Using Stir Bar Sorptive Extraction (SBSE) for Taste and Odour Measurements in Drinking Water

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Purpose of this presentation

- Brief introduction into Twister SBSE (focussed on Taste and Odour water contaminants)
Who are Anatune?

- **Where?** - Girton, Cambridge
- **Focus?** - Customer specific chromatography solutions
- **Technology?** - Novel automation, sample prep, introduction
- **Provide?** - complete sample preparation, automation & analytical packages
Partners, platforms and markets

- Agilent Technologies Value Added Reseller (VAR) since Oct 1999
- GERSTEL UK & Ireland Distributor since Apr 2003

- GC and LC platforms - MSD, QqQ, qTOF
- Environmental, Flavour/Fragrance, Food/Beverage Markets
What do our customers need?

- Customers need more than just a standard system

Dear Anatune,

I need my analysis to be:

1. Faster
2. Cheaper
3. More reproducible
4. Higher throughput
5. Less labour intensive
6. More sensitive
7. Safer

Can you help me PLEASE????

Signed,
Laboratory Manager
How we help our customers

NO MORE SAMPLES PLEASE!!!
How we help our customers
GERSTEL Multi-Purpose Sampler

- Dynamic Headspace (DHS)
- TDU Thermal desorption and PYROlysis
- Solid Phase Extraction (SPE)
- ATEX Thermal Extraction in μVials
- Disposable Pipette Extraction (DPX)
- SPME & Multi-Fiber EXchange (MFX)
- Headspace
- ALEX Automated Liner EXchange
Turnkey solution example

- Anatune VOC Headspace solution
  - 160/240 sample capacity
  - Auto addition of internal standards & surrogates
  - Minimal manual work, low cost per sample
  - parallel processing of samples (PrepAhead)
Stir Bar Sorptive Extraction

- Current situation – Analysis of T&O Compounds
- Problems and Implications
- Introduction to Twister SBSE
- Twister Method
- Advantages of using Twister
- Results
- Developments and alternative ways of thinking?
Current Situation

Taste and Odour Panel
Possible situation?

Add Twister → Extraction → WATER → MPS → Analysis → Data Processing

Taste and Odour Panel
<table>
<thead>
<tr>
<th>Problem</th>
<th>Implication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow extraction time</td>
<td>Takes longer to get results</td>
</tr>
<tr>
<td>Many long manual extraction steps</td>
<td>Large staff resource</td>
</tr>
<tr>
<td>Error prone sample prep</td>
<td>Result reproducibility issue?</td>
</tr>
<tr>
<td>Can’t hit LOD’s without pre-concentration</td>
<td>Time/staff needed for prep</td>
</tr>
<tr>
<td>High solvent usage/staff exposure</td>
<td>Cost for purchasing solvent, disposal &amp; staff safety</td>
</tr>
<tr>
<td>Glassware contamination</td>
<td>Inaccurate results/repeat analysis, investigations etc.</td>
</tr>
</tbody>
</table>
What else?

- Liquid-liquid extraction most used technique
- Solid Phase Extraction (SPE) as an alternative?
- Miniaturisation techniques (SPME) developed
  - Simple
  - Fast
  - Environmentally Friendly
  - More sensitivity?
- Stir Bar Sorptive Extraction......?
Stir Bar Sorptive Extraction

- Marketed by GERSTEL as ‘Twister’
- 1.5cm long magnetic stir bar sealed in glass
- High capacity PDMS phase on glass
- Adsorbs compounds from water onto PDMS phase whilst stirring in sample
- Different sizes and phase thicknesses
  - thickness 0.5 mm, 10 mm length
  - thickness 0.5 mm, 20 mm length
  - thickness 1.0 mm, 10 mm length
  - thickness 1.0 mm, 20 mm length
Recovery of Analytes onto Twister

- Same principle as liquid/liquid extraction
  - with a small amount of immobilized “solvent” in the form of polydimethyl siloxane (PDMS)

