

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



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

REPORT

Submitted to

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE AND CARBON MONOXIDE

GLOBAL GAW STATION ZUGSPITZE / HOHENPEISSENBERG PLATFORM ZUGSPITZE

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Submitted by

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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 global GAW station Zugspitze, 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 Zugspitze (chemiluminescence and UVmethod), considerably increases confidence in data quality concerning parallel measurements as well as detection of potential interferences with other trace species. However, the calibration of both instruments has to be traceable back to the UV-absorption method since it is the preferred method in the GAW programme.

Carbon Monoxide Analysers:

As well for the carbon monoxide parameter parallel measurements considerably increase confidence in data quality.

We welcome the efforts in characterising the effect and influence of differently processed zero air and suggest to involve the GC / HgO system again.

Data Handling:

Splitting up responsibilities requires well implemented communication tools to ensure that important information gets not lost on the way down to IFU. With the new data acquisition software it is presumed that the comprehensibility of the whole procedure will be improved.

The relative comparison between two instruments is seen as a useful instrument to judge data and adjust span or zero factors in a small term. The basis for changes of a correction function, however, should always be an absolute calibration using a traceable standard from the IFU calibration laboratory.

Operation and Maintenance:

The appearance inside the station is clean and functional.

It is noted that maintenance on a case by case basis has its advantage due to no unnecessary interruption of the operating of the instruments. However, it requires a lot of experience and knowledge about the instruments. Since this is the case at Zugspitze we do not recommend any change to this procedure. Even though it differs from the description in the SOP of GAW report No. 97.

Documentation:

At the audit in spring 1996, in agreement with the responsible group, the documentation was seen as a major weak point. Since then, some extra efforts were made to build up or upgrade the necessary logbooks which has lead to a significant improvement 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.

However, the pressure on the group has increased to perform the same work with less personnel and raises the hope that, nevertheless, the high quality standard of the measurements can be maintained.

Ozone Intercomparisons:

The ozone concentrations observed at Zugspitze (1996) usually ranged between 36 and 71 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 reasonable good condition.

Carbon Monoxide Intercomparisons:

The carbon monoxide concentrations observed at Zugspitze (1996) usually ranged between 95 and 235 ppb (5- and 95-percentile of hourly mean values).

Because of the calibration system in use, differences to the concentration of the transfer standard and to different kinds of zero air were detected.

Because of new calibration factors (from a new set-up of the calibration system) the ambient air concentration measurements are well comparable to the results of the transfer standard instrument (Horiba).

It can be assumed, that with the new set-up of the calibration system these differences, detected during the audit, are eliminated.

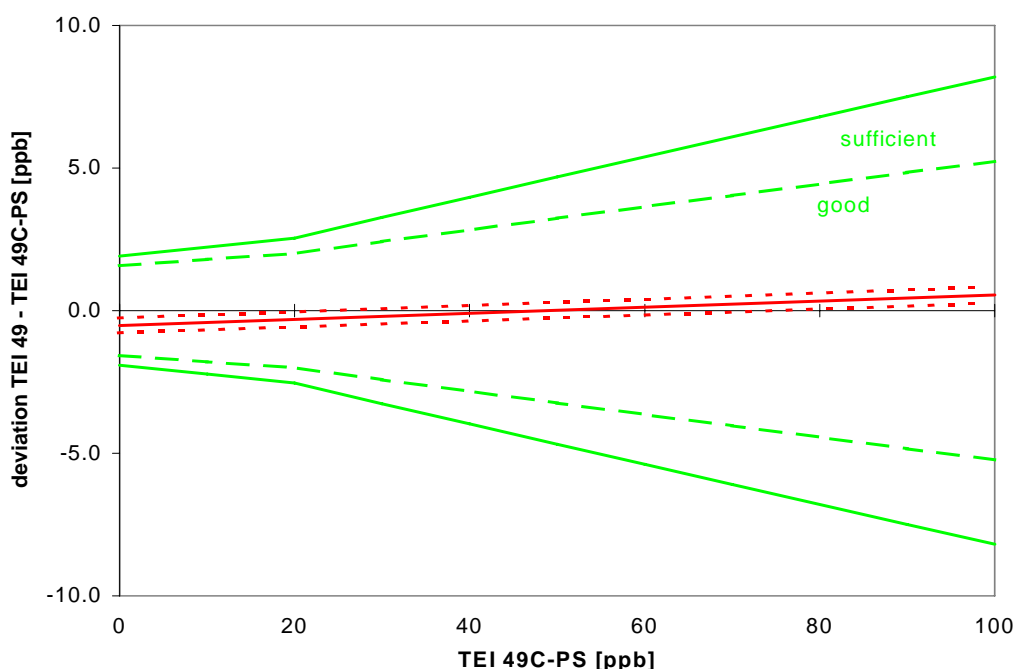


Figure 1: Intercomparison of instrument TEI 49 "C"

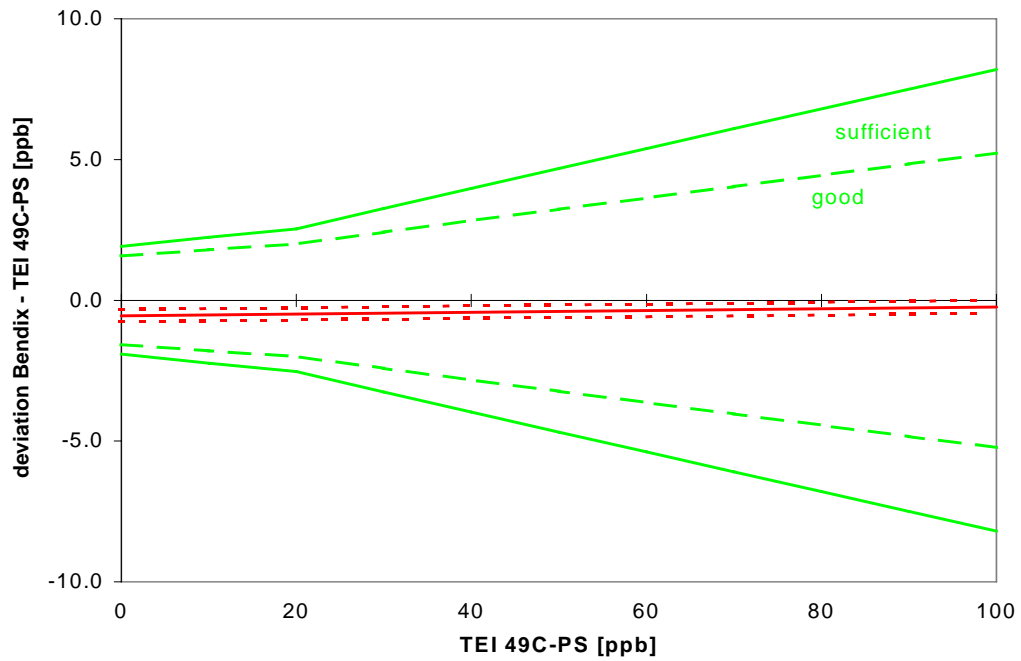


Figure 2: Intercomparison of instrument Bendix 8002

Dübendorf, 21. February, 1998

EMPA Dübendorf, WCC

Project engineer

Project manager

A. Herzog

Dr. B. Buchmann

Dr. A. Fischer

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 agreement with the group of IFU (Institute for Atmospheric Environmental Research) who is in charge of O₃ and CO measurements a system and performance audit at the global GAW station Zugspitze, Germany, 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 November 10 to 14, 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. 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, 1996, 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 IFU, the World Meteorological Organization in Geneva and the Quality Assurance and Scientific Activity Centre (QA / SAC) for Europe and Africa.

System and performance audits at global GAW stations will be regularly conducted on mutual arrangement every 12 to 18 months.

3. Global GAW Site Platform Zugspitze

3.1. Site Characteristics

Zugspitze, near Garmisch-Partenkirchen, is the highest mountain of the German Alps (2964 m above sea level). It is located in south-east Germany, approximately 90 km south-west of Munich, at the Austrian border. Because of the high elevation of the mountain station, the site can be considered to be in the free troposphere and far away from regional contamination for most of the time. A cable car leads directly to the summit of the Zugspitze.

The new monitoring station (co-ordinates: 47°25' N, 10°59' E; elevation: 2962 m above sea level) is installed in an aluminium sheltered cabin on the view point terrace (see picture). The air inlet system and the meteorological sensors are mounted on the flat roof of the shelter.

Over the past year, 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 Zugspitze

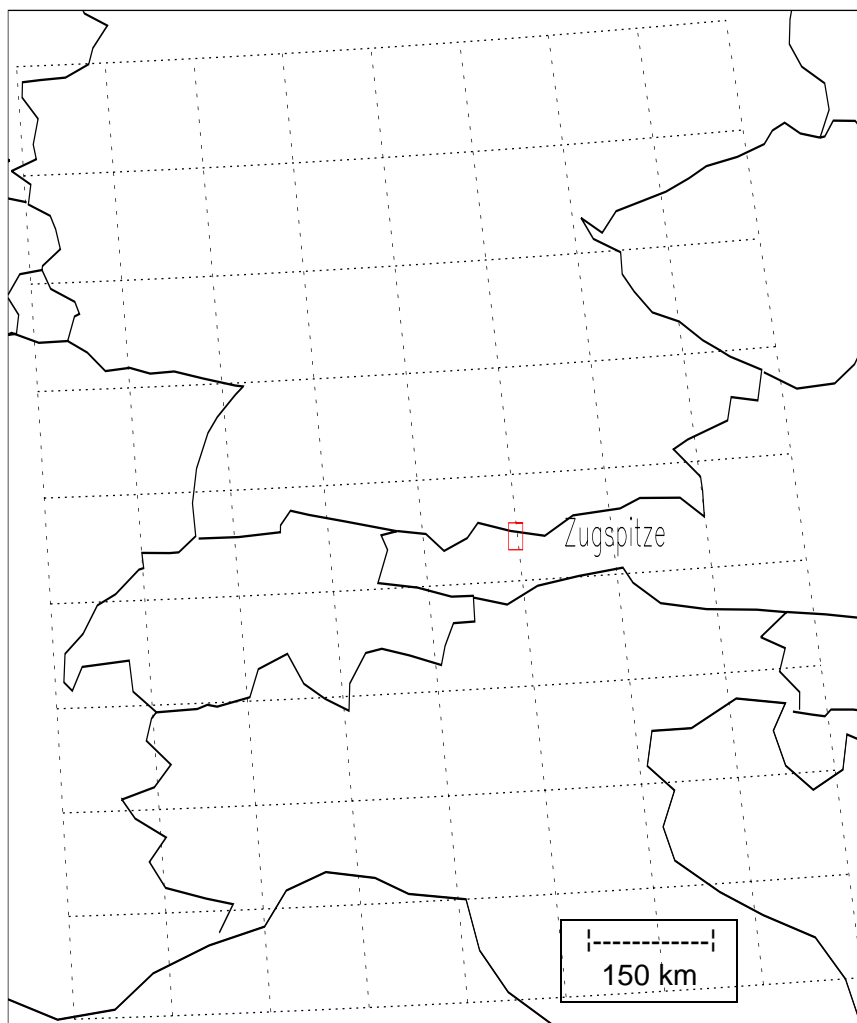


Figure 4: Map of Central Europe:

3.2. Operators

The Fraunhofer Institute for Atmospheric Environmental Research (IFU) in Garmisch-Partenkirchen, Germany, has an international reputation in the field of atmospheric research. The personnel of IFU consists of an interdisciplinary team of about 70 scientists and technicians. The group of Dr. Scheel is responsible for the operation of the station at Zugspitze. His team conducts the measurements on behalf of the Umweltbundesamt Berlin (UBA). The structure of the station management at IFU is shown in Table 1.

