Global Atmosphere Watch
World Calibration Centre for Surface Ozone
Carbon Monoxide and Methane

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

EMPA-WCC REPORT 01/3

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE

GLOBAL GAW STATION ZEPPELIN MOUNTAIN

NY-ÅLESUND, SVALBARD, SEPTEMBER 2001

Submitted by

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WMO World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane

EMPA Dübendorf, Switzerland

Contents:

EMPA is accredited as a calibration laboratory for ozone measuring instruments in accordance with EN SN 45'001

1. Abstract

A system and performance audit was conducted at the Global Atmosphere Watch station Zeppelin Mountain from September 6 to 12, 2001 by the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide and Methane. The results can be summarised as follows:

System Audit of the Observatory

During 1999, the station was completely rebuilt. It offers now excellent facilities for atmospheric research and measurement campaigns.

Audit of the Surface Ozone Measurement

The inter-comparison, consisting of three multipoint runs between the WCC transfer standard and the ozone instrument of the station, demonstrated good agreement between the station analyser and the transfer standard. The recorded differences fulfilled the defined assessment criteria as "good" over the tested range up to 100 ppb (Figure 1).

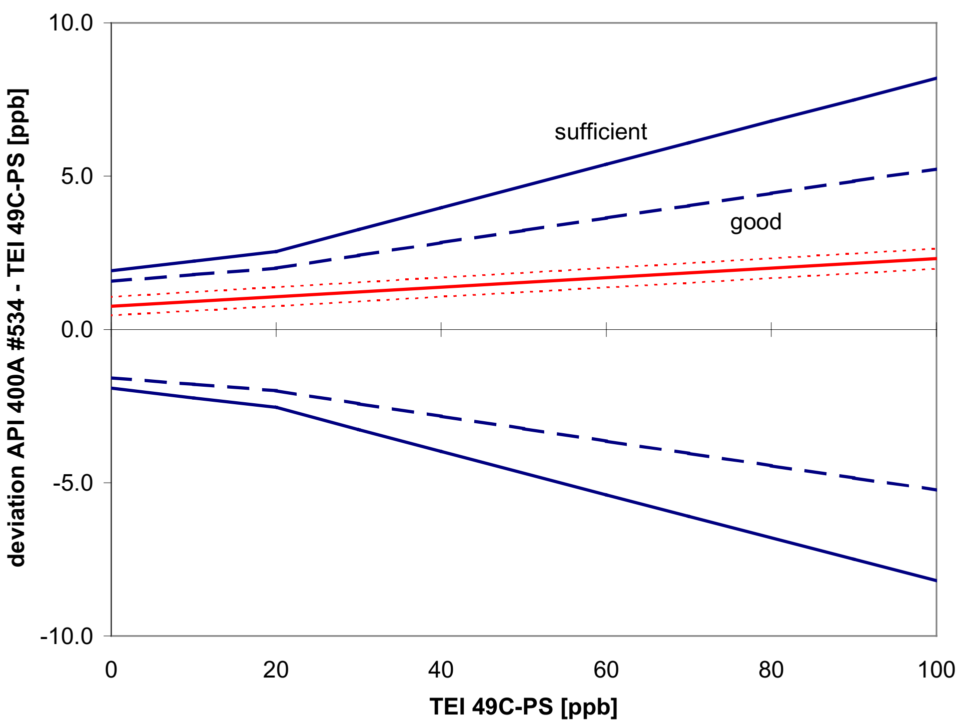

Figure 1: Intercomparison of the API 400A S/N 534 field instrument with the WCC transfer standard

The API 400A instrument is in use at the station since February 2001, and before its use as the station analyser only one full calibration with a TEI 49C-PS ozone calibrator has been performed at NILU. The zero offset should be carefully watched, and a re-calibration of the instrument is encouraged by EMPA-WCC.

Audit of the Carbon Monoxide Measurement

The results of the inter-comparisons between the five EMPA-WCC transfer standards and the RGA-3 system of the Zeppelin station showed a difference of 5 to 7 ppb in the concentration range of 50 to 200 ppb. The difference could be explained by the recent revision of the CMDL scale for carbon monoxide. A multipoint calibration of the RGA-3 instrument is encouraged by EMPA-WCC to characterise the calibration function of the instrument. For this purpose it should be considered to purchase additional carbon monoxide standards in the concentration range of 50 to 200 ppb CO.

Audit of the Methane Measurement

The results of the inter-comparisons between the five EMPA-WCC transfer standards and the GC system of the Zeppelin station showed good agreement for the relevant concentration range of 1740 to 2000 ppb. The deviation was within ±0.4%. No further recommendations are suggested by EMPA-WCC for the methane measurements.

Conclusions

All measurements of the audited parameters (O_3, CO, CH_4) at Ny Ålesund were performed at a high level of accuracy. The whole system from the air inlet to the instrumentation, including maintenance and data handling, is operated with great care. The staff involved in measurements and data evaluation is highly motivated and experienced.

The station was completely re-built in 1999 and offers now an excellent infrastructure for atmospheric research and measurement campaigns.

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Dübendorf, 26. March 2002 EMPA Dübendorf, WCC

Project scientist Project manager

Dr. C. Zellweger Dr. B. Buchmann

2. Introduction

The **Global GAW Station Zeppelin Mountain at Ny Ålesund on Svalbard** is part of Norway's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) programme. The observatory on the Zeppelin Mountain is an established site for long-term measurements of greenhouse gases, ozone and physical and meteorological parameters.

The air pollution and environmental technology section of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) was assigned by the WMO to operate the GAW **World Calibration Center** (WCC) for Surface Ozone, Carbon Monoxide and Methane, thereby establishing a co-ordinated quality assurance programme for this part of GAW. The detailed goals and tasks of the WCC concerning surface ozone are described in the GAW report No. 104. System and performance audits at global GAW stations are conducted regularly based on mutual agreement about every two years.

In agreement with the co-ordinator of GAW activities in Norway, Øystein Hov from the Norsk Institutt for Luftforsking (NILU), and the measurement responsible Dr. Norbert Schmidbauer and Chris Lunder (both NILU), a **system and performance audit** at the Observatory Zeppelin Mountain was conducted by the WCC between September 6 and 12, 2001.

The scope of the audit was the whole measurement system in general and surface ozone, carbon monoxide and methane measurements in particular. The entire system from the air inlet to the data processing and the quality assurance was reviewed during the audit procedure. The ozone audit was performed according to the "Standard Operating Procedure (SOP) for performance auditing ozone analysers at global and regional WMO-GAW sites", WMO-GAW Report No. 97. The assessment criteria for the ozone inter-comparison have been developed by EMPA based on WMO-GAW Report No. 97 (EMPA-WCC Report 98/5, "Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements", July 2000, available on request from EMPA or downloadable from www.empa.ch/gaw). The present audit report is distributed to NILU and the World Meteorological Organization in Geneva.

Staff involved in the audit

Ny Ålesund	Dr. Norbert Schmidbauer	contacts, general program, organisation
	Chris Lunder	contacts, general program, organisation
	Ine-Therese Pedersen	technical assistance at the observatory
EMPA-WCC	Dr. Christoph Zellweger	lead auditor
	Dr. Stefan Reimann	assistant auditor

Previous audits at the GAW station Ny Ålesund:

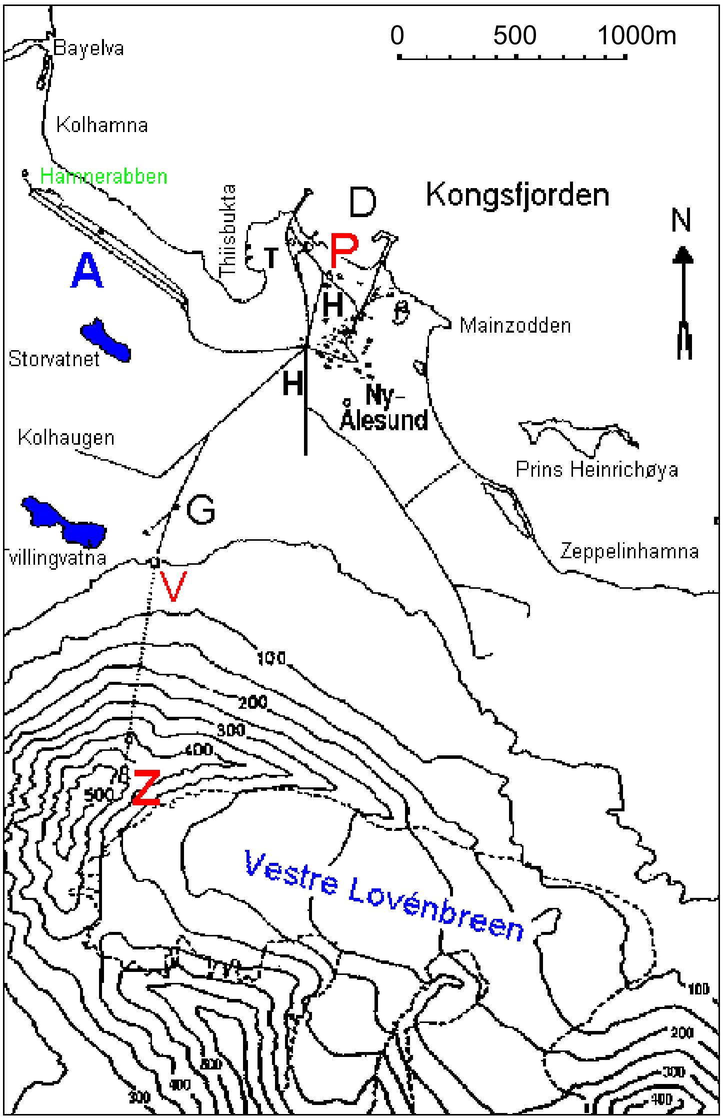
- September 1997 by EMPA-WCC for surface ozone.

