Centri applications

From farm to fork…

Common challenges facing todays analytical laboratories

Complexity of analysis

Changes in regulation/customer requests

- Compounds of interest
- Limit levels
- Analytical technique required

Environmental considerations

Updating equipment

Introducing new methods and techniques

Cost per sample

Analyst time

Validation

Solvent-free techniques for solid/liquid analysis




Desirables	Headspace	HS–trap	SPME	Sorptive extraction
Solvent-free	✓	✓	✓	✓
Preconcentration	✗	✓	✓	✓
Entirely automated	✓	✓	✓	✗
Re-collection	✗	✗	✗	✗

Solvent-free techniques for solid/liquid analysis





Desirables	Headspace	HS–trap	SPME	Sorptive extraction	Thermal desorption
Solvent-free	✓	✓	✓	✓	✓
Preconcentration	✗	✓	✓	✓	✓
Entirely automated	✓	✓	✓	✗	✓
Re-collection	✗	✗	✗	✗	✓

Solvent-free techniques for solid/liquid analysis

The uniqueness of Centri



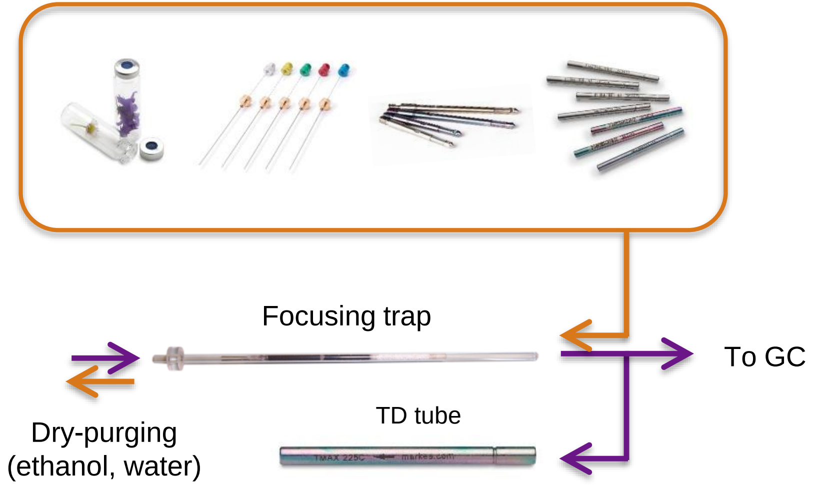



Desirables	Headspace	HS–trap	SPME	SPME–trap	HiSorb sorptive extraction	Thermal desorption
Solvent-free	✓	✓	✓	✓	✓	✓
Preconcentration	×	✓	✓	✓	✓	✓
Entirely automated	✓	✓	✓	✓	✓	✓
Re-collection	×	✓	×	✓	✓	✓

Uniqueness of Centri

Unique features, thanks to our electrically cooled focusing trap

- Sampling using headspace syringe, SPME, HiSorb or from TD tube
- Pre-concentration onto focusing trap
- Dry-purge
- Re-collection



Trap focusing and peak shape

Headspace analysis: Odorants in 10 mL water at 500 ppt

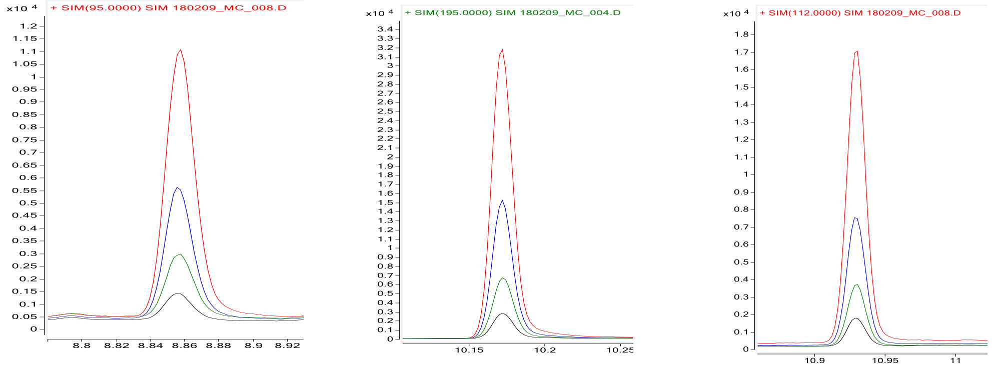
<u>Injection volume</u>

0.5mL

1mL

2mL

5mL



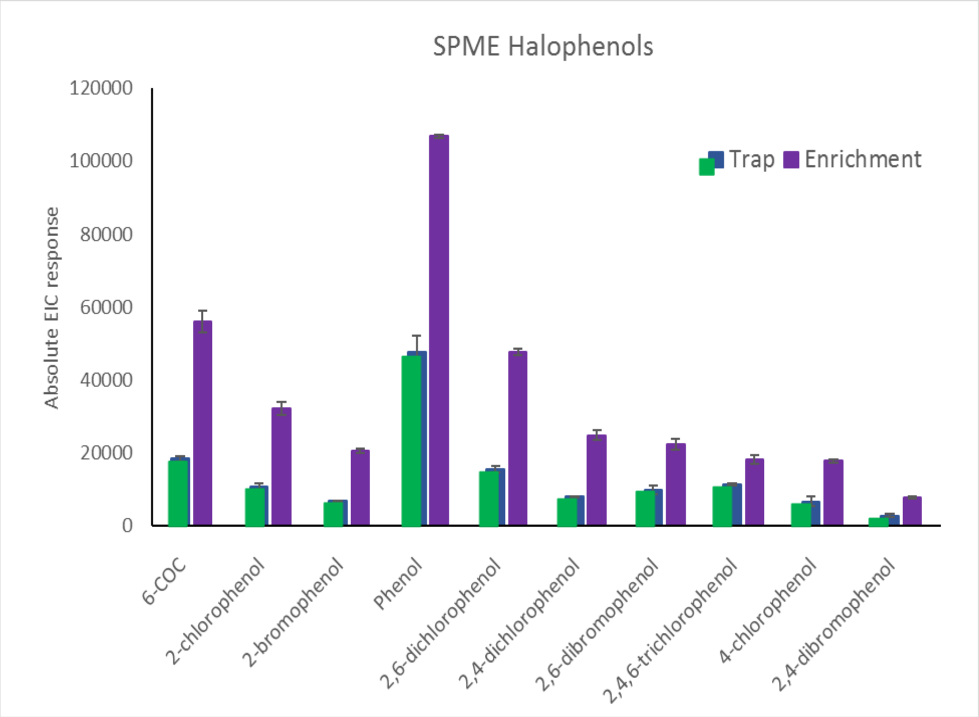
2-MIB | 2,4,6-TCA | Geosmin

- Increasing the HS sample volume by a factor of 10
- No loss in peak shape/symmetry across this range
- No peak splitting observed at higher volume
- Incremental gain in sensitivity
- Splitless analysis

Trapping technology

Multiple injections

- SPME-trap-enrichment:
  multiple SPME extractions from one sample
- Increase in response
- Re-collection is possible



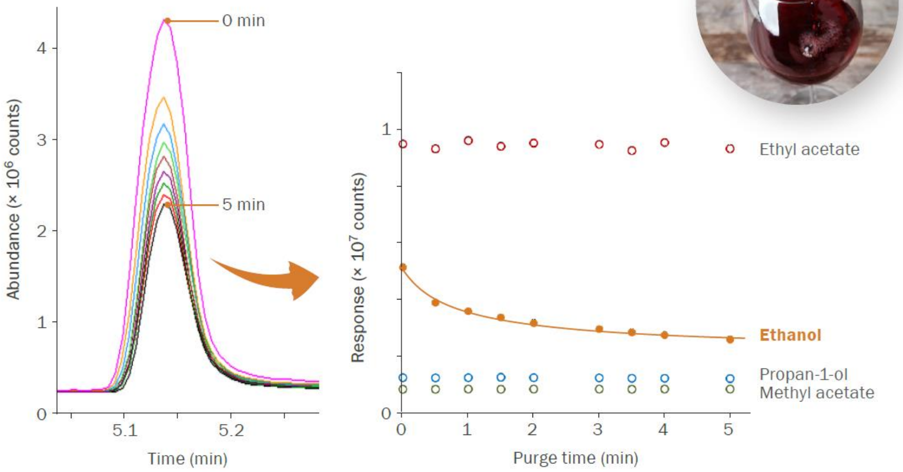
Selective elimination of interferences

Analyte selectivity prior to trap injection

- High-abundance sample interferents such as water and ethanol make it difficult to detect minor compounds of interest
- Ability to selectively purge these from the focusing trap prior to injection
- No effect on analytes of interest

