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

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

EMPA-WCC REPORT 98/2

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE

GLOBAL GAW STATION IZAÑA

TENERIFE, FEBRUARY 1998

Submitted by

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WMO World Calibration Centre for Surface Ozone and Carbon Monoxide

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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 Izaña, Tenerife. Below, the findings, comments and recommendations are summarised:

Air Inlet System:

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. In investigations during the last audit no loss of ozone could be detected.

Instrumentation:

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. With the TEI 49C, a well maintained analyser which is in very good condition, had been defined as the basic instrument.

Operation and Maintenance:

The appearance of the station is clean and functional.
Regular intercomparisons between the analyser and an ozone reference by multipoint calibration are regarded as an important factor of quality assurance. Since the purchase of a TEI 49C-PS calibrator last year this gap could be filled.
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. Since the required experience for such a practice is present we do not recommend any change to this procedure, even though it differs from the description in the SOP of GAW report No. 97.

Data Handling:

The procedure of data treatment for each instrument is well organised and clearly arranged.
The recommendation of the last audit to reprocess the data on a monthly interval has been implemented. The feature to compare ozone data of the two analysers using the reprocessing software has not yet been adapted but is still planned.

Documentation:

At the audit in November 1996, in agreement with the responsible group, the documentation was classified as "not easy to survey and to obtain quickly the desired information by an external person ". Since then, some extra effort to build up or upgrade the necessary logbooks was made and has lead to an improvement of the documentation.

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.

Ozone Intercomparisons:

The ozone concentration observed at Izaña (1997) usually ranged between 31 and 67 ppb (5- and 95- percentile of hourly mean values).
The basic field instrument, TEI 49C, clearly fulfils the assessment criteria as "good" over the tested range up to 100 ppb (figures 1). A very small deviation among the three intercomparisons is the reason for a very narrow prediction interval which implies that the instrument is in good condition.
The Dasibi 1008RS instrument, considering the range relevant to the site, fulfils the assessment criteria as "good". For concentrations lower than 30 ppb it only partly satisfies them (figure 2). This is due to a relatively wide prediction interval, which had significantly increased, reflecting the comparatively poor stability of the instrument (see Fig. 10).
The linear regression analysis from the intercomparisons obtained in November '96 and during this audit are very similar. However, it should be noted that the stability of the backup instrument, the Dasibi 1008-RS, has declined.

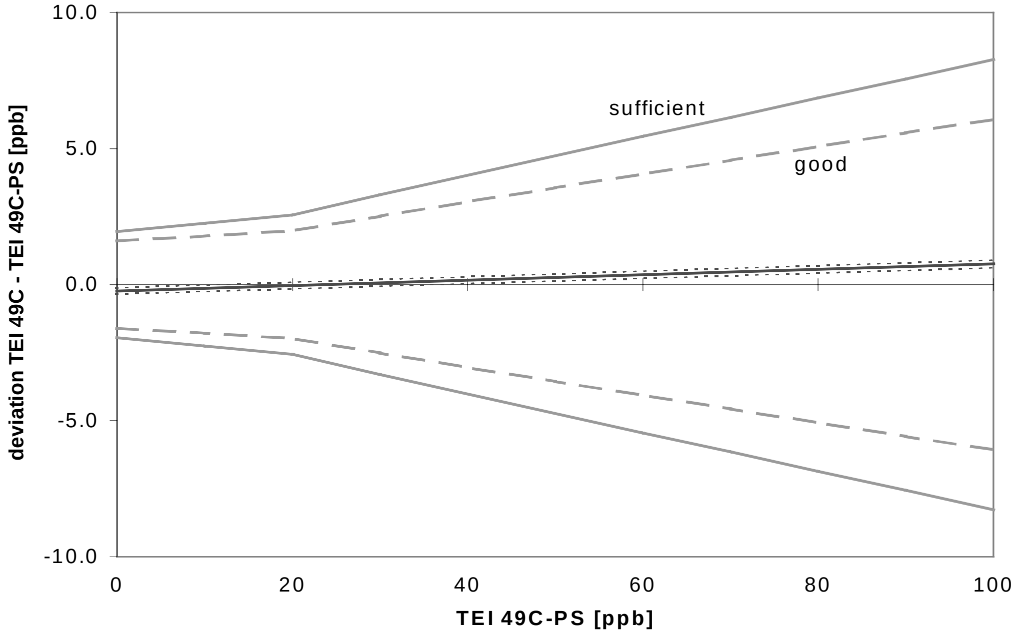

Figure 1: Intercomparison of instrument TEI 49C

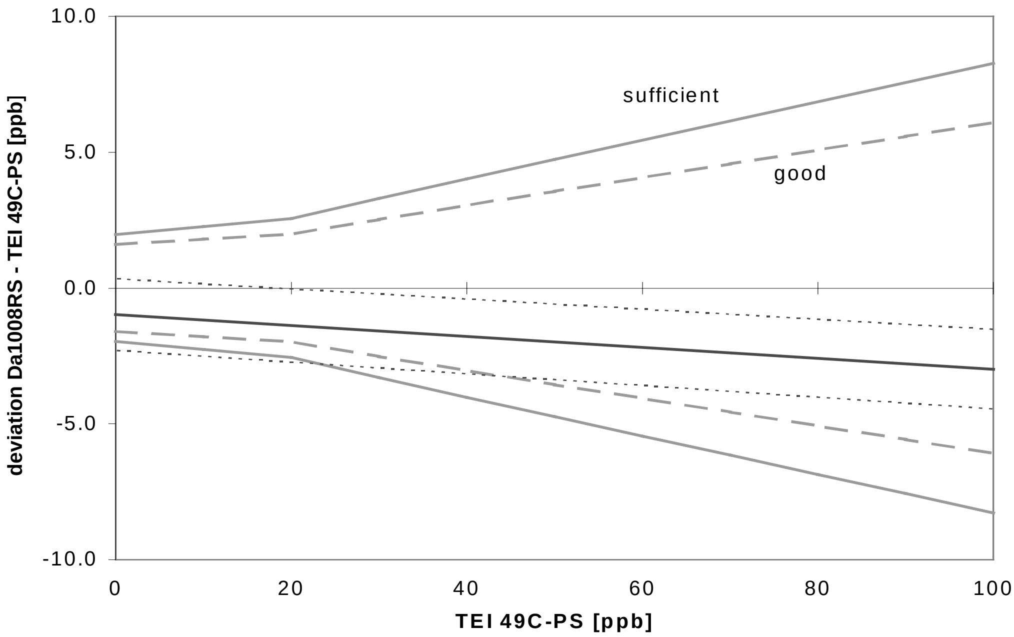

Figure 2: Intercomparison of instrument Dasibi 1008-RS

Dübendorf, 1. September 2000

EMPA Dübendorf, WCC

Project engineer

Project manager

A. Herzog

Dr. B. Buchmann

Technical assistant and CO expert: M. Hill

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 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 responsible persons in charge of O_3 and CO measurements at the Instituto National Meteorologia (INM), Tenerife, the second 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 distributed pollution in the free troposphere.

The scope of the audit, which took place from February 20 to 26, 1998, 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 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. 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, June 1998, available on request from the authors at: EMPA, Section 134, Ueberlandstr. 129, CH-8600 Dübendorf).

The recently re-established carbon monoxide measurements were not audited since the instrumentation has not yet reached the state of routine operation. Instead, the entire CO system had been analysed, set up to operation and discussed in order to support the operators.

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.

The last audit at Izaña had been performed in November 1996. System and performance audits at global GAW stations will be regularly conducted on mutual arrangement about every 18 months.

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 equipment 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).

Over the past year, the near environment of the site has not changed in a way that could have influenced the ozone measurements.

