Overview on Ten Years of WCC-N_2O

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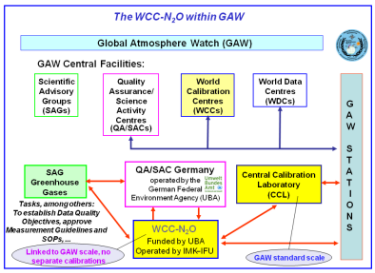
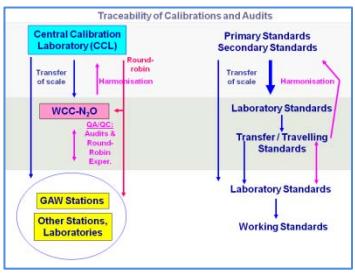
Introduction

The World Calibration Centre for N_2O (WCC-N_2O) has been established in 2001 as a central GAW facility according to the requirements of the GAW Strategic Plan 2001–2007 (WMO/GAW Report No. 142) and is operating in agreement with the current Strategic Plan: 2008 - 2015 (WMO/GAW Report No. 172). The overall goal is the improvement of the N_2O data quality and compatibility within the network.

The major tasks of the WCC-N_2O comprise the development of quality control procedures, conducting audits at stations and intercomparison experiments as well as providing training and technical advice to GAW station personnel.

http:// imk-ifu.fzk.de/wcc-n2o/





Analytical Laboratory of the WCC-N_2O

Gas chromatograph with electron capture detector (ECD) for comparisons of N_2O standards of different levels in the traceability chain and dedicated to different purposes.

Link to the GAW N_2O scale through 8 laboratory standards (range 253 – 358 ppb), recalibrated by the Central Calibration Laboratory (CCL) in 2009.

Suite of 22 gas mixtures: 5 as scale back-up, 17 suitable as travelling standards for audits and intercomparisons, usually comprising sets of 5 cylinders.

Traceability Chain

Based on the NOAA calibration scale – with primary and secondary standards kept at the CCL – standards on the tertiary level are used as "Laboratory Standards" by the WCC-N_2O and GAW laboratories/stations.

Data Quality Objectives (DQO)

Repeatability:Target value 0.1 ppb (0.03% at ambient levels) as driven by scientific needs (GAW Report No. 185 (2009), p. 13).

Compatibility of measurements from different laboratories of 0.1 ppb (range 290 – 350 nmol/mol). Reproducibility of NOAA N_2O calibrations (2 sigma): 0.16 nmol/mol at the 95% confidence level (GAW Report No. 194 (2011), p. 14). *Note: nmol/mol = ppb*

The uncertainty of WCC-N_2O standards is determined from comparisons at the CCL.

Comparisons WCC-N_2O / CCL

Conducted in 2007 and 2011, employing 5 Travelling Standards of the WCC-N_2O. Total range 296 – 347 ppb.

2007: Differences (WCC - CCL) between -0.12 and +0.12 ppb.

2011: Differences for four standards between 0.09 and 0.15 ppb, and one outlier at 0.27 ppb.

International Intercomparisons

IHALACE (2005): Organized by NOAA/ESRL . 3 standards; differences WCC - Reference of 0.22 and 0.24 ppb at 318 ppb, and 0.46 ppb at 259 ppb.

CCQM-K68 (2008): Organized by KRISS (Korea). 1 standard; difference WCC - Reference of 0.76 ppb. Value reduced to 0.36 ppb if a propable analytical error of about 0.3 ppb by the WCC-N_2O is taken into account.

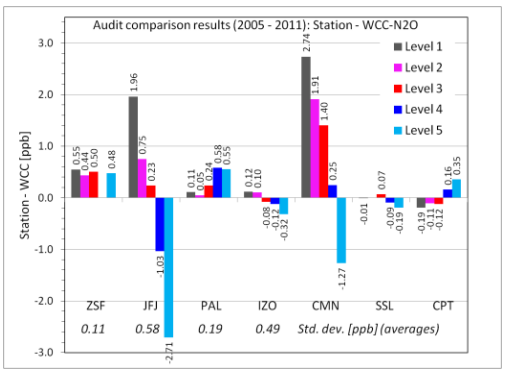
System and Performance Audits

Audits were conducted according to audit guidelines approved by the Scientific Advisory Group for Greenhouse Gases (SAG GG).

