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

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

REPORT

Submitted to the

World Meteorological Organisation

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE

GLOBAL GAW STATION IZAÑA

TENERIFE, NOVEMBER 1996

Submitted by

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WMO World Calibration Centre for Surface Ozone for Europe and Africa

EMPA Dübendorf, Switzerland

Contents:

1. Abstract

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

Air Inlet System:

The inlet system, concerning construction materials as well as residence time, is adequate for gas analysis. No loss of ozone could be detected.

Instrumentation:

The operation of two ozone analysers in parallel at Izaña, considerably increases confidence in quality of the data. However, the data submitted to the GAW data centre can only originate from one ozone analyser. Therefore, in aiming for continuity, one instrument should be clearly defined as the basic instrument for a longer term.
In order to minimise interferences with other trace species, the different processing of zero air for zero check and span check should be avoided.

Data Handling:

The procedure of data treatment for each instrument is organised and clearly arranged. Since the two instruments are operated in parallel, it is recommended to compare the data with regard to deviations. Thereby, the practice of removal of suspect data could be carried out on a more certain basis. Furthermore, by means of other parameters, like wind speed and relative humidity, the data plausibility check would be improved.
The reprocessing of the data at a more regularly, at least a monthly interval is recommended. In this manner detecting irregularities would be possible earlier.

Operation and Maintenance:

The appearance of the station is clean and functional.
One of the main factors of quality assurance is the regular intercomparison by multipoint calibration between the analyser and an ozone reference that is traceable to the NIST. High priority should be given to the purchase of such an instrument.
It is noted that the advantage of maintenance on a case by case basis is due to the fact that there is no unnecessary interruption of the instruments. However, we recommend a timetable for periodical maintenance. For the instrument protection the use of a dust inlet filter is advised.
In order to benefit most from the daily two-point span checks, they should be set within the relevant range of the site, i.e. 30 and 60 ppb.

Documentation:

It is recommended that some extra effort should be made to implement, or upgrade the necessary documents. Some specific examples have already been discussed with the operators.

Competence:

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

Instrument Intercomparisons:

The ozone concentration observed at Izaña (1994) usually ranged between 26 and 58 ppb (5- and 95- percentile of hourly mean values). Both field instruments fulfil the assessment criteria as "good" over the tested range up to 100 ppb (figures 1 and 2).

Figure 1: Intercomparison of instrument TEI 49C

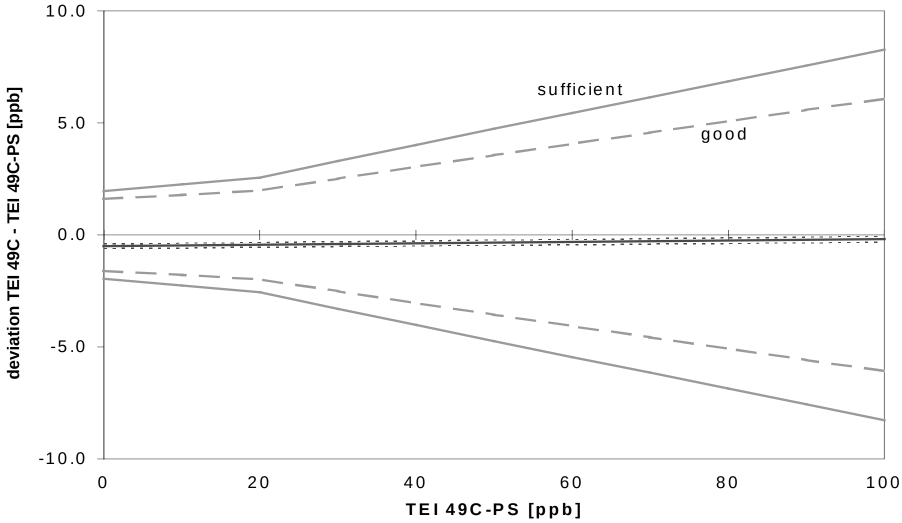
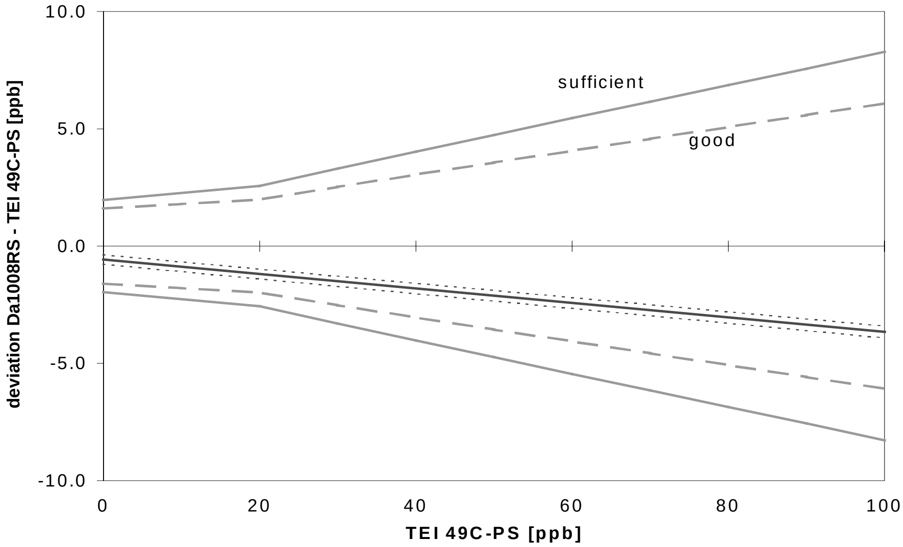


Figure 2: Intercomparison of instrument Dashibi 1008-RS



Dübendorf, 1. September 2000

EMPA Dübendorf, WCC-O_3

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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 Center for Surface Ozone for Europe and Africa (WCC-O_3). At the beginning of 1996 our work started within the GAW programme. The detailed goals and tasks of the WCC-O_3 are described in WMO-GAW Report No. 104.

In agreement with the responsible persons in charge of surface ozone measurements at the Instituto National Meteorologia (INM), Tenerife, a system and performance audit at the global GAW station Izaña was conducted. The station is an established site for long-term measurements of several chemical compounds and physical and meteorological parameters. With regard to the location in the Atlantic, in combination with its high altitude, it offers an excellent opportunity for monitoring of large scale pollution in the free troposphere.

The scope of the audit, which took place from November 21 to 28 in 1996, was confined to the surface ozone 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 at Izaña 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. The assessement criteria for the 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, the World Meteorological Organisation in Geneva and the Quality Assurance and Scientific Activity Centre (QA / SAC) for Europe and Africa.

3. Global GAW Site Izaña

3.1. Site Characteristics

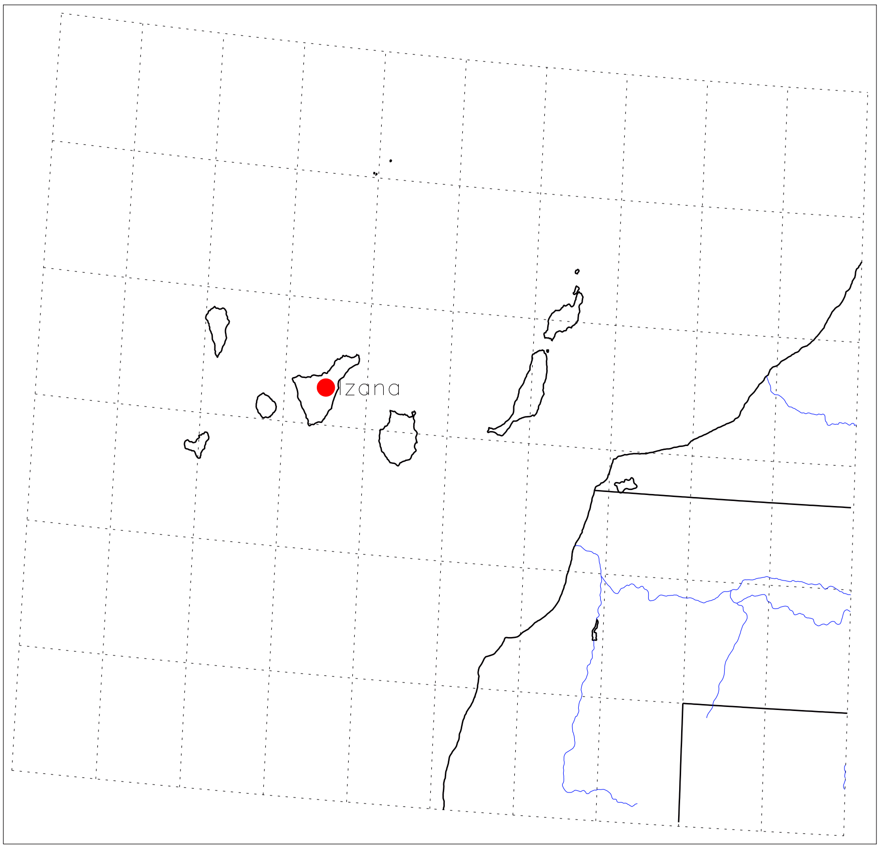
The station Izaña is located on the Island of Tenerife, Spain, (coordinates: 28°18' N, 16°30' W) roughly 300 km west of the African coast (figure 4). The meteorological observatory is situated on a mountain platform at an altitude of 2367 m a.s.l., 15 km north-east of the volcano Teide (3718 m a.s.l.). The local wind field at the site is dominated by north-westerly winds. A predominant meteorological attribute of the Canary Islands region is the presence of the trade wind inversion that persists through most of the year and is well below the altitude of the station.

