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THE QUEEN'S AWARDS FOR ENTERPRISE: INNOVATION 2019

Versatile options for extending analyte range and sensitivity for monitoring volatile organic compounds (VOCs) in water and soil by automated, cryogen-free headspace– and SPME–trap with GC–MS

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Outline

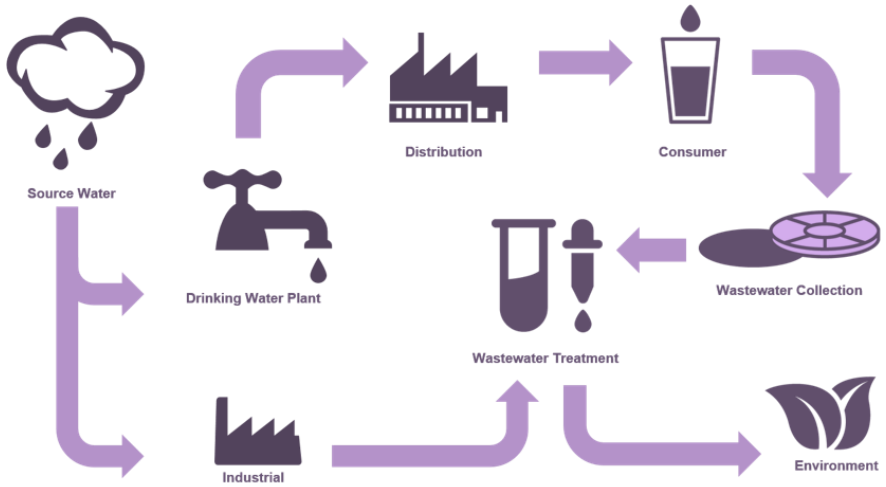
- Regulations connected with VOCs in water
- Importance of soil health, relevance to agriculture and the global impact
- Advantages & drawbacks of traditional techniques
- Case studies to demonstrate alternative techniques:
  1) VOCs in water: Exceptional sensitivity enhancements for routine analysis
  2) Volatiles in soil: Understanding contamination and effects on soil health
  3) Chlorophenols in water: Eliminating sample prep
- Summary

Water: A fundamental resource for life

- Water is one of the most valuable resources
- More than one-quarter of all bottled water comes from a municipal water supply
  - The same place that tap water comes from
- Safe drinking-water is:
  - Essential to health
  - A basic human right
  - A component of effective policy for health protection
- Each person uses about 80-100 gallons of water per day
  - 92.5% goes to waste

Regulations connected with VOCs in water

- Water is the most regulated substance
- VOCs and SVOCs are major contaminants
- Many stakeholders in the water cycle:



Water type	Regulation	Technique
Drinking	Method 524	Purge-and-trap (P&T)
Waste	Method 624	P&T
Environmental	SW-846 (8260D)	Performance-based criteria. Choice of extraction methods (5000 series)
Ground		

The importance of soil health

- Fundamental to a wide range of ecosystem services, including water purification.
- Affects the whole earth system[1]→ monitoring is essential.
- Anthropogenic sources can cause degradation of soil health.
- Soil remediation: Reducing concentration levels of contaminants within soil[2] to 'suitable for use' levels.

VOC pollution **negatively impacts human health**, causing:

- Irritation of eyes, nose, throat
- Fatigue
- Dizziness
- Allergic skin reaction
- Nausea
- Headaches

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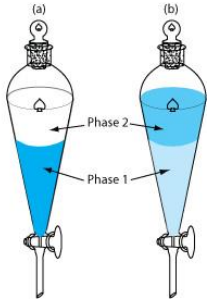
[1] FAO, *Status of the World's Soil Resources. Main report |Policy Support and Governance| Food and Agriculture Organization of the United Nations*, 2015.
[2] https://www.soilutions.co.uk/services/soil-remediation/

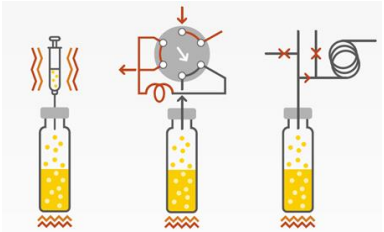
Existing techniques

Solvent extraction

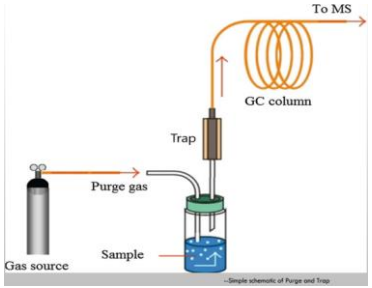


Static headspace

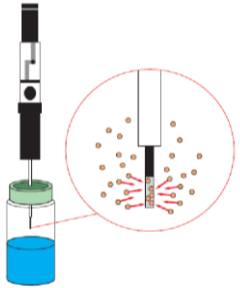
Syringe / Valve & loop / Pressure balance



Purge & trap

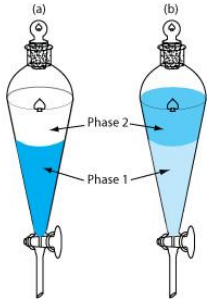


Solid-phase microextraction



Advantages with existing techniques

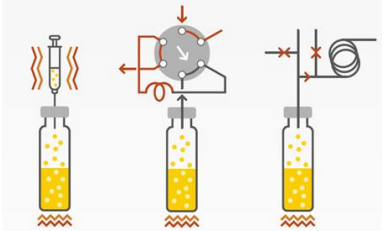
Solvent extraction



- ✓ Easy operation
- ✓ Simple apparatus

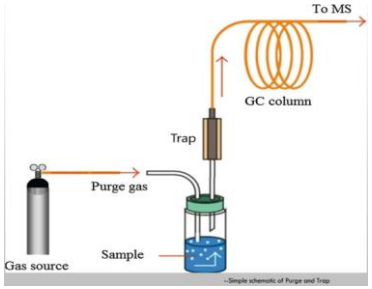
Static headspace

Syringe / Valve & loop / Pressure balance



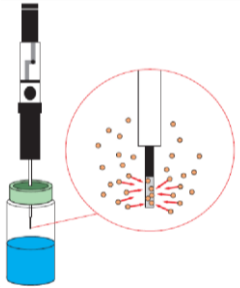
- ✓ Easily automated
- ✓ Solvent-free
- ✓ Low cost/sample

Purge & trap



- ✓ More sensitive than static HS
- ✓ Solvent-free

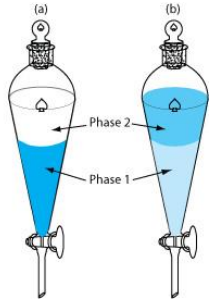
Solid-phase microextraction



- ✓ Easily automated
- ✓ Solvent-free
- ✓ Short extraction time

Drawbacks with existing techniques

Solvent extraction

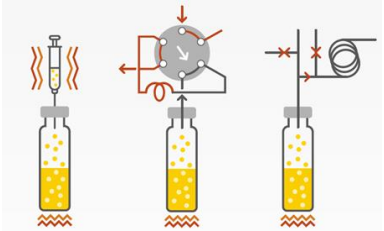


- ✓ Easy operation
- ✓ Simple apparatus

- × Labour intensive
- × Lengthy extraction time
- × Prone to human error
- × Costly disposal of hazardous solvents

Static headspace

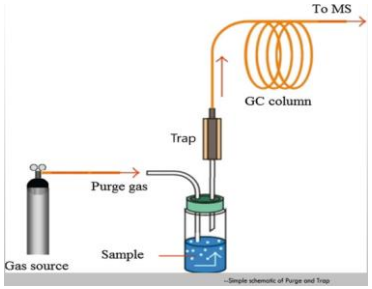
Syringe / Valve & loop / Pressure balance



