

Environmental

Sensitive and cryogen-free analysis of epichlorohydrin and other VOCs in drinking water by using In-Tube Extraction Dynamic Headspace (ITEX-DHS) sampling coupled to GC-MS

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Goal

The aim of this study is to demonstrate the suitability of In-Tube Extraction Dynamic Headspace (ITEX-DHS) for the analysis of very volatile organic compounds (VVOCs), volatile organic compounds (VOCs), and epichlorohydrin (ECH) in drinking water, when coupled to a cryogen-free refocusing into a programmed temperature vaporizer (PTV) injector.

Keywords

Epichlorohydrin, ECH, volatile organic compounds, VVOCs, VOCs, drinking water, ITEX-DHS, dynamic headspace, gas chromatography, TRACE 1610 GC, single quadrupole mass spectrometry, ISQ 7610 GC-MS

Introduction

Volatile organic compounds (VOCs) are a matter of concern as they are considered ubiquitous pollutants in the environment. They are common components or additives in many commercial and industrial products as well as some household and personal care products and pharmaceuticals. Once released into groundwater, many VOCs are persistent and can migrate to drinking water supplies and pose adverse effects on human health.

Epichlorohydrin (ECH) can leach from epoxy resin coatings on pipes or through the water treatment process and enter drinking water supplies. Due to the presence of chlorine and an epoxy bridge, ECH is a highly reactive molecule that tends to hydrolyze in water at ambient temperature to form 3-MCPD (3-monochloropropane-1,2-diol or 3-chloro-1,2-propanediol), which is a known carcinogen.

The Drinking Water Directive (DWD),¹ recast in 2020, is the EU's main regulation on drinking water to ensure its access and quality to protect human health. This directive strictly regulates the presence of VVOCs, VOCs, and ECH in water intended for human consumption by establishing their allowed limits.

These compounds are usually present at trace concentrations, and therefore they need to be extracted and pre-concentrated prior to analysis. Multiple sample preparation techniques can be considered for extracting these compounds, such as solid-phase microextraction (SPME), purge-and-trap (P&T), and headspace analysis (HS). Among these, P&T and HS sampling are the most common techniques for the analysis of aqueous samples.

In particular, the analytical method commonly used for quantifying ECH in drinking water according to regulatory requirements is GC-MS coupled to P&T sample enrichment. This method is highly sensitive and capable of detecting ECH at very low concentrations, which is essential given the strict limit of 0.10 µg/L in drinking water set by European regulations.

Next to these well-known sampling techniques, In-Tube Extraction Dynamic Headspace (ITEX-DHS) is a solventless extraction technique that uses a gas-tight syringe with a needle body filled with a sorbent material to efficiently trap and concentrate the volatile compounds (Figure 1). Samples are 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). The analytes are then concentrated from the sample headspace by performing multiple syringe plunger strokes (dynamic extraction) and trapped onto the

sorbent material (e.g., Tenax™). The syringe needle is then rapidly heated through a dedicated heater, and the analytes are thermally desorbed into the GC inlet independently from the injector temperature profile. After thermal desorption, the sorbent material is flushed with nitrogen at a high temperature for cleaning. Depending on the number of strokes, ITEX-DHS can provide an exhaustive collection of the analytes from the sample headspace allowing for low detection limits. Moreover, this syringe-based approach does not require the installation of transfer lines or switching valves, assuring high robustness and ease of use.

In this study, the reliability of ITEX-DHS for analysis of VVOCs, VOCs, and ECH in drinking water was evaluated by assessing linearity, method detection limits (MDLs), absolute peak area repeatability, and carryover. Additionally, the refocusing into the PTV injector was evaluated to improve peak shape and sensitivity for the most volatile compounds.

Experimental

Instrumentation

A Thermo Scientific™ TriPlus™ RSH SMART autosampler² equipped with an ITEX-DHS tool was coupled to a Thermo Scientific™ TRACE™ 1610 GC, configured with a Thermo Scientific™ iConnect™ programmed temperature vaporizer (iConnect-PTV) injector, and a Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer.

The PTV injector was equipped with a liner packed with Tenax TA (P/N 45312145-UI), suitable for a cryogen-free refocusing of the most volatile compounds.

