

Report of the WCC-N₂O

H.E. Scheel

Forschungszentrum Karlsruhe
Institute for Meteorology and Climate Research, IMK-IFU



WCC-N₂O



*15th WMO/IAEA Meeting of Experts on Carbon Dioxide,
other Greenhouse Gases and Related Tracer Measurement Techniques
Jena, 7 - 10 September 2009*

Report of the World Calibration Centre for Nitrous Oxide

Activities and Results 2007 - 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**

World Calibration Centre for Nitrous Oxide (WCC-N₂O)

1. Introduction

The WCC-N₂O 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)

G
A
W

S
T
A
T
I
O
N
S

SAG
Greenhouse
Gases

Tasks, among others:
To establish Data Quality
Objectives, approve
Measurement Guidelines and
SOPs, ...

Linked to GAW scale, no
separate calibrations

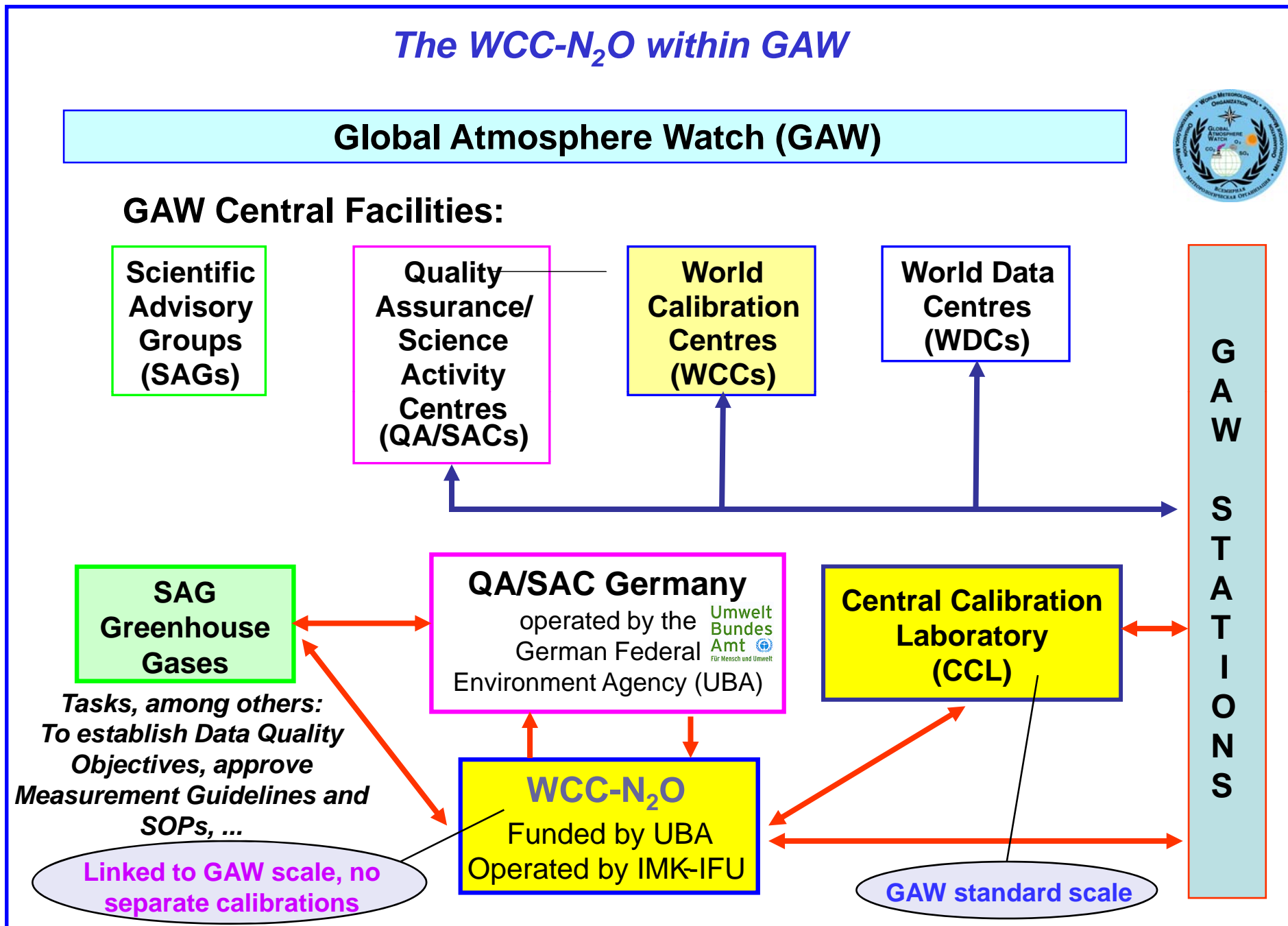
QA/SAC Germany
operated by the
German Federal
Environment Agency (UBA)



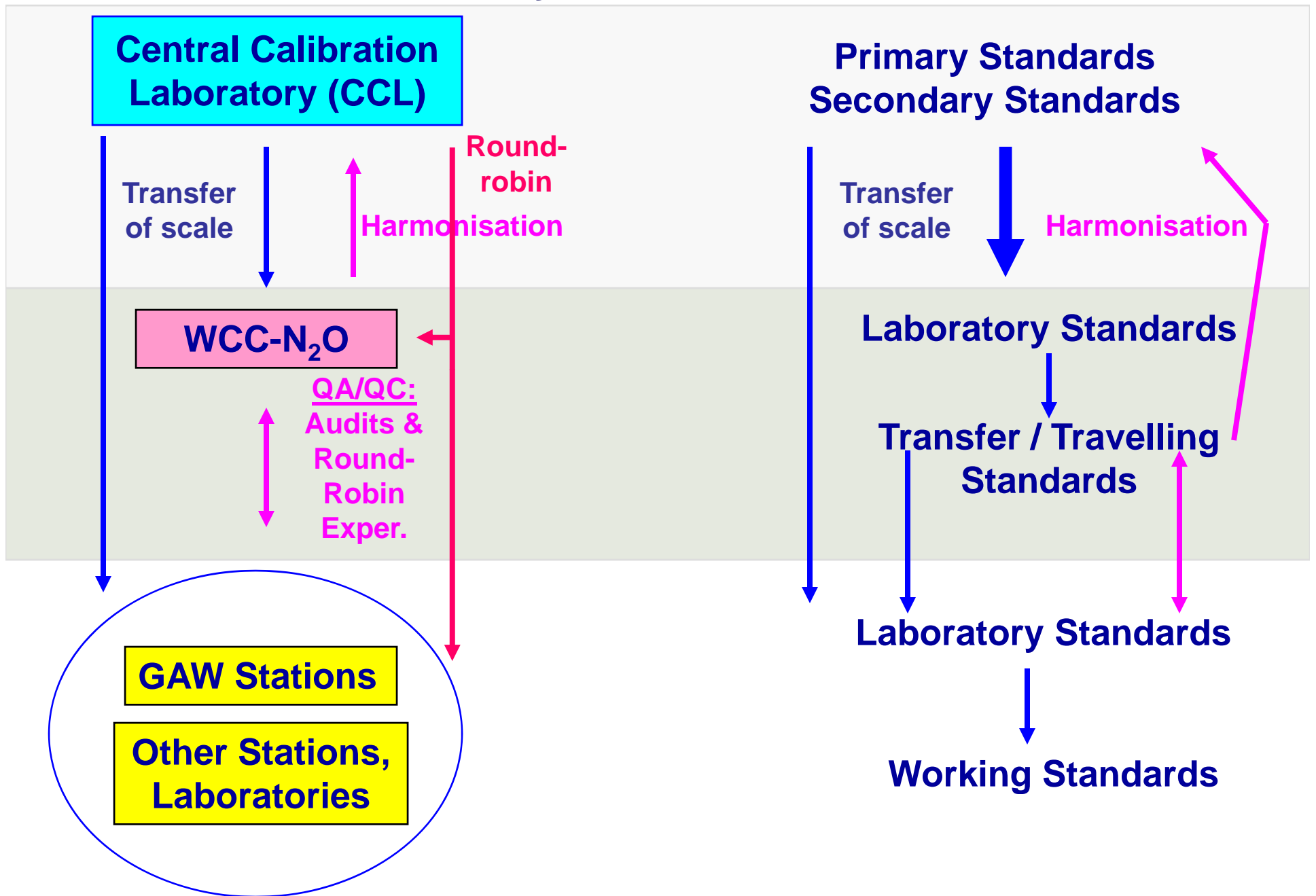
Central Calibration
Laboratory
(CCL)

WCC-N₂O
Funded by UBA
Operated by IMK-IFU

GAW standard scale



Traceability of Calibrations and Audits



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)

The screenshot shows the WMO Global Atmosphere Watch (GAW) website. The page title is "WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 - 2015". The main content is divided into two columns: "Recent and upcoming meetings" and "Recent reports".

