Report of the WCC-N_2O

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WCC-N_2O

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

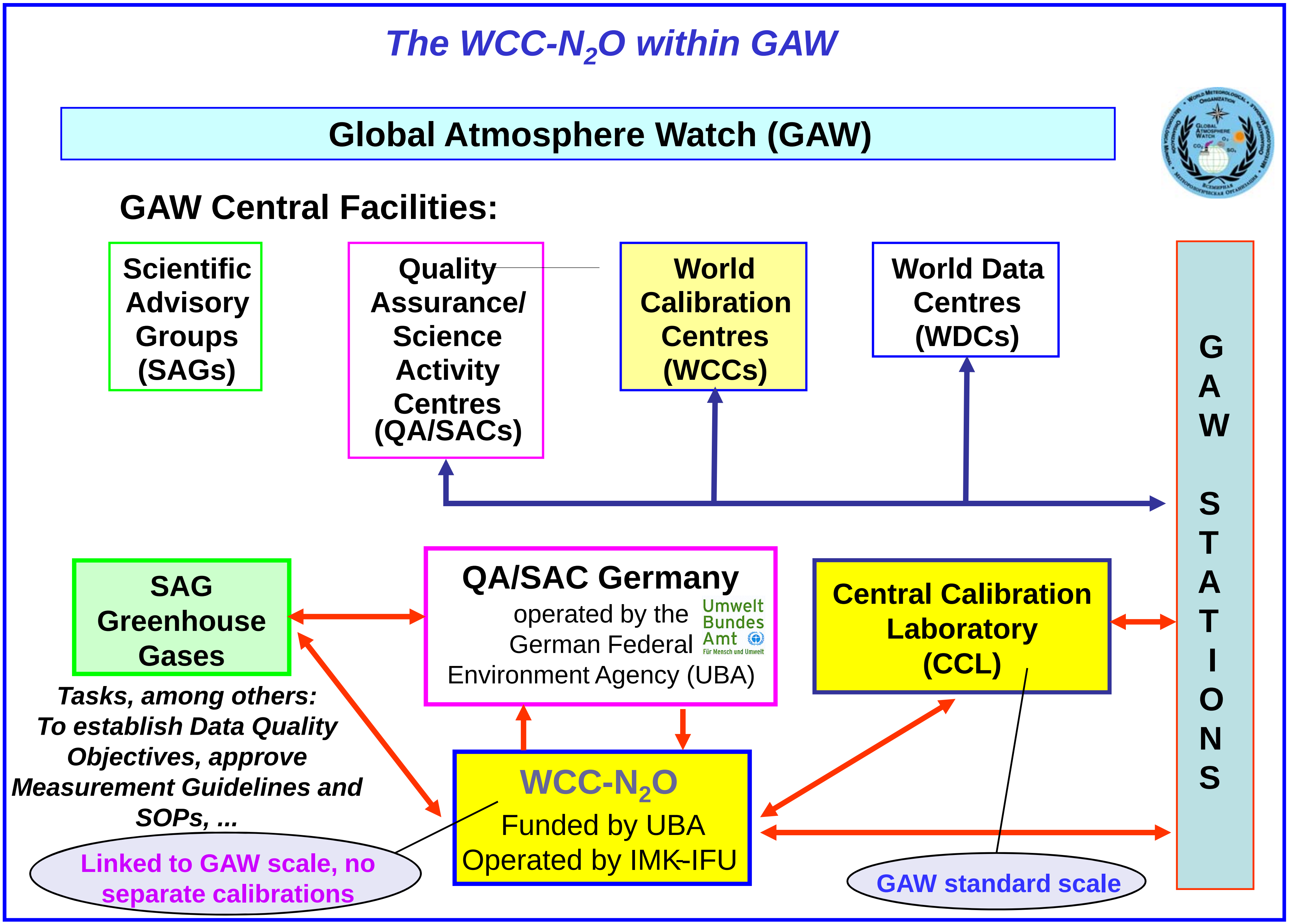
Report of the World Calibration Centre for Nitrous Oxide

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

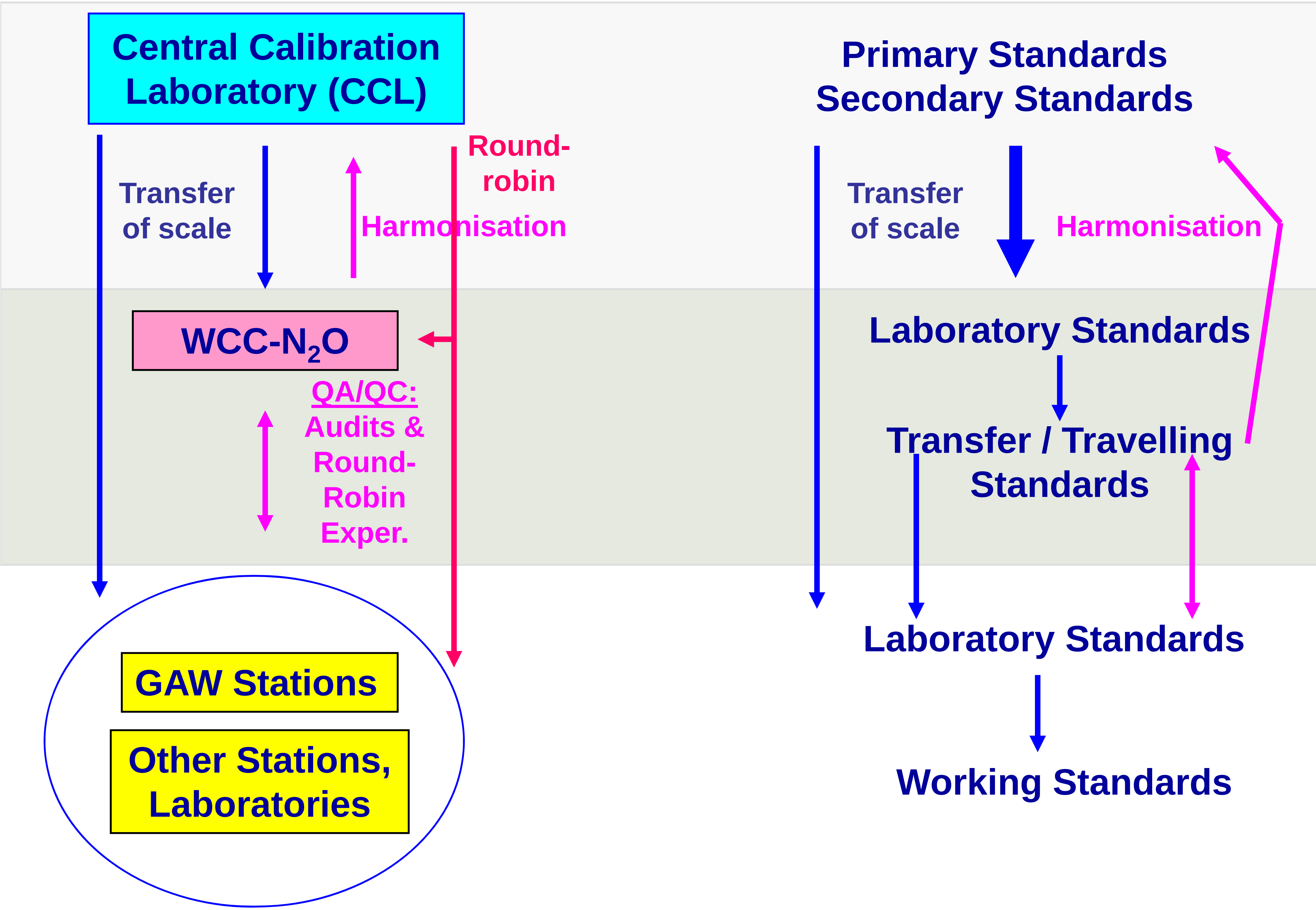
WCC-N_2O website: http://imk-ifu.fzk.de/wcc-n2o/

