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

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

EMPA-WCC REPORT 99/1

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE AND CARBON MONOXIDE

REGIONAL GAW STATION JUNGFRAUJOCH

SWITZERLAND, JANUARY 1999

Submitted by

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WMO World Calibration Centre for Surface Ozone and Carbon Monoxide

EMPA Dübendorf, Switzerland

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1. Abstract

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

Air Inlet System:

All teflon tubes and glass manifolds were clean and free of dust and adequate for trace gas measurements in particular with regard to minimal loss of ozone. Nevertheless, it is recommended to rethink the manifold configuration with its many teflon to glass connections, as a preventive action, in order to avoid possible leakage problems in the future. Although tight at the moment, a small leak would be very difficult to notice but still can have a significant effect on the results.

Instrumentation:

Ozone Analysers:
The operation of an ozone analyser and a backup instrument (both UV method), considerably increases confidence in data quality concerning parallel measurements as well as data availability.

Carbon Monoxide Analyser:
The CO NDIR analyser in use is a very stable instrument and adequate to the pollution level of the site of Jungfraujoch.

Operation and Maintenance:

The appearance inside the station is clean and functional. The room is well equipped with electronic devices for instrumental control and data acquisition.
The maintenance of the site is clearly structured and organised. The regular calibrations for both the ozone and CO measurements are regarded as very important means of quality assurance.

Data Handling:

The procedure of data treatment is well organised and clearly arranged. The first reviewing of the data is done on a regular, mostly daily interval, so that irregularities can be detected early. The review of the final data set is well done and transparent to the outside, which increases the reliability of the data.

Documentation:

The documentation of the ozone and CO measurement meets the requirements of the guidelines for GAW stations. It can be taken as a good example for complete and clearly arranged documentation. However, a practice orientated SOP for maintenance and operation should be implemented as a preventive action to avoid loss of accumulated knowledge.

Ozone Intercomparisons:

The ozone concentrations observed at the Jungfraujoch (1997) usually ranged between 36 and 67 ppb (5- and 95-percentile of hourly mean values).
The instrument clearly fulfils the assessment criteria as "good" over the tested range up to 100 ppb (figure 1). Fairly small deviations among the three intercomparisons are the reason for narrow prediction intervals which implies that the instrument is in good condition.

Carbon Monoxide Intercomparisons:

The results of the CO intercomparison measurements (figure 14) deviate only by about 1 to 3% from the conventional true value with a measurement uncertainty of approximately 2%. Regarding the relevant range (99 and 193 ppb, 5- and 95-percentile respectivley) and the methode in operation this is a very good result.

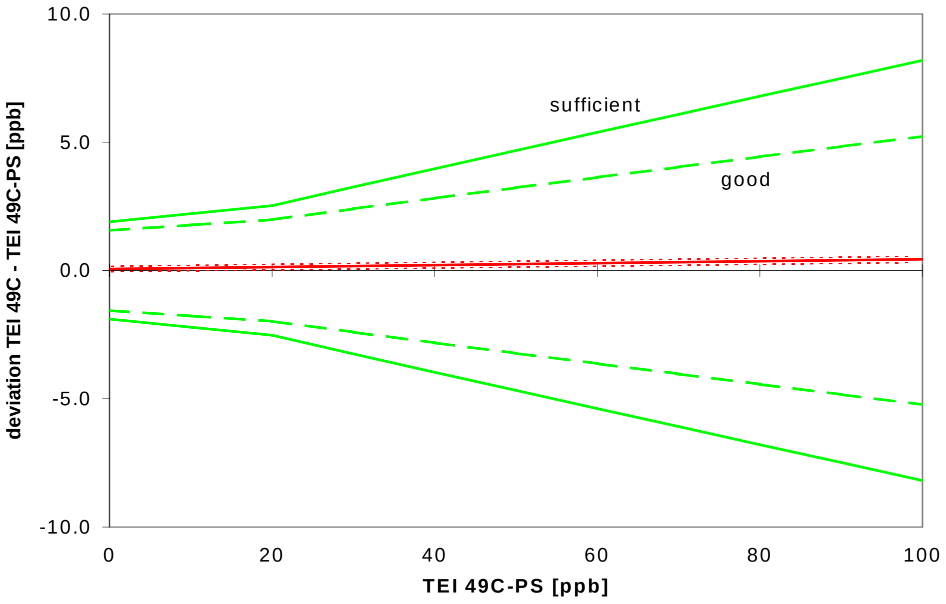

Figure 1: Intercomparison of instrument TEI 49C

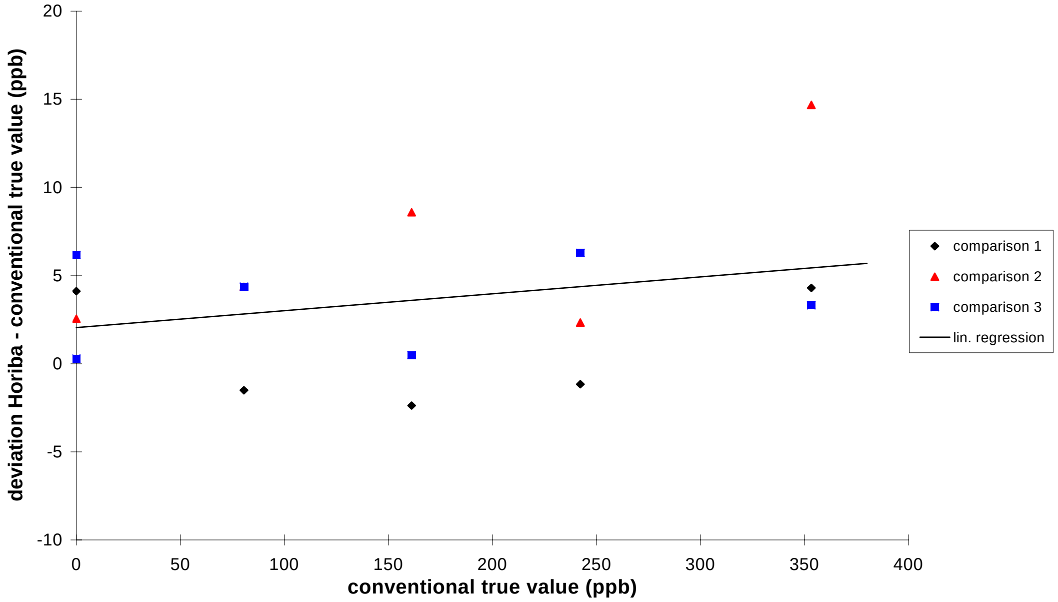

Figure 2: Intercomparison of CO analyser Horiba APMA-360

Dübendorf, 9. February, 1999

World Calibration Centre

Project engineer

Project manager

A. Herzog

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. At the beginning of 1996 our work had started within the GAW programme with the parameter surface ozone. The activities were extended for 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.

From January 11 to 13 in 1999,a system and performance audit at the Jungfraujoch, Switzerland, was conducted. This station is an established site for long-term measurements of several chemical compounds and physical and meteorological parameters.

The scope of the audit 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. No Standard Operation Procedures (SOP) have been established for CO measurements by QA/SAC until now. For this reason the ozone SOP was adapted for carbon monoxide. The assessment criteria for the ozone intercomparison have been developed by EMPA-WCC and are based on WMO-GAW Report No. 97 (EMPA-WCC report 98/5 "Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements" by P. Hofer, B. Buchmann and A. Herzog, September 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 EMPA, the World Meteorological Organization in Geneva and the Quality Assurance and Scientific Activity Centre (QA / SAC) for Europe and Africa.

3. Regional GAW Site Jungfraujoch

3.1. Site Characteristics

The high Alpin research station Jungfraujoch (3580 m a.s.l.) is situated in a mountain saddle in the Berner Oberland (Switzerland) between the two mountains Jungfrau (4158 m a.s.l.) and the Mönch (4099 m a.s.l.). This topographical condition strongly influences the local wind field. The main wind directions measured at the site are therefore north-west and south-east. The station can be reached by a rack-railway.

The chemical monitoring station (co-ordinates: 46°33' N, 7°59' E;) is placed in the second floor of the Research Station (see picture) in the so-called "Sphinx", approx. 120 m higher than the railway station. The air inlet system is mounted on top of the flat roof of the building.