Table 1: Operators

Dr. L. Ries, GAW co-ordinator at the UBA Berlin

Prof. W. Seiler Director of the Fraunhofer Institute for Atmospheric Environmental Research (IFU)
<p style="text-align: center;">Operators and Observers</p> Dr. H.E. Scheel, Responsible for the station Mr. S. Glück, Station maintenance Mr. R. Sladkovic, Data management and supervision
<p style="text-align: center;">Experts</p> Prof. V.A. Mohnen Mr. H.J. Kanter

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 36 and 71 ppb according to the 5 and 95 percentile values. The annual data capture of ozone was considerably improved from 85 % in 1995 to 97%.

Source of data: received from IFU, December 1997

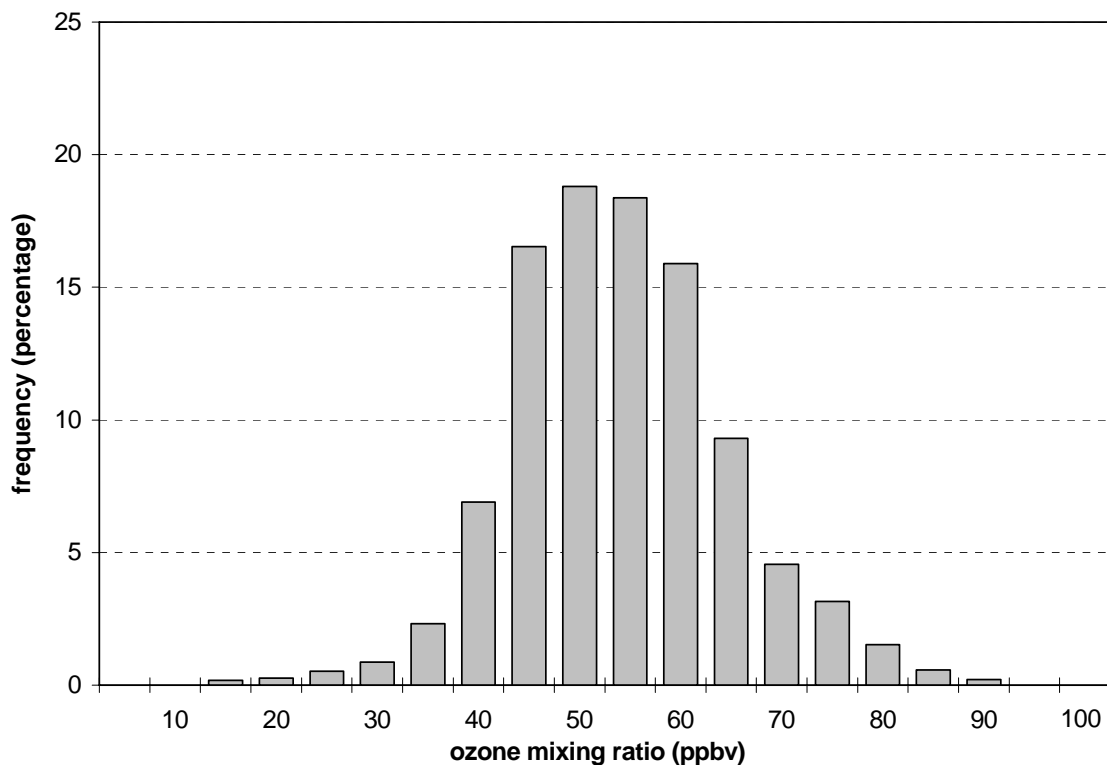


Figure 5: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Zugspitze of the year 1996. Data capture is around 97 per cent.

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 95 and 235 ppb according the 5 and 95 percentile values. The annual data capture of carbon monoxide was about 95 %.

Source of data: received from IFU, December 1997

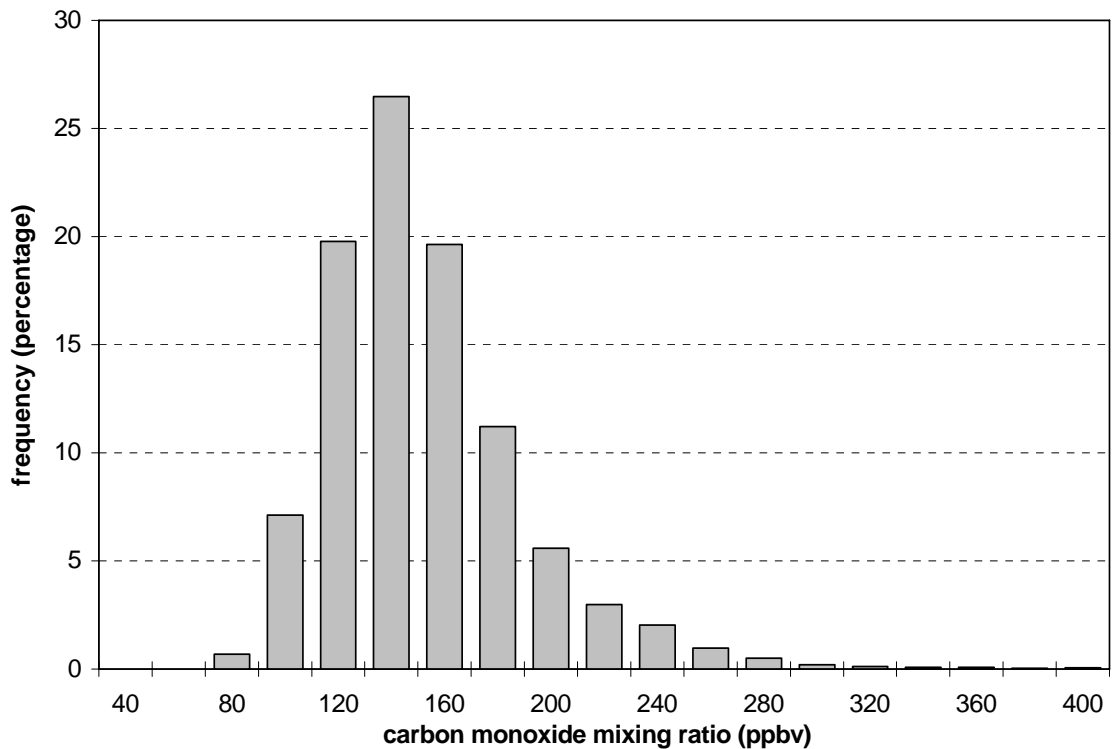


Figure 6: Frequency distribution of the hourly mean values of the carbon monoxide mixing ratio (ppb) at Zugspitze of the year 1996. Data capture is around 95 per cent.

4. Measurement Technique

4.1. Air Inlet System

The air inlet system is located on top of the flat roof of the measurement cabin. It consists of a heated, glass coated inlet, which is protected from rain and snow. Additionally, a punched sheet of metal shields the outdoor inlet from heavy precipitation under strong wind conditions. The main glass manifold (ID approx. 8 cm) leads directly into the shelter and is flushed by about 1000m³ (STP) ambient air a day. For the ozone measurements a thinner glass manifold branches off (flushed with an extra pump) from where a 4mm ID, 2m long PFA tubing goes to the inlet filter and to the instrument. The total residence time is estimated at 15 seconds.

Since the last audit, the air inlet system has not been modified.

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 (about 20°C).

The instrumentation used for measuring ozone at Zugspitze during this audit was identical with the configuration during the last audit in April 1996 and is shown below in table 2.

Instrumental details for the carbon monoxide analyser on site are listed in table 3.

Investigations are in progress aiming on characterising the effect and influence of differently processed zero air (wet or dry) supplies in operation at the site.

4.2.1. Ozone Analysers

Table 2: Field instruments

type	TEI 49 internal Code "C" #40-483-263	Bendix 8002 #5514880-2x
method	UV absorption	chemiluminescence
usage	basic instrument	backup instrument
at Zugspitze	since March 11, 1996	for several years
range	0-1000 ppb	0-100 ppb
analog output	0-10 V	0-1 V
instruments specials	internal ozone source	

According to the experience by IFU, the long-term stability and the sensitivity of the chemiluminescence instrument (Bendix 8002) has been comparable with the stability of the different UV instruments used in the course of time.

Zero air: for investigation purposes

- ambient air - MnO₂ filter
- pressurised ambient air - molecular sieve - activated charcoal (dewpoint: -40°C)

Comment

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

4.2.2. Carbon Monoxide Analysers

Table 3: Field instruments

type	TEI 48 S, internal code "B" #520 27-290	TEI 48 S, internal code "A" #290479 85-279
method	NDIR / GFC	NDIR / GFC
usage	basic instrument	backup instrument
at Zugspitze	since 1995	8.10.97
range	0-1000 ppb	0-1000 ppb
analog output	0-10 V	0-10 V

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 present, two continuously monitoring analysers (NDIR / GFC) are working in parallel at the Zugspitze. A GC / HgO system had been in operation for parallel measurements as well, but only for a certain time in spring 1997 and it is therefore not part of this audit.

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 analysers (NDIR / GFC), in use at present, show a continuous drift for the zero point potentiometer which makes a frequent zeroing of the system necessary. Thus, in a five-minute interval ambient air and zero is measured alternatingly. In this report we just show the audit-results of the basic instrument (TEI 48 S "B", #520 27-290), because the second instrument (internal code "A") is only used as a backup instrument. According to the operator these results are less precise than the results of the basic instrument.

Comment

Also for the carbon monoxide parallel measurements considerably increase confidence in data quality.

We appreciate the efforts in characterising the effect and influence of differently processed zero air and suggest to operate the GC / HgO system again.

4.3. Data Handling

At the time of the audit the data acquisition system at the site was in the process of renewal. The IFU constructed system (IDAS software and 12-bit A/DC) is being replaced by a self-developed TestPoint® application and a 16-bit A/D conversion. All data is stored on a server at the Zugspitze and transmitted on a daily basis via modem to the IFU.

The fields of responsibility of the operational group is split up into two parts. The technician at the site is responsible for the maintenance, while a different person is in charge of data reviewing and processing 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 of each analyser. These parameters are evaluated usually from a monthly data file but may also be extracted from a longer time period. Finally the data sets from the parallel measurements are compared by regarding differences for each parameter. With respect to creating a final data set, small deviations are accepted while greater differences point to problems. In such a case, based on the experience with the instruments, it is often known which of the two analysers is probably the more stable one. The values are accordingly adjusted. All raw data sets are stored.

Comment

Splitting up responsibilities requires well implemented communication tools to ensure that important information does not get lost on the way down to IFU. With the new data acquisition software it is presumed that the comprehensibility of the whole procedure will be improved.

The relative comparison between two instruments is seen as a useful instrument to judge data and adjust span or zero factors in a small term. The basis for changes of the calibration parameters (span and zero), however, should always be an absolute calibration using a traceable standard from the IFU calibration laboratory.

4.4. Operation and Maintenance

About once a week, a station technician visits the site for general maintenance. Exchange of the teflon filters at the instrument inlets is made every 6 weeks. Maintenance of the zero air supply on site includes semi-annually renewing of the absorbent cartridges of activated charcoal and molecular sieve. The same interval is chosen for the Sofnocat® (CO measurements). Preventive maintenance of the ozone and carbon monoxide instruments is performed on a case by case basis. Automatic combined zero and span checks are made as a daily check of the analysers (O₃ and CO) and are used for recalculating the final data set (approx. span check values: TEI 49: 65 ppb and 180 ppb ozone, Bendix: 65 ppb ozone, TEI 48 "A" and "B": 250 ppb CO).

