

## Environmental

# 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

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## Keywords

VOC, VVOC, water, dynamic  
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PTV, TRACE 1610 GC, TriPlus RSH  
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## Goal

To demonstrate how the technological development of dynamic headspace extraction/enrichment techniques, such as ITEX-DHS (In-Tube Extraction-Dynamic Headspace) coupled to a cryogen-free refocusing in the PTV injector, enables the achievement of lower detection limits for volatile and very volatile organic compounds.

## Introduction

Volatile organic compounds (VOCs) are a group of organic chemicals with low vapor pressure that can easily evaporate into the air, even at room temperature. These compounds can originate from various sources, including industrial processes, vehicle emissions, and natural sources. While VOCs are often associated with air pollution, they can also contaminate water, thus posing potential risks to human health and the environment.<sup>1</sup> VOCs can enter water through direct discharges, atmospheric deposition, or runoff from contaminated areas. Common VOCs found in water include benzene, toluene, ethylbenzene, and xylene (BTEX), as well as chlorinated compounds such as trichloroethylene (TCE) and tetrachloroethylene (PCE). These compounds can cause adverse health effects, ranging from short-term irritation to long-term chronic conditions, depending on the concentration and duration of exposure.

Regulatory authorities all over the world have established limits to control the maximum 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, monitoring and analyzing VOCs in water play crucial roles in identifying and addressing potential contamination issues, guiding remediation efforts, and ensuring compliance with water quality regulations.<sup>4</sup>

Common methods to analyze VOCs in water include headspace, purge and trap, solid-phase microextraction, and liquid-liquid extraction as possible sample preparation techniques employed to extract and concentrate VOCs before GC-MS analysis. As technology advances, continuous improvements in analytical methods and instrumentation contribute to more accurate and efficient VOC analysis, enhancing the ability to safeguard water resources and public health.

When dealing with drinking water testing, the limits of detection are particularly challenging, requiring an efficient enrichment before GC-MS analysis.

In-Tube Extraction-Dynamic Headspace (ITEX-DHS) is a sample preparation technique for the extraction and preconcentration of volatile compounds from different matrices, such as water, soil, or biological samples. One of the key advantages of ITEX-DHS is its high sensitivity and selectivity for volatile compounds. It allows for the extraction of low concentrated analytes from complex matrices while minimizing interference from non-volatile matrix components. Additionally, the technique offers an automated and efficient sampling process through a robotic autosampler, making it suitable for unattended and time-sensitive analyses.

ITEX-DHS has found applications in various fields, including environmental monitoring, food analysis, and forensic science. Its versatility makes it particularly valuable in situations where trace-level analysis of volatile compounds is crucial. An example of the use of ITEX-DHS for the detection of odorants in water at ng/L level is reported in a previous application note.<sup>5</sup>

In this study, the performance of the ITEX-DHS sampling technique has been evaluated for trace level detection of volatile and very volatile compounds (VVOCs) in water, in combination with peak refocusing into a Programmed Temperature Vaporizer (PTV) injector, to enhance peak shape and signal-to-noise ratio.

## Experimental

The Thermo Scientific™ TriPlus™ RSH SMART autosampler equipped with the ITEX-DHS tool has been coupled to the Thermo Scientific™ TRACE™ 1610 gas chromatograph connected to a Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer, which features the Thermo Scientific™ ExtractaBrite™ EI ion source with NeverVent™ technology. The AEI ion source, offering even higher sensitivity, is optional in case lower detection limits are required.

The ITEX-DHS technique involves the use of a small trap embedded into a gas-tight syringe (Figure 1), which selectively adsorbs and enriches the target compounds from the sample headspace during the withdrawing step. The adsorbent material used in this study was the standard Tenax™ TA 80/100 mesh, suitable for volatile compounds. The collection of the headspace through repeated strokes of the syringe allows for a scalable sensitivity level according to the number of strokes, making this approach versatile towards low and high concentration samples.

