



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



**Swiss Federal Laboratories for Materials Testing  
and Research (EMPA)**

## **EMPA-WCC REPORT 97/6**

**Submitted to the  
World Meteorological Organization**

# **SYSTEM AND PERFORMANCE AUDIT FOR SURFACE OZONE AND CARBON MONOXIDE GLOBAL GAW STATION ZUGSPITZE / HOHENPEISSENBERG PLATFORM HOHENPEISSENBERG GERMANY, NOVEMBER 1997**

**Submitted by**

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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 GAW platform Hohenpeissenberg, Germany. Below, the findings, comments and recommendations are summarised:

### **Air Inlet System:**

All teflon tubes and glass 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 Analysers:**

The operation of two ozone analysers at the MOHp (chemiluminescence and UV method), considerably increases confidence in data quality concerning parallel measurements as well as detection of potential interferences with other trace species. Still, the calibration of both instruments are traceable back to the UV-absorption method which is the preferred method in the GAW programme.

#### **Carbon Monoxide Analyser:**

The CO NDIR / GFC analyser in use is adequate to the pollution level of the site of Hohenpeissenberg.

### **Data Handling:**

The procedure of data treatment is well organised and clearly arranged with different people. 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.

### **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 structured and organised. It is further noted that the regularly and frequently performed calibrations for both the ozone and CO measurements are regarded as very important means of quality assurance.

### **Documentation:**

The documentation of the ozone measurement meets all the requirements of the guidelines for global GAW stations and can be taken as a good example of practice orientated implementation.

### **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 the adequate education, the staff was very familiar with the techniques and problems associated with ozone measurements.

### **Ozone Intercomparisons:**

The ozone concentrations observed at the MOHp (1996) usually ranged between 12 and 67 ppb (5- and 95-percentile of hourly mean values).

Both instruments clearly fulfil the assessment criteria as "good" over the tested range up to 100 ppb (figure 1 and 2). For each analyser, fairly small deviations among the three intercomparisons are the reason for narrow prediction intervals which implies that the instruments are in good condition.

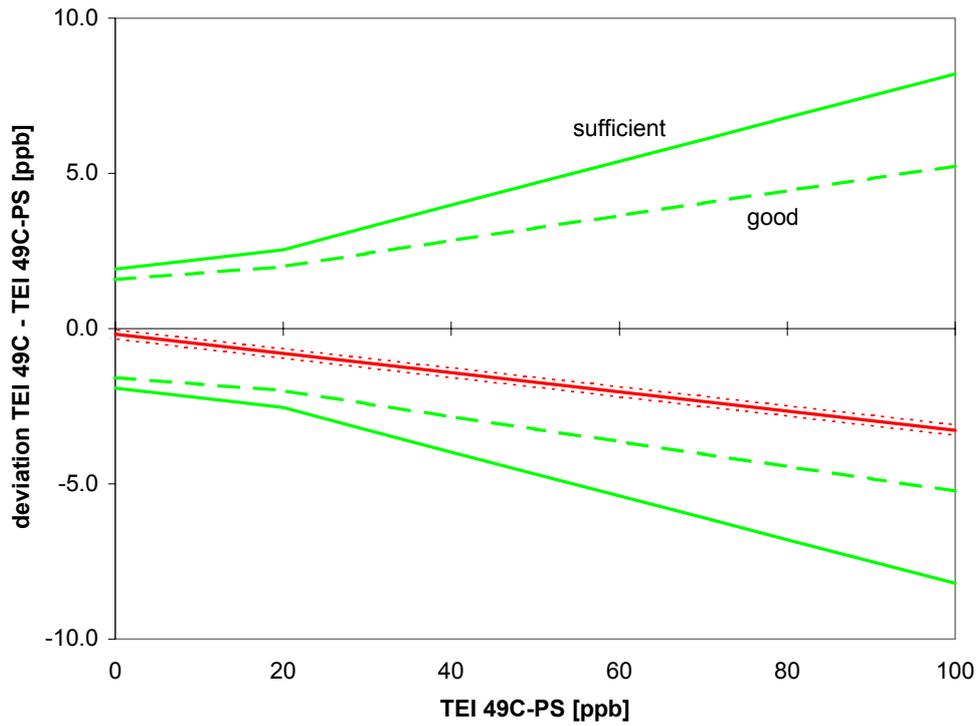


Figure 1: Intercomparison of instrument TEI 49C

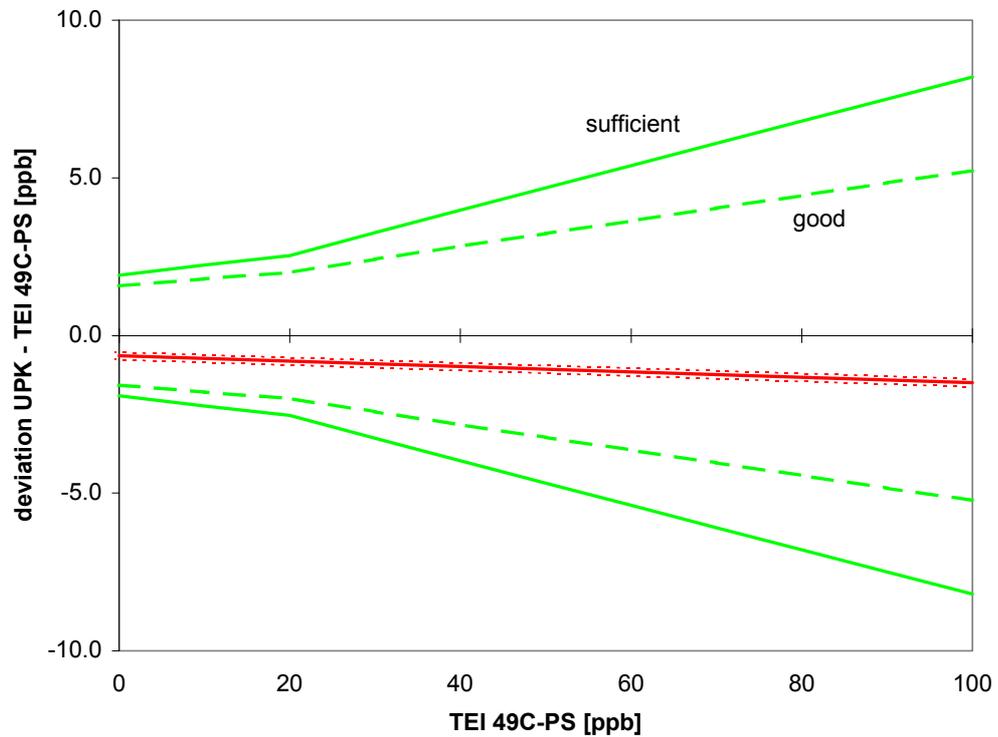


Figure 2: Intercomparison of instrument UPK 8002

**Carbon Monoxide Intercomparisons:**

The carbon monoxide concentrations observed at Hohenpeissenberg (1996) usually ranged between 99 and 339 ppb (5- and 95-percentile of hourly mean values).

The ambient air concentration measurements with the TEI 48S are well comparable to the results of the transfer standard instrument (Horiba). The results of the different concentrations during the audit demonstrate only small deviations from the transfer standard.

The good results of the different concentrations during the audit and the ambient air measurements, demonstrate that the calibration factors (dry/dry) are well applicable to the humid/humid (zero mode/ measurement mode) measurements of ambient air.

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Dübendorf, 9. June, 1998

EMPA Dübendorf, WCC

Project engineer

Project manager

A. Herzog

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## 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.

In agreement with the GAW-group of the DWD site Hohenpeissenberg (German Meteorological Service) who is in charge of O<sub>3</sub> and CO measurements a system and performance audit at the GAW platform Hohenpeissenberg, Germany, 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 which took place from November 14 to 19 in 1997, 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 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, 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 the DWD, the World Meteorological Organization in Geneva and the Quality Assurance and Scientific Activity Centre (QA / SAC) for Europe and Africa.

## 3. Global GAW Site Platform Hohenpeissenberg

### 3.1. Site Characteristics

Hohenpeissenberg, is an isolated mountain at 985 m above sea level (300 m above the surrounding area) in the German Pre-Alpin Region. It is located in south-east Germany, approximately 55 km south-west of Munich. A small road leads from the village Hohenpeissenberg directly to the summit of the Hohenpeissenberg.

The chemical monitoring station (co-ordinates: 47°48' N, 11°01' E; ) is placed in the fourth floor of the tower which is attached to the main building of the Meteorological Observatory of Hohenpeissenberg (see picture). The air inlet system is mounted on the outside wall (approx. 1 m apart) at the same level while the meteorological sensors (i.e. wind) are mounted on the flat roof of the building.



Figure 3: Picture of the station Hohenpeissenberg:

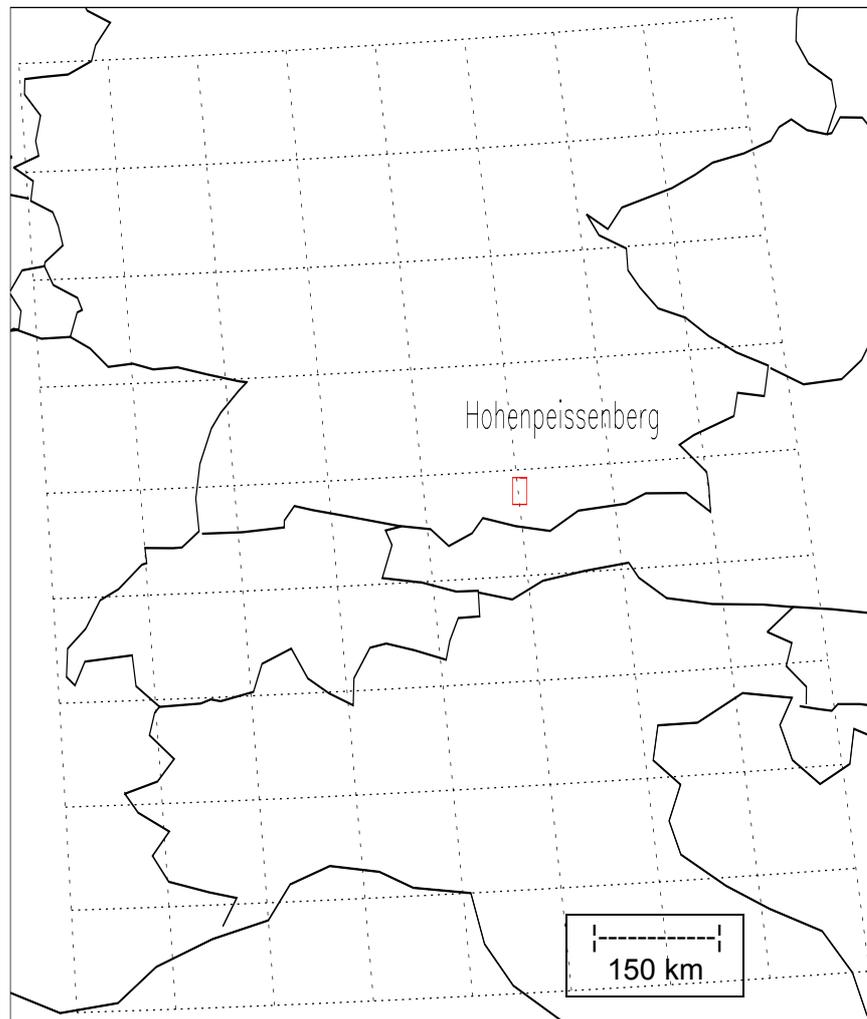


Figure 4: Map of Central Europe:

### 3.2. Operators

The Meteorological Observatory on the top of Hohenpeissenberg (MOHp) is one out of three observatories run by the German Meteorological Service (DWD). The personnel of MOHp consists of an interdisciplinary team of scientists and technicians. The group of Dr. Fricke is responsible for the operation of the GAW station. The structure of the station management is shown in Table 1.