1. Introduction



The WCC-N_2O 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)
GAW STATIONS
SAG Greenhouse Gases
Tasks, among others: To establish Data Quality Objectives, approve Measurement Guidelines and SOPs, ...
QA/SAC Germany
operated by the German Federal Environment Agency (UBA)
Umwelt Bundes Amt
Für Mensch und Umwelt
Central Calibration Laboratory (CCL)
WCC-N_2O
Funded by UBA
Operated by IMK-IFU
Linked to GAW scale, no separate calibrations
GAW standard scale

Traceability of Calibrations and Audits



2. Contributions to GAW Documents and Training Courses

Involvement of the WCC-N_2O 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

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

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-N_2O-calibrated WCC-Empa travelling standards. →
- CCQM-K68 N_2O 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_2O)

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)

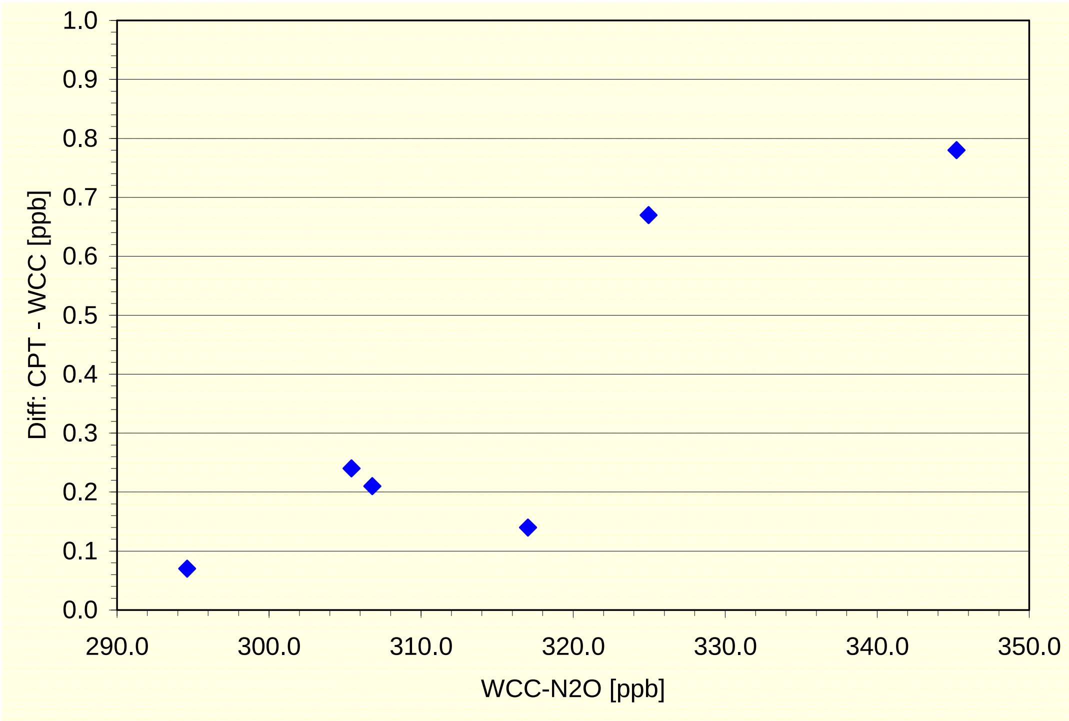
IHALCE results of the WCC-N_2O:
N_2O mole fractions [ppb] expressed in NOAA-2000 scale

Tank number	#3527	#3536	#3538
WCC-N_2O [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-N_2O 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_2O [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

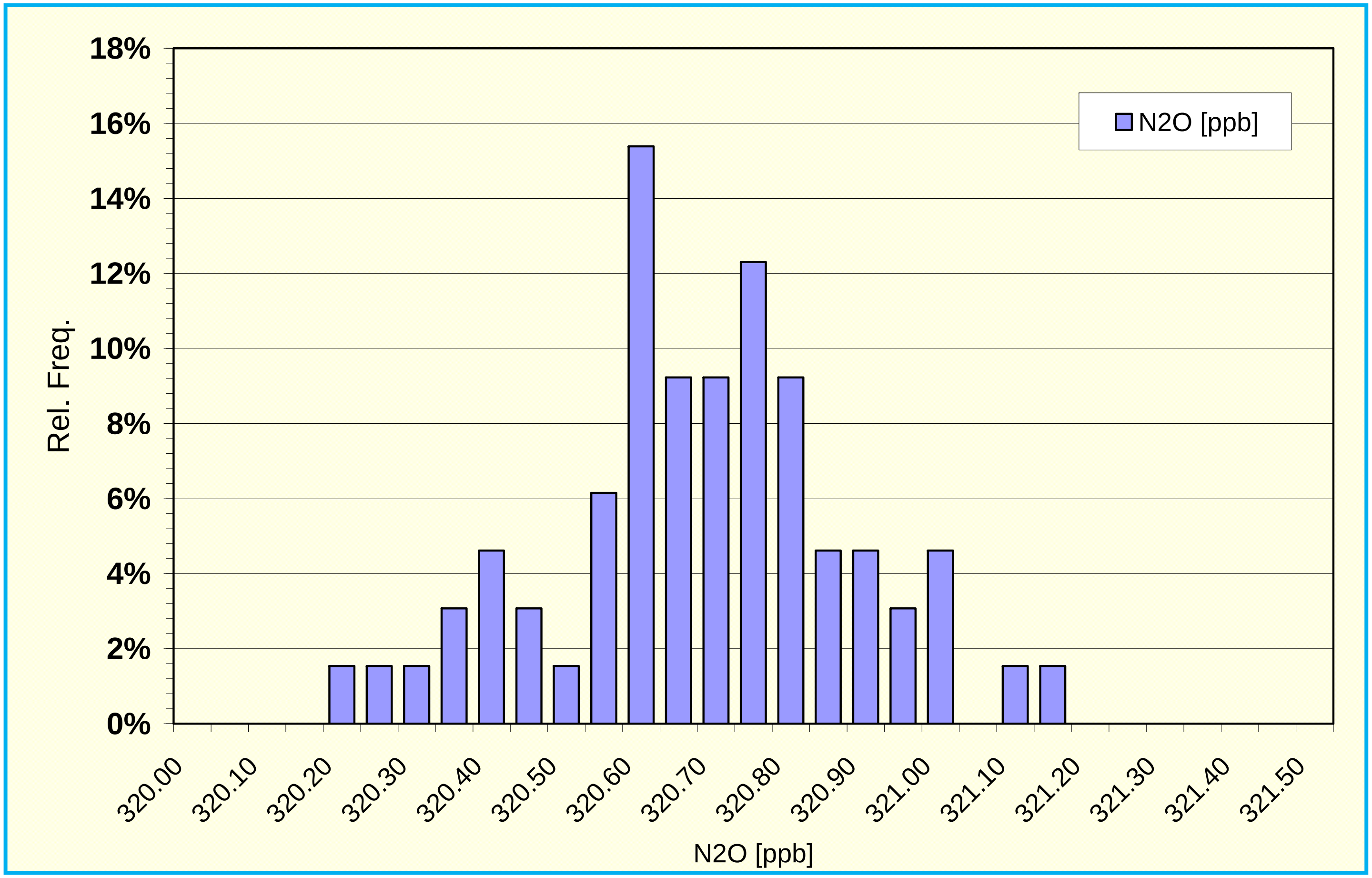


CCQM-K68 N_2O International Comparison (2008)

1 cylinder with gas mixture containing nominally 320 ppb N_2O, 21 % mol/mol oxygen and nitrogen as balance.

