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

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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
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:

<table>
<thead>
<tr>
<th>Country</th>
<th>Agency</th>
<th>Regulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>US EPA</td>
<td>The Safe Drinking Water Act (SDWA)</td>
</tr>
<tr>
<td>EU</td>
<td>EEA</td>
<td>EU Drinking Water Directive</td>
</tr>
<tr>
<td>India</td>
<td>BIS</td>
<td>BIS Code 10500: Revised 2012</td>
</tr>
<tr>
<td>Canada</td>
<td>CDWQG</td>
<td>Safe Drinking Water Act 2002</td>
</tr>
<tr>
<td>China</td>
<td>China EPA</td>
<td>National Drinking Water Quality Standard</td>
</tr>
</tbody>
</table>
## Maximum/reporting levels

...for a few contaminants, globally.

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

1\textsuperscript{st} stage

- Common to all sampling modes
- Allows \textbf{high uptake} flows for VOCs
- After the 1\textsuperscript{st} stage a \textbf{dry purge} is optional

2\textsuperscript{nd} stage

- Narrow design allows \textit{split or splitless} injection
- \textbf{Backflushed} to the GC-MS
- \textbf{Re-collection} of split is possible
VOCs in water

Increasing sensitivity using Headspace-trap
Reliable trapping for all compounds

Headspace–trap analysis

TIC of spiked water
Trapping across the whole volatility range
Headspace–trap analysis
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%
Low detection limits

Reproducibility and linearity

- Seven-point calibration curves and R² values for the six most volatile compounds
- Seven-point calibration curves and R² 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

![Diagram of EPA 524.2 compounds]

**A** Original sample

**B** Re-collected sample

Retention time (min)
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

<table>
<thead>
<tr>
<th>Compound</th>
<th>MDL (ppt)</th>
<th>PQL (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl chloride</td>
<td>1.3</td>
<td>11</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.9</td>
<td>17</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>1.3</td>
<td>11</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.6</td>
<td>5</td>
</tr>
<tr>
<td>Xylenes</td>
<td>0.3</td>
<td>3 - 14</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>US EPA (MCL)</th>
<th>Scan-Mode (MDL)</th>
<th>SIM-Mode (MDL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.005 mg/L (5 ppb)</td>
<td>0.11 ppb</td>
<td>0.0019 ppb</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.7 mg/L (700 ppb)</td>
<td>0.06 ppb</td>
<td>0.0006 ppb</td>
</tr>
<tr>
<td>Xylenes (total)</td>
<td>10 mg/L (10,000 ppb)</td>
<td>0.02 ppb</td>
<td>0.0016 ppb</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>0.002 mg/L (2 ppb)</td>
<td>0.29 ppb</td>
<td>0.0013 ppb</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>0.003 mg/L (3 ppb)</td>
<td>0.46 ppb</td>
<td>0.0027 ppb</td>
</tr>
</tbody>
</table>
High reliability with maximum throughput

Optimising GC-MS run-time with HS-trap

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

<table>
<thead>
<tr>
<th>Action</th>
<th>Time (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incubation</td>
<td>10</td>
</tr>
<tr>
<td>Trap loading</td>
<td>2</td>
</tr>
<tr>
<td>GC-run</td>
<td>15</td>
</tr>
<tr>
<td>GC-cooldown</td>
<td>3</td>
</tr>
</tbody>
</table>
# Approaches to handling the analysis of water

## Summary

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

*Centri*
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