### Forschungszentrum Karlsruhe

in der Helmholtz-Gemeinschaft

## Report of the WCC-N<sub>2</sub>O

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WCC-N<sub>2</sub>O



14th WMO/IAEA Meeting of Experts on Carbon Dioxide, other Greenhouse Gases and Related Measurement Techniques Helsinki, 10 - 13 September 2007

### Report of the World Calibration Centre for Nitrous Oxide

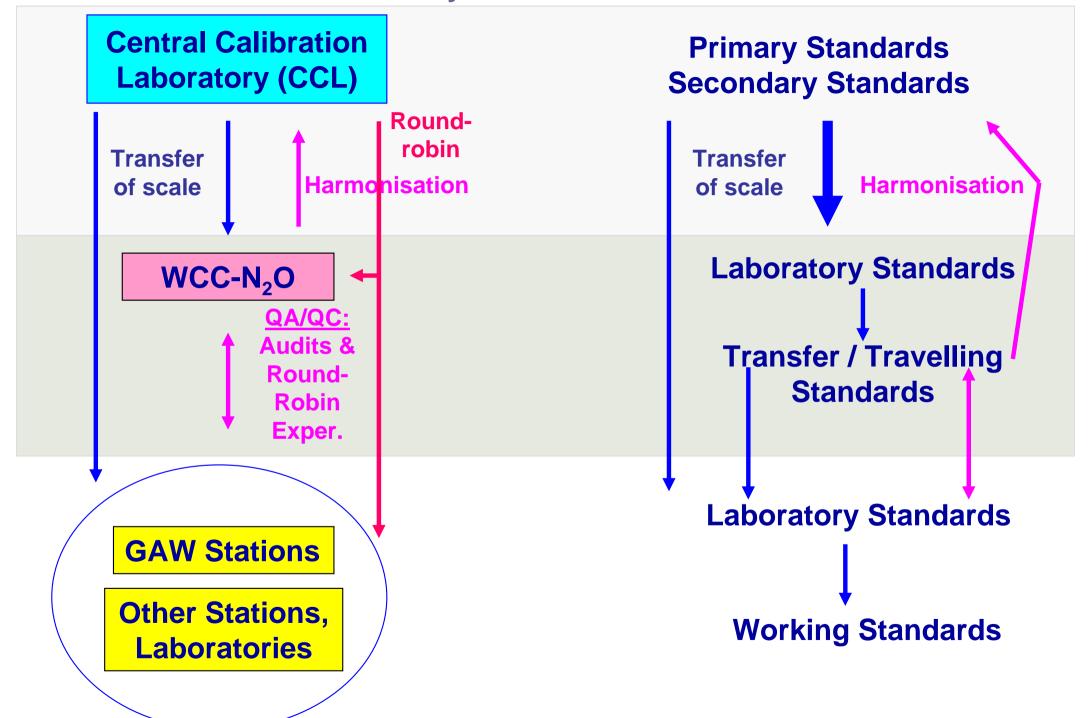
### **Outline**

- 1. Introduction
- 2. Contributions to GAW documents
- 3. Comparison of standards
- 4. Audits
- 5. Contributions to training courses
- 6. Summary and Outlook

### World Calibration Centre for Nitrous Oxide (WCC-N<sub>2</sub>O)

### 1. Introduction

### **Traceability of Calibrations and Audits**



## 2. Contributions to GAW documents

## Involvement of the WCC-N<sub>2</sub>O in the Development of Guidelines and Related GAW Documents

# Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance

Status: Several modifications during recent years, draft currently reviewed by SAG GG. Draft posted on the GAW website soon.

### Audit Questionnaire (Gases)

Status: Document based on joint input from QA/SAC Switzerland, WCC-Empa and WCC- $N_2O$ . Approved by SAG GG.

### Audit SOP (Gases)

Status: Document based on outline by WCC-Empa with edits of WCC- $N_2O$ . Approved by SAG GG.

