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Environmental

An automated approach for the analysis of VOCs in drinking and surface water by using the TriPlus RSH SMART VOC Sample Prep Station

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Keywords

Automated sample preparation, TriPlus RSH SMART Sample Prep Station, volatile organic compounds, VOCs, drinking water, surface water, gas chromatography, TRACE 1610 GC, single quadrupole mass spectrometry, ISQ 7610 GC-MS

Goal

The aim of this study is to demonstrate the suitability of the Thermo Scientific™ TriPlus™ RSH SMART VOC Sample Prep Station for the analysis of volatile organic compounds (VOCs) in drinking and surface water by using a fully automated sample preparation workflow.

Introduction

Organic chemicals are widely used as ingredients in household products as well as fuels, industrial uses, and manufacturing. Through inappropriate use or disposal, they are released into the air as gases and can leach into ground water and wastewater. Consequently, they need to be considered as ubiquitous pollutants in the environment. In environmental analysis, classification is usually accomplished using a compound's volatility, either classifying them as volatile or semi-volatile organic compounds (VOCs and SVOCs, respectively). VOCs have a higher vapor pressure and lower water solubility than SVOCs. This compound class includes a variety of chemicals, some of which may have short- and long-term adverse health effects.[1] Environmental agencies worldwide strictly regulate the presence of VOCs in drinking[2] and surface water[3] by establishing the allowed limits and providing analytical methods[1] that may be considered when determining VOCs in water samples. The recent update to the Drinking Water Directive,[2] entered into force in January 2021, is the EU's main law in regulating the contaminant

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thresholds in drinking water, whereas the Environmental Quality Standard Directive establishes the allowed limits for contaminants in surface water.[3]

One of the main challenges in VOCs analysis is the sample preparation. These compounds are usually present at trace concentrations in a variety of complex matrices; therefore, they need to be extracted and pre-concentrated prior the analysis. Because of their chemical properties, they are also prone to evaporate or degrade, thus having limited stability for analysis. When dealing with VOCs analysis in water, multiple sample preparation techniques can be considered for extracting these compounds, such as solid-phase microextraction (SPME), purge-and-trap (P&T), liquid-liquid extraction (LLE), and headspace analysis (HS). Among these, P&T and HS sampling are the most common techniques for the analysis of aqueous samples. Headspace is a straightforward approach that allows for the extraction of volatile and very volatile compounds from non-volatile matrix in a fast and simple way, without the need for time-consuming sample preparation. Water samples are simply heated and maintained at a constant temperature in closed vials to promote the migration of volatile compounds from the matrix to the vapor phase (headspace). After equilibration, an aliquot of headspace is injected for analysis. Compared to other dynamic techniques like P&T where the volatile compounds are stripped continuously with an inert gas through the sample, the static headspace technique is not affected by foam formation and minimal maintenance of the system is required.

Internal standards are usually added to the sample vials prior to the sample preparation and used to monitor extraction efficiency. To achieve a reliable quantitative analysis, they are used in the data processing to compensate for sample loss, matrix effects, and variability of the detector. When dealing with HS sampling, the sample preparation is minimal, typically consisting of transferring the water sample into a HS vial and adding the ISTDs to a batch of samples before starting the analytical sequence (sample incubation followed by GC analysis). However, with this approach, sample vials may remain on the autosampler tray for hours, especially in case of long sequences, with possible impact on sample integrity and overall data repeatability, affecting quantitative analysis.

With the TriPlus RSH SMART VOC Sample Prep Station, reagents can be added immediately before the sample incubation by using a dedicated dual head configuration (Figure 1). One head is equipped with a liquid tool to dispense the reagents (e.g., ISTD or calibration standard) into the sample vial, whereas the second head moves the vial into the incubator for headspace analysis. The possibility of adding fresh reagents just before the incubation increases the stability of samples, therefore increasing the accuracy of the quantitation of target analytes during data reprocessing. Table 1 shows the absolute peak area %RSD comparison for two batches of samples bracketed by QCs spiked with a VOC mix at 10 ng/mL and ISTD/surrogate solutions. In batch 1 the reagents were automatically spiked before starting the sequence using a dedicated script, whereas in batch 2, the reagents were added to each sample just before incubation, with an improvement of the average RSD from 8.4% to 3.2%.

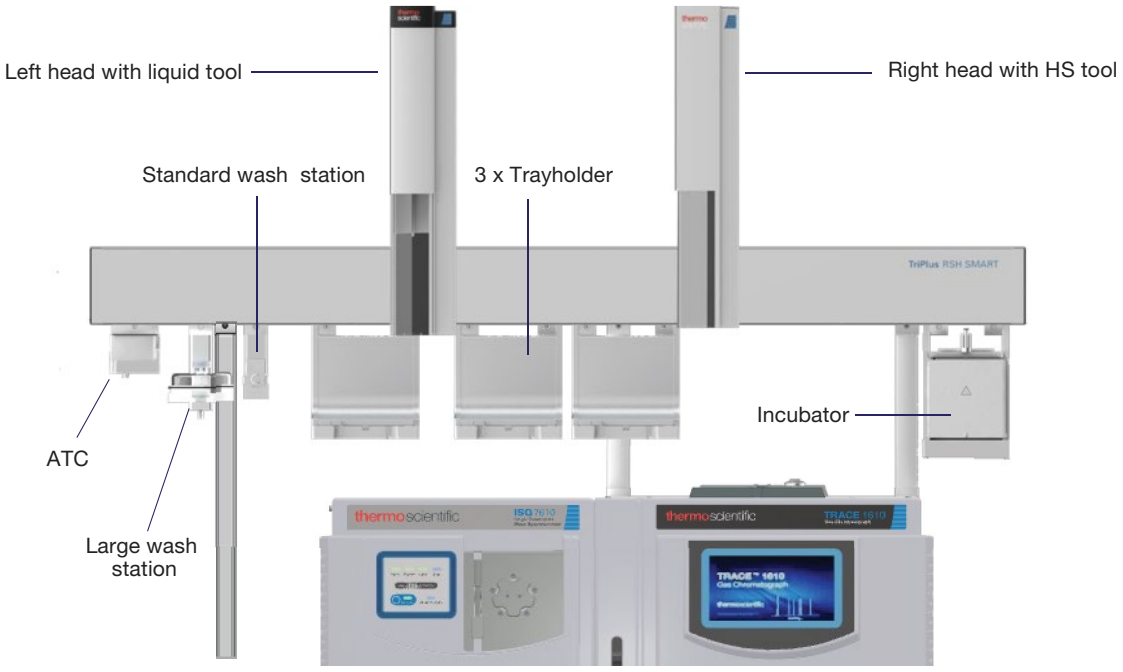


Figure 1. TriPlus RSH SMART VOC Sample Prep Station configuration for automated analysis of VOCs

Table 1. Absolute peak area %RSD comparison between two batches of samples bracketed by QCs spiked with a VOC mix at 10 ng/mL and ISTD/surrogate solutions. In batch 1 the reagents were automatically spiked before starting the sequence, whereas in batch 2 the reagents were added to each sample just before incubation.