Recent and upcoming meetings:

- 2009**
- GAW 2009 Workshop** (Geneva, 5-7 May 2009)
Deadline abstracts: 22 May 2009
- Ozone Theme Meeting 2009** (Geneva, 11-13 May 2009)
- 15th WMO/IAEA CO₂ Experts Meeting** (Jena, Germany, 7-10 September 2009)
- Meeting of GAW Scientific Advisory Group on Greenhouse Gases** (Jena, Germany, 11 September 2009)
- 8th International Carbon Dioxide Conference** (Jena, Germany, 13-19 September 2009)

Recent reports:

- New GAW Aerosol Optical Depth Newsletter**
- WMO Greenhouse Gas Bulletins**
- DRAFT GAW 188** - Revision of the WDCGG Data Submission and Dissemination Guide (Comments before 1 September to OTarasova@wmo.int)
- DRAFT GAW 187** - Joint Report of COST Action 728 and GURME - Review of the Capabilities of Meteorological and Chemistry-Transport Models for Describing and Predicting Air Pollution Episodes
- GAW 186** - 14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (Helsinki, Finland, 10-13 September 2007)
- GAW 185** - Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance
- GAW 184** - Technical Report of Global Analysis Method for Major Greenhouse Gases by the World Data Center for Greenhouse Gases
- WMO/UNEP Scientific Assessment of Ozone**

A red arrow points from the title "Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance (GAW Report No. 185)" to the "GAW 185" entry in the "Recent reports" section.



WCC-N₂O 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)
- N₂O 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>

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>

Table of Contents

Introduction

Glossary

Recommendations

References

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 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. →**
- **IHALACE round-robin: Analyses and submission of data in mid-2005. Results received in May 2008. →**
- **Intercomparison with Cape Point based on WCC-N₂O-calibrated WCC-Empa travelling standards. →**
- **CCQM-K68 N₂O 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-N₂O)

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 (International HALocarbon in Air Comparison Experiment)

IHALACE results of the WCC-N₂O:

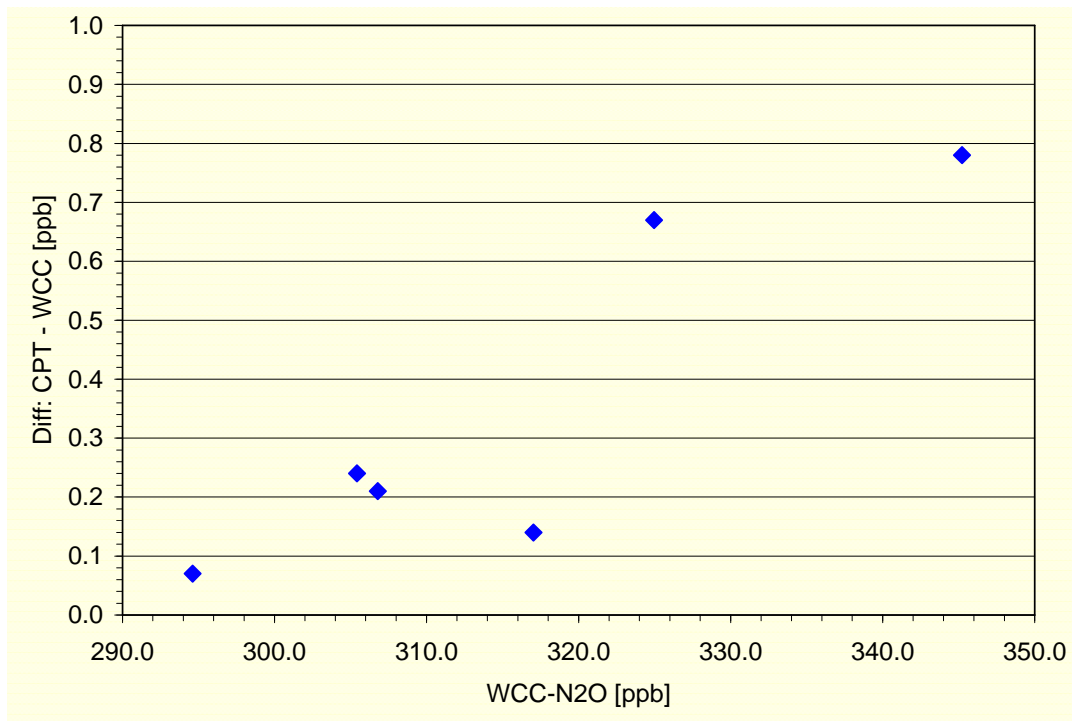
N₂O mole fractions [ppb] expressed in NOAA-2000 scale

Tank number	#3527	#3536	#3538
WCC-N ₂ O [ppb]	318.57	259.30	318.43
CCL reference [ppb]	318.35	258.84	318.19
Deviation of WCC [ppb]	0.22	0.46	0.24

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)

Cylinder #	WCC-N ₂ O [ppb]	CPT [ppb]	Diff: CPT - WCC [ppb]
FA02786	294.61	294.68	0.07
FA02783	305.42	305.66	0.24
FA02769	306.79	307.00	0.21
FF30491	317.03	317.17	0.14
FA02773	324.97	325.64	0.67
FF31496	345.21	345.99	0.78

