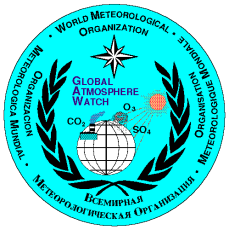

Global Atmosphere Watch
World Calibration Centre for Surface Ozone
Carbon Monoxide and Methane

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

EMPA-WCC REPORT 02/1

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE

GLOBAL GAW STATION MT. KENYA

FEBRUARY 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

1. Abstract

A system and performance audit was conducted at the Global Atmosphere Watch station Mt. Kenya from 29. January to 11 February 2002 by the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide and Methane. Additionally, a performance audit of the ozone calibrator used for ozone sounds checks at the Kenya Meteorological Department (KMD) was performed. The results can be summarised as follows:

System Audit of the Observatory

The Mt. Kenya research station offers laboratory and office facilities. The infrastructure supports the measurements of the atmospheric composition as well as measurements of physical and meteorological parameters. To date the main problems have been an unstable power supply and infrequent station visits. The power line to the station was operational by the end of the audit. Station staff is scheduled to move from Nairobi to Nanyuki by March 2002.

Audit of the Surface Ozone Measurement

The inter-comparison, consisting of three multipoint runs between the WCC transfer standard and the 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).

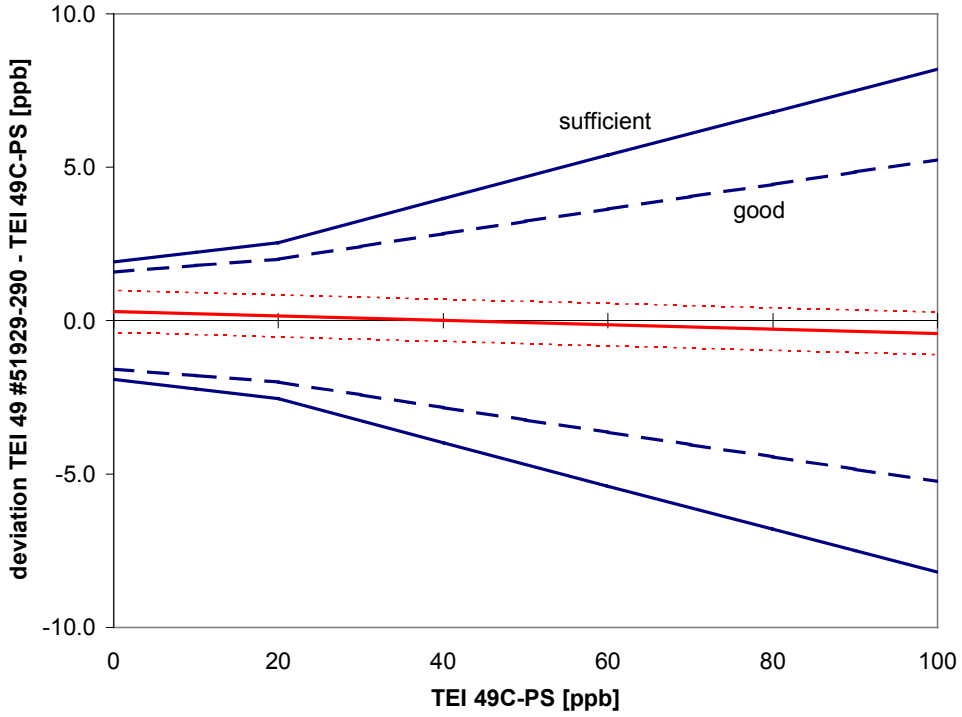

Figure 1: Intercomparison of the TEI 49-003 #51959-290 field instrument with the WCC transfer standard

In addition, an inter-comparison of the EMPA-WCC transfer standard with the ozone calibrator used for the check of ozone sounds at KMD was performed. The results confirmed the inter-comparison carried out by EMPA-WCC in January 2000, and also fulfils the assessment criteria as good.

Implementation of Carbon Monoxide Measurements

A carbon monoxide instrument (TEI 48C) including calibration facilities was installed by EMPA-WCC during the audit as part of WMO/GEF project No. 340-99 (GLO/91/G32) 1115-99. The operators were intensively trained on the new instrument, and first CO data is available from the Mt. Kenya GAW station.

Further activities of EMPA-WCC

The data acquisition and transmission system (MILOS/DCP) and the aethalometer were also checked during the audit. The communication of the DCP with the satellite was not operational. The DCP unit was taken to Nairobi for repair. Checks of the aethalometer indicated that the instrument is working. However, the pump needs to be replaced.

Conclusions and Recommendations

The global GAW station Mt. Kenya was operational concerning ozone measurements as well as for the meteorological parameters by the end of the audit by EMPA-WCC. In addition, instrumentation for continuous carbon monoxide measurements was implemented during the audit by EMPA-WCC.

The geographical position of the Mt. Kenya station within the GAW programme is regarded as important, since ground based measurements of air pollutants from equatorial regions are very limited. Furthermore, the station offers excellent infrastructure concerning laboratory facilities. To take advantage of this, national and international co-operation for both technical and scientific staff (workshops, exchange programs, scientific partnerships) is regarded as important.

Several recommendations were made by EMPA-WCC concerning not only ozone measurements but the general operation of the station. The main recommendations are summarised below:

- The station should be visited on regular intervals, e.g. weekly.
- The situation concerning the power line should be checked daily, and measures should be taken in case of a power outage.
- The UPS unit available at the site should be installed as soon as possible.
- Persistent problems with any of the measurements at Mt. Kenya should be communicated to external partners and WMO. Communication should be re-established where necessary and maintained to ensure continuing support of external partners. E-mail and internet access should be re-established for all persons involved in the GAW activities. This is also of highest priority at the new location in Nanyuki.
- A budget, for example in accordance to the GAW measurement guide, should be available for the long-term operation and maintenance of the station. Part of the budget should be at the immediate disposal of the station manager.
- The road up to Old Moses Camp was in fairly good condition during the audit. However road maintenance is regarded as important to ensure the accessibility of the station.

Dübendorf, 12. July 2002 EMPA Dübendorf, WCC

Project scientist Project manager

Dr. C. Zellweger Dr. B. Buchmann

2. Introduction

The **Global GAW Station Mt. Kenya** is part of Kenya's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) programme. The observatory was established within the framework of UNDP's Global Environment Facility (GEF) and is designated for long-term measurements of several chemical compounds and physical and meteorological parameters in the lower troposphere. The station has started its operation in June 2001 with a reduced measurement programme and was officially opened in December 1999. The leading office is the Kenya Meteorological Department (KMD).

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 of the Mt. Kenya station, Wilson Kimani from the Kenya Meteorological Department, a **system and performance audit** for surface ozone was conducted at the station by EMPA-WCC from 1. to 8. February 2002.

The scope of the audit was the whole measurement system in general and surface ozone measurements in particular. The entire system from the 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 were 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).

In addition, the ozone calibrator used for the checks of the ozone sounds at KMD was traced back to the designated standard for ozone within the GAW programme during the visit of EMPA-WCC.

Furthermore, EMPA-WCC installed a carbon monoxide instrumentation based on a TEI 48C analyser as part of the GEF project No 340-99 (GLO/91/G32) 1115-99. The operators were trained on the new instrument during the audit.

The present audit report is distributed to the Director of the KMD, the station manager, the Institut für Atmosphärische Umweltforschung (IFU) in Garmisch-Partenkirchen, the Swiss Meteorological Institute (SMI) in Payerne and the World Meteorological Organization in Geneva.

Staff involved in the audit

KMD / station	Mr Wilson Kimani	Meteorologist, contacts, general program, organisation
	Mr Josiah Kariuki	Meteorologist, technical assistance at station and KMD
	Mr John Aseyo	Technician, technical assistance at station and KMD
	Mr John Rotich	Meteorologist, technical assistance at station and KMD
	Mr Dominic Mutungi	Technician, technical assistance at station and KMD
EMPA-WCC	Dr. Christoph Zellweger	lead auditor
EMPA-QA/SAC	Dr. Jörg Klausen	assistant auditor

Previous audits at the GAW station Mt. Kenya:

- January 2000: System audit for surface ozone by EMPA-WCC.

