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

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

EMPA-WCC REPORT 02/2

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE

GLOBAL GAW STATION CAPE POINT

SOUTH AFRICA, APRIL 2002

Submitted by

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

EMPA Dübendorf, Switzerland

Contents:

EMPA is accredited as a calibration laboratory for ozone measuring instruments in accordance with EN SN 45'001

S	SCHWEIZERISCHER KALIBRIERDIENSTDIENST	**EN SN 45'001 accredited calibration service**	
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S	SWISS CALIBRATION SERVICE		

1. Abstract

A system and performance audit was conducted at the Global Atmosphere Watch station Cape Point from 23. to 30. April 2002 by the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide and Methane. The results can be summarised as follows:

System Audit of the Observatory

The Cape Point global GAW station offers excellent facilities for atmospheric research and measurement campaigns. Spacious laboratories are available in the new part of the building. The former lighthouse cottage serves now as an information centre about GAW activities at Cape Point and is open to the public.

Audit of the Surface Ozone Measurement

The inter-comparison, consisting of three multipoint runs between the WCC transfer standard and the main ozone instrument of the station, demonstrated good agreement between the station analyser and the transfer standard. The recorded differences fulfilled the defined assessment criteria as "good" over the tested range up to 100 ppb (Figure 1).

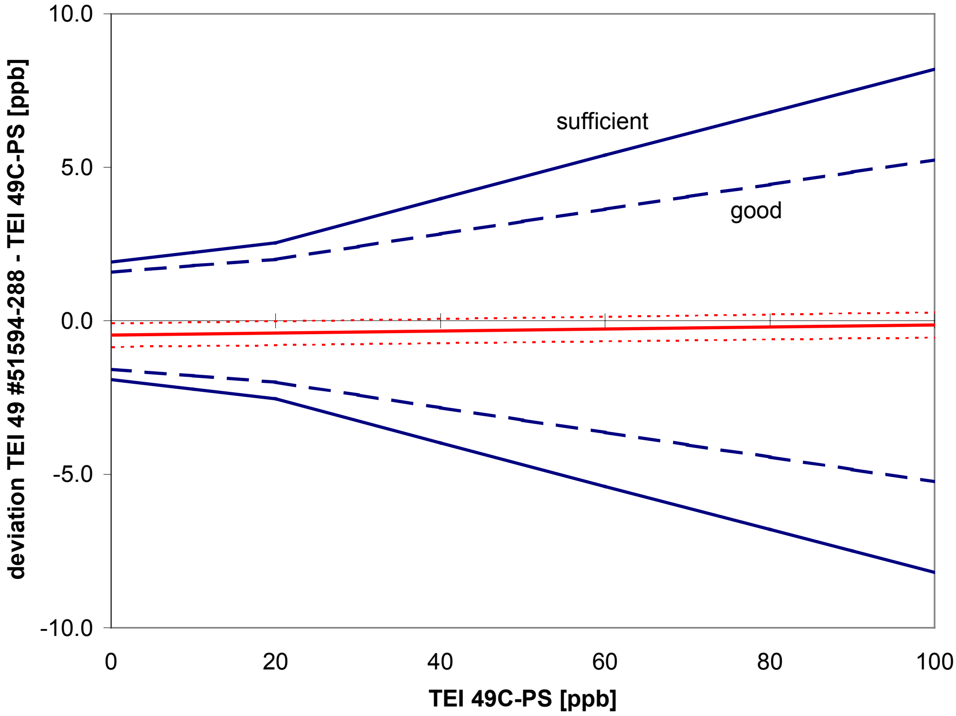


Figure 1: Inter-comparison of the TEI 49 #51594-288 field instrument with the WCC transfer standard

The inter-comparison confirmed the results of the EMPA-WCC audit from 1998, and only minor recommendations were made by EMPA-WCC concerning ozone measurements.

Audit of the Carbon Monoxide Measurement

The results of the inter-comparisons between the eight EMPA-WCC transfer standards and the RGA-3 system of the Cape Point station showed a difference of 2 to 4 ppb in the relevant concentration range of 35 to 75 ppb. Higher differences were found for higher concentrations. Both EMPA-WCC and the Cape Point GAW station refer to the revised CMDL scale. However, the CO standards at Cape Point have never been re-calibrated since the revision of the CO scale. This could explain part of the differences. In view of the uncertainties of the CO scale, the result of the inter-comparison can still be considered as good.

Audit of the Methane Measurement

The results of the inter-comparisons between the eight EMPA-WCC transfer standards and the GC system of the Cape Point station showed good agreement over a concentration range of 1550 to 2010 ppb. The deviation was within ±0.5%. No further recommendations are suggested by EMPA-WCC concerning methane measurements.

Conclusions

All measurements of the audited parameters (O_3, CO, CH_4) at Cape Point were performed at a high level of accuracy. The whole system from the air inlet to the instrumentation, including maintenance and data handling, is operated with great care. The staff involved in measurements and data evaluation is highly motivated and experienced.

The station was completely re-built in 1995 and offers now an excellent infrastructure for atmospheric research and measurement campaigns.

Dübendorf, 23. September 2002 EMPA Dübendorf, WCC

Project scientist Project manager

Dr. C. Zellweger Dr. B. Buchmann

2. Introduction

The **Global GAW Station Cape Point** is part of South Africa's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) programme. The observatory at Cape Point is an established site for long-term measurements of greenhouse gases, ozone and physical and meteorological parameters.

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 GAW **World Calibration Center** (WCC) for Surface Ozone, Carbon Monoxide and Methane, thereby establishing a co-ordinated quality assurance programme 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 years.

In agreement with the station manager, Ernst-Günther Brunke from the South African Weather Service (SAWS), a **system and performance audit** at the Cape Point observatory was conducted by EMPA-WCC between 23. and 30. April 2002.

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 ozone audit 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 inter-comparison have been developed by EMPA based on WMO-GAW Report No. 97 (EMPA-WCC Report 98/5, "Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements", July 2000, available on request from EMPA or downloadable from www.empa.ch/gaw). The present audit report is distributed to the station manager and the World Meteorological Organization in Geneva.

Staff involved in the audit

Cape Point	Ernst-Günther Brunke	contacts, general program, organisation
	Casper Labuschagne	technical assistance at the observatory
	Danie van der Spuy	technical assistance at the observatory
	Bhawoodien Parker	technical assistance at the observatory
EMPA-WCC	Dr. Christoph Zellweger	lead auditor
EMPA-QA/SAC	Dr. Jörg Klausen	assistant auditor

Previous audits at the GAW station Cape Point:

- January 1997 by EMPA-WCC for surface ozone
- September 1998 by EMPA-WCC for surface ozone and carbon monoxide

3. Global GAW Site Cape Point, South Africa

3.1. Description of the Site

The Cape Point station is located in a nature reserve at the southern end of the Cape Peninsula, South Africa, (coordinates: 34°21' S, 18°29' E). The monitoring station is exposed to the sea on top of a cliff 230 m a.s.l., about 60 km south from the city of Cape Town. Since the dominant wind direction is SE - S - SW, the station is subjected to maritime air from the South Atlantic most of the time. Due to its very special location on a peninsula extremity, the vicinity around Cape Point (sector larger than 300°) is primarily ocean and the only ground in the surrounding area consists of sparsely vegetated rock. In the last few years the Cape Point area has developed into a major tourist attraction with hundreds of daily visitors from Cape Town arriving by cars and busses. About 400 m north of the station a large parking lot was built for the public traffic. From there, the station is approximately 150 m uphill and is reached by a funicular. To date, only a few Mini-busses and the station operators are permitted to travel up the steep drive to the station. As tourist activities increase in the future, care should be taken not to compromise the scientific needs.

Figure 2: Map of the Cape Peninsula with the location of the station at Cape Point (from www.sunsetbeach.co.za/Western_Cape_map.htm)

Ozone-, Carbon Monoxide and Methane Levels at Cape Point

The frequency distribution of 30 minute mean values of O_3, CO and CH_4 for 2001 are shown in Figure 3 to 5. The data shown is filtered according to the usual station method (clean air sector from SW to SE), i.e. only background data is shown. Note that frequency distributions are broadened by seasonal cycles.

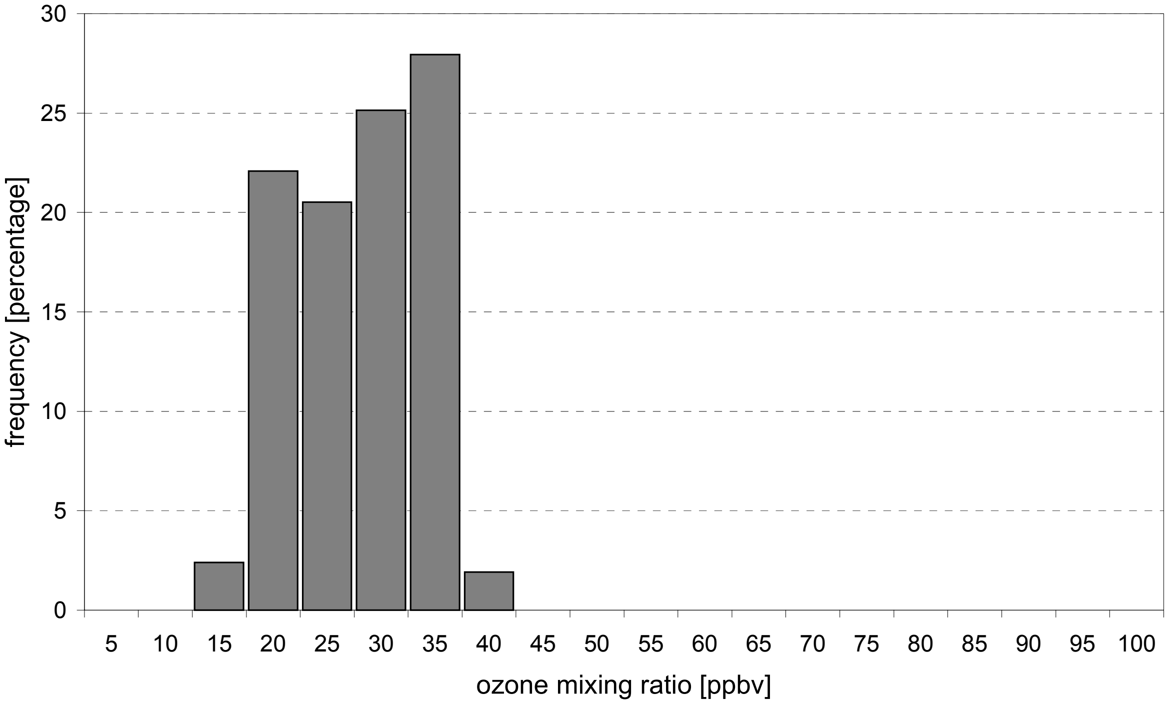


Figure 3: Frequency distribution of the 30 minutes mean ozone mixing ratio (2001) at Cape Point. Only data for clean conditions are shown. Availability of data: 68.2%.

