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

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 04/4

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE

GLOBAL GAW STATION IZAÑA

TENERIFE, SPAIN, DECEMBER 2004

Submitted by

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WMO World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
Empa Dübendorf, Switzerland

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APPENDIX

Empa is accredited as a calibration laboratory for ozone measuring instruments in accordance with ISO/IEC 17025

1 EXECUTIVE SUMMARY

A system and performance audit was conducted at the Global Atmosphere Watch station Izaña from 30. November to 4. December 2004 by the World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-Empa). The results of the fourth WCC-Empa audit can be summarized as follows:

1.1 System Audit of the Observatory

The Izaña global GAW station was completely re-built since the last audit of WCC-Empa in 2000. It offers excellent facilities for atmospheric research and measurement campaigns.

1.2 Audit of the Ozone Measurements

The station ozone analysers and calibrator were inter-compared with the travelling standard of WCC-Empa. The inter-comparison, consisting of three multipoint runs between the WCC transfer standard and the ozone instruments of the station, demonstrated good agreement between the station analyzer and the transfer standard. The recorded differences fulfilled the assessment criteria as "good" over the tested range from 0 to 100 ppb (Figure 1, main station instrument).

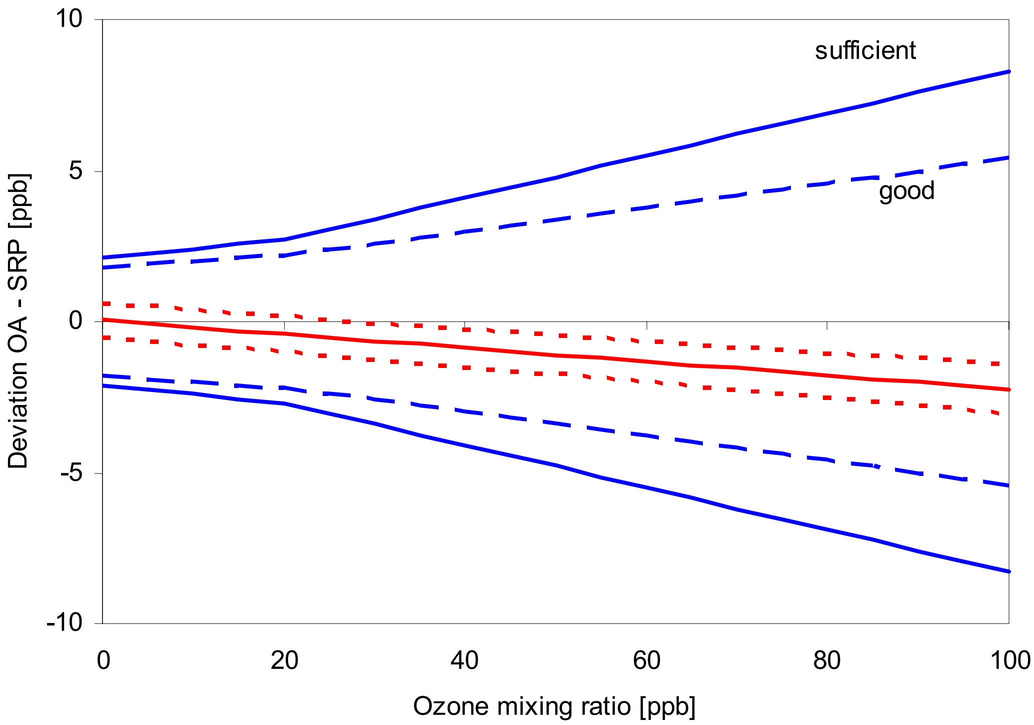

Figure 1: Inter-comparison of instrument TEI 49C #62900-337

The second ozone instrument also fulfilled the WCC-Empa criteria and was in a good condition.

The ozone calibrator at the station also fulfilled the WCC-Empa criteria and was in a good condition (Figure 2). Inter-comparisons between the station calibrator and the ozone analyzers of the station made since the last WCC-Empa audit were reviewed during the audit and were consistent with the results of WCC-Empa.

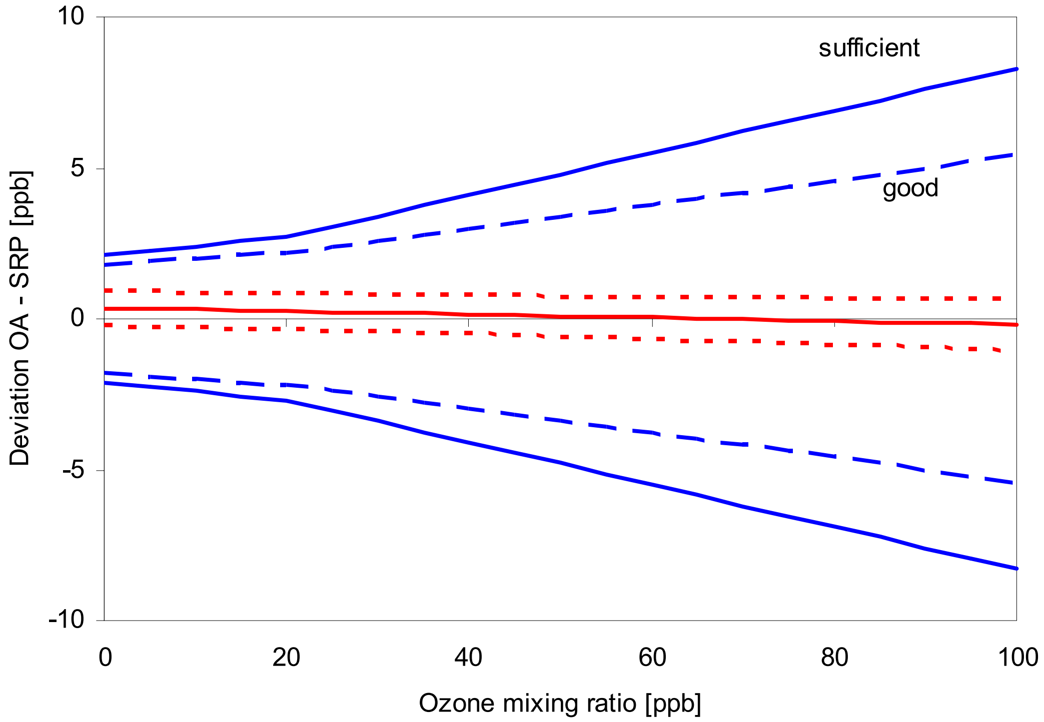

Figure 2: Inter-comparison of instrument TEI 49CPS #56085-306

Due to the good results of the inter-comparison, only minor recommendations were made by WCC-Empa. An executive summary of the surface ozone audit results is given in Appendix VII

1.3 Audit of the Carbon Monoxide Measurements

The analysis of the WCC-Empa transfer standards by the Izaña station resulted in lower values (-9.0 to -6.0 ppb or -3.4 to -13.5%) for concentrations between 70 and 175 ppb compared to the reference (Figure 3). Differences can be directly attributable to the set of standards used at Izaña. These standards refer to the WMO-88 scale of NOAA-CMDL. WCC-Empa refers to the NOAA-CMDL WMO-2000 scale but calibration standards at lower concentrations (below 200 ppb CO) are determined using a higher concentration standard on a UV-Fluorescence instrument. Inconsistencies within the two CO scales explain most of the observed differences.

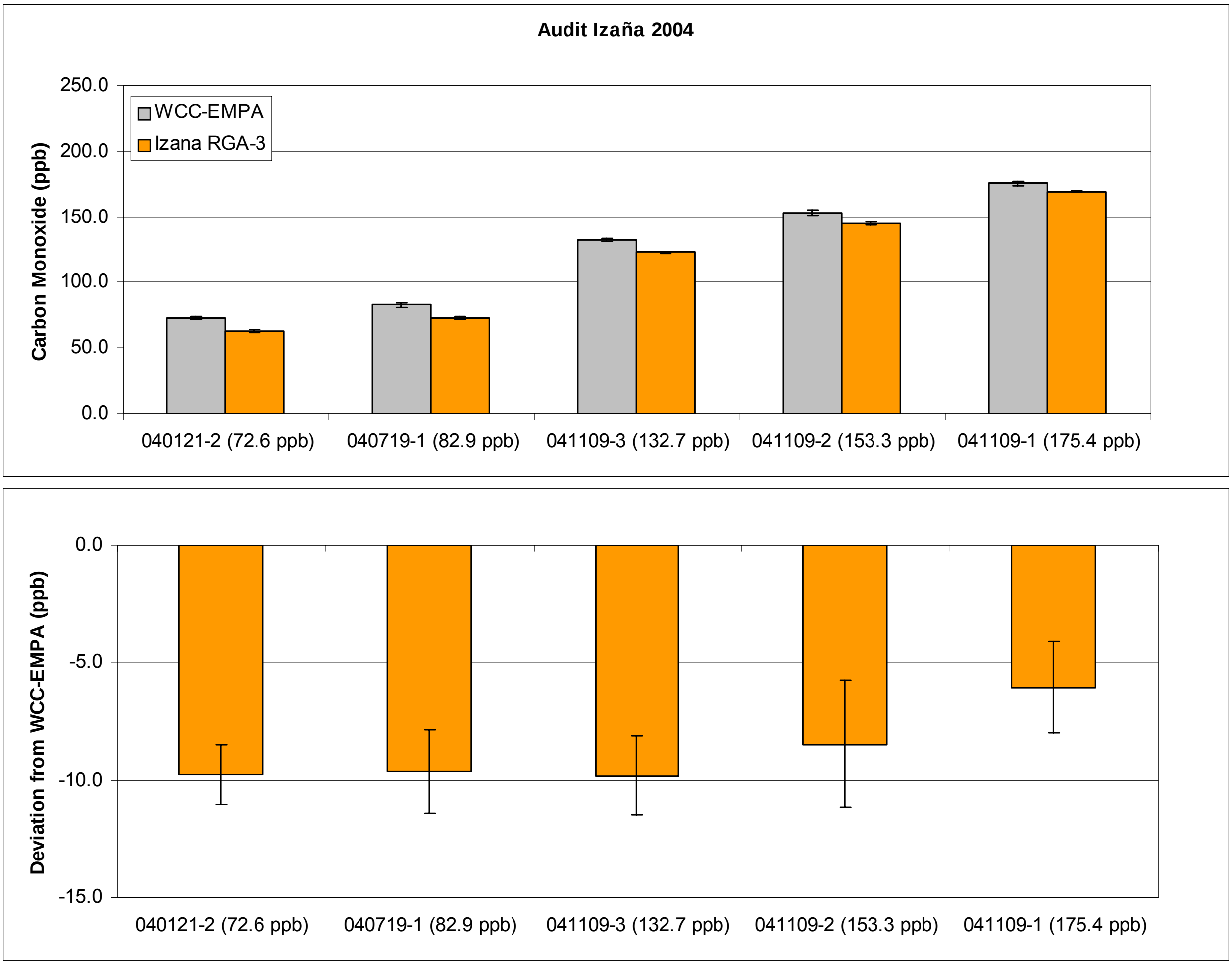

Figure 3: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Izaña (orange).
lower panel: deviation of the Izaña station from the reference.
The error bars represent the 95% confidence interval.

1.4 Audit of the Methane Measurements

The results of the inter-comparisons between the five WCC-Empa travelling standards and the GC system of Izaña showed good agreement over the concentrations range of 1790 to 1880 ppb (Figure 4). The audit results at Izaña are good when compared to methane audits conducted by WCC-Empa at other GAW sites. The station instrument also showed reasonable repeatability. Due to the good results no technical recommendations are made by WCC-Empa.

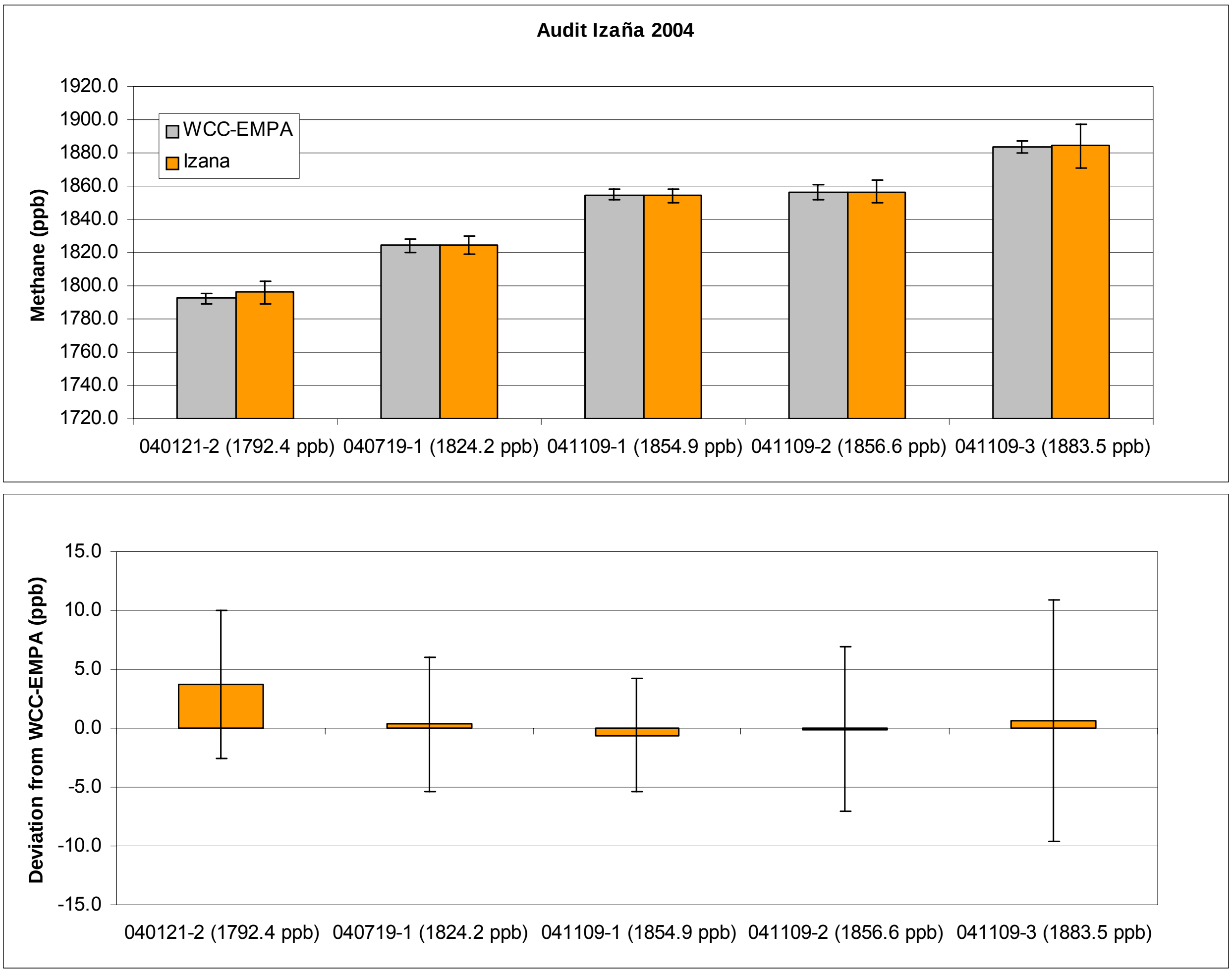

Figure 4: upper panel: concentrations of the WCC transfer standards (grey) measured with the GC system of Izaña (orange).
lower panel: deviation of Izaña from the reference.
The error bars represent the 95% confidence interval.

1.5 Data Submission

Data submission to the GAW World Data Centres is one of the obligations of stations participating in the GAW program. Surface ozone and methane data were submitted to the World Data Centre for Greenhouse Gases (WDCGG), but submission of more recent data was delayed due to the renovation of the station. Carbon monoxide data has not yet been submitted due to unresolved issues with the carbon monoxide scale.

1.6 Conclusions

The global GAW station Izaña is an established monitoring site within the GAW program. Several decades of high quality data series exist for many parameters. The Izaña site also provides a good platform for extensive atmospheric research studies.

The results of the inter-comparisons for surface ozone, carbon monoxide and methane showed good agreement between WCC-Empa and the station instruments for ozone, carbon monoxide and methane.

The analysis of the WCC-Empa transfer standards at the Izaña station for CO resulted in lower values for the concentrations between 70 and 300 ppb when compared to the WCC-Empa reference scale. Differences observed between Izaña and WCC-Empa at lower CO concentrations are attributable to uncertainties of the CO scale provided by CMDL.

Dübendorf, 21. February 2006

Empa Dübendorf, WCC-Empa

Project leader

Dr. C. Zellweger

Head of the laboratory

Dr. B. Buchmann

2 INTRODUCTION

The global GAW station Izaña is an established site for long-term measurements of greenhouse gases, ozone and physical and meteorological parameters. The observatory is maintained by the Instituto Nacional de Meteorología (INM).

The Laboratory for Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (Empa) was assigned by the WMO to operate the **GAW World Calibration Centre (WCC)** for Surface Ozone, Carbon Monoxide and Methane, thereby establishing a coordinated quality assurance program for this part of GAW. The detailed goals and tasks of the WCC concerning surface ozone are described in the GAW report No. 104. System and performance audits at global GAW stations are conducted regularly based on mutual agreement about every two to four years.

In agreement with the GAW country contact and station manager, Dr. Emilio Cuevas (INM), a system and performance audit was conducted at the global GAW station Izaña, Spain, from November 30 to December 4, 2004.

The scope of the audit was the whole measurement system in general and surface ozone, carbon monoxide and methane measurements in particular. The entire system from the air inlet to the data processing and the quality assurance was reviewed during the audit procedure. The assessment criteria for the ozone inter-comparison have been developed by WCC-Empa and QA/SAC Switzerland [*Hofer, et al.*, 2000; *Klausen, et al.*, 2003]. The present audit report is distributed to the GAW station Izaña and the World Meteorological Organization in Geneva.