Figure 3: Picture of the research station at the Jungfraujoch:

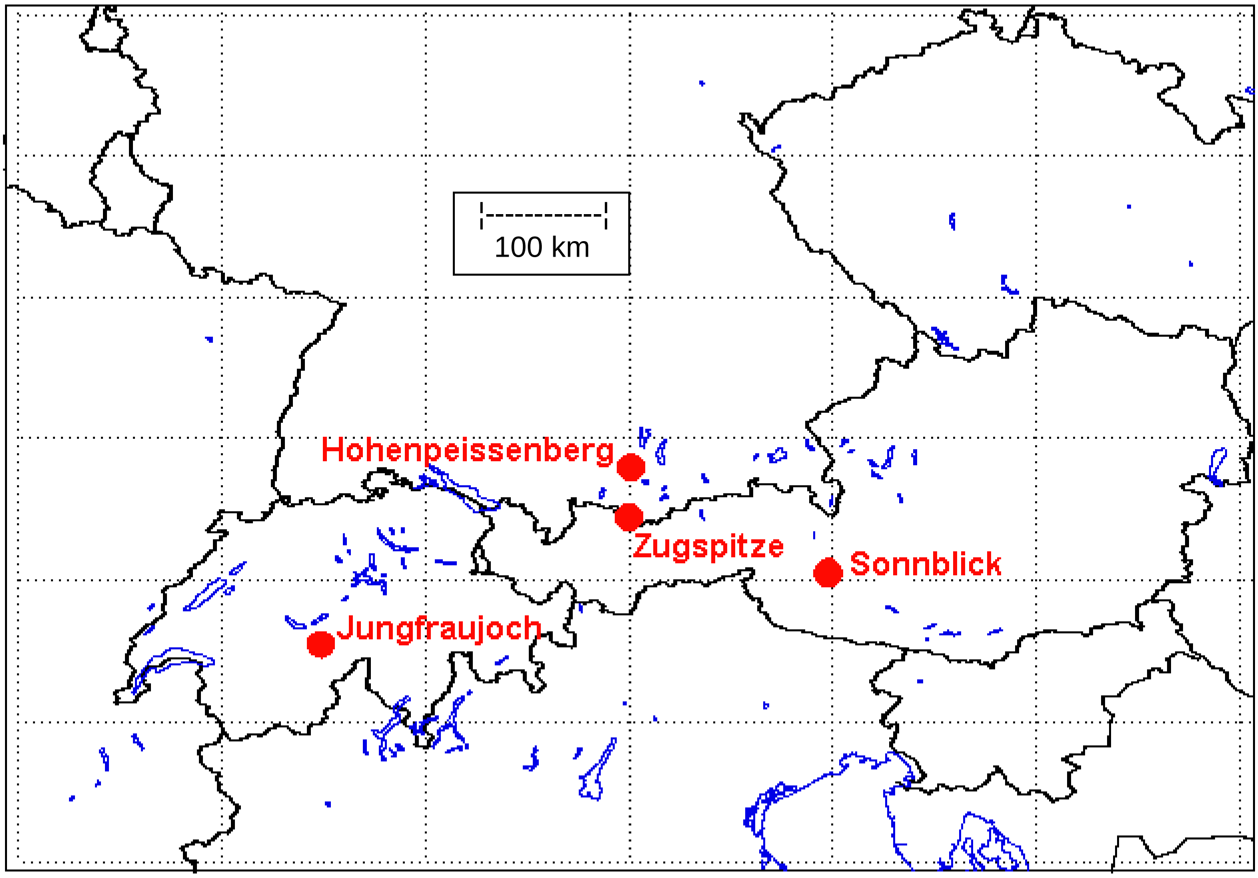

Figure 4: Map of Central Europe with all the GAW-DACH sites:

3.2. Operators

The section Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) runs the Swiss Air Pollution Monitoring Network (NABEL). The network is operated on behalf of the Federal Office of Environment, Forests and Landscape (BUWAL). The group of Dr Buchmann is responsible for the operation of the NABEL to which the audited parameters of the regional GAW station Jungfraujoch belong. The structure of the management is shown in Table 1.

During the entire audit procedure Mr R. Rüttimann was present.

Table 1: Operators

Dr P. Hofer, Head of the Section Air Pollution / Environmental Technology at EMPA
Dr B. Buchmann, Manager of the Swiss Air Pollution Network (NABEL)
Operator Mr R. Rüttimann, Station operator, data correction

3.3. Ozone Level

The site characteristics and the relevant surface ozone concentration range can be well defined by the frequency distribution. In figure 5 the frequency distribution of the half-hourly mean values from the year 1997 is shown. The relevant ozone concentrations were calculated, ranging between 36 and 67 ppb according the 5 and 95 percentile values. The annual data capture of ozone was about 98 %.
Source of data: NABEL database

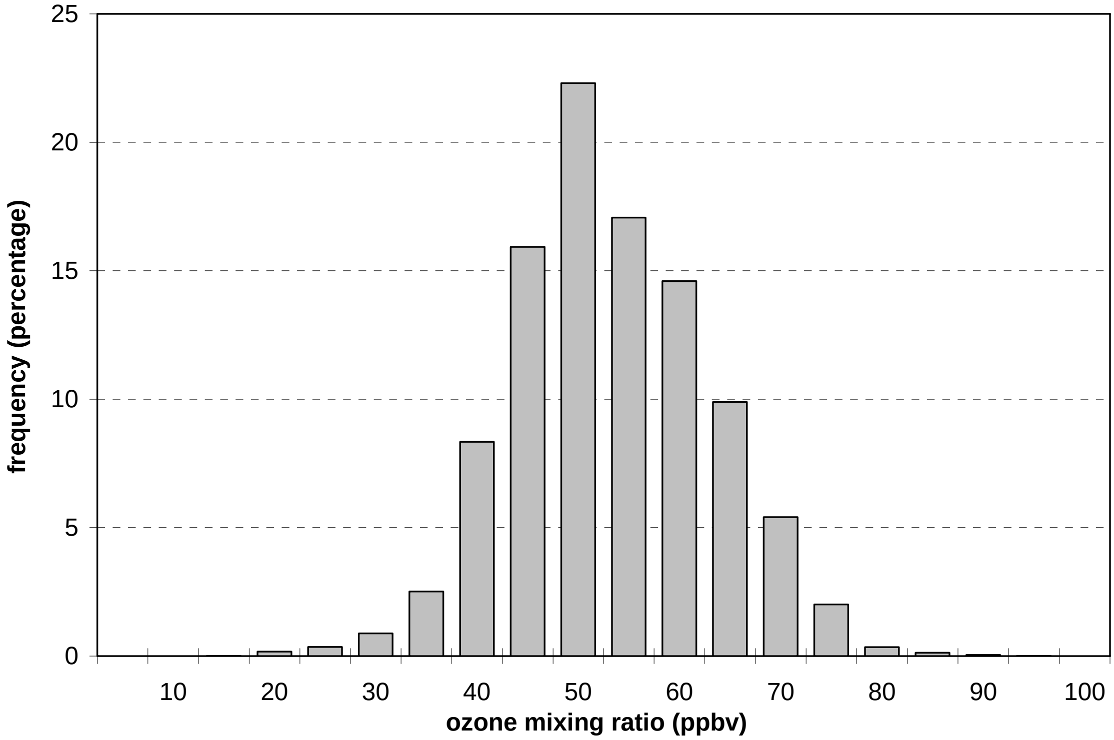

Figure 5: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at the Jungfraujoch of the year 1997. Data capture is about 98 per cent.

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 1997 is shown. The relevant carbon monoxide concentrations were calculated, ranging between 99 and 193 ppb according the 5 and 95 percentile values. The annual data capture of carbon monoxide was about 89 %.

Source of data: CO database at EMPA

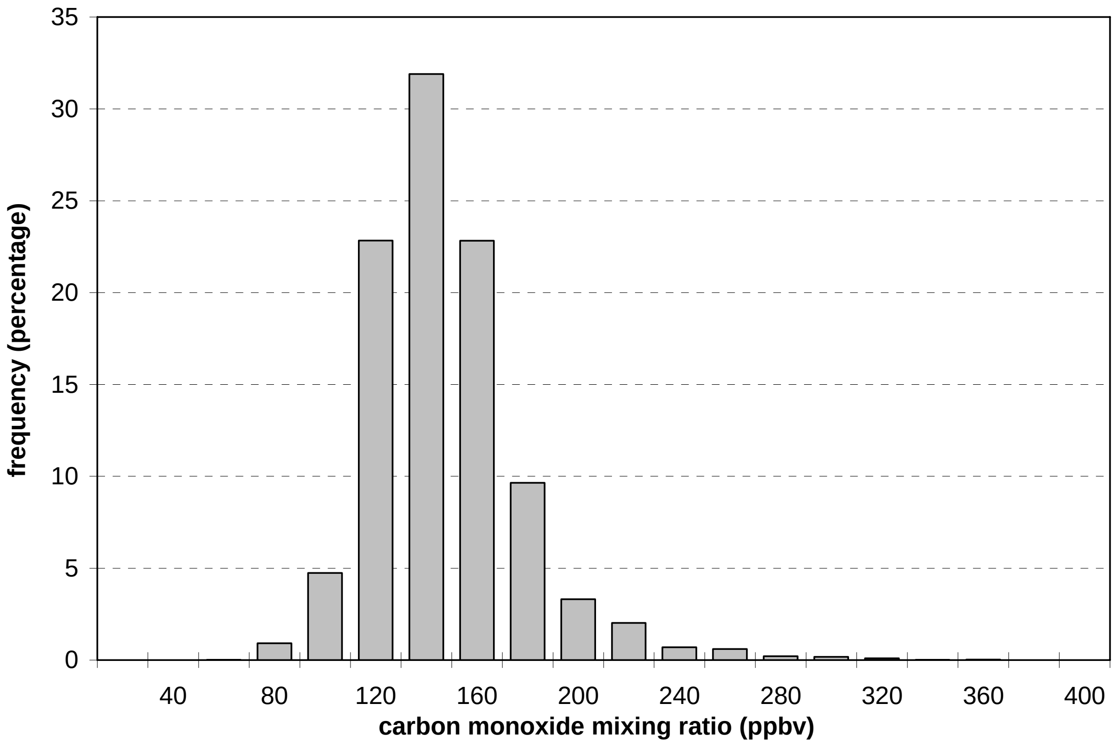

Figure 6: Frequency distribution of the hourly mean values of the carbon monoxide mixing ratio (ppb) at the Jungfraujoch of the year 1997. Data capture is around 89 per cent.