- Recovery of analytes onto stir bar
  - How well the analyte can adsorb onto PDMS phase?
  - Depend on hydrophobic and lipophilic characteristics of analyte
  - Use calculated and theoretical octanol/water ratios (Log K o/w)
  - PDMS behaves similarly to octanol
Conditioning of Twisters

• Conditioned before/after analysis
  – Thermally cycle PDMS up to 280 deg C
  – Flow of clean N2 at 80-100ml/min
  – 40 bars per conditioning cycle
  – Twisters are reusable – >50x
Easy to use - method

- Add Twister to sample
Easy to use - method

- Add Twister to sample
- Stir for 1 hour
Easy to use - method

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• Remove Twister and rinse with DI water
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- Dry with lint-free tissue
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- Place rack on MPS Autosampler
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- Dry with lint-free tissue
- Insert into TDU Tube
- Place tube in Twister rack
- Place rack on MPS Autosampler
- Automated Thermal Desorption and analysis
GERSTEL CIS/TDU Setup

- CIS – Cooled Injection System
  - PTV Inlet or
  - Cryotrap (-150C)
- TDU – Thermal Desorption System
  - Automated TD of
    1. Stir Bars
    2. Adsorbent tubes
    3. Solid samples
    4. High matrix liquid samples
Benefits of using Twister

• High productivity
  - parallel extraction – multiple using stir plate
  - automated analysis using MPS Auto sampler
• Time and cost savings through minimal sample preparation
• Very sensitive – ng/l in SIM mode
• Good reproducibility – 4-15%
• Reliable results - simple sample handling, reduced risk of error
• Green technology - Low solvent usage/disposal
• Safer
• Multiple reuse of each twister after easy reconditioning
  - 1 Twister = £35.00. 50 extractions = £0.70 each
• Can be applied to other analysis – pesticides, PAH’s etc
Extraction location?

- Can be carried out at customer tap/WTW instead of lab
- ‘Captures’ problem compounds immediately
- No time for compounds to degrade (sample point to lab extraction)
- Twisters stable for 7 days before analysis (4°C)
- Veolia Water – Twister analysis in Paris, extraction worldwide
Example

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Taste</th>
<th>Odor threshold, ng/L</th>
<th>CAS number</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylisoborneol</td>
<td>MIB</td>
<td>Earthy</td>
<td>5–10</td>
<td>N/A</td>
</tr>
<tr>
<td>2,4,6-trichloroanisole</td>
<td>2,4,6-TCA</td>
<td>Musty</td>
<td>0.1–2</td>
<td>6130-75-2</td>
</tr>
<tr>
<td>2,3,6-trichloroanisole</td>
<td>2,3,6-TCA</td>
<td>Musty</td>
<td>0.1–2</td>
<td>50375-10-5</td>
</tr>
<tr>
<td>Geosmin</td>
<td>Geosmin</td>
<td>Camphor</td>
<td>1–10</td>
<td>19700-21-1</td>
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<tr>
<td>2,3,4-trichloroanisole</td>
<td>2,3,4-TCA</td>
<td>Musty</td>
<td>0.2–2</td>
<td>54135-80-7</td>
</tr>
<tr>
<td>2,4,6-tribromoanisole</td>
<td>2,4,6-TBA</td>
<td>Musty</td>
<td>0.15–10</td>
<td>607-99-8</td>
</tr>
</tbody>
</table>

- 100ml Water
- 40ul Internal Standard
- 2hr extraction
- Thermal Desorption
- GC-MS Analysis
Tap water spiked with 2ng/l

