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

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

EMPA-WCC REPORT 98/4

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE AND CARBON MONOXIDE

REGIONAL GAW STATION SONNBLICK

AUSTRIA, AUGUST 1998

Submitted by

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WMO World Calibration Centre for Surface Ozone and Carbon Monoxide

EMPA Dübendorf, Switzerland

Contents:

Figures:

Tables:

1. Abstract

A system and performance audit was conducted by the World Calibration Centre for Surface Ozone and Carbon Monoxide at the regional GAW station Sonnblick, Austria. Below, the findings, comments and recommendations are summarised:

Air Inlet System:
All teflon tubes and manifolds were clean and free of dust. The inlet system concerning materials as well as residence time is adequate for trace gas measurements in particular with regard to minimal loss of ozone.

Instrumentation:
Ozone Analyser: The measurement technique used is the UV-method which is the preferred method in the GAW programme. Considering its age, the analyser TEI 49 is in good condition.

Carbon Monoxide Analyser: The NDIR method in use is adequate for the pollution level of the site. Though, the signals of the instrument are fairly noisy and the drift of the zero point is relatively large.
The leak of the cooling trap needs to be repaired with highest priority or is to be replaced by another facility to dry the ambient air.

Operation and Maintenance:
The appearance inside the station is clean and functional. However, an air-condition for controlling the indoor temperature would be very desirable, since the larger fluctuations can influence the measurements.
The regularly and frequently performed calibrations for both the ozone and carbon monoxide measurements are of fundamental importance for the quality assurance.
It is known that the type of CO analyser, actually in use, shows a continuous drift for the zero point potentiometer making a very frequent zeroing of the system necessary. As is shown in 6.2. the present interval of 5.5 hours is too long. It is recommended to change this procedure, thus ambient air and zero air should be measured in a five-minute or 10-minute interval, alternatingly.

Data Handling:
Splitting up responsibilities requires well implemented communication tools to ensure that important information does not get lost. Thus, it is recommended that the person who is responsible for the station maintenance, should also have direct access to the data.

Documentation:
For an external person, it has not always been easy to survey and obtain the desired information quickly. Due to the mentioned separation of maintenance and data processing this may be even more important. Therefore it is recommended that the efforts that have been made should be continued to improve the transparency of the documentation.

Competence:
All persons directly or indirectly involved in the operation of the station are highly motivated and experts in their fields. Obviously, due to long-standing experience and adequate education, the staff was very familiar with the techniques and problems associated with ozone and CO measurements.

Ozone Intercomparisons:
The ozone concentrations observed at Sonnblick (1997) usually ranged between 37 and 64 ppb (5- and 95-percentile of hourly mean values).
The instrument fulfils the assessment criteria as "good" over the tested range up to 100 ppb (figure 12). Fairly small deviations among the three intercomparisons are the reason for narrow prediction intervals which implies that the instrument is in reasonably good condition.

Carbon Monoxide Intercomparisons:
The results of the CO intercomparison measurements (figure 17) deviate by about 1 to 5% from

the conventional true value, for concentrations between 120 and 350 ppb CO. The measurement uncertainty is approximately 2%. However, as parallel measurements showed (figure 16), the assessed error for ambient air values must be considered to be very significant. This due to the actual practice of zeroing the instrument. Either, a much more frequent zeroing of the system or an exchange of the analyser is strongly recommended. Regarding the detected leak of the cooling trap, the ambient air data of the period with the leaking trap, needs to be examined very carefully.

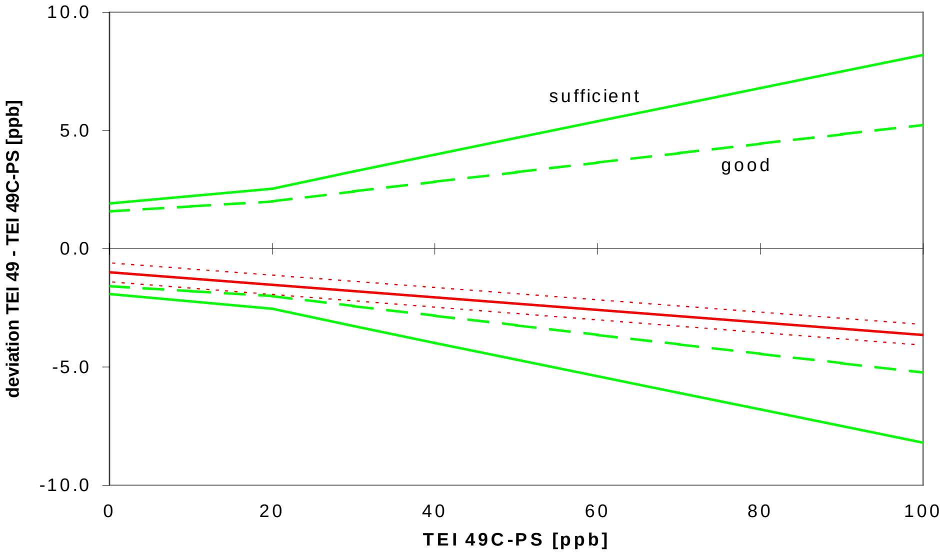

Figure 1: Intercomparison of ozone instrument TEI 49

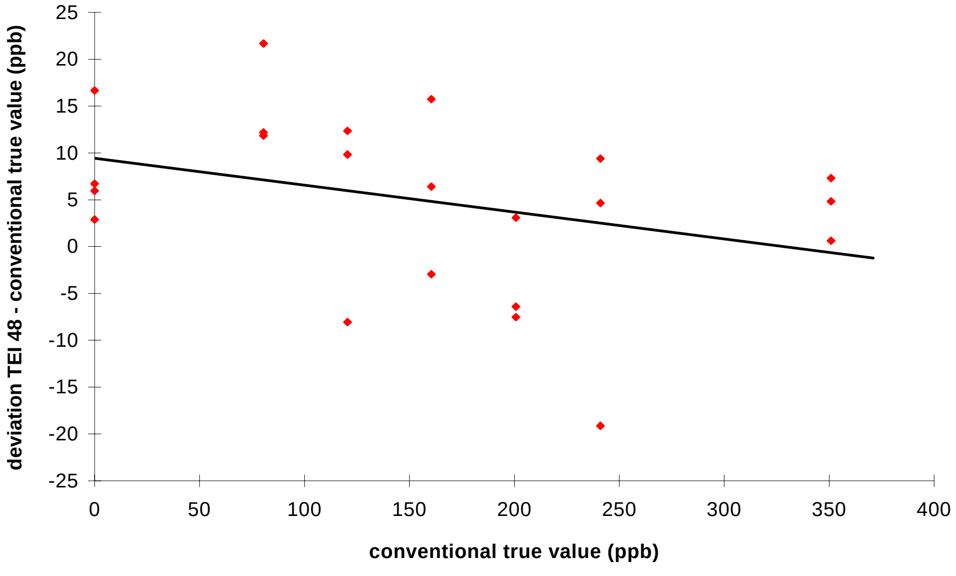

Figure 2: Intercomparison of CO instrument TEI 48

Dübendorf, 9. April, 1999 EMPA Dübendorf, WCC

Project manager

A. Herzog A. Fischer B. Buchmann

2. Introduction

In establishing a co-ordinated quality assurance programme for the WMO Global Atmosphere Watch programme, 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 WMO-GAW World Calibration Centre (WCC) for Surface Ozone and Carbon Monoxide for Europe and Africa. At the beginning of 1996 our work had started within the GAW programme with the parameter surface ozone. The activities were extended to carbon monoxide in the middle of the year 1997. The detailed goals and tasks of the WCC concerning surface ozone are described in the WMO-GAW report No. 104. In June '98, on the occasion of the GAW OSG meeting in Geneva (Node 14), the EMPA-WCC responsibility for the components surface ozone and carbon monoxide was extended from regional (Europe and Africa) to global.

In agreement with the group of UBA Vienna (Umweltbundesamt Wien) who is in charge of O_3 and CO measurements a system and performance audit at the regional GAW station Sonnblick, Austria, was conducted. This station is an established site for long-term measurements of several chemical compounds and physical and meteorological parameters in the lower free troposphere.

The scope of the audit which took place from August 6 to 10, 1998, was confined to the tropospheric ozone and carbon monoxide measurements. The entire process, beginning with the inlet system and continuing up to the data processing, and also the supporting measures of quality assurance, were inspected during the audit. The audit concerning ozone 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. For carbon monoxide the SOP was adapted accordingly but has still a draft character. The assessment criteria for the ozone intercomparison have been developed by EMPA and are based on WMO-GAW Report No. 97 ("Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements" by P. Hofer, B. Buchmann and A. Herzog, Sept. 1998, available on request from the authors at: EMPA, 134, Ueberlandstr. 129, CH-8600 Dübendorf).

The present audit report is submitted to the station manager at UBA, to the person who is responsible for the station maintenance at ZAMG, the project manager of the GAW-DACH co-operation, the World Meteorological Organization in Geneva and the Quality Assurance and Scientific Activity Centre (QA / SAC) for Europe and Africa.

This was the first audit to be performed at the regional GAW station Sonnblick. System and performance audits at GAW stations will be regularly conducted on mutual arrangement.

3. Regional GAW Site Sonnblick

3.1. Site Characteristics

The Sonnblick Observatory is located on top of the Hoher Sonnblick (coordinates: 47°03’ N, 12°58’ E, elevation 3106 m above sea level) in the Austrian Alps. The observatory was originally built in 1886. It can either be reached with a small cable car that is closed for public or by feet, so there is only negligible abundance of tourism. The site is within the national park “Hohe Tauern” and can be considered to be in the free troposphere and far away from local or regional contamination for most of the time. A real improvement of the site, as a measurement platform for trace gases, could be realised with the new construction of the observatory in 1986 (right part of the picture 3).

The air inlet system is located on the flat roof of the observatory and is exposed to all wind directions. The meteorological sensors are mounted on a 20 m high tower and on the old tower, where the data have been measured for the last 112 years.
The station is a well established site for long-term measurements of several chemical compounds and physical and meteorological parameters in the free troposphere. It is also an important platform for scientific research investigating the global climate. For decades the near environment of the site has not changed in a way, that could have influenced the ozone or carbon monoxide measurements significantly.