4. Measurement Technique

4.1. Air Inlet System

The air inlet system is located on top of the flat roof of the research platform "Sphinx" and goes directly into the building. It consists of a heated, stainless steal inlet tube, which is protected from rain and snow. The sound (8 cm ID, 3.5 m long) is flushed with 50 m3 / h. While the main stream goes to a high volume sampler a 10 m3 / h flow branches off through a teflon manifold (2.2 cm ID, 10 m long) leading downstairs where the analysers are located. On its way down the manifold bends several times following the ceiling and the stair. The bends are made of right-angled glass pieces and the teflon tube are slid over the glass connectors a few centimetres.
From the manifold, tubings (4mm ID, 1.5 to 2 m long) go to the inlet filters and to the instruments.
The total residence time of the ambient air in the inlet line lies around 4 seconds for both the CO and the ozone measurements.
The indoor concentration for CO can be a few times higher than ambient air.

Comment

All teflon tubes and glass manifolds were clean and free of dust and adequate for trace gas measurements in particular with regard to minimal loss of ozone. Nevertheless, it is recommended to rethink the manifold configuration with its many teflon to glass connections, as a preventive action, in order to avoid possible leakage problems in the future. Although tight at the moment, a small leak would be very difficult to notice but still can have a significant effect on the results.

4.2. Instrumentation

This autumn, a system to regulate the temperature in the instruments room had been installed. To date, indoor temperatur is around 20 to 25°C. In the past years in summer temperatures up to 35°C could be reached. However, this problem is expected to be solved.

The zero air supply unit consists of an air compressor and a Pd-Catalyst (CO/CO_2 converter) followed by a purafil ® and a charcoal cartridge. For the CO measurements the zero air tubing tees off just before the charcoal cartridge and instead flows through a molecular sieve and a sofnocat ® cartridge.

Instrumental details for the ozone and carbon monoxide analyser on site are listed in table 2 and 3, respectively.

4.2.1. Ozone Analysers

Table 2: Field instruments, ozone

type	TEI 49C #58106-318	Environics S300 #1093
method	UV absorption	UV absorption
usage	basic instrument	"backup" instrument (CRANOX)
at Jungfraufoch	since June, 1997	since February, 1991
range	0-250 ppb	0-1000 ppb

analog output	0-1 V	0-1 V

The "backup" instrument is part of a CRANOX ® system operated at the Jungfraujoch but is not regarded as a parallel ozone analyser. It is not directly calibrated with a transfer standard but the measurements are adjusted with coefficients to the basic instrument. The data is usually not used as ambient air data although the data quality is sufficient. Therefore only the basic analyser was part of the ozone performance audit.

Comment

The operation of an ozone analyser and a backup instrument (both UV method), considerably increases confidence in data quality concerning parallel measurements as well as data availability.

4.2.2. Carbon Monoxide Analyser

Table 3: Field instrument, carbon monoxide

type	Horiba APMA-360 #8512640106
method	NDIR
usage	basic instrument
at Jungfraujoch	since December 1997
range	0-10'000 ppb
analog output	0-1 V

A continuously monitoring analyser (NDIR) is in operation at the site.

Not like most other type of monitoring analyser with NDIR detection, the Horiba analyser does not show continuous drift for the zero point potentiometer. Thus a frequent (every few minutes) "zero defining" of the system is not necessary in that case. Thus, ambient air is measured continuously.

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

Comment

The CO NDIR analyser in use is a very stable instrument and adequate to the pollution level of the site of Jungfraujoch.

4.3. Operation and Maintenance

Daily, the person performing the synoptical observervations inspects the measurements for a quick check of general operation of the analysers. They also exchange the teflon filters at the ozone instrument inlet every two weeks and make some additional works. The major maintenance is carried out by the station operator (EMPA) during a station visit and is listed in table 4.

Ozone calibration: Every three month the ozone analyser is calibrated on site with a TEI 49-PS reference instrument (traceable to NIST SRP#15). The procedure follows a multipoint calibration at approximately 20, 40, 60, 90, 120 ppb ozone and a zero point check. The analyser is corrected accordingly if the offset varies >0.5 ppb and/or the slop deviates >0.5 %. The last calibration was performed on 10. November '98.

CO calibration: A working gas-standard (cylinder B0274) from Messer-Griesheim that is containing 1.10 ppm CO is utilised for manual calibration purposes every three weeks. The working standard is traceable to a 10 ppm NIST standard and also to the CMDL laboratory standards of the WCC at EMPA. The span value is corrected only when the average of the last two span checks deviates by more than 1 % from the given value. For the zero point determination the analyser is flushed with zero air for 50 minutes while the last 30 minutes are averaged. Every month the mean trend value is calculated and taken into account.

Table 4: Maintenance schedule

Maintenance on the analysers	interval ozone	interval CO
Filter exchange	2 weeks	3 weeks
Check of: T, flows, lamp V	3 weeks	3 weeks
Check of: p-sensor	3 month	-
Cell cleaning	6 month	annually
General service (manufacturer)	-	annually
Automatic span check	Daily, 70 ppb (not used for recalc.)	-
Automatic zero check	Daily (not used for recalc.)	6 days (used for recalculation)

Maintenance on the zero air	interval ozone	interval CO
Adsorbents exchange	annually	Not yet determined

Comment

The appearance inside the station is clean and functional. The room is well equipped with electronic devices for instrumental control and data acquisition.

The maintenance of the site is clearly structured and organised. The regular calibrations for both the ozone and CO measurements are regarded as very important means of quality assurance.

4.4. Data Handling

The data acquisition facility (software and hardware) from the German company Breitfuss is installed at the site next to the ambient air analysers. It consists of several ADC circuit boards for analog signals and interfaces for serial data of the analysers and uses Breitfuss ANAVIS and ANACOMP software. The one- and 10-minute mean values are stored on the station PC. The one minute values are kept at the site for three month before entitled while the 10-minute means are automatically transferred to EMPA via modem every six hours.

The operator responsible for the station maintenance is also in charge of data reviewing and data management at the institute. Data processing consists, in a first step, of daily or second daily visual inspection of the raw data. To get the final results, the raw data are recalculated by applying the appropriate values for zero and span (each analyser). This parameters are evaluated from the calibrations (see 4.3. Operation and Maintenance). Invalid values (according logbook), i.e. data from manual calibrations or automatic zero/span checks are flagged as maintenance data and removed from the database. Analytically invalid data (local influences, e.g. construction) has to be manually removed from the database. Every month the data are reprocessed and recalculated. The final data set for the ozone includes a 10' raw data set; and a 30' validated data set within the network database. The 10' raw data of the CO parameter is up to date extracted from the network database and reprocessed on MS-EXCEL resulting in a 10' validated data set.

Comment

The procedure of data treatment is well organised and clearly arranged. The first reviewing of the data is done on a regular, mostly daily interval, so that irregularities can be detected early. The review of the final data set is well done and transparent to the outside, which increases the reliability of the data.

4.5. Documentation

Within the GAW guidelines for documentation the transparency and the access to the station documents are required. During the audit the documentation was reviewed for availability and usefulness.

At the Jungfraujoch, each analyser has its separate instrument logbook containing all necessary information about major maintenance or exchange. During the three-weekly maintenance procedure a very detailed checklist is filled in and kept in a file. In such a checklist, which is in fact a combination of station- and maintenance logbook, a lot of instrument parameters, a brief description of the works carried out, and special events are documented. The logbooks were easy accessible at the site and contained all necessary information about maintenance, changes, events and special investigations. Data omissions or circuit breaks are noted in a separate list kept at EMPA. Most of the instrument manuals were available at the site, the rest was at EMPA. A station specific system operating procedure (SOP) for maintenance was not available.

Comment

The documentation of the ozone and CO measurement meets the requirements of the guidelines for GAW stations. It can be taken as a good example for complete and clearly arranged documentation. However, a practice orientated SOP for maintenance and operation should be implemented as a preventive action to avoid loss of accumulated knowledge.

5. Intercomparison of Ozone Instrument

5.1. Experimental Procedure

At the site, the WCC transfer standard (detailed description see Appendix Ozone I) was hooked up to power for warming up over night (deviation to the GAW report No. 97 in which only one hour of warm-up time is required). In the morning, before the intercomparison was 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 the 12. January, three comparison runs between the field instrument and the WCC transfer standard were performed. In the meantime the inlet system and the instrument maintenance were inspected and discussed. Table 5 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.

