Report of the WCC-N$_2$O

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Jena, 7 - 10 September 2009
1. Introduction

2. Contributions to GAW Documents and Training Courses

3. Comparisons of Standards & Round-robin Experiments

4. Audits

5. Conclusions

6. Summary and Outlook

WCC-N$_2$O website: http://imk-ifu.fzk.de/wcc-n2o/
1. Introduction
The WCC-N$_2$O within GAW

Global Atmosphere Watch (GAW)

GAW Central Facilities:

- Scientific Advisory Groups (SAGs)
- Quality Assurance/Science Activity Centres (QA/SACs)
- World Calibration Centres (WCCs)
- World Data Centres (WDCs)

QA/SAC Germany
operated by the
German Federal Environment Agency (UBA)

WCC-N$_2$O
Funded by UBA
Operated by IMK-IFU

Linked to GAW scale, no separate calibrations
2. Contributions to GAW Documents and Training Courses
Involvement of the WCC-N₂O in the Development of Guidelines and Related GAW Documents

Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance (GAW Report No. 185)
WCC-$N_2O$ contributions to GAWTEC courses
http://www.gawtec.de/

Location: Environmental Research Station Schneefernerhaus (Zugspitze, Germany)
http://www.schneefernerhaus.de

Lectures (2007 till present):

- Graphical Presentation of Measurement Data (5)
- GAW Terminology and ISO Definitions (5)
- $N_2O$ in the Atmosphere (1)

Please remember:

WMO/GAW Glossary of QA/QC-Related Terminology

Document on the web.
http://www.empa.ch/gaw/glossary.html
The evaluation and characterisation of data obtained from measurements made within WMO/GAW involve a number of statistical parameters and specific terms to characterise data quality. At present, several of these terms (e.g. precision) are frequently used with different meaning by different people. Efforts for standardization have been made in the past, involving contributions from a number of international organizations, and are coordinated under the umbrella of ISO.

With the aim of ensuring the comparability and consistency of measurements, the GAW Strategic Plan recommends adoption and use of internationally accepted methods and vocabulary to deal with measurement uncertainty as outlined in various ISO publications. Since each term should have the same meaning for all of its users, efforts are called for to familiarize all individuals involved in WMO/GAW and the associated scientific community with the relevant terminology. The following glossary is intended as a step in this direction. GAW members are encouraged to use these terms in their own publications and to suggest their use when reviewing manuscripts of others.

**Glossary**

**accuracy of measurement**
3. Comparisons of standards

- Laboratory work (ongoing): Internal comparisons of WCC standards. In total: 8 Laboratory Standards, 22 others gas mixtures, incl. 16 Travelling Standards (TS). Tests of pressure regulators.


- Intercomparison with Cape Point based on WCC-\(\text{N}_2\text{O}\)-calibrated WCC-Empa travelling standards.

- CCQM-K68 \(\text{N}_2\text{O}\) International Comparison, organised by the Division of Metrology for Quality Life, Korea Research Institute of Standards and Science (KRISS)

- Recalibration of Laboratory Standards by the CCL
Tests of pressure regulators (Laboratory WCC-N$_2$O)

A few regulators yielded mole fraction results of a few tenths of a ppb above the values typically obtained with other regulators.

For improved quality control, identification numbers were assigned to the regulators in 2008.

Laboratory protocols of analysis runs were supplement with the regulator ID.

For the audits, dedicated regulators were assigned to the five travelling standards involved.
IHALACE results of the WCC-N$_2$O:
N$_2$O mole fractions [ppb] expressed in NOAA-2000 scale

<table>
<thead>
<tr>
<th>Tank number</th>
<th>#3527</th>
<th>#3536</th>
<th>#3538</th>
</tr>
</thead>
<tbody>
<tr>
<td>WCC-N$_2$O [ppb]</td>
<td>318.57</td>
<td>259.30</td>
<td>318.43</td>
</tr>
<tr>
<td>CCL reference [ppb]</td>
<td>318.35</td>
<td>258.84</td>
<td>318.19</td>
</tr>
<tr>
<td>Deviation of WCC [ppb]</td>
<td>0.22</td>
<td>0.46</td>
<td>0.24</td>
</tr>
</tbody>
</table>
Results from a comparison between Cape Point and WCC-N₂O conducted in mid-2008. The cylinders are travelling standards of the WCC Empa and contain natural air.

### Cape Point inter-comparison (2008)

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>FA02786</td>
<td>294.61</td>
<td>294.68</td>
<td>0.07</td>
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<tr>
<td>FA02783</td>
<td>305.42</td>
<td>305.66</td>
<td>0.24</td>
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<tr>
<td>FA02769</td>
<td>306.79</td>
<td>307.00</td>
<td>0.21</td>
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<tr>
<td>FF30491</td>
<td>317.03</td>
<td>317.17</td>
<td>0.14</td>
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<tr>
<td>FA02773</td>
<td>324.97</td>
<td>325.64</td>
<td>0.67</td>
</tr>
<tr>
<td>FF31496</td>
<td>345.21</td>
<td>345.99</td>
<td>0.78</td>
</tr>
</tbody>
</table>

![Graph showing the comparison between WCC-N₂O and CPT values with a scatter plot of the differences]
CCQM-K68 N₂O International Comparison (2008)

1 cylinder with gas mixture containing nominally 320 ppb N₂O, 21 % mol/mol oxygen and nitrogen as balance.