Figure 3: Picture of the station Sonnblick

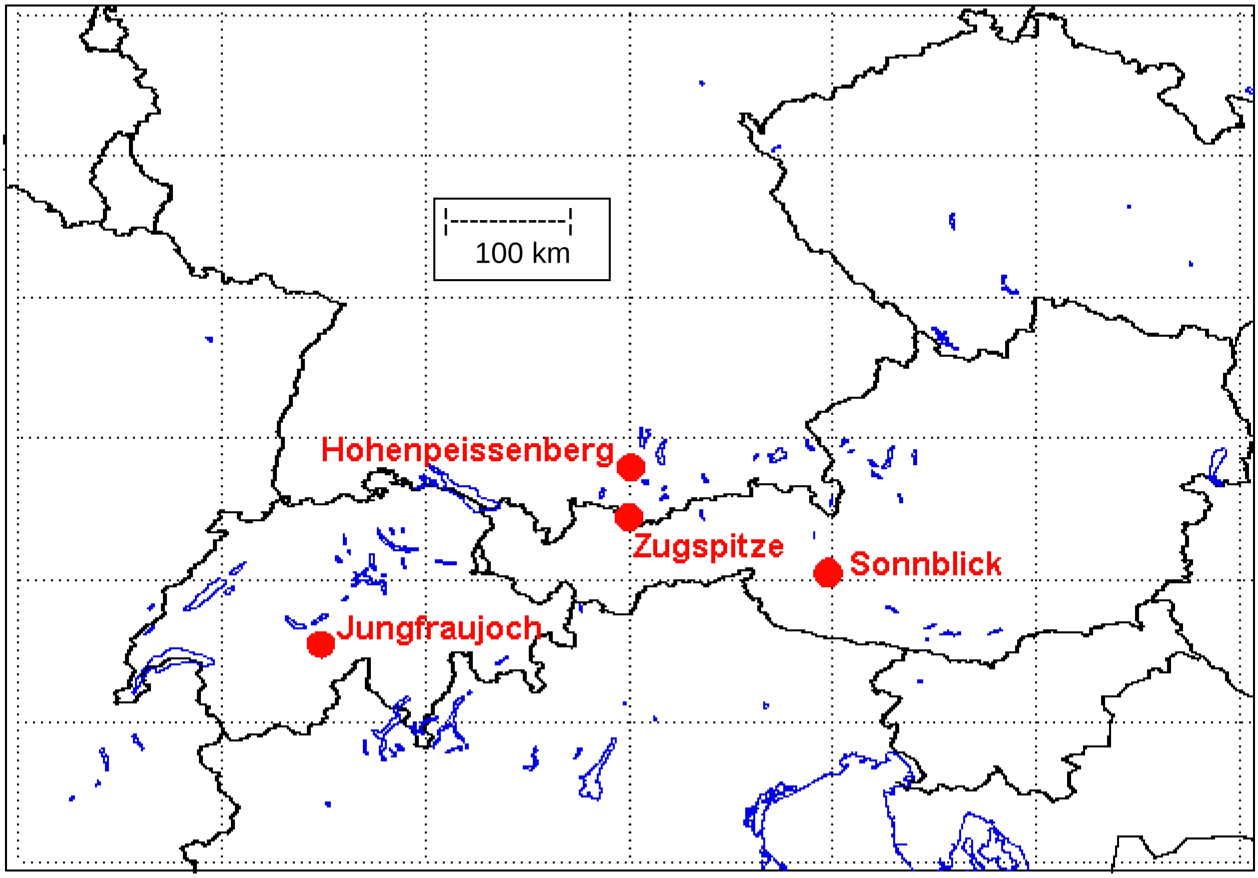

Figure 4: Map of Central Europe:

3.2. Operators

The station is an established site for long-term measurements of several chemical compounds and physical and meteorological parameters. The technical staff of Umweltbundesamt Vienna (UBA) and Zentralanstalt für Meteorologie (ZAMG) are responsible for the operation of the station at Sonnblick. The team of UBA conducts the Measurements of the chemical compounds and the team of ZAMG of the physical and meteorological parameters. The structure of the station management (for the chemical compounds) is shown in Table 1.

Table 1: Operators

Umweltbundesamt (UBA) Zentralanstalt für Meteorologie und Geodynamik (ZAMG)
Operators and Observers Mrs. M. Fröhlich (UBA), Responsible for the station and the network Mr. M. Mandl (UBA, ZAMG), Station maintenance Mr. F. Zimmerl (UBA), calibration, service O3 Mr. F. Rokop (UBA), service CO, data transfer Mr. W. Spangl (UBA), Data management and supervision

3.3. Ozone Level

The site characteristics and the relevant ozone concentration range can be well described by the frequency distribution. In figure 5 the frequency distribution of the hourly mean values from the year 1996 is shown. The relevant ozone concentrations were calculated, ranging between 37 and 64 ppb according the 5 and 95 percentile values.

Source of data: UBA Vienna

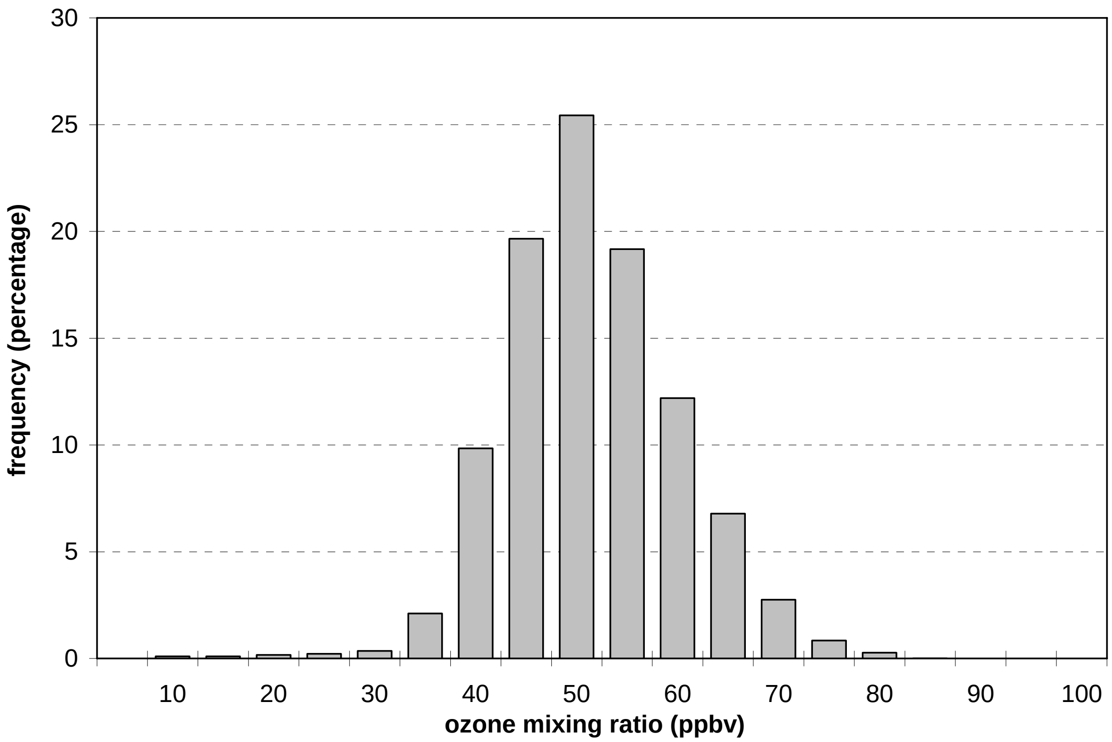

Figure 5: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Sonnblick of the year 1997. Data capture is around 99 per cent.

3.4. Carbon Monoxide Level

The relevant carbon monoxide concentration range can be well defined by the frequency distribution. In figure 6 the frequency distribution of the hourly mean values from the year 1996 is shown. The relevant carbon monoxide concentrations were calculated, ranging between 90 and 240 ppb according the 5 and 95 percentile values. The annual data capture of carbon monoxide was only about 50 %.
Source of data: UBA Vienna

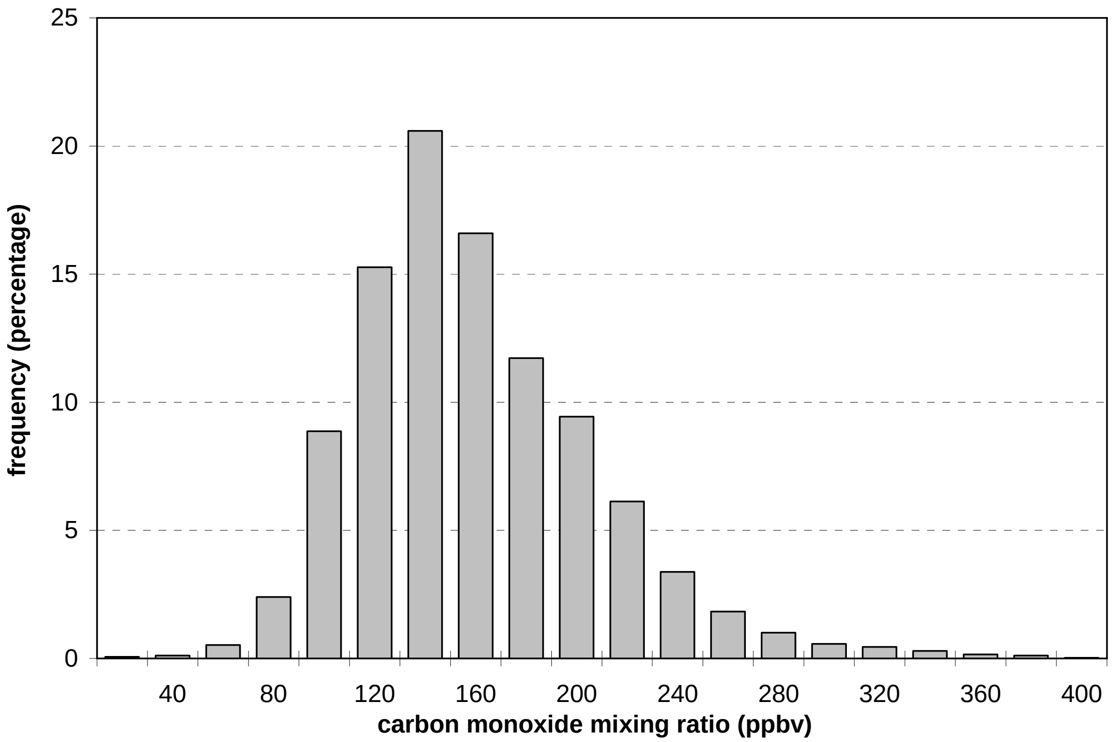

Figure 6: Frequency distribution of the hourly mean values of the carbon monoxide mixing ratio (ppb) at Sonnblick of the year 1997. Data capture is around 50 per cent.

4. Measurement Technique

4.1. Air Inlet System

The air inlet system is located on top of the flat roof of the observatory (it is free exposed to all directions). It consists of a heated, teflon coated inlet, which is protected from rain and snow. The main manifold (2 m outdoor and 0.6 m indoor; ID approx. 20 cm) is coated on the inside with teflon. It leads down along the northern side of the observatory through the wall into the measurement room on the top floor, and is flushed by about 1000 litres ambient air an hour. For the ozone measurements a 4 mm ID, 1.2 m long PFA tubing goes to the inlet filter and to the instrument. For the CO measurement a 4 mm ID, 4 m long PFA tubing is used. The total residence time is estimated at 5 seconds.

Comment

All teflon tubes and manifolds were clean and free of dust. The inlet system concerning materials as well as residence time is adequate for trace gas measurements in particular with regard to minimal loss of ozone and carbon monoxide.

4.2. Instrumentation

The instruments are installed in a room (average temperature 25°C) without air-condition. If the temperature is too high, the room will be ventilated manually. Because of this procedure sometimes there are big changes in temperature in the room. There are plans for the future, to install a temperature control in this room.
The instrumentation used for measuring ozone and CO at Sonnblick during this audit is shown below in table 2 and 3, respectively.