3. Global GAW Site Zeppelin Mountain, Ny Ålesund

3.1. Description of the Site

Ny-Ålesund in the European Arctic is one of the world's northernmost human settlements. It is situated on Kongsfjorden - the King's fjord - on north-western Spitsbergen, which is the largest of the Svalbard islands. The town is surrounded by mountains and glaciers, which at several places stretch well out into the sea. Large areas of Svalbard (about 60 %) are covered with glaciers. Svalbard with an area of 62'049 km^2 is very sparsely populated. Approximately 3'200 inhabitants live in one of five small settlements on Spitsbergen. The Norwegian town Ny-Ålesund is permanently maintained by about 30 people. Additionally approx. 150 scientists live there during the summer peak season.

The global GAW station Zeppelin Mountain (coordinates: 78°54'29" N, 11°52'53" E) near Ny-Ålesund lies south of the town (see Figure 2). The monitoring station was built in 1988 / 89 on a small plateau 473 m above sea level, east of the Zeppelin Mountain top. The station can be accessed by cable car. The station was completely re-built in 1999 and offers now space for different scientific activities. Several air inlets and some meteorological equipment are mounted on the top of the roof.



Z Zeppelin research station
V valley station for the cable-car
G pre-Zeppelin station (before 1989)
D dock where visiting ships stop
P oil burning power plant
A airstrip
H helicopter landing sites
T former trash burning (discontinued)

Figure 2: The topography surrounding the Zeppelin Mountain Station (from www.misu.su.se/~kim)

Svalbard has a milder climate than might be expected in an area so far north. This is because a branch of the North Atlantic current flows north along the west coast of Spitsbergen. The average temperature for Ny Ålesund in February, which is the coldest month, is about -15°C. In July, which commonly is the warmest month, the average temperature is about +5°C. Strong winds are common during the winter months, while fog is a typical summer phenomenon. Svalbard is often described as an 'Arctic desert' because of its low precipitation. Average precipitation in Ny-Ålesund is about 370 mm / year (measurements from 1975 to 1989).

Ozone-, Carbon Monoxide and Methane Levels at Ny Ålesund

The distribution of the hourly mean values of O_3 from 1996 is shown in Figure 3.

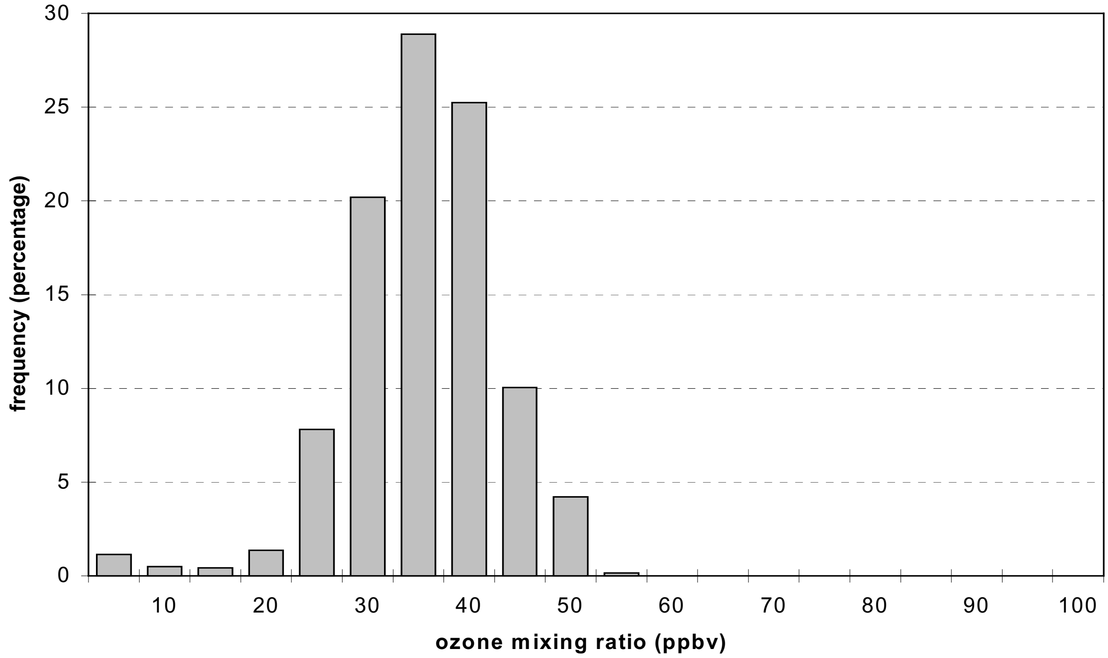


Figure 3: Frequency distribution of the hourly mean ozone mixing ratio (1996) at Ny Ålesund. Availability of data: almost 100%.

Carbon monoxide was measured at Ny Ålesund form 1992 to 1994, before the measurements became again operational in 2001. The CO data from the 1992 to 1994 period averaged 159 ppb, with a standard deviation of 46 ppb. The 10- and 90-percentile was 100 ppb and 218 ppb, respectively.

No data is yet available for methane since measurements became operational only recently.

3.2. Description of the Observatory

The observatory on Zeppelin Mountain (Figures 4 and 5) was completely re-built in 1999. It offers now several laboratories for atmospheric research and measurement campaigns. The laboratory of NILU (Figure 6) is 25 square meters and offers all necessary infrastructure for atmospheric research.

Comment

- The new station on Zeppelin Mountain offers spacious laboratories which meet all requirements for the measurement of air pollutants. No significant changes regarding location and inlet types were made since the station was re-built.

Figure 4: View of the Zeppelin Station from east

Figure 5: View over Zeppelin Station to Kongsfjorden

Figure 6: Inside the new laboratory at the Zeppelin Station

3.3. Staff / Operators

Table 1: Staff responsible for the GAW site Ny Ålesund (by September 2001)

Name	**Position and duty**
Prof. Dr. Øystein Hov	Director of NILU, Co-ordinator of GAW activities
Kjetil Tørseth	GAW Country contact
Sverre Solberg	Measurement leader
Jan Wasseng	Instrument responsible (O_3)
Ove Hermansen	Instrument responsible (CH_4)
Dr. Norbert Schmidbauer	Instrument responsible (CO)
Chris Lunder	Instrument responsible (CO)
Ine-Therese Pedersen	PhD student (working with CH_4 and CO data)

4. System- and Performance Audit for Surface Ozone

4.1. Monitoring Set-up and Procedures

Changes since the last audit of EMPA-WCC in September 1997:

- The station was completely re-built in 1999.
- The former field instrument Monitor Labs ML 8810 #1150 was replaced by an API 400A ozone instrument in February 2001

4.1.1. Air Inlet System

Sampling-location: Zeppelin Mountain, on the west side of the building close to the building wall and a ladder leading up to the roof.

Sample inlet:

Rain protection: The Inlet is protected against rain and snow by an upside-down teflon beaker.

Inlet-filter: Teflon inlet filter inside analyser, exchanged approx. every 3 months.

Sampling-line:

Dimensions: inlet line: length = 5 m, i.d. = 4 mm

Material: PFA

Flow rate: inlet line: 800 ml/min

Residence time in the sampling line: ca. 5 s

Comment

The PFA tube was clean and free of dust. Materials as well as residence time of the inlet system are adequate for trace gas measurements in particular with regard to minimal loss of ozone. However, the inlet location is very close to the building wall and a metal ladder. At this location a potential ozone loss can not be excluded, and it should be considered to move the inlet location to the flat terrace above the laboratory.

4.1.2. Instrumentation

Ozone Analyser

At the Zeppelin Mountain one O_3 analyser model API 400A (Table 2) from Advanced Pollution Instruments Inc. is in use. The instrument is installed in the air-conditioned laboratory and is protected from direct sunlight.

Table 2: Ozone analyser at the Zeppelin Research Station

Type	API 400A S/N 534
Method	UV absorption at 254 nm
purchase date	late 2000
at Zeppelin Mountain	since February 2001
Range	0-250 ppb
Analog output	0-1 and 0-10 V
Offset [ppb]	-5.1
Slope	0.972

Ozone Calibrator

No ozone calibrator is available at the site. A calibrator model 49C PS from Thermo Environmental Instruments Inc. is available at NILU, and yearly instrument calibrations are performed at the site or at NILU.

Operation and Maintenance

Preventive maintenance includes frequent checks of several instrument parameters (test points according to instrument manual) by remote access from NILU. If malfunction is detected, measures are taken.

Manual zero and span checks are performed weekly with the internal span/zero check. This is also done by remote access from NILU. Until now these checks were not used for data correction. A full calibration is done yearly with the NILU transfer standard (TEI 49C PS) either at the site or at NILU.

4.1.3. Data Handling

Data Acquisition and –transfer

At the site a NILU model NDL2 data logger collects data (in ppb) from the ozone monitor every 10 seconds via the RS232 serial interface. The 10 seconds instantaneous data is averaged by the data logger to 1 minute, 5 minute and 1 hour averages. The 1 minute and 5 minute averages are only used for service and trouble shooting. At NILU a data acquisition systems collects the 1 hour averages automatically once every day via a modem and dial up telephone line. Both the data logger and the data collection system have been developed at NILU.

Data Treatment

A monthly data report is prepared at NILU. The raw data as it was collected from the data logger is inspected by the site technician and any invalid data is marked as invalid. A correction is made for deviation in offset and slope. The correction is based on the last calibration of the ozone monitor. The corrected data is converted to $\mu g/m^3$ and inspected again by the site technician. Finally the data report is signed by the Head of department. The data report, both on paper and electronically, is made available to the site's project manager.

Data Submission

Surface ozone data is reported to the GAW World Data Centre for Surface Ozone (WDCSO) at NILU.

4.1.4. Documentation

Logbooks

Electronic logbooks are available for the ozone instrument. The notes are up to date and describe all important events. The log files can be accessed both from the station and from NILU.

Standard Operation Procedures (SOPs)

The manual for the instrument is available at the site.

Comment

The frequent instrument checks and the up-to-date logbooks support the quality of the data. No change of the current practice is suggested.