Ozone Calibration: Around twice a year the ozone instruments are compared (multipoint) against a reference which is calibrated in the calibration laboratory at IFU.

CO Calibration: A synthetic CO working standard (low ppb) is prepared by IFU and calibrated against CMDL standards (ppb range). This working standard is used for the daily span checks and around every 3 months for manual calibration purposes.

Comment

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

It is noted that maintenance on a case by case basis has its advantage due to no unnecessary interruption of the operating of the instruments. However, it requires a lot of experience and knowledge about the instruments. Since this is the case at Zugspitze we do not recommend any change to this procedure, even though it differs from the description in the SOP of GAW report No. 97.

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 (bound) contained the necessary information for all parameters about maintenance, changes, events and special investigations listed chronologically in a bound book. A copy (carbon paper) of the station logbook is stored at the IFU for the purpose of data review. Additionally, since the middle of last year, a monitor logbook is attached to each instrument on site. It contains specific facts concerning the instrument as for example start of operation, calibrations or failures. The instrument manuals were either at the site or at the IFU available.

For data review the responsible person prints out time series diagrams. Further plots are made on demand, i. e. for data correction of parallel monitoring of a parameter or for special event studies. The acquired data is regularly sent to the GAW co-ordinator of the UBA Berlin. Part of the data is issued in scientific publications.

Comment

At the audit in spring 1996, in agreement with the responsible group, the documentation was seen as a major weak point. Since then, some extra effort to build up or upgrade the necessary logbooks was made and has led to an improvement 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. 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.

However, the pressure on the group has increased in terms of performing the same work with less personnel. Nevertheless, it is hoped that the high quality standard of the measurements can be maintained.

We enjoyed working with the people at IFU and had a pleasant stay in Garmisch-Partenkirchen.

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 the 11. and 12. 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.

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 IFU). 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

audit-team, EMPA	A. Fischer, A. Herzog
reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instruments:	- Bendix 8002 #5514880-2x - TEI 49 "C" #40-483-263
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: 697 hPa \pm 2 hPa and T_{indoor} : approximately 20°C
pressure transducers reading:	TEI 49C-PS: 697 hPa TEI 49 "C": 697 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:	2 x on November 11, 1997 1 x on November 12, 1997
connection between instruments:	less than 1 meter of 1/4" PFA tubing

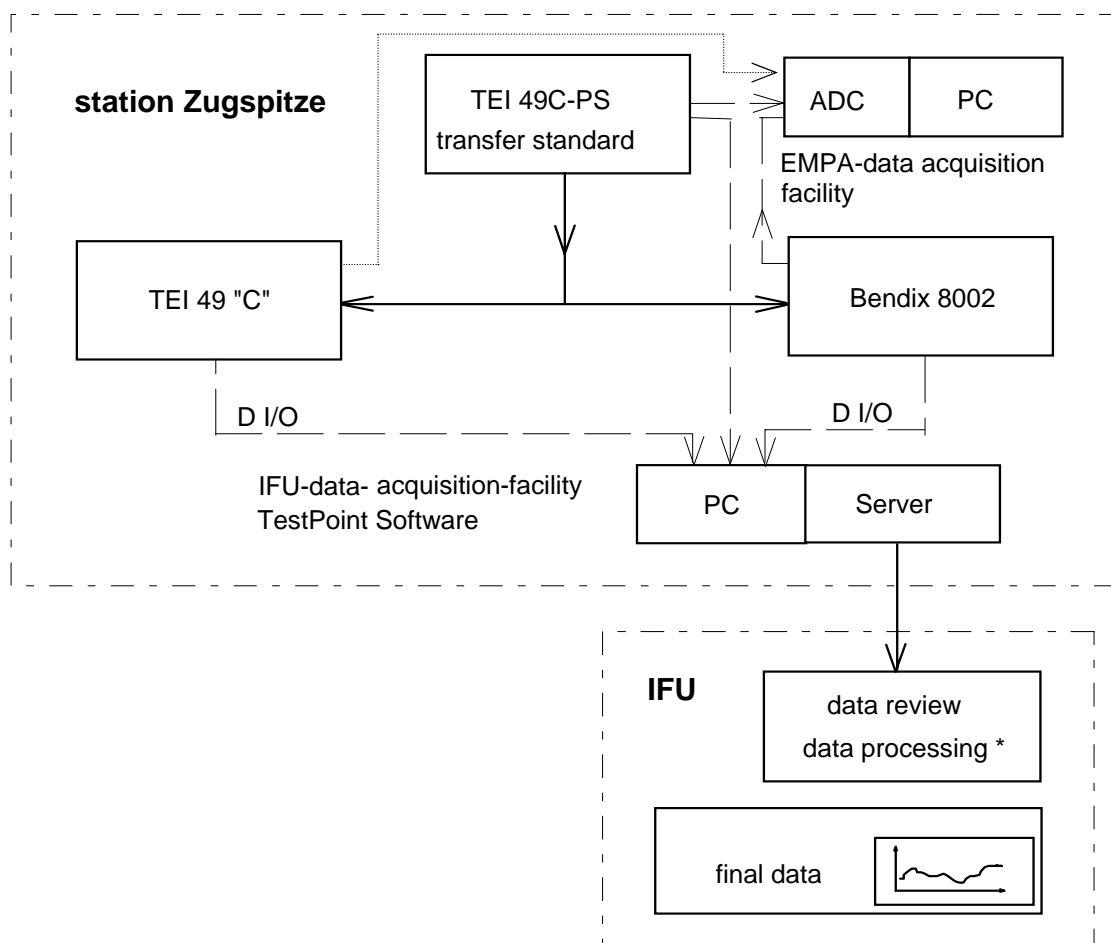


Figure 7: Experimental set up

* data processing = calculation of final results from the raw data by applying the appropriate values for zero and span. This may include corrections of previously used instrument parameters.
The software in use is TestPoint® a product of CEC (Capital Equipment Corp.)

5.2. Results

The results comprise three intercomparisons between the field instruments TEI 49 "C", Bendix 8002 and the transfer standard TEI 49C-PS, carried out on November 11 and 12, 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		TE 49 "C"				Bendix 8002			
	TE 49C-PS conc.	s _d	conc.	s _d	deviation from reference		conc.	s _d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	%
1	1.0	0.86	0.5	0.31	-0.5		0.2	0.10	-0.8	
2	34.9	0.16	35.0	0.52	0.1	0.3%	34.6	0.15	-0.4	-1.1%
3	54.9	0.12	55.2	0.19	0.3	0.5%	54.7	0.14	-0.2	-0.4%
4	95.0	0.15	95.2	0.28	0.3	0.3%	94.8	0.19	-0.2	-0.2%
5	75.0	0.22	75.6	0.42	0.6	0.9%	75.0	0.20	0.0	0.0%
6	15.0	0.13	14.7	0.57	-0.4	-2.4%	14.6	0.11	-0.4	-2.8%
7	0.5	0.30	0.1	0.35	-0.5		0.0	0.14	-0.5	

Table 6: 2. Intercomparison

No.	transfer standard		TE 49 "C"				Bendix 8002			
	TE 49C-PS conc.	s _d	conc.	s _d	deviation from reference		conc.	s _d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	%
1	0.7	0.43	0.0	0.35	-0.7		-0.1	0.11	-0.8	
2	75.0	0.38	75.5	0.43	0.4	0.6%	74.6	0.26	-0.4	-0.6%
3	35.0	0.16	35.0	0.39	0.0	0.1%	34.7	0.16	-0.3	-0.8%
4	95.0	0.18	95.0	0.18	0.0	0.1%	94.8	0.18	-0.2	-0.2%
5	55.0	0.18	55.2	0.17	0.2	0.3%	54.8	0.12	-0.2	-0.4%
6	15.1	0.20	14.4	0.28	-0.7	-4.7%	14.8	0.11	-0.3	-2.0%
7	0.8	0.54	0.0	0.30	-0.8		-0.1	0.06	-0.9	

Table 7: 3. Intercomparison

No.	transfer standard		TE 49 "C"				Bendix 8002			
	TE 49C-PS conc.	s _d	conc.	s _d	deviation from reference		conc.	s _d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	%
1	0.4	0.17	0.1	0.28	-0.3		0.2	0.08	-0.2	
2	54.8	0.14	54.6	0.31	-0.2	-0.3%	54.2	0.16	-0.6	-1.2%
3	94.9	0.26	95.3	0.33	0.4	0.4%	94.5	0.29	-0.4	-0.4%
4	34.9	0.20	34.6	0.18	-0.4	-1.1%	34.5	0.11	-0.4	-1.3%
5	74.9	0.13	75.5	0.31	0.6	0.8%	74.2	0.24	-0.7	-0.9%
6	15.0	0.19	14.7	0.85	-0.3	-2.1%	14.6	0.14	-0.4	-2.7%
7	0.6	0.12	0.2	0.38	-0.4		0.0	0.06	-0.5	

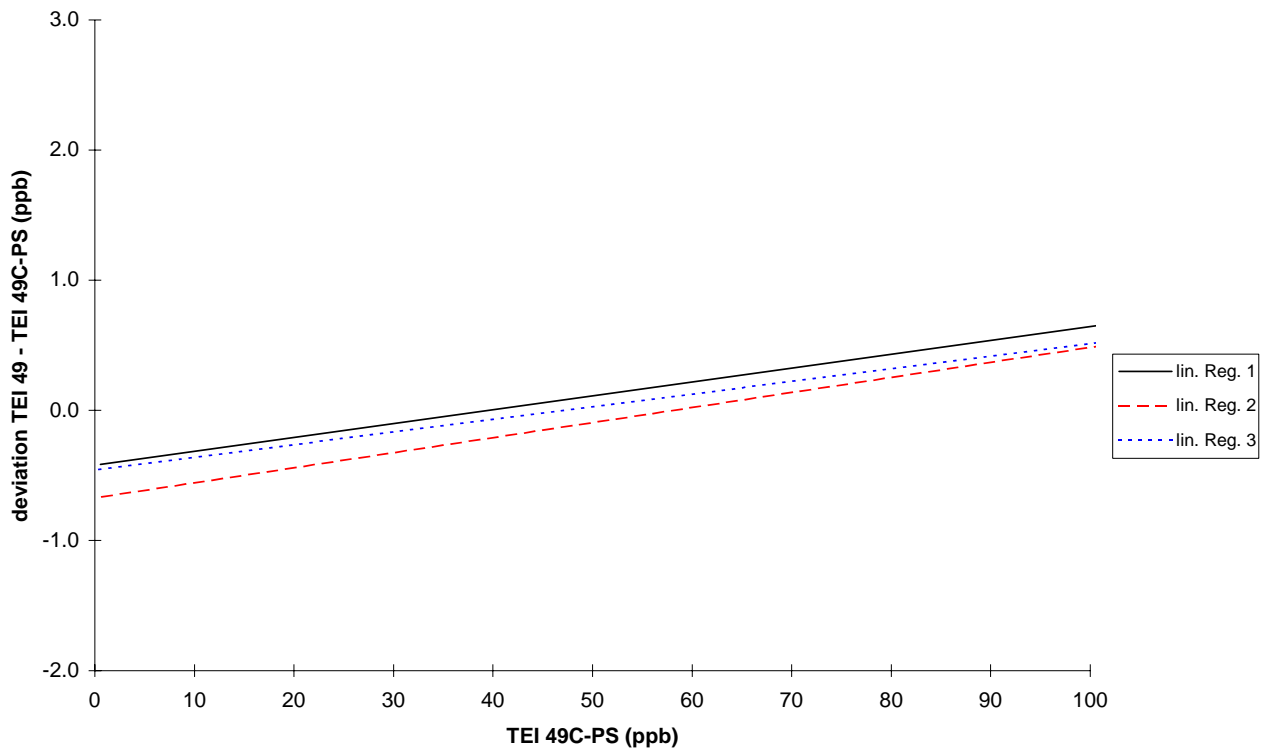


Figure 8: Individual linear regressions of intercomparisons 1 to 3, TEI "C"

