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Quantitative Determination of Volatile Organic Pollutants in Water Using Headspace–Trap GC–MS

Jan Peter Mayser, Ph.D.; Nicola Watson, Ph.D.

Volatile Organic Pollutants in Water

Outline

- Global water standards
- Challenges
- Solutions
  - Headspace-Trap
  - Selective dry purging
- Results
  - Scan Mode
  - SIM Mode
- Summary

A fundamental resource for life

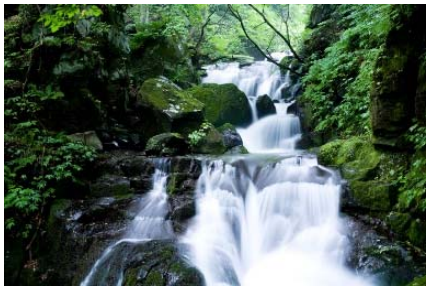
Water's importance

- 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

Drinking water

Waste water

Environmental water

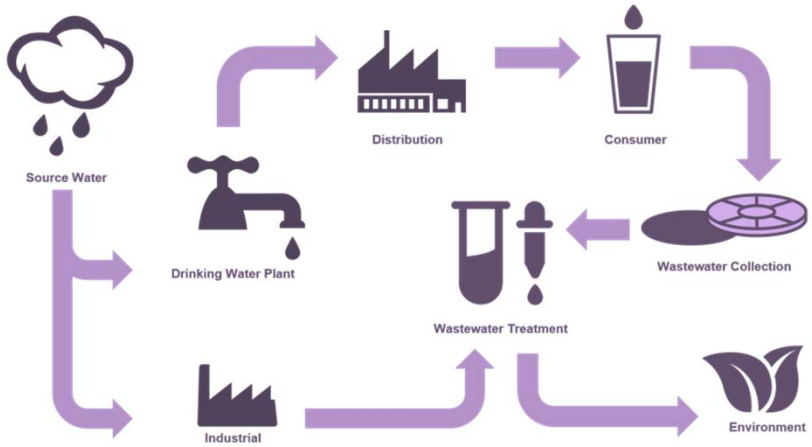


Groundwater

Global water standards

Regulations connected with VOCs in water

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



Drinking Water standards		
Country	Agency	Regulation
USA	US EPA	The Safe Drinking Water Act (SDWA)
EU	EEA	EU Drinking Water Directive
India	BIS	BIS Code 10500: Revised 2012
Canada	CDWQG	Safe Drinking Water Act 2002
China	China EPA	National Drinking Water Quality Standard

Maximum/reporting levels

…for a few contaminants, globally.

Compound	US EPA	China EPA	European EEA	Canadian CDWQG	WHO guidelines
Benzene	0.005 mg/L	0.01 mg/L	0.001 mg/L	5 µg/L	10 ppb
Ethylbenzene	0.7 mg/L	0.3 mg/L	—	140 µg/L	300 ppb
Xylenes (total)	10 mg/L	0.5 mg/L	—	90 µg/L	500 ppb
Vinyl chloride	0.002 mg/L	0.005 mg/L	0.0005 mg/L	2 µg/L	—

VOCs in drinking water

Compounds of interest

- Pollution of water from:
  - Agriculture
  - Petrochemical extraction and processing
  - Major industry
  - Waste-water processing plants
  - and much more…
- US EPA 524.2 and US EPA 524.3
  - Surface water
  - Ground water
  - Drinking water in any stage of treatment

- Major challenges for analysis:
  - Low detection limits required (0.02–1.6 ppb)
  - Trapping gases at ambient temperatures
  - Trapping SVOC and VVOCs
  - Water management

Challenges associated with Environmental Monitoring

Why use Thermal Desorption?

- Low levels in the water
  (parts per billion/trillion; ppb/ppt).

  → **Pre-concentration**

- Wide volatility range

  → **Multiple sorbent beds**

- Extremely volatile

  → **Strong sorbents required**

Automated Concentration Platform

Centri®

- Sample introduction from
  - Water
  - Air
  - Soil
- Pre-concentration of analytes via focusing trap
- 4 different operational modes
- Re-collection
- Low-running costs
  - no liquid cryogen

HiSorb high-capacity sorptive extraction

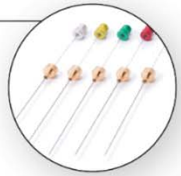
Convenient probes for immersive or HS sampling of liquids & solids.

HS & HS–trap

Versatile sampling from solids and liquids contained in regular headspace vials.

Thermal desorption

The ideal option for analysis of trace VOCs and SVOCs.



SPME & SPME–trap

Fast and sensitive sample extraction, with a range of selective fiber types.

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Advantages of Static Headspace and HS-Trap

Why?

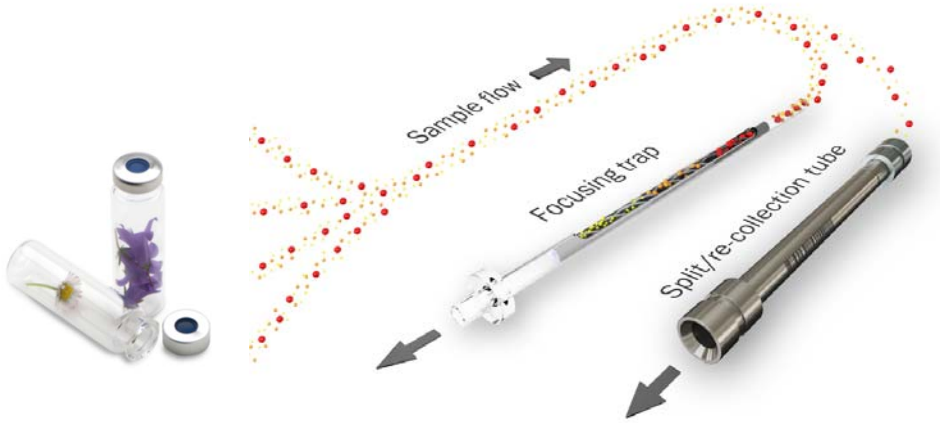
- Easily automated and increased productivity with prep-ahead functionality
- Excess purging can lead to loss of very volatile VOCs
- Samples that foam pose no added difficulty
- Virtually any matrix can be analysed, including water, soil, sludge, or waste drum contents
- The glassware is all disposable
- Headspace samples could be prepared directly in the field, saving a transfer step
- Lower detection limits achieved with trapping in-line