Figure 3: Picture of the station Izaña

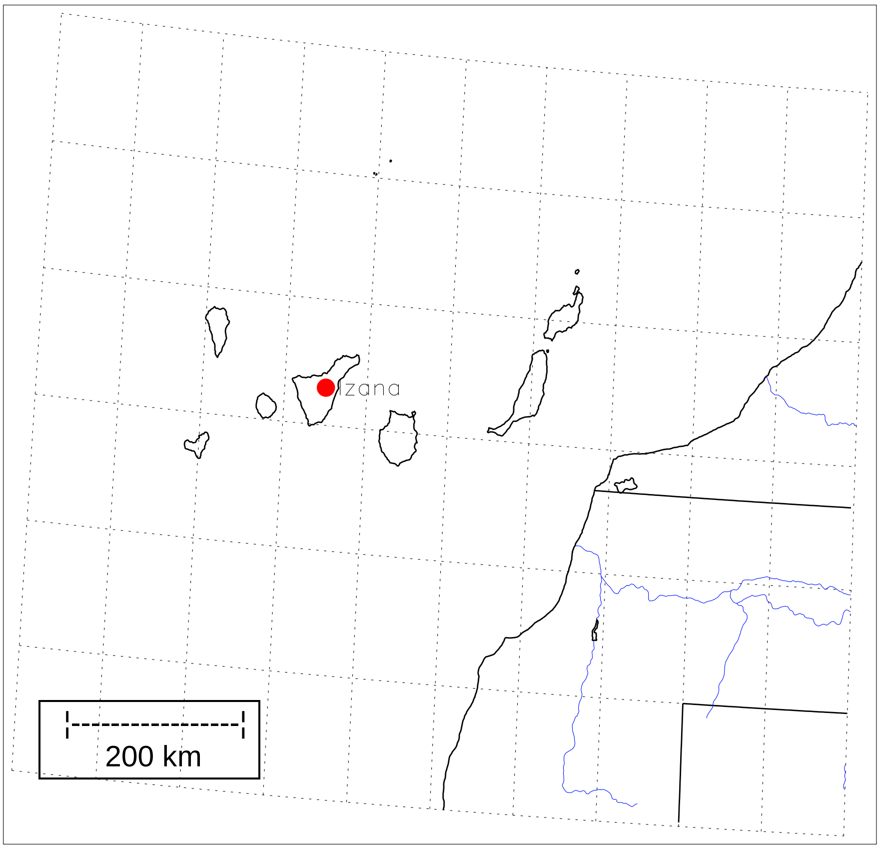

Figure 4: Map of the Canary Islands and African Continent

3.2. Operators

The meteorological observatory at Izaña (IZO) was set up in 1984 by the Instituto Nacional de Meteorologia (INM).

Dr E. Cuevas' team, who is in charge of the operation of the station at Izaña, consists of an interdisciplinary group of physicists, technicians and supporting staff. The structure of the station management at Izaña is shown in Table 1.

Table 1: Operators

Dr. Emilio Cuevas, Station Chief and Head for the Ozone and UV Group (Physics PhD)
Operators and Specialists Mr Juanma Sancho, Ozone and UV Group, Responsible for the tropospheric ozone programme, (Physics graduate) Mr Alberto Redondas, Ozone and UV Group, Responsible for the stratospheric ozone and UV radiation programme, (Physics graduate) Mr Sergio Afonso, Ozone and UV Group, Ozonesounding instrument specialist Mr Braulio Aguilar, actual surface ozone instrument specialist, (Physics student) Dr Xavier Calbet, Head of the Aerosol and Radiation Group, (Physics PhD) Mrs Carmen Romero, Aerosol and Radiation Group, (Physics graduate) Mr Pedro Romero, Aerosol and Radiation Group, (Physics graduate)

Mrs Pilar Ripodas, Head of the Carbon Cycle Group, (Physics graduate) Mr Ramon Ramos, Carbon Cycle Group, (Physics graduate) Mr Juanjo Bustos, Meteorological support, (Physics graduate) Mr Pedro Carretero, Former surface ozone instrument specialist Mr Ramon Juega, Instrument specialist Mr Nacho Abad, Instrument specialist Mr Jaime Estevez, Instrument specialist Mr Carlos Marsal, Electronic Technician Mr Manuel Estevez, Maintenance Technician
Support personal Mrs Pilar Salamo, Secretary Mrs Concha Salamo, Secretary

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 1997 is shown. The relevant ozone concentrations were calculated, ranging between 31 and 67 ppb according the 5 and 95 percentile of the hourly mean values.

Source of data: received from J. Sancho, INM, March. 1998

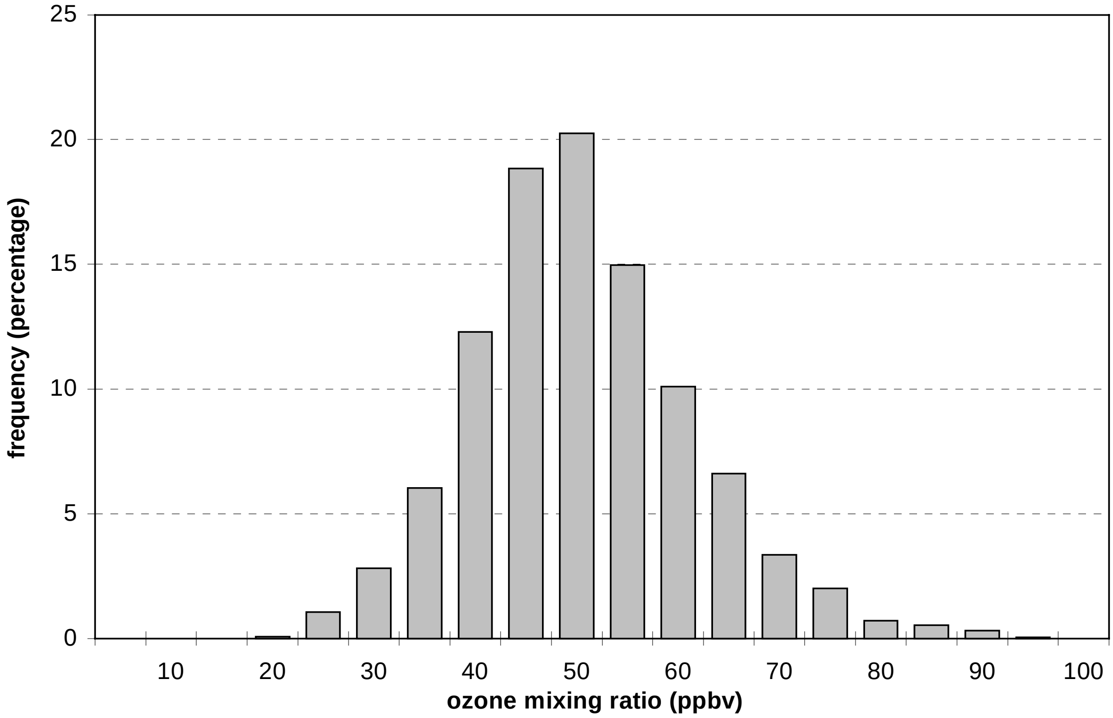

Figure 5: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Izaña of the year 1997. Data capture higher 94 per cent

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 m3 per minute with ambient air. For the ozone measurements, a PFA teflon tube (4 mm i.d., 2 m long) branches off within the first 0.5 m from the glass manifold passing a teflon inlet filter (dust and particles) from where the air stream splits 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. The total residence time of the ambient air, through the inlet line to the instruments, lies between 2 to 3 seconds.

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

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. In investigations during the last audit no loss of ozone could be detected.

4.2. Instrumentation

The instruments are installed in an environmentally controlled room (between 20 to 25°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 (identical to the instrumentation of the audit in November 1996).

In April 1997, an ozone calibrator of the type TEI 49C-PS had been purchased (financed by WMO) for the Izaña Observatory and is used for regular calibration of the analysers on site as well as for conducting ozone audits within the SCO_3P Project and the GAW Programme in South America. This ozone calibrator was integrated into the intercalibration procedure by EMPA and the results are presented in Appendix I.

Table 2: Field instruments

type	TEI 49C #55912-305	Dasibi 1008-RS #5797
method	UV absorption	UV absorption
usage	basic instrument	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	1.028	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.