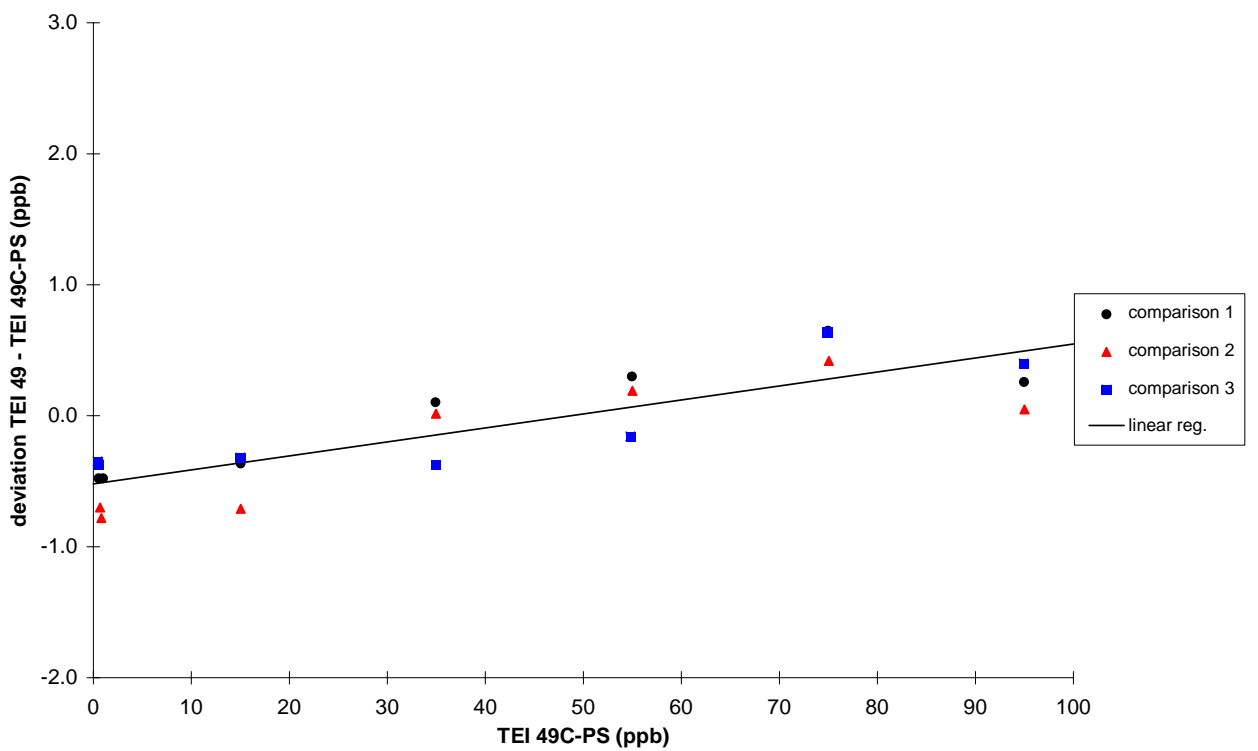


Figure 9: Mean linear regression of intercomparisons 1 to 3, TEI "C"

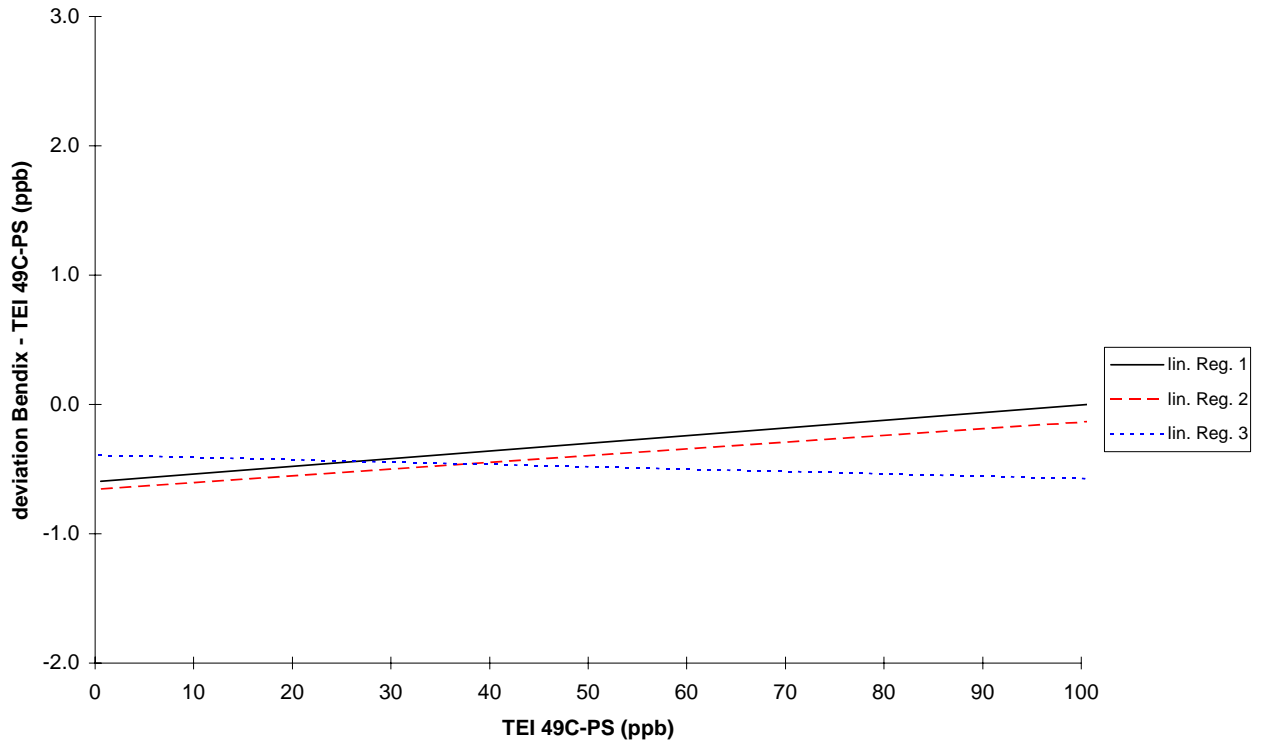


Figure 10: Individual linear regressions of intercomparisons 1 to 3, Bendix 8002

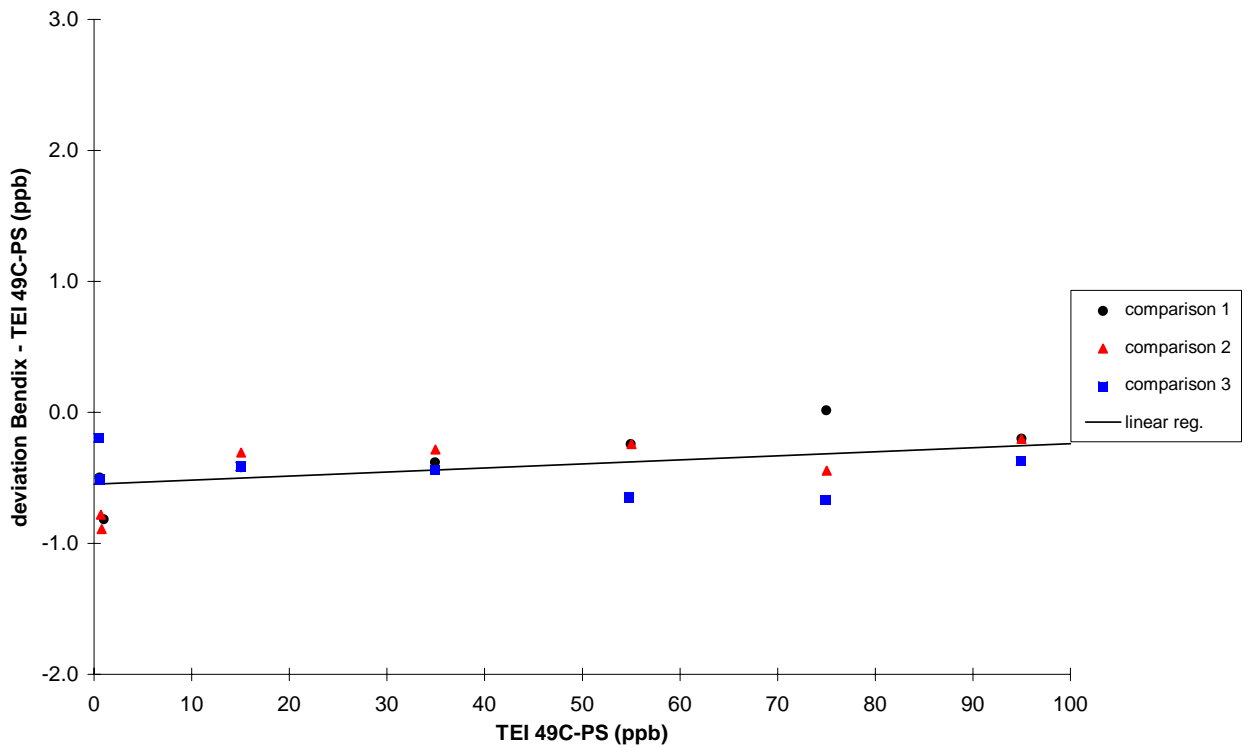


Figure 11: Mean linear regression of intercomparisons 1 to 3, Bendix 8002

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

-TEI 49 "C":

$$\text{TEI 49 "C"} = 1.011 \times \text{TEI 49C-PS} - 0.5 \text{ ppb}$$

TEI 49 "C" = O₃ mixing ratio in ppb, determined for TEI 49 #40-483-263

TEI 49C-PS = O₃ mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0015 (f = 3) f=degree of freedom
	- offset S_b in ppb	0.08 (f = 3)
	- residuals in ppb	0.24 (f = 19)

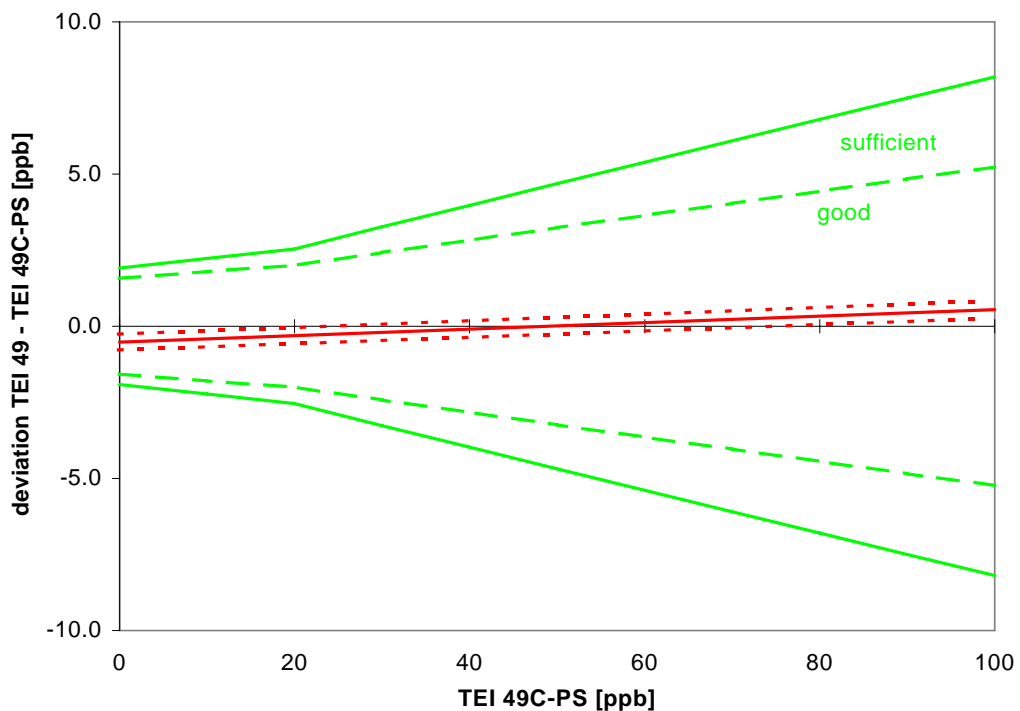


Figure 12: Intercomparison of instrument TEI 49 "C"