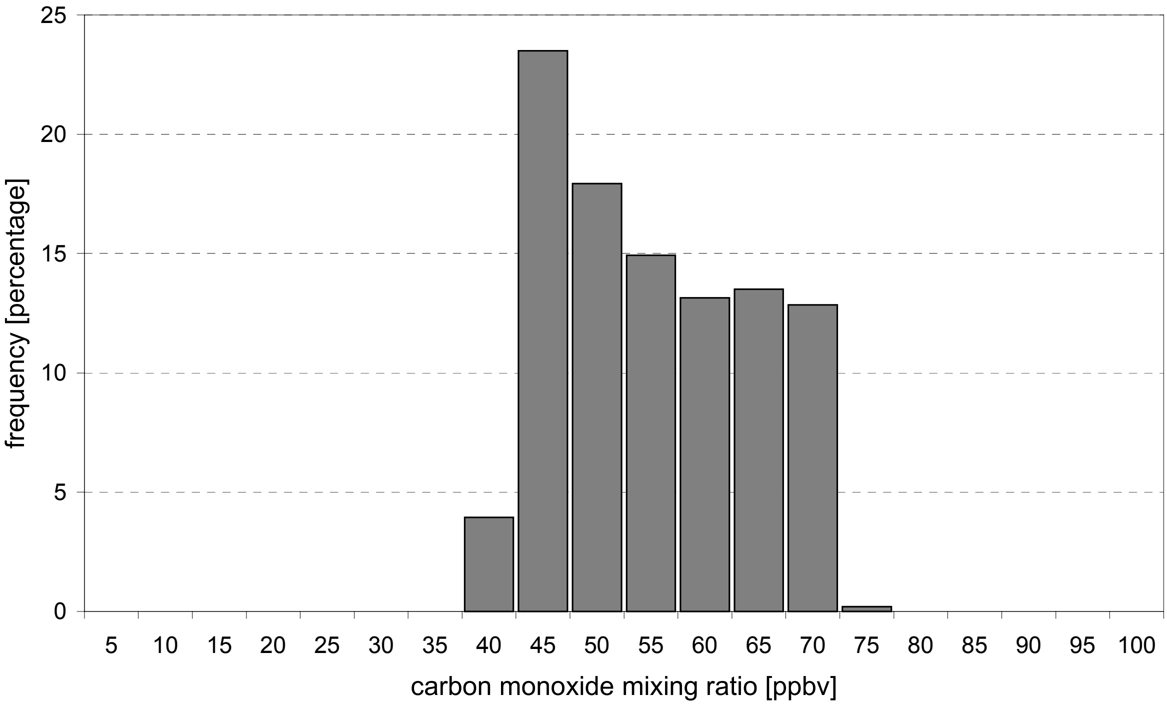


Figure 4: Frequency distribution of the 30 minutes mean carbon monoxide mixing ratio (2001) at Cape Point. Only data for clean conditions are shown. Availability of data: 38.3%.

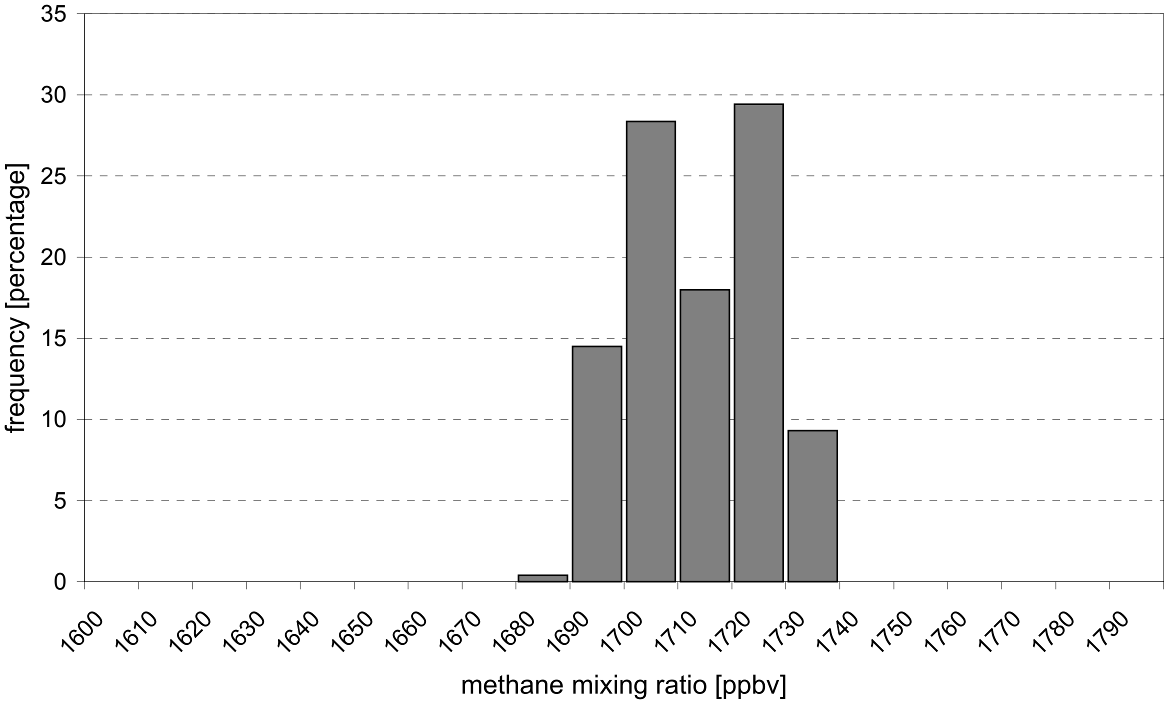


Figure 5: Frequency distribution of the 30 minutes mean methane mixing ratio (2001) at Cape Point. Only data for clean conditions are shown. Availability of data: 63.3%.

3.2. Description of the Observatory

In 1995, the station moved from the two former lighthouse cottages to a newly built one-story measurement station (Figure 6). The new location provides excellent space (Figure 7) for present and future measurement activities and underlines the importance given to the site by the government. It is situated next to the old station beneath the 30 m sampling tower and is built partially into the rock. The air inlet and several pieces of meteorological equipment are mounted on a platform at the top of the flat roof.

Comment

- The Cape Point GAW station offers spacious laboratories which meet all requirements for the measurement of air pollutants.

3.3. Staff / Operators

Table 1: Staff responsible for the GAW site Cape Point (as of April 2002)

Name	**Position and duty**
Gerrie J. R. Coetzee	GAW country contact
Ernst-Günther Brunke	Station manager, atmospheric chemist
Casper Labuschagne	Station operator, atmospheric chemist
Danie van der Spuy	Station operator, electronic engineer
Bhawoodien Parker	Station operator, meteorologist

Figure 6: View of the Cape Point GAW station with the 30 m tower and the lighthouse in the back. The former lighthouse cottage (right) serves now as a visitor centre for GAW activities at Cape Point.

Figure 7: Inside the laboratory at the Cape Point station

4. System- and Performance Audit for Surface Ozone

4.1. Monitoring Set-up and Procedures

There are at present three ozone analysers in use at the Cape Point station. The main instrument is a TEI 49 (operational since August 1996), which draws its air from a 4m-glass tube, through which the sample air is flushed by means of a high-volume fan.

In addition, there are two Dasibi instruments. One samples air from the 30m mast (PTFE tubing), whilst the other toggles between the two air intakes on a half-hourly basis. A metal bellow pump pushes ambient air through the two Dasibis, whose internal pumps have been switched off. The main reason for this plumbing arrangement was to reduce the residence time of the sampling air within the 30m tubing. From a quality point of view, the TEI 49 data is considered to be superior to those of the Dasibis and will hence be submitted to the recently established WDC in Tokyo. The data from the two Dasibis, which are “SPAN” adjusted against the TEI 49, are considered to be of secondary importance.

As a consequence, only the results for the TEI 49 instruments are shown in this section. The inter-comparison with the Dasibi instruments is shown in Appendix I.

4.1.1. Air Inlet System

Sampling-location: on the flat roof of the laboratory building.

Sample inlet:

Rain protection:	The Inlet is protected against rain and snow by an upside-down stainless steel bucket.
Inlet-filter:	Teflon inlet filter before analyser, exchanged monthly or when dirty.
Inlet:	length = 4.3 m, i.d. = 100 mm, with SCHOTT glass tube (50 mm o.d.) inside. Flow rate 1.5 m^3 per minute.
Manifold:	length = 0.4 m, i.d. = 80 mm, SCHOTT glass, flow rate 1.5 m^3 per minute.
Sample line:	length = ca. 1.5 m, i.d. = 4 mm, PFA, flow rate approx. 2 l/min.

Residence time in the sampling line: approx. 2 s

Comment

The PFA tube was clean and free of dust. Materials as well as residence time of the inlet system are adequate for trace gas measurements in particular with regard to minimal loss of ozone.

4.1.2. Instrumentation

Ozone Analysers

Three O_3 analysers are is in use at the Cape Point station (Table 2). The instruments are installed inside the laboratory and are protected from direct sunlight. There is no air-conditioning available, but the laboratory temperature remains usually stable at approx. 22°C.

Table 2: Ozone analysers at the Cape Point Research Station

Type	TEI 49 #51594-288	Dasibi 1008RS #4840	Dasibi 1008-PC #4243
Method	UV absorption	UV absorption	UV absorption
used as	main instrument	backup instrument	backup instrument
at CPT	since August 1996	since 1991	since 1991
Range	0-1000 ppb	0-1000 ppb	0-1000 ppb
Analog output	0-10 V	0-10 V	0-10 V
Offset	56	0	3
Slope	507	307	308
Instrument specials	internal ozone generator	toggles between 4m and 30 m inlet	

Ozone Calibrator

No ozone calibrator is available at the site. However, a calibrator model 49C PS from Thermo Environmental Instruments Inc. is shipped on a regular basis (once every one or two years) to the station from the Institut Atmosphärische Umweltforschung (IFU) in Garmisch-Partenkirchen (Germany).