### WMO/GAW Glossary of QA/QC-Related Terminology

Status: Document on the web. http://www.empa.ch/gaw/glossary.html

### WMO/GAW Glossary of QA/QC-Related Terminology

Version 0.4 2007-04-26

Editors: J. Klausen and H.-E. Scheel

http://www.empa.ch/gaw/glossary.html

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#### Introduction

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 [5] recommends adoption and use of internationally accepted methods and vocabulary to deal with measurement uncertainty as outlined in various ISO publications [1-3, 5, 6]. 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 encoouraged to use these terms in their own publications and to suggest their use when reviewing manuscripts of others.

### **Glossary**

accuracy of measurement

## Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance

- 1. Introduction
- 2. Terminology and Definitions

Extract for web glossary → Editing (lead: J. Klausen) → Recirculated to MGs

- 3. Data Quality Objectives for CH<sub>4</sub>
- 4. Data Quality Objectives for N<sub>2</sub>O
- 5. Representativeness Criteria for Trace Gas Measurements
- 6. Measurement Guidelines for CH₄
- 7. Measurement Guidelines for N<sub>2</sub>O
- 8. Concepts for Audits at WMO/GAW Sites -

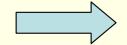
Questionnaire now as separate document

- 9. References
- 10.Annex 1: Abbreviations and Acronyms
- 11.Annex 2: List of Contributors and Reviewers

Status: Several modifications during recent years, draft currently reviewed by SAG GG.

## 3. Comparison of standards

- Laboratory work (ongoing): Internal comparisons of WCC standards: travelling standards vs. laboratory standards
- Participitation in IHALACE round-robin: Analyses and submission of results in mid-2005
- Informal analysis of a series of WCC-Empa travelling standards (2006)
- Intercomparison with the Central Calibration Laboratory, CCL (NOAA/ESRL GMD) in early 2007



# Results of a CCL–WCC intercomparison experiment (10-L cylinders) 5 WCC-N<sub>2</sub>O travelling standards analyzed by the CCL (Brad Hall)

Cylinder		Additional gases in mixture		N₂O [ppb] as assigned by WCC-N₂O		CCL results (intercom -parison 2007) [ppb]	Diff.: WCC – CCL [ppb]
Number	Short name	CO <sub>2</sub>	SF <sub>6</sub>	Based on NOAA-2000 scale	Converted to NOAA- 2006 scale	NOAA- 2006 scale	
6061	DS 11	+	+	296.30	296.26	295.89	0.37
4616D	DS 14	+	+	306.03	305.95	305.89	0.06
4586D	DS 15	+	+	319.12	318.97	318.90	0.07
4563D	DS 13	+	+	332.91	332.65	332.77	-0.12
4594D	DS 10	+		347.90	347.47	347.35	0.12

