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 01/1

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE

AT THE GLOBAL GAW STATION ZUGSPITZE / HOHENPEISSENBERG, PLATFORM ZUGSPITZE, GERMANY

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Submitted by

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

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Contents:

1. Abstract

A system and performance audit was conducted at the Global Atmosphere Watch station Zugspitze from February 5 to 8, 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 2001, the Zugspitze GAW station is going to be moved from the Zugspitze summit to the recently renovated Schneefernerhaus 300 m below the summit site. During the audit, part of the instrumentation had already been installed at the new site. The Schneefernerhaus offers now spacious laboratories with an excellent infrastructure to support an efficient GAW station work. However, parallel measurements at both sites are considered to be important by EMPA-WCC to ensure the consistency of the existing and future time series.

Audit of the Surface Ozone Measurement

The intercomparison, consisting of three multipoint runs, between the WCC transfer standard and the ozone instruments of the station (analyser and calibrator) demonstrated excellent 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). The station calibrator (TEI 49PS) was also compared to the WCC transfer standard. It was found that the station calibrator was not working properly during the audit. The station operators were aware of the problem, and the instrument was sent for repair after the audit.

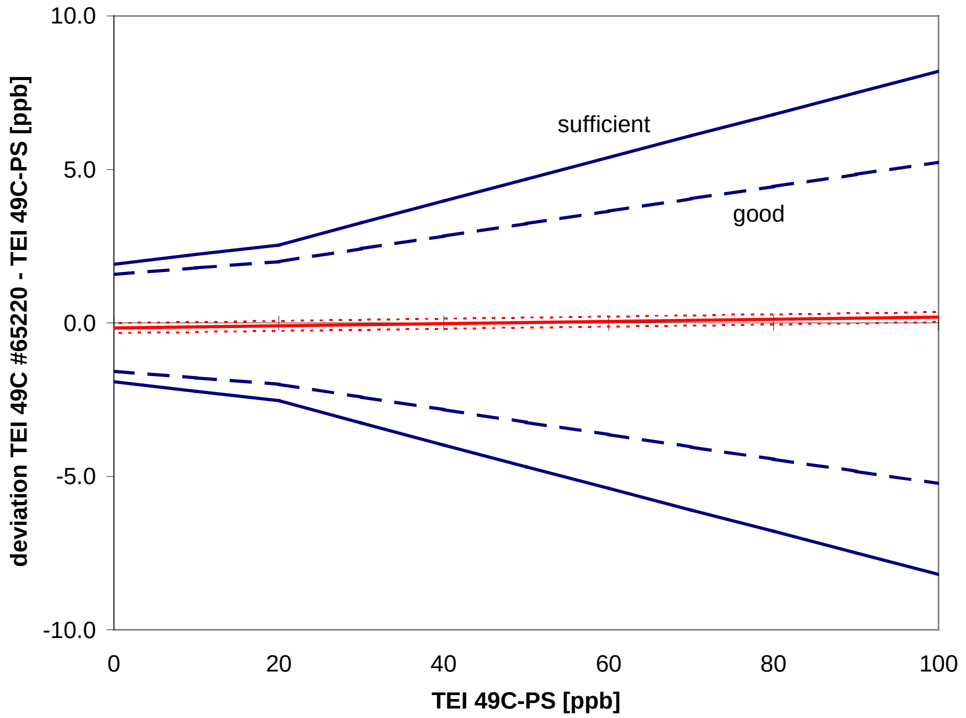


Figure 1: Intercomparison of the TEI 49C S/N 65220-347 with the WCC transfer standard

Audit of the Carbon Monoxide Measurement

A significant difference between the EMPA-WCC transfer standards and the results of the Zugspitze CO gas chromatograph was observed during the audit. Only part of the difference can be explained by the revision of the carbon monoxide scale of the National Oceanic and

Atmospheric Administration / Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL). The observed differences were also confirmed by inter-comparison measurements of ambient air with the EMPA-WCC transfer CO instrument (AeroLaser AL 5001). However, the deviations of the station GC system from the EMPA-WCC transfer standards were reproducible, indicating an incorrect calibration function. With the correct calibration function, reliable CO measurements should be achievable with the Zugspitze GC system.

The two NDIR CO instruments (TEI 48S) also deviated significantly from the EMPA-WCC transfer CO instrument (AeroLaser AL 5001) during instrument inter-comparison using ambient air. The type of instrument used at Zugspitze is not state-of-the-art technology, and a replacement with modern instrumentation should be considered by the station operators.

Audit of the Methane Measurement

The results of the inter-comparisons between the four EMPA-WCC transfer standards and the Zugspitze GC system showed good agreement for the relevant concentration range of 1780 to 2000 ppb. The deviation was within ±0.4%.

Conclusion

All measurements of the audited parameters (O_3, CO, CH_4) at Zugspitze were performed at a high level. 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 measurement of CO with the NDIR instruments is regarded as a weak point of the system. Since it is planned to move part of the instrumentation to the Schneefernerhaus, a re-design of the system concerning zero point measurements and correction should be considered. The NDIR instruments should be replaced by more modern instrumentation.

Since the measurements of the GAW programme are moved from the Zugspitze summit site to the Schneefernerhaus 300 m below the old site, parallel measurements at both sites are considered to be important by EMPA-WCC to ensure the consistency of the existing and future time series and to characterise differences between the two sites.

The new laboratories at the Schneefernerhaus offer very good infrastructure that supports the measurements of several parameters within the GAW programme.

Dübendorf, 23. August 2001 EMPA Dübendorf, WCC

Project scientist Project manager

Dr. C. Zellweger Dr. B. Buchmann

2. Introduction

The **Global GAW Stations Hohenpeissenberg and Zugspitze** are part of Germany's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) programme. The observatory on top of the Zugspitze is an established site for long-term measurements of greenhouse gases, ozone and physical and meteorological parameters. In response to the German Federal Government's intention of contributing to the United Nation's Global Atmosphere Watch programme, the State of Bavaria re-built the former Hotel Schneefernerhaus just below the Zugspitze summit from 1993 to 1997 to serve now as Germany's highest environmental research station.

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 arrangement about every two years.

In agreement with the station manager Dr. Ludwig Ries from the Umweltbundesamt (UBA) and Dr. H.E. Scheel from the Institut für Atmosphärische Umweltforschung (IFU), a **system and performance audit** at the Observatory Zugspitze / Schneefernerhaus was conducted. The scope of the audit that took place from February 5 to 8, 2001, 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 intercomparison 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 the station manager, the QA/SAC Germany and the World Meteorological Organization in Geneva.

Staff involved in the audit

Zugspitze	Dr. Ludwig Ries	contacts, general program, organisation
	Christian Propst	technical assistance on the observatory
	Ralf Sohmer	technical assistance on the observatory
	Dr. H. E. Scheel	data evaluation for CO and CH_4
EMPA-WCC	Dr. Christoph Zellweger	lead auditor
EMPA-QA/SAC	Dr. Jörg Klausen	assistant auditor

Previous audits at the GAW station Zugspitze:

- April 1996 by EMPA-WCC for surface ozone.
- November 1997 by EMPA-WCC for surface ozone and carbon monoxide.

3. Global GAW Site Zugspitze

3.1. Description of the Site

Zugspitze, near Garmisch-Partenkirchen, is the highest mountain of the German Alps (2962 m above sea level). It is located in south-east Germany, approximately 90 km south-west of Munich, at the Austrian border. Because of the high elevation of the mountain station, the site is considered to be in the free troposphere, and not influenced by regional pollution sources most of the time. Access to the station is by cable car directly to the summit of the Zugspitze.

The monitoring station on the summit (co-ordinates: 47°25.0' N, 10°59.0' E; elevation: 2962 m above sea level) is housed in a temperature-controlled room next to the view point terrace. The air inlet system and the meteorological sensors are mounted on the flat roof of the shelter.

It is planned to perform all future measurements for the GAW programme at the newly renovated Schneefernerhaus (co-ordinates: 47°25.0' N, 10°58.9' E; elevation: 2660 m above sea level). The Schneefernerhaus is located approx. 600m south-west of the summit station and is accessible by cog wheel train or cable car. In contrast to the summit site there are almost no tourist activities at the Schneefernerhaus. Parallel measurements of surface ozone are currently performed at both sites to ensure the consistency in the long-term data series. Such measurements are also planned for carbon monoxide and methane. However, at the time of the audit, only ozone measurements were operational at the Scheefernerhaus.

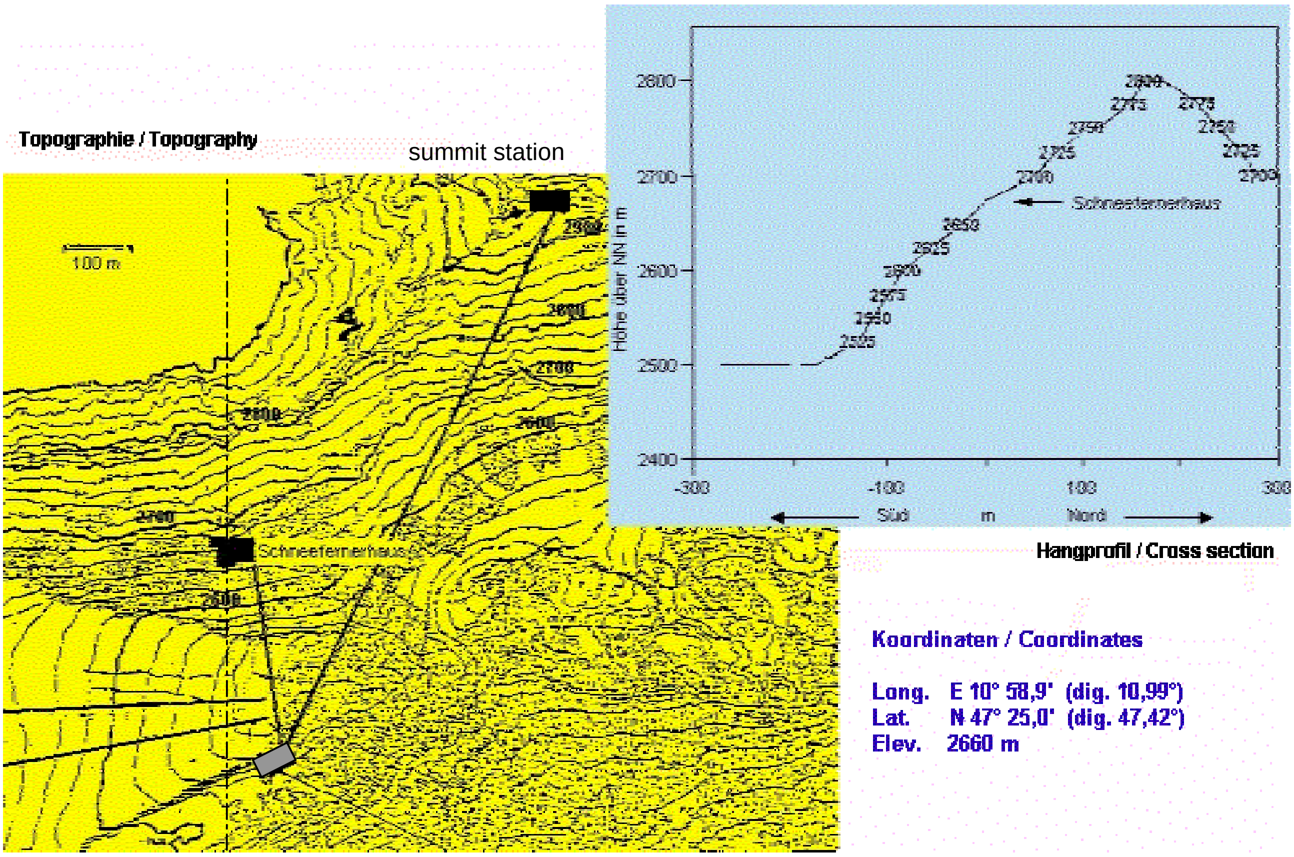


Figure 2: The topography surrounding the Schneefernerhaus (from www.schneefernerhaus.de)

The annual mean temperature at the Zugspitze site is –4.8°C. The main wind directions are N, W, and SSE. The influence of the meteorology is well described for the Zugspitze, and filter functions are used for the interpretation of the data [W. Fricke *et. al*., Filterung luftchemischer Messreihen im Alpenraum zur Charakterisierung ihrer Repräsentanz, *Berichte des Deutschen Wetterdienstes*, Nr. 211, 2000].