→ Powerful combination of headspace and pre-concentration technology

Loading the trap

Headspace Trap workflow

1st stage

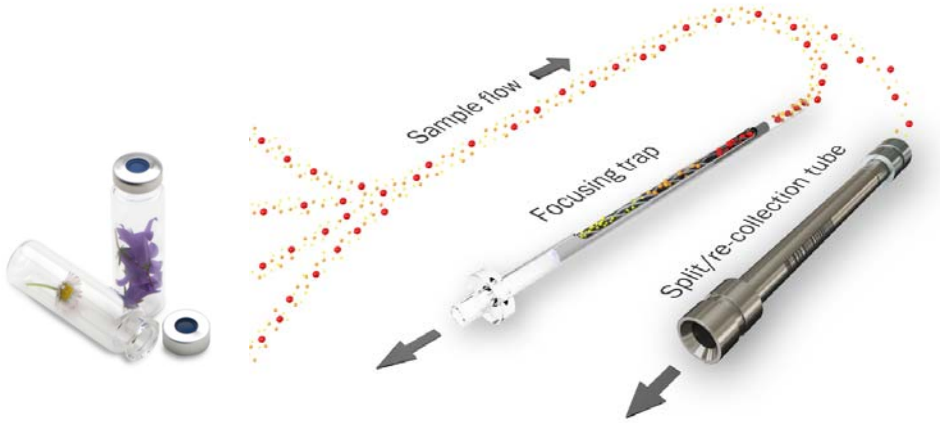


- Common to **all** sampling modes
- Allows **high uptake** flows for VOCs
- After the 1st stage a **dry purge** is optional

Water removal

Dry purging

1st stage



- Common to **all** sampling modes
- Allows **high uptake** flows for VOCs
- After the 1st stage a **dry purge** is optional

Dry purging:

- Setting the trap at slightly higher temperatures
- Purging excess water from the sorbents

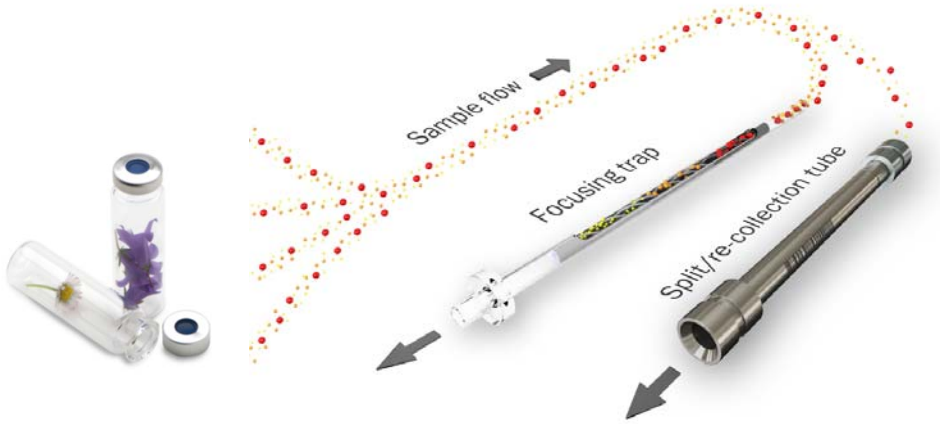
Possible because:

- Multiple sorbent beds
- Stronger sorbents can be used

Desorbing the trap to the GC

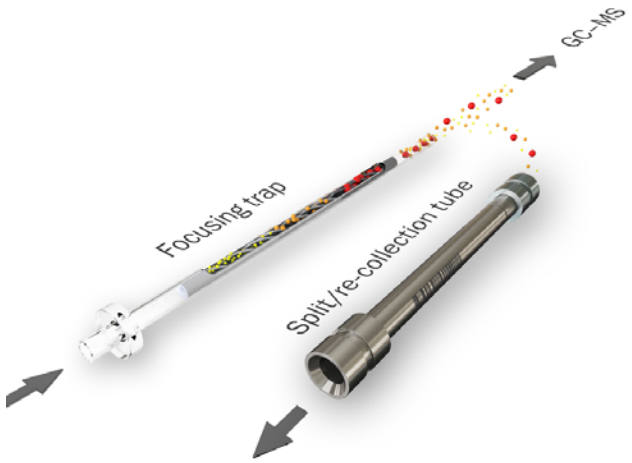
Headspace Trap workflow

1st stage



- Common to **all** sampling modes
- Allows **high uptake** flows for VOCs
- After the 1st stage a **dry purge** is optional

2nd stage



- Narrow design allows **split or splitless** injection
- **Backflushed** to the GC-MS
- **Re-collection** of split is possible

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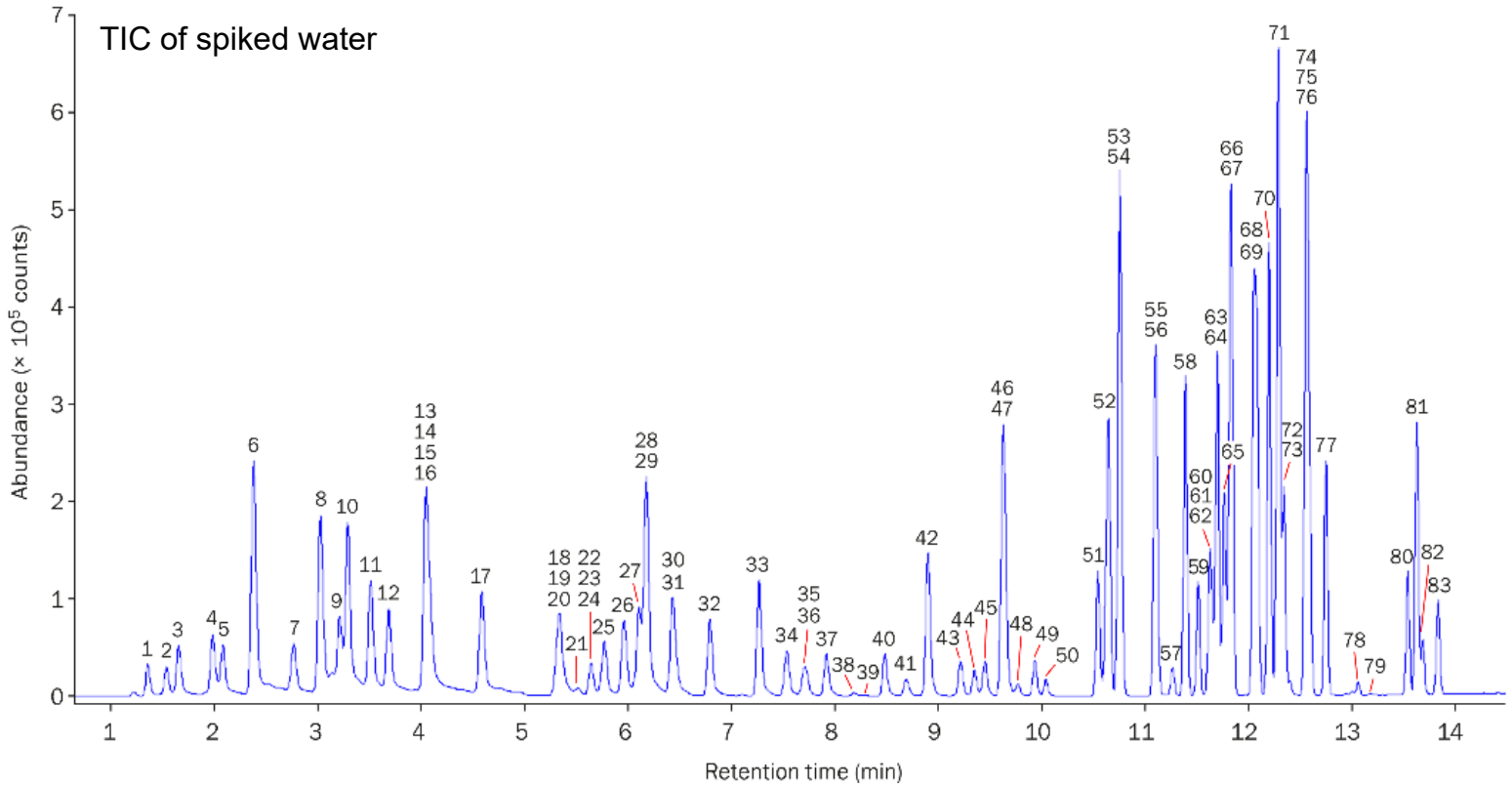
VOCs in water