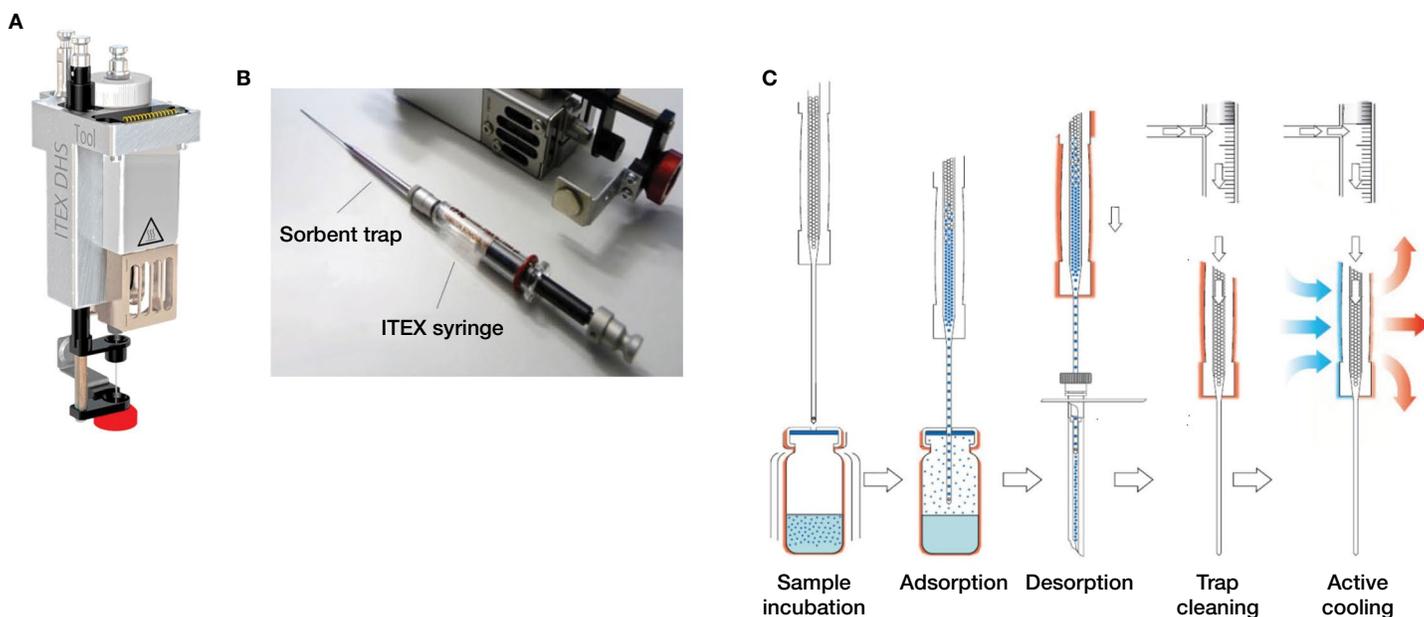


Figure 1. TriPlus RSH SMART ITEX-DHS tool (A) and ITEX syringe (B) as well as a schematic of the ITEX-DHS sample extraction and desorption process (C)

Chromatographic separation was achieved using a Thermo Scientific™ TraceGOLD™ TG-624 SiIMS, 60 m × 0.25 mm × 1.4 μm column (P/N 26085-3330). 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.

Instrument parameters as well as a complete list of the target compounds, including quantifier and qualifier ions, are reported in Appendix 1.

Data acquisition, processing, and reporting

Data were 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 analytical workflow combined with an intuitive user interface for data analysis, processing, customizable reporting, and storage in compliance with the U.S. Food and Drug Administration (FDA) Title 21 Code of Federal Regulations Part 11 (Title 21 CFR Part 11).

Standard and calibration curve preparation

Multi-component standard solutions were purchased from Restek (8260 Volatile Organics Kit, 2,000 μg/mL in methanol, P/N 30076) and diluted in methanol (Optima™ LC/MS grade, Fisher Scientific™, P/N A456-1) to obtain a calibration stock solution at 50 mg/L (ppm) and an internal standard and surrogate stock solution at 62.5 mg/L.

The calibration stock solution was further diluted in ultra-pure water (18.2 Ω) to obtain three working solutions at 5, 50, and 500 μg/L (ppb) that were dispensed into 20 mL screw top headspace vials (P/N 6ASV20-1, caps P/N 6PMSC18-ST2), previously filled with 10 mL of ultra-pure water, to prepare an 8-point calibration curve ranging from 0.025 to 5 μg/L (ppb) according to the scheme reported in Appendix 3. Each calibration standard was prepared in duplicate.

The internal standard / surrogate stock solution was diluted in ultra-pure water to a final concentration of 625 μg/L. An aliquot (40 μL) of this solution was then added to each calibration vial to reach a final concentration of 2.5 μg/L.

An aliquot (0.5 mg) of sodium chloride (NaCl, >99%, Fisher Scientific, P/N 10055850) was added to each standard prior to spiking to decrease the solubility of polar organic volatiles and promote their transfer into the headspace.

Results and discussion

Chromatography

When analyzing volatile organics, re-focusing at sub-ambient temperature is typically used to avoid peak broadening and co-elution of compounds such as chloromethane and vinyl chloride. Focusing the analytes on a sorbent trap represents a viable alternative to cryo-focusing, allowing for easier system configuration and management without the need for additional hardware or valves. In this application note, a PTV liner packed with Tenax TA was used to trap and refocus the analytes into the iConnect-PTV inlet at low temperature and transfer them into a very narrow band. This preserves column efficiency and improves the peak shapes of early eluting compounds as demonstrated in a previous application note³ where peak shapes obtained with and without re-focusing on Tenax TA packed liner were compared. A single ion monitoring (SIM) acquisition method allowed for 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.

An example of the SIM trace of a standard spiked at 0.5 μg/L with VOC mix, ISTD/surrogate mix (2.5 μg/L) is shown in Figure 2. The high thermal stability and superior inertness of the TraceGOLD TG-624 SiIMS column ensured adequate peak shapes and baseline chromatographic separation for most of the target compounds.

Linearity and method detection limits (MDLs)

Linearity was assessed by injecting a matrix-matched 8-point calibration curve in ultra-pure water. Each calibration level was prepared in duplicate. The calibration plot was fitted using a linear type and an internal standard method, with the exception of vinyl chloride for which an external method was applied. The response values of each calibration level were averaged before curve fitting. Laboratory environment and purity of reagents used for sample preparation can impact the cleanliness of the background; therefore, blank subtraction was applied, when needed, to compensate for possible contaminations from the ambient air and reagents.

All target analytes showed a linear trend within the ranges specified in Appendix 2 with coefficient of determination (R^2) > 0.9920 and average calibration factor (AvCF) %RSD < 14%. Details of the linearity ranges, as well as R^2 and AvCF% RSD for each individual analyte are reported in Appendix 1. Full range calibration curves for vinyl chloride (0.05–5 μg/L) and ECH (0.025–5 μg/L) as well as an extracted ion chromatogram (XIC) showing the quantifier and qualifier ions for a matrix-matched standard spiked at the lowest calibration point are reported as an example in Figure 3.

