

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

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Overview

- Static headspace (SHS) and In-Tube Extraction Dynamic Headspace (ITEX-DHS) sampling techniques combined with the use of hydrogen (H_2) as carrier gas were 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.
- These sampling 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 solutions do not require the installation of transfer lines or switching valves.
- The results demonstrated that both SHS and ITEX-DHS techniques achieved sensitive detection of VOCs with method detection limits (MDLs) below 1.4 $\mu\text{g/L}$ and coefficients of determination (R^2) greater than 0.990. The reliability of the sampling workflows was confirmed with absolute peak area repeatability (RSD) below 20% over multiple injections of matrix-matched standards.

Introduction

Volatile organic compounds (VOCs) are significant environmental pollutants found in many commercial, industrial, and household products. These compounds, including solvents, degreasers, and gasoline components, can be released during manufacturing, usage, or disposal processes. When VOCs enter groundwater, they can persist for long periods due to their chemical stability, leading to contamination of drinking water supplies and posing serious health risks. Exposure to VOCs has been linked to a range of adverse health effects, including respiratory problems, neurological damage, and an increased risk of cancer. VOCs require extraction and pre-concentration prior to analysis to ensure accurate detection and quantification. Common techniques for analyzing VOCs in aqueous samples include P&T and SHS sampling. Recently ITEX-DHS came to the scene as an attractive alternative to traditional sampling techniques for VOC analysis. It uses a gas-tight syringe with a needle body filled with a sorbent material to efficiently trap and concentrate the volatile compounds from the sample headspace allowing for low detection limits combined with a simplified hardware that does not require transfer lines or switching valves (Figure 1). H_2 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.

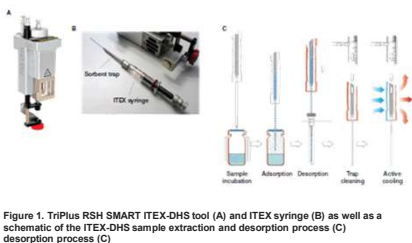


Figure 1. TriPlus RSH SMART ITEX-DHS tool (A) and ITEX syringe (B) as well as a schematic of the ITEX-DHS sample extraction and desorption process (C) desorption process (C)

Materials and methods

Standard and sample preparation

Multi-component standards were diluted to 0.5, 0.05, and 0.005 mg/L, and internal standards/surrogate to 0.025 mg/L. Aliquots were dispensed into 20 mL headspace vials previously filled with 10 mL ultra-pure water to obtain 7-point calibration curves ranging from 0.05 to 5 $\mu\text{g/L}$ for ITEX-DHS and from 0.1 to 100 $\mu\text{g/L}$ for SHS. Each vial was spiked with internal standard/surrogate solution (final concentration 2.5 $\mu\text{g/L}$ for ITEX-DHS and 25 $\mu\text{g/L}$ for SHS) and added with 0.5 mg NaCl to enhance headspace transfer.

Test Method(s)

A Thermo Scientific™ TriPlus™ RSH SMART autosampler equipped with ITEX-DHS and SHS configurations were coupled to a Thermo Scientific™ TRACE™ 1610 GC equipped with a Thermo Scientific™ iConnect™ split/splitless injector, upgraded to work in HeSaver-H2Safer mode, and a Thermo Scientific™ iScan™ programed temperature vaporizer (iConnect-PTV) injector, and to a Thermo Scientific™ ISQ™ 7610 single quadrupole mass spectrometer. The PTV injector was equipped with a liner packed with Tenax TA (PN-45312145-11), suitable for a cryogen-free refocusing of the most volatile compounds. Chromatographic separation for ITEX-DHS was achieved using a Thermo Scientific™ TraceGOLD™ TG-624 SILMS, 60 m \times 0.25 mm \times 1.4 μm column whereas for SHS a Thermo Scientific™ TraceGOLD™ TG-624 SILMS, 20 m \times 0.18 mm \times 1.0 μm column was used.

Data Analysis

Data were acquired, processed, and reported using the Thermo Scientific™ Chromleon™ 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).

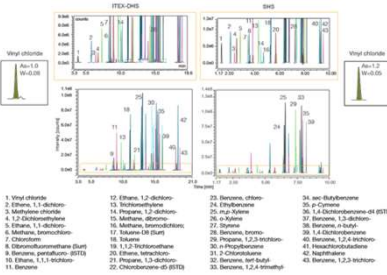


Figure 2. SIM traces showing an example of the chromatographic separation obtained for a matrix-matched standard using ITEX-DHS (concentration: 5 $\mu\text{g/L}$) and SHS (concentration: 100 $\mu\text{g/L}$) sampling. Peak asymmetry and width (calculated at 50% height) for the first eluting compound (vinyl chloride) are annotated.