The ground in the vicinity around Izaña is loosely covered with light volcanic soil. The vegetation in the surrounding area is sparse, consisting mainly of broom.

About 100 m south of the station a road leads to the meteorological observatory, and also serves the astrophysical institute of the Canaries and a nearby military camp. Because the road is closed to public traffic, only approximately 5 to 10 cars a day pass the vicinity. The facilities at the site consist of the main building which provides space for offices, meeting rooms and accommodation on two floors. Attached to this building is a four-story laboratory tower, housing the instrumentation for gas analysis. On the platform at the top of the flat roof, the air inlet and several pieces of meteorological equipement are mounted. The ozone analyser is installed on the uppermost floor close to the air inlet. Nearby are an unused building and an extensive warm-water preparation facility (figure 3).

Figure 3: Picture of the station Izaña:

Figure 4: Map of the Canary Islands and African Continent:



3.2. Operators

The meteorological observatory at Izaña was set up in 1984 by the Instituto Nacional de Meteorologia (INM), Spain, in co-operation with the German Environmental Protection Agency (UBA) and the Meteorologie Consult GmbH. Dr E. Cuevas' team, who is in charge of the operation of the station at Izaña, consists of an interdisciplinary group of physicians, meteorologists and supporting staff. The structure of the station management at Izaña is shown in Table 1.

Table 1: Operators

Dr. Emilio Cuevas, Station Director (Physics PhD)
Operators and Specialists Mr Juanma Sancho, (Physics graduate), Responsible for the tropospheric surface ozone group Mr Pedro Carretero, Former surface ozone instrument specialist Mr Braulio Aguilar, (Physics student), Current surface ozone instrument specialist Mr Sergio Afonso, Ozonesounding instrument specialist Mr Alberto Redondas, (Physics graduate), Responsible for total ozone and UVB Mr Ramon Ramos, (Physics graduate), Responsible for carbon cycle (CO2, CH4, CO) group

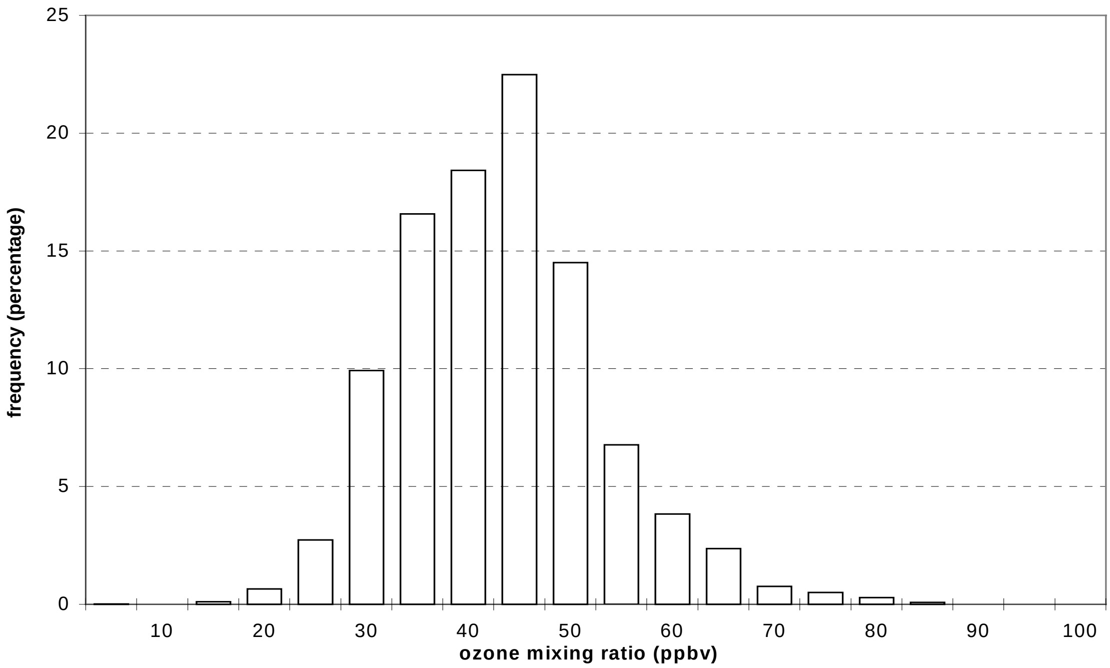
Mr Ramon Juega, Instrument specialist Mrs Carmen Romero, (Physics graduate), Responsible for the radiation group Mr Julian Perez, Instrument specialist Mr Pedro Romero, (Physics graduate), Responsible for aerosol group Mr Juanjo Bustos, (Physics graduate), Meteorological support Mr Nacho Abad, Meteorological instrument specialist Mr Carlos Marsal, Electronic technician
Support personal Mrs Concha Salamo, Secretary Mrs Pili Salamo, Secretary

3.3. Ozone Level

The site characteristics and the relevant 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 1995 is shown. The relevant ozone concentrations were calculated, ranging between 26 and 58 ppb according the 5 and 95 percentile of the hourly mean values.

Source of data: received from Dr E. Cuevas, Nov. 1996

Figure 5: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Izaña of the year 1995. Data capture higher 95 per cent



4. Measurement Technique

4.1. Air Inlet System

The air inlet system for the ozone measurements is mounted on the flat platform at the top of the four-story laboratory tower. The inlet part of the system on the flat roof is 2.5 m high and about 15 m above the ground and consists of an inverse stainless steel bucket, stacked on a stainless steel tube (50 mm i.d., 4 m long), shielding the system from rain and snow. The sampling line is a combination of the 4 m long stainless steel tube leading directly through a hole in the side-wall to the ceiling of the uppermost floor and a glass manifold indoors (50 mm i.d., 3 m long). It is continuously flushed at 1.5 m^3 per minute with ambient air. For the ozone measurements, two PFA teflon tubes (4 mm i.d., 2 m long) branch off within the first 0.5 m from the glass manifold leading to the ozone analysers. The sample pumps of the analysers are being used to draw ambient air through these teflon tubes according to the instrument's specified internal flows. There is no further protection from dust and particles with a teflon inlet filter. The total residence time of the ambient air, through the inlet line to the instruments, lies between 2 to 3 seconds.

The inlet line was checked with regard to loss of ozone. For this experiment a teflon tube (4 mm i.d., 5.5 m long) was pushed up backwards, inside the glass manifold and the stainless steel tube to the top of the air intake on the roof. Inside the laboratory, the other end of this tube and the connection tube usually used (between glass manifold and instrument) were connected to a teflon three-way valve from where a third tube led to the instrument. Prior to the test the installed teflon tube and the valve were well conditioned with ambient air. By manually switching the valve at a two minute interval, ambient air was drawn once through the air inlet system and, during the other period through the installed teflon tube. In this way the ozone analyser TEI 49C was continuously measuring ambient air indeed but alternately from the two different inlet lines. The other analyser, the Dashibi 1008-RS, was connected to the glass manifold as usual and was not involved in this experiment. No difference between the measurements with the two different inlet lines was found.