Staff involved in the audit

INM	Dr. Emilio Cuevas	contacts, general program
	Mr. Ramon Ramos	technical assistance at the observatory
	Mr. Carlos Marrero	technical assistance at the observatory
WCC-Empa	Dr. Christoph Zellweger	lead auditor
	Mr. Beat Schwarzenbach	

Previous audits at the GAW station Izaña:

November 1996, February 1998 and June 2000 by WCC-Empa

3 GLOBAL GAW SITE IZAÑA, SPAIN

3.1 Site description

The GAW site Izaña is located on the island of Tenerife, Spain, (28.300 N, 16.50° W) roughly 300 km west of the African coast (Figures 5 and 6). 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 is predominately from the north-western sector. Typical for 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 of 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 pass the vicinity per day.

The facilities at Izaña were renovated and enlarged between 2000 and 2004. During this period some of the measurements were made in the provisional site about 100 m south of the main laboratory building. Whenever possible parallel measurements were made to ensure comparable measurement series at the two sites.

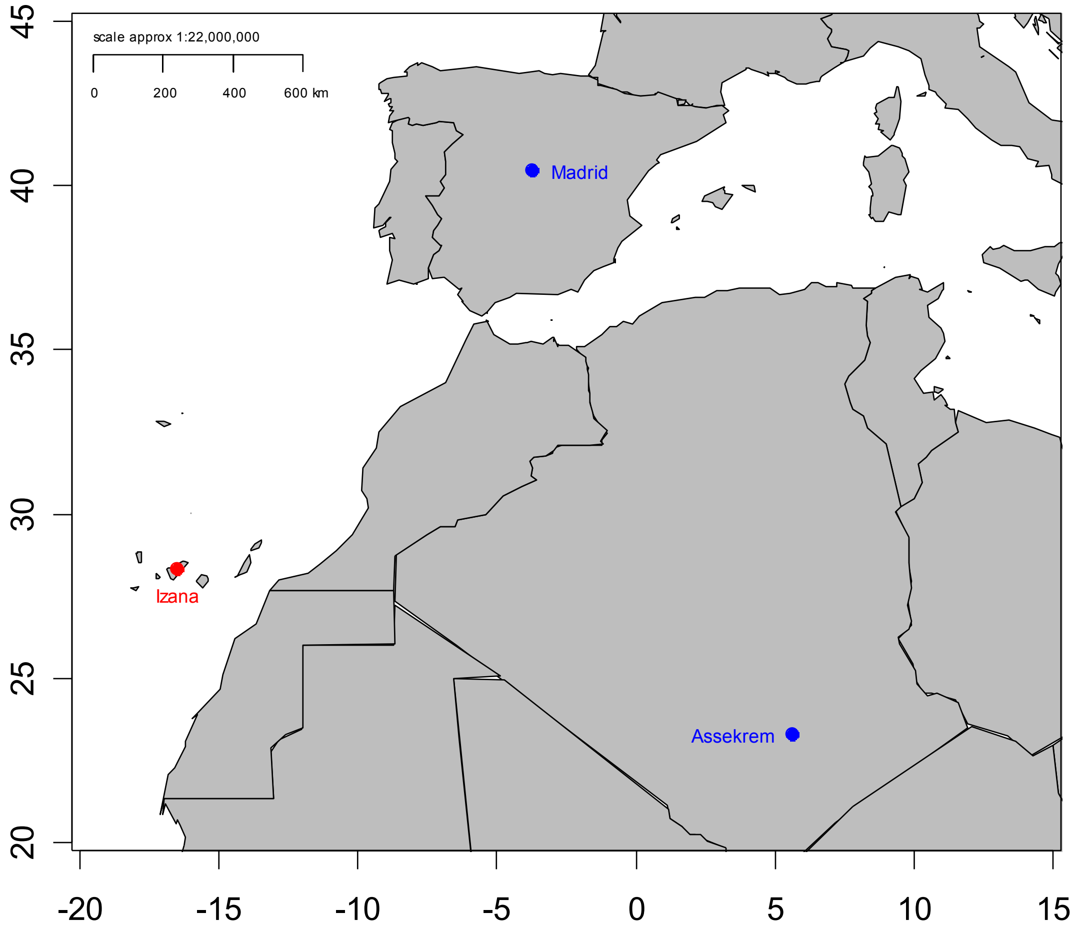

Figure 5: Location of Izaña

Figure 6: Izaña observatory

3.2 Ozone, carbon monoxide and methane levels at Izaña

The frequency distributions of one hourly mean values for surface ozone, carbon monoxide and methane are shown in Figures 7 to 9.

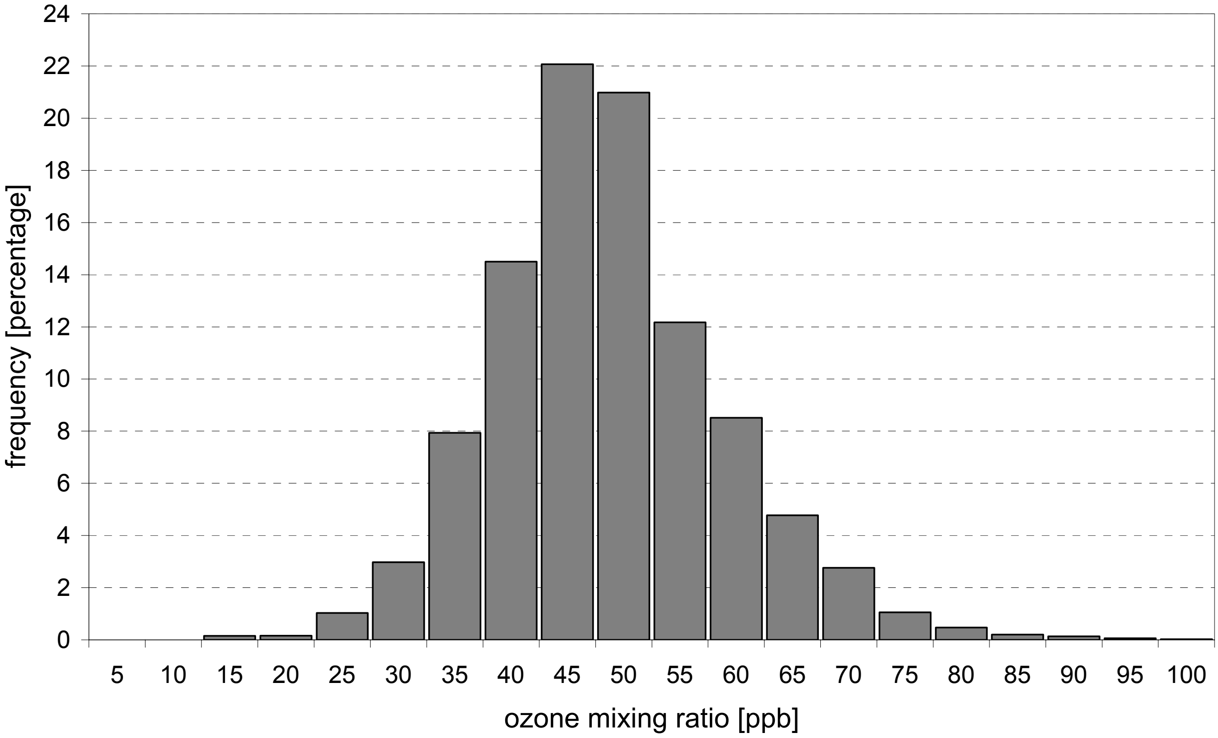

Figure 7: Frequency distribution of hourly ozone mixing ratios (ppb) at Izaña for the year 2003. Data availability 91.7%.

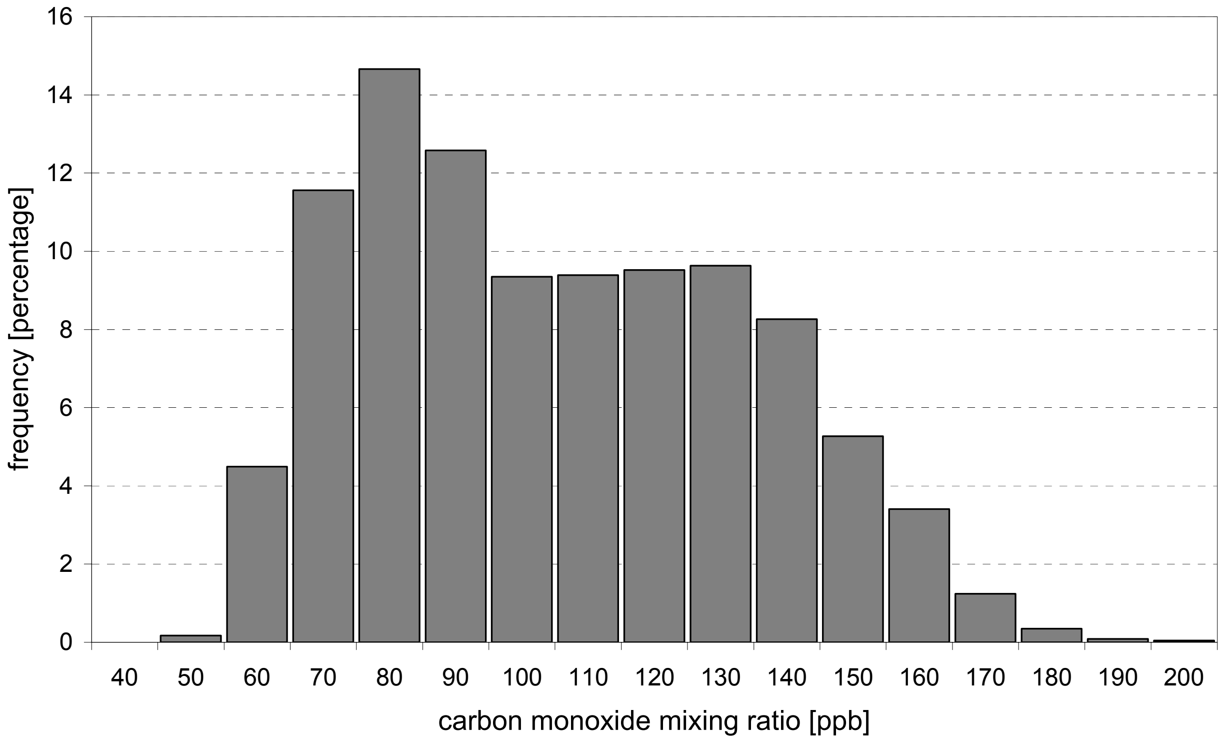

Figure 8: Frequency distribution of hourly carbon monoxide mixing ratios (ppb) at Izaña for the year 1999. Data availability 52.6%.

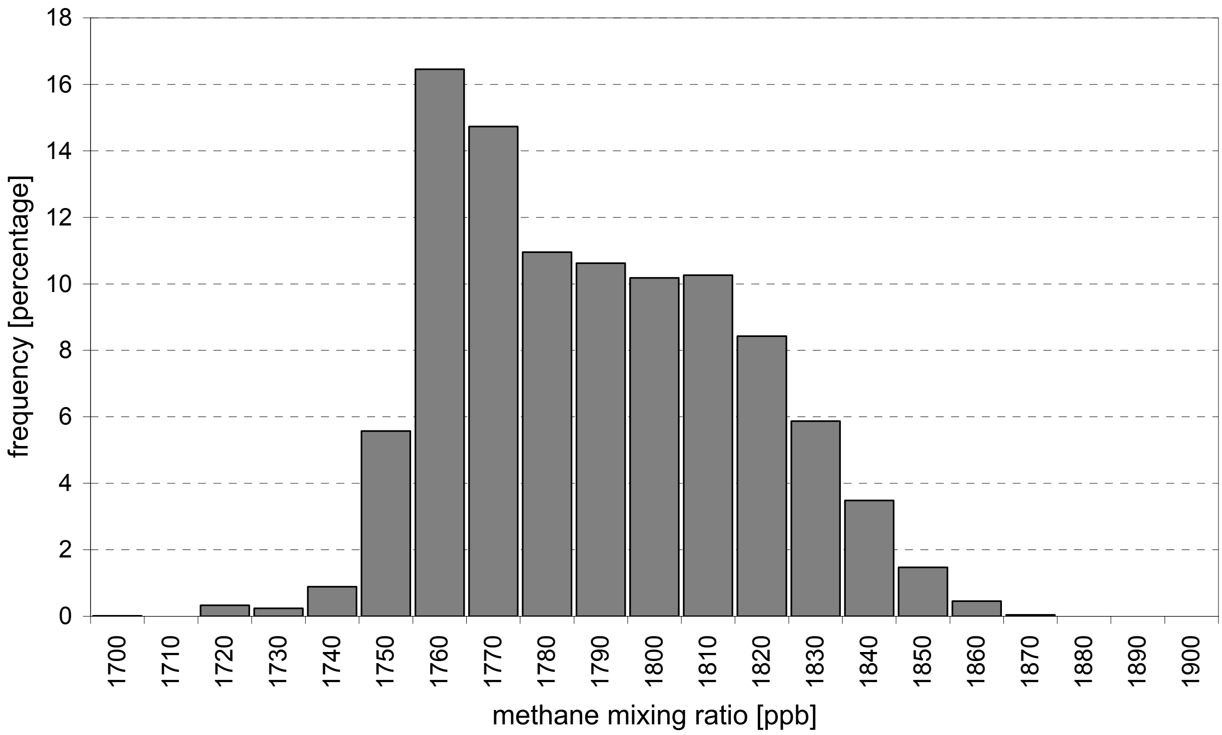

Figure 9: Frequency distribution of hourly methane ratios (ppb) at Izaña for the year 2002. Data availability 82.2%.

3.3 Izaña Staff

The GAW station Izaña is approximately one hour drive from the headquarters in St. Cruz. During working days the station is visited by the station operators. At night and during weekends and holidays the station is staffed with a security guard. Table 1 shows the staff responsible as of December 2004.

Table 1: Staff responsible for the GAW station Izaña (November 2004)

Dr Emilio Cuevas, Director of Izaña Atmospheric Observatory (Physics PhD)
Technical staff: Instrument operators and specialists Mr. Ramon Ramos, Field Manager (Physics graduate) Mr. Victor Ayala, Computer network, communications and software applications (Electronic Engineer) Mr. César López, Instrument maintenance (Electronic Engineer) Mr. Sergio Afonso, Ozonesonde instrument specialist Mr. Carlos Torres, Radiation and aerosol instrument specialist (Physics graduate, PhD in course) Mr. Julián Pérez, trace gas instrument specialist Mr. José Manuel Rodríguez, lidar instrument specialist (Physics graduate, PhD in course) Mr. Ramon Juega, Observer Mr. Daniel Martín, Observer (Physics graduate) Ms. Cándida Hernández, Observer (Biology graduate) Mr. Juan Canino, building maintenance (Electricity technician) Mr. Manuel Estevez, building maintenance (Technician)
Permanent position research staff Mr. Alberto Redondas, Total column ozone, ozonesonde and UV radiation programs, Principal Investigator of the WMO Regional Brewer Calibration Centre for Europe (RBCC-E) (Physics graduate, PhD in course) Mr. Pedro Romero, Optical Aerosol Program (Physics graduate) Mr. Carlos Marrero, Surface ozone and carbon monoxide programs (50%) and air quality forecasting modelling (50%) (Physics graduate, PhD in course) Mr. Juanjo Bustos, Meteorological support, McIdas Forecasting and analysis system (Physics graduate) Mr. Angel Gómez-Peláez, Greenhouse gases Program (Physics graduate, PhD in course)
Contracted research staff Dr. Sergio Rodríguez, Physical and Chemical Aerosol Program (Physics PhD) Dr. Celia Milford, Air quality forecasting program (Physics PhD) Dr. Matthias Schneider, NDSC-FTIR program (Physics PhD) Dr. Sergio Chueca, Aerosol MPL Lidar program (Physics PhD) Mr. Virgilio Carreño, UVI forecasting program, Brewer calibration (Physics graduate, PhD in course)
Students Ms. Silvia Alonso, Dust forecasting system (Physics graduate, PhD in course) Ms. Carmen Guirado, UV and Radiation Program (Physics graduate, PhD in course)
Supporting staff Ms. Julieta Bethencourt, Financial Section Chief Ms. Pilar Salamo, Secretary Ms. Concha Salamo, Secretary Mr. Marcos Damas, Driver

4 SYSTEM AND PERFORMANCE AUDIT FOR SURFACE OZONE

4.1 Monitoring Set-up and Procedures

4.1.1 Air Inlet System

The air inlet is on top of the renovated tower. A service channel in the centre of the tower is running from the upper most level to the ground level. All laboratories have access to this inlet system.

Sampling-location:

on top of the tower building, 5 m above the tower terrace and 30 m above ground.

Sample inlet:

The inlet consists of a stainless steel inlet running from the tower terrace through the central service channel. The upper part is heated. A pump flushes the inlet with 2180 l/min. Inner diameter approx. 10 cm. The Inlet is protected against rain by an upside-down stainless steel bucket. Ozone instruments are installed at the 6th floor 23.5 m above ground.

Sampling-line:

Dimensions:	length = ca. 4 m, inner diameter = 4 mm
Material:	PFTE
Inlet-filter:	Teflon inlet filter before instrument, exchanged weekly
Flow rate:	ca. 2 l/min

Total residence time in the sampling line and the inlet: ca. 3 s

Materials as well as the residence time of the inlet system are adequate for surface ozone measurements.