Operation and Maintenance

Preventive instruments maintenance includes several instrument checks, and adjustment of the pressure transducer is made when necessary. The instrument cells are cleaned yearly. Inlet filters are exchanged monthly or when dirty.

Automatic zero and span checks are performed daily. The monthly average of the daily zero check data are used for zero offset correction. The zero offset for the TEI 49 instrument was 5.65 ppb for the audit period. This value was subtracted from all data obtained during the audit.

4.1.3. Data Handling

Data Acquisition and –transfer

A new data acquisition (Testpoint, Keithley) was installed at the station in January 2000. All analog signals of the ozone instruments are acquired, and 1-minute and 30-minute average signals are stored on the data acquisition computer. Data back-ups are made weekly, and the data evaluation is made at the office in Stellenbosch.

Data Treatment

The raw data as it was collected from the data acquisition is inspected by the station operators (time series plot, check with instrument log book). A correction is made for the zero offset based on the monthly average value of the daily zero checks.

Data Submission

Ozone data have not been submitted to the GAW data centre at NILU, but submission to the recently established WDC for surface ozone at JMA is planned.

4.1.4. Documentation

Logbooks

A logbook is available for each of the ozone instruments. The notes are up to date and describe all important events.

Standard Operation Procedures (SOPs)

The manual for the instrument is available at the site.

Comment

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

4.2. Inter-comparison of the Ozone Instrument

4.2.1. Experimental Set-up

Inter-comparisons were made for all of ozone instruments at the Cape Point GAW station, but only the results for the TEI 49 are shown in this section. Since the Dasibi instruments are considered to be of secondary importance and no data of these instruments will be submitted to any data centre, the results for the Dasibis are summarised in Appendix I.
The WCC transfer standard TEI 49C PS (details see Appendix II-III) was operated in stand-by mode for warming up for 40 hours. During this stabilisation time the transfer standard and the PFA tubing connections to the instrument were conditioned with 250 ppb ozone for 60 minutes. Afterwards, three comparison runs between the field instrument and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 8 the experimental set-up during the audit. No modifications of the ozone analysers which could influence the measurements were made for the inter-comparisons.
It was noticed during the instrument tests prior to the inter-comparison that the analog output of the TEI 49 field instrument was not adjusted properly. Agreement was observed for the zero reading, but full scale was 10.48 V instead of 10.00 V. The analog output of the field instrument was adjusted to 0.00 – 10.00 V by EMPA-WCC. Based on the daily span check it was possible to isolate the period when the drift happened (Sept. 2001). All data for the period between September 2001 and the audit can be corrected accordingly.

The audit procedure included a direct inter-comparison of the TEI 49C-PS WCC 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 III.

Table 3: Experimental details of the ozone inter-comparison

reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instrument:	TEI 49 #51594-288
ozone source:	WCC: TEI 49C-PS, internal ozone 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:	16-channel ADC with acquisition software
pressure transducer readings:	TEI 49C-PS (WCC): 982.0 hPa adjusted to ambient pressure (985.0 hPa) before the inter-comparison. TEI 49 #51594-288: 985 hPa (no adjustment made)
concentration range	0 - 100 ppb
number of concentrations:	5 plus zero air at start and end
approx. concentration levels:	10 / 20 / 30 / 50 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	3 x on 25. April 2002
connection between instruments:	approx. 1.5 meter of 1/4" PFA tubing

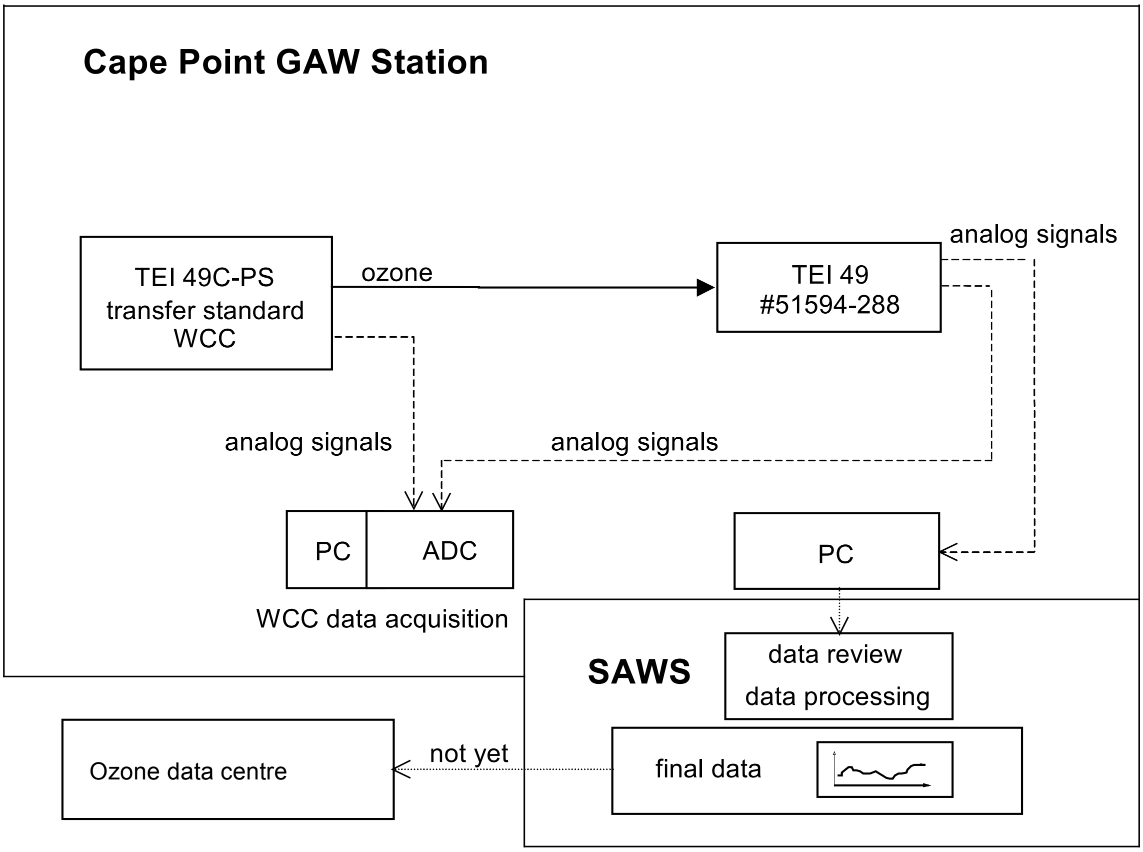


Figure 8: Experimental set up for the ozone inter-comparison

4.2.2. Results

Ozone Analyser

The results comprise the inter-comparison between the TEI 49 #51594-288 field instrument (Slope 507) and the WCC transfer standard TEI 49C-PS, carried out on 25. April 2002.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty 30-second-means are presented in Table 4. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Figures 9 and 10 show the residuals of the linear regression analysis of the field instrument compared to the EMPA transfer standard. The residuals versus the run index are shown in Figure 9 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 10 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 11).

The data used for the evaluation was recorded by the EMPA data acquisition system. This raw data was treated according to the usual station method. Corresponding to this procedure the zero offset determined by the daily zero checks was averaged over a month (5.65 ppb) and subtracted from all data.

Table 4: Inter-comparison of the ozone field instrument

	TEI 49C-PS		TEI 49 #51594-288			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.2	0.08	0.2	0.30	0.1	
2	89.8	0.10	89.7	0.32	-0.1	-0.1%
3	10.0	0.18	9.7	0.34	-0.3	-3.4%
4	29.8	0.13	29.5	0.37	-0.4	-1.2%
5	20.0	0.08	19.4	0.32	-0.6	-3.0%
6	49.9	0.11	49.8	0.41	-0.1	-0.2%
7	0.2	0.10	-0.4	0.32	-0.6	
8	0.2	0.11	-0.2	0.29	-0.4	
9	10.0	0.13	9.5	0.29	-0.5	-5.0%
10	29.9	0.09	29.6	0.32	-0.3	-1.2%
11	49.9	0.11	49.6	0.30	-0.3	-0.7%
12	20.0	0.11	19.4	0.28	-0.6	-2.8%
13	89.9	0.09	89.8	0.36	-0.1	-0.1%
14	0.2	0.09	-0.4	0.25	-0.5	
15	0.2	0.08	-0.2	0.37	-0.3	
16	89.9	0.08	89.7	0.38	-0.2	-0.3%
17	50.0	0.10	49.6	0.37	-0.4	-0.8%
18	29.9	0.11	29.4	0.19	-0.5	-1.7%
19	10.1	0.11	9.3	0.22	-0.8	-7.8%
20	20.0	0.07	19.5	0.40	-0.5	-2.7%
21	0.2	0.10	-0.2	0.40	-0.4	

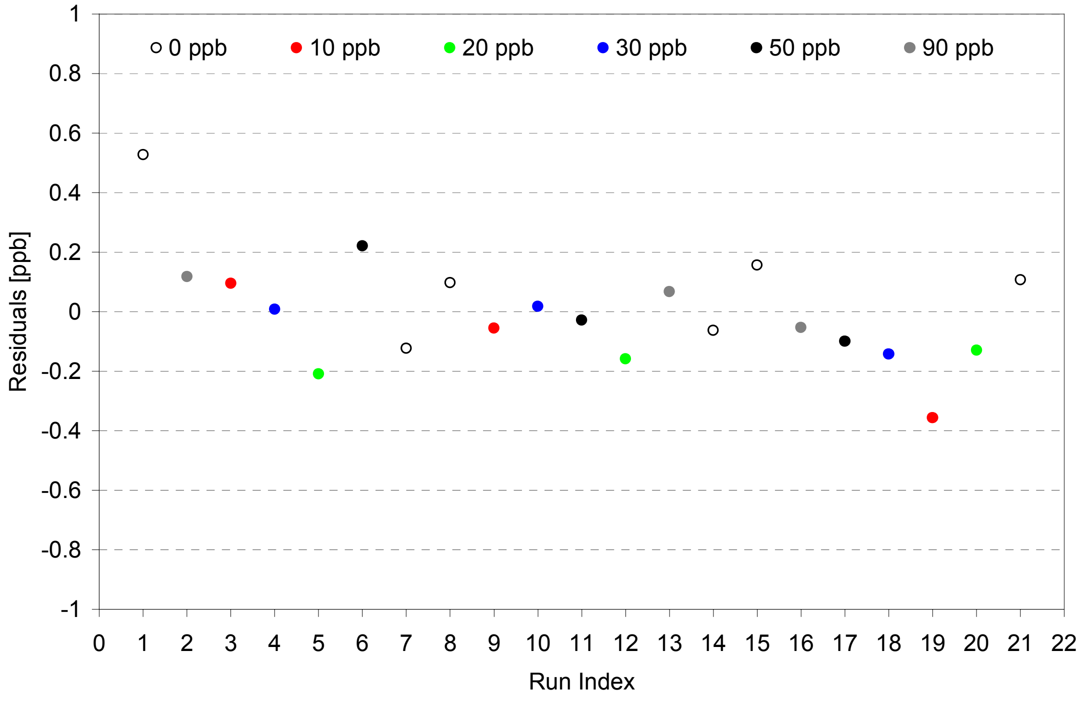


Figure 9: Residuals to the linear regression function (TEI 49 #51594-288) vs the run index (time dependence)

