Quality Assurance and Quality Control in the WMO-GAW-VOC Network

Rainer Steinbrecher
and
Stephan Thiel

http://imk-ifu.fzk.de/wcc-voc/
GAW Network for VOC

Provides a framework for the next generation GAW program 2008-2015
The WCC-VOC Activities

- Operation of the WCC-VOC
- Quality assurance of the WCC-VOC
- Round-Robin Exercises and Audits
- Central Calibration Laboratories (CCLs)
- Training in WCC-VOC and GAWTEC
- Workshops and international co-operations
- Interactions WCC-VOC and GAW institutions
- Outreach
The GAW-VOC QA/QC Strategy

Traceability of Calibrations and Audits

Central Calibration Laboratory (CCL)

Transfer of scale

Harmonisation

WCC- VOC

QA/QC: Audits & Round Robin Exper.

GAW Stations

Other Stations, Laboratories
The GAW-VOC QA/QC Control of Success

**Round robin Exercises**
- Evaluate Results on the basis of data quality objectives
- Report findings to the participants
- Enquire reasons for deviations in bilateral meetings
- Suggest joint measures to improve quality
- Check progress by repeating QC/QA experiments

**Audits**
- Report discovered discrepancies to station staff
- Take possibilities to solve detected problems on-site
- Set up an action priority list with deadlines to solve encountered problems together with station personal in the final audit meeting
- Check progress by repeating audit
### The GAW-VOC Target Compounds

<table>
<thead>
<tr>
<th>Ethane</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>DMS</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Benzene</td>
</tr>
<tr>
<td>Isoprene</td>
<td>Toluene</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Iso-Butane</td>
</tr>
<tr>
<td>Monoterpenes</td>
<td>n-Butane</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>Iso-Pentane</td>
</tr>
<tr>
<td>Methanol</td>
<td>n-Pentane</td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
</tr>
</tbody>
</table>

#### Realisation of QA/QC

- **Stage approach**
  - hydrocarbons
  - other compounds

- Full suite in 2011

---

*WMO Report 171; 2007*
## Current WCC-VOC Standards

### high precision VOC standard NPL_D296263

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nominal value /ppb</th>
<th>Uncertainty 2σ ppb</th>
<th>Overall uncertainty 2σ of analysis/ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethan</td>
<td>2.70</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Ethine</td>
<td>2.66</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>2.67</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>i-Butane</td>
<td>2.68</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>2.60</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>i-Pentan</td>
<td>2.59</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>n-Pentane</td>
<td>2.63</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Isoprene</td>
<td>2.60</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>2.62</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>2.59</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>α-Pinene</td>
<td>2.01</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>
### Current WCC-VOC Standards

Recalibrated laboratory/working/travelling standard

Apel/Riemer 2006

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nominal value after recalibration/ ppb</th>
<th>Uncertainty 2σ/ ppb</th>
<th>Δx after recalibration / %</th>
<th>Uncertainty specified /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>13,8</td>
<td>0,13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethine</td>
<td>8,69</td>
<td>0,11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>12,56</td>
<td>0,17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-Butane</td>
<td>6,13</td>
<td>0,07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>10,99</td>
<td>0,08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-Pentane</td>
<td>7,96</td>
<td>0,08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Pentane</td>
<td>9,58</td>
<td>0,08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isoprene</td>
<td>5,57</td>
<td>0,07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>2,36</td>
<td>0,21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>3,3</td>
<td>0,52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Pinene</td>
<td>10,47</td>
<td>0,15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Prospective GAW VOC Network
The GAW-VOC Audits

Title:
STANDARD OPERATING PROCEDURE (SOP) FOR SYSTEM AND PERFORMANCE AUDITS OF ATMOSPHERIC TRACE GAS MEASUREMENTS AT WMO/GAW SITES

Version:
Version 1.1-20080131

Contributors:
J. Klausen (QA/SAC Switzerland), Ch. Zellweger (WCC Empa), H.-E. Scheel (WCC N2O); R. Steinbrecher (WCC-VOC)

Approval:
SAG Reactive Gases: pending

Scope:
This document gives guidelines on how to conduct combined system and performance audits of measurement systems at WMO Global Atmosphere Watch (GAW) stations. It is intended to be used in the context of audits of trace gas systems that use either a gas chromatographic method or continuous gas analysers. This SOP has been optimized for audits of VOCs.