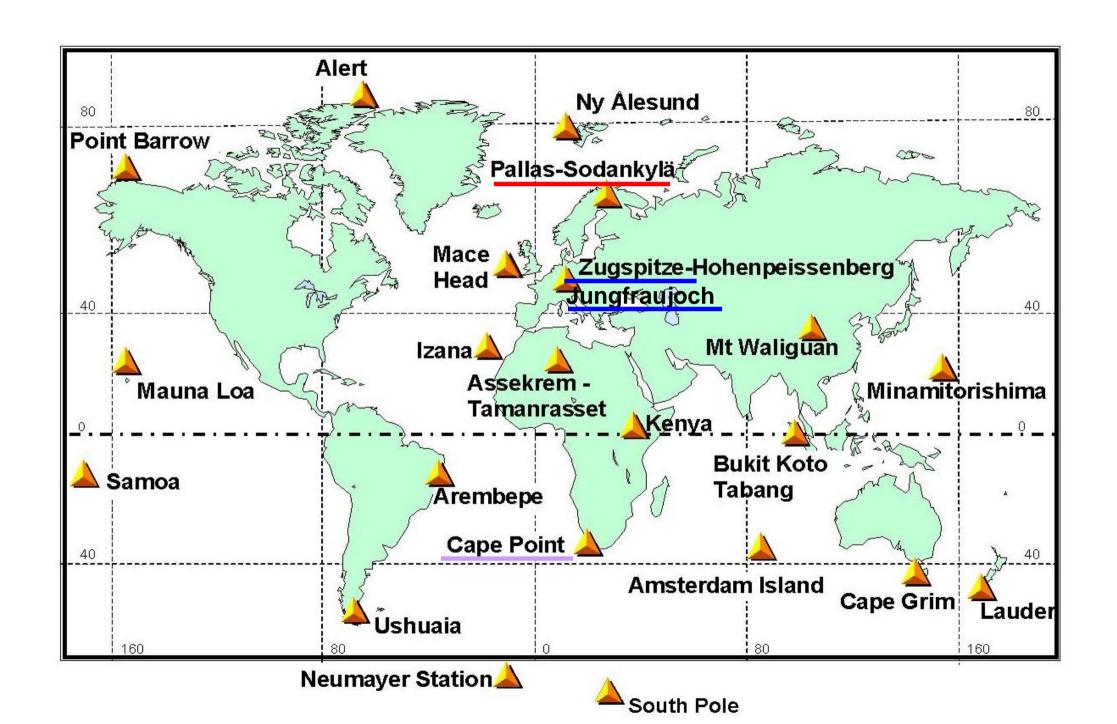
Related to Lab Stds calibrated at the CCL in 2005

## 4. Audits

### Criteria for selection of stations to be audited

- N<sub>2</sub>O measurements recently started
- Station not directly part of well-established global networks (such as NOAA/ESRL or AGAGE)
- Major changes, in particular upgrade of N<sub>2</sub>O instrumentation

### WMO Global Atmosphere Watch (GAW) network of Global Stations



### Some details from two stations

Similarities: Up-to-date instrumentation, measurements related to SIO-98 scale

**Differences noticed with respect to:** 

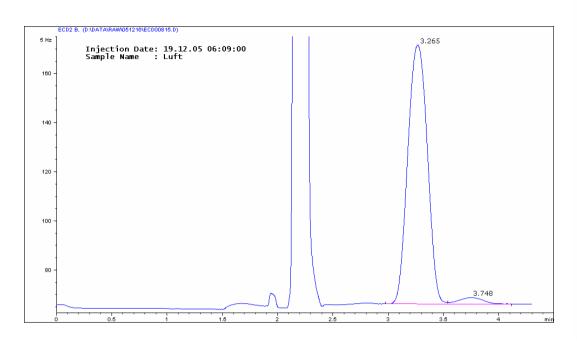
- ➤ Shape of chromatograms (separation of N₂O peak)
- > Handling of 1-point calibration for routine operation (ECD response curve not through zero).

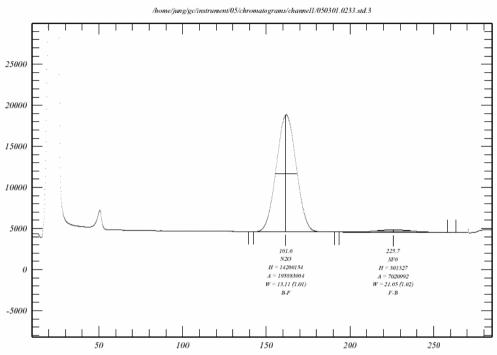
Station A: Corrections applied.

Station B: Working standard very close to ambient level. No correction applied before audit.