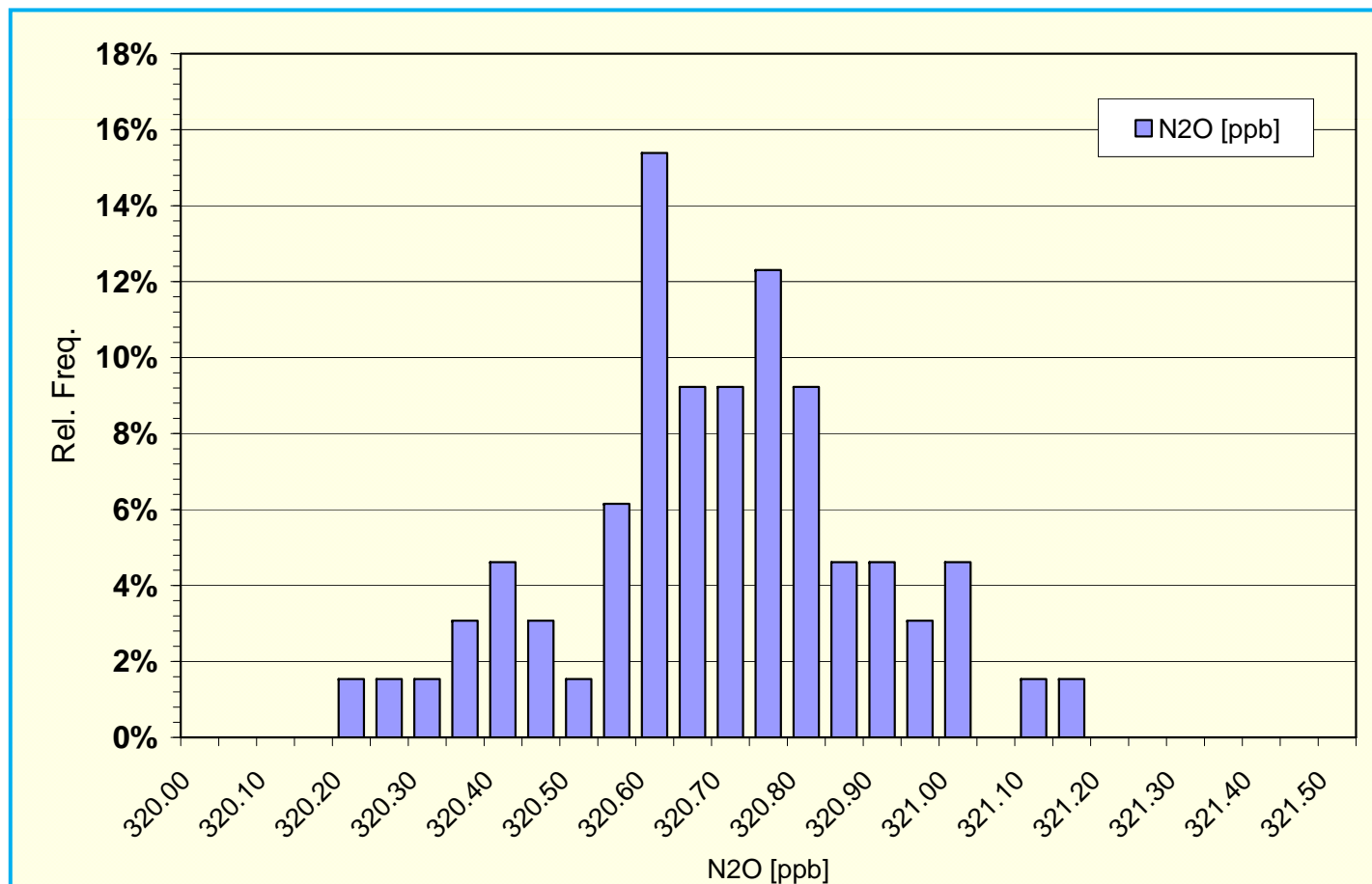


CCQM-K68 N₂O International Comparison (2008)

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

Result of the WCC-N₂O:

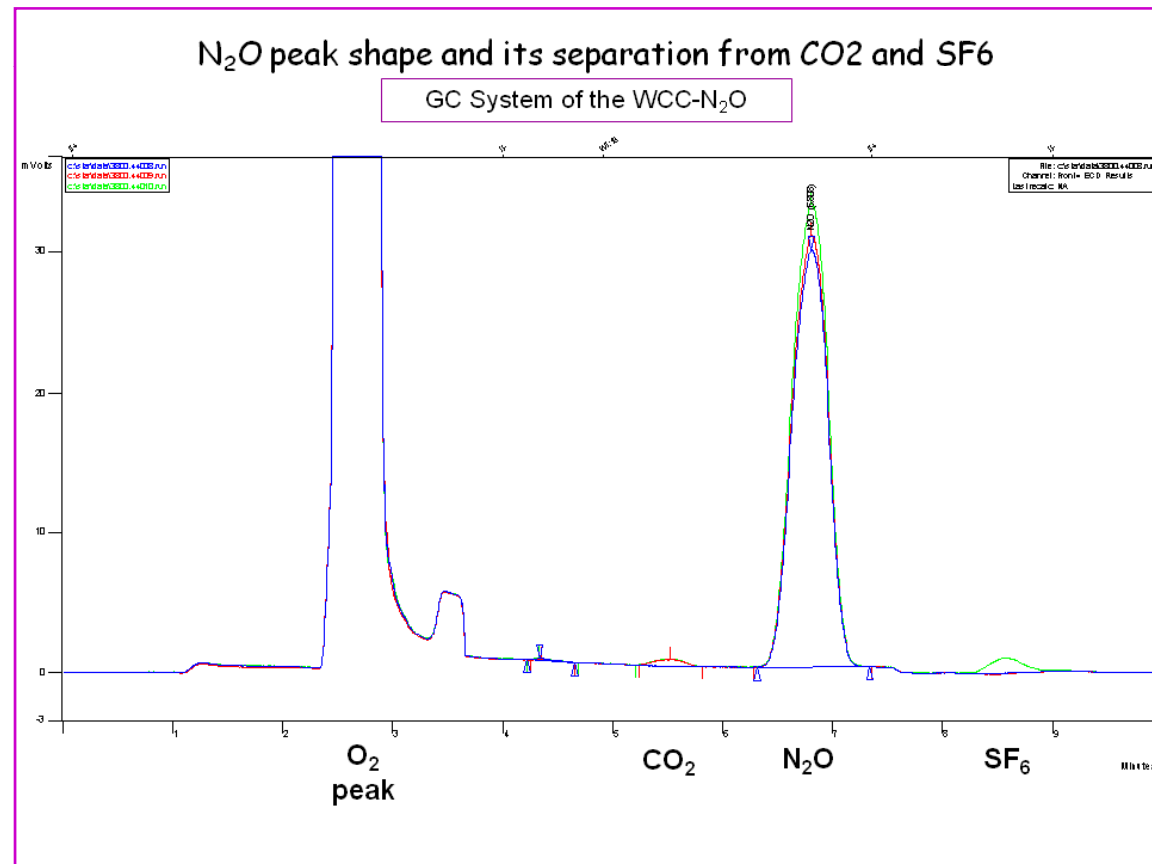
n = 65, rel. std. dev. 0.065 %



CCQM-K68 N₂O International Comparison (2008)

Remarks:

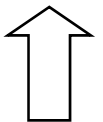
- Focus on N₂O mole fraction only
- 1 level
- No concurrent check of the analytical performance (separation of CO₂ and SF₆, detector response characteristics)



Recalibration of Laboratory Standards by the CCL, Feb 2009

Cyl ID	N2O	Recalibration results (CCL, Brad Hall)			
	before recal.	Mean	Std dev	Rel. std.dev.	old - new
CA06234	293.27★	293.34	0.11	0.04%	-0.07
CA04785	312.42	312.26	0.08	0.03%	0.16
CA06246	320.67	320.58	0.11	0.03%	0.09
CA04800	325.95	325.84	0.09	0.03%	0.11
CA04743	333.23	333.36	0.14	0.04%	-0.13
CA04752	358.10	358.12	0.14	0.04%	-0.02

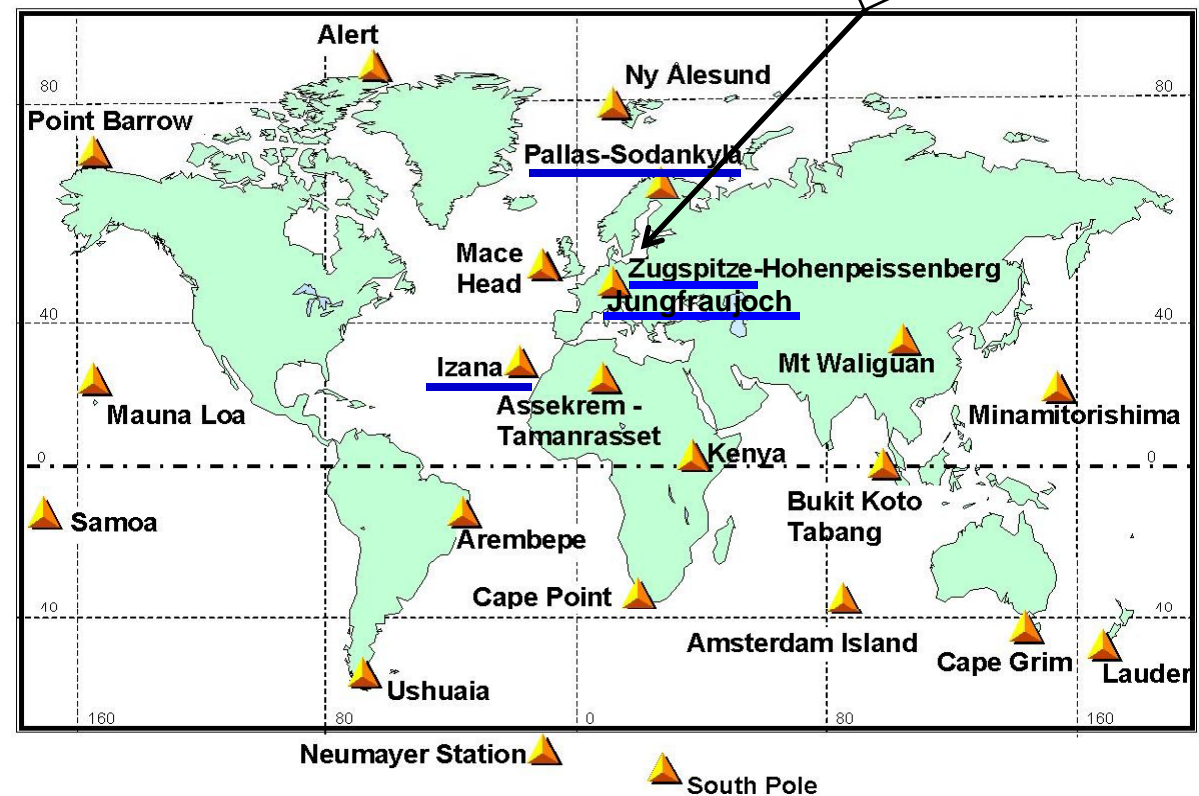
★ Original CCL value lowered by 0.3 ppb based on CCL – WCC.N₂O intercomparison of 5 gas mixtures (TS) in 2007.