Comment

The teflon tube and the rain protection at the inlet were clean and free of dust. The inlet system, concerning construction materials as well as residence time, is adequate for gas analysis. No loss of ozone could be detected.

4.2. Instrumentation

The instruments are installed in an environmentally controlled room (about 20°C) in an instrument rack and are protected from direct sunlight.

The instrumentation used for measuring ozone at Izaña during the audit is shown in table 2 below.

Since July '95, several redefinition of the purpose of the ozone analysers on site have been made. As clarification, the usage during this period is listed in table 2. The used terminology is:

- basic instrument: analyser from which the final data results
- backup instrument: instrument that is monitoring in parallel to the basic instrument; for checking the basic instrument in general.
- reference instrument: analyser for calibration purposes (not used for ambient air measurements)

Before July ’95 the Dashibi ozone analyser 1008-AH #4283 was the basic instrument and the present backup instrument was used as reference. The reason for an exchange was a sudden major drop of about ten percent of the basic instrument compared to the reference. The operators of Izaña had detected this deviation in a regularly (twice a year) performed calibration.

For completeness reasons, the former basic instrument, the Dashibi 1008-AH, was integrated into the intercalibaration procedure by EMPA. The results are presented in Appendix I

Table 2: Field instruments

type	TEI 49C #55912-305	Dashibi 1008-RS #5797
method	UV absorption	UV absorption
usage	basic instrument	reference instrument: until 7. '95, basic instrument: 7. '95 - 7. '96 now as backup instrument
at Izaña	since July 22., 1996	for several years
range	0-100 ppb	0-100 ppb
analog output	0-10 V	0-100 mV, amplified to 0-10 V
electronic offset	1.0 ppb	5 units (corresponding ppb)
electronic coefficient	1.027	308 (absorption coeff.)

The zero air unit consists of an activated charcoal cartridge (approx. 1 litre volume) and a particulate filter. It is used to determine the analyser's daily zero. For the span checks the ambient air is only treated by an ozone scrubber (no activated charcoal).

For the daily span checks a Dashibi 1007 PG #011 ozone generator is used. About half an hour in advance it is switched on manually (stabilising the UV-lamp) while the procedure of the zero and span check at 16:00 GMT is controlled automatically by the data acquisition software. The detailed procedure of span and zero check is described in "4.4. Operation and Maintenance".

Comment

The measurement technique used is the UV-method which is the preferred method in the GAW programme.

The operation of two ozone analysers in parallel at Izaña, considerably increases confidence in data quality. However, the data submitted to the GAW data centre can only originate from one ozone analyser. Therefore, in aiming for continuity, one instrument should be clearly defined as the basic instrument for a longer term.

In order to minimise interferences with other trace species, the different processing of zero air for zero check and span check should be avoided.

4.3. Data Handling

The person who is responsible for the instrument operation is also in charge of data reviewing and processing.

The data acquisition facility is installed at the site next to the ozone analysers. It consists of an ADC circuit board to store the data on the computer. Around every two months the data is reprocessed and recalculated on a specifically designed software from INM. In a preliminary step, two ozone data files are prepared; one consisting the ten-minute mean values and the other one, the daily zero readings (5 one-minute means) from the automatically performed zero checks at 16:00 GMT. Then the invalid values (according logbook) or suspect data from each data file are manually removed from the database. The validated data is averaged to the appropriate mean values; hourly means for the ozone data and 5 minute means for the zero readings. Defined as suspect data are hourly means with a standard deviation higher than 8 ppb. Based on long term experience of the operators, such high deviation is generally due to instrument malfunction and does not respond to real ambient air measurements. However, for cases of sharp changes in the 10 minute values, the plausibility of the data is additionally checked by means of meteorological parameters, like wind speed and relative humidity and chemical parameters, like carbon dioxide, methane and Aitken nuklei. The final results are achieved by subtracting the daily zero mean value from the hourly mean values of the day according, using the two cleared data files. Diagrams for visual control are plotted from the final data.

From the final data, the daily mean and the highest hourly mean of each day are extracted and saved in a defined data format. Once a year these reformatted data are submitted to the database of the World Ozone Data Centre (WODC) at AES in Canada.

Comment

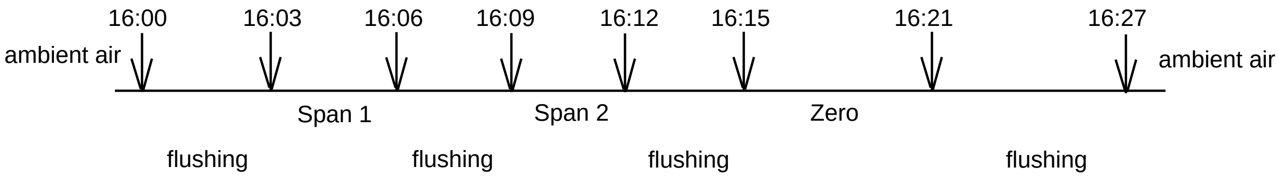
The procedure of data treatment for each instrument is organised and clearly arranged. Since the two instruments are operated in parallel, it is recommended to compare the data with regard to deviations. Thereby, the practice of removal of suspect data could be carried out on a more certain basis.

The reprocessing of the data at a more regularly, at least a monthly interval is recommended. In this manner detecting irregularities would be possible earlier.

4.4. Operation and Maintenance

Preventive maintenance of the instruments incorporates adjustment of the pressure transducers and cleaning of the instruments glass cell, and is performed on a case by case basis (every 2-6 month). The instruments are not protected with a dust inlet filter due to an investigation by the operators which showed that the measurements are not affected when operated with or without filters.

Automatic zero and span checks are made as a daily check of the ozone analysers. At 16:00 GMT, a two-point span (10 and 15 ppb) checks is made as a routine check of the ozone analyser. These data are stored in a separate file and are not used for correcting the ambient air measurement values because the precision and stability of ozone generators would be generally too poor to be used for calibration purposes. At the same time, a zero check is performed. The data is also stored in a separate file (one-minute means) but is used later for data reprocessing. The time schedule for the checks is visualised below:



Regular multipoint calibrations of the analysers can not be carried out at Izaña, because there is no ozone calibrator for reference that is traceable to the NIST. The only accuracy check, therefore, is the long-term parallel measurement of ambient air between the two field instruments.

Comment

The appearance of the station is clean and functional.

One of the main factors of quality assurance is the regular intercomparion by multipoint calibration between the analyser and an ozone reference that is traceable to the NIST. High priority should be given to the purchase of such an instrument.

It is noted that the advantage of maintenance on a case by case basis is due to the fact that there is no unnecessary interruption of the instruments. However, we recommend a timetable for periodical maintenance. For the instrument protection the use of a dust inlet filter is advised.

In order to benefit most from the daily two-point span checks, they should be set within the relevant range of the site, i.e. 30 and 60 ppb.

4.5. Documentation

Within the GAW guidelines for documentation, the transparency as well as the access to the station documents are required. During the audit the documentation was reviewed for availability and usefulness. The maintenance logbook of the station (bound, copy with carbon paper) was at the site and contained all necessary information. A checklist, in which primary function controls namely actual value and zero check results are noted, is filled in daily by the observers in charge and stored in a file.

Comment

However, for an external person, it was not easy to survey and obtain the desired information quickly. Therefore it is recommended that some extra effort should be made to implement, or upgrade the necessary documents. Some specific examples have already been discussed with the operators.

4.6. Competence

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

5. Intercomparison of Ozone Instruments

5.1. Experimental Procedure

At the site, the transfer standard (detailed description see Appendix II) was hooked up to power for warming up over night in deviation to 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 200 ppb ozone. During the next day, three comparison runs between the field instrument and the EMPA transfer standard were performed. In the meantime the inlet system and the station documentation were inspected. Table 3 shows the experimental details and Figure 6 the experimental set up of the audit. In general, no modifications of the ozone analysers which could influence the measurements were made for the intercomparisons.