Increasing sensitivity using Headspace-trap

Reliable trapping for all compounds

Headspace–trap analysis



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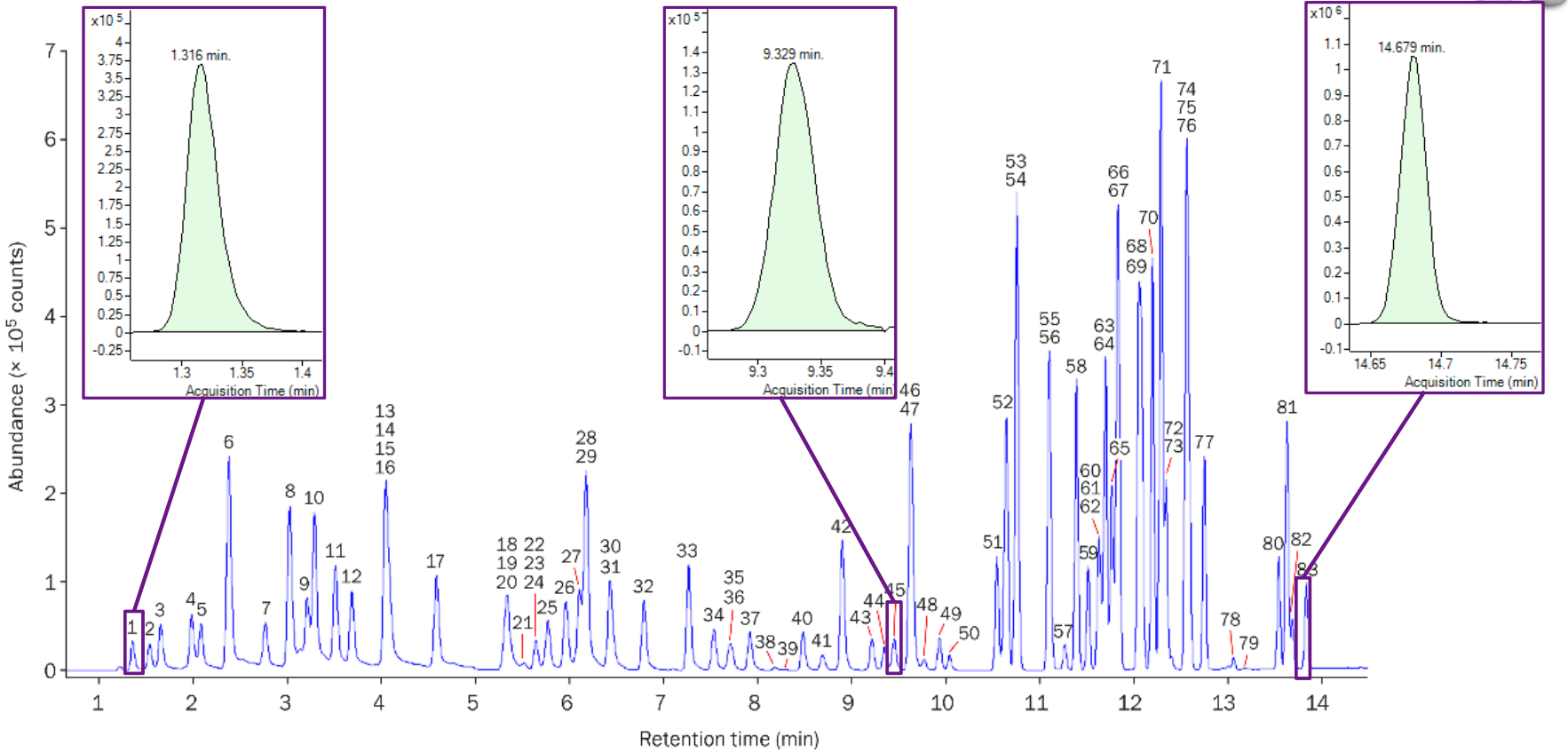
Trapping across the whole volatility range