3. Global GAW Site Mt. Kenya

3.1. Description of the Site

The global GAW station Mt. Kenya is located on the north-western side of Mount Kenya within the Mt. Kenya national park (Figure 2) (GPS coordinates: 00° 03' 40" S – 37° 17' 50" E) at an altitude of approximately 3650 m above sea level (a.s.l.). The closest town is Nanyuki with a population of approx. 30000 inhabitants. The surrounding terrain of the station is gently sloping shrub with several smaller streams nearby. The station itself is exposed in all directions on a 10 m high rock outcrop. Access to the site requires a one hour drive from Nanyuki by a 4WD vehicle up to "Old Moses" camp at 3300 m a.s.l. and a 30 to 40 minutes uphill walk. The national park is entered at the Sirimon Gate following a steep unpaved road, which is closed to public traffic. The road is in fairly good condition, but road maintenance is of crucial importance to keep the station accessible also during the wet season.

About 10% of the meteorological data is available for the period between 20.12.99 and 3.03.02. For this period the following averages were observed: Temperature 6.5°C (range 2.2 – 13.8), rel. humidity 73% (9 – 100), wind speed 7.9 m/s (0 – 45.2).

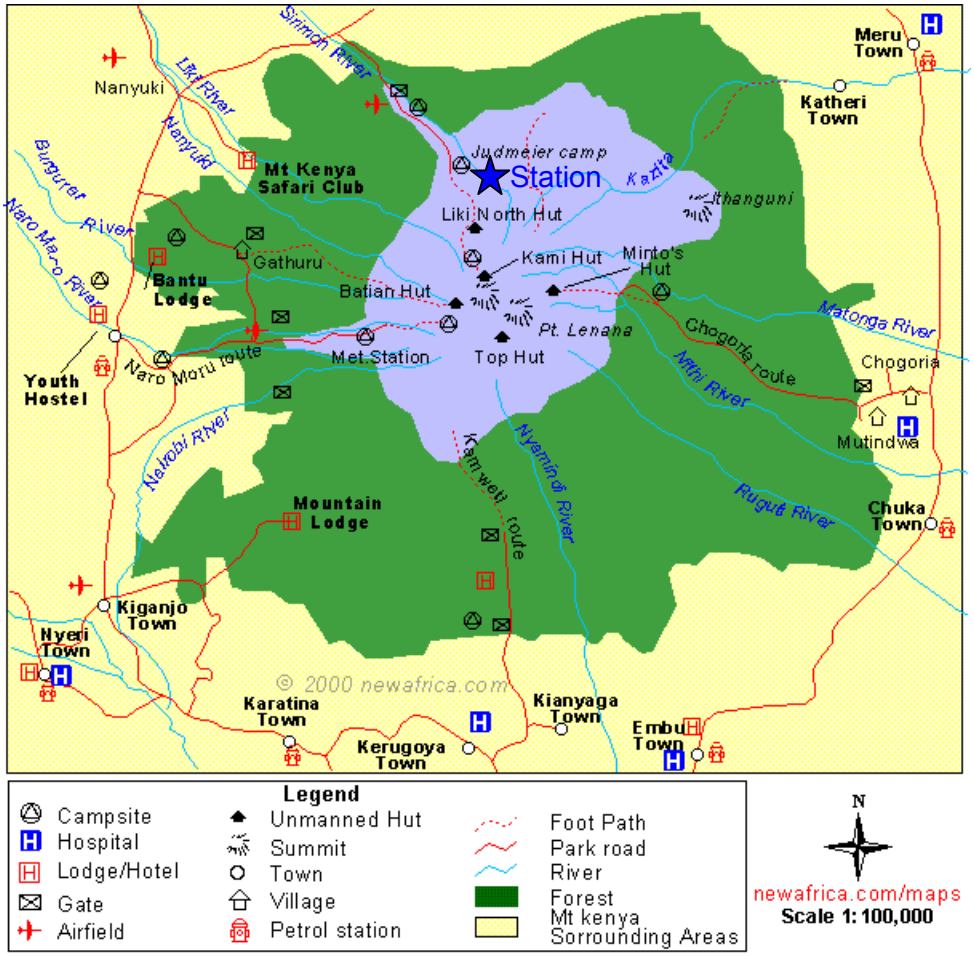

Figure 2: Map of Mt. Kenya National Park (from www.newafrica.com/maps)

Ozone and Carbon Monoxide Level at Mt. Kenya

Since the station became fully operational only recently, very little ozone data is available. The frequency distribution for 10-minute averages of all available ozone data between 20.12.1999 and 3.03.2002 is shown in Figure 3. Note that only 8 % of the data was collected during this period. The presented frequency distribution therefore can not account for seasonal variation, and more data will be necessary to fully characterise the Mt. Kenya ozone level.

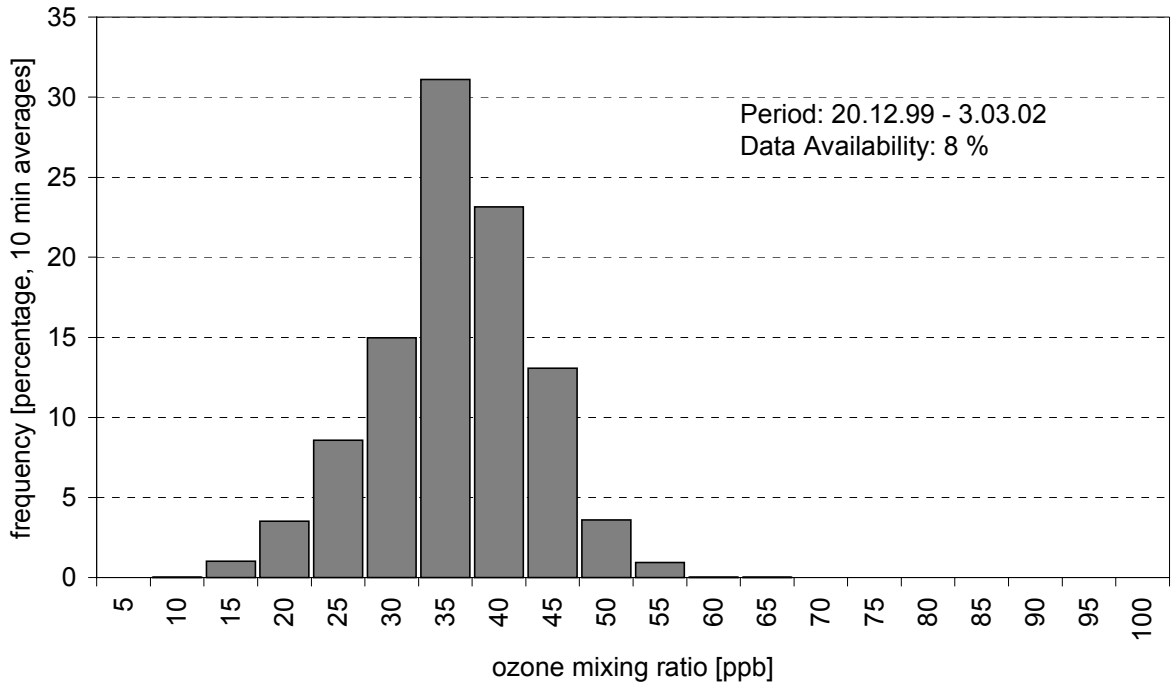

Figure 3: Frequency distribution of the ozone mixing ratio at Mt. Kenya for the period between 20.12.99 to 3.03.02. Availability of data: 8%.

The carbon monoxide instrument was installed during the audit of EMPA-WCC, and data collection started in February 2002. Therefore no frequency distributions can be shown for this parameter yet.

3.2. Description of the Station

The facilities at the site (Figure 4 and 5) consist of two 2.5 m x 6 m steel containers attached to each other, which provide space for an office and measurement racks. The air inlet and several radiation and meteorological instruments are mounted on the flat roof of the laboratory (walk on).

Comment

- The facilities at Mt. Kenya support the measurements of atmospheric parameters.

Figure 4: View of Mt. Kenya Station with Mt. Kenya in the Background

Figure 5: Inside the laboratory at the Mt. Kenya station

3.3. Staff / Operators

The staff responsible for the Mt. Kenya GAW station moved from Nairobi to Nanyuki in March 2002. The responsible staff at Nanyuki is listed in Table 1. Furthermore, a four-wheel drive vehicle (Landrover Defender) with a driver is located in Nanyuki for station access.

Table 1: Staff responsible for the GAW site Mt. Kenya at Nanyuki (March 2002)

Name	**Position and duty**
Wilson Kimani	Station manager, Meteorologist
Joshia Kariuki	Station operator, Meteorologist
John Aseyo	Station operator, Technician

4. System- and Performance Audit for Surface Ozone

Ozone measurements started at the Mt. Kenya station in late 1999. However, only very few data is available due to long periods with power outages. The situation improved in June 2001, but the station was not accessible for the station operators within a day or two. This resulted in further data loss.