- Results in:
  - Higher sensitivity
  - Better repeatability
  - Improved peak shape
  - Extended column and detector lifetime

Purging of ethanol from wine



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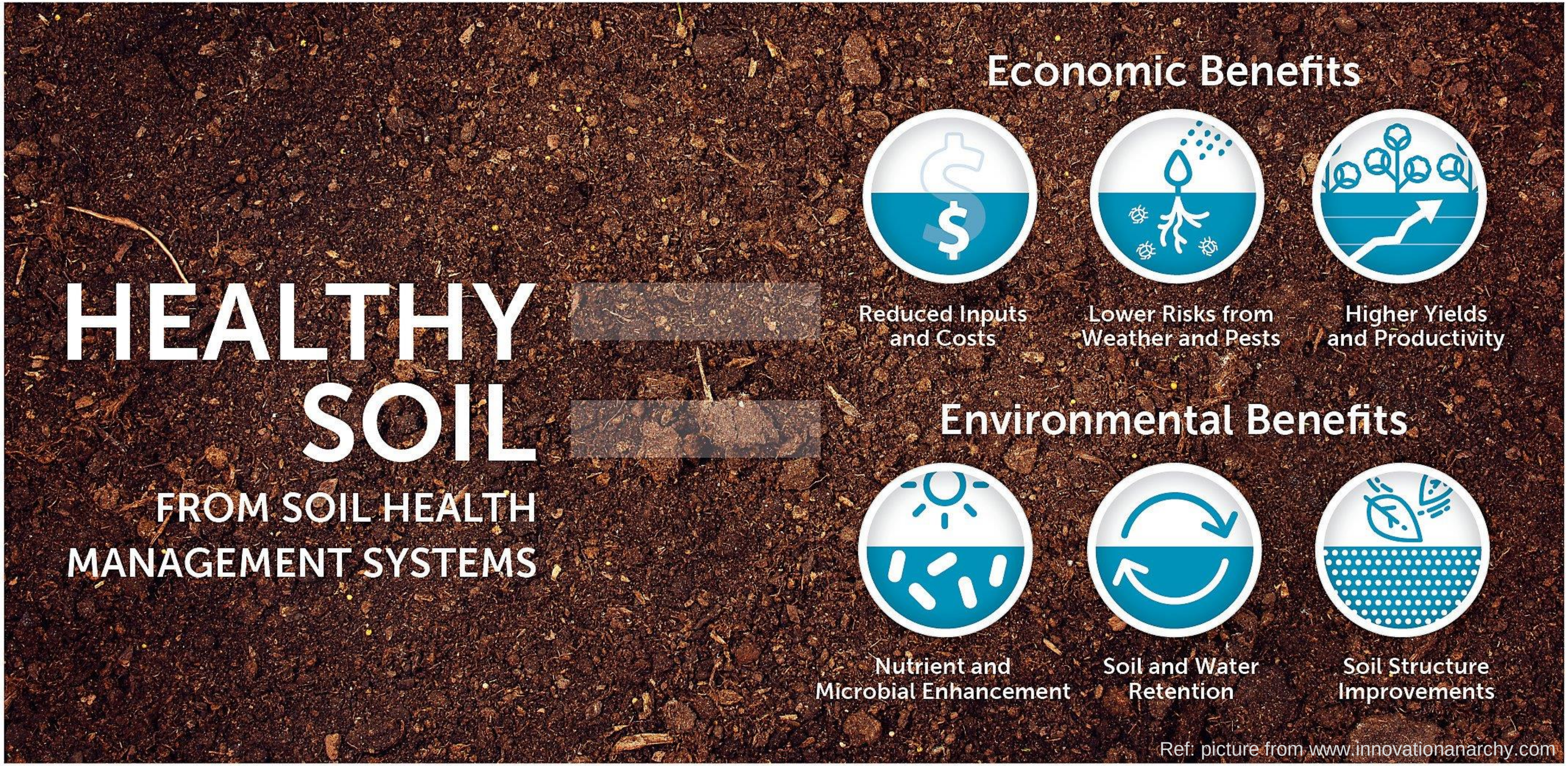
Soil analysis

THE QUEEN'S AWARDS FOR ENTERPRISE: INTERNATIONAL TRADE 2015

Why carry out soil analysis?



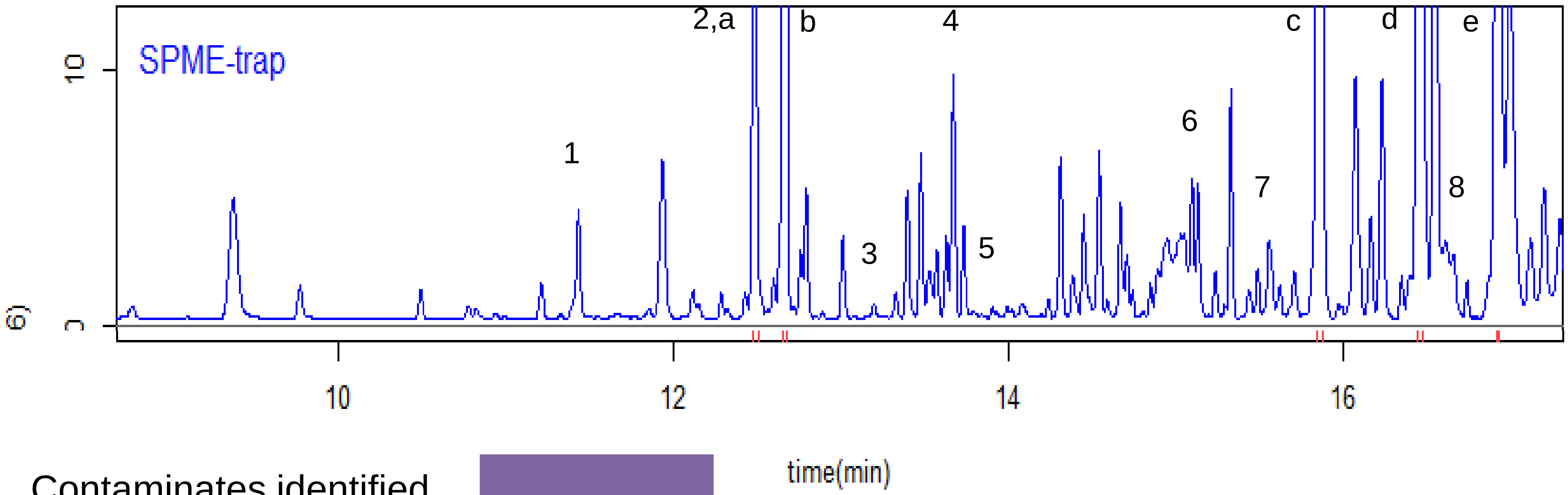
Organic contaminants in soil

- Wide range of compounds which are known to be bad for human health and environmental health
- Common sources are Industrial, Agricultural and manufacturing activities

- Soils once contaminated can act as a sink, accumulating more and more contaminants.
- These can then be released back out of the soil into the air, water sources and be adsorbed by plant life