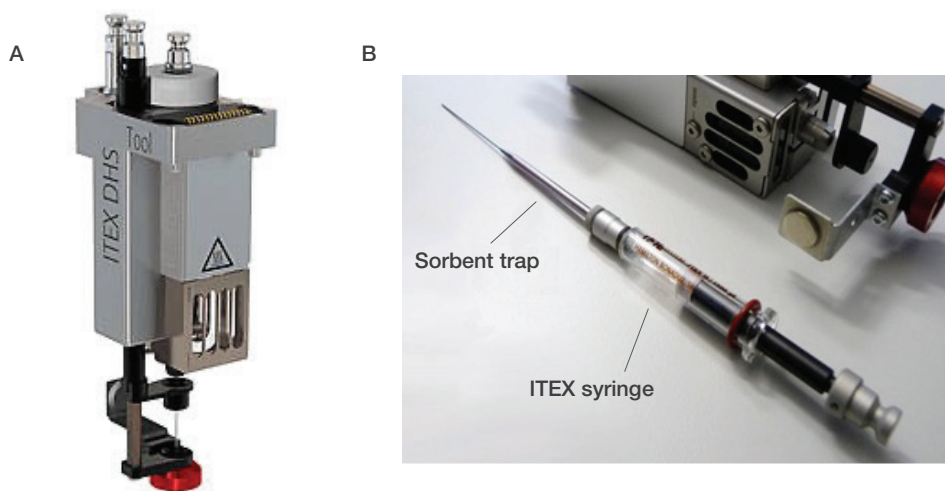


Figure 1. ITEX-DHS tool for the TriPlus RSH SMART autosampler (A) and ITEX gas-tight syringe (B)

This enrichment provides a clear benefit in terms of sensitivity compared to the static headspace sampling approach where only a limited headspace volume (typically 1 mL) is sampled and analyzed. As more strokes of the gas-tight syringe typically result in higher enrichment of the volatile compounds in the trap, this setup is suitable to deliver sensitivity levels comparable to those obtained using a purge and trap system, however, with a less complex setup and more flexible operations.

Following the adsorption step, the trap is thermally desorbed by rapid heating while the syringe delivers the desorbed analytes into the GC inlet for the analysis (Figure 2).

A refocusing step after the trap desorption can be achieved into the Thermo Scientific™ iConnect™ PTV injector by using a packed liner dedicated to VOCs analysis (Figure 3), improving peak shape and sensitivity especially for very volatile compounds such as vinyl chloride.

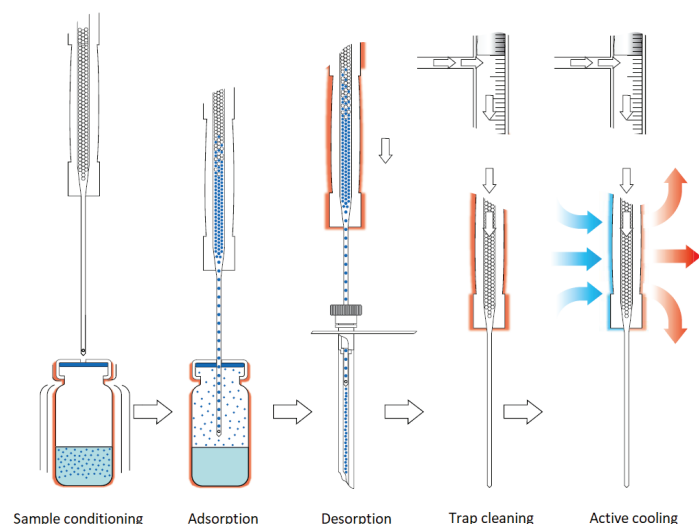


Figure 2. Schematic of the ITEX-DHS sample extraction and desorption process



Figure 3. 2 mm ID packed deactivated glass liner for the iConnect PTV injector module

The method parameters are summarized in Tables 1 and 2, while the list of target compounds along with SIM Quan/Qual ions are reported in Appendix Table A1.

