Odour Management – Sulfurous Compounds

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Content

• UNSW odour Laboratory
• Odorants
• Odorant sampling
• Online monitoring
  • Chemical analysis
• Odorant analysis
  • Sample pre-concentration
  • GC analysis
  • ODP analysis
• Biosolid monitoring
UNSW Odour Laboratory (est. 1999)

- Chemical analysis
  - VOC & S analysis - GC-MS/FPD
  - VSC & VNCO analysis - GC-SCD/NCD
  - GHG & PG analysis - FTIR Spectrometer
  - TD-GC-QTOF
  - Portable TD-GC-MS
- Olfactometry
  - Dilution olfactometry (AS/NZS 4323.3:2001)
  - Olfactory analysis - GC-MS/ODP
- Future instruments
  - Mobile chemical analysis – SIFT-MS

Research staff

- Dr Eric Sivert (Group manager)
- Dr Gavin Parcsi (Chemical analysis)
- Dr Xinguang Wang (Olfactometry)
- Dr Nhat Le (Chemical analysis and treatment)
- Dr Kate Murphy (Chemometric analysis)

PhD students

- Bei Wang (emission characterisation)
- Hung Le (sulfur degradation and sampling)
- Mark Dunlop (litter emission formation)
- James Hayes (olfactory annoyance-public engagement)
Research Projects

- Intensive livestock practices (poultry sheds)
- WWTP and biosolid emissions
- Sewer odours
- Landfill emissions
- Composting operations
- Odour abatement performance
- Material emissions
- Taste & odours (drinking water)
- Indoor air quality
- Medical applications (breath analysis)
Odorant emissions

Hydrogen sulfide – 0.5 ppb
Methyl mercaptan – 0.0014-18 ppb
Dimethyl sulfide – 0.12-0.4 ppb
Methylamine – 0.9-53 ppb
Dimethylamine – 23-80 ppb

Odour thresholds

Sulfides
Volatile acids C_2-C_6
Phenols
Indoles
Odorant sampling

- Source - where - type
- Multi-component ppb-ppt range
- Labile components e.g. thiol
- Humidity interferes with the adsorption of polar odorants
- Transportation and transformation of compounds
- Sample collection
- Pre-concentration of samples

Sample collection

- Odour bags
  - Inert bag materials
- Canisters
- Sorbent tubes
  - Porous polymers e.g. Tenax TA
  - Carbon based sorbents e.g. Carbotrap B
  - Others multiple bed sorbent tubes e.g. Chromosorb Silica gel
- Sample pre-concentrations
  - Cryogenic sampling
- Solid-phase micro extraction (SPME)
  - Equilibrium technique based on partitioning of analytes between gaseous and silicone phase
Chemical analysis

- Online monitoring
  - Odour abatement monitoring
  - Continuous infield measurements
    - sewer systems
- Offline monitoring
  - Spot or grab measurements

H₂S measurements and methods

- A good marker compound for:
  - Anaerobic processes
  - Acidic conditions
- A poor marker for:
  - Aerobic processes
  - Basic conditions
- Paper tape
  - Lead-acetate / colorimetric
- Gold film
  - Resistance change by adsorption onto gold film
- UV Fluorescence
  - Catalytic conversion of H₂S to SO₂
H$_2$S interference issues

Gas Chromatography (GC)

- A separation technique
  - Separates individual compounds from complex mixtures
  - Qualitative/quantitative determination of odorants present
- Components detected as they exit the GC column at different times using detectors

- Separation by differential affinities to the column surface
- Column dimensions
  - longer-better separation
- Column surfaces
  - porous solid film for light VOCs/gases
  - thicker films better retention
**Choice of Detector**

- **Known analytes**
  - FID - C & H $10^6$ dynamic range
  - ECD - electron affinity - halides & N
  - Sulfur – sulfur chemiluminescence detector (SCD)
  - Nitrogen – nitrogen chemiluminescence detector (NCD)

- **Unknown analytes**
  - Mass spectrometer (MS) - almost universal

- **MS detection**
  - Molecular identification
  - pg detection limits
  - set mass range and single ion monitoring (SIM) e.g. 64 SO$_2$
  - gas flows are important
  - concentration stage
  - mostly laboratory based but transportable systems now available
Air server-TD-GC-SCD

Odour bag
AirServer
Unity
GC
SCD

MS data presentation

• Qualitative assessment
• Relative quantification
• Quantification
  • standard solution
  • calibration curves
• method detect limits
• storage recovery
  • sulfur compounds
Analytical methods

**US EPA Method TO-17**

- Standard Method for Air Toxics
- BTEX, halo-hydrocarbons
- 44 compounds ~ 50 minutes
- Last Revision 1999
- Few known odorants in the matrix