4.2. Intercomparison of Ozone Instruments

4.2.1 Experimental Set-up

The WCC transfer standard TEI 49C PS (details see Appendix I-II) was operated in stand-by mode for warming up for 20 hours. During this stabilisation time the transfer standard and the PFA tubing connections to the instrument were conditioned with 250 ppb ozone for 30 minutes. Afterwards, three comparison runs between the field instrument and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 7 the experimental set up during the audit. No modifications of the ozone analysers which could influence the measurements were made for the inter-comparisons.

The audit procedure included a direct inter-comparison of the TEI 49C-PS WCC transfer standard with the Standard Reference Photometer SRP#15 (NIST UV photometer) before and after the audit in the calibration laboratory at EMPA. The results are shown in Appendix II.

Table 3: Experimental details of the ozone inter-comparison

reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instrument:	API 400A S/N 534
ozone source:	WCC: TEI 49C-PS, internal ozone generator
zero air supply:	EMPA: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition system:	16-channel ADC with acquisition software
pressure transducer readings:	TEI 49C-PS (WCC): 961.9 hPa adjusted to ambient pressure (958.0 hPa) before the inter-comparison. No adjustments were made for the field instrument.
concentration range	0 - 100 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	10 / 20 / 30 / 50 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	3 x on September 7, 2001
connection between instruments:	approx. 1.5 meter of 1/4" PFA tubing

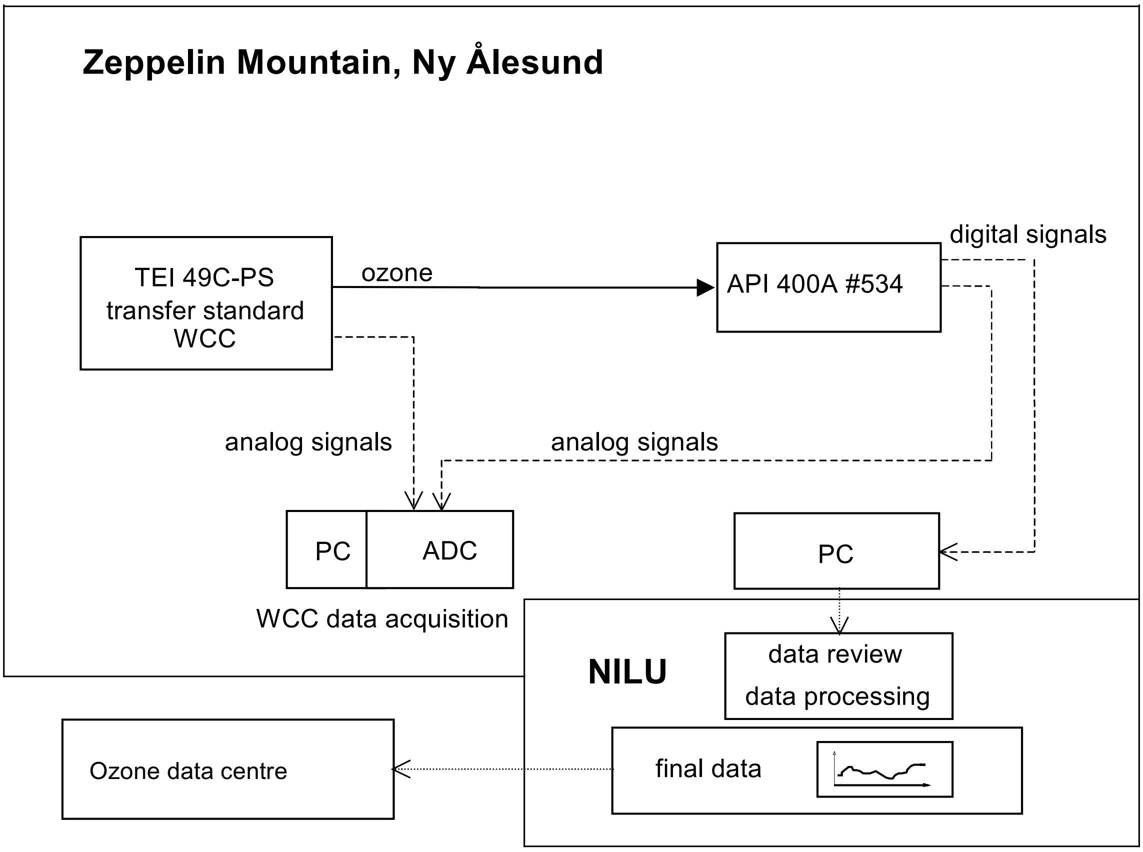


Figure 7: Experimental set up for the ozone inter-comparison

4.2.2. Results

Ozone Analyser

The results comprise the inter-comparison between the API 400A field instrument and the WCC transfer standard TEI 49C-PS, carried out on September 7, 2001.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty 30-second-means are presented in Table 4. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Figures 8 and 9 show the residuals of the linear regression analysis of the field instrument compared to the EMPA transfer standard. The residuals versus the run index are shown in Figure 8 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 9 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 10).

The data used for the evaluation was recorded by the EMPA data acquisition system. This raw data was treated according to the usual station method. Corresponding to this procedure the zero offset determined at the last calibration of the instrument with the NILU transfer standard (+1.0 ppb) was subtracted from all data. These offset is also confirmed by the weekly zero checks (range 0.9 to 1.4 ppb, ten values).

Table 4: Inter-comparison of the ozone field instrument

	TEI 49C-PS		API 400A S/N 534			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.0	0.10	0.8	0.17	0.9	
2	30.1	0.12	31.3	0.20	1.2	4.0%
3	10.2	0.10	10.8	0.21	0.6	5.8%
4	50.2	0.12	51.7	0.19	1.5	3.0%
5	90.2	0.06	92.2	0.17	2.0	2.3%
6	20.2	0.09	21.2	0.16	1.0	4.8%
7	-0.1	0.08	0.8	0.17	0.9	
8	-0.1	0.09	0.7	0.21	0.8	
9	50.2	0.11	51.8	0.22	1.6	3.2%
10	20.0	0.07	21.2	0.22	1.2	5.9%
11	30.0	0.10	31.2	0.17	1.2	3.8%
12	90.1	0.08	92.3	0.26	2.1	2.4%
13	10.1	0.11	11.0	0.23	0.9	9.1%
14	-0.1	0.17	0.8	0.20	0.9	
15	-0.2	0.13	0.5	0.20	0.7	
16	30.1	0.17	31.3	0.16	1.2	4.1%
17	10.1	0.09	11.2	0.16	1.1	10.9%
18	20.0	0.07	21.3	0.30	1.3	6.5%
19	50.0	0.13	51.7	0.31	1.7	3.3%
20	90.2	0.08	92.4	0.28	2.2	2.4%
21	-0.2	0.09	0.3	0.20	0.4	

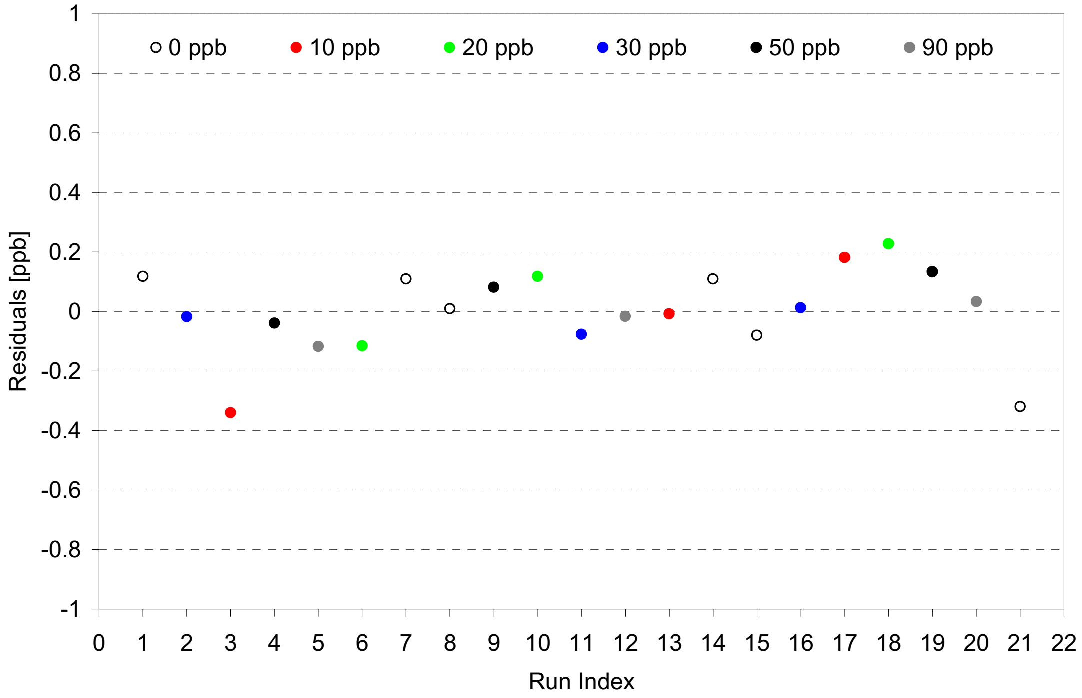


Figure 8: Residuals to the linear regression function (API 400A #534) vs the run index (time dependence)