	QC absolute peak area %RSD (n=6)	
Peak name	Batch 1	Batch 2
Dichlorodifluoromethane	5.9	5.7
Vinyl chloride	5.8	8.1
Chloroethane	7.2	2.6
Trichlorofluoromethane	4.8	2.8
1,1-Dichloroethene	5.9	3.6
Methylene chloride	5.1	1.2
1,2-Dichloroethene (Z cis)	5.9	2.9
1,1-Dichloroethane	5.6	1.9
1,2-Dichloroethene (E)	5.9	3.2
Bromochloromethane	8.1	1.5
Chloroform (Trichloromethane)	4.8	1.6
1,1,1-Trichloroethane	5	2
2,2-Dichloropropene	4.9	2.1
Surr Dibromofluoromethane	5	1.5
ISTD Pentafluorobenzene	6.5	3.8
Carbon tetrachloride	5.1	2.5
Benzene	6.1	2.7
1,2-Dichloroethane	5.3	4
ISTD 1,4-Difluorobenzene	6.5	4
Trichloroethene	5.9	3.2
1,2-Dichloropropane	5.7	2
Dibromomethane	7	1.8
Bromodichloromethane	5.3	1.5
Surr Toluene D8	7.2	4.1
1.3-Dichloropropene (Z)	8.5	3.7
Toluene	7.6	4.2
1,1,2-Trichloroethane	5.3	2.9
Tetrachloroethene	7	2.5
1,3-Dichloropropane	7.5	1.7
Dibromochloromethane	6.2	1.4
1,2-Dibromoethane	18.6	2.1
ISTD Chlorobenzene D5	7.6	3.2

	QC absolute peak area %RSD (n=6)	
Peak name	Batch 1	Batch 2
Chlorobenzene	7	3.6
1,1,1,2-Tetrachloroethane	6.2	1.4
Ethylbenzene	8.9	4.6
m,p-Xylene	9.7	4.6
o-Xylene	9	4.1
Styrene	9.7	4.5
Bromoform	6.1	2.1
Isopropylbenzene (Cumene)	10.2	4.7
BFB 1-Bromo-4-fluorobenzene	8.6	3.4
1,1,2,2-Tetrachloroethane	4.4	2.1
Bromobenzene	7.1	3.5
1,2,3-Trichloropropane	14.7	3
n-Propylbenzene	12.3	4.4
1,3,5-Trimethylbenzene	12.9	4.7
2-Chlorotoluene	9.8	4.5
4-Chlorotoluene	11.2	3.7
tert-Butylbenzene	13.4	4.5
1,2,4-Trimethylbenzene	12.3	4.6
sec-Butylbenzene	14.4	4.3
4-Isopropyltoluene (*p*-Cymene)	15.3	4.9
1,3-Dicholorobenzene	9.9	2.2
ISTD 1,4-Dichlorobenzene D4	11	2.6
1,4-Dicholorobenzene	9.9	2.7
n-Butylbenzene	17.6	4.2
1,2-Dichlorobenzene	9	2.7
1,2-Dibromo-3-chloropropane	6.7	2.7
1,2,4-Trichlorobenzene	9.4	4.5
Hexachlorobutadiene	17.6	2.7
Naphtalene	8.8	4.3
1,2,3-Trichlorobenzene	8.3	4.3
Average RSD%	**8.4**	**3.2**

By using an automated approach, the analyst is only required to transfer the samples into the headspace vials, place them on the autosampler tray, and place the stock solutions containing the reagents to be dispensed, thus saving valuable analyst time, reducing the risk of human errors, and ensuring a safer laboratory environment with less exposure to harmful chemicals.

The TriPlus RSH SMART VOC Sample Prep Station is capable of processing up to 150 samples unattended. Sample capacity can be further extended up to 210 samples.

In this study, the reliability of an automated workflow including the generation of calibration curves, as well as internal standard addition for analysis of VOCs in drinking and surface water, was evaluated.

Experimental

Instrumentation

In these experiments, a TriPlus RSH SMART VOC Sample Prep Station was used to automate the calibration curve dilution and the internal standard addition by using a pre-compiled sequence of operations that is fully embedded in the Thermo Scientific™ Chromeleon™ 7.3 Chromatography Data System (CDS) for seamless and straightforward method set-up and instrument control (Figure 2). A detailed description of the autosampler configuration, including a complete list of suggested consumables, is reported in Appendix 1.

The TriPlus RSH SMART VOC Sample Prep Station was installed on top of a Thermo Scientific™ TRACE 1610 GC, equipped with a Thermo Scientific™ iConnect™ split/splitless injector working in HeSaver-H_2Safer mode, and coupled to a Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer.

Chromatographic separation was achieved using a Thermo Scientific™ TraceGOLD™ TG-624 SilMS, 20 m × 0.18 mm × 1.0 µm column (P/N 26059-4950). This column provided high inertness and thermal stability with maximum temperatures up to 320 °C. The phase thickness makes this column ideal for volatile organics analysis. Helium was used as carrier gas providing high chromatographic efficiency and inertness. The Thermo Scientific™ Helium Saver technology[4] ensured reduced helium consumption by using a cheaper gas (e.g., nitrogen) for inlet pressurization, analyte vaporization, and transfer to the analytical column and using helium only to feed the chromatographic column for the separation process.

Instrument parameters as well as a complete list of the target compounds, including quantifier and qualifier ions, are reported in Appendix 2.

Data acquisition, processing, and reporting

The TriPlus RSH SMART VOC Sample Prep Station instrument control is fully integrated in Chromeleon 7.3 CDS, ensuring a streamlined automated workflow covering on-line sample preparation, sequence setup, data acquisition, and reporting. The Chromeleon Environmental Analysis Extension Pack for U.S. EPA-based environmental applications provides a comprehensive set of GC-MS eWorkflow™ procedures for quick sequence set-up and reporting templates to make data review and reporting easier. Moreover, with the ever-evolving compliance requirements for data integrity and data security, Chromeleon CDS provides a secure platform for analytical laboratories to comply with modern regulatory guidelines including FDA 21 CFR Part 11 and European Commission (EU) Annex 11.

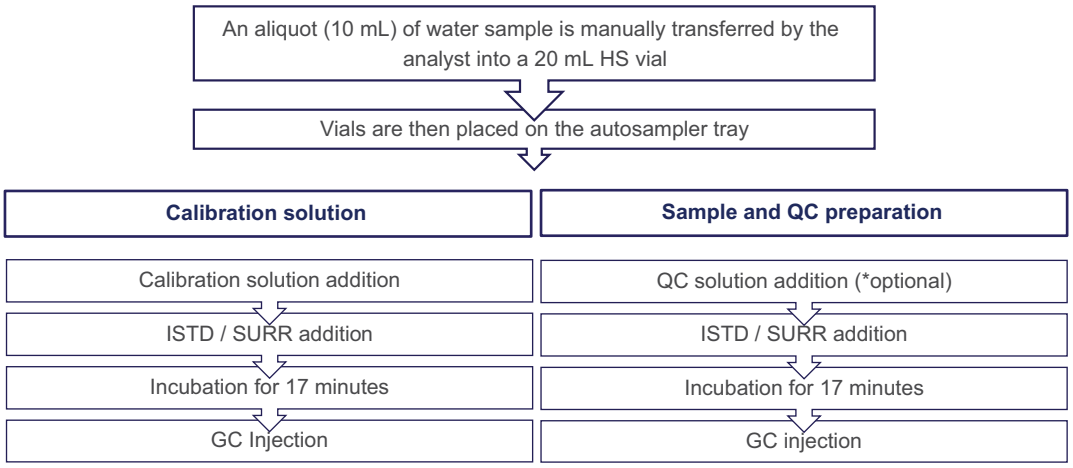


Figure 2. Schematic showing the workflow for automated preparation of calibration solution and addition of ISTD/surrogate mix to sample vials for analysis of VOCs

Standard and sample preparation

Calibration curve preparation

Multi-component standard solutions were purchased from Restek (8260 Volatile Organics Kit, 2000 µg/mL in methanol, P/N 30076) and diluted in methanol (Optima™ LC/MS grade, Fisher Scientific™, P/N A456-1) to obtain:

- Four calibration solutions (20 µg/mL, 2 µg/mL, 0.2 µg/mL, and 0.02 µg/mL)
- Internal standard and surrogate solution (20 µg/mL and 25 µg/mL, respectively).

These stock solutions were placed in the autosampler tray and different aliquots were automatically dispensed by the autosampler into 20 mL screw top headspace vials (P/N 6ASV20-1, caps P/N 6PMSC18-ST2), previously filled with tap water (10 mL) and containing solid sodium thiosulphate (>99,99%, Sigma-Aldrich, P/N 563188) to neutralize any residual chlorine, to produce a 10-point calibration curve and QC samples. The calibration curve ranged from 0.1 to 100 ng/mL according to the scheme reported in Appendix 3.