- ✓ Easily automated
- ✓ Solvent-free
- ✓ Low cost/sample

- × Poor sensitivity
- × Difficult to establish optimal conditions for multi-component mixtures

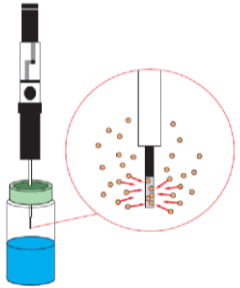
Purge & trap



- ✓ More sensitive than static HS
- ✓ Solvent-free

- × Foaming/aerosol formation leading to carryover
- × Ice blockages due to use of cryogen

Solid-phase microextraction

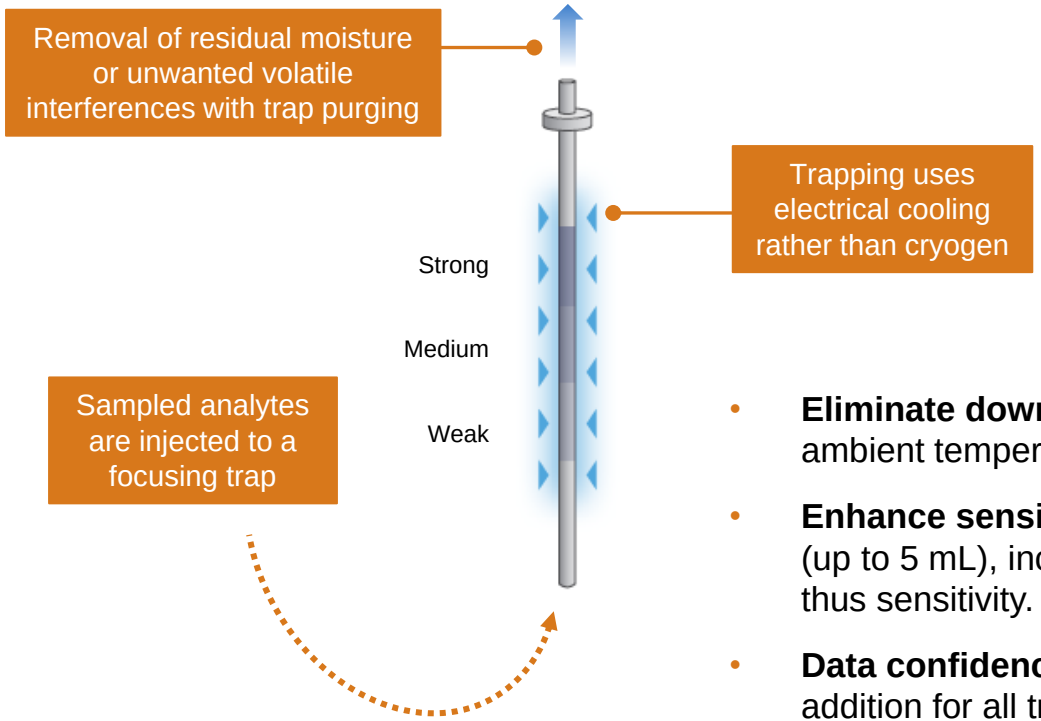


- ✓ Easily automated
- ✓ Solvent-free
- ✓ Short extraction time

- × Selective towards compound classes
- × Difficult to quantitatively sample VVOCs

Analyte focusing and preconcentration…

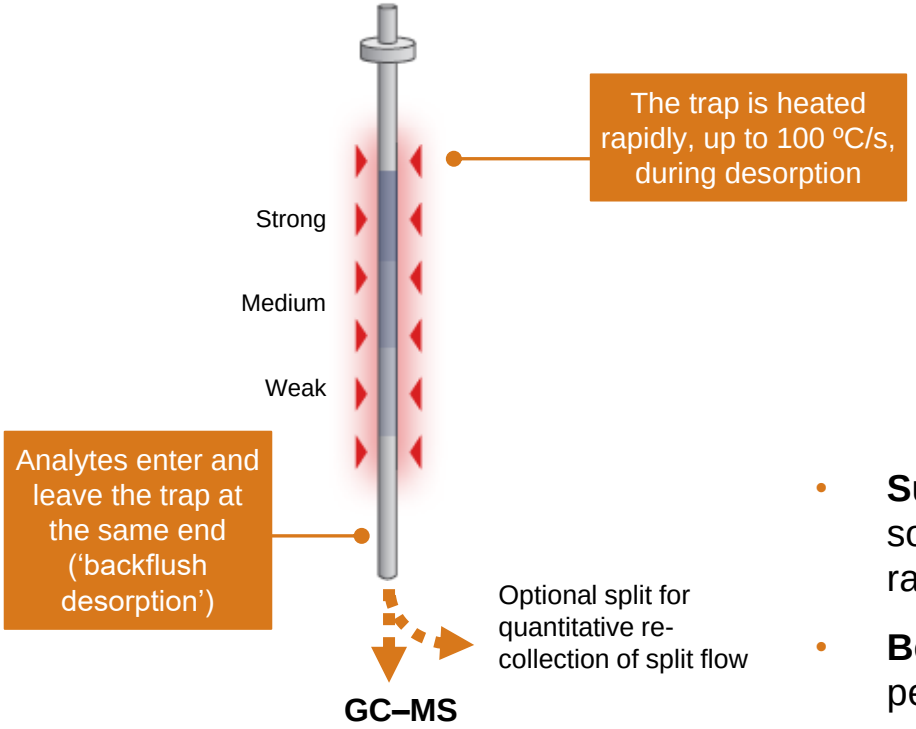
Step 1: Injection of sampled analytes and focusing of volatiles



- **Eliminate downtime**: Controlled, cryogen-free trapping at ambient temperatures, therefore, no risk of ice blockages.
- **Enhance sensitivity**: Allows larger HS volume extraction (up to 5 mL), increasing analyte amount for detection, and thus sensitivity.
- **Data confidence**: Unique gas-phase internal standard addition for all trap-enabled sampling modes.

…combined with rapid GC injection

Step 2: Rapid desorption and transfer/injection to the GC



- **Superior chromatographic performance**: Multi-sorbents and backflush operation for wide-ranging VOC analysis.
- **Better peak shape**: Fast injection provides sharp peaks, significantly enhancing analyte response.

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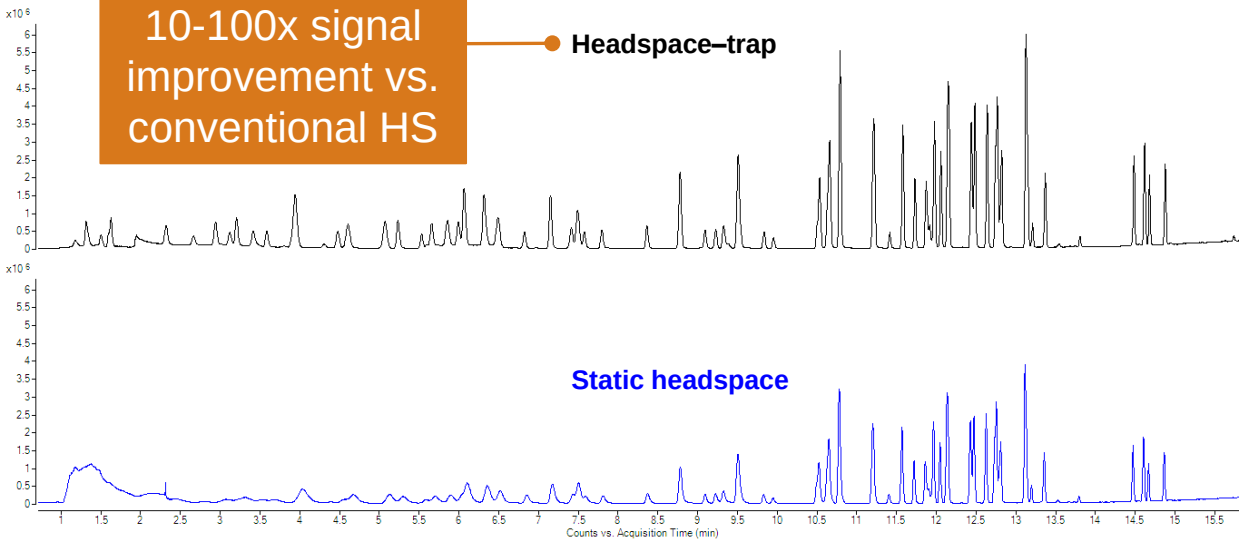
1. VOCs in water: Exceptional sensitivity enhancements for routine analysis

