Simplified and cost-effective approaches for the determination of volatile organics in water

Using GC-MS with static headspace and In-tube Extraction Dynamic Headspace coupled to hydrogen carrier gas

Keywords
Volatile organic compounds, VOCs, water, GC-MS, static headspace (SHS) and In-Tube Extraction Dynamic Headspace (ITEX-DHS), hydrogen carrier gas

Goal

The aim of this study is to demonstrate the suitability of In-Tube Extraction Dynamic Headspace (ITEX-DHS) for the analysis of volatile organic compounds (VOCs) in drinking water, when using hydrogen carrier gas to provide a cost-effective alternative to helium.

Introduction

Volatile organic compounds (VOCs) can enter water supplies through spills or underground leaks and contaminate surface and groundwater. These pollutants are usually present at trace concentrations; therefore, they need to be extracted and pre-concentrated prior the analysis.

In this study, static headspace (SHS) and In-Tube Extraction Dynamic Headspace (ITEX-DHS) sampling techniques were used for the determination of VOCs in drinking water. Both these techniques use a syringe-based approach that allows for a simplified hardware configuration delivering high robustness and ease of use. In contrast to purge and trap (P&T), often a reference method for preconcentration of volatile analytes, both aforementioned solutions do not require the installation of transfer lines or switching valves.

Hydrogen was selected as carrier gas as it reduces running costs significantly, is renewable, and provides high optimal linear velocity, which translates to shorter analysis times and increased productivity without compromising efficiency. However, the use of hydrogen may not always be an option, as sensitivity may be negatively affected, and some compounds may undergo chemical reactions in the inlet, leading to potentially false negative results. In the following, the use of both sampling techniques was evaluated in the context of the applicable regulations as per the European Parliament Directive (EU) 2020/2184 on the quality of water intended for human consumption.[1]

Experimental

In this study a Thermo Scientific™ TRACE™ 1610 gas chromatograph equipped with a Thermo Scientific™ iConnect™ split/splitless injector, upgraded to work in HeSaver-H_2Safer mode, and a Thermo Scientific™ iConnect™ programmed temperature vaporizer (iConnect-PTV) injector was coupled to a Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer. A Thermo Scientific™ TriPlus™ RSH SMART autosampler equipped with both ITEX-DHS and SHS configuration was used. Instrument set up conditions are summarized in Table 1. Comparative data with helium used as carrier gas, including complete method settings, are listed in two application notes previously published.[1,2]