Result of the WCC-N₂O:

\[
\text{n} = 65, \text{rel. std. dev.} \ 0.065 \%
\]
CCQM-K68 $\text{N}_2\text{O}$ International Comparison (2008)

Remarks:
- Focus on $\text{N}_2\text{O}$ mole fraction only
- 1 level
- No concurrent check of the analytical performance (separation of $\text{CO}_2$ and $\text{SF}_6$, detector response characteristics)
Recalibration of Laboratory Standards by the CCL, Feb 2009

<table>
<thead>
<tr>
<th>Cyl ID</th>
<th>N2O before recal.</th>
<th>Recalibration results (CCL, Brad Hall)</th>
<th>Mean</th>
<th>Std dev</th>
<th>Rel. std.dev.</th>
<th>old - new</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA06234</td>
<td>293.27★</td>
<td>293.34</td>
<td>0.11</td>
<td>0.04%</td>
<td>-0.07</td>
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<tr>
<td>CA04785</td>
<td>312.42</td>
<td>312.26</td>
<td>0.08</td>
<td>0.03%</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>CA06246</td>
<td>320.67</td>
<td>320.58</td>
<td>0.11</td>
<td>0.03%</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>CA04800</td>
<td>325.95</td>
<td>325.84</td>
<td>0.09</td>
<td>0.03%</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>CA04743</td>
<td>333.23</td>
<td>333.36</td>
<td>0.14</td>
<td>0.04%</td>
<td>-0.13</td>
<td></td>
</tr>
<tr>
<td>CA04752</td>
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<td>358.12</td>
<td>0.14</td>
<td>0.04%</td>
<td>-0.02</td>
<td></td>
</tr>
</tbody>
</table>

★Original CCL value lowered by 0.3 ppb based on CCL – WCC.N$_2$O intercomparison of 5 gas mixtures (TS) in 2007.
4. Audits

Overview on results of 4 audits

- Zugspitze (ZSF)
- Jungfraujoch (JFJ)
- Pallas (PAL)
- Izaña (IZO)
Shape of chromatograms
Fig. 4.3: Example of a chromatogram obtained with the ECD channel of the GC system.

Fig. 4.4: Zoom into the chromatogram of Fig. 4.3.
Fig. 1. Example of a chromatogram obtained with the ECD channel of the GC system. The inset enlarges the peaks for better visibility. The mole fractions of the working standard sample were 321.6 ppb N₂O and 5.5 ppt SF₆. Figure taken from a draft version of a publication (Steinbacher et al., 2008).
Comparison of ECD response curves (extrapolated)

Range of standards: 296 - 347 ppb
Comparison of standard deviations
(average of audit intercomparison of 5 N2O standards)

Target value

<table>
<thead>
<tr>
<th>ZSF</th>
<th>JFJ</th>
<th>PAL</th>
<th>IZO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>0.58</td>
<td>0.19</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Intercomparison: Individual analysis results for 319 ppb

Comparison of audit results

Number

N2O [ppb]

0 5 10 15 20 25 30

WCC_318.97

Avg (JFJ)

Avg (IZO)

Avg (PAL)

N2O_PAL

N2O_JFJ

N2O_IZO
Intercomparison: Differences between reported and assigned values

Audit intercomparisons: N2O differences, Station - WCC-N2O

Station - WCC [ppb]

WCC-N2O [ppb]
Audit intercomparison results (2005 - 2008): Station - WCC-N2O

- **Partly explained by response curve**
- **Best overall performance**

**Station - WCC [ppb]**

- **ZSF**
  - Bias: -1.03
- **JFJ**
  - Matter of response curve: -2.71
- **PAL**
  - Bias: -1.0
  - Matter of response curve: -3.0
- **IZO**
  - Bias: -0.32

**Levels**

- **Level 1**
- **Level 2**
- **Level 3**
- **Level 4**
- **Level 5**
5. Conclusions

- Intercomparisons: Standard deviation (repeatability) of minor importance for the analysis series. No obvious relationship with reported mole fraction results.

- Intercomparisons: Agreement within ± 0.2 ppb at ambient levels seems to be achievable at present.

- Careful determination of the response curve is of importance if one wants to quantify gas mixtures over the entire range between 290 and 350 ppb.
6. Summary and outlook

- Laboratory activities = ongoing work
- Link of WCC travelling standards to the CCL (GAW scale) has been proven. Lab Standards are up-to-date. New standards to be checked.
- Audits have yielded valuable results. Next steps to be planned.
- Post-audit contacts with the stations as a continuous task (control of success).
- Participation in the current WMO 2009 Intercomparison.
- WCC-N₂O round-robin experiments involving a small number of participants. Repetition of audit intercomparisons.