4.1.2 Instrumentation

Ozone Analyzers

Two TEI 49C ozone analyzers are used for surface ozone measurements. The instruments are installed in the air-conditioned laboratory, and are protected from direct sunlight. One instrument is assigned to be the main instrument, and the other analyzer runs mainly for QA/QC reasons. Data of the two analyzers are compared and further measures are taken when a significant difference is present. Data of the main instrument are used for scientific data analysis.

Ozone Calibrator

A TEI 49C-PS is available at the site. It is used approximately every three months for an inter-comparison with the station instrument. No changes of the calibration settings are done by the station operators. Instrument details are summarized in Table 2.

Table 2: Ozone instruments at Izaña. Analyzer #1 is the main station instrument.

	Analyzer #1	Analyzer #2	Station calibrator
Type	TEI 49C #62900-337	TEI 49C #72491-371	TEI 49CPS #56085-306
Method	UV absorption		
At Izaña	Since February 1999	Since November 2003	Since April 1997
Cal. before audit	BKG -4.0, Span 1.006	BKG -2.0, Span 1.048	BKG -1.0, Span 1.000
Cal. after audit	No changes were made		
Analogue output	0-10 V		
Digital output	RS-232		

Operation and Maintenance

Preventive maintenance of the instruments includes adjustment of the pressure transducers and cleaning of the instruments cells, and is performed on a case by case basis (every 2-6 month). The instruments are protected with an inlet filter. The filter is changed every one to three months, depending on the season or Sahara dust events.

Automatic zero checks are performed daily at 16:00 UTC. Zero data is used for data reprocessing and correcting the zero offset. The station calibrator is used weekly for a manual span check (90 ppb). Every three weeks, the analyzers are checked at three ozone levels (10, 45, 90 ppb for 10 min). However, these tests are not considered as calibrations, and further actions are only taken if a considerable disagreement is noticed. Three times a year, a multipoint calibration using the TEI 49C-PS #56085-306 is performed. The photometer was certified with the NIST Standard Reference Photometer #16 in July 1996 and was inter-compared with the WCC-Empa transfer standard in February 1998 (TEI 49C-PS #54509-300), June 2000 (TEI 49C-PS #62026-333) and during this audit TEI 49C-PS #54509-300).

4.1.3 Data Handling

Data Acquisition and –transfer

The data acquisition is installed at the site next to the ozone analyzers. It consists of an ADC circuit board and data acquisition software.

Data Treatment

The data is reprocessed on a monthly basis. Two ozone data files are generated, one file containing ten-minute average values and the other one the daily zero readings (12 one-minute means) from the zero checks at 16:00 UTC. Invalid values (according to the logbook) or questionable data is flagged. All data is visually inspected before a validated data set is created.

Data Submission

Ozone data have been submitted to the World Data Centre for Surface Ozone at JMA (World Data Centre for Greenhouse Gases, WDCGG). Submitted data currently span the period from 1996 to 2001. Submission of more recent data was delayed by re-construction work of the station. Submission of missing data is planned for 2005.

Documentation

Electronic station and instrument logbooks are available. The notes are up to date and describe all important events. All instrument manuals are available at the site.

Comment

The frequent instrument checks and the up-to-date electronic logbook support the quality of the data. No change of the current practice is suggested.

4.2 Inter-comparison of the Ozone Instrument

Inter-comparisons were made for the both station instrument and the station calibrator. The analyzer TEI 49C #62900-337 is considered as the main station instrument, whereas TEI 49C #72491-371 operates as a backup instrument.

4.2.1 Experimental Set-up

The WCC transfer standard TEI 49C PS (details see Appendix III-IV) was operated in stand-by mode to warm up for more than 24 hours. During this stabilization time the transfer standard and the PFA tubing connections to the instrument were conditioned with 400 ppb ozone for 30 minutes. Afterwards, three comparison runs between the field instruments and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 10 the experimental set-up during the audit. No modifications of the ozone analyzers which could influence the measurements were made for the inter-comparisons.

The audit procedure included a direct inter-comparison of the WCC-Empa 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 Appendix IV.

Table 3: Experimental details of the ozone inter-comparison

reference	Empa: TEI 49C-PS #5409-300 transfer standard
field instruments	TEI 49C #72491-371(main analyzer) TEI 49C #62900-337 (backup analyzer) TEI 49CPS #56085-306 (calibrator)
ozone source	WCC: 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 systems	16-channel ADC circuit board with acquisition software (Hunter & Caprez) TEI internal data logger (WCC-Empa) Station data acquisition
pressure transducer readings	Ambient Pressure: 765.7 hPa TEI 49C-PS (WCC): adjusted to 765.7 hPa TEI 49C #72491-371: 765.6 hPa, not adjusted TEI 49C #62900-337: 765.4 hPa, not adjusted TEI 49CPS #56085-306: 765.7 hPa, not adjusted
concentration range	0 - 100 ppb
number of concentrations	5 + zero air at start and end
approx. concentration levels	15 / 35 / 55 / 75 / 90 ppb
sequence of concentration	random
averaging interval per concentration	5 minutes
number of runs	3 runs per instrument, between December 1 and 3, 2004
connection between instruments	about 1.5 meter of 1/4" PFA tubing

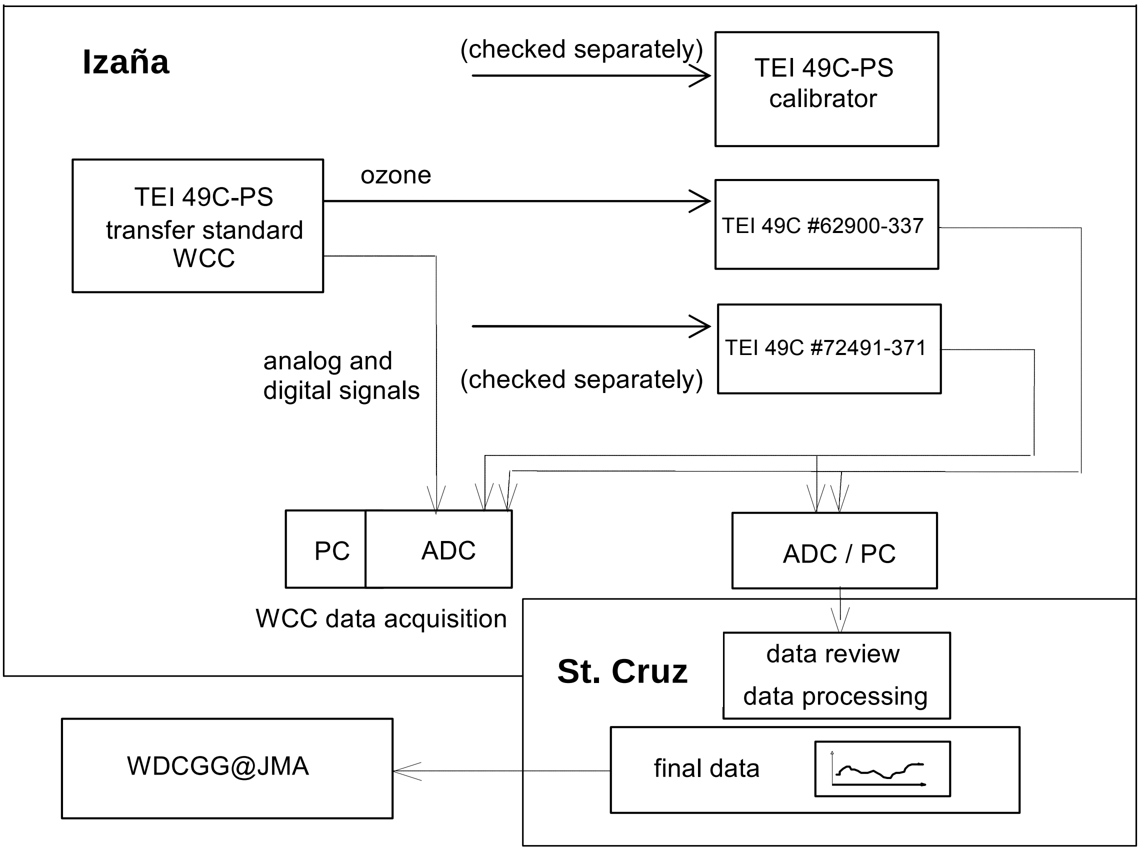

Figure 10: Experimental set up for the ozone inter-comparison

4.2.2 Results

The assessment of the inter-comparison was done according to [*Klausen, et al.*, 2003]. The results shown below refer to the calibration factors as given in Table 2 and was corrected for the zero offset (see below).

Ozone Analyzer – Main Instrument

The results comprise the inter-comparison between the TEI 49C #62900-337 field instrument and the WCC transfer standard TEI 49C-PS, carried out on December 2, 2004.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 60-second-means are presented in Table 4. For each mean value the differences between the concentrations assigned by the station and the WCC-Empa transfer standard are calculated in ppb and in %.

Figures 11 and 12 show the residuals of the linear regression analysis of the field instrument compared to the WCC-Empa transfer standard. The residuals versus the run index are shown in Figure 11 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 12 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 13).

The data used for the evaluation was recorded by both WCC-Empa and Izaña data acquisition systems. The raw data was treated according to the usual station method, which implied a zero offset correction of -4.05 ppb based on the average observed zero reading of 4.05 ppb during the inter-comparison.

Table 4: Inter-comparison of the ozone field instrument TEI 49C #62900-337

run index	WCC TEI 49C-PS conc.		TEI 49C #62900-337 conc.		deviation from reference	
	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	-0.14	0.16	-0.10	0.15	0.03	
2	34.97	0.08	34.17	0.15	-0.81	-2.30
3	14.96	0.08	14.56	0.16	-0.40	-2.67
4	74.87	0.13	73.52	0.19	-1.36	-1.81
5	89.93	0.07	88.28	0.20	-1.65	-1.83
6	54.97	0.10	54.04	0.14	-0.93	-1.68
7	-0.13	0.11	-0.01	0.19	0.12	
8	-0.12	0.08	-0.03	0.19	0.09	
9	89.89	0.06	88.14	0.19	-1.75	-1.95
10	35.02	0.03	34.42	0.13	-0.60	-1.72
11	15.01	0.11	14.71	0.14	-0.30	-2.01
12	54.95	0.14	53.84	0.18	-1.11	-2.02
13	74.90	0.13	73.58	0.04	-1.32	-1.76
14	-0.05	0.11	0.08	0.09	0.14	
15	-0.02	0.07	0.05	0.14	0.07	
16	15.09	0.15	14.85	0.18	-0.23	-1.53
17	55.06	0.04	53.84	0.16	-1.22	-2.21
18	35.00	0.16	34.18	0.19	-0.83	-2.36
19	89.91	0.07	88.22	0.23	-1.69	-1.88
20	74.93	0.09	73.74	0.15	-1.19	-1.59
21	0.10	0.31	0.01	0.12	-0.09	

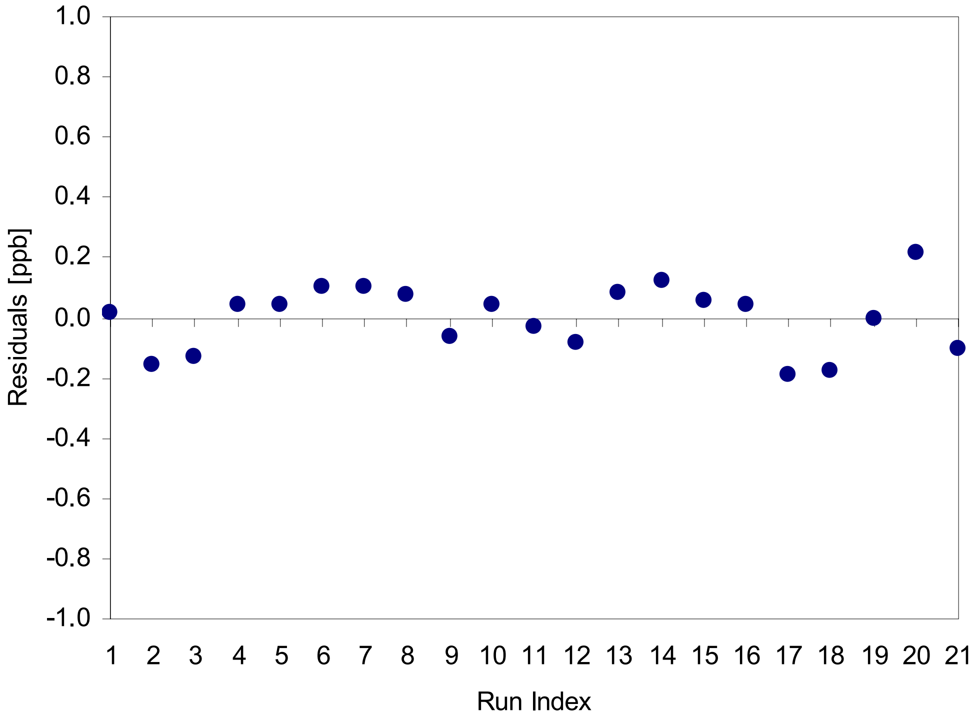

Figure 11: Residuals to the linear regression function (TEI 49C #62900-337) vs. the run index (time dependence)

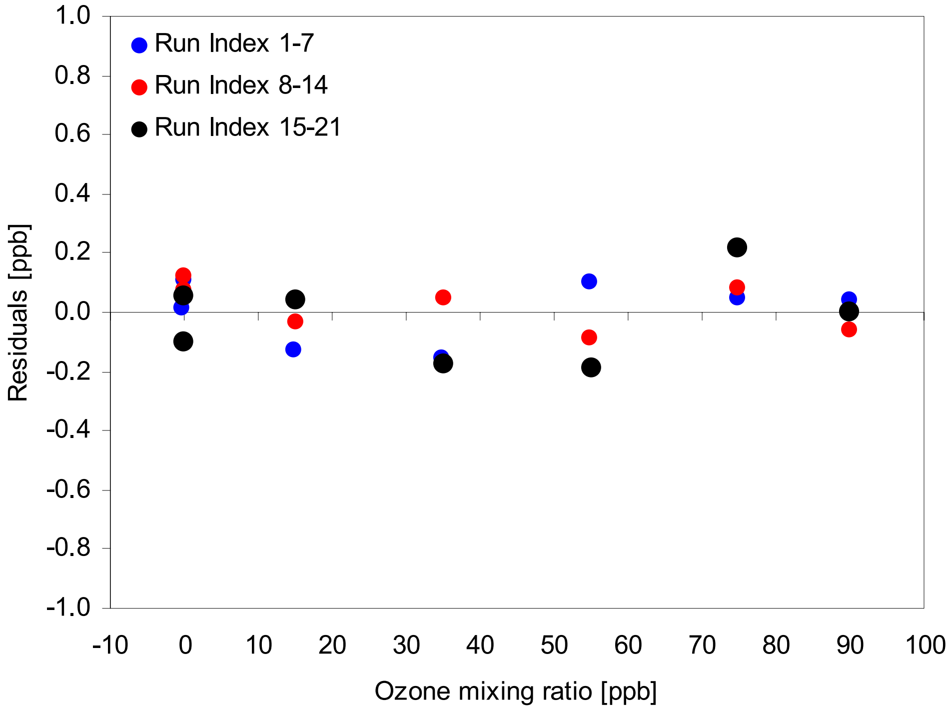

Figure 12: Residuals to the linear regression function (TEI 49C #62900-337) vs. the concentration of the WCC transfer standard (concentration dependence)

An unbiased ozone concentration was calculated using equation (4) of [*Klausen, et al.*, 2003]. The remaining standard uncertainty of the analyzer was calculated using equation (26). The regression statistics between instruments were calculated using the procedure `fitexy` given in Press et al. (1995).

TEI 49C #62900-337:

$$\text{Unbiased } O_3 = (\text{TEI 49C} - 0.04) / 0.9773$$

Unbiased O_3= O_3 mixing ratio in ppb, unbiased to SRP#15

TEI 49C = O_3 mixing ratio in ppb, determined with TEI 49C #62900-337

The remaining standard uncertainty u_c after compensation of the calibration bias is

$$u_C \approx \{(0.58 \text{ ppb})^2 + (0.00606 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 13 shows the deviation of the TEI 49C #62900-337 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-Empa. The red dotted line shows the remaining standard uncertainty.

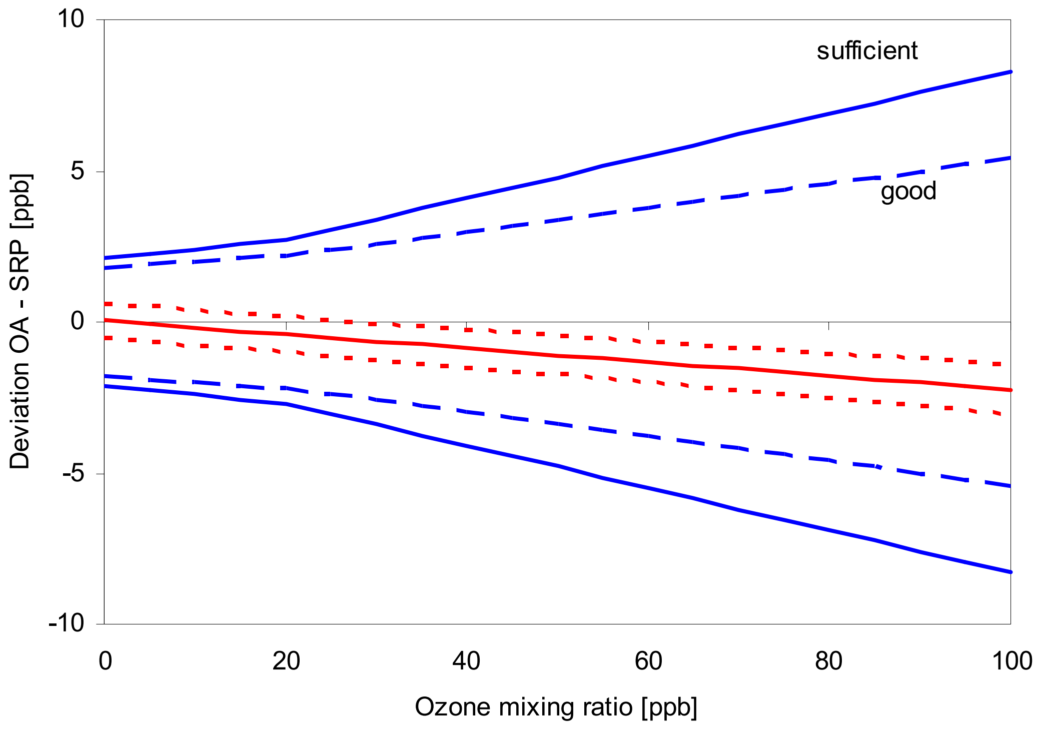

Figure 13: Inter-comparison of instrument TEI 49C #62900-337

Ozone Analyzer – Backup Instrument

The results comprise the inter-comparison between the TEI 49C #72491-371 field instrument and the WCC transfer standard TEI 49C-PS, carried out on December 1, 2004.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 60-second-means are presented in Table 5. For each mean value the differences between the concentrations assigned by the station and the WCC-Empa transfer standard are calculated in ppb and in %.

