Global Atmosphere Watch
World Calibration Centre for Surface Ozone
WCC-O_3

Swiss Federal Laboratories for Materials Testing and Research (EMPA)

REPORT

Submitted to

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE

GLOBAL GAW STATION ZUGSPITZE

GERMANY, APRIL 1996

Submitted by

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WMO World Calibration Centre for Surface Ozone for Europe and Africa

Contents:

1. Abstract

A system and performance audit was conducted by the World Calibration Center for Surface Ozone, at the global GAW station Zugspitze, Germany. Below, the findings, comments and recommendations are summarised:

Air Inlet System:

The inlet system concerning materials as well as residence time is adequate with regard to minimal loss of ozone.

Instrumentation:

The operation of two ozone analysers in parallel at Zugspitze (chemiluminescence and UV-method), considerably increases confidence in data quality. However, since in the GAW programme the UV method is the preferred method it is regarded as important that the chemiluminescence instrument's (Bendix 8002) calibration is based on comparisons with UV instruments.

Data Handling:

It is suggested that the comprehensibility of the whole procedure could be simplified to increase the responsibility of all the persons involved.

The relative comparison between two field instruments should not be considered as a method for disregarding data but rather for detecting problems. An exception for disregarding data could be for example an obviously systematic temporal change of one of the instrument.

Operation and Maintenance:

The appearance inside the station is clean and functional.
Because the IFU staff has the required experience in operating an air monitoring station, carrying out maintenance on a case by case basis is the right choice. Even though it differs from the description in the SOP of the GAW report No. 97.

The calibrations should always be supplemented by a manual multipoint calibration using a transfer standard for reference.

Documentation:

It is recommended that some extra effort should be made to build up or upgrade the necessary documents.

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.

Instrument Intercomparisons:

In the usual range of ozone concentration level at the Zugspitze (above 20 ppb), both field instruments fulfil the assessment criteria as "good" (Figures 1 and 2).

Figure 1: Assessment criteria for GAW field instruments; TEI 49 "C"

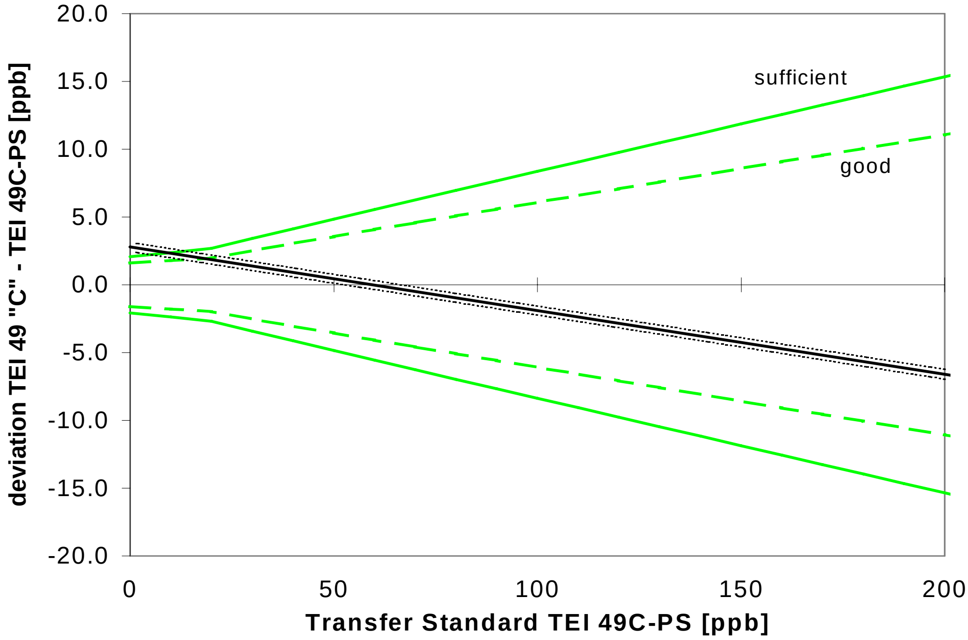
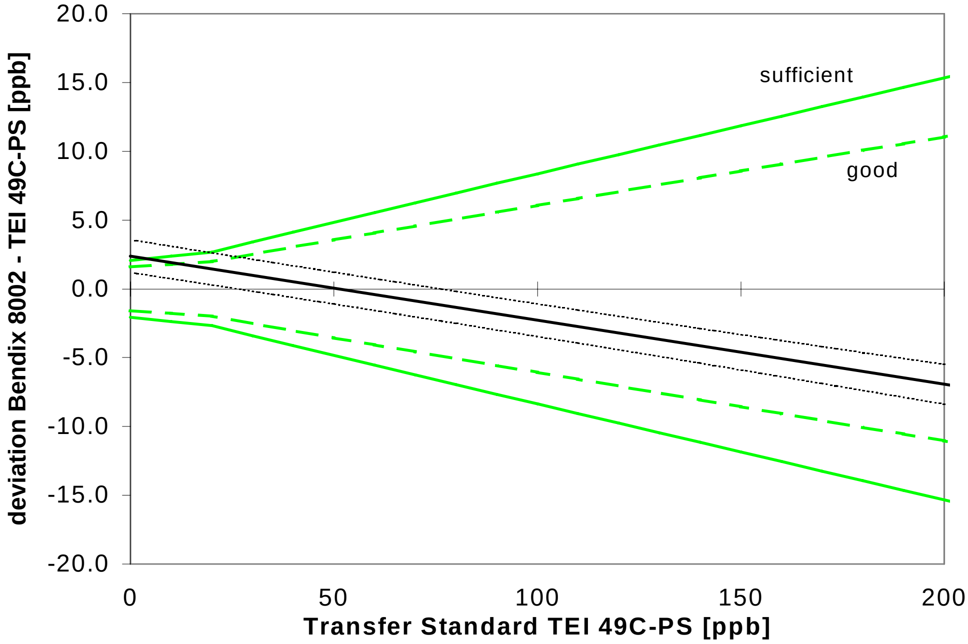