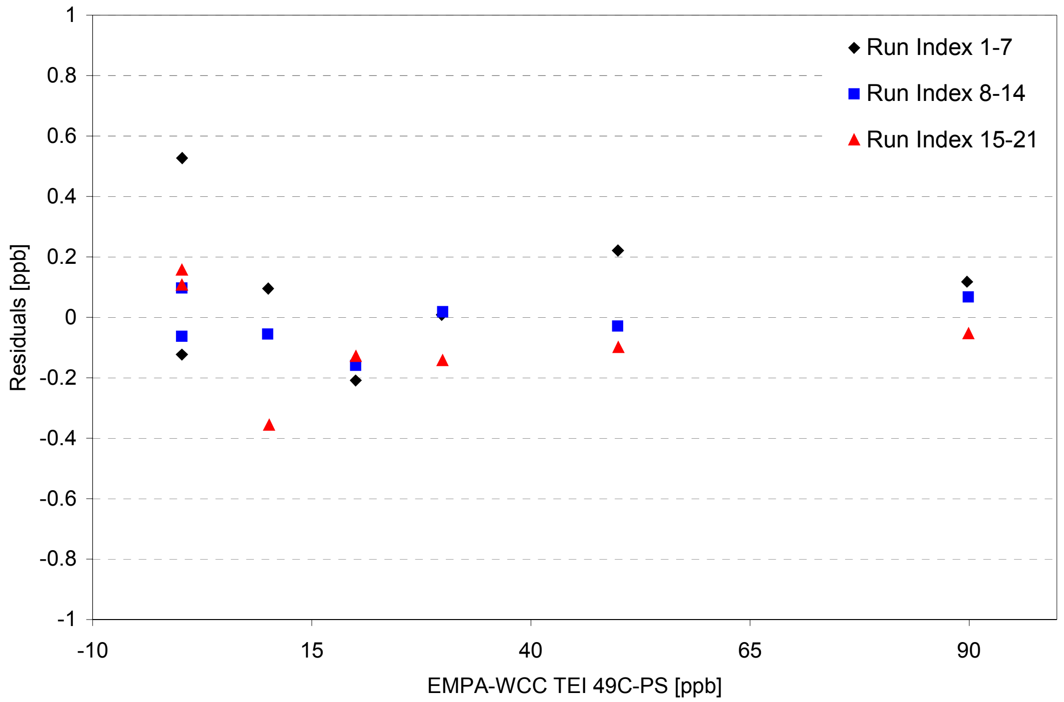


Figure 10: Residuals to the linear regression function (TEI 49 #51594-288) vs the concentration of the WCC transfer standard (concentration dependence)

From the inter-comparisons of the TEI 49 #51594-288 field instrument with the TEI 49C-PS transfer standard from EMPA, the resulting linear regression (for the range of 0-100 ppb ozone) is:

TEI 49 #51594-288:

TEI 49 #51594-288 = 1.003 x TEI 49C-PS - 0.47 ppb

TEI 49 #51594-288= O3 mixing ratio in ppb, determined with TEI 49 #51594-288

TEI 49C-PS = O_3 mixing ratio in ppb, determined with TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.001	(f = 19) f = degree of freedom
	- offset S_b in ppb	0.06	(f = 19)
	- residuals in ppb	0.12	(n = 21)

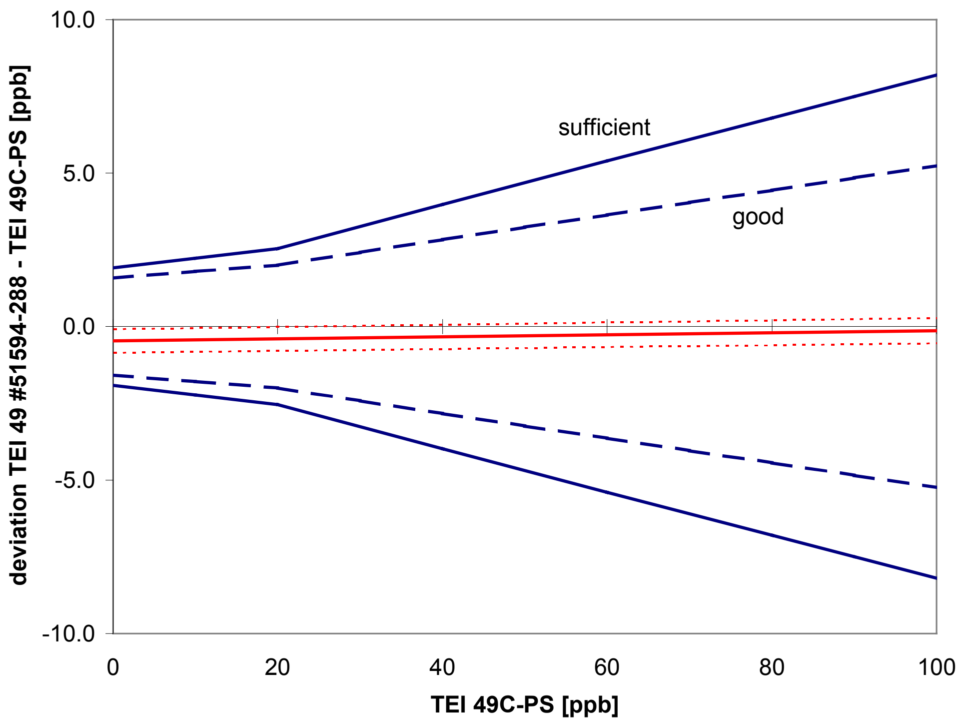


Figure 11: Inter-comparison of instrument TEI 49 #51594-288

Comment

The ozone concentrations observed at Cape Point (2001) ranged between 16 and 34 ppb (5- and 95-percentile of 30 min mean values). The main ozone instrument TEI 49 fulfils the assessment criteria of “good” over the tested range between 0 and 100 ppb ozone.

4.3. Recommendation for the Ozone Measurements

The TEI 49 ozone instrument at Cape Point is in a good condition and fulfils the assessment criteria as "good" over the tested range of 0 to 100 ppb. Two Dasibi instruments are used as backup instruments, one of which toggles between two sampling heights. The data of the Dasibi analysers is only used for quality assurance purposes, and is not submitted to any data centre. The recommendations of EMPA-WCC for ozone measurements can be summarised as follows:

TEI 49 instrument:

- The agreement between display reading, analog output voltage and data acquisition reading should be checked more frequently. It is suggested to add this to a station specific check list, which should be completed at regular intervals.
- A yearly comparison of the instrument with a ozone calibrator (for example from IFU) would be beneficial.
- Submission of the ozone data to the GAW data centre is encouraged.

Dasibi instruments:

- The pumps in the inlet line potentially destroy ozone. An instrument set-up with the pumps after the analyser should be considered.

5. System- and Performance Audit for Carbon Monoxide

Carbon monoxide measurements started at Cape Point in 1978 and a continuos time series is available.

5.1. Monitoring Set-up and Procedures

5.1.1. Air Inlet System for CO and CH_4

Sampling-location: on top of the 30 m tower

Inlet description: 43 m long stainless steel tube (1/4'') - two stage freezing traps (– 4°C and - 40°C) – pump and overflow (~12 l/min) - 50 ml/min is split off – instrument - pump

Residence time in the sampling line: approx. 3 s

Comment

The inlet system is adequate for analysing CO and CH_4 concerning materials and residence time.

5.1.2. Instrumentation

An RGA-3 GC-system of Trace Analytical Inc. is used as an in-situ CO analyser. Instrumental details are listed in Table 5.

Table 5: Carbon monoxide gas chromatograph at Cape Point

instrument	Trace Analytical Inc.
model, S/N	RGA3, S/N 113087-003
at Cape Point	since 1989
configuration	one analytical column
method	GC / HgO Detector
loop	1 ml
columns	analytical column: Mole sieve 5Å 60/80
carrier gas	synthetic air - Mole sieve - Hopcalite - Sofnocat
operating temperatures	Detector: 200 °C, Column: 100 °C
analog output	0 - 1 V
calibration interval	every 180 min (working standard)
instrument's specials	a few seconds before injection, the flow through the loop is stopped (solenoid valve) to equilibrate loop pressure with ambient pressure

Gas Standards

Table 6 shows the gas standards that are used for the verification of the measurements. A Scott-Marrin cylinder (traced back to the station reference) is available at the site to serve as working standards. The original certificates of the CMDL standards were corrected to the new CMDL scale in early 2002. However, no re-calibration of the CMDL cylinders has been performed yet.

Table 6: Station CO cylinders

Gas cylinder	Description	Conc. [ppb][1]	Conc. [ppb][2]	Conc. [ppb][3]
CA02907	Scott Marrin / station reference (CMDL certified)	45.0	49.7	51.0
CA02929	Scott Marrin / station reference (CMDL certified)	69.4	74.1	74.3
CA04037	Scott Marrin / working standard			61.8

[1] CMDL certified (old scale)
[2] newly assigned by CMDL in early 2002 (new scale); the standards were not re-calibrated at CMDL
[3] concentrations based on the working standard CA04037 (61.8 ppb)

The working gas used during the audit was calibrated against the MPI flow dilution system using a 10 ppm CO standard. This system was supplied by the Institut Atmosphärische Umweltforschung (IFU) and has been used as a reference since the beginning of CO measurements at Cape Point. The data were never adjusted to the NOAA CMDL scale, but the recent revision of the CMDL scale brought the Cape Point measurements and the NOAA CMDL scale together within instrumental error.