Improving sensitivity for VVOC analysis in water

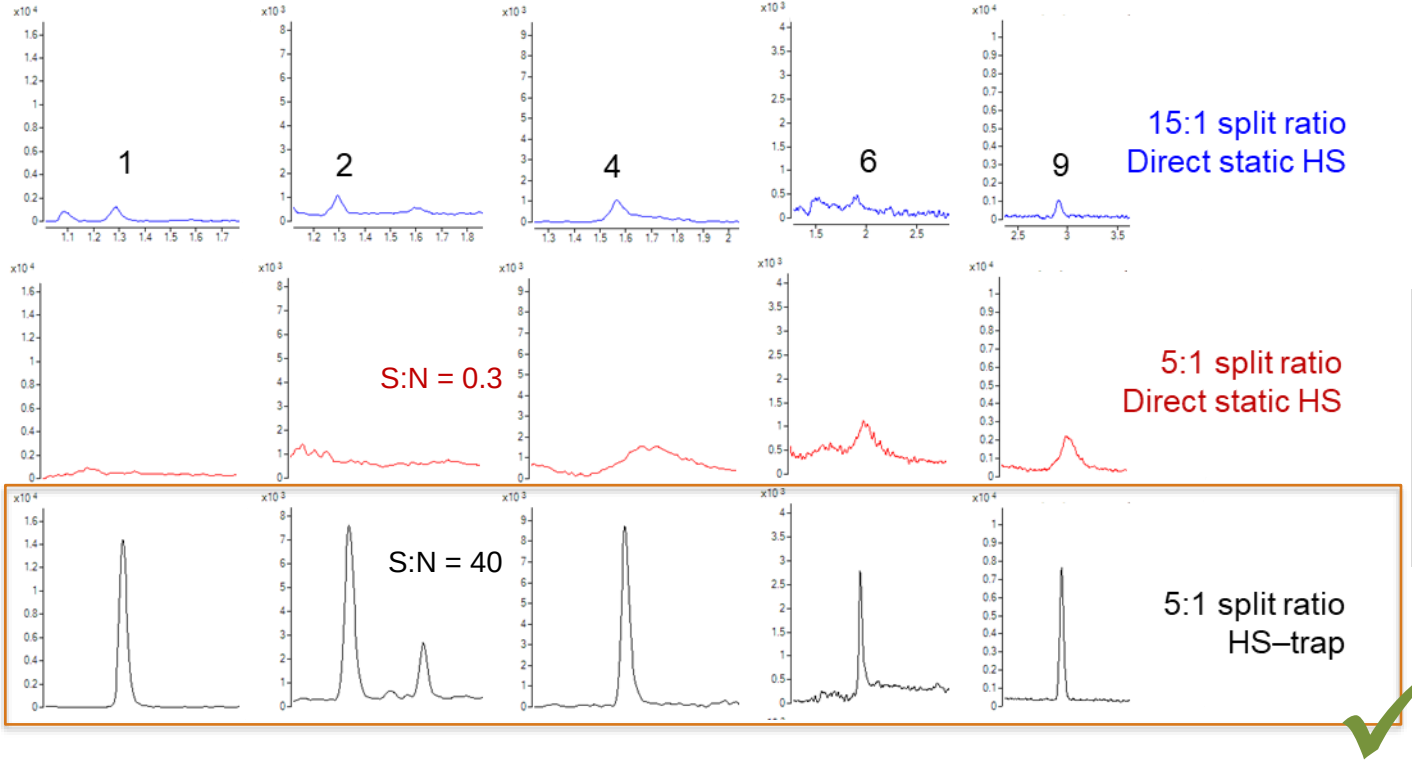
- Exceptional concentration enhancements to achieve trace-level detection of VOCs
- Refocusing and fast injection of VVOCs ensures good peak shape & signal-to-noise to boost sensitivity

10-100x signal improvement vs. conventional HS



80-component mix of VOCs in water at 20 µg/L (ppb)

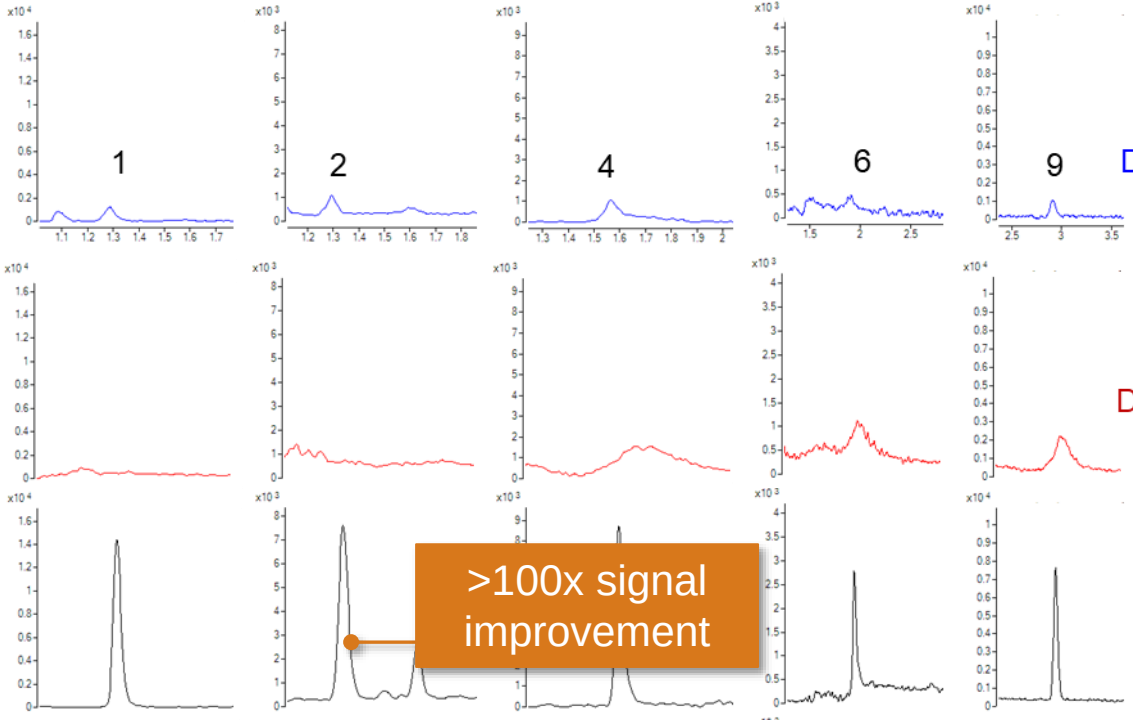
Excellent peak shapes for VVOCs at 1 ppb