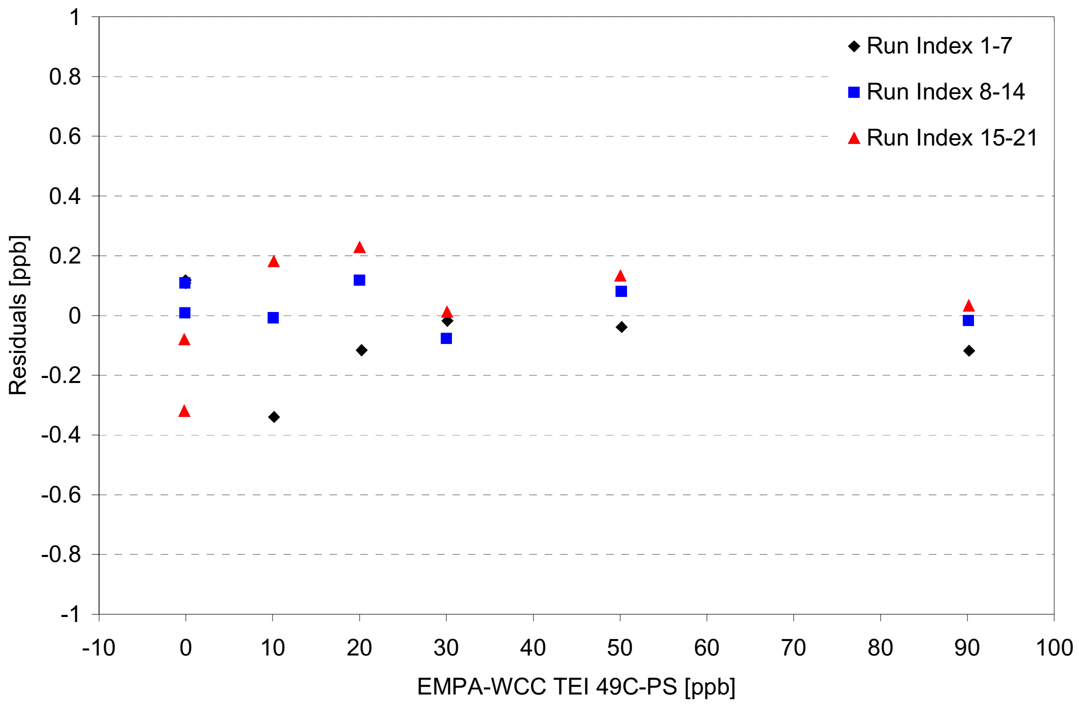


Figure 9: Residuals to the linear regression function (API 400A #534) vs the concentration of the WCC transfer standard (concentration dependence)

From the inter-comparisons of the API 400A field instrument with the TEI 49C-PS transfer standard from EMPA, the resulting linear regression (for the range of 0-100 ppb ozone) is:

API 400A #534:

$$\text{API 400A} = 1.015 \times \text{TEI 49C-PS} + 0.8 \text{ ppb}$$

API 400A = O_3 mixing ratio in ppb, determined with API 400A #534

TEI 49C-PS = O_3 mixing ratio in ppb, determined with TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.001	(f = 19) f = degree of freedom
	- offset S_b in ppb	0.04	(f = 19)
	- residuals in ppb	0.11	(n = 21)

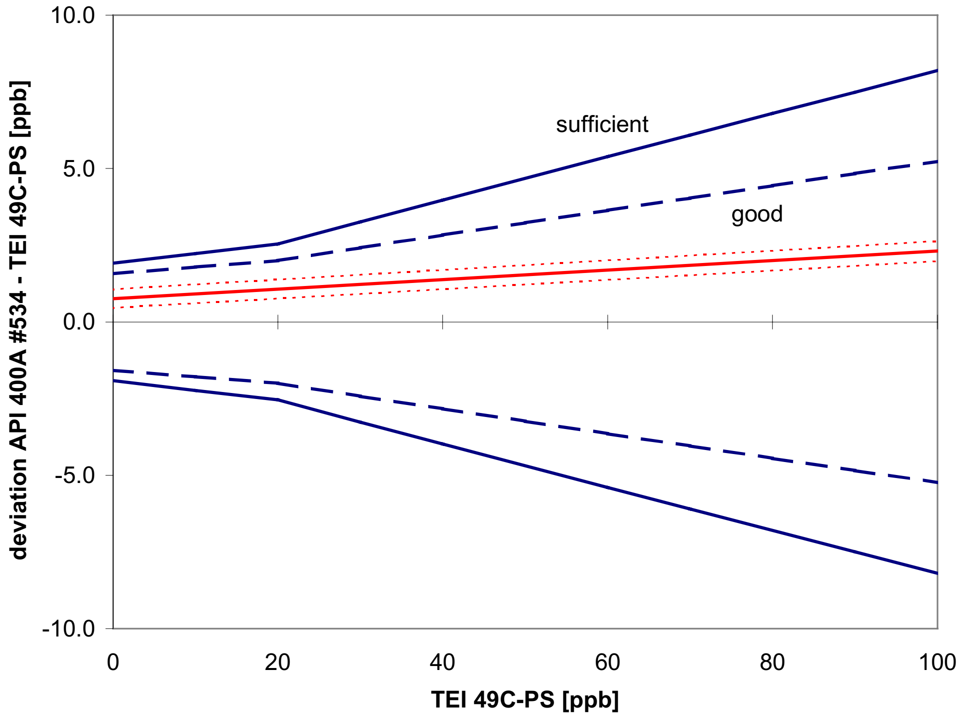


Figure 10: Inter-comparison of instrument API 400A #534

Comment

The ozone concentrations observed at Ny-Ålesund (1996) usually ranged between 23 and 45 ppb (5- and 95-percentile of hourly mean values). However, episodes of very low ozone concentrations are a common feature in spring. These events are interesting regarding atmospheric chemistry. The instrument fulfils the assessment criteria of “good” over the tested range between 0 and 100 ppb ozone.

4.3. Recommendation for the Ozone Measurements

The API 400A ozone instrument at Zeppelin Mountain is in a good condition and fulfilled the assessment criteria as "good" over the tested range of 0 to 100 ppb. However, an offset of 0.8 ppb was found during the inter-calibration. It is therefore strongly recommended that the zero checks of the instrument be carefully watched and that the data be corrected accordingly. The calibration interval of one year is regarded as an upper limit, but acceptable considering the frequent zero and span checks.

The location of the inlet for the ozone measurement is regarded as not optimal. It is recommended to move the inlet, for example to the terrace above the laboratory.

5. System- and Performance Audit for Carbon Monoxide

Carbon monoxide measurements were performed at Zeppelin Mountain from 1994 to 1997 and from 1997 to 1999. The measurements became again operational three weeks before the audit of EMPA-WCC, and are planned to continue in the future.

5.1. Monitoring Set-up and Procedures

5.1.1. Air Inlet System for CO and CH_4

Sampling-location: on top of the building, 3 meters above the roof.

Inlet description: aluminium inlet (i.d. 12 cm), length 5 m, protected from rain and snow, flow rate 510 l/min. From there connections with 1/16" stainless steel tubing to the pump with overflow, length ca. 1.2 m, flow rate 330 ml/min. From pump to CO instrument: 1/16" stainless steel tubing, length ca. 1.0 m, flow rate 16 ml/min.

Residence time in the sampling line: approx. 7 s

Comment

The inlet system is adequate for analysing CO concerning materials and residence time.

5.1.2. Instrumentation

An RGA-3 GC-system of Trace Analytical Inc. is used as an in situ CO analyser. Instrumental details are listed in Table 5, and a flow schematic is shown in Figure 11.

Table 5: Carbon monoxide gas chromatograph at the Zeppelin research station

instrument	Trace Analytical Inc.
model, S/N	RGA3, S/N 020190-005
at Zeppelin station	1991 - 1994, 1997 – 1999, since August 2001
configuration	E-001 (Trace Analytical terminology)
method	GC / HgO Detector
loop	1 ml
columns	pre-column: Unibeads 1S 60/80 analytical column: Mole sieve 5Å 60/80
carrier gas	N_2 99.999 %
operating temperatures	Detector: 265 °C, Column: 105 °C
analog output	0 - 1 V
calibration interval	every 120 min (working standard)
instrument's specials	flow through the sample loop is adjusted to 16 ml/min for both air samples and standards.

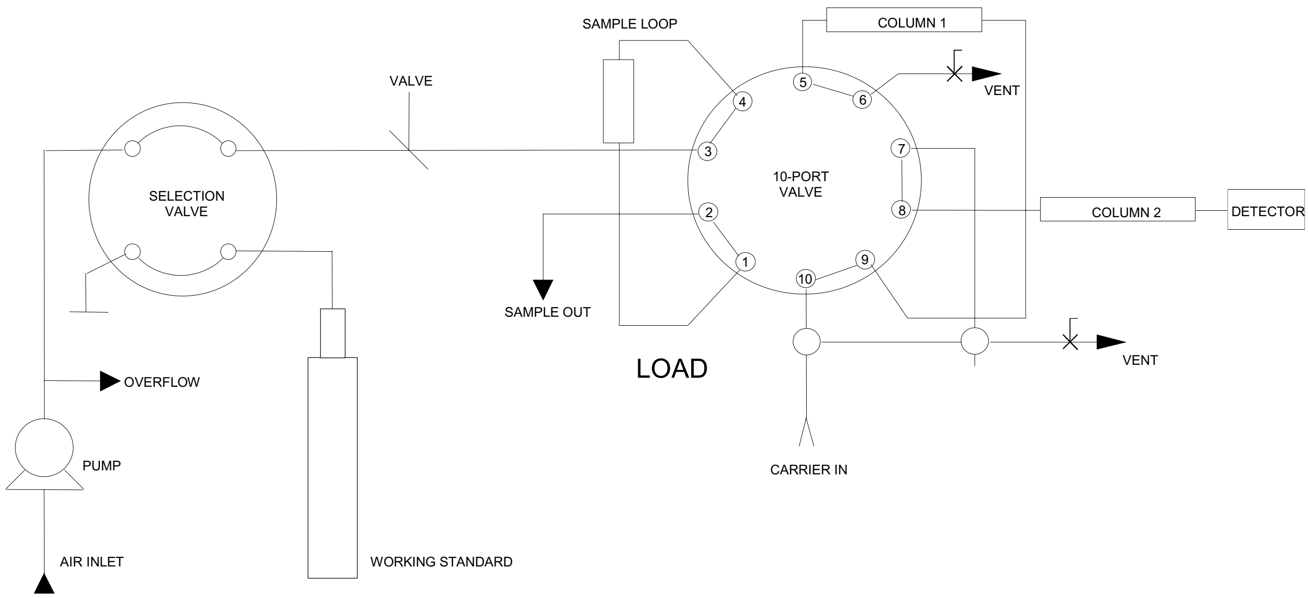


Figure 11: Flow schematic of the CO GC system at the Zeppelin research station

Gas Standards

Table 6 shows the gas standards that are used for the verification of the measurements. Cylinders with ambient air from the Zeppelin station are available at the site to serve as working standards. These working standards were traced back to the station reference.