During the entire audit procedure Mr. Gilge, Mr Schafranek and Mrs Plörer were mostly present.

Table 1: Operators

Dr. P. Winkler, Head of the Meteorological Observatory Hohenpeissenberg
Dr. W. Fricke, GAW Station Manager

### Operators for reactive gases

Dr. S. Gilge, Data correction and supervision

Mr B. Schafranek, Data management and station maintenance

Mrs E. Plörer, Station maintenance

## 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 hourly mean values from the year 1996 is shown. The relevant ozone concentrations were calculated, ranging between 12 and 67 ppb according to the 5 and 95 percentile values. The annual data capture of ozone was about 91.5 %.

Source of data: received from MOHp

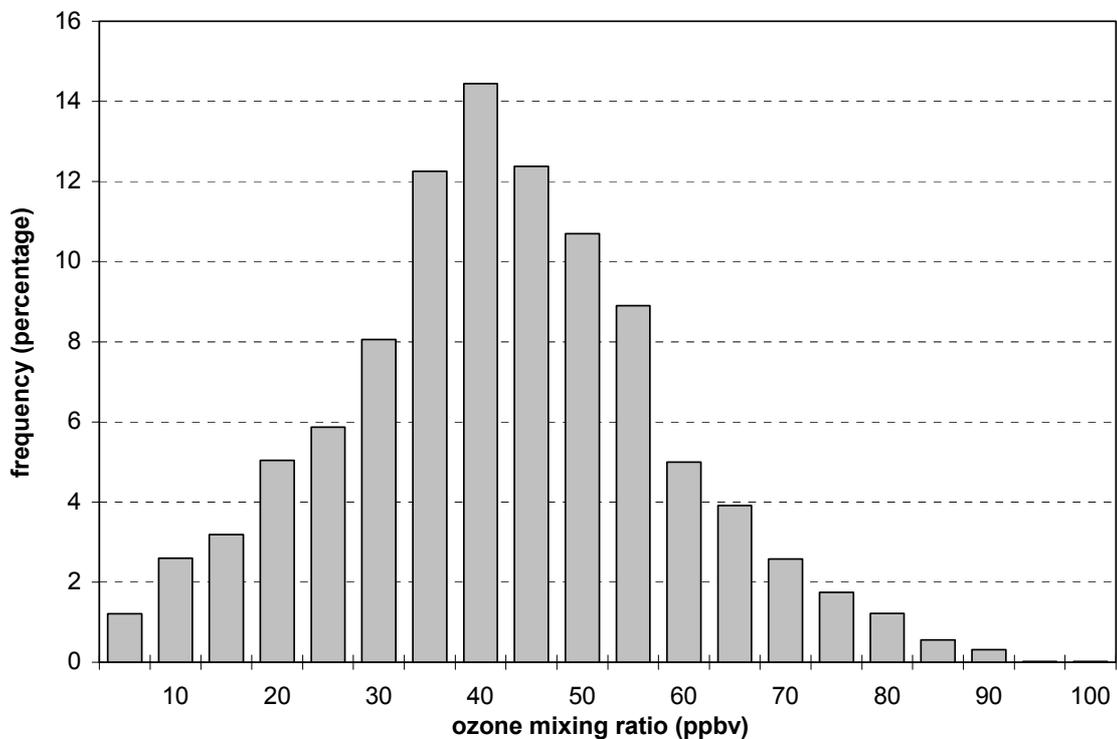


Figure 5: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at MOHp of the year 1996. Data capture is about 91.5 per cent.

### 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 99 and 339 ppb according to the 5 and 95 percentile values. The annual data capture of carbon monoxide was about 66 %.

Source of data: received from MOHp

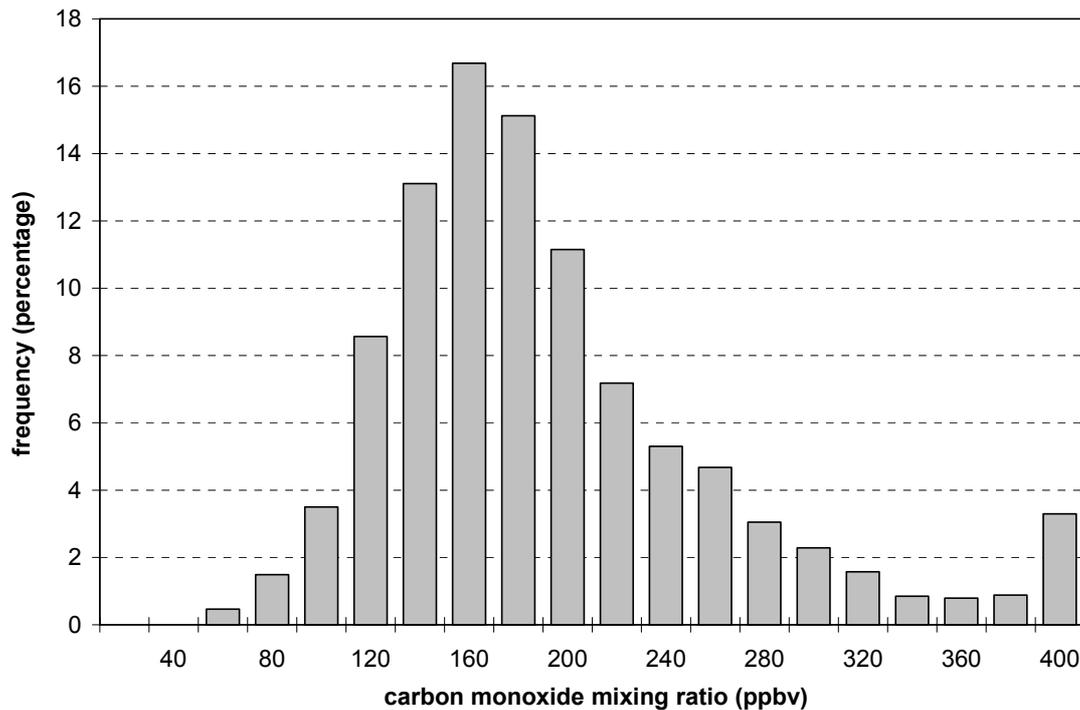


Figure 6: Frequency distribution of the hourly mean values of the carbon monoxide mixing ratio (ppb) at MOHp of the year 1996. Data capture is around 66 per cent.

## 4. Measurement Technique

### 4.1. Air Inlet System

The air inlet system is mounted approximately one meter outside the wall of the tower building at the same level as the ozone and CO analysers. It consists of a ½" teflon tube that is heated to 2 °C above ambient temperature. To protect it from rain and snow it is covered by a stainless steel tube. The 2.5 m long main teflon manifold (ID 0.9 cm) leads directly into the shelter and is flushed by about 5 l/min ambient air. For the ozone and CO measurements a 2 m, ¼", teflon tube branches off (flushed with the instruments pumps connected to this line) from where three 4mm ID, 0.5 m long PFA tubings go to the inlet filters and to the instruments. The total residence time of the ambient air in the inlet line lies around 3 seconds for both the CO and the ozone measurements.

The butanol of the nuclei counter in the same room is frozen out before vented to the outside.

#### Comment

All teflon tubes and glass 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.

### 4.2. Instrumentation

The instruments are installed in an environmentally controlled room at 25°C but can rise to 30°C in summer.

The zero air supply consists of a JunAir 600-25M (pressurised air and molecular sieve) with an additional silikagel and charcoal cartridge. At the output a 1µm particle filter is installed. For the CO measurements the zero air is also treated with a Pd-Catalyst (150C).

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

#### 4.2.1. Ozone Analysers

Table 2: Field instruments

type	TEI 49C #56028-306	UPK 8002 #92062
method	UV absorption	chemiluminescence
usage	basic instrument	backup instrument
at MOHp	since April, 1996	since May, 1992
range	0-200 ppb	0-100 ppb
analog output	0-10 V	0-1 V

#### Comment

The operation of two ozone analysers at the MOHp (chemiluminescence and UV method), considerably increases confidence in data quality concerning parallel measurements as well as detection of potential interferences with other trace species. Still, the calibration of both instruments is traceable back to the UV-absorption method which is the preferred method in the GAW programme.

#### 4.2.2. Carbon Monoxide Analysers

Table 3: Field instruments

type	TEI 48 S,#50873-286
method	NDIR / GFC
usage	basic instrument
at MOHp	since January 1995
range	0-2000 ppb
ambient air / zero interval	every 10 minutes
analog output	0-5 V

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

It is well known that this type of monitoring analyser with NDIR / GFC detection shows a continuous drift for the zero point potentiometer which makes a frequent "zero defining" of the system necessary. Thus, ambient air and zero is measured alternately in a ten minute interval.

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 / GFC analyser in use is adequate to the pollution level of the site of Hohenpeissenberg.

### 4.3. Data Handling

An MOHp developed data acquisition facility is installed at the site next to the ambient air analysers. It consists of an ADC circuit board and a PC to store the one-minute actual point concentration.

The fields of responsibility of the operational group is split up into three parts. The technicians at the site are responsible for the maintenance and the data processing, meanwhile a different person is 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). These parameters are evaluated usually from a every two month calibration. Invalid values (according logbook), i.e. data from manual calibration or two times a week zero/span checks, or analytically invalid data, are manually removed from the database. Analytical invalid data, are evaluated considering the logbook on obvious local influences, e.g. construction activities or the central heating of the laboratory (is important if the wind direction is SE). Every week the data are reprocessed and recalculated, but at the moment this data processing is little behind the schedule.

The final data set includes: 1' raw data set; with instrumental parameters  
10', 30', 60' validated data sets.

The minima criteria for a valid mean value is 50% data.

#### Comment

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

### 4.4. Operation and Maintenance

Daily, a station technician inspects the measurement for a quick check of general operation of the analysers. Exchange of the teflon filters at the instruments inlet is made every two weeks. Before and after this a manual multipoint check is performed for the ozone measurements. An external ozone generator of the type Environics 100 is used for this.

Preventive maintenance of the ozone and carbon monoxide instruments is performed on a case by case basis. The silikagel cartridge of the zero air supply on site is renewed if required.

Ozone calibration: Every two month the ozone analysers are calibrated on site with a TEI 49-PS reference instrument (provided from the ozone group of MOHp). The procedure follows a multipoint calibration at approximately 30, 50, 100, 150 ppb ozone and a zero point check. The analysers are corrected accordingly if necessary. The last calibration was performed on 13. November.

CO calibration: A certified gas-standard (aluminium cylinder GLB-056095 00 470) from Messer-Griesheim containing 40.5 ppm CO is utilised for calibration purposes twice a week. By dynamic dilution using mass-flow-controllers the ppm standard is diluted with synthetic air to about 160 ppb CO. Using the span inlet the analyser is flushed in a 10 minute interval with standard gas and CO-free synthetic air. This procedure using dry gases is verified around every three month by adding different defined amounts of the CO standard into the ambient air flow.

#### 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 structured and organised. It is further noted that the regularly and frequently performed calibrations for both the ozone and CO measurements are regarded as very important means of quality assurance.

## **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.

In the scope of quality assurance the GAW group of the Meteorological Observatory of Hohenpeissenberg established a documentation. In several SOPs, i.e. for maintenance, calibration, span check or verifying flow controllers the working processes are described in a very detailed and practically oriented way. Furthermore, station instrument logbooks and a maintenance logbook (bound, copy) were kept in an organised manner and contained all necessary information about special investigations, maintenance or unusual events. The instrument manuals were available at the site.