Result of the WCC-N_2O:

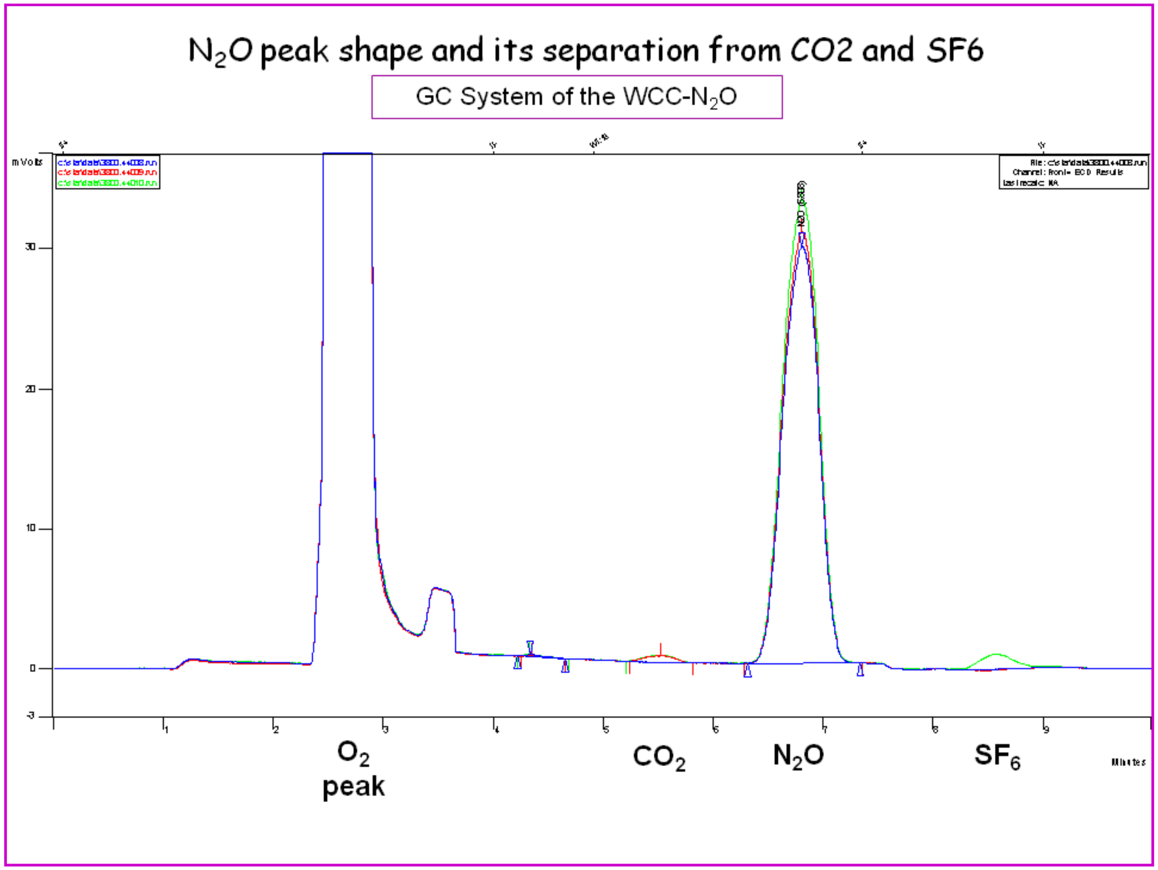
n = 65, rel. std. dev. 0.065 %



CCQM-K68 N_2O International Comparison (2008)

Remarks:

- o Focus on N_2O mole fraction only
- o 1 level
- o No concurrent check of the analytical performance (separation of CO_2 and SF_6, detector response characteristics)



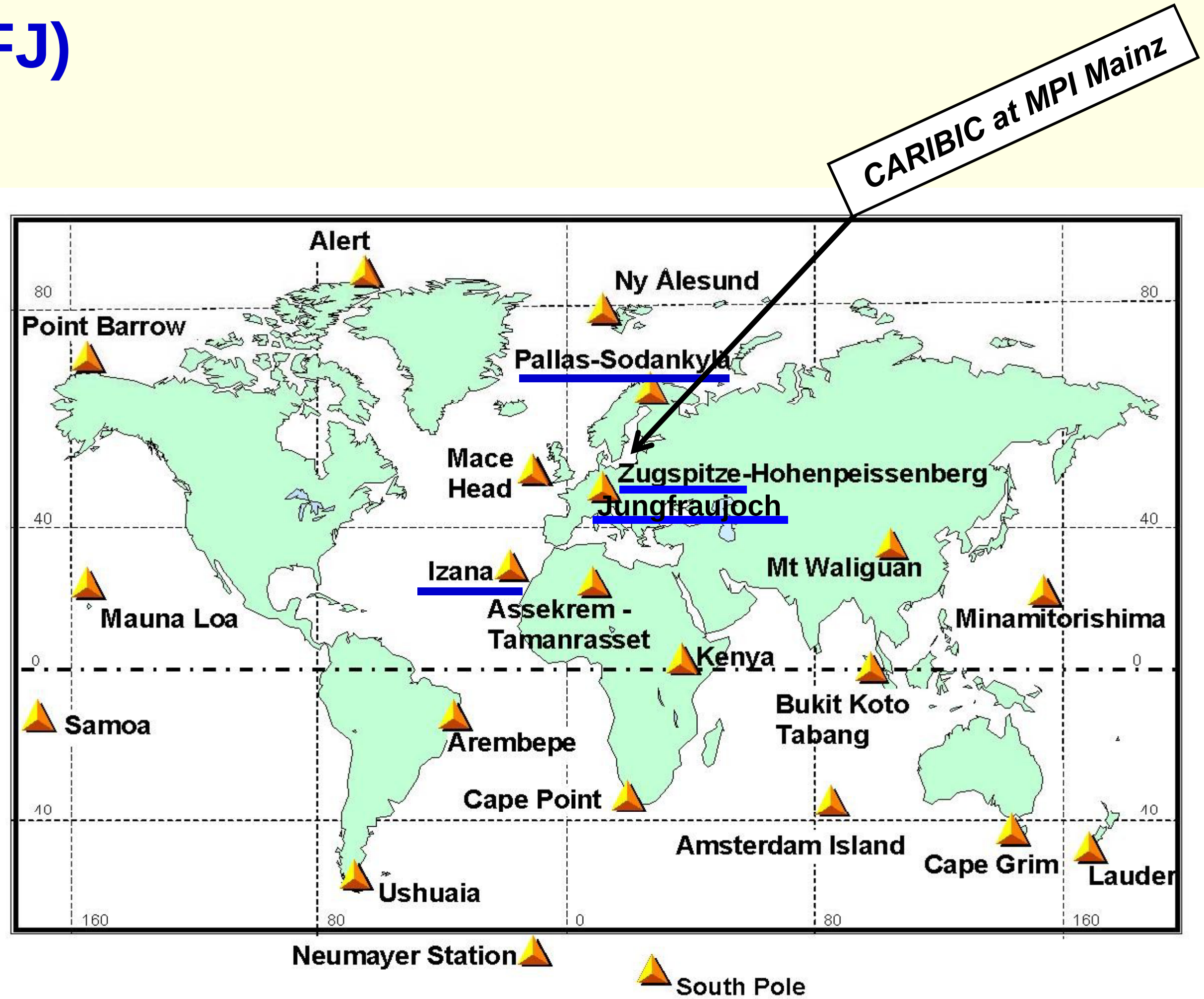
Recalibration of Laboratory Standards by the CCL, Feb 2009					
	N2O	Recalibration results (CCL, Brad Hall)			
Cyl ID	before recal.	Mean	Std dev	Rel. std.dev.	old - new
CA06234	293.27★	293.34	0.11	0.04%	-0.07
CA04785	312.42	312.26	0.08	0.03%	0.16
CA06246	320.67	320.58	0.11	0.03%	0.09
CA04800	325.95	325.84	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.N_2O 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