Table 6: Station CO cylinders

Gas cylinder	Description	Conc. [ppb]
CA03178	Scott Marrin / station reference (not CMDL certified)	193.7
CO0708STD1	working standard (used before audit)	78.8
CO1109STD5	working standard (after audit)	93.1

Operation and Maintenance

Analysis: 6 measurements are performed within 2 hours: 5 of ambient air and one of the working standard. Additionally, the reference standard is injected when the station is visited by the instrument responsible (approx. every 3 months).

Daily checks: UV-lamp
chromatogram / peak width / CO-retention time
cylinder pressures

A baseline reset is done if necessary.

Instrument checks according to the RGA-3 manual are performed on a monthly basis.

Comment

- Gas chromatography for CO analysis followed by mercury reduction detection is a sophisticated method. Applied with care it is characterised by excellent specificity, very low detection limits and high precision. Unfortunately, the detectors are not perfectly linear.

5.1.3. Data Handling

Data Acquisition and –transfer

HP ChemStation Chromatography Software is used for data acquisition. Both reports and chromatograms are stored as raw data.

Data Treatment

Ambient air mixing ratios are calculated based on peak area by using the concentrations of the working standard. Data evaluation includes consistency checks with charts (in particular retention time, peak start, peak end), checks with the instrument logbook and time series review. The final data evaluation is done weekly at NILU.

Data Submission

For scientific reasons data have been submitted to different teams. At present CO data are not submitted to any data centre, but it is planned for the future to submit data to the GAW Data centre for Greenhouse Gases at JMA.

Comment

Remote access to the data acquisition system from NILU allows the inspection of the data for plausibility. If malfunction is detected, measures are initiated.

5.1.4. Documentation

Logbooks

During the audit the documentation was reviewed for availability and usefulness. The electronic station logbook contained for all parameters all necessary information about maintenance, instrument changes, events and special investigations. The logbook files are accessible from NILU for use in the final data evaluation. The instrument manuals are available at the site.

Comment

The log files were kept up-to-date. All the necessary information was available at the site.

5.2. Intercomparison of the in-situ Carbon Monoxide Analyser

5.2.1. Experimental Procedure

Since no Standard Operation Procedure (SOP) has been established for CO measurements until now, the "SOP for performance auditing ozone analysers at global and regional WMO-GAW sites" (WMO-GAW Report No 97) also serves as a guideline for CO audits.

The inter-comparison of the CO measurements was comprised of the following experiments.

The four transfer standards of the WCC (approx. 50, 100, 150 and 200 ppb CO) were stored in the same room as the CO measurement system to equilibrate for one day. The transfer standards were previously calibrated against CMDL laboratory standards (CA03209, CA02803, CA03295, CA02859) at EMPA. Before the inter-comparison measurements, the pressure regulators and the stainless steel tubing were extensively flushed and leak checked (no pressure drop for half an hour with main cylinder valve closed). All transfer standards were injected and analysed 5 times on September 9. No modifications of the RGA-3 carbon monoxide analyser were made for the inter-comparison. The WCC transfer standards were injected at the working standard inlet. One WCC transfer standard was also injected as an ambient air sample. No difference could be observed for the two methods. The data was acquired by the station software. This data (mean values and standard deviations) was reprocessed by the station operators during the audit. The experimental details are summarised in Table 7.

Table 7: Experimental details of the carbon monoxide inter-comparison

field instrument:	RGA3, S/N 020190-005
reference:	EMPA-WCC transfer standards 001201-3, 001201-1, FF30491, FA01467
data acquisition system:	HP ChemStation Chromatography Software
approx. concentration levels:	50 /100 / 150 / 200 ppb
injections per concentration:	5
Sequence	injected as working standards, every 10 min

5.2.2. Results

The results of the inter-comparison between the RGA-3 field instrument and the four WCC transfer standards are shown in Table 8. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 12 shows the absolute differences (ppb) between the measurements of the RGA-3 and the WCC transfer standards (TS) (conventional true value). The WCC TS were calibrated before and after the audit against the CMDL scale (Reference: CMDL CA02859, 194.7 pbb) with the Aerolaser AL5001. No significant differences were found between the calibrations before and after the audit (t-test at 95% confidence interval). The error bars represent the combined 95% confidence interval for the calibration of the transfer standards against the CMDL standard and of the multiple injection of the transfer standards at the Zeppelin station. The data of the RGA-3 field instrument were processed during the audit by the station operators and are based on calibration of the instrument against the reference standards available at the site.

Table 8: Carbon monoxide inter-comparison measurements at the Zeppelin station

No.	WCC standard	RGA-3 (Peak Area) of Zeppelin station				
	conc.	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	52.4 ± 1.0	46.9	1.2	5	-5.5	-10.5
2	102.4 ± 1.6	95.8	0.6	5	-6.6	-6.4
3	158.7 ± 1.8	151.7	1.0	5	-7.0	-4.4
4	209.6 ± 2.6	204.6	1.0	5	-5.0	-2.4

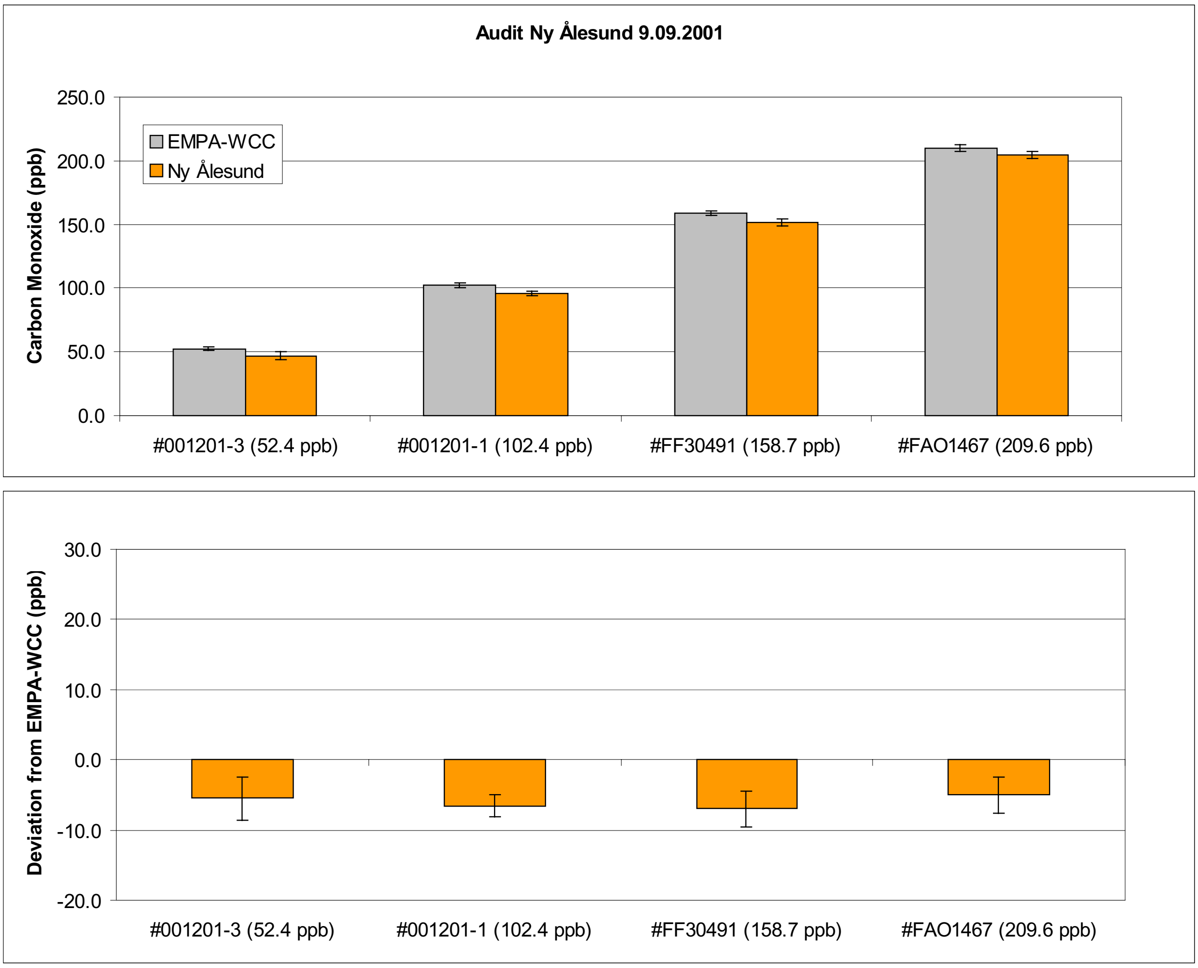


Figure 12: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02859, 194.7 ppb) measured with the GC system of the Zeppelin station (orange). lower panel: deviation of Zeppelin station from the conventional true value.

5.3. Discussion of the Inter-Comparison Results

The transfer standards of EMPA-WCC analysed by the station resulted in lower values (5 to 7 ppb) compared to the conventional true value. The transfer standard of EMPA-WCC were traced back to the revised CMDL scale (see Appendix III). The CMDL scale as revised by Paul Novelli also changed in the order of 5.0 to 8.2 ppb. Therefore, the differences in the inter-comparison measurements could be explained by the different scales.

The RGA-3 system of the Zeppelin station was not checked for linearity. Nevertheless, the instrument response seems to show rather linear characteristics.

5.4. Recommendation for the Measurement of Carbon Monoxide

- EMPA-WCC recommends a re-calibration of the GC system for the relevant concentration range of 100 to 200 ppb. A multipoint calibration should be performed to characterise the (non-linear) calibration function in the mentioned concentration range. For this purpose, additional standards should be available at the station.