At the time of the audit the power was off first, but the problem could be solved during the audit by the Kenya Power Company (KPLC). However, the inter-comparison of the ozone instruments could only be made using the station generator (Honda EB3000S). As a consequence, only a two hour warm-up period of the instruments was possible. However, this relatively short warm-up period is not expected to have an influence on the inter-comparison results.

Recommendations concerning ozone measurements are summarised in section 4.4. General, parameter independent recommendations can be found in section 6.

4.1. Monitoring Set-up and Procedures

4.1.1. Air Inlet System

Sampling-location: The air inlet is mounted on top of the flat roof, approx. 1.7 m above the cabin and 4.5 m above the ground.

Sample inlet:

- Rain protection: The Inlet is protected against rain and snow by an upside-down aluminum beaker.
- Inlet-filter: Teflon inlet filter before analyser, to be exchanged approx. every 3 months.

Sampling-line:

- Inlet / Mainfold
- Dimensions: length = ca. 3 m, i.d. = 5 cm
- Material: glass
- Sample line
- Dimensions: length = ca. 1.5 m, i.d. = 4 mm

Flow rate: inlet / manifold: High volume pump, flow rate unknown
sample line: 2 l/min

Residence time in the sampling line: estimated to be < 10 s

Comment

The tubing 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. However, the inlet filter was never exchanged because no spare filters were available. EMPA-WCC left 50 teflon filters at the site, and an exchange interval every 3 months or depending on the pollution level was agreed on.

4.1.2. Instrumentation

Ozone Analyser

The monitoring system at the global GAW station Mt. Kenya consists of an ozone analyser with an internal ozone generator, plus an external zero air unit consisting of a pump and a charcoal

cartridge. The ozone instrument is installed in a 19" rack in a 6m x 2.5m cabin unit. The room has no air conditioning. Temperatures dropping below 10°C during the night and rising up to 20°C during daytime can be expected. The instruments are not exposed to direct sunlight. Instrumental details for the ozone analyser are summarised in Table 2.

Table 2: Ozone analyser at the Mt. Kenya Research Station

Type	TEI 49-003 #51959-290
Method	UV absorption at 254 nm
at Mt. Kenya	since December 1999
Range	0-1000 ppb
Analog output	0-10 V
Settings	Span: 509; Offset: 49
Instrument specials	Internal ozone generator

Ozone Calibrator

No ozone calibrator is available at the site. A calibrator model 49 PS from Thermo Environmental Instruments Inc. is available at KMD in Nairobi and is mainly used to check the ozone sounds. Instrumental details can be found in the EMPA-WCC audit report 00/1. The instrument was also compared with the WCC transfer standard during this audit, and the results are summarised in section 4.3.

Operation and Maintenance

Checklists were developed during the last audit by EMPA-WCC in February 2000. They include all necessary information for instrument checks and maintenance. Due to infrequent station visits and power outages, these checklists were not completed regularly. However, all activities were noted in a station log book. It was agreed with the station operators that the checklists provided during the first audit should be completed during the planned weekly station visits.

Zero and span checks are performed automatically with the internal span/zero check.

4.1.3. Data Handling

Data Acquisition and –transfer

The ozone analyser is connected to the MILOS 500 data acquisition system. One minute averages are stored together with meteorological data. The logger has a capacity for two weeks data storage. The transmission of the data via the DCP to EUMESAT was not working during the audit. The DCP unit was taken to IfU for servicing. As a consequence, the station must be visited at least every two weeks to avoid data loss.

Data Treatment

To date only few data were collected. Data treatment includes consistency checks with time series plots.

Data Submission

Surface ozone data is not yet reported to the GAW World Data Centre for Surface Ozone (WDCSO) at NILU.

4.1.4. Documentation

Logbooks

A logbooks is available for the ozone instrument. The notes are up to date and describe all important events. Furthermore, a log book for the general operation of the station is available.

Standard Operation Procedures (SOPs)

The manual for the instrument is available at the site. The checklists provided by EMPA-WCC during the audit of 2000 are also available.

Comment

The station was visited infrequently over the past two years. This situation should improve once the station staff has settled in Nanyuki.

4.2. Inter-comparison of ozone analyser at Mt. Kenya

4.2.1. Experimental set-up

The WCC transfer standard TEI 49C PS (details see Appendix I-II) was operated in stand-by mode for warming up for 2 hours. This rather short warm-up period was chosen because at the inter-comparison had to be performed relying on the station generator. During the stabilisation time the transfer standard and the PFA tubing connections to the instrument were conditioned with 300 ppb ozone for 30 minutes. Afterwards, three comparison runs between the field instrument and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 6 the experimental set up during the audit. No modifications of the ozone analysers which could influence the measurements were made for the inter-comparisons.

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 II.

Table 3: Experimental details of the ozone inter-comparison

reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instrument:	TEI 49-003 #51959-290
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): 669.2 hPa TEI 49-003 (Mt. Kenya): 670 hPa no adjustments were made for the inter-comparison.
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 on 3. February 2002
connection between instruments:	approx. 1.5 meter of 1/4" PFA tubing

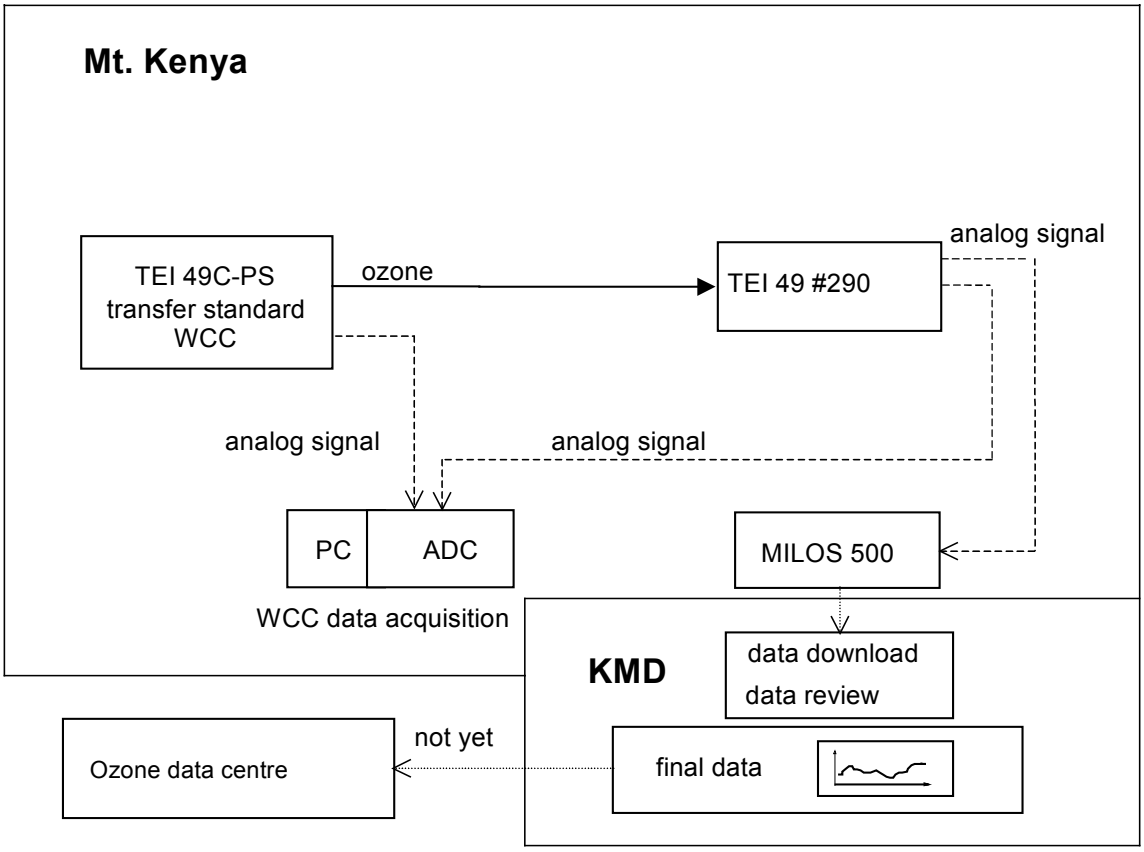

Figure 6: Experimental set up for the ozone inter-comparison

4.2.2. Results

The results comprise the inter-comparison between the TEI 49-003 field instrument and the WCC transfer standard TEI 49C-PS, carried out on 3 February 2002.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 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 7 and 8 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 7 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 8 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 9).