A daily zero check at 16:00 GMT is automatically triggered by the data acquisition software. The data of twelve one minute means is stored in a separate file. The performance of daily span checks had been stopped since multipoint calibrations are carried out every two months.

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. With the TEI 49C, a well maintained analyser which is in very good condition, had been defined as the basic instrument.

4.3. 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). Since April last year, the instruments are protected with a dust inlet filter. This although an investigation by the operators had showed that the measurements are not affected when operated without filters. The filter is changed monthly.

Automatic zero checks are made as a daily check of the ozone analysers at 16:00 GMT. This data is stored in a separate file and is used later for data reprocessing and correcting the ambient air measurement values. The two-point span (10 and 15 ppb) routine checks had been stopped in April last year and replaced by a multipoint calibration every two months using a transfer standard. The applied ozone levels are 0 / 10 / 30 / 45 / 60 / 90 ppb. The transfer standard used for this multipoint calibrations, TEI 49C-PS #56085-306, was certified with the NIST Standard Reference Photometer #12 of the AES in Canada in July 1996. During this audit it was supplementary intercompared with the EMPA transfer standard TEI 49C-PS #54509-300 (results see Appendix I).

Comment

The appearance of the station is clean and functional.

Regular intercomparisons between the analyser and an ozone reference by multipoint calibration are regarded as an important factor of quality assurance. Since the purchase of a TEI 49C-PS calibrator last year this gap could be filled (multipoint calibration every two months).

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. Since the required experience for such a practice is present we do not recommend any change to this procedure, even though it differs from the description in the SOP of GAW report No. 97.

4.4. 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 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 (12 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 12 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.

The group of INM had not been informed yet by the new World Data Centre for Surface Ozone (WDCSO) at NILU about its activity. Thus the data of the global GAW station Izaña is still being sent to the WODC in Canada only.

Comment

The procedure of data treatment for each instrument is well organised and clearly arranged.

The recommendation of the last audit to reprocess the data on a monthly interval has been implemented. The feature to compare ozone data of the two analysers using the reprocessing software has not yet been adapted but is still planned.

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 station logbook (bound, copy with carbon paper) is found at the site or at the institute in Santa Cruz where it is needed for the purpose of data review. It contained all necessary information listed chronologically. Since the middle of last year, a monitor logbook is attached to the instruments on site. It contains specific facts concerning the instrument as for example putting into operation, calibrations or failures. The instrument manuals were available at the site. A checklist, in which primary function controls namely actual value and zero check results are noted, is filled in daily by the observer in charge and stored in a file. Additionally, a form is pined to a billboard at the station where special observations of the environment, i. e. sand storms or forest fires are marked.

Comment

At the audit in November 1996, in agreement with the responsible group, the documentation was classified as "not easy to survey and to obtain quickly the desired information by an external person". 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 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 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 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

audit team:	M. Hill, A. Herzog
reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instruments:	TEI 49C #55912-305 Dasibi 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 (EMPA): 771 hPa TEI 49C: 770 hPa (no adjustment necessary) Dasibi 1008-RS: 770 hPa (no adj. necessary)
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 February 25, 1998
connection between instruments:	about 1.5 meter of 1/4" PFA tubing

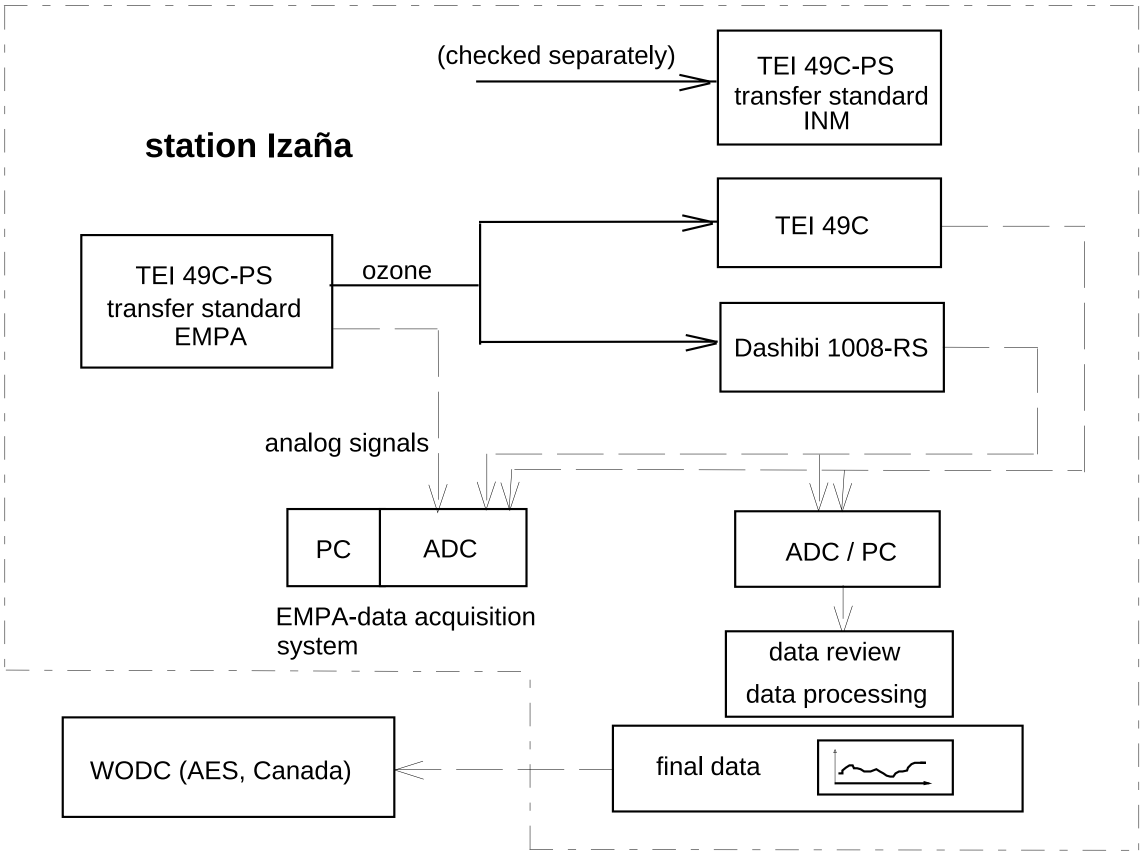

Figure 6: Experimental set up

5.2. Results

The results comprise the three runs of the intercomparison between the two field instruments TEI 49C and Dasibi 1008-RS and the EMPA transfer standard TEI 49C-PS, carried out on February 25, 1998.

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

Furthermore, the diagrams show the results of the linear regression analysis of both field instruments compared to the EMPA transfer standard. The results of the three runs are then summarised to the mean regression equation and presented in a graph with the assessment criteria for GAW field instruments (Figure 11 and 12).

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 offset was determined by zero check at 16:00 GMT. The individual resulting offsets were subtracted from the data of the intercomparison (see 4.4.). The offsets were: TEI 49C: 1.7 ppb; Dasibi 1008-RS: 4.6 ppb. In table 4 to 6 the recalculated data are listed.