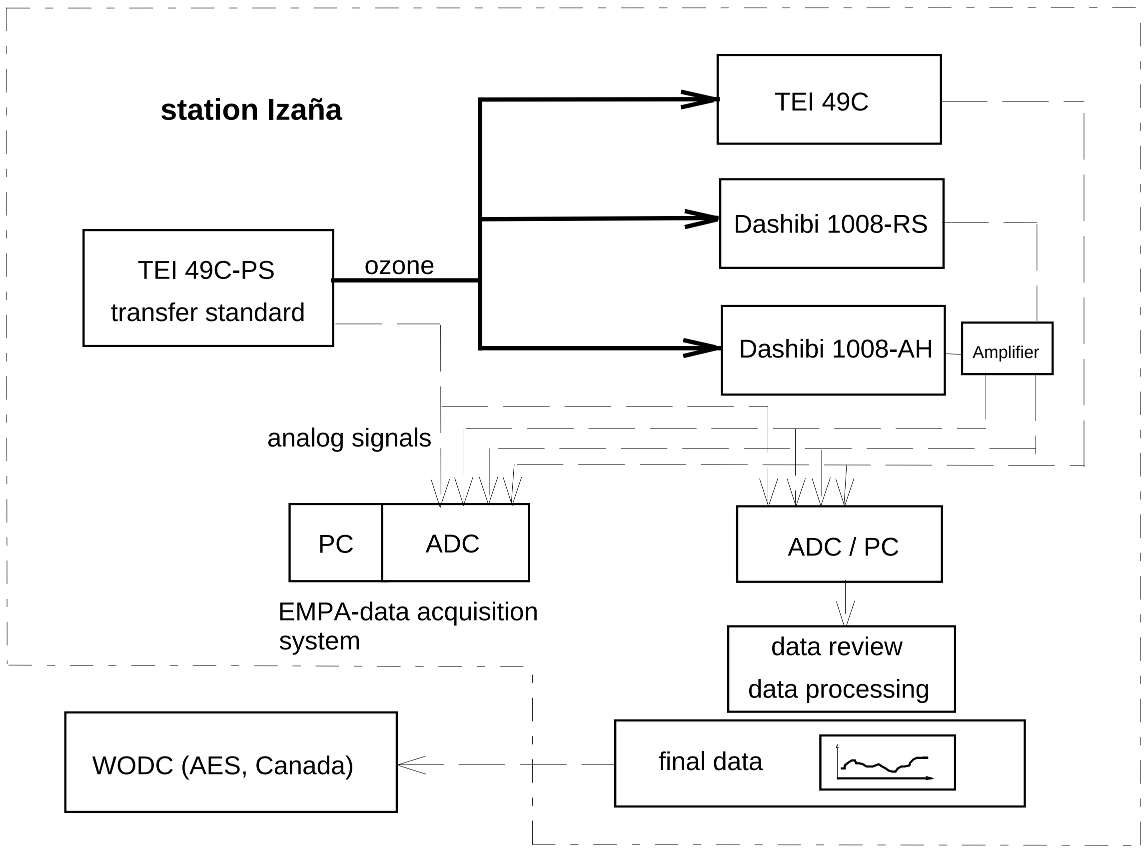
The EMPA acquisition system, which was used for the audit, consisted of a 16 channel ADC circuit board and a PC with the corresponding software. Hooked up to the analog output of the field instruments and of the transfer standard the data was collected by both data acquisition systems (EMPA and INM) and showed no discrepancy. For data interpretation the EMPA data is used. Finally, the observed results were discussed in an informal review with the person involved.

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

Table 3: Experimental details

reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instruments:	TEI 49C #55912-305 Dashibi 1008-RS #5797
ozone source:	EMPA: TEI 49C-PS, internal generator
zero air supply:	EMPA: silica gel - 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
pressure transducers reading:	TEI 49C-PS: 770.1 hPa TEI 49C: 758.0 hPa, Dashibi 1008-RS: 771.0 hPa
concentration range	0 - 100 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	10 / 30 / 45 / 60 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	3 x on November 25, 1996
connection between instruments:	about 1.5 meter of 1/4" PFA tubing

Figure 6: Experimental set up



5.2. Results

The results comprise the three runs of the intercomparisons between the two field instruments TEI 49C, Dashibi 1008-RS and the transfer standard TEI 49C-PS, carried out on November 25, 1996.

In the following tables the resulting mean values of each ozone concentration and the standard deviations (s_d) of 10 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 %.

Furthermore, the diagrams show the results of the linear regression analysis of the field instruments compared to the EMPA transfer standard. The results of the runs are then summarised to the mean regression equation and presented with the assessment criteria for GAW field instruments (Figure 11 and 12). Short before the start of the intercomparison a leak at the ozone supply tube leading to the Dashibi 1008-RS was detected and fixed. Clearly, due to this problem, the Dashibi 1008-RS was not yet fully stabilised in the first run and is regarded as not representative for the real condition of the instrument. So the calculated regression equation is based on runs two and three, while the first run is neglected.
The data used for the evaluation were recorded by the EMPA data acquisition system. This raw data was treated according the usual station method. Corresponding to this procedure the daily zero offsets were determined by zero check at 16:00 GMT. The individual resulting offsets were subtracted from the data of the intercomparison (see 4.3.). The offsets were: TEI 49C: 0.5 ppb; Dashibi 1008-RS: 4.8 ppb; Dashibi 1008-AH: 5.8 ppb.

In table 4 to 6 the recalculated data are listed.

Table 4: 1. Intercomparison, field instruments

No.	transfer standard		TE 49C				Dashibi 1008-RS			
	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	0.15	0.2	0.22	-0.6		-1.9	1.62	-2.7	
2	59.7	0.16	59.1	0.15	-0.6	-1.0	54.9	1.89	-4.8	-8.1
3	29.8	0.18	29.5	0.21	-0.3	-1.2	26.7	1.26	-3.1	-10.4
4	10.0	0.21	9.7	0.17	-0.2	-2.4	8.7	1.22	-1.3	-12.7
5	44.8	0.16	44.5	0.19	-0.4	-0.8	41.6	1.05	-3.2	-7.2
6	89.7	0.17	89.5	0.20	-0.3	-0.3	85.0	1.51	-4.7	-5.3
7	0.7	0.14	0.2	0.17	-0.4		-0.8	1.57	-1.5	

Table 5: 2. Intercomparison, field instruments

No.	transfer standard		TE 49C				Dashibi 1008-RS			
	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	0.6	0.17	0.3	0.19	-0.3		-0.2	0.32	-0.8	
2	44.9	0.13	44.7	0.26	-0.2	-0.4	42.6	0.56	-2.3	-5.1
3	29.9	0.16	29.7	0.19	-0.2	-0.7	28.7	0.58	-1.2	-4.1
4	89.8	0.13	89.8	0.20	0.0	0.0	86.3	0.45	-3.5	-3.9
5	59.9	0.11	59.7	0.13	-0.3	-0.4	57.4	0.51	-2.5	-4.1
6	10.2	0.14	9.6	0.23	-0.7	-6.4	9.5	0.59	-0.7	-6.5
7	0.7	0.18	0.1	0.19	-0.6		0.2	0.44	-0.4	

Table 6: 3. Intercomparison, field instruments

No.	transfer standard		TE 49C				Dashibi 1008-RS			
	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	0.8	0.12	0.3	0.16	-0.4		0.4	0.76	-0.3	
2	44.9	0.13	44.5	0.18	-0.4	-0.9	43.0	0.65	-1.8	-4.1
3	9.8	0.22	9.4	0.24	-0.4	-4.3	8.8	0.75	-1.1	-10.8
4	89.9	0.14	89.6	0.19	-0.2	-0.3	86.9	0.61	-3.0	-3.3
5	59.9	0.17	59.5	0.24	-0.4	-0.7	57.5	0.58	-2.4	-4.1
6	30.0	0.12	29.5	0.16	-0.6	-1.9	28.1	0.71	-1.9	-6.4
7	0.8	0.12	-0.1	0.25	-0.9		0.2	0.48	-0.6	