Figure 2: Assessment criteria for GAW field instruments; Bendix 8002



Dübendorf, 21. Decembre, 1996

EMPA Dübendorf, WCC-O_3

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2. Introduction

In establishing a coordinated 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 Center for Surface Ozone for Europe and Africa (WCC-O_3). At the beginning of this year our work started within the GAW programme. The detailed goals and tasks of the WCC-O_3 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 ozone 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 free troposphere.

The scope of the audit which took place from April 1 to 3 in 1996, was confined to ozone measurements including the whole process beginning with the inlet system on the roof of the station up to the data correction at IFU. The audit procedure at Zugspitze was performed according to the Standard Operating Procedure (SOP) for "Performance auditing ozone analysers at global and regional WMO-GAW sites" in the WMO-GAW report No. 97.

3. Global GAW Site 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 from Garmisch directly to the summit of the Zugspitze.

The new monitoring station (coordinates: 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.

Picture of the station Zugspitze:

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 120 scientists and technicians. The group of Dr. Scheel, head of the section measurement techniques and analytical, is responsible for the operation of the station at Zugspitze. The structure of the station management at IFU is shown in Table 1.

Table 1: Operators

Prof. W. Seiler Director of the Fraunhofer Institute for Atmospheric Environmental Research (IFU)
Operators and Observers Dr. H.E. Scheel, Responsible for the station Mr S. Glück, Station maintenance Mr R. Müller, Data processing Mr R. Sladkovic, Data management and supervision
Experts Prof. V.A. Mohnen, QA/SAC Europe/Africa Dr. W. Junkermann Mr H.J. Kanter

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 in strong wind conditions. The main glass manifold (ID approx. 8 cm) leads directly into the shelter and is flushed by about 1000m^3 (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.

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 with regard to minimal loss of ozone.

4.2. Instrumentation

The instruments are installed in an environmentally controlled room (about 20°C) and are protected from direct sunlight in an instrument rack.
The instrumentation used for measuring ozone at Zugspitze during the audit is shown in table 2 below.

Table 2: Field instruments

type	TEI 49 internal Code "C" #40-483-263	Bendix 8002 #5514880-2x
method	UV absorption	chemiluminescence
usage	backup instrument	basic 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	
	direct signal output from the instruments digital board	

The zero air supply at Zugspitze consists of pressurised air filtered through two cartridges, one packed with molecular sieve and the other with activated charcoal.

Due to the experience by IFU, the long-term stability of the sensitivity of the chemiluminescence instrument (Bendix 8002) has been comparable or even better than the stability of the different UV instruments used in the course of time. Therefore and because the Bendix 8002 has been in operation for several years without major interruptions IFU regards it as the basic instrument at the Zugspitze. Nonetheless, its calibration is based on comparisons with UV instruments.

Comment

The operation of two ozone analysers in parallel at Zugspitze (chemiluminescence and UV-method), considerably increases confidence in data quality. Moreover, the fact that two different analytical methods (UV and chemiluminescence) are used increases the possibility of detecting interferences with other trace species. However, since in the GAW programme the UV method is the preferred method it is regarded as important that the chemiluminescence instrument's (Bendix 8002) calibration is based on comparisons with UV instruments.

4.3. Data Handling

An IFU constructed data acquisition facility is installed at the site and is connected via modem to the laboratory at IFU. Data transmission is carried out automatically.

The fields of responsibility of the operational group is split up into two parts. The technicians at the site are responsible for the maintenance meanwhile the staff at the institute is in charge of data reviewing and processing. 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. This may include corrections of previously used parameters. Finally these data are compared with each other by regarding differences. With respect to create a final data set deviations up to 1 ppb 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. Still the raw data sets are stored.