-Bendix 8002:

$$\text{Bendix 8002} = 1.003 \times \text{TEI 49C-PS} - 0.5 \text{ ppb}$$

Bendix 8002 = O₃ mixing ratio in ppb, determined for Bendix 8002 #5514880-2x

TEI 49C-PS = O₃ mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0013 (f = 3) f=degree of freedom
	- offset S_b in ppb	0.07 (f = 3)
	- residuals in ppb	0.21 (f = 19)

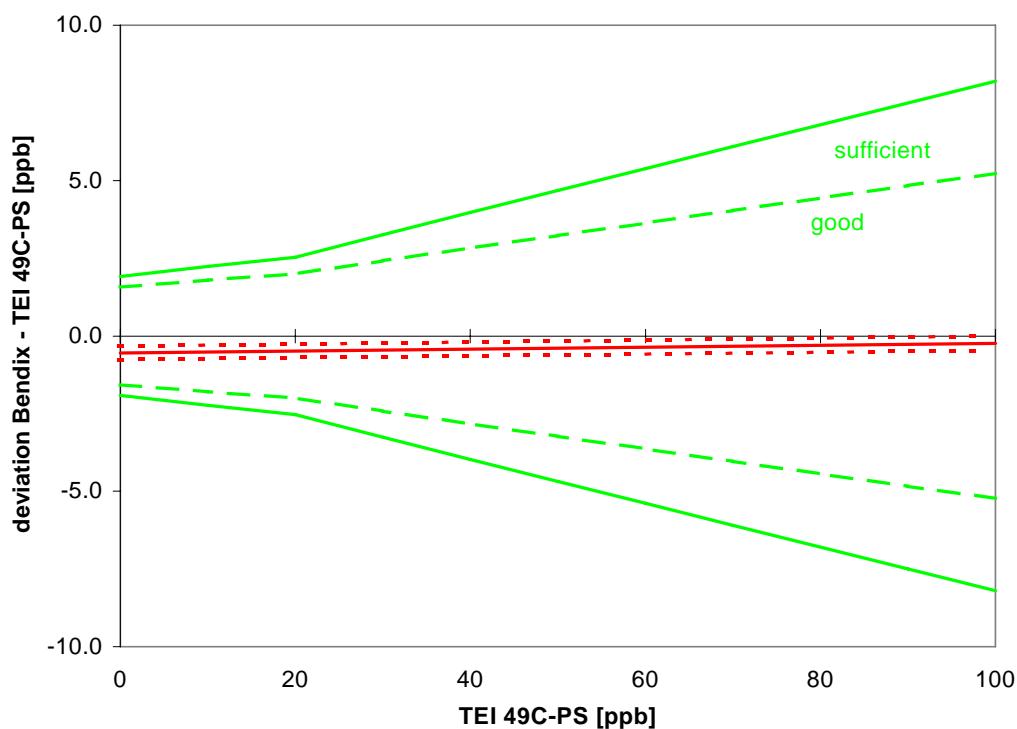


Figure 13: Intercomparison of instrument Bendix 8002

Comment

In the linear regressions of both instruments (figures 8 and 10) no trend as a function of time could be observed during the two days.

The ozone concentrations observed at Zugspitze (1996) usually ranged between 36 and 71 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 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 November 11 until November 14 the intercomparison was made with two field instruments by repeated switching between the measurement mode with calibration gas and zero-mode about every 5 minutes for 50 minutes for each concentration. The instruments were supplied with different concentration levels (figure 14). 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. The signals of the two field instruments were acquired by the EMPA data acquisition system. Because of the drifts of the instruments, the average zero signals were subtracted from the average measurement signals. These average signals were calculated after reaching stable values. IFU provided all data for the final results, except the data of the ambient air intercomparison.

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.

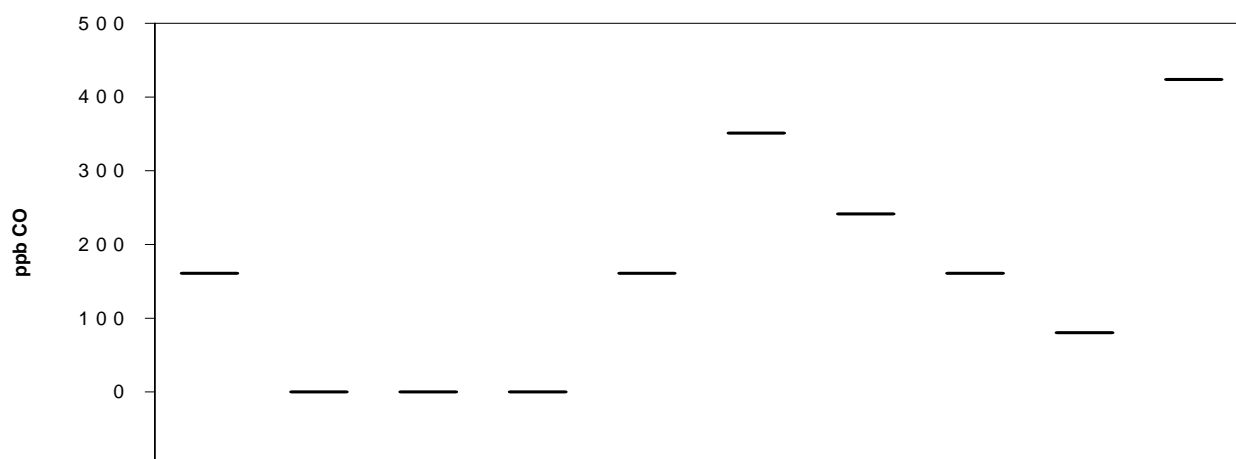


Figure 14: Sequence of concentrations during audit.

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 #520 27-290, "#B" (basic instrument) - TEI 48S #479 85-279, "#A" (backup instrument)
air inlet system (pre-treatment)	dried air (cooling trap)
zero air supply:	EMPA: synthetic air + Sofnocat IFU: #B ambient air + Sofnocat #A ambient air + Sofnocat
data acquisition system:	EMPA: 16 channel ADC circuit board, software
surrounding conditions:	p: 698 hPa \pm 2 hPa and T _{indoor} : approx. 20°C
concentration range:	0 - 1000 ppb
number of concentrations:	5 + zero air
approx. concentration levels:	80 / 160 / 240 / 350 / 420 ppb
sequence of concentration:	160/0/0/0/160/350/240/160/80/420 (figure 14)
averaging interval per concentration:	50 minutes
measuring cycle	5 minutes measurement-mode 5 minutes zero-mode
connection between instruments:	less than 3 meter of 1/4" PFA tubing

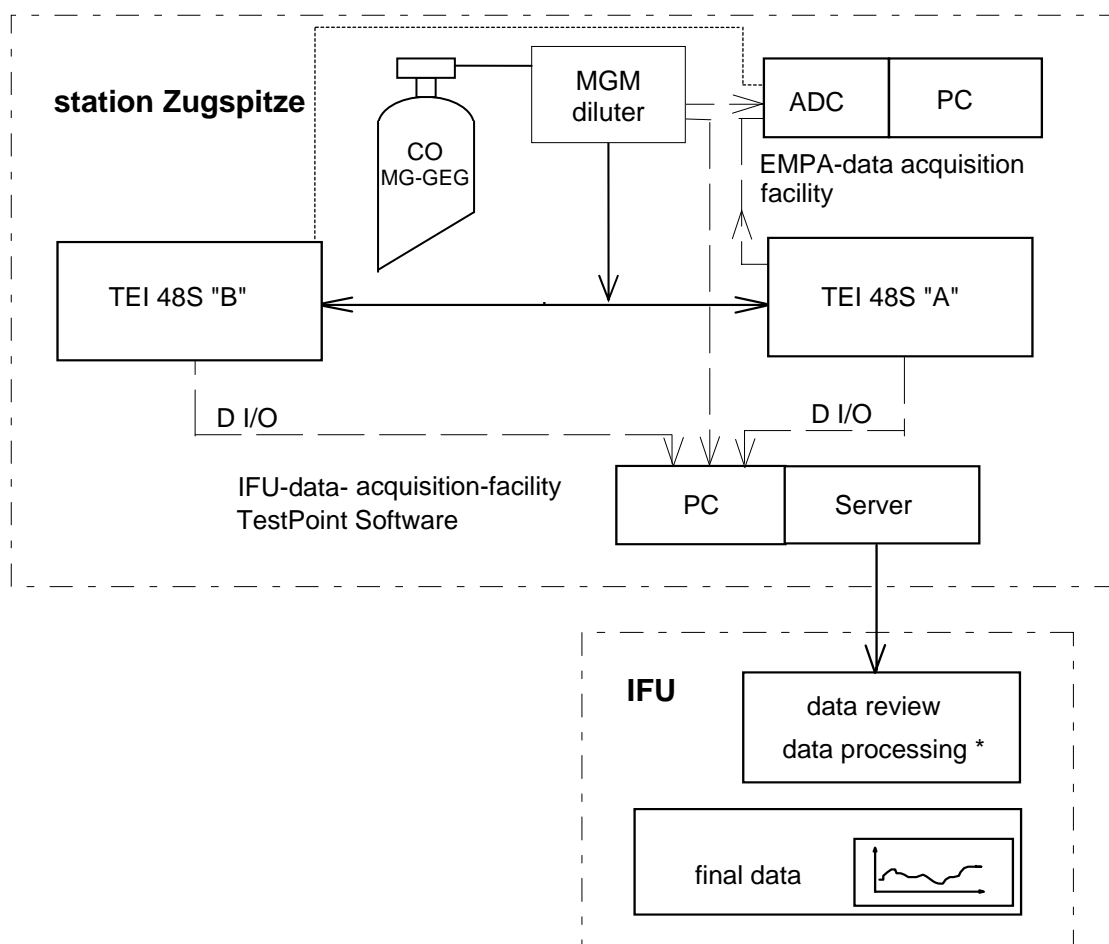


Figure 15: Experimental set up

* data processing = calculation of final results from the raw data by applying the appropriate values for zero and span. This may include corrections of previously used instrument parameters.

The software in use is TestPoint® a product of CEC

Before and during the audit the operator used ambient air (+Sofnocat) as zero air for calibration. During the audit the instruments of Zugspitze detected increased values for the zero air (synth. air + Sofnocat) of the audit team. Because of this the operator performed different tests during and after the audit with different kinds of zero air. There are different results for the two instruments used, at the site. Based on laboratory experiments, the operators had already been aware of this problem. At this time there is no explanation for these results. The operator of the site had planned to use synth. air (+Sofnocat) as zero air for the calibration, but it couldn't be installed in time for the audit (see Appendix IV).