Ozone-, Carbon Monoxide and Methane Levels at the Zugspitze

The distribution of the hourly mean values of O_3, CO and CH_4 from 1999 are shown in Figures 3 to 5.

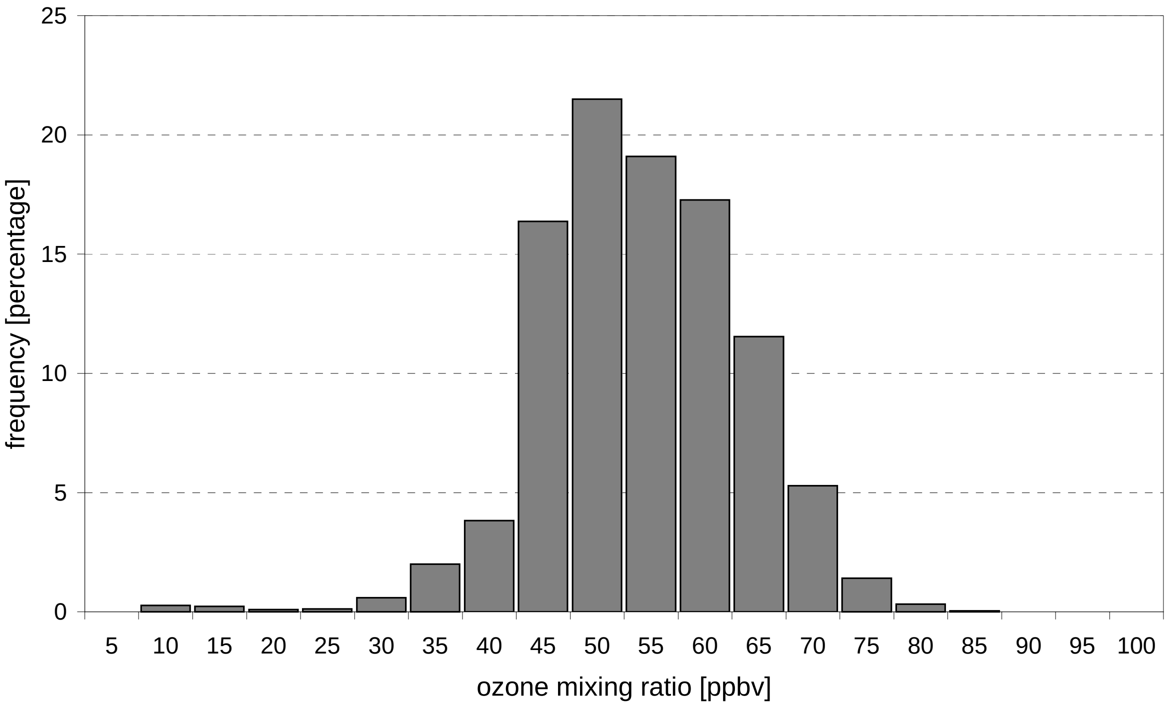


Figure 3: Frequency distribution of the hourly mean ozone mixing ratio (1999) at the Zugspitze summit station. Availability of data: 91%.

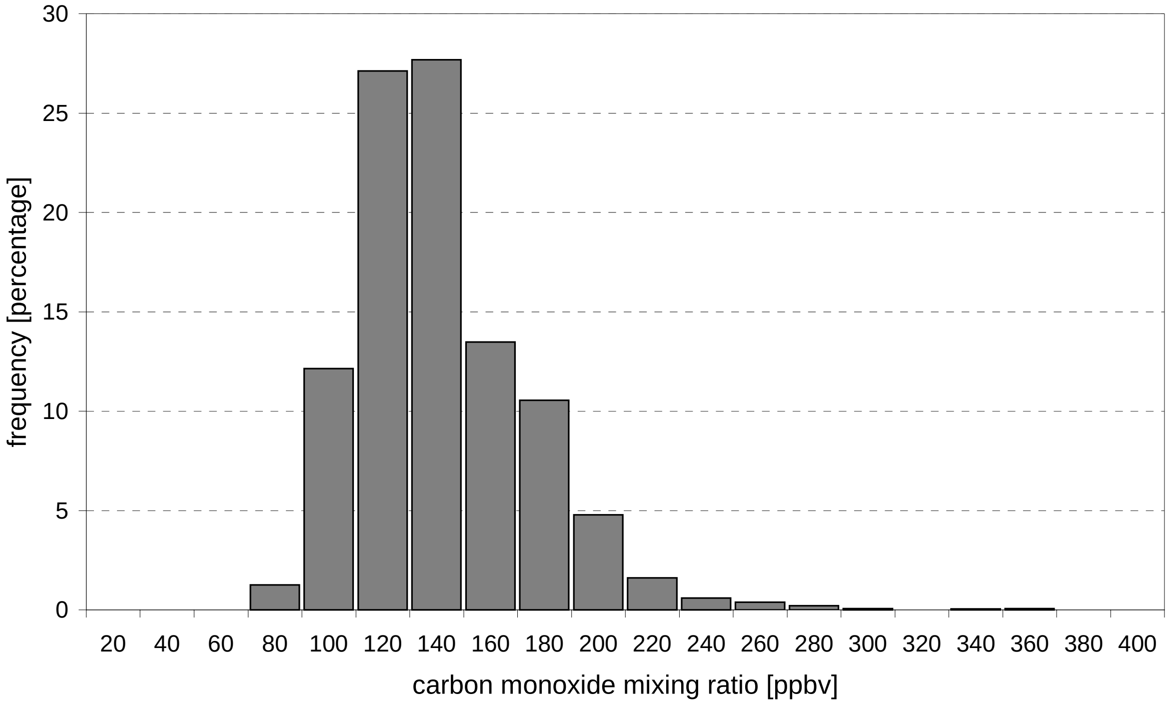


Figure 4: Frequency distribution of the hourly mean carbon monoxide mixing ratio (1999) at Zugspitze. Availability of data: 85%.

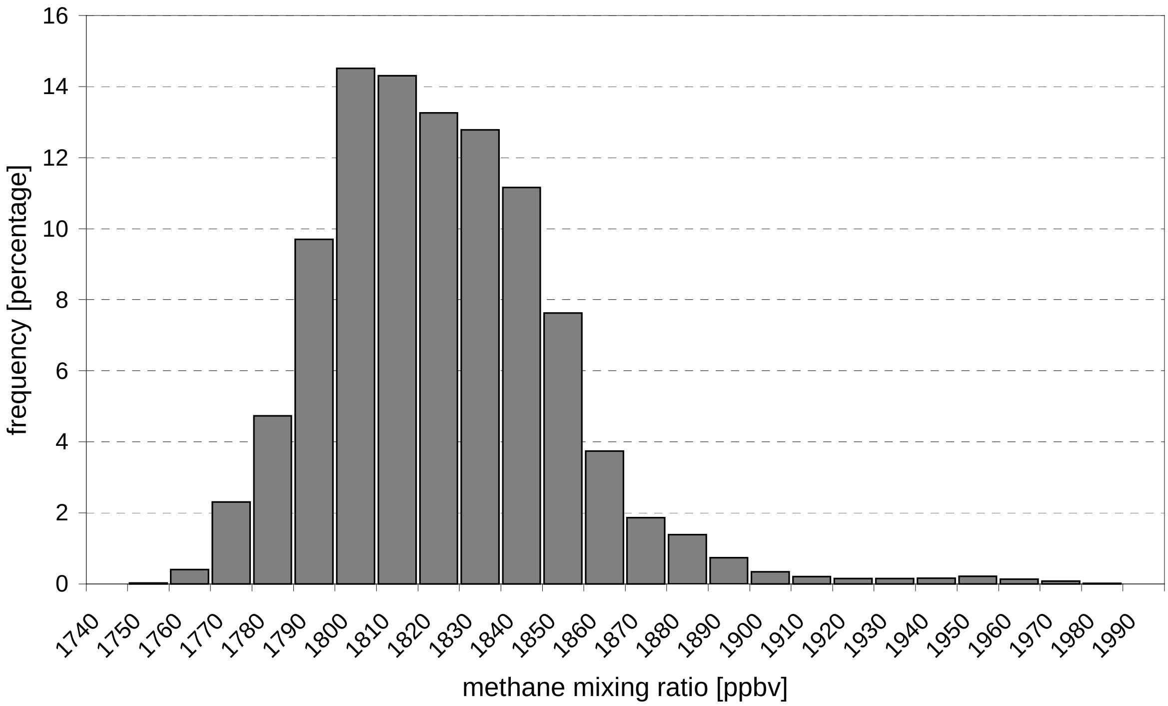


Figure 5: Frequency distribution of the hourly mean methane mixing ratio (1999) at Zugspitze. Availability of data: 90%.

3.2. Description of the Observatory

Zugspitze summit (old GAW site)

The laboratories of the old site are housed in a temperature controlled facility on the view point terrace. The air inlet system and the meteorological sensors are mounted on the flat roof of the shelter.

Schneefernerhaus (new GAW site)

The former Hotel Schneefernerhaus was renovated from 1993 to 1997 and offers now spacious laboratories with excellent infrastructure. The GAW measurements performed by UBA are located on the 4th floor, with air inlet facilities directly on a terrace above the laboratory.

Comment

- Compared to the old GAW site on the summit, the Schneefernerhaus offers spacious laboratories which meet all requirements for the measurement of air pollutants.
- The relative absence of tourist activities is regarded as an advantage over the old summit site.
- Parallel measurements are regarded as important to ensure the consistency of the time series. Such measurements are currently performed for ozone, and are planned for carbon monoxide and methane. Since the new site is at a significantly lower altitude and less exposed, such parallel comparison measurement should be performed for all parameters for at least one year.

Figure 6: View of Zugspitze (bottom left: Schneefernerhaus: top right: Zugspitze summit)

Figure 7: Inside the new laboratory at Schneefernerhaus

3.3. Staff / Operators

Table 1: Staff responsible for the GAW site Zugspitze (by early 2001)

Name	Position and duty
Dr. Wolfgang Fricke	GAW Country contact
Dr. Horst Werner	station manager (Administration)
Dr. Ludwig Ries	station manager (Operation)
Mr. Christian Propst	station operator
Mr. Ralf Sohmer	station operator
Dr. H.E. Scheel (IFU)	data evaluation, consulting
Prof. Dr. V.A. Mohnen	scientific support / expert

4. System- and Performance Audit for Surface Ozone

Ozone measurements became operational at the Schneefernerhaus in late 1999, and now replace the data from the summit site. Therefore the system and performance audit for surface ozone was carried out at the Schneefernerhaus. Parallel measurements at the Zugspitze summit site are still ongoing.

4.1. Monitoring Set-up and Procedures

4.1.1. Air Inlet System

Sampling-location:	Schneefernerhaus, on a terrace above the laboratory, 2.5 m above the roof		
Sample inlet:			
Rain protection:	The Inlet is protected against rain and snow by a stainless steel beaker.		
Inlet-filter:	Teflon inlet filter before analyser, exchanged every 6-8 weeks.		
Sampling-line:			
Dimensions:	inlet / manifold:	length = 4.2 m,	inner diameter = 8 cm
	manifold to TEI 49C:	length = 1 m,	inner diameter = 4 mm
Material:	inlet and manifold: glass		
	manifold to analyser: PFA		
Flow rate:	inlet / manifold:	350 ℓ/min	
	manifold to TEI 49C:	0.6 ℓ/min	

Residence time in the sampling line: ca. 5 s

Comment

All teflon tubes and glass manifolds were 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.

4.1.2. Instrumentation

Ozone Analyser

At the Schneefernerhaus one O_3 analyser model 49C (Table 2) from Thermo Environmental 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 Schneefernerhaus

Type	TEI 49C #65220-347
Method	UV absorption at 254 nm
purchase date	autumn 1999
at Schneefernerhaus	since November 1999
Range	0-1000 ppb
Analog output	0-10 V
O_3 Background [ppb]	0.0
Cal. Factor	1.025

Ozone Calibrator

An UV photometric O_3-Calibrator model 49C PS from Thermo Environmental Instruments Inc. is in use. The calibrator was used in the German national monitoring network as a transfer standard before its use as a station calibrator at the Schneefernerhaus. The instrument was compared to the TEI 49C PS transfer standard of the Fraunhofer Institute for Atmospheric Environmental Research (IFU), Garmisch-Partenkirchen, Germany in January 2000 and January 2001. The IFU transfer standard is traceable to EMPA-WCC (last intercomparison with SRP#15 October 2000 at EMPA).