Table 4: 1. Intercomparison, field instruments

No.	transfer standard		TEI 49C				Dasibi 1008-RS			
	TEI 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		TEI 49C				Dasibi 1008-RS			
	TEI 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	0.1	0.22	-0.1	0.18	-0.2		-0.7	1.23	-0.8	
2	29.8	0.15	29.8	0.17	0.0	-0.1%	29.2	1.47	-0.6	-2.1%
3	59.8	0.13	60.3	0.20	0.5	0.8%	57.7	0.66	-2.1	-3.4%
4	9.9	0.22	9.7	0.17	-0.2	-2.1%	8.5	1.05	-1.4	-14.1%
5	44.8	0.16	45.0	0.25	0.2	0.3%	42.6	1.02	-2.2	-4.9%
6	89.8	0.11	90.2	0.21	0.5	0.5%	86.3	1.94	-3.5	-3.9%
7	0.2	0.16	0.0	0.11	-0.2		-1.8	1.12	-1.9	

Table 6: 3. Intercomparison, field instruments

No.	transfer standard		TEI 49C				Dasibi 1008-RS			
	TEI 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	0.3	0.15	0.1	0.20	-0.1		-1.3	1.52	-1.5	
2	89.8	0.08	90.7	0.23	0.9	1.0%	87.6	0.72	-2.1	-2.4%
3	44.8	0.14	45.1	0.19	0.4	0.8%	43.6	1.56	-1.1	-2.5%
4	10.0	0.14	9.8	0.17	-0.2	-1.6%	8.5	1.21	-1.4	-14.5%
5	59.8	0.09	60.2	0.21	0.4	0.7%	56.5	0.91	-3.3	-5.6%
6	29.8	0.19	29.8	0.23	0.0	0.0%	28.2	1.22	-1.7	-5.5%
7	0.2	0.18	0.1	0.19	-0.1		-0.8	1.16	-0.9	