Comment

Splitting up responsibilities requires well implemented communication tools to ensure that important information gets not lost on the way down to IFU. It is suggested that the comprehensibility of the whole procedure could be simplified to increase the responsibility of all the persons involved.

The relative comparison between two field instruments should not be considered as a method for disregarding data but rather for detecting problems which should be investigated by absolute calibration using a NIST traceable transfer standard (UV method). An exception for disregarding data could be for example an obviously systematic temporal change of one of the instrument.

4.4. Operation and Maintenance

Maintenance of the zero air supply includes semi-annually renewing of the absorbents and monthly exchange of the teflon filters at the instrument's inlet. Preventive maintenance of the instruments is performed on a case by case basis. Automatic zero and span checks are made as a daily check of the ozone analysers and are used for recalculating the final data set. As a routine, parallel measurements of ambient air between the field instruments and a calibrated ozone analyser are carried out on site over a period of time. The ozone instrument used as reference is calibrated in the calibration laboratory at IFU. Additionally, but only if major drifts of sensitivity are noticed without their cause being obvious, the problem is tried to localise by concurrent measurements of ambient air or by multipoint calibration.

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.

The disadvantage of performing calibrations based on parallel measurements of ambient air only is that, given by an average ozone variation during several days at Zugspitze of about 20 ppb, only a small range of ozone concentrations can be covered. This results in a large uncertainty of the calibration curve for all other concentration levels. Therefore parallel measurements should always be supplemented by a manual multipoint calibration using a transfer standard for reference.

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's maintenance logbook (bound, copy with carbon paper) was at the site and contained all necessary information.

Comment

However, for an external person, it has not been easy to survey and obtain the desired information quickly. The lack of SOPs for maintenance and operation is well known by the group. This will be improved as soon as possible. Due to the mentioned separation of maintenance and data processing this may be even more important. Therefore it is recommended that some extra effort should be made to build up or upgrade the necessary documents.

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 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) was hooked up to power for warming up over night in deviation from the GAW report No. 97 which recommends only one hour of warm-up. During this stabilisation time the standard and the PFA tubing connections to the instruments were conditioned with air containing 100 ppb ozone. The next day three comparison runs between the two field instruments and the EMPA transfer standard were performed. In the meantime the inlet system and the station's documentation were inspected. Table 3 shows the experimental details and Figure 3 the experimental set up of the audit.

In general, no modifications of the ozone analysers were made for the intercomparison. An exception was the Bendix 8002 instrument which is usually used in the 100 ppb range. Therefore, for the first two comparisons with the transfer standard TEI 49C-PS the higher ozone concentrations (120 and 180 ppb) could not be measured. For the third comparison the range of the Bendix 8002 was switched to 0-200 ppb.

It was noticed that the data acquisition system of the EMPA, consisting of an ADC circuit board and a PC with the corresponding software, when hooked up to the analog output of the field instruments influenced the TEI 49 "C" (decreased values), but not the Bendix 8002. So, the regular data acquisition facility of IFU was used for collecting the data of all instruments. In parallel the signals from the Bendix 8002 and of the transfer standard were acquired by the EMPA system. IFU provided all data for the final results. This was justified, since only minor differences occurred between the two data acquisition systems.