4.2.1. Ozone Analyser

Table 2: Field instrument, ozone

type	TEI 49 #26030
method	UV absorption
usage	basic instrument
at Sonnblick	for 1 year (2 different instruments are used with a annual replacement interval)
range	0-500 ppb
analog output	0-1 V
instruments specials	internal ozone source

Present zero air supply of the station:

- Ozone measurements: ambient air - activated charcoal cartridge
- CO measurements: ambient air – cooling trap of company SMK, Peltier element (dewpoint: -50°C) – SMK CO scrubber (Pd on AlOx)

Comment

The operation of the ozone analyser at Sonnblick (UV method), is corresponding to the method, which is preferred in the GAW programme. Considering its age, the analyser TEI 49 is in good condition.

4.2.2. Carbon Monoxide Analyser

Table 3: Field instrument, carbon monoxide

type	TEI 48 #25429-220
method	GFC (instrument with a modified gas-flow and pressure sensor)
usage	basic instrument
at Sonnblick	since April 1996 (before the instrument was in service on an other site)
range	0-2000 ppb
analog output	0-1 V

In general, two different principles of measuring carbon monoxide can be distinguished and are in practical use at several global GAW stations:

- method: NDIR / GFC, continuous monitoring
- method: GC / HgO, discreet

At Sonnblick since spring 1996 a continuously monitoring analyser (GFC) is in operation.

Distinct characteristics and capabilities of current instruments are discussed in WMO-GAW Report No. 98, WMO meeting of experts on global CO measurements.

The monitoring analyser (NDIR / GFC), in use at present, shows a continuous drift for the zero point potentiometer which makes a frequent zeroing of the system necessary. Thus, every 5.5 hours the zero point is determined during half an hour. However, based on field experience made by other operators of the same type of instrument, this interval is by far too long and should be reduced to a few minutes. For further information see also the diagrams of the ambient air measurements in chapter "6.2 Results".

During the audit it was detected that the SMK cooling trap had a leak in one of the chambers, thus, frequently indoor air was mixed into the ambient air stream. Indoors, high concentrations of a few ppm of CO could be found.

Comment

The NDIR method in use is adequate for the pollution level of the site. Though, the signals of the instrument are fairly noisy and the drift of the zero point is relatively large.
The leak of the cooling trap needs to be repaired with highest priority or is to be replaced by another facility to dry the ambient air.

4.3. Operation and Maintenance

About every 9 days, a station technician visits the site for general maintenance. Exchange of the teflon filters at the instrument inlets is made every 2 weeks. Maintenance of the zero air supply on site includes semi-annually renewing of the absorbent cartridges of activated charcoal. Preventive maintenance of the ozone and carbon monoxide instruments is performed on a case by case basis. Automatic combined zero and span checks (approx. values: 148 ppb) are made as a daily check of the ozone analyser and are not used for recalculating the final data set. In case of an instrument failure, the analyser is replaced with a backup instrument and repaired at UBA. For the CO-analyser, a automatic zero check is performed every 5.5 hours. No backup instrument is available, so during the annual instrument maintenance or while a repair no measurements can be performed.

Ozone Calibration: During the station visits the operator manually checks the zero and span. Twice a year the ozone instruments are compared (multipoint) against a reference which is calibrated once a year (last check January 98) at EMPA.

CO Calibration: A CO working standard (AGA, 1.69 ppm) is used for the weekly manual span check. The cylinder is traceable to a NIST standard (9.18 ppm) at UBA Vienna. Twice a year the CO-instrument is calibrated with a transfer standard (around 7 ppm), which is calibrated at UBA Vienna against a NIST standard (9.18 ppm).

Comment

The appearance inside the station is clean and functional. However, an air-condition for controlling the indoor temperature would be very desirable, since the larger fluctuations can influence the measurements.

The regularly and frequently performed calibrations for both the ozone and carbon monoxide measurements are of fundamental importance for the quality assurance.

It is known that the type of CO analyser, actually in use, shows a continuous drift for the zero point potentiometer making a very frequent zeroing of the system necessary. As is shown in 6.2. the present interval of 5.5 hours is too long. It is recommended to change this procedure, thus ambient air and zero air should be measured in a five-minute or 10-minute interval, alternatingly.

4.4. Data Handling

The data acquisition system at the site is UWEDAT, a product of the Research Centre Seibersdorf. All data are transmitted on a hourly basis via modem to the UBA. Data from the last two weeks are stored at the site on a PC.

The fields of responsibility of the operational group is split up into different parts. One person is in charge for the maintenance and operation, located at the ZAMG, Salzburg, and has no direct access to the actual data. Whereas a person, at the UBA Vienna, reviews and processes the data.

At UBA, data processing follows three phases. In a first step, the raw data is daily visually inspected for assessing general operation. Every month the data set is reviewed for invalid values (according fax sheet from the station operator) to be removed, i.e. data from manual calibrations and maintenance. In a last process, any drift of the transfer standards, which are used for the semi-annual calibrations, is taken into account to recalculate and to obtain the final data set.

Comment

Splitting up responsibilities requires well implemented communication tools to ensure that important information does not get lost. Thus, it is recommended that the person who is responsible for the station maintenance, should also have direct access to the data.

4.5. Documentation

Within the GAW guidelines for documentation, the transparency and the access to the station's documents are required. During the audit the documentation was reviewed for availability and usefulness. The station logbook (excel file on PC) contained the information of all parameters concerning analyser test points, maintenance and calibration. This data is presented in diagrams by the station operator. Changes, events and special investigations are noted in a bound logbook since the beginning of 1998. The relevant information from the station maintenance, that is used for data recalculation, is communicated (phone or FAX) to the UBA Vienna. The instrument manuals are stored at the site. Further we have been informed that the UBA Vienna had started producing monthly data reports.

Comment

For an external person, it has not always been easy to survey and obtain the desired information quickly. Due to the mentioned separation of maintenance and data processing this may be even more important. Therefore it is recommended that the efforts that have been made should be continued to improve the transparency of the documentation.

4.6. Competence

All persons directly or indirectly involved in the operation of the station are highly motivated and experts in their fields. Splitting up the responsibilities requires well implemented communication tools to ensure that important information does not get lost. Specially because most of the technical staff is domiciled in Vienna, a good communication between the person who is responsible for the station maintenance (working in Salzburg) is absolute necessary.

We enjoyed working with the people from UBA and because of Mr. M. Mandl (responsible for the station maintenance) we had a very pleasant stay at the Observatory Hoher Sonnblick.

5. Intercomparison of Ozone Instruments

5.1. Experimental Procedure

At the site, the transfer standard (detailed description see Appendix Ozone) was hooked up to power for warming up over night (deviation from the GAW report No. 97 which recommends only one hour of warm-up time). In the morning, before the intercomparison runs were started the transfer standard, the PFA tubing connections to the instrument and the instrument itself were conditioned with about 200 ppb ozone for 20 min. On August 7th , three comparison runs between the field instrument and the EMPA transfer standard were performed. In the meantime the inlet system and the instrument maintenance were inspected and discussed. Table 4 shows the experimental details and figure 7 the experimental set up of the audit. In general, no modifications of the ozone analyser which could influence the measurements were made for the intercomparisons.

The EMPA acquisition system, which was used for the audit, consists of a 16-channel ADC circuit board and a PC with the corresponding software. Hooked up to the analog output of the field instrument and of the transfer standard the data was collected by both data acquisition systems (EMPA and UBA). In advance, it was checked that the readings of the two acquisition systems were equal at zero (ozone) and at 200 ppb ozone respectively. For data interpretation the EMPA data is used.

Finally, the observed results were discussed in an informal review with the persons involved.

The audit procedure included a direct intercomparison of the TEI 49C-PS 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 the Appendix.

Table 4: Experimental details, ozone

audit-team, EMPA	B. Buchmann, A. Herzog
reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instrument:	TEI 49 #26030
ozone source:	EMPA: TEI 49C-PS, internal generator
zero air supply:	EMPA: silicagel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition system:	EMPA: 16 channel ADC circuit board, software
surrounding conditions:	p: 707 hPa ±2 hPa and T_{indoor}: approximately 25°C
pressure transducers reading:	TEI 49C-PS: 707 hPa TEI 49: 707 hPa
concentration range:	0 - 100 ppb
number of concentrations:	5 + zero air at beginning and end
approx. concentration levels:	15 / 35 / 55 / 75 / 95 ppb

sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 x August 7, 1998
connection between instruments:	around 1 meter of 1/4" PFA tubing

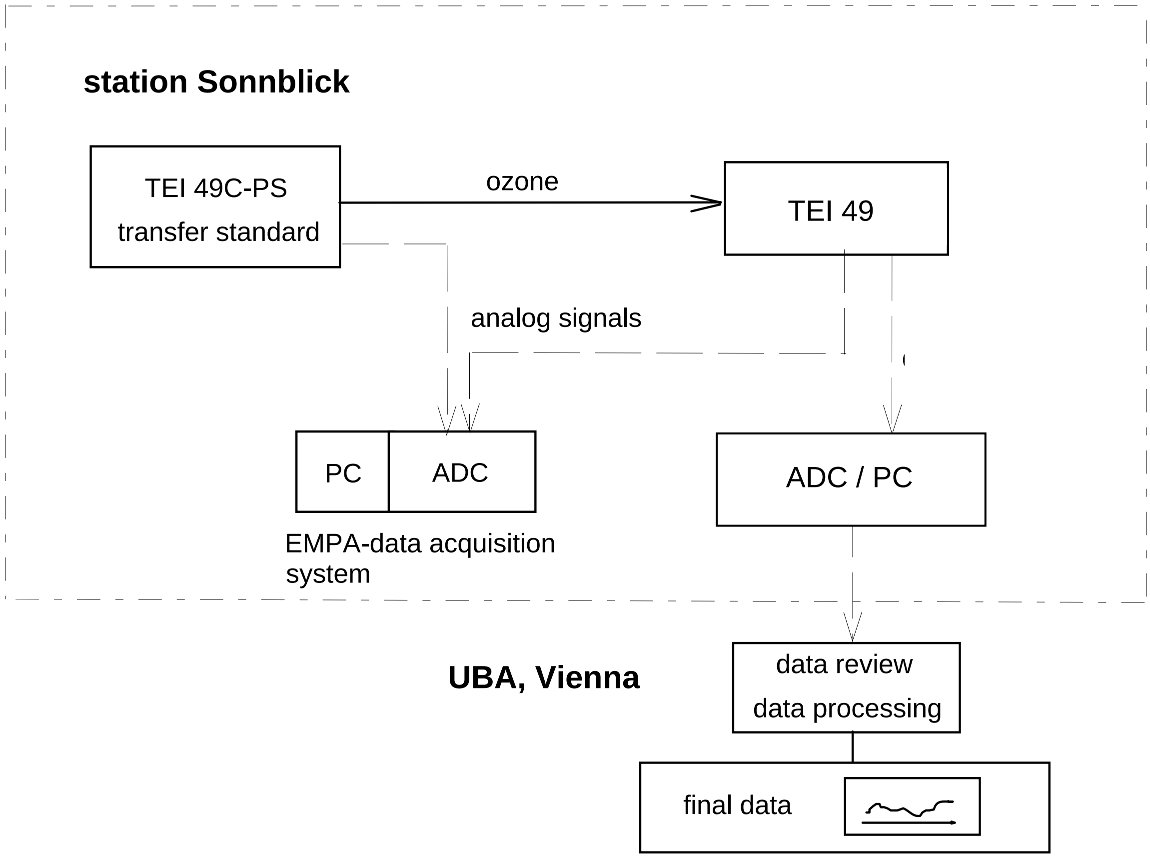

Figure 7: Experimental set up, ozone

5.2. Results

The results comprise three intercomparisons between the field instrument TEI 49 and the transfer standard TEI 49C-PS, carried out on August 7, 1998.