Soil VOCs via SPME-trap

Welsh roadside soil

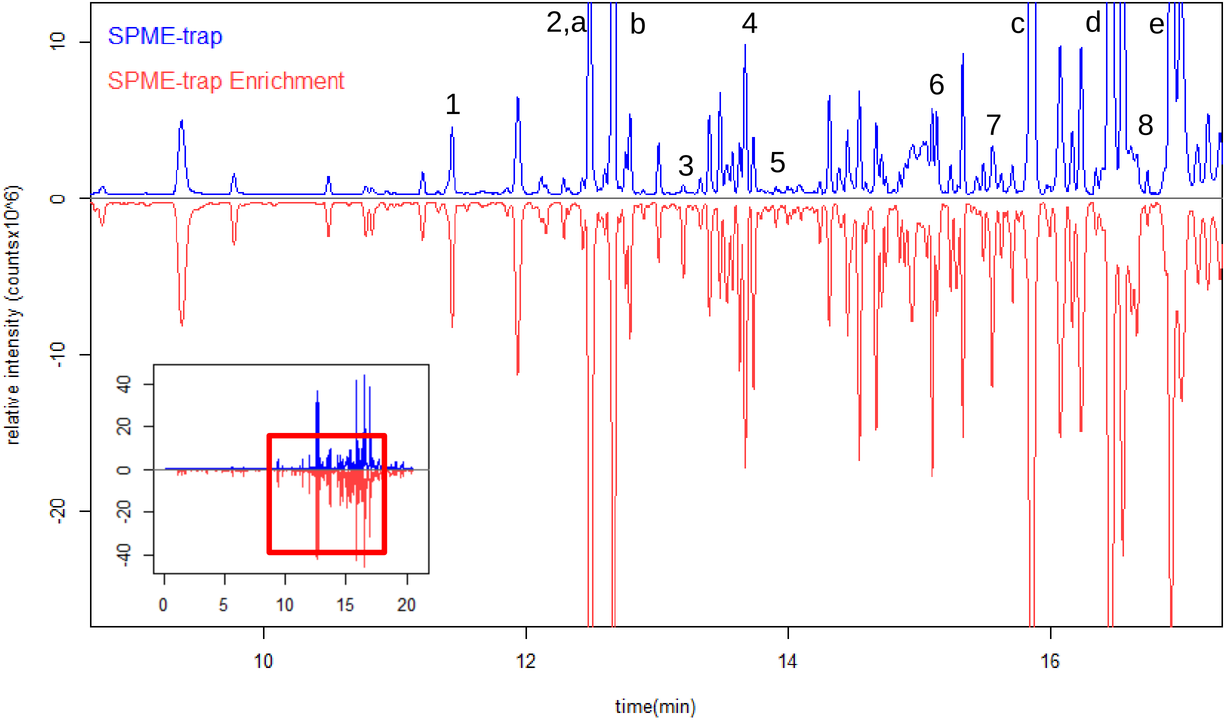


Contaminates identified from EPA 5035 (97 contaminates)

SPME-trap
22

Soil VOCs via SPME-trap + Enrichment

Welsh roadside soil



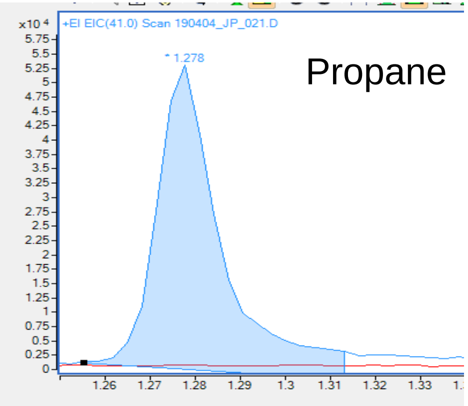
Contaminates identified from EPA 5035 (97 contaminates)

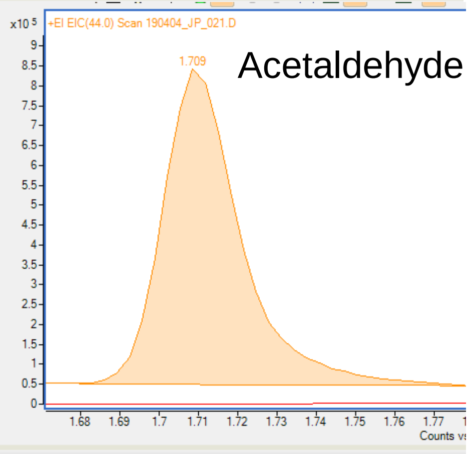
SPME-trap	SPME-trap + Enrichment
22	26

Soil VOCs via SPME-trap

Welsh roadside soil

- Great peak shape for early eluting compounds compared to direct SPME injection
- Propane (blue) and Acetaldehyde (orange) can be particularly useful to determine soil health
- Studies into how VOCs in our soil actually help improve soil health are now also of interest with a view to soil improvement specifically for food production





Food and beverage analysis

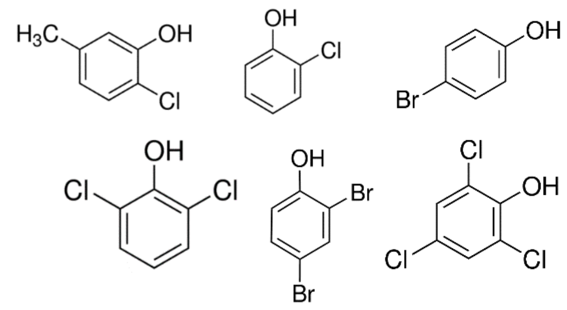
Taints in food and drinks

- Taints are unpleasant odours or flavours in food and drinks which come from external sources
- One of these can be contamination of water or soil
- Other common sources of taints are:
  - Direct contact with packaging
  - Vapour phase contamination
  - And internal chemical reaction

Tea analysis – Main challenges

- Low-level VOC analysis in tea sample
  - Complex VOC profiles (different chemical structures, trace amounts)
  - Off-flavours: compounds associated to unpleasant smells/tastes, sometimes a few ng/L are enough to cause problems

- For this analysis, we used a tea sample spiked with **halophenols**



Ubiquitous, man-made pollutants.
Accidental contamination of many food types.
Toxic, unpleasant smells (damp, musty, mouldy)

Technique 1: SPME / SPME-trap / with enrichments

Analytical process

The SPME fiber is normally positioned in the sample headspace and incubated/agitated to facilitate extraction.

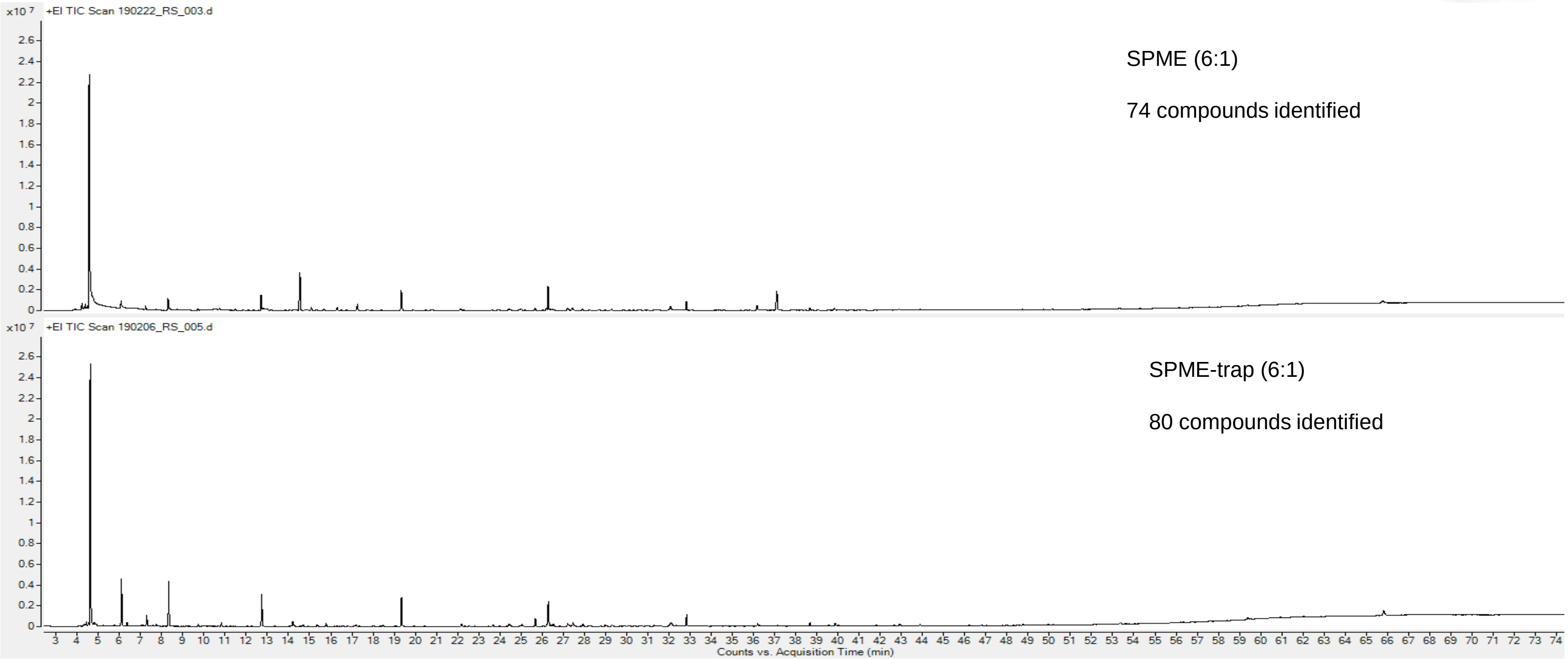
The fiber is inserted into the injection port and the vapours transferred to the focusing trap (or sent directly to the GC–MS).