Results and discussion

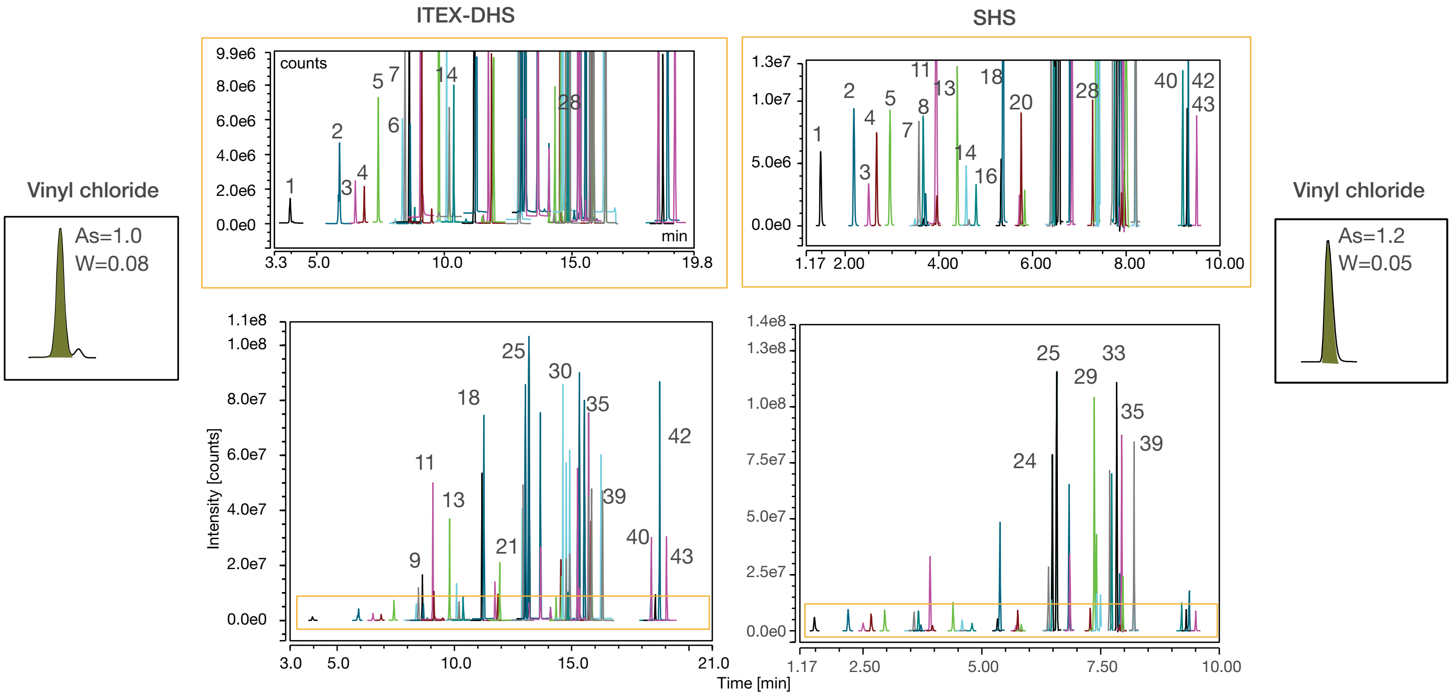
Peak broadening of early eluting compounds can occur due to a poor re-focalization of the analytes at the head of the GC column. Focusing the analytes into the iConnect-PTV inlet at low temperature by using a PTV Tenax™ TA liner allowed for analyte transfer into a very narrow band ensuring Gaussian peak shapes for early eluting compounds. Moreover, the use of hydrogen as carrier gas provided improved peak shapes when injecting at high temperature into the HeSaver-H_2Safer injector (Figure 1).

Hydrogen is a reactive gas that can affect the ionization process resulting in some spectral differences, such as number of fragments and relative ion abundances, compared to helium. Figure 2 shows an example of spectral comparison between mass spectra acquired with hydrogen for both PTV and HeSaver-H_2Safer injectors as well as a comparison with the NIST23 mass spectral library. Overall, the search index scores (SI) fit well to the NIST library, demonstrating that hydrogen is not a concern in terms of spectral fidelity.

Linearity was assessed by injecting seven calibration levels ranging from 0.05 to 5 µg/L for ITEX-DHS and from 0.1 to 100 µg/L for SHS sampling. Coefficients of determination (R^2) were better than >0.990 for both sampling techniques with residual values (measured as %RSD of average response factors, AvCF %RSD) <20% (Figure 3).

Table 1. Instrument set up applied for analysis of VOCs in drinking water using ITEX-DHS and SHS sampling

Parameter	ITEX-DHS	SHS
TRACE 1610 GC inlet	i-Connect PTV	i-Connect HeSaver-H_2Safer
Liner	Thermo Scientific™ LinerGOLD™, Tenax™ PTV liner (P/N 45312145-UI)	SSL Direct Straight Liner (P/N 453A1335)
Carrier gas, flow (mL/min)	H_2, 1.5	H_2, 0.7
GC oven program	35 °C, hold 3.0 min 11.7 °C/min to 260 °C, hold 3 min	35 °C, hold 1.8 min 15 °C/min to 85 °C 25 °C/min to 260 °C, hold 2 min
Column	Thermo Scientific™ TraceGOLD™ TG 624 SILMS 60 m × 0.25 mm, 1.4 µm (P/N 26059-3330)	Thermo Scientific™ TraceGOLD™ TG-624 SILMS 20 m × 0.18 mm, 1.0 µm (P/N 26059-4950)