Figures 14 and 15 show the residuals of the linear regression analysis of the field instrument compared to the WCC-Empa transfer standard. The residuals versus the run index are shown in Figure 14 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 15 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 16).

The data used for the evaluation was recorded by both WCC-Empa and Izaña data acquisition systems. The raw data was treated according to the usual station method, which implied a zero offset correction of -2.10 ppb based on the average observed zero reading of 2.10 ppb during the inter-comparison.

Table 5: Inter-comparison of the ozone field instrument TEI 49C #72491-371

	WCC TEI 49C-PS		TEI 49C #72491-371			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	-0.08	0.06	0.09	0.08	0.17	
2	15.11	0.05	15.45	0.11	0.34	2.27
3	55.04	0.11	56.27	0.18	1.24	2.25
4	35.04	0.04	35.93	0.15	0.89	2.55
5	89.91	0.09	92.16	0.13	2.26	2.51
6	75.00	0.06	76.79	0.21	1.79	2.38
7	-0.03	0.08	-0.03	0.15	0.00	
8	-0.09	0.05	0.09	0.19	0.18	
9	54.90	0.08	56.53	0.15	1.62	2.96
10	89.94	0.12	92.13	0.15	2.19	2.44
11	35.07	0.06	35.88	0.17	0.81	2.31
12	74.95	0.09	76.88	0.14	1.93	2.58
13	15.07	0.06	15.46	0.12	0.39	2.57
14	-0.18	0.07	-0.04	0.18	0.14	
15	-0.23	0.09	-0.08	0.14	0.15	
16	15.09	0.08	15.59	0.08	0.50	3.32
17	89.91	0.09	92.11	0.23	2.19	2.44
18	35.07	0.16	36.00	0.20	0.93	2.67
19	74.94	0.11	76.74	0.14	1.80	2.40
20	55.02	0.14	56.32	0.15	1.30	2.36
21	-0.14	0.08	-0.04	0.12	0.11	

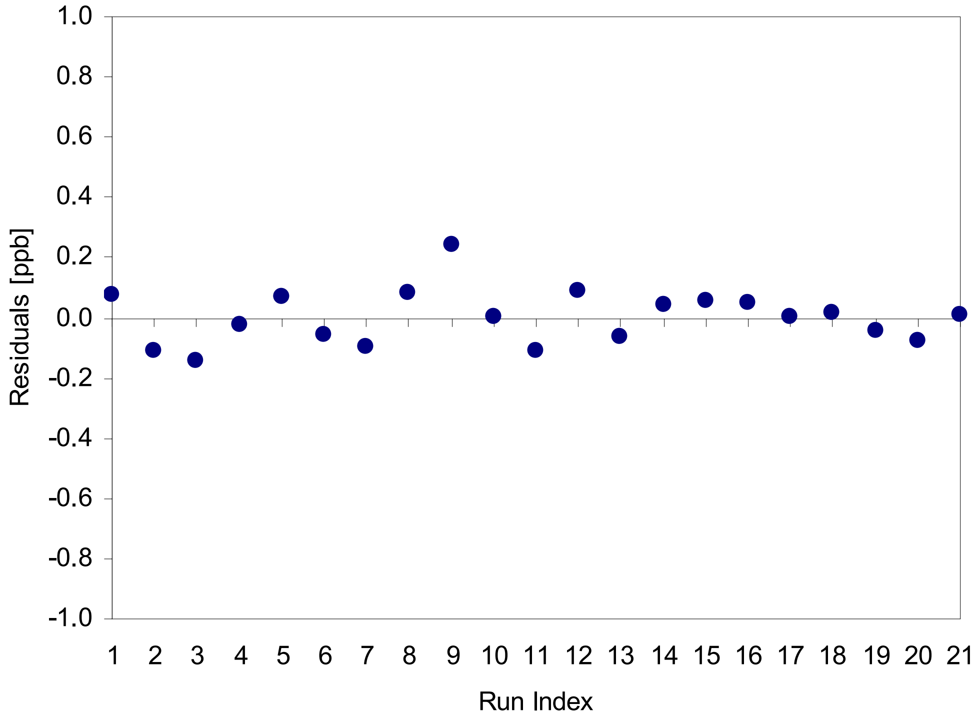

Figure 14: Residuals to the linear regression function (TEI 49C #72491-371) vs. the run index (time dependence)

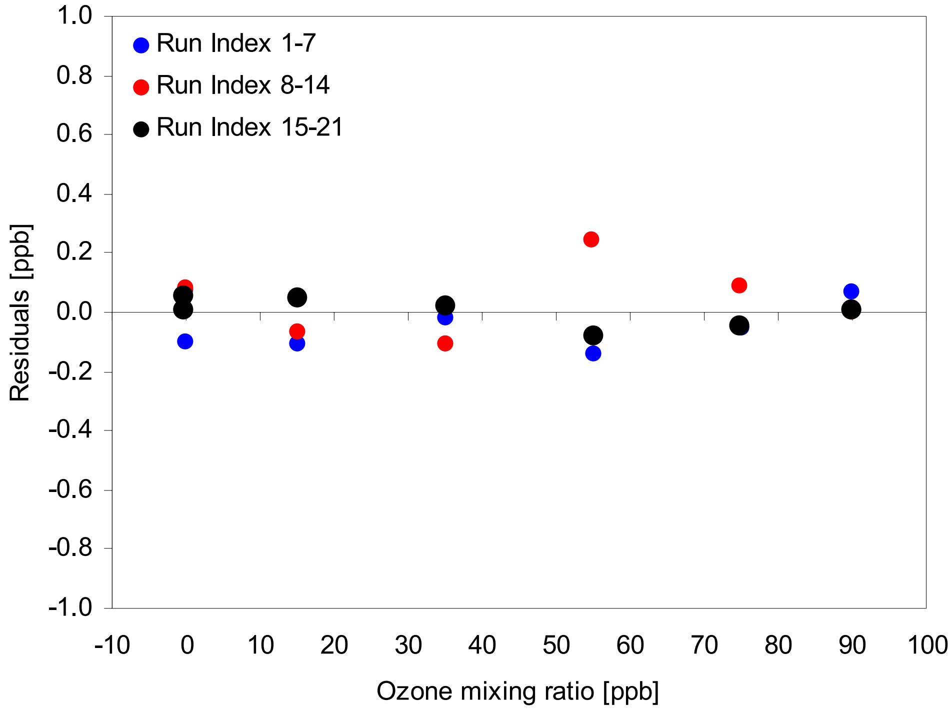

Figure 15: Residuals to the linear regression function (TEI 49C #72491-371) vs. the concentration of the WCC transfer standard (concentration dependence)

An unbiased ozone concentration was calculated using equation (4) of [*Klausen, et al.*, 2003]. The remaining standard uncertainty of the analyzer was calculated using equation (26). The regression statistics between instruments were calculated using the procedure `fitexy` given in Press et al. (1995).

TEI 49C #72491-371:

$$\text{Unbiased } O_3 = (\text{TEI 49C} - 0.13) / 1.0193$$

Unbiased O_3= O_3 mixing ratio in ppb, unbiased to SRP#15

TEI 49C = O_3 mixing ratio in ppb, determined with TEI 49C #72491-371

The remaining standard uncertainty u_c after compensation of the calibration bias is

$$u_C \approx \{(0.55\text{ ppb})^2 + (0.00586 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 16 shows the deviation of the TEI 49C #72491-371from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-Empa. The red dotted line shows the remaining standard uncertainty.

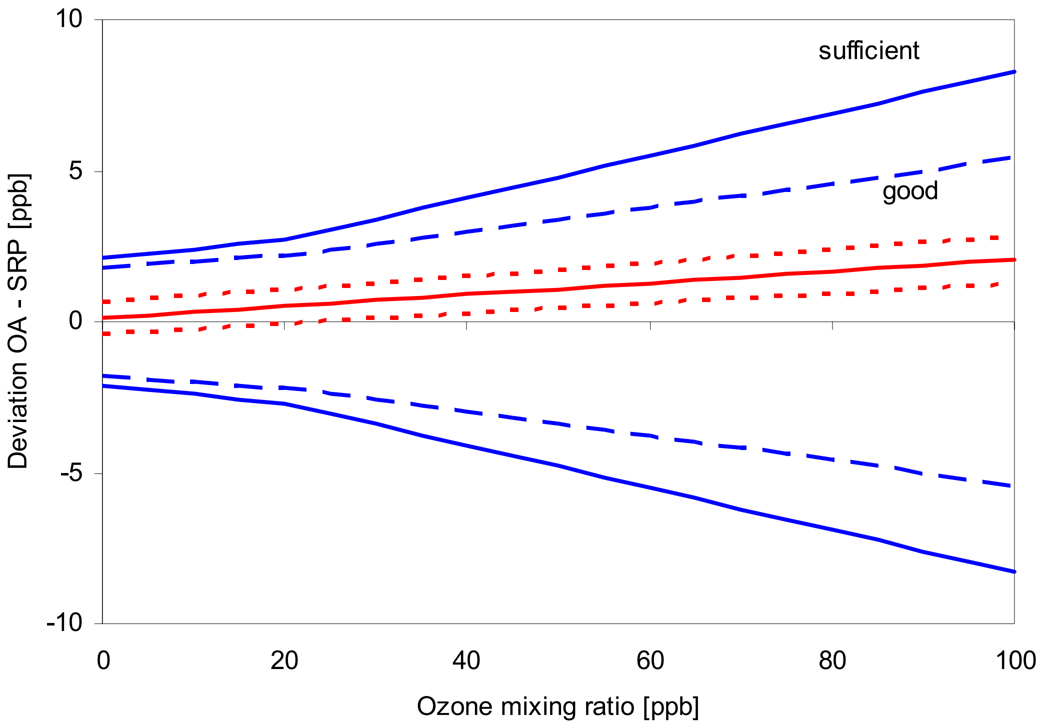

Figure 16: Inter-comparison of instrument TEI 49C #72491-371

Ozone Calibrator

The results comprise the inter-comparison between the TEI 49CPS #56085-306 field calibrator and the WCC transfer standard TEI 49C-PS, carried out between December 2 and 3, 2004.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 60-second-means are presented in Table 6. For each mean value the differences between the concentrations assigned by the station and the WCC-Empa transfer standard are calculated in ppb and in %.

Figures 17 and 18 show the residuals of the linear regression analysis of the field instrument compared to the WCC-Empa transfer standard. The residuals versus the run index are shown in Figure 17 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 18 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 19).

The data used for the evaluation was recorded by both WCC-Empa and Izaña data acquisition systems. The raw data was treated according to the usual station method, and no further corrections were applied.

Table 6: Inter-comparison of the ozone field calibrator TEI 49CPS #56085-306

	WCC TEI 49C-PS		TEI 49CPS #56085-306			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.04	0.14	0.20	0.16	0.16	
2	14.94	0.14	15.19	0.14	0.25	1.67
3	54.93	0.06	55.01	0.15	0.08	0.15
4	34.98	0.11	35.25	0.13	0.27	0.77
5	89.94	0.07	89.93	0.17	-0.02	-0.02
6	74.95	0.08	74.81	0.12	-0.14	-0.18
7	0.00	0.09	0.18	0.11	0.18	
8	-0.02	0.09	0.14	0.09	0.15	
9	55.00	0.10	55.13	0.10	0.13	0.24
10	89.96	0.06	90.03	0.15	0.08	0.09
11	34.98	0.05	35.26	0.12	0.28	0.80
12	74.97	0.08	75.17	0.13	0.19	0.26
13	15.05	0.10	15.42	0.11	0.37	2.47
14	-0.02	0.09	0.42	0.13	0.44	
15	-0.02	0.10	0.38	0.09	0.40	
16	15.06	0.16	15.55	0.16	0.50	3.29
17	89.94	0.08	90.41	0.11	0.47	0.52
18	35.01	0.06	35.47	0.12	0.46	1.31
19	74.99	0.10	75.56	0.22	0.57	0.76
20	54.99	0.08	55.56	0.22	0.57	1.03
21	-0.05	0.11	0.41	0.13	0.45	

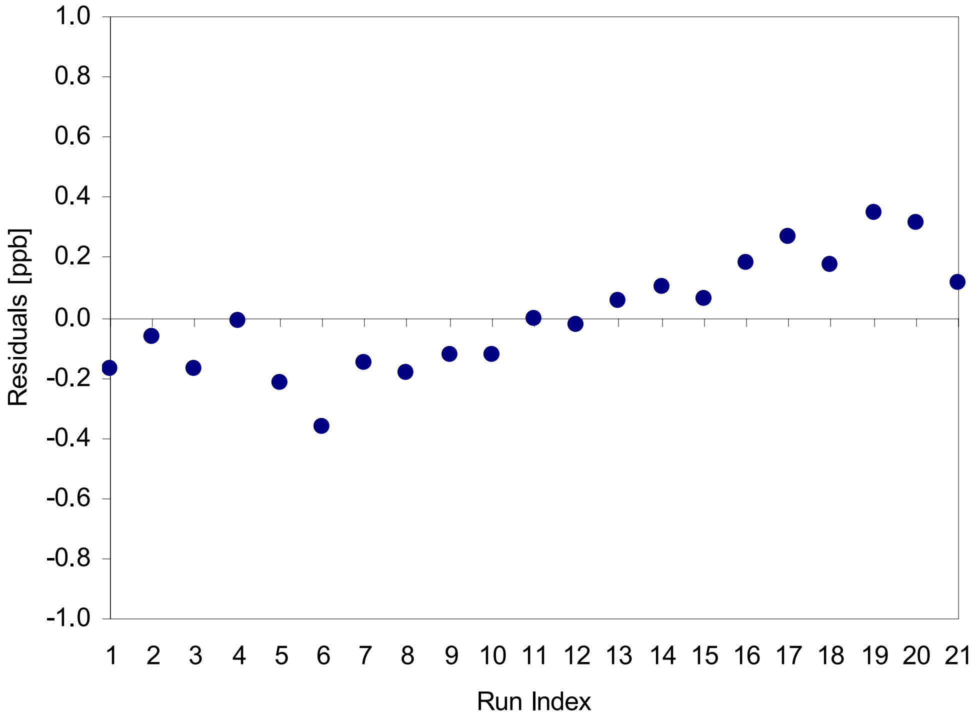

Figure 17: Residuals to the linear regression function (TEI 49CPS #56085-306) vs. the run index (time dependence)

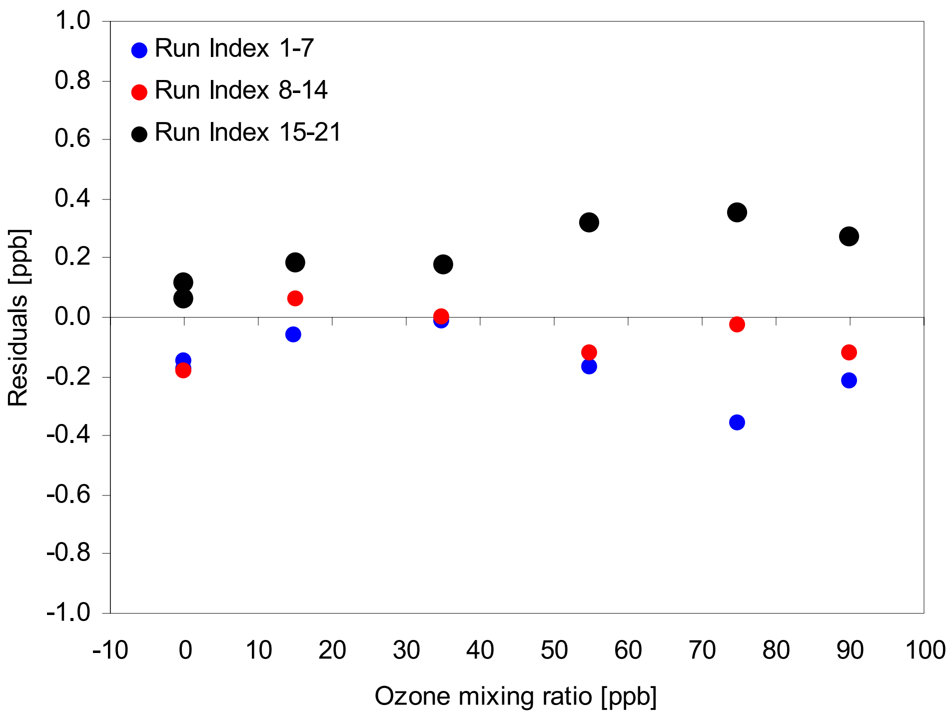

Figure 18: Residuals to the linear regression function (TEI 49CPS #56085-306) vs. the concentration of the WCC transfer standard (concentration dependence)

An unbiased ozone concentration was calculated using equation (4) of [*Klausen, et al.*, 2003]. The remaining standard uncertainty of the analyzer was calculated using equation (26). The regression statistics between instruments were calculated using the procedure `fitexy` given in Press et al. (1995).