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

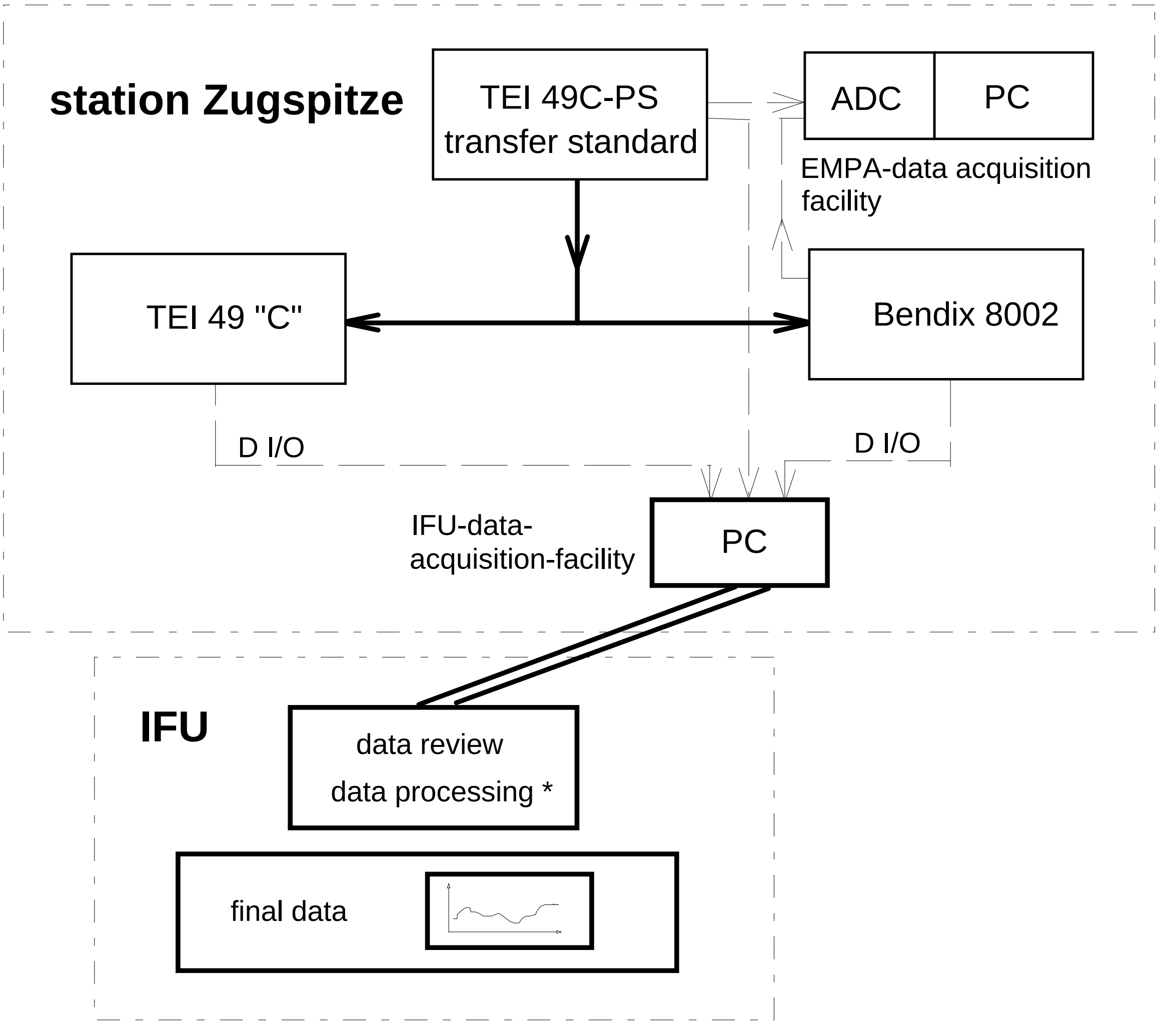
The audit procedure included a direct intercomparison of the TEI 49C-PS transfer standard with the Standard Reference Photometer SRP#15 (NIST UV photometer) before and after the audit in the calibration laboratory at EMPA. The results are shown in the Appendix.

Table 3: Experimental details

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:	IFU constructed system
surrounding conditions:	p: 693hPa ±2hPa and T_{indoor}: around 20°C
pressure transducers reading:	on April 2., 15:00 : surrounding: 694hPa TEI 49C-PS: 693.5hPa TEI 49 "C": 649.8hPa
concentration range:	0 - 200 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 120 / 180 ppb
sequence of concentration:	random

averaging interval per concentration:	5 minutes
number of runs:	3 x on April 2, 1996
connection between instruments:	less than 1 meter of 1/4" PFA tubing

Figure 3: 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.

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 April 2, 1996.

In the following tables the resulting mean values of each ozone concentration and the standard deviations of five one-minute-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 4: 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	-1.2	0.11	1.7	0.24	2.9		1.6	0.17	2.8	
2	60.2	0.10	59.9	0.22	-0.3	-0.4	60.6	0.13	0.4	0.7
3	180.1	0.04	174.4	0.30	-5.7	-3.2				
4	90.2	0.15	88.9	0.13	-1.3	-1.4	89.2	0.09	-1.0	-1.1
5	30.2	0.26	31.7	0.15	1.5	4.8	32.0	0.18	1.8	6.1
6	120.3	0.17	117.2	0.25	-3.0	-2.5				
7	-0.9	0.29	1.9	0.26	2.8		1.7	0.24	2.6	

Table 5: 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	-0.9	0.29	1.9	0.26	2.8		1.7	0.24	2.6	
2	90.0	0.13	89.0	0.16	-1.0	-1.1	88.5	0.15	-1.6	-1.7
3	180.1	0.14	174.2	0.15	-5.9	-3.3				
4	60.1	0.06	60.3	0.17	0.2	0.4	59.2	0.17	-0.8	-1.4
5	120.2	0.19	117.6	0.18	-2.6	-2.2				
6	30.1	0.11	31.5	0.42	1.5	4.8	31.0	0.27	0.9	3.0
7	-1.0	0.33	1.4	0.18	2.4		-0.7	0.09	0.3	

