GAW-ACTRIS: OVOC Systems

Jennifer Englert, Werner, Plass-Dülmer, Reimann, Hill, Hopkins, Roukos, ... and ACTRIS community

REFERENCES


The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n°262254.
Comparison of OVOC GC systems

1. GC-MS
   Institution: Swiss Federal Institute for Materials Science and Technology (Empa), Dübendorf, Switzerland

2. GC-FID
   Institution: Ecole des Mines de Douai (EMD), Département Chimie et Environnement, Douai, France

3. GC-FID
   Institution: National Centre for Atmospheric Science (NCAS), Department of Chemistry, University of York, Heslington, York, UK

4. GC-MS/FID
   Institution: Hohenpeissenberg Meteorological Observatory (HPB), German Meteorological Service (DWD), Germany
Water in ambient air samples – problems in OVOC analysis:

1. Reduction of the system performance e.g. the capacity of adsorbents (ROUKOS, 2009).

2. Losses of OVOC (high water solubility) or chemical transformation.

3. Ice plugging in cryogen focussing units and sub-zero cooled adsorbent traps.

4. Shift in retention times up to 2 minutes on PLOT columns e.g. CP-LowOx and GS-OxyPLOT, bad peak shapes.

5. Mass spectrometer detects water, high peak that coelutes with OVOC.

6. Reduced lifetime of the GC column.

![Graph showing safe sampling volume at 80% RH](image)
Water management techniques

1. Empa GC-MS:
   Preconcentration on a hydrophobic adsorbent (Hayesep D – polydivinylbenzene) held at room temperature; before desorption flushing the trap with dry helium in sampling direction.

2. EMD GC-FID:
   Humidity reduced by the trap composition (hydrophobic graphitized carbons – Carbopack B/Carbopack X), the trap temperature (held at 12.5°C), by diluting (50:50) the sample with dry air before the preconcentration step and purging the trap with helium after sampling.

3. NCAS GC-2FID:

4. HPB GC-FID/MS:
   Water is frozen out with a cryostatic temperature regulator at -30°C in a 1/8” Silcosteel tubing, trap temperature is held at 18°C, trap purge with helium.
Water management techniques

1. Empa GC-MS: Preconcentration on a hydrophobic adsorbent (Hayesep D – polydivinylbenzene) held at room temperature; before desorption flushing the trap with dry helium in sampling direction.
2. EMD GC-FID: Humidity reduced by the trap composition (hydrophobic graphitized carbons – Carbopack B/Carbopack X), the trap composition (Carbopack B/Carbopack X) is held at 20°C; before the preconcentration step and purging the trap with helium after sampling.
4. HPB GC-FID/MS: Water is frozen out with a cryostatic temperature regulator at -30°C in a 1/8” Silcosteel tubing, trap temperature is held at 18°C, trap purge with helium.

RH < 5% - With dilution

1  Furan
2  2-Methyl furan
3  Toluene
4  Acetaldehyde
5  ETBE
6  Propanal
7  Acrolein
8  Methacrolein
9  Acetonitrile
10  Butanal
11  Acetone
12  Ethane
13  Ethanol
14  Isopropanol
15  Pentanenitrile
16  Isobutanol
17  Benzaldehyde
18  Butyl acetate
19  Heptanenitrile
20  Octanenitrile

RH = 90% - With dilution

RH = 90% - Without dilution
Ozone removal

1. Empa GC-MS:
   Ozone effects on aldehydes were detected > correlations with ozone concentration;
   NO titration (10 ml/min of 20 ppm NO) for ozone removal.

2. EMD GC-FID:
   No ozone removal.

3. NCAS GC-2FID:
   All gas transfer lines within the system are made from stainless steel and heated to
   70°C to reduce ozone mixing ratios, but ozone is not actively removed.

4. HPB GC-FID/MS:
   Until now no ozone removal, NO titration tests are planned.
Sampling

1. Empa GC-MS:
   Preconcentration on 600 mg of 40-60 mesh Hayesep D adsorbent at room temperature and afterwards flushing with helium, refocusing on 30 mg of 40-60 mesh Hayesep D cooled to -40°C with Peltier elements.