1. Vinyl chloride
2. Ethene, 1,1-dichloro-
3. Methylene chloride
4. 1,2-Dichloroethylene
5. Ethane, 1,1-dichloro-
6. Methane, bromochloro-
7. Chloroform
8. Dibromofluoromethane (Surr)
9. Benzene, pentafluoro- (ISTD)
10. Ethane, 1,1,1-trichloro-
11. Benzene
12. Ethane, 1,2-dichloro-
13. Trichloroethylene
14. Propane, 1,2-dichloro-
15. Methane, dibromo-
16. Methane, bromodichloro;
17. Toluene-D8 (Surr)
18. Toluene
19. 1,1,2-Trichloroethane
20. Ethene, tetrachloro-
21. Propane, 1,3-dichloro-
22. Chlorobenzene-d5 (ISTD)
23. Benzene, chloro-
24. Ethylbenzene
25. *m,p*-Xylene
26. o-Xylene
27. Styrene
28. Benzene, bromo-
29. Propane, 1,2,3-trichloro-
30. *n*-Propylbenzene
31. 2-Chlorotoluene
32. Benzene, *tert*-butyl-
33. Benzene, 1,2,4-trimethyl-
34. *sec*-Butylbenzene
35. *p*-Cymene
36. 1,4-Dichlorobenzene-d4 (ISTD)
37. Benzene, 1,3-dichloro-
38. Benzene, *n*-butyl-
39. 1,4-Dichlorobenzene
40. Benzene, 1,2,4-trichloro-
41. Hexachlorobutadiene
42. Naphthalene
43. Benzene, 1,2,3-trichloro-

Figure 1. SIM traces showing an example of the chromatographic separation obtained for a matrix-matched standard using ITEX-DHS (concentration: 5 µg/L) and SHS (concentration: 100 µg/L) sampling. Peak asymmetry and width (calculated at 50% height) for the first eluting compound (vinyl chloride) are annotated.