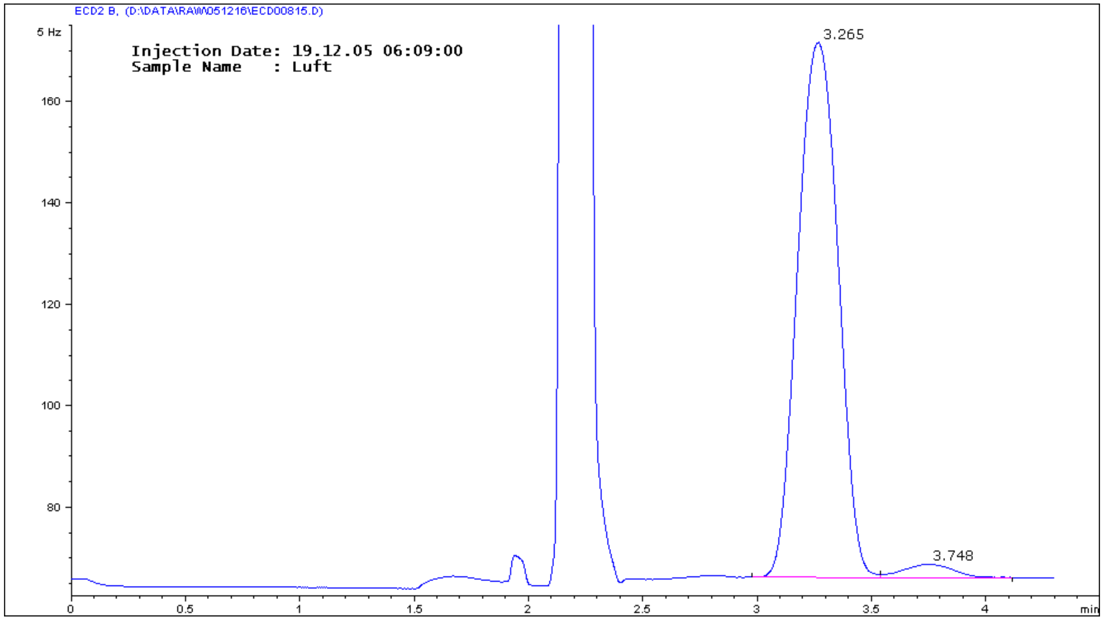


Fig. 4.3: Example of a chromatogram obtained with the ECD channel of the GC system.

ZSF

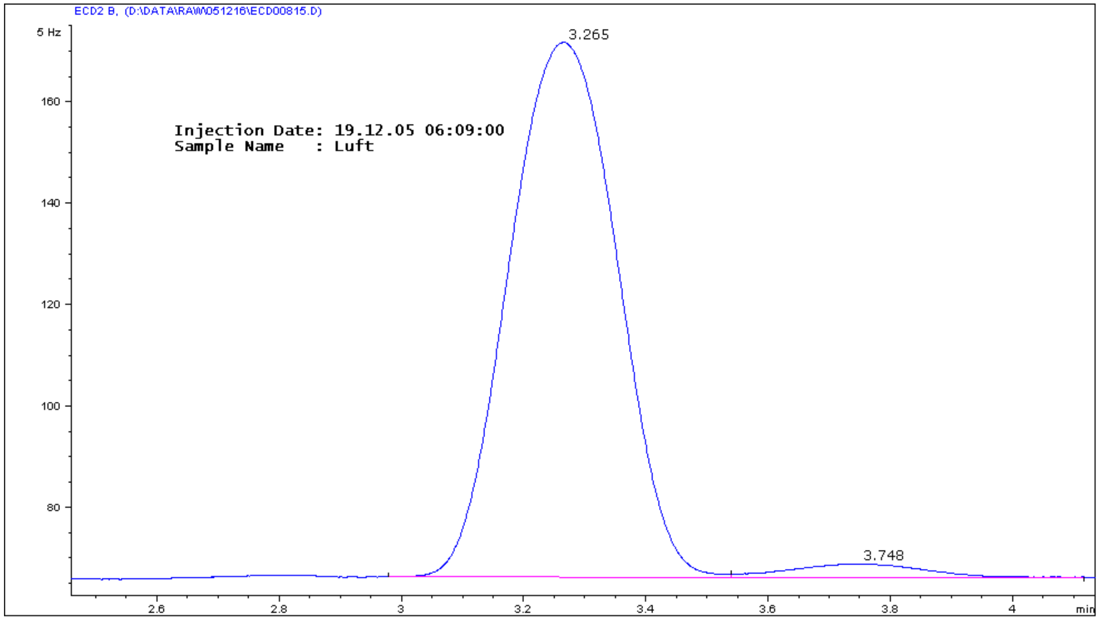


Fig. 4.4: Zoom into the chromatogram of Fig. 4.3.