6.2. Results

The results consists of 10 measurements between the field instruments TEI 48S "B" (basic instrument) and the transfer standard carried out on November 11 until November 14, 1997.

In the following table the resulting mean values of each carbon monoxide concentration and the standard deviations of a 50-minute interval with 5 measuring cycles (5 minutes measurement mode + 5 minutes zero mode) are 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 "B" compared to the EMPA transfer standard. In this report we just show the audit results of the basic instrument TEI 48S „B“, because the second instrument is only used as a backup instrument at the site. According to the operator, the results of the backup instrument are less exact than the results of the basic instrument.

Table 9: Intercomparisons

No.	transfer standard		TEI 48S "B"			
	MGM conc.	sd	conc.	sd	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	161.0	0.5	172.1	12.4	11.1	6.9
2	0		21.2	14.8	21.2	
3	0		8.0	10.2	8.0	
4	0		15.2	15.6	15.2	
5	161.0	0.5	160.5	10.6	-0.5	-0.3
6	351.1	1.2	336.3	12.2	-14.8	-4.2
7	241.5	0.6	241.1	16.4	-0.4	-0.2
8	161.0	0.5	166.4	18.3	5.4	3.4
9	80.4	0.2	96.1	10.3	15.7	19.5
10	423.8	2.1	391.2	14.4	-32.6	-7.7

The summary of the CO comparisons (for the CO range 0 - 420 ppb) of the TEI 48S "B" with the EMPA transfer standard is the following linear regression line:

-TEI 48S "B":

$$\text{TEI 48S "B"} = 0.8992 \times \text{TS} + 18.75 \text{ ppb}$$

TEI 48S "B" = CO mixing ratio in ppb, determined for TEI 48S #520 27-290

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 "B" and the Transfer standard.

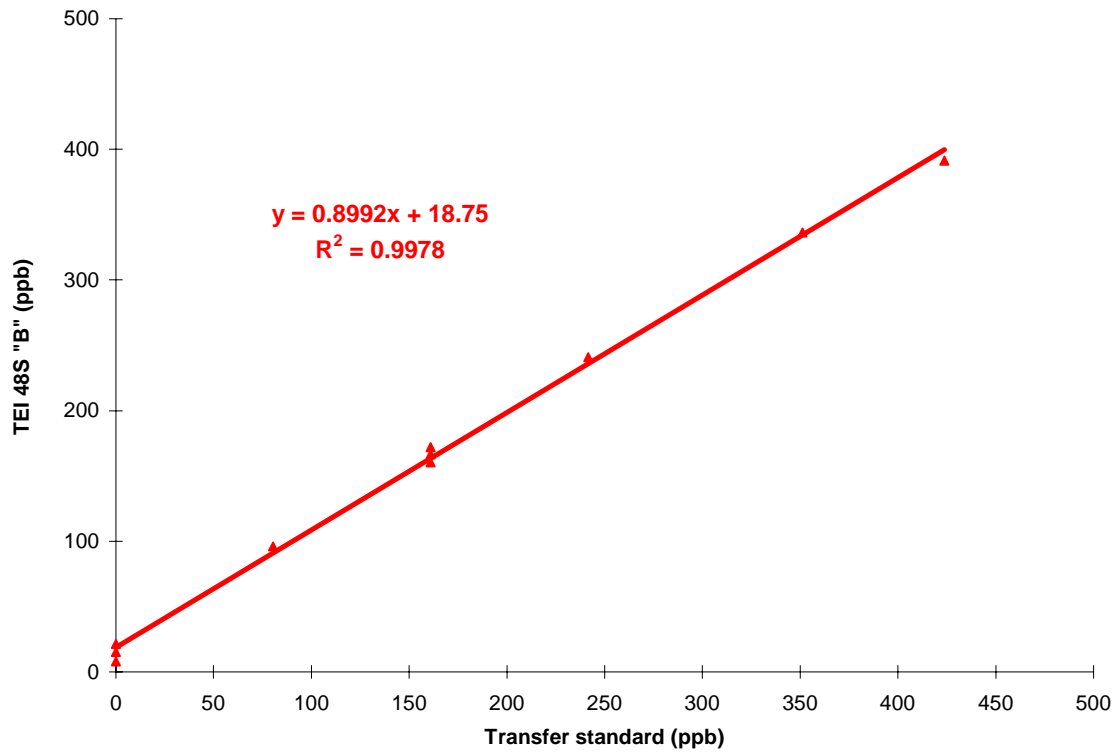


Figure 16: Mean linear regression analysis of field instrument TEI 48S "B".

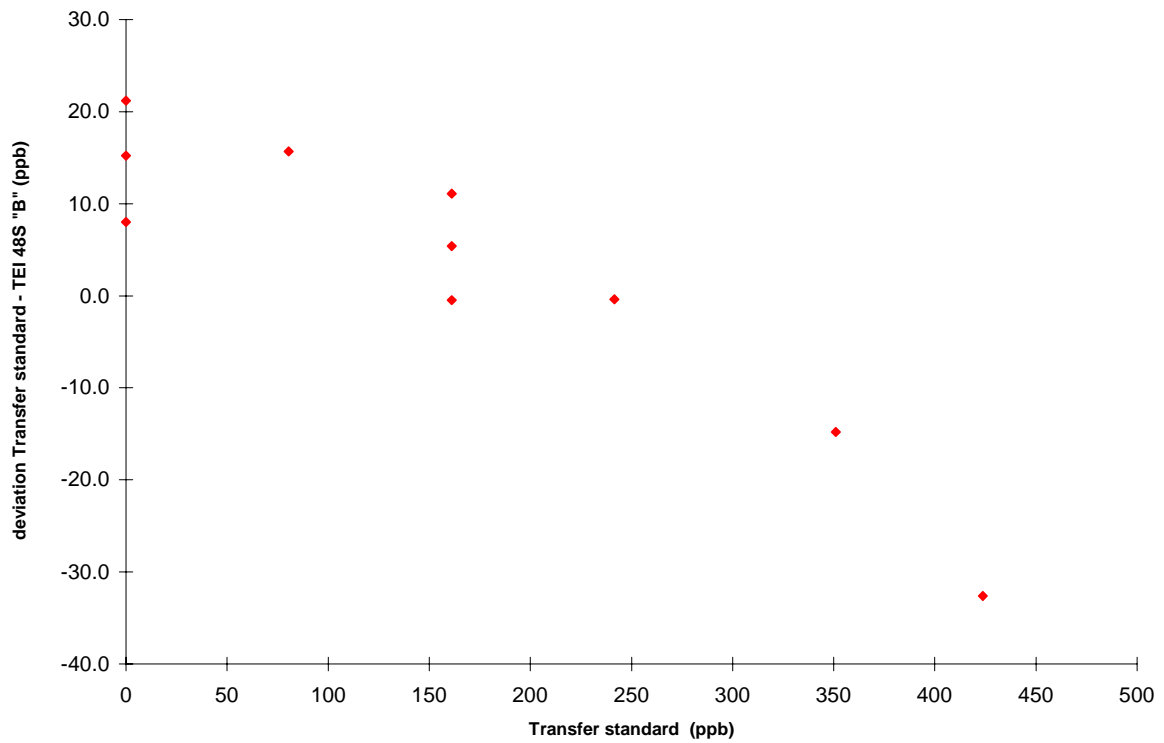


Figure 17: Absolute differences between TEI 48S "B" and the Transfer standard.

Figure 18 shows the relative differences (%) between TEI 48S "B" 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.

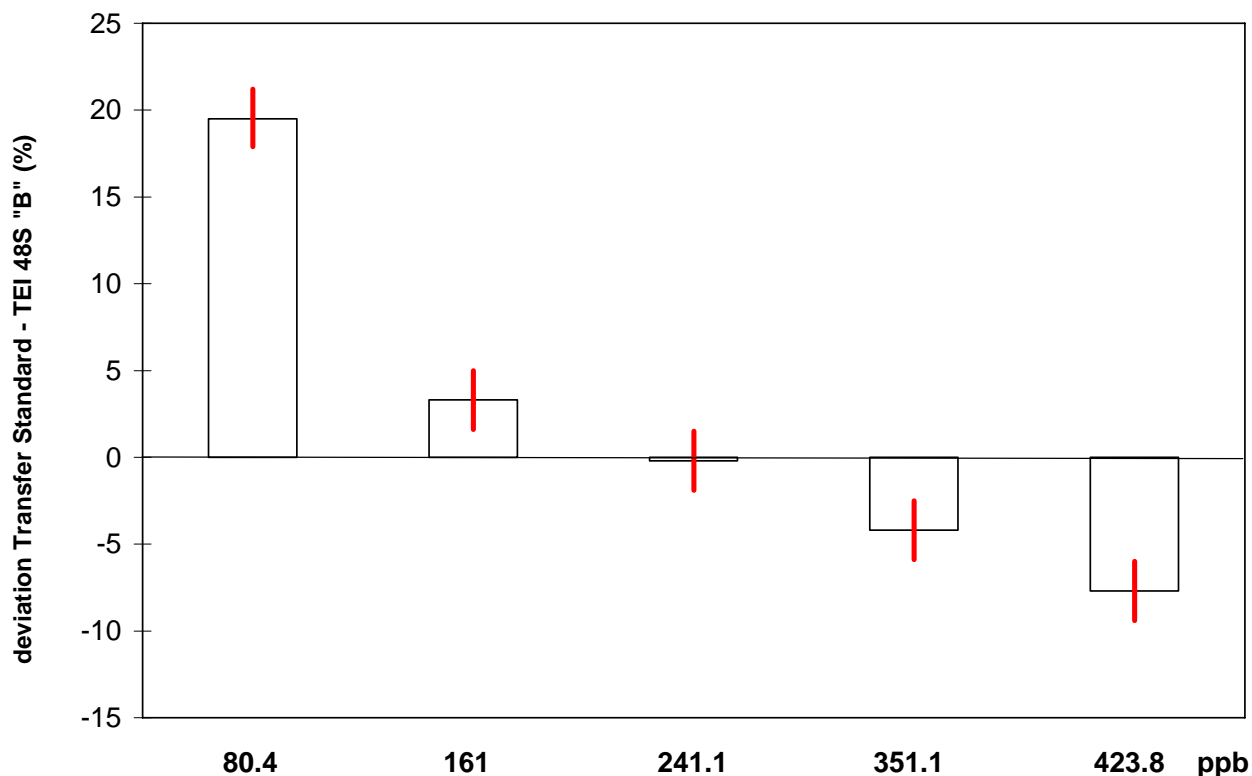


Figure 18: Differences (%) between TEI 48S "B" and the Transfer Standard. The red line shows the uncertainty of the Transfer Standard.

Because of the detected differences to the transfer standard, the audit team decided to perform an ambient air intercomparison during the night-time. During 16.5 hours (November 13, 3.30 p.m. until November 14, 8.00 a.m.) we carried out an ambient air intercomparison between the field instruments TEI 48S "B", and the transfer standard Horiba 360 APMA. In figure 19 the half hourly mean values (mean of 3 x 3minutes measurements) of the results of the TEI 48S "B" and the transfer standard are shown. The calculated mean values of the whole period are: 125 ± 12 ppb for TEI 48S "B" and 130 ± 14 ppb for the Horiba 360 APMA.