### **Comment**

The documentation of the ozone measurement meets all the requirements of the guidelines for global GAW stations and can be taken as a good example of practice orientated implementation.

## **4.6. 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 the adequate education, the staff was very familiar with the techniques and problems associated with ozone measurements.

We enjoyed working with the people at the Meteorological Observatory and had a pleasant stay at Hohenpeissenberg.

## 5. Intercomparison of Ozone Instruments

### 5.1. Experimental Procedure

At the site, the transfer standard (detailed description see Appendix I) was hooked up to power for warming up over the weekend (deviation to the GAW report No. 97 which recommends only one hour of warm-up time). 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 18. November, 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.

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

audit-team, EMPA	A. Fischer, A. Herzog
reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instruments:	- TEI 49C #56028-306 - UPK 8002 #92062
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: 888 hPa ± 2 hPa and T <sub>indoor</sub> : approx. 25°C
pressure transducers reading:	TEI 49C-PS: 888 hPa TEI 49C #306: 887 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 November 18,
connection between instruments:	approx. 1.5 meter of 1/4" PFA tubing

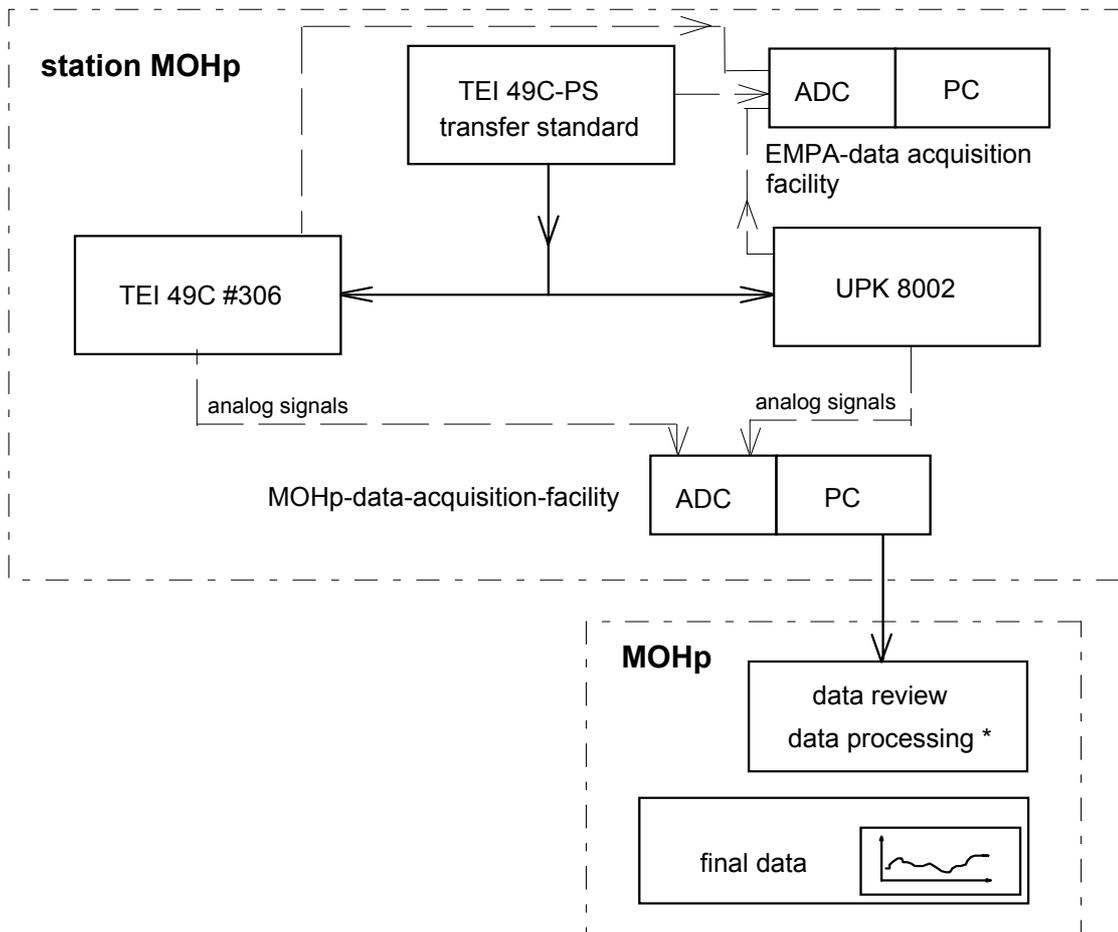


Figure 7: Experimental set up

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 all the instruments involved the data was collected by the data acquisition systems of EMPA. 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 EMPA data is used.

## 5.2. Results

The results comprise three intercomparisons between the field instruments TEI 49C, UPK 8002 and the transfer standard TEI 49C-PS, carried out on 18. November, 1997.

In the following tables the resulting mean values of each ozone concentration and the standard deviations of ten 30 second-means are presented. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Further, the diagrams show the results of the linear regression analysis of both field instruments compared to the EMPA transfer standard.

Table 5: 1. Intercomparison

No.	transfer standard			TEI 49C			UPK 8002			
	TEI 49C- PS conc.	s <sub>d</sub>	conc.	s <sub>d</sub>	deviation from reference		conc.	s <sub>d</sub>	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	%
1	0.2	0.15	-0.1	0.21	-0.2		-0.8	0.11	-1.0	
2	74.8	0.19	72.4	0.29	-2.5	-3.3%	73.4	0.22	-1.4	-1.9%
3	14.9	0.21	14.6	0.22	-0.3	-2.1%	14.0	0.11	-0.9	-5.9%
4	54.9	0.21	53.1	0.17	-1.8	-3.3%	53.8	0.20	-1.1	-2.0%
5	94.9	0.16	92.0	0.21	-3.0	-3.1%	93.6	0.20	-1.3	-1.4%
6	35.0	0.17	34.0	0.14	-1.0	-2.8%	34.1	0.15	-0.9	-2.6%
7	0.0	0.20	-0.1	0.19	-0.1		-0.6	0.07	-0.6	

Table 6: 2. Intercomparison

No.	transfer standard		TEI 49C				UPK 8002			
	TEI 49C- PS conc.	s <sub>d</sub>	conc.	s <sub>d</sub>	deviation from reference		conc.	s <sub>d</sub>	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	%
1	0.0	0.15	-0.2	0.14	-0.2		-0.6	0.10	-0.6	
2	35.0	0.25	33.5	0.20	-1.5	-4.3%	33.9	0.13	-1.0	-3.0%
3	15.0	0.16	14.1	0.13	-0.9	-6.0%	14.2	0.15	-0.7	-5.0%
4	95.0	0.31	91.6	0.28	-3.4	-3.6%	93.4	0.19	-1.5	-1.6%
5	55.0	0.22	53.0	0.11	-2.0	-3.6%	54.0	0.19	-1.0	-1.9%
6	75.0	0.26	72.4	0.23	-2.5	-3.4%	73.8	0.30	-1.2	-1.6%
7	0.0	0.15	-0.2	0.12	-0.3		-0.5	0.06	-0.6	

Table 7: 3. Intercomparison

No.	transfer standard		TEI 49C				UPK 8002			
	TEI 49C- PS conc.	s <sub>d</sub>	conc.	s <sub>d</sub>	deviation from reference		conc.	s <sub>d</sub>	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	%
1	0.0	0.15	-0.2	0.12	-0.3		-0.5	0.06	-0.6	
2	54.9	0.22	53.0	0.25	-1.9	-3.5%	53.8	0.19	-1.1	-2.0%
3	75.0	0.18	72.4	0.25	-2.6	-3.4%	73.5	0.27	-1.5	-2.0%
4	35.0	0.16	33.8	0.22	-1.2	-3.4%	34.2	0.11	-0.8	-2.3%
5	95.0	0.25	92.0	0.27	-3.0	-3.1%	93.5	0.30	-1.4	-1.5%
6	15.0	0.20	14.5	0.17	-0.6	-3.9%	14.3	0.13	-0.8	-5.1%
7	0.0	0.18	-0.2	0.19	-0.2		-0.6	0.07	-0.6	