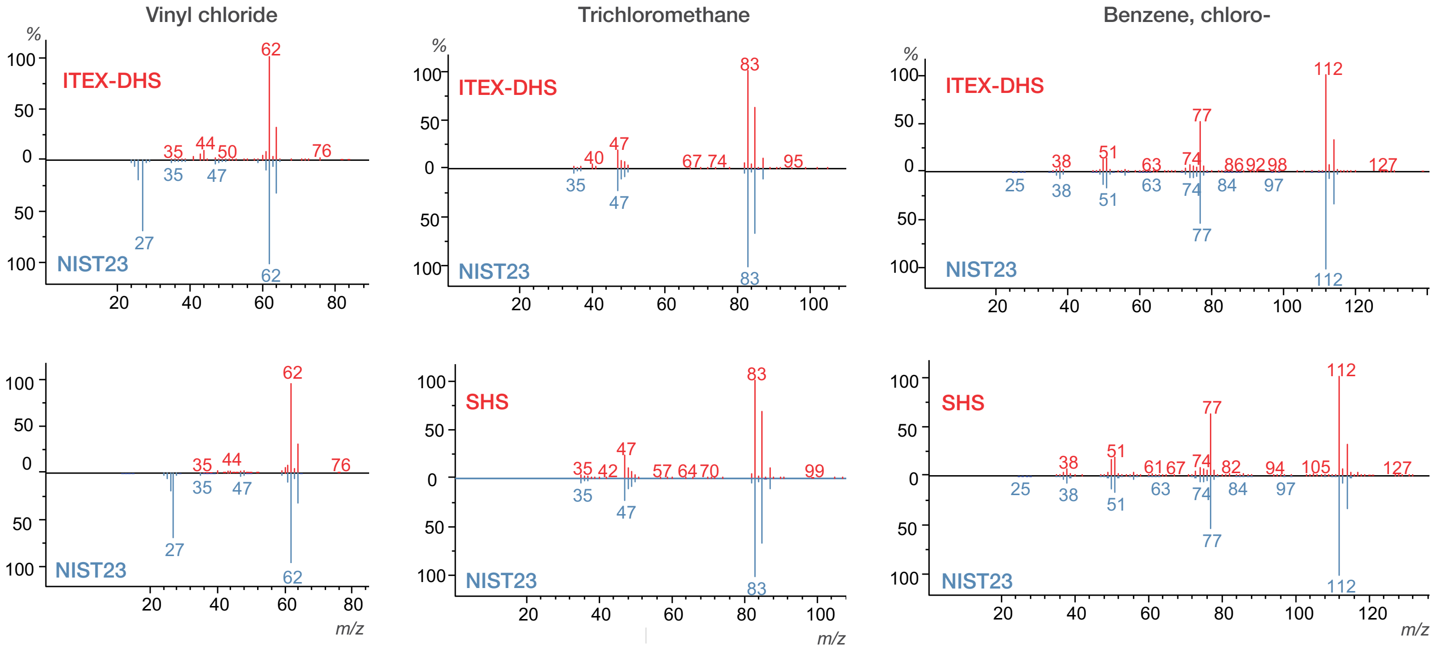


Figure 2. Examples of acquired spectra for PTV and HeSaver-H_2Safer injectors (carrier gas: hydrogen) versus NIST23 spectral library (carrier gas: helium). Acquisition range: *m/z* 35–300.