Table 1. ITEX-DHS parameters

Parameter	Setting
Vial size	20 mL
ITEX-DHS trap	Tenax TA 80/100 mesh (P/N 1R77010-1126)
Incubation time	15 min
Incubation temperature	70 °C
Agitator speed	500 rpm
Trap pre-cleaning temperature	280 °C
Trap pre-cleaning time	240 s
Extraction strokes	40
Trap extraction temperature	35 °C
Syringe temperature	50 °C
Extraction volume	1,000 µL
Extraction aspirate flow rate	100 µL/s
Extraction dispense flow rate	100 µL/s
Sample volume in vial	10 mL
Sample prefill ratio	40%
Water removal	Disabled
Desorb temperature	280 °C
Injector aspirate flow rate	10 µL/s
Desorb flow rate	80 µL/s
Sample volume	1,300 µL
Injector penetration speed	50 mm/s
Trap post cleaning time	240 s

Table 2. GC-MS parameters

Parameter	Setting
Inlet	PTV
PTV program	35 °C (0.3 min), 14 °C/s to 280 °C (30 min)
Inlet mode	Split
Split flow	2 mL/min
Carrier gas	Helium (99.999% purity)
Carrier gas flow rate	1.2 mL/min
Oven temperature program	35 °C (5 min), 7 °C/min to 250 °C (3 min)
GC run time	38.7 min
MS transfer line temperature	250 °C
Ionization mode	EI, 70 eV
MS acquisition mode	Timed SIM see table Appendix Table A1
Ion source temperature	250 °C

## Data acquisition, processing, and reporting

Data was acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. The 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

A 50 µg/L dilution in water was prepared from a stock solution containing 1,000 µg/mL of the VOCs analyzed in this study, dissolved in methanol. 50 µg/L 1-bromo-2-chloroethane and 30 µg/L fluorobenzene were also added to this solution as internal standards.

Of this solution, 1,000 µL were diluted with 9,000 µL deionized water containing NaCl at a concentration of 55 g/L. This operation was done directly into a 20 mL headspace vial, which was immediately sealed with magnetic crimp caps.

## Results and discussion

### PTV refocusing

VVOCs are characterized by low boiling points, and their chromatographic separation can be challenging. Due to their

low retention (primarily influenced by the low boiling point), they may initially overload the GC column, causing band broadening with reduced peak intensity. The refocusing effect is particularly beneficial when analyzing these highly volatile compounds to improve the precision and sensitivity of the analysis.

In this work, the refocusing effect has been achieved inside of the PTV injector by using a dedicated liner packed with Tenax TA and has had an impactful effect without the use of any cryogenic device. This means a simplification of the hardware setup and method parameters and the avoidance of issues related to moisture potentially frozen out in a cryogenic trap. By concentrating the analytes before they enter the GC column, better peak shapes and improved signal-to-noise ratios can be achieved, leading to more accurate and reliable results. Figure 4 shows the effect of using the packed liner on some very volatile compounds.

### Chromatography

The separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-624SiIMS GC column, 60 m x 0.25 mm x 1.4 µm (P/N 26059-3330), which offers a medium polarity and a suitable phase ratio for a good separation over a wide range of volatile compounds from vinyl chloride to trichlorobenzene.