If applicable, the trap is thermally desorbed at up to 100°C/s to inject the sample into the GC–MS as a narrow band.

- Incubation: 60 ºC, 15 minutes, 500 rpm
- Enrichment: total number of extractions from same vial = 3

Sample profile: SPME direct v SPME-trap

Full profile comparison



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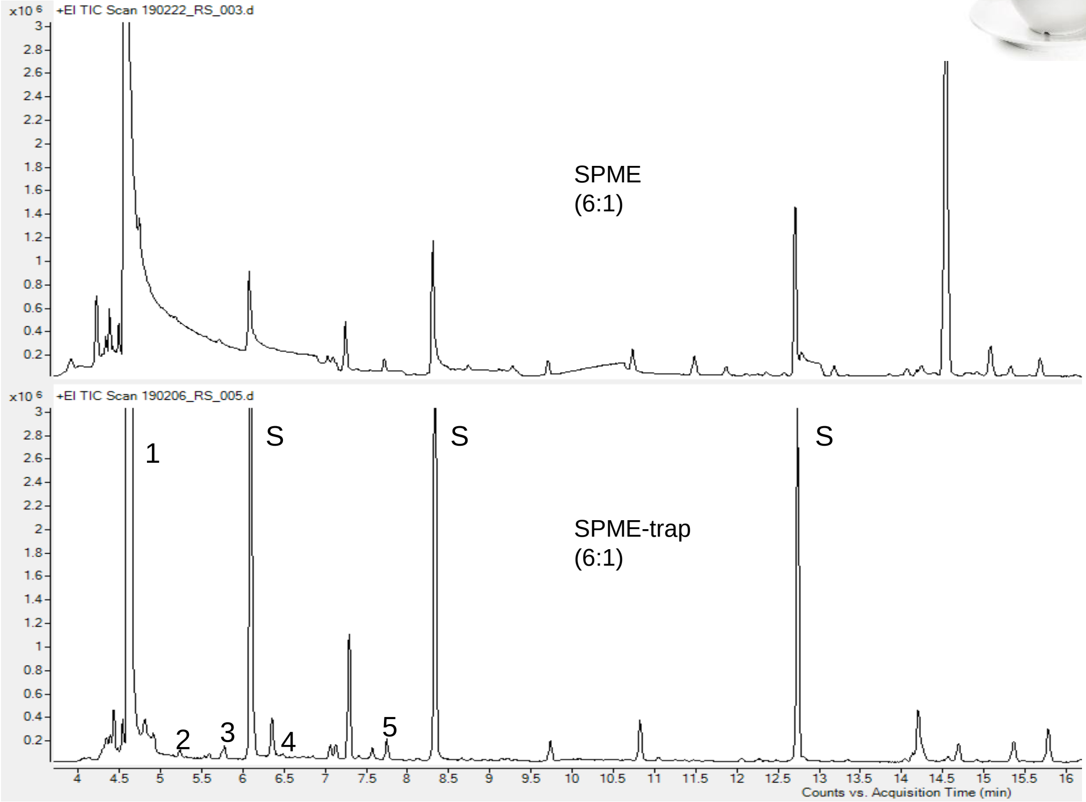
Sample profile: SPME direct v SPME-trap

- Improvement in peak shape for earlier eluting compounds when trap is in-line
- Low-level compounds identified which were previously masked by peak tailing (*)
- Get benefit when trying to concur with challenge 1 – Complex VOC profiles



1. Ethyl ether
2. Dimethyl sulphide*
3. Acetone*
4. Butanal*
5. 2-Ethylfuran

S = siloxane

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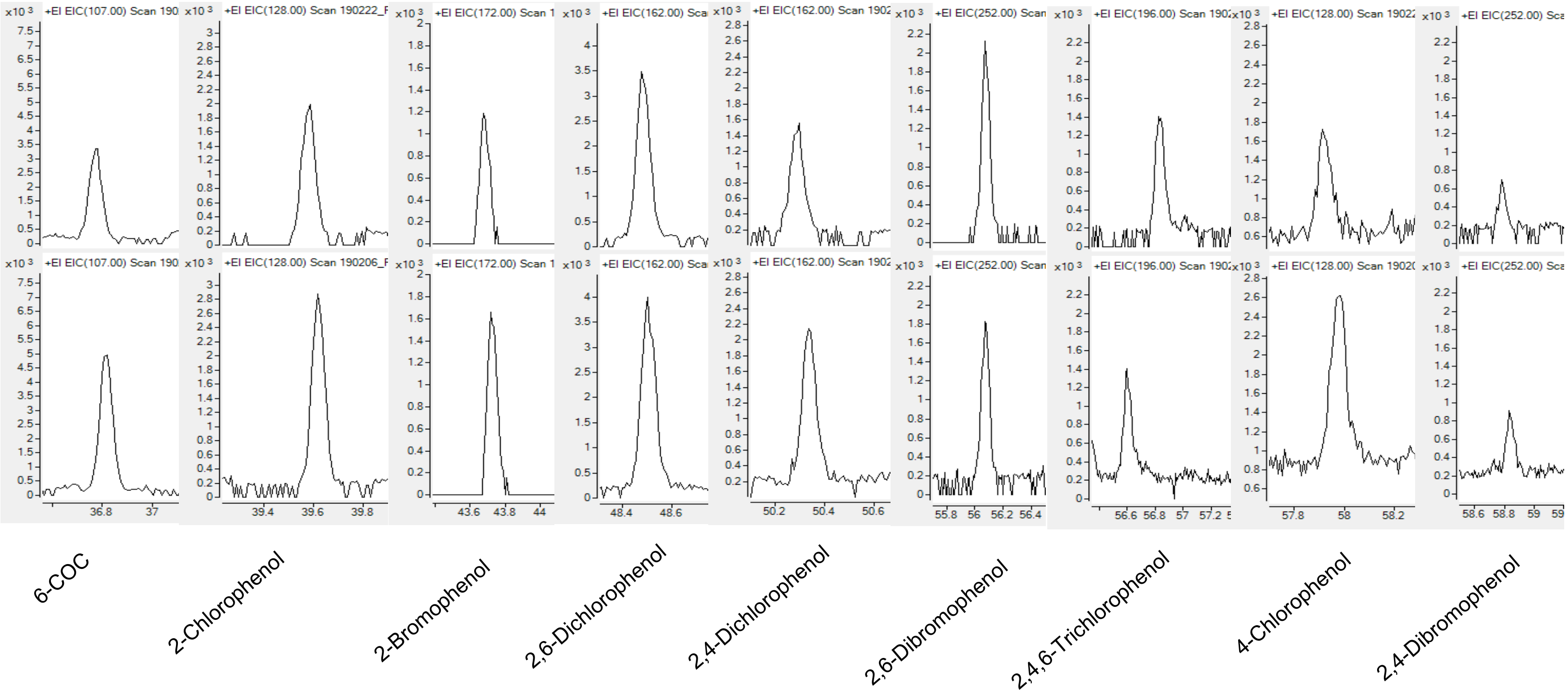
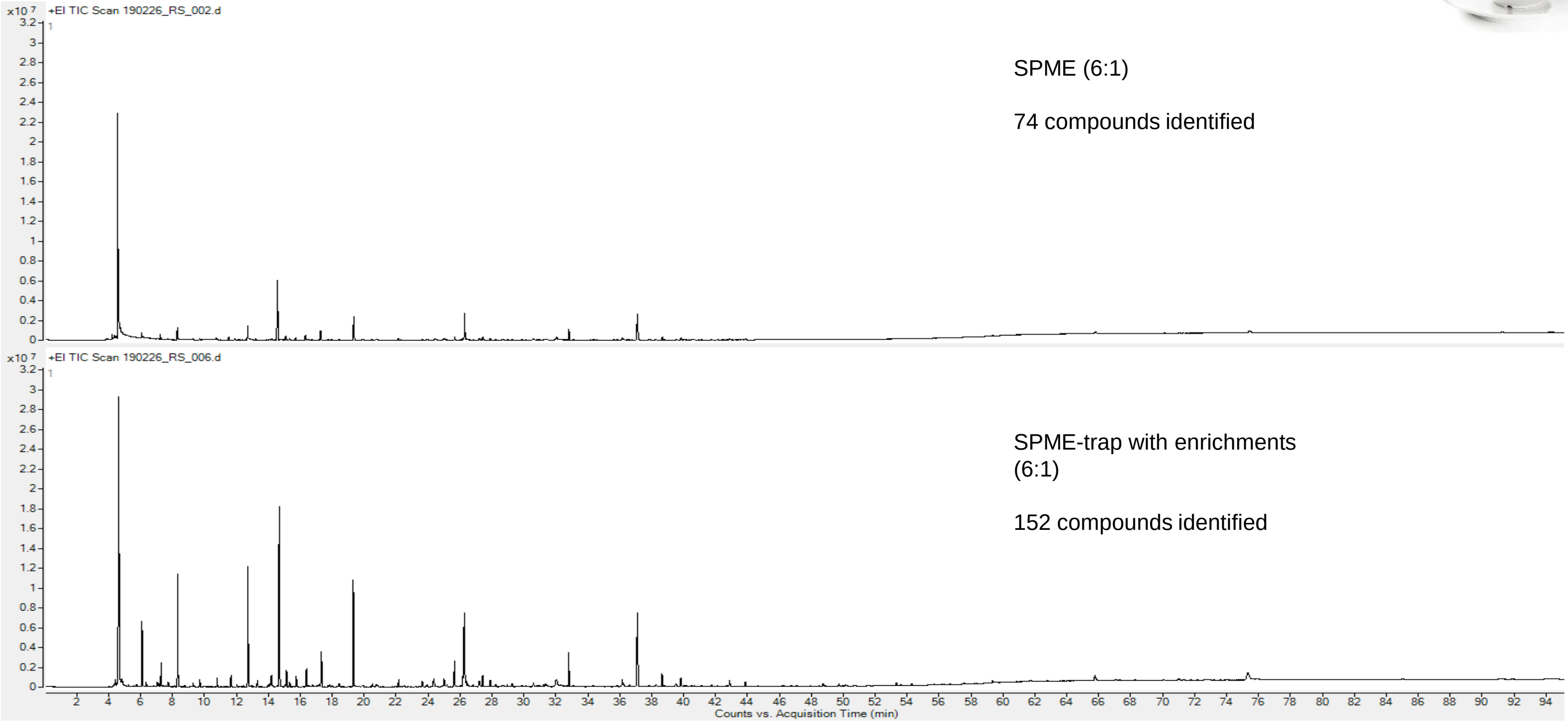
Halophenols