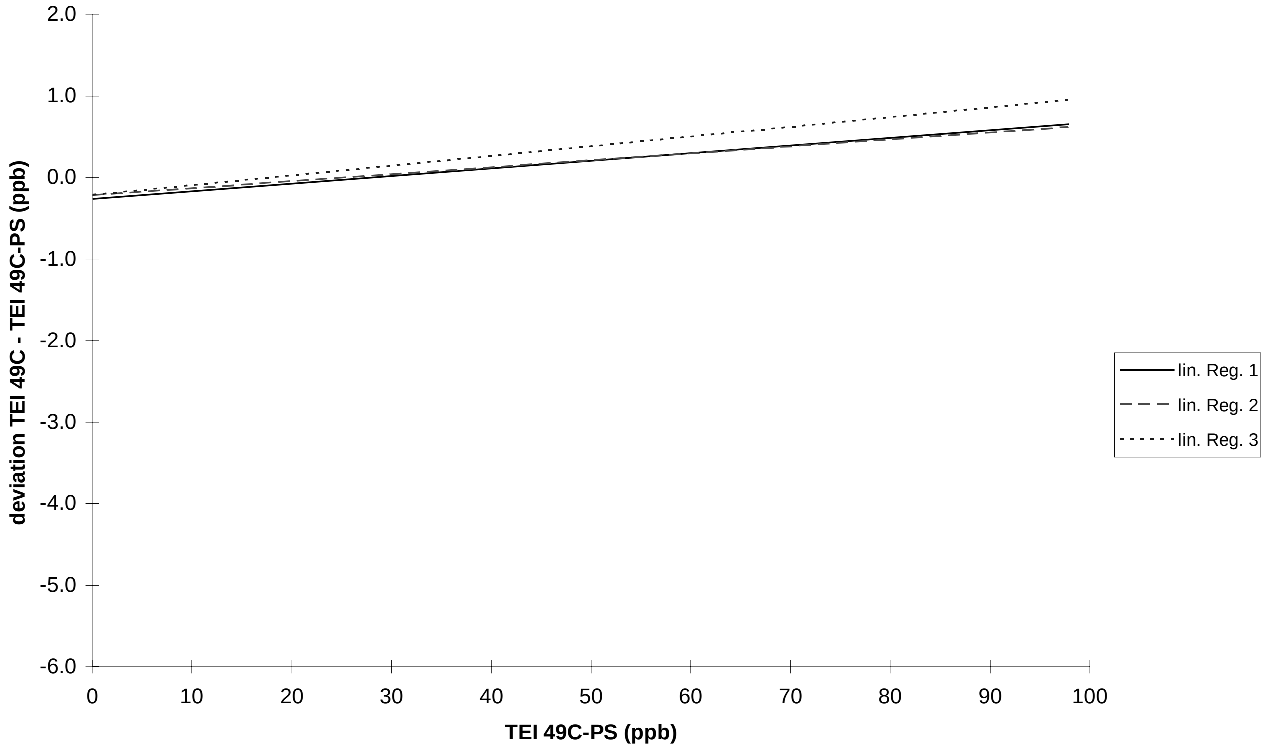

Figure 7: Individual linear regressions of intercomparisons 1 to 3, TEI 49C

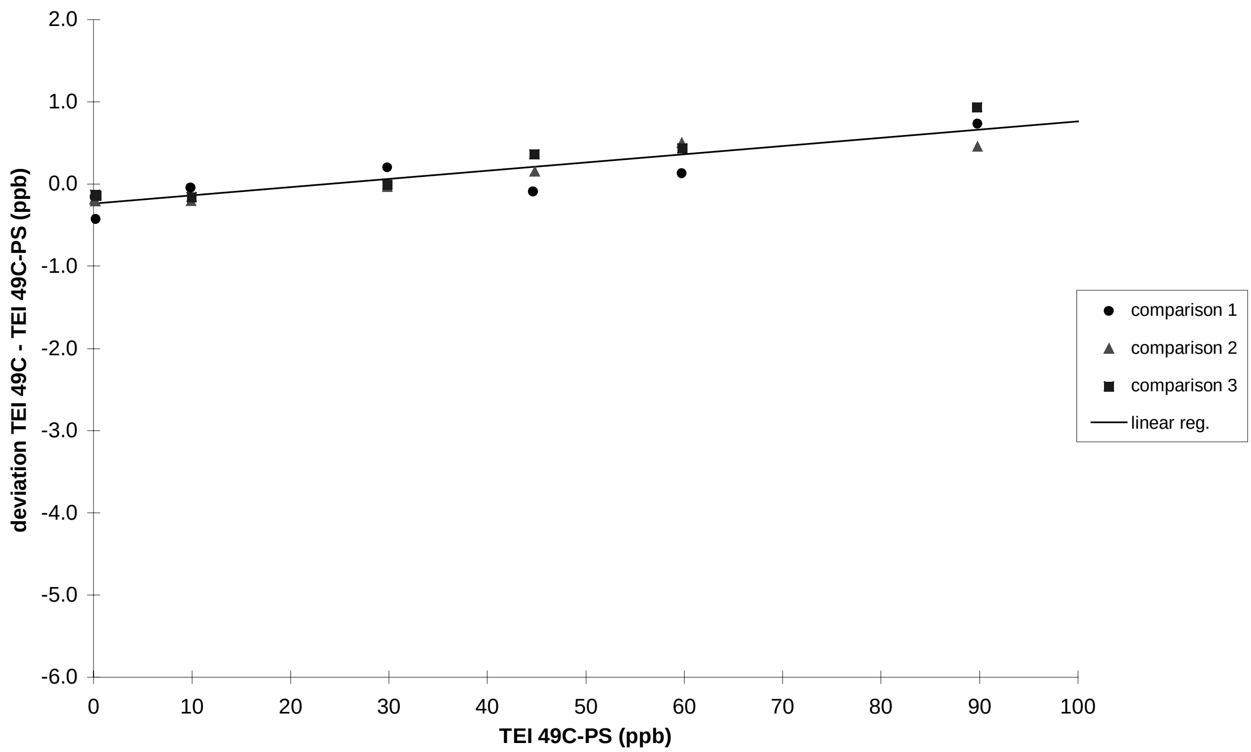

Figure 8: Mean linear regression of intercomparisons 1 to 3, TEI 49C

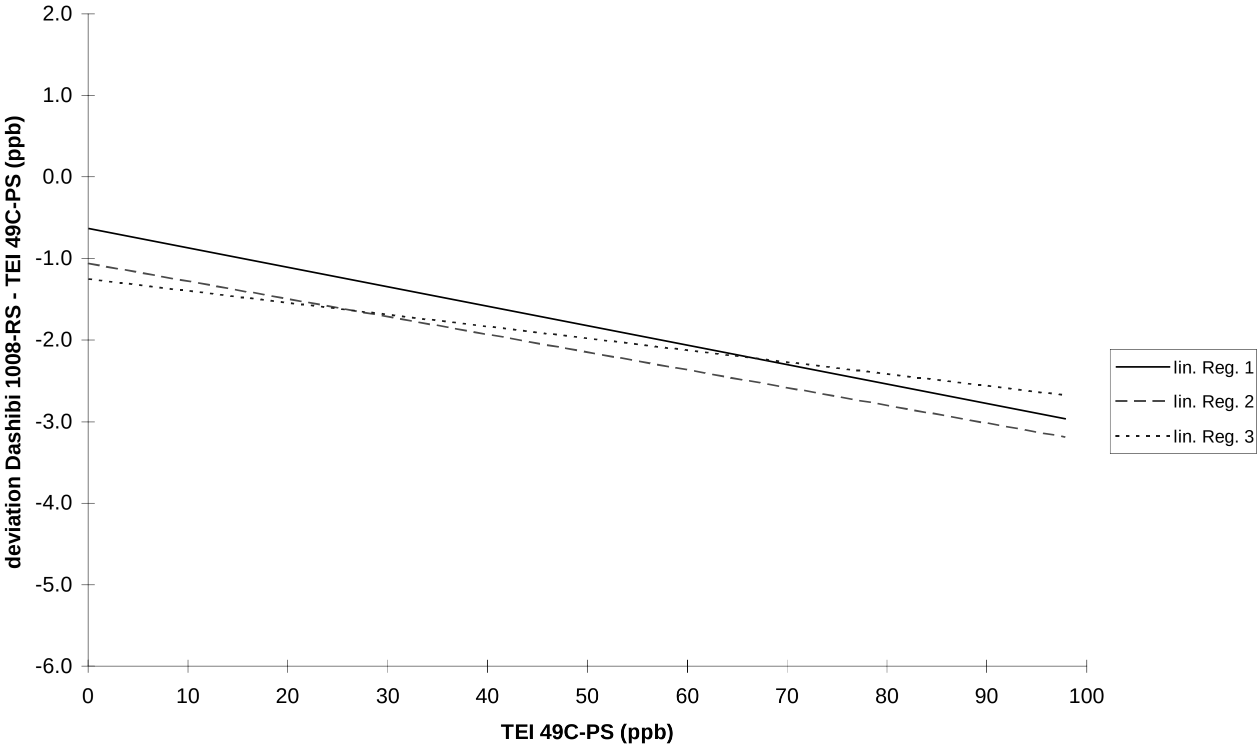

Figure 9: Individual linear regressions of intercomparisons 1 to 3, Dasibi 1008-RS

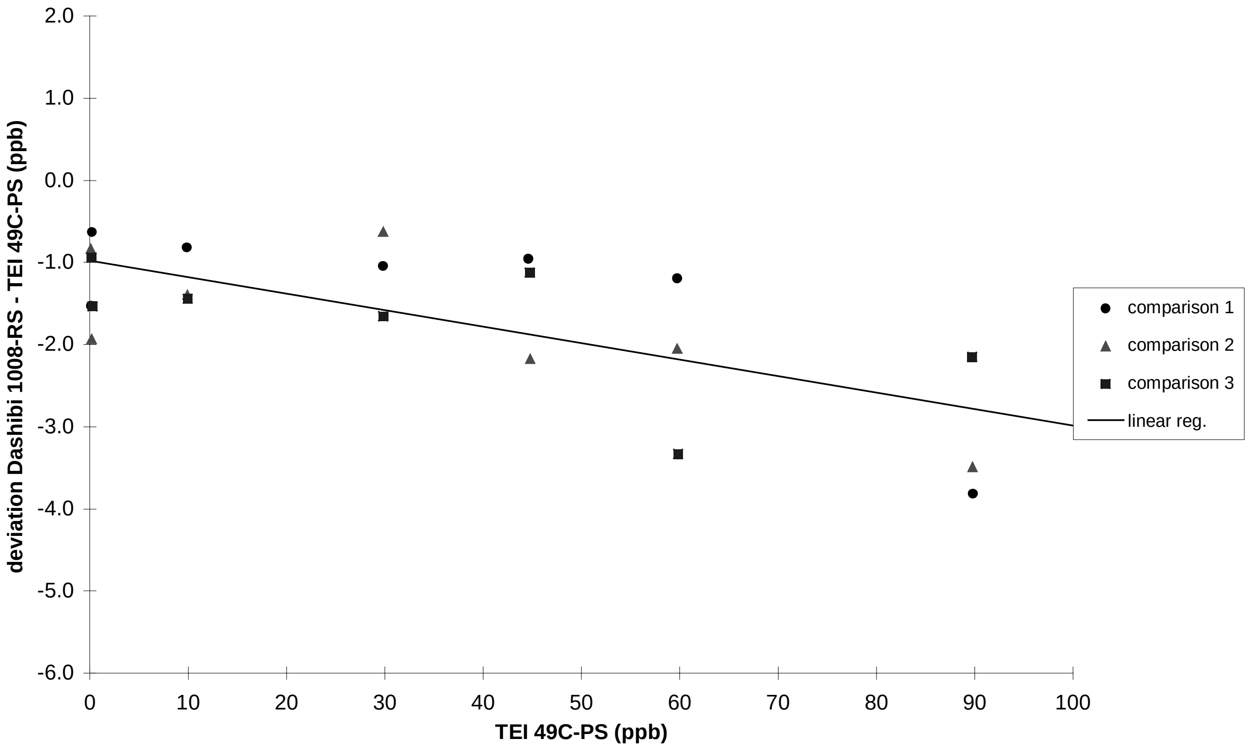

Figure 10: Mean linear regression of intercomparisons 1 to 3, Dasibi 1008-RS

From the intercomparisons of the TEI 49C #55912-305 and the Dasibi 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:

<u>-TEI 49C:</u>

$$\text{TEI 49C} = 1.001 \times \text{TEI 49C-PS} - 0.2 \text{ ppb}$$

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	0.0010	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.05	(f = 3)
	- residuals in ppb	0.13	(f = 19)

<u>-Dasibi 1008-RS:</u>

$$\text{Dasibi 1008-RS} = 0.980 \times \text{TEI 49C-PS} - 1.00 \text{ ppb}$$

Dasibi 1008-RS = O_3 mixing ratio in ppb, determined for Dasibi 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	0.0048	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.22	(f = 3)
	- residuals in ppb	0.63	(f = 19)