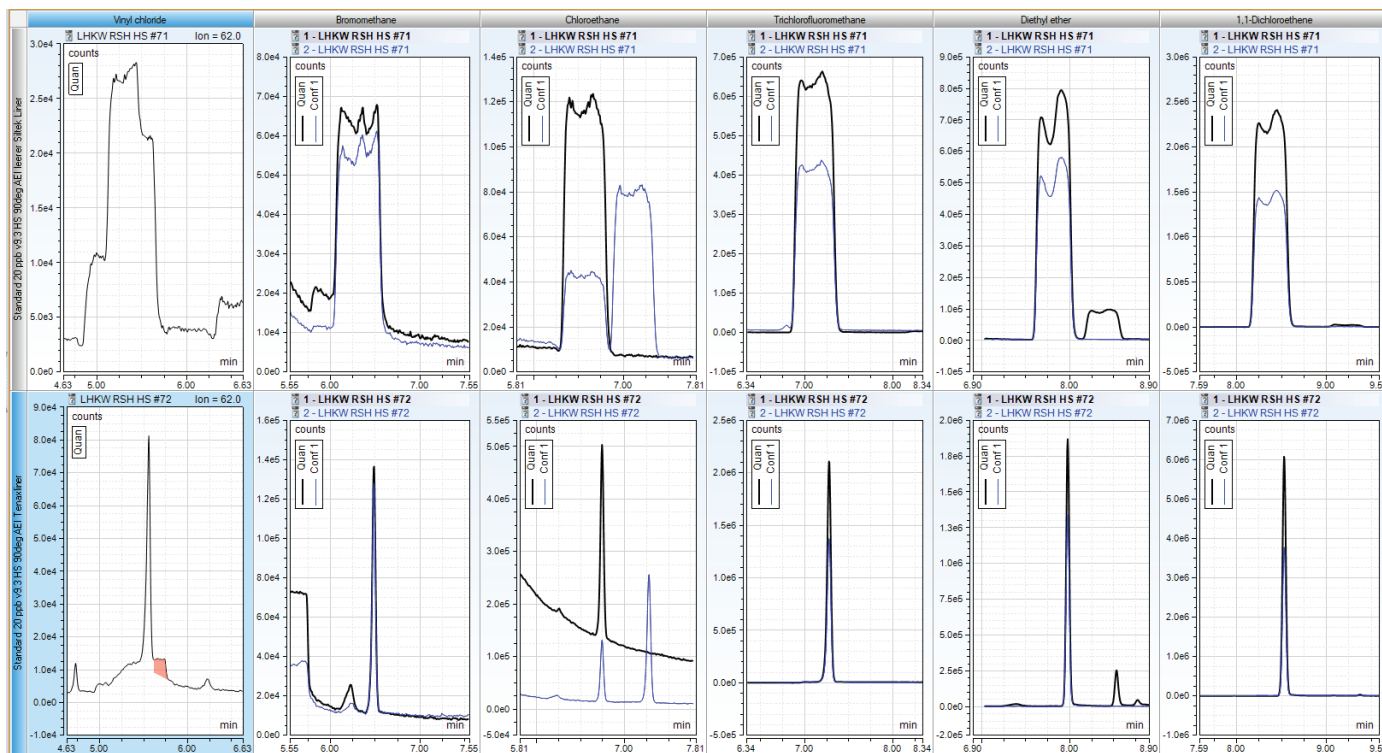


Figure 4. Comparison of VVOC peak shape with a standard PTV liner (upper) and the PTV with the packed VOC-liner (bottom)

The use of the ITEX-DHS technique to perform a dynamic headspace sampling effectively removed the matrix so that a clean sample was injected onto the GC, which helped in turn to reduce baseline noise and simplify operations by using a t-SIM acquisition mode.

### Linearity and limit of detection

Linearity of the recovery has been assessed across the concentration range from 0.005 µg/L to 10 µg/L with a coefficient of determination  $R^2 > 0.995$  and an average calibration factor

%RSD < 3.17%, as reported in Appendix Table A2. Figures 5 and 6 show examples of linearity for chlorinated hydrocarbons and aromatics compounds, respectively.

Considering the targeted low detection limits, the blank contamination from the environment was found to be an issue for some aromatic compounds used as solvents in the lab, as evident in Figure 6. For those compounds, it was not possible to evaluate a limit of quantification below the contamination level.