Finally, the observed results were discussed in an informal review with the person 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 WCC calibration laboratory at EMPA. The results are shown in the Appendix Ozone II.

Table 5: Experimental details, ozone

auditor, WCC	A. Herzog
reference:	WCC: TEI 49C-PS #54509-300 transfer standard
field instrument:	TEI 49C #-318
ozone source:	WCC: TEI 49C-PS, internal generator
zero air supply:	WCC: silicagel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition system:	WCC: 16 channel ADC circuit board, software
surrounding conditions:	p: 638.4 hPa ± 2 hPa and T_{indoor}: approx. 23°C
pressure transducers reading:	TEI 49C-PS: 638.9 hPa TEI 49C #318: 639.3 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 on January 12
connection between instruments:	approx. 1.2 meter of 1/4" PFA tubing

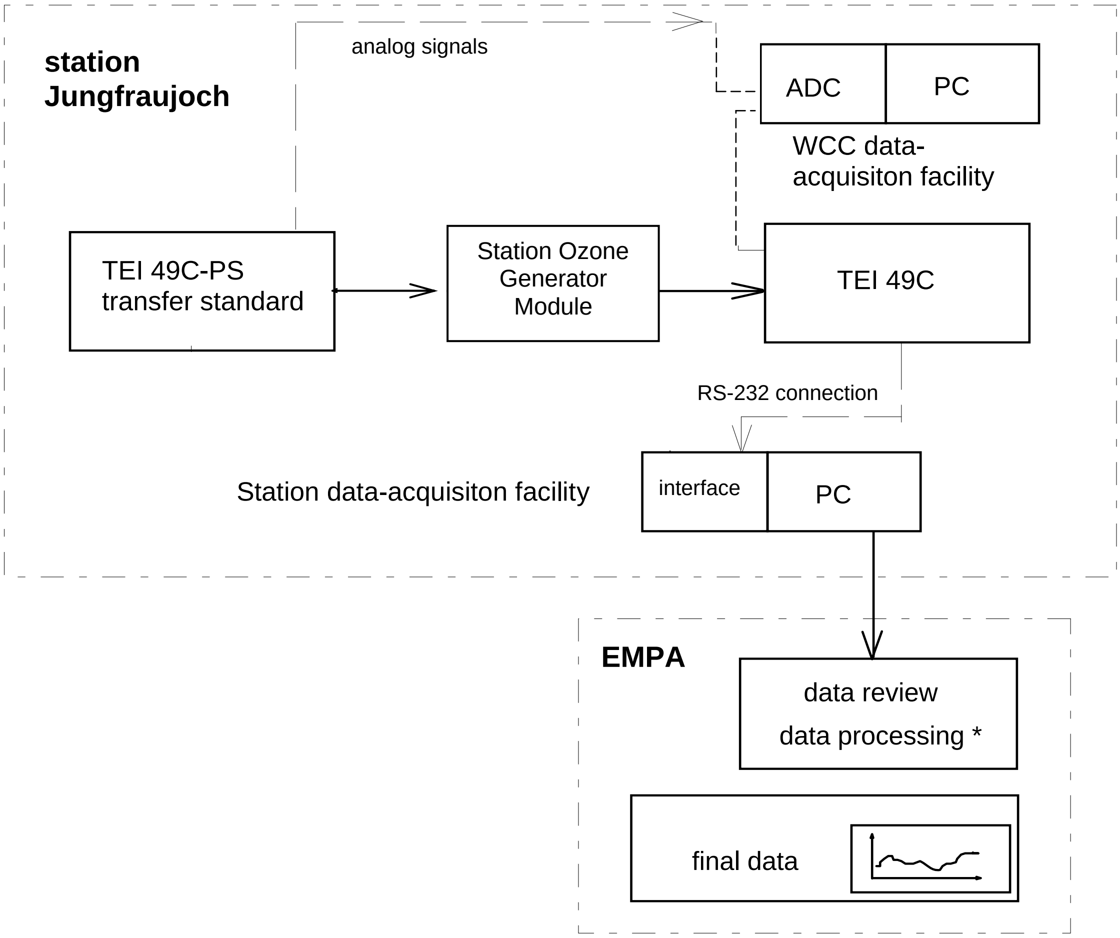

Figure 7: Experimental set up, ozone

The WCC 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 all the instruments involved the data was collected by the data acquisition system of the WCC. In advance, it was checked that the readings of the two acquisition systems were equal at zero (ozone) and at 200 ppb ozone. For data interpretation the WCC data is used.

5.2. Results

The results comprise three intercomparisons between the field instrument TEI 49C and the WCC transfer standard TEI 49C-PS, carried out on 12. January, 1999.

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 show the results of the linear regression analysis of the field instrument compared to the WCC transfer standard.

Table 6: 1. Intercomparison

No.	transfer standard TEI 49C-PS conc.	S_d	TEI 49C #-318 conc.	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	1.0	0.19	1.0	0.14	0.0	
2	34.5	0.14	34.6	0.14	0.1	0.4%
3	74.6	0.26	74.9	0.45	0.3	0.4%
4	14.7	0.19	14.7	0.26	0.0	-0.1%
5	54.6	0.15	54.8	0.16	0.2	0.3%
6	89.7	0.27	89.9	0.17	0.2	0.3%
7	0.9	0.14	1.0	0.18	0.1	

Table 7: 2. Intercomparison

No.	transfer standard TEI 49C-PS conc.	S_d	TEI 49C #-318 conc.	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.9	0.14	1.0	0.18	0.1	
2	14.7	0.14	14.8	0.24	0.2	1.0%
3	54.6	0.16	55.0	0.25	0.3	0.6%
4	34.7	0.10	34.6	0.14	0.0	-0.1%
5	89.6	0.14	90.0	0.21	0.4	0.4%
6	74.7	0.14	74.9	0.23	0.2	0.3%
7	0.9	0.17	1.1	0.16	0.2	

Table 8: 3. Intercomparison

No.	transfer standard TEI 49C-PS conc.	S_d	TEI 49C #-318 conc.	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.9	0.17	1.1	0.16	0.2	
2	74.7	0.13	75.2	0.29	0.5	0.7%
3	34.7	0.14	34.9	0.21	0.2	0.5%
4	14.8	0.12	15.0	0.12	0.2	1.4%
5	89.7	0.16	90.3	0.28	0.6	0.7%
6	54.8	0.16	55.2	0.23	0.4	0.7%
7	0.9	0.13	0.9	0.14	-0.1	