VVOCs in water at **1 µg/L** (ppb)

1 Dichlorodifluoromethane
2 Difluorochloromethane
4 Vinyl chloride
6 Bromomethane
9 1,1-Dichloroethene

Significant improvement in signal-to-noise

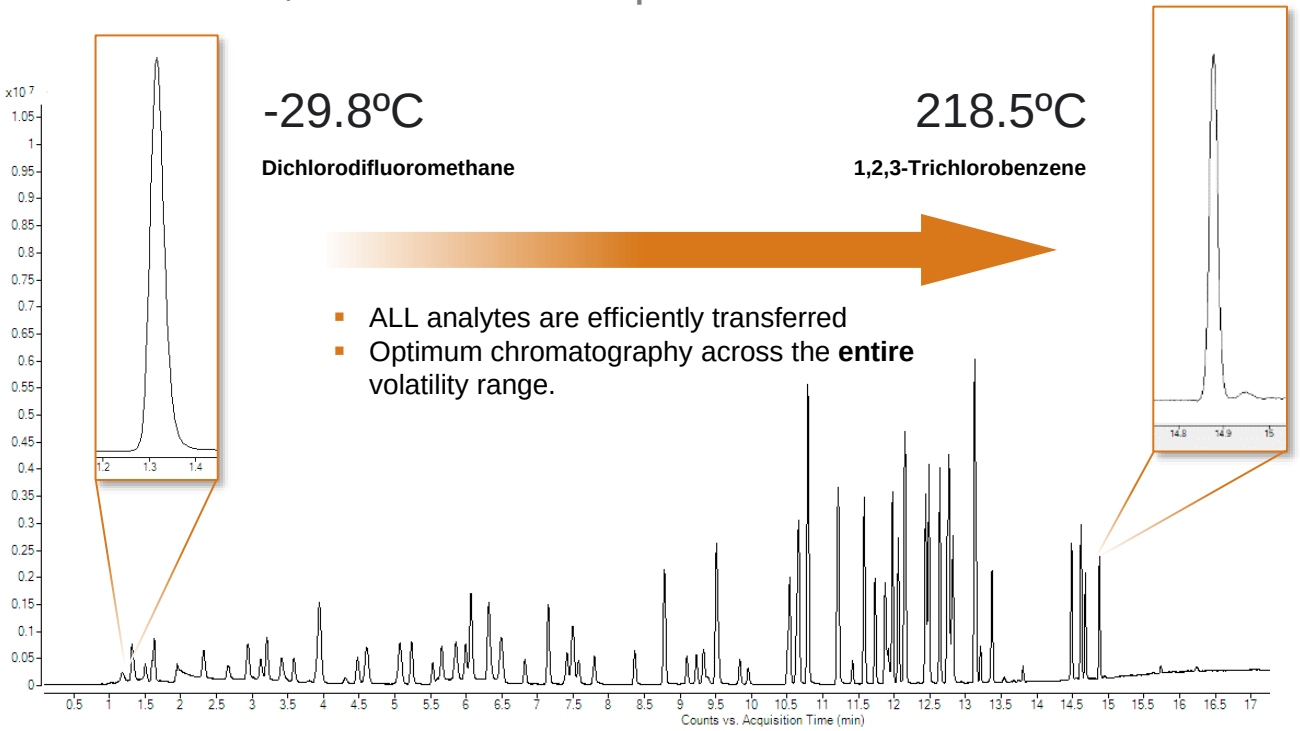


VVOCs in water at **1 µg/L** (ppb)

1 Dichlorodifluoromethane
2 Difluorochloromethane
4 Vinyl chloride
6 Bromomethane
9 1,1-Dichloroethene

Analysis of wide-ranging volatile organics in a single run

Multi-sorbent, backflushed trap



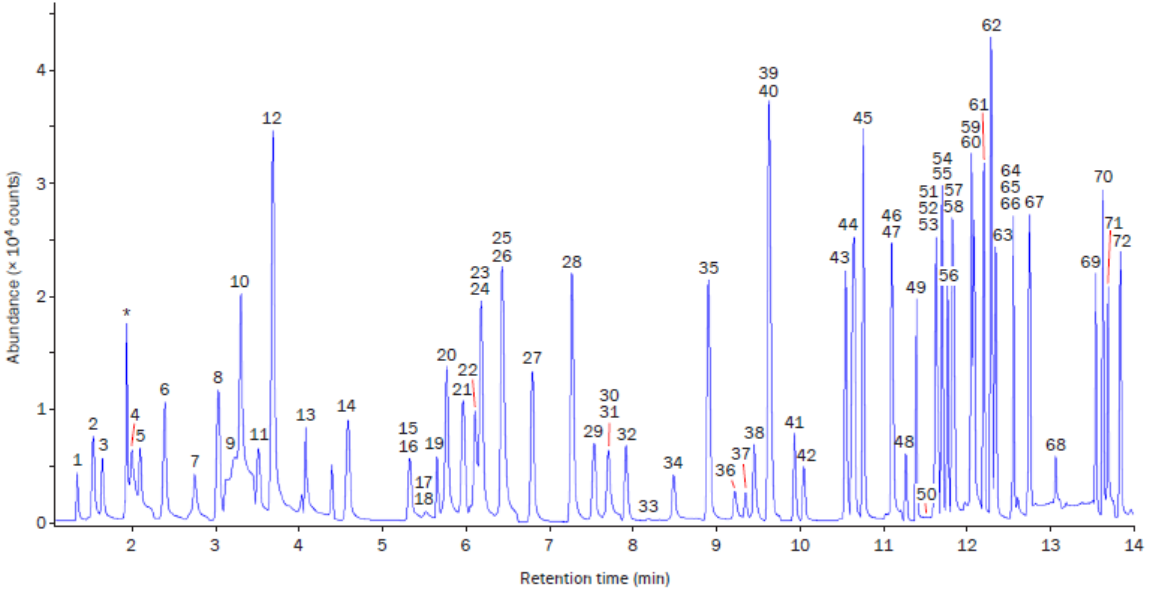
80-component mix of VOCs in water at 20 µg/L (ppb) by headspace–trap

With HS-trap into the ppt-world!

…using a MS-single quad

By using:

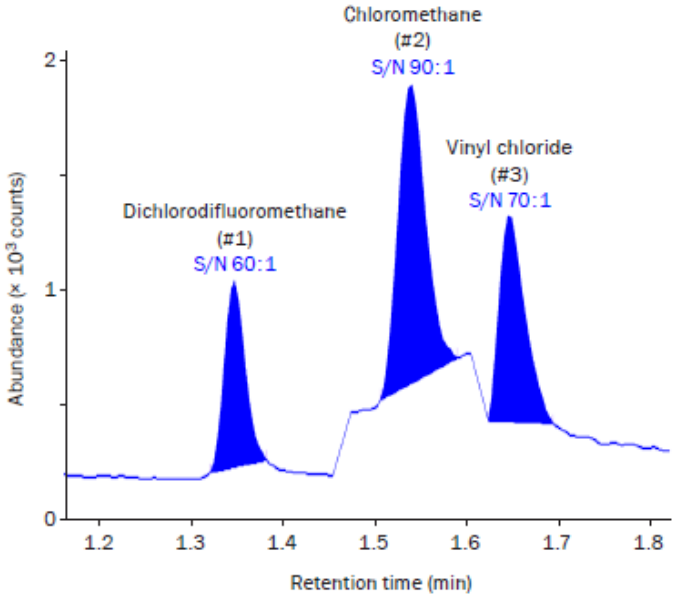
- Pre-concentration
- Higher injection volume
- Splitless injection
- MS in SIM mode



Headspace–trap SIM analysis of the standard mix at 100 ppt on-column.