2. EMD GC-FID:
   Adsorbent trap of Carbopack B and Carbopack X Peltier-cooled at 12.5 °C.

3. NCAS GC-2FID:
   Adsorbent trap of Carbotrap B and Carboxen1000 (90 mg in total), Peltier-cooled at -20°C.

4. HPB GC-FID/MS:
   Trapping on a 3-phase adsorbent tube (Tenax TA/Carbopack X/Carboxen 569) at 18°C (cooled with compressed air). Refocussing on a cryogenic trap (fused silica capillary) with liquid nitrogen at -180°C.
Transfer lines and valves

1. Empa GC-MS:
   1/16” sulfinated Silcosteel (Restek), transfer into the GC by a heated deactivated fused silica capillary, all transfer lines heated to 80°C, VICI Valcon E rotor valves at 80°C, inlet line Teflon (ambient temperature) with a Silcosteel particle filter.

2. EMD GC-FID:
   All transfer lines and valves stainless steel, inlet line 1/8” stainless steel with a stainless steel particulate filter.

3. NCAS GC-2FID:
   All transfer lines out of stainless steel and heated to 70°C, inlet line ¼” Teflon at 55°C.

4. HPB GC-FID/MS:
   1/16” Silcosteel (Restek) and Ultimetal (Varian), deactivated fused silica capillaries for cryogenic trap and transfer lines to the GC column and detectors, all transfer lines heated to 50°C, inlet line 1/16” Ultimetal at 50°C (samples split from a permanently flushed glass manifold with 375 L/min), VICI Valcon R rotor valves at 50°C.
**GC columns**

1. Empa GC-MS:
   CP-PoraBond U (Varian), 25 m x 0.32 mm x 7 µm, semi-polar bonded porous polymer, water resistant – retention times are not influenced by water in the sample.

2. EMD GC-FID:
   CP-LowOx (Varian), 30 m x 0.53 mm x 10 µm, high polar PLOT column that separates the polar compounds from the hydrocarbon/aromatic matrix, extended length for a very selective separation.

3. NCAS GC-2FID:
   Two columns with a 50:50 split ratio, for NMHCs: Na$_2$SO$_4$ deactivated aluminium oxide PLOT column, 50 m x 0.53 mm (Varian); for OVOCs: two CP-LowOX columns (Varian) in series, each 10 m x 0.53 mm; 50 µm flow restrictors upstream of the LowOx column to balance the flow through each channel.

4. HPB GC-FID/MS:
   GS-OxyPLOT (Agilent), 10 m x 0.53 mm x 10 µm, similar to CP-LowOx, high polar.
GC columns

1. Acetaldehyde
2. Propanal
3. Methacrolein
4. Butanal
5. Acetone
6. Methanol
7. MVK
8. MEK
9. Ethanol
10. Isopropanol
11. Methylbutenol
12. Benzene
13. Toluene
14. Benzaldehyde
## Detection limits, accuracy and precision

<table>
<thead>
<tr>
<th></th>
<th>Empa GC-MS</th>
<th>EMD GC-FID</th>
<th>NCAS GC-2FID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limits [pptv]:</td>
<td>1 - 730</td>
<td>40</td>
<td>1</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>640</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Methacrolein</td>
<td>20</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Propanal</td>
<td>40</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>Butanal</td>
<td>70</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>90</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Acetone</td>
<td>40</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Methylvinylketone</td>
<td>40</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>Methanol</td>
<td>10</td>
<td>70</td>
<td>9</td>
</tr>
<tr>
<td>Ethanol</td>
<td>90</td>
<td>9</td>
<td>40</td>
</tr>
<tr>
<td>Propanol</td>
<td>90</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Butanol</td>
<td>40</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td><strong>Accuracy</strong></td>
<td>1 – 30 %</td>
<td>7 – 11 %</td>
<td>7 – 11 %</td>
</tr>
<tr>
<td><strong>Precision</strong></td>
<td>1 – 5 %</td>
<td>10 %</td>
<td>0.5 – 10 %</td>
</tr>
</tbody>
</table>
Comparison of Empa GC-MS with UHEL PTR-MS
Empa GC-MS and NCAS GC-2FID at the SAPHIR atmosphere simulation chamber

Apel et al., 2006
Empa GC-MS and NCAS GC-2FID at the SAPHIR atmosphere simulation chamber

Apel et al., 2006
Outlook

- An ambient air intercomparison is currently taking place (July-September 2012) between EMPA, DWD and MPI Mainz PTR-MS (only July)
- Data of Hyytiälä intercomparison EMPA – PTR-MS by UHEL are evaluated
- Bring together test and characterization information
- Draft for OVOC module will be available in October 2012 (Reimann et al., ACTRIS Delivery)
- Further field intercomparisons are planned

Who is interested to contribute?
What are WCC activities and contributions?
What are the reference values in field intercomparisons?
Should we go for another SAPHIR-like intercomparison experiment?