Sample preparation

Tap water samples and surface water samples were collected from different locations around the Milan metropolitan area. Solid sodium thiosulphate was added immediately after sample collection in the field. Samples were prepared for analysis by transferring 10 mL of the collected water into 20 mL screw top headspace vials.

An aliquot (10 µL) of the internal standard and surrogate solution (20 µg/mL and 25 µg/mL, respectively) was then automatically added by the autosampler to each sample immediately before vial incubation.

Results and discussion

Chromatography

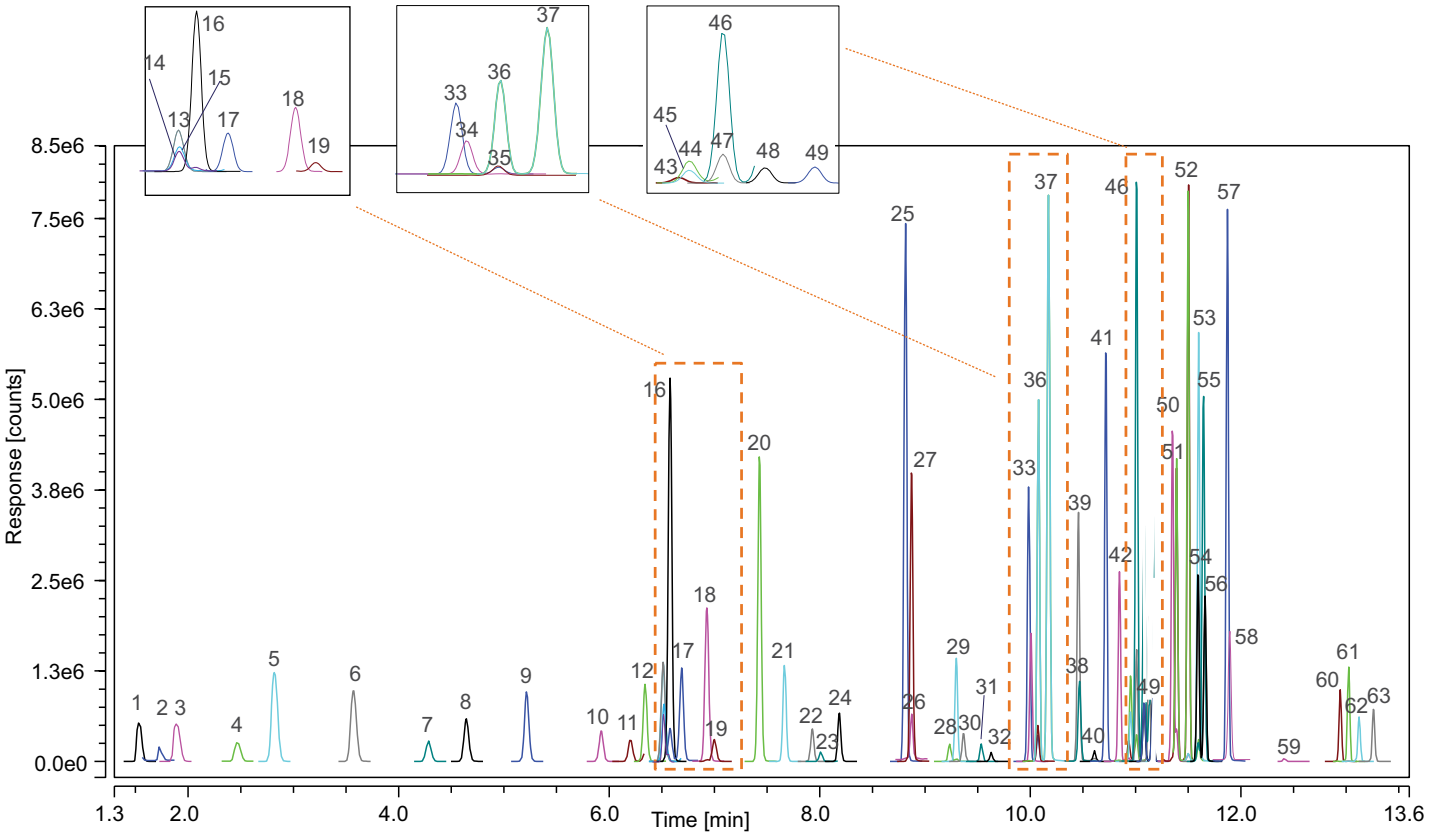
Headspace sampling allowed for the extraction of the target volatile analytes in a fast and simple way without the need for time-consuming sample preparation. A single ion monitoring (SIM) acquisition method allowed for simultaneous acquisition of multiple characteristic ions for each compound of interest, combining sensitivity with high selectivity, and thus ensuring a confident identification and subsequent quantification of analytes.

As an example, the SIM trace of a tap water sample spiked at 10 ng/mL with VOC mix, ISTD (20 ng/mL) and surrogate (25 ng/mL) is shown in Figure 3. The high thermal stability and superior inertness of the TraceGOLD TG-624 SilMS column ensured baseline chromatographic separation in a short analysis time (<14 minutes) for most of the target compounds. Very few exceptions could be identified based on their characteristic *m/z*.

Linearity and method detection limits (MDLs)

Two matrix-matched calibration curves in tap water ranging from 0.1 to 100 ng/mL were automatically diluted by the TriPlus RSH SMART VOC Sample Prep Station and used to evaluate the system repeatability for calibration curve preparation. All target analytes showed a linear trend with coefficient of determination (R^2) > 0.990, relative response factor (RRF) %RSD < 20% and calculated amount within 20% the expected values as reported in Appendix 4. Full range calibration curves (0.1–100 ng/mL) for benzene, dibromomethane, and 1,2,4-trimethylbenzene as well as an extracted ion chromatogram (XIC) showing the quantifier and qualifier ions for a tap water sample spiked at 0.1 ng/mL are reported as an example in Figure 4. The SIM trace showing all the target compounds in a tap water sample spiked with VOC mix at 0.1 ng/mL is also presented in Figure 4.

MDLs and precision were assessed using n=10 replicates of matrix-matched water samples spiked with VOC solution at 0.5 ng/mL, ISTD (20 ng/mL) and surrogate mix (25 ng/mL). Calculated MDLs were ≤ 0.17 ng/mL, with calculated absolute peak area %RSD < 20% for all compounds (Appendix 4).



Peak name	Peak no.
Dichlorodifluoromethane	1
Chloromethane	2
Vinyl chloride	3
Chloroethane	4
Trichlorofluoromethane	5
1,1-Dichloroethene	6
Methylene chloride	7
1,2-Dichloroethene (Z)	8
1,1-Dichloroethane	9
1,2-Dichloroethene (E)	10
Bromochloromethane	11
Chloroform (Trichloromethane)	12
1,1,1-Trichloroethane	13
2,2-Dichloropropene	14
Surr Dibromofluoromethane	15
ISTD Pentafluorobenzene	16
Carbon tetrachloride	17
Benzene	18
1,2-Dichloroethane	19
ISTD 1,4-Difluorobenzene	20
Trichloroethene	21
1,2-Dichloropropane	22
Dibromomethane	23
Bromodichloromethane	24
Surr Toluene D8	25
1.3-Dichloropropene (Z)	26
Toluene	27
1,1,2-Trichloroethane	28
Tetrachloroethene	29
1,3-Dichloropropane	30
Dibromochloromethane	31
1,2-Dibromoethane	32

Peak name	Peak no.
ISTD Chlorobenzene D5	33
Chlorobenzene	34
1,1,1,2-Tetrachloroethane	35
Ethylbenzene	36
m,p-Xylene	37
o-Xylene	38
Styrene	39
Bromoform	40
Isopropylbenzene (Cumene)	41
BFB 1-Bromo-4-fluorobenzene	42
1,1,2,2-tetrachloroethane	43
Bromobenzene	44
1,2,3-Trichloropropane	45
n-Propylbenzene	46
1,3,5-Trimethylbenzene	47
2-Chlorotoluene	48
4-Chlorotoluene	49
tert-Butylbenzene	50
1,2,4-Trimethylbenzene	51
sec-Butylbenzene	52
4-Isopropyltoluene (*p*-Cymene)	53
1,3-Dicholorobenzene	54
ISTD 1,4-Dichlorobenzene D4	55
1,4-Dicholorobenzene	56
n-Butylbenzene	57
1,2-Dichlorobenzene	58
1,2-Dibromo-3-chloropropane	59
1,2,4-Trichlorobenzene	60
Hexachlorobutadiene	61
Naphtalene	62
1,2,3-Trichlorobenzene	63