Operation and Maintenance

Analysis: 5 measurements are performed per hour and the working standard is injected every 3 hours. Additionally, the station reference standards are injected when ever the station is visited by the instrument responsible.

Weekly checks: RGA-3 test points
chromatogram / peak width / CO-retention time
cylinder pressures

A linearity check (range 40 to 80 ppb) with a dilution system is performed when significant changes of the instrument are made (e.g. replacement of the mercury bed).

Comment

- CO analysis by GC followed by mercury reduction detection is a sophisticated method. Applied with care it is characterised by excellent specificity, very low detection limits and high precision. Unfortunately, the detectors are not perfectly linear.

5.1.3. Data Handling

Data Acquisition and –transfer

Currently (at time of audit) AZUR GC control software has been used for data acquisition and processing. Since mid-1997 raw data including chromatograms have been archived on CD on a monthly basis.

Data Treatment

From the results of the working standard, a moving average encompassing three calibrations is run over the whole set of monthly calibrations. The individual value (moving average) from the calibration peak adjacent to the corresponding ambient air peak is used to calculate the ambient air concentration. Chromatogram integration is carried out for peak height. Invalid values (according to logbook), i.e. data from manual calibration or zero checks or analytically invalid data, are manually removed from the database. The validated 12-minute CO values are averaged to 30 minutes mean values. In a second step, the data set is filtered to achieve a data set for background conditions. Since wind direction criteria alone are not satisfactory to remove local and/or regional pollution effects from the "all data sets", various routines for baseline filtering have been tested over the years by the Cape Point team. Currently, the raw data sets are being filtered using Excel spreadsheets and appropriate algorithms. The filtering procedure itself makes use of 11-day moving percentiles for the parameter under consideration. Two freely selectable percentiles, each one tuneable by a factor, serve as upper and lower cut-off limits for background concentrations for the trace gas being measured. The data sets are stored on a PC and archived monthly on CD (two copies).

Data Submission

For scientific reasons data have been submitted to different teams. At present CO data are not submitted to any data centre, but it is planned for the future to submit data to the GAW World Data Centre for Greenhouse Gases at JMA.

5.1.4. Documentation

Logbooks

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

Standard Operation Procedures (SOPs)

The manual for the instrument is available at the site.

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. Intercomparison of the in-situ Carbon Monoxide Analyser

5.2.1. Experimental Procedure

Since no Standard Operation Procedure (SOP) has been established for CO measurements until now, the "SOP for performance auditing ozone analysers at global and regional WMO-GAW sites" (WMO-GAW Report No 97) also serves as a guideline for CO audits.

The inter-comparison of the CO measurements was comprised of the following experiments.

The eight transfer standards of the WCC (concentration range 40-160 ppb CO) were stored in the same room as the CO measurement system to equilibrate for several days. The transfer standards were calibrated against the CMDL scale at EMPA before and after the audit (Appendix IV). 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 analysed between 6 and 21 times in the period from 18. to 30. April 2002. No modifications of the RGA-3 carbon monoxide analyser were made for the inter-comparison. The WCC transfer standards were injected at the sample inlet. The data was acquired by the station software. This data (mean values and standard deviations) was reprocessed by the station operators during and after the audit. The experimental details are summarised in Table 7.

Table 7: Experimental details of the carbon monoxide inter-comparison

field instrument:	RGA3, S/N 113087-003
reference:	EMPA-WCC transfer standards
data acquisition system:	APEX GC control software
approx. concentration levels:	40 to 160 ppb
injections per concentration:	6 to 21
Sequence	injected as sample, every 12 min

5.2.2. Results

The CO concentrations determined by the RGA-3 field instrument for the eight WCC transfer standards are shown in Table 8. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 12 shows the absolute differences (ppb) between the measurements of the RGA-3 and the WCC transfer standards (TS) (conventional true value). The WCC TS were calibrated before and after the audit against the CMDL scale (Reference: CMDL CA02859, 194.7 pbb) with the 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 injection of the transfer standards at Cape Point. The data of the RGA-3 field instrument were processed during the audit by the station operators and are based on calibration of the instrument against the reference standards available at the site.

Table 8: Carbon monoxide inter-comparison measurements at Cape Point

No.	WCC standard	Cape Point analysis (RGA-3, Peak Height)				
	conc. ± 1σ (N)	conc.	sd	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	38.2 ± 1.1* (59)	35.8	0.1	6	-2.4	-6.3
2	43.5 ± 0.9 (107)	41.6	0.3	11	-1.9	-4.4
3	53.2 ± 1.1 (113)	50.3	0.1	18	-2.9	-5.5
4	71.6 ± 1.1 (109)	67.9	0.2	16	-3.6	-5.1
5	75.4 ± 1.0 (109)	71.4	0.2	17	-3.9	-5.2
6	99.2 ± 0.9 (111)	93.0	0.2	19	-6.2	-6.2
7	109.8 ± 0.9 (113)	103.6	0.3	21	-6.2	-5.6
8	159.8 ± 0.9 (125)	148.3	0.2	15	-11.5	-7.2

* no re-calibration of this transfer standard could be made after the audit because the cylinder was emptied during the audit

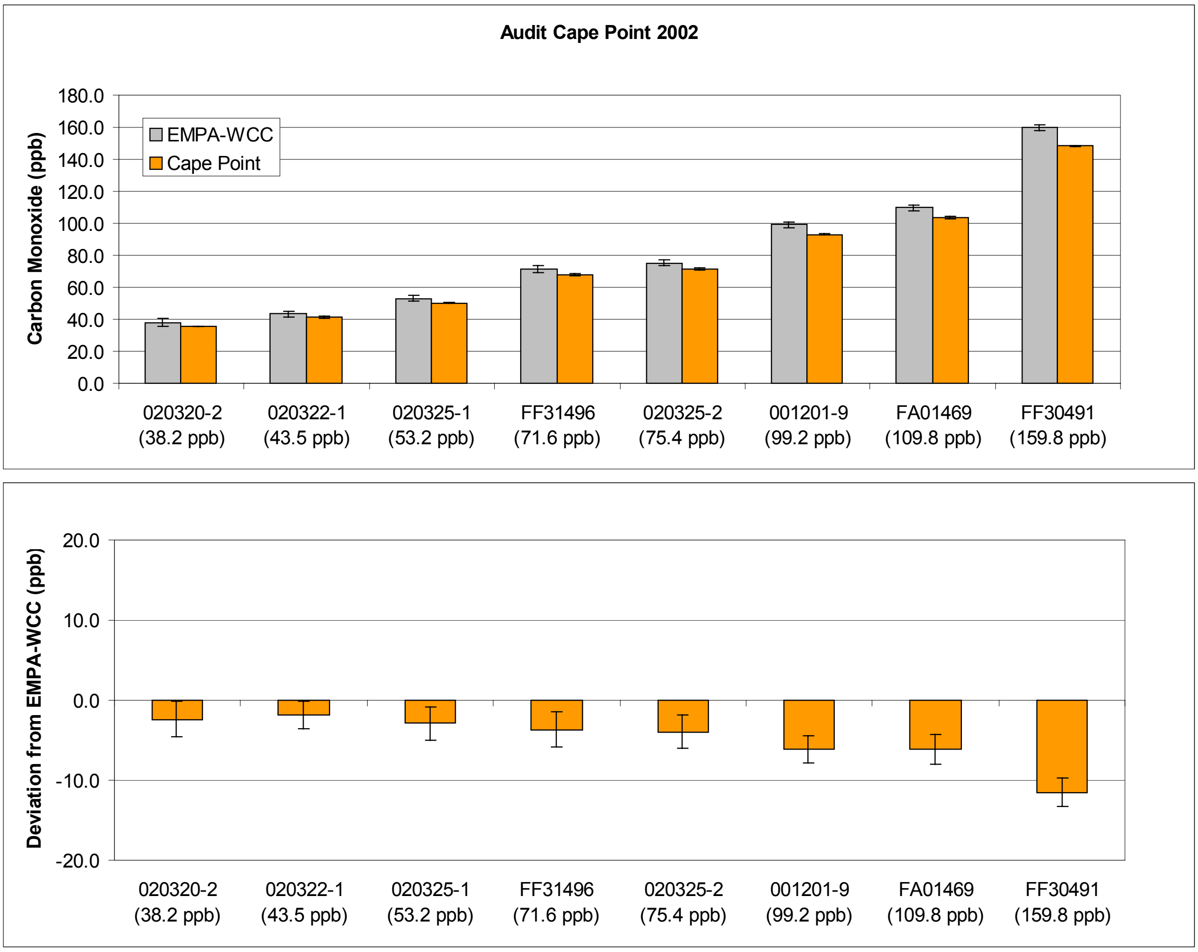


Figure 12: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02859, 194.7 ppb) measured with the GC system of Cape Point (orange). lower panel: deviation of the Cape Point station from the conventional true value. The error bars represent the 95% confidence interval.

5.3. Discussion of the Intercomparison Results

The analysis of the EMPA-WCC transfer standards by the station resulted in lower values (1.9 to 11.5 ppb) compared to the conventional true value. Both the transfer standards of EMPA-WCC and the station reference gases are traceable to the revised CMDL scale (see Appendix IV). The results improved significantly in comparison to the audit in 1998 for the relevant concentration range (40 to 80 ppb), which can be explained by the revision of the CMDL scale. The remaining differences could be explained as follows:

Concentrations > 80 ppb

The highest deviation (–7.2 to -5.6%) from the conventional true value were found for CO concentrations >80 ppb. Concentrations >80 ppb are above the relevant concentration range for background data of Cape Point. The instrument was not calibrated for this range, and a linear extrapolation was made for the calculation of the results. The RGA-3 instrument was not checked for linearity above 80 ppb during the audit.

Concentrations < 80 ppb

Smaller deviations of –1.9 to –3.9 ppb (-6.3 to –4.4%) were found for CO concentrations below 80 ppb. The CMDL certificates for the cylinders of Cape Point were corrected to the new CMDL scale in early 2002 (by P. Novelli, CMDL), but the cylinders have not been re-calibrated at CMDL. Analysis of the Cape Point CMDL cylinders with the working standard (calibrated with the MPI dilution system using a 10 ppm CO standard) still results in higher concentrations than assigned by CMDL, but the differences are significantly smaller compared to the old scale (see Table 6).