Headspace–trap analysis



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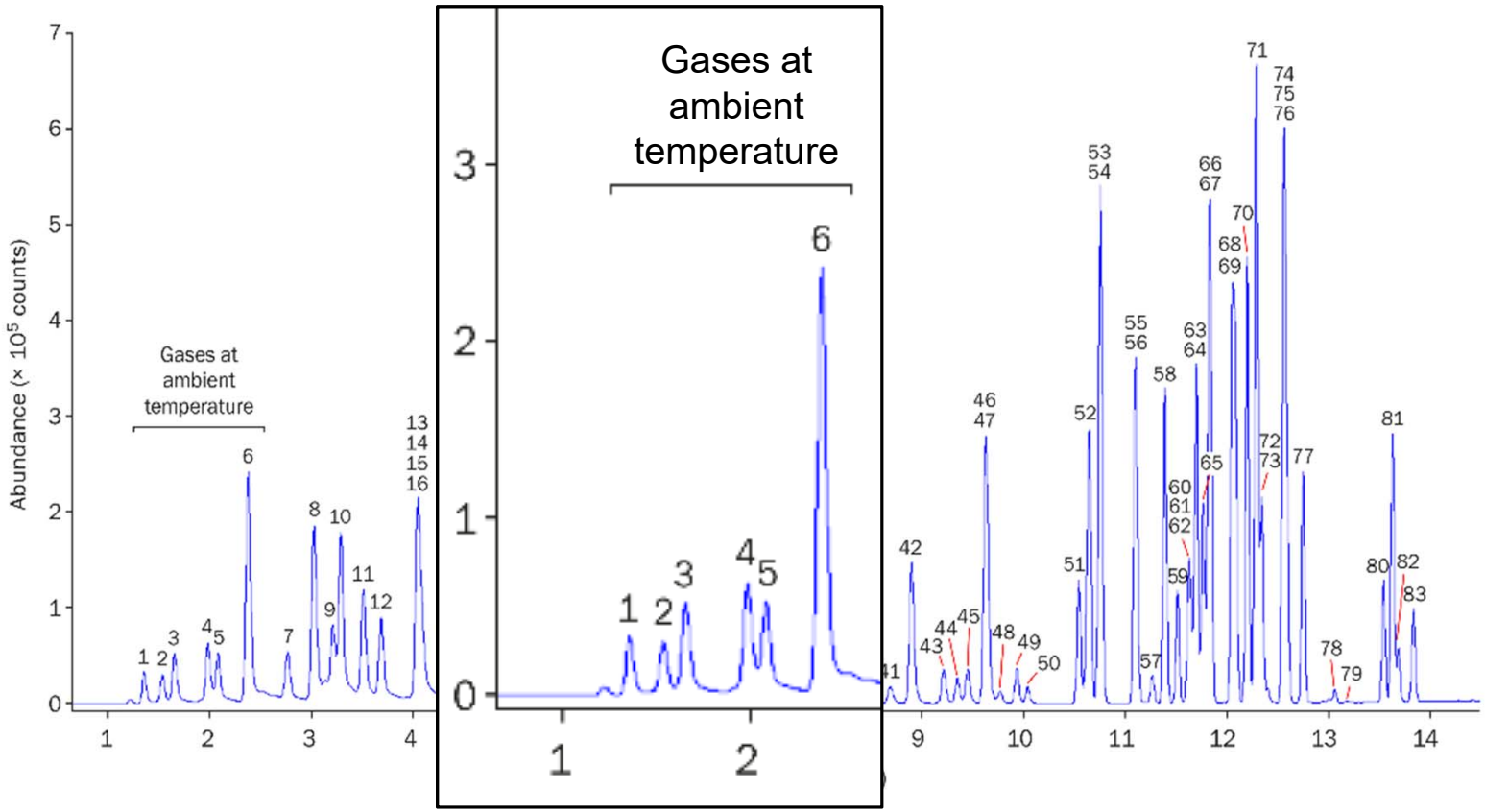
Very volatile compounds

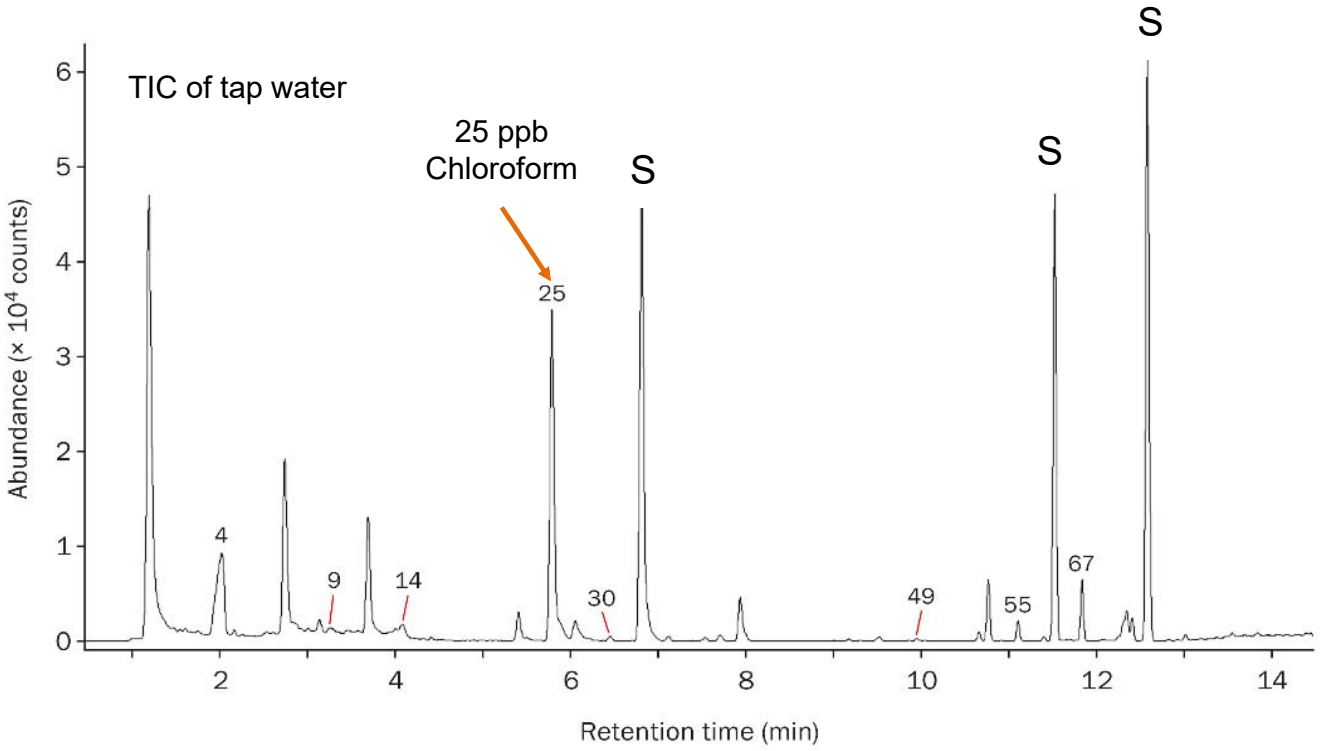
Retained and released, reliably



What is in our tap water?