Definitions:
According to the GAW Strategic Implementation Plan (WMO/GAW Report 142), a performance audit is defined as a voluntary check of conformity of a measurement where the audit criteria are the DQOs for that parameter. In the absence of formal DQOs, an audit will at least involve ensuring the traceability of measurements to the Reference Standard. A system audit is more generally defined as a check of the overall conformity of a station with the principles of the GAW QA system. The reference for conformity of a station will evolve as the GAW QA system evolves.
## Audit Results

<table>
<thead>
<tr>
<th>Compound</th>
<th>WCC-VOC Nominal value /ppb</th>
<th>WCC-VOC Overall uncertainty 2σ of analysis/ppb</th>
<th>GAW Station Reported Values /ppb</th>
<th>Δx to WCC-VOC /%</th>
<th>GAW Station Reported uncertainty 2σ /%</th>
<th>GAW VOC DQO Accuracy /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethan</td>
<td>2.70</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Ethine</td>
<td>2.66</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Propane</td>
<td>2.67</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>i-Butane</td>
<td>2.68</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>n-Butane</td>
<td>2.60</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>i-Pentan</td>
<td>2.59</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>2.63</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Isoprene</td>
<td>2.60</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.62</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.59</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>α-Pinene</td>
<td>2.01</td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>
## Audit Results

<table>
<thead>
<tr>
<th>Compound</th>
<th>WCC-VOC Nominal value /ppb</th>
<th>WCC-VOC Overall uncertainty 2σ of analysis/ppb</th>
<th>GAW Station Reported Values /ppb</th>
<th>δx to WCC-VOC /%</th>
<th>GAW Station Reported uncertainty 2σ /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>2.70</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethine</td>
<td>2.66</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>2.67</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-Butane</td>
<td>2.68</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>2.60</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-Pentan</td>
<td>2.59</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Pentane</td>
<td>2.63</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isoprene</td>
<td>2.60</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>2.62</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>2.59</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Pinene</td>
<td>2.01</td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Audit Results Summary

**GAW Station R**
- No major flaws
- All reported GAW target compounds within DQO
  Uncertainty < 6%
- No monoterpenes

**GAW Station J**
- No major flaws
- All reported GAW target compounds within DQO
  Uncertainty < 9%, except i-butane and n-pentane
- No ethane, ethine, propane, isoprene, monoterpenes

**GAW Station H**
- No major flaws
- All reported GAW target compounds within DQO
  Uncertainty < 1%
- No ethine, n-butane, monoterpenes
Audit Results Summary

GAW Station Y
- No major flaws
- All reported GAW target compounds within DQO, except ethane
  Uncertainty < 10%
- No monoterpenes

GAW Station i
- No major flaws
- All reported GAW target compounds within DQO except ethane and isoprene, Uncertainty < 10%
- No monoterpenes

GAW Station B
- No major flaws
- All reported GAW target compounds within DQO
  Uncertainty < 2%
- No monoterpenes
What comes next in 2008?

- Further promotion for CCLs for VOC in co-operation with NMIs and GAW-VOC.
- A CCQM-GAWG-GAW-VOC expert workshop in July at EMPA.
- Inter-comparisons, audits and re-audits are going to be performed at GAW central laboratories at UC, Irvine, CA, AQRDE, Toronto, MPI, Mainz, and at the global GAW station Cap Verde.
Thank You for Your Attention
and we appreciate
the Excellent Co-operation of the GAW Stations in Audits and Inter comparison experiments