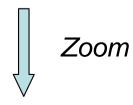
- Reproducibility (based on intercomparison results)
- Results obtained for the travelling standards

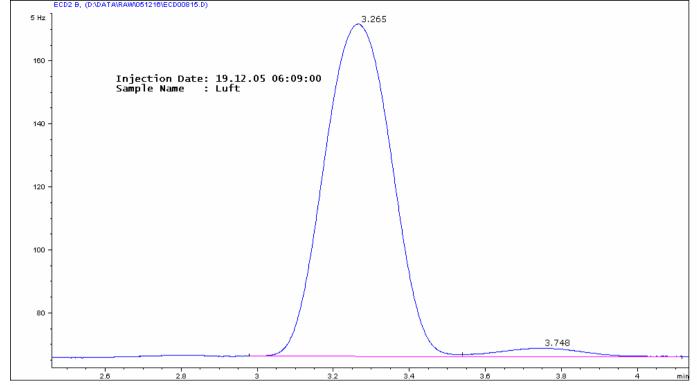
## N<sub>2</sub>O peak shape



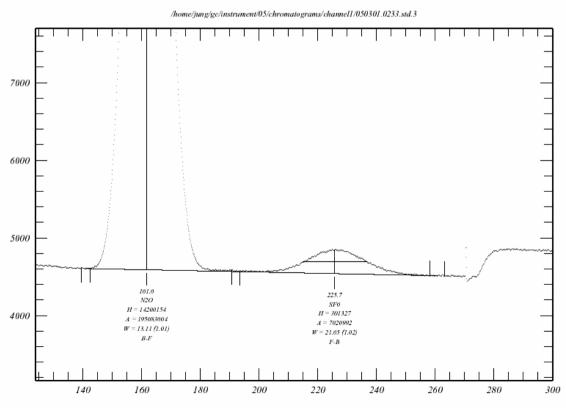


Working standard with 323.3 ppb N2O and 5.85 ppt SF6

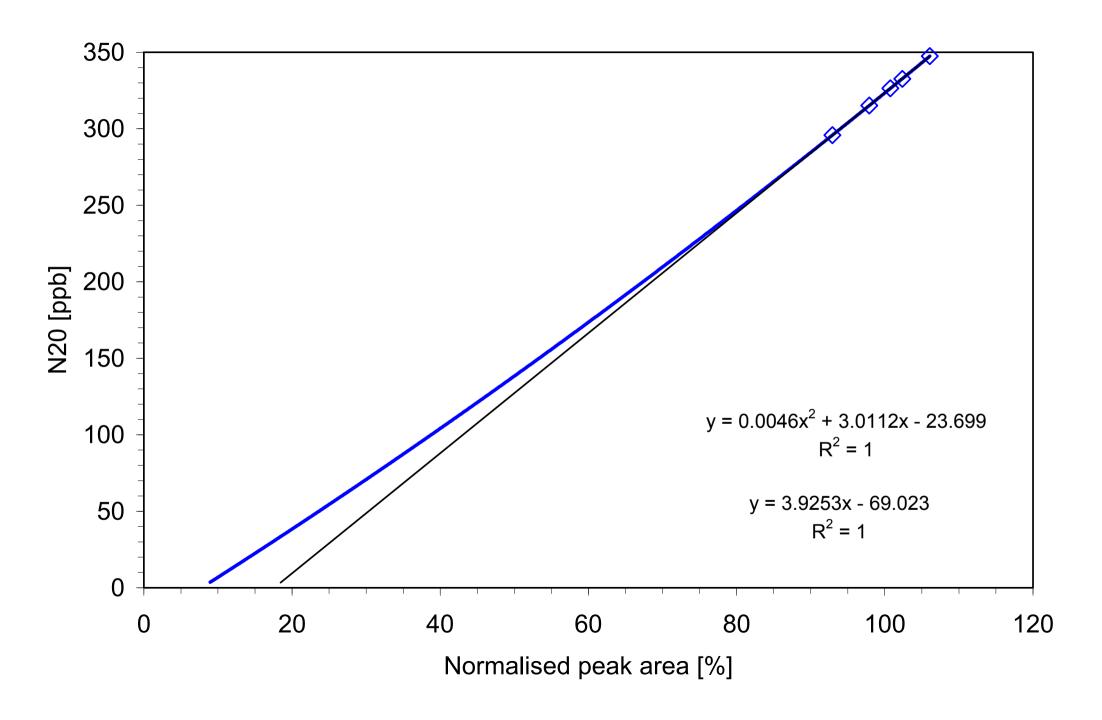




# Separation of peaks: $N_2O$ and $SF_6$



### Response curve of ECD, extrapolated

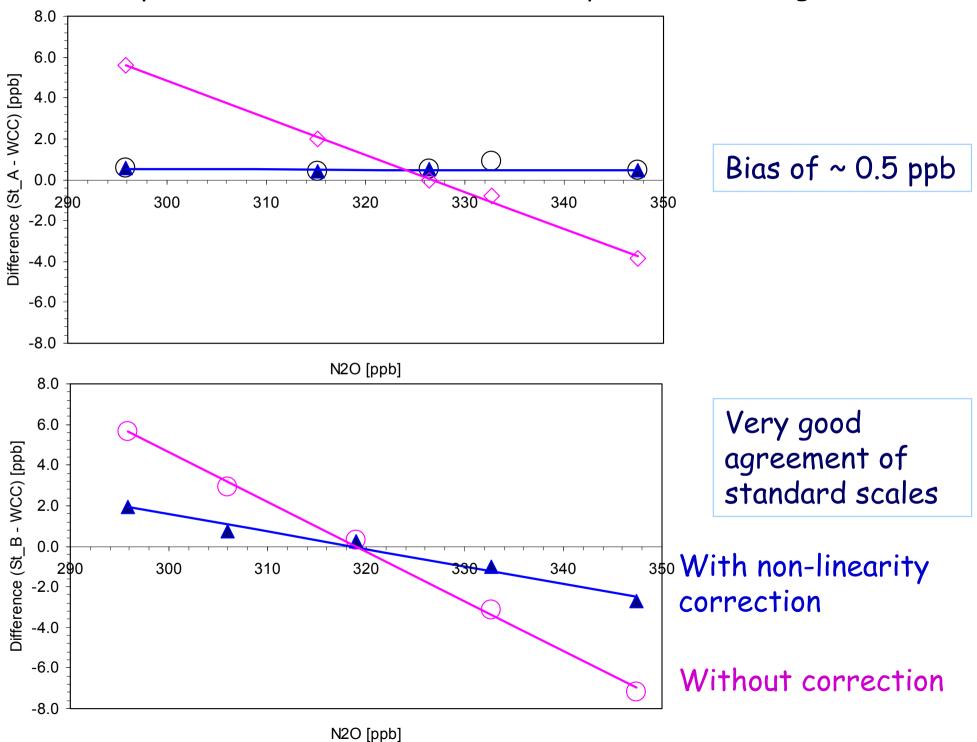


Audit results as reported by 'Station\_A' and 'Station\_B'. Comparison of statistics (modern instrumentation at both stations)

N20 (St_A) [ppb]	St. dev.	Rel. s.d [%]	n
296.44	0.12	0.04	24
315.60	0.09	0.03	32
326.88	0.15	0.05	38
333.57	0.09	0.03	38
347.95	0.09	0.03	32

N20 (St_B) [ppb]	St. dev.	Rel. s.d [%]	n
301.55	0.40	0.13	10
308.90	0.46	0.15	9
319.25	0.44	0.14	9
329.48	0.48	0.14	10
340.28	0.62	0.18	10

### Intercomparison: Differences between reported and assigned values



## 5. Contributions to training courses



# WCC-N<sub>2</sub>O contributions to GAWTEC courses

Location: Environmental Research Station Schneefernerhaus (Zugspitze)

http://www.schneefernerhaus.de/ufs.htm

### Lectures:

Graphical Presentation of Measurement Data

> GAW Terminology and ISO Definitions

## 6. Summary and outlook

- GAW documents requested by the Strategic Plan will be finalized till the end of 2007, if not yet ready.
- Laboratory activities = ongoing work
- Link of WCC travelling standards to the CCL (GAW scale) has been proven
- Audits have yielded valuable results. Next steps to be planned.
- Post-audit contacts with the stations might be intensified.
- A round-robin experiment organised by the WCC-N<sub>2</sub>O will be envisaged.