Table 4: Inter-comparison of the ozone field instrument

run index	TEI 49C-PS		TEI 49-003 #51959-290			
	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	-0.1	0.1	0.5	0.3	0.6	
2	15.0	0.1	15.5	0.4	0.5	3.1%
3	35.2	0.1	35.0	0.4	-0.2	-0.6%
4	75.2	0.2	75.0	0.5	-0.2	-0.3%
5	90.2	0.1	90.4	0.4	0.2	0.2%
6	55.2	0.1	54.9	0.6	-0.3	-0.5%
7	0.0	0.2	0.2	0.6	0.2	
8	0.1	0.1	0.0	0.5	-0.1	
9	90.5	0.1	90.1	0.5	-0.3	-0.4%
10	75.2	0.1	74.9	0.5	-0.3	-0.3%
11	35.4	0.1	34.8	0.5	-0.6	-1.8%
12	55.2	0.1	55.1	0.5	-0.1	-0.2%
13	15.4	0.2	15.4	0.8	0.0	0.3%
14	0.0	0.1	1.0	0.5	1.0	
15	0.0	0.1	0.8	0.7	0.7	
16	75.2	0.2	74.9	0.5	-0.4	-0.5%
17	55.0	0.2	55.0	0.9	0.0	0.0%
18	35.3	0.2	35.0	0.5	-0.3	-0.7%
19	15.3	0.2	15.3	0.4	-0.1	-0.4%
20	90.1	0.1	89.9	0.9	-0.3	-0.3%
21	-0.1	0.2	0.2	0.3	0.3	

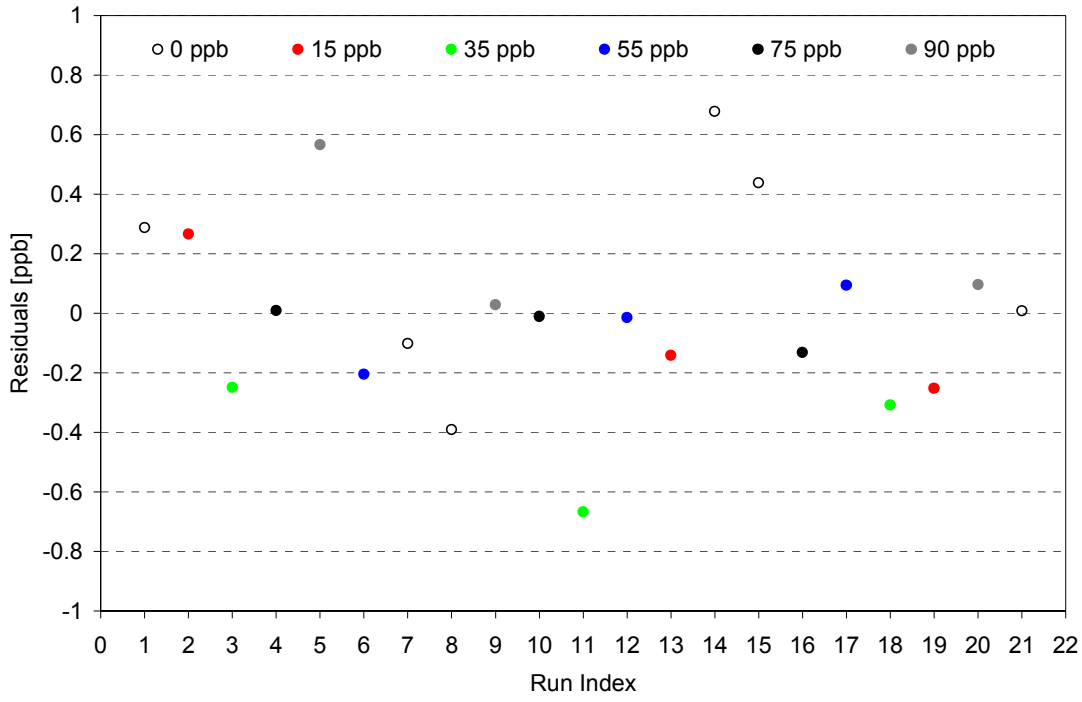

Figure 7: Residuals to the linear regression function (TEI 49-003 #290) vs the run index (time dependence)

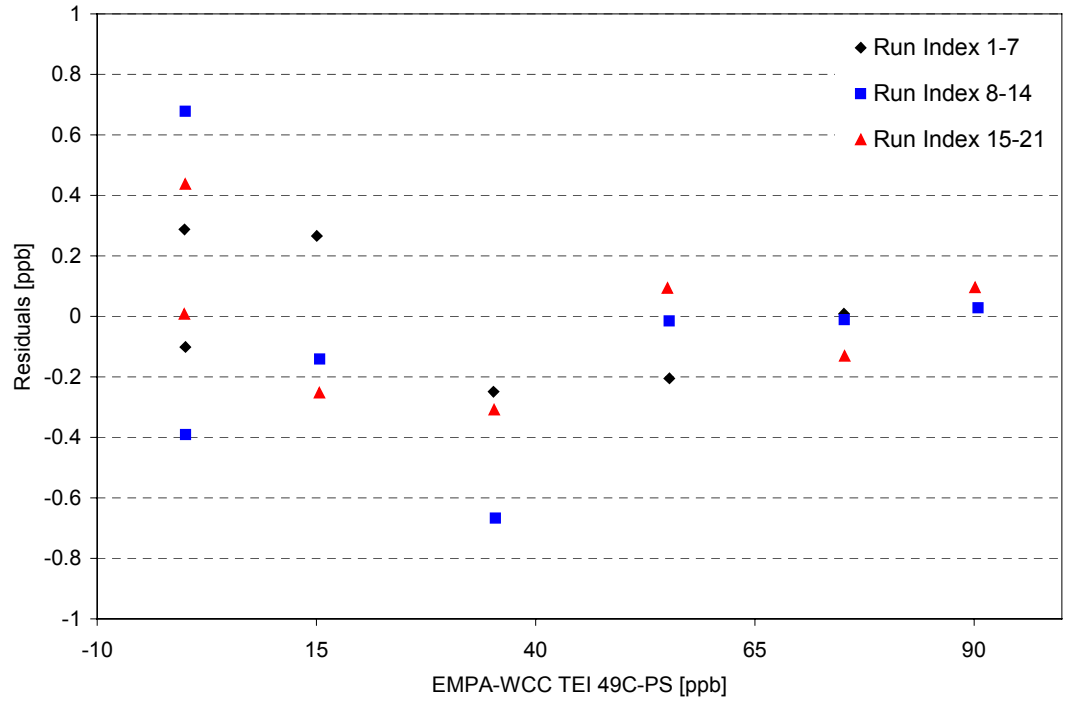

Figure 8: Residuals to the linear regression function (TEI 49-003 #290) vs the concentration of the WCC transfer standard (concentration dependence)

From the inter-comparisons of the TEI 49-003 #290 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 49-003 #290:

$$\text{TEI 49-003} = 0.993 \times \text{TEI 49C-PS} + 0.3 \text{ ppb}$$

TEI 49-003 = O_3 mixing ratio in ppb, determined with TEI 49-003 #51959-290

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	0.11	(f = 19)
	- residuals in ppb	0.28	(n = 21)

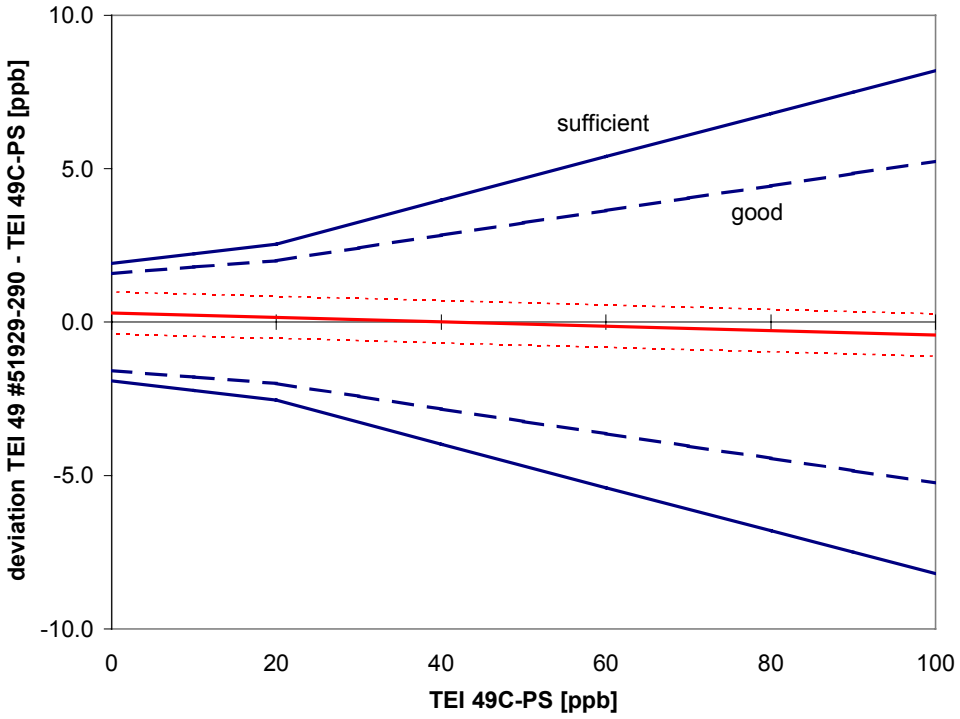

Figure 9: Inter-comparison of instrument TEI 49-003 #51959-290

Comment

The instrument fulfils the assessment criteria of “good” over the tested range between 0 and 100 ppb ozone.