Figure 7: Individual linear regressions of intercomparisons 1 to 3, TEI 49C

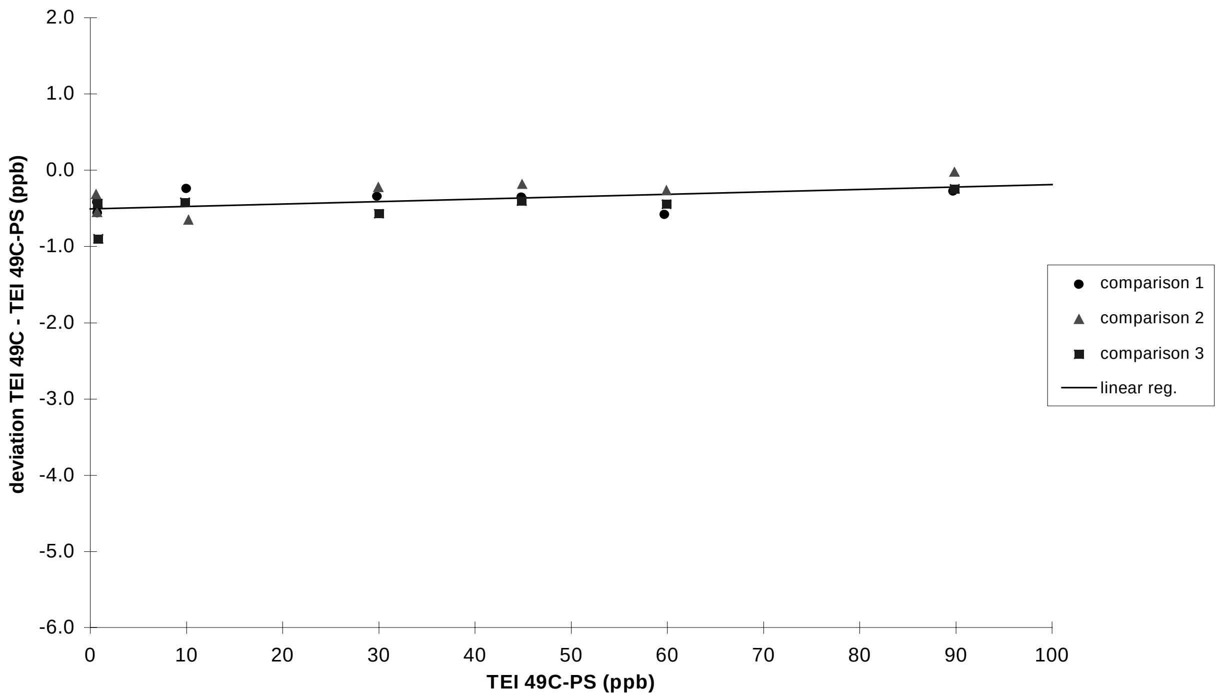


Figure 8: Mean linear regression of intercomparisons 1 to 3, TEI 49C

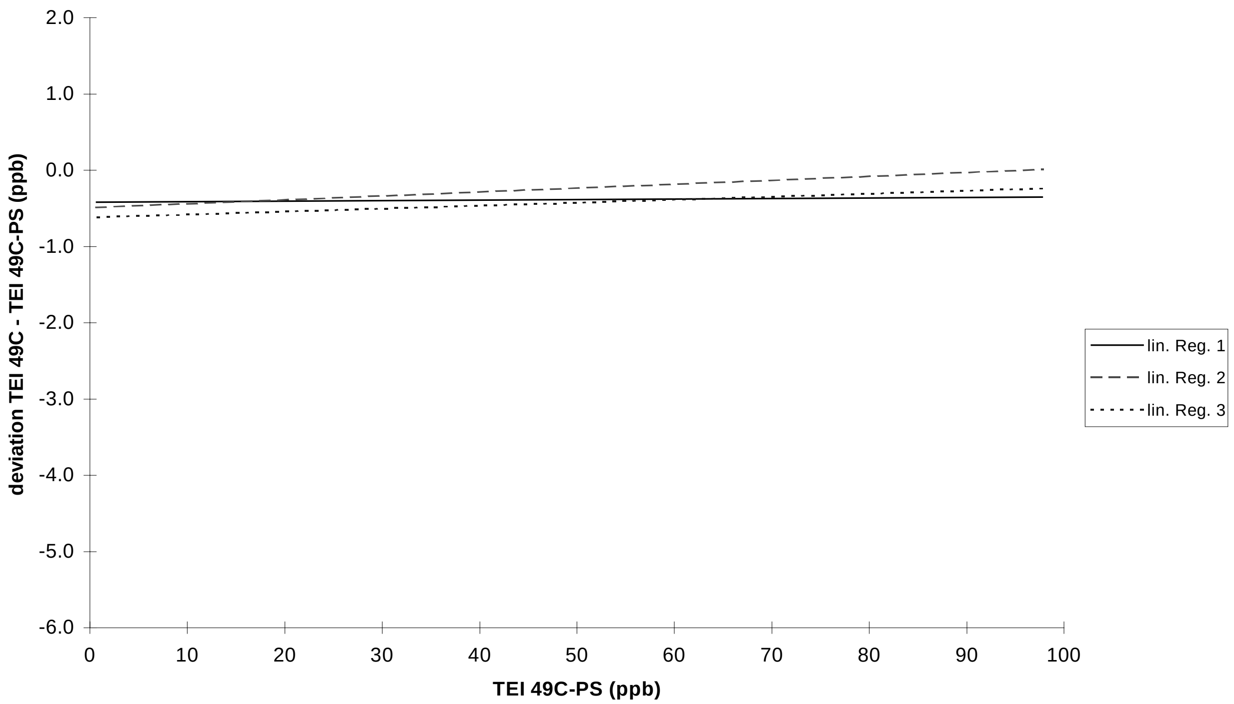


Figure 9: Individual linear regressions of intercomparisons 1 to 3, Dashibi 1008-RS