4. Audits

Overview on results of 4 audits

- Zugspitze (ZSF)
- Jungfraujoch (JFJ)
- Pallas (PAL)
- Izaña (IZO)



Shape of chromatograms

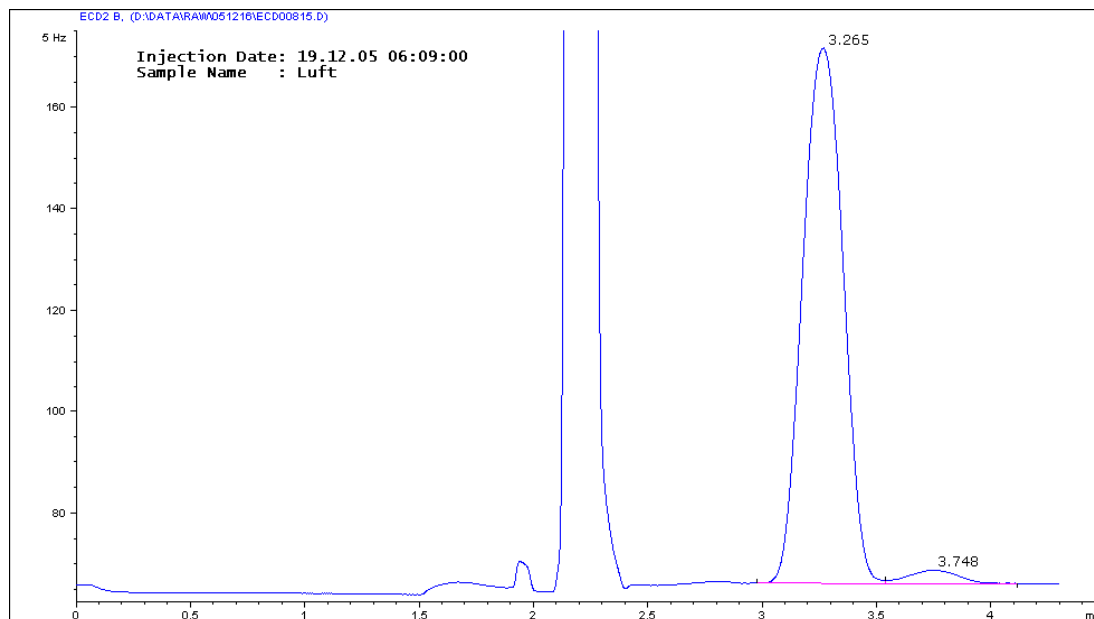


Fig. 4.3: Example of a chromatogram obtained with the ECD channel of the GC system.

ZSF

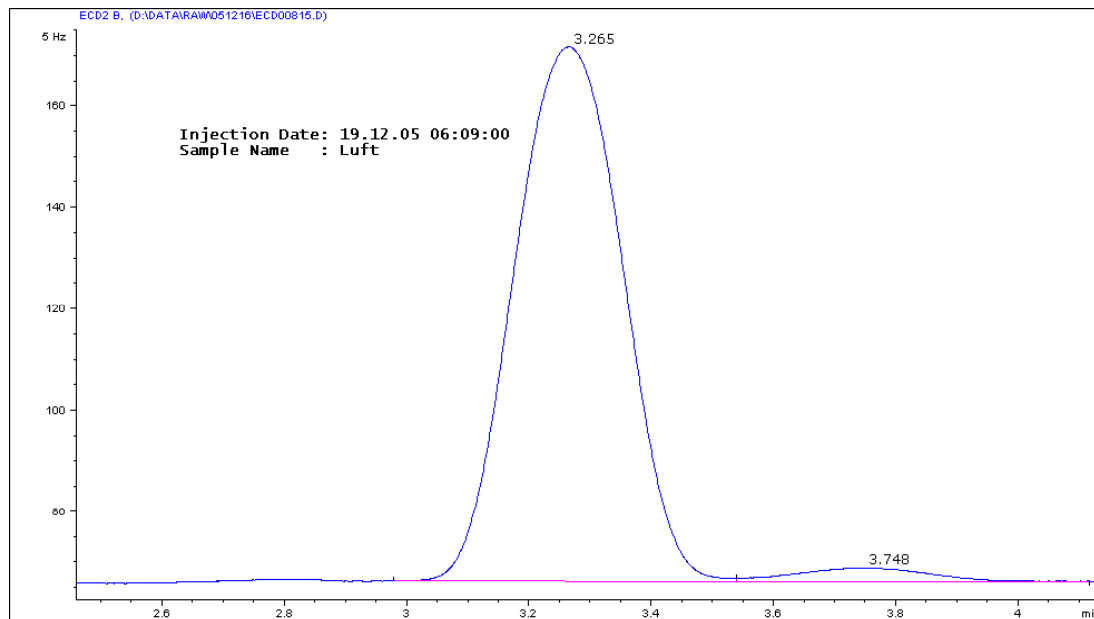


Fig. 4.4: Zoom into the chromatogram of Fig. 4.3.