4.3. Inter-comparison of ozone calibrator at KMD

An inter-comparison of the ozone calibrator at the KMD was also performed during the audit.
The WCC transfer standard TEI 49C PS (details see Appendix I-II) was operated in stand-by mode for warming up for 21 hours. During the stabilisation time the transfer standard and the PFA tubing connections to the instrument were conditioned with 300 ppb ozone for 30 minutes. Afterwards, three comparison runs between the calibrator and the WCC transfer standard were

performed. Experimental details are shown in Table 5. No modifications of the ozone calibrator which could influence the measurements were made for the inter-comparisons.

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 II.

Table 5: Experimental details of the ozone inter-comparison

reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instrument:	TEI 49PS #53677-297, Gain 6
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): 824 hPa TEI 49PS (KMD): 824 hPa no adjustments were made for the inter-comparison.
concentration range	0 - 250 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	50 / 100 / 150 / 200 / 245 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 x on 30 January 2002
connection between instruments:	approx. 1.5 meter of 1/4" PFA tubing

4.3.1. Results

The results comprise the inter-comparison between the TEI 49PS field instrument and the WCC transfer standard TEI 49C-PS, carried out on January 30, 2002.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 30-second-means are presented in Table 6. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Figures 10 and 11 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 10 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 11 (concentration dependence).

Table 6: Inter-comparison of the ozone calibrator at KMD

run index	TEI 49C-PS		TEI 49PS #53677-297			
	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.1	0.1	0.3	0.4	0.2	
2	99.8	0.1	98.5	0.3	-1.3	-1.3%
3	149.9	0.1	148.6	0.3	-1.3	-0.9%
4	250.0	0.2	247.7	0.2	-2.3	-0.9%
5	50.3	0.1	49.4	0.3	-1.0	-1.9%
6	199.9	0.4	197.8	0.3	-2.1	-1.1%
7	0.0	0.2	-0.2	0.5	-0.2	
8	0.0	0.1	-0.1	0.4	-0.1	
9	244.9	0.1	242.6	0.4	-2.3	-0.9%
10	149.9	0.1	148.7	0.2	-1.2	-0.8%
11	50.0	0.1	49.4	0.3	-0.6	-1.2%
12	199.9	0.1	197.9	0.2	-2.0	-1.0%
13	100.0	0.1	98.7	0.2	-1.3	-1.3%
14	0.0	0.1	-0.1	0.3	-0.2	
15	0.0	0.1	-0.3	0.2	-0.2	
16	99.9	0.1	98.7	0.3	-1.2	-1.2%
17	149.9	0.1	148.6	0.3	-1.4	-0.9%
18	50.0	0.1	49.2	0.3	-0.8	-1.6%
19	200.0	0.1	197.6	0.2	-2.3	-1.2%
20	245.0	0.1	242.0	0.3	-3.0	-1.2%
21	-0.1	0.1	-0.4	0.2	-0.4	

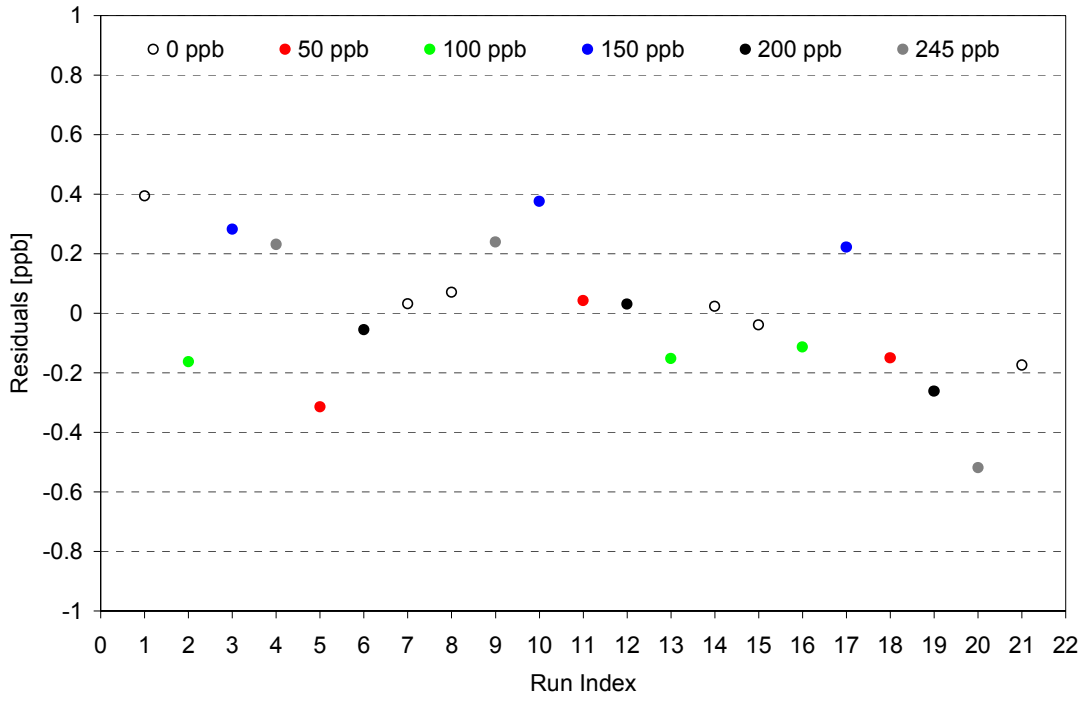

Figure 10: Residuals to the linear regression function (TEI 49PS #297) vs the run index (time dependence)

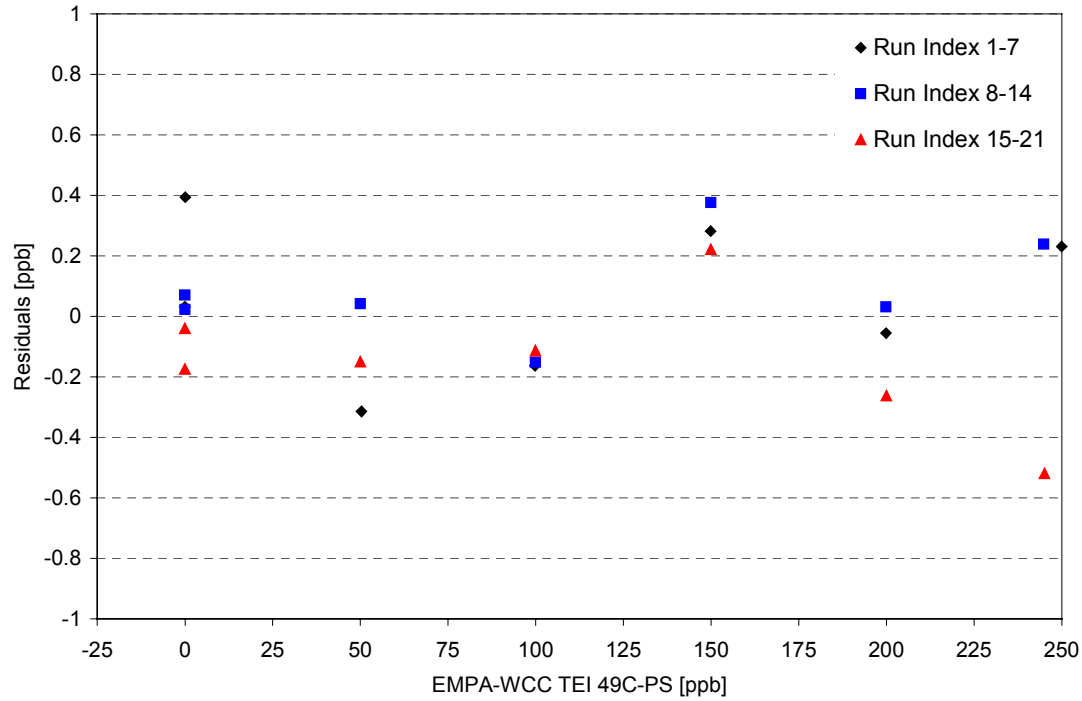

Figure 11: Residuals to the linear regression function (TEI 49-PC #297) vs the concentration of the WCC transfer standard (concentration dependence)

From the inter-comparisons of the TEI 49PS #297 field instrument with the TEI 49C-PS transfer standard from EMPA, the resulting linear regression (for the range of 0-250 ppb ozone) is:

TEI 49PS #297:

$$\text{TEI 49PS} = 0.991 \times \text{TEI 49C-PS} - 0.2 \text{ ppb}$$

TEI 49PS = O_3 mixing ratio in ppb, determined with TEI 49PS #53677-297

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	0.08	(f = 19)
	- residuals in ppb	0.19	(n = 21)

Comment

The inter-comparison confirmed the results of the previous audit by EMPA-WCC in January 2000, and the instrument is in a good condition.