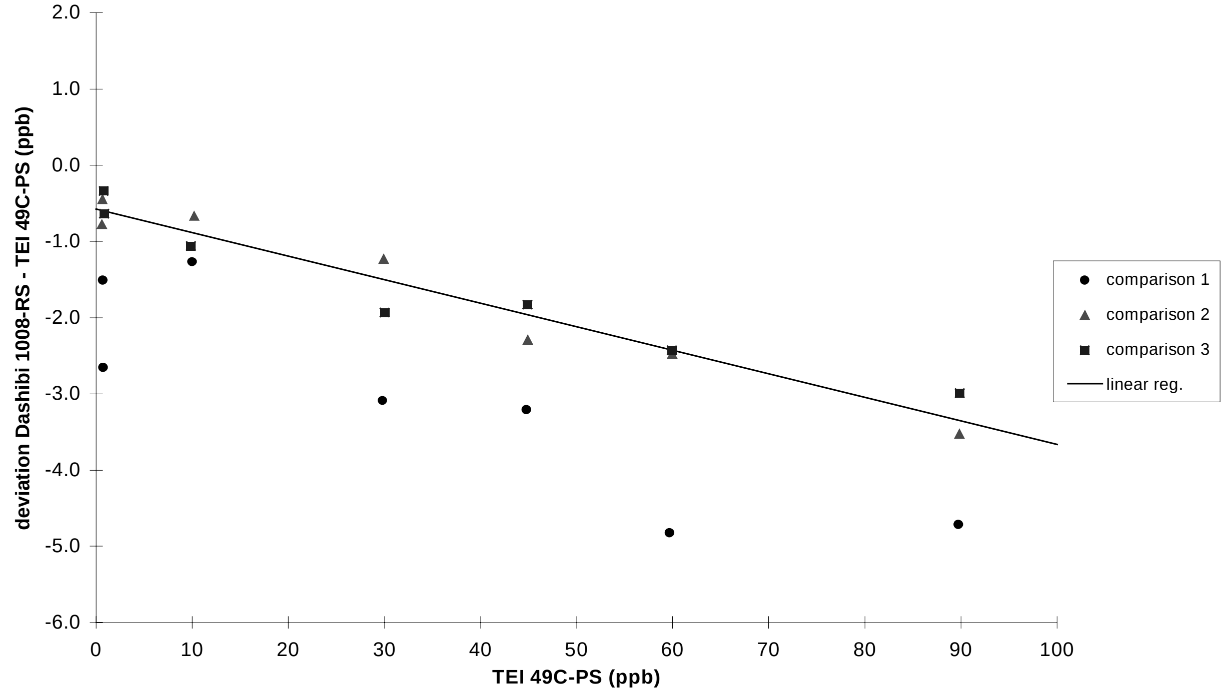
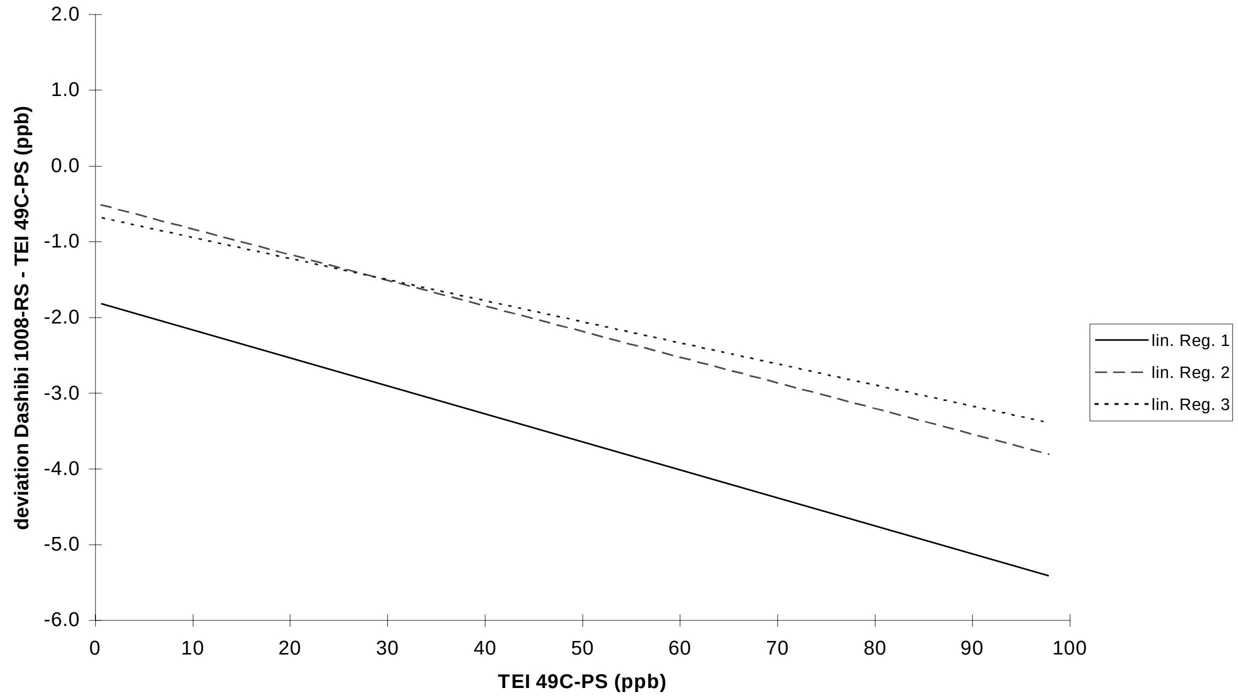


Figure 10: Mean linear regression of intercomparisons 1 to 3, Dashibi 1008-RS



From the intercomparisons of the TEI 49C #55912-305 and the Dashibi 1008-RS #5797 field instruments with the TEI 49C-PS transfer standard, from EMPA, the resulting linear regression (for the range of 0-100 ppb ozone) are:

-TEI 49C:

$$\text{TEI 49C} = 1.003 \times \text{TEI 49C-PS} - 0.51 \text{ ppb}$$

TEI 49C = O_3 mixing ratio in ppb, determined for TEI 49C #55912-305

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

Standard deviation of:	- slope s_m	0.0012	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.05	(f = 3)
	- residuals in ppb	0.12	(f = 19)

-Dashibi 1008-RS:

$$\text{Dashibi 1008-RS} = 0.969 \times \text{TEI 49C-PS} - 0.57 \text{ ppb}$$

Dashibi 1008-RS = O_3 mixing ratio in ppb, determined for Dashibi 1008-RS #5797

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

Standard deviation of:	- slope s_m	0.0022	(f = 2) f=degree of freedom
	- offset S_b in ppb	0.10	(f = 2)
	- residuals in ppb	0.23	(f = 12)

Figure 11: Intercomparison of instrument TEI 49C

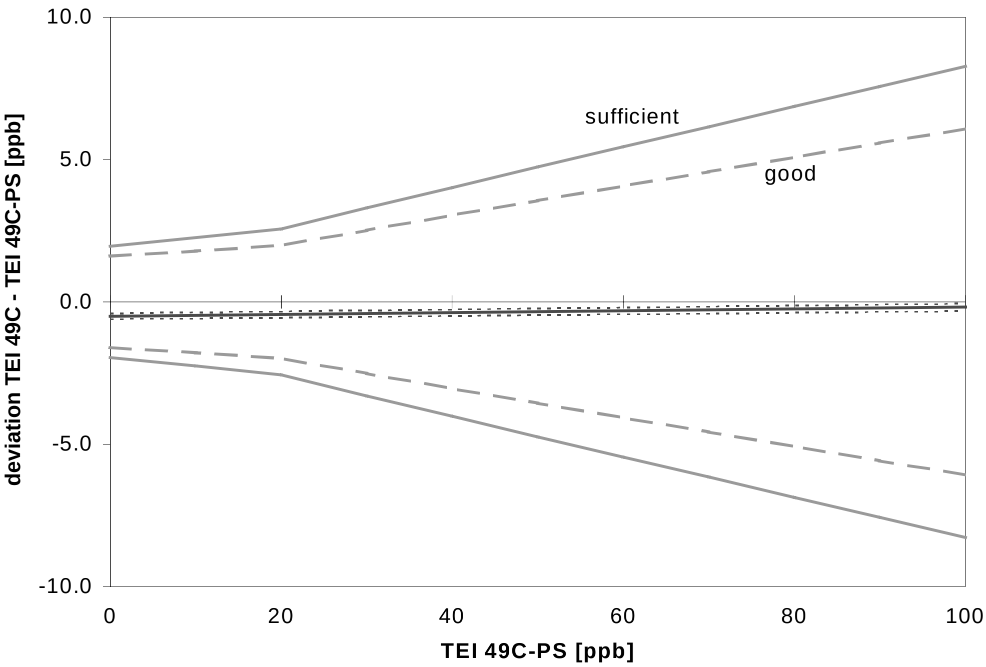
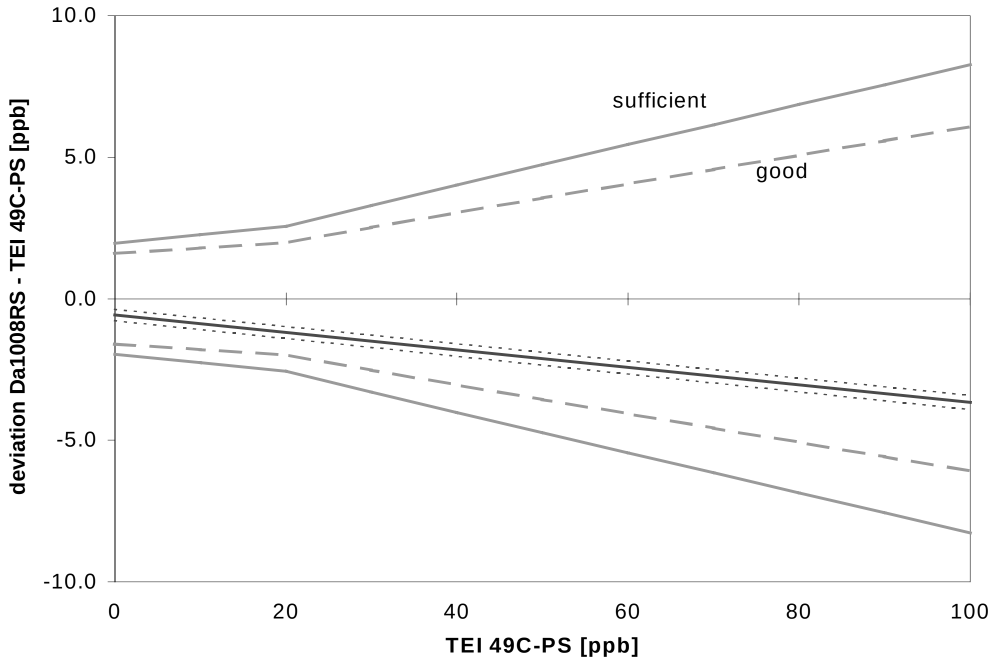


Figure 12: Intercomparison of instrument Dashibi 1008-RS



Comment

In figures 7 of the linear regressions, for the TEI 49C, no clear trend could be observed during the day when the intercalibration took place. Such a drift could indicate insufficient warm up time (stability) or pollution in the measurement cell of the instrument. However, in figure 9 and 10 (Dashibi 1008-RS) a substantial deviation between the first run and the followings is noticed. This is due to the fact of a leak at the ozone supply tube, leading to the Dashibi 1008-RS, that was detected and fixed shortly before the start of the intercomparison. Clearly, due to this problem, the Dashibi 1008-RS was not yet fully stabilised in the first run and is regarded as not representative for the real condition of the instrument. (For the Dashibi 1008-RS, the calculated regression equation is based on runs two and three).