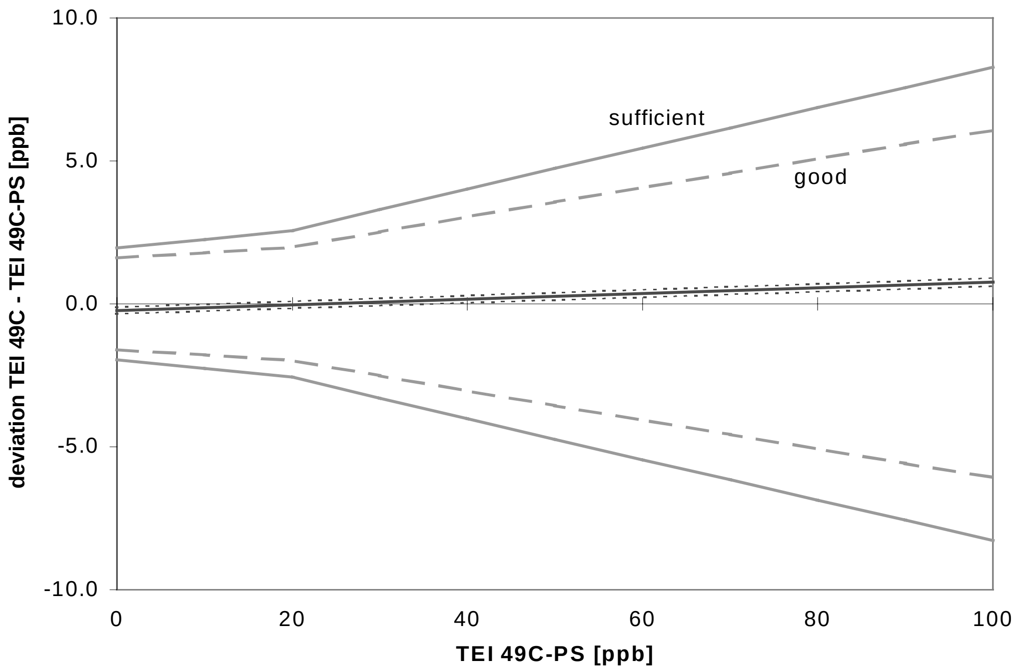

Figure 11: Intercomparison of instrument TEI 49C

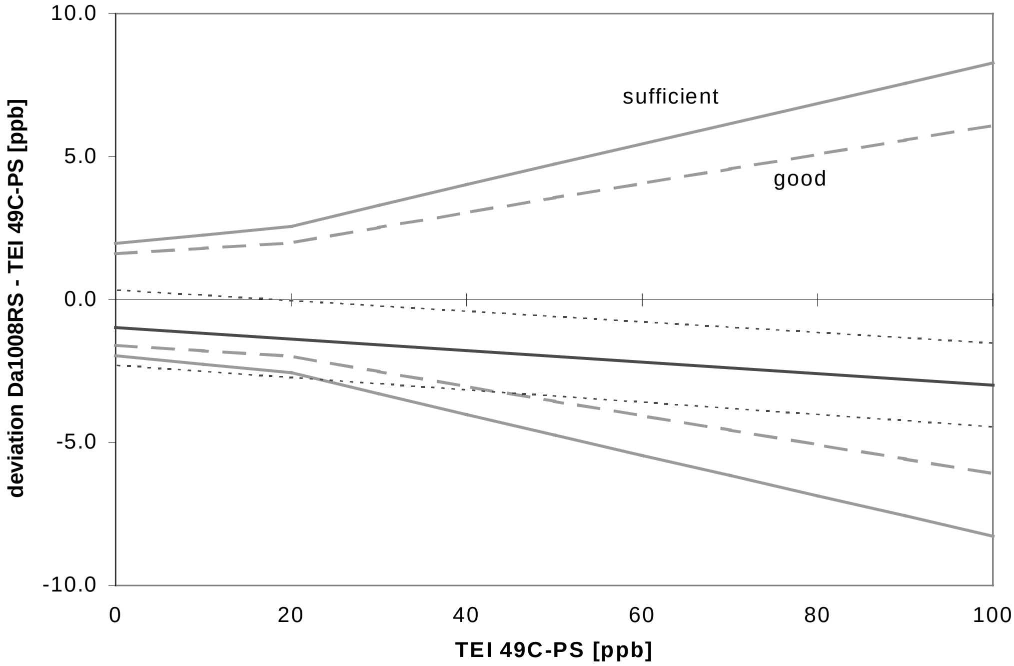

Figure 12: Intercomparison of instrument Dasibi 1008-RS

Comment

The ozone concentration observed at Izaña (1997) usually ranged between 31 and 67 ppb (5- and 95- percentile of hourly mean values).

In the linear regressions of both instruments (figures 7 and 9) no trend as a function of time could be observed.

The basic field instrument, TEI 49C, clearly fulfils the assessment criteria as "good" over the tested range up to 100 ppb (figures 11). Very small deviation among the three intercomparisons is the reason for a very narrow prediction interval which implies that the instrument is in good condition.

The Dasibi 1008PC instrument, considering the range relevant to the site, fulfils the assessment criteria as "good". For concentrations lower than 30 ppb it only partly satisfies them (figure 12). This is due to a relatively wide prediction interval, which had significantly increased, reflecting the comparatively poor stability of the instrument (see Fig. 10).

The linear regression analysis from the intercomparisons obtained in November '96 and during this audit are very similar. However, it should be noted that the stability of the backup instrument, the Dasibi 1008-RS, has declined.

6. Carbon Monoxide Measurements at Izaña

The trace gas carbon monoxide had been measured at Izaña for different projects, i.e. the TOR/EUROTRAC, for several years. After the end of TOR the INM had decided to go on with these continuous measurements and had recently started to re-establish the former instrumentation. At the time of the audit the instrumentation had not yet reached the state of routine operation. Thus, the CO was not audited. Instead, the entire CO system had been analysed, set up to operation and discussed in order to support the operators.

6.1. Instrumentation

The actual CO system is shown below in a schematic. The pro and cons of a different instrument configuration had been discussed. It was agreed that the recommendations below will improve the measurements and thus should be implemented.

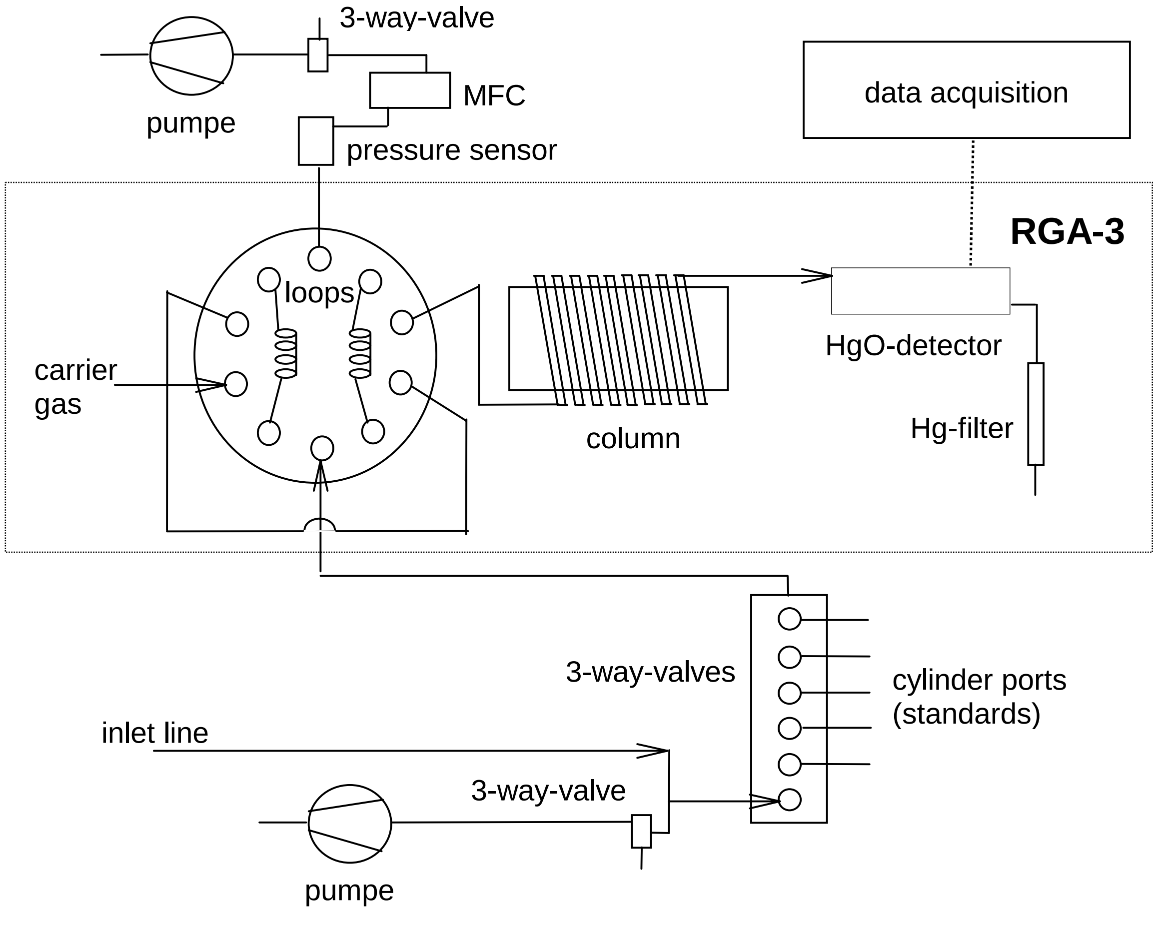

Figure 13: Actual gas sampling schematic of the RGA-3 CO analyser at Izaña

6.2. Recommendations

Table 7: Actual state and its agreed changes of the CO system

Component / Problems	Actual state / Possible cause	Agreed change / Solution
• cooling trap for ambient air:	none	pre-treatment of ambient air with a cooling trap (-55°C) that is already available
• noisy signal	old HgO-bed	replace HgO-bed (check of linearity)
• column	one column system: mole sieve 13X 60/80 (application for CO determination in high purity inerts)	two column system: unibeads 1S 60/80 and mole sieve 5A 60/80
• data acquisition	a basic software which does not have the possibility to reintegrate peaks	replace the actual software with a more sophisticated integration system
• calibration	procedure not fixed yet	hourly calibration with a working tank, working tank compared to CMDL cylinders
• flow schematic	specific application S-001, according the "RGA-3 operating manual"	specific application E-001, according the "RGA-3 operating manual" (one loop, two columns)
• documentation	laboratory journal	additionally an instrument logbook