SPME direct (top) v SPME-trap (bottom)



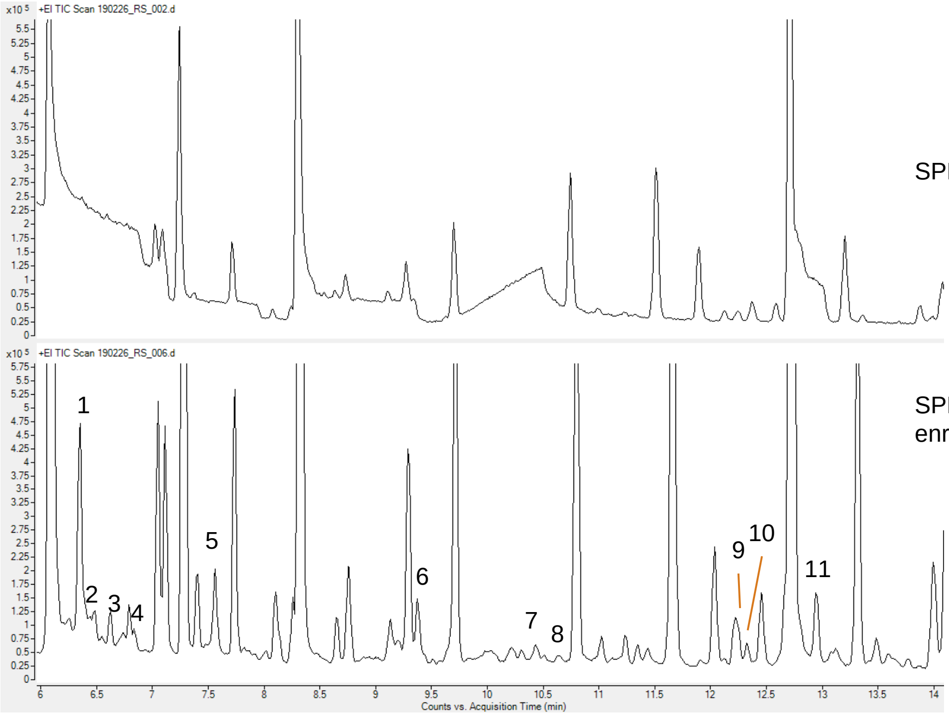
SPME direct v SPME-trap with enrichments

Full profile comparison



SPME direct v SPME-trap with enrichments

Greater abundance of compounds previously identified, additional compounds identified



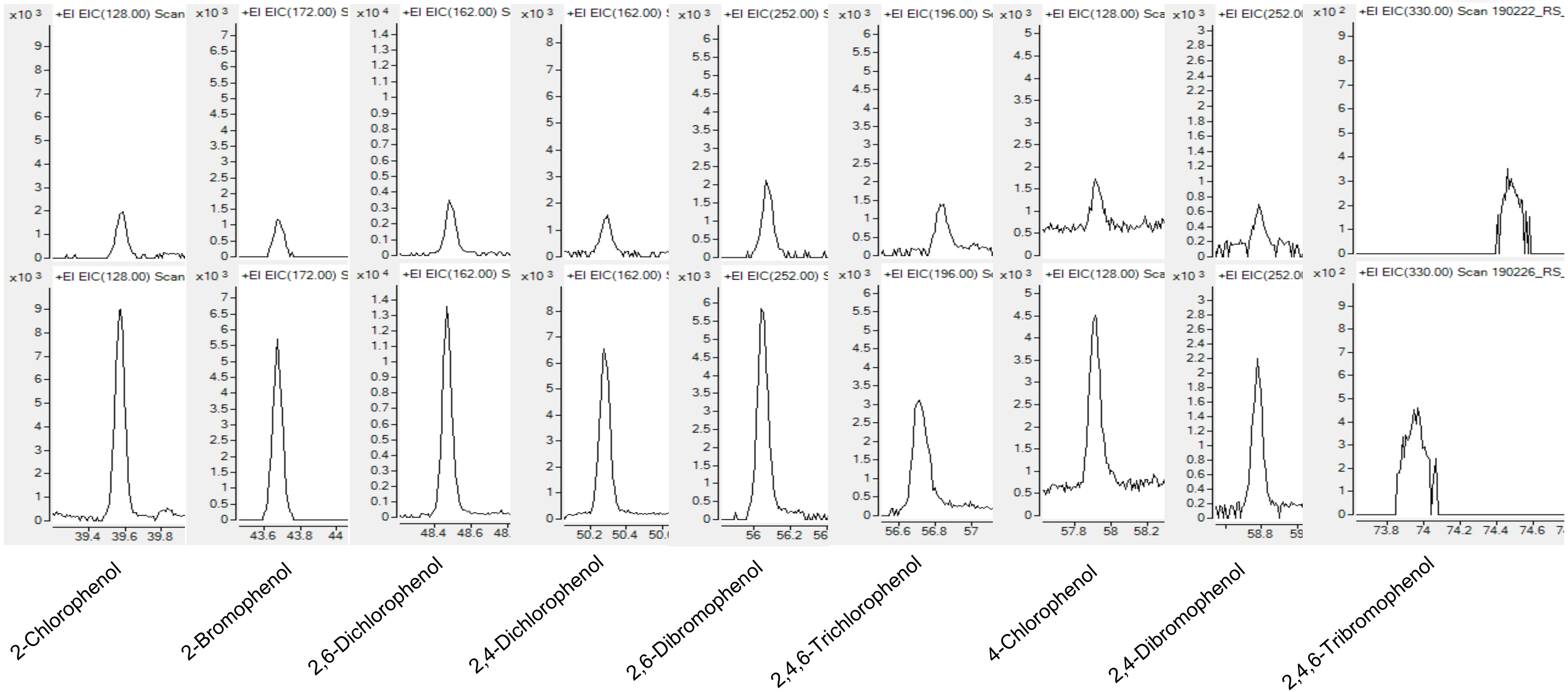
SPME (6:1)

SPME-trap with enrichments (6:1)

#	Compound
1	Tetrahydrofuran
2	Butanal
3	3-Methylfuran
4	2-Butanone
5	Benzene
6	α-Thujene
7	Camphene
8	Dimethyl disulphide
9	3-Methyl-2-butenal
10	2-n-Butyl furan
11	3-Carene