The ozone concentration observed at Izaña (1994) usually ranged between 26 and 58 ppb (5- and 95- percentile of hourly mean values). Both field instruments fulfil the assessment criteria as "good" over the tested range up to 100 ppb (figures 11 and 12). Small deviation among the three intercomparisons (exception is discussed above) is the reason for a very narrow precision interval for both analysers.

Appendix

I Results, Intercomparison Dashibi 1008-AH

In the course of the intercomparisons of the actual ozone analysers at Izaña, an intercomparison of the former basic instrument, Dashibi 1008-AH #4283, was additionally performed in parallel. The experimental procedure was exactly the same as for the other analysers and is described in chapter 5.1. Some technical data is listed in table 7. The results are shown below in table 8 to 10 and confirm the results of a former comparison measurement performed by the operators at Izaña. The deviation of about 10 % between the former basic instrument compared to the reference had already then been detected (28.8.95) and resulted in an exchange of the analyser.

Table 7: Former field instrument

type	Dashibi 1008-AH #4283
method	UV absorption
at Izaña	since 1984
range	0-100 ppb
analog output	0-100 mV amplified to 0-10 V
electronic offset	5 units (corresponding ppb)
electronic coefficient	308 (absorption coeff.)

Table 8: 1. Intercomparison, Dashibi 1008-AH

	TE 49C-PS		Dashibi 1008-AH #4283			
No.	conc.	S_d	conc.	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.7	0.15	-2.1	0.67	-2.9	
2	59.7	0.16	50.8	0.45	-8.9	-15.0%
3	29.8	0.18	24.5	0.36	-5.3	-17.9%
4	10.0	0.21	7.3	0.35	-2.7	-26.6%
5	44.8	0.16	38.2	0.51	-6.6	-14.8%
6	89.7	0.17	77.7	0.29	-12.1	-13.5%
7	0.7	0.14	-1.0	0.43	-1.7	

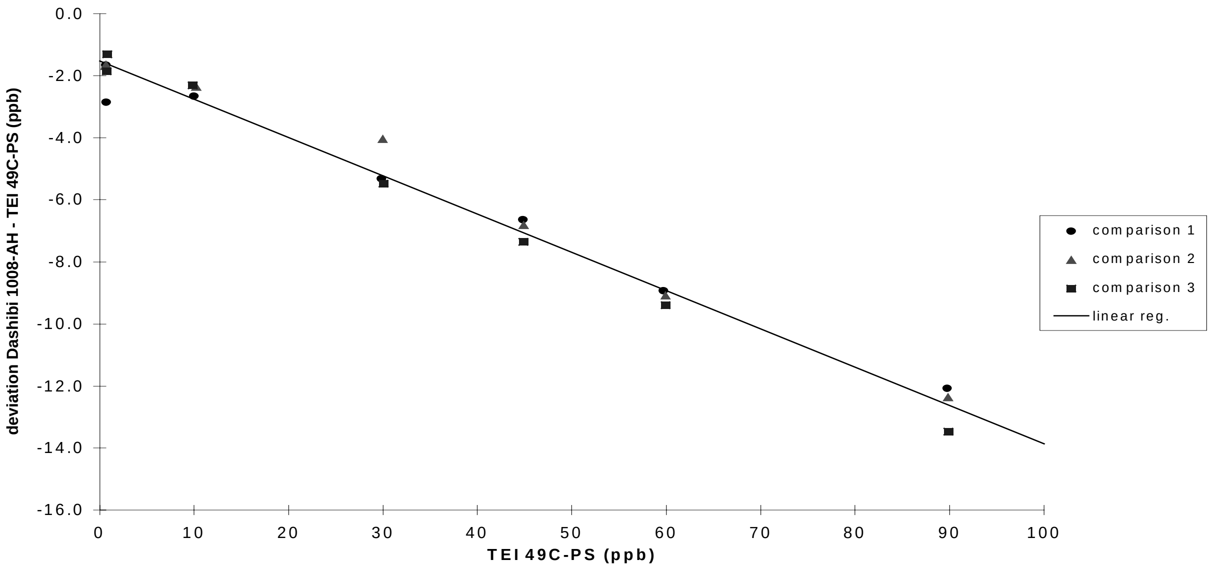
Table 9: 2. Intercomparison, Dashibi 1008-AH

No.	TE 49C-PS conc.	TE 49C-PS S_d	Dashibi 1008-AH #4283 conc.	Dashibi 1008-AH #4283 S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.6	0.17	-1.1	0.46	-1.7	
2	44.9	0.13	38.1	0.12	-6.8	-15.2%
3	29.9	0.16	25.9	0.35	-4.0	-13.5%
4	89.8	0.13	77.5	0.50	-12.4	-13.8%
5	59.9	0.11	50.8	0.27	-9.1	-15.2%
6	10.2	0.14	7.8	0.87	-2.4	-23.1%
7	0.7	0.18	-1.0	0.49	-1.7	

Table 10: 3. Intercomparison, Dashibi 1008-AH

No.	TE 49C-PS conc.	TE 49C-PS S_d	Dashibi 1008-AH #4283 conc.	Dashibi 1008-AH #4283 S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.8	0.12	-1.1	0.49	-1.9	
2	44.9	0.13	37.5	0.43	-7.4	-16.4%
3	9.8	0.22	7.5	0.50	-2.3	-23.5%
4	89.9	0.14	76.4	0.44	-13.5	-15.0%
5	59.9	0.17	50.5	0.40	-9.4	-15.7%
6	30.0	0.12	24.6	0.41	-5.5	-18.2%
7	0.8	0.12	-0.5	0.18	-1.3	

Figure 13: Mean linear regression of intercomparisons 1 to 3 , Dashibi 1008-AH



From the intercomparisons of the Dashibi 1008-RS #4283 field instrument with the TEI 49C-PS transfer standard from EMPA the resulting linear regression (for the range of 0-100 ppb ozone) is:

Dashibi 1008-AH = 0.877 x TEI 49C-PS - 1.53

Dashibi 1008-AH = O_3 mixing ratio in ppb, determined for Dashibi 1008-AH #4283
TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0037	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.17	(f = 3)
	- residuals in ppb	0.38	(f = 19)

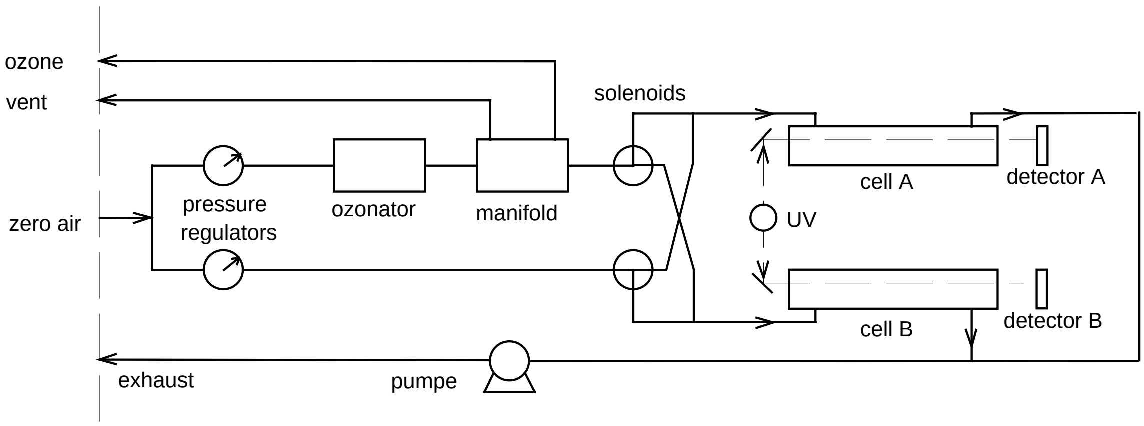
II EMPA Transfer Standard TEI 49C-PS

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 14. 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, manifold and 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 14: Flow schematic of TEI 49C-PS