Appendix

I Calibrator TEI 49C-PS #306 of the Izaña Observatory

In April 1997, an ozone calibrator of the type TEI 49C-PS had been purchased for the Izaña Observatory and is used for regular calibration of the analysers on site as well as for conducting ozone audits within the SCO_3P Project and the GAW Programme in South America.

In the course of the intercomparisons of the ozone analysers at Izaña, an intercomparison of the recently purchased ozone calibrator, TEI 49C-PS #306, was additionally performed. In principal, the experimental procedure was the same as for the analysers described in chapter 5.1. The data about the calibrator is listed in table 9. The results are shown below in table 10 to 12.

Table 8: Experimental details

reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
station calibrator:	INM: TEI 49C-PS #56085-306 transfer standard
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 (EMPA): 772 hPa TEI 49C-PS (INM): 758.4 hPa, for the intercomparison adjusted to 772 hPa
concentration range	0 - 200 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 130 / 185 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	3 x on February 24, 1998
connection between instruments:	about 1.0 meter of 1/4" PFA tubing, ozone connected to station calibrator between manifold and solenoid valve

It should be noted that the pressure transducer of the INM transfer standard had to be adjusted from 758.4 mbar to 772 or by about 1.8 %. Increasing the pressure reading of the sensor has an indirect proportional effect on the ozone reading.

Table 9: Ozone calibrator at global GAW station Izaña

type	TEI 49C-PS #306
method	UV absorption
at Izaña	since April 1997
range	0-200 ppb
analog output	0-10 V
electronic offset	- 1 ppb, artificial electronic offset
calibration coefficient	1.000

Table 10: 1. Intercomparison, TEI 49C-PS #306

No.	TEI 49C-PS (EMPA) conc. ppb	S_d ppb	TEI 49C-PS #306 conc. ppb	S_d ppb	deviation from reference ppb	deviation from reference %
1	0.7	0.09	0.1	0.10	-0.6	
2	60.1	0.13	58.3	0.18	-1.8	-3.0%
3	130.0	0.21	127.4	0.19	-2.6	-2.0%
4	185.1	0.24	181.6	0.20	-3.5	-1.9%
5	90.2	0.24	88.1	0.18	-2.2	-2.4%
6	30.1	0.22	28.9	0.14	-1.2	-4.1%
7	0.8	0.12	0.0	0.23	-0.8	

Table 11: 2. Intercomparison, TEI 49C-PS #306

No.	TEI 49C-PS (EMPA) conc. ppb	S_d ppb	TEI 49C-PS #306 conc. ppb	S_d ppb	deviation from reference ppb	deviation from reference %
1	0.8	0.19	0.1	0.18	-0.7	
2	130.3	0.17	127.3	0.25	-2.9	-2.3%
3	60.2	0.14	58.3	0.20	-2.0	-3.3%
4	185.2	0.11	181.5	0.18	-3.7	-2.0%
5	30.1	0.25	28.9	0.11	-1.3	-4.2%
6	60.1	0.19	58.2	0.23	-2.0	-3.3%
7	0.8	0.12	0.0	0.13	-0.8	

Table 12: 3. Intercomparison, TEI 49C-PS #306

No.	TEI 49C-PS (EMPA) conc. ppb	TEI 49C-PS (EMPA) S_d ppb	TEI 49C-PS #306 conc. ppb	TEI 49C-PS #306 S_d ppb	deviation from reference ppb	deviation from reference %
1	0.7	0.14	-0.1	0.19	-0.8	
2	30.2	0.14	28.8	0.13	-1.4	-4.6%
3	90.2	0.18	87.9	0.15	-2.4	-2.6%
4	185.3	0.21	181.4	0.19	-3.9	-2.1%
5	60.5	0.19	58.2	0.13	-2.2	-3.7%
6	130.1	0.24	127.4	0.22	-2.8	-2.1%
7	0.5	0.21	-0.1	0.12	-0.6	

From the intercomparisons of the TEI 49C-PS #306 ozone calibrator with the TEI 49C-PS transfer standard from EMPA the resulting linear regression (for the range of 0-200 ppb ozone) is:

calibrator Izaña = 0.984 x TEI 49C-PS (EMPA) - 0.8 ppb

calibrator Izaña = O_3 mixing ratio in ppb, determined for TEI 49C-PS #306
TEI 49C-PS (EMPA) = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:			
	- slope s_m	0.0006	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.06	(f = 3)
	- residuals in ppb	0.14	(f = 19)

Comment

The deviation of the INM transfer standard to the one of the EMPA is with 1.2 % for the slope and -0.8 ppb offset is relatively high and should be adjusted accordingly. However, since the results of the comparison measurements (EMPA transfer standard vs. SRP) between prior and after the audit deviated more than generally observed we recommend to apply half of the above regression function only.

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.

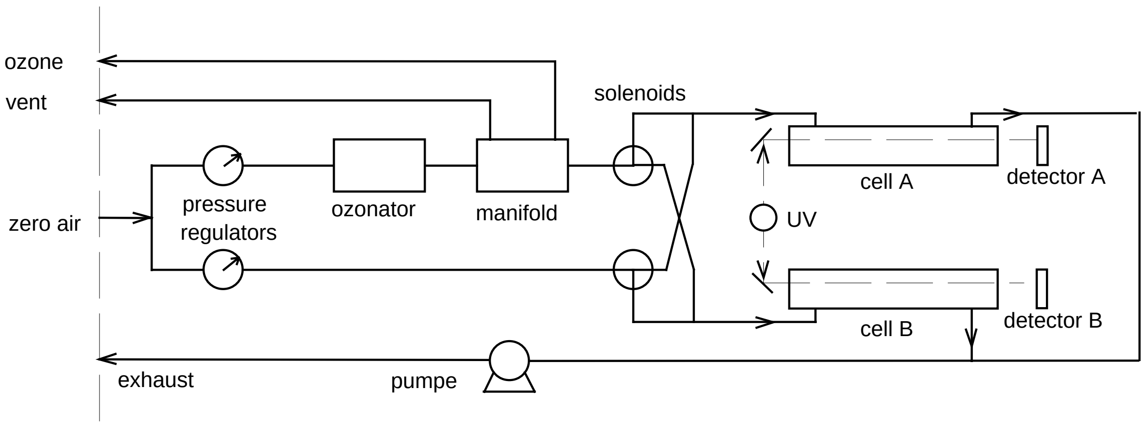

Figure 14: Flow schematic of TEI 49C-PS

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 13 and Figure 15.