In the following tables the resulting mean values of each ozone concentration and the standard deviations of twenty 30-second-means are presented. For each mean value the differences between the tested instrument and the transfer standard are calculated in ppb and in %.
Further, the diagrams 8 and 9 show the results of the linear regression analysis of the field instrument compared to the EMPA transfer standard.

Table 5: 1. Intercomparison, ozone

No.	transfer standard		TEI 49 #26030			
	TE 49C-PS conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	1.1	0.13	0.2	0.77	-0.9	
2	34.9	0.14	33.4	0.68	-1.5	-4.2%
3	94.9	0.15	92.0	0.63	-2.9	-3.1%
4	54.9	0.13	52.4	0.48	-2.5	-4.5%
5	14.9	0.12	13.4	0.49	-1.5	-10.0%
6	74.9	0.15	71.7	0.51	-3.2	-4.3%
7	1.0	0.18	0.2	0.54	-0.8	

Table 6: 2. Intercomparison, ozone

No.	transfer standard		TEI 49 #26030			
	TE 49C-PS conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	1.0	0.15	-0.1	0.48	-1.1	
2	54.9	0.17	53.0	0.42	-1.9	-3.4%
3	35.0	0.20	33.2	0.76	-1.8	-5.0%
4	95.0	0.17	91.2	0.78	-3.8	-4.0%
5	75.0	0.19	71.7	0.61	-3.3	-4.5%
6	15.1	0.19	13.2	0.84	-1.9	-12.3%
7	1.0	0.17	-0.3	0.56	-1.3	

Table 7: 3. Intercomparison, ozone

No.	transfer standard		TEI 49 #26030			
	TE 49C-PS conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	1.0	0.17	-0.3	0.56	-1.3	
2	75.0	0.22	71.6	0.52	-3.4	-4.5%
3	55.0	0.24	52.7	0.73	-2.3	-4.1%
4	94.9	0.14	91.3	0.83	-3.5	-3.7%
5	34.8	0.14	33.2	0.70	-1.7	-4.8%
6	14.9	0.13	13.3	0.57	-1.6	-10.9%
7	1.0	0.20	0.3	0.50	-0.7	

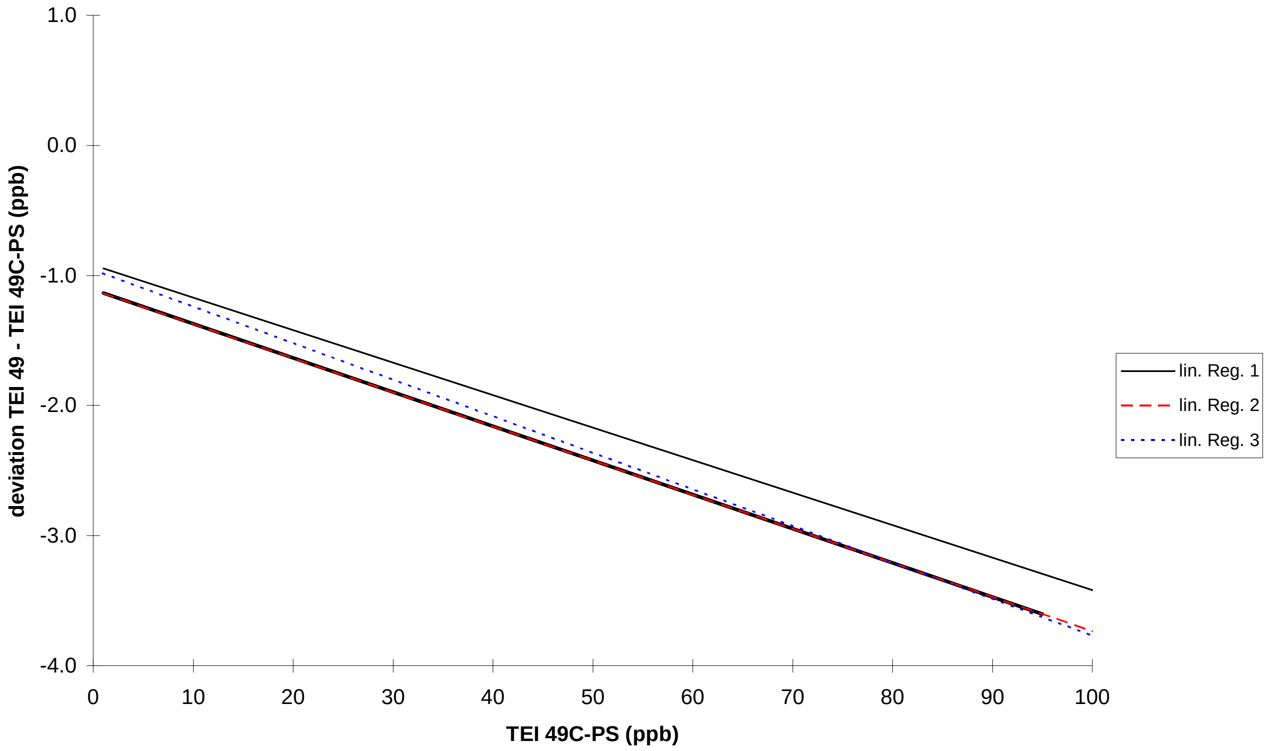

Figure 8: Individual linear regressions of intercomparisons 1 to 3, ozone

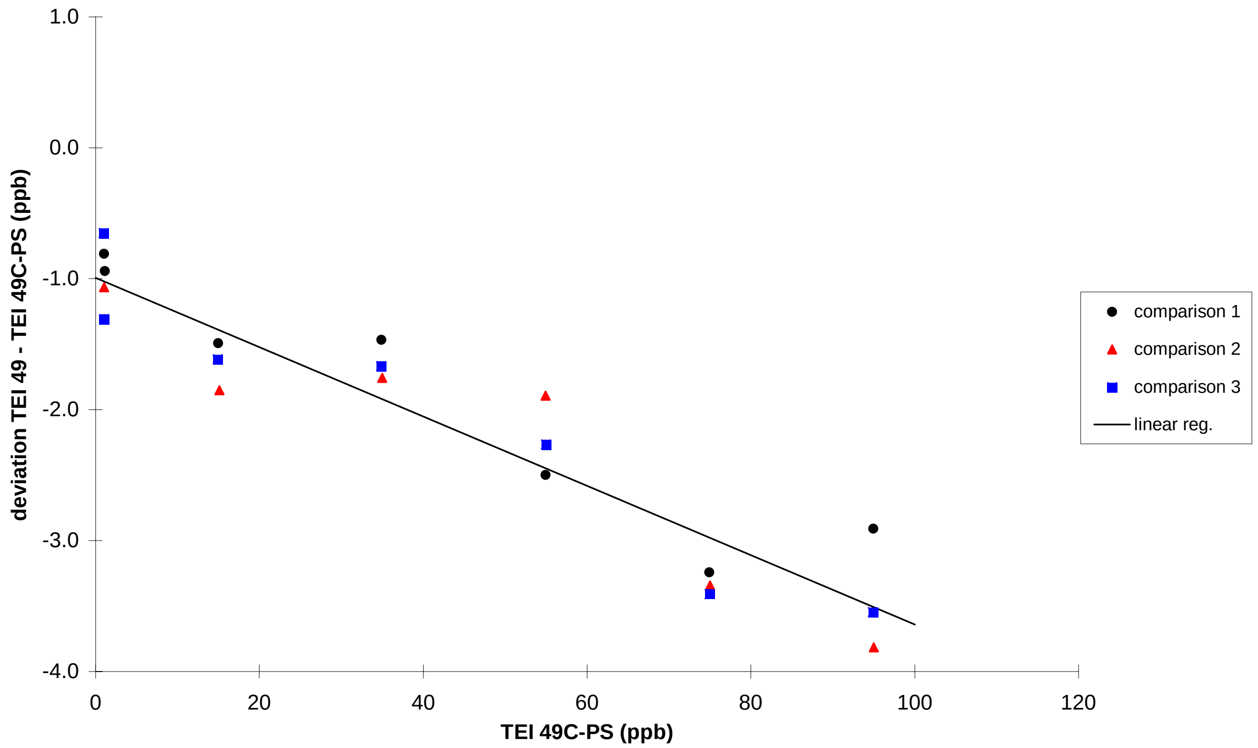

Figure 9: Mean linear regression of intercomparisons 1 to 3, ozone

From the comparisons of the TEI 49 field instrument with the EMPA transfer standard the following linear regression (for the range of 0-100 ppb ozone) is resulting:

TEI 49 = 0.974 x TEI 49C-PS - 1.0 ppb

TEI 49 = O_3 mixing ratio in ppb, determined for TEI 49 #26030
TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0021	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.11	(f = 3)
	- residuals in ppb	0.26	(f = 19)

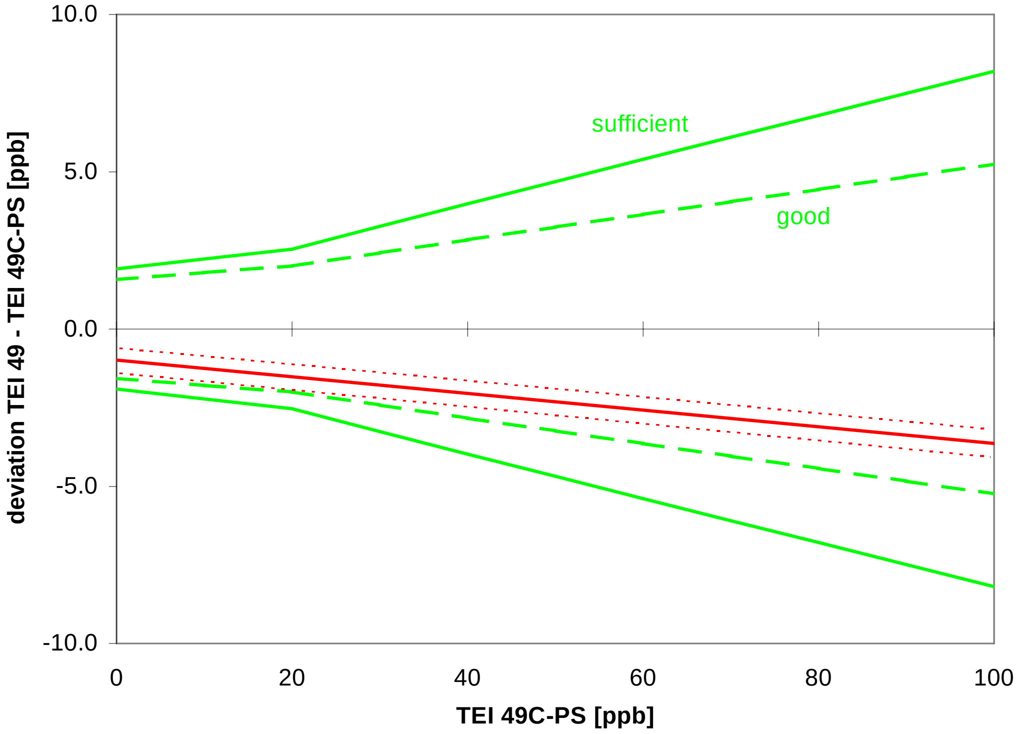

Figure 10: Intercomparison of ozone instrument TEI 49

Comment

In the linear regressions of the instrument (figure 8) no trend as a function of time could be observed.