The transfer standards that were used by EMPA-WCC were calibrated against a CMDL certified cylinder with 194.7 ppb CO (new scale), see Appendix IV. Measurements of the lower EMPA-WCC CMDL standards using the 194.7 ppb cylinder as a reference also result in higher findings (2.6 to 3.9 ppb) in comparison to the CMDL certificates.

The differences between EMPA-WCC and Cape Point can therefore be explained by the uncertainty of the CMDL carbon monoxide scale.

5.4. Recommendation for Carbon Monoxide Measurements

Since the major problem for the CO measurements seems to be the uncertainty of the CO scale, EMPA-WCC can only make minor recommendations, which can be summarised as follows:

- Continuation of the measurements at Cape Point using various standards for calibrations and consistency checks is encouraged.
- A re-calibration of the Cape Point CO standards at CMDL is encouraged.
- The RGA instrument used at Cape Point seems to show a rather linear response for low concentrations up to 80 ppb. Linearity checks with the dilution system for concentrations up to 200 ppb are encouraged.
- Submission of the CO data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is recommended.

6. System-and Performance Audit for Methane

Methane measurements became operational at Cape Point in 1982. The average CH_4 concentration measured at Cape Point increased from approx. 1550 ppb to over 1700 ppb since then. Since such a long time series is available from Cape Point, the continuation of these measurements at Cape Point is of great importance.

6.1. Monitoring Set-up and Procedures

6.1.1. Air Inlet System for CH_4

Inlet: same as for Carbon Monoxide (see 5.1.1)

Comment

The inlet system is adequate for analysing CH_4 concerning materials and residence time.

6.1.2. Analytical System

Gas chromatograph

A Carlo Erba FRACTOVAP 2450 gas chromatograph with an FID detector is used for ambient methane measurements at Cape Point. Instrument details are summarised in Table 9.

Table 9: Gas chromatograph for methane at the Cape Point station

Instrument	Carlo Erba FRACTOVAP 2450, S/N 152884 FID: Carlo Erba Mod. 180, S/N 125268
at Cape Point since	November 2001
method	GC / FID Detector
sample loop	7 ml
column	Molecular sieve 13x, ¼", length 135 cm
carrier gas	N_2 99.999%
operating temperatures	Injector: 125°C, Column: 70°C
analog output	0 - 10 V
calibration interval	working standard once per hour station reference once per day
instrument specials	a few seconds before injection, the flow through the loop is stopped to equilibrate pressure.

Gas Standards

Table 10 shows an overview of the methane standards available at the site.

Table 10: Station CH_4 cylinders

Gas cylinder	Description	Conc. [ppb]
CA02907	Scott Marrin / station reference (CMDL certified)	1709.0
CA02929	Scott Marrin / station reference (CMDL certified)	1766.0
CA03712	Scott Marrin / working standard calibrated against station reference	1822.0

Operation and Maintenance

Analysis: five ambient air and one working standard samples are analysed per hour. Additionally, the station reference is injected every 24 hours. Weekly checks of general instrument operation are performed (retention times, flows, cylinder pressures etc). A zero check is made twice a year. If malfunction is detected, measures are taken.

6.1.3. Data Handling

Data Acquisition and –transfer

The data is acquired on both a AZUR GC integration package and the Testpoint software (Keithley). Both reports and chromatograms are stored as raw data.

Data Treatment

Ambient air mixing ratios are calculated based on peak area by using the concentrations of the working standard. Data evaluation includes consistency checks with charts (in particular retention time, peak start, peak end), checks with the instrument logbook and time series review. The final data evaluation is done at the Stellenbosch office.

Data Submission

Data are submitted to the GAW World Data Centre for Greenhouse Gases at JMA.

6.1.4. Documentation

Logbooks

During the audit the documentation was reviewed for availability and usefulness. The logbook for the methane instrument contained all necessary information about maintenance, instrument changes, events and special investigations.

Comment

The log files were kept up-to-date. All the necessary information was available at the site.

6.2. Inter-Comparison of in-situ Methane Measurements

6.2.1. Experimental Procedure

Since no Standard Operation Procedure (SOP) has been established for CH_4 measurements until now, the "SOP for performance auditing ozone analysers at global and regional WMO-GAW sites" (WMO-GAW Report No 97) also serves as a guideline for CH_4 audits.

The eight transfer standards of the WCC (approx. concentration range 1550 - 2000 ppb CH_4) were stored in the same room as the CH_4 measurement system to equilibrate for several days. The transfer standards were calibrated against CMDL laboratory standards (CA04462, CA04580) at EMPA before and after the audit (see 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 14 to 20 times and analysed between 18. to 30. April 2002. No modifications of the GC system were made for the inter-comparison. The WCC transfer standards were injected at the sample port. The data was acquired by the station software. This data (mean values and standard deviations) was processed during and after the audit by the station operators. The experimental details are summarised in Table 11.

Table 11: Experimental details of the methane inter-comparison

field instrument:	Carlo Erba FRACTOVAP 2450, S/N 152884
reference:	8 EMPA-WCC transfer standards
data acquisition system:	AZUR GC integration package / Testpoint software
approx. concentration levels:	concentration range approx. 1550 – 2000 ppb
injections per concentration:	14 to 20
Sequence	injection at sample port, every 12 minutes

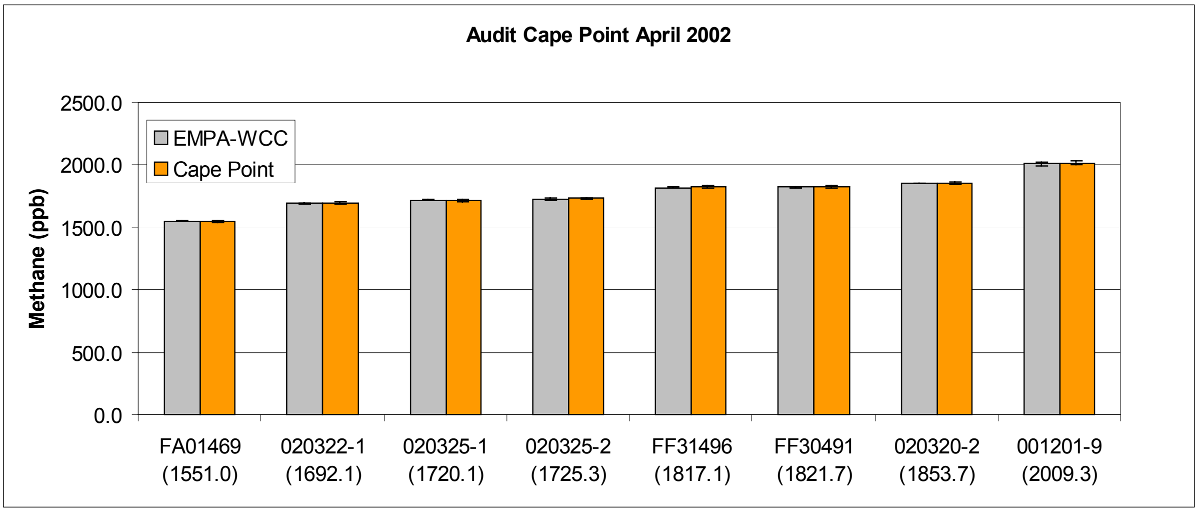
6.2.2. Results of the Methane Intercomparison

The results of the inter-comparison between the Carlo Erba field instrument and the eight WCC transfer standards are shown in Table 12. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 13 shows the absolute differences (ppb) between the measurements of the Carlo Erba GC and the WCC transfer standards (TS) (conventional true value). 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 Cape Point. The data from the Carlo Erba field instrument were reprocessed during and after the audit and are based on the comparison with the working standard and the station references.

Table 12: Methane inter-comparison measurements at Cape Point

No.	WCC standard	Cape Point analysis (Carlo Erba GC-FID, Peak Area)				
	conc. ± 1σ (N)	conc.	sd	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	1551.0 ± 3.2 ppb (20)	1549.3	3.7	15	-1.7	-0.1
2	1692.1 ± 3.9 ppb (20)	1695.9	5.3	15	3.8	0.2
3	1720.1 ± 3.4 ppb (20)	1719.8	4.2	17	-0.3	0.0
4	1725.7 ± 3.9 ppb (20)	1731.5	4.2	19	5.8	0.3
5	1817.1 ± 2.8 ppb (20)	1824.8	5.3	20	7.7	0.4
6	1821.7 ± 3.4 ppb (20)	1825.0	4.1	19	3.3	0.2
7	1853.7 ± 1.0 ppb* (4)	1858.0	4.2	14	4.3	0.2
8	2009.3 ± 5.6 ppb (20)	2018.6	5.3	15	9.3	0.5

* no re-calibration of this transfer standard could be made after the audit because the cylinder was emptied



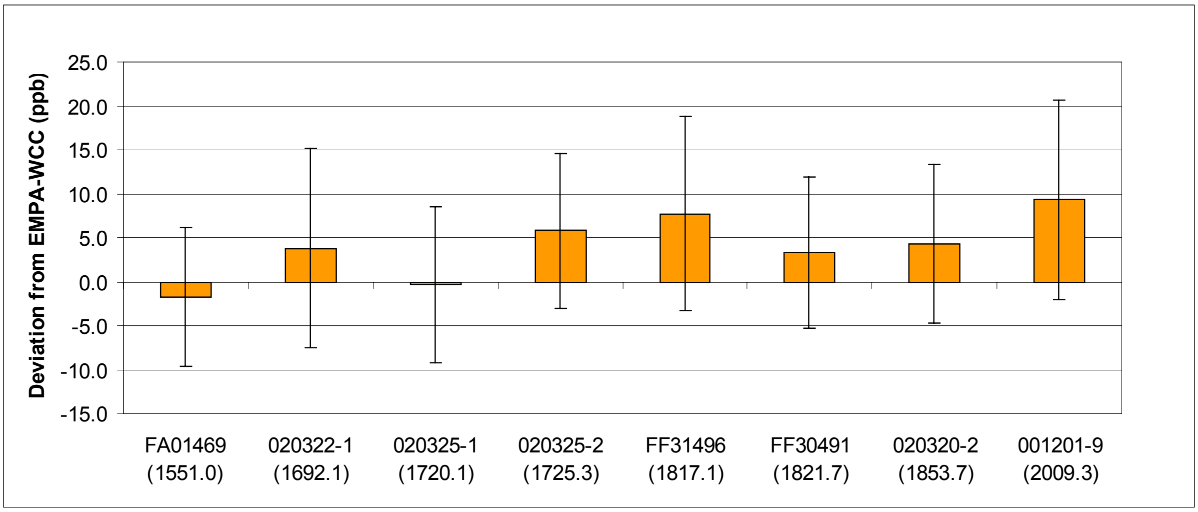


Figure 13: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL scale, Appendix V) measured with the GC system of Cape Point (orange).
lower panel: deviation of Cape Point from the conventional true value.
The error bars represent the 95% confidence interval.

