.2
1,1,2-Trichloroethane	6.04	0.1–2.0	0.9928	6.6	0.04	89	4.5
Tetrachloroethylene	6.07	0.1–2.0	0.9992	3.0	0.01	89	3.3
Dibromochloromethane	6.24	0.1–2.0	0.9911	9.1	0.03	72	5.9
1,2-dibromoethane	6.31	0.1–2.0	0.9955	6.8	0.02	76	5.8
Bromoform	7.17	0.1–2.0	0.9974	8.2	0.03	60	7.0
Benzene	3.87	0.1–2.0	0.9998	1.2	0.05	98	2.6
Toluene	5.75	0.1–2.0	0.9997	1.8	0.07	98	2.4
Ethylbenzene	6.67	0.1–2.0	0.9996	2.0	0.06	98	2.7
<i>m+p</i> -Xylene	6.76	0.1–2.0	0.9997	1.7	0.12	98	2.9
<i>o</i> -Xylene	7.03	0.1–2.0	0.9995	2.0	0.06	99	2.9
Styrene	7.04	0.1–2.0	0.9995	2.1	0.06	99	3.1

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