JFJ

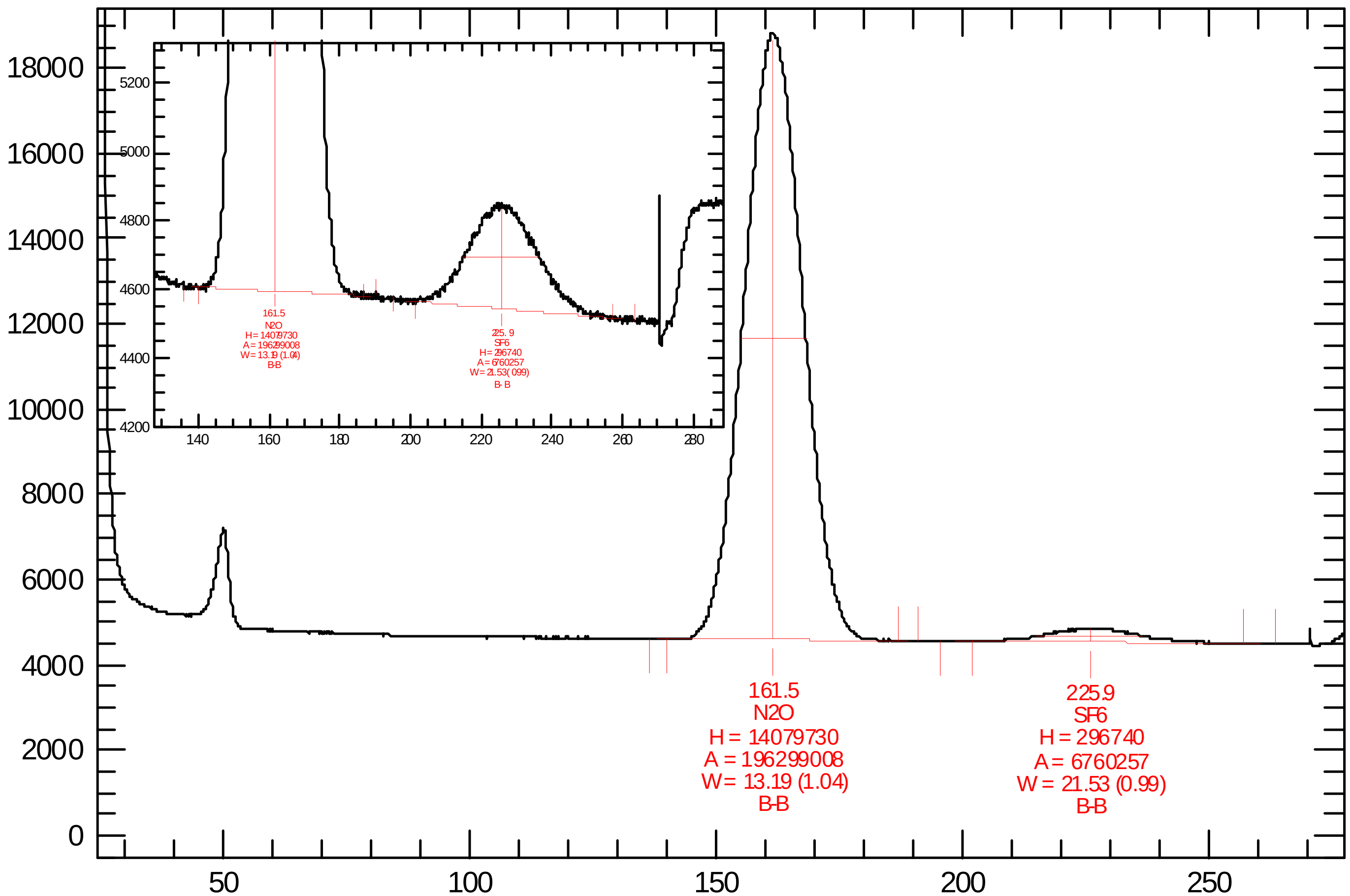
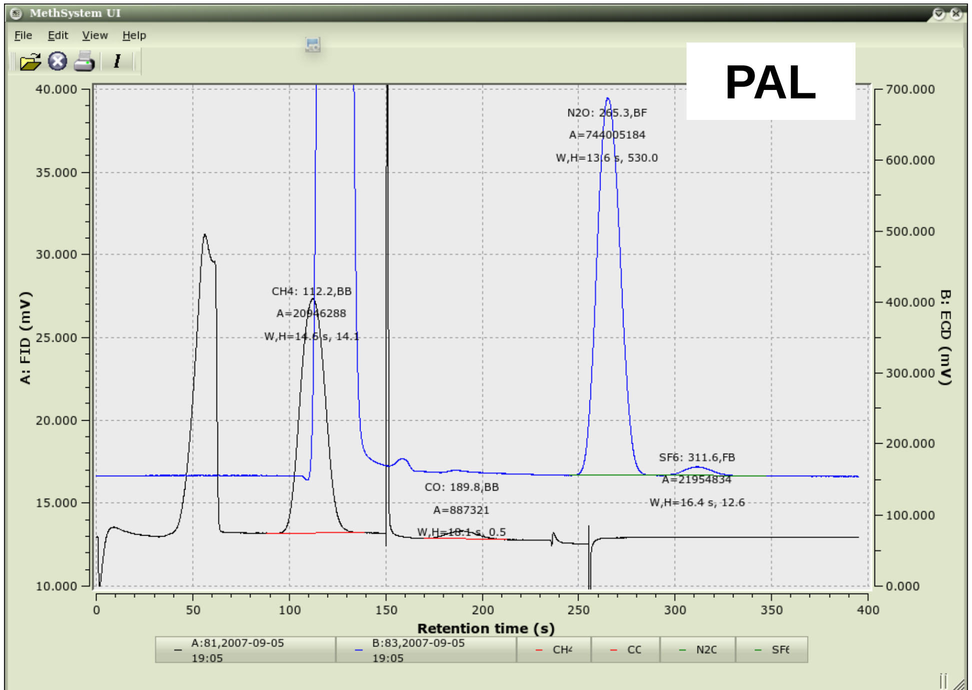
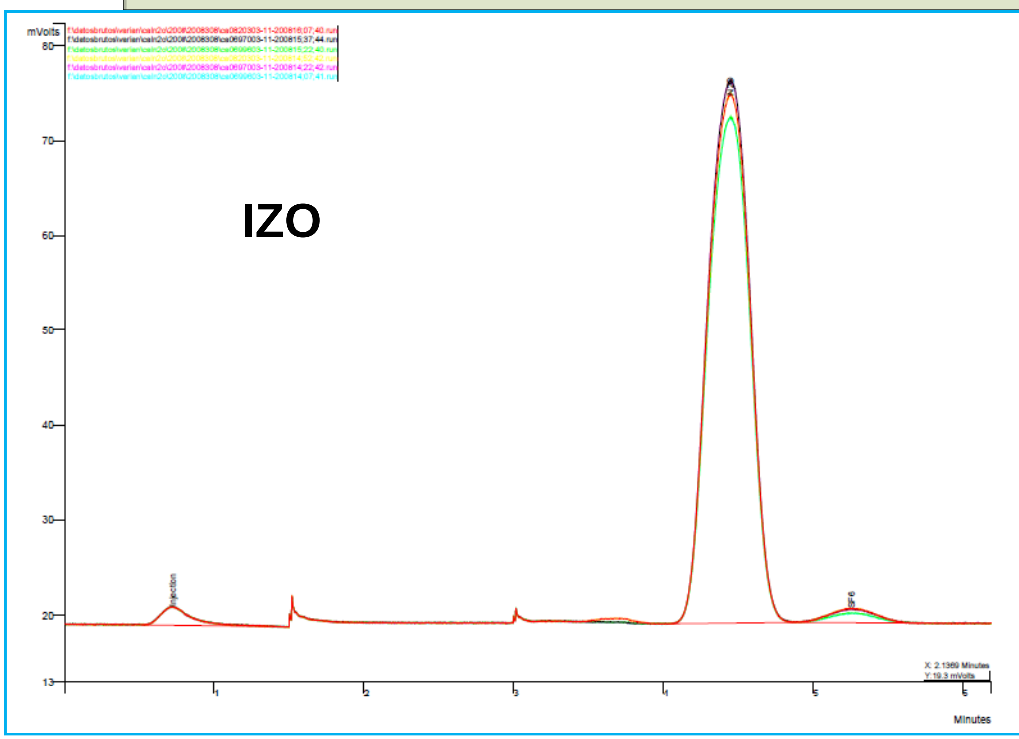
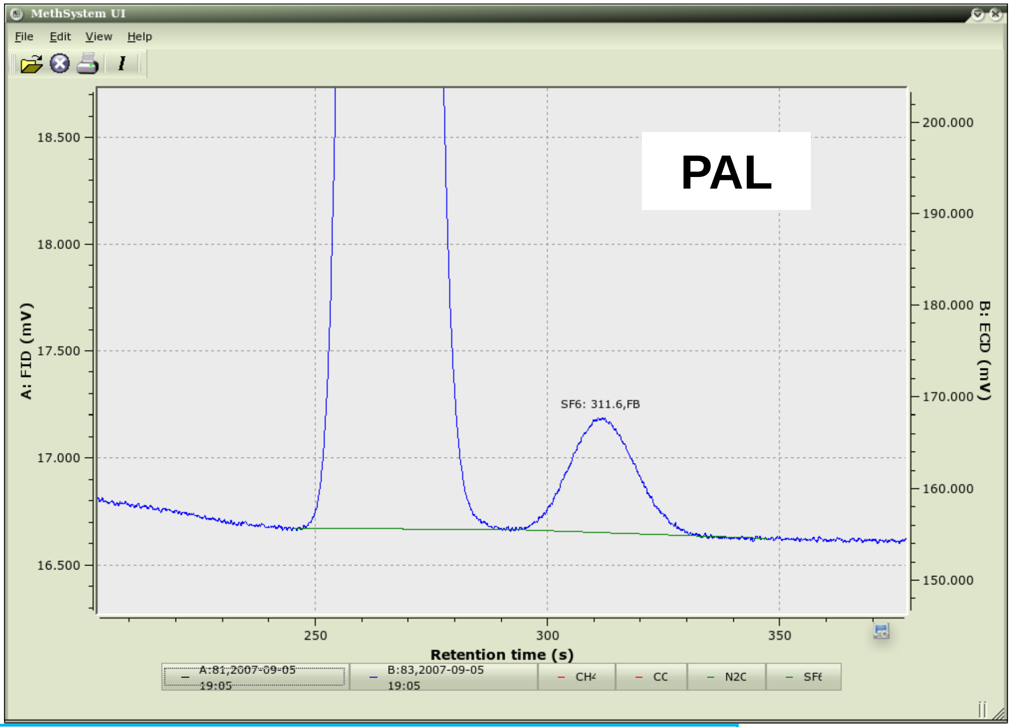
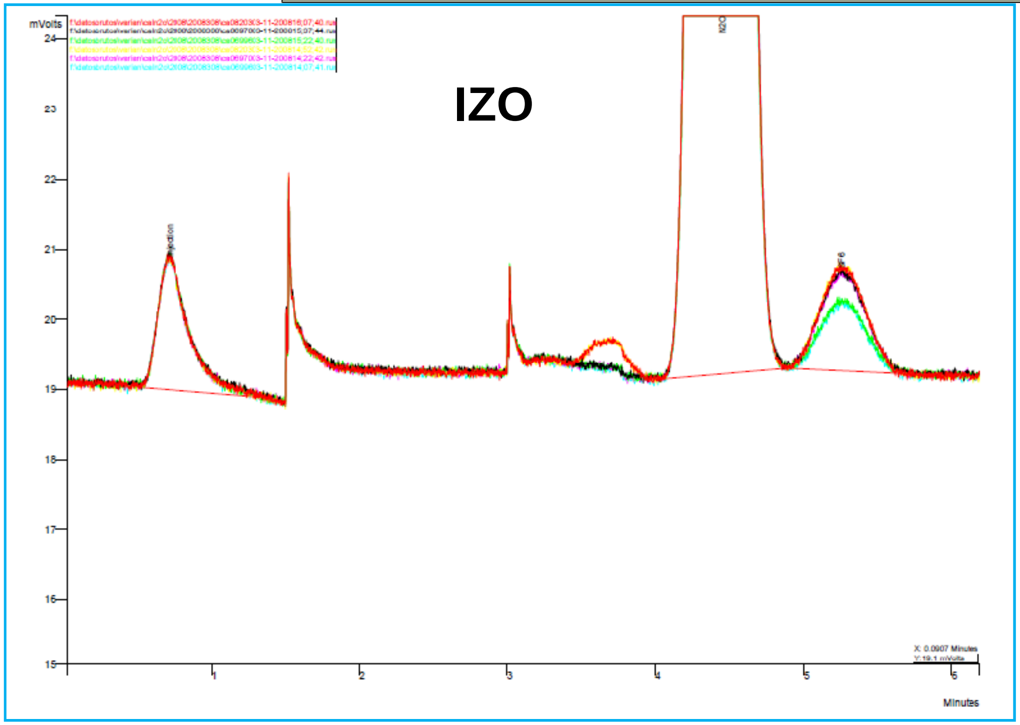