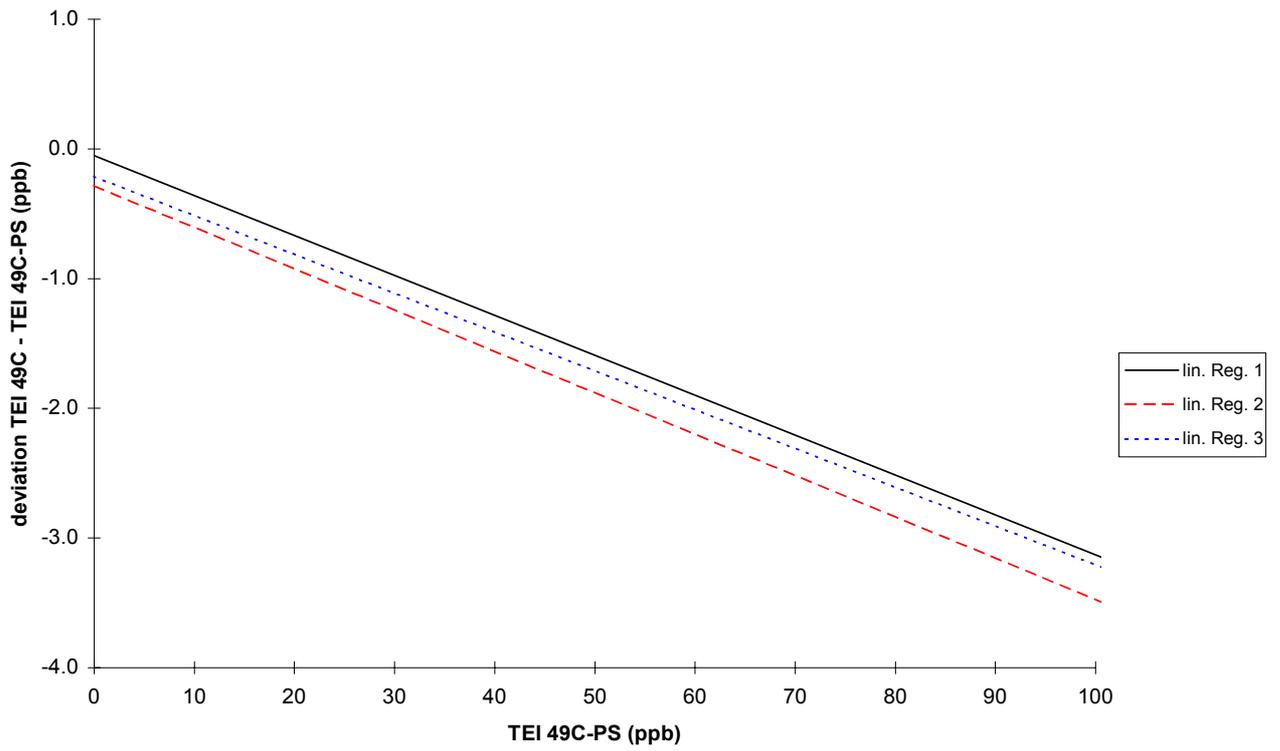


Figure 8: Individual linear regressions of intercomparisons 1 to 3, TEI 49C

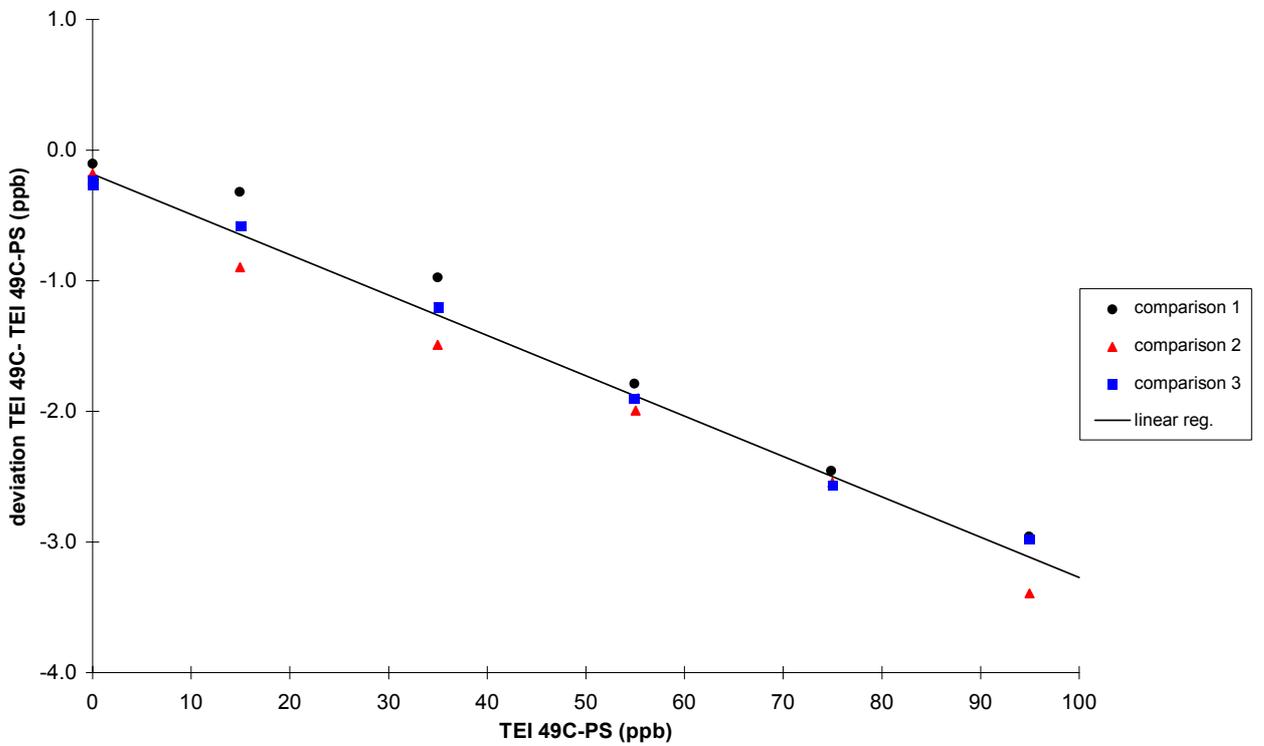


Figure 9: Mean linear regression of intercomparisons 1 to 3, TEI 49C

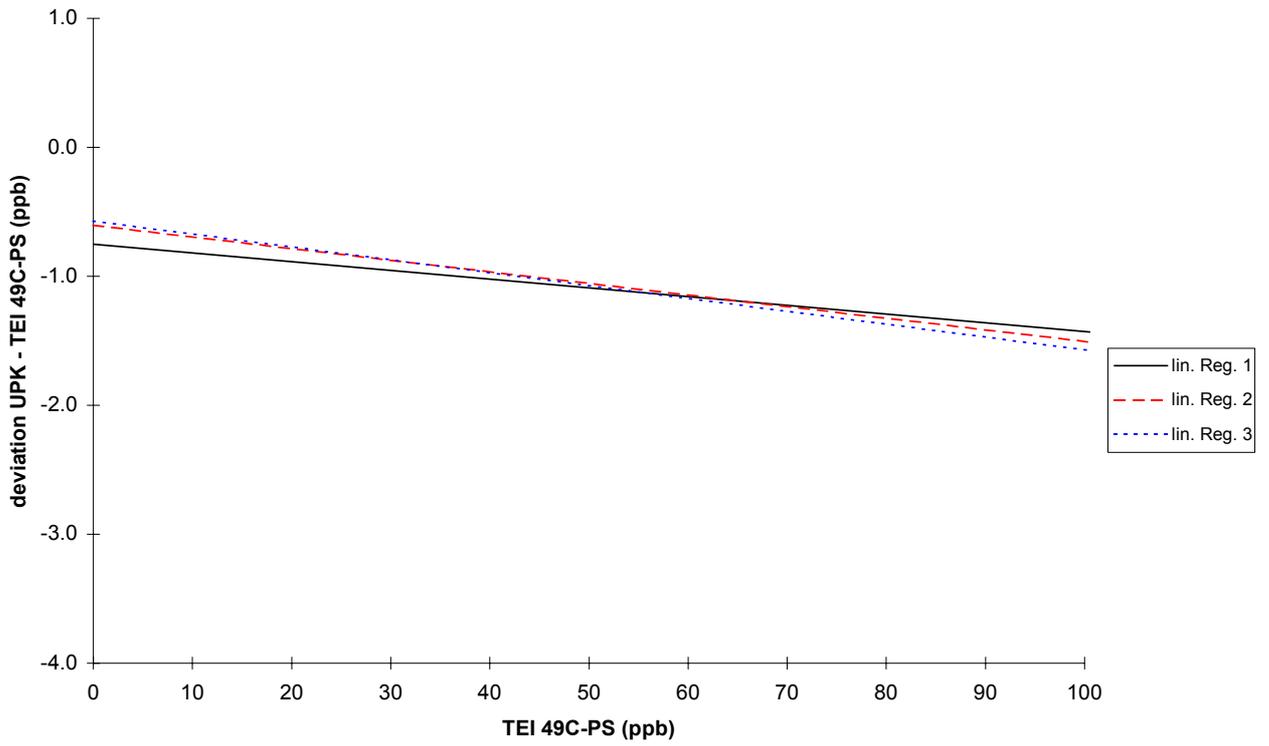


Figure 10: Individual linear regressions of intercomparisons 1 to 3, UPK 8002

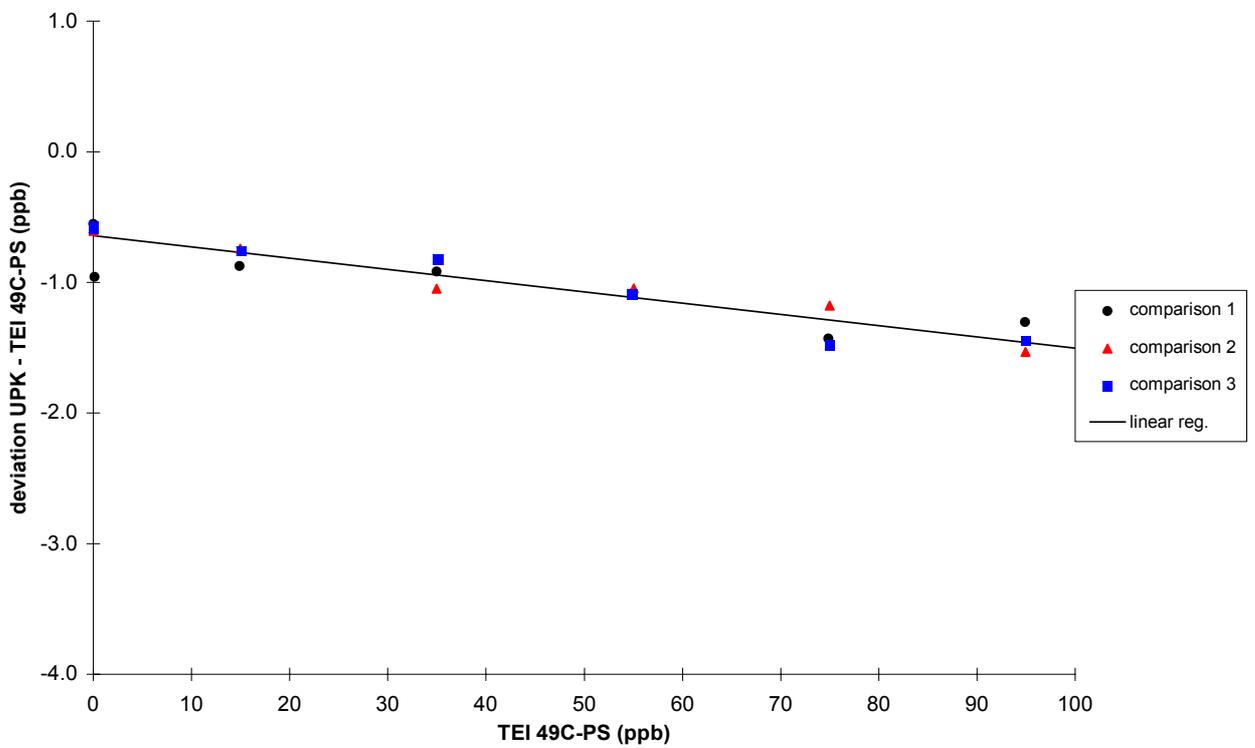


Figure 11: Mean linear regression of intercomparisons 1 to 3, UPK 8002

From the comparisons of the TEI 49C and the UPK 8002 field instruments with the EMPA transfer standard the resulting linear regressions (for the range of 0-100 ppb ozone) are:

-TEI 49C:

$$\text{TEI 49C} = 0.969 \times \text{TEI 49C-PS} - 0.2 \text{ ppb}$$

TEI 49C = O<sub>3</sub> mixing ratio in ppb, determined for TEI 49C #56028-306

TEI 49C-PS = O<sub>3</sub> mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope $s_m$	0.0010 (f = 3) f=degree of freedom
	- offset $S_0$ in ppb	0.05 (f = 3)
	- residuals in ppb	0.16 (f = 19)

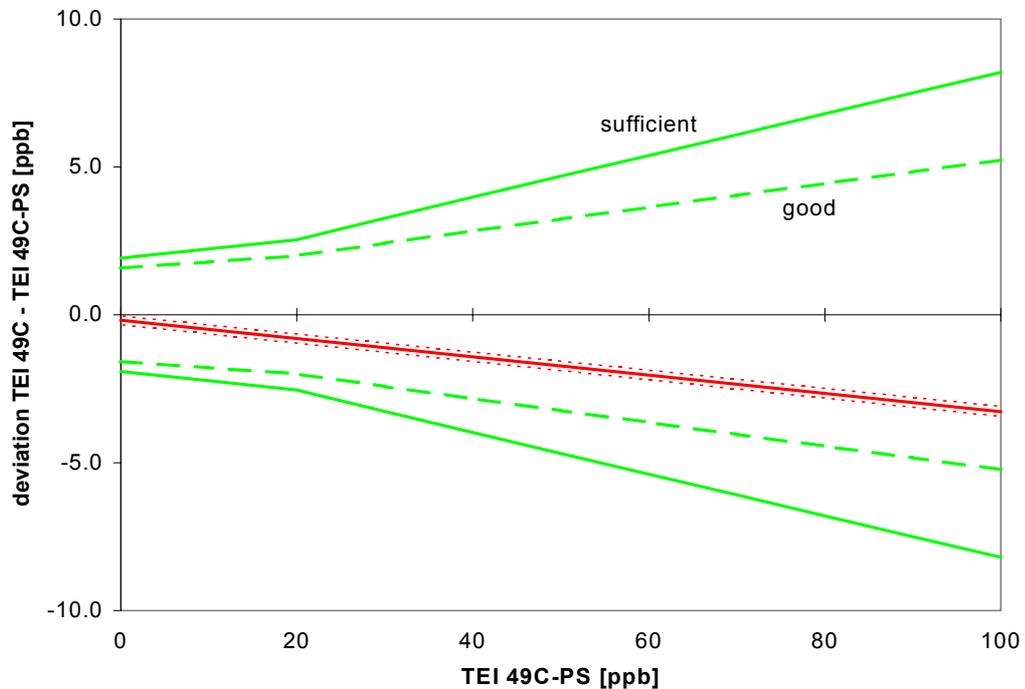


Figure 12: Intercomparison of instrument TEI 49C

-UPK 8002:

$$\text{UPK 8002} = 0.991 \times \text{TEI 49C-PS} - 0.6 \text{ ppb}$$

UPK 8002 = O<sub>3</sub> mixing ratio in ppb, determined for UPK 8002 #92062

TEI 49C-PS = O<sub>3</sub> mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope sm	0.0008 (f = 3) f=degree of freedom
	- offset Sb in ppb	0.04 (f = 3)
	- residuals in ppb	0.12 (f = 19)