The ozone concentrations observed at Sonnblick (1997) usually ranged between 37 and 64 ppb (5- and 95-percentile of hourly mean values).

The instrument fulfils the assessment criteria as "good" over the tested range up to 100 ppb (figure 10). Fairly small deviations among the three intercomparisons are the reason for narrow prediction intervals which implies that the instrument is in reasonably good condition.

6. Intercomparison of CO Instruments

6.1. Experimental Procedure

No Standard Operation Procedures (SOP) have been established for CO measurements by QA/SAC until now. For this reason, the "SOP for performance auditing ozone analysers at global and regional WMO-GAW sites" (WMO-GAW Report No 97), was adapted for CO, but the document has still a draft character.

At the site the MGM diluter (see Appendix Carbon Monoxide) was hooked up to power for warming up and for stabilisation for several hours. The calibration gases (see Appendix Carbon Monoxide) were stored at the site over night before the audit measurements were started. At the end of the stabilisation time the whole dilution system including PFA tubing was flushed with 350 ppb CO for one hour. From August 6 until August 8 the intercomparison on the instrument was made with different concentration levels (figure 11). The instrument was supplied with calibration gas for 10 minutes for each concentration. Table 8 shows the experimental details and figure 15 the experimental set up of the audit. In general, no modifications of the carbon monoxide analyser was made for the intercomparison. The signal of the field instrument was acquired by the EMPA data acquisition system.

Finally, the observed results were discussed in an informal review with the persons involved.

The audit procedure included a direct intercomparison of the MGM diluter transfer standard with the Califlow (Standard Reference) and the Calibration Gases (Transfer Standard) with the Standard Reference Gases (CMDL) before and after the audit in the calibration laboratory at EMPA. The results of these intercomparisons are shown in the Appendix.

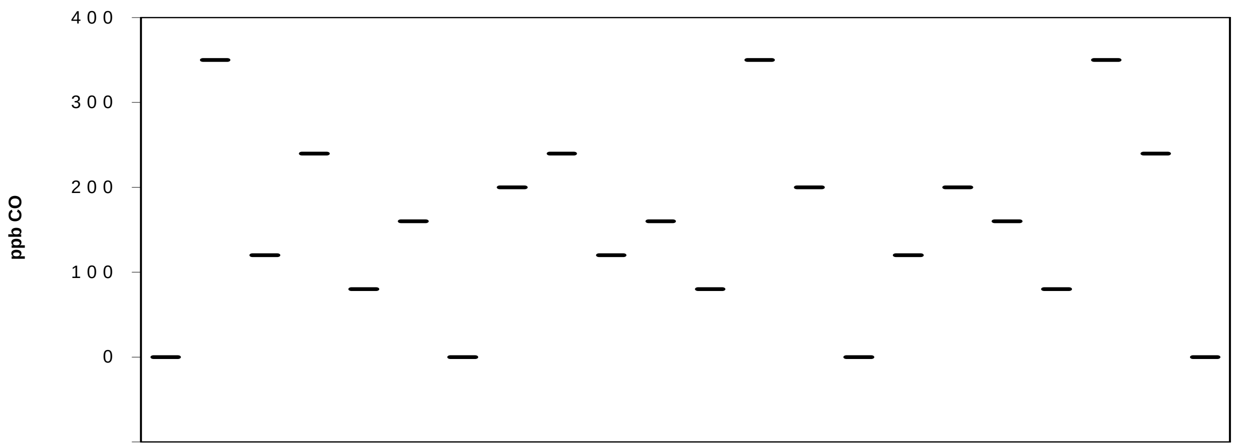

Figure 11: Sequence of concentrations during audit.

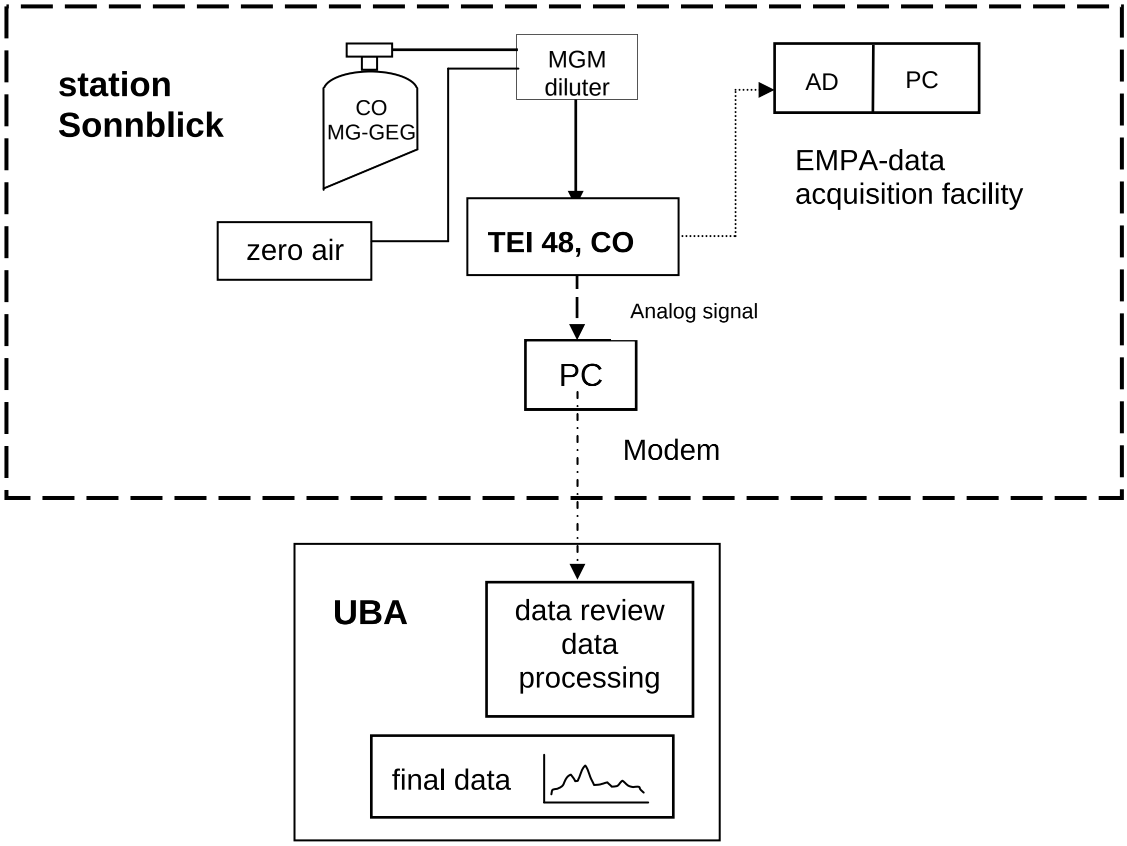

Figure 12: Experimental set up, CO

Table 8: Experimental details, CO

audit-team, EMPA	B. Buchmann, A. Herzog
reference:	Transfer standards: MGM diluter, MG-GEG Calibration Gas
field instrument:	- TEI 48 #25429-220
air inlet system (pre-treatment)	dried air (cooling trap)
zero air supply:	EMPA: synthetic air + Sofnocat UBA: ambient air – drying - CO scrubber (Pd on AlOx) of SMK company
data acquisition system:	EMPA: 16 channel ADC circuit board, software
surrounding conditions:	p: 707 hPa ±2 hPa and T_{indoor}: approx. 25°C
concentration range:	0 - 2000 ppb
number of concentrations:	5 + zero air

approx. concentration levels:	80 / 120 / 160 / 200 / 240 / 350 ppb
sequence of concentration:	(figure 14)
averaging interval per concentration:	10 minutes
connection between instruments:	less than 3 meter of 1/4" PFA tubing

6.2. Results

The results consists of 22 measurements between the field instruments TEI 48 and the transfer standard carried out on 7. and 8. August, 1998.
In the following table the resulting mean values of each carbon monoxide concentration and the standard deviations of a 10-minute interval (20 x 30-second means) are presented. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and in %. Further figure 13 shows the results of the linear regression analysis of field instrument TEI 48 compared to the EMPA transfer standard.

Table 9: Intercomparisons, CO

No.	transfer standard		TEI 48			
	MGM conc.	S_d	conc.	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0		6.7	20.4	6.7	
2	350.9	0.21	355.7	13.0	4.8	1.4
3	120.5	0.07	130.3	19.0	9.8	8.2
4	241.0	0.52	245.6	12.6	4.6	1.9
5	80.5	0.25	92.3	10.9	11.8	14.7
6	160.4	0.27	166.8	17.8	6.4	4.0
7	0		5.9	18.1	5.9	
8	200.7	0.43	194.3	16.6	-6.4	-3.2
9	241.0	0.52	221.9	15.4	-19.1	-7.9
10	120.5	0.07	132.8	17.2	12.3	10.3
11	160.4	0.27	176.1	12.7	15.7	9.8
12	80.5	0.25	102.2	15.7	21.7	26.9
13	350.9	0.21	358.2	16.2	7.3	2.1
14	200.7	0.43	203.8	15.9	3.1	1.5
15	0		2.9	15.8	2.9	
16	120.5	0.07	112.4	19.2	-8.1	-6.7
17	200.7	0.43	193.2	17.7	-7.5	-3.8
18	160.4	0.27	157.5	13.2	-2.9	-1.8

19	80.5	0.25	92.7	17.4	12.2	15.1
20	350.9	0.21	351.5	13.8	0.6	0.2
21	241.0	0.52	250.4	14.0	9.4	3.9
22	0		16.7	16.1	16.7	

The summary of the CO comparisons (for the CO range 0 - 350 ppb) of the TEI 48 with the EMPA transfer standard is the following linear regression line:

TEI 48 = 0.97 x TS + 9 ppb

TEI 48 = CO mixing ratio in ppb, determined for TEI 48 #25429-220
TS = CO mixing ratio in ppb, produced by the Transfer standards (MGM diluter + Calibration gases) and related to the Standard References at EMPA (Califlow, CMDL + NIST gases).