JFJ

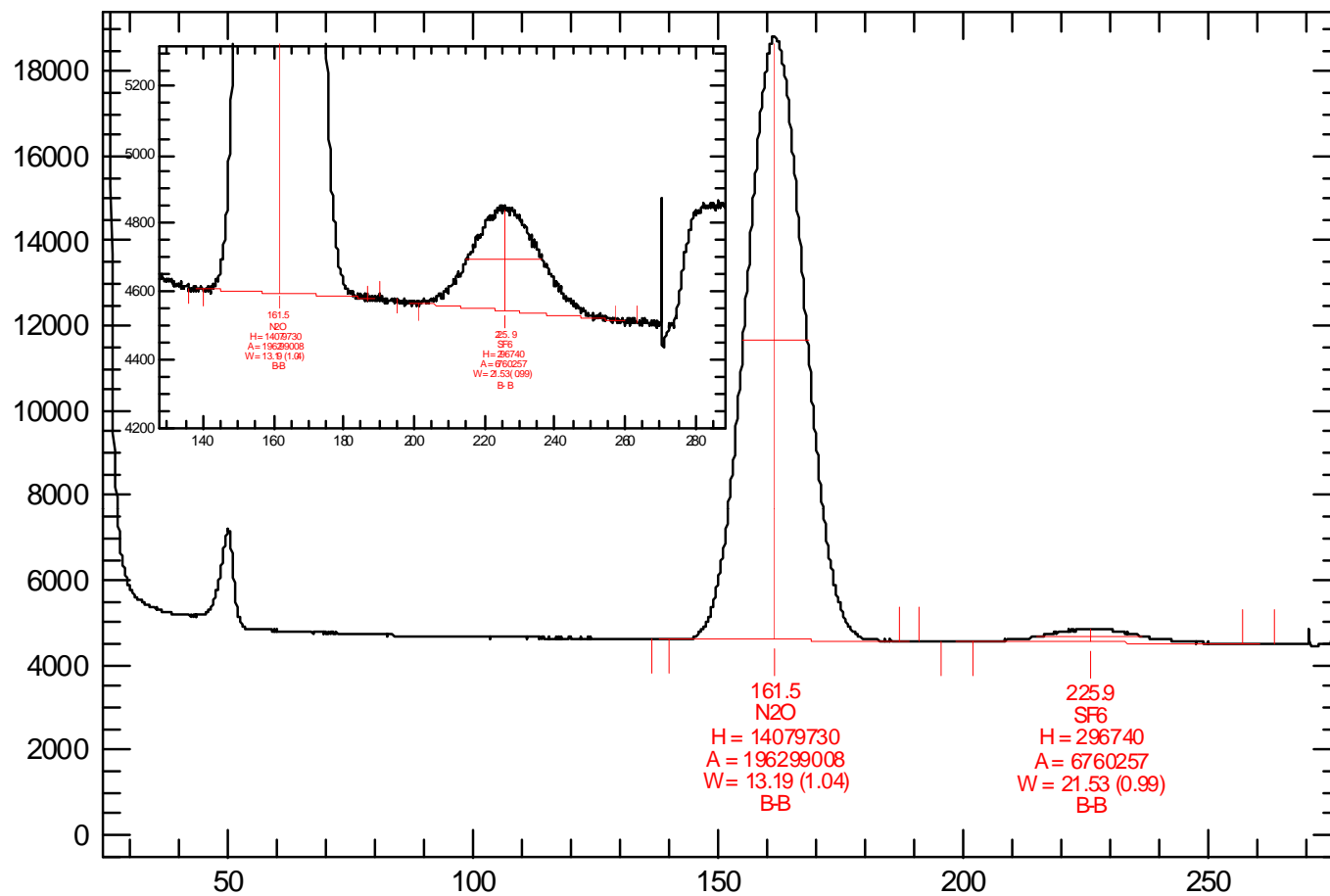
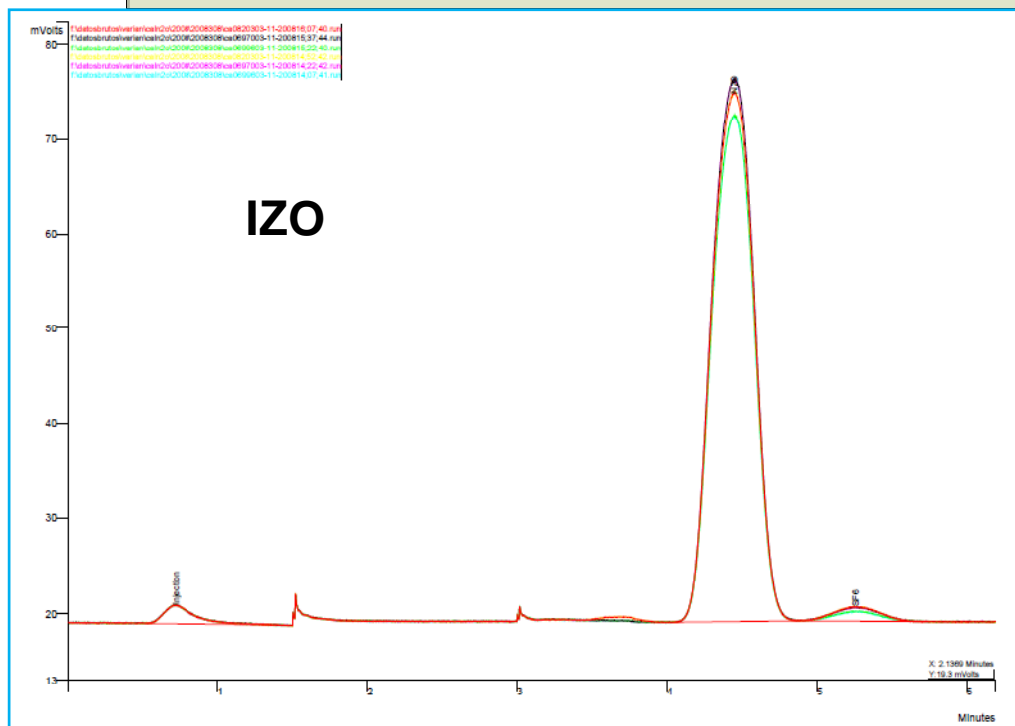
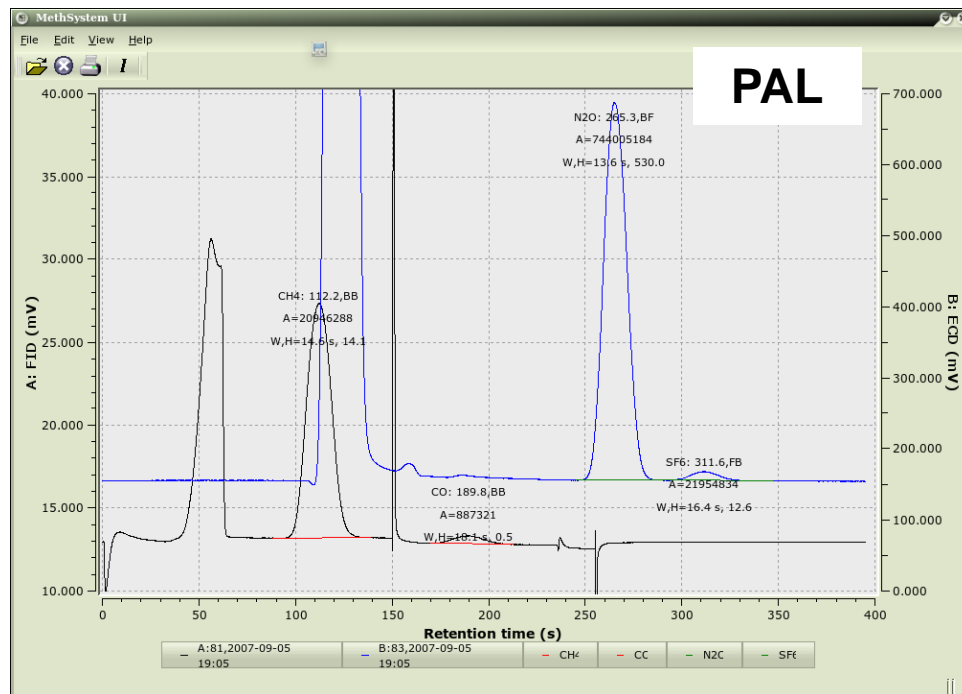
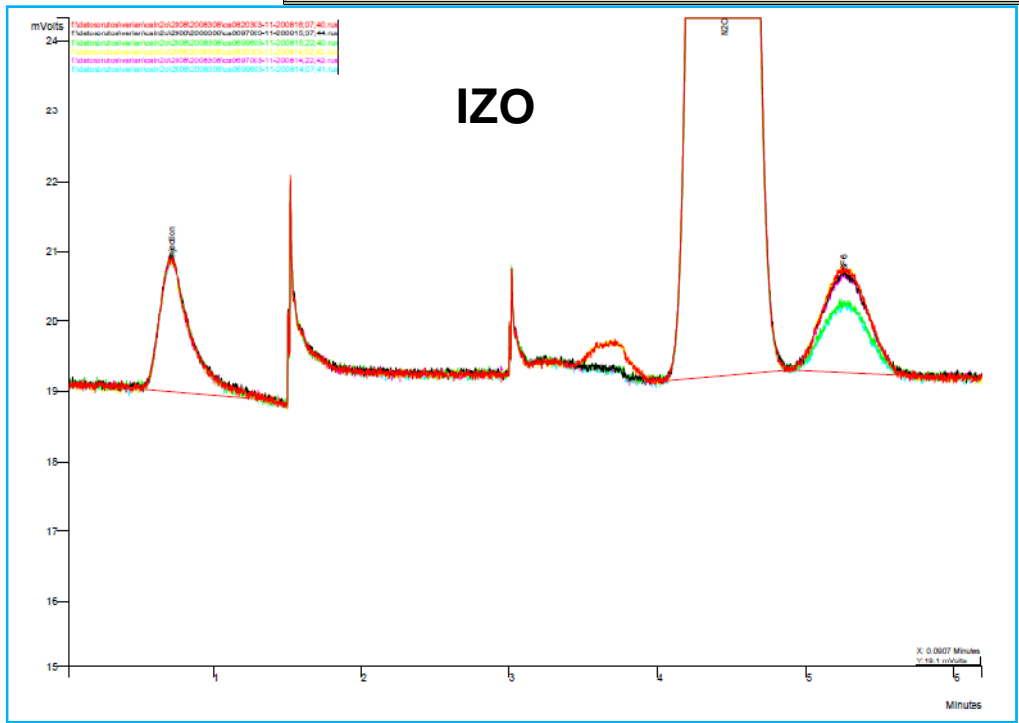