The zero air unit consists of a VOC removing catalyst followed by activated charcoal.

Operation and Maintenance

Preventive maintenance includes the weekly check of sample flow rates, intensities, noise, pressure and temperatures. If malfunction is detected, measures are taken.

Manual zero and span checks are performed weekly with the station calibrator. Until now these checks were not used to calibrate the instrument. A calibration was done yearly with the IFU transfer standard (TEI 49C PS) for both the station analyser and calibrator.

Comment

The station calibrator was not used for the calibration of the analyser at the site mainly because the station calibrator was not as stable as the analyser.

4.1.3. Data Handling

Data Acquisition and –transfer

Data Acquisition is made with the C series communication software (version 2.2.0) from Thermo Environmental Instruments. The data (5 minute average values) is stored weekly on a notebook, and the data transfer is done by floppy disc.

Data Treatment

Data treatment is performed once per month at the measurement site. This data treatment includes:
- plausibility checks
- data check with station logbook

Data Submission

At present surface ozone data is not reported to the database of GAW World Data Centre for Surface Ozone (WDCSO) at NILU.

4.1.4. Documentation

Logbooks

Logbooks are available for the ozone instrument. The notes are up to date and describe all important events.

Standard Operation Procedures (SOPs)

The manuals for all instruments are available. For a lot of operations specific check lists have been developed.

Comment

The weekly checklists and the up-to-date logbooks support the quality of the data. No change of the current practise 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-III) was operated in stand-by mode for warming up for 12 hours (in deviation from the GAW Report No. 97 which recommends only one hour of warm-up). During this stabilisation time the transfer standard and the PFA tubing connections to the instruments were conditioned with 250 ppb ozone for 150 minutes. Afterwards, three comparison runs between the field instruments (analyser and calibrator) and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 8 the experimental set up during the audit. No modifications of the ozone analysers which could influence the measurements were made for the intercomparisons.

The audit procedure included a direct intercomparison 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 instruments:	TEI 49C #65220-347 (analyser) TEI 49C-PS #58686-319 (calibrator)
ozone source:	WCC: TEI 49C-PS, internal 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:	C Series Communication Software Version 2.2.0 (TEI), WCC reference and station analyser 16-channel ADC circuit board with acquisition software for the inter-comparison of the station calibrator
pressure transducer readings:	TEI 49C-PS (WCC): 550.8 hPa TEI 49C #65220-347: 550.4 hPa TEI 49C-PS #58686-319: 550.8 hPa (no adjustment made)
concentration range	0 - 100 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	15 / 35 / 55 / 75 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	3 x on Feb. 6, 2001
connection between instruments:	about 1.5 meter of 1/4" PFA tubing

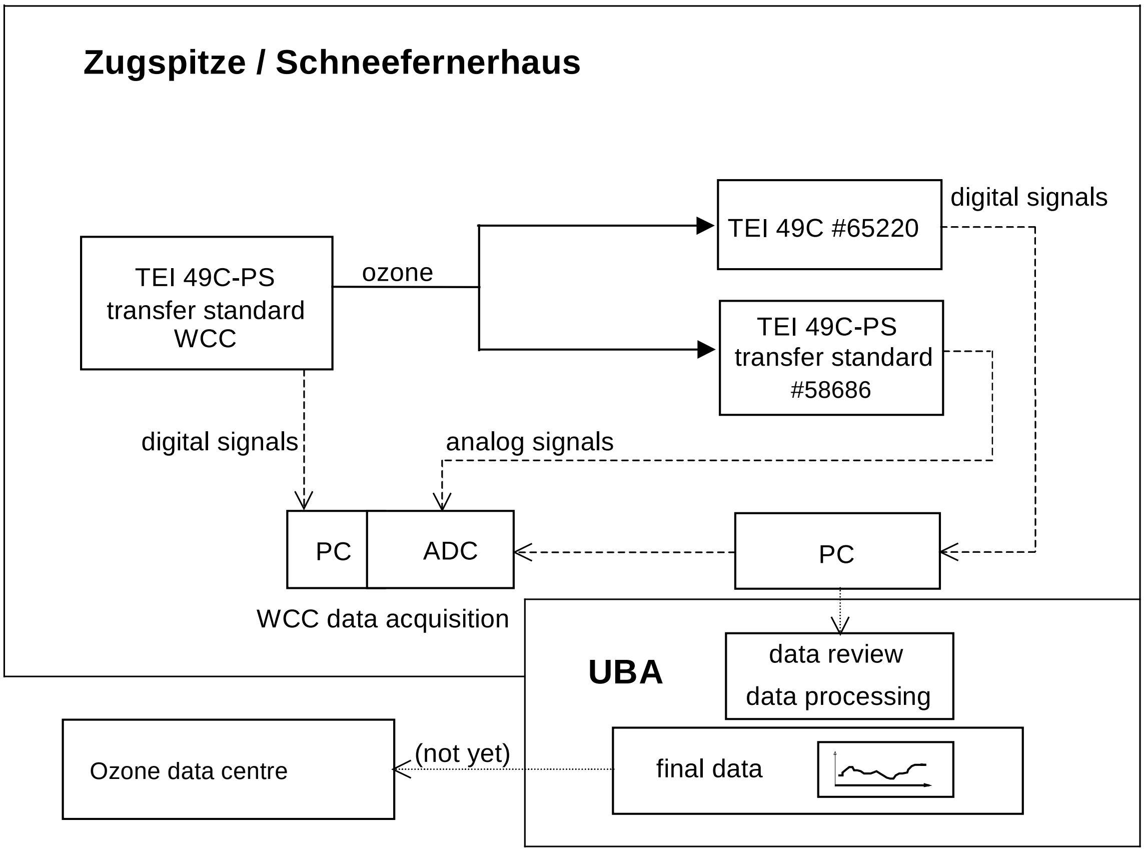


Figure 8: Experimental set up for the ozone intercomparison

4.2.2. Results

Ozone Analyser

The results comprise the intercomparison between the TEI 49C field instrument and the WCC transfer standard TEI 49C-PS, carried out on February 6, 2001.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 1-minute-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 9 and 10 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 9 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 10 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 11).

The data used for the evaluation was acquired by the C series communication software from TEI by the RS-232 interface. This is the usual station data acquisition method at present.

Table 4: Inter-comparison of the ozone field instrument

	TEI 49C-PS		TEI 49C #65220			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.4	0.16	0.4	0.17	0.0	
2	89.9	0.11	90.0	0.31	0.0	0.0%
3	15.1	0.10	15.0	0.39	-0.1	-0.5%
4	74.9	0.16	75.1	0.29	0.1	0.2%
5	55.0	0.10	55.1	0.22	0.1	0.1%
6	35.0	0.11	35.1	0.24	0.0	0.1%
7	0.6	0.15	0.4	0.12	-0.2	
8	0.4	0.10	0.2	0.20	-0.2	
9	14.9	0.27	14.7	0.32	-0.2	-1.3%
10	34.8	0.22	34.9	0.19	0.0	0.1%
11	74.9	0.14	75.0	0.32	0.2	0.2%
12	55.0	0.13	55.0	0.16	0.0	0.0%
13	89.9	0.12	90.1	0.31	0.2	0.2%
14	0.4	0.11	0.4	0.06	0.0	
15	0.5	0.06	0.3	0.13	-0.2	
16	74.9	0.13	75.1	0.18	0.2	0.3%
17	15.0	0.18	14.7	0.16	-0.3	-1.7%
18	54.7	0.24	54.6	0.32	-0.1	-0.2%
19	35.0	0.17	34.9	0.25	-0.1	-0.3%
20	89.7	0.11	89.9	0.21	0.1	0.1%
21	0.4	0.05	0.2	0.33	-0.2	

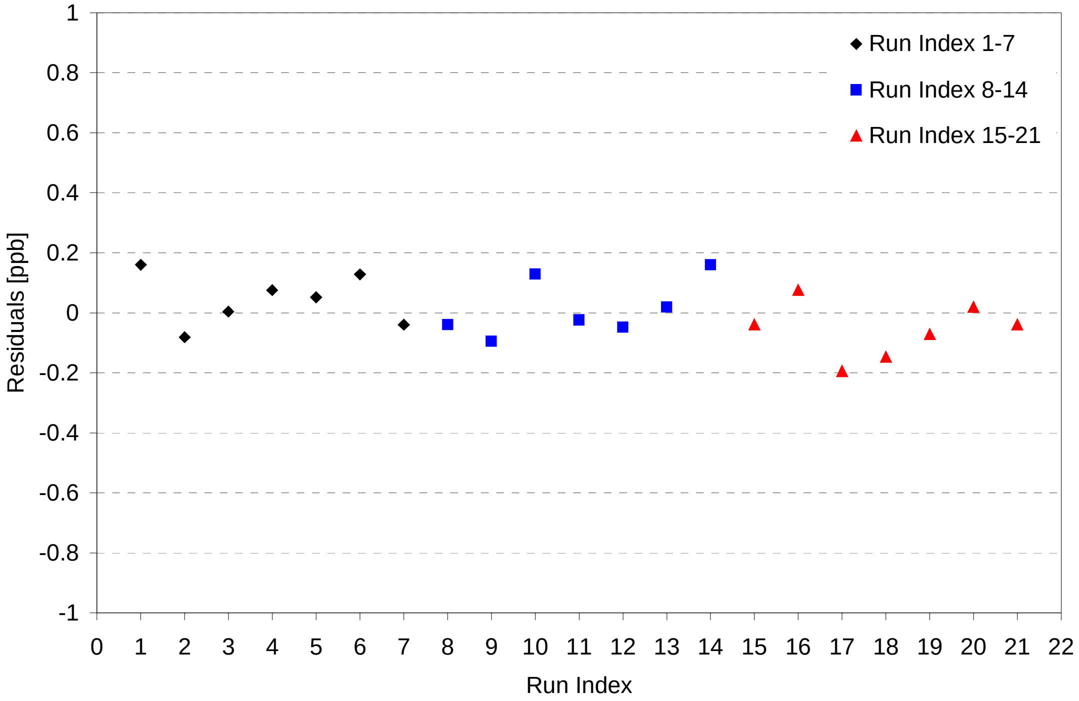


Figure 9: Residuals to the linear regression function (TEI 49C #65220-347) vs the run index (time dependence)

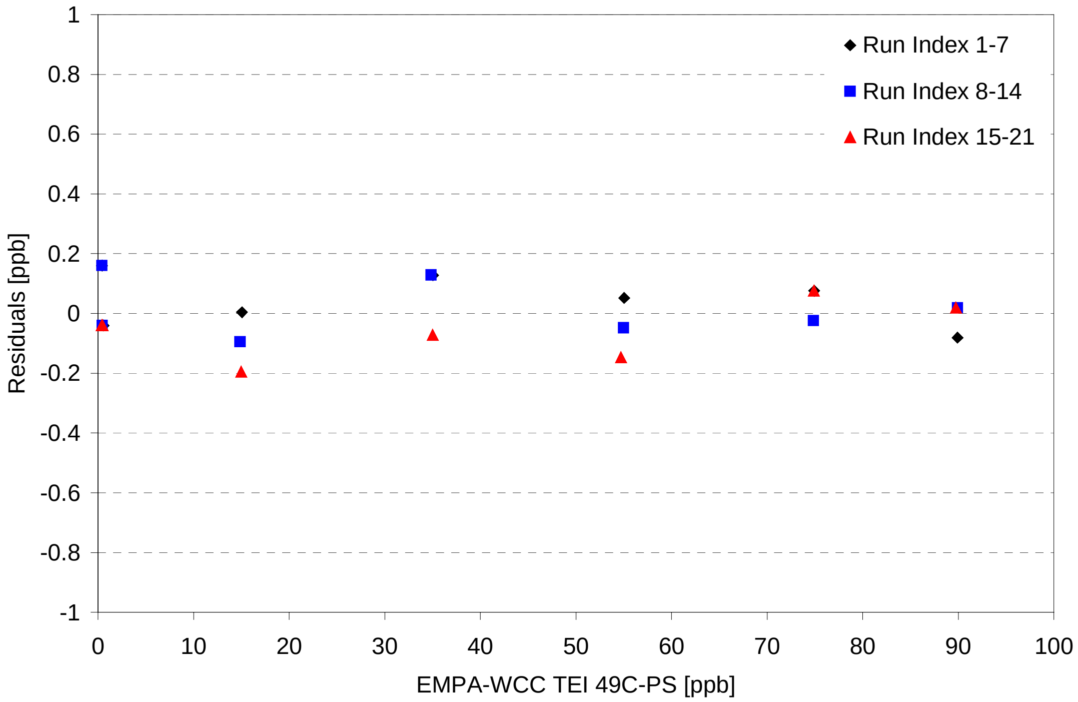


Figure 10: Residuals to the linear regression function (TEI 49C #65220-347) vs the concentration of the WCC transfer standard (concentration dependence)