Fig. 1. Example of a chromatogram obtained with the ECD channel of the GC system. The inset enlarges the peaks for better visibility. The mole fractions of the working standard sample were 321.6 ppb N_2O and 5.5 ppt SF_6. Figure taken from a draft version of a publication (Steinbacher et al., 2008).

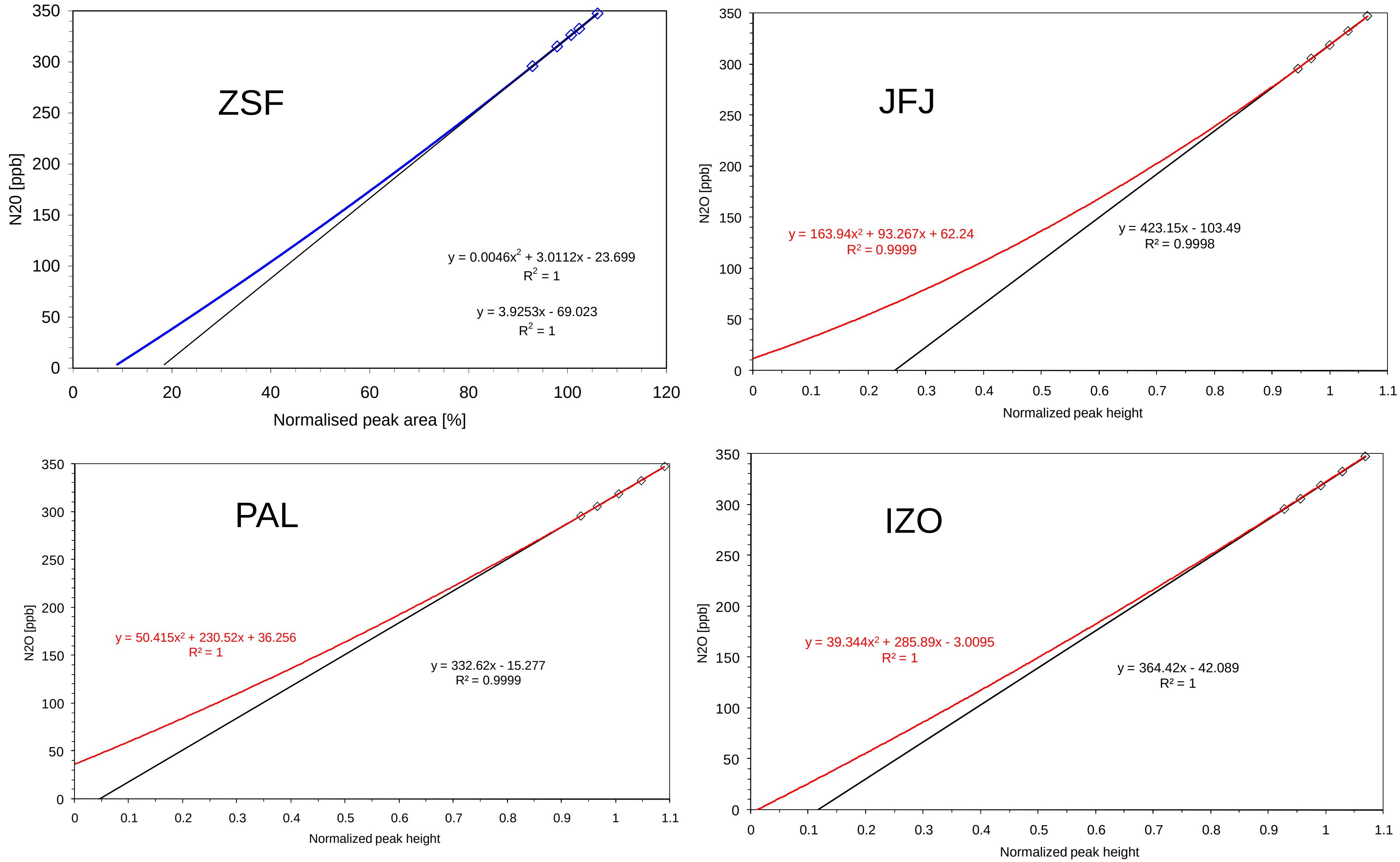

MethSystem UI
File
Edit
View
Help
PAL
A: FID (mV)
B: ECD (mV)
Retention time (s)
N2O: 265.3,BF
A=744005184
W,H=13.6 s, 530.0
CH4: 112.2,BB
A=20946288
W,H=14.6 s, 14.1
CO: 189.8,BB
A=887321
W,H=10.1 s, 0.5
SF6: 311.6,FB
A=21954834
W,H=16.4 s, 12.6
A:81,2007-09-05 19:05
B:83,2007-09-05 19:05
CH4
CC
N2C
SF6


IZO
mVolts
Minutes


MethSystem UI
File Edit View Help
PAL
SF6: 311.6,FB
A: FID (mV)
B: ECD (mV)
18.500
18.000
17.500
17.000
16.500
200.000
190.000
180.000
170.000
160.000
150.000
250
300
350
Retention time (s)
A:81,2007-09-05 19:05
B:83,2007-09-05 19:05
CH4
CC
N2C
SF6