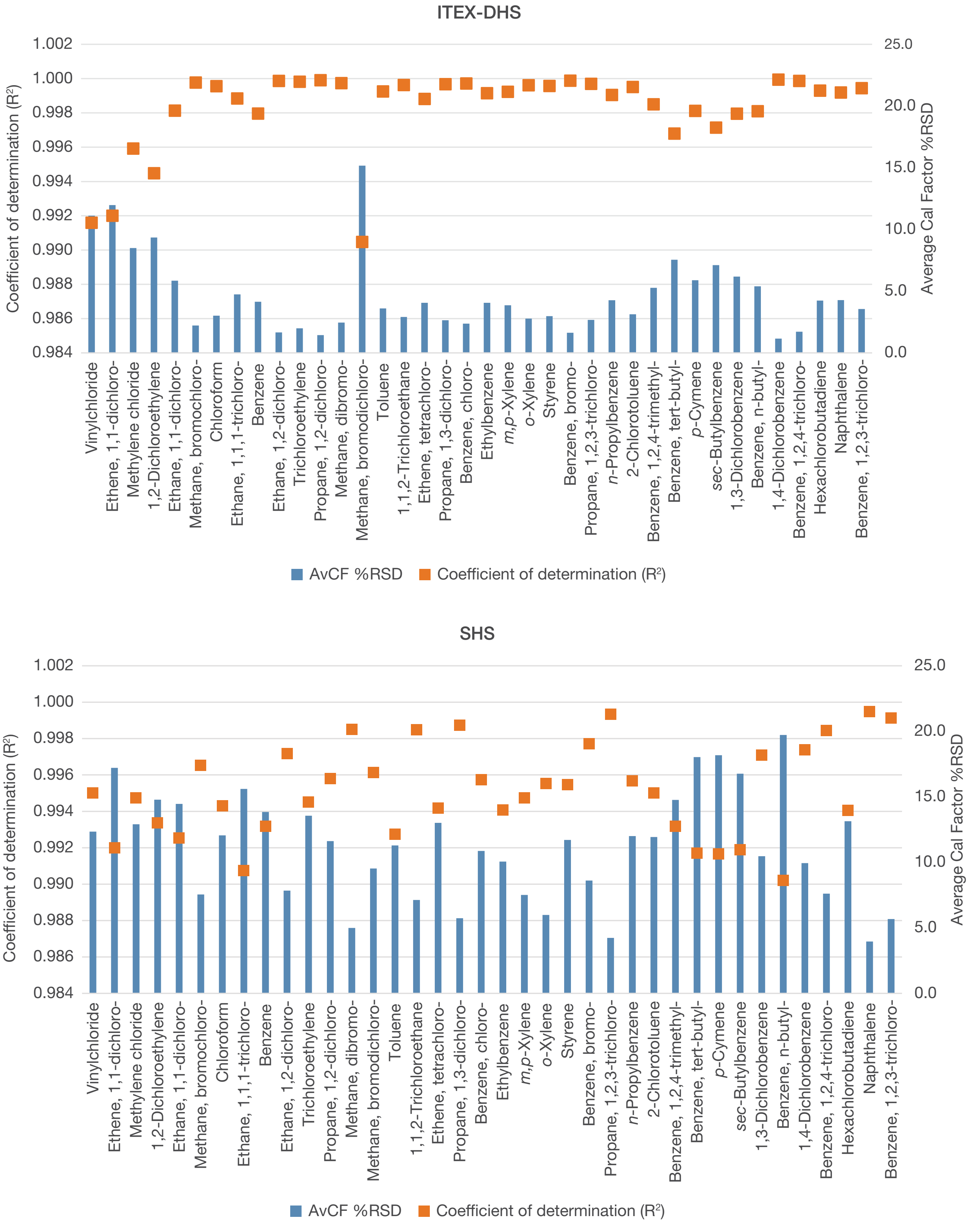


Figure 3. Coefficient of determination (R^2) and residual values (measured as %RSD of average response factors, AvCF %RSD) obtained by injecting seven calibration levels ranging from 0.05 to 5 µg/L for ITEX-DHS and from 0.1 to 100 µg/L for SHS sampling

MDLs and precision were assessed using n=9 replicates of matrix-matched standards spiked with VOC solution at 1.0, 2.0, and 2.5 µg/L. ITEX-DHS provided better sensitivity with calculated IDLs for all analytes <0.9 µg/L, whereas calculated MDLs for HS sampling ranged from 0.05 to 1.4 µg/L (Figure 4).

The repeatability of both sampling techniques was evaluated by analyzing n=9 matrix-matched standards spiked at 1.0 µg/L (ITEX-DHS) and 2.0 µg/L (SHS). The reliability of both ITEX-DHS as well as SHS was demonstrated with overall absolute peak area %RSD <20 as reported in Figure 5.