Figure 3. SIM trace showing an example of the chromatographic separation obtained for a tap water sample spiked at 10 ng/mL with VOC mix, ISTD (20 ng/mL), and surrogate (25 ng/mL)

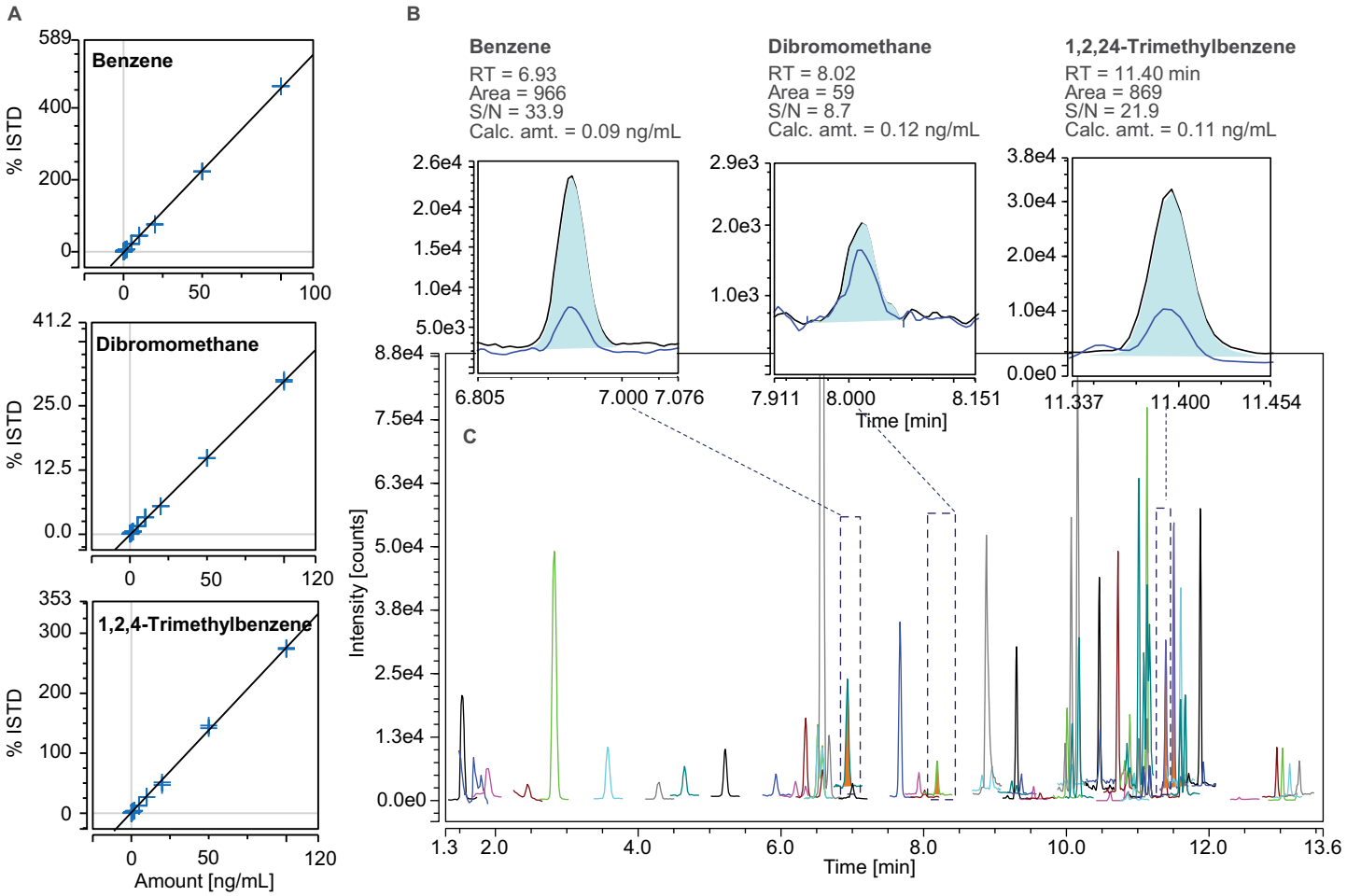


Figure 4. Full range calibration curves (0.1–100 ng/mL) for benzene, dibromomethane, and 1,2,4-trimethylbenzene (A), XIC showing the quantifier and qualifier ions for a tap water sample spiked at 0.1 ng/mL (B), and SIM trace showing the target compounds in a tap water sample spiked with a VOC mix at the lowest calibration point (0.1 ng/mL), ISTD (20 ng/mL) and surrogates (25 ng/mL) (C)

Inter-day repeatability

Analytical testing laboratories need to process a high number of samples every day. Therefore, it is critical that the instrument performs consistently every day.

The repeatability of the TriPlus RSH SMART VOC Sample Prep Station and system performance for everyday analysis were evaluated over six days of continuous operation by preparing three batches of samples (n=44 samples each) consisting of blank matrix, a calibration set ranging from 0.1 to 100 ng/mL, matrix-matched QCs spiked with VOC standard solution at 10 ng/mL bracketing series of n=5 samples of tap and surface water samples collected in different locations in the Milan area. Samples were spiked with internal standard solution and surrogate at 20 ng/mL and 25 ng/mL, respectively.

The precise mechanical control of the TriPlus RSH SMART VOC Sample Prep Station ensured reproducible addition of both the ISTD/surrogate solution as well as the VOC mix with average absolute peak area %RSD across the entire evaluation period <20%, QC calculated amount with respect to the batch ran on day 1 within 20%, and calculated recovery within 70–130%, with the only exception of 1,2-dibromo-3-chloropropane for which the % recovery was 132% (Appendix 5). As an example, the ISTD/surrogate peak area %RSD for the analyzed samples across the batches across the evaluation period is reported in Figure 5.

The analyzed samples results were compliant with the allowed threshold limits established by the current EU directives on the quality of water intended for human consumption and for the surface waters. Quantitative results are detailed in Appendix 6.