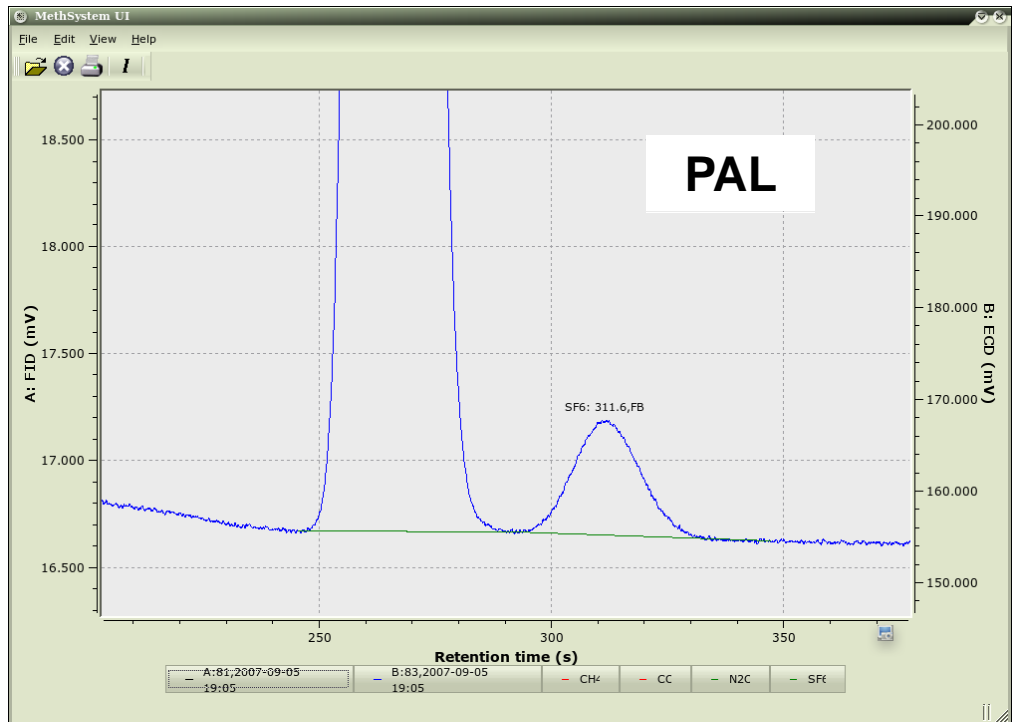
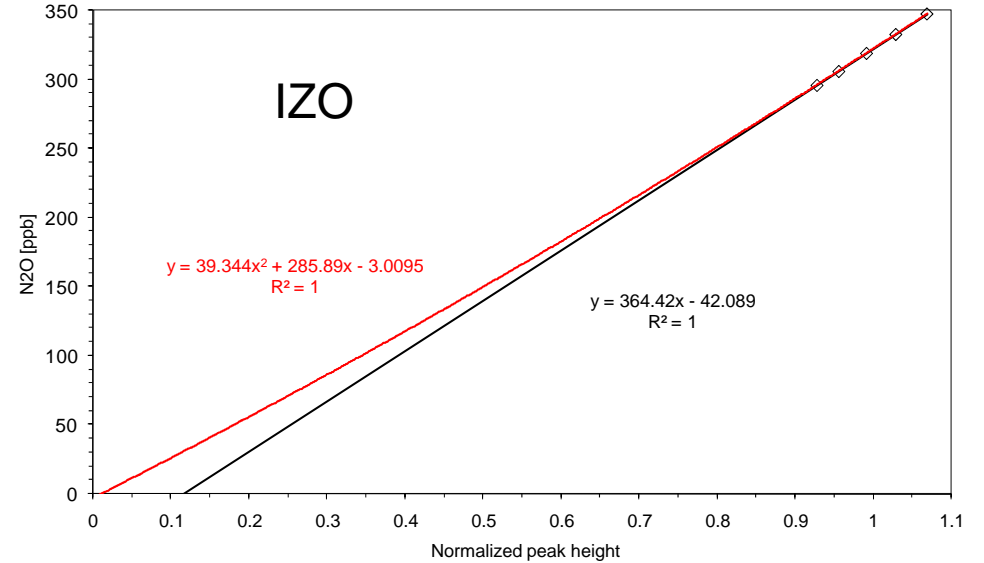
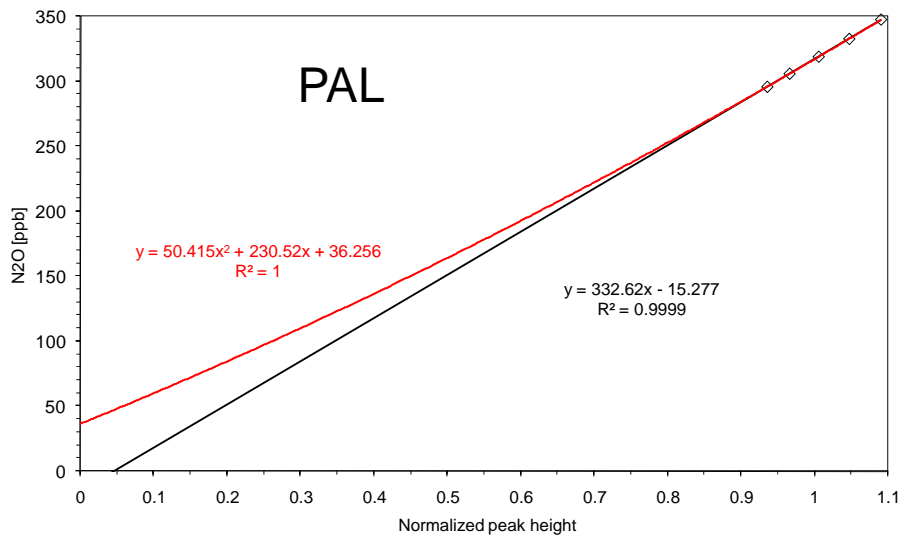
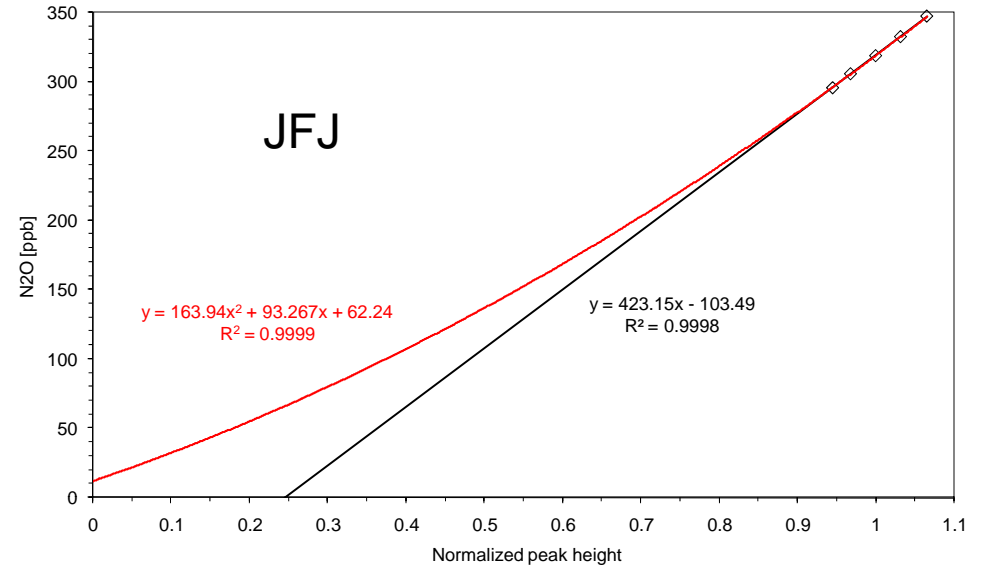
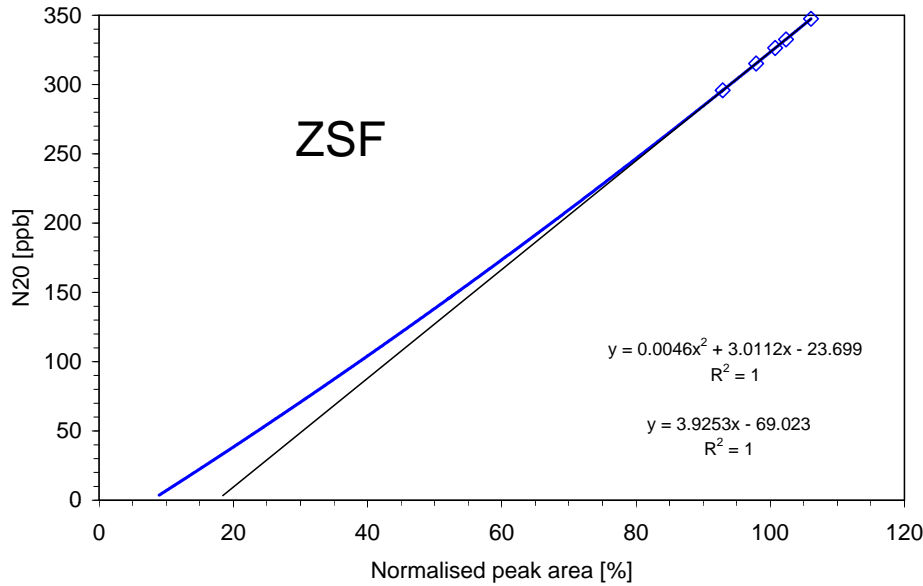