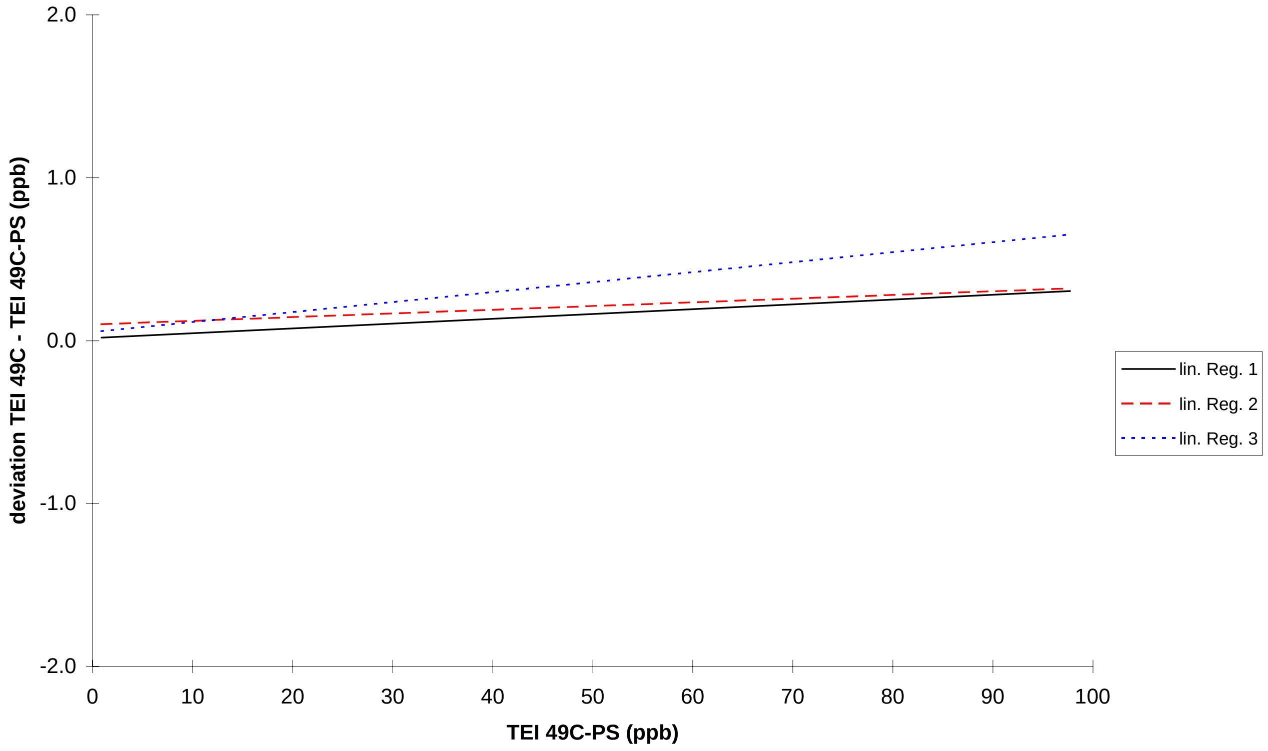

Figure 8: Individual linear regressions of intercomparisons 1 to 3, TEI 49C

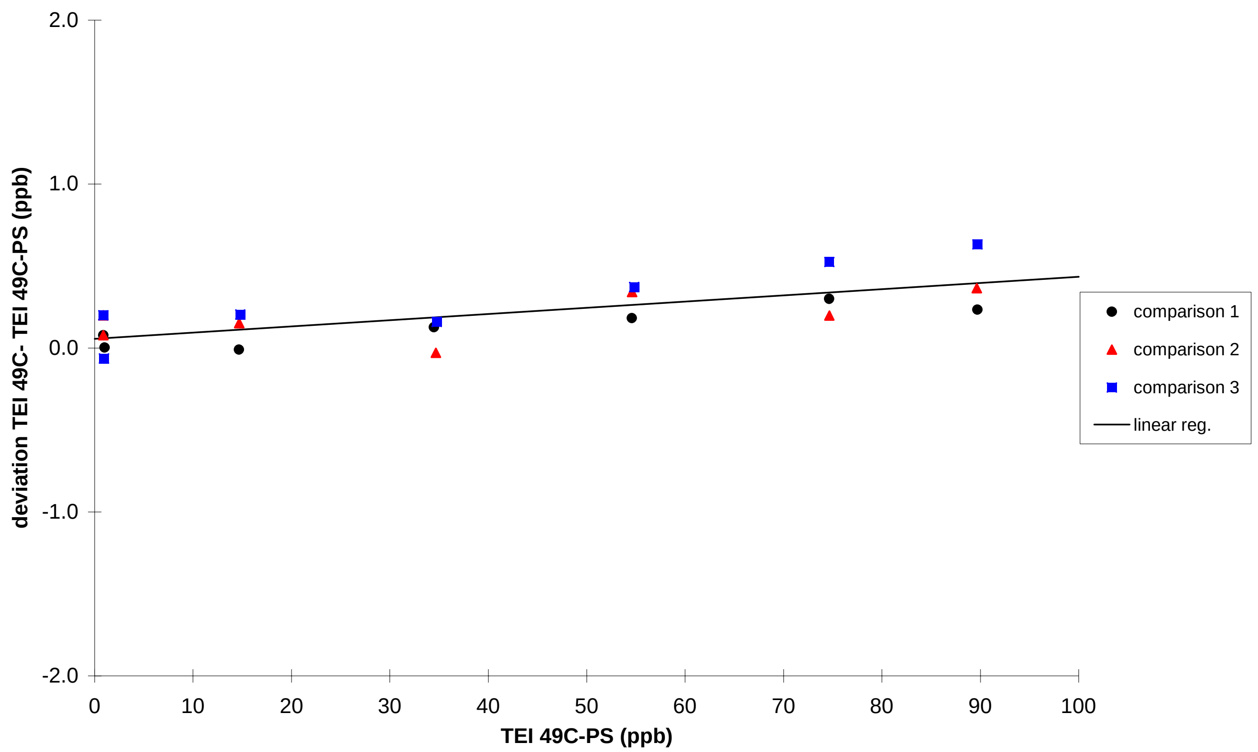

Figure 9: Mean linear regression of intercomparisons 1 to 3, TEI 49C

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

TEI 49C = 1.004 x TEI 49C-PS + 0.1 ppb

TEI 49C = O_3 mixing ratio in ppb, determined for TEI 49C #58106-318
TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0008	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.04	(f = 3)
	- residuals in ppb	0.08	(f = 19)

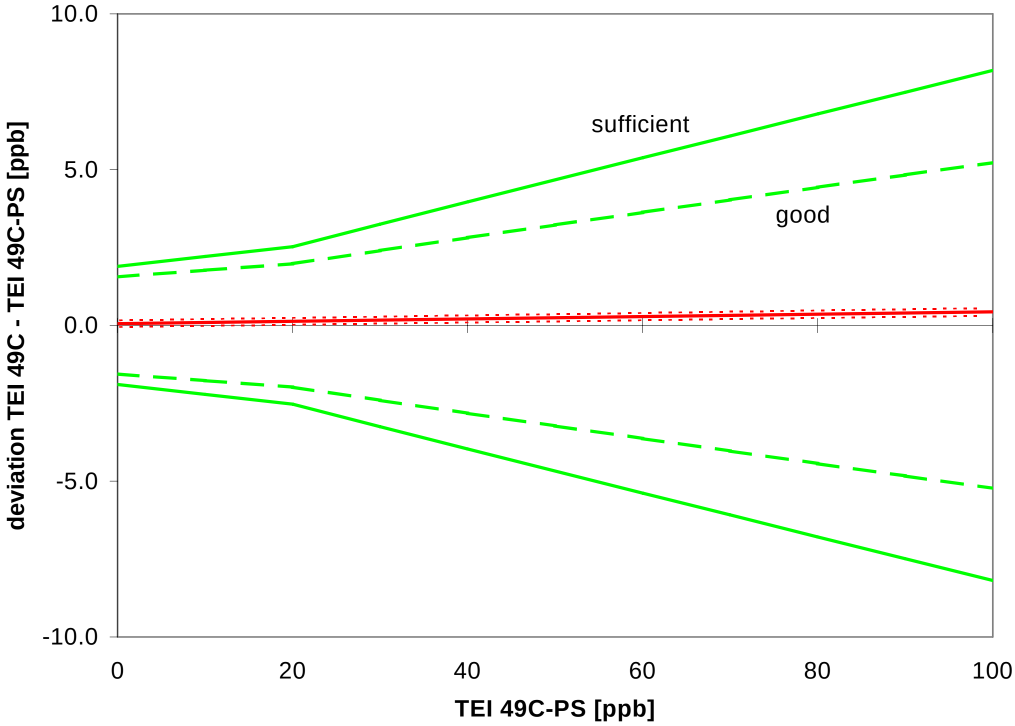

Figure 10: Intercomparison of instrument TEI 49C

Comment

In the linear regressions of the instrument (figures 8), no trend as a function of time could be observed during the intercomparison.

The ozone concentrations observed at the Jungfraujoch (1997) usually ranged between 36 and 67 ppb (5- and 95-percentile of hourly mean values).

The instrument clearly fulfils the assessment criteria as "good" over the tested and relevant 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 good condition.

6. Intercomparison of CO Instrument

6.1. Experimental Procedure

No Standard Operation Procedure (SOP) has 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 accordingly.

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 gas (NMI reference gas) was 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 20 minutes. On January 12 the intercomparison was made with the field instrument Horiba AMPA-360. Different concentration levels between 80 and 350 ppb were applied (figure 11). Table 9 shows the experimental details and figure 12 the experimental set up of the CO performance audit. In general, no modification of the carbon monoxide analyser was made for the intercomparison. The signal of the field instrument was acquired by the WCC data acquisition system. During the audit WCC zero air (synthetic air + Sofnocat) was used. The station zero air was tested and there was no significant difference between the site zero air and the WCC zero air.

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

The audit procedure included a direct intercomparison of the MGM diluter transfer standard with the Califlow (Standard Reference) before and after the audit in the calibration laboratory at (see Appendix CO, MGM Diluter). The NMI-Reference Gas (Transfer Standard) is traceable to NIST and the CMDL Laboratory Standard Gases.