Large S/N ratios for easy determination

…down to single digit ppt levels

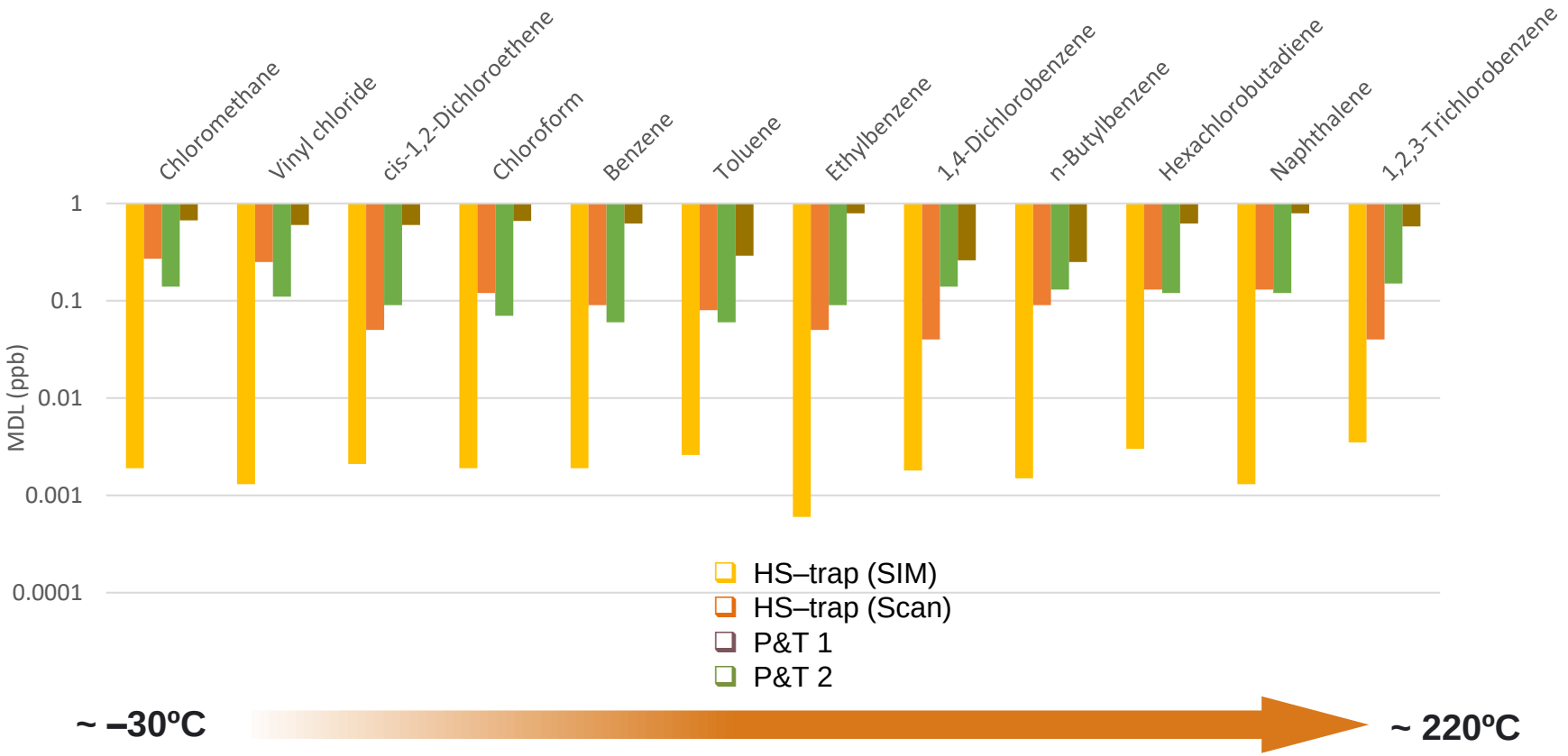


Headspace–trap SIM analysis of the **three most volatile components** in the standard mix, at **20 ppt** on-column.

Compound	MDL (ppt)	PQL (ppt)
Vinyl chloride	1.3	11
Benzene	1.9	17
Trichloroethene	1.3	11
Ethylbenzene	0.6	5
Xylenes	0.3	3 - 14

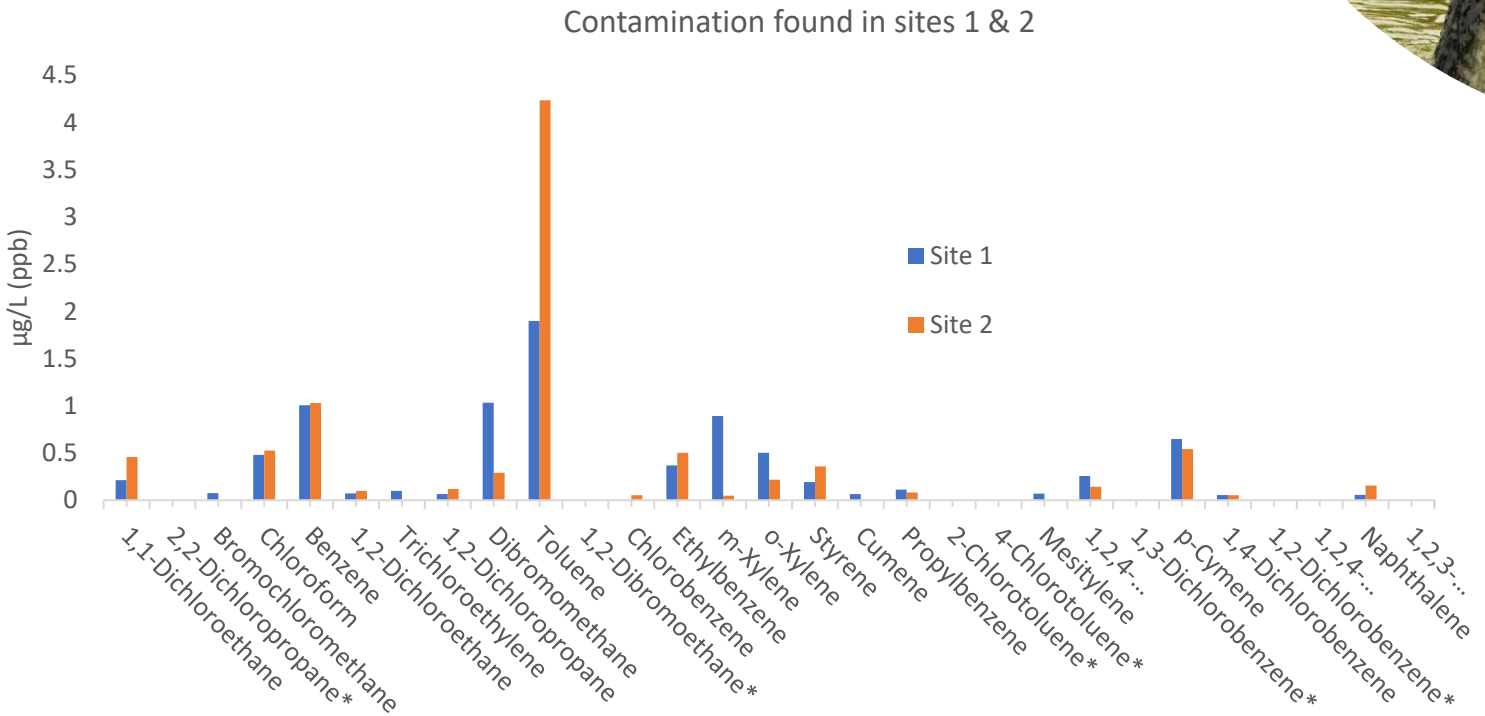
MDLs for a range of VOCs across the volatility range demonstrate **superior sensitivity in the low- to sub-ppt** range using HS–trap SIM analysis.