Table 6: 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	-1.3	0.12	1.8	0.22	3.1		1.6	0.15	2.9	
2	180.1	0.10	174.4	0.32	-5.7	-3.2	173.8	0.51	-6.2	-3.5
3	120.1	0.12	117.4	0.11	-2.8	-2.3	116.5	0.29	-3.7	-3.0
4	90.0	0.14	88.5	0.15	-1.5	-1.7	87.7	0.23	-2.3	-2.5
5	60.0	0.17	59.8	0.20	-0.2	-0.3	59.4	0.32	-0.6	-1.0

6	29.9	0.23	31.2	0.22	1.3		31.0	0.19	1.1	

Figure 4: Individual linear regressions of intercomparisons 1 to 3, TEI "C"

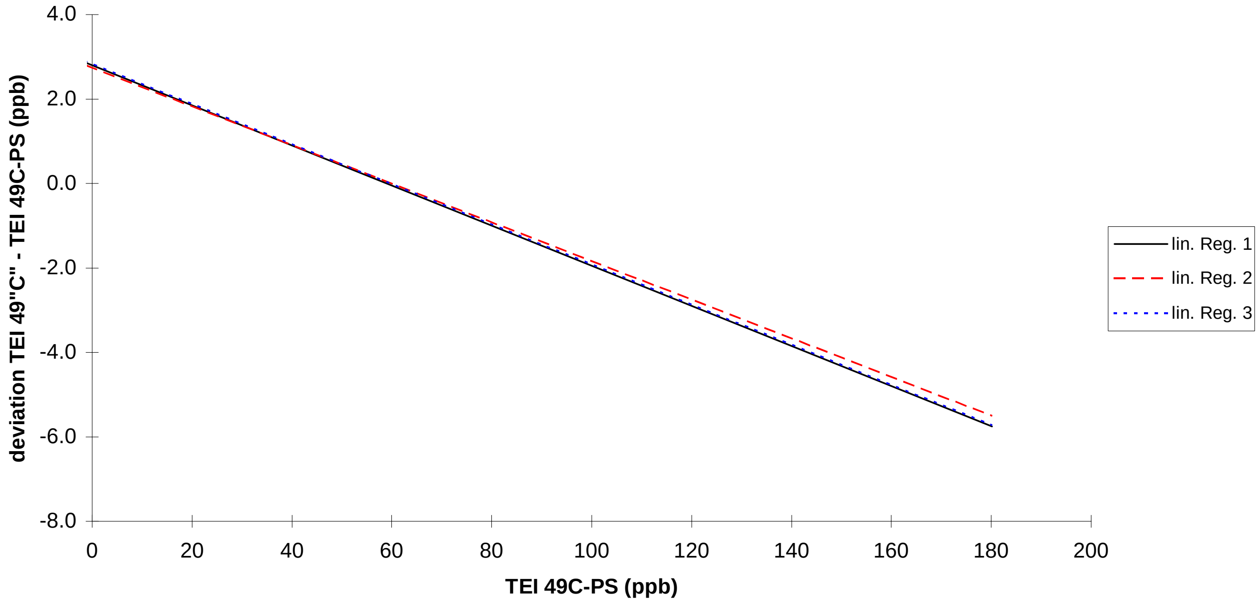


Figure 5: Mean linear regression of intercomparisons 1 to 3, TEI "C"