Results

Chromatography

Peak broadening of early eluting compounds can occur due to a poor re-focusing 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 H_2 as carrier gas provided improved peak shapes when injecting at high temperature into the HeSaver-H2 Safer injector. H_2 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 3 shows an example of spectral comparison between mass spectra acquired with H_2 for both PTV and HeSaver-H2 Safer injectors as well as a comparison with the NIST mass spectral library. Overall, the search index scores (SI) fit well to the NIST library, demonstrating that H_2 is not a concern in terms of spectral fidelity.

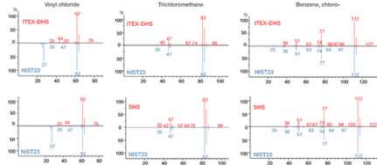


Figure 3. Examples of acquired spectra for PTV and HeSaver-H2 Safer injectors (carrier gas: H_2) versus NIST23 spectral library (carrier gas: helium). Acquisition range: m/z 35–300.

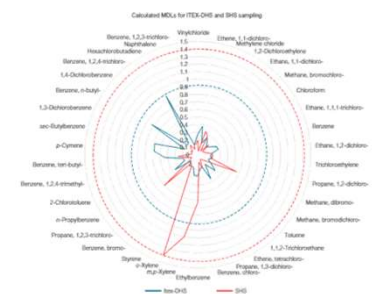


Figure 4. Coefficient of determination (R^2) and residual values (measured as %RSD of average response factors) for ITEX-DHS and SHS

Linearity and method detection limits (MDLs)

Linearity was assessed by injecting seven calibration levels ranging from 0.05 to 5 $\mu\text{g/L}$ for ITEX-DHS and from 0.1 to 100 $\mu\text{g/L}$ for SHS sampling. R^2 were better than >0.990 for both sampling techniques with %RSD of average response factors <20% (Figure 4). MDLs and precision were assessed using n=9 replicates of matrix-matched standards spiked with VOC solutions at 1.0, 2.0, and 2.5 $\mu\text{g/L}$. ITEX-DHS provided better sensitivity with calculated IDLs for all analytes <0.9 $\mu\text{g/L}$, whereas calculated MDLs for SHS sampling ranged from 0.05 to 1.4 $\mu\text{g/L}$ (Figure 5).

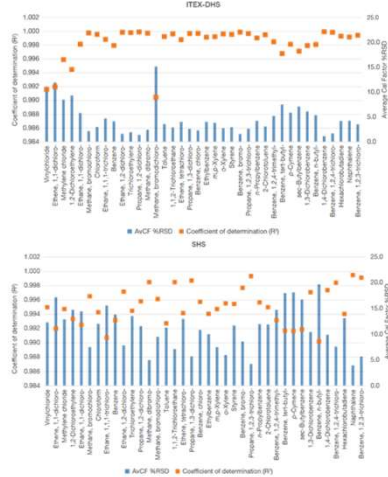


Figure 5. Calculated MDLs for ITEX-DHS and SHS sampling

Repeatability

The repeatability of both sampling techniques was evaluated by analyzing n=9 matrix-matched standards spiked at 1.0 $\mu\text{g/L}$ (ITEX-DHS) and 2.0 $\mu\text{g/L}$ (SHS). The reliability of both ITEX-DHS as well as SHS was demonstrated with overall absolute peak area %RSD <20 as reported in Figure 6.

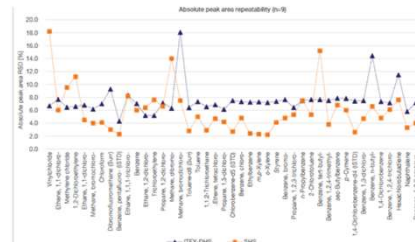


Figure 6. %RSD obtained for n=9 matrix-matched standards spiked at 1.0 $\mu\text{g/L}$ (ITEX-DHS) and 2.0 $\mu\text{g/L}$ (SHS).

Conclusions

- 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.
- H_2 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 $\mu\text{g/L}$ and 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 $\mu\text{g/L}$ (ITEX-DHS) and 2.0 $\mu\text{g/L}$ (SHS).

References

- 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)

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