Method detection limits of HS-trap vs P&T



Applicability to real-world wastewater samples

Screening from two industrial sites (ppb-level)



Summary

Case study 1

- Low level VOCs in water (parts per billion/trillion; ppb/ppt)
  - ✓ Automated pre-concentration thanks to cryogen-free trap focusing
- Wide volatility range
  - ✓ Multiple sorbent beds and backflush operation
- Extremely volatile challenging compounds
  - ✓ Strong sorbents for VVOC re-focusing
  - ✓ Electrically-controlled at ambient temperature to allow breakthrough of sample moisture
  - ✓ Subsequent rapid injection, sharp chromatographic peaks, high sensitivity
- Removal of water interferences
  - ✓ Separation of extraction and injection enabled trap purging, removing water away from the GC-MS

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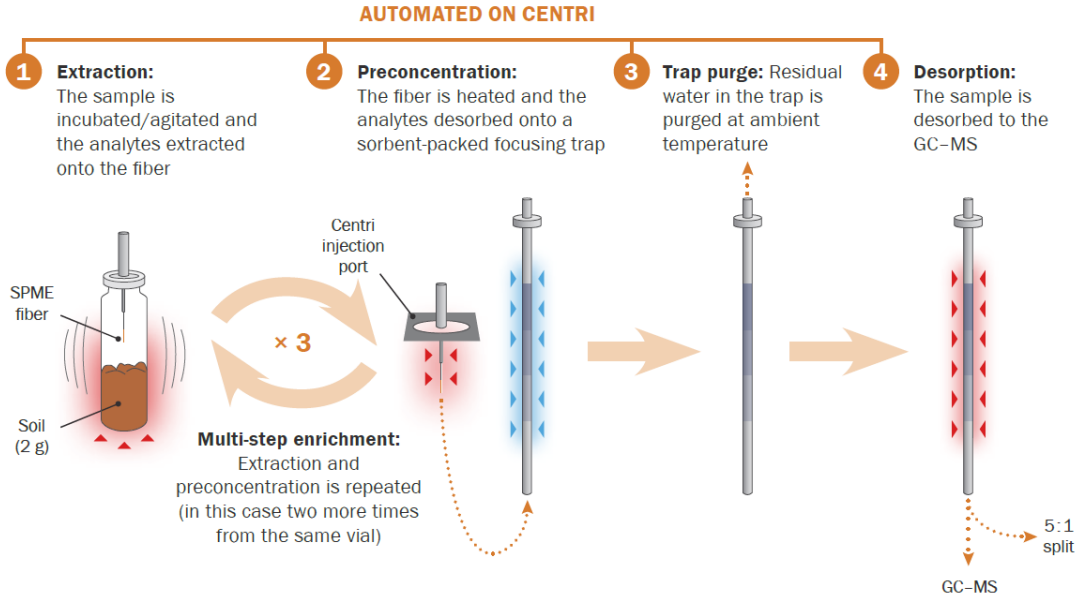
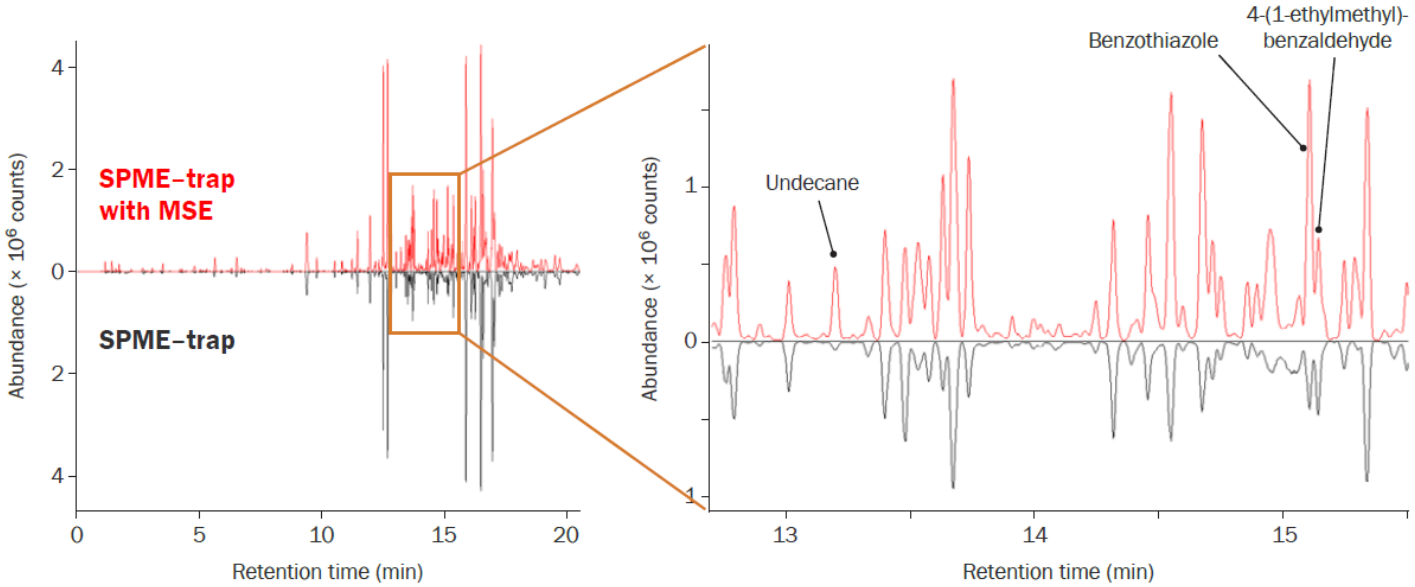
2. Volatiles in soil: Understanding contamination and effects on soil health

Extending performance of traditional SPME



- **Fast, simple sampling**: SPME is ideal for sampling wide-ranging VOCs from a variety of tricky matrices
- **Increase sensitivity**: Analyte refocusing and preconcentration on a sorbent-packed trap
- **Confident identification**: Unique multi-step enrichment boosts analyte extraction for trace-level VOCs

Screening of volatiles in soil near roadside

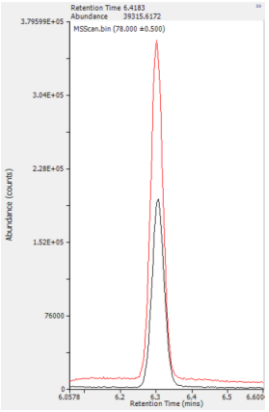


Multi-step enrichment revealed **112 more compound peaks** with >50% confidently identified (MF >850 in NIST library).