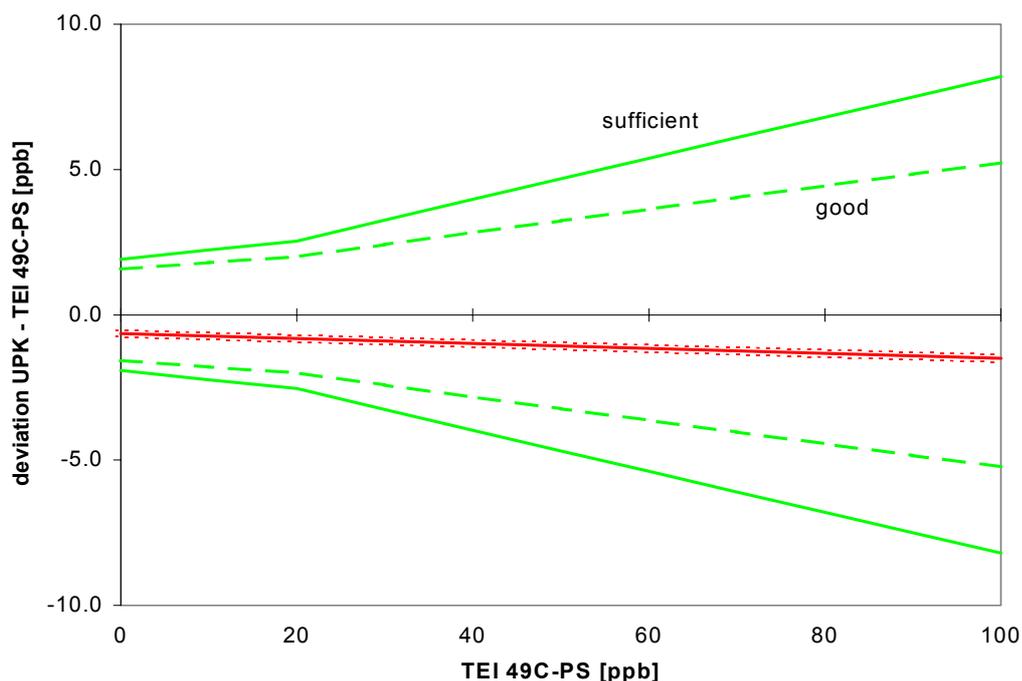


Figure 13: Intercomparison of instrument UPK 8002

### Comment

In the linear regressions of both instruments (figures 12 and 13), no trend as a function of time could be observed during the intercomparison.

The ozone concentrations observed at MOHp (1996) usually ranged between 12 and 67 ppb (5- and 95-percentile of hourly mean values).

Both instruments clearly fulfil the assessment criteria as "good" over the tested range up to 100 ppb (figure 12 and 13). For each analyser, fairly small deviations among the three intercomparisons are the reason for narrow prediction intervals which implies that the instruments are in 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.

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 the weekend 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 November 17 until November 19 the intercomparison was made with the field instrument TEI 48S. Different concentration levels were applied (figure 14) by repeated switching in the measurement mode between calibration gas and zero gas about every 10 minutes. Table 8 shows the experimental details and figure 15 the experimental set up of the audit. In general, no modifications of the carbon monoxide analysers were made for the intercomparison. During the night-time of the 17th and 18th of November an ambient air intercomparison between the field instrument TEI 48S (#50873-286) and the transfer standard Horiba 360 APMA was performed. The signal of the field instrument was acquired by the EMPA data acquisition system. Because of the drifts of the instruments, the average measurements signals (after reaching a stable value) are subtracted from average zero signals before and after switching (after reaching a stable value). During the audit EMPA zero air (synthetic air + Sofnocat) was used. The zero air for calibration at the site was tested and there was no significant difference between the site zero air and the EMPA zero air.

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.

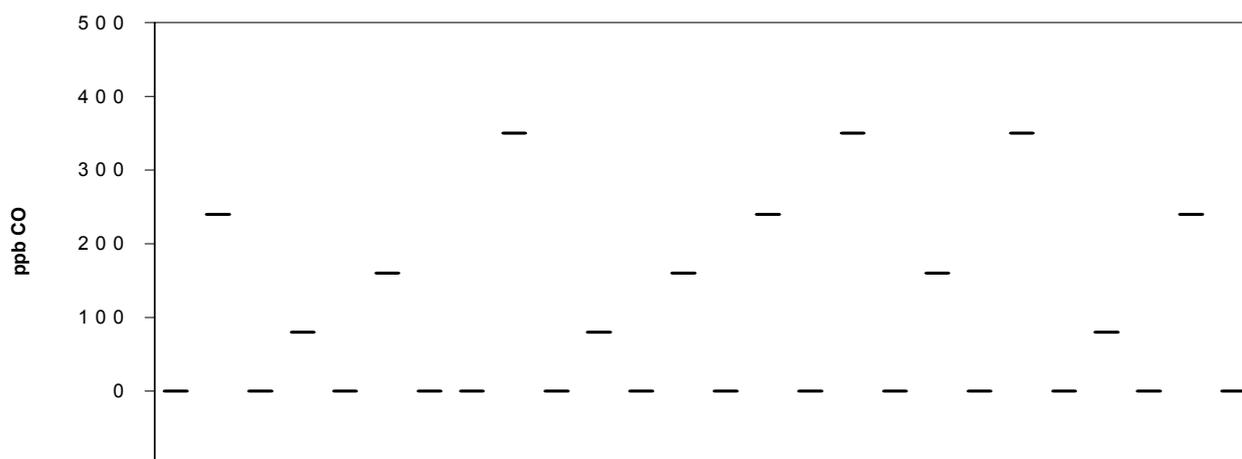


Figure 14: Sequence of concentrations during audit.

Table 8: Experimental details during audit (see changes after audit in Appendix Carbon Monoxide)

audit-team, EMPA	A. Fischer, A. Herzog
reference:	Transfer standards: MGM diluter, MG-GEG Calibration Gas, Horiba 360 APMA
field instruments:	- TEI 48S #50873 - 286
air inlet system (pre-treatment)	no
zero air supply:	EMPA: synthetic air + Sofnocat MOHp: ambient air + Pd-catalyst + Silicagel (Calibr.) MOHp: ambient air + Pd-catalyst (measurements)
data acquisition system:	EMPA: 16 channel ADC circuit board, software
surrounding conditions:	p: 888 hPa $\pm$ 2 hPa and T <sub>indoor</sub> : approx. 25°C
concentration range:	0 - 2000 ppb
number of concentrations:	4 + zero air
approx. concentration levels:	80 / 160 / 240 / 350 ppb
sequence of concentration:	see figure 14
averaging interval per concentration:	10 minutes
measuring cycle	10 minutes measurement-mode 10 minutes zero-mode
connection between instruments:	less than 3 meter of 1/4" PFA tubing

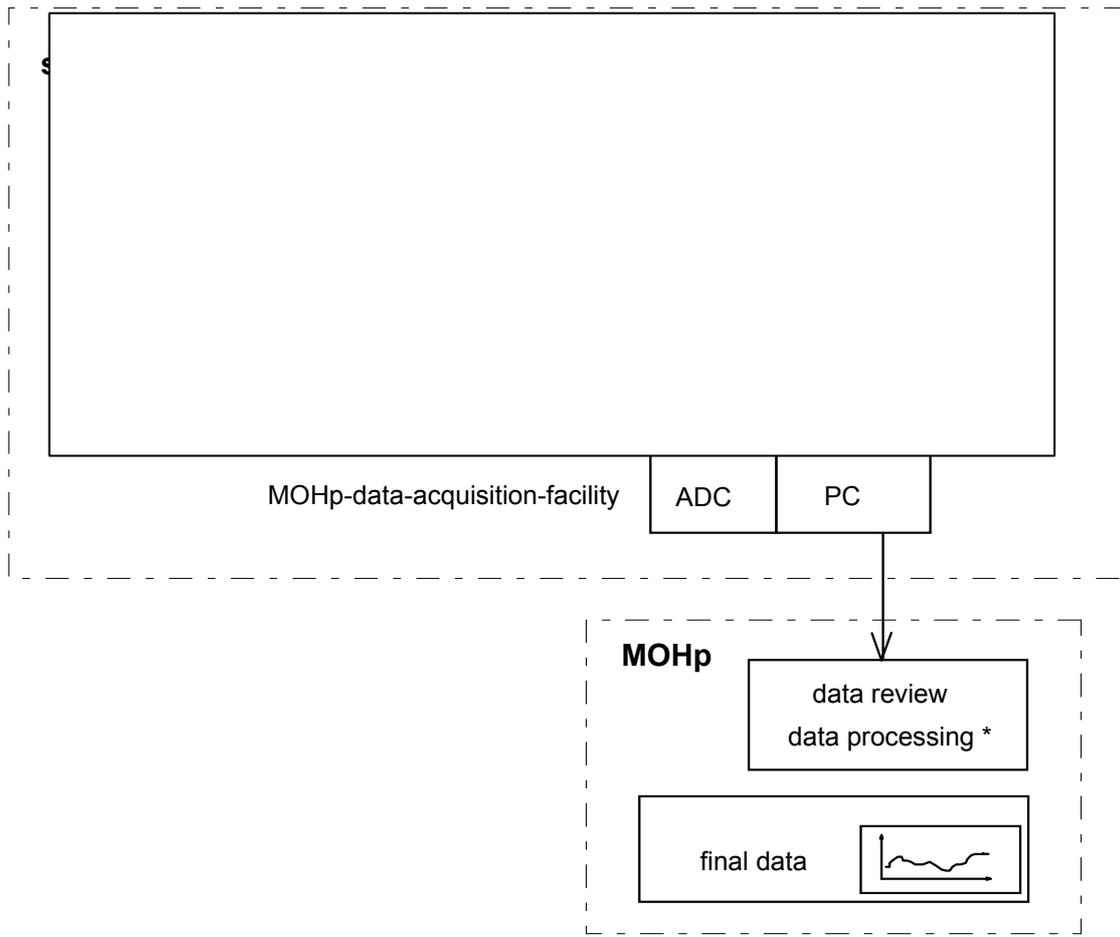


Figure 15: Experimental set up

## 6.2. Results

The results consist of 12 intercomparisons between the field instrument TEI 48S (#50873-286) and the transfer standard carried out on November 17 until November 19, 1997.

In the following table the resulting mean values of each carbon monoxide concentration and the standard deviations of a 10 minute interval (n = 20) is presented. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and in %. Further figure 16 shows the results of the linear regression analysis of field instrument TEI 48S compared to the EMPA transfer standard.