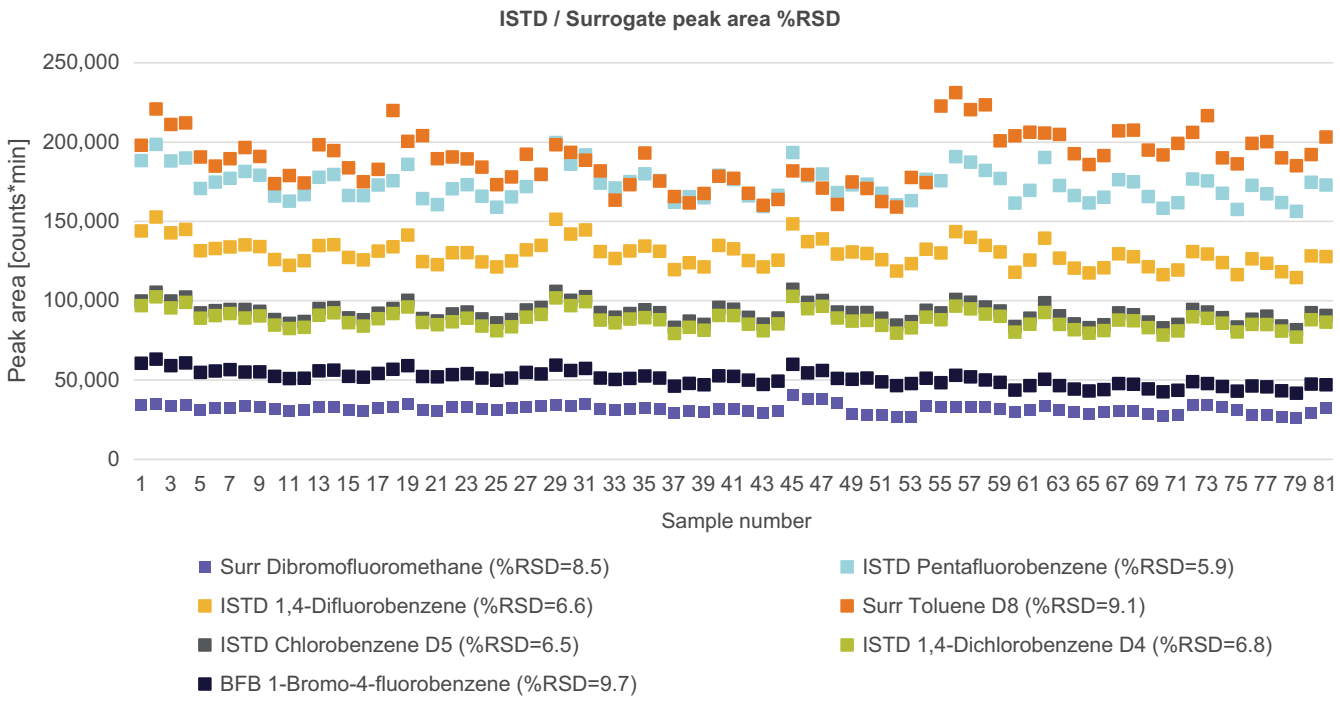


Figure 5. ISTD/surrogate peak area %RSD across the samples in the evaluation period of six working days

Conclusions

The results of these experiments demonstrate that the automated sample preparation capability of the TriPlus RSH SMART VOC Sample Prep Station coupled to the ISQ 7610 GC-MS system provides an ideal solution for water testing laboratories looking to improve productivity and deliver confident results.

- Static headspace is a convenient solventless extraction technique for volatiles in water with almost no sample preparation required.
- Unattended operations of up to 210 samples can be achieved with the automated calibration dilution and ISTD addition workflows.
- The automated addition of fresh reagent just before the incubation increases the stability of ISTD/surrogates mix, therefore improving the accuracy of the quantitation of target analytes during data reprocessing.
- The TriPlus RSH SMART VOC Sample Prep Station ensures increased sample integrity for highly reliable quantitative analysis, and reduced errors or possible cross-contaminations, maximizing the productivity of the laboratory. Additionally, it allows saving valuable analyst time and improving safety by limiting the user's exposure to toxic chemicals.
- The integrated control for both autosampler and GC-MS in a single CDS ensures a streamlined automated workflow from on-line sample preparation to sequence setup, data acquisition, and reporting.
- Suitability of headspace sampling for analysis of VOCs was demonstrated with $R^2 > 0.990$, RRF %RSD < 20%, and calculated amount within 20% of the spiked concentration.
- Inter-day reproducibility was demonstrated by running three batches of samples bracketed with QCs. Average absolute peak area %RSD across the entire evaluation period was <20%, the QC calculated amount was within 20% of the expected value, and the calculated recovery was within 70–130%, with the only exception of 1,2-dibromo-3-chloropropane for which the % recovery was 132.
- Reliable quantitative analysis was achieved for drinking water samples and surface water samples analyzed in three different batches across six working days. All the sample results were compliant with the thresholds set by the current EU regulation.

References

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2. Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption, EUR-Lex - 32020L2184 - EN - EUR-Lex (europa.eu)
3. Directive 2008/105/ec of the european parliament and of the council of 16 December 2008 on environmental quality standards in the field of water policy, https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0105
4. Thermo Fisher Scientific, Technical Note 001218: Addressing gas conservation challenges when using helium or hydrogen as GC carrier gas, https://assets.thermofisher.com/TFS-Assets/CMD/Technical-Notes/tn-001218-gc-hesaver-h2safer-trace1600-tn001218-na-en.pdf

Appendix 1. TriPlus RSH SMART VOC Sample Prep Station configuration and list of suggested consumables

TriPlus RSH SMART VOC Sample Prep Station configuration*	Part number
TriPlus RSH SMART VOC Sample Prep Station including:	1R77010-2010
• mounting brackets for TRACE 1600/1610 GC (P/N 1R77010-1005)	
• one extra single leg for TRACE 1600/1610 GC, 667 mm (P/N 1R77010-1141)	
• one Automatic Tool Change Station (ATC) Station (P/N 1R77010-1019)	
• one universal liquid syringe tool, for syringes of 0.5, 1.0, 5, 10, 25, 50 or 100 µL with a 57 mm needle length (P/N 1R77010-1007)	
• two 100 µL SMART syringes, 57 mm needle length, 26S gauge, cone needle type (P/N 365H2141-SM)	
• three tray holders (P/N 1R77010-1021)	
• one VT54 tray, for 54 vials of 2 mL (P/N 1R77010-1023)	
• one standard washing station with 5 x 10 mL vials (P/N 1R77010-1029)	
• one large wash station for 2 × 100 mL solvent bottles and one waste position (P/N 1R77010-1030)	
• one headspace tool for 2.5 mL syringe (P/N 1R77010-1013)	
• two vial tray R60 aluminum tray for 60 vials of 10/20 mL (P/N 1R77010-1025)	
• two VT 15 trays, for 15 vials of 10/20 mL (P/N 1R77010-1022)	
• one Incubator/Agitator (P/N 1R77010-103)	
• two HT 2.5 mL GT SMART syringes (P/N 365L2321-SM)	
Suggested consumables	**Part number**
Thermo Scientific™ GC SMART Gas tight syringe, 100 µL, Fixed needle, 57 mm length, 26s gauge, Cone	365H2161-SM
Thermo Scientific™ GC SMART Gas tight syringe, 2.5 mL, Fixed needle, 65 mm length, 23 gauge, Side hole	365L2321-SM
Thermo Scientific™ SureSTART™ 20 mL Glass screw top headspace vials, Level 2 High-Throughput Applications	6ASV20-1
Thermo Scientific™ SureSTART™ 18 mm Precision screw caps, Level 3 High Performance Applications	6PMSC18-ST2
TraceGOLD TG-624SilMS column, 20 m × 0.18 mm × 1.0 µm	26059-4950
Thermo Scientific™ Deactivated direct straight liner, 1.2 mm ID, 78.5 mm, 5/P	453A1335

*This configuration provides a 150-vial capacity.

For more details about orders and quotations, please refer to your Thermo Fisher Scientific sales representatives.

Appendix 2. Instrument parameters and list of the target compounds, including quantifier and qualifier ion

TriPlus RSH SMART VOC Sample Prep Station parameters

ISTD addition	
ISTD volume (µL)	10
ISTD fill speed (µL/s)	2
ISTD dispense speed (µL/s)	5
ISTD rinsing cycles	1
ISTD rinsing volume (µL)	20
ISTD filling stokes cycles	4
ISTD filling stokes volume (µL)	20
Sample vial penetration depth (mm)	20
Syringe pre-cleaning cycles	1
Syringe pre-cleaning volume (methanol)	70%
Syringe post-cleaning cycles	1
Syringe post-cleaning volume (isopropanol)	70%
Calibration reagent	
Reagent volume (µL)	According to table in Appendix 3
Reagent fill speed (µL/s)	10
Reagent dispense speed (µL/s)	25
Reagent rinsing cycles	1
Reagent rinsing volume (µL)	Reagent volume
Reagent filling stokes cycles	4
Regaent filling stokes volume (µL)	Reagent volume
Sample vial penetration depth (mm)	20
Syringe pre-cleaning cycles	1
Syringe pre-cleaning volume (methanol)	70%
Syringe post-cleaning cycles	1
Syringe post-cleaning volume (isopropanol)	70%
Syringe	Thermo Scientific™ GC SMART Gas tight syringe, 100 µL (P/N 365H2161-SM)