Welsh drinking water

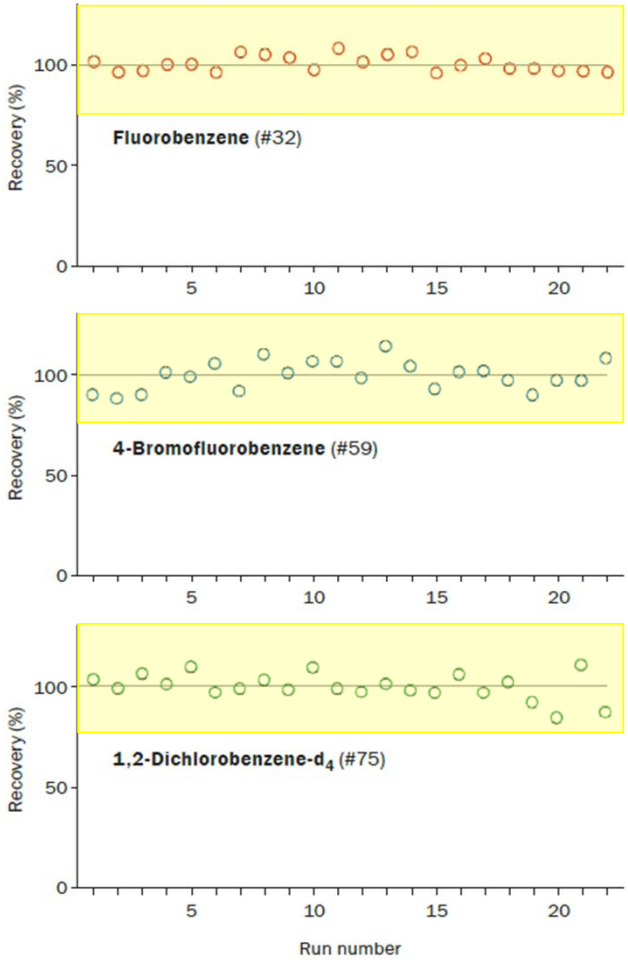
- Real-world sample of tap water
- Surrogates added at 25 ppb
- Chloroform @ 25 ppb
- 82 compounds <2 ppb



Reliable and consistent results

Reproducibility and linearity

- The recoveries for the internal standard and the two surrogates
- 22 consecutive analyses of the 25 ppb standard
- Falls within the 80–120% range
- RSDs below 10%



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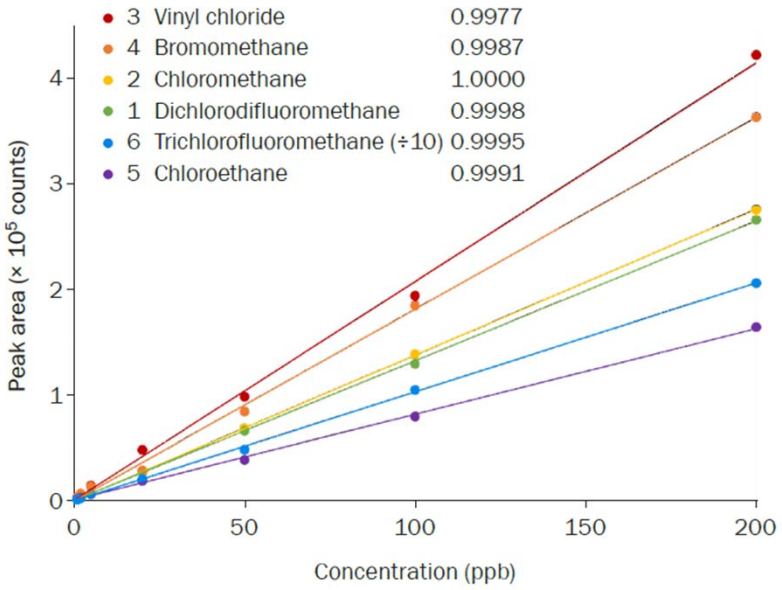
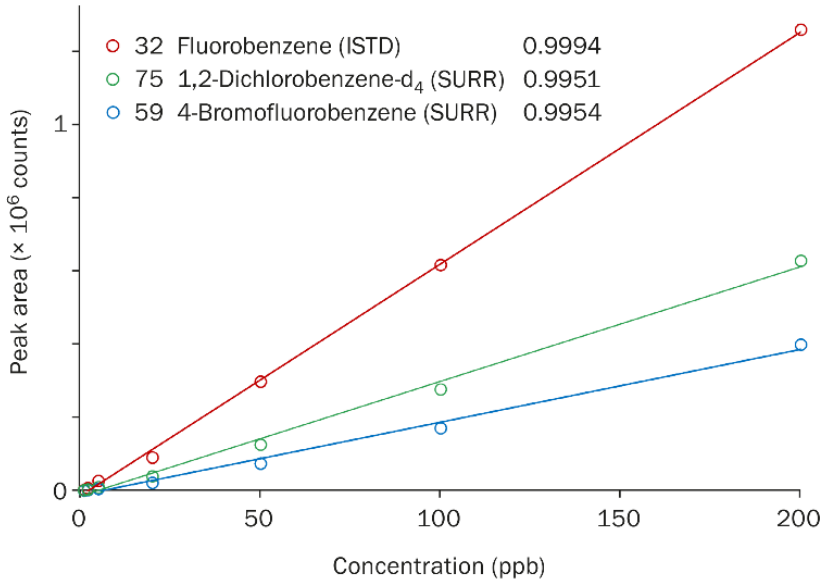
Low detection limits

Reproducibility and linearity

- Seven-point calibration curves and R^2 values for the six most volatile compounds



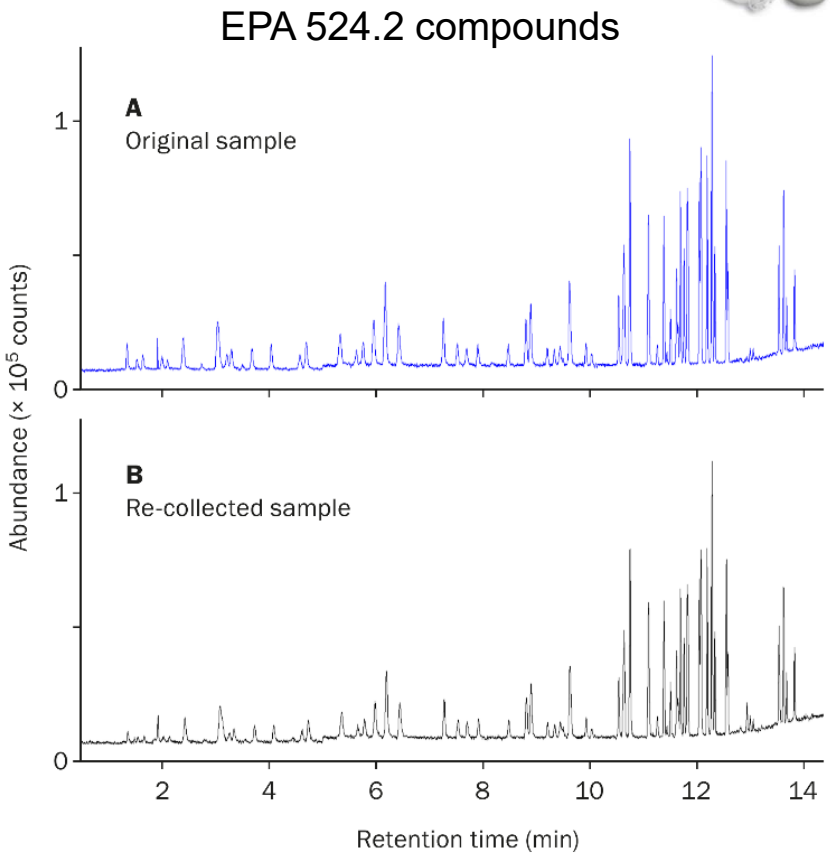
- Seven-point calibration curves and R^2 values for the internal standard and the two surrogates



Can we re-analyse?