6. System-and Performance Audit for Methane

Methane measurements became operational at the Zeppelin research station in 1997. The data have not yet been submitted to the GAW data center for greenhouse gases at JMA. The reason for this was mainly that the station operators were not completely confident with the calibration of their system.

6.1. Monitoring Set-up and Procedures

6.1.1. Air Inlet System for CH_4

Main Inlet: same as for Carbon Monoxide (see 5.1.1)

Connection to Instrument: approx. 5 m stainless steel tubing, 1/8'', flow rate 110 ml/min

Residence time in the sampling line: approx. 20 s

Comment

The inlet system is adequate for analysing CH_4 concerning materials and residence time.

6.1.2. Analytical System

Gas chromatograph

A Carlo Erba FRACTOVAP 4160 gas chromatograph with an FID detector is used for ambient methane measurements at the Zeppelin research station. Instrument details are summarised in Table 9, and a flow scheme is shown in Figure 13.

Table 9: Gas chromatograph for methane at the Zeppelin station

Instrument	Carlo Erba FRACTOVAP 4160, S/N 1150392 FID: Carlo Erba Mod. 380
at Zeppelin since	1997
method	GC / FID Detector
sample loop	1 ml
column	plot fused silica: Molecular sieve 5 Å length 250 cm, ID 0.53 mm
carrier gas	N_2 99.999%
operating temperatures	Injector: 270°C, Column: 70°C
analog output	0 - 1 V
calibration interval	working standard once per hour station reference during station visits
instrument specials	a few seconds before injection, the flow through the loop is stopped to equilibrate pressure. sample loop and injection valve reside inside GC oven

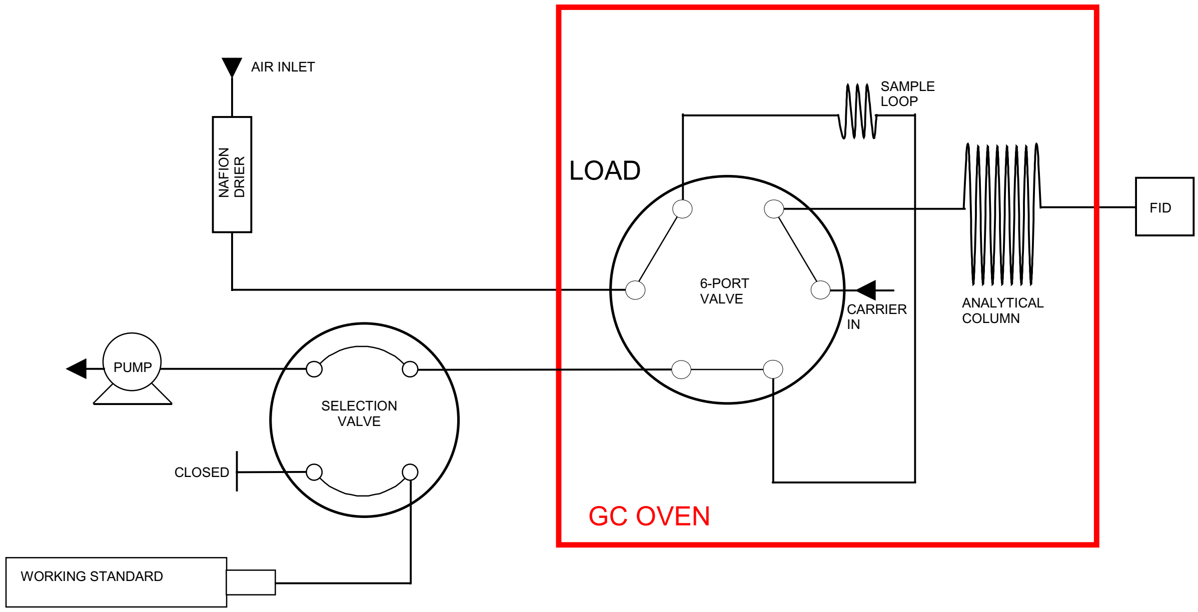


Figure 13: Flow scheme of the methane GC at the Zeppelin station

Gas Standards

Table 10 shows an overview of the methane standards available at the site. Ambient air from Zeppelin Mountain is used for working standards. The station reference is a real air standard from Mace Head (Ireland), which is traced back to the AGAGE / SCRIPPS scale.

Table 10: Station CH_4 cylinders

Gas cylinders	Conc. [ppb]
0509MET2 (working standard)	1838.9
164STD1 (station reference)	1834.7

Operation and Maintenance

Analysis: three ambient air and one working standard samples are analysed per hour. The instrument is calibrated with the station reference when the station is visited by the instrument responsible (approx. every 3 months).

Daily checks: cylinder pressures, temperatures
visual inspection of chromatograms

6.1.3. Data Handling

Data Acquisition and –transfer

HP ChemStation Chromatography Software is used for data acquisition. Both reports and chromatograms are stored as raw data.

Data Treatment

Ambient air mixing ratios are calculated based on peak area by using the concentrations of the working standard. Data evaluation includes consistency checks with charts (in particular retention time, peak start, peak end), checks with the instrument logbook and time series review. The final data evaluation is done weekly at NILU.

Data Submission

At present CH_4 data are not submitted to any data centre, but it is planned to submit data to the GAW Data centre for Greenhouse Gases at JMA.

Comment

Remote access to the data acquisition system from NILU allows the inspection of the data for plausibility. If malfunction is detected, measures are initiated.

6.1.4. Documentation

Logbooks

During the audit the documentation was reviewed for availability and usefulness. The electronic station logbook contained for all parameters all necessary information about maintenance, instrument changes, events and special investigations. The logbook files are accessible from NILU for use in the final data evaluation. The instrument manuals are available at the site.

Comment

The log files were kept up-to-date. All the necessary information was available at the site.

6.2. Inter-Comparison of in situ Methane Measurements

6.2.1. Experimental Procedure

Since no Standard Operation Procedure (SOP) has been established for CH_4 measurements until now, the "SOP for performance auditing ozone analysers at global and regional WMO-GAW sites" (WMO-GAW Report No 97) also serves as a guideline for CH_4 audits.

The five transfer standards of the WCC (approx. 1640, 1745, 1780, 1820 and 2000 ppb CH_4) were stored in the same room as the CH_4 measurement system to equilibrate for one day. The transfer standards were calibrated against CMDL laboratory standards (CA04462, CA04549, CA04580) at EMPA before and after the audit (see Appendix IV). Before the inter-comparison measurements, the pressure regulators and the stainless steel tubing were extensively flushed and leak checked (no pressure drop for half an hour with main cylinder valve closed). All transfer standards were injected 5 times and analysed on September 8 and 9. No modifications of the GC system were made for the inter-comparison. The WCC transfer standards were injected at the working standard port. One transfer standard was also analysed as an ambient air sample. No difference between the two methods could be found. The data was acquired by the station software. This data (mean values and standard deviations) was processed during the audit The experimental details are summarised in Table 11.

Table 11: Experimental details of the methane inter-comparison

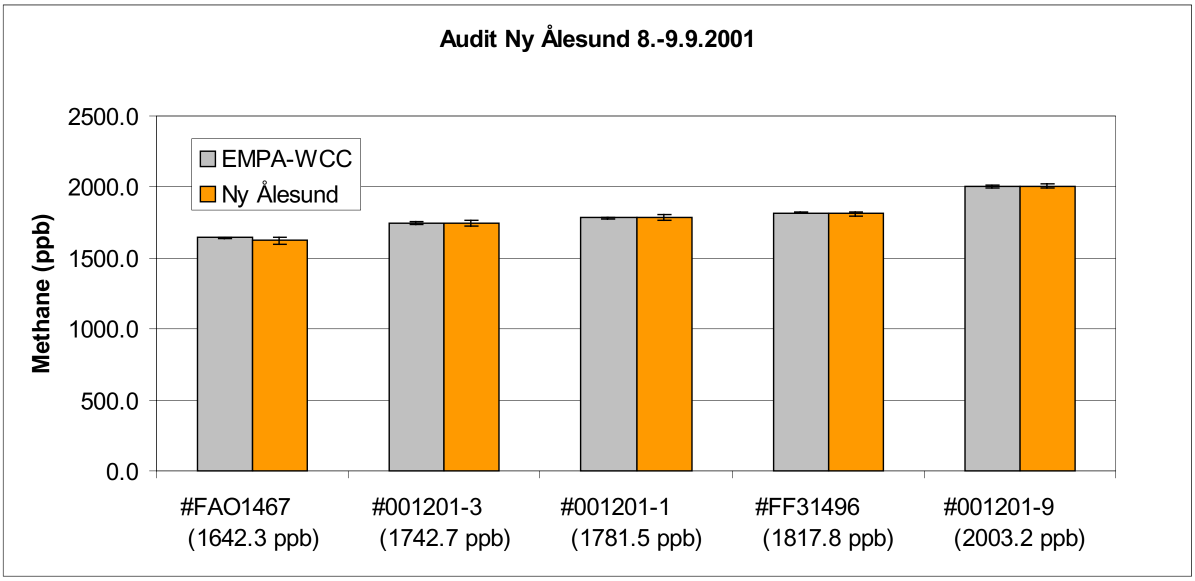
field instrument:	Carlo Erba FRACTOVAP 4160, S/N 1150392
reference:	EMPA-WCC transfer standards 001201-1, 001201-3,001201-9, FF31496, FA01469
data acquisition system:	HP ChemStation
approx. concentration levels:	1640 / 1745 / 1780 / 1820 / 2000 ppb
injections per concentration:	5
Sequence	injection as working standards, every 10 minutes

6.2.2. Results of the Methane Inter-Comparison

The results of the inter-comparison between the Carlo Erba field instrument and the five WCC transfer standards are shown in Table 12. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 14 shows the absolute differences (ppb) between the measurements of the Carlo Erba GC and the WCC transfer standards (TS) (conventional true value). The transfer standards were analysed before and after the audit, and no significant differences were found (t-test at 95% confidence interval). The error bars represent the 95% confidence interval for the calibration of the transfer standards against the CMDL standard and of the multiple injections of the transfer standards at the Zeppelin station. The data from the Carlo Erba field instrument were reprocessed during the audit and are based on the comparison with the working standard.