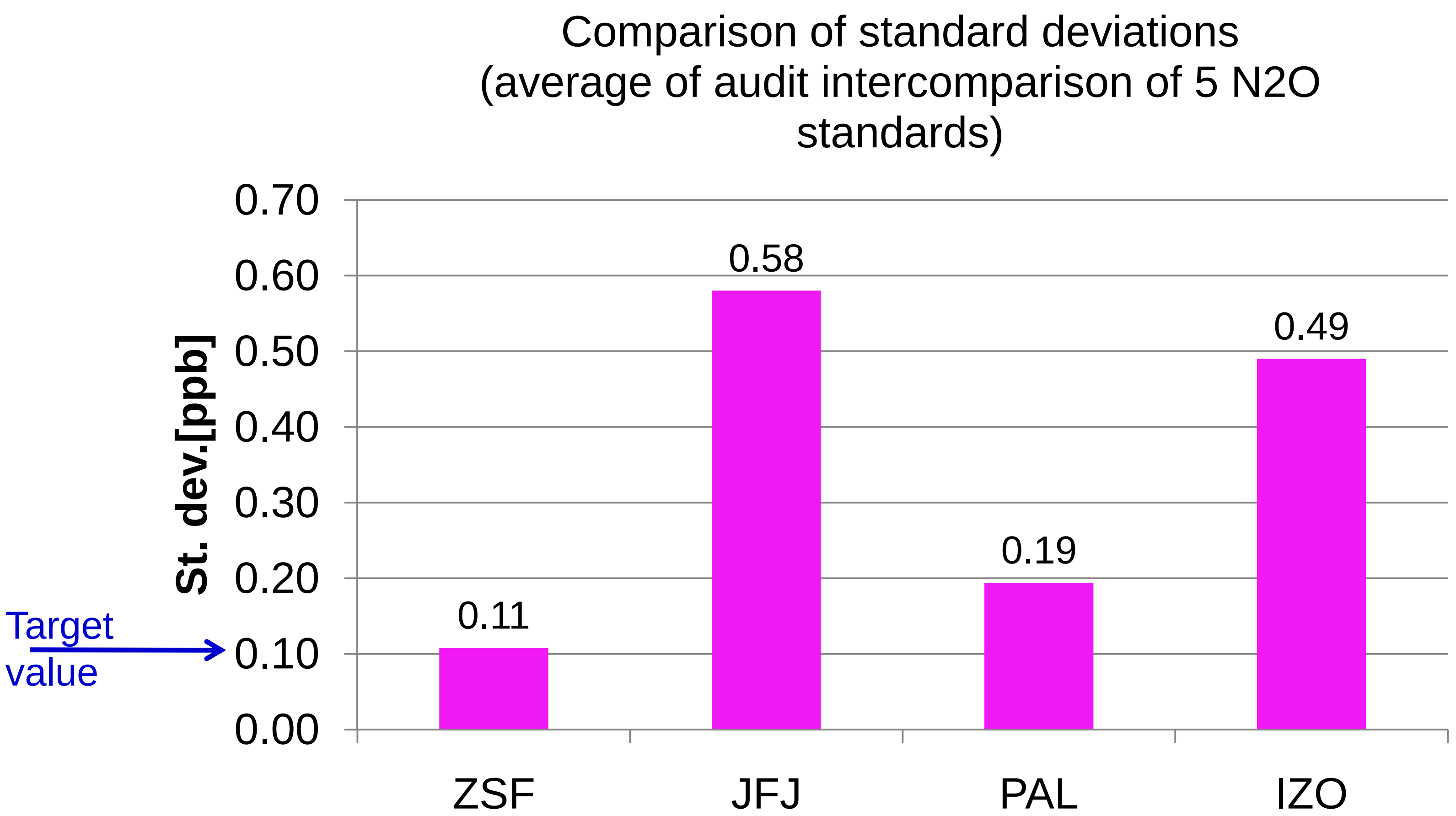

IZO
mVolts
24
23
22
21
20
19
18
17
16
15
1
2
3
4
5
6
Minutes

Comparison of ECD response curves (extrapolated)