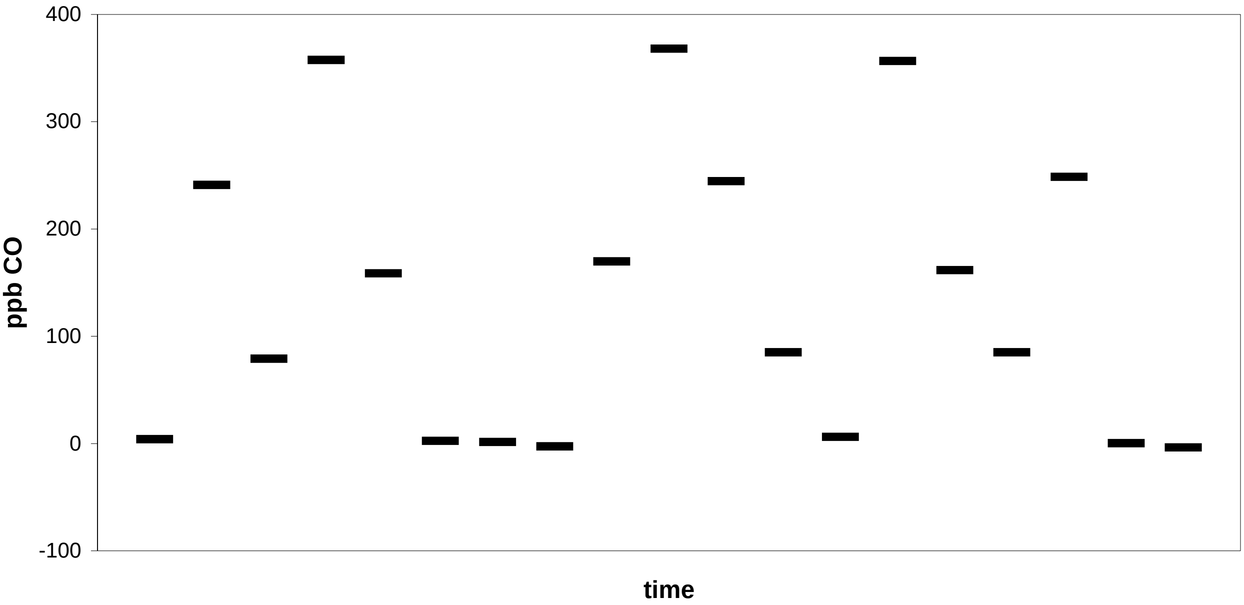

Figure 11: Sequence of concentrations during audit, CO

Table 9: Experimental details, carbon monoxide

auditor, WCC	A. Herzog
reference:	Transfer standards: MGM diluter, NMI Reference Gas
field instrument:	Horiba APMA-360 #8512640106
zero air supply:	WCC: synthetic air + Sofnocat station: ambient air (compressed) - Pd-catalyst – purafil – molecular sieve - Sofnocat
data acquisition system:	WCC: 16 channel ADC circuit board, software
surrounding conditions:	p: 640 hPa ± 2 hPa and T_{indoor}: approx. 23°C
instrument range:	0 – 10'000 ppb
number of concentrations:	4 + zero air of station and WCC
approx. concentration levels:	80 / 160 / 240 / 350 ppb
sequence of concentration:	see figure 14
averaging interval per concentration:	15 minutes
connection to instrument:	less than 3 meter of 1/4" PFA tubing

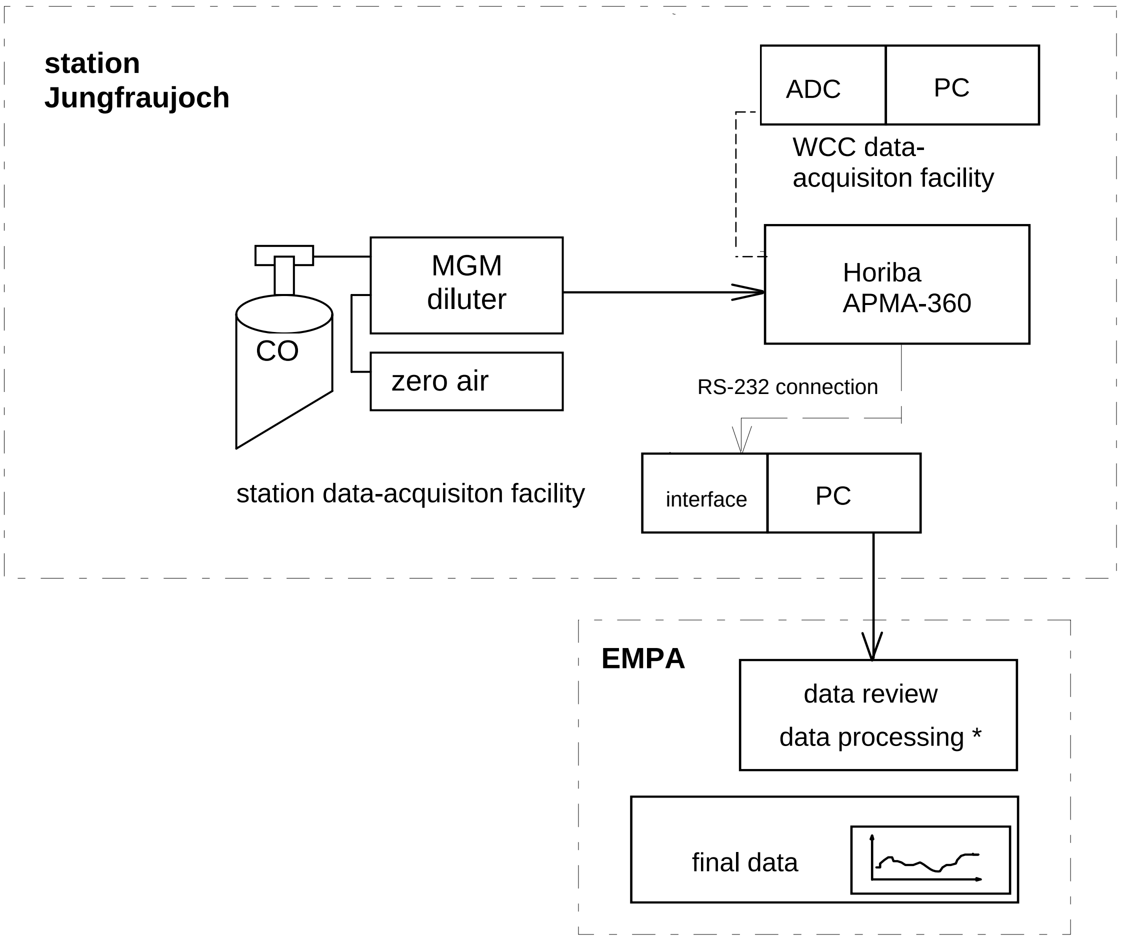

Figure 12: Experimental set up, carbon monoxide

6.2. Results

The results consist of 3 intercomparisons between the field instrument Horiba APMA-360 and the WCC transfer standard carried out on January 12, 1999.
In the following table the resulting mean values of each carbon monoxide concentration and the standard deviations of thirty 30 second-means (15 minutes) 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 the field instrument compared to the WCC transfer standard.

Table 10: Intercomparisons, CO

No.	**transfer standard**	**Horiba APMA-360**			
	MGM conc.	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	%
1	0	4	12	4	
2	242	241	13	-1	0
3	81	79	8	-2	-2
4	353	358	10	4	1
5	161	159	17	-2	-1
6	0	3	9	3	
7	161	170	10	9	5
8	353	368	18	15	4
9	242	245	14	2	1
10	81	85	14	4	5
11	0	6	15	6	
12	353	357	15	3	1
13	161	162	10	0	0
14	81	85	12	4	5
15	242	249	24	6	3
16	0	0	13	0	

The summary of the CO comparisons (for the CO range 0 - 350 ppb) of the Horiba CO analyser with the WCC transfer standards is the following linear regression line:

Horiba = 1.01 x TS - 2 ppb

Horiba = CO mixing ratio in ppb, determined for Horiba APMA-360 #8512640106
TS = CO mixing ratio in ppb, produced by the Transfer standards (MGM diluter + NMI Reference gas) and related to the Standard References at the EMPA-WCC (Califlow, CMDL + NIST gases).

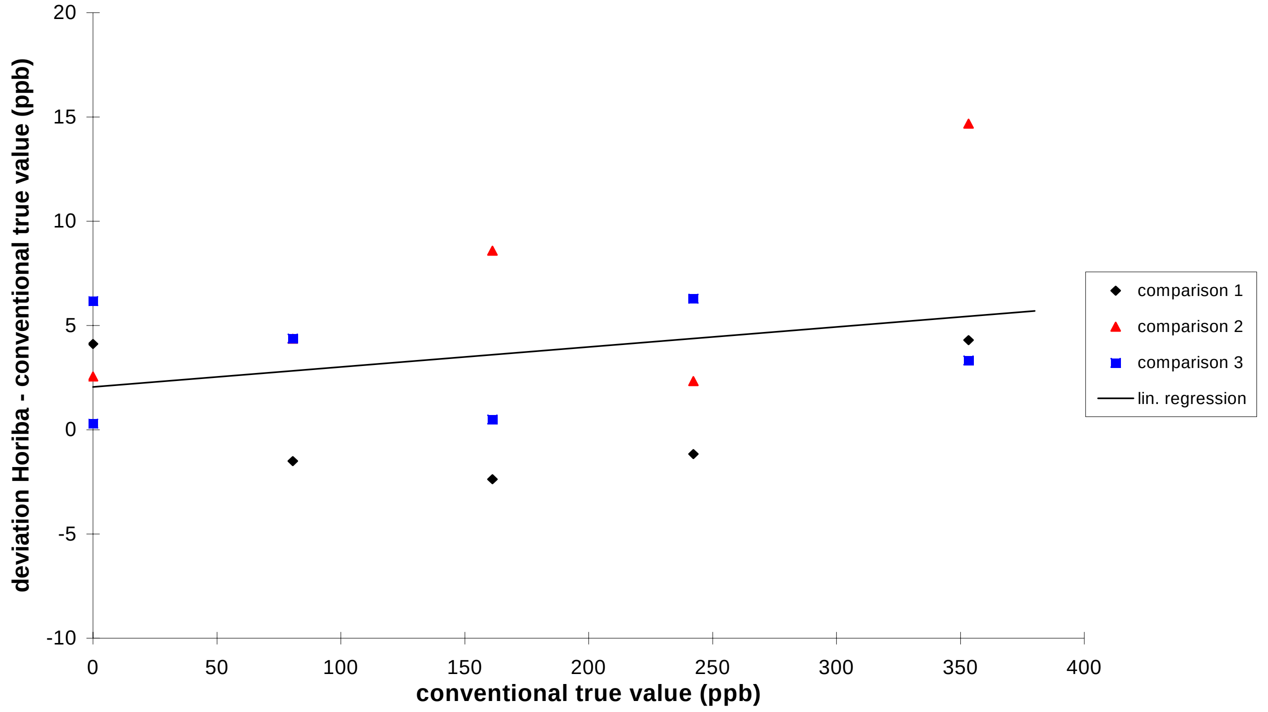

Figure 13: Absolute differences between the Horiba analyser and the transfer standard

Figure 14 shows the relative differences (%) between Horiba 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.