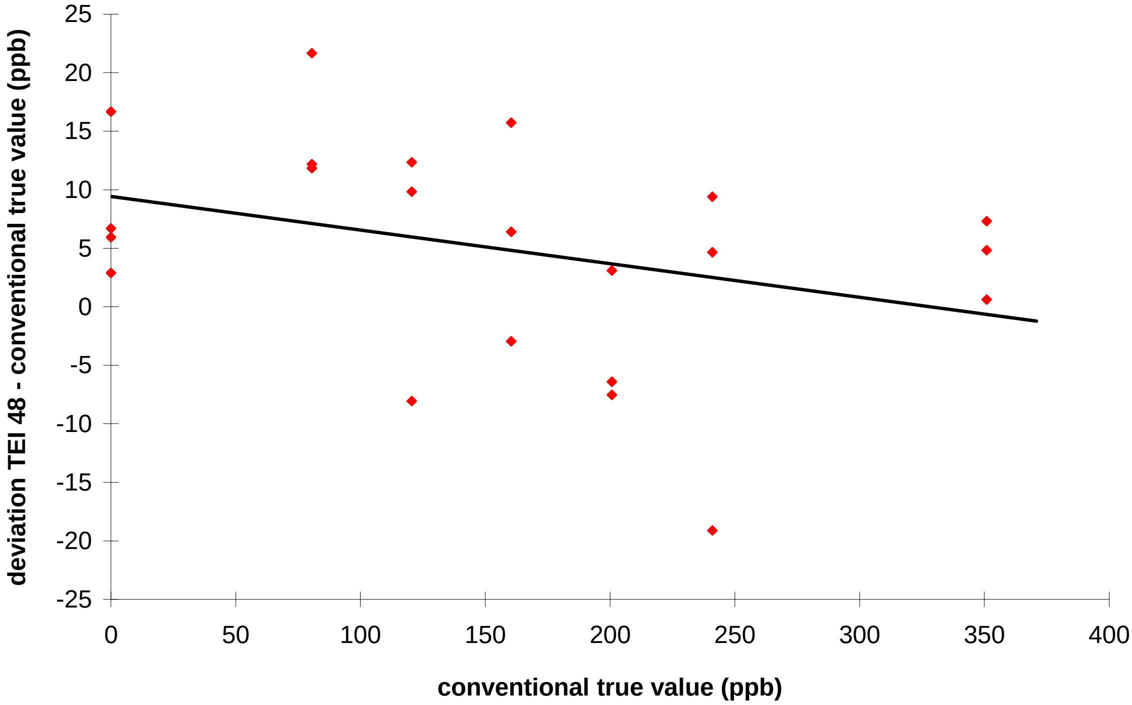

Figure 13: Differences (ppb) between the TEI 48 and the transfer standard

Figure 14 shows the relative differences (%) between TEI 48 and the transfer standard. The total uncertainty of the transfer standard (red line in figure 14) has been calculated for the whole audit procedure. Most of the uncertainty is caused by the uncertainties of the Reference gases.

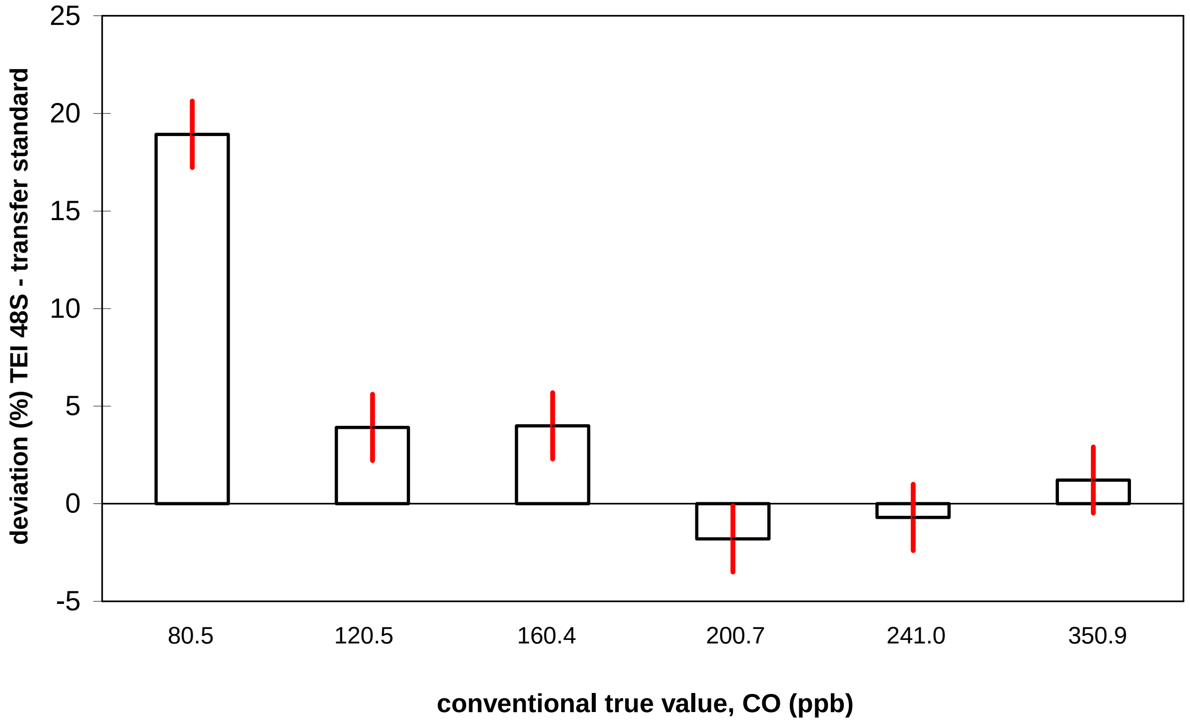

Figure 14: Differences (%) between TEI 48 and the transfer standard (the red lines show the whole uncertainty of the audit procedure)

During two nights (August 7/8th and 8/9th) we carried out parallel measurements of ambient air between the station instrument TEI 48 and a CO monitor of the EMPA, Horiba 360 APMA. The principle of the Horiba instrument is the NDIR method without gas filter correlation. Unlike most other NDIR CO analysers, the Horiba instrument shows only minor interference for water vapour and nearly no drift for the zero point potentiometer. In figure 15 and 16, the 10 -minute mean values of the results of the TEI 48S and the Horiba 360 APMA are shown.

When we processed the data of the first night (7/8th) it became very apparent that there was a problem with the CO ambient air measurements of the station. The values were generally higher then expected regarding the actual meteorological conditions. It was further noticed, that at the same time when a valve in the SMK cooling trap switched, the time series of the TEI 48 station analyser either dropped or raised (see figure 14). A leak in the cooling trap was found to be the problem. Since the ambient air for the Horiba instrument does not need any pre-treatment (drying) this instrument was directly conected with the main sampling line (without cooling trap) and thus was not effected by this leak.

So for the second night two large silicagel cartridges were used for drying the ambient air for the TEI 48 station instrument. These results look much more encouraging, however, another problem became apparent. It is known from field experience, made by other operators of the same type of instrument in use at present, that they show a continuous drift for the zero point potentiometer making a frequent zeroing of the system necessary. At Sonnblick, only every 5.5 hours the zero point is determined (figure 16), while an interval of only a few is commonly recommended. But in that case much less ambient air data would be acquired, which seems to be critical for the data objectives. Nevertheless, since the drift of the instrument is relatively large, and the zero determined at the end of a 5.5 hour period is applied to the whole period of ambient air data, the error is considered to be very significant.

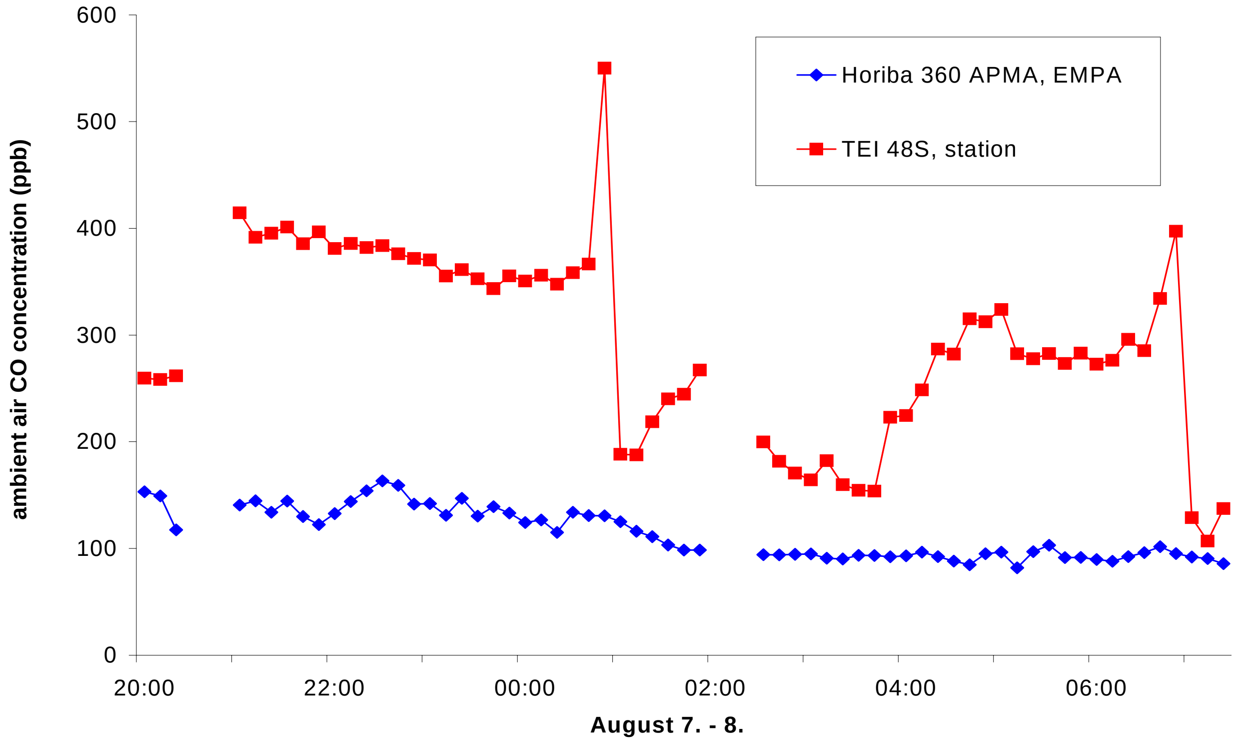

Figure 15: Ambient air concentrations during 1. night, measured with the field instrument TEI 48 and the transfer standard Horiba 360 APMA, leakage in the cooling trap of the station

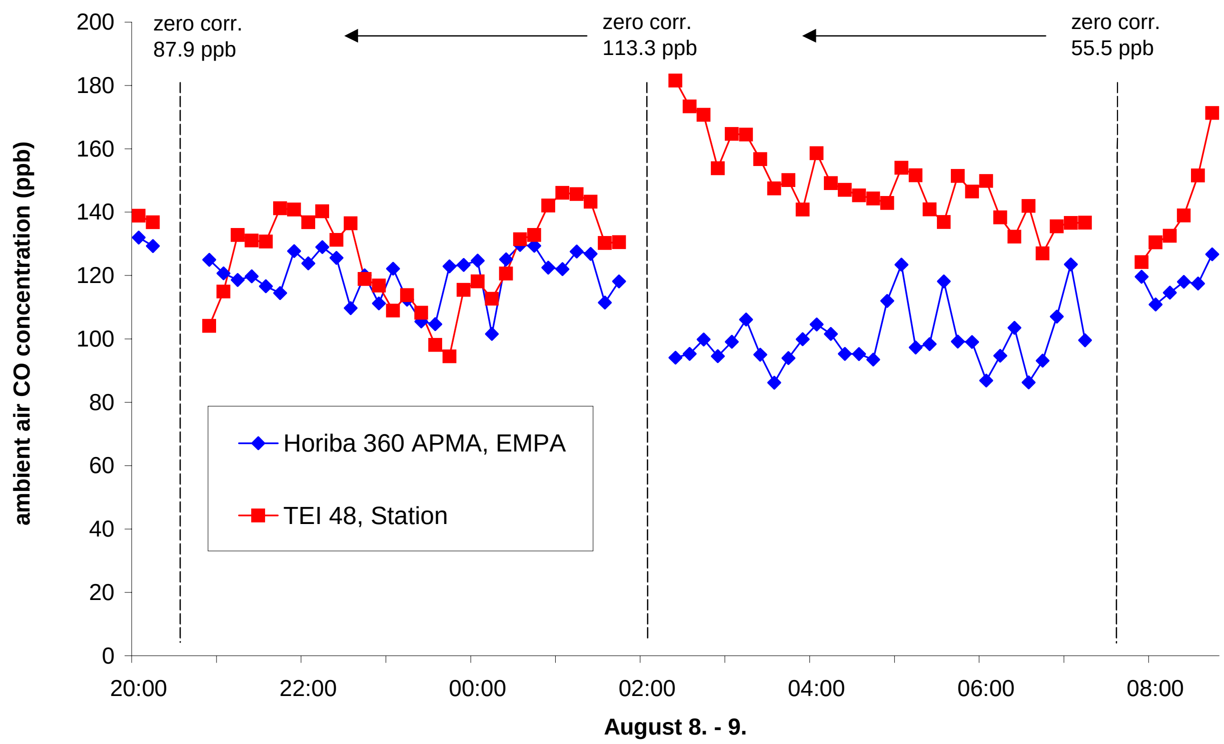

Figure 16: Ambient air concentrations during 2. night, measured with the field instrument TEI 48 and the transfer standard Horiba 360 APMA, by-passing the cooling trap

Comment

The carbon monoxide concentrations observed at Sonnblick (1997) usually ranged between 90 and 240 ppb (5- and 95 percentile of hourly mean values).