- Peaks:
- | | | | |
|------------------------------------|-----------------------------|----------------------------------|-----------------------------------|
| 1. Dichlorodifluoromethane | 14. Benzene | 27. Ethane, 1,2-dibromo- | 40. 2-Chlorotoluene |
| 2. Chloromethane | 15. Ethane, 1,2-dichloro- | 28. Chlorobenzene-d5 (ISTD) | 41. Benzene, <i>tert</i> -butyl- |
| 3. Vinylchloride | 16. Trichloroethylene | 29. Benzene, chloro- | 42. Benzene, 1,2,4-trimethyl- |
| 4. Ethene, 1,1-dichloro- | 17. Propane, 1,2-dichloro- | 30. Ethane, 1,1,1,2-tetrachloro- | 43. <i>sec</i> -Butylbenzene |
| 5. Methylene chloride | 18. Methane, dibromo- | 31. Ethylbenzene | 44. <i>p</i> -Cymene |
| 6. Ethylene, 1,2-dichloro- | 19. Methane, bromodichloro- | 32. <i>m,p</i> -Xylene | 45. 1,4-Dichlorobenzene (ISTD) |
| 7. Ethane, 1,1-dichloro- | 20. Epichlorohydrine | 33. <i>o</i> -Xylene | 46. 1,3-Dichlorobenzene |
| 8. Methane, bromochloro- | 21. Toluene-D8 (Surr) | 34. Styrene | 47. Benzene, <i>n</i> -butyl- |
| 9. Chloroform | 22. Toluene | 35. Bromoform | 48. 1,4-Dichlorobenzene |
| 10. Benzene, pentafluoro- (ISTD) | 23. 1,1,2-Trichloroethane | 36. Benzene, 1,3,5-trimethyl- | 49. Propane, 1,2-dibromo-3-chloro |
| 11. Methane, dibromofluoro- (Surr) | 24. Ethene, tetrachloro- | 37. Benzene, Bromo- | 50. Benzene, 1,2,4-trichloro |
| 12. Ethane, 1,1,1-trichloro- | 25. Propane, 1,3-dichloro | 38. Propane, 1,2,3-trichloro | 51. Hexachlorobutadiene |
| 13. Carbon Tetrachloride | 26. Methane, dibromochloro- | 39. <i>n</i> -Propylbenzene | 52. Naphthalene |
| | | | 53. Benzene, 1,2,3-trichloro |

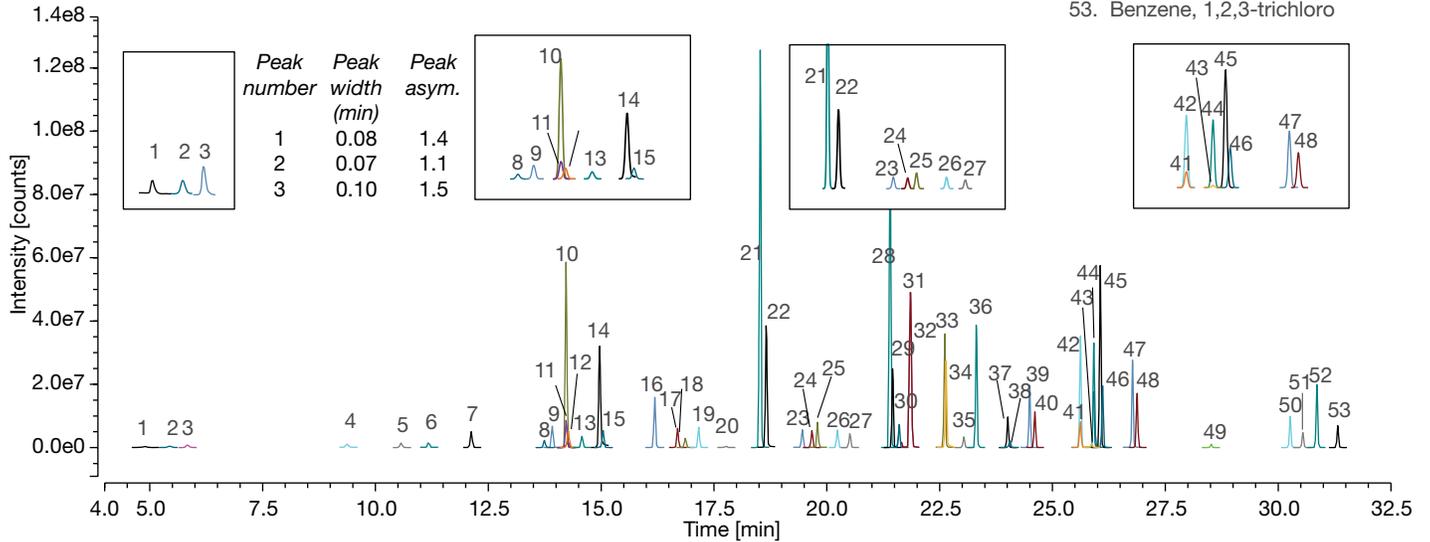


Figure 2. SIM trace showing an example of the chromatographic separation obtained for a matrix-matched standard spiked at 0.5 µg/L with VOC, ISTD/surrogate (2.5 µg/L) solutions. Peak width (calculated at 50% height) and peak asymmetry for the first eluting compounds are annotated.