Table 12: Methane inter-comparison measurements at the Zeppelin station

No.	WCC standard	Carlo Erba / FID (Peak Area) of the Zeppelin station				
	conc.	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	1642.3 ± 8.0 ppb	1623.9	10.2	5	-18.4	-1.1
2	1742.7 ± 8.8 ppb	1745.7	8.2	5	3.0	0.2
3	1781.5 ± 8.9 ppb	1785.2	6.8	5	3.7	0.2
4	1817.8 ± 7.2 ppb	1810.6	5.9	5	-7.7	-0.4
5	2003.3 ± 8.3 ppb	2007.6	6.4	5	4.4	0.2



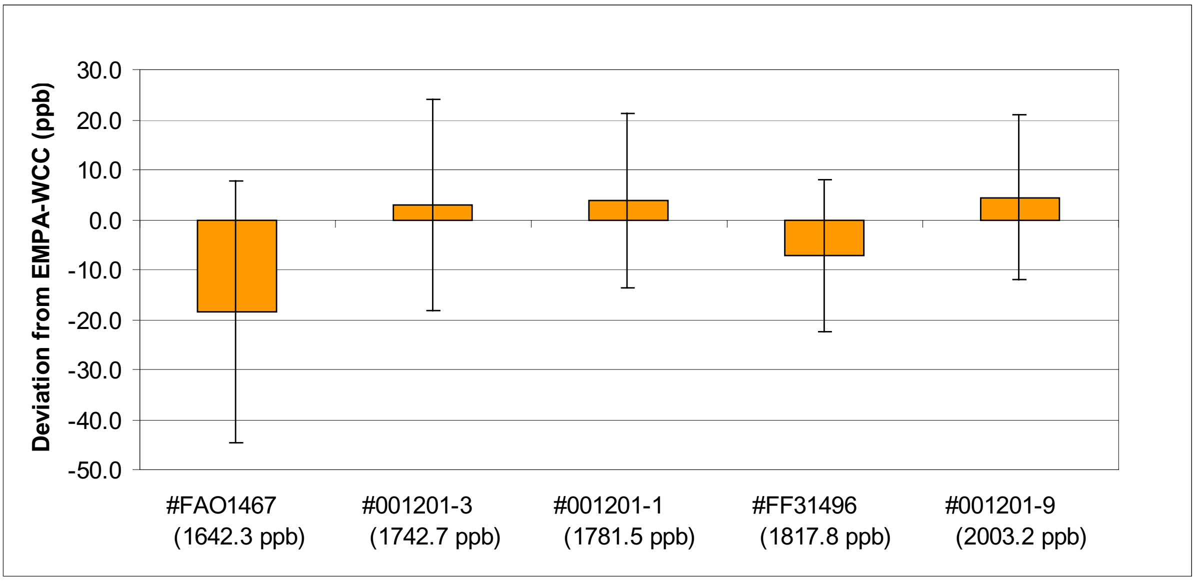


Figure 14: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL scale, Appendix V) measured with the GC system of the Zeppelin station (orange). lower panel: deviation of Zeppelin station from the conventional true value.

Comment

The results for the EMPA-WCC transfer standards obtained with the Zeppelin field instrument agrees very well with the conventional true value in the concentration range between 1740 and 2000 ppb methane. The deviation from the transfer standards is less than 0.4%. A higher deviation of -1.1% was found for the low concentration transfer standard (1620 ppb). However, with respect to the expected concentration range at the Zeppelin site, the result for the lowest concentration is not as relevant. Thus, the Zeppelin methane measurements can be considered to be traceable to the GAW reference standards.

6.3. Recommendation for the Measurement of Methane

The good result of the inter-comparison measurements show that the whole measurement system, beginning at the air inlet and ending at the data treatment is appropriate for the measurement of methane. Therefore no further technical recommendations are made by the WCC.

The submission of the data to the GAW data center for greenhouse gases at JMA is encouraged.

7. Conclusions

The global GAW station Zeppelin Mountain on Svalbard is an established site within the GAW programme. An optimal platform for extensive atmospheric measurements is now available with the new laboratory facilities in the rebuilt station.

The results of the inter-comparisons for surface ozone, carbon monoxide and methane showed good agreement between EMPA-WCC and the station instruments for all parameters. However, CO measurements could be improved if more reference gases would be available to characterise the non-linearity of the CO instrument.

Due to the good audit results, only minor recommendations were made by EMPA-WCC concerning surface ozone, carbon monoxide and methane measurements.

Appendix

I EMPA Transfer Standard TEI 49C-PS

The Model 49C-PS is based on the principle that ozone molecules absorb UV light at a wavelength of 254 nm. The UV absorption is proportional to the concentration as described by the Lambert-Beer Law.

Zero air is supplied to the Model 49C-PS through the zero air bulkhead and is split into two gas streams, as shown in Figure 15. One gas stream flows through a pressure regulator to the reference solenoid valve to become the zero reference gas. The second zero air stream flows through a pressure regulator, ozonator, manifold and the sample solenoid valve to become the sample gas. Ozone from the manifold is delivered to the ozone bulkhead. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa.

The UV light intensities of each cell are measured by detectors A and B. After the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The Model 49C-PS then determines the ozone concentration for each cell and outputs the average concentration.

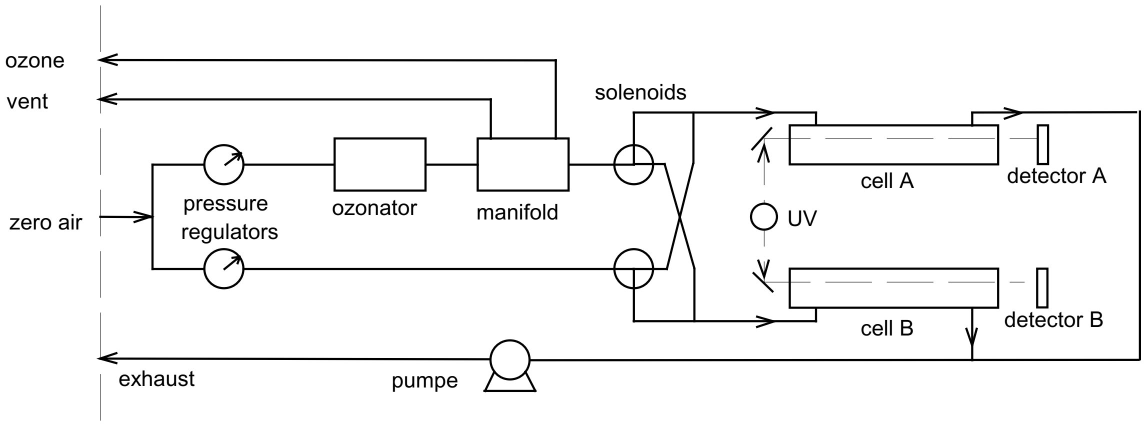


Figure 15: Flow schematic of TEI 49C-PS

II Stability of the Transfer Standard TEI 49C-PS

To exclude errors that might result from transportation of the transfer standard, the TEI 49C PS #54509-300 was compared with the SRP#15 before and after the field audit.

The procedure and instrumental details of this inter-comparison at the EMPA calibration laboratory are summarised in Table 13 and Figure 16.

Table 13: Intercomparison procedure SRP - TEI 49C-PS

pressure transducer:	zero and span check (calibrated barometer) at start and end of procedure
concentration range:	0 - 200 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 140 / 190 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 before and 3 after audit
zero air supply:	Pressurised air - zero air generator (CO catalyst, Purafil, charcoal)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

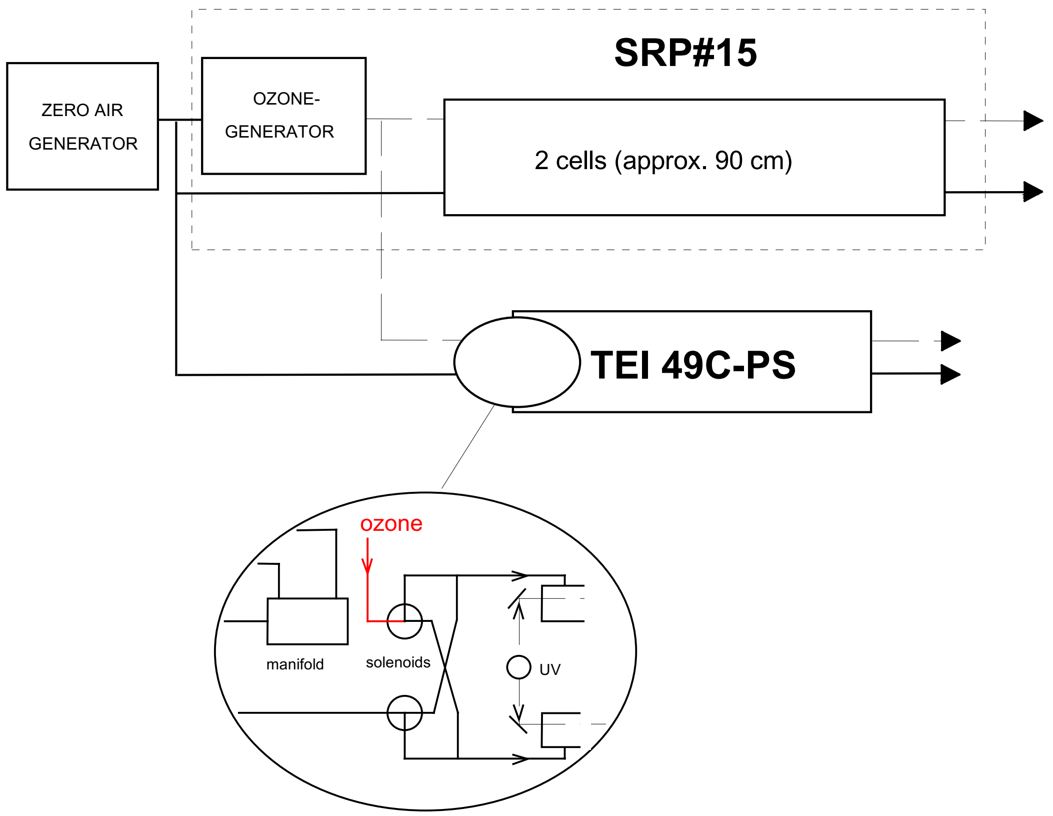


Figure 16: Instruments set up SRP -TEI 49C-PS

The stability of the transfer standard was thoroughly examined with respect to the uncertainties of the different components (systematic error and precision). For the GAW transfer standard of the WCC-O_3 (TEI 49C-PS) the assessment criteria, taking into account the uncertainty of the SRP, are defined to approximately ±(1 ppb + 0.5%).