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

TEI 49C #65220:

$$TEI\ 49C = 1.004 \times TEI\ 49C\text{-}PS - 0.2\ ppb$$

TEI 49C = O_3 mixing ratio in ppb, determined with TEI 49C #65220-347

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 = 1) f=degree of freedom
	- offset S_b in ppb	0.03	(f = 1)
	- residuals in ppb	0.08	(f = 19)

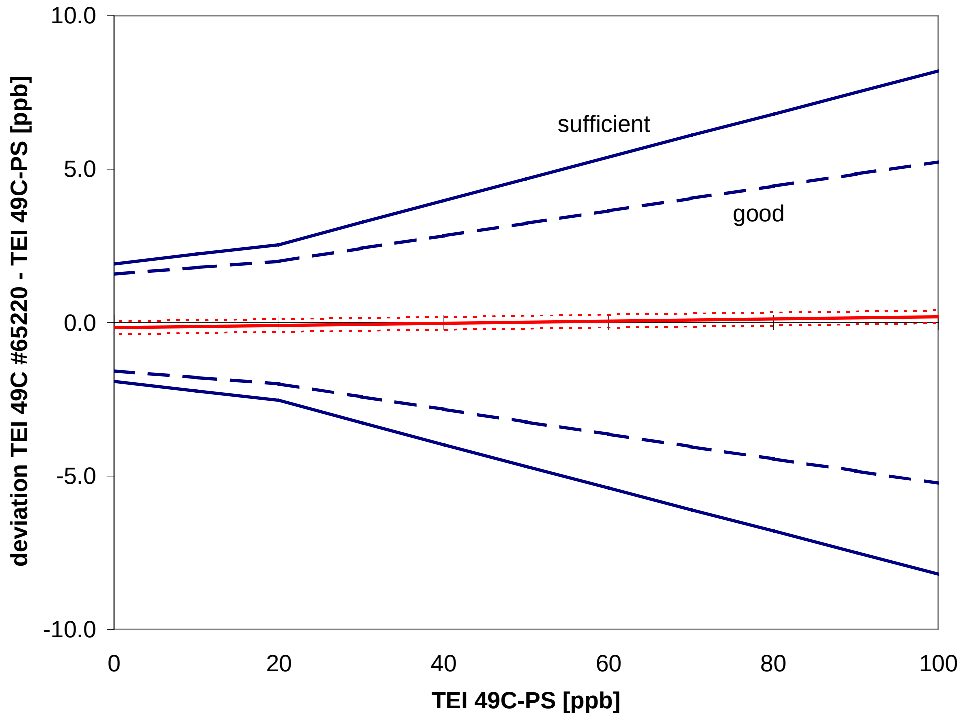


Figure 11: Inter-comparison of instrument TEI 49C #65220-347

Comment

In 1999 the ozone concentration observed at Zugspitze ranged between 38 and 66 ppb (5- and 95- percentile of hourly mean values). The TEI 49C field instruments clearly fulfils the assessment criteria as "good" over the tested range up to 100 ppb.

Ozone Calibrator

In addition to the ozone analyser, an inter-comparison of the station ozone calibrator TEI 49C PS with the WCC transfer standard was made. Experimental details are also summarised in Table 3.

The results comprise the three runs of the inter-comparison between the TEI 49C PS calibrator and the WCC transfer standard TEI 49C-PS, carried out on February 6, 2001. In contrast to the inter-comparison of the ozone analyser, the analog signal of the calibrator was acquired on the EMPA-WCC 16-channel ADC circuit board data acquisition.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 1-minute-means are shown in Tables 5. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Table 5: Inter-comparison of the ozone calibrator TEI 49C PS

	TEI 49C-PS		**TEI 49C PS #58686-319**			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.4	0.16	0.2	0.30	-0.3	
2	89.9	0.11	87.8	0.41	-2.1	-2.4%
3	15.1	0.10	14.5	0.44	-0.6	-3.8%
4	74.9	0.16	73.2	0.36	-1.7	-2.3%
5	55.0	0.10	54.0	0.38	-1.1	-2.0%
6	35.0	0.11	34.2	0.42	-0.9	-2.5%
7	0.6	0.15	0.3	0.47	-0.3	
8	0.4	0.10	0.3	0.42	-0.1	
9	14.9	0.27	14.3	0.36	-0.6	-3.8%
10	34.8	0.22	34.1	0.39	-0.7	-2.1%
11	74.9	0.14	73.3	0.28	-1.6	-2.1%
12	55.0	0.13	53.8	0.46	-1.2	-2.2%
13	89.9	0.12	87.9	0.53	-2.1	-2.3%
14	0.4	0.11	0.4	0.26	-0.0	
15	0.5	0.06	0.3	0.41	-0.2	
16	74.9	0.13	73.1	0.42	-1.8	-2.4%
17	15.0	0.18	14.5	0.42	-0.5	-3.3%
18	54.7	0.24	53.5	0.42	-1.2	-2.3%
19	35.0	0.17	34.2	0.39	-0.8	-2.4%
20	89.7	0.11	87.7	0.65	-2.1	-2.3%
21	0.4	0.05	0.2	0.40	-0.2	

The resulting average linear regression from the intercomparison is (for the range 0-100 ppb):

Calibrator Zugspitze = 0.979 x TEI 49C-PS (WCC) - 0.1 ppb

Calibrator Zugspitze = O_3 mixing ratio in ppb, determined with TEI 49C PS #58686-319
TEI 49C-PS (WCC) = O_3 mixing ratio in ppb, determined with TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.001	(f = 1) f=degree of freedom
	- offset S_b in ppb	0.03	(f = 1)
	- residuals in ppb	0.10	(f = 19)

Comment

The agreement between the station calibrator and the WCC transfer standard was significantly worse compared to the station analyser. The station calibrator was never used to calibrate the analyser, and only span checks have been made so far. The station operators were aware of the problems with the station calibrator. During the audit, several malfunctions of the station calibrator were noted, as summarised below.

- Within the diagnostics menu, cell A/B O_3 did not display the average ozone concentration in the first line.
- In the flows sub-menu of the diagnostics menu flow rates of up to one liter per minute were displayed (instead of approx. 0.6 lpm) for short periods.
- The difference between the intensities of cells A and B was extremely large (A: 101950 Hz, B:63050 Hz) and should be adjusted.
- The internal data logger was not working during the audit.

4.3. Recommendation for the Ozone Measurements

The TEI 49C ozone instrument at Scnmeefernerhaus is in a good condition and fulfilled the assessment criteria as "good" over the tested range of 0 to 100 ppb and. The station calibrator was in a less satisfactory condition. The following recommendations are suggested by EMPA-WCC:

Station calibrator

The ozone calibrator was not working properly during the audit. Several checks were made, but the problem could not be resolved during the audit procedure. It was therefore agreed with the station operators that the calibrator should be sent to the instrument manufacturer or representative for an instrument check/service. After this and before its use at the Zugspitze the calibrator should again be compared to the ozone calibrator at IFU, which is traceable to WCC-EMPA.

Calibration interval

Calibrations of the ozone instrument are performed yearly at IFU, and the station calibrator is only used for span checks. EMPA-WCC suggests to perform calibrations on a three-monthly basis with the station calibrator. The yearly intercomparison of the station calibrator with the calibrator of IFU supports the quality of the ozone measurements.

Data submission

Submission of the data to the GAW World Data Centre for Surface Ozone (WDCSO) at NILU is recommended.

5. System- and Performance Audit for Carbon Monoxide

The instrumentation for the carbon monoxide measurements has not yet been moved to the Schneefernerhaus and is still installed at the Zugspitze summit station. There are currently three CO instruments in operation at the summit site, namely one GC with HgO detector, and two NDIR monitors. The EMPA-WCC audit focused mainly on the GC system and the NDIR monitor that will become the main CO instrument for the GAW programme at the Schneefernerhaus, but the other NDIR instrument was also considered.

5.1. Monitoring Set-up and Procedures

5.1.1. Air Inlet System for CO and CH_4

Sampling-location: on top of the flat roof of the building.

Inlet description: glass tube (i.d. 8 cm) inside a stainless steel inlet, length 2.2 m, protected from rain and snow. Inside the laboratory glass manifold, i.d. 8 cm, length ca. 2.1 m, flow rate 1000 l/min. From there connections with ¼" PFTE tubing to the instruments, length ca. 2 m. Flow rates: CO GC 180 ml/min, CO monitors 0.8 to 0.9 l/min.

Residence time in the sampling line: < 10 s

Drying of the air: Cryotrap ca. - 65°C (for instrument TEI 48S "A")

Nafion drier PermaPure PD-625-24 PP (for the other instruments)

Comment

Concerning materials and residence time the used inlet system is adequate for analysing CO and CH_4.

5.1.2. Instrumentation

A Perkin Elmer gas chromatograph with a Trace Analytical RGD-2 detector is used as an in-situ CO analyser. Instrumental details are listed in Table 6. Furthermore, two TEI 48S CO monitors are in use. Instrumental details for the monitors are shown in Table 7.

Table 6: Carbon monoxide gas chromatograph at Zugspitze

method	GC / HgO Detector
instrument	GC: Perkin Elmer, model F22, S/N 1809 Detector: Trace Analytical RGD-2, S/N 091191-003
at Zugspitze	since 1998
configuration	one column system
loop	1.6 ml
columns	analytical column: Molecular sieve 5Å 60/80 100 cm, 1/8'' O.D.
carrier gas	synth. air (hydrocarbon free, Messer Griessheim)
operating temperatures	Detector: 240 °C, Column: 100 °C
analog output	0 - 1 V
calibration interval	every 60 min (working standard)
instrument's specials	a few seconds before injection, the flow through the sample loop is stopped (solenoid valve) to equilibrate pressure

Table 7: CO NDIR monitors at Zugspitze

method	NDIR, Gas Filter Correlation (GCF)	
instrument	TEI 48 S, internal code "B" #52027-290	TEI 48 S, internal code "A" #47985-279
usage	main instrument	backup instrument
at Zugspitze	since 1995	8.10.97
range	0-1000 ppb	0-1000 ppb
analog output	0-10 V	0-10 V

Gas Standards

Table 8 shows a summary of the gas standards that are used for the verification of the measurements. Four CMDL certified cylinders are used for calibration purposes. The concentrations refer to the old CMDL scale and are not adjusted to the new scale. It should be noted that the new values have not yet been communicated to CMDL's customers. This remains to be done in the future. Furthermore, station calibration and reference gases are available at the site to serve as working standards. These station standards were traced back to the CMDL scale at IFU.

Table 8: Station CO cylinders

Gas cylinder	Purpose / Location	Conc. [ppb]
CAO 1456	CMDL scale / IFU*	51.6
CAO 1480	CMDL scale / IFU*	98.8
CAO 1447	CMDL scale / IFU*	151.1
CAO 1499	CMDL scale / IFU*	199.6
#1899547	calibration gas (GC) / Zugspitze = reference (target)	105.0
#29230	calibration gas (GC) / Zugspitze	155.0
#A3291	calibration gas (NDIR) / Zugspitze	624.0

* the concentrations refer to the old CMDL scale and are not adjusted to the new scale yet

Operation and Maintenance

GC system

Analysis: 4 measurements are performed per hour: 3 of ambient air and one of the working standard (155 ppb). Additionally, the reference standard (105 ppb) is injected twice every 12 hours. A full calibration of the instrument is performed 2 to 4 times per year.