SPME-trap with enrichments: Halophenols

SPME direct (top) v SPME-trap with enrichments (bottom)



Technique 2: HiSorb, high-capacity sorptive extraction

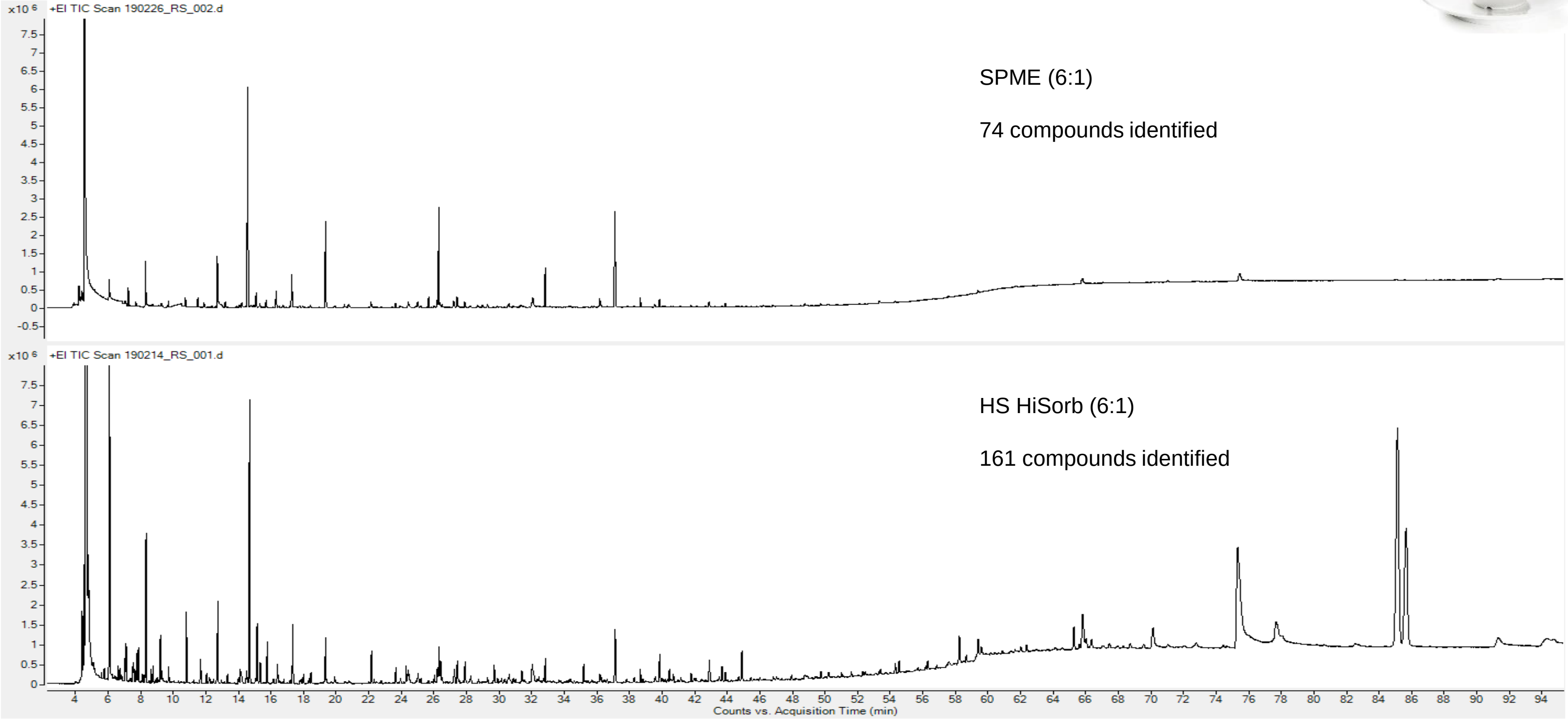
Analytical process

The robot inserts the probe into the vial, and the assembly is incubated/agitated to ensure analyte equilibration.	The probe is removed from the vial, and a wash/dry station removes residual sample matrix.	The probe is thermally desorbed and vapours transferred to the focusing trap.	The trap is thermally desorbed at up to 100°C/s to inject the sample into the GC–MS as a narrow band.	The headspace vials are re-sealed with special caps to avoid contamination of laboratory air.

- Incubation: 60 ºC, 60 minutes, 500 rpm
- Probe mode: Headspace, short length probes

SPME direct v HS HiSorb

Full profile comparison



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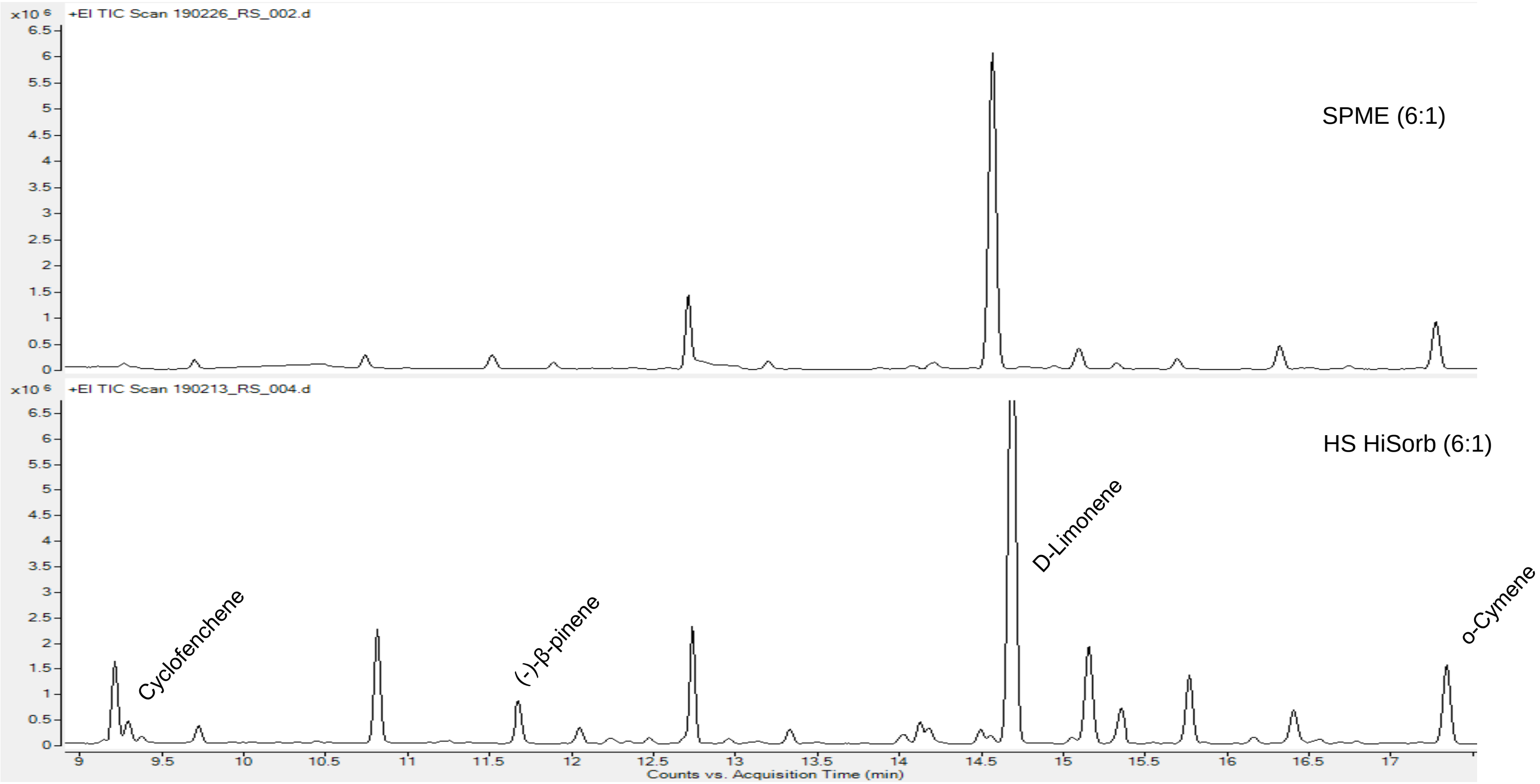
SPME direct v HS HiSorb