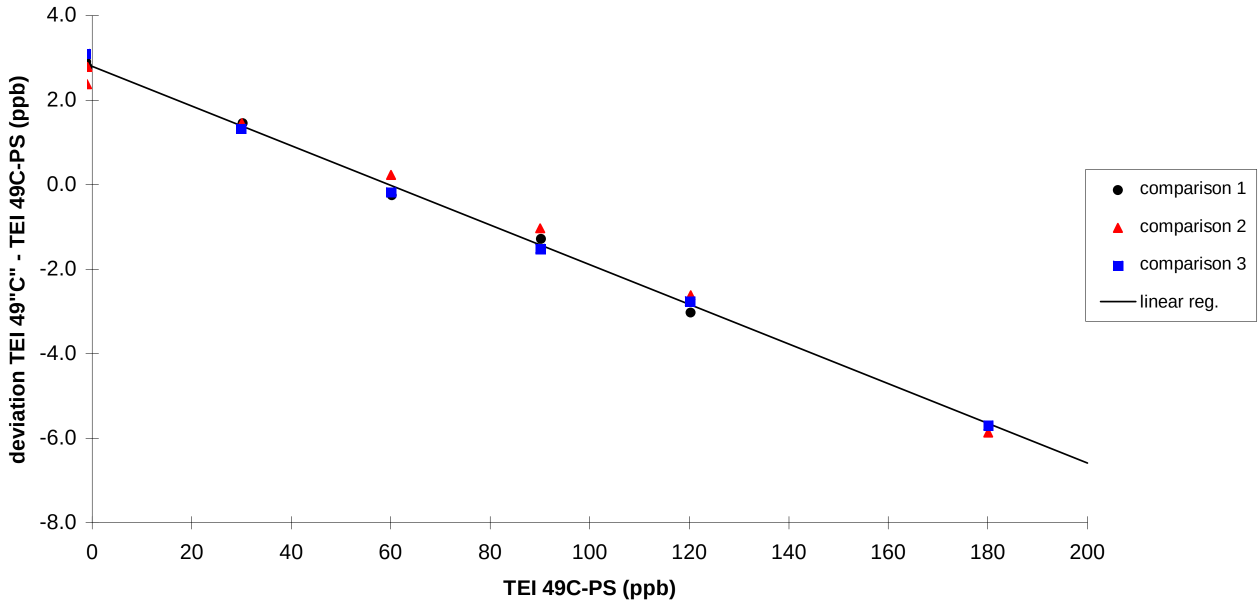


Figure 6: Individual linear regressions of intercomparisons 1 to 3, Bendix 8002

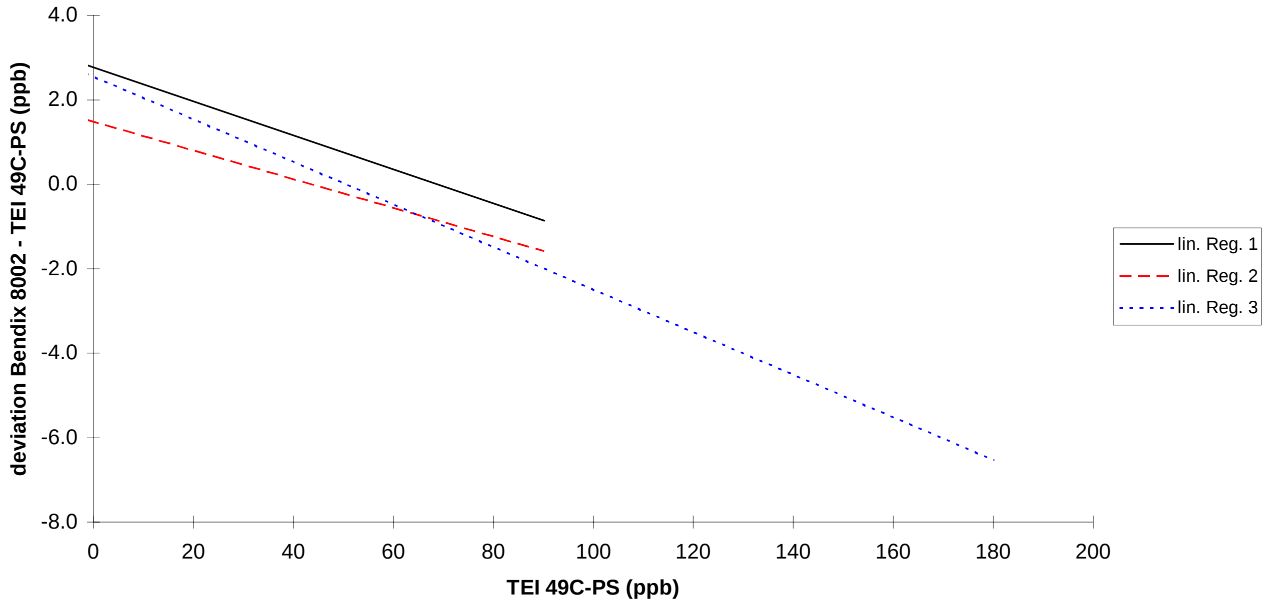
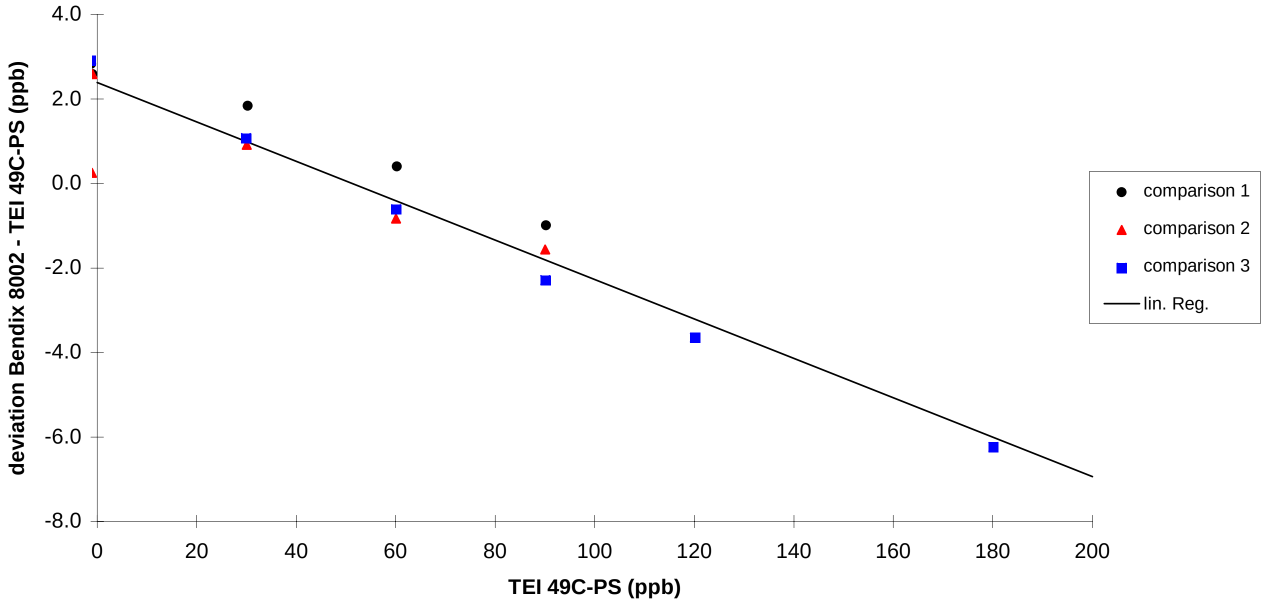