Daily checks:	air pump pressure	UV-lamp	peak width
	cylinders pressure	integrator time	
	sample- and carrier flow	CO-retention time	
	check of the daily plot concerning working standards and target		

A baseline reset is done if necessary.

Comments

- 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.

NDIR (GFC) instruments

The two TEI 48S analysers in use show a continuous drift of the zero point that makes a frequent zeroing of the system necessary. Thus, in a five-minute interval ambient air and zero is measured alternatingly. Of the two CO analysers only the main instrument (TEI 48 S ”B”, #52027-290) was audited, because the second instrument (internal code ”A”) is only used as a backup instrument. The audited instrument will become the main CO monitor within the GAW programme at the Scheefernerhaus.

A schematic overview of the current instrumental set-up of the NDIR CO measurements is given in Figure 12.

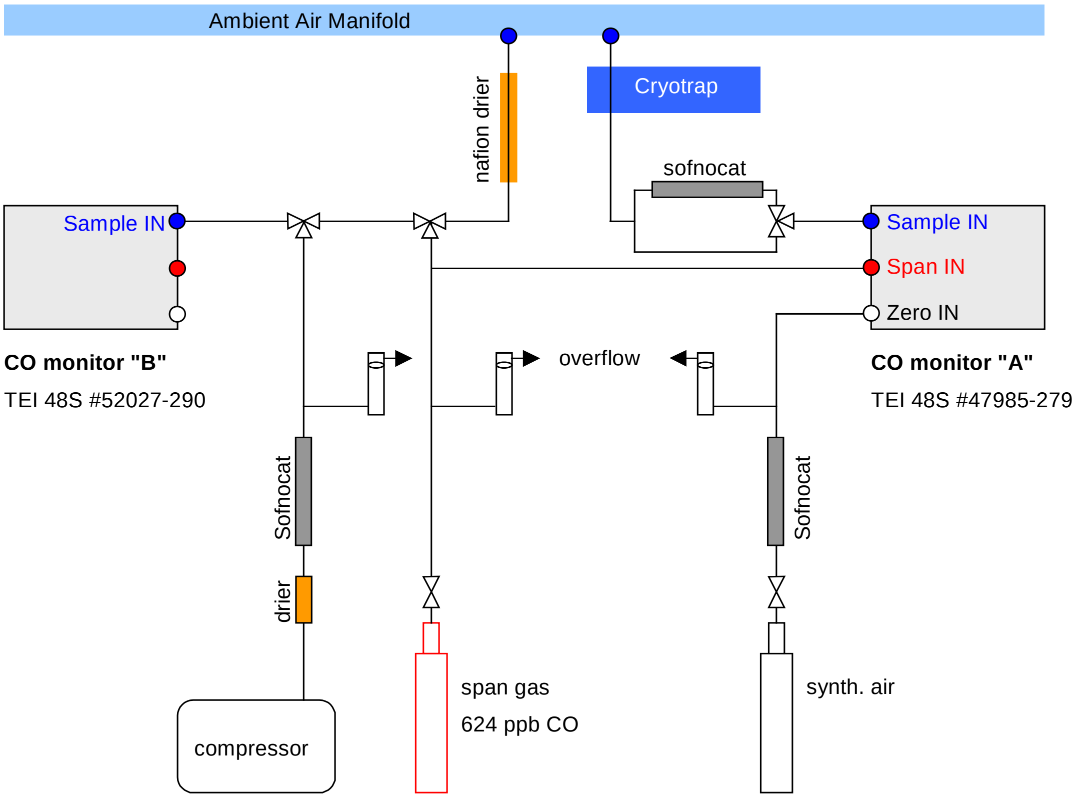


Figure 12: Schematic overview of the instrumental set-up of the CO NDIR instruments at Zugspitze.

As shown in Figure 12, three different methods for zeroing of the station analysers are used. Ambient air and zero air measurement alternate every five minutes. For zeroing, instrument "B" samples station zero air, whereas instrument "A" samples dried and CO scrubbed ambient air. No differences were observed for these two zeroing procedures. However, once per day CO scrubbed synthetic air is used for zeroing as part of the daily span check. This procedure gives an offset compared the other two methods. The offset with the scrubbed synthetic air was confirmed for both analysers. No explanation could be found for this behaviour so far. Since the calibration gas that is used is also in synthetic air, the station operators assume that this offset is also present during the calibration. As a consequence, a "net span signal" is calculated from the difference between span and CO scrubbed synthetic air, which is applied to the ambient CO measurements.

The different methods of zeroing and its implication on the calibration (net span signal) are shown schematically in Figure 13.

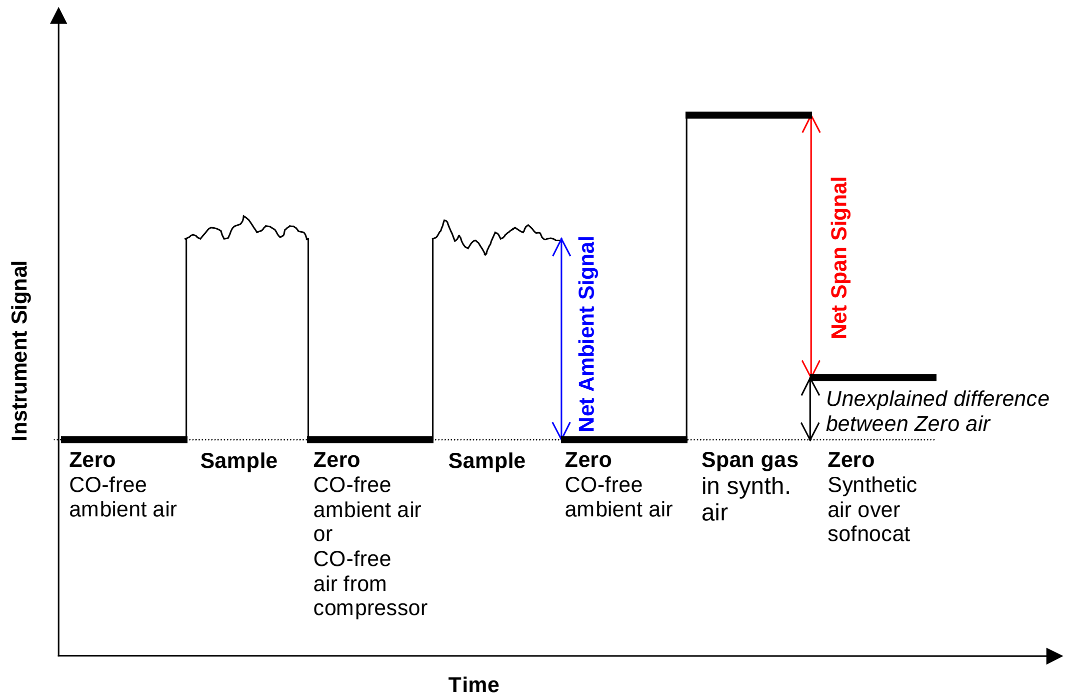


Figure 13: Different methods of zeroing of the NDIR CO monitors at the Zugspitze

5.1.3. Data Handling

Data Acquisition and –transfer

GC: Apex Chromatography Peak Integration Software is used for data acquisition. Only the reports are stored as raw data, but an integrator is used to plot chromatograms for the weekly checks.

NDIR monitors: An IFU-developed 16-bit A/D data acquisition system is used. All data is stored on a server at the Zugspitze which is part of IFU's network.

Data Treatment

GC: Ambient air mixing ratios are calculated based on peak height by using the concentrations of the working standards. Data evaluation includes consistency checks with graph plots (in particular retention time, peak start, peak end), checks with the instrument logbook and time series review. The final data evaluation is done monthly at IFU in Garmisch-Partenkirchen.

NDIR monitors: The data processing is performed once per month at IFU in Garmisch-Partenkirchen. Monthly averages of the zero and span points are used to calculate the "net span signal", which is then applied to the ambient air measurements. The data treatment includes the consideration of the station log files.

Data Submission

CO data have been submitted to various scientists. Data are also submitted to the GAW World Data centre for Greenhouse Gases at JMA.

Comment

Remote access to the data acquisition system from IFU 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 submitted to IFU for use in the final data evaluation. Additionally, monitor logbooks are available for each instrument. They contain specific information about the operation of each instrument. The instrument manuals are available either at the site or at IFU.

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 by the QA/SAC 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 intercomparison of the CO measurements was comprised of the following experiments.

Gas Chromatograph

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 intercomparison 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 4 to 5 times on February 6 and 7. No modifications of the GC/RGD-2 carbon monoxide analyser were made for the intercomparison. The automated analysis procedure with 4 injections per hour was used with one injection of the working standard. The data was acquired by the station software. This data (mean values and standard deviations) was reprocessed by Dr. H. E. Scheel at IFU in Garmisch Partenkirchen and was submitted afterwards to the WCC. The experimental details are summarised in Table 9.

Table 9: Experimental details of the carbon monoxide intercomparison (GC system)

field instrument:	GC: Perkin Elmer F22, S/N 1809 Detector: Trace Analytical RGD-2, S/N 091191-003
reference:	EMPA-WCC transfer standards 001201-3, 001201-2, FF30491, FA01467
data acquisition system:	Apex Chromatography Workstation Software
approx. concentration levels:	50 /100 / 150 / 200 ppb
injections per concentration:	4 -5
Sequence	4 injections per hour (3 WCC transfer standards, 1 working standard)

NDIR instruments

For the NDIR instruments the following intercomparisons with EMPA-WCC were made:

1) A gas mixture was fed to CO TEI 48S "B" by diluting a CO calibration gas with CO free synthetic air (treated with Sofnocat). However, the automated zeroing of the system was not in operation during this inter-comparison, and due to a significant drift of the instrument during the intercomparison no stable CO levels were observed with the TEI instrument.
2) CO calibration gases (EMPA-WCC transfer standards) were directly fed to TEI 48S "B" for 20 minutes. Again, no stable CO signal could be observed during the inter-comparison.
3) During the night from February 6 to 7 an intercomparison with the EMPA-WCC transfer standard CO monitor (AeroLaser AL 5001 ppt) was made for ambient air with all CO instruments. Instrumental details of the AL 5001 are given in Appendix IV.

5.2.2. Results

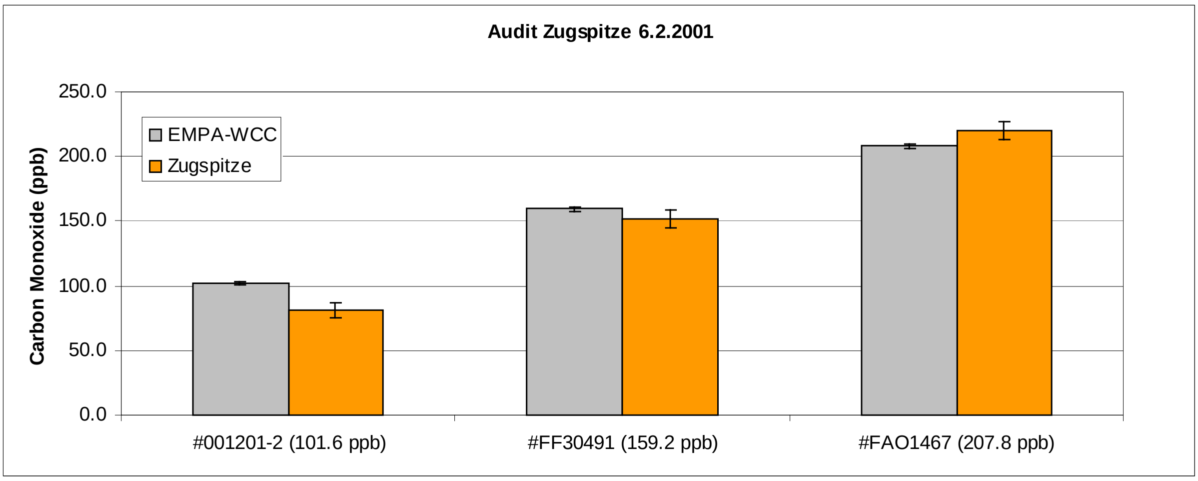
Gas Chromatograph

The results of the intercomparison between the Perkin Elmer / RGD-2 field instrument and the four WCC transfer standards are shown in Table 10. 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 Perkin Elmer / RGD-2 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 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 Zugspitze. The data from the Perkin Elmer / RGD-2 field instrument field instrument at Zugspitze were submitted to the WCC by Dr. E. Scheel from IFU and are based on calibration of the instrument against the standards available at IFU.