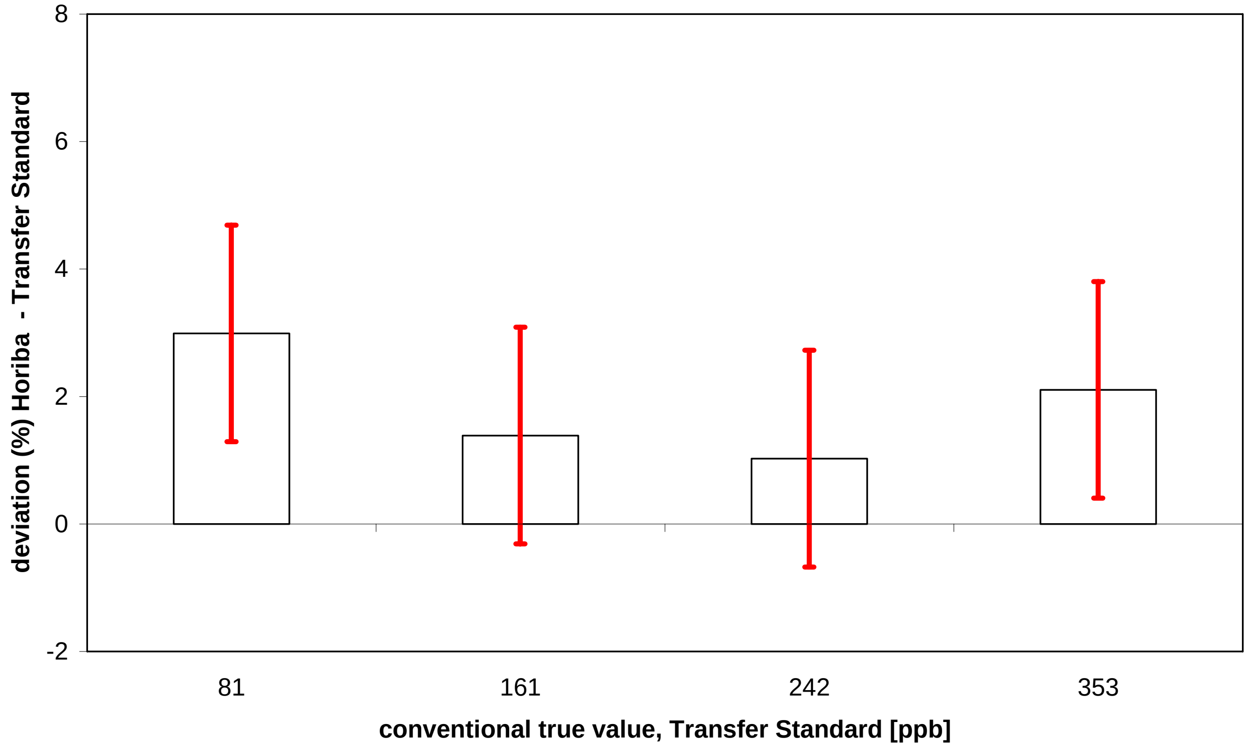

Figure 14: Differences (%) between the Horiba and the transfer standard (the red lines show the total uncertainty for the whole audit procedure)

Comment

The results of the CO intercomparison measurements (figure 14) deviate only by about 1 to 3% from the conventional true value with a measurement uncertainty of approximately 2%. Regarding the relevant range (99 and 193 ppb, 5- and 95-percentile respectivley) and the methode in operation this is a very good result.

Appendix Ozone

I. WCC 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 15. 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.

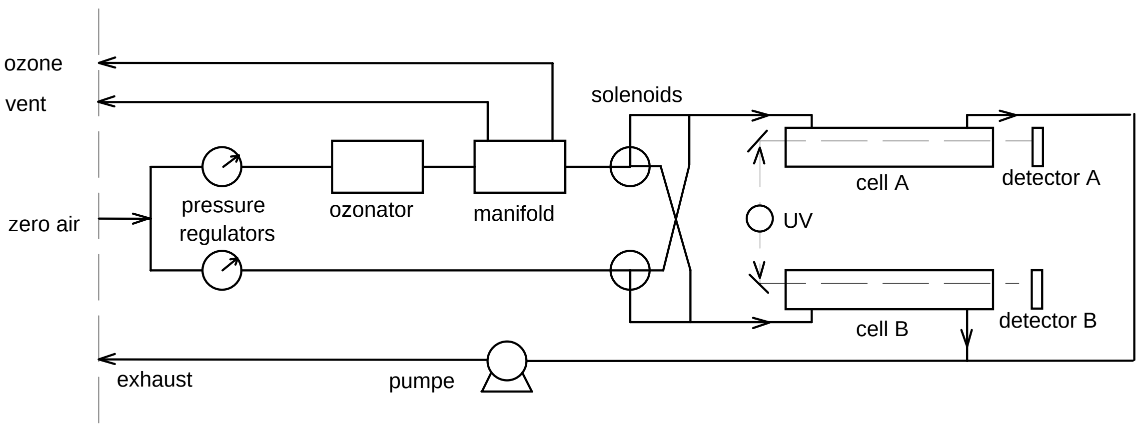

Figure 15: Flow schematic of TEI 49C-PS

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 the EMPA-WCC are summarised in Table 11 and Figure 16.

Table 11: Intercomparison procedure SRP - TEI 49C-PS

pressure transducer:	span check (calibrated barometer)
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

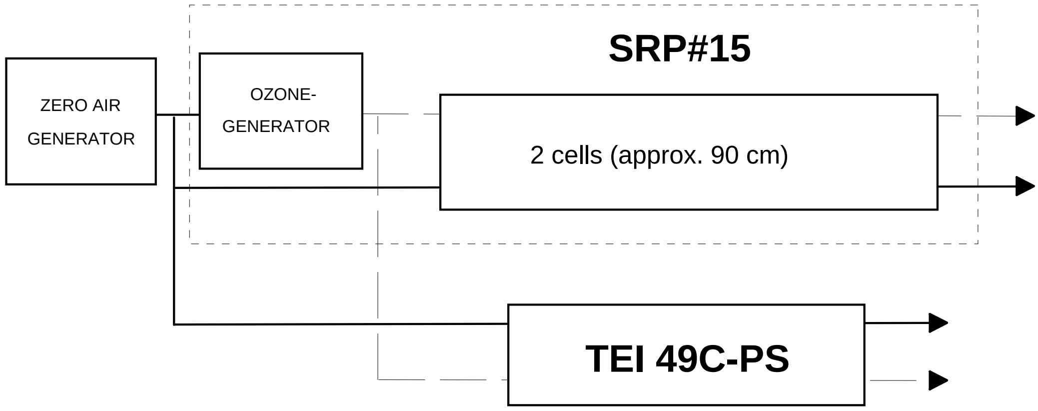

Figure 16: Instruments set up SRP -TEI 49C-PS

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 + 0.7%).

Figures 17 and 18 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.