Fig. 1. Example of a chromatogram obtained with the ECD channel of the GC system. The inset enlarges the peaks for better visibility. The mole fractions of the working standard sample were 321.6 ppb N₂O and 5.5 ppt SF₆. Figure taken from a draft version of a publication (Steinbacher et al., 2008).





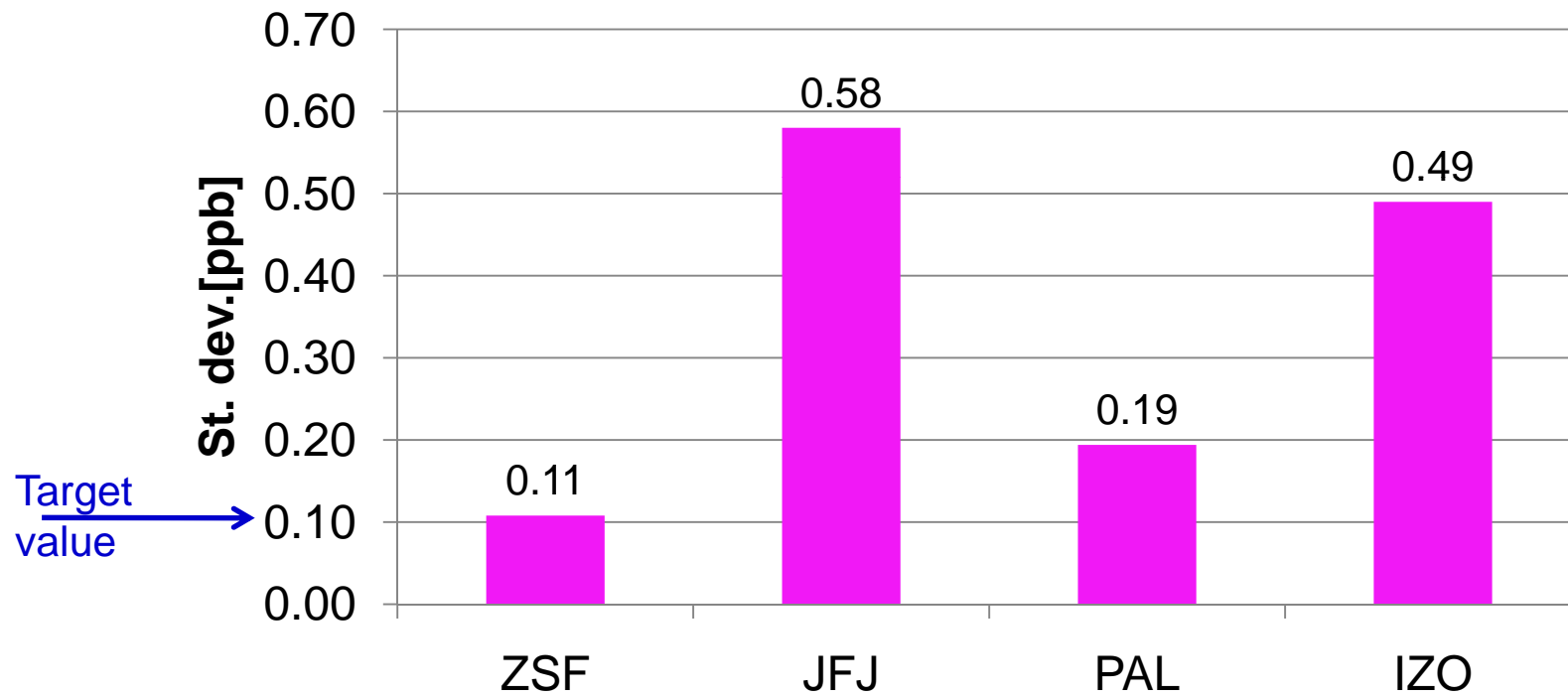
Comparison of ECD response curves (extrapolated)



Range of standards: 296 - 347 ppb

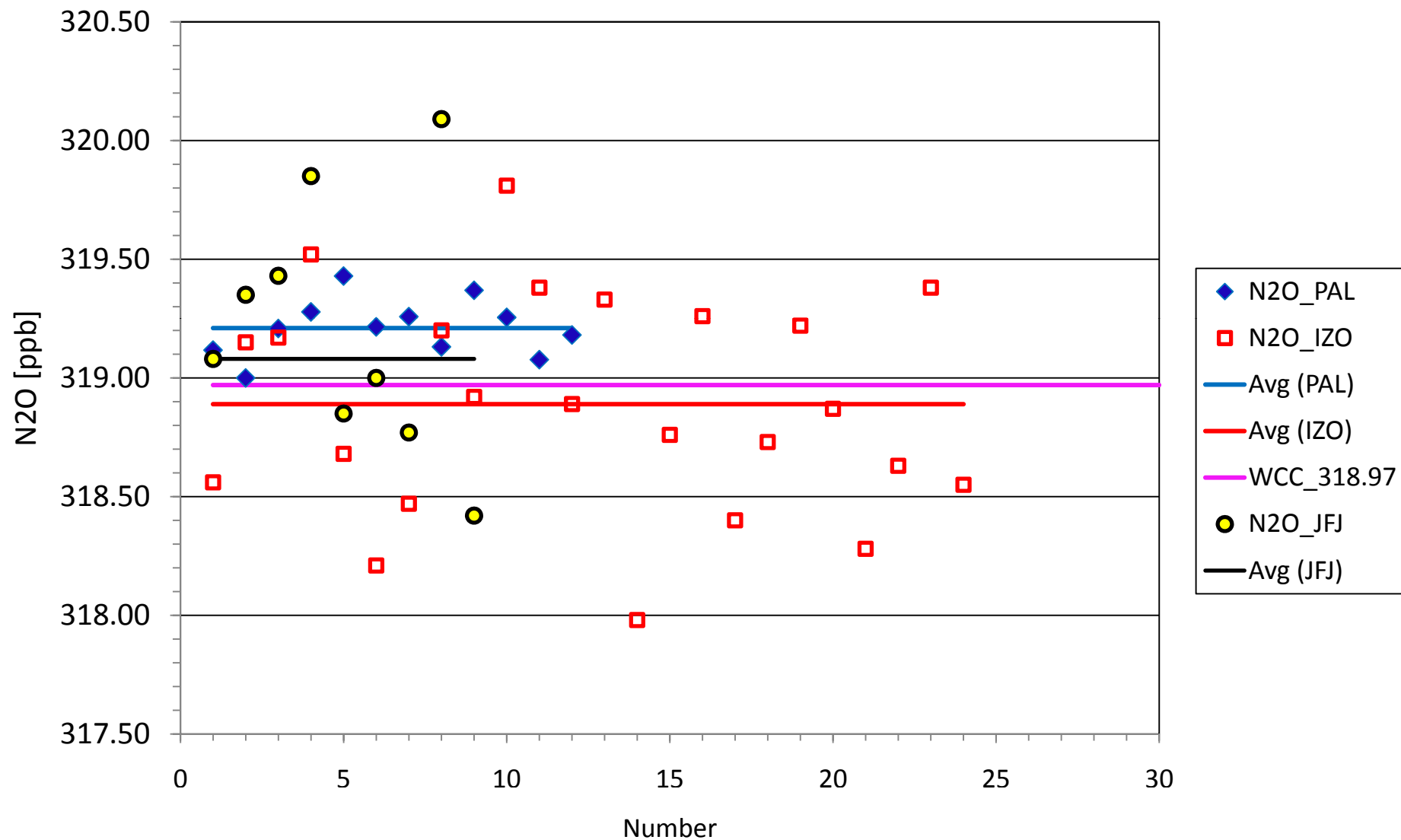
Comparison of standard deviations

Comparison of standard deviations
(average of audit intercomparison of 5 N₂O standards)