Table 10: Carbon monoxide intercomparison measurements at Zugspitze

No.	**WCC standard**	**Perkin Elmer / RGD-2 (Peak Height) of Zugspitze**				
	conc.	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	51.5 ± 0.9	N/A*	N/A*	4	N/A*	N/A*
2	101.6 ± 0.9	81.0	2.1	5	-20.7	-20.4
3	159.2 ± 1.8	151.8	2.4	4	-7.4	-4.6
4	207.8 ± 2.2	220.0	2.8	5	12.2	5.9

* concentration was below the threshold value of the instrument



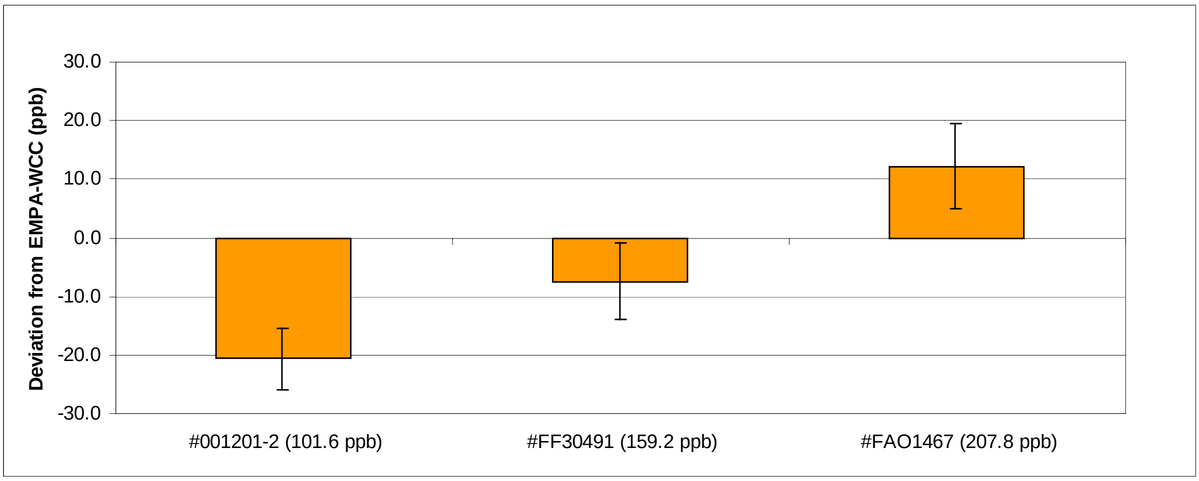


Figure 14: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02859, 194.7 ppb) measured with the GC system of the Zugspitze station (orange). lower panel: deviation of Zugspitze from the conventional true value.

NDIR Instruments

As already mentioned above, the direct addition of gas mixture to the TEI 48S "B" CO monitor gave no stable signals. For the gases that were added by the dilution of a standard gas, this might be explained by the instrument drift during the inter-comparison. Additionally, the WCC transfer standards listed in Table 10 were directly analysed by the TEI 48S "B" monitor for 20 minutes. A stable CO concentration was also not observed during this experiment. Therefore no direct comparison of the WCC transfer standards and the NDIR CO monitors of Zugspitze could be made.

Ambient Air Inter-Comparison Measurements

During the night from February 6 to 7, 2001, an inter-comparison with the EMPA-WCC transfer standard (AeroLaser AL 5001 ppt) CO monitor was made for ambient air with all CO instruments of the Zugspitze station. Instrumental details of the AL 5001 are given in Appendix IV. Figure 15 shows half-hour mean values for the different instruments. These values are summarised in Table 11 for all instruments, including the deviation to the EMPA-WCC transfer instrument AL5001 ppt.

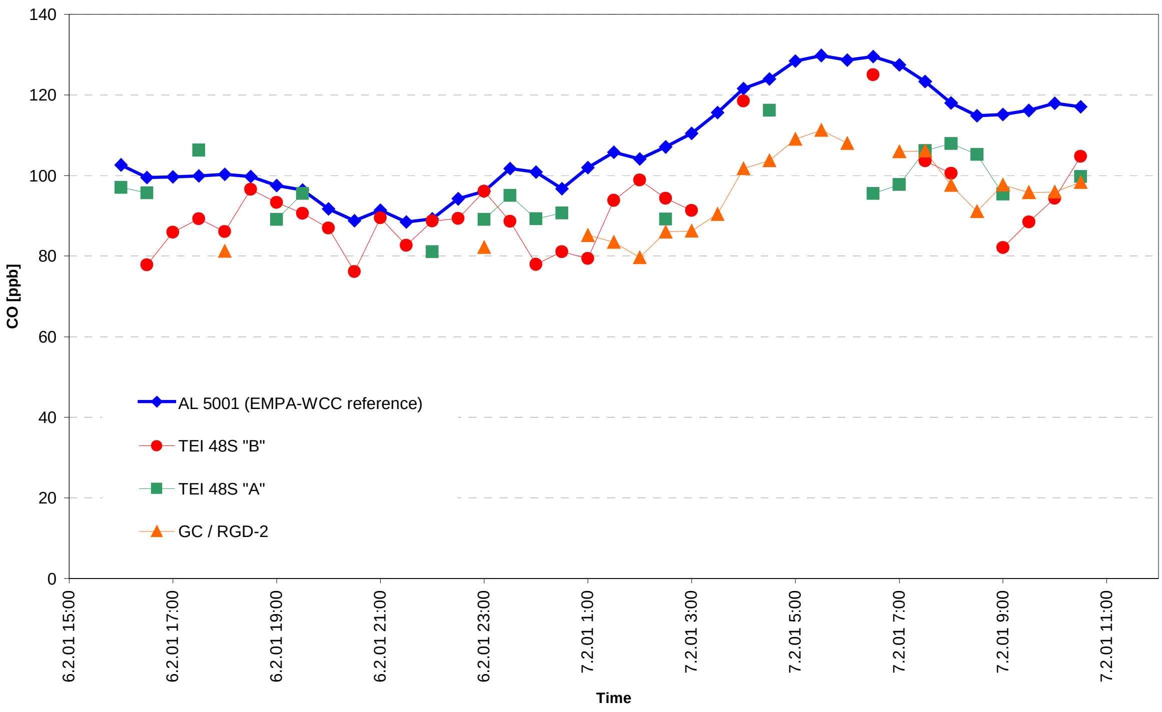


Figure 15: 30 min average values of ambient CO concentrations measured at Zugspitze with the station CO instrument and the EMPA-WCC transfer standard AL 5001.

Table 11: Half hour mean values of ambient air at Zugspitze measured with different instruments.

Time	**AL5001**	**TEI 48S "B"**		**TEI 48S "A"**		**GC / RGD-2**	
	conv. true value [ppb]	**measured value [ppb]**	**deviation [ppb]**	**measured value [ppb]**	**deviation [ppb]**	**measured value [ppb]**	**deviation [ppb]**
6.2.01 16:00	102.7	N/A	N/A	97.0	-5.6	N/A	N/A
6.2.01 16:30	99.5	77.8	-21.7	95.7	-3.8	N/A	N/A
6.2.01 17:00	99.7	85.9	-13.8	N/A	N/A	N/A	N/A
6.2.01 17:30	99.9	89.3	-10.6	106.3	6.4	N/A	N/A
6.2.01 18:00	100.3	86.1	-14.2	N/A	N/A	81.3	-19.0
6.2.01 18:30	99.7	96.6	-3.1	N/A	N/A	N/A	N/A
6.2.01 19:00	97.5	93.3	-4.3	89.1	-8.4	N/A	N/A
6.2.01 19:30	96.4	90.6	-5.8	95.5	-0.9	N/A	N/A
6.2.01 20:00	91.8	87.0	-4.8	N/A	N/A	N/A	N/A
6.2.01 20:30	88.8	76.1	-12.6	N/A	N/A	N/A	N/A
6.2.01 21:00	91.4	89.5	-2.0	N/A	N/A	N/A	N/A
6.2.01 21:30	88.5	82.7	-5.8	N/A	N/A	N/A	N/A
6.2.01 22:00	89.3	88.7	-0.6	81.1	-8.2	N/A	N/A
6.2.01 22:30	94.2	89.3	-4.9	N/A	N/A	N/A	N/A
6.2.01 23:00	96.1	96.1	0.1	89.1	-6.9	82.2	-13.9
6.2.01 23:30	101.7	88.6	-13.1	95.1	-6.6	N/A	N/A
7.2.01 00:00	100.9	78.0	-22.9	89.3	-11.6	N/A	N/A
7.2.01 00:30	96.7	81.0	-15.7	90.7	-6.0	N/A	N/A
7.2.01 01:00	101.9	79.4	-22.5	N/A	N/A	85.1	-16.8
7.2.01 01:30	105.7	93.8	-11.9	N/A	N/A	83.4	-22.3
7.2.01 02:00	104.1	98.9	-5.2	N/A	N/A	79.6	-24.5

7.2.01 02:30	107.1	94.4	-12.7	89.2	-18.0	86.0	-21.1
7.2.01 03:00	110.5	91.4	-19.1	N/A	N/A	86.3	-24.2
7.2.01 03:30	115.6	N/A	N/A	N/A	N/A	90.4	-25.2
7.2.01 04:00	121.6	118.5	-3.1	N/A	N/A	101.7	-19.9
7.2.01 04:30	124.0	N/A	N/A	116.2	-7.8	103.7	-20.2
7.2.01 05:00	128.4	N/A	N/A	N/A	N/A	109.1	-19.3
7.2.01 05:30	129.8	N/A	N/A	N/A	N/A	111.3	-18.5
7.2.01 06:00	128.7	N/A	N/A	N/A	N/A	108.0	-20.6
7.2.01 06:30	129.5	125.0	-4.5	95.6	-33.9	N/A	N/A
7.2.01 07:00	127.5	N/A	N/A	97.8	-29.7	106.0	-21.5
7.2.01 07:30	123.3	103.6	-19.7	106.2	-17.2	106.1	-17.2
7.2.01 08:00	118.0	100.6	-17.4	108.0	-10.1	97.6	-20.4
7.2.01 08:30	114.8	N/A	N/A	105.2	-9.6	91.1	-23.7
7.2.01 09:00	115.2	82.1	-33.1	95.4	-19.8	97.7	-17.5
7.2.01 09:30	116.1	88.5	-27.6	N/A	N/A	95.8	-20.3
7.2.01 10:00	117.9	94.3	-23.6	N/A	N/A	95.9	-22.0
7.2.01 10:30	117.1	104.7	-12.4	99.8	-17.3	98.4	-18.7
mean deviation to reference [ppb]			**-12.3**		**-11.3**		**-20.3**
standard deviation [ppb]			**8.7**		**9.6**		**2.8**

5.3. Discussion of the Inter-Comparison Results

The CO measurements performed at Zugspitze deviate significantly from the transfer standards of the EMPA-WCC. Possible reasons for the deviation are discussed below.

5.3.1. GC Instrument

It can be seen from Table 10 that the CO GC of the Zugspitze deviates significantly from the EMPA-WCC transfer standards. For the lower concentrations of about 100 ppb, a deficit of up to ~20 pbb is observed. This finding is also confirmed by the inter-comparison measurements of ambient air at Zugspitze during the night form February 6 to 7, 2001. The deviation was slightly smaller for the 159.2 ppb and 207.8 ppb transfer standards (-4.6% and +5.9%). The reason for this discrepancy between the WCC transfer standards and the GC instrument might be by the following:

1) Different scales: The CO scale of the CMDL was used by both the EMPA-WCC and the Zugspitze station operators. However, the CO scale of the EMPA-WCC was recently revised (Dec. 2000) by CMDL. For the low concentrations a significant shift in the CO scale was recognised by CMDL. Details are shown in Appendix III. This shift of the CMDL scale can explain about half of the difference for the low concentrations.
2) The mercury reduction detector has a non-linear response to different CO levels. Therefore, a calibration function has to be applied. This function has to be checked at regular intervals, in particular after instrument modifications.