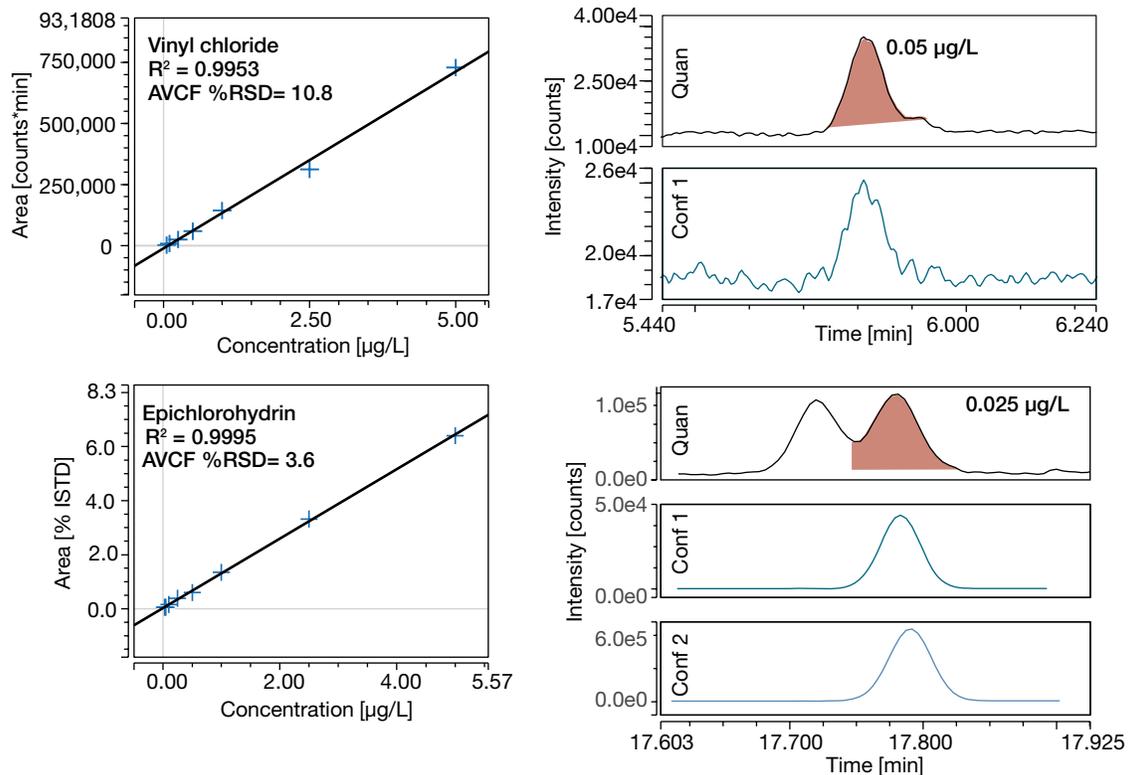


Figure 3. Full range calibration curves for vinyl chloride (0.05–5 µg/L) and epichlorohydrin (0.025–5 µg/L) (A); XIC showing the quantifier and qualifier ions a matrix-matched standard spiked at the lowest calibration point (B)

MDLs and precision were assessed using n=10 replicates of matrix-matched standards spiked with VOC solution at 0.05, 0.10, and 0.25 µg/L. Calculated MDLs were between 0.002 and 0.22 µg/L with calculated absolute peak area %RSD at MDL level <20% and calculated amounts within 20% of the expected value for all compounds (Appendix 2), allowing for equivalent sensitivity to the P&T sampling technique.⁴ Some examples of analytes spiked in ultra-pure water at the calculated MDL levels are reported in Figure 4.

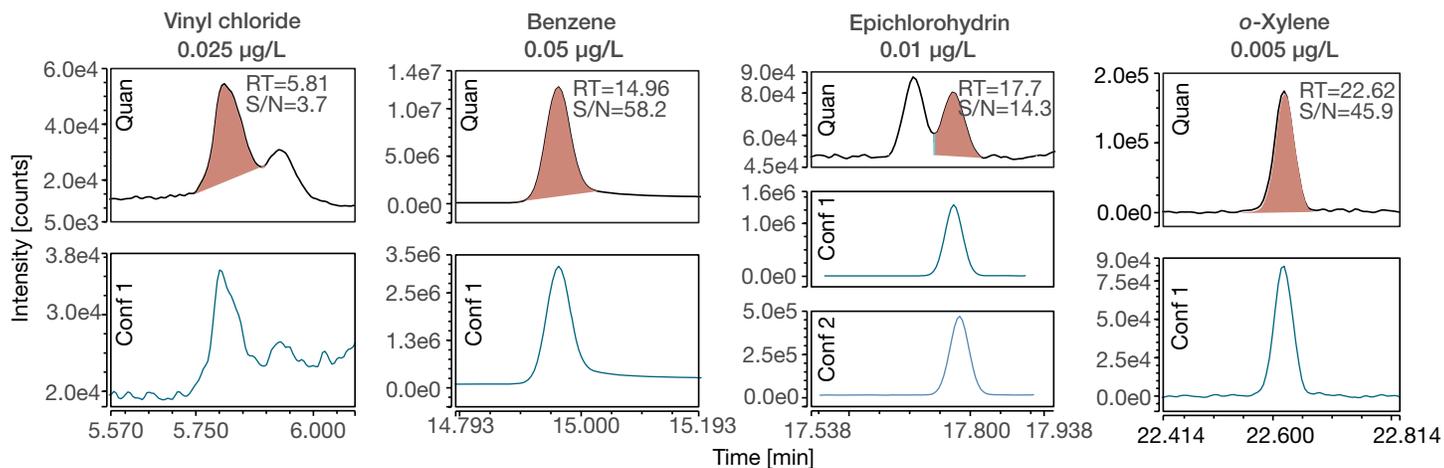


Figure 4. Examples of analytes spiked in ultra-pure water at the calculated MDL levels. Peak-to-peak signal-to-noise (S/N) is annotated.

Repeatability

The repeatability of the analytical system was evaluated by analyzing n=10 matrix-matched standards spiked at 0.25 µg/L. The reliability of the entire workflow from sample extraction, enrichment and injection, to data acquisition was demonstrated with absolute peak area %RSD < 14 as reported in Figure 5.