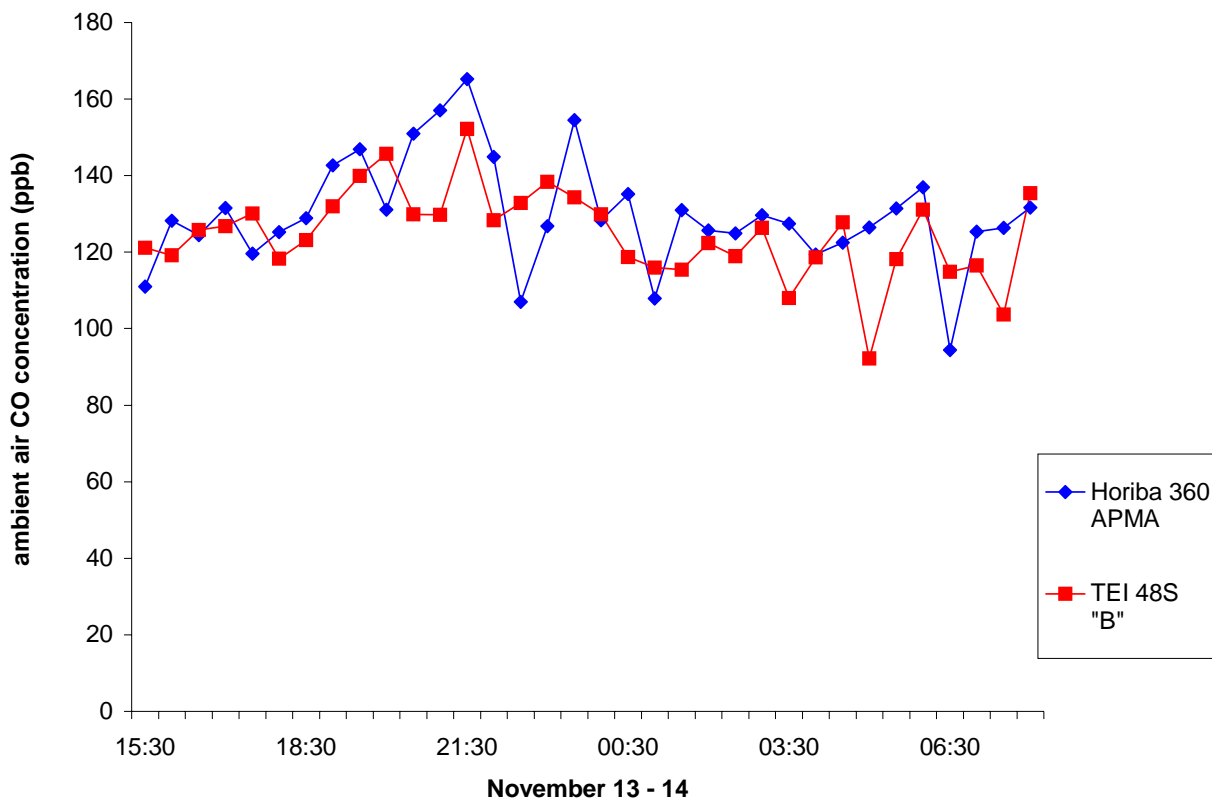


Figure 19: Ambient air concentrations measured with the field instrument TEI 48S "B" and the transfer standard Horiba 360 APMA.

Comment

The carbon monoxide concentrations observed at Zugspitze (1996) usually ranged between 95 and 235 ppb (5- and 95-percentile of hourly mean values).

Before and during the audit the operator used ambient air (+ Sofnocat) as zero air and span gas for calibration. So he used a humid/dry calibration (zero air / dry span gas) for his measurements. During the audit differences from a humid/dry to a dry/dry (zero air and span gas) calibration were detected. New calibration factors of a dry/dry calibration (after the audit) were applied to the audit results and to the ambient air intercomparison. Because of these factors the ambient air concentration measurements are well comparable to the results of the transfer standard instrument (Horiba). This suggests that calibration factors of a dry/dry calibration are applicable for ambient air measurements (humid/humid). The results of the different concentrations during the audit, demonstrate larger differences, because the calibration factors (dry/dry), determined after the audit are not well applicable to the humid/dry (zero mode/measurement mode) - measurement of the calibration gas.

It can be assumed, that with the new set-up of the calibration system (see „Changes after audit“ in Appendix Carbon Monoxide) these differences, detected during the audit, are eliminated.

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 20. 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.

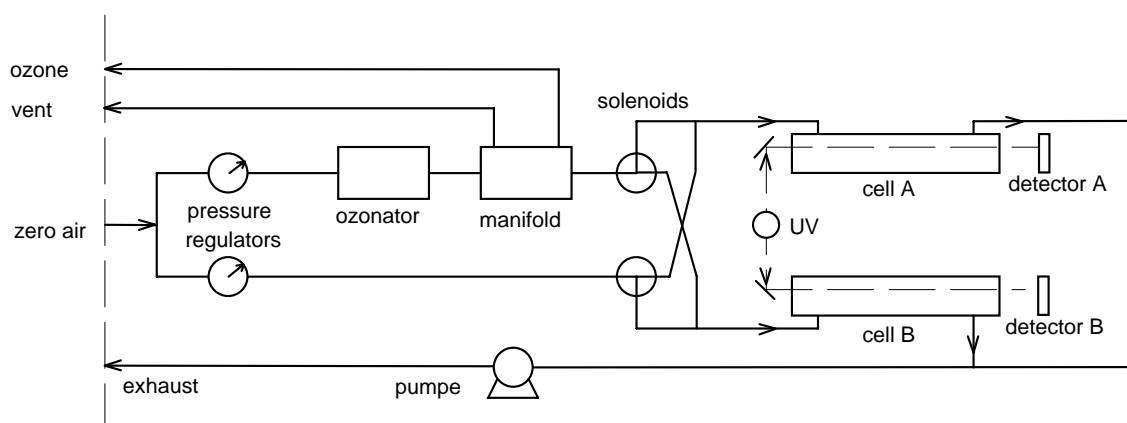


Figure 20: Flow schematic of TEI 49C-PS

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 21.

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

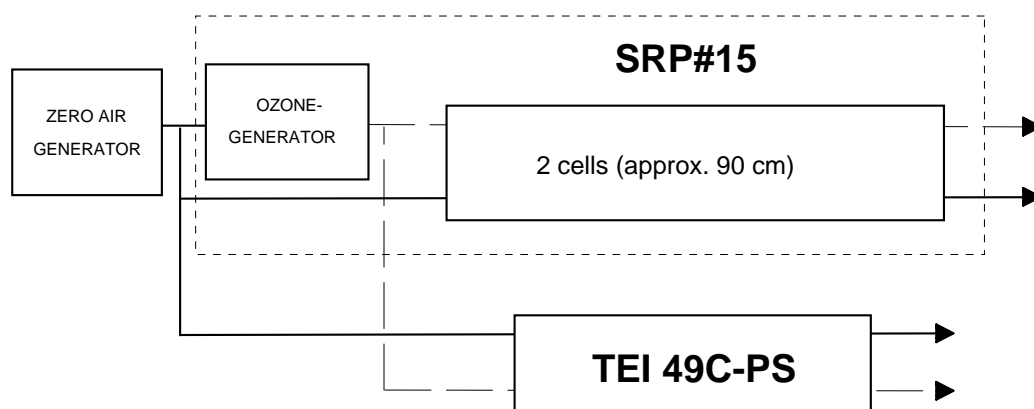


Figure 21: Instruments set up SRP -TEI 49C-PS

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 22 and 23 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.

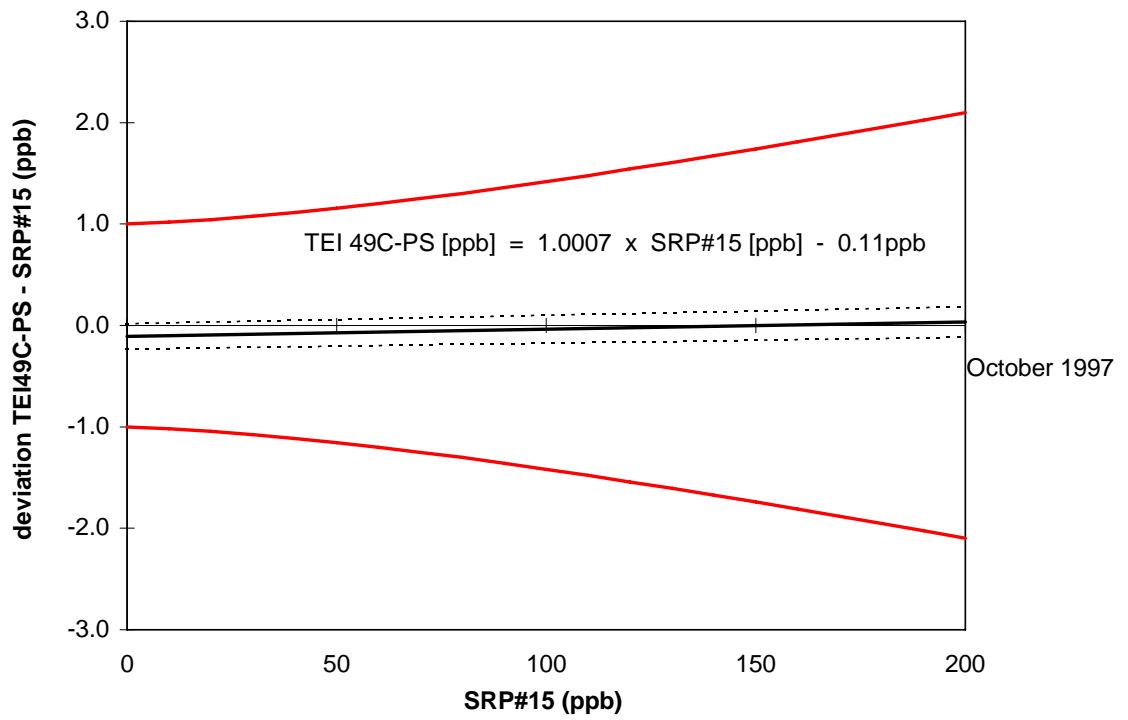


Figure 22: Transfer standard before audit

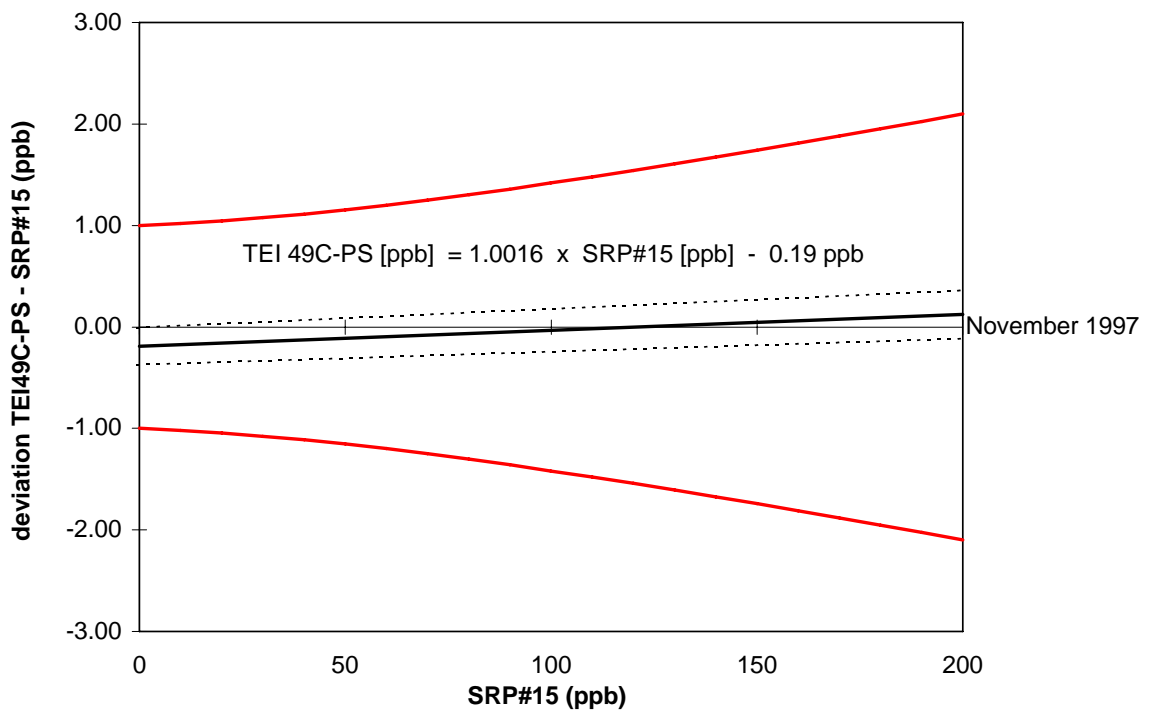


Figure 23: Transfer standard after audit

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 24 the traceability-chain of the carbon monoxide audit, used by the WCC-CO is shown.