Figure 7: Mean linear regression of intercomparisons 1 to 3, Bendix 8002



From the comparisons of the TEI 49 "C" and the Bendix 8002 field instruments with the EMPA transfer standard the resulting linear regression (for the range of 0-200 ppb ozone) are:

-TEI 49 "C":

$$\text{TEI 49 "C"} = 0.9531 \times \text{TEI 49C-PS} + 2.79 \text{ ppb}$$

TEI 49 "C" = O_3 mixing ratio in ppb, determined for TEI 49 #40-483-263
TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.00075 (f = 19) f=degree of freedom
	- offset S_b in ppb	0.071 (f = 19)
	- residuals in ppb	0.192 (f = 3)

-Bendix 8002:

$$\text{Bendix 8002} = 0.9534 \times \text{TEI 49C-PS} + 2.38 \text{ ppb}$$

Bendix 8002 = O_3 mixing ratio in ppb, determined for Bendix 8002
TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.00373 (f = 15) f=degree of freedom
	- offset S_b in ppb	0.272 (f = 15)
	- residuals in ppb	0.482 (f = 3)

Comment

In Figures 4 and 6 of the linear regressions of both instruments, no trend as a function of time could be observed during the day. Such an occurrence could indicate insufficient warm up time (stability) or pollution in the measurement cells or chambers of the instrument.

Figures 5 and 7 as well as the standard deviations of the slope, the offset and the residuals indicate that the repeatability of the TE 49 "C" was better than that of the Bendix 8002 during the audit.

The resulting mean linear regressions of the two field instruments, which show only minor differences, certainly reflect the way IFU adjusts the data of their ozone meters (see 4.3. Data Handling). The absolute deviations of the mean regressions of the two instruments from the EMPA transfer standard are small and fulfil the assessment criteria as "good" for ozone concentrations higher than 20 ppb. For lower values (< 20 ppb) the instruments were assessed outside tolerance. However, for the concentration range which is relevant for the site Zugspitze the deviations were very low, at only about 1%.

Appendix

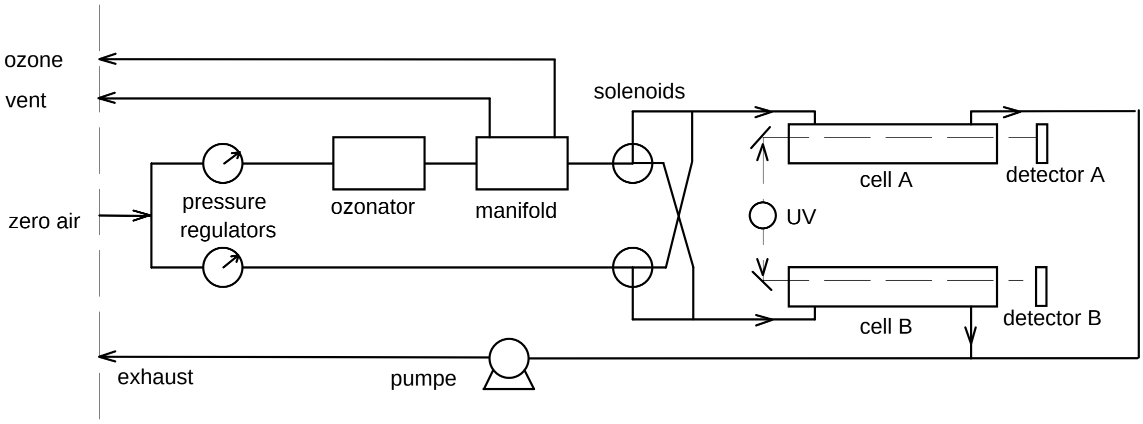
EMPA Transfer Standard TEI 49C-PS

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 8. 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 8: Flow schematic of TEI 49C-PS