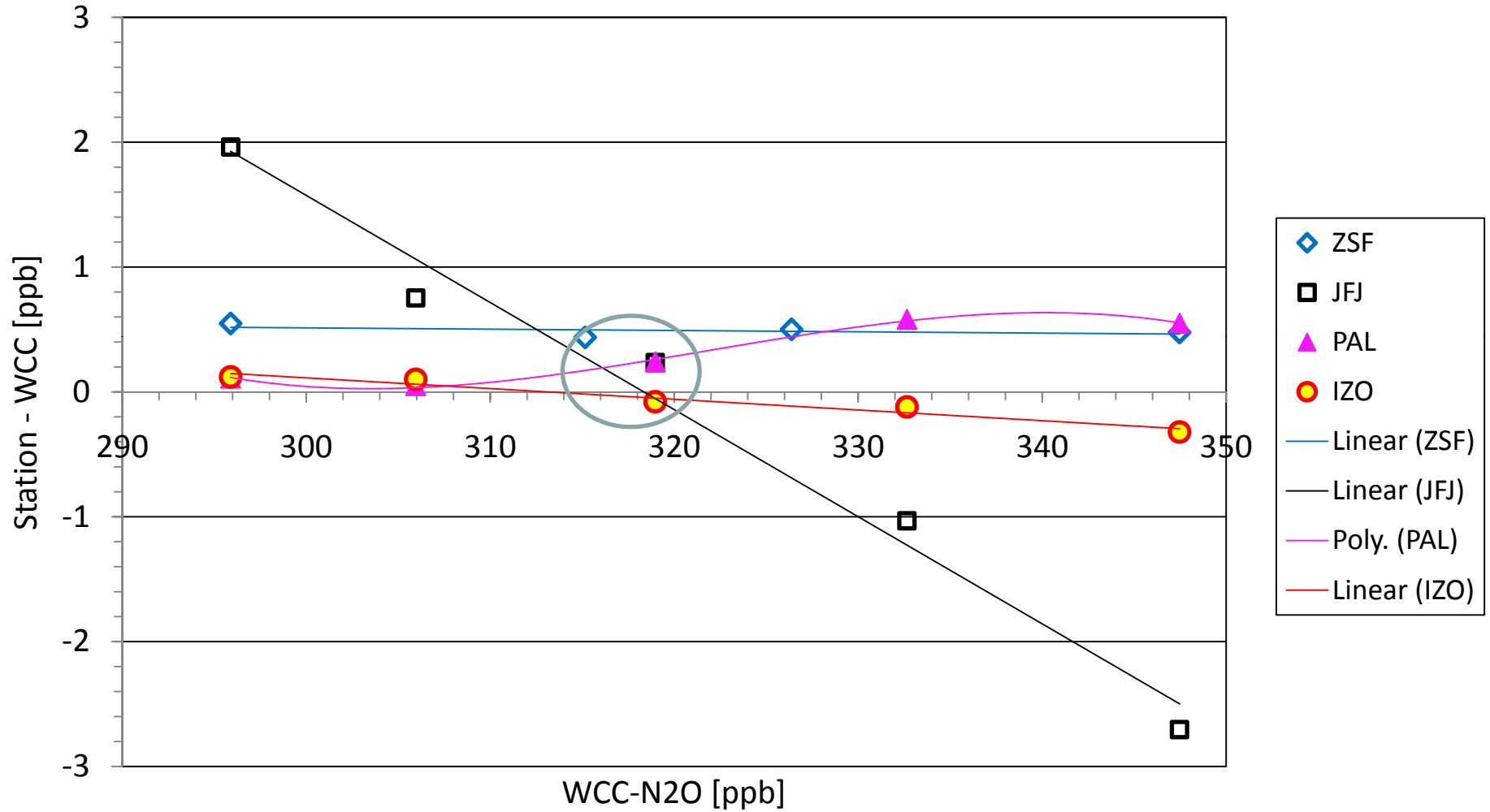
Intercomparison: Individual analysis results for 319 ppb

Comparison of audit results

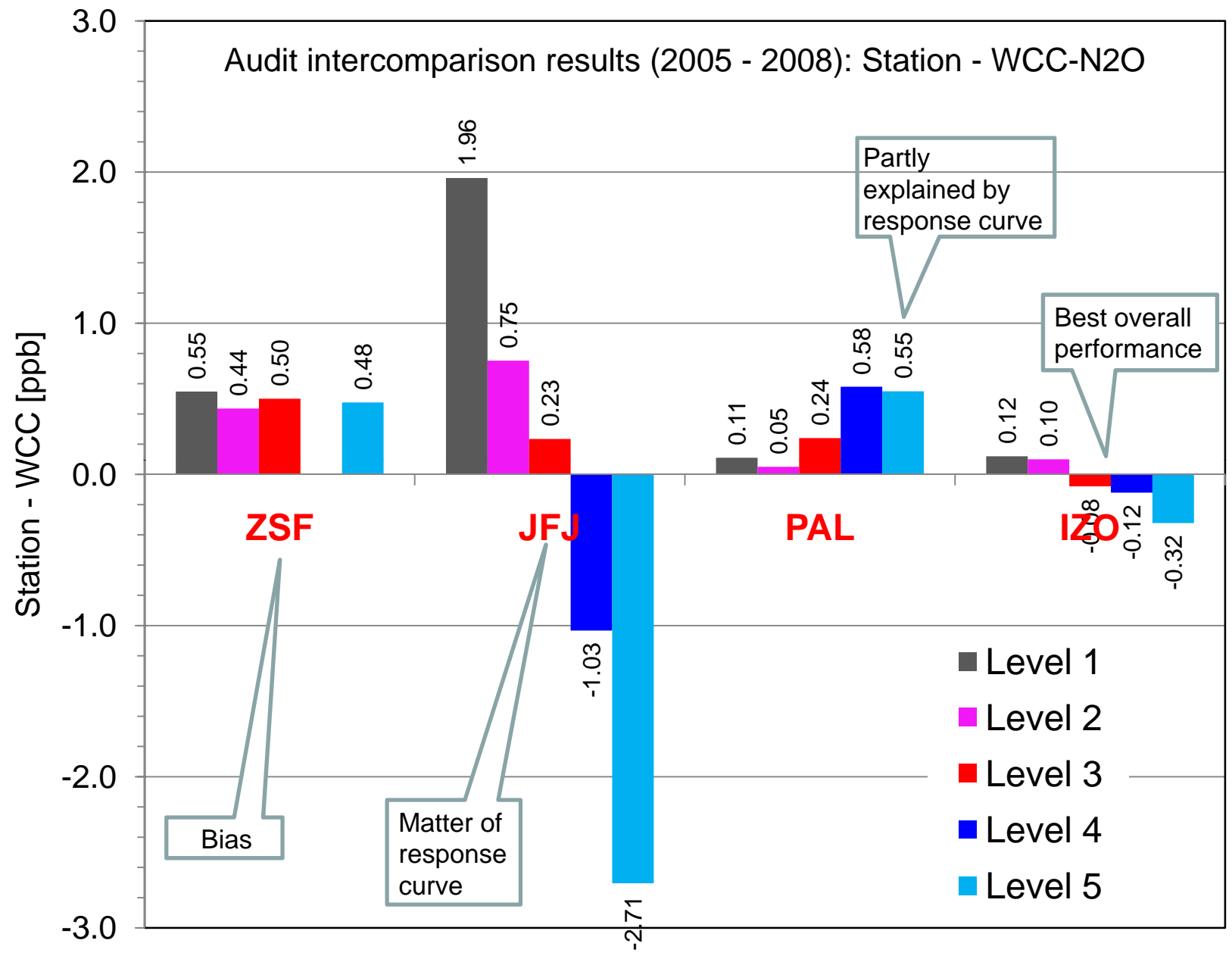


Intercomparison: Differences between reported and assigned values

Audit intercomparisons: N2O differences, Station - WCC-N2O



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



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.**