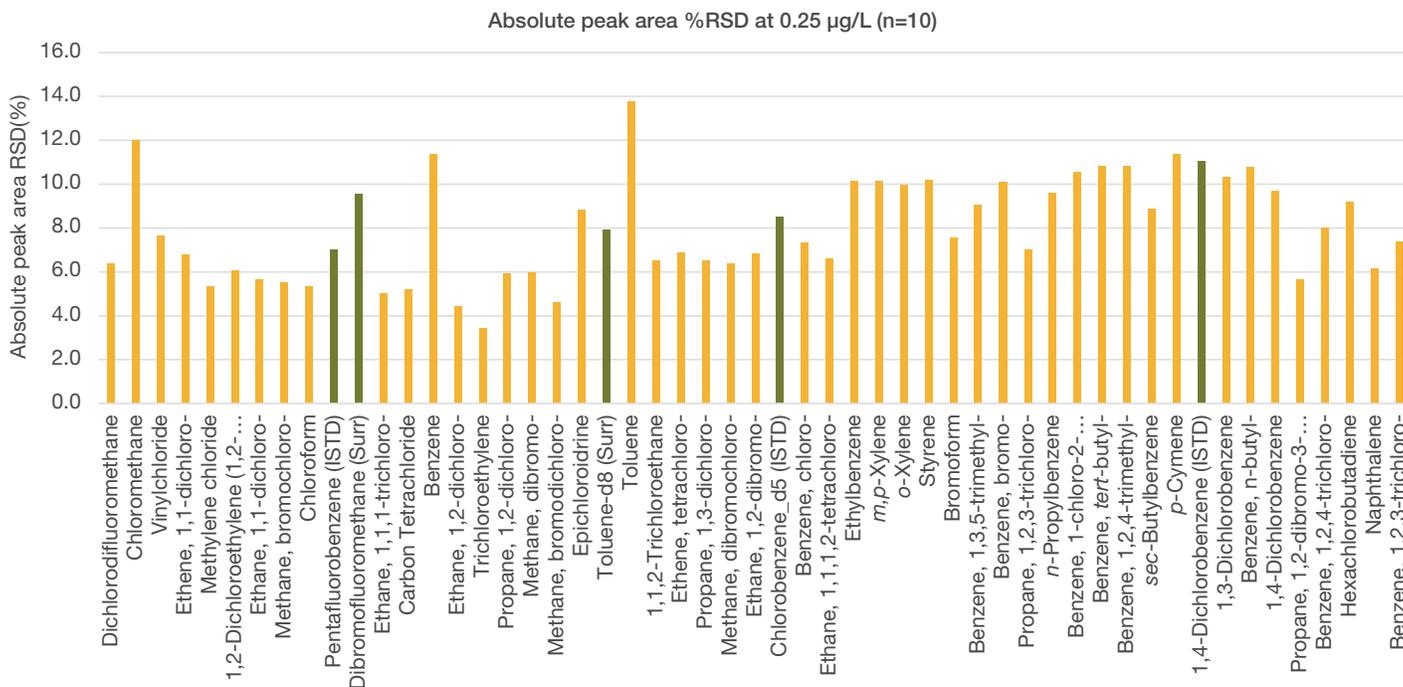


Figure 5. Absolute peak area repeatability (%RSD) obtained for n=10 matrix-matched standards spiked at 0.25 µg/L. ISTDs and surrogates spiked at 2.5 µg/L are shown in green.

Carryover

Carry-over was assessed by injecting a matrix-matched standard spiked at 10 µg/L followed by a blank (ultra-pure water). All analytes showed carryover $\leq 0.5\%$ except for benzene, naphthalene, and trichlorobenzene for which the carryover was 1.5, 0.9, and 0.8%, respectively, as reported in Appendix 2. Figure 6 shows some examples of overlaid chromatograms at 10 µg/L versus a blank sample.