Table 13: 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 / 190 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

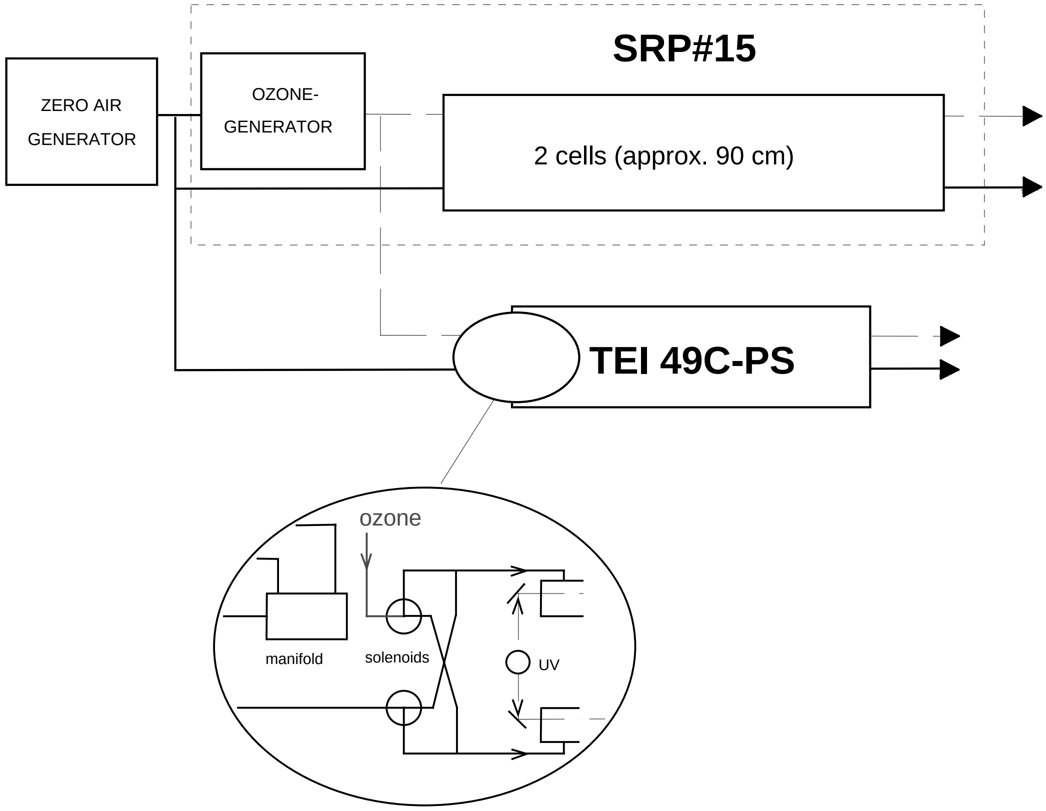

Figure 15: Instruments set up SRP -TEI 49C-PS

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 approximately ±(1 ppb + 0.5%).

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 fulfilled the recommended criterias for the period of the audit, including transportation. However, it should be noted that the results of the comparison measurements between prior and after the audit deviated more than generally observed.

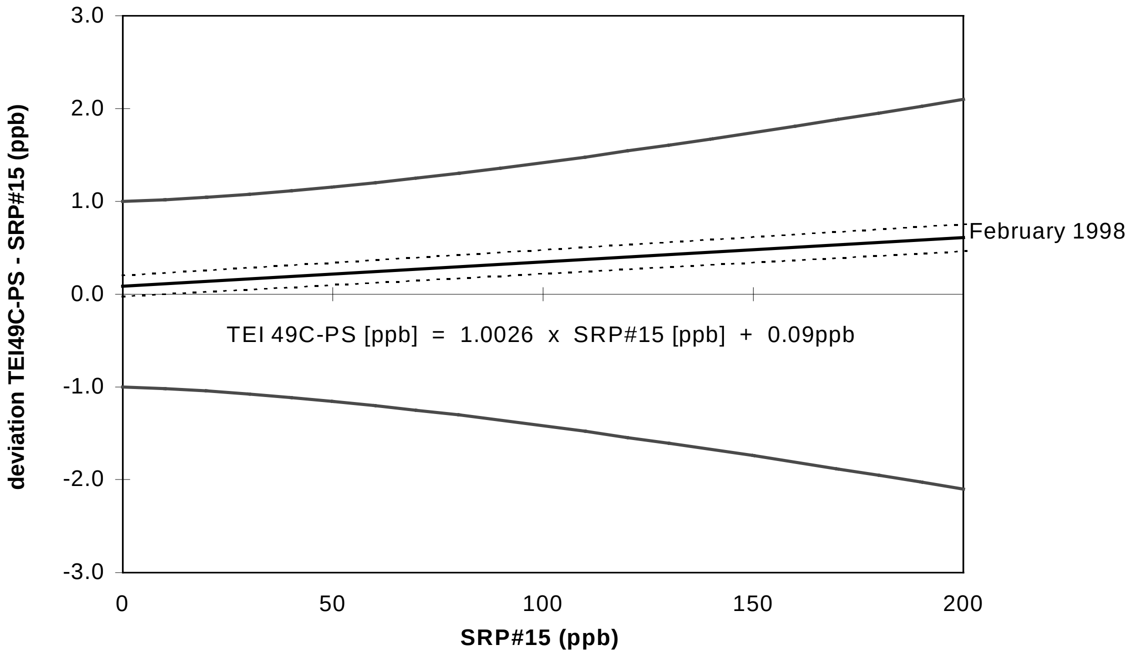

Figure 16: Transfer standard before audit

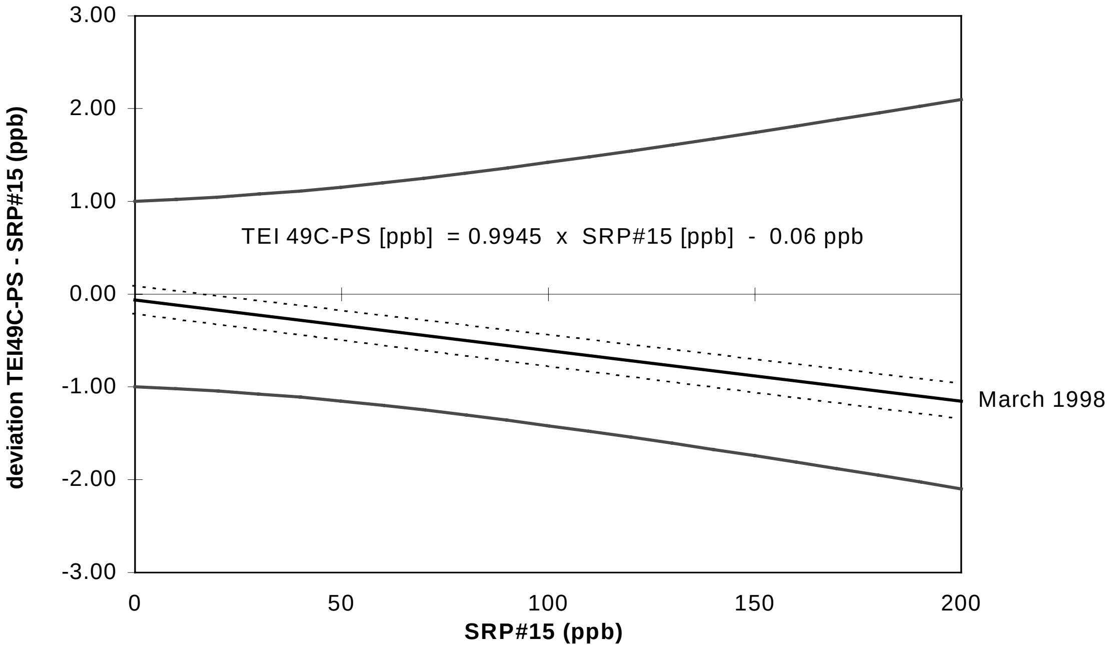

Figure 17: Transfer standard after audit

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 data of Izaña to add the information in this first audit report already.

- A cooling trap (-55°C) for pre-treatment of ambient air has been implemented.
- The money had been approved to buy the recommended replacement and additional parts, i.e. two analytical columns, HgO bed, 2 UV lamps and a loop. Thereafter, the flow schematic will be adapted according the E-001 sketch in the "RGA-3 operating manual".
- An improved integration software had been installed so the chromatograms are stored and could be reintegrated anytime using different integration methods.
- At the time, the system is calibrated every 20 minutes with a working standard. The working standard is traced back to CMDL standards around every two to three weeks.