Figures 17 and 18 show the resulting linear regression and the corresponding 95% precision interval for the comparisons of TEI 49C-PS vs. SRP#15. The results show that the EMPA transfer standard fulfilled the recommended criteria for the period of the audit, including transportation.

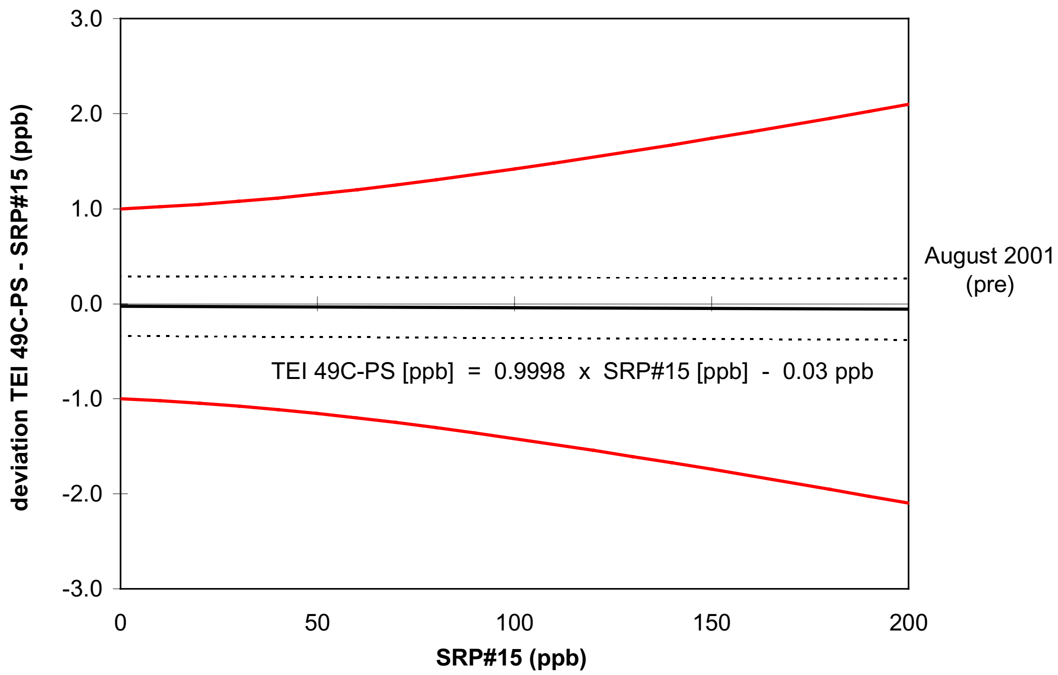


Figure 17: Transfer standard before audit

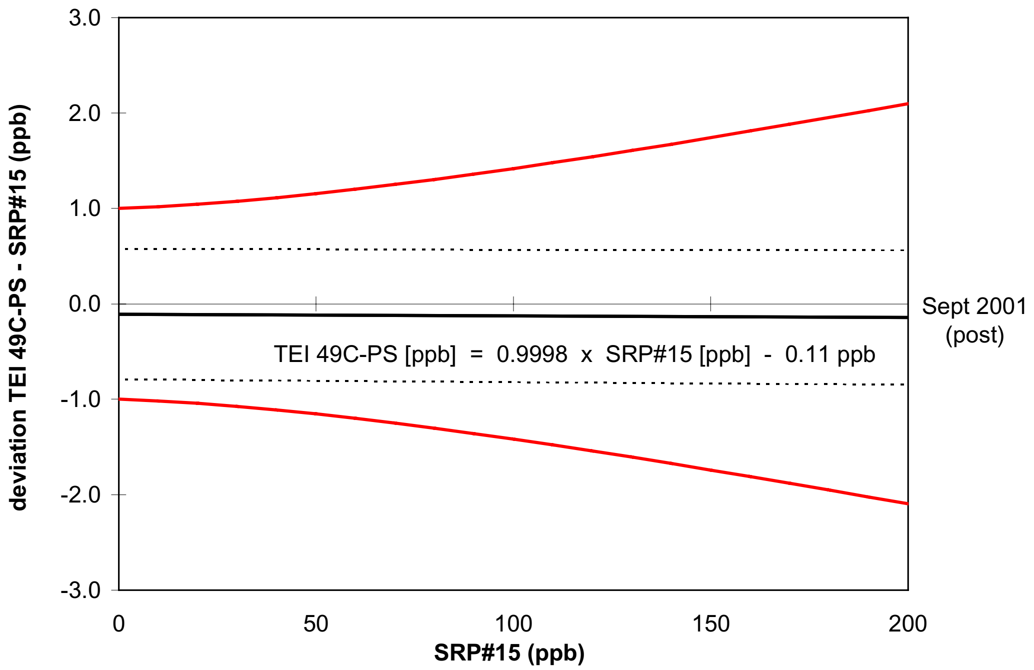


Figure 18: Transfer standard after audit

III WCC Carbon Monoxide Reference

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CO in the atmosphere, calibrate standards of other laboratories and to otherwise provide reference gases to the community measuring atmospheric CO. This CO reference scale developed at CMDL was designated by WMO as the reference for the GAW programme. The standards used at the WCC are listed in Table 14:

The CO scale of the CMDL was recently revised. EMPA-WCC refers to the **new** scale. The EMPA-WCC transfer standards used during the audit are listed in Table 15.

Table 14: CMDL CO Standards at the WCC. The error represents the measured standard deviation and the ultimate determination of the primary standard.

Standard (Gas Cylinders)	CMDL old scale*	CMDL new scale**	Cylinder
CMDL Laboratory Standard (basis for WCC)	44.0 ± 1.0 ppb	52.1 ± 1.1 ppb	CA03209
CMDL Laboratory Standard (")	97.6 ± 1.0 ppb	105.8 ± 1.1 ppb	CA02803
CMDL Laboratory Standard (")	144.3 ± 1.4 ppb	149.7 ± 1.5 ppb	CA03295
CMDL Laboratory Standard (")	189.3 ± 1.9 ppb	194.7 ± 1.9 ppb	CA02859
CMDL Laboratory Standard (")	287.5 ± 8.6 ppb	295.5 ± 3.0 ppb	CA02854

* Certificates from 5.8.97 (97.6, 189.3, 287.5 ppb) and 7.01.98 (44.0, 144.3 ppb)
** Revised scale (by P. Novelli), 23.01.01

Table 15: CO transfer standards of the WCC (average of calibrations from 16.05.01 and 01.10.01). The error represents the measured standard deviation.

Transfer Standard (Gas Cylinders)	CO (calibrated against CMDL new scale CA02859) with AL5001		Cylinder
	before audit	after audit	
WCC Transfer Standard (2 l cylinder)	52.2 ± 0.6 ppb	52.3 ± 0.5 ppb	001201-3
WCC Transfer Standard (2 l cylinder)	102.4 ± 0.7 ppb	102.3 ± 0.8 ppb	001201-2
WCC Transfer Standard (6 l cylinder)	158.9 ± 1.0 ppb	158.5 ± 0.7 ppb	FF30491
WCC Transfer Standard (6 l cylinder)	209.6 ± 1.6 ppb	209.6± 1.0 ppb	FA01467

IV WCC Methane Reference

The methane reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CH_4 in the atmosphere. This CH_4 reference scale developed at CMDL was designated by WMO as the reference for the GAW programme. The CMDL standards used at the WCC are listed in Table 16. The EMPA-WCC transfer standards (Table 17) are traced back to the CMDL standards shown below.

Table 16: CMDL CH_4 Standards at the WCC. The error represents the measured standard deviation and the ultimate determination of the primary standard.

CMDL Standard	Methane [ppb]*	Cylinder
CMDL Laboratory Standard (basis for WCC)	1598.9 ± 0.28 ppb	CA04549
CMDL Laboratory Standard (")	1795.1 ± 0.19 ppb	CA04462
CMDL Laboratory Standard (")	1882.0 ± 0.24 ppb	CA04580

* Certificates from 13.09.2000

Table 17: CH_4 transfer standards of the WCC (average of calibrations from 25.01/9.02.01 and 25.09.01). The error represents the measured standard deviation.

Transfer Standard (Gas Cylinders)	CH_4 (calibrated against CMDL standards listed in Table 19)		Cylinder
	before audit	after audit	
WCC Transfer Standard (6 l cylinder)	1643.6 ± 5.2 ppb	1641.5 ± 2.4 ppb	FA01467
WCC Transfer Standard (2 l cylinder)	1743.7 ± 6.6 ppb	1742.1 ± 2.2 ppb	001201-3
WCC Transfer Standard (2 l cylinder)	1784.0 ± 4.0 ppb	1780.0 ± 3.4 ppb	001201-1
WCC Transfer Standard (6 l cylinder)	1819.8 ± 4.4 ppb	1816.8 ± 2.6 ppb	FF31496
WCC Transfer Standard (6 l cylinder)	2004.6 ± 6.0 ppb	2002.5 ± 2.5 ppb	001201-9