Need a benchmarked method that addresses relevant odorous compounds

<table>
<thead>
<tr>
<th>Halocarbon 114</th>
<th>Tetrachloroethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Dichloroethane</td>
<td>Chloroform</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>1,2-Dibromoethane</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>Acetone</td>
</tr>
<tr>
<td>Halocarbon 111</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>Trichloroethane</td>
<td>1,1,1-Trichloroethane</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>Ethylbenzene</td>
</tr>
<tr>
<td>Methyl tert-Butyl Ether</td>
<td>2-Propanol</td>
</tr>
<tr>
<td>Halocarbon 113</td>
<td>m-Xylene</td>
</tr>
<tr>
<td>1,2-Dichloropropane</td>
<td>Carbon tetrachloride</td>
</tr>
<tr>
<td>Dichlorobenzenes</td>
<td>p-Xylene</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>Acrylonitrile</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>α-Xylene</td>
</tr>
<tr>
<td>cis-1,3-Dichloropropene</td>
<td>Benzene</td>
</tr>
<tr>
<td>1,2,4-Trichlorobenzene</td>
<td>1,1,2,2-Tetrachloroethane</td>
</tr>
<tr>
<td>Ethyl Acrylate</td>
<td>Isoprene</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
</tr>
</tbody>
</table>
| Hexachloro-1,3,5-
| Butadiene | |
| Methyl Acrylate | |
| 1,1 Dichloroethane | |
| Trans-1,3-
| Dichloropropene | |
| 1,3 Butadiene | |
| Methyl Isobutyl Ketone | |
| cis-1,2-Dichloroethene | |
| Furfural | |
| Acetonitrile | |

Odors of interest

**Key Compounds**

- Volatile Organic Compounds (VOCs)
  - Butyl compounds
  - Aromatics
  - Terpenes

- Volatile Organic Sulfur Compounds (VOSCs) and H₂S
  - Sulfides
  - Thiols

- Volatile Nitrogen Compounds (VNCs)
  - Non-permeable Gases (NPGs) - Methane

GC-MS

GC-SCD/NCD

GC-FID
Sorbent tube selection

- Field samples
- Tedlar bags
- Drawn onto sorbent tubes
- 3 sorbents

3 significant compounds detected in all samples

- Toluene
- N,N-dimethyl acetamide
- Phenol

Carbotrap 300
Tenax TA + Carbograph 1TD
Tenax TA

Carbotrap 300
Tenax TA + Carbograph 1TD
Tenax TA

N,N-dimethyl acetamide
N,N-dimethyl acetamide
N,N-dimethyl acetamide

SWC-AC-6

Sorbent tube selection
Sampling artifacts

- Blank sample
- Tenax TA sorbent
- Tedlar bag
- Significant artefacts from the Tedlar bag

*Bags not suitable for VOC sample collection*

Sample pre-concentration

Thermal desorption (TD)

- Improves resolution of GC peaks
- Samples are heated in a flow of inert gas to extract target compounds into the vapour stream via a process of dynamic gas extraction
- The techniques combines sample extraction, with selective analyte concentration and transfer of target compounds to the detector
Impact of sorbent tube age on compound capture

Tenax TA + Carbograph 1TD sorbent tubes

New Tube (<10 cycles)

Late Life Tube (~75 cycles)

No significant degradation in absorptive capacity

Column selection

Non-Polar Stationary Phase (HP-5ms column)

A – 2,3-butanedione
B – 3-methyl-2-butanal
C – 1-butanol
D – 3-hydroxy-2-butanol
E – Dimethyl disulfide
F – Toluene
G – Styrene
H – 2-ethyl-1-hexanol

Polar Stationary Phase (HP-INNOWax column)

A – 2,3-butanedione
B – 3-methyl-2-butanal
C – 1-butanol
D – 3-hydroxy-2-butanol
E – Dimethyl disulfide
F – Toluene
G – Styrene
H – 2-ethyl-1-hexanol
ODP analysis

- Coupling an olfactory detection port (ODP) to a GC-MS or GC
- Techniques allows odorants to be separated and identifies individually

TD-GC-MS/O

- Allows odor contribution for each compound to be characterised in terms of character and intensity
• Variations between ODP operators based n-butanol threshold
Biosolid sampling

Sorbent tubes and bag samples being collected

Sample preparation using US EPA Flux Hoods

Biosolid emissions (VOCs and VOSCs)

Low abundance and diversity, dominated by sulfurs
Sulfur Compounds: Odorants

- Different characters
- Low detection thresholds

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Character</th>
<th>OTV (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>Rotten egg</td>
<td>0.002</td>
</tr>
<tr>
<td>DMS</td>
<td>Sulfury onion</td>
<td>0.049</td>
</tr>
<tr>
<td>MeSH</td>
<td>Decomposing cabbage</td>
<td>0.0013</td>
</tr>
<tr>
<td>DMDS</td>
<td>Sulfurous vegetable</td>
<td>0.82</td>
</tr>
<tr>
<td>EtSH</td>
<td>Sulfurous fruity</td>
<td>0.0008</td>
</tr>
<tr>
<td>DEDS</td>
<td>Gassy ripe onion</td>
<td>0.09</td>
</tr>
<tr>
<td>EMDS</td>
<td>Sulfurous truffle</td>
<td>0.062</td>
</tr>
<tr>
<td>DMTS</td>
<td>Sulphorous cooked onion</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Sulfur Transformation

\[ \text{EtSH} + \text{MeSH} \rightarrow \text{EMDS} \]

\[ \text{EtSH} = \text{DEDS} \]
Summary

• In order to compare VOC emissions from different sources we need to benchmark sampling and analysis approaches
• Several hundred different VOCs and VOSCs are present in odour emissions, often compounds in low abundance are most odorous
• Sites-specified VOCs are often present and can be related to the source or the process functionality
  • eg. sewer catchment, household waste, composting operation, biosolids processing

Acknowledgements

www.odour.unsw.edu.au