Improvement in peak shape, more confident compound identification



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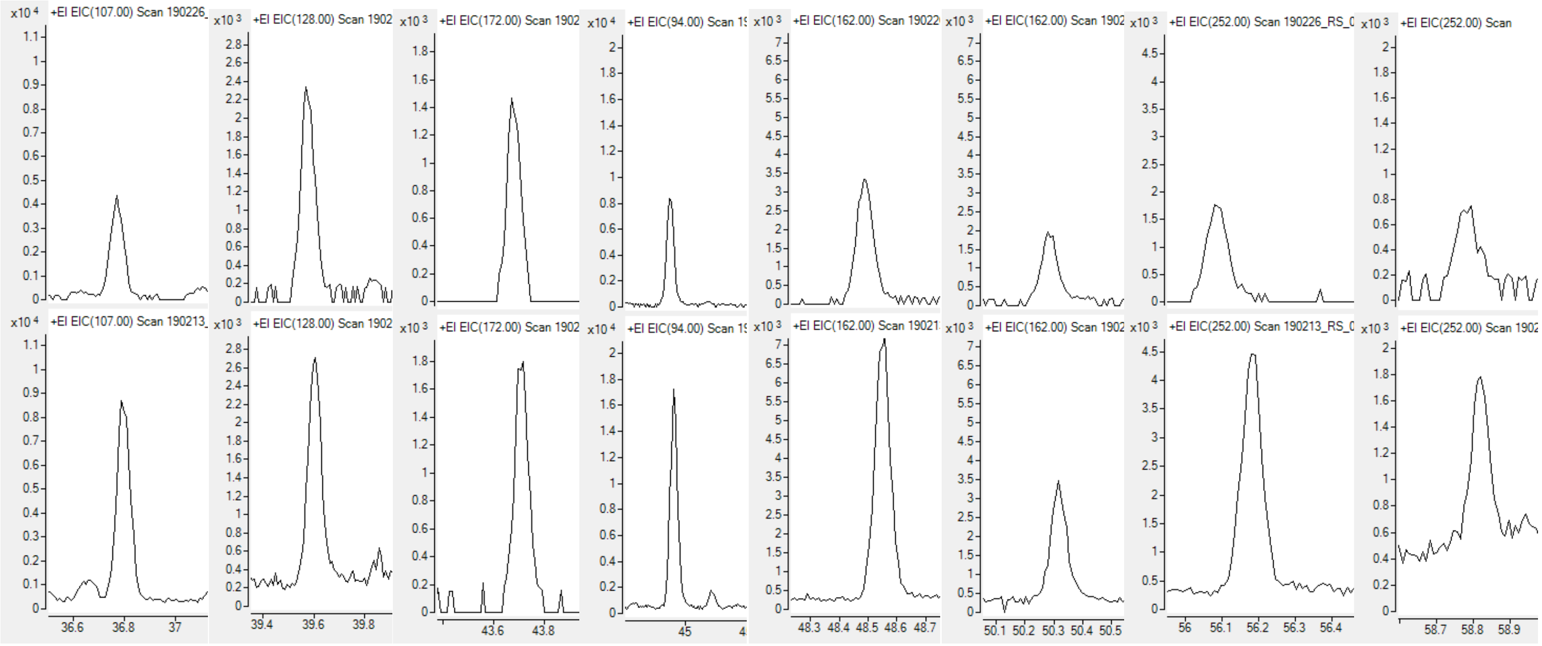
HS HiSorb: Halophenol compounds

SPME direct (top) v HS HiSorb (bottom)



6-COC
2-Chlorophenol
2-Bromophenol
Phenol
2,6-Dichlorophenol
2,4-Dichlorophenol
2,6-Dibromophenol
2,4-Dibromophenol

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Technique comparison: VOC profiling

Technique	Compounds identified
SPME direct	**74**
SPME trap	**80**
SPME trap with enrichment	**152**
HS HiSorb	**161**

Technique comparison: VOC profiling

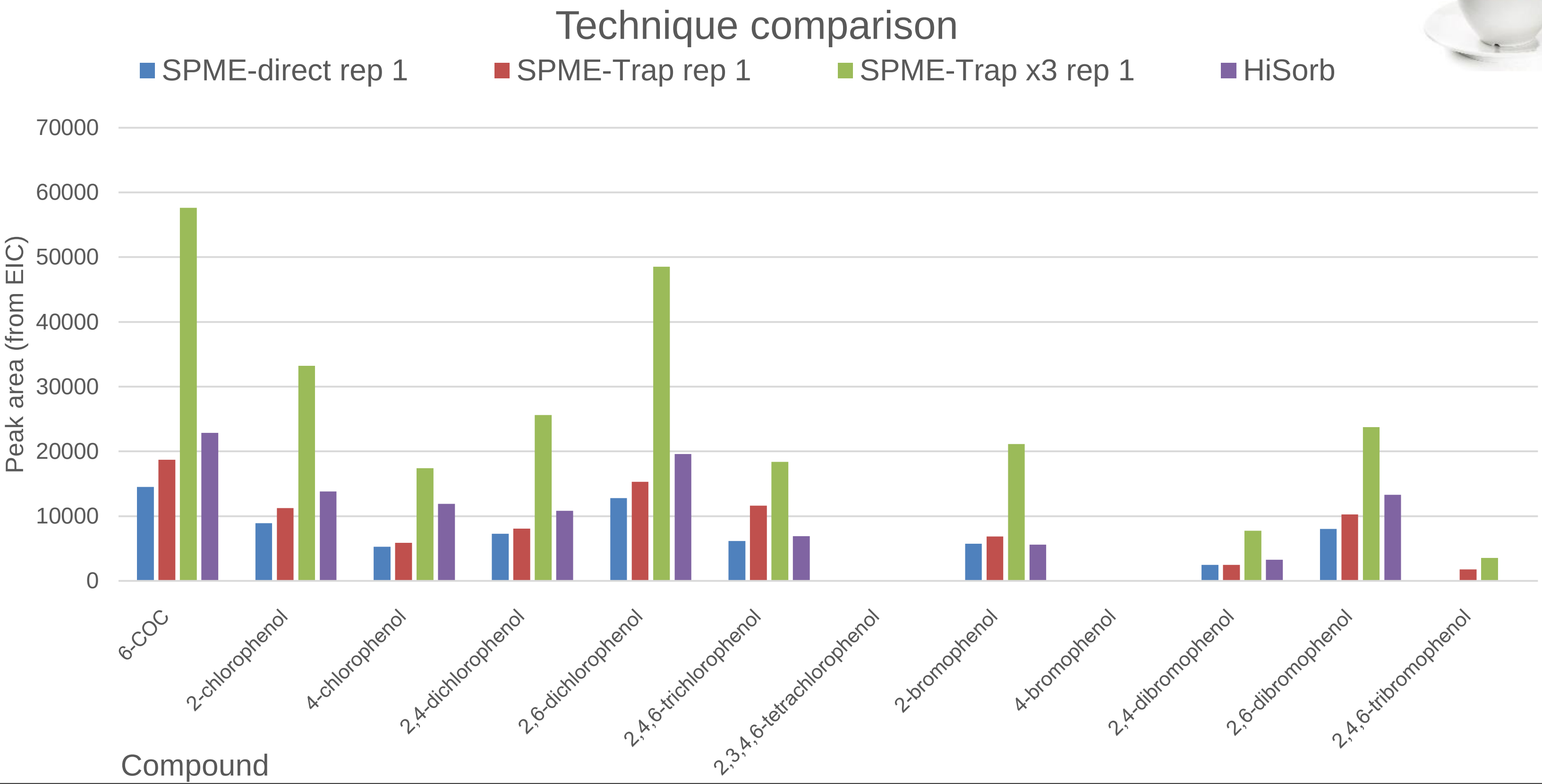
Technique	Compounds identified
SPME direct	**74**
SPME trap	**80**
SPME trap with enrichment	**152**
HS HiSorb	**161**