III Stability of the Transfer Standard TEI 49C-PS

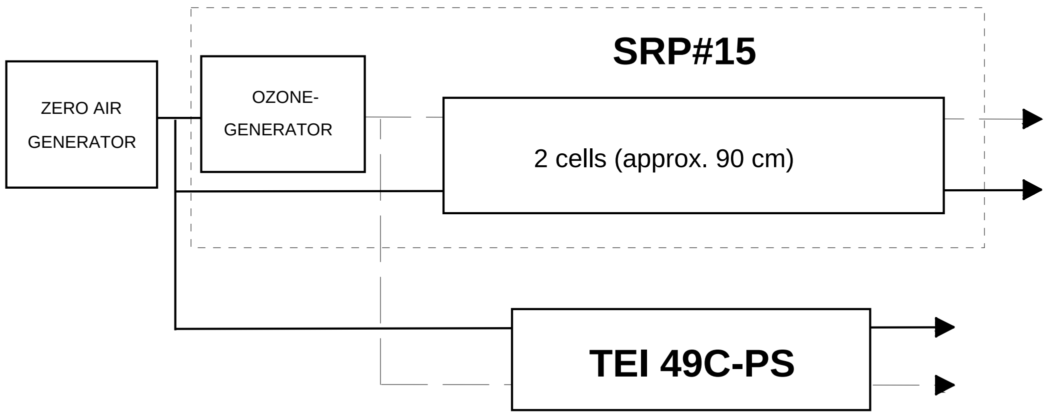
To exclude errors which might occur through transportation of the transfer standard, the TEI 49C-PS #54509-300 has to be compared with the SRP#15 before and after the field audit.

The procedure and the instruments set up of this intercomparison in the calibration laboratory at EMPA are summarised in Table 11 and Figure 15.

Table 11: 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 15: 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 16 and 17 show the resulting linear regression and the corresponding 95% precision interval for the comparisons of TEI 49C-PS vs. SRP#15. Clearly, the results show that the EMPA transfer standard fullfiled the recommended criterias for the periode of the audit, including transportation.

Figure 16: Transfer standard before audit

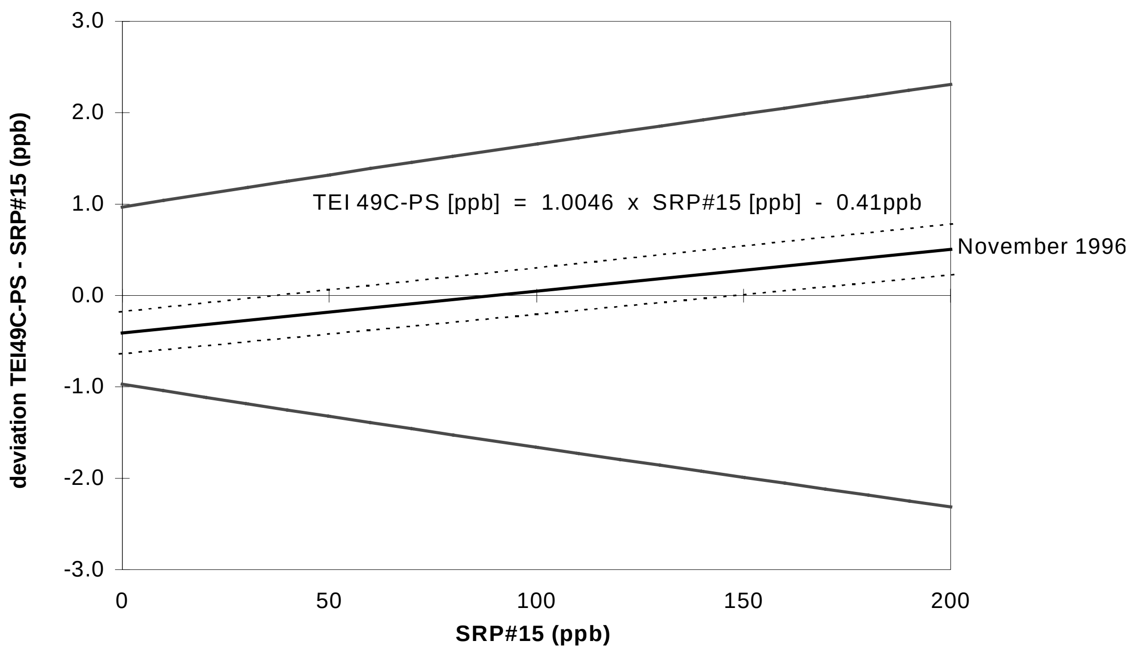
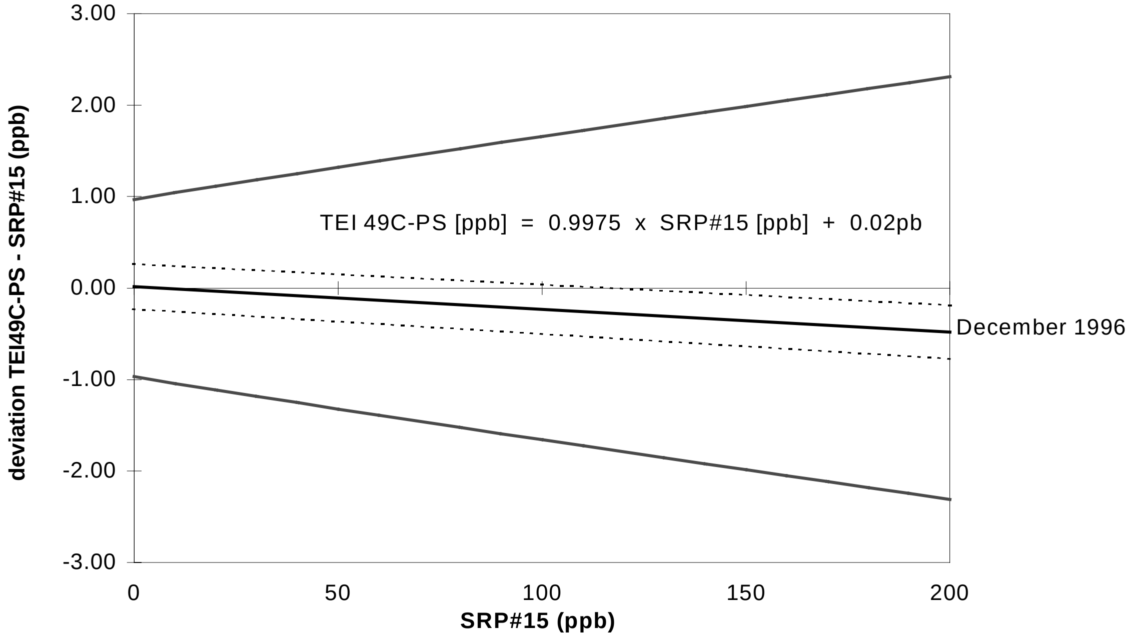


Figure 17: Transfer standard after audit



IV Changes after the Audit

The below listed improvements at the GAW site Izaña have been, according to the information of the station operators, subsequently implemented as a consequence of the audit discussion and have not been proved by the audit team. Subject of a following audit in the future will be to verify these changes on site. Nevertheless, it was regarded as helpful to users of ozone data of Izaña to add the information in this first audit report already.

- Since February 1997 the ozone analysers at Izaña are protected with a teflon dust filter.
- With the purchase of a reference photometer TEI 49C-PS, in April 1997, that is traceable to the NIST, multipoint calibrations can now be performed on a regular basis.
- After the audit procedure in November 1996, the scrubber of the Dashibi 1008-AH #4283 was replaced and an intercomparison with the new reference instrument was conducted. The operators found out a significant improvement of the instrument that is now operating at a sea-level station in a lighthouse in the northern part of the island.