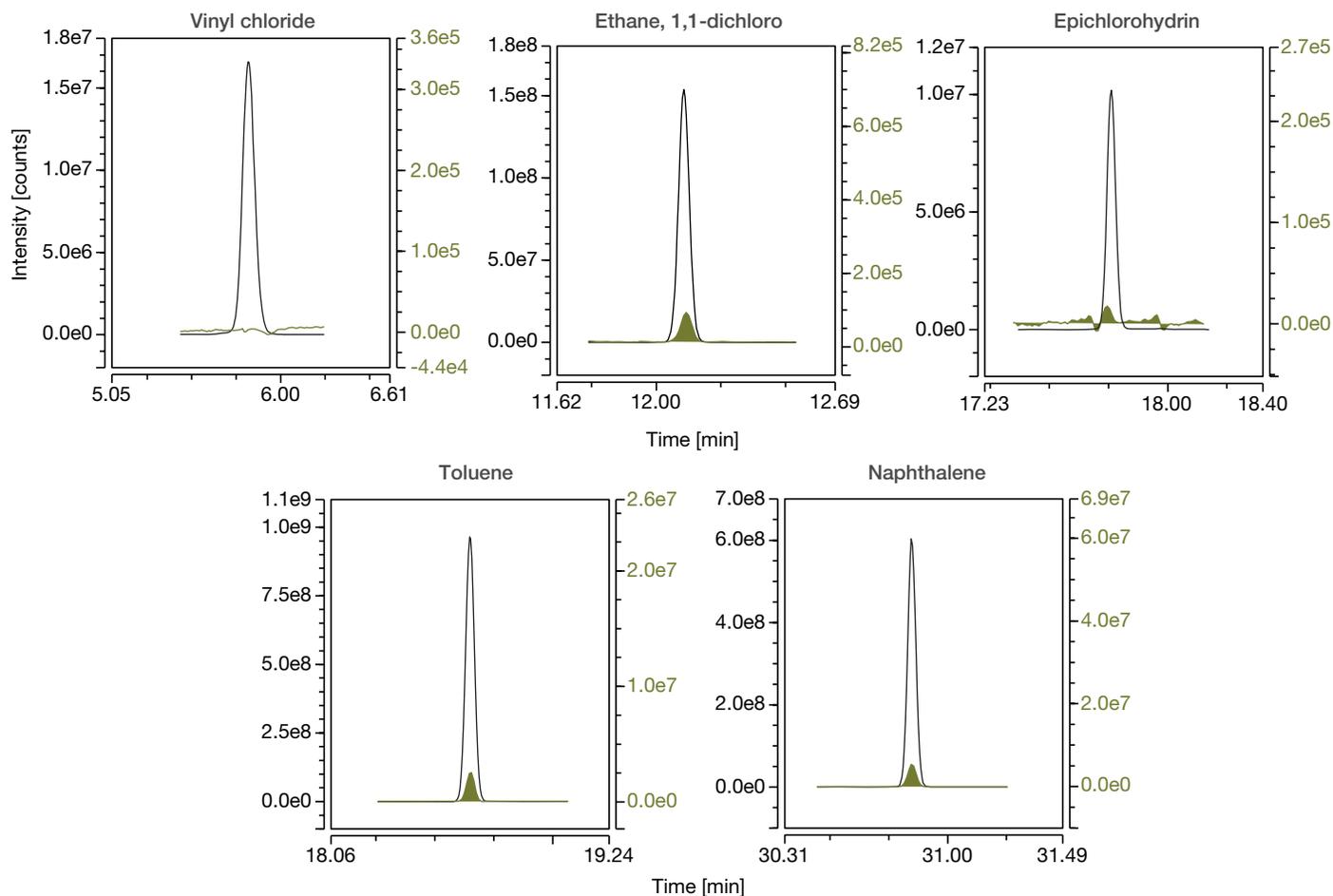


Figure 6. Examples of overlaid chromatograms of a matrix-matched standard at 10 µg/L (black trace) versus a blank sample of ultra-pure water (green trace)

Conclusions

The results of these experiments demonstrate that the In-Tube Extraction Dynamic Headspace (ITEX-DHS) coupled to the ISQ 7610 GC-MS system equipped with an iConnect PTV injector provides an ideal solution for analytical science laboratories monitoring critical contaminants in drinking water.

- Dynamic headspace is a convenient solventless extraction and enrichment technique for VVOCs, VOCs, and ECH in drinking water with almost no sample preparation required.
- The ITEX-DHS sampling technology offers a robust and powerful enrichment of volatiles, removing typical issues involved when purging the aqueous samples and allowing for equivalent limits of detection to the P&T sampling technique.
- The ITEX-DHS sampling technology coupled to a Tenax TA packed liner and PTV injector allows for analyte trapping and refocusing prior to column transfer so that improved peak shapes for the early eluting compounds can be achieved.
- The ITEX-DHS enrichment capability combined with SIM acquisitions allows for sensitive analysis of ECH and other VOCs with limits of detection in the low ppt range (from 2 to 220 ng/L) ensuring adequate performance to meet the thresholds set by the current EU regulation.
- The reliability of the entire workflow (analyte extraction, enrichment, injection, and data acquisition) was demonstrated with absolute peak area repeatability $<14\%$ over $n=10$ injections of matrix-matched standards spiked at 0.25 µg/L.
- The integrated control for both autosampler and GC-MS in a single CDS ensures a streamlined automated workflow from sample extraction to sequence set up, data acquisition, and reporting.

References

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2. Thermo Fisher Scientific, BR52235-EN 0921C, TriPlus RSH SMART robotic sampling system, <https://assets.thermofisher.com/TFS-Assets/CMD/brochures/br-52235-gc-autosampler-br52235-en-lr.pdf>
3. Thermo Fisher Scientific, AN 002784, Improvements for the analysis of volatile (VOC) and very volatile (VVOC) organic compounds using In-Tube Extraction Dynamic Headspace (ITEX-DHS) and cryogen-free refocusing, <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-002784-gc-triplus-rsh-smart-autosampler-vocs-an002784-em-en.pdf>
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Appendix 1

Table A1 (part 1). Instrument parameters

TriPlus RSH SMART ITEX-DHS parameters	
General	
Sample volume (µL)	1,300
Sampling depth mode (mm)	Custom, 27
Extraction volume (µL)	1,000
Aspirate flow (µL/s)	100
Dispense flow (µL/s)	100
Incubation temperature (°C)	70
Incubation time (min)	15
Agitation speed (rpm)	500
Pull up delay (s)	1
Number of stokes	40
Pre-fill ratio (%)	40
Syringe	
Syringe temperature (°C)	75
Trap pre cleaning temperature (°C)	100
Trap pre cleaning time (s)	0
Trap extraction temperature (°C)	35
Trap purge time (s)	5
Trap post cleaning temperature (°C)	280
Injection	
Injection depth (mm)	30
Injection speed (µL/s)	60
Injection temperature (°C)	280
Penetration speed (mm/s)	50
Injection aspiration flow rate (µL/s)	10
Injection aspiration delay (s)	0
Analysis time (min)	80
Liner	LinerGold PTV Liner, Tenax TA, 2 × 2.75 × 12 (P/N 45312145-UI)
Trap	ITEX Trap Tenax TA 80/100 (P/N 1R77010-1126)
Syringe	SMART ITEX Syringe 1.3 mL (P/N 1R77010-1127)

TRACE 1610 GC parameters	
iC-PTV	
Inlet module and mode	PTV, split
Injection temperature (°C)	35
Injection time (min)	0.30
Transfer rate (°C/s)	14.0
Transfer temperature (°C)	280
Transfer time (min)	5
Cleaning rate (°C/s)	5.0
Cleaning temperature (°C)	280
Cleaning time (min)	15.0
Cleaning flow (mL/min)	50
Post cycle temperature	Maintain
Split flow (mL/min)	2.0
Septum purge flow (mL/min)	3, constant
Carrier gas, flow (mL/min)	He, 1.2
Oven temperature program	
Temperature (°C)	35
Hold time (min)	5
Rate (°C/min)	7
Temperature 2 (°C)	260
Hold time (min)	5
GC run time (min)	42.143
Oven equilibration time (min)	0.2
Analytical column	
TraceGOLD TG-624SiIMS	30 m × 0.25 mm × 1.4 µm (P/N 26085-3330)