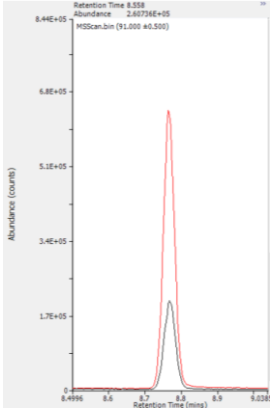
- *Undecane*: Can irritate skin and eyes.[4]
- *Benzothiazole*: Central nervous system & respiratory depression. Kidney & liver toxicity.[5]
- *4-(1-Ethylmethyl)-benzaldehyde*: Eye, skin and respiratory irritation.[6]

[4] https://nj.gov/health/eoh/rtkweb/documents/fs/1963.pdf
[5] https://link.springer.com/article/10.1007/s11356-018-2448-6
[6] https://www.synerzine.com/docs/sds/W0313%20SDS%20(US-English).pdf

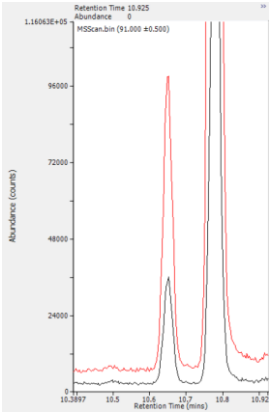
BTEX contamination within soil



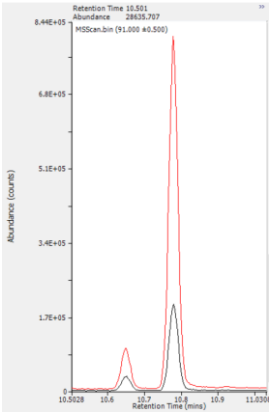
Benzene



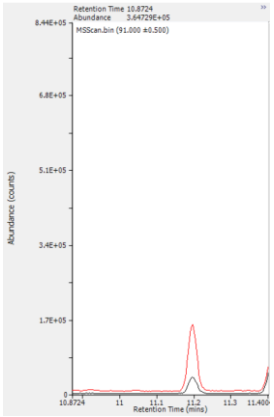
Toluene



Ethylbenzene



m-/p-*Xylene*



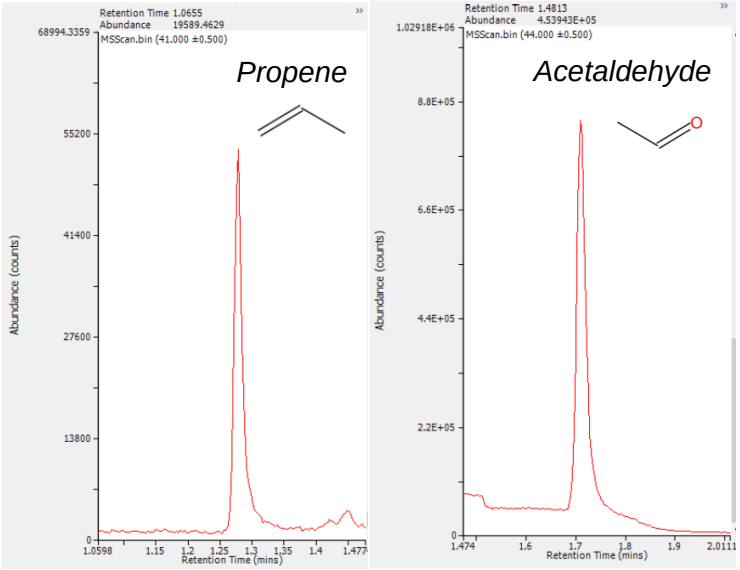
o-*Xylene*

– SPME-trap
– MSE-SPME-trap

- Known carcinogens and endocrine disruptors, often detected around roads and areas affected by emissions from combustion of gasoline and diesel fuels
- Have a high affinity for apolar matrices like soil and so, can be difficult to monitor especially at low levels
- MSE-SPME-trap enabled increased responses, ideal for detecting and identifying components if present at trace levels with increased confidence

In the agricultural sector

- VOC profiles provide non-destructive fingerprints indicative of health
- Allows the monitoring of organisms and understanding of microorganism, plant and invertebrate interactions in soil
- Offers valuable insights of the agronomic effects of composts and mineral fertiliser on soil properties (i.e., chemical, biological and physiological)



Analyte refocusing provides **excellent peak shape** for these **difficult early-eluting compounds** of interest that have the potential to be used as **indicators for monitoring soil health**.

[7] M. Schloter, P. Nannipieri, S.J. Sørensen and J.D. van Elsas, Microbial indicators for soil quality, *Biol. Fertil. Soils*, 2018, 54: 1–10.

Summary

Case study 2

- Soil health is important globally as VOC concentration can have a negative effect on human health
- Monitoring ensures environmental health and safety is upheld
- Requires fast, sensitive and non-target screening methods
  - MSE-SPME-trap can be used to increase detection of low-level unknowns
  - Also used for monitoring target VOCs like BTEX in the same run
- This enables:
  - Reuse of land, e.g., for a residential housing development, that is safe and does not negatively impact human health
  - Authorities to be informed of the level of remediation needed to remove contamination
  - An understanding of how to implement sustainable land management, monitoring and remediation processes to reduce global impact

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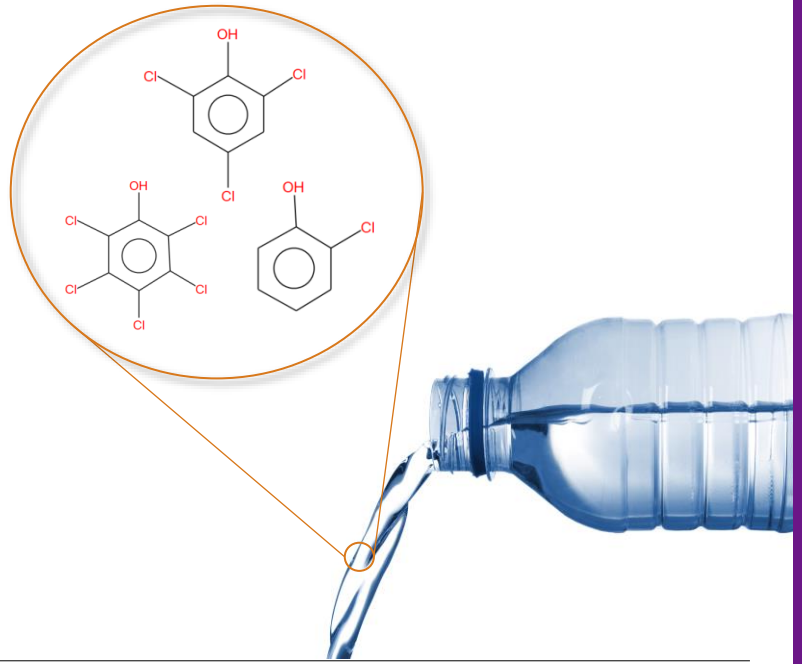
3. Chlorophenols in water: Eliminating sample prep

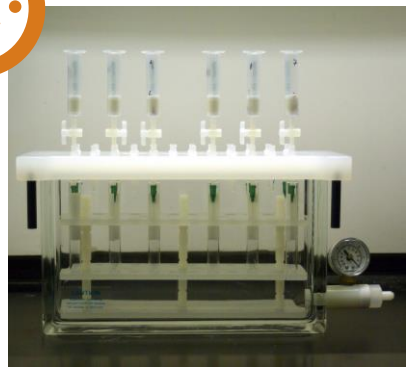
Monitoring disinfection by-products in water

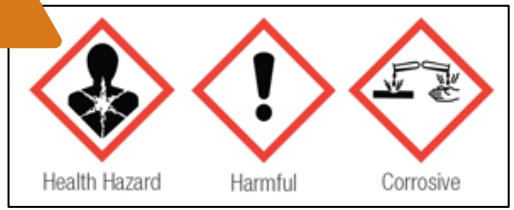
- Water pollution occurs when harmful substances contaminate streams, rivers, lakes or other bodies of water.
- Different processes are used for removing these substances, including disinfection.
- Halogenated disinfection by-products are often formed as a result.
- These substances are being investigated to understand their effect on human health.
- Toxic and persist in water for longer than in air.
- Contribute malodours to water, detectable by humans at very low levels.