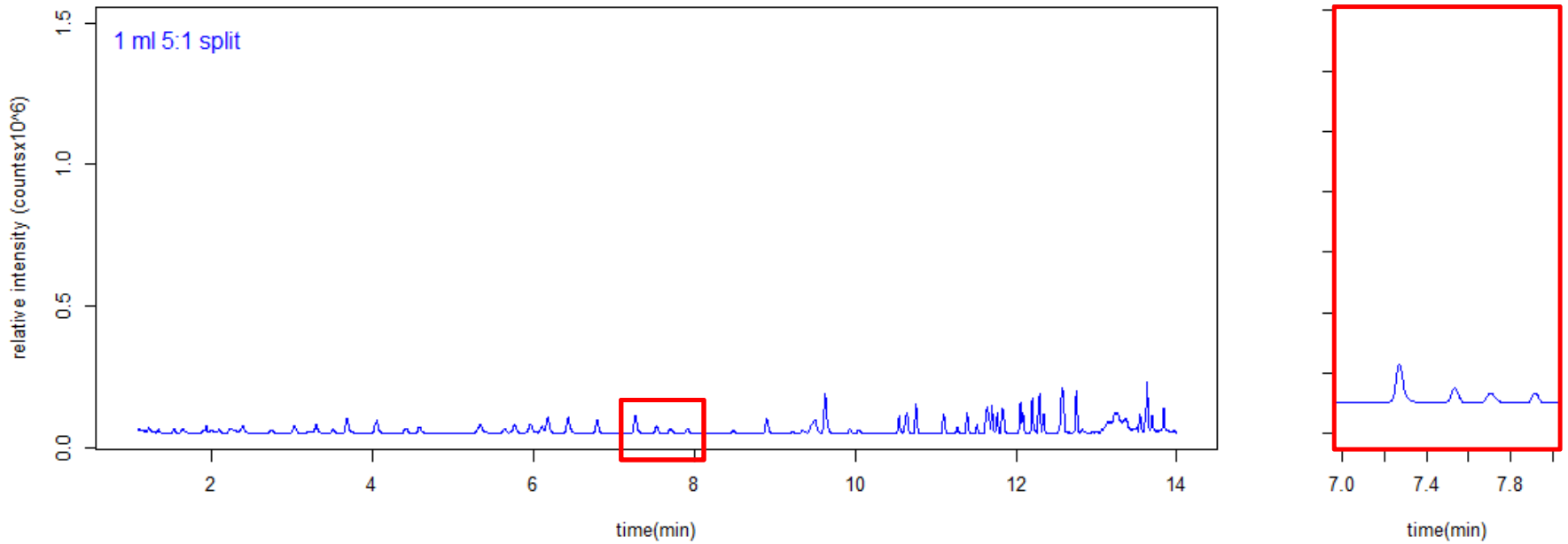
Reproducibility – Re-collection

- Repeat analysis without repeating lengthy sample preparation
- Different split conditions possible (‘High–Low’ analysis)
- Protecting the GC column and MS
- Sample security
- Storing samples for later analysis or re-analysis