Injection volume (µL)	1,000
Syringe temperature (°C)	80
Incubation temperature (°C)	60
Incubation time (min)	17
Agitation speed (rpm)	750
Sample vial penetration depth (mm)	25
Pre-filling sample vial	TRUE
Pre-filling volume (%)	90
Sample fill speed (incubation temperature) (µL/s)	100
Sample filling stokes counts	1
Sample filling stokes volume (mL)	1,000
Delay after filling strokes (s)	10
Sample post-aspirate delay (s)	0
Injector penetration depth (mm)	45
Injection speed (µL/s)	500
Pre-injection delay (s)	0
Post-injection delay (s)	0
Pre-injection syringe purge time (s)	5
Post-injection syringe purge time (s)	150
Analysis time (min)	25
Syringe	Thermo Scientific™ GC SMART Gas tight syringe, 2.5 mL (P/N 365L2321-SM)

TRACE 1610 GC parameters

iC-SSL HeSaver - H_2Safer	
Temperature (°C)	80
Liner	SSL direct straight liner (P/N 453A1335)
Inlet module and mode	SSL upgraded to HeSaver - H_2Safer, split
Split flow (mL/min)	10
Septum purge flow (mL/min)	5, constant
Hydrogen delay (min)	0.15
Carrier gas, flow (mL/min)	He, 0.3

Oven temperature program	
Temperature (°C)	35
Hold time (min)	3
Rate (°C/min)	12
Temperature 2 (°C)	85
Rate (°C/min)	25
Temperature 3 (°C)	260
Hold time (min)	3
GC run time (min)	17.167
Oven equilibration time (min)	0.2
Ready delay (min)	1.2
Analytical column	
TraceGOLD TG-624SilMS	20 m × 0.18 mm × 1.0 µm (P/N 26059-4950)

ISQ 7610 mass spectrometer parameters	
Transfer line temperature (°C)	270
Ion source type and temperature (°C)	Thermo Scientific™ ExtractaBrite™, 280
Ionization type	EI
Emission current (µA)	50
Aquisition mode	SIM
Tuning parameters	BFB Tune

Compound name	RT (min)	Quantitation ion (*m/z*)	Confirming ion 2 (*m/z*)	Confirming ion 3 (*m/z*)
Dichlorodifluoromethane	1.54	85	87	
Chloromethane	1.72	50	52	
Vinyl chloride	1.88	62	64	
Chloroethane	2.47	64	66	
Trichlorofluoromethane	2.82	101	103	
1,1-dichloroethene	3.58	61	96	63
Methylene chloride	4.3	84	86	49
1,2-Dichloroethene (Z cis)	4.65	96	61	98
1,1 Dichloroethane	5.22	63	65	
1,2-Dichloroethene (E)	5.94	96	91	98
Bromochloromethane	6.18	49	130	128
Chloroform (Trichloromethane)	6.39	83	85	
2,2-Dichloropropene	6.51	61	99	
1,1,1,-Trichloroethane	6.53	97	61	
Surr Dibromofluoromethane	6.53	111	113	192
ISTD Pentafluorobenzene	6.58	168	99	137
Carbon tetrachloride	6.69	117	119	
Benzene	6.94	78	77	
1,2-dichlroethane	7.01	62	64	98
ISTD 1,4-Difluorobenzene	7.44	114	63	
Trichloroethene	7.67	95	130	97
1,2-Dichloropropane	7.94	63	112	
Dibromomethane	8.02	93	95	174
Bromodichloromethane	8.2	83	85	
Surr Toluene D8	8.82	98	100	
1,3-Dichloropropene (Z)	8.87	39	75	77
Toluene	8.89	91	92	
1,1,2-Trichloroethane	9.24	83	97	85
Tetrachloroethene	9.31	164	129	131
1,3-Dichloropropane	9.38	76	78	
Dibromochloromethane	9.54	129	127	

Compound name	RT (min)	Quantitation ion (*m/z*)	Confirming ion 2 (*m/z*)	Confirming ion 3 (*m/z*)
1,2-Dibromoethane	9.64	107	109	
ISTD Chlorobenzene D5	9.99	117	119	
Chlorobenzene	10.02	112	77	114
1,1,1,2-Tetrachloroethane	10.08	131	133	119
Ethylbenzene	10.08	91	106	
m,p-Xylene	10.18	91	106	
o-Xylene	10.47	91	106	
Styrene	10.48	78	103	104
Bromoform	10.62	173	175	254
Isopropylbenzene (Cumene)	10.72	105	120	
BFB 1-Bromo-4-fluorobenzene	10.85	95	174	176
1,1,2,2-tetrachloroethane	10.95	83	131	85
1,2,3-Trichloropropane	10.95	77	75	
Bromobenzene	10.96	156	77	158
1,3,5-Trimethylbenzene	11	120	105	
n-Propylbenzene	11.02	91	120	92
2-Chlorotoluene	11.09	126	91	
4-Chlorotoluene	11.16	126	91	
tert-Butylbenzene	11.36	119	91	134
1,2,4-Trimethylbenzene	11.4	105	120	
sec-Butylbenzene	11.51	105	134	
4-Isopropyltoluene (*p*-Cymene)	11.6	119	134	
1,3-Dicholorobenzene	11.6	146	111	148
ISTD 1,4-Dichlorobenzene D4	11.64	150	152	
1,4-Dicholorobenzene	11.67	146	111	148
n-Butylbenzene	11.89	91	92	134
1,2-Dibromo-3-chloropropane	12.5	157	155	
1,2,4-Trichlorobenzene	12.95	180	182	145
Hexachlorobutadiene	13.03	225	223	227
Naphtalene	13.11	128		
1,2,3-Trichlorobenzene	13.27	180	182	145

Appendix 3. Schematics for automated calibration curve preparation

Calibration level	Concentration in vial (ng/mL)	Bulk calibration solution (µg/mL)	Spiking amount (µL)	ISTD / Surrogate concentration in vial (ng/mL)	Bulk ISTD / Surrogate solution (µg/mL)	ISTD/ Surrogate spiking amount (µL)
Blank	--					
1	0.1	0.02	50	20 / 25	20 / 25	10
2	0.2	0.02	100	20 / 25	20 / 25	10
3	0.5	0.2	25	20 / 25	20 / 25	10
4	1	0.2	20	20 / 25	20 / 25	10
5	2	0.2	100	20 / 25	20 / 25	10
6	5	2	25	20 / 25	20 / 25	10
7	10	2	50	20 / 25	20 / 25	10
8	20	2	100	20 / 25	20 / 25	10
9	50	20	25	20 / 25	20 / 25	10
10	100	20	50	20 / 25	20 / 25	10

Appendix 4. Coefficient of determination (R^2), relative response factor (RRF) %RSD, calculated amount (ng/mL) and absolute peak area %RSD at MDL (0.5 ng/mL, n=10)