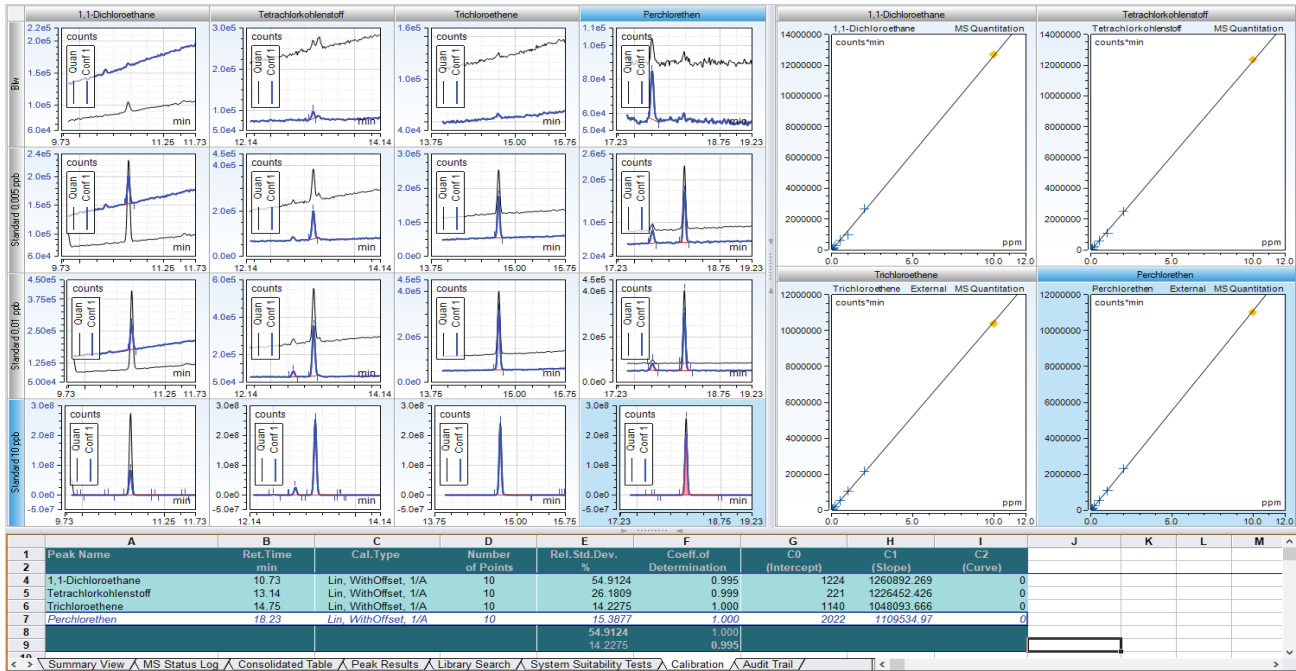


Figure 5. Examples of linearity response for some chlorinated hydrocarbons. Top to bottom: blank, 0.005 µg/L, 0.01 µg/L, 10 µg/L