Table 9: Intercomparisons

No.	transfer standard		TEI 48S (#50873-286)			
	MGM conc.	s <sub>d</sub>	conc.	s <sub>d</sub>	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	241.5	0.6	235.0	11.3	-6.5	-2.7
2	80.4	0.2	78.0	10.7	-2.4	-3.0
3	161	0.5	160.5	13.0	-0.5	-0.3
4	351.1	1.2	342.3	14.4	-8.8	-2.5
5	80.4	0.2	76.4	8.7	-4.0	-5.0
6	161	0.5	155.3	11.6	-5.7	-3.5
7	241.5	0.6	237.7	10.2	-3.8	-1.6
8	351.1	1.2	346.3	10.4	-4.8	-1.4
9	161	0.5	150.1	12.2	-10.9	-6.8
10	351.1	1.2	342.3	11.8	-8.8	-2.5
11	80.4	0.2	77.0	10.9	-3.4	-4.2
12	241.5	0.6	238.9	13.5	-2.6	-1.1

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

-TEI 48S:

$$\text{TEI 48S} = 0.9872 \times \text{TS} - 2.52 \text{ ppb}$$

TEI 48S = CO mixing ratio in ppb, determined for TEI 48S #50873-286

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 17 shows the absolute differences, calculated in ppb between TEI 48S and the transfer standard.

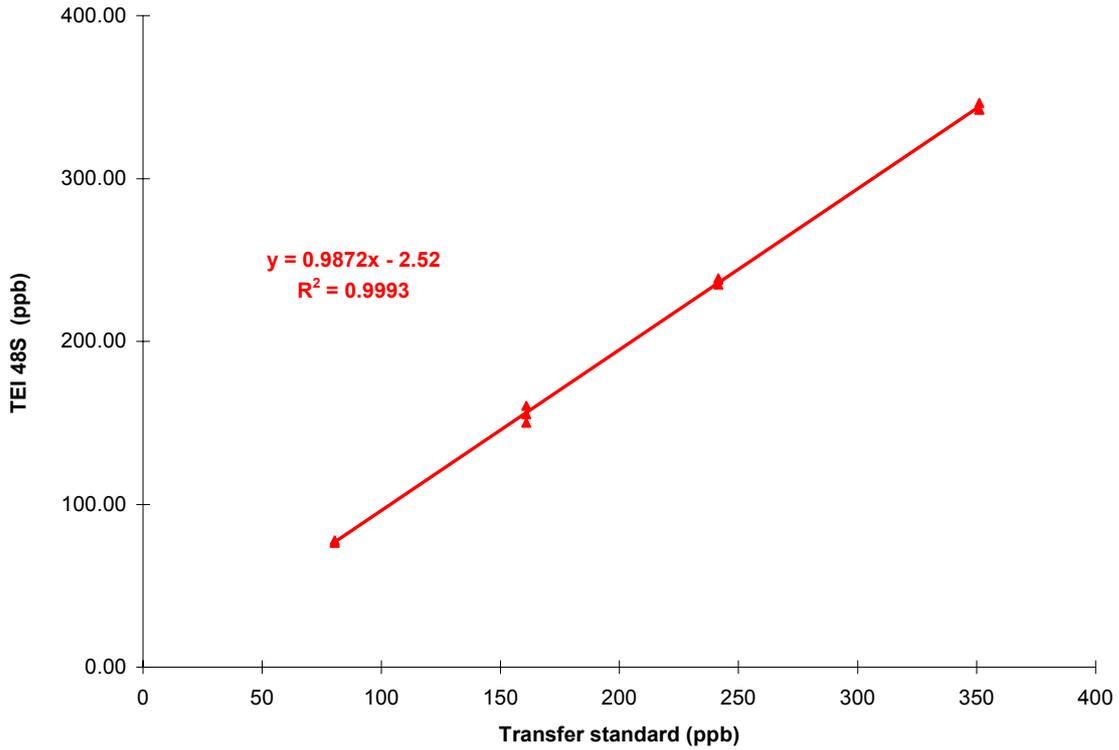


Figure 16: Mean linear regression analysis of field instrument TEI 48S.

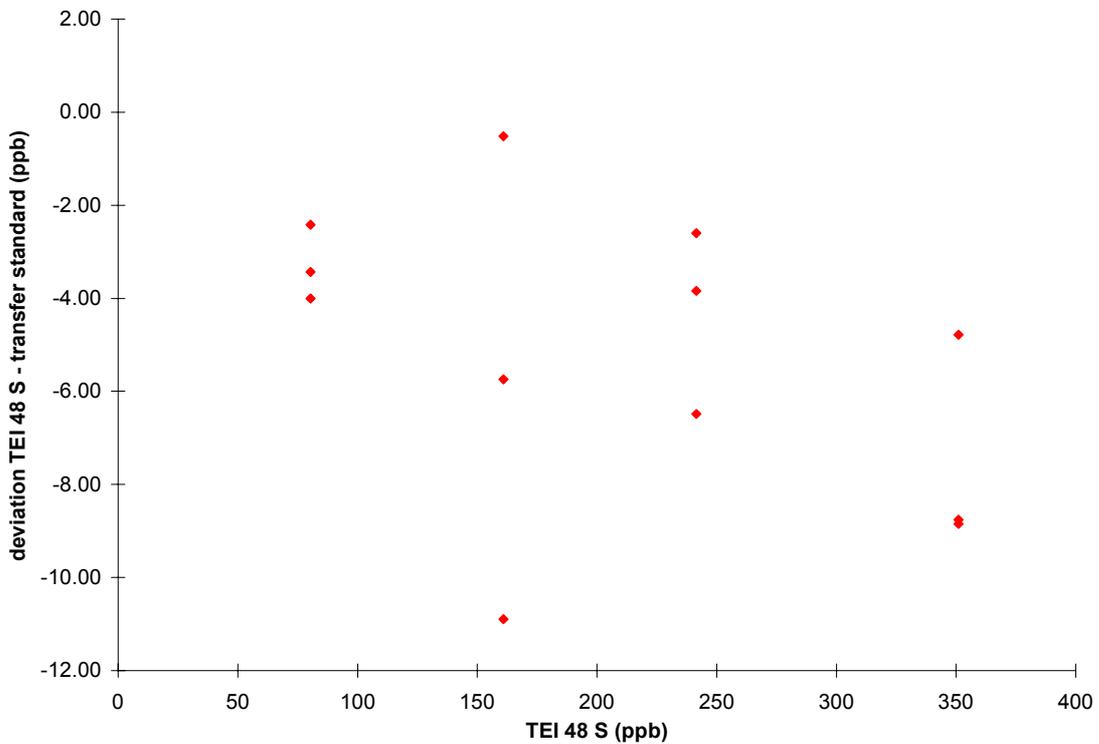


Figure 17: Absolute differences between TEI 48S and the transfer standard.

Figure 18 shows the relative differences (%) between TEI 48S and the transfer standard. The total uncertainty of the transfer standard (red line in figure 18) has been calculated for the whole audit procedure. Most of the uncertainty is caused by the uncertainties of the Reference gases.

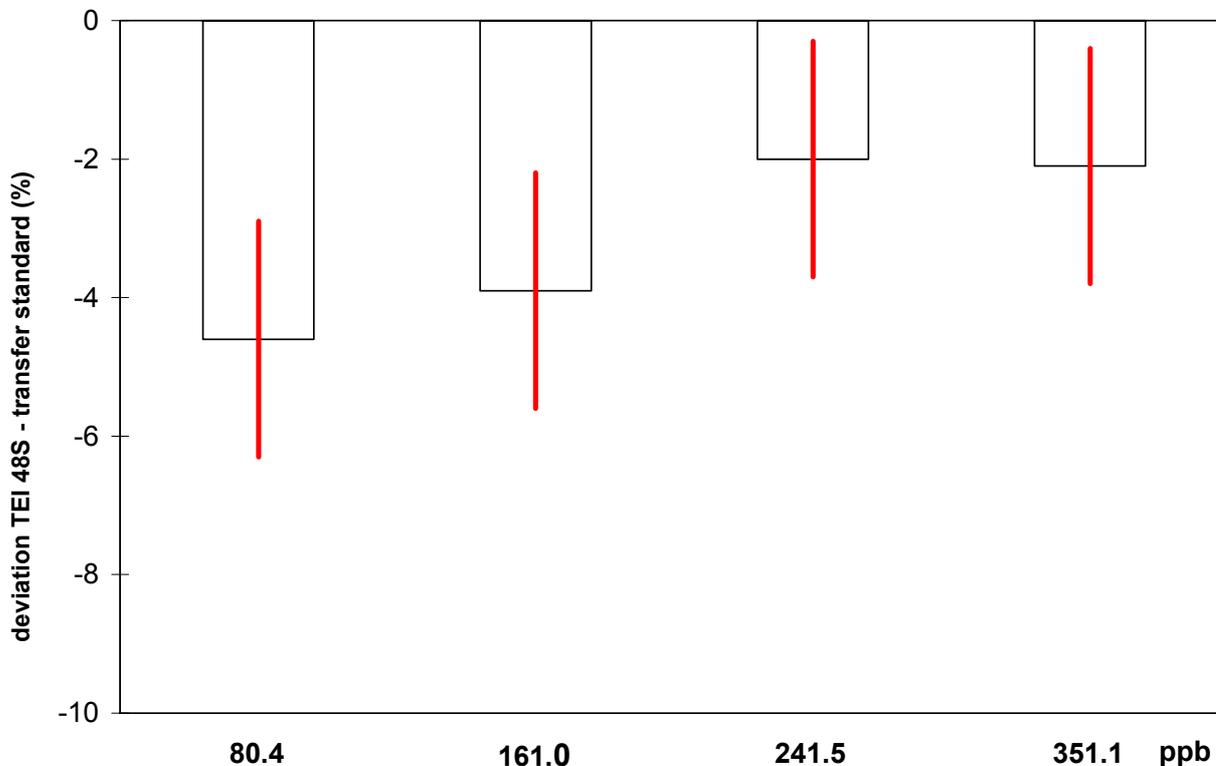


Figure 18: Differences (%) between TEI 48S and the transfer standard. The red line shows the uncertainty of the transfer standard.

During 2 nights (November 17/18th, 18/19th) we carried out ambient air intercomparisons between the field instruments TEI 48S and the transfer standard Horiba 360 APMA. In figures 19 and 20 the 10 minutes mean values of the results of the TEI 48S and the transfer standard are shown. The calculated mean values of the whole period are:  $243 \pm 17$  and  $217 \pm 23$  ppb for TEI 48S and  $259 \pm 16$  and  $234 \pm 24$  ppb for the Horiba 360 APMA.