5.3.2. NDIR Instruments

During the inter-comparison procedure the TEI 48S "B" did not produce stable concentration readings when gas mixtures were added by the EMPA-WCC. As it can be seen from Figure 15 both NDIR instruments also deviated significantly from the EMPA-WCC transfer instrument AL 5001 during the inter-comparison measurements of ambient air at Zugspitze. They also deviated from the station GC instrument. As a consequence no reliable CO measurements could be made with these two instruments. A further discussion is given in the recommendations section.

5.4. Recommendation for the Measurement of Carbon Monoxide

GC system

The GC / RGD-2 system installed at Zugspitze fulfils the criteria for carbon monoxide measurements. The calibration procedures as well as the documentation and data treatment are performed on a high level of expertise. Despite this, a rather high deviation was found between the WCC transfer standards and the GC instrument, especially for the lower concentrations. Regarding the relevant concentration range (98.1 and 188.2 ppb according to the 5- and 95%-percentile) the result should be improved. Only part of the deviation can be explained by the revision of the CO scale (see Appendix III).

- 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.

Further minor recommendations of the EMPA-WCC are summarised below.

- The transfer standard with the lowest concentration (51.5 pbb) was not detected because it was below the threshold level of the integrator. It is recommended to lower the threshold level.

NDIR monitors

The NDIR monitors deviated significantly from both the WCC transfer instrument and the station GC during the intercomparison measurements. The recommendations of the EMPA-WCC are summarised below.

- The TEI 48S monitors are rather old models. This type of instrument may not be appropriate for CO measurements at a background station. The EMPA-WCC therefore suggests the replacement of these instruments by state-of-the-art instrumentation.
- The problem that different (dry) zero air supplies lead to a different response is still not resolved. This difference should not exist, and might disappear if the instrumentation is replaced by up-to-date models. The EMPA WCC suggests to re-consider the current calibration procedure where the "net span signal" is calculated by the difference between span gas and CO scrubbed synthetic air. For this purpose the span gas should also be scrubbed by sofnocat, and the result should be comparable to the CO free synthetic air.
- One major disadvantage of the current system is that no actual data is available at the site. This is mainly due to the significant drift of the zero point of the analysers in use. Again, the problem might disappear upon replacement of the instrument.

6. System-and Performance Audit for Methane

The instrumentation for the methane measurements has been installed at the Schneefernerhaus but was not operational during the audit. However, the methane measurements of the summit site were still operational. Therefore a system- and performance audit was carried out by EMPA-WCC for methane at Zugspitze summit station.

6.1. Monitoring Set-up and Procedures

6.1.1. Air Inlet System for CH_4

Same as for Carbon Monoxide (see 5.1.1)

6.1.2. Analytical System

Gas chromatograph

A Carlo Erba FRACTOVAP 021AC gas chromatograph with an FID detector is used for ambient methane measurements at Zugspitze. Instrumental details are summarised in Table 12.

Table 12: Gas chromatograph for methane at Zugspitze

Instrument	Carlo Erba FRACTOVAP 021AC, S/N 124595
at Zugspitze since	~ 1990
method	GC / FID Detector
sample loop	4.7 ml
column	packed column: Molecular sieve 13X (60/80 mesh) length 120 cm, ID ca. 5 mm
carrier gas	N_2 99.999%
operating temperatures	Injector: 100°C, Column: 80°C
analog output	0 - 1 V
calibration interval	working standard (2062 ppb) once per hour station reference (1949 ppb) two times per day
instrument specials	20 seconds before injection, the flow through the loop is stopped (solenoid valve) to equilibrate pressure

Gas Standards

Messer Griessheim gas standards (Table 13) are used at the site for the verification of the measurements. All standards were traced back to CMDL by way of cylinder CA0 1408, which is kept at the site.

Table 13: Station CH_4 cylinders

	Gas cylinders	Conc. [ppb]
S1	MG 588A (working standard)	2061.5
S2	MG 2054C (station reference)	1949.0

Operation and Maintenance

Analysis: three ambient air and one working standard are performed per hour. Additionally two measurements of the station reference are performed per day.

Daily checks: cylinders pressure, temperatures
sample- and carrier flow
visual inspection of integrator plots

Weekly checks: check of peak shape using an integrator plot
peak width
CH_4-retention time

6.1.3. Data Handling

Data Acquisition and –transfer

Apex Chromatography Workstation Software is used for data acquisition. Only the reports are stored but an integrator is used to plot chromatograms for the weekly checks.

Data Treatment

Ambient air mixing ratios are calculated based on peak area by using the concentrations of the working standards. Data evaluation includes consistency checks with graph plots (in particular retention time, peak start, peak end), checks with the instrument logbook and time series review. The final data evaluation is done monthly at IFU in Garmisch-Partenkirchen.

Data Submission

Data have been submitted to various scientists. Data are also submitted to the GAW World Data centre for Greenhouse Gases at JMA.

6.1.4. Documentation

During the audit the documentation was reviewed for availability and usefulness. For all parameters the electronic station logbook contained all necessary information about maintenance, instrument changes, events and special investigations. The logbook files are accessible from IFU for daily survey and the final data evaluation.

Comments

The log book 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 by QA/SAC 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 four transfer standards of the WCC (approx. 1560, 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 V). Before the intercomparison 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 4 to 5 times and analysed on February 6 and 7. No modifications of the GC system were made for the inter-comparison. The automated analysis procedure with 4 injections per hour was used with one injection of the working standard. The data was acquired by the station software. This data (mean values and standard deviations) was processed by Dr. H. E. Scheel for methane at IFU in Garmisch-Partenkirchen and was submitted to the WCC afterwards. The experimental details are summarised in Table 14.

Table 14: Experimental details of the methane inter-comparison

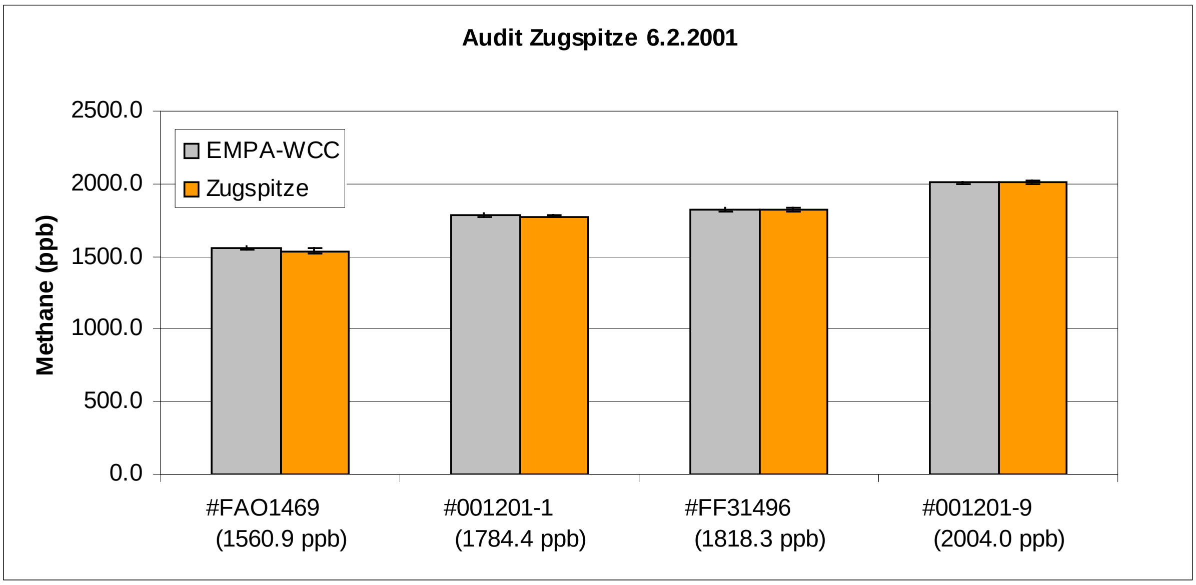
field instrument:	Carlo Erba FRACTOVAP 021AC, S/N 124595
reference:	EMPA-WCC transfer standards 001201-1, 001201-9, FF31496, FA01469
data acquisition system:	Apex Chromatography Workstation
approx. concentration levels:	1560 /1780 / 1820 / 2000 ppb
injections per concentration:	4 -5
Sequence	4 injections per hour (3 WCC transfer standards, 1 working standard)

6.2.2. Results of the Methane Inter-Comparison

The results of the intercomparison between the Carlo Erba field instrument and the four WCC transfer standards are shown in Table 15. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 16 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 Zugspitze. The data from the Carlo Erba field instrument at Zugspitze were submitted to the WCC by Dr. E. Scheel from IFU and based on comparisons of the working standards with the CMDL-analysed cylinder CA01408.

Table 15: Methane intercomparison measurements at Zugspitze

No.	WCC standard	Carlo Erba / FID (Peak Area) of Zugspitze				
	conc.	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	1560.9 ± 12.3 ppb	1538.2	7.6	5	-22.7	-1.4
2	1784.4 ± 8.0 ppb	1776.9	4.0	5	-7.5	-0.4
3	1818.3 ± 13.6 ppb	1817.7	4.6	4	-0.6	0.0
4	2004.0 ± 10.3 ppb	2009.7	7.1	5	5.7	0.3



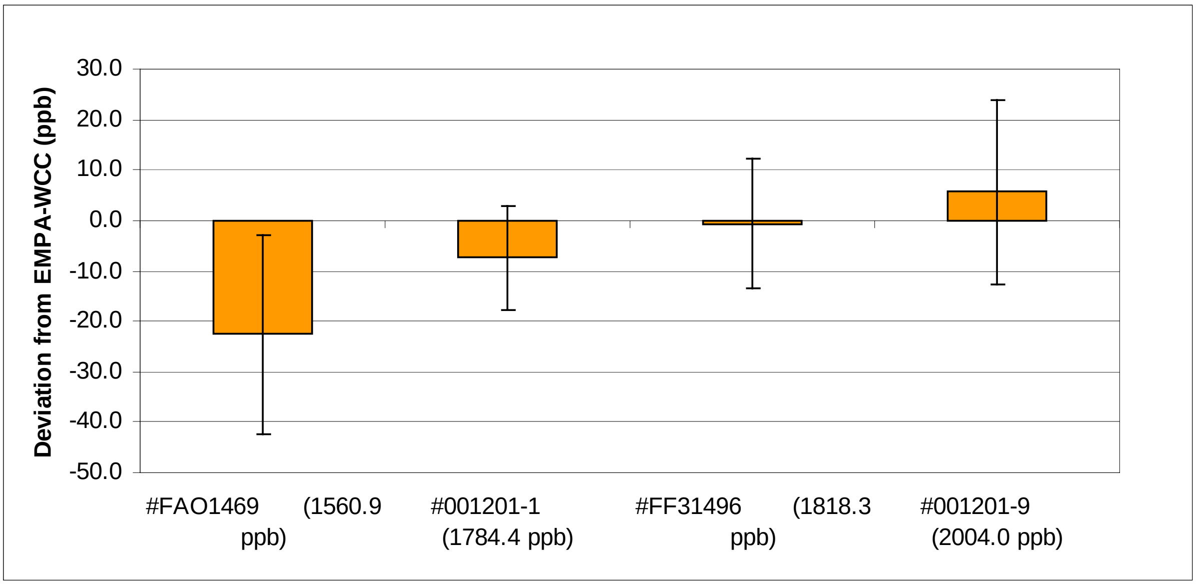


Figure 16: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL scale, Appendix V) measured with the GC system of the Zugspitze station (orange). lower panel: deviation of Zugspitze from the conventional true value.

Comment

The results for the EMPA-WCC transfer standards obtained during the Zugspitze measurements agrees very well with the conventional true value in the concentration range between 1780 and 2000 ppb methane. The deviation from the transfer standards is less than 0.4%. A higher deviation of -1.4% was found for the low concentration transfer standard (1560 ppb). However, with respect to the relevant concentration range at the Zugspitze (1776 to 1861 ppb according to the 5- and 95-percentile of the 1999 methane data), the result for the lowest concentration is not relevant. Thus, the Zugspitze 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.