Peak name	RT (min)	Linear range (ng/mL)	R^2	AvCF %RSD	RRF% RSD	Calculated MDL (ng/mL)	Absolute peak area %RSD at MDL (n=10)
Dichlorodifluoromethane	1.53	2-100	0.999	5	15.2	0.11	5.6
Chloromethane	1.73	2-100	0.998	6	14.4	0.17	6.8
Vinyl chloride	1.89	0.1-100	0.999	4.3	16.6	0.04	5
Chloroethane	2.47	0.1-100	1	3.6	9.3	0.04	4.5
Trichlorofluoromethane	2.82	1-100	0.999	4.2	13.9	0.1	4.9
1,1-Dichloroethene	3.57	0.1-100	0.999	6.4	9.5	0.02	4.1
Methylene chloride	4.28	0.1-100	0.999	4	15.4	0.03	2.9
1,2-Dichloroethene (Z)	4.65	0.1-100	0.998	7	10.4	0.02	3.5
1,1-Dichloroethane	5.22	0.1-100	0.999	5	9.8	0.02	3.2
1,2-Dichloroethene (E)	5.93	0.1-100	0.998	7.2	10.8	0.02	4
Bromochloromethane	6.2	0.1-100	1	3.3	9.2	0.04	3.1
Chloroform (Trichloromethane)	6.35	0.1-100	1	3.5	19	0.03	3
1,1,1-Trichloroethane	6.51	0.1-100	0.999	4.9	10.8	0.01	2.5
2,2-Dichloropropene	6.52	0.1-100	0.999	3.8	12.2	0.04	4.2
Surr Dibromofluoromethane	6.53	--	--	--	--	--	3.3
ISTD Pentafluorobenzene	6.58	--	--	--	--	--	3.6
Carbon tetrachloride	6.69	0.1-100	0.999	4.7	10.6	0.02	3.1
Benzene	6.93	0.1-100	0.999	6.5	10.8	0.01	3.3
1,2-Dichloroethane	7	0.1-100	0.999	4.1	10.6	0.03	3.7
ISTD 1,4-Difluorobenzene	7.43	--	--	--	--	--	4
Trichloroethene	7.67	0.5-100	0.999	4.8	12.6	0.02	3.7
1,2-Dichloropropane	7.93	0.1-100	0.999	5.2	9.7	0.02	3.5
Dibromomethane	8.01	0.1-100	0.999	3.6	11.5	0.05	4.1
Bromodichloromethane	8.19	0.1-100	0.999	3.7	10	0.04	3
Surr Toluene D8	8.82	--	--	--	--	--	4.1
1,3-Dichloropropene (Z)	8.87	0.5-100	0.999	5.1	14.5	0.08	5
Toluene	8.87	0.2-100	0.997	7.7	13.4	0.12	6.2

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Appendix 4. Continued from previous page

Peak name	RT (min)	Linear range (ng/mL)	R^2	AvCF %RSD	RRF% RSD	Calculated MDL (ng/mL)	Absolute peak area %RSD at MDL (n=10)
1,1,2-Trichloroethane	9.24	0.1-100	0.999	3.7	10.6	0.05	4.7
Tetrachloroethene	9.3	0.2-100	0.999	5.2	15.6	0.03	4.5
1,3-Dichloropropane	9.37	0.1-100	0.999	4.1	10.3	0.02	4.5
Dibromochloromethane	9.54	0.1-100	0.999	4.4	12.3	0.03	5.2
1,2-Dibromoethane	9.63	0.1-100	0.999	3.9	12.9	0.04	4.2
ISTD Chlorobenzene D5	9.99	--	--	--	--	--	4.1
Chlorobenzene	10.01	0.1-100	0.998	7.1	10.8	0.01	4.7
1,1,1,2-Tetrachloroethane	10.08	0.1-100	0.999	4.9	11.3	0.06	3.3
Ethylbenzene	10.08	0.1-100	0.994	13.7	15	0.01	4.1
m,p-Xylene	10.18	0.2-50	0.99	17.3	12	0.01	4.9
o-Xylene	10.46	0.1-100	0.995	12.3	17.9	0.01	4.9
Styrene	10.47	0.2-100	0.995	12.6	18.2	0.01	4.5
Bromoform	10.61	0.1-100	0.999	6.1	13	0.07	6.7
Isopropylbenzene (Cumene)	10.72	0.1-100	0.999	4.4	10.3	0.02	4.1
BFB 1-Bromo-4-fluorobenzene	10.85	--	--	--	--	--	4.6
1,1,2,2-tetrachloroethane	10.94	0.5-100	0.999	3.7	10.5	0.18	9.7
Bromobenzene	10.96	0.1-100	0.996	9.1	17.7	0.06	5.1
1,2,3-Trichloropropane	10.96	0.2-100	0.999	4.9	18.6	0.02	4.5
n-Propylbenzene	11.01	0.1-100	0.999	4.8	10.1	0.02	4.5
1,3,5-Trimethylbenzene	11.01	0.1-100	0.999	4.3	10.5	0.03	4.8
2-Chlorotoluene	11.08	0.1-100	0.998	6.6	10.3	0.05	5.1
4-Chlorotoluene	11.17	0.2-100	0.998	6.3	12.8	0.05	5.7
tert-Butylbenzene	11.35	0.1-100	0.999	4.9	10.9	0.05	5.3
1,2,4-Trimethylbenzene	11.39	0.1-100	0.999	4.9	12.5	0.03	6.7
sec-Butylbenzene	11.5	0.1-100	0.999	4.8	10.2	0.01	4.2
4-Isopropyltoluene (*p*-Cymene)	11.6	0.1-100	0.999	4.9	12.9	0.02	5.2
1,3-Dicholorobenzene	11.6	0.2-100	0.993	12.5	15.2	0.04	5.4
ISTD 1,4-Dichlorobenzene D4	11.65	--	--	--	--	--	4.2
1,4-Dicholorobenzene	11.67	0.2-100	0.993	12.2	13.7	0.05	5.4
n-Butylbenzene	11.88	0.1-100	0.999	4.7	10.7	0.02	5.1
1,2-Dichlorobenzene	11.92	0.2-100	0.994	11.1	12	0.04	4.3
1,2-Dibromo-3-chloropropane	12.42	0.2-50	0.99	13.6	14.1	0.06	3.4
1,2,4-Trichlorobenzene	12.95	1.0-100	0.997	7.9	17.6	0.15	10.1
Hexachlorobutadiene	13.03	0.1-50	0.993	11.2	13	0.04	3
Naphtalene	13.13	0.2-100	0.998	6	17.7	0.06	6.4
1,2,3-Trichlorobenzene	13.27	1.0-100	0.997	7.6	19.3	0.11	8.2

Appendix 5. QC absolute peak area %RSD as well QC calculated amount deviation with respect to batch 1 and % recovery obtained injecting three batch of samples over a period of six working days

Peak name	RT (min)	QC delta respect to batch 1	QC delta respect to batch 1	QC % Recovery	QC absolute peak area %RSD (n=18)
Dichlorodifluoromethane	1.53	1	1.8	80	9.4
Chloromethane	1.73	0.6	0.8	98	8
Vinyl chloride	1.89	0.8	1	94	8.7
Chloroethane	2.47	0.6	0.8	102	5.8
Trichlorofluoromethane	2.82	0.6	0.7	101	4.4
1,1-Dichloroethene	3.57	0.4	0.4	94	4.8
Methylene chloride	4.28	-2.8	-2.7	118	18.5
1,2-Dichloroethene (Z)	4.65	0.4	0.4	94	4.5
1,1-Dichloroethane	5.22	0.4	0.5	103	3.3
1,2-Dichloroethene (E)	5.93	0.4	0.4	95	5.6
Bromochloromethane	6.2	0.3	0.5	108	5.3
Chloroform (Trichloromethane)	6.35	0.4	0.5	109	4
1,1,1-Trichloroethane	6.51	0.4	0.4	104	4
2,2-Dichloropropene	6.52	0.4	0.4	107	3.1
Surr Dibromofluoromethane	6.53	0.4	0.2	103	1.8
ISTD Pentafluorobenzene	6.58	0	0	100	3.4
Carbon tetrachloride	6.69	0.3	0.3	100	4.6
Benzene	6.93	0.3	0.3	90	5.9
1,2-Dichloroethane	7	0.5	0.5	106	6.8
ISTD 1,4-Difluorobenzene	7.43	0	0	100	3.9
Trichloroethene	7.67	0.1	0.2	98	5.1
1,2-Dichloropropane	7.93	0.4	0.4	102	7.4
Dibromomethane	8.01	0.3	0.5	106	4.8
Bromodichloromethane	8.19	0.3	0.5	107	3.9
Surr Toluene D8	8.82	-0.1	0	100	7.2
1.3-Dichloropropene (Z)	8.87	0.1	0	97	6.3
Toluene	8.87	0.3	0.3	87	6.1
1,1,2-Trichloroethane	9.24	0.3	0.7	108	4.8
Tetrachloroethene	9.3	0.6	0.6	97	4.9
1,3-Dichloropropane	9.37	0.4	0.4	103	3.5
Dibromochloromethane	9.54	0.3	0.5	105	4.1

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Appendix 5. Continued from previous page