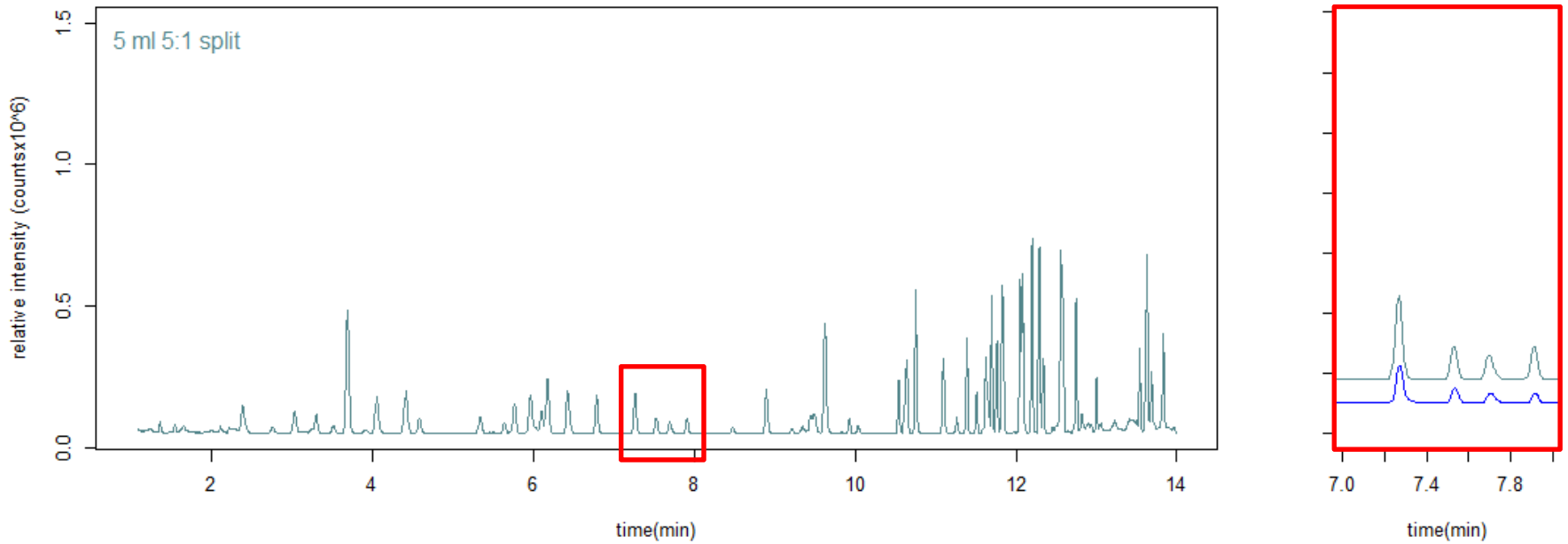
Conventional HS-trap with 1 mL

Benefits of adding a cold trap: injection volume



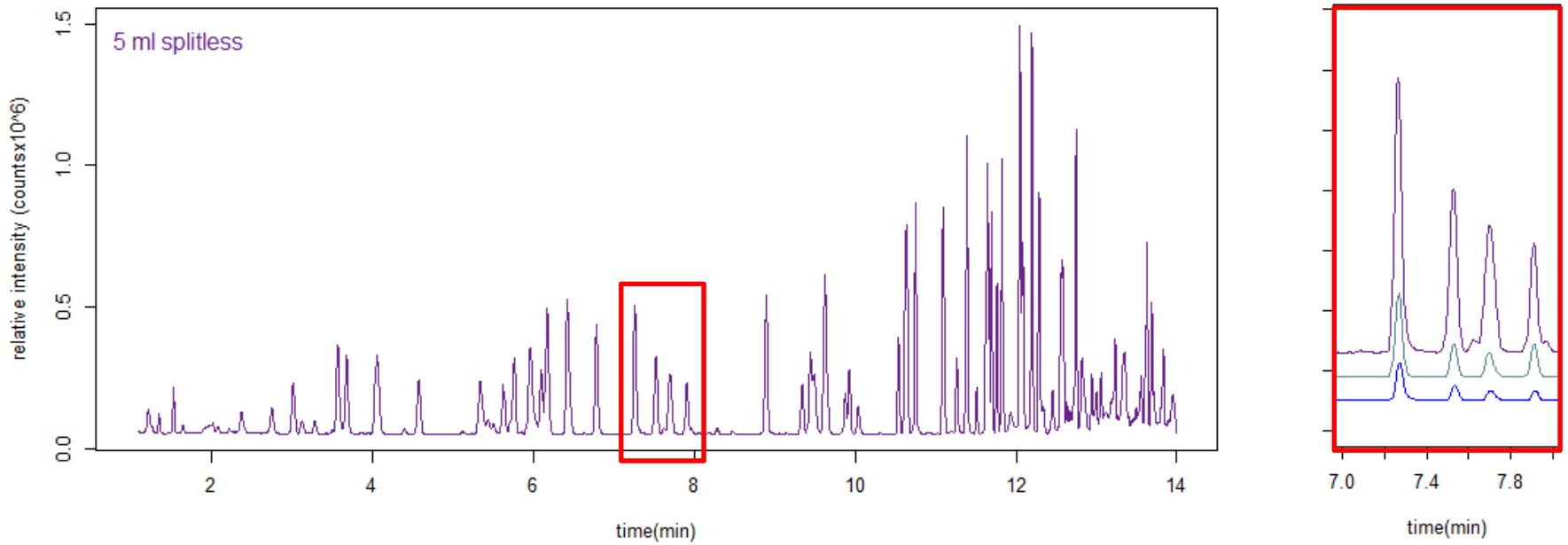
Extending HS-trap with 5 mL injection

Benefits of adding a cold trap: injection volume



Further extending HS-trap by going splitless

Narrow-bore and rapid trap heating

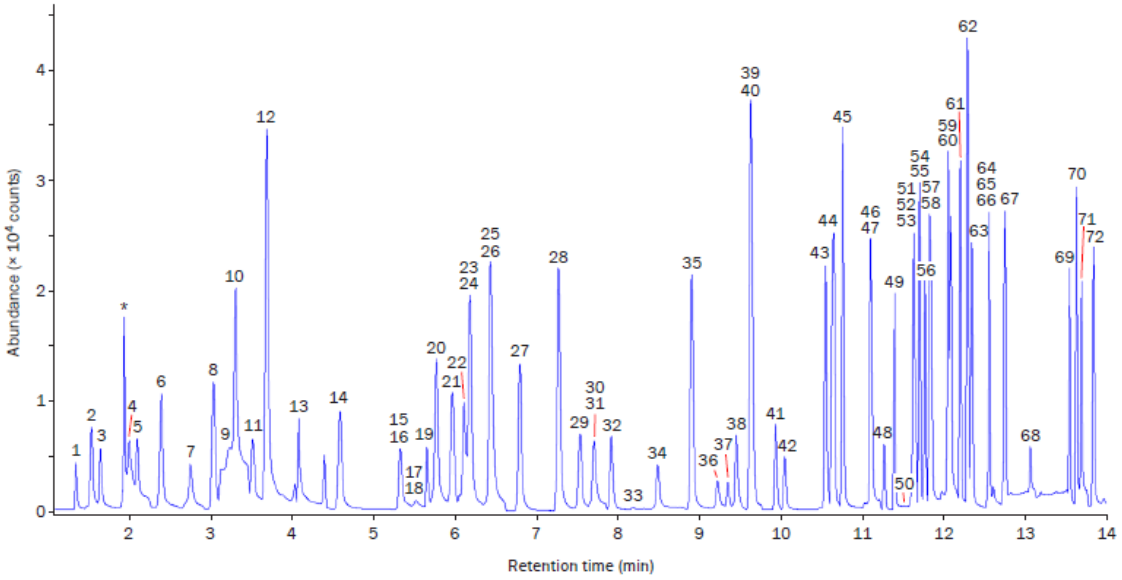


With HS-trap into the ppt-world!

…using a MS-single quad

By using:

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

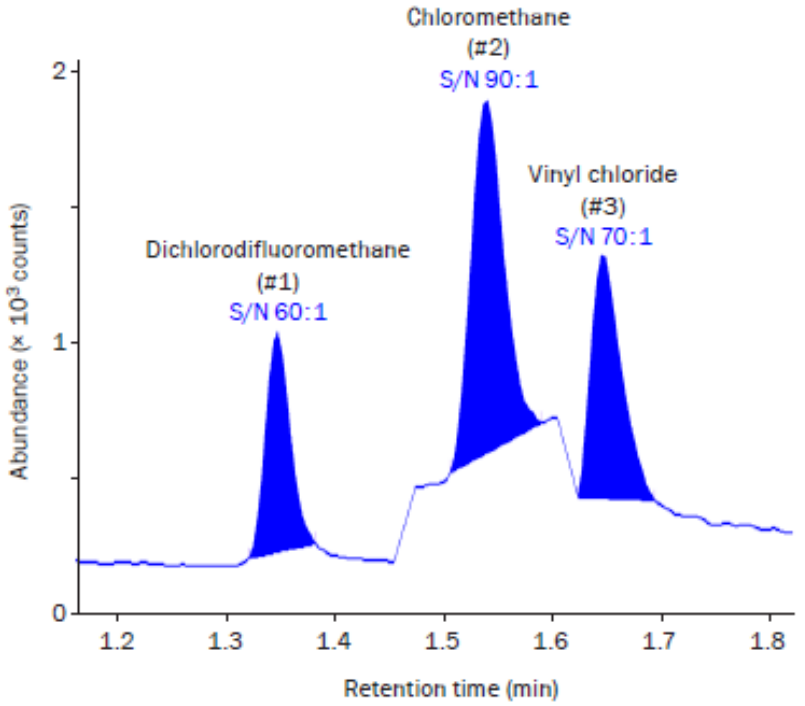


Headspace–trap SIM analysis of the standard mix at 100 ppt on-column.