4.4. Recommendation for the Ozone Measurements

The TEI 49-003 ozone instrument at the Mt. Kenya station is in a good condition and fulfilled the assessment criteria as "good" over the tested range of 0 to 100 ppb. However, it was noticed during the audit that the instrument is sensitive to an unstable power supply.

The following recommendations are made by EMPA-WCC concerning the ozone measurements. Refer also to section 6 for general recommendations suggested by EMPA-WCC.

- The UPS available at the station (Powerware PW9150) should be installed to guard the instruments from high voltage peaks. This is of highest priority.
- Since the DCP is not working at the moment, the station should be visited at least every two weeks to avoid data loss.
- The weekly checklists should be completed by the responsible person for the ozone measurements.
- Data should be checked weekly for plausibility using time series plots.
- Regular back-ups of the measurement data are strongly encouraged.
- It was agreed data should be submitted to EMPA-WCC.
- Submission of the data to the GAW World Data Centre for Surface Ozone (WDCSO) at NILU is recommended as soon as longer time series will become available. QA/SAC Switzerland is ready to offer assistance as needed.

5. Carbon Monoxide Measurements at Mt. Kenya

As part of the WMO/GEF program No. 340-99 (GLO/91/G32) 1115-99 and a proposal by EMPA-WCC to WMO from 15. November 1999, a measurement system for carbon monoxide was installed by EMPA-WCC during the audit. The installation of the system was carried out in close collaboration with the station staff and included an intensive training on the new instrument. The instrument set-up is described below.

5.1. Monitoring Set-up and Procedures

5.1.1. Air Inlet System

Sampling-location:

The same air inlet system (inlet, manifold) as for the ozone measurements is used. The instrument is connected to the manifold with approx. 1.5 m teflon tubing, and the residence time is estimated to be less than 10 s.

5.1.2. Instrumentation

CO Instrument

The CO monitoring system at the global GAW station Mt. Kenya consists of a commercially available NDIR CO monitor that was modified with a drying system to remove all water vapor in the sample air. Details of the instrument are shown in Table 7.

The following tests were performed at the EMPA-WCC laboratory before installation:

- CO loss in the drying system
- Zero drift
- Multipoint calibration and linearity check for the range 0 to 1500 ppb CO
- Interference of humidity with and without drying system
- Inter-comparison measurements with a different measurement technique (AL5001, VUV Fluorescence)

The results of the above tests showed that the instrumentation and the set-up is suitable for carbon monoxide measurements at remote sites.

Table 7: CO Instrument at Mt. Kenya

	CO Instrument
type	TEI 48C Trace Level #66838-352
method	NDIR, Gas Filter Correlation Technique
modification	nafion drier PERMAPURE PD-50-24'' reflux mode using critical orifice and pump of instrument
at Mt. Kenya	since February 2002, installed by EMPA-WCC
range	0-1000 ppb
settings	CO COEFF: 1.115; BKG: frequent calibrations
analog output	0-1 V
serial output	RS 232

Calibration Equipment

The calibration equipment used for zero / span checks and calibrations is listed in Table 8.

Table 8: CO calibration equipment at Mt. Kenya

Standard gas for direct calibrations	1060 ppb CO ± 2%, 3845H (CO 99.997% in synth. air 99.9995%) traced back to NIST at EMPA-WCC
Standard gas for span checks (dilution)	15000 ppb CO ± 2%, 6395E (CO 99.997% in synth. air 99.9995%) traced back to NIST at EMPA-WCC
Zero air unit (for dilution)	Custom built by EMPA-WCC Inlet Filter – Pump – Rubin Gel – Sofnocat 423 – Outlet Filter
Dilution unit	MFC Bronkhorst HI-TEC S/N 413212.A 0 – 100 ml/min MFC Bronkhorst HI-TEC S/N 413212.B 0 – 5000 ml/min Bronkhorst Control Unit S/N M1206113A

A schematic overview of the instrumental set-up is shown in Figure 12, and a picture of the installation at Mt. Kenya is shown in Figure 13.