Parallel methane measurements at both sites are recommended to ensure the consistency of the time series.

7. Conclusions

The global GAW station Zugspitze is an established site within the GAW programme. With the new laboratory facilities at the Schneefernerhaus, an optimal platform for extensive atmospheric measurements is now available.

The results of the inter-comparisons for surface ozone, carbon monoxide and methane showed excellent agreement between EMPA-WCC and the station instruments for O_3 and CH_4, but the CO measurements could be improved. Only part of the disagreement for the CO measurements between EMPA-WCC and the station can be explained by the uncertainty / revision of the CO reference scale of the CMDL.

Since Zugspitze is an established site with existing long time series, parallel measurements are regarded as very important by EMPA-WCC for the compounds that will be measured at the Schneefernerhaus in the future.

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 17. 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.

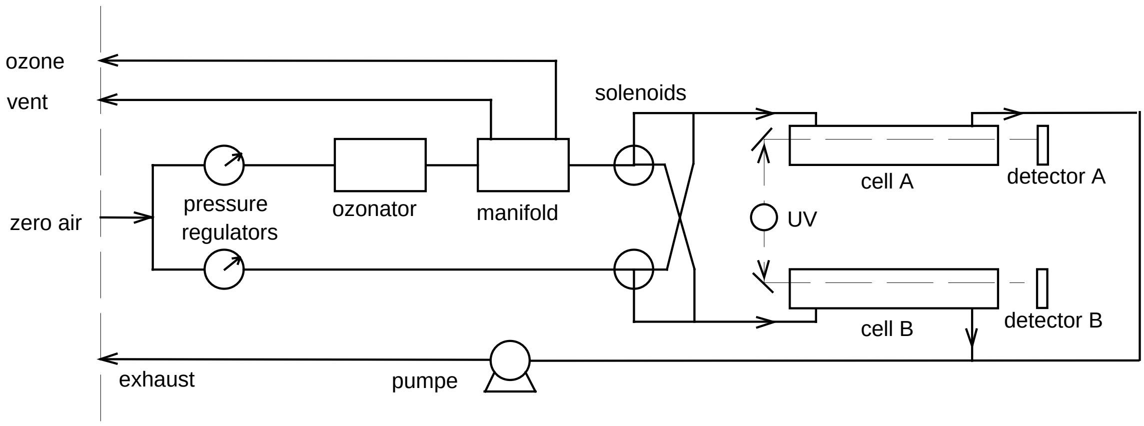


Figure 17: Flow schematic of TEI 49C-PS

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 intercomparison at the EMPA calibration laboratory are summarised in Table 16 and Figure 18.

Table 16: 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 / 125 / 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

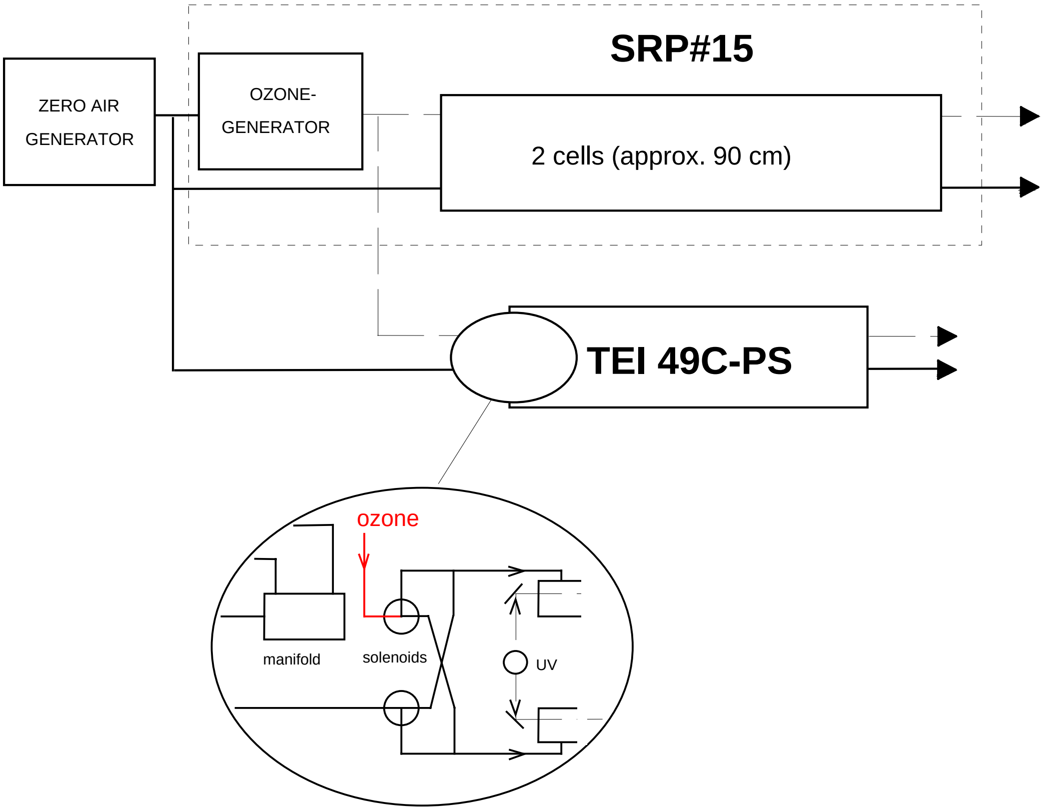


Figure 18: Instruments set up SRP -TEI 49C-PS

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 19 and 20 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.

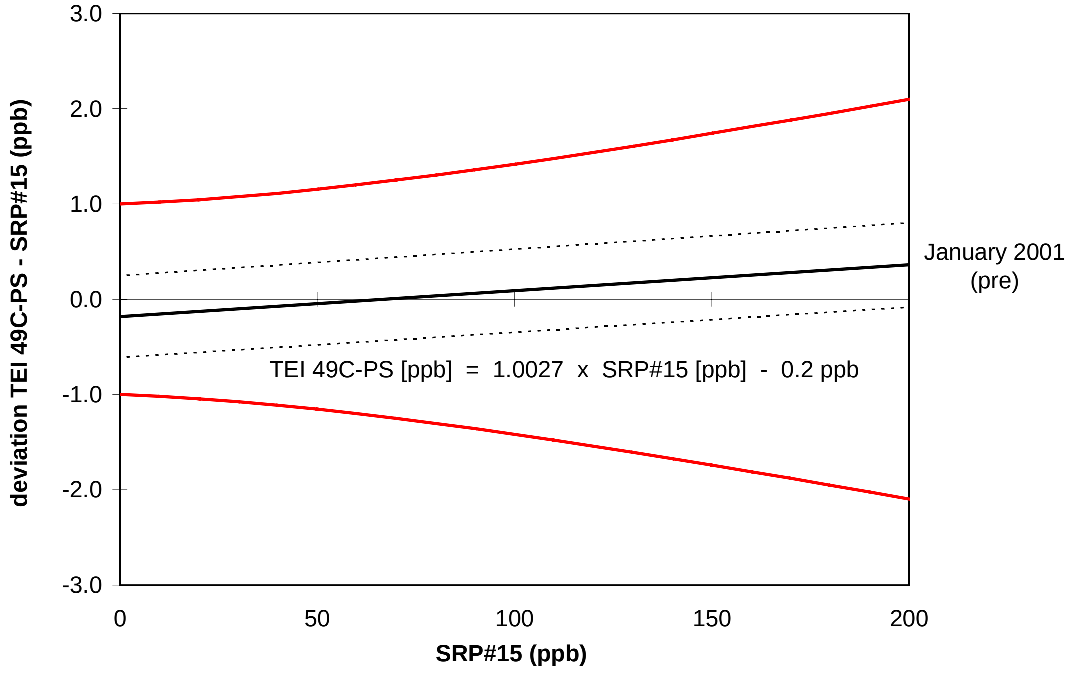


Figure 19: Transfer standard before audit

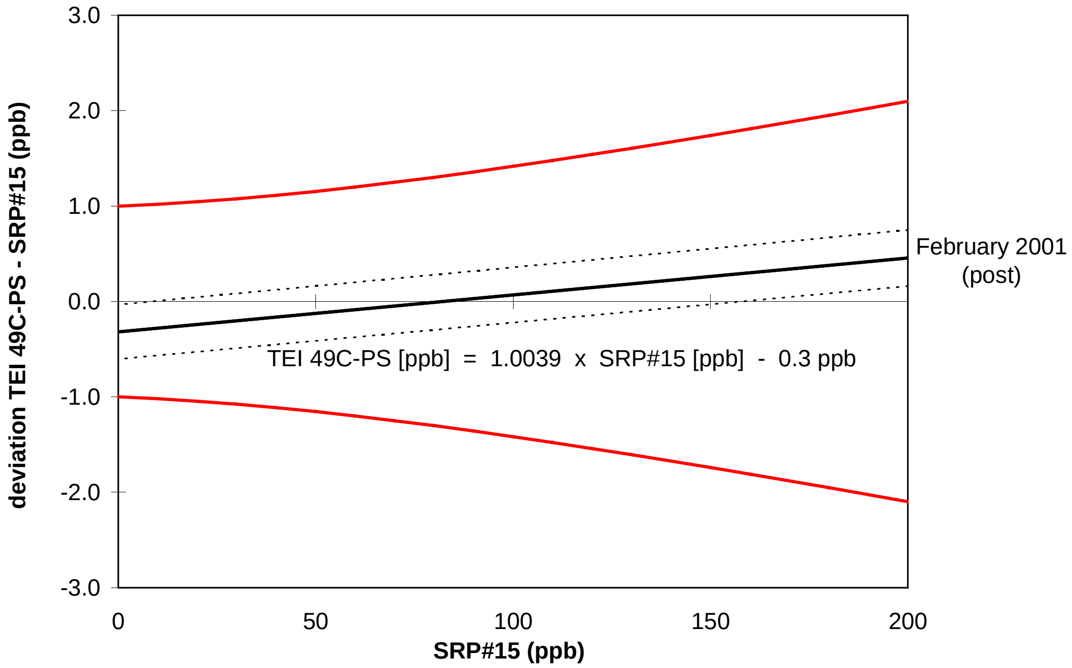


Figure 20: Transfer standard after audit

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 17:

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 22.

Table 17: 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 18: CO transfer standards of the WCC (average of calibrations from 29.01.01 and 14.02.01). 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)	51.7 ± 0.5 ppb	51.5 ± 0.4 ppb	001201-3
WCC Transfer Standard (2 l cylinder)	101.7 ± 0.4 ppb	101.5 ± 0.5 ppb	001201-2
WCC Transfer Standard (6 l cylinder)	159.0 ± 1.0 ppb	159.5 ± 0.5 ppb	FF30491
WCC Transfer Standard (6 l cylinder)	208.2 ± 0.6 ppb	207.3 ± 1.2 ppb	FA01467

IV WCC Transfer CO instrument

An AL5001 ppt CO monitor (AeroLaser GmbH, Garmisch Partenkirchen) was used by EMPA-WCC as a transfer standard instrument for ambient CO measurements at Zugspitze. The measurement method is based on the fluorescence of CO in the VUV at 150 nm. The fluorescence in the wavelength range between 160 nm and 190 nm is detected by a VUV photomultiplier followed by a fast counter. The instrument was calibrated every 90 minutes (zero and span) with CO calibration gas in synthetic air (SL7033, 407.7 ppb, traced back to CMDL CA02859) during the inter-comparison.

V 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 19. The EMPA-WCC transfer standards (Table 24) are traced back to the CMDL standards shown below.

Table 19: 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 20: CH_4 transfer standards of the WCC (average of calibrations from 25.01.01 and 9.02.01). 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)	1560.3 ± 4.9 ppb	1561.4 ± 6.5 ppb	FA01469
WCC Transfer Standard (2 l cylinder)	1784.7 ± 3.4 ppb	1784.0 ± 4.0 ppb	001201-1
WCC Transfer Standard (6 l cylinder)	1819.5 ± 8.1 ppb	1818.3 ± 3.5 ppb	FF31496
WCC Transfer Standard (6 l cylinder)	2003.5 ± 3.2 ppb	2004.6 ± 6.0 ppb	001201-9