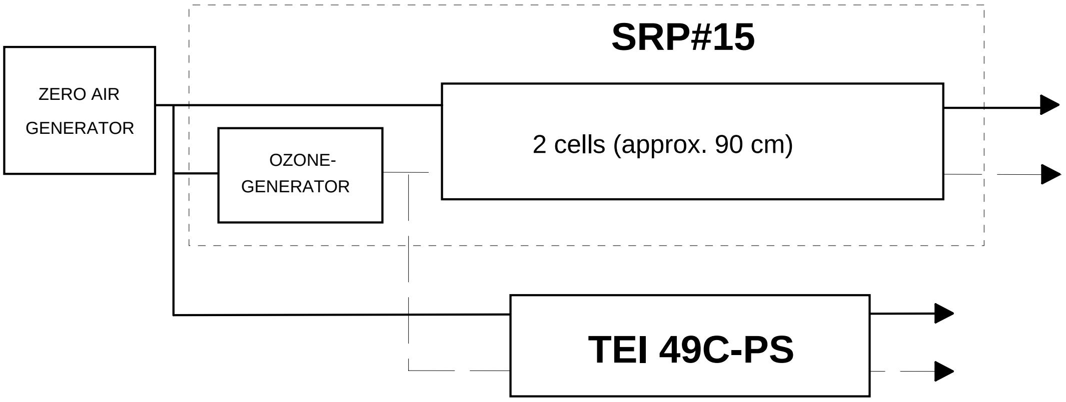
Stability of the Transfer Standard TEI 49C-PS

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 9.

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 - 250 ppb
number of concentrations:	6 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 120 / 180 / 240 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	2 before and 2 after audit
zero air supply:	Pressurised air - activated charcoal - zero air generator (AADCO)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

Figure 9: Instruments set up SRP -TEI 49C-PS



The stability of the transfer standard is well examined in respect of the component's uncertainties (systematic error and precision). For the GAW transfer standard of the WCC-O_3 (TEI 49C-PS) the assessment criteria, taking in account the uncertainty of the SRP, is defined to ±(1 ppb + 0.7%).

Figures 10 and 11 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 10: Transfer standard before audit

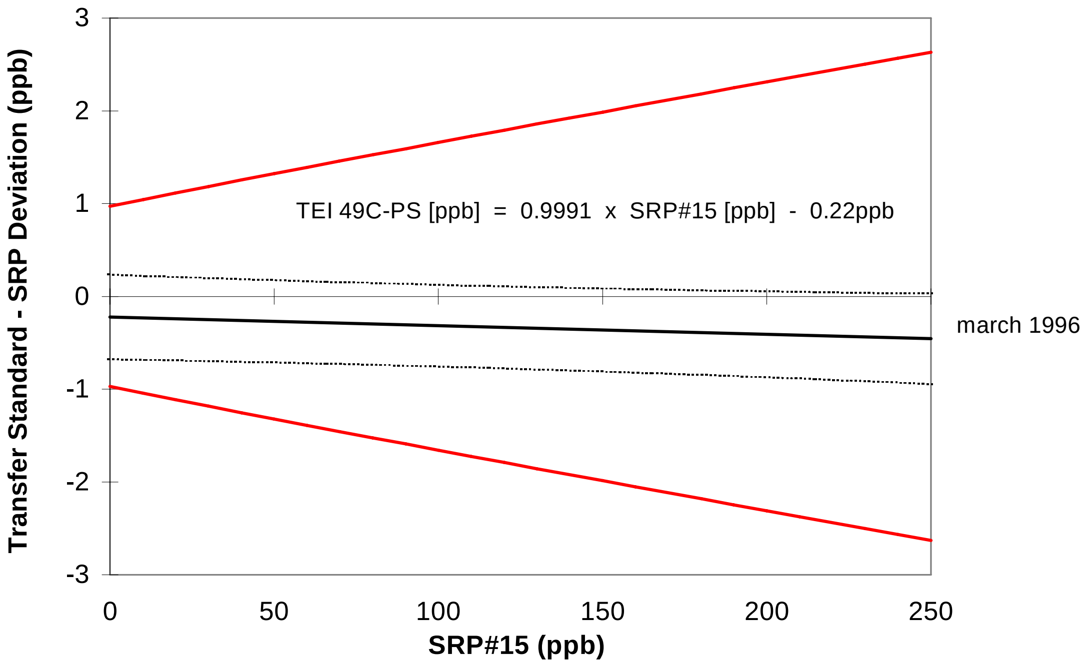


Figure 11: Transfer standard after audit