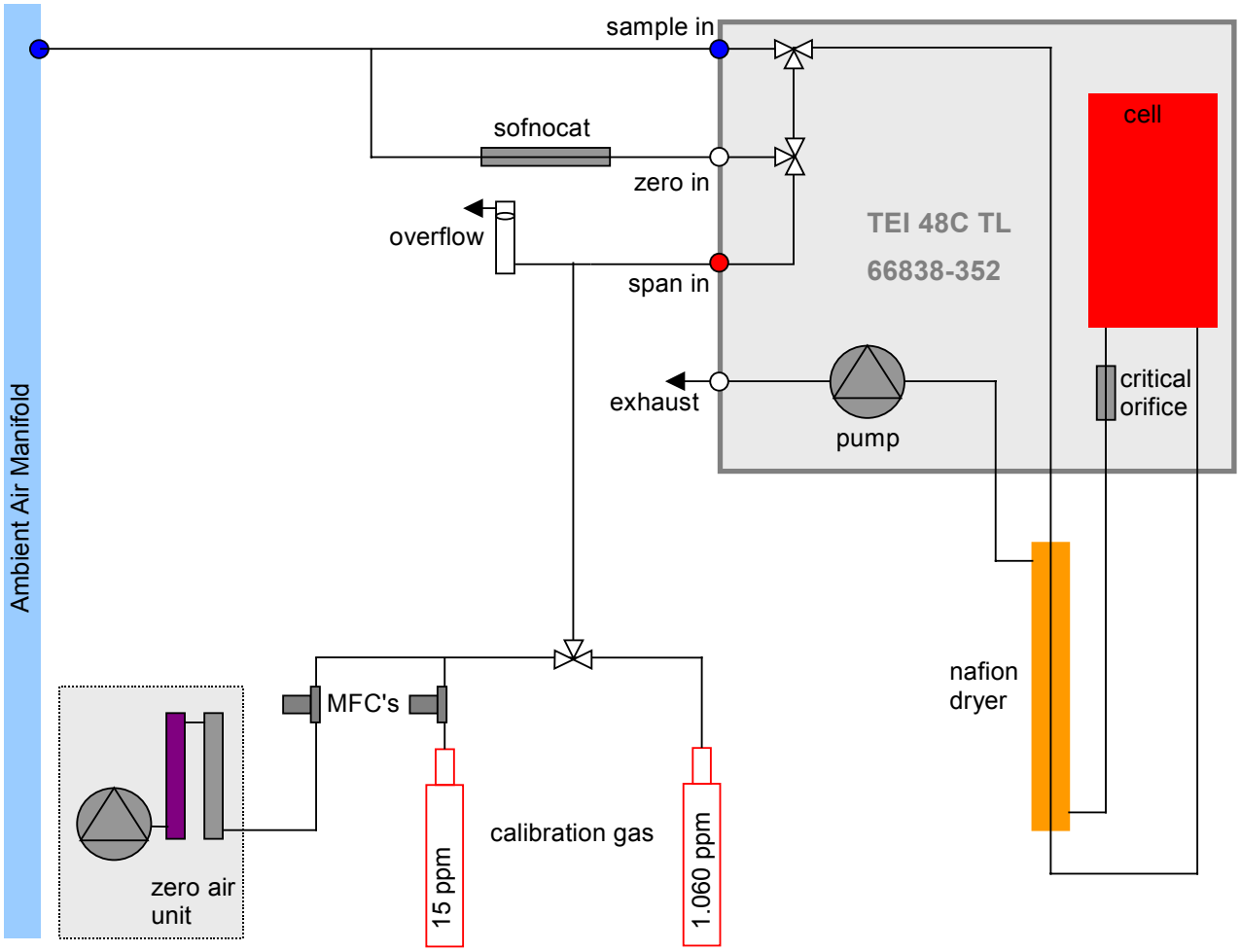

Figure 12: Instrument set-up (carbon monoxide) at Mt. Kenya

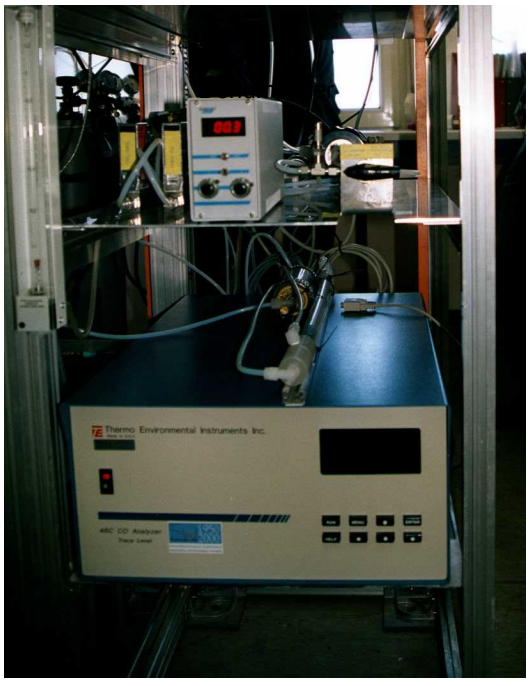

Figure 13: CO Instrumentation at Mt. Kenya

Operation and Maintenance

The following operation and maintenance schedule has been agreed upon for the CO measurements at Mt. Kenya:

- On a regular working day, the person in charge inspects the instruments for general operation.
- A station specific check list (Appendix III) should be completed weekly for the CO analyser. It includes basic instrument checks as well as download and storage of the CO data. It was agreed with the station manager that he regularly informs EMPA-WCC about the instrument status. Data files should be submitted to EMPA-WCC.
- A full instrument calibration using the 1.06 ppm CO standard should be performed every three months. For this purpose, a specific check list / SOP is available (Appendix IV).

Automatic zero checks are performed every 2 hours for 30 minutes (at 1, 3, 5, 7, 9, and 11 am/pm). This data is used for data processing (correction of zero drift).

5.1.3. Data Handling

Data Acquisition and –transfer

Data Acquisition is made with the C series communication software (version 2.2.0) from Thermo Environmental Instruments. The data (5 minute average values) is downloaded weekly to a notebook, and the data transfer is done by floppy disc. The settings of the internal data logger are 5 minute averages for the short records (max. 4096 values or approx. 2 weeks) and 15 minute averages for the long records respectively (max. 1792 values).

In addition, the analog output (0-1 V, corresponding to 0-1000 ppb CO) of the instrument is logged by the MILOS 500 data acquisition unit.

Data Treatment

Data treatment is performed after data download and includes:
- correction of zero drift with the zero values of the automatic zero check
- time series plot, plausibility checks
- data check with station logbook

Data Submission

CO measurements became operational during the audit of EMPA-WCC. Data submission to the GAW World Data centre for Greenhouse Gases at JMA should start as soon as the system is fully operational and a longer data set is available.

5.1.4. Documentation

The Station was supplied by EMPA-WCC with all instrumentation manuals (TEI 48C, Bronkhorst MFCs) including TEI data acquisition programme Version 2.2.0 on floppy disk. A log book including information on instrument operation and maintenance is available at the site.

5.1.5. CO data from Mt. Kenya

CO measurements became operational at the Mt. Kenya station in February 2002 after the installation of the instrument by EMPA-WCC during the audit. Thus, no data is available yet.

5.2. Recommendations for Carbon Monoxide Measurements

The following recommendations are made by EMPA-WCC concerning carbon monoxide measurements.

- All actions concerning CO measurements should be carefully documented in the log book. If malfunction of the instrument is noticed and the problem persists, contact EMPA-WCC for assistance.
- The checklists should be filled in by the responsible person for the CO measurements. It was also agreed that checklist and data should be submitted to EMPA-WCC.
- Data should be checked weekly for plausibility with time series plots.
- Regular back-ups of the CO data are strongly encouraged.
- The installation of the UPS to avoid frequent cold-starts of the instrument is encouraged.
- Submission of the data to the GAW World Data Centre for Greenhouse Gases (WDCGG) at JMA is recommended as soon as more data become available.

6. General Recommendations

The following recommendations are made to ensure the long-term operation of the GAW station Mt. Kenya. The reason for part of these recommendations is the problem that occurred with the power line to the station and infrequent station visits.

- The station should be visited on regular intervals, e.g. weekly. This should be possible as soon as the station staff will be located in Nanyuki (planned for March 2002).
- The situation concerning the power line should be checked daily, and measures should be taken in case of a power outage.
- The UPS unit available at the site should be installed as soon as possible.
- Persistent problems with any of the measurements at Mt. Kenya should be communicated to external partners and WMO. Communication should be re-established where necessary and maintained to ensure continuing support of external partners. E-mail and internet access should be re-established for all persons involved in the GAW activities. This is also of highest priority at the new location in Nanyuki.
- A budget, for example in accordance to the GAW measurement guide, should be available for the long-term operation and maintenance of the station. Part of the budget should be at the immediate disposal of the station manager.
- The road up to Old Moses Camp was in fairly good condition during the audit. It is of high priority that a 4WD vehicle is available for the station staff in Nanyuki to access the station.
- An extensive measurement program is important for a global station. Existing but dormant equipment should be activated/repaired.

7. Conclusions

The global GAW station Mt. Kenya opened in December 1999. Since then, ozone data have become available but time series are incomplete due to technical problems and infrequent station visits. This was recognised by KMD and measures were taken. The station staff was to be relocated from Nairobi to Nanyuki by March 2002. This should resolve some of the issues. Furthermore, the power line to the station could be repaired by the Kenya Power Company during the audit. The station was operational concerning ozone measurements as well as meteorological parameters at the end of the audit of EMPA-WCC. In addition, instrumentation for continuous carbon monoxide measurements was implemented during the audit by EMPA-WCC.

The geographical position of the Mt. Kenya station within the GAW programme is regarded as important, since ground based measurements of air pollutants from equatorial regions are very limited. Furthermore, the station offers excellent infrastructure concerning laboratory facilities. To take advantage of this, national and international co-operation for both technical and scientific staff (workshops, exchange programs, scientific partnerships) is regarded as important.

The station will require regular training for some years to come. All possibilities for twinning should be explored.

Appendix

I 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.

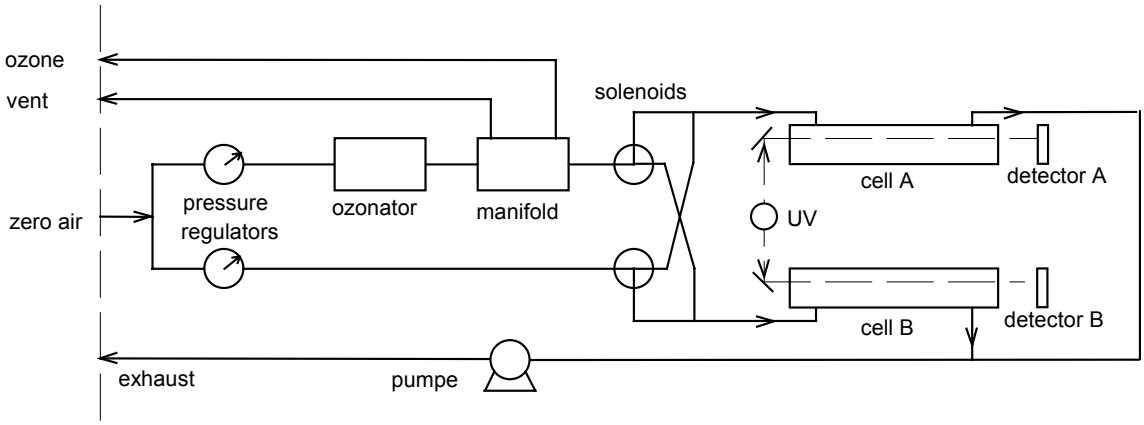

Figure 14: Flow schematic of TEI 49C-PS

II 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 9 and Figure 15.