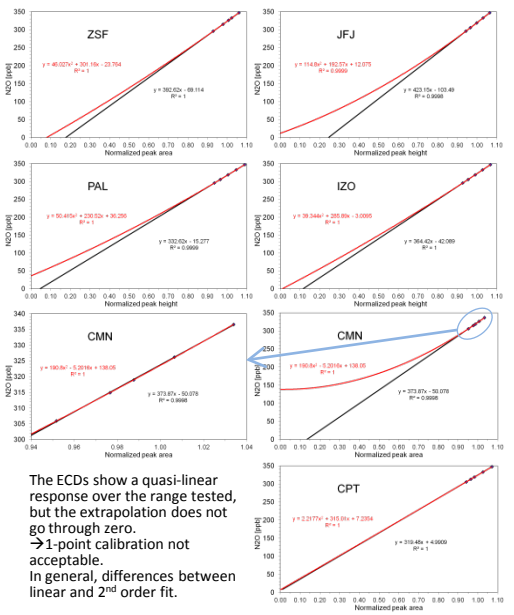
In practice the audit consists of 2 parts: (i) General inspection of the station facilities (system audit), and (ii) performance check of the N_2O instrumentation. This involves 5 Travelling Standards for on-site comparisons.

System and performance audits by the WCC-N_2O

	Station	Date	Comment
1	Schauinsland (SSL)	Nov 2002	Station not yet prepared for audit requirements
2	Cape Point (CPT)	Feb 2003	Old GC, performance not sufficient
3	Zugspitze (ZSF)	Dec 2005	Bias
4	Jungfraujoch (JFJ)	Jul 2006	Response curve undetermined, good at ambient level
5	Pallas (PAL)	Sep 2007	Good at ambient level
6	Izaña (IZO)	Nov 2008	Good
7	MPI Mainz	Dec 2008	Unclear result of comparisons
8	Monte Cimone (CMN)	Aug 2010	Response curve undetermined, bias unexplained
9	Schauinsland (SSL)	Nov 2010	Very good (close to DQO target)
10	Cape Point (CPT)	Feb 2011	Good near ambient levels



Comparison of ECD response curves (extrapolated)
Range of standards: 296 – 347 ppb



The ECDs show a quasi-linear response over the range tested, but the extrapolation does not go through zero.
→1-point calibration not acceptable.
In general, differences between linear and 2nd order fit.

Collaboration with WCC-Empa

Aim: Increasing the number of stations with N_2O comparisons.

(i) Quantification of N_2O for 10 cylinders in 2008 (295 - 355 ppb) with no N_2O values previously assigned, and 6 cylinders in 2011.

(ii) Analysis of the standards at stations as part of a WCC-Empa audit.

Δ [ppb] = Station - Assigned value.

Results: Cape Point (2008); range 295 - 317 ppb: $0.07 \le \Delta$ [ppb] ≤ 0.24; for 325, 345 ppb: Δ [ppb] = 0.67, 0.78, respectively.

Point Barrow (2008); Δ [ppb] = 0.01 at 315.7 ppb.

Mace Head (2009); range 245 - 323 ppb: $-0.17 \le \Delta$ [ppb] ≤ 0.29.

Comparison WCC-Empa/ WCC-N_2O (2011); 4 standards yielding Δ [ppb] within ± 0.08, for 2 others $-0.17 \le \Delta$ [ppb] ≤ 0.30.

Summary of Audit Findings

- Crucial point in the gas chromatogram: Sufficient separation of the N_2O peak from CO_2 and SF_6.
- No relationship between standard deviation of analysis runs and quality of comparison results (see bar graph).
- 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
- 1-point calibration is insufficient, does not yield correct results, except in very special cases.
- For comparisons, agreement within ± 0.2 ppb at ambient levels seems to be achievable at present.
- Post-audit contacts with the stations are a continuous task (control of success)
- The audits have revealed significant differences in the performance of gas chromatographic systems, even if equipped with similar instrumentation.

Summary of WCC-N_2O Activities

- Laboratory analyses: Performance checks of the GC, comparisons of standards: (i) working & travelling standards (notably pre- and post-audit analyses, (ii) bilateral cooperations, (iii) 3 international round-robin experiments
- 10 audits, two of them as repetitions
- Contributions to Guidelines for N_2O measurements (incl. Data Quality Objectives) and for audits as well as to terminology issues
- Presentation of the WCC-N_2O concept at meetings and workshops
- Contributions to GAWTEC (www.gawtec.de/) courses
- Rendering advice to GAW stations
- Collaboration with WCC-Empa

Conclusions

From the 10 system and performance audits, considerable progress over the years can be noted regarding the network compatibility of N_2O measurements.

Major factors that have contributed to the achievements at the individual stations are:

- Recommendations compiled at GAW meetings (see WMO/GAW Reports)
- GAW Measurement Guidelines including DQOs (GAW Report No. 185)
- Acquisition of a set of CCL-calibrated standards and recalibrations. Several stations improved or newly established their link to the GAW N_2O scale.
- In most cases there are no obvious parameters of the GC system promising major future improvements.
- The fulfilment of the DQOs still remains a challenge. Expectations for the future are with laser-based instruments.