ISQ 7610 mass spectrometer parameters	
Transfer line temperature (°C)	260
Ion source type and temperature (°C)	Thermo Scientific™ ExtractaBrite™, 270
Ionization type	EI
Emission current (µA)	50
Aquisition mode	SIM
Tuning parameters	SMART Tune

Table A1 (part 2). List of the target compounds, including quantifier and qualifier ions

Compound name	RT (min)	Quantifier ion (m/z)	Qualifier ion 1 (m/z)	Qualifier ion 2 (m/z)
Dichlorodifluoromethane	4.89	85	87	--
Chloromethane	5.43	50	52	--
Vinylchloride	5.82	62	64	--
Ethene, 1,1-dichloro-	9.35	61	96	63
Methylene chloride	10.55	84	86	49
1,2-Dichloroethylene	11.16	96	61	98
Ethane, 1,1-dichloro-	12.11	63	65	--
Methane, bromochloro-	13.73	49	130	128
Chloroform	13.91	83	85	--
Pentafluorobenzene (ISTD)	14.20	168	137	--
Dibromofluoromethane (Surr)	14.21	111	113	192
Ethane, 1,1,1-trichloro-	14.26	97	61	--
Carbon Tetrachloride	14.56	117	119	--
Benzene	14.95	78	77	--
Ethane, 1,2-dichloro-	15.03	62	64	98
Trichloroethylene	16.17	95	130	97
Propane, 1,2-dichloro-	16.68	63	112	--
Methane, dibromo-	16.85	93	95	174
Methane, bromodichloro-	17.15	83	85	--
Epichlorohydrine	17.76	57	62	49
Toluene-D8 (Surr)	18.51	98	100	--
Toluene	18.65	91.1	92.1	--
1,1,2-Trichloroethane	19.45	97	83	85
Ethene, tetrachloro-	19.66	164	129	131
Propane, 1,3-dichloro-	19.79	76	78	--
Methane, dibromochloro-	20.23	129	127	131

Compound name	RT (min)	Quantifier ion (m/z)	Qualifier ion 1 (m/z)	Qualifier ion 2 (m/z)
Ethane, 1,2-dibromo-	20.51	107	109	--
Chlorobenzene-D5 (ISTD)	21.39	117	119	--
Benzene, chloro-	21.45	112	77	114
Ethane, 1,1,1,2-tetrachloro-	21.60	131	133	119
Ethylbenzene	21.85	91	106	--
<i>m,p</i> -Xylene	21.85	91	106	105
<i>o</i> -Xylene	22.61	91	106	--
Styrene	22.63	104	103	78
Bromoform	23.03	173	175	254
Benzene, 1,3,5-trimethyl-	23.31	105	120	77
Benzene, bromo-	24.00	156	158	77
Propane, 1,2,3-trichloro-	24.04	110	75	77
<i>n</i> -Propylbenzene	24.49	120	91	92
2-Chlorotoluene	24.60	126	91	--
Benzene, <i>tert</i> -butyl-	25.61	134	91	119
Benzene, 1,2,4-trimethyl-	25.61	105	120	--
<i>sec</i> -Butylbenzene	25.91	105	134	--
<i>p</i> -Cymene	25.91	119	134	--
1,4-Dichlorobenzene (ISTD)	26.05	152	150	--
1,3-Dichlorobenzene	26.11	146	148	111
Benzene, <i>n</i> -butyl-	26.77	91	92	134
1,4-Dichlorobenzene	26.87	146	148	111
Propane, 1,2-dibromo-3-chloro-	28.51	157	155	--
Benzene, 1,2,4-trichloro-	30.26	180	182	145
Hexachlorobutadiene	30.54	225	223	227
Naphthalene	30.85	128	--	--
Benzene, 1,2,3-trichloro-	31.31	180	182	145

Appendix 2

Table A2 (part 1). Linearity range, coefficient of determination (R^2), average calibration factor (AvCF) %RSD, calculated MDLs ($\mu\text{g/L}$), as well as absolute peak area %RSD at MDL level