Current methodologies

- Low odour thresholds require sensitive detection.
- Current methods include lengthy and manual solvent extraction steps or SPE.
- In the US:
  - EPA Method 528 (drinking water)
    - Describes SPE
    - Liquid injection of an aliquot of concentrated analytes in **methylene chloride**
  - EPA Method 604 (wastewaters)
    - Many solvent extraction steps
    - Use of harmful **derivatising agent** (pentafluorobenzyl bromide, PFB).

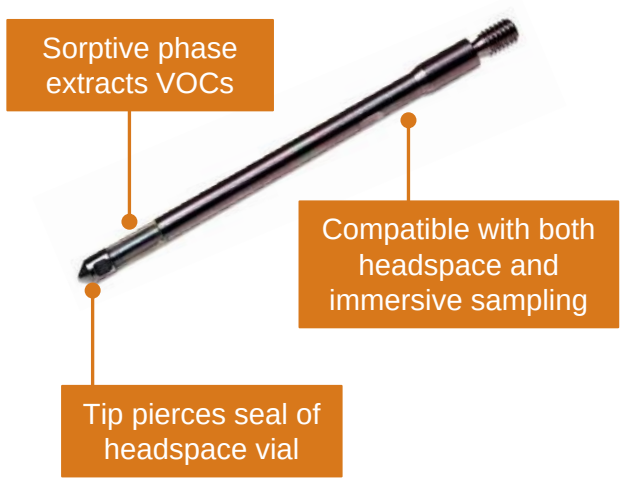




Overcoming challenges of solvent-based methods

Steps towards a greener lab…

- **Sorptive extraction** allows for:
  - Large concentration enhancements
  - Small sample sizes
  - Easy handling
  - Fast extraction
  - Simple methodology
  - Elimination of solvent use
- Next steps to investigate **high-capacity** sorptive extraction, similar principles to SPME.
- Can sorptive extraction modernise the way labs test for phenols in water?
  - **US EPA Methods 528, 604 and 8041 (SW-846)**



Fast, simple extraction of chlorophenols in water

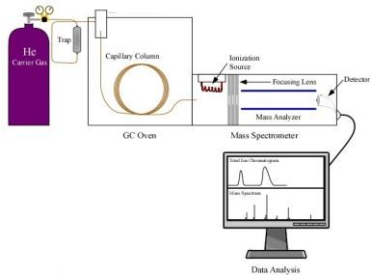
Preparation	Extraction	Analysis	Detection

Water at a spiked concentration of 2 µg/L (ppb) placed into standard 20 mL vial and capped

High-capacity sorptive probes were inserted to sample by direct immersion with agitation

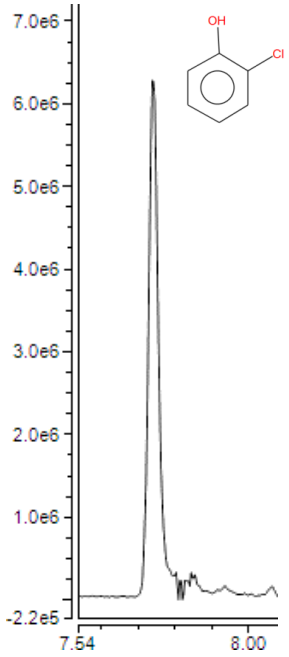
Probes fit inside empty TD tubes for automated analysis by thermal desorption (TD)

TD system connected to GC-MS for separation and detection of target analytes

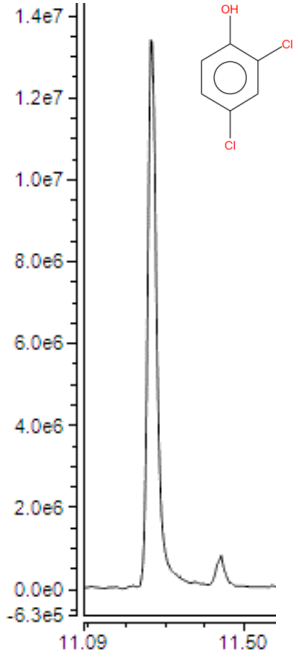


Note: Extraction and analysis using high-capacity probes can be automated, providing hands-free operation

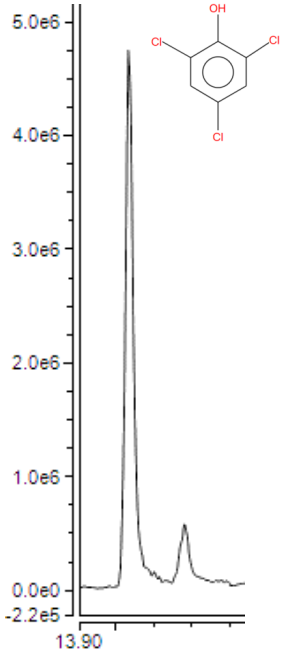
Initial results for the detection of chlorophenols in water



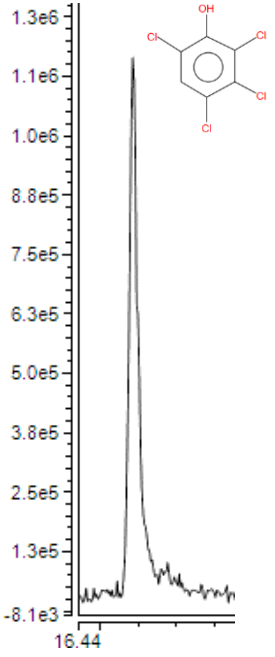
2-Chlorophenol (m/z 128)



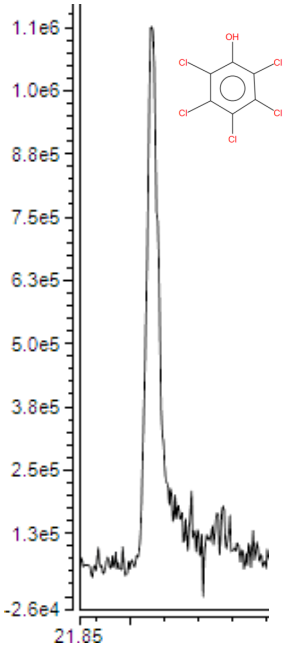
2,4-Dichlorophenol (m/z 162)



2,4,6-Trichlorophenol (m/z 196)



2,3,4,6-Tetrachlorophenol (m/z 232)



Pentachlorophenol (m/z 266)

Summary

Case study 3

- High-capacity sorptive extraction has the potential for rapid, sensitive analysis of chlorophenols in water
- Eliminates sample preparation steps, use of hazardous solvents and derivatising agents
- Simplifies and expedites the process compared to conventional techniques
- Provides huge improvements in health & safety for the operator
- Can be automated from sampling to GC injection, enabling hands-free approach

Conclusions

- **HS-trap**, **SPME-trap** and **high-capacity sorptive extraction** overcome analytical challenges with existing techniques.
- These alternatives provide **versatile options** for a variety of environmental analyses, enabling:
  - **Simplified sample preparation**, removing many manual handling steps
  - **Superior sensitivity** for trace-level analysis thanks to analyte preconcentration
  - **Excellent peak shape** across a wide volatility range of analytes in a single run
  - **Enhanced chromatographic performance** by removal of residual sample moisture prior to analysis
- High sample throughput is maintained, ideal for high productivity labs.
- Multi-step enrichment boosts sensitivity further, ideal for trace-level non-target screening.
- New techniques are allowing labs to move towards greener ways for sample extraction that are safer and more environmentally friendly.

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