← better chromatography un-masking trace analytes

← Increased sensitivity

← large phase volume enhances extraction

Technique comparison: Halophenol abundance



Packaging analysis

Quantitation of residual solvents in packaging materials

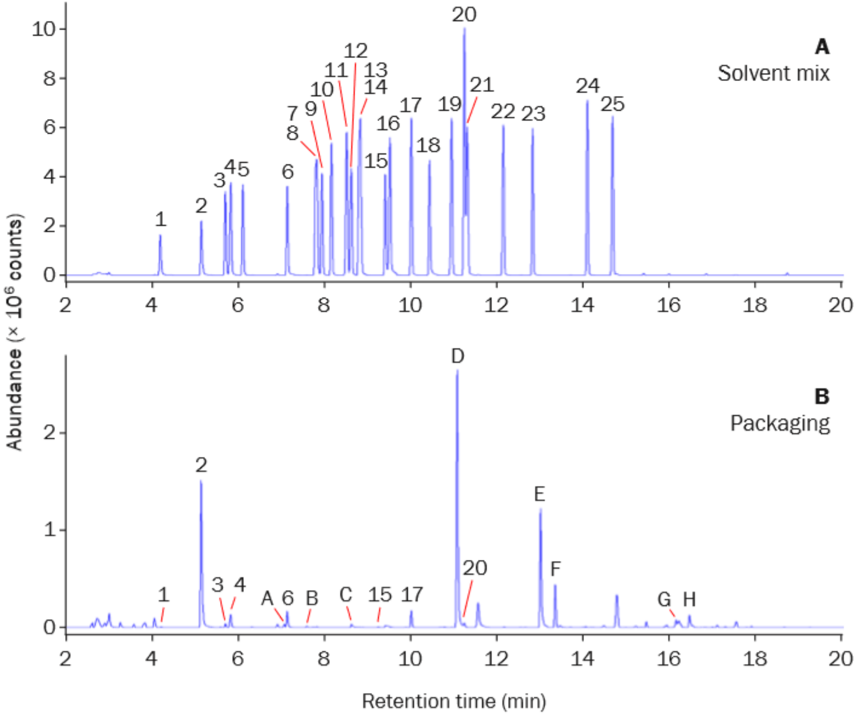
Sensitive, automated sampling and analysis by headspace–trap GC–MS

- Packaging conveys information about the product and protects it during shipping and storage.
- The packaging itself can be a source of contaminants, including residual solvents, monomers and additives.
- As well as off-odours, such contaminants can also give rise to health concerns.
- Residual solvents in food packaging are regulated in the US (under 21CFR175) and the EU (under EC 1935/2004).
- The analysis of flexible packaging for the determination of residual solvents typically uses static headspace–GC in accordance with EN 13628-1 or -2.

Quantitation of residual solvents in packaging materials

Sensitive, automated sampling and analysis by headspace–trap GC–MS

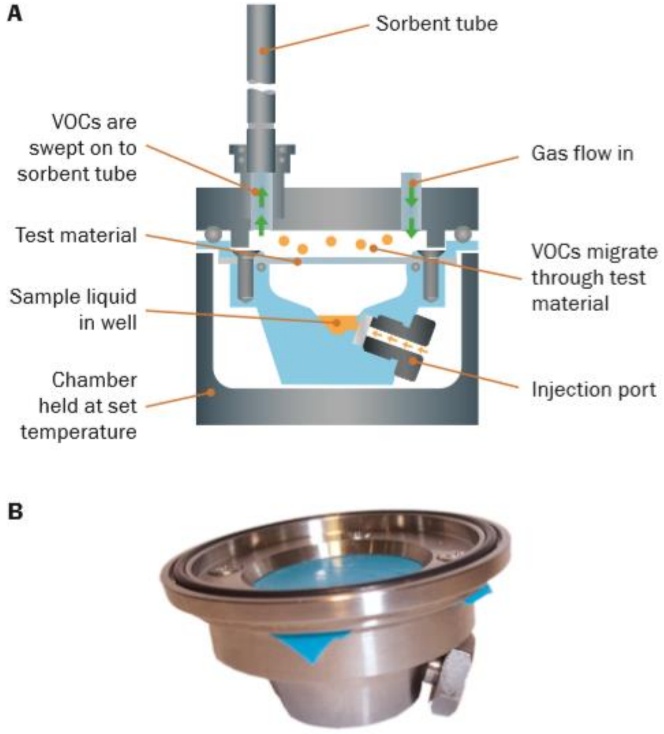
- The headspace of thin flexible packaging for savoury snacks was analysed using syringe headspace trap
- The HS–trap GC–MS profile for a standard containing 25 solvents commonly found in food packaging shows elution of all components within 15 min.
- The HS–trap profile from a 64 cm^2 sample of food packaging, which indicates the presence of a number of solvents and some other components that likely derive from the manufacturing process.
- Ethanol is the most significant component (at 1.92 mg/m^2), with seven other solvents at trace levels.
- Thanks to trap focusing, good peak shapes are obtained, in spite of a very low (3.5:1) split ratio.



Permeability of packaging materials

A simple and reliable method using microchamber and TD–GC–MS

- Permeation of chemicals into (and out of) food packaging has an impact on the shelf-life and safety of pre-prepared and food products.
- Permeation studies are possible using microchamber, using a dedicated tool.
- A thin film of material is secured in horizontal position.
- The bottom well is filled with a standard containing the compounds of interest.
- The upper part of the chamber is flushed with 50 mL/min of dry nitrogen.



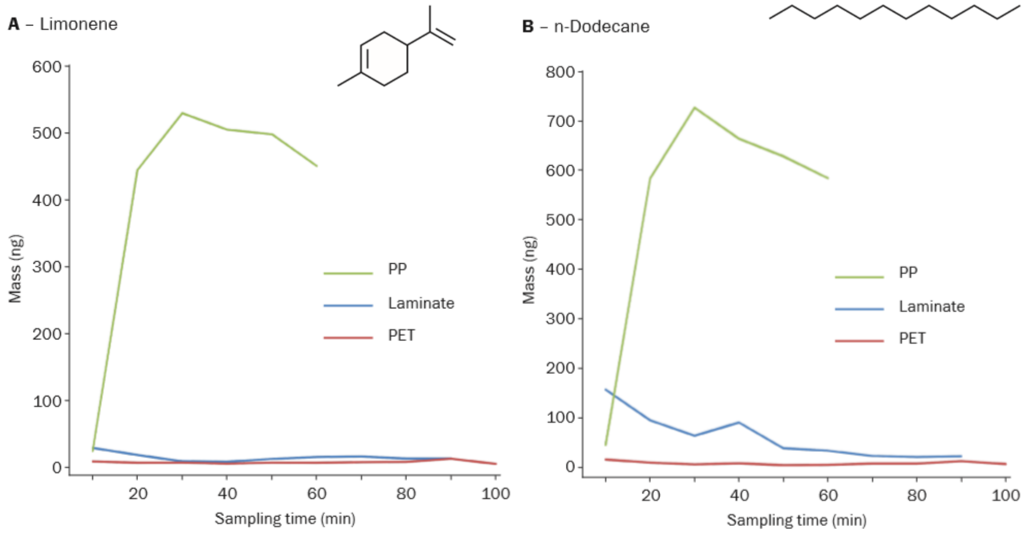
Ref.: Application Note 121

Permeability of packaging materials

A simple and reliable method using microchamber and TD–GC–MS

- Three types of food packaging materials: polypropylene (PP), polyethylene terephthalate (PET) and laminate (silicon-oxide coated PET + PP)

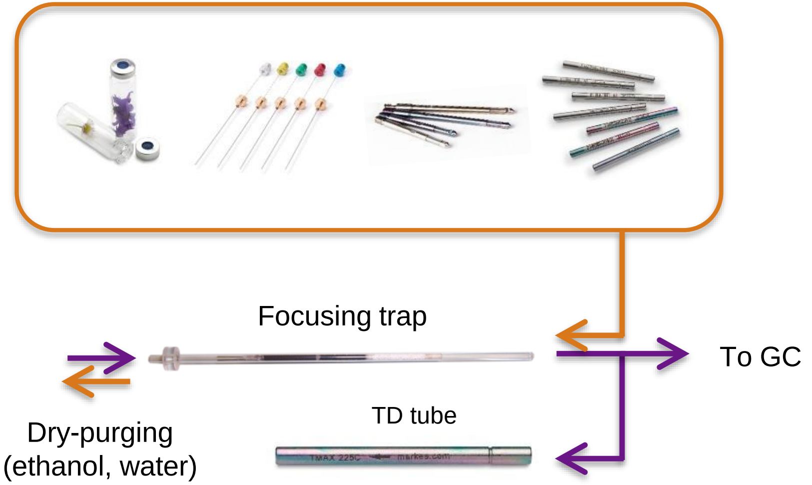
- Possibility to simulate the outward migration of an aroma compound (limonene) or the inward migration of a toxic chemical (dodecane)



Uniqueness of Centri

Unique features, thanks to our electrically cooled focusing trap

- Sampling using headspace syringe, SPME, HiSorb or from TD tube
- Pre-concentration onto focusing trap
- Dry-purge
- Re-collection



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