TEI 49CPS #56085-306:

$$\text{Unbiased } O_3 = (\text{TEI 49CPS} - 0.36) / 0.9946$$

Unbiased O_3= O_3 mixing ratio in ppb, unbiased to SRP#15

TEI 49CPS = O_3 mixing ratio in ppb, determined with TEI 49CPS #56085-306

The remaining standard uncertainty u_c after compensation of the calibration bias is

$$u_C \approx \{(0.59 \text{ ppb})^2 + (0.00622 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 19 shows the deviation of the TEI 49CPS #56085-306from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-Empa. The red dotted line shows the remaining standard uncertainty.

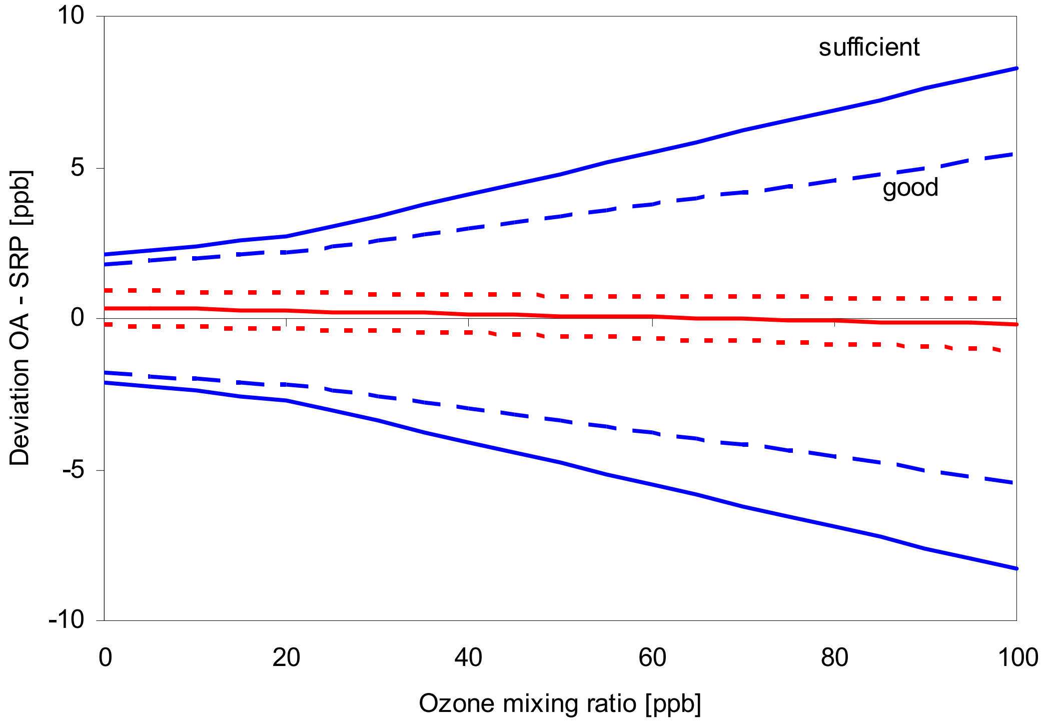

Figure 19: Inter-comparison of instrument TEI 49CPS #56085-306

Conclusions

The ozone concentrations observed at Izaña (2003) ranged between 30.8 and 64.8 ppb (5- and 95-percentile of 60 min mean values). Both ozone analyzers and the station calibrator of Izaña fulfil the assessment criteria of “good” over the tested range between 0 and 100 ppb ozone.

The results of the three-monthly comparisons of the station calibrator with the analysers of Izaña were also reviewed during the audit. These results were consistent with the findings of WCC-Empa during the performance audit, which further supports the quality of the Izaña ozone measurements.

4.3 Recommendation for Surface Ozone Measurements

Due to the good results of the audit WCC-Empa only makes a few minor recommendations, which can be summarized as follows:

- It should be considered to adjust the calibration factors of the two analyzers to reduce the bias to the ozone calibrator.
- Data should be corrected based on the 3-monthly inter-comparison with the station calibrator. The station calibrator does not show a significant bias compared to the WCC-Empa transfer standard, and proved to be stable over time since the WCC-Empa audit in June 2000.
- Data submission to the GAW data centre on a more regular basis is strongly encouraged. Ozone data is currently only available until the end of 2001.

5 SYSTEM AND PERFORMANCE AUDIT FOR CARBON MONOXIDE

On-going measurement of carbon monoxide at Izaña commenced in 1998, and continuous data series are available since then. Carbon monoxide measurements at Izaña are made using GC with HgO detector technique. Since the end of 2004 an additional NDIR instrument is available. Inter-comparison results of the NDIR instrument are considered as preliminary and are shown in Appendix II.

5.1 Monitoring Set-up and Procedures

5.1.1 Air Inlet System

Carbon monoxide measurements are currently being made at two locations in Izaña. The RGA-3 instrument is still operating in the provisional measurement site, while NDIR measurements commenced in the new tower building. It is planned to continue parallel measurements at two sites to have an overlap before the RGA-3 is moved to the new building. Both measurements are planned to continue; the RGA-3 is considered as the main instrument for carbon monoxide measurements.

RGA-3 sampling-location:

Sample inlet / manifold:

The air inlet system for the CO measurements is mounted on the flat platform at the top of the provisional measurement station. The inlet part of the system on the flat roof is 2.5 m high and about 10 m above 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 near the ceiling of the station and a glass manifold indoors (50 mm i.d., 0.5 m long). It is continuously flushed at 1.5 m^3 per minute with ambient air. From the manifold to the instrument a total length of 7 m Teflon tubing (4 mm i.d.) is used with a flow rate of 800 ml min^{-1}. The air is dried using a glass trap submerged in a cryo cooler set at -60°C. The air is then distributed to the 2 separate GC systems (for CO and for CH_4). Individual needle valves located on each system are used to control their respective flow rates.

Residence time in the sampling line: < 10 s

Comment

The inlet systems, including all parts and materials are adequate for the analysis of CO (and CH_4).

5.1.2 Instrumentation

Currently two measurement techniques are used for CO measurements at Izaña. The primary method is based on GC with a mercury oxide reduction detector (RGA-3). A backup system based on NDIR technique was installed before the audit. This system was running but still considered to be in a test phase. Calibration including zero and span check frequencies were still not established. Inter-comparison results are shown for both techniques; however, the NDIR results have to be considered as preliminary since they might improve with a better instrument calibration and appropriate zero and span checks.

GC/HgO Detector

A RGA-3 GC-system from Trace Analytical Inc. is used for in-situ CO analysis. A schematic illustrating the automated CO gas chromatographic RGA analyzer and calibration tank setup at Izaña is shown in Figure 20. System specifications are listed in Table 7.

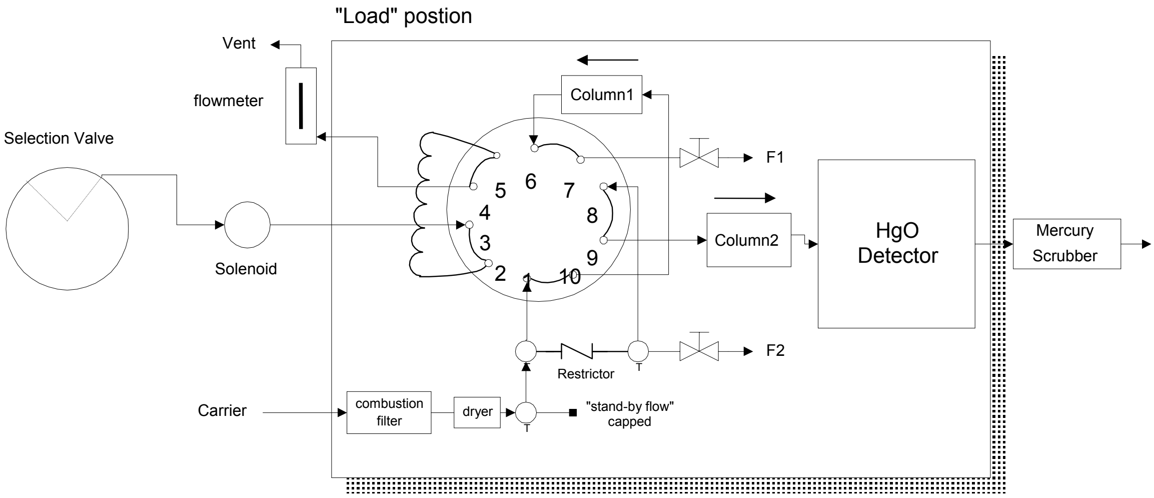

Figure 20: Schematic of RGA CO analyzer used at Izaña (load position)

Table 7: Carbon monoxide gas chromatograph at Izaña

Instrument	Trace Analytical Inc.
model, S/N	RGA3, S/N 070188-006
at Izaña	since 1998
Method	GC / HgO Reduction Detector
Loop	1 ml
Columns	pre-column: Unibeads 1S 60/80 analytical column: Mole sieve 5Å 60/80
carrier gas	synthetic air – Sofnocat - Mole sieve, 20 ml/min
operating temperatures	Detector: 265°C, Column: 105°C
analogue output	1 V
Instrument's specials	A few seconds before injection, the flow through the loop is stopped (solenoid valve) to equilibrate loop pressure with ambient pressure

Operation and Maintenance

Analysis: 6 Injections are made every hour. The sequence alternating between ambient air and working standard. Every 15 days the working standard is calibrated against the four station reference tanks.

The RGA CO GC is potentially non-linear and therefore a single calibration point is insufficient to determine the ambient mixing ratios. The ambient data is determined as follows: A potential calibration curve is determined every two weeks by passing 4 calibration gases through the system. Based on this calibration a concentration is assigned to the working standard, which will be further used for the calculation of the ambient data.

Frequent checks are made of tank pressures, temperatures, flow rates, and retention times. The cold trap is exchanged when necessary. Further measures are taken when something unusual is observed.

Gas Standards

The standard CO scale, to which the Izaña CO measurements are referenced, is based on a set of four 37.5 L aluminium cylinders purchased from NOAA/CMDL (see Table 8). These standards refer to the WMO-88 scale, and no re-certification to the WMO-2000 scale has been made. The working standard is calibrated against the CMDL standards every two weeks.

Table 8: Station CO cylinders

Cylinder	Content	CO [ppb]
Working standard	Dried ambient air from Izaña	165.2
CMDL CA03037	natural dry air	64.6
CMDL CA03083	natural dry air	162.7
CMDL CA02635	natural dry air	73.7
CMDL CC115003	natural dry air	146.0

5.1.3 Data Handling

Data Acquisition and –transfer

The data acquisition consists of a Perkin Elmer Integrator 900 with Perkin Elmer Software. Additional software developed at INM is used to trigger the solenoid valves and the integrator. All the raw data and chromatograms are stored, regularly back-upped and transferred to INM for data evaluation. Peak integration is carried out both for area and area. Data evaluation has been carried out using peak area, but peak height will be used in future for the final dataset.

Data Treatment

All data is in a first step being quality controlled by the station operator. Chromatograms are visually inspected. The final data evaluation includes the recalculation of the raw data by applying the calibration function. The peak area of the working standard is used to correct for instrument drift. One hourly averages are calculated for the final data set.

Data Submission

To date carbon monoxide data have not been submitted to the GAW data centre for greenhouse gases (WDCGG) at JMA.

5.1.4 Documentation

Logbooks

An electronic logbook is available for the carbon monoxide instrument. The notes are up-to-date and describe all important events.

Comment

The frequent instrument checks and the up-to-date logbook support the quality of the data. No change of the current practice is suggested.

5.2 Inter-comparison of the in-situ Carbon Monoxide Analyzer

5.2.1 Experimental Procedure

The five transfer standards of WCC-Empa (concentration range approx. 70-180 ppb CO) were stored in the same room as the CO measurement system to equilibrate over night. The transfer standards were calibrated against the CMDL WMO-2000 scale [*Novelli, et al.*, 2003] at Empa before the audit (Appendix V). Before the inter-comparison measurements, the pressure regulators and the stainless steel tubing were extensively flushed and leak checked (no pressure drop for half an hour with main cylinder valve closed). All transfer standards were injected and analyzed 8 to 13 times in the period from November 30 to December 1, 2004. The data was acquired by the station software. This data (mean values and standard deviations) was reprocessed by the measurement leader after the audit. The experimental details are summarized in Table 9.

Table 9 Experimental details of the carbon monoxide inter-comparison

field instrument:	RGA3, S/N 070188-006
reference:	WCC-Empa transfer standards
data acquisition system:	Station data acquisition
approx. concentration levels:	70 to 180 ppb
injections per concentration:	8 – 13

5.2.2 Results

The CO concentrations determined by the RGA-3 field instrument for the five WCC transfer standards are shown in Table 10. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 21 shows the absolute differences (ppb) between the measurements of the RGA-3 and the WCC transfer standards (TS) (reference). The WCC TS were calibrated before and after the audit against the CMDL scale (Reference: CMDL CA02854, 295.5 pbb) with an Aerolaser AL5001. The error bars represent the combined 95% confidence interval for the calibration of the transfer standards against the CMDL standard and of the multiple injections of the transfer standards at Izaña. The data of the RGA-3 field instrument were re-processed after the audit and are based on calibration of the instrument against the reference standards available at the site.

Table 10: Carbon monoxide inter-comparison measurements at Izaña

No.	**WCC standard**	**Izaña analysis (RGA-3, Peak Area)**				
	conc. ± 1σ	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	72.6 ± 0.6	62.8	0.3	8	-9.8	-13.5
2	82.9 ± 0.7	73.2	0.6	9	-9.7	-11.7
3	132.7 ± 0.8	122.8	0.4	9	-9.9	-7.4
4	153.3 ± 1.2	144.8	0.7	13	-8.5	-5.5
5	175.4 ± 1.0	169.4	0.3	8	-6.0	-3.4

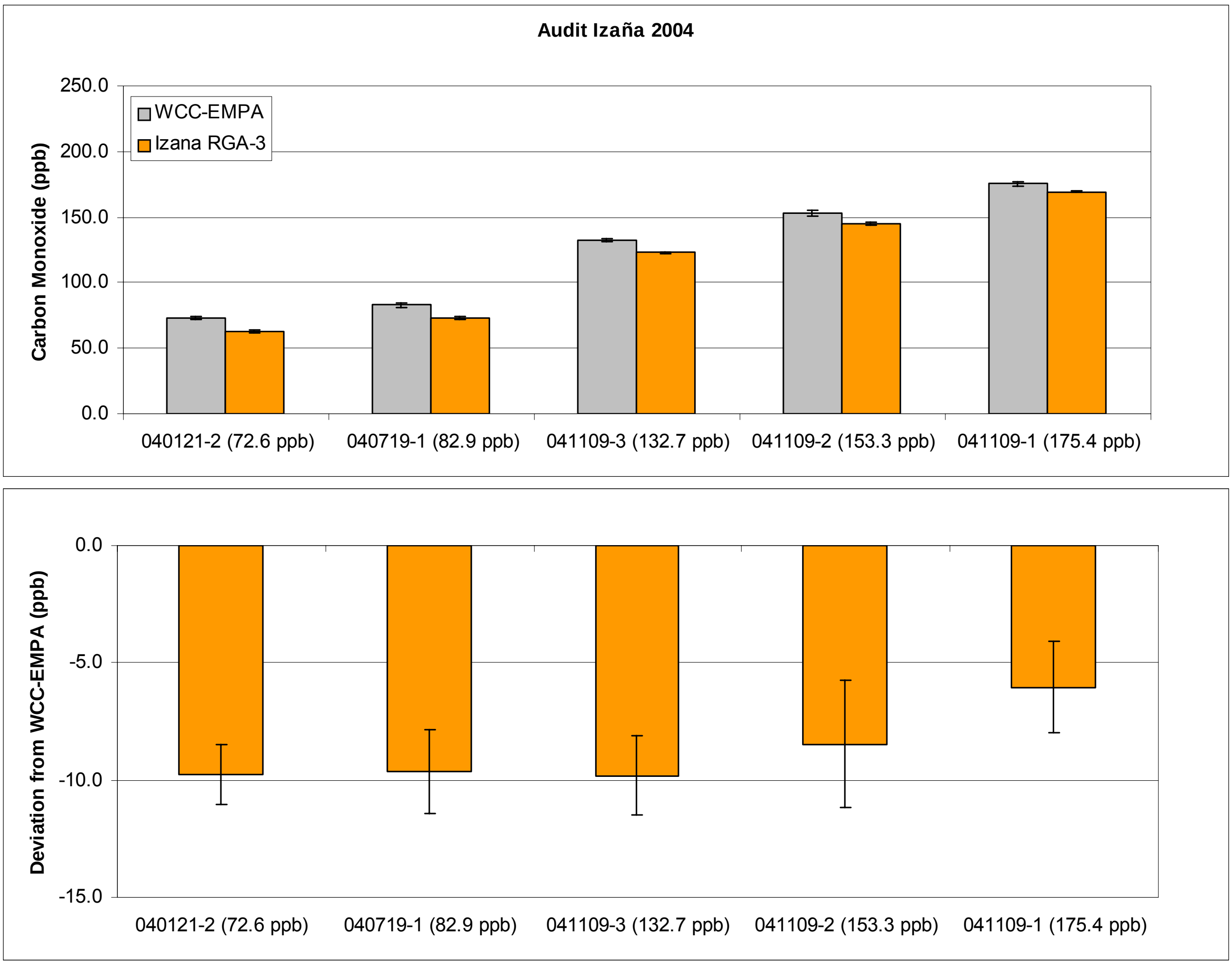

Figure 21: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Izaña (orange).
lower panel: deviation of the Izaña station from the reference.
The error bars represent the 95% confidence interval.