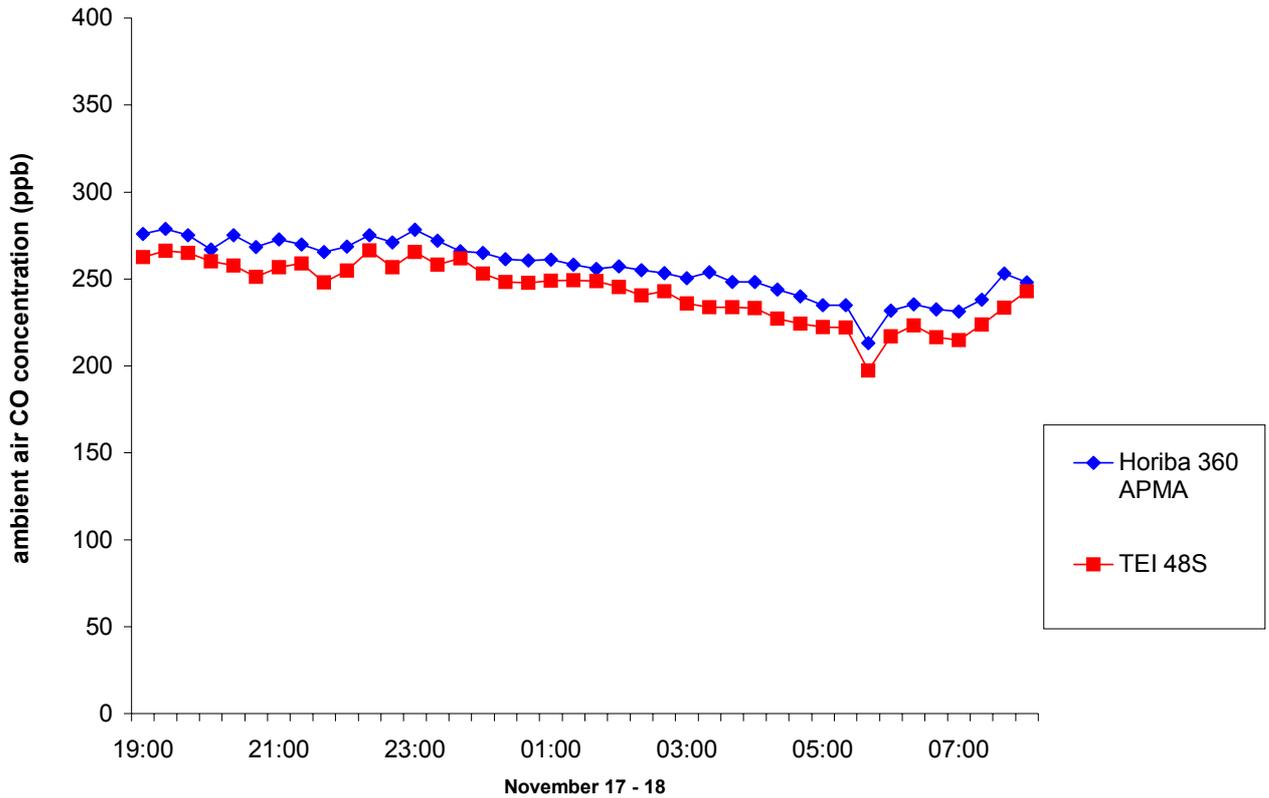


Figure 19: Ambient air concentrations measured with the field instrument TEI 48S and the transfer standard Horiba 360 APMA during the night (17th/18th).

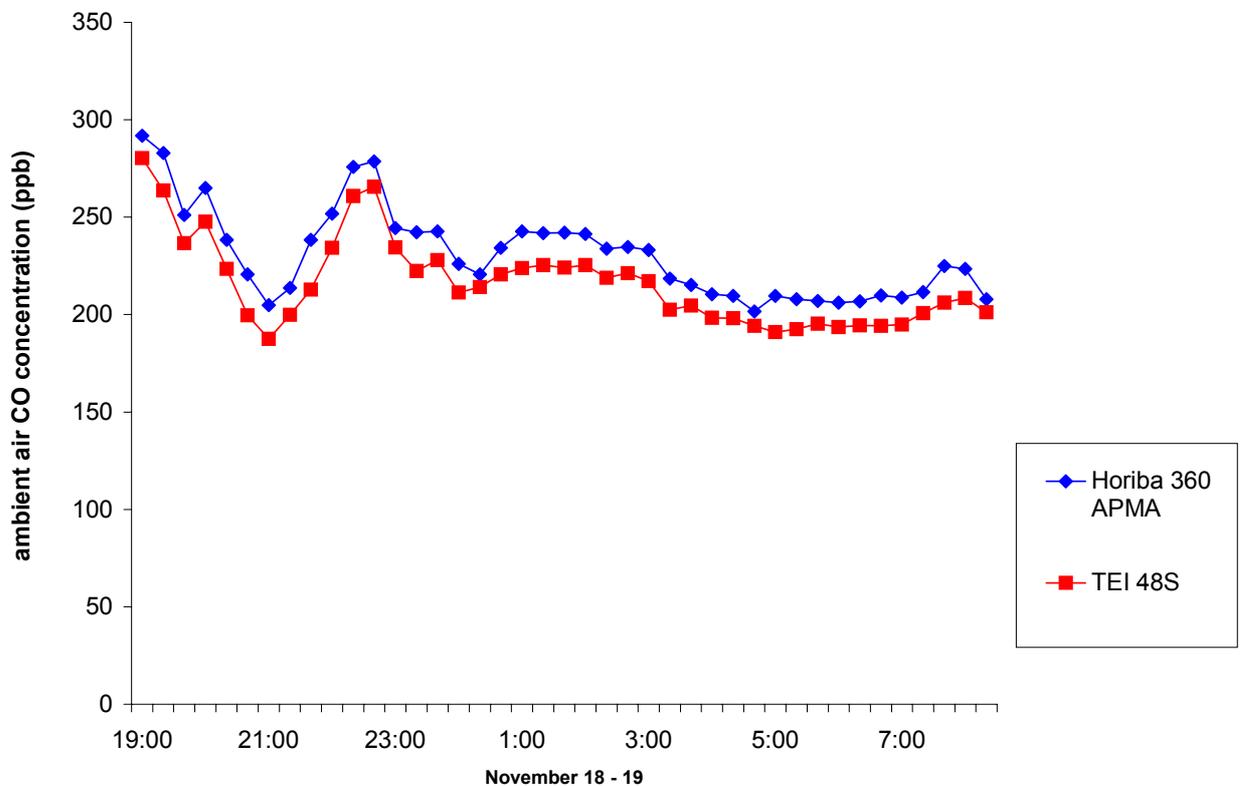


Figure 20: Ambient air concentrations measured with the field instrument TEI 48S and the transfer standard Horiba 360 APMA during the night (18th/19th).

## Comment

The carbon monoxide concentrations observed at Hohenpeissenberg (1996) usually ranged between 99 and 339 ppb (5- and 95-percentile of hourly mean values).

Before and during the audit the operator used ambient air (+ Pd-Catalyst + Silicagel) as zero air and span gas for calibration. So he used a dry/dry calibration (zero air / dry span gas) for his humid/humid measurements (zero mode: ambient air + Pd-catalyst; measurement mode: ambient air).

The ambient air concentration measurements with the TEI 48S are well comparable to the results of the transfer standard instrument (Horiba). The results of the different concentrations during the audit demonstrate only small deviations from the transfer standard.

The good results of the different concentrations during the audit and the ambient air measurements, demonstrate that the calibration factors (dry/dry) are well applicable to the humid/humid (zero mode/ measurement mode) measurements of ambient air.

## 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 21. 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.

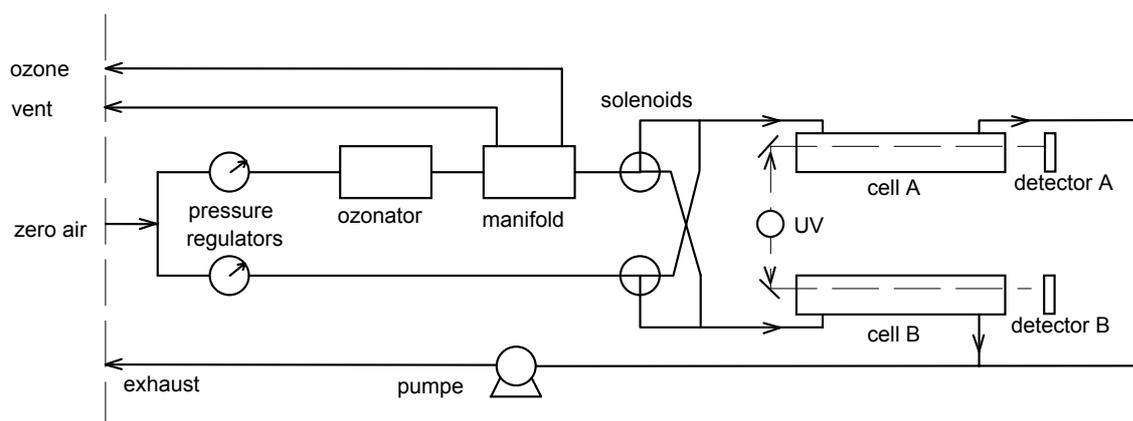


Figure 21: Flow schematic of TEI 49C-PS

### 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 7 and Figure 22.

Table 7: 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

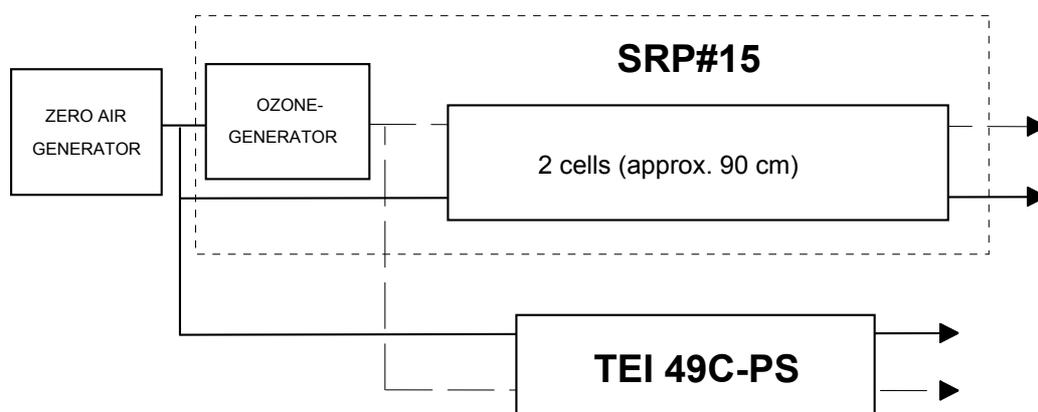


Figure 22: Instruments set up SRP -TEI 49C-PS

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  $(1 \text{ ppb} + 0.7\%)$ .

Figures 23 and 24 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.