Comment

The CH_4 concentrations of the EMPA-WCC transfer standards as obtained with the Cape Point field instrument agrees very well with the conventional true value in the concentration range between 1550 and 2010 ppb methane. The deviation from the transfer standards is less than 0.5%. Thus, the Cape Point methane measurements can be considered to be fully traced to the GAW reference standards.

6.3. Recommendation for the Measurement of Methane

The good result of the inter-comparison measurements show 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 the WCC.

7. Conclusions

The global GAW station Cape Point is a well-established site within the GAW programme, and long time series of high quality exist for ozone, carbon monoxide, methane and other parameters. An excellent platform for extensive atmospheric research is available with the laboratory facilities in the rebuilt station.

The results of the inter-comparisons for surface ozone, carbon monoxide and methane showed good agreement between EMPA-WCC and the station instruments for ozone and methane. The results of the CO inter-comparison improved since the last audit in 1998 for the relevant concentration range of 40 to 80 ppb. This was mainly because the CO scale was recently revised by CMDL, and both EMPA-WCC and the station now refer to this new scale. The differences that were found might be explained by the remaining uncertainty of the CMDL scale and/or non-linearity of the GC system in the higher concentration range (>80 ppb).

Due to the good audit results, only minor recommendations were made by EMPA-WCC concerning surface ozone, carbon monoxide and methane measurements.

Appendix

I Intercomparison of the Dasibi instruments with EMPA-WCC

There are two Dasibi instruments (Dasibi 1008PC and Dasibi 1008RS, see Table 2) at Cape Point that were also inter-compared against the WCC transfer standard. The Dasibi 1008PC gets its air from the 30m mast (PTFE tubing), whilst Dasibi 1008RS toggles between the 30 m and 4 m air intakes on a half-hourly basis. For both Dasibis MB-41 pumps push ambient air through the instruments, whose internal pumps are switched off. The main reason for this plumbing arrangement has been to reduce the residence time of the sampling air within the 30 m tubing. The data from the two Dasibis, which are “SPAN” adjusted against the TEI 49, are considered to be of secondary importance.

The monthly Dasibi data (30-min values) are adjusted to the TEI 49 data in the following way:

For each month, the 30-min O_3 data common to both the TEI 49 (primary instrument) and Dasibi 1008RS analysers are plotted against each other. By means of a “tuneable” SPAN factor as well as by an “adjustable” zero in an Excel worksheet, the Dasibi 1008RS data is aligned in such a way as to achieve the best straight-line fit. Should the monthly zero average (obtained from the daily wet external zeros) for Dasibi 1008RS contribute towards a misfit on the X-Y plot, they are changed until optimal correlation is achieved.

Once the Dasibi 1008RS data are adjusted to that of the TEI 49, the O_3 data common to both Dasibi 1008PC and Dasibi 1008RS (30m values) are then in turn tuned against Dasibi 1008RS now acting as the primary instrument.

The following zero offsets and span factors were applied for the audit period:

Dasibi 1008PC: Zero offset: -0.50 ppb, Span 1.16

Dasibi 1008RS: Zero offset: -1.35 ppb, Span 1.09

For the inter-comparison with the WCC transfer standard, the internal pumps of the Dasibi instruments were used. The original set-up of the station could not be used for the inter-comparison because of excessively high flow rates using the MB-41 pumps.

Tables 13 and 14 show the results of the inter-comparisons with the WCC transfer standard. Note that no zero comparisons could be made for the Dasibi 1008PC due to the inability of this instrument to produce negative output signals.

Table 13: Inter-comparison of the Dasibi 1008PC

	TEI 49C-PS		Dasibi 1008PC #4243			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	89.8	0.07	97.6	0.24	7.8	8.7%
2	29.9	0.08	32.0	0.50	2.2	7.2%
3	10.2	0.14	11.3	0.45	1.2	11.4%
4	49.8	0.09	54.3	0.46	4.4	8.9%
5	19.9	0.11	21.1	0.40	1.2	5.9%
6	9.8	0.10	11.6	0.59	1.8	18.4%
7	29.9	0.13	32.1	0.41	2.2	7.3%
8	20.0	0.11	22.0	0.61	2.0	9.8%
9	49.9	0.06	54.3	0.60	4.4	8.8%
10	89.9	0.10	97.5	0.39	7.6	8.5%
11	49.9	0.13	54.1	0.46	4.2	8.4%
12	30.0	0.07	32.1	0.62	2.1	7.2%
13	20.1	0.11	21.9	0.44	1.9	9.3%
14	9.8	0.11	10.9	0.57	1.1	11.3%
15	90.0	0.14	97.8	0.46	7.8	8.7%

Table 14: Inter-comparison of the Dasibi 1008PC

	TEI 49C-PS		Dasibi 1008RS #4840			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.2	0.07	-1.1	0.01	-1.4	
2	89.8	0.07	92.9	0.02	3.1	3.4%
3	29.9	0.08	30.4	0.28	0.5	1.6%
4	10.2	0.14	9.8	0.46	-0.4	-3.6%
5	49.8	0.09	51.2	0.23	1.4	2.8%
6	19.9	0.11	19.6	0.35	-0.3	-1.7%
7	0.2	0.12	-1.6	0.44	-1.8	
8	0.2	0.09	-1.2	0.16	-1.4	
9	9.8	0.10	9.4	0.10	-0.4	-4.0%
10	29.9	0.13	30.2	0.07	0.3	1.2%
11	20.0	0.11	19.5	0.36	-0.5	-2.7%
12	49.9	0.06	51.1	0.42	1.3	2.5%
13	89.9	0.10	92.9	0.11	3.1	3.4%
14	0.2	0.08	-1.7	0.38	-1.9	
15	0.2	0.08	-1.5	0.38	-1.7	
16	49.9	0.13	51.0	0.20	1.0	2.0%
17	30.0	0.07	30.3	0.38	0.3	1.0%
18	20.1	0.11	19.9	0.38	-0.2	-1.0%
19	9.8	0.11	9.4	0.02	-0.4	-3.7%
20	90.0	0.14	93.0	0.29	3.1	3.4%
21	0.2	0.09	-1.2	0.41	-1.4	

The following relations between the two Dasibis and the WCC transfer standards were observed:

Dasibi 1008PC:

Dasibi 1008PC = 1.083 x TEI 49C-PS + 0.11 ppb

Dasibi 1008PC = O3 mixing ratio in ppb, determined with Dasibi 1008PC #4243

TEI 49C-PS = O_3 mixing ratio in ppb, determined with TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.004	(f = 13) f = degree of freedom
	- offset S_b in ppb	0.17	(f = 13)
	- residuals in ppb	0.13	(n = 15)

Dasibi 1008RS:

Dasibi 1008RS = 1.051 x TEI 49C-PS – 1.33 ppb

Dasibi 1008PC = O3 mixing ratio in ppb, determined with Dasibi 1008RS #4840

TEI 49C-PS = O_3 mixing ratio in ppb, determined with TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.002	(f = 19) f = degree of freedom
	- offset S_b in ppb	0.09	(f = 19)
	- residuals in ppb	0.24	(n = 21)

Comment

The two Dasibis deviate significantly from the EMPA-WCC transfer instrument. Part of this might be explained by ozone loss over the pumps. Since data of the Dasibi instrument are “adjusted” to the values of the TEI 49 instrument, they can not be regarded as independent measurements.

In the present configuration, the use of the two Dasibis makes sense for quality control purposes only. Data of these instruments should not be used for scientific purposes.

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 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 14. 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.

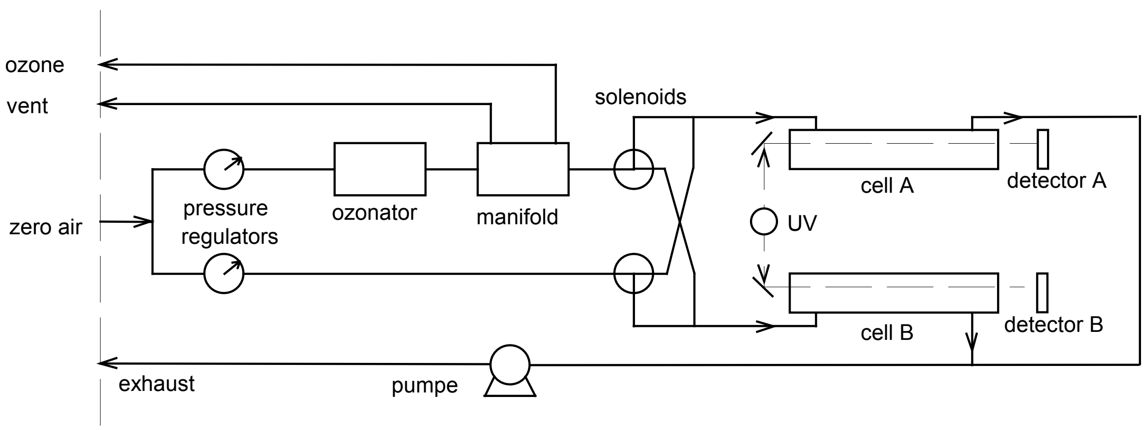


Figure 14: Flow schematic of TEI 49C-PS

III 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 summarised in Table 15 and Figure 15.