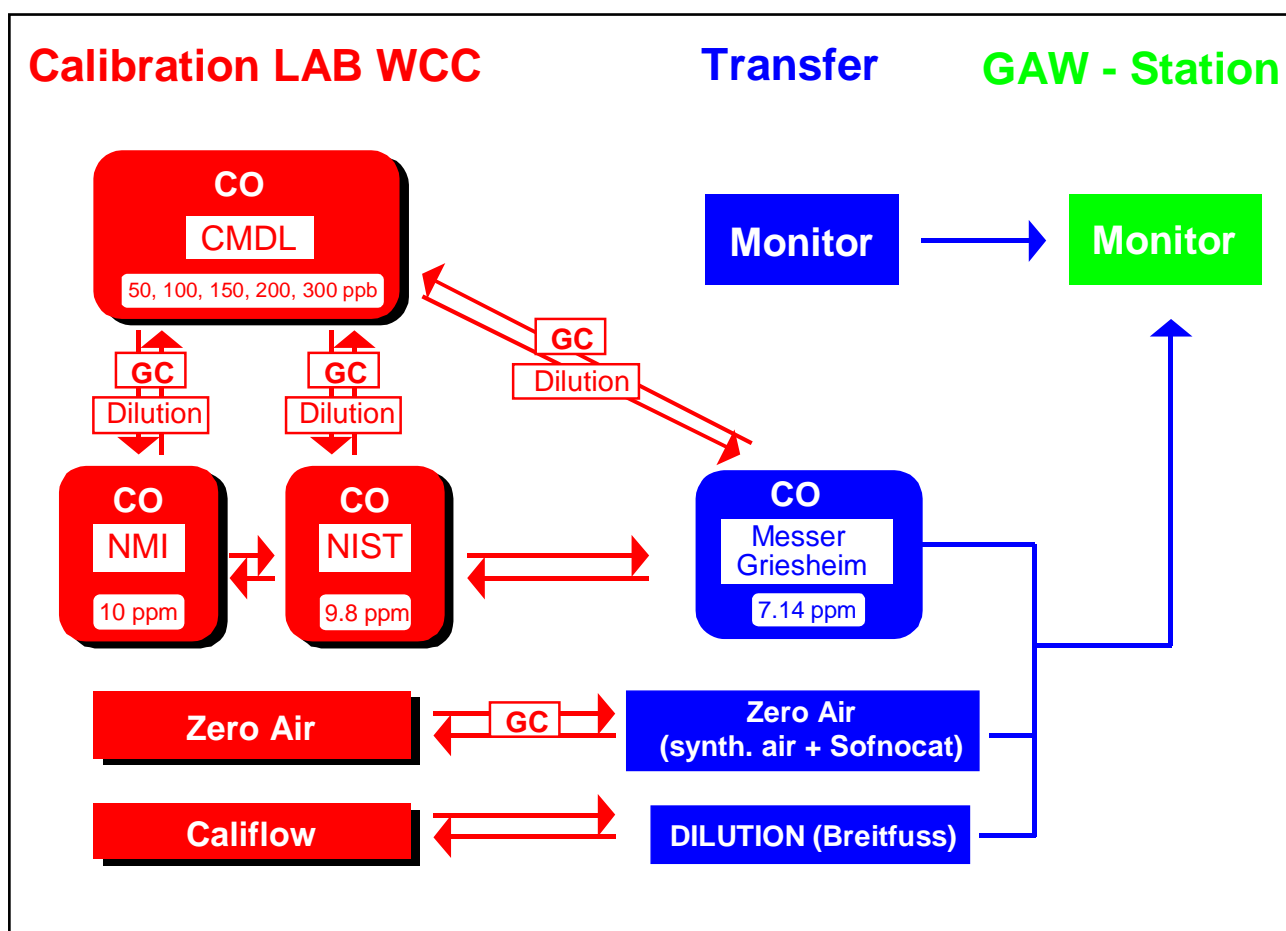


Figure 24: Traceability chain of the carbon monoxide audit.

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 widely used standard for measurements of atmospheric CO all over the world.

At EMPA we use the 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% (Kitzis D.R., NOAA/CMDL Carbon Cycle Group calibration laboratory, 1998, Personal Communication).

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, 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 (7.14 ± 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 25 (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

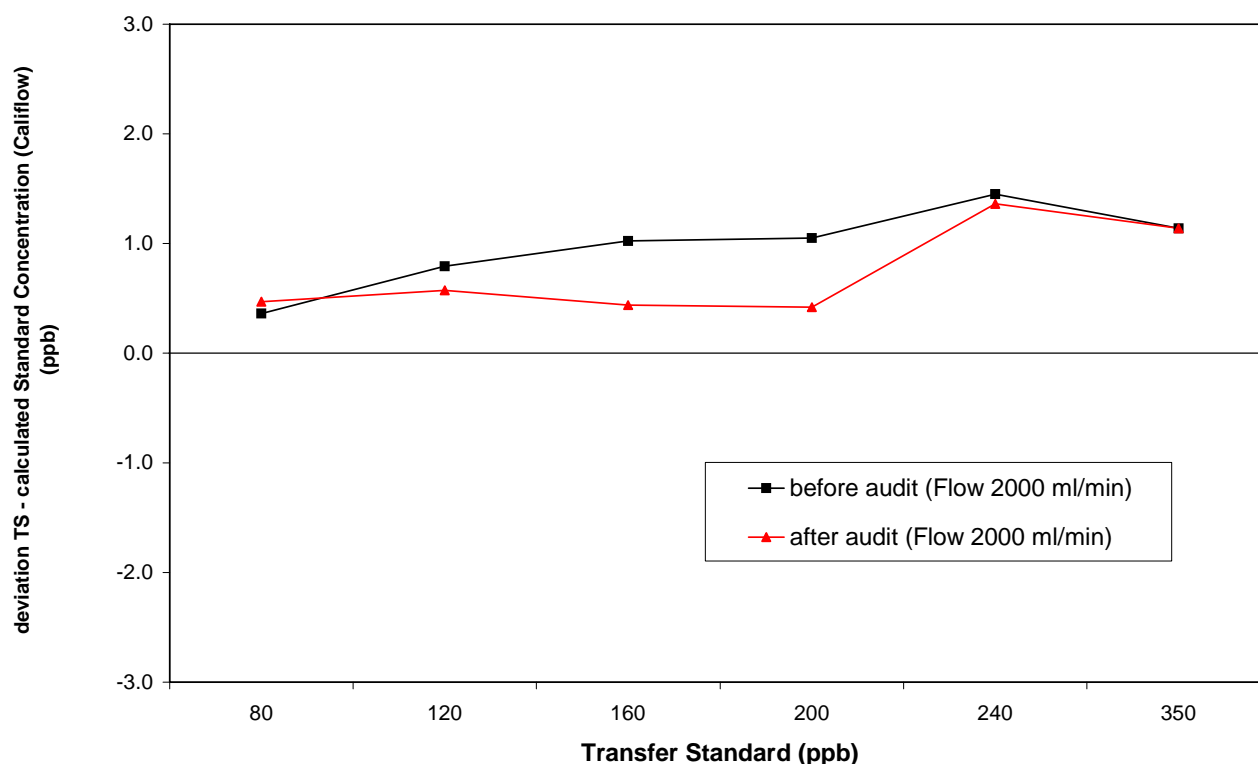


Figure 25: Transfer standard (TS) before and after audit.

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 instruments at Zugspitze and the transfer standard (Horiba 360 APMA) we made a calibration of the Horiba 360 APMA with zero-air and span-gas (350 ppb).

IV. Changes after audit

- New CO-set up at Zugspitze

This set-up was planned by the operator before the audit, but it couldn't be installed in time before the audit took place.

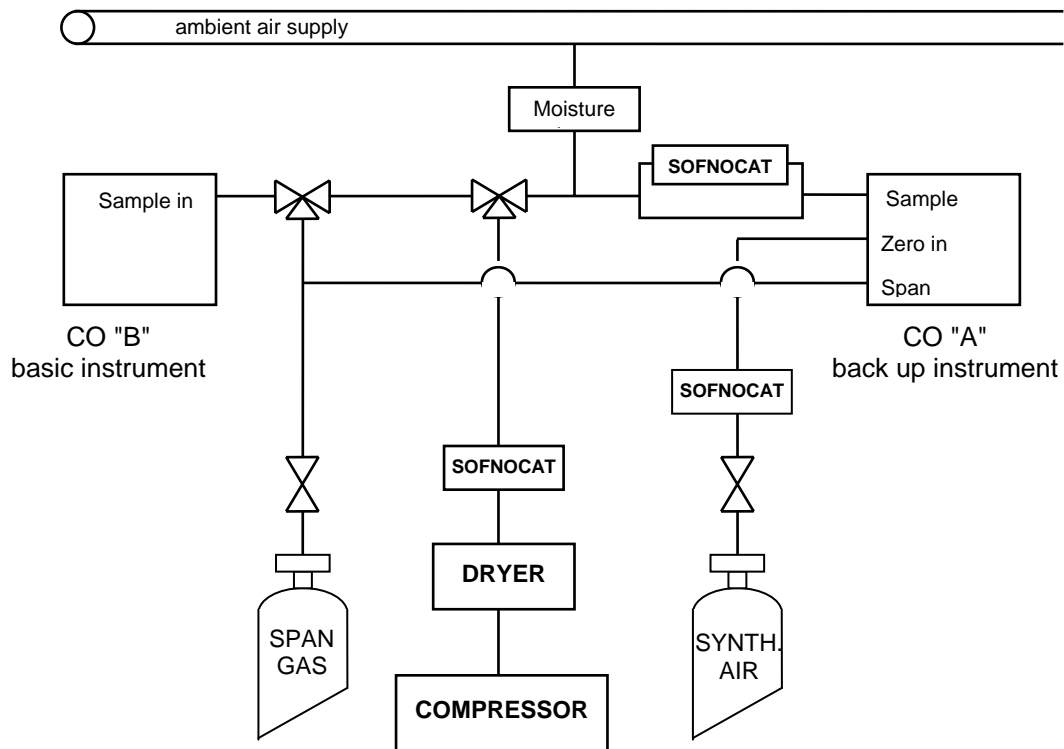


Figure 26: CO set up at Zugspitze.

- GC / HgO System (RGD 2)

The operator wants to bring the GC / HGO - System in operation again.