5.3 Discussion of the Inter-comparison Results

The analysis of the WCC-Empa transfer standards by the Izaña station resulted in lower values (-9.0 to -6.0 ppb or -3.4 to -13.5%) for concentrations between 70 and 175 ppb compared to the reference.

Transfer standards of WCC-Empa are traceable to the CMDL scale (see Appendix V). The scale was revised in 2000 (WMO-2000 scale), and significant corrections were applied to the previous WMO-88 scale. All transfer standards of WCC-Empa were calibrated using the 295.5 ppb CMDL (scale WMO-2000) CO standard with an Aerolaser AL5001 CO instrument. The instrument linearity and zero was checked for the calibrations of the WCC-Empa transfer standards. Measurements of the lower WCC-Empa CMDL standards using the above standards as a reference also result in higher findings (2.6 to 3.9 ppb) in comparison to the CMDL certificates (WMO-2000 scale).

The standards used at Izaña refer to the WMO-88 scale [*Novelli, et al.*, 2003]. The revision and uncertainty of the CO scale explains most of the observed differences between Izaña and WCC-Empa.

5.4 Recommendation for Carbon Monoxide Measurements

The major issue for CO measurements is the uncertainty of the CO scale. This task needs to be addressed in the recently established SAG Reactive Gases.

Furthermore, WCC-Empa makes the following recommendation concerning CO measurements at Izaña:

- The station standards should be re-calibrated against the revised CMDL scale.
- Previous data needs to be corrected when new values of the station standards become available.
- Submission of the CO data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is strongly encouraged. Data submission is one of the obligations of a GAW station.

6 SYSTEM AND PERFORMANCE AUDIT FOR METHANE

Continuous methane measurements became operational at Izaña in September 1984. Annual average CH_4 concentration at Izaña increased from approx. 1650 ppb in 1984 to 1785 ppb in 2002. The continuation of these CH_4 measurements at Izaña is considered to be of importance to the international community.

6.1 Monitoring Set-up and Procedures

6.1.1 Air Inlet System for CH_4

At the time of the audit methane measurements were still made in the provisional laboratory building. It is planned to install an additional GC in the new lab. When long enough time series are available at both sites the instrument will also be moved to the new building. The same inlet system is used for both methane and carbon monoxide (see 5.1.1)

6.1.2 Instrumentation

The analysis of CH_4 at Izaña as well as CO_2 is made using a Dani-3800 gas chromatograph employing flame ionization detection. System specifications are listed in Table 11.

Table 11: Specifications of the Dani-3800 CH_4 GC at Izaña

GC	Dani-3800
S/N	011109
at Izaña	since September 1984
Method	GC / FID Detector
Loop size	10 ml
Column	analytical column: Molsieve 13 X 60/80 MESH; 1.20 m x 6 mm
Carrier gas	Synthetic Air
Operating temperatures	Detector: 110 °C, Column: 55 °C
Calibration interval	Injections alternating between working standard and ambient air
Instrument's specials	a few seconds before injection, the flow through the loop is stopped (solenoid valve) to equilibrate pressure differences

Operation and Maintenance

Analysis: Injections are made every 15 minutes and are alternating between working standard and ambient air.

Daily checks are made for tank pressures, temperatures, flow rates, and retention times. The moisture cold trap is exchanged when necessary. Further measures are taken when something unusual is observed.

CH_4 Measurement Scale

Two NOAA/CMDL station standards are available at the site (CA03075 1773.5 ppb and CA03794 1817.1 ppb). These two standards are used every second week to calibrate the working standard, which consists of ambient air from Izaña.

6.1.3 Data Handling

Data Acquisition and –transfer

The data acquisition consists of a workstation and a GC control software. The detector signal is amplified by a factor of 1000 to be acquired by a digital Me-26 12-bit A/D board. All chromatograms are stored. Peak integration is carried out for area which is used for the final data set.

Data Treatment

Peak integration is performed automatically, and two consecutive working tank signals are used to calculate the ambient air concentration. If one or both working standard injections are missing or invalid, the result of the injection of ambient air is rejected. The difference of the two working tank injections must further be below a certain threshold to be considered as valid data. The working tank is calibrated using the station standards every two week. Peak area is used for data evaluation, and a linear fit through zero is used as a calibration function.

Data Submission

In-situ methane data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG) at JMA. Submitted data currently span the period from 1984 to 2002. Submission of more recent data was delayed by re-construction work of the station. Further submission of methane data is planned for 2005.

6.1.4 Documentation

Logbooks

An electronic logbook is available for the methane instrument. The notes are up-to-date and describe all important events.

Standard Operation Procedures (SOPs)

The instrument manual is available at the site. In addition, instrument specific check lists are used.

Comment

The frequent instrument checks and the up-to-date logbook support the quality of the data. No change of the current practice is suggested.

6.2 Inter-Comparison of in-situ Methane Measurements

6.2.1 Experimental Procedure

The five transfer standards of the WCC (approx. concentration range 1790 - 1880 ppb CH_4) were stored in the same room as the CH_4 measurement system to equilibrate over night. The transfer standards were calibrated against CMDL laboratory standards (CA05316, CA04462, CA04580) at WCC-Empa before and after the audit (see Appendix VI). Before the inter-comparison measurements, the pressure regulators and the stainless steel tubing were extensively flushed and leak checked (no pressure drop for half an hour with main cylinder valve closed). All transfer standards were injected 4 to 7 times and analyzed between November 30 and December 1, 2004. No modifications of the GC system were made for the inter-comparison. The station software acquired the data. The data (mean values and standard deviations) was processed after the audit. The experimental details are summarized in Table 12.

Table 12: Experimental details of the methane inter-comparison

field instrument:	Dani-3800 GC
Reference:	5 WCC-Empa transfer standards
data acquisition system:	Station GC control software
approx. concentration levels:	concentration range approx. 1790 – 1880 ppb
Injections per concentration:	4 to 7

6.2.2 Results of the Methane Inter-comparison

The results of the inter-comparison between the DANI-3800 field instrument and the five WCC transfer standards are shown in Table 13. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 22 shows the absolute differences (ppb) between the measurements of the DANI-3800 GC and the WCC transfer standards (TS) (reference). The transfer standards were analysed before and after the audit. The error bars represent the combined 95% confidence interval for the calibration of the transfer standards against the CMDL standard and of the multiple injections of the transfer standards at Izaña. The data from the DANI-3800 field instrument were reprocessed after the audit and are based on the comparison with the station standard. Data of Izaña used for the audit refer to the NOAA/CMDL scale.

Table 13: Methane inter-comparison measurements at Izaña

No.	**WCC standard**	**Izaña analysis (DANI-3800 GC-FID, Peak Area)**				
	conc. $\pm 1\sigma$	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	1792.4 ± 1.6	1796.1	2.7	5	3.7	0.21
2	1824.2 ± 1.9	1824.5	2.1	6	0.3	0.02
3	1854.9 ± 1.7	1854.3	1.7	7	-0.6	-0.03
4	1856.6 ± 2.3	1856.5	2.7	5	-0.1	-0.01
5	1883.5 ± 1.7	1884.1	4.8	4	0.6	0.03

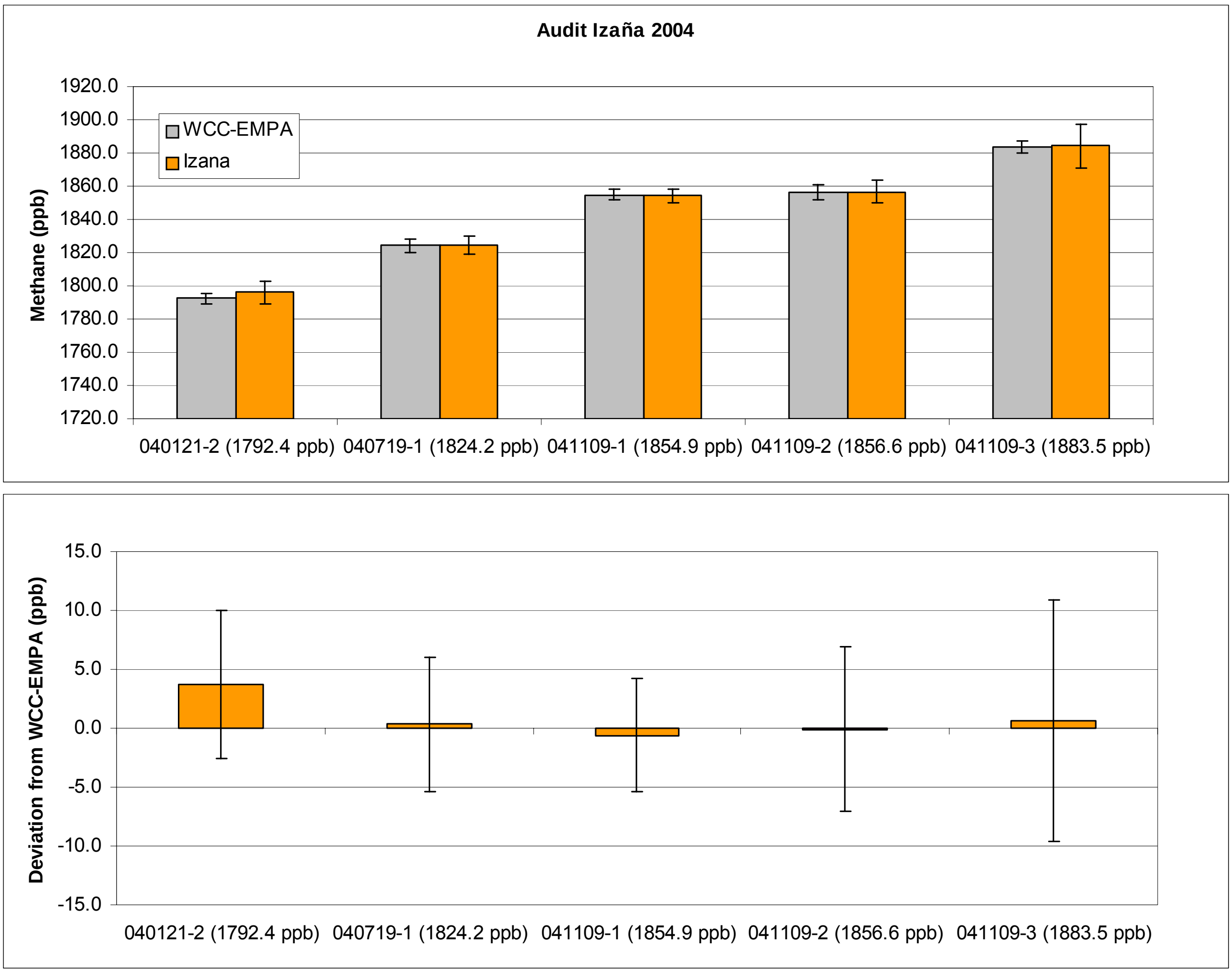

Figure 22: upper panel: concentrations of the WCC transfer standards (grey) measured with the GC system of Izaña (orange).
lower panel: deviation of Izaña from the reference.
The error bars represent the 95% confidence interval.

The repeatability of multiple injections was acceptable, with an average standard deviation of 0.15% from the tested concentrations. The best instruments at GAW stations reach a repeatability of approximately 0.05%.

Conclusions

The CH_4 inter-comparison between WCC-Empa and Izaña agreed very well in the concentration range between 1790 and 1890 ppb methane. The deviation from the transfer standards is less than 0.2 %. The overall instrument performance was good.

6.3 Recommendation for Methane Measurements

The good result of the inter-comparison measurements shows that the whole measurement system, beginning at the air inlet and ending at the data treatment is appropriate for the measurement of methane. Therefore no further technical recommendations are made by WCC-Empa.

Methane data were submitted to the World Data Centre for Greenhouse Gases (WDCGG) at JMA, and data until the end of 2002 were available at the WDC by the time of the audit. It is recommended that data submission continues.

7 REFERENCES

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Klausen, J., et al. (2003), Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *J. Geophys. Res.-Atmos.*, *108*, art. no.-4622.

Novelli, P. C., et al. (2003), Re-analysis of tropospheric CO trends: Effects of the 1997-1998 wild fires, *J. Geophys. Res.-Atmos.*

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APPENDIX

I. Santa Cruz ozone measurements

An ozone inter-comparison was made at the regional GAW station St. Cruz. The ozone instrument is installed in a small laboratory building on top of the INM office building in St. Cruz. The site is located near the sea shore and both clean and polluted conditions can be observed at the station depending on wind direction. The installations are appropriate for ozone measurement. The results of the inter-comparison are shown below, and the inter-comparison was done as described in section 4.2. The result is valid for the calibration settings O3 BKG 0.0, O3 COEF 1.030.

The results comprise the inter-comparison between the TEI 49C #032060000000731 field instrument and the WCC transfer standard TEI 49C-PS, carried out on November 30, 2004.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 60-second-means are presented in Table 14. For each mean value the differences between the concentrations assigned by the station and the WCC-Empa transfer standard are calculated in ppb and in %.

Figures 23 and 24 show the residuals of the linear regression analysis of the field instrument compared to the WCC-Empa transfer standard. The residuals versus the run index are shown in Figure 23 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 24 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 25).

The data used for the evaluation was recorded by both WCC-Empa and St. Cruz data acquisition systems. The raw data was treated according to the usual station method, and no further corrections were applied.

Table 14: Inter-comparison of the ozone field instrument TEI 49C #032060000000731

	WCC TEI 49C-PS		**TEI 49C #032060000000731**			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.12	0.08	0.31	0.07	0.19	
2	10.11	0.10	10.46	0.18	0.35	3.41
3	89.99	0.09	91.70	0.15	1.72	1.91
4	20.03	0.05	20.49	0.12	0.46	2.29
5	50.00	0.07	51.04	0.08	1.04	2.09
6	30.08	0.09	30.73	0.11	0.66	2.18
7	0.15	0.07	0.22	0.12	0.07	
8	0.10	0.07	0.25	0.10	0.16	
9	10.01	0.10	10.20	0.13	0.19	1.86
10	30.02	0.05	30.59	0.13	0.57	1.89
11	20.00	0.06	20.43	0.11	0.43	2.15
12	89.93	0.05	91.71	0.14	1.78	1.98
13	50.01	0.07	51.04	0.07	1.03	2.06
14	0.11	0.08	0.26	0.09	0.14	
15	0.08	0.07	0.25	0.07	0.17	
16	29.97	0.07	30.61	0.12	0.64	2.13
17	89.93	0.09	91.75	0.17	1.82	2.03
18	19.99	0.07	20.47	0.07	0.48	2.40
19	49.96	0.05	50.97	0.10	1.02	2.04
20	10.06	0.07	10.40	0.11	0.33	3.30
21	0.11	0.10	0.21	0.13	0.10	

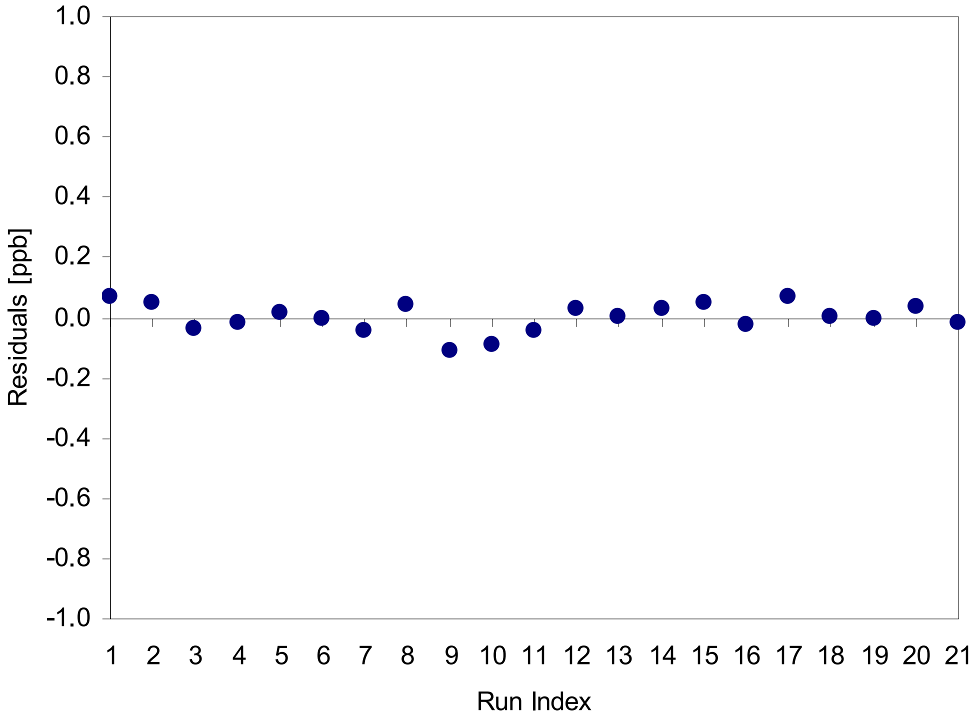

Figure 23: Residuals to the linear regression function (TEI 49C #032060000000731) vs. the run index (time dependence)

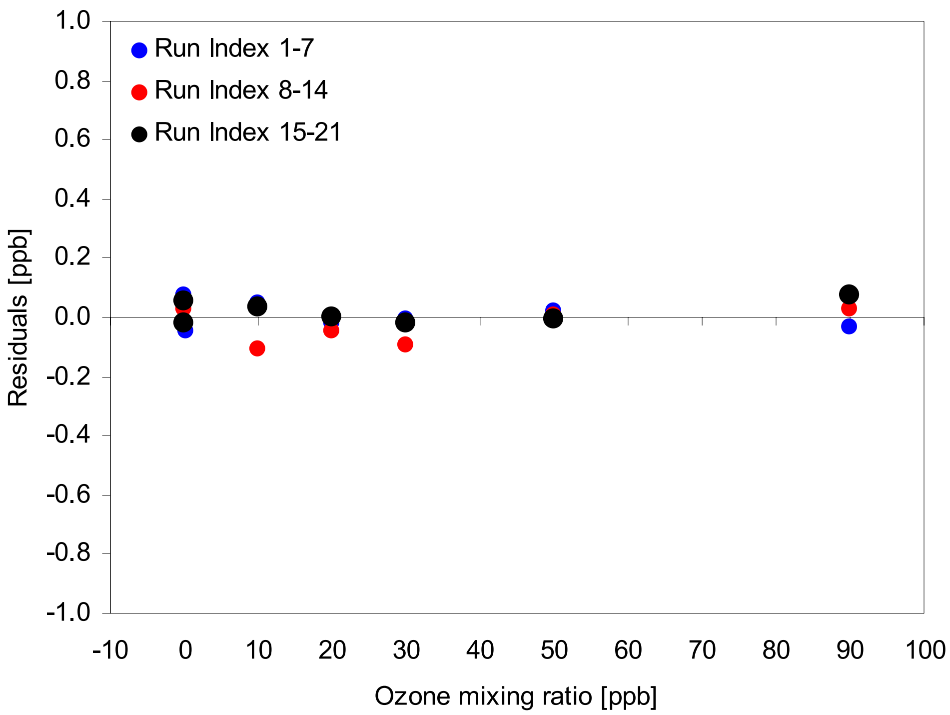

Figure 24: Residuals to the linear regression function (TEI 49C #032060000000731) vs. the concentration of the WCC transfer standard (concentration dependence)

An unbiased ozone concentration was calculated using equation (4) of [*Klausen, et al.*, 2003]. The remaining standard uncertainty of the analyzer was calculated using equation (26). The regression statistics between instruments were calculated using the procedure `fitexy` given in Press et al. (1995).