Peak name	RT (min)	QC delta respect to batch 1	QC delta respect to batch 1	QC % Recovery	QC absolute peak area %RSD (n=18)
1,2-Dibromoethane	9.63	0.5	0.6	106	4.7
ISTD Chlorobenzene D5	9.99	0	0	100	3.4
Chlorobenzene	10.01	0.3	0.4	92	5.3
1,1,1,2-Tetrachloroethane	10.08	0.3	0.5	99	3.8
Ethylbenzene	10.08	0.2	0.1	76	7.7
m,p-Xylene	10.18	0	0	77	7.9
o-Xylene	10.46	0.1	0	71	7.6
Styrene	10.47	-0.1	-0.2	71	10
Bromoform	10.61	0.3	0.5	99	5.3
Isopropylbenzene (Cumene)	10.72	0.2	0	98	7.8
BFB 1-Bromo-4-fluorobenzene	10.85	0.2	0.3	97	6.9
1,1,2,2-tetrachloroethane	10.94	0.7	0.7	108	3.7
Bromobenzene	10.96	0.6	0.7	121	7.7
1,2,3-Trichloropropane	10.96	-0.1	0.1	89	4.2
n-Propylbenzene	11.01	0.3	0.1	100	7.7
1,3,5-Trimethylbenzene	11.01	0.1	0	91	7.7
2-Chlorotoluene	11.08	0.2	0	101	6.9
4-Chlorotoluene	11.17	0.1	-0.1	100	6.3
Tert-butylbenzene	11.35	0	-0.2	95	8.3
1,2,4-Trimethylbenzene	11.39	0.2	-0.1	88	8.6
sec-Butylbenzene	11.5	0.4	0	94	8.1
4-Isopropyltoluene (*p*-Cymene)	11.6	0	-0.4	88	8.2
1,3-Dicholorobenzene	11.6	-0.8	0.2	121	4
ISTD 1,4-Dichlorobenzene D4	11.65	0	0	100	2.4
1,4-Dicholorobenzene	11.67	0.4	0.4	125	4.1
n-Butylbenzene	11.88	0.2	-0.2	99	8
1,2-Dichlorobenzene	11.97	0.3	0.4	127	4.1
1,2-Dibromo-3-chloropropane	12.42	0.1	0.3	132	3.6
1,2,4-Trichlorobenzene	12.95	0.2	0.3	120	6.3
Hexachlorobutadiene	13.03	0.6	0.5	125	5.5
Naphtalene	13.13	0.2	0.4	113	7.2
1,2,3-Trichlorobenzene	13.27	0	0.1	116	5.8

Appendix 6. Results obtained for analysis of tap water samples (three locations) and surface water samples (two locations)

		Drinking water samples (ng/mL)				Surface water samples (ng/mL)		
Peak name	RT (min)	1	2	3	Limits[2] (ng/mL)	1	2	Limits[3] (ng/mL)
Dichlorodifluoromethane	1.53	< MDL	< MDL	< MDL		< MDL	<MDL	
Chloromethane	1.73	--	--	--		--	--	
Vinyl chloride	1.89	--	--	--	**0.5**	< MDL	< MDL	
Chloroethane	2.47	--	--	--		--	--	
Trichlorofluoromethane	2.82	0.13	--	--		--	--	
1,1-Dichloroethane	3.57	--	0.06			--	0.07	
Methylene chloride	4.28	0.23	0.23	0.27		0.26	0.23	
1,2-Dichloroethene (Z)	4.65	--	--	--		--	--	
1,1 Dichloroethane	5.22	--	0.02	0.02		--	0.02	
1,2-Dichloroethene (E)	5.93	--	0.17	0.05		--	0.2	
Bromochloromethane	6.2	--	--	--		--	--	
Chloroform (Trichloromethane)	6.35	0.06	0.07	< MDL	**100****	0.03	0.08	**2.5**
1,1,1,-Trichloroethane	6.51	--	0.04	--		--	0.05	
2,2-Dichloropropene	6.52	--	--	--		--	--	
Carbon tetrachloride	6.69	--	--	--		--	--	**12**
Benzene	6.93	--	--	--	**1**	--	--	**50**
1,2-Dichloroethane	7	--	--	--	**3**	--	--	**10**
Trichloroethene	7.67	0.13	0.12	--	**10***	--	0.14	
1,2-Dichloropropane	7.93	--	--	--		--	--	
Dibromomethane	8.01	--	--	--		--	--	**20**
Bromodichloromethane	8.19	--	--	--	**100****	--	--	
1,3-Dichloropropene (Z)	8.87	--	--	--		--	--	
Toluene	8.87	0.13	0.14	0.12		0.17	0.12	
1,1,2-Trichloroethane	9.24	--	--	--		--	--	
Tetrachloroethene	9.3	0.09	1.28	< MDL	**10***	--	1.42	
1,3-Dichloropropane	9.37	--	--	--		--	--	
Dibromochloromethane	9.54	--	--	--	**100****	--	--	

* = Sum of tetrachloroethene and trichloroethene
** = Sum of chloroform, bromoform, dibromochloromethane, and bromodichloromethane

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Appendix 6. Continued from previous page

Peak name	RT (min)	Drinking water samples (ng/mL) 1	2	3	Limits[2] (ng/mL)	Surface water samples (ng/mL) 1	2	Limits[3] (ng/mL)
1,2-Dibromoethane	9.63	--	--	--		--	--	
Chlorobenzene	10.01	0.01	0.01	0.01		0.01	0.01	
1,1,1,2-Tetrachloroethane	10.08	--	--	--		--	--	
Ethylbenzene	10.08	0.01	0.01	0.01		0.01	0.01	
m,p-Xylene	10.18	0.01	0.01	0.01		0.01	0.01	
o-Xylene	10.46	0.01	0.01	0.01		0.01	0.01	
Styrene	10.47	--	--	--		0.02	--	
Bromoform	10.61	--	--	--	**100****	--	--	
Isopropylbenzene (Cumene)	10.72	--	--	--		--	--	
1,1,2,2-Tetrachloroethane	10.94	--	--	--		--	--	
Bromobenzene	10.96	--	--	--		--	--	
1,2,3-Trichloropropane	10.96	--	--	-		--	--	
n-Propylbenzene	11.01	< MDL	< MDL	< MDL		< MDL	0.02	
1,3,5-Trimethylbenzene	11.01	< MDL	< MDL	--		< MDL	< MDL	
2-Chlorotoluene	11.08	--	--	--		--	--	
4-Chlorotoluene	11.17	--	--	--		--	--	
tert-Butylbenzene	11.35	--	--	--		--	--	
1,2,4-Trimethylbenzene	11.39	< MDL	< MDL	< MDL		< MDL	< MDL	
sec-Butylbenzene	11.5	--	--	--		--	--	
4-Isopropyltoluene (*p*-Cymene)	11.6	< MDL	< MDL	< MDL		--	< MDL	
1,3-Dicholorobenzene	11.6	< MDL	< MDL	< MDL		< MDL	< MDL	
1,4-Dicholorobenzene	11.67	< MDL	< MDL	< MDL		< MDL	< MDL	
n-Butylbenzene	11.88	< MDL	< MDL	< MDL		< MDL	0.02	
1,2-Dichlorobenzene	11.92	< MDL	< MDL	<MDL		< MDL	< MDL	
1,2-Dibromo-3-chloropropane	12.42	--	--	--		--	--	
1,2,4-Trichlorobenzene	12.95	< MDL	< MDL	< MDL		< MDL	< MDL	**0.4**
Hexachlorobutadiene	13.03	< MDL	< MDL	< MDL		< MDL	0.01	**0.6**
Naphtalene	13.13	0.1	0.08	0.07		0.08	0.07	**1.2**
1,2,3-Trichlorobenzene	13.27	< MDL	< MDL	< MDL		< MDL	< MDL	**0.4**

* = Sum of tetrachloroethene and trichloroethene
** = Sum of chloroform, bromoform, dibromochloromethane, and bromodichloromethane

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