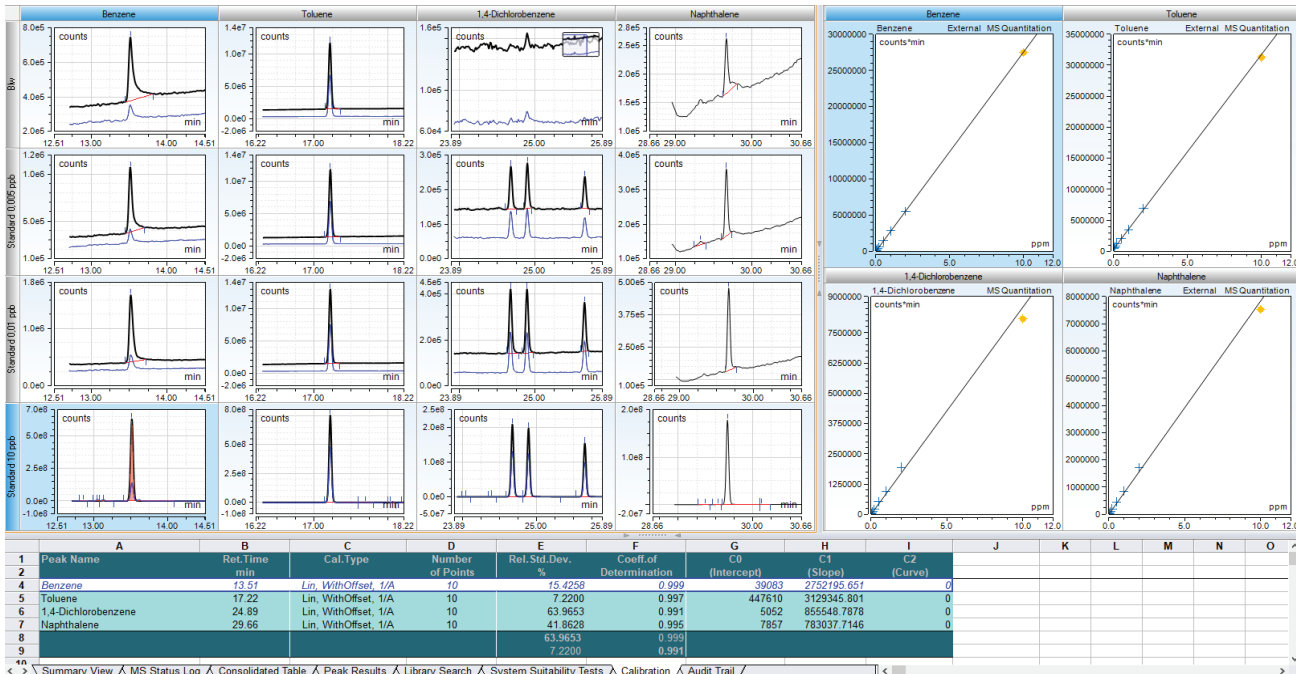


Figure 6. Examples of linearity response for some aromatic hydrocarbons. Top to bottom: blank, 0.005 µg/L, 0.01 µg/L, 10 µg/L

The headspace enrichment capacity of the ITEX-DHS technique, combined with a SIM mode MS acquisition, allows the achievement of low ppt level sensitivity (Appendix Table A2), suitable to meet stringent regulatory requirements for drinking water testing. The limits of detection reported in Table A2 were extrapolated to S/N=3 after blank subtraction.

### Repeatability

The entire process of extraction, enrichment, injection, and re-focusing is very repeatable as demonstrated over a sequence of 12 subsequent injections of fresh aliquots of the same sample with and without internal standard.

As shown in Table 3, the analysis demonstrates the excellent precision of the process, with an average of 4.4% RSD on quantitative recovery from a standard solution at 2.5 µg/L with the use of an external standard. The precision is further improved to an average of 2.7% RSD with the use of the internal standard.

Even if the average RSD has improved with the use of the IS, such improvement is not visible for all the compounds. In fact, the IS should be individually selected. Some recommendations on the IS selection are reported in the new EN ISO 20595:2023.

### Carryover

When dealing with trace analysis, possible carryover from more concentrated samples can pose a critical challenge. In this study, carryover has been checked by running clean DI-water after the analysis of a standard mixture at 10 µg/L, obtaining for all analytes a carryover less than 0.027%, without blank subtraction, as shown in Figure 7.

**Table 3. Recovery precision over n=12 repetitions with and without internal standard**

Compound	ESTD	ISTD
Dichlorodifluoromethane	5.0%	4.4%
Trichlorofluoromethane	3.1%	2.0%
1,1-Dichloroethene	3.0%	1.7%
Dichloro-methane	4.4%	1.8%
<i>trans</i> -1,2-Dichloroethene	3.6%	0.9%
<i>cis</i> -1,2-Dichloroethene	4.4%	0.9%
Chloroform	4.1%	0.8%
1,1,1-Trichloroethane	3.3%	1.3%
Carbon tetrachloride	4.1%	1.9%
Benzene	5.6%	2.3%
1,2-Dichloroethane	6.0%	3.1%
Fluorobenzene (ISTD)	4.1%	--
Trichloroethene	3.9%	4.3%
Bromodichloromethane	5.0%	1.5%
1-Bromo-2-chlorethane (ISTD)	6.4%	--
Toluene	3.4%	3.6%
Perchloroethylene	3.1%	4.8%
Dibromochloromethane	6.4%	2.2%
Ethylbenzene	3.5%	4.3%
<i>m/p</i> -Xylene	3.6%	4.2%
<i>o</i> -Xylene	3.9%	4.1%
Bromoform	7.9%	4.2%
<b>Average value</b>	<b>4.4%</b>	<b>2.7%</b>



**Figure 7. Carryover for all analytes is <0.027%. Top traces: clean DI-water before standard mix analysis. Middle traces: standard mixture at 10 µg/L. Bottom traces: clean DI-water after standard mix analysis.**

## Conclusion

The use of the ITEX-DHS technique for headspace enrichment coupled to cryogen-free refocusing into the PTV injector is a suitable approach for trace level analysis of VOC and VVOC in water samples, offering a clean method to comply with more stringent regulatory limits of quantitation.