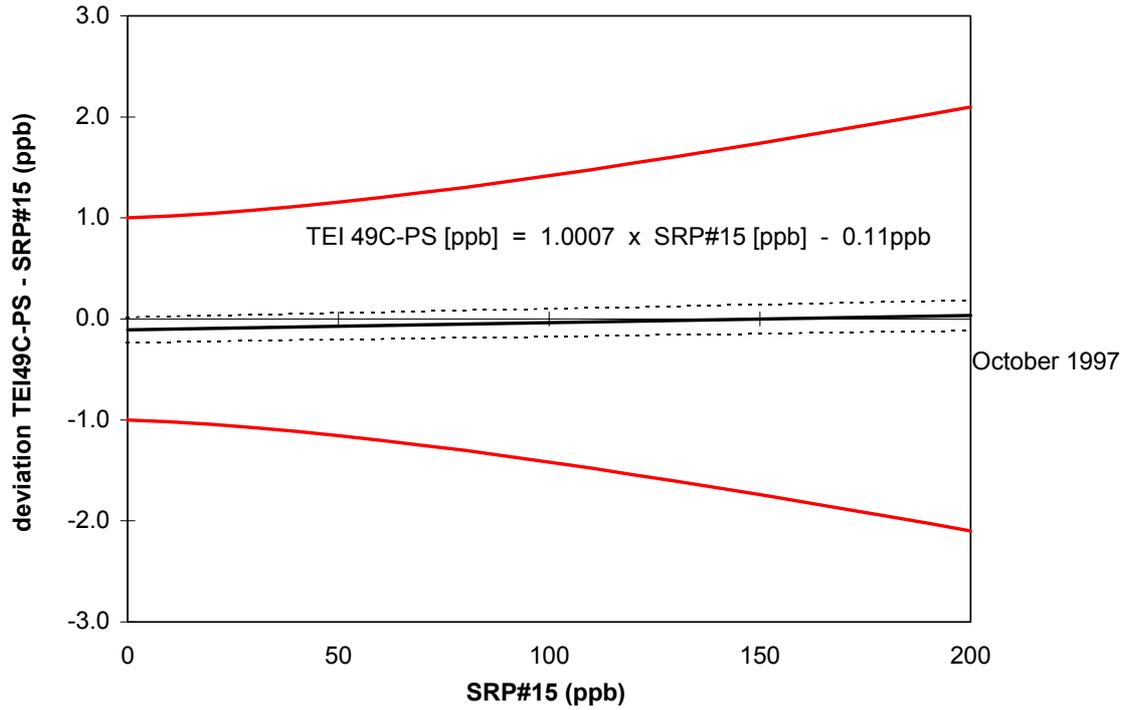


Figure 23: Transfer standard before audit

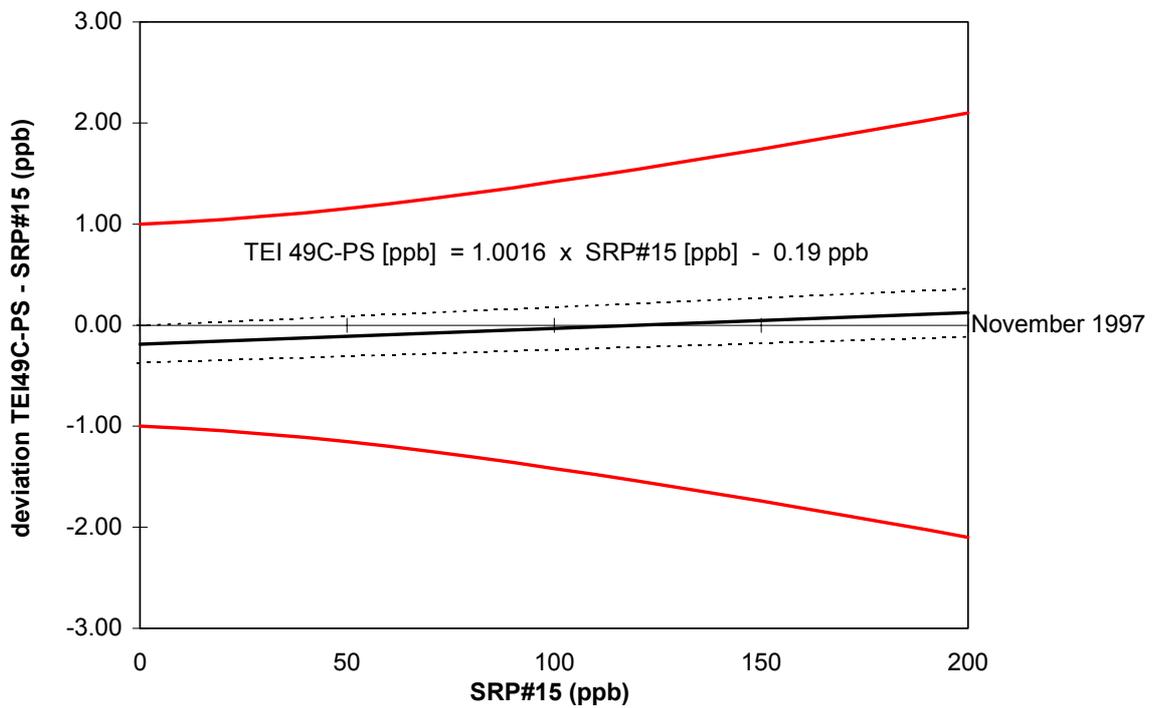


Figure 24: Transfer standard after audit

## Appendix Carbon Monoxide

### I. Traceability Chain

No Standard Operation Procedures (SOP) have been established for CO measurements until now by the QA/SAC. In figure 25 the traceability chain of the carbon monoxide audit, used by the WCC-CO is shown.

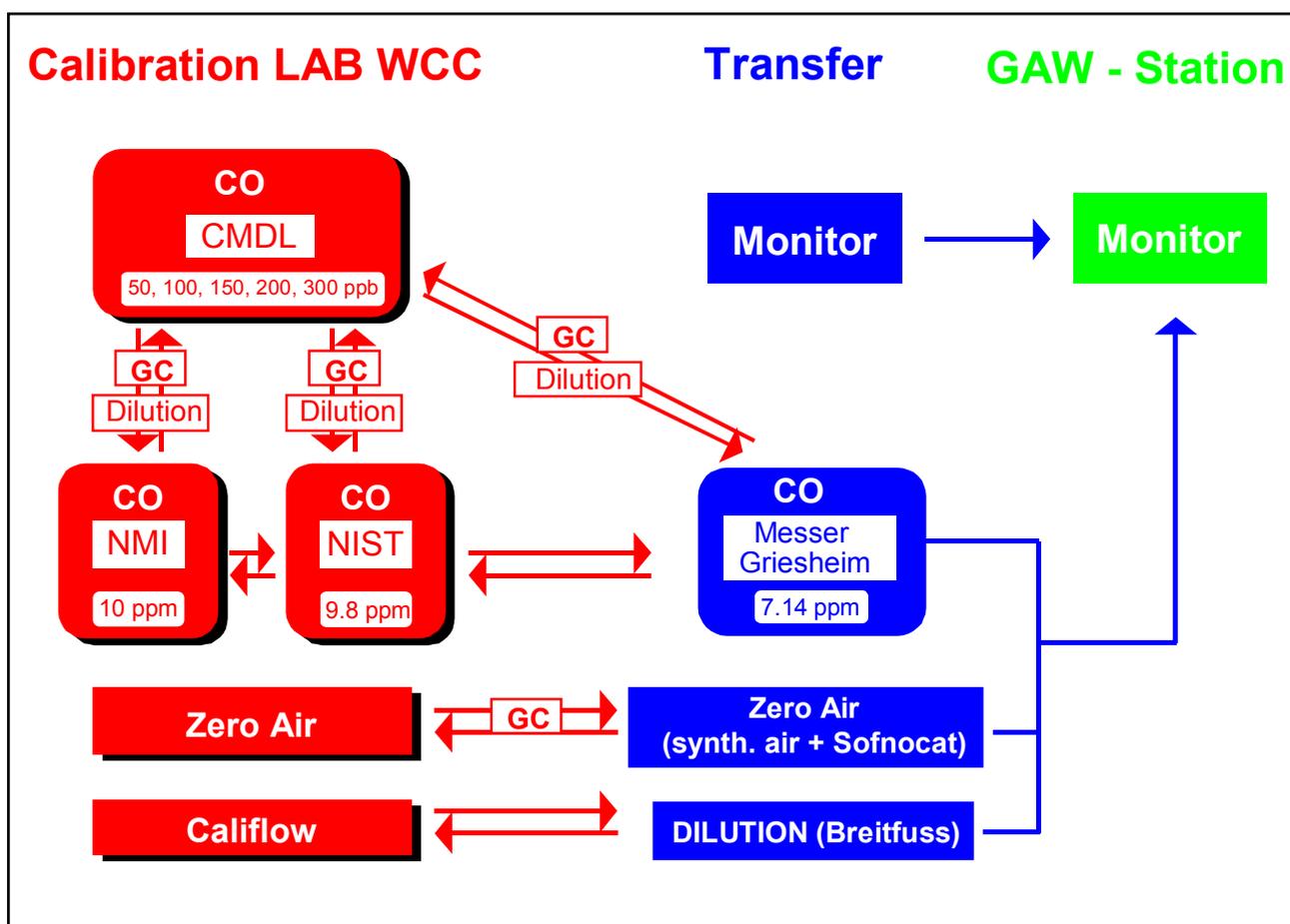


Figure 25: Traceability-Chain of the Carbon monoxide audit.

### 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 EMPA we use following standards of NOAA/CMDL:

Table 11: CO-Standards at EMPA.

Cylinder	CO nanomole/mole	Standard
CA03209	44.0 ± 1.0	Primary Standard
CA02803	97.6 ± 1.0	Primary Standard
CA03295	144.3 ± 1.4	Primary Standard
CA02859	189.3 ± 1.9	Primary Standard
CA02854	287.5 ± 8.6	Primary Standard
FAO1469	98.7 ± 1.0	Transfer Standard (for gas chromatography)
FAO1467	202.1 ± 2.0	Transfer Standard (for gas chromatography)
FAO1477	305.9 ± 9.1	Transfer Standard (for gas chromatography)

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 flowrates. Gas flowrates 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 flowrate. 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)**

The CO mixing ratios in ppb for the intercomparison were produced by the Transfer standards, the MGM diluter and the MG GEG-Calibration gas ( $7.14 \pm 0.03$  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 pure 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 produced by 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 transportation 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 26 (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
flow range:	1000 – 3000 ml/min

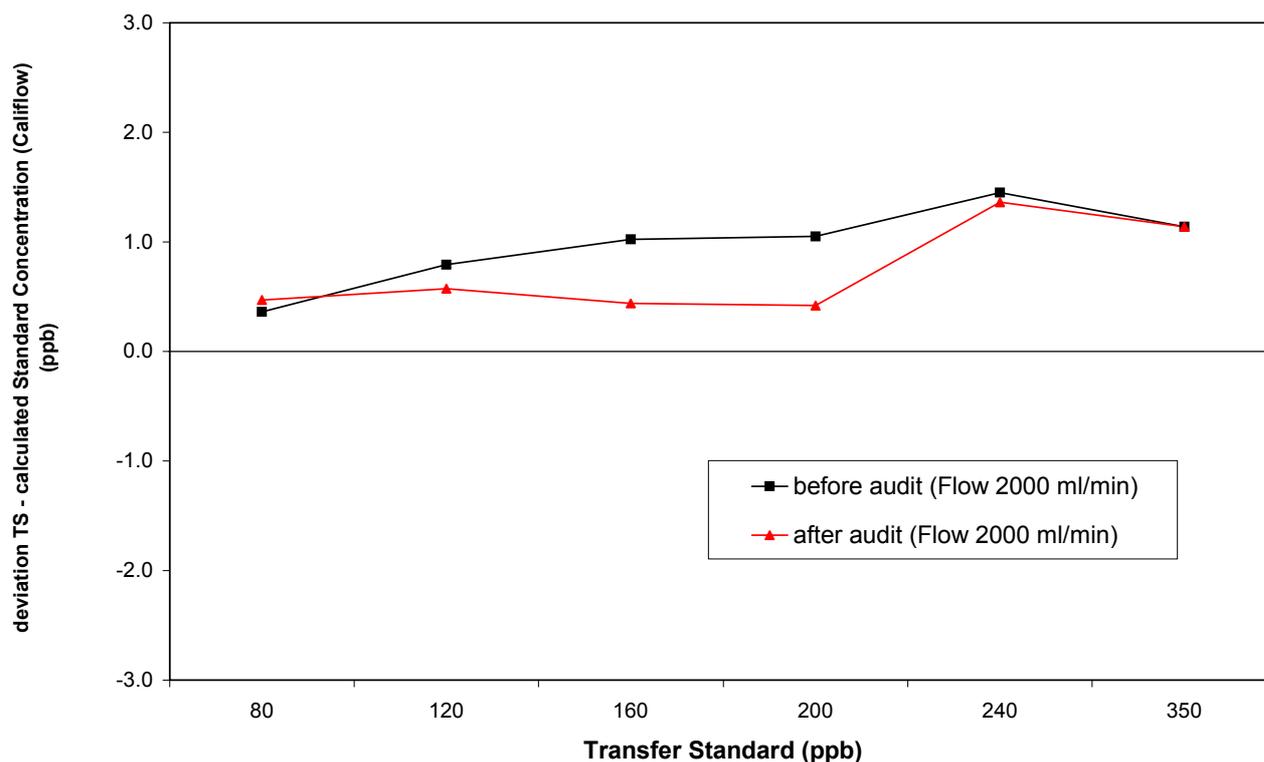


Figure 26: Transfer standard (TS) before and after audit.

### 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 intercomparison between the field instrument at MOHp and the transfer standard (Horiba 360 APMA) we made a calibration of the Horiba 360 APMA with zero-air and span-gas (350 ppb).