- GC-MS Analysis – Agilent 5973/6890

- MIB
- 2,3,6-TCA
- 2,4,6-TCA
- 2,3,4-TCA
- Geosmin
- 2,4,6-TBA

Ion 95
Ion 212 qualifier: 210
Ion 112 qualifier: 120
Ion 346 qualifier: 344
<table>
<thead>
<tr>
<th></th>
<th>R</th>
<th>LOQ, ng/L</th>
<th>Repeatability</th>
<th>Trueness</th>
<th>Reproducibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIB</td>
<td>0.9987</td>
<td>1</td>
<td>4–10</td>
<td>89–110</td>
<td>13</td>
</tr>
<tr>
<td>2,4,6-TCA</td>
<td>0.9998</td>
<td>0.1</td>
<td>1–5</td>
<td>97–110</td>
<td>4</td>
</tr>
<tr>
<td>2,3,6-TCA</td>
<td>0.9998</td>
<td>0.1</td>
<td>4–11</td>
<td>97–117</td>
<td>5</td>
</tr>
<tr>
<td>Geosmin</td>
<td>0.9991</td>
<td>0.5</td>
<td>2–10</td>
<td>83–101</td>
<td>9</td>
</tr>
<tr>
<td>2,3,4-TCA</td>
<td>0.9998</td>
<td>0.2</td>
<td>7–15</td>
<td>87–110</td>
<td>13</td>
</tr>
<tr>
<td>2,4,6-TBA</td>
<td>1.0000</td>
<td>0.2</td>
<td>2–9</td>
<td>91–104</td>
<td>15</td>
</tr>
</tbody>
</table>
GC-SBSE-Olfactometry-MS

- Optional Olfactory Detection with voice recognition
- Olfactory detection in parallel with GC/MS analysis
- Voice descriptors added directly to Chromatogram
- Olfactogram (Intensity input) added to chromatogram
- Widely used for off odours, flavour and fragrance
Using the ODP with SBSE

- Closes loop between complaint, analysis and T+O Panel
- Help to determine the complaint compound
Dual SBSE

First Extraction

SBSE 1h
1500 rpm

LogK_{ow} > 4

30 % NaCl

Second extraction

SBSE 1h
1500 rpm

LogK_{ow} < 4
Ethylene Glycol Twister

• Sorbent phase is a mixture of silicone and ethylene glycol
  – Efficient concentration of non-polar analytes similar to the PDMS Twister
  – Concentration of polar analytes that form hydrogen bonds acting as proton donors, for example phenols
  – Low limits of detection and good recovery due to large phase volume
Further Developments – Veolia France – David Benanou

- Easy & quick installation (tap nozzle dismounting)
- Continuous bars enrichment at each tap opening

**ARISTOTEL**

- Advanced relevant investigation amplifier for taste and odor at tap

**Components:**
- PDMS: PolyDiMethylSiloxane (silicone gum)
- Glass jacket
- Magnetic stirring rod

**Dimensions:**
- 40 mm
- 24 mm Ø
System flexibility – using same hardware as Twister - MultiFlex

Single System - multiple uses, easily reconfigurable

1. Remove TDU - Use CIS for Large Volume/Liquid Injection

2. Headspace Analysis with autospiking

3. Automated Thermal Extraction

4. Internal Std, Surrogate, Cal Prep, Dilution

5. Add more GERSTEL Hardware to MPS Rail
Anatune MPS Multi-Flex

The Ultimate R&D Tool

Agilent SQ, QQQ and QTOF Platforms
Anatune developments with Multi-Flex

Automated extraction and analysis
- Dual Head MPS
- ITSP Micro SPE
1. NDMA & Metaldehyde
2. T+O Compounds & Phenol
GC-QTOF Multi-Flex Developments

- Highly sensitive and selective Mass Spectrometer
- Accurate mass on a familiar platform
- Known unknown analysis
- Sold 1\textsuperscript{st} system to University of York in September
- GC-QTOF Workshops next week
- Applications work/demos planned
Conclusion - Payoff

- Cheaper – Labour/Consumables
- Fast, easy, reliable
- Less solvent consumption/exposure
- Low LOD’s reached
- Capture of analytes close to source
- Olfactory detection enhances results/investigation
- Analysis of non-T&O compounds
- GERSTEL MPS flexible
- Anatune happy to collaborate with customers – any ideas?
- Think outside the box
Any questions &
Thank you for your attention