The results of the CO intercomparison measurements (figure 14) deviate by about 1 to 5% from the conventional true value, for concentrations between 120 and 350 ppb CO. The measurement uncertainty is approximately 2%. However, as parallel measurements showed (figure 16), the assessed error for ambient air values must be considered to be very significant. This due to the actual practice of zeroing the instrument. Either, a much more frequent zeroing of the system or an exchange of the analyser is strongly recommended.
Regarding the detected leak of the cooling trap, the ambient air data of the period with the leaking cooling trap, needs to be examined very carefully.

Appendix Ozone

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 degree to which the UV light is absorbed is directly related 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 reference gas. The second zero air stream flows through a pressure regulator, ozonator and manifold 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. When 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 calculates the ozone concentration for each cell and outputs the average concentration.

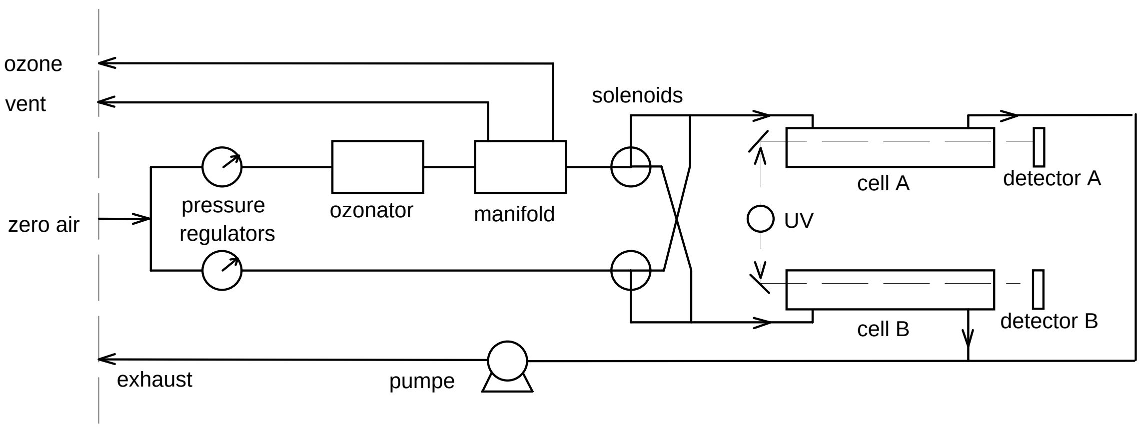

Figure 17: Flow schematic of TEI 49C-PS

II. Stability of the Transfer Standard TEI 49C-PS

To exclude errors which might occur through transportation of the transfer standard, the TEI 49C-PS #54509-300 has to be compared with the SRP#15 before and after the field audit.

The procedure and the instruments set up of this intercomparison in the calibration laboratory at EMPA are summarised in Table 10 and Figure 18.

Table 10: 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 / 185 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

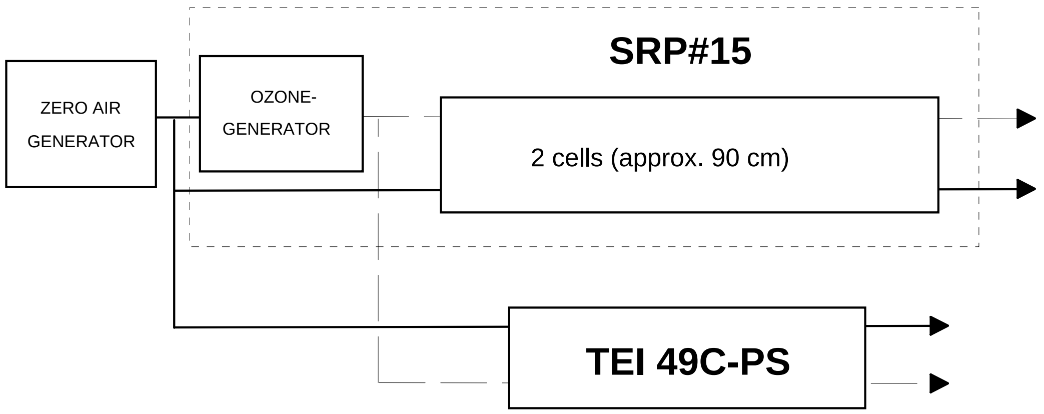

Figure 18: Instruments set up SRP -TEI 49C-PS

The stability of the transfer standard is 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 ± (1 ppb + 0.6%).

Figures 19 and 20 show the resulting linear regression and the corresponding 95% prediction interval for the comparisons of TEI 49C-PS vs. SRP#15. Clearly, the linear regression and the prediction interval remain within the recommended tolerance.

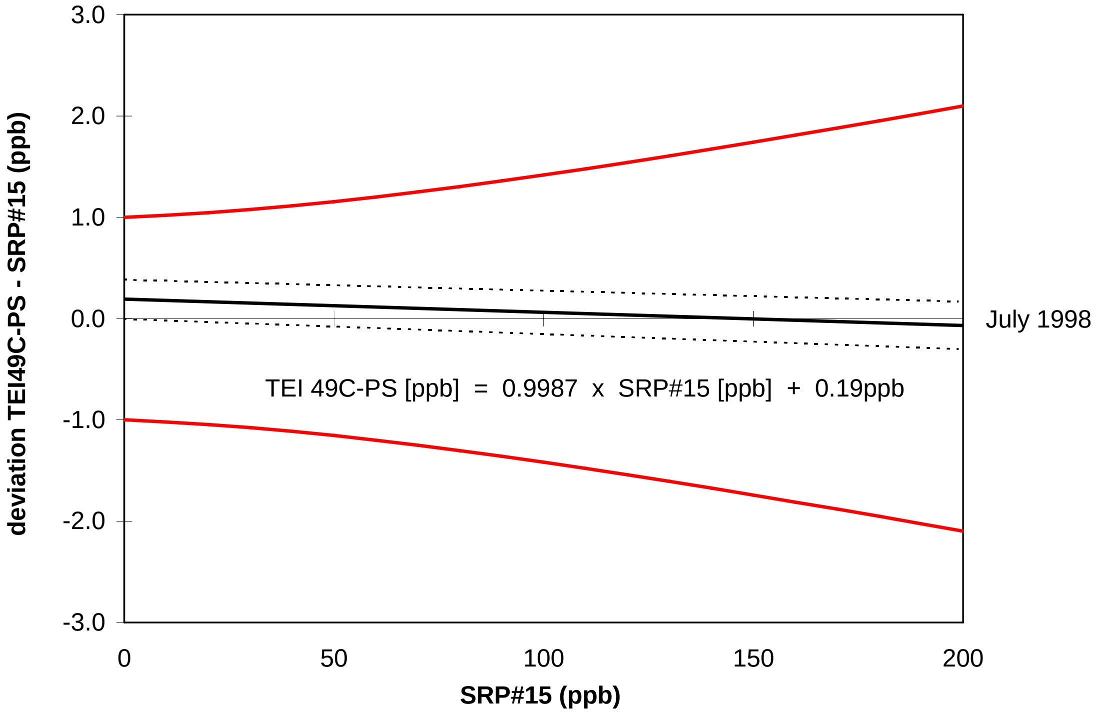

Figure 19: Transfer standard (O_3) before audit

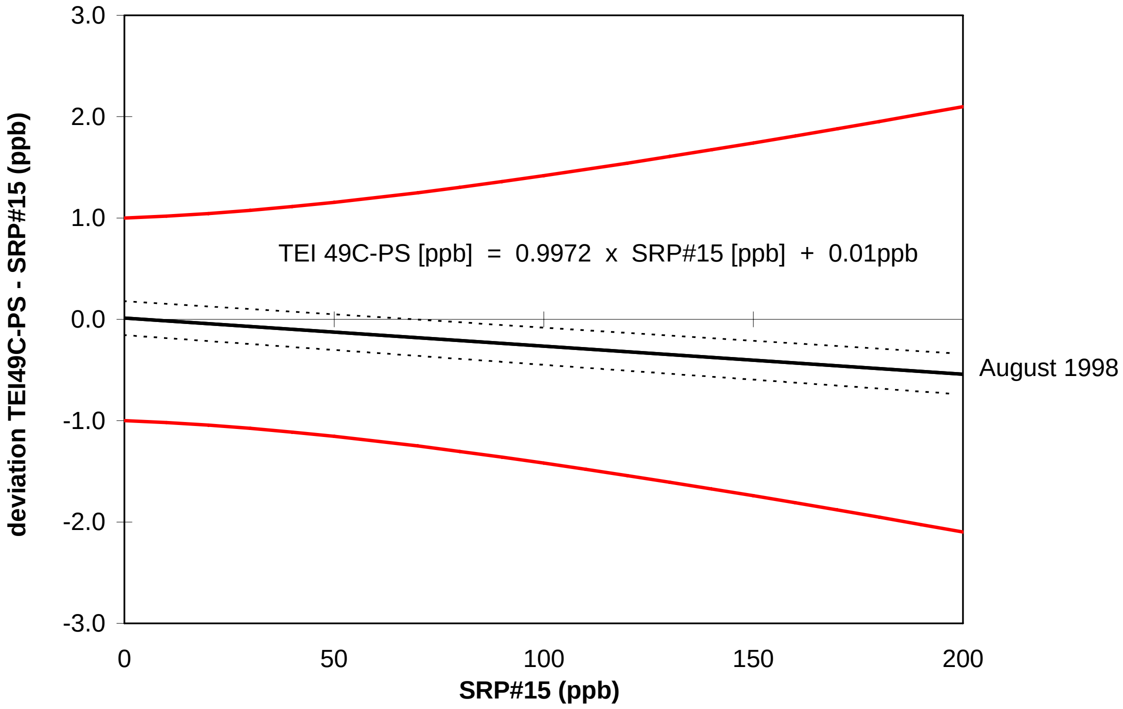

Figure 20: Transfer standard (O_3) after audit

Appendix Carbon Monoxide

I. Traceability chain

No Standard Operation Procedure (SOP) has been established yet for CO measurements. In figure 21 the traceability chain for the carbon monoxide, used by the WCC-CO is shown.