- Combined with refocusing prior to transfer into the column and SIM acquisition mode, the ITEX-DHS technique achieves limits of quantification at low ppt levels and extrapolated limits of detection in the sub-ppt range, even for VVOC such as vinyl chloride, with high recovery precision (<5% RSD) and a linear response over four orders of magnitude.
- ITEX-DHS offers a flexible enrichment technique capable of handling low and high concentrated samples to comply with different sensitivity requirements.
- The complete workflow, from method set up to data processing and reporting, can be fully controlled through Chromeleon CDS, which greatly facilitates operations on a day-to-day basis.

## Appendix

Table A1. List of target VOC compounds with RT and Quan/Qual ions

Component	Retention time (min)	Quantifier ion	Qualifier ion
Dichlorodifluoromethane	4.863	85	87
Trichlorofluoromethane	7.843	101	103
1,1-Dichloroethene	9.236	61	96
Dichloromethane	10.482	84	49
<i>trans</i> -1,2-Dichloroethene	10.917	96	61
<i>cis</i> -1,2-Dichloroethene	13.092	96	61
Chloroform	13.677	83	85
1,1,1-Trichloroethane	13.978	97	99
Carbon tetrachloride	14.217	117	119
Benzene	14.686	78	51
1,2-Dichloroethane	14.863	62	64
Fluorobenzene (ISTD)	15.227	96	70
Trichloroethene	15.878	130	132
Bromodichloromethane	16.892	83	85
1-Bromo-2-chloroethane (ISTD)	17.577	63	144
Toluene	18.313	91	92
Perchloroethylene	19.321	166	164
Dibromochloromethane	19.956	129	127
Ethylbenzene	21.269	91	106
<i>m/p</i> -Xylene	21.506	91	106
<i>o</i> -Xylene	22.338	91	106
Bromoform	22.86	173	79
1,4-Dichlorobenzene	24.89	146	148
Naphthalene	29.66	128	-

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**Table A2. List of compounds with coefficient of variation (%), extrapolated limit of detection, and coefficient of correlation R<sup>2</sup> (in the conc. range 0.005 µg/L to 10 µg/L)**

Peak name	Var. coeff. (%)	Detection limit* (µg/L)	R <sup>2</sup>
Dichlorodifluoromethane	2.39	0.0043	0.9994
Trichlorofluoromethane	2.42	0.0001	0.9994
1,1-Dichloroethene	2.3	0.0001	0.9995
Dichloromethane	2.06	0.0001	0.9995
<i>trans</i> -1,2-Dichloroethene	2.82	0.0001	0.9992
<i>cis</i> -1,2-Dichloroethene	2.81	0.0001	0.9989
Chloroform	1.63	0.0001	0.9997
1,1,1-Trichloroethane	2.03	0.0006	0.9996
Carbon tetrachloride	3.68	0.0047	0.9986
Benzene**	5.41	0.132	0.9953
1,2-Dichloroethane	2.03	0.0003	0.9996
Fluorobenzene (ISTD)	n.a.	n.a.	n.a.
Trichloroethene	3.43	0.0002	0.9949
Bromodichloromethane	2.56	0.0002	0.9993
1-Bromo-2-chloroethane (ISTD)	n.a.	n.a.	n.a.
Toluene**	2.53	0.102	0.9972
Perchloroethylene	4.24	0.0003	0.9976
Dibromochloromethane	3.2	0.0001	0.9989
Ethylbenzene	2.78	0.0001	0.9992
<i>m/p</i> -Xylene	3.35	0.0001	0.9988
<i>o</i> -Xylene	3.23	0.0001	0.9989
Bromoform	5.04	0.0004	0.9974
1,4-Dichlorobenzene	14.6	0.0005	0.9780
Naphthalene	13.2	0.0082	0.9724

\*Extrapolated to S/N = 3 after blank subtraction

\*\*Detection limits are influenced by laboratory blanks from ambient air in the lab or DI-water used for sample preparation.

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