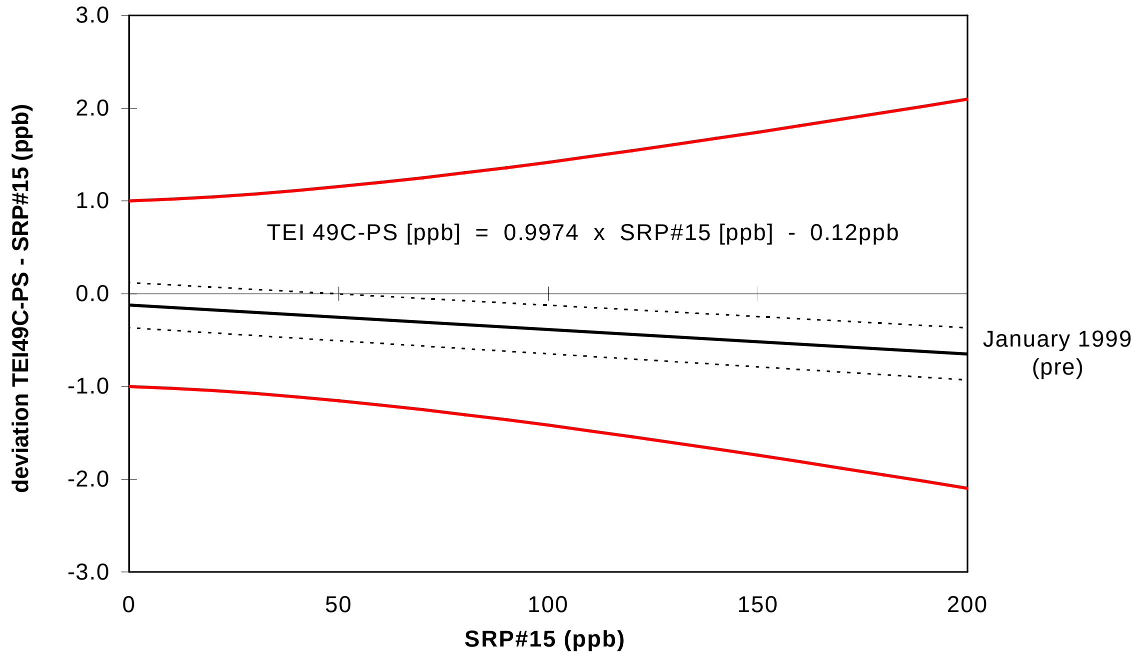

Figure 17: Transfer standard (O_3) before audit

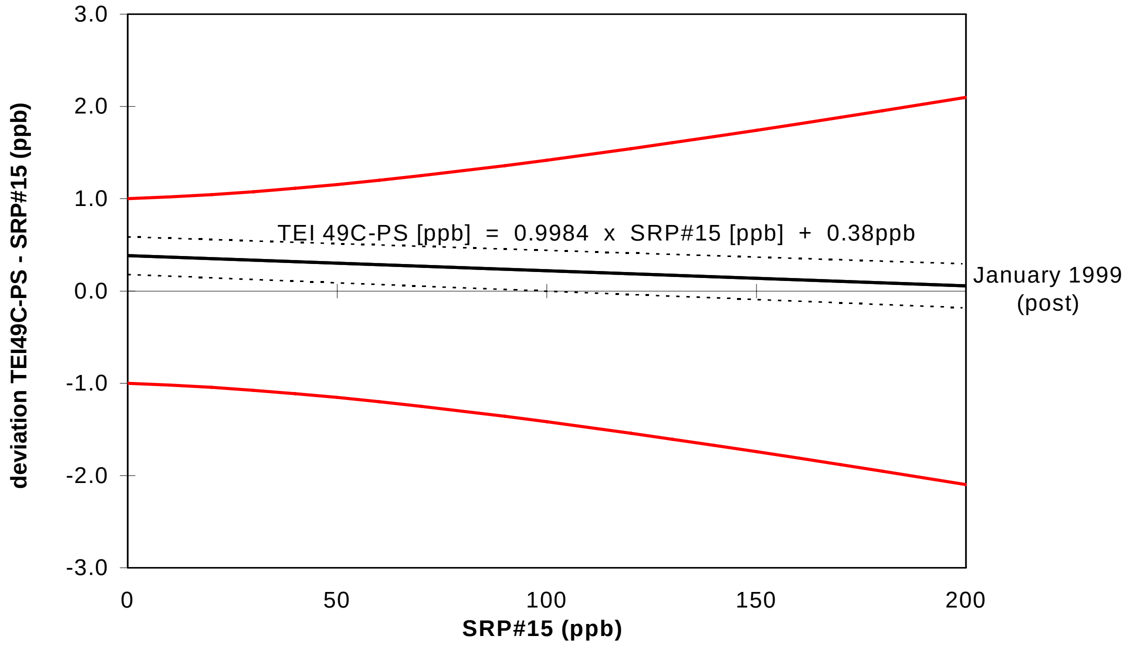

Figure 18: Transfer standard (O_3) after audit

Appendix Carbon Monoxide

I. Traceability Chain

No Standard Operation Procedure (SOP) has been established yet for CO measurements. In figure 19 the traceability chain for the carbon monoxide, used by the WCC-CO is shown.

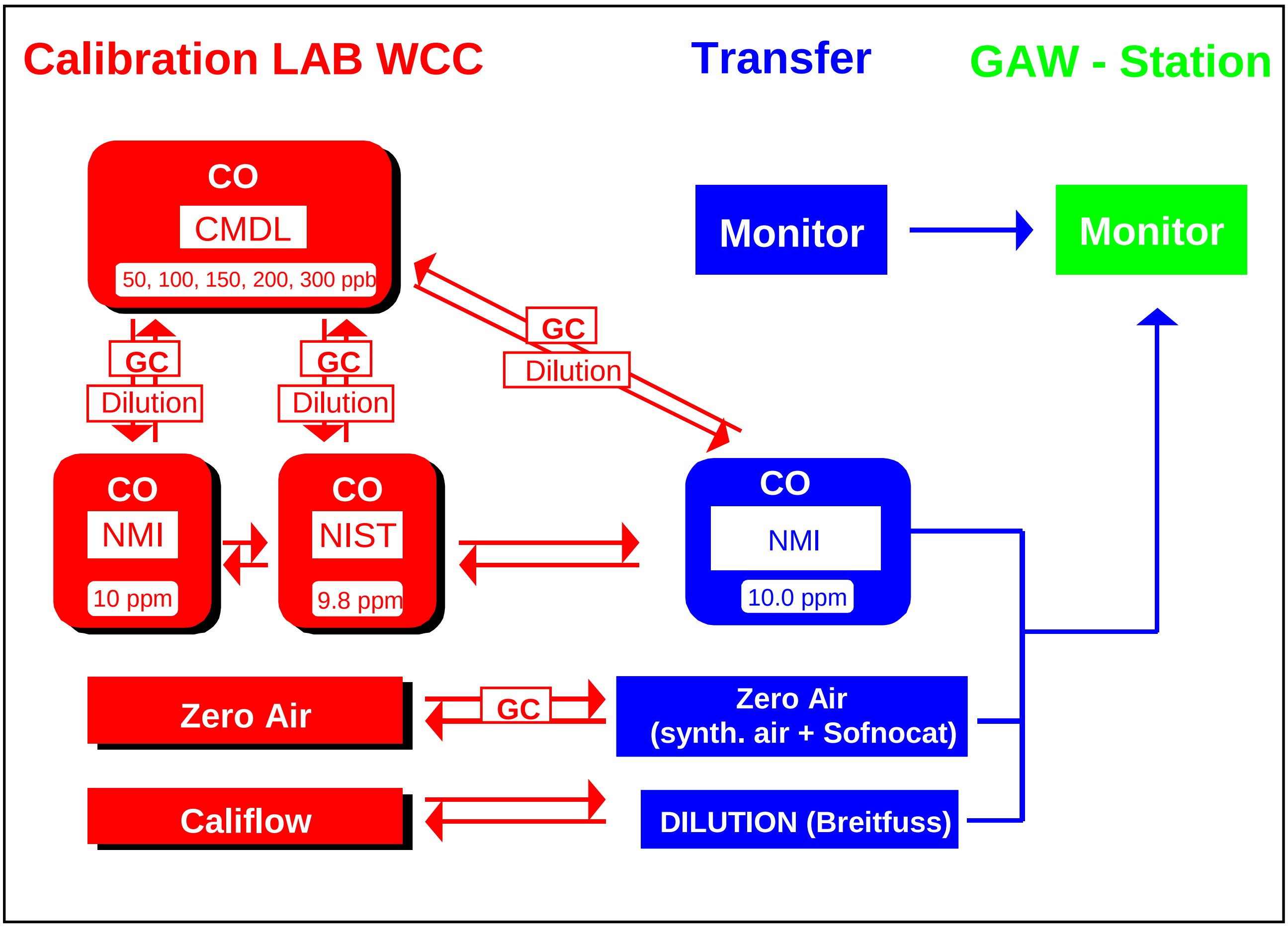

Figure 19: Traceability-Chain for the Carbon monoxide

II. WCC CO Standards

Laboratory 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 we use the following standards:

Table 12: CO-Standards at the WCC

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%.

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. WCC Transfer Standards

NMI-Calibration Gas (Nederlands Meetinstituut, Netherlands)

The CO mixing ratios in ppb for the intercomparison were produced by the Transfer standards, the MGM diluter and the NMI-Reference gas (10.01 ± 0.04 ppm). The NMI standard was related pure to the NIST standard (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 MGM diluter (S/N 2262/97/1) consists of two thermal mass flow controllers (BRONKHORST HI TEC, Serial number 9720369 and B), a mixing chamber and electronics to produce the different mixing ratios. To exclude errors which might occur through transportation of the diluter its Mass Flow Controllers (MFC) were compared to the Califlow (Primary Standard) before and after the field audit. The deviation of the MFCs were around 1% and taken into account for calculating the mixing ratio. The stability of the transfer standard is thoroughly examined with respect to the uncertainties of the different components (systematic error and precision).