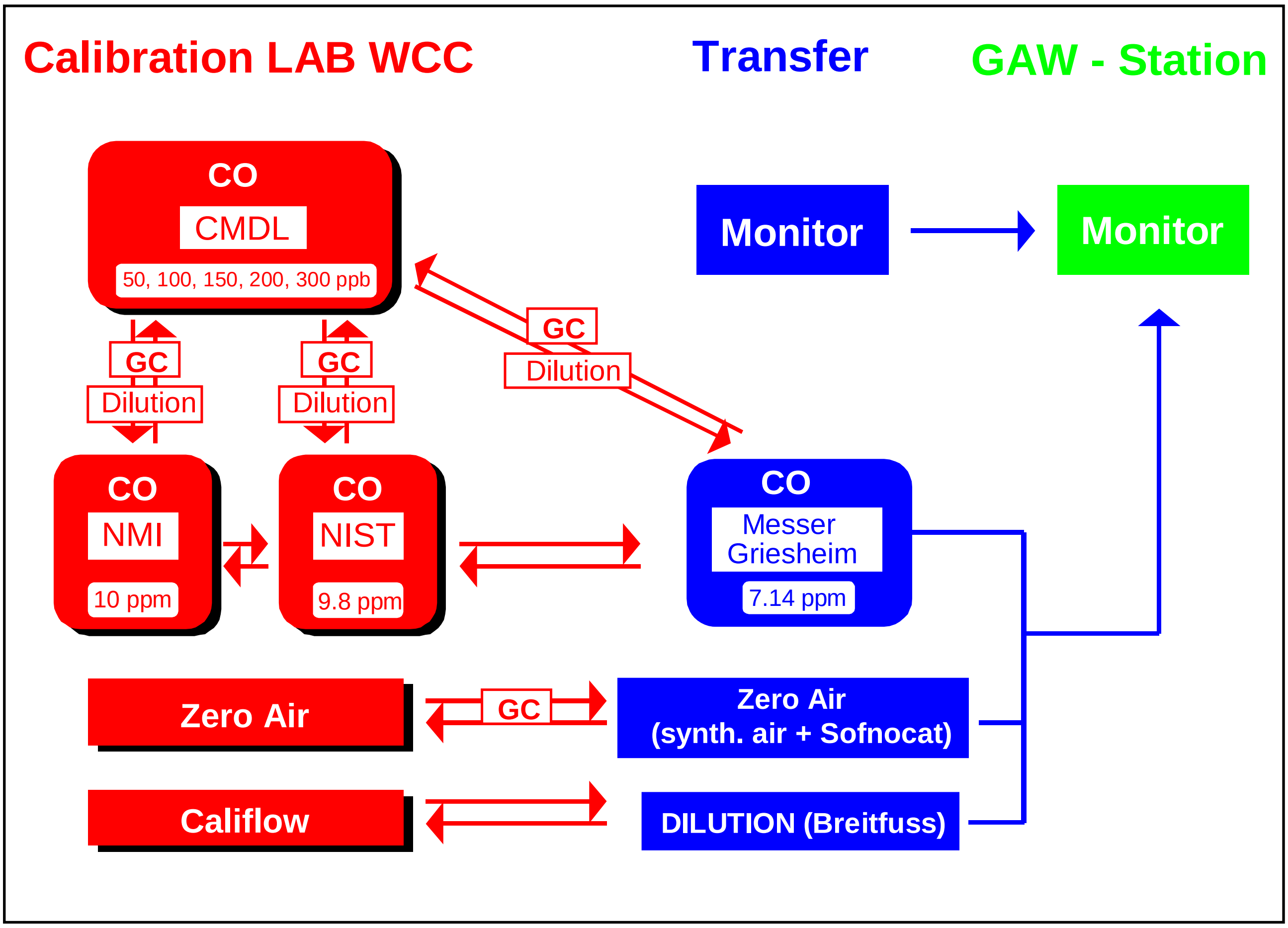

Figure 21: Traceability chain of the carbon monoxide audit.

II. EMPA Primary Standards

CMDL Primary Gas Standards

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is 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 is now the most used standard for measurements of atmospheric CO all over the world.
At the WCC at EMPA we use the following CO standards:

Table 11: CO-Standards at the EMPA

Standard	CO	Cylinder
CMDL Laboratory Standard (basis for WCC)	44.0 ± 1.0 nmole/mole	CA03209
CMDL Laboratory Standard (")	97.6 ± 1.0 nmole/mole	CA02803
CMDL Laboratory Standard (")	144.3 ± 1.4 nmole/mole	CA03295
CMDL Laboratory Standard (")	189.3 ± 1.9 nmole/mole	CA02859
CMDL Laboratory Standard (")	287.5 ± 8.6 nmole/mole	CA02854

NIST Reference Standard	9.8 ± 0.05 μmol/mol	CLM006694
NMI Reference Standard	10.01 ± 0.04 μmol/mol	316511

The absolute accuracy of the NOAA/CMDL CO scale has not been rigorously determined, but based on the uncertainties of the gravimetric and analytical procedures, and comparisons to the NIST CO scale, the NOAA/CMDL scale is probably accurate to within 3% (Kitzis D.R., NOAA/CMDL Carbon Cycle Group calibration laboratory, 1998, Personal Communication).
The listed μmol/mol standards from NIST and NMI are checked against the CMDL standards by using dynamic dilution and analysis on an RGA-3 system.

CALIFLOW (MKS, USA)

Califlow is a high accuracy Primary Standard, designed for accurate and efficient measurement of gas flow rates. Gas flow rates are measured by collecting a volume of gas under a piston, with a frictionless seal, which moves inside precision-bore borosilicate glass tube. The unit automatically places this volume measurement on a precision time base to establish flow rate. The Primary Standard Califlow shows these capabilities: traceable to National Institute of Standards and Technology (NIST, USA), high accuracy of 0.2% of reading and wide range calibration up to 50 l/min.

III. EMPA Transfer Standards

MG GEG-Calibration Gas (Messer Griesheim, Duisburg, Germany)

The CO mixing ratios in ppb for the intercomparison were obtained with the transfer standards , the MGM diluter and the MG GEG-Calibration gas (7.13 ± 0.03 ppm, cylinder 9751B). The MG GEG-Calibration gas was related before and after the audit to the Standard References at EMPA. The transfer standard was related without dilution to the NIST standards (National Institute of Standards and Technology, USA) and the mixing ratios, used in the intercomparison were related to the NOAA/CMDL (National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory) reference scale.

MGM Diluter (Breitfuss, Germany)

The CO mixing ratios in ppb for the intercomparison were obtained with the transfer standards, the MGM diluter (S/N 2262/97/1) and the MG GEG-Calibration gas. The MGM diluter consists two thermal mass flow controllers (BRONKHORST HI TEC, Serial number 9720369 and B), a mixing chamber and electronics to produce the different mixing ratios.

Stability of the Transfer Standard MGM Diluter

To exclude errors which might occur through transport of the transfer standard, the MGM diluter has to be compared to the Califlow (Primary Standard) before and after the field audit.

The procedure and the instruments set up of this intercomparison in the calibration laboratory at EMPA are summarised in Table 12 and Figure 22 (flow 2000 ml/min). The stability of the transfer standard is thoroughly examined with respect to the uncertainties of the different components (systematic error and precision).

Table 12: Intercomparison procedure MGM diluter – MKS Califlow.

concentration range:	0 - 350 ppb
number of concentrations:	6 + zero air
approx. concentration levels:	80 / 120 / 160 / 200 / 240 / 350 ppb

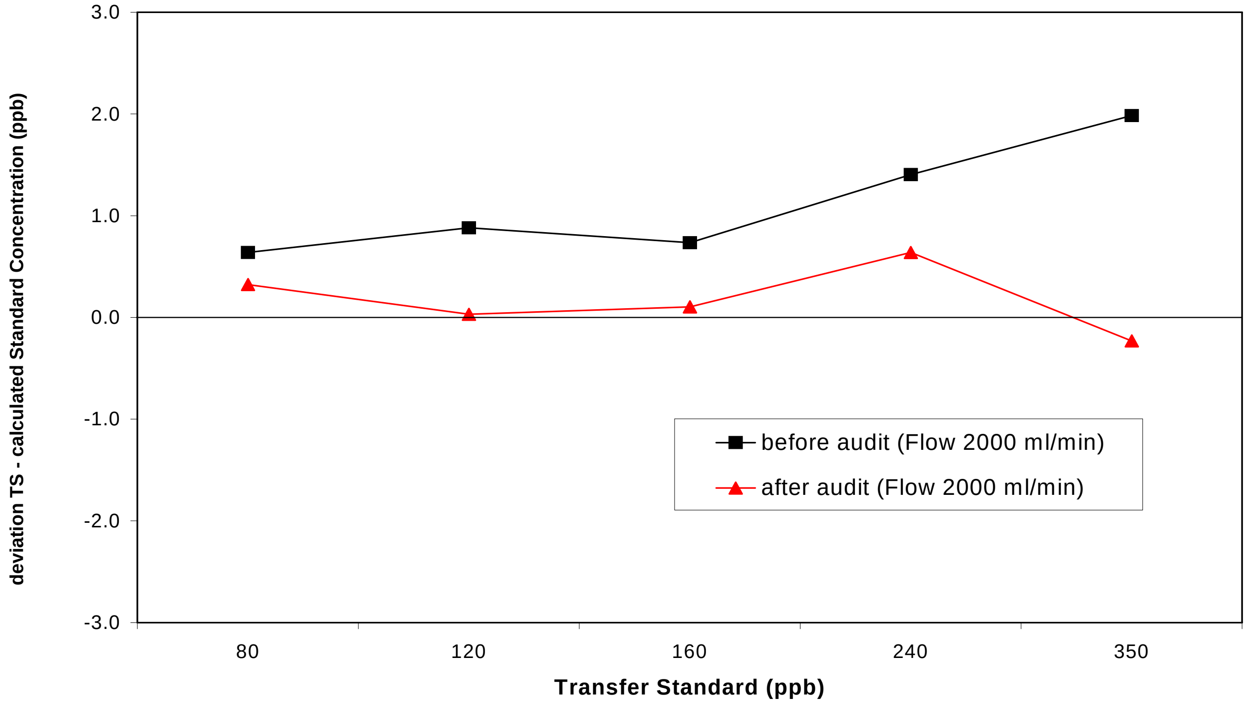

Figure 22: Transfer standard (MGM diluter) before and after audit.

The deviations of the really applied CO calibration gas concentrations to the theoretical values, are shown in figure 22 and are taken into account when calculating the dilution ratio of the MGM dilution unit.

Horiba CO Monitor APMA – 360

The APMA-360 has been designed to measure the concentration of carbon monoxide in ambient air using the non-dispersive infrared analysis method (NDIR) as its operating principle.
Before and after the ambient air parallel measurements, between the station instrument of the Sonnblick and the EMPA CO analyser Horiba 360 APMA, we made a calibration of the Horiba 360 APMA with zero-air and span gas (350 ppb).