Table 15: 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 / 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:	Pressurised air - zero air generator (CO catalyst, Purafil, charcoal)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

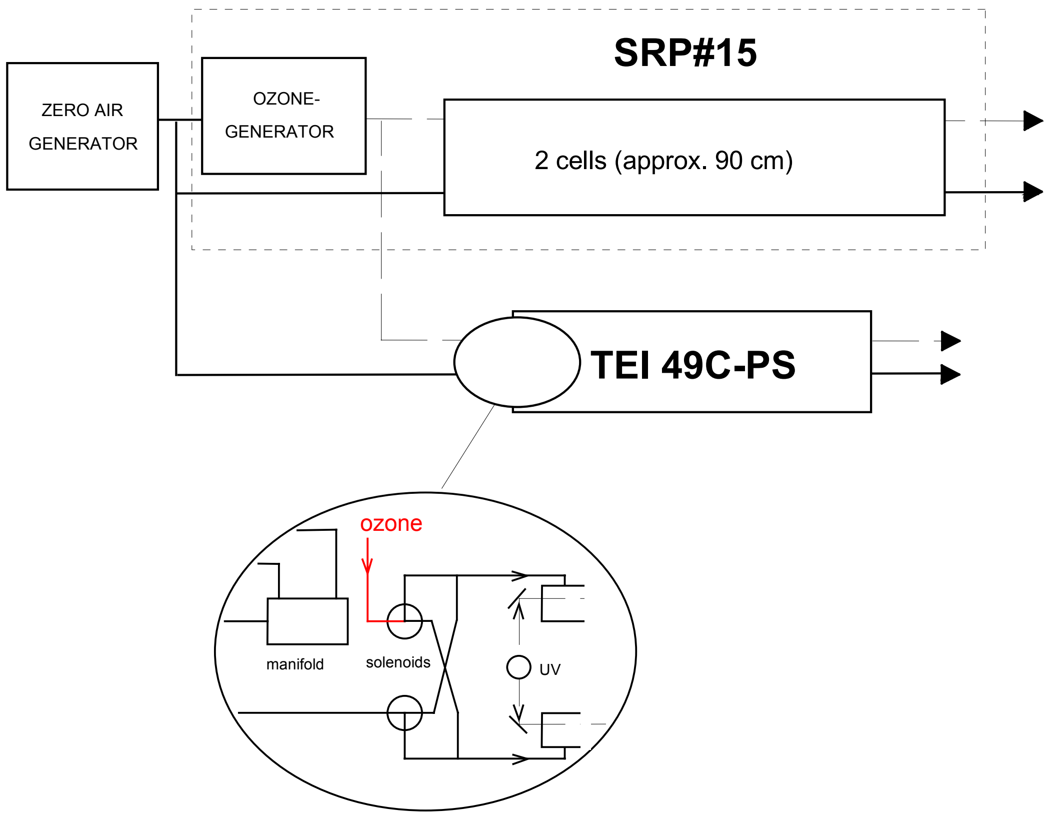


Figure 15: Instruments set up SRP -TEI 49C-PS

The stability of the transfer standard was 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. The results show that the EMPA transfer standard fulfilled the recommended criteria for the period of the audit, including transportation.

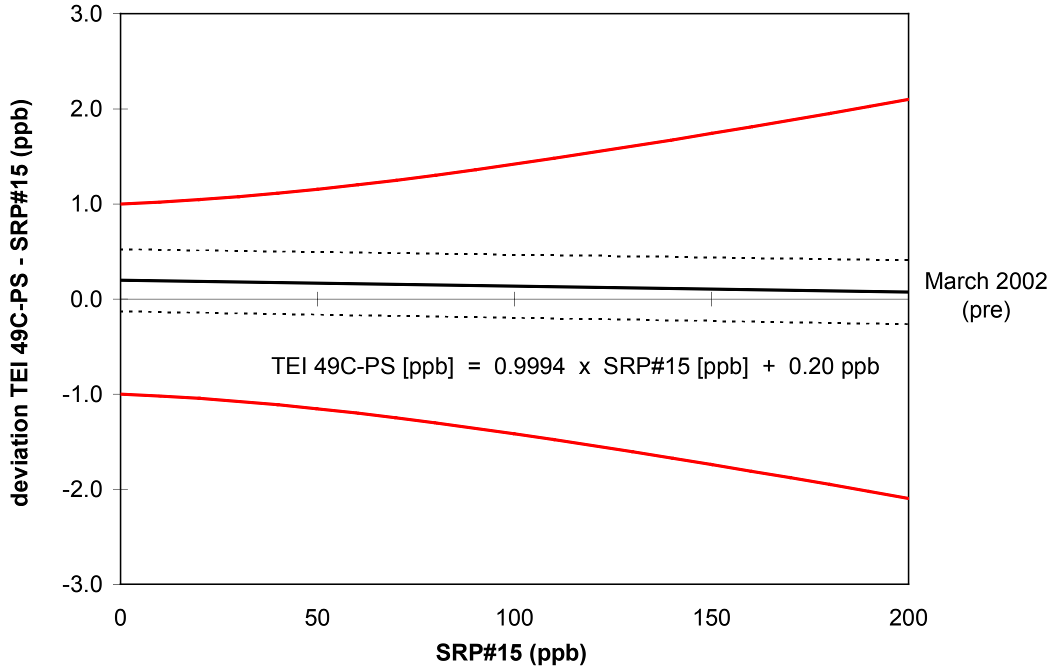


Figure 16: Transfer standard before audit

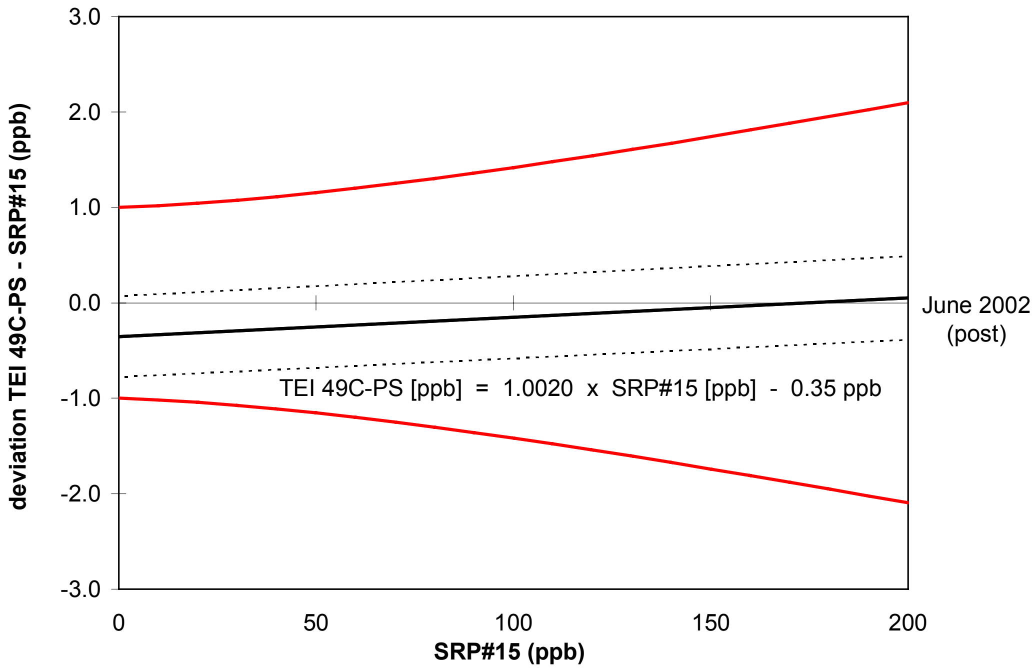


Figure 17: Transfer standard after audit

IV 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 programme. The standards used at the WCC are listed in Table 16:

The CO scale of the CMDL was recently revised. EMPA-WCC refers to the **new** scale. The EMPA-WCC transfer standards used during the audit are listed in Table 17.

Table 16: 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 (")	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

Table 17: CO transfer standards of the WCC (average of calibrations from March 02 and July 02). The error represents the measured standard deviation.

Transfer Standard (Gas Cylinders)	CO (calibrated against CMDL new scale CA02859) with AL5001		Cylinder
	before audit	after audit	
WCC Transfer Standard (2 l cylinder)	38.2 ± 1.1 ppb	N/A	020320-2
WCC Transfer Standard (2 l cylinder)	43.6 ± 0.8 ppb	43.4 ± 0.8 ppb	020322-1
WCC Transfer Standard (2 l cylinder)	53.2 ± 1.2 ppb	53.2 ± 0.9 ppb	020325-1
WCC Transfer Standard (6 l cylinder)	72.0 ± 1.2 ppb	71.1 ± 0.7 ppb	FF31496
WCC Transfer Standard (2 l cylinder)	75.7 ± 1.0 ppb	75.0 ± 0.9 ppb	020325-2
WCC Transfer Standard (2 l cylinder)	99.9 ± 1.2 ppb	98.4 ± 0.6 ppb	001201-9
WCC Transfer Standard (6 l cylinder)	110.0 ± 1.2 ppb	109.5 ± 0.7 ppb	FA01469
WCC Transfer Standard (6 l cylinder)	160.1 ± 1.0 ppb	159.5 ± 0.7 ppb	FF30491

V 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 programme. The CMDL standards used at the WCC are listed in Table 18. The EMPA-WCC transfer standards (Table 19) are traced back to the CMDL standards shown below.

Table 18: CMDL CH_4 Standards at the WCC. 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)	1795.1 ± 0.19 ppb	CA04462
CMDL Laboratory Standard (")	1882.0 ± 0.24 ppb	CA04580

* Certificates from 13.09.2000

Table 19: WCC CH_4 transfer standards (average of calibrations from March 02 and June 02). The error represents the 95% confidence interval.

Transfer Standard (Gas Cylinders)	CH_4 (calibrated against CMDL standards CA04462 and CA04580)		Cylinder
	before audit	after audit	
WCC Transfer Standard (6 l cylinder)	1550.7 ± 5.4 ppb	1551.3 ± 9.1 ppb	FA01469
WCC Transfer Standard (2 l cylinder)	1693.5 ± 7.4 ppb	1690.7 ± 9.5 ppb	020322-1
WCC Transfer Standard (2 l cylinder)	1720.9 ± 6.8 ppb	1719.2 ± 8.5 ppb	020325-1
WCC Transfer Standard (2 l cylinder)	1728.4 ± 6.7 ppb	1723.0 ± 5.8 ppb	020325-2
WCC Transfer Standard (6 l cylinder)	1817.9 ± 6.2 ppb	1816.4 ± 6.0 ppb	FF31496
WCC Transfer Standard (6 l cylinder)	1822.1 ± 9.2 ppb	1821.3 ± 6.2 ppb	FF30491
WCC Transfer Standard (2 l cylinder)	1853.8 ± 3.2 ppb	N/A	020320-2
WCC Transfer Standard (2 l cylinder)	2013.2 ± 7.4 ppb	2005.3 ± 6.2 ppb	001201-9