Large S/N ratios for easy determination

…down to single digit ppt levels

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



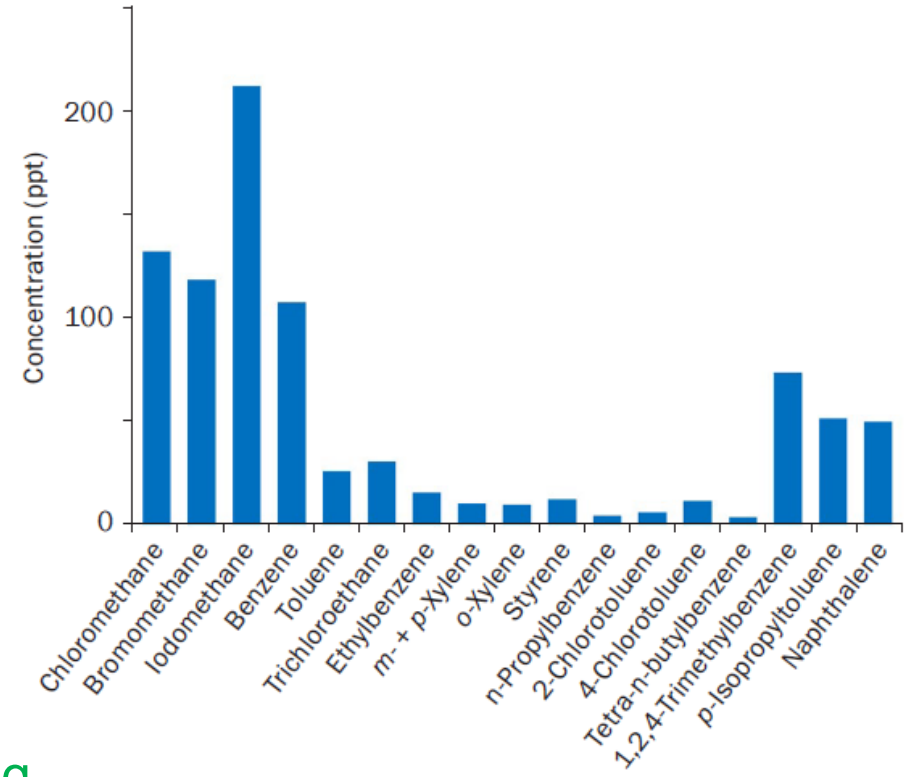
Headspace–trap SIM analysis of the three most volatile components in the standard mix, at 20 ppt on-column.

What is REALLY in our tap water?

When you REALLY want to know

- Additional to the Chloroform at 25 ppb

- Number of ppt-level VOCs
  - BTEX
  - CHC
  - a PAH



→ Welsh tap water is fine for drinking

What can be reported?

Maximum contamination levels for example contaminants

Compound	US EPA (MCL)	Scan-Mode (MDL)	SIM-Mode (MDL)
Benzene	0.005 mg/L (5 ppb)	0.11 ppb	0.0019 ppb
Ethylbenzene	0.7 mg/L (700 ppb)	0.06 ppb	0.0006 ppb
Xylenes (total)	10 mg/L (10.000 ppb)	0.02 ppb	0.0016 ppb
Vinyl chloride	0.002 mg/L (2 ppb)	0.29 ppb	0.0013 ppb
1,1,2-Trichloroethane	0.003 mg/L (3 ppb)	0.46 ppb	0.0027 ppb

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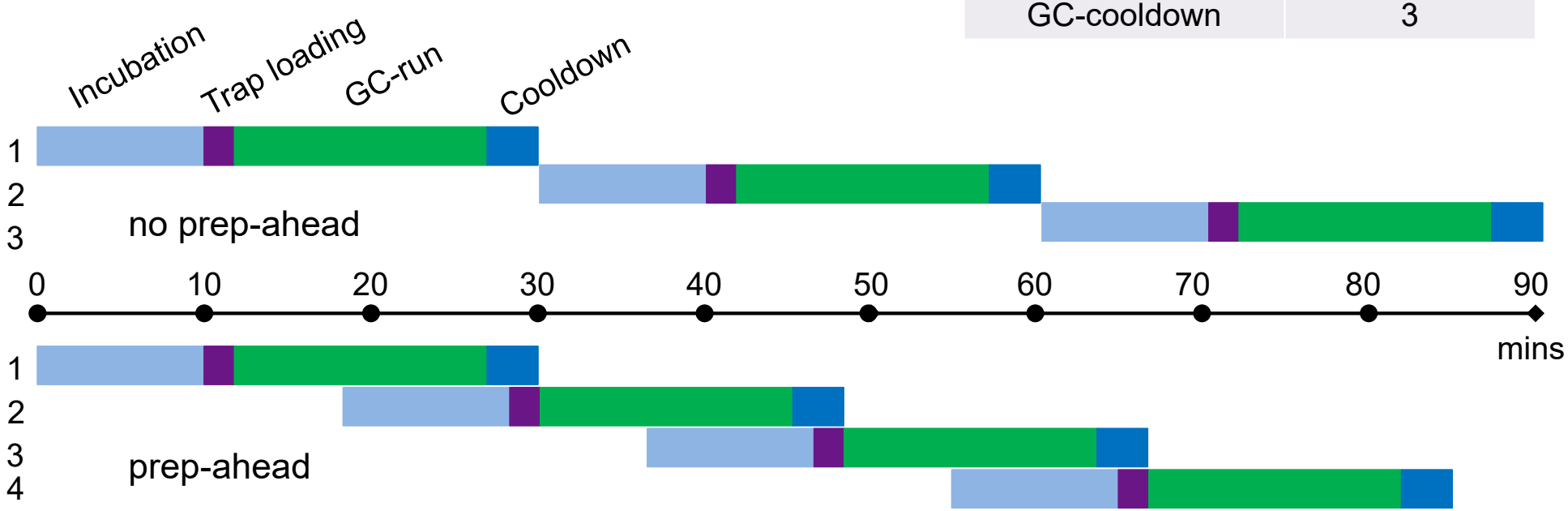
High reliability with maximum throughput

Optimising GC-MS run-time with HS-trap

Action	Time (mins)
Incubation	10
Trap loading	2
GC-run	15
GC-cooldown	3

Using prep-ahead you can ensure that there is always a sample ready to be analysed



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Approaches to handling the analysis of water

Summary

Challenges	The Centri Solution
High sample number	• Full automation
High contaminant levels (e.g. waste water)	• Classic headspace • Large split range (1:125,000)
Low contaminant levels (e.g. drinking water)	• SPME fibre preconcentration • Trapping capabilities • Multiple injection modes • Multiple enrichment steps • Splitless analysis
Different sample types: • Drinking water • Waste water • Slurry water	• SPME / HiSorb / Classic headspace / Matrix modification
Wide analytical target list from VVOCs to SVOCs	• Multi-bed trap
Reproducibility	• Re-collection
Sample traceability	• TubeTAG (RIFD) • Barcode scanner

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