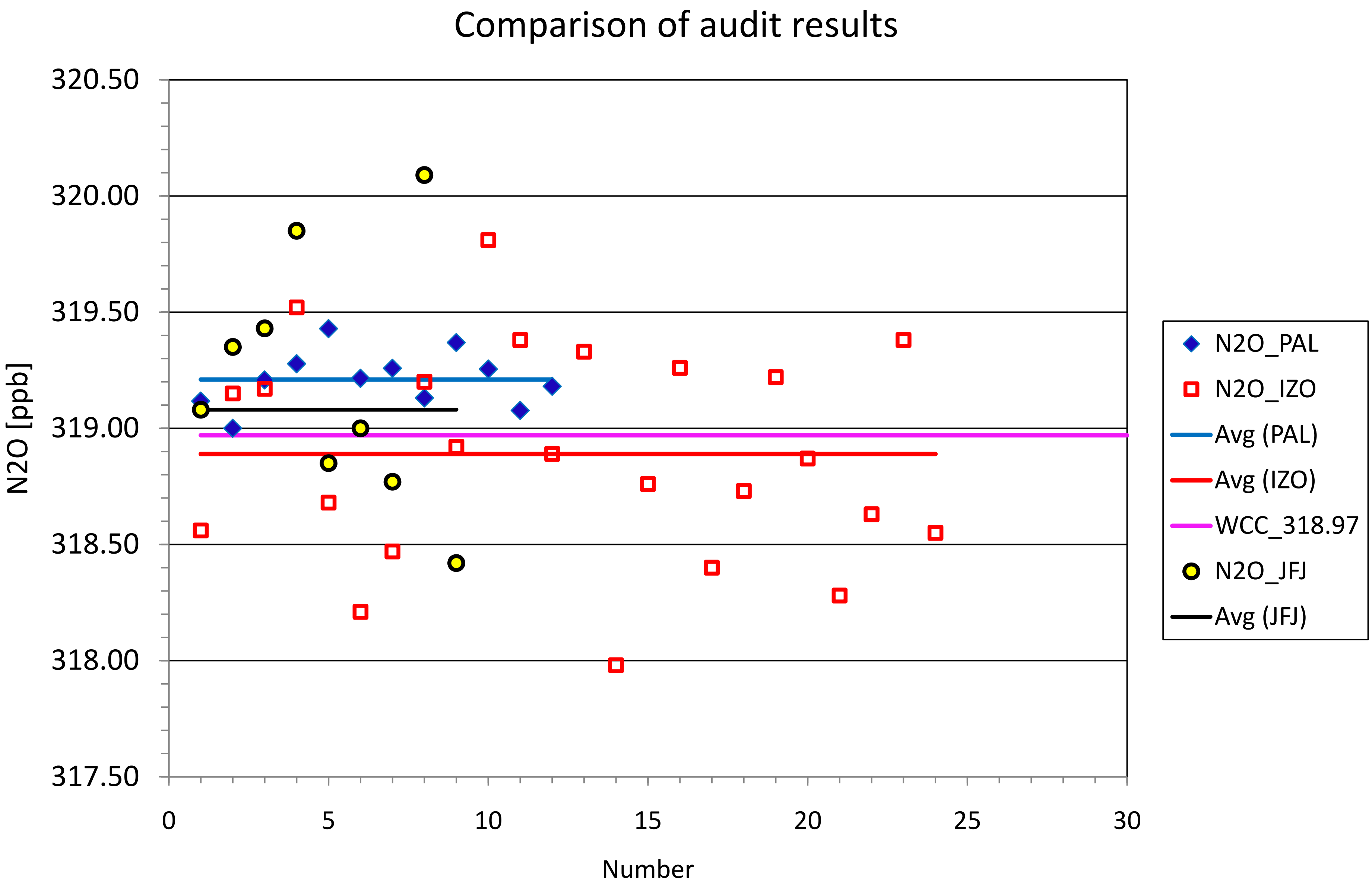


Range of standards: 296 – 347 ppb

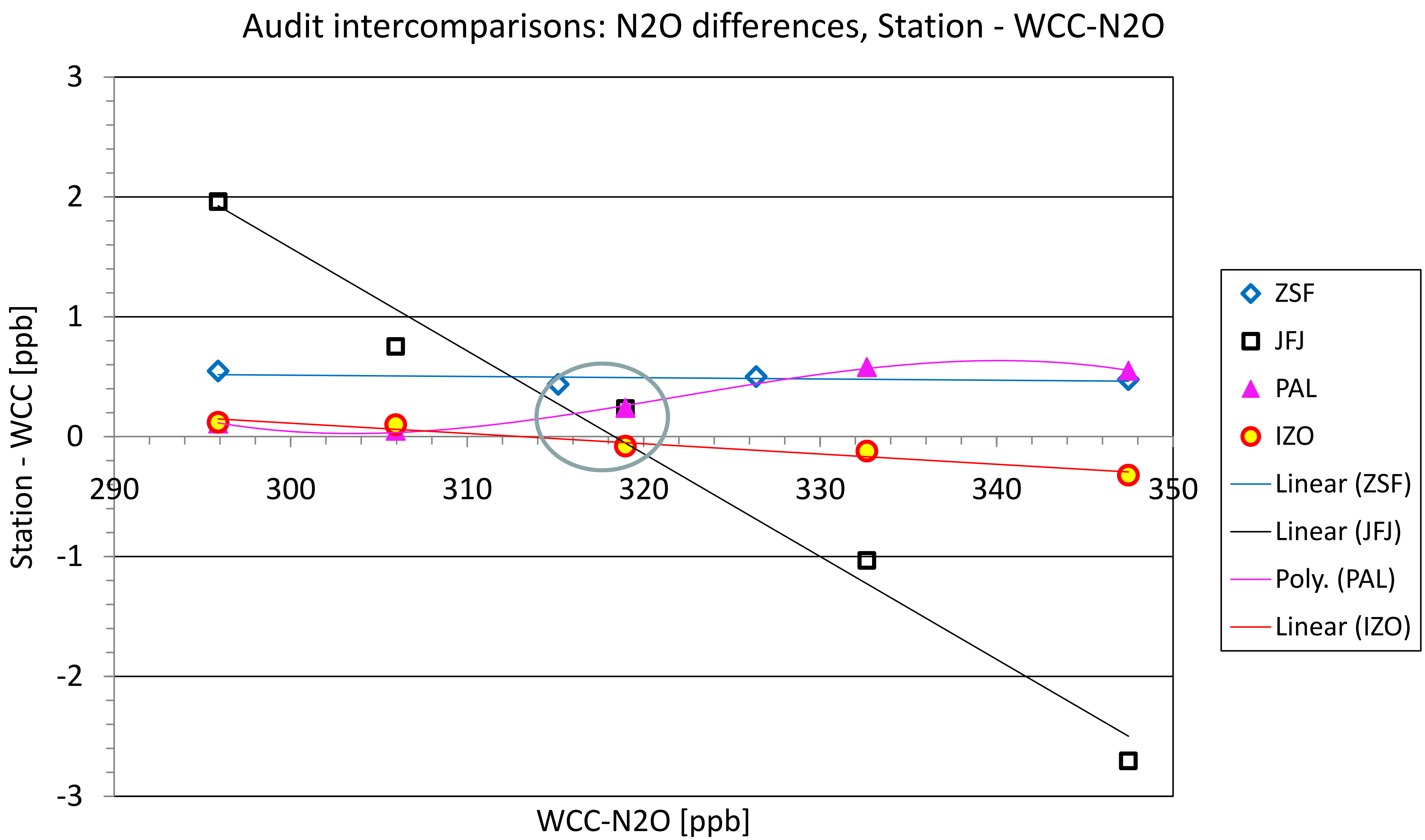
Comparison of standard deviations

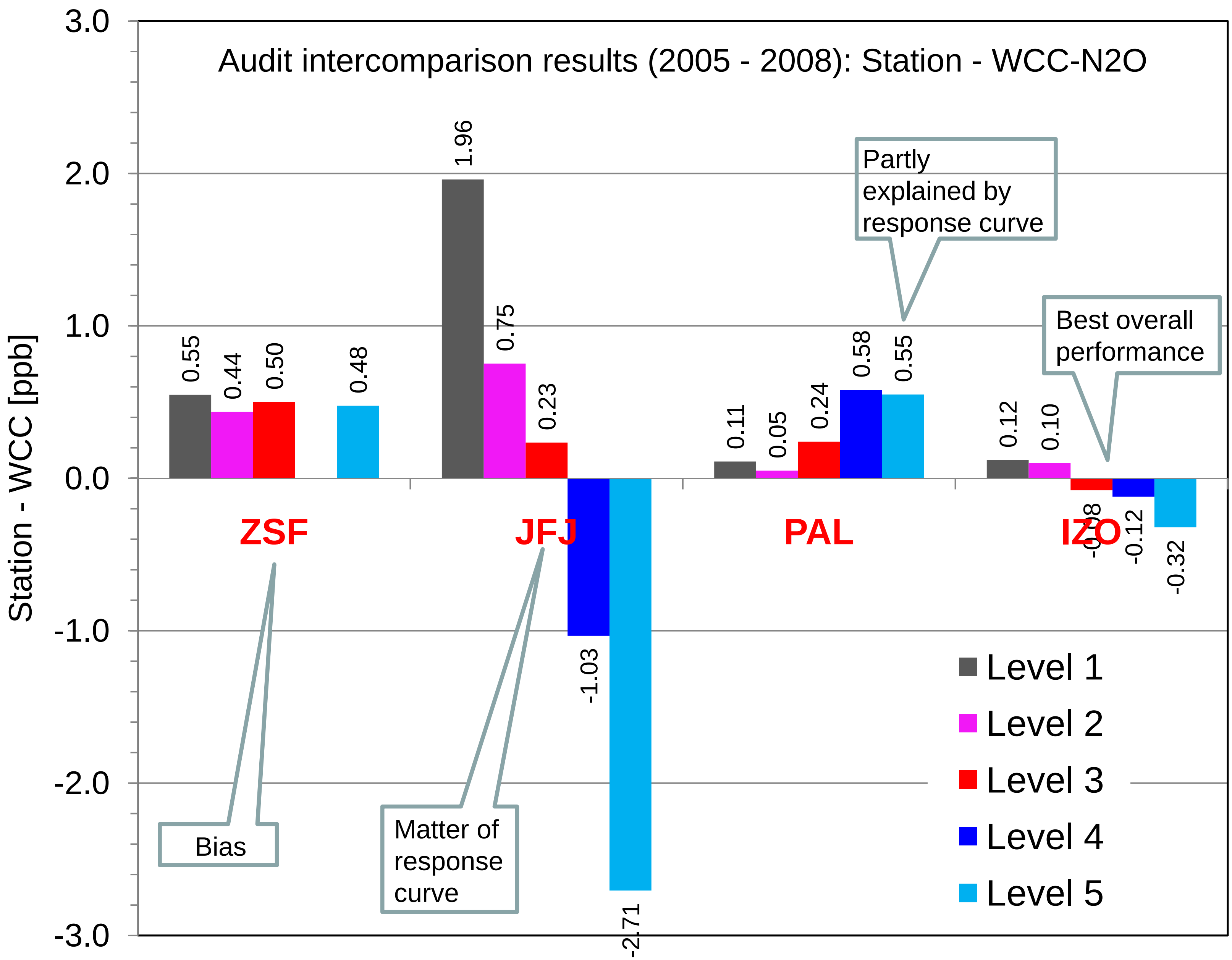


Intercomparison: Individual analysis results for 319 ppb



Intercomparison: Differences between reported and assigned values





Audit intercomparison results (2005 - 2008): Station - WCC-N2O
Station - WCC [ppb]
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
ZSF
JFJ
PAL
IZO
0.55
0.44
0.50
0.48
1.96
0.75
0.23
-1.03
-2.71
0.11
0.05
0.24
0.58
0.55
0.12
0.10
-0.08
-0.12
-0.32
Partly explained by response curve
Best overall performance
Bias
Matter of response curve
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-N_2O round-robin experiments involving a small number of participants. Repetition of audit intercomparisons.