Compound name	RT (min)	Cal range ($\mu\text{g/L}$)	AvCF %RSD	Coefficient of determination (R^2)	MDL level* ($\mu\text{g/L}$)	Calculated MDL ($\mu\text{g/L}$)	Absolute peak area %RSD at MDL level	Carryover (%)
Dichlorodifluoromethane	4.89	0.05-5	4.9	0.9989	0.25	0.02	6.4	0.1
Chloromethane	5.43	0.05-5	5.5	0.9986	0.25	0.05	12.0	0.5
Vinylchloride	5.82	0.05-5	10.8	0.9953	0.25	0.03	7.6	< 0.1
Ethene, 1,1-dichloro-	9.35	0.05-5	5.8	0.9985	0.10	0.01	11.0	0.3
Methylene chloride	10.55	0.05-5	6.2	0.9984	0.10	0.01	4.8	0.1
1,2-Dichloroethylene	11.16	0.05-5	5.3	0.9988	0.05	0.002	11.0	0.1
Ethane, 1,1-dichloro-	12.11	0.05-5	5.0	0.9989	0.05	0.004	12.3	0.1
Methane, bromochloro-	13.73	0.05-5	6.9	0.9981	0.10	0.01	5.0	0.1
Chloroform	13.91	0.05-5	5.7	0.9986	0.10	0.01	5.8	0.1
Pentafluorobenzene (ISTD)	14.20	--	--	--	--	--	--	--
Dibromofluoromethane (Surr)	14.26	--	--	--	--	--	--	--
Ethane, 1,1,1-trichloro-	14.26	0.05-5	5.6	0.9986	0.25	0.03	5.0	0.1
Carbon Tetrachloride	14.56	0.05-5	6.8	0.9980	0.25	0.03	5.2	0.1
Benzene	14.95	0.10-5	1.9	0.9997	0.25	0.06	11.3	1.5
Ethane, 1,2-dichloro-	15.03	0.05-5	4.6	0.9991	0.05	0.007	9.0	0.2
Trichloroethylene	16.17	0.05-5	2.5	0.9997	0.05	0.004	7.3	0.2
Propane, 1,2-dichloro-	16.68	0.05-5	5.1	0.9989	0.05	0.003	9.9	0.1
Methane, dibromo-	16.85	0.05-5	4.0	0.9993	0.05	0.004	8.5	0.2
Methane, bromodichloro-	17.15	0.05-5	14.0	0.9927	0.10	0.01	4.9	0.1
Epichlorohydrin	17.76	0.025-5	3.6	0.9995	0.05	0.01	5.1	0.1
Toluene-d8 (Surr)	18.51	--	--	--	--	--	--	--
Toluene	18.65	0.05-5	4.0	0.9993	0.10	0.01	6.6	0.3
1,1,2-Trichloroethane	19.45	0.05-5	6.3	0.9983	0.10	0.01	19.8	0.4
Ethene, tetrachloro-	19.66	0.05-5	6.0	0.9984	0.25	0.03	6.9	0.3
Propane, 1,3-dichloro-	19.79	0.05-5	6.7	0.9981	0.10	0.01	3.9	0.2
Methane, dibromochloro-	20.23	0.05-5	5.0	0.9990	0.10	0.01	4.9	0.2
Ethane, 1,2-dibromo-	20.51	0.05-5	6.1	0.9985	0.10	0.01	4.6	0.2
Chlorobenzene-d5 (ISTD)	21.39	--	--	--	--	--	--	--
Benzene, chloro-	21.45	0.05-5	3.5	0.9995	0.05	0.003	10.1	0.3
Ethane, 1,1,1,2-tetrachloro-	21.60	0.05-5	3.5	0.9995	0.05	0.003	9.2	0.2
Ethylbenzene	21.85	0.05-5	4.3	0.9992	0.10	0.004	5.3	0.3
<i>m,p</i> -Xylene	21.85	0.05-5	4.3	0.9992	0.10	0.004	5.3	0.3
<i>o</i> -Xylene	22.61	0.05-5	3.5	0.9995	0.10	0.005	5.4	0.3
Styrene	22.63	0.05-5	3.6	0.9994	0.25	0.03	10.2	0.3

(*) Standard concentration used for the MDL calculation

Table A2 (part 2). Linearity range, coefficient of determination (R^2), average calibration factor (AvCF) %RSD, calculated MDLs ($\mu\text{g/L}$), as well as absolute peak area %RSD at MDL level

Compound name	RT (min)	Cal range ($\mu\text{g/L}$)	AvCF %RSD	Coefficient of determination (R^2)	MDL level* ($\mu\text{g/L}$)	Calculated MDL ($\mu\text{g/L}$)	Absolute peak area %RSD at MDL level	Carryover (%)
Bromoform	23.03	0.05-5	4.5	0.9991	0.25	0.02	7.6	0.2
Benzene, 1,3,5-trimethyl-	23.31	0.05-5	4.5	0.9991	0.05	0.003	10.3	0.2
Benzene, bromo-	24.00	0.05-5	3.0	0.9996	0.05	0.004	9.2	0.3
Propane, 1,2,3-trichloro-	24.04	0.05-5	6.5	0.9982	0.25	0.02	7.0	0.3
n-Propylbenzene	24.49	0.05-5	4.3	0.9992	0.05	0.003	10.6	0.3
2-Chlorotoluene	24.60	0.05-5	3.3	0.9995	0.05	0.004	10.9	0.4
Benzene, 1,2,4-trimethyl-	25.61	0.05-5	5.3	0.9988	0.05	0.002	12.2	0.2
Benzene, <i>tert</i> -butyl-	25.61	0.05-5	5.4	0.9988	0.05	0.002	11.8	0.2
<i>p</i> -Cymene	25.91	0.05-5	5.3	0.9982	0.05	0.003	11.6	0.3
<i>sec</i> -Butylbenzene	25.91	0.05-5	6.4	0.9988	0.10	0.004	4.8	0.3
1,4-Dichlorobenzene (ISTD)	26.05	--	--	--	--	--	--	--
1,3-Dichlorobenzene	26.11	0.05-5	3.7	0.9994	0.25	0.03	10.3	0.4
Benzene, <i>n</i> -butyl-	26.77	0.05-5	4.5	0.9991	0.05	0.003	11.4	0.3
1,4-Dichlorobenzene	26.87	0.05-5	2.4	0.9998	0.05	0.005	11.0	0.4
Propane, 1,2-dibromo-3-chloro-	28.51	0.05-5	5.5	0.9987	0.25	0.02	5.6	0.2
Benzene, 1,2,4-trichloro-	30.26	0.05-5	3.0	0.9996	0.05	0.006	10.3	0.5
Hexachlorobutadiene	30.54	0.05-5	6.6	0.9981	0.10	0.004	6.1	0.2
Naphthalene	30.85	0.05-5	4.3	0.9993	0.25	0.22	6.1	0.9
Benzene, 1,2,3-trichloro-	31.31	0.05-5	3.3	0.9996	0.10	0.01	5.2	0.8

(* Standard concentration used for the MDL calculation)

Appendix 3

Table A3. Schematics for calibration curve preparation

Calibration level	Concentration in vial ($\mu\text{g/L}$)	Bulk calibration solution ($\mu\text{g/L}$)	Spiking amount (μL)	ISTD / Surrogate concentration in vial ($\mu\text{g/L}$)	Bulk ISTD / Surrogate solution ($\mu\text{g/L}$)	ISTD/ Surrogate spiking amount (μL)
Blank	--	--	--	2.5	625	40
1	0.025	5	50	2.5	625	40
2	0.05	5	100	2.5	625	40
3	0.1	50	20	2.5	625	40
4	0.25	50	50	2.5	625	40
5	0.5	50	100	2.5	625	40
6	1.0	500	20	2.5	625	40
7	2.5	500	50	2.5	625	40
8	5.0	500	100	2.5	625	40

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