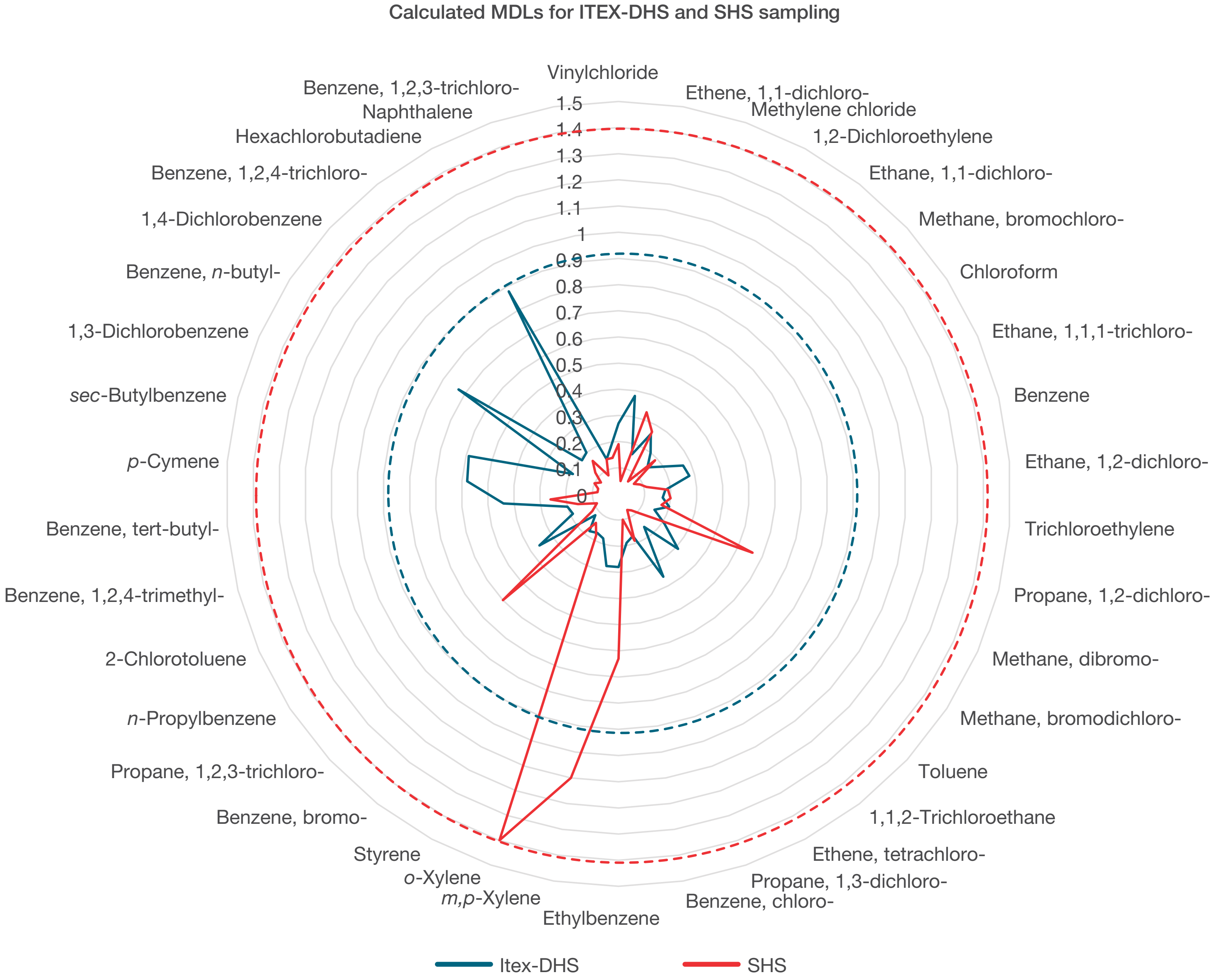


Figure 4. Calculated MDLs for ITEX-DHS and SHS sampling

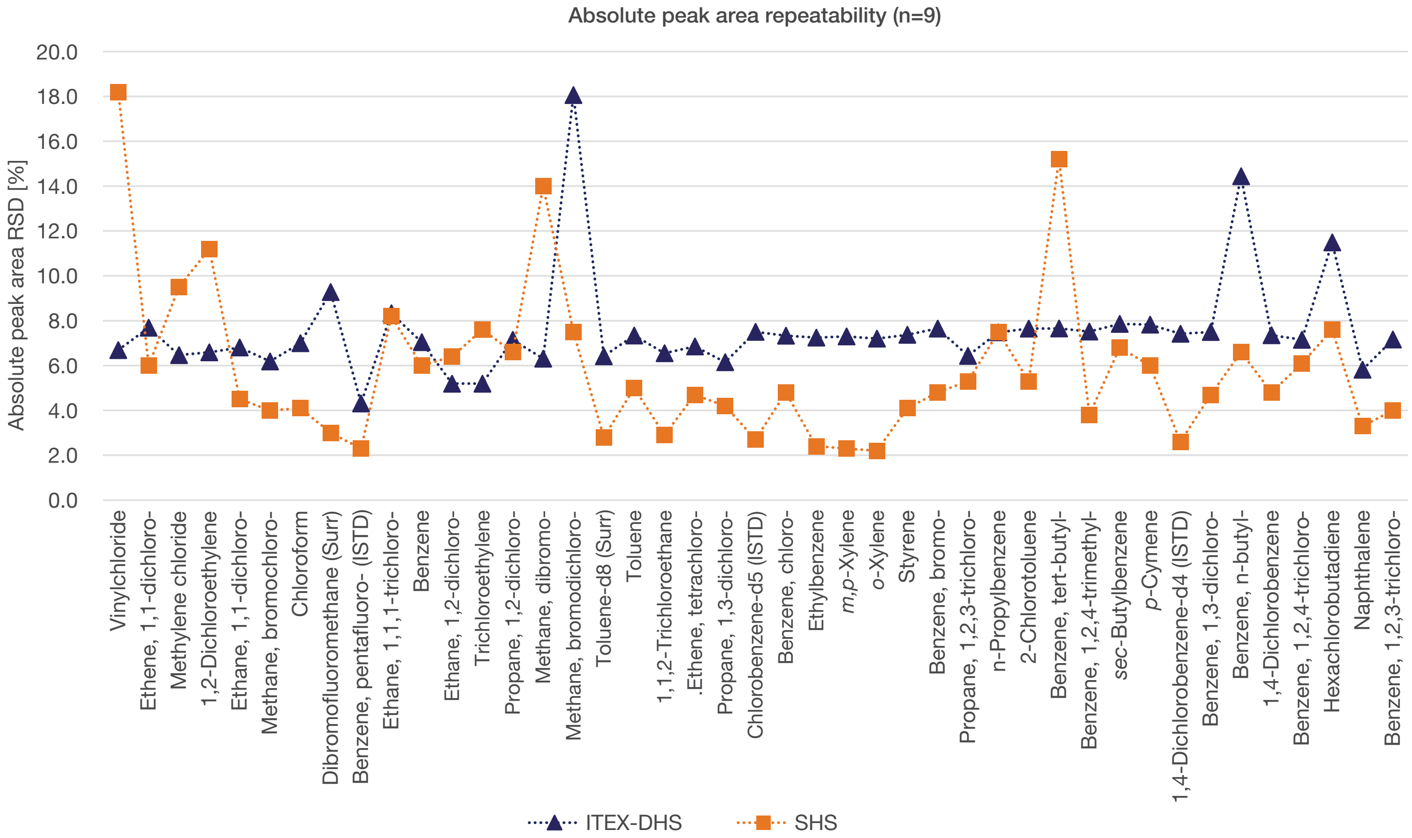


Figure 5. Absolute peak area repeatability (%RSD) obtained for n=9 matrix-matched standards spiked at 1.0 µg/L (ITEX-DHS) and 2.0 µg/L (SHS). ISTDs and surrogates were spiked at 2.0 µg/L (ITEX-DHS) and 20 µg/L (HS).

Summary

- ITEX-DHS and SHS sampling offer robust and powerful extraction of volatiles. Based on a syringe approach, both sampling techniques allow for simplified hardware configuration and straightforward operations.

- Hydrogen carrier gas provides a cost-effective alternative to helium, allowing for reliable GC-MS performance in compliance with the current EU regulation and ensuring spectral fidelity with matches to commercial libraries commonly used for spectral search.

- Sensitive detection of VOCs was achieved for both sampling techniques with overall calculated MDLs <1.4 µg/L and coefficient of determination (R^2) >0.990 with residual values <20%.

- The reliability of both sampling workflows was demonstrated with absolute peak area repeatability (RSD) <20% over n=9 injections of matrix-matched standards spiked at 1.0 µg/L (ITEX-DHS) and 2.0 µg/L (HS).

References

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3. Thermo Fisher Scientific, AN003503 - 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. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-003503-gc-ms-itex-dhs-vocs-an003503-na-en.pdf

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