TEI 49C #032060000000731:

$$\text{Unbiased } O_3 = (\text{TEI 49C} - 0.14) / 1.0143$$

Unbiased O_3 = O_3 mixing ratio in ppb, unbiased to SRP#15

TEI 49C = O_3 mixing ratio in ppb, determined with TEI 49C #032060000000731

The remaining standard uncertainty u_c after compensation of the calibration bias is

$$u_C \approx \{(0.53 \text{ ppb})^2 + (0.00604 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 25 shows the deviation of the TEI 49C #032060000000731from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-Empa. The red dotted line shows the remaining standard uncertainty.

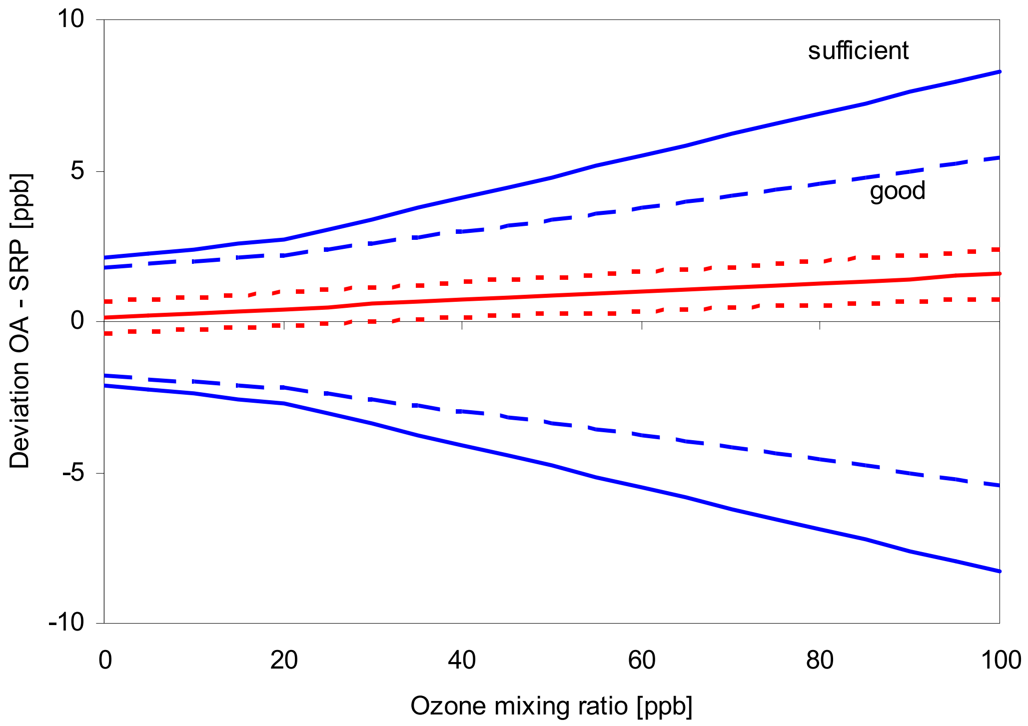

Figure 25: Inter-comparison of instrument TEI 49C #032060000000731

II. Inter-comparison of the NDIR CO measurements

Carbon monoxide measurements with NDIR technique were installed a few days before the WCC-Empa audit. The instrument was running in a pre-operational mode at the time of the audit. The instrument was not yet calibrated. Results shown below have to be considered as preliminary.

NDIR sampling-location:

Sample inlet / manifold:

The air sampling for the NDIR CO measurement is on top of the new tower building 30 m above ground. The inlet consists of a stainless steel inlet running from the tower terrace through the central service channel. The upper part is heated. A pump flushes the inlet with 2180 l/min. Inner diameter approx. 10 cm. The Inlet is protected against rain by an upside-down stainless steel bucket. The NDIR CO instrument is installed 11.5 m above ground.

Sampling-line:

Dimensions:	length = ca. 6 m, inner diameter = 4 mm
Material:	PFTE
Inlet-filter:	Teflon inlet filter before instrument, exchanged weekly
Flow rate:	ca. 2 l/min
Drying:	cryo trap at -60°C

Residence time in the sampling line and inlet: < 10 s

Instrumentation

A TEI48C NDIR monitor was installed at Izaña just before the WCC-Empa audit. Instrumental details are listed in Table 15.

Table 15: NDIR analyzer at Izaña

Instrument type and S/N	TEI 48C Trace Level #75723-380
Analytical method	NDIR, Gas Filter Correlation Technique
Dryer	Cold trap -60°C
at Izaña	Since November 2004
range	0-1000 ppb
calibration settings	CO COEFF: 1.000; BKG: 0.000 ppm
analogue output	0-10 V (not used)
serial output	RS 232

Inter-comparison

WCC-Empa provided different CO concentrations to the TEI48C-TL using a high concentration CO standard and a dilution unit. Details and traceability to CMDL are described in Appendix V. Each concentration was measured by the station instrument three times (each concentration 30 minutes bracketed by 30 minute zero checks). The first 10 one-minute average values after valve switching were discarded. A linear interpolation was made between the two zero checks to calculate zero corrected data. 1 minute averages were acquired and averaged to 20 minutes values. The final result thus comprises an average of 3 zero drift corrected 20 minute values. The experimental details are summarized in Table 16.

Table 16: Experimental details of the carbon monoxide inter-comparison

Field instruments:	TEI 48C Trace Level #75723-380
Reference:	WCC-Empa dilution unit (MGM, Breitfuss)
Data acquisition system:	Internal TEI48C data logger
Approx. concentration levels:	0 to 1000 ppb

Results

The CO concentrations determined by the main station instrument TEI 48C-TL #75723-380 for six different concentrations provided by the WCC-Empa dilution system are shown in Table 17. For each value the difference between the tested instrument and the dilution unit is calculated in ppb and %. Figure 26 shows the absolute differences (ppb) between the measurements of the TEI 48C-TL #75723-380 and WCC-Empa (reference). The WCC-Empa dilution system was calibrated against a flow reference and tested with an Aerolaser AL5001 CO instrument (before and after the audit) which was calibrated with a CMDL certified standard (CMDL CA02854, 295.5 pbb). The error bars represent the combined 95% confidence interval for the calibration of the dilution system against the CMDL standard and of the average values of Izaña.

Table 17: Carbon monoxide inter-comparison measurements at Izaña

No.	**WCC standard**	**Izaña Analysis (TEI 48C-TL #75723-380)**				
	conc. ± uncertainty*	conc.	s_d	No. of 20 min values	deviation from reference	
	ppb	ppb	ppb		ppb	%
1	0.0 ± 2.0	-0.1	2.2	3	-0.1	N/A
2	155.0 ± 3.1	138.6	1.2	3	-16.4	-10.6
3	205.1 ± 4.1	188.3	3.6	3	-16.9	-8.2
4	407.3 ± 8.1	374.3	2.5	3	-33.0	-8.1
5	609.9 ± 12.2	552.2	10.1	3	-57.7	-9.5
6	1015.2 ± 20.2	926.6	2.8	3	-88.6	-8.7

* Uncertainties were estimated to be ± 2 ppb (conc. ≤ 100 ppb) or 2 % (conc. > 100 ppb)

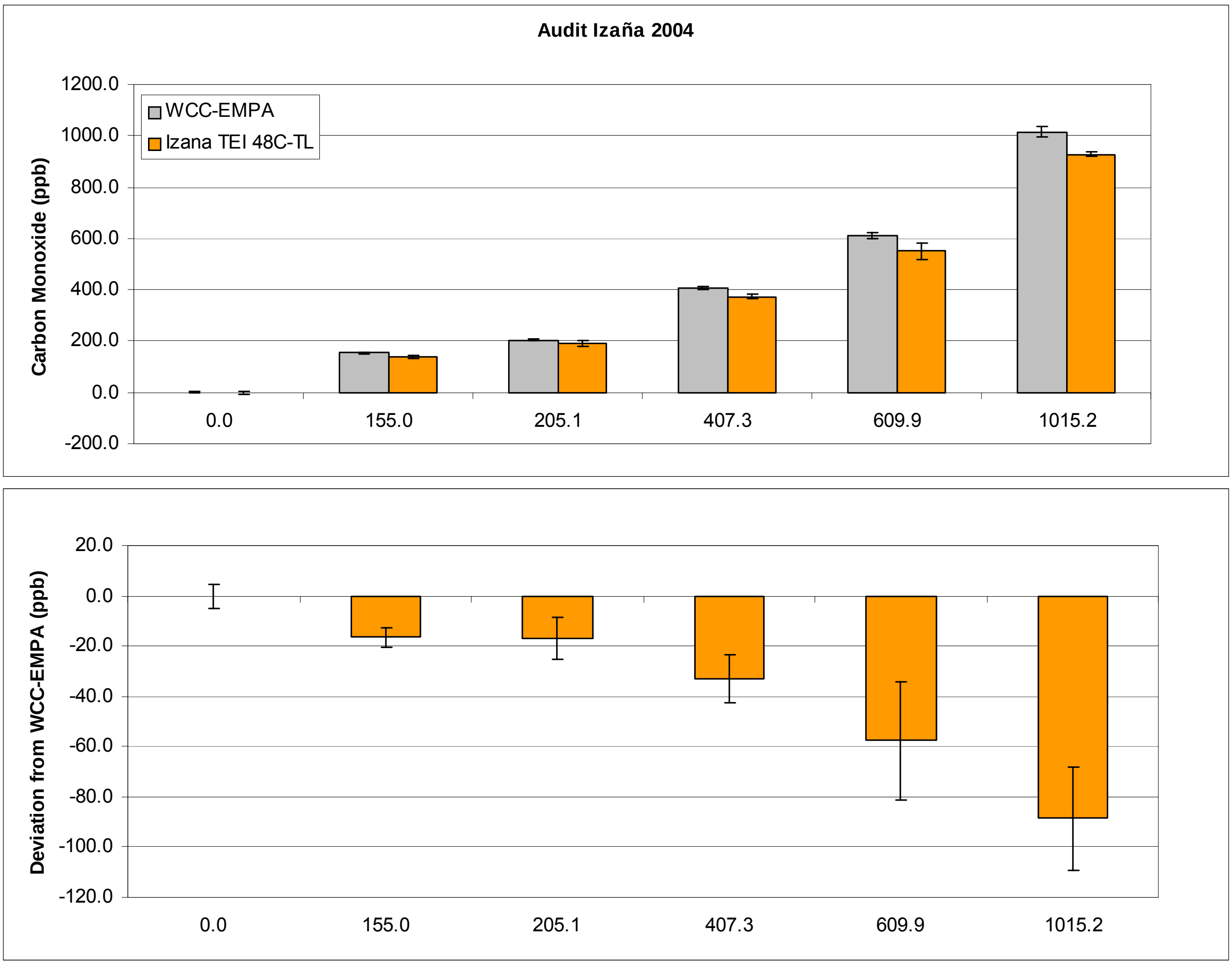

Figure 26: upper panel: concentrations of the WCC dilution unit (grey, reference: CMDL CA02854, 295.5 ppb) measured with the main CO analyzer of Izaña (orange). lower panel: deviation of the Izaña station from the conventional true value. The error bars represent the 95% confidence interval. Data are averages of three 20 minute values.

Discussion of the Inter-comparison Results

The inter-comparison between WCC-Empa and the station showed relatively large deviations from the reference value with relatively high uncertainties. The reason for this is discussed below:

a) Instrument calibration

The TEI 48C was not calibrated at the time of the audit. The lower readings of 8-10% of the TEI 48C compared to the WCC-Empa reference could be explained by this fact.

b) Instrument drift

The TEI 48C shows a significant zero drift. The drift seems to be correlated with the laboratory temperature. Figure 27 shows the raw data that was used for the inter-comparison.

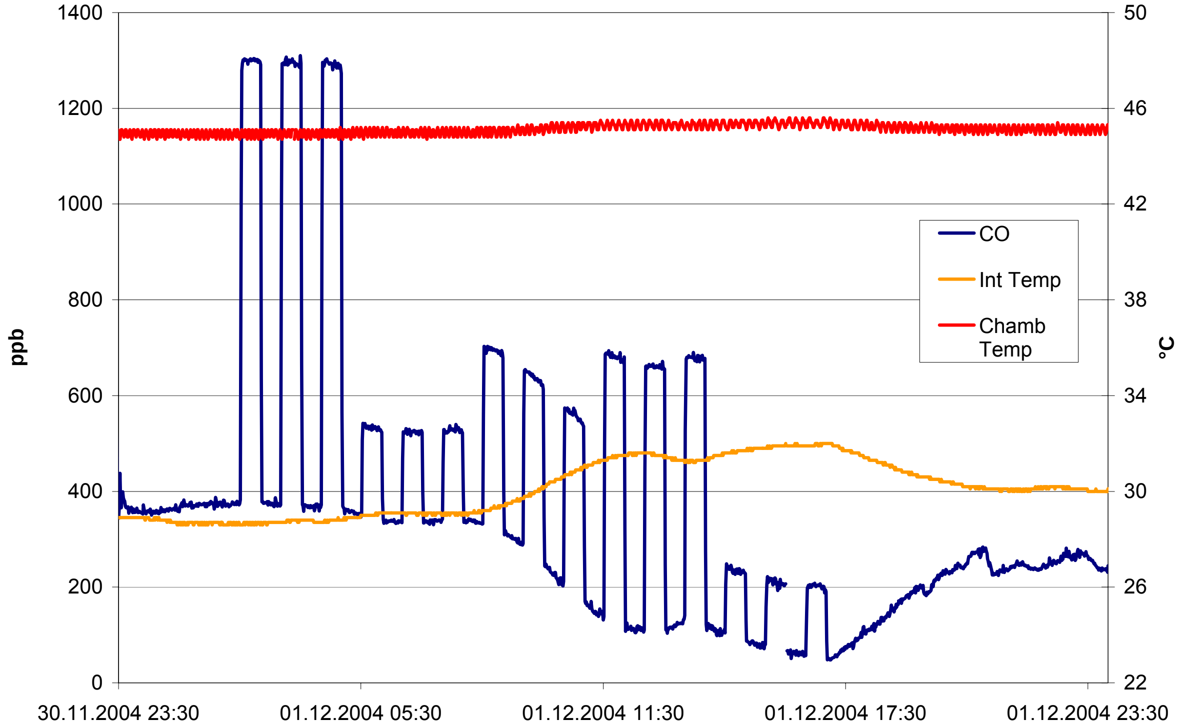

Figure 27: Raw measurement values (blue line), instrument temperature (internal temp., yellow line) and optical bench temperature (chamber temp., red line).

It can be seen that instrument drift significantly adds to the uncertainty of the TEI 48C. The drift seems to be strongly correlated with the internal instrument temperature.

c) Instrument noise

Instrument noise is also limiting the precision of NDIR instruments. Series of 10 or more one minute averages of zero or span measurements show usually a standard deviation of to 10 ppb or higher. This instrument noise is however typical for NDIR instruments and the TEI 48C of Izaña does not show higher noise compared to other NDIR analyzers.

Recommendation for NDIR Carbon Monoxide Measurements

Zero drift and instrument noise of the TEI 48C were identified to be the most limiting factor for accurate CO measurements with NDIR technique. However, the system can be optimized for the measurements of low concentrations with following recommendations:

- Frequent automatic zero checks are important to correct for zero drift. During the audit zero check were alternating with ambient air measurements (both 30 min). The duration of zero and ambient air measurements was reduced to 15 min after the audit. This is regarded as a good sequence to correct zero drift.
- Automatic span checks should be made. This was also implemented after the audit. Automatic span is now performed once per day.
- The air-conditioning of the laboratory building could be optimized. The internal temperature largely controls the zero reading of the instrument and correlates with the temperature of the laboratory.

III. 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 UV absorption is proportional 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 28. One gas stream flows through a pressure regulator to the reference solenoid valve to become the zero 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. After 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 then determines the ozone concentration for each cell and outputs the average concentration.

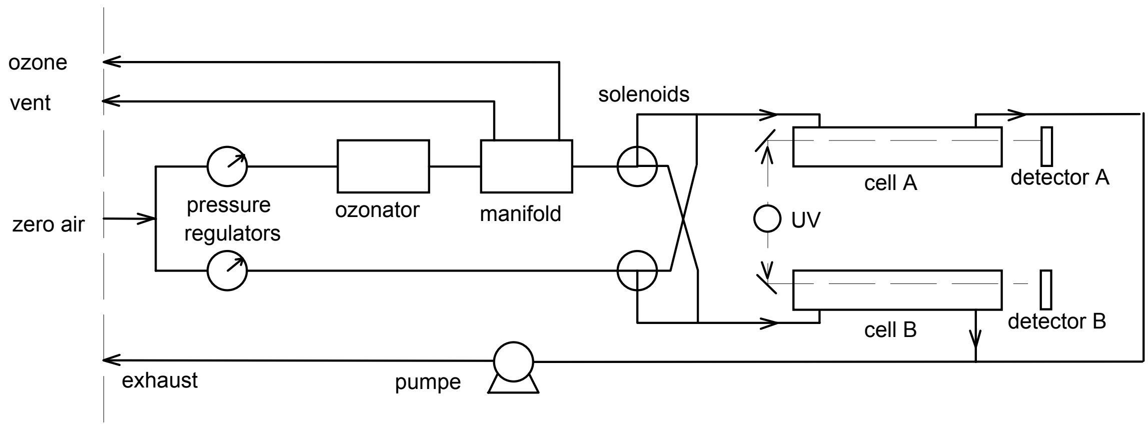

Figure 28: Flow schematic of TEI 49C-PS

IV. Stability of the Transfer Standard TEI 49C-PS

To exclude errors that might result from transportation of the transfer standard, the TEI 49C PS #54509-300 was compared with the SRP#15 before and after the field audit.

The procedure and instrumental details of this inter-comparison at the Empa calibration laboratory are summarized in Table 18 and Figure 29.

Table 18: Inter-comparison 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 / 140 / 190 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 before and 3 after audit
zero air supply:	Pressurized air - zero air generator (CO catalyst, Purafil, charcoal, filter)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

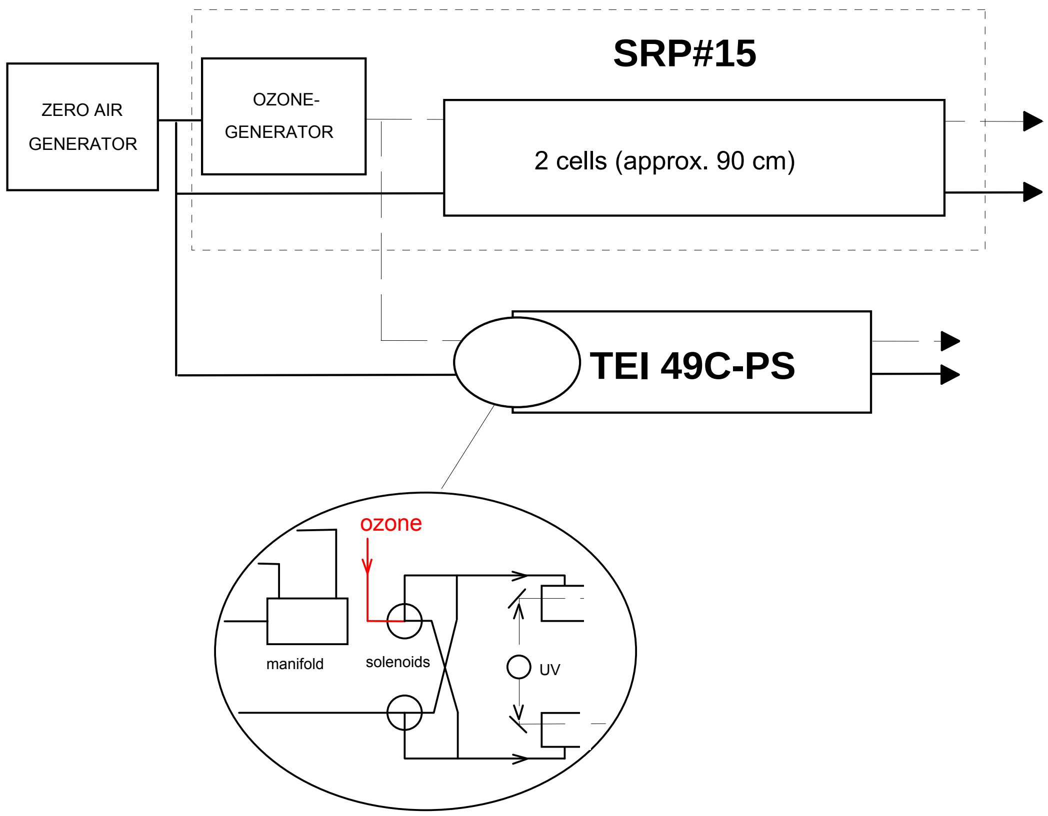

Figure 29: Instruments set up SRP -TEI 49C-PS

The transfer standard fulfilled the criteria given in [*Klausen, et al.*, 2003], which means that neither intercept nor slope were different from 0 and 1,respectively, on the 95% confidence level.

Figure 30 shows the deviation of the transfer standard from SRP#15 before and after the audit. The maximum allowed deviation is also shown in this figure. The regression statistics between the WCC-Empa transfer standard and SRP#15 were calculated using the procedure `fitexy` given in [*Press, et al.*, 1995]. The following relationship was found for the pooled data of the inter-comparisons before and after the audit:

TEI 49C-PS #54509-300 = 0.9961 x SRP#15 + 0.02 ppb

This relationship was used for the calculation of the unbiased ozone concentrations.

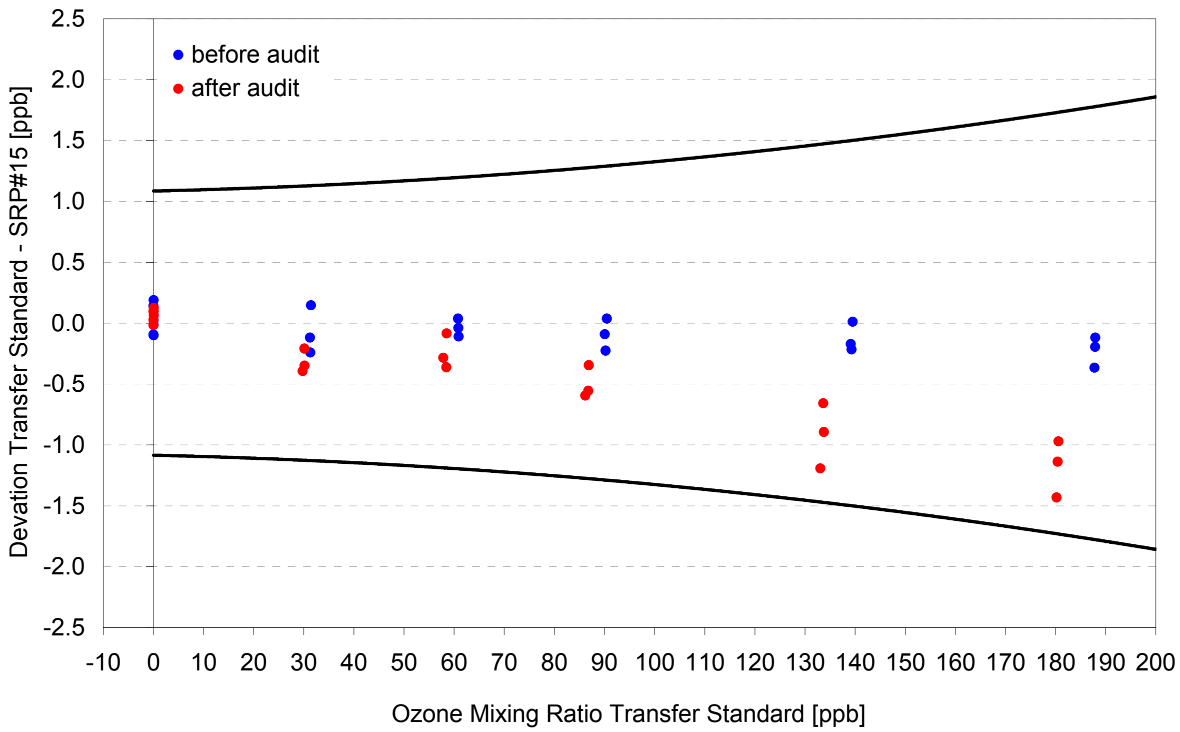

Figure 30: Deviation of the WCC-Empa transfer standard from SRP#15 before and after the audit

V. WCC Carbon Monoxide Reference

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CO in the atmosphere, calibrate standards of other laboratories and to otherwise provide reference gases to the community measuring atmospheric CO. This CO reference scale developed at CMDL was designated by WMO as the reference for the GAW program. The standards used at the WCC are listed in Table 19:

The CO scale of the CMDL was recently revised (Novelli et al., 2003). WCC-Empa refers to the **new** scale (WMO 2000). The WCC-Empa transfer standards used during the audit are listed in Table 20.

A MGM dilution unit (Breitfuss, Serial # 2262/91/1) was used to generate different CO concentrations for the inter-comparison of the NDIR instrument. This dilution unit was calibrated against a flow reference (DH Instruments, Inc., MOLBOX #396 and #643, MOLBLOC #850 and #851) before and after the audit. Zero air was generated using a zero air generator (Ambient Air – Rubingel – Sofnocat – Filter – Pump – Purafil – Sofnocat – Filter). This zero air system was tested and completely removed CO from ambient levels of > 1 ppm at 3.5 litres per minute. A CO standard (Sauerstoffwerk Lenzburg) in synthetic air was used for the dilution system. This standard was calibrated against CMDL revised scale CA02854 with the Aerolaser AL5001, resulting in a concentration of 50.117 ppm CO. In addition, the whole dilution system was checked by measuring the resulting concentrations with the AL5001. The results (flows, expected and measured CO concentrations) are listed in Table 21. The expected CO concentration from the dilution was assigned to be the conventional true value.

Table 19: CMDL CO Standards at the WCC. The error represents the measured standard deviation and the ultimate determination of the primary standard.

Standard (Gas Cylinders)	CMDL old scale*	CMDL new scale**	Cylinder
CMDL Laboratory Standard (basis for WCC)	44.0 ± 1.0 ppb	52.1 ± 1.1 ppb	CA03209
CMDL Laboratory Standard (")	97.6 ± 1.0 ppb	105.8 ± 1.1 ppb	CA02803
CMDL Laboratory Standard (")		129.8 ± 1.3 ppb	CA05373
CMDL Laboratory Standard (")	144.3 ± 1.4 ppb	149.7 ± 1.5 ppb	CA03295
CMDL Laboratory Standard (")	189.3 ± 1.9 ppb	194.7 ± 1.9 ppb	CA02859
CMDL Laboratory Standard (")	287.5 ± 8.6 ppb	295.5 ± 3.0 ppb	CA02854

* Certificates from 5.8.97 (97.6, 189.3, 287.5 ppb) and 7.01.98 (44.0, 144.3 ppb)
** Revised scale (by P. Novelli), re-calibrated at CMDL, 23.01.01; Certificate from 15.4.04 (129.8 ppb)

Table 20: CO transfer standards of the WCC (average of calibrations from November 04 and January 05). The error represents the measured standard deviation.

Transfer Standard (Gas Cylinders)	CO (calibrated against CMDL new scale CA02854) with AL5001		Cylinder
	before audit	after audit	
WCC Transfer Standard (2 l cylinder)	72.7 ± 0.7 ppb	72.4 ± 0.5 ppb	040121-2
WCC Transfer Standard (2 l cylinder)	82.9 ± 0.5 ppb	82.8 ± 0.8 ppb	040719-1
WCC Transfer Standard (6 l cylinder)	132.7 ± 0.7 ppb	132.6 ± 0.8 ppb	041109-3
WCC Transfer Standard (2 l cylinder)	153.2 ± 1.4 ppb	153.3 ± 1.0 ppb	041109-2
WCC Transfer Standard (2 l cylinder)	175.4 ± 1.1 ppb	175.4 ± 0.8 ppb	041109-1

Table 21: Breitfuss MGM dilution system

Mass Flow Controller Setpoint [ml/min]		Mass Flow Controller Actual value before audit [ml/min]		Expected CO concentration before audit [ppb]	Measured CO concentration before audit [ppb ± 1σ]	Mass Flow Controller Actual value after audit [ml/min]		Expected CO concentration after audit [ppb]	Measured CO concentration after audit [ppb ± 1σ]	Average expected CO concentration [ppb]
MFC1	MFC2	MFC1	MFC2			MFC1	MFC2			
2000.0	0.0	1996.9	0.0	0.0		1991.3	0.0	0.0		0.0
1994.0	6.0	1991.7	6.2	154.3	154.2 ± 1.0	1984.8	6.2	155.7	156.0 ± 0.8	155.0
1992.0	8.0	1990.5	8.1	204.3	204.2 ± 0.9	1983.1	8.2	206.0	205.3 ± 0.8	205.1
1984.0	16.0	1982.2	16.2	405.9	406.2 ± 1.7	1974.7	16.2	408.6	408.5 ± 1.2	407.3
1976.1	23.9	1973.0	24.2	608.2	608.8 ± 1.6	1966.4	24.3	611.6	611.6 ± 2.0	609.9
1960.1	39.9	1957.8	40.4	1012.4	1012.1 ± 1.7	1949.1	40.4	1018.0	1016.3 ± 3.5	1015.2

VI. WCC Methane Reference

The methane reference scale maintained by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CH_4 in the atmosphere. This CH_4 reference scale developed at CMDL was designated by WMO as the reference for the GAW program. The CMDL standards used at WCC-Empa are listed in Table 22. The WCC-Empa transfer standards (Table 23) are traced back to the CMDL standards shown below.

Table 22: CMDL CH_4 Standards at WCC-Empa. The error represents the measured standard deviation and the ultimate determination of the primary standard.

CMDL Standard	Methane [ppb]*	Cylinder
CMDL Laboratory Standard (basis for WCC)	1691.6 ± 0.30 ppb	CA05316
CMDL Laboratory Standard (basis for WCC)	1795.1 ± 0.19 ppb	CA04462
CMDL Laboratory Standard (")	1882.0 ± 0.24 ppb	CA04580

* Certificates from 13.09.2000 (CA04462 and CA04580) and 1.04.2003 (CA05316)

Table 23: WCC-Empa CH_4 transfer standards (average of calibrations from November 04 and January 05). The error represents the measured standard deviation.

Transfer Standard (Gas Cylinders)	CH_4 (calibrated against CMDL standards CA04462 and CA04580)		Cylinder
	before audit	after audit	
WCC Transfer Standard (2 l cylinder)	1794.2 ± 1.7 ppb	1790.5 ± 1.5 ppb	040121-2
WCC Transfer Standard (2 l cylinder)	1823.4 ± 2.1 ppb	1824.9 ± 1.7 ppb	040719-1
WCC Transfer Standard (2 l cylinder)	1853.7 ± 2.1 ppb	1856.1 ± 1.3 ppb	041109-1
WCC Transfer Standard (2 l cylinder)	1855.0 ± 2.4 ppb	1858.2 ± 2.1 ppb	041109-2
WCC Transfer Standard (6 l cylinder)	1883.2 ± 2.4 ppb	1883.7 ± 1.0 ppb	041109-3

VII. Ozone Audit Executive Summary

GAW World Calibration Centre for Surface Ozone
GAW QA/SAC Switzerland
Swiss Federal Laboratories for Materials Testing and Research (Empa)
Empa Dübendorf, CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

Ozone Audit Executive Summary

0.1	Station Name:	Izaña
0.2	GAW ID:	
0.3	Coordinates/Elevation:	28.30 N, 16.50 W (2367 m a.s.l)
0.4	Parameter:	Surface Ozone

1.1	Date of Audit: 30. November to 4. December 2004	
1.2	Auditors: Dr. C. Zellweger and B. Schwarzenbach	
1.3	Station staff involved in audit: Dr. E.. Cuevas, Mr. R. Ramos, Mr. C. Marrero	
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C PS S/N: 54509-300
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	$(0.9961 \pm 0.0010) \times [SRP] + (0.02 \pm 0.11)$
1.6	Ozone Analyzer [OA]	
1.6.1	Model:	TEI 49C S/N 62900-337
1.6.2	Coefficients prior to audit	BKG: -4.0 SPAN: 1.006
1.6.3	Coefficients during and after audit	BKG: -4.0 SPAN: 1.006
1.6.4	Range of calibration: 0 – 100 ppb	
1.6.5	Calibration before audit (ppb):	$[OA] = (0.9811 \pm 0.0031) \times [TS] + (0.01 \pm 0.15)$
1.6.6	Calibration after audit (ppb):	$[OA] = (0.9811 \pm 0.0031) \times [TS] + (0.01 \pm 0.15)$
1.6.7	Unbiased ozone concentration (ppb):	$C = ([OA] - 0.0360) / 0.9773$
1.6.8	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_C \approx \{0.57\ ppb)^2 + (0.0061 \times C)^2\}^{1/2}$
1.7	Comments:	
1.8	Reference:	Empa-WCC Report 04/4