Table 9: 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

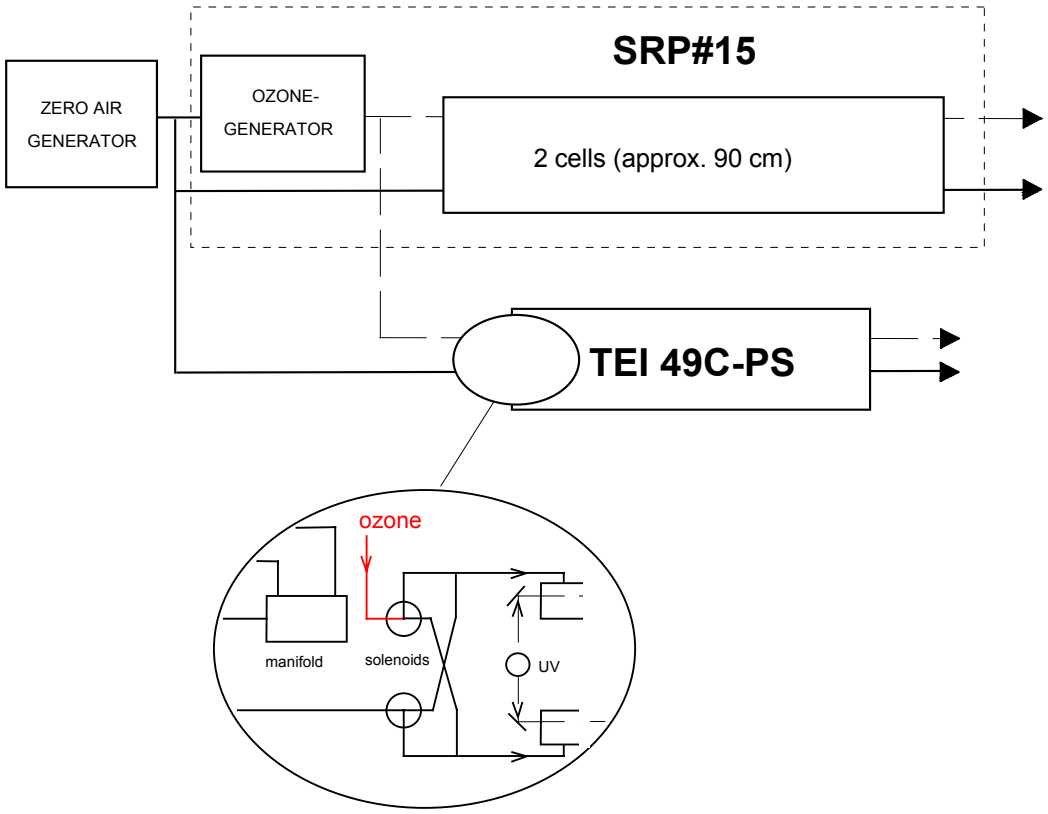

Figure 15: Instruments set up SRP -TEI 49C-PS

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.

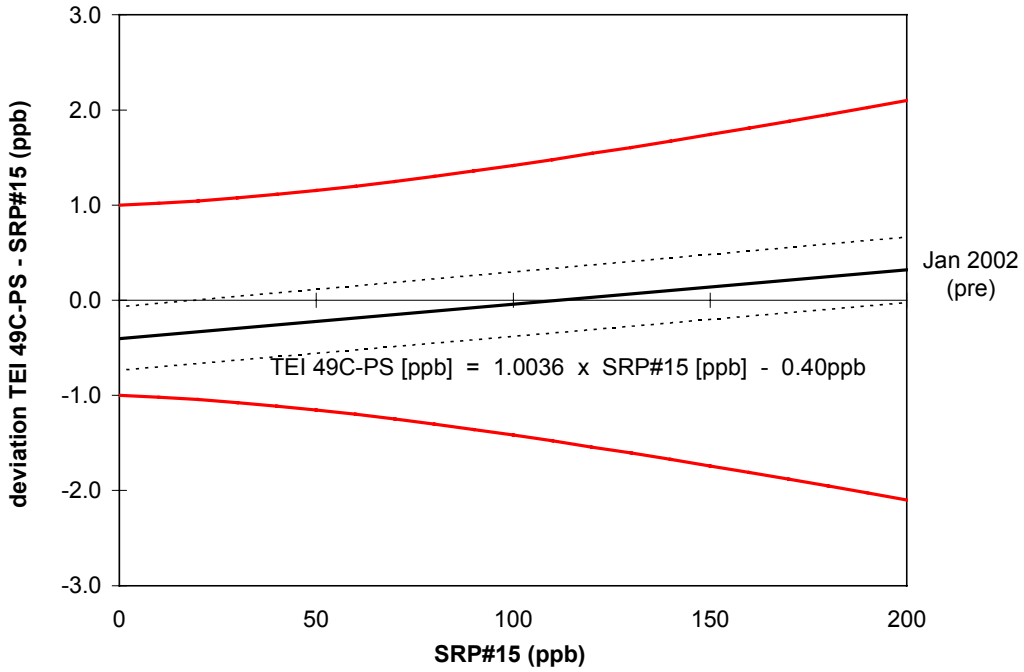

Figure 16: Transfer standard before audit

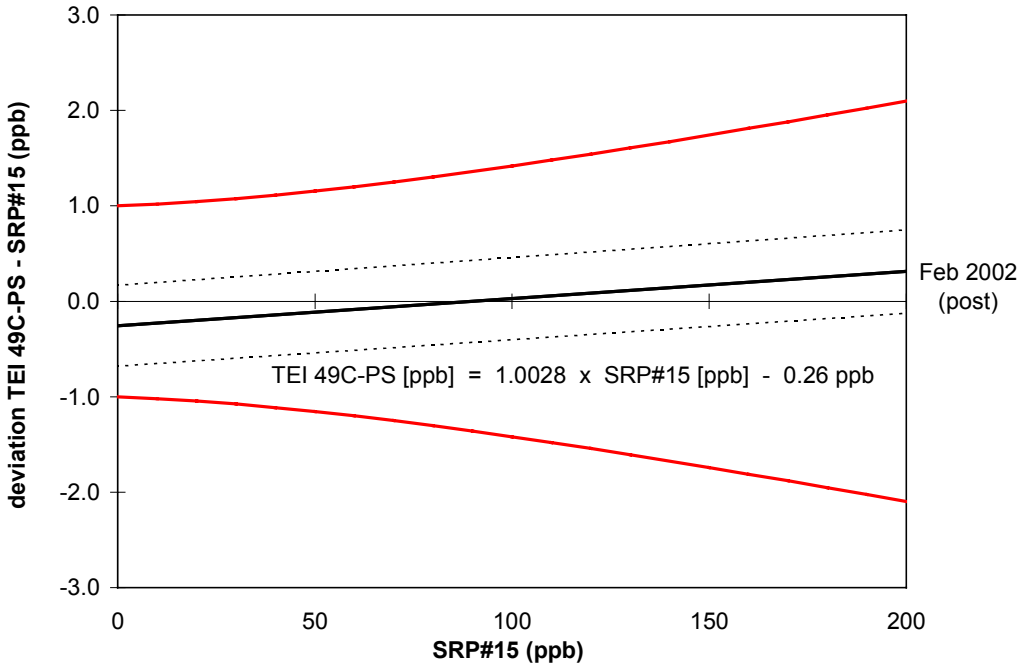

Figure 17: Transfer standard after audit

III CO Checklist (weekly)

Date:

Operator:

1. **Check for Alarms** if yes, specify
2. **Check Time** ☐ OK; if not, what was the time? ..... ☐ corrected
3. **Check Date** ☐ OK; if not, what was the date? ..... ☐ corrected
4. **Download Data**

   Long records (15 min AVG), max 1792: Filename: .....
   Short records (5 min AVG), max 4096: Filename: .....

5. **Instrument Checks**

Internal Temp.	°C	8-47
Chamber Temp.	°C	40-50
Pressure	mm Hg	250-1000
Flow	LPM	0.350-1.500
BIAS Voltage	V	-120 to –100
AGC Intensity	Hz	150000-300000
Motor Speed	%	100
CO BKG	ppm	
CO COEFF		

6. **Span Check** (only if instrument was running for more than 6 hours)

   not between 1:00 to 1:30, 3:00 to 3:30, 5:00 to 5:30 etc (automatic zero checks)

A. Press RUN until ZERO and wait until zero concentration has stabilised

B. Calibrate ZERO (Menu Calibration)

C. Switch calibration selection valve to position 1

D. Start zero air and open cal gas valve (15 ppm)

E. Check flow rates of MFCs (1: 25.9 %, 2: 15.0%)

F. Check span flow rate at overflow rotameter (> 1 LPM)

G. Press RUN until SPAN and wait until span has stabilised

H. SPAN ..... ppb (Expected 500 ppb, OK if 450-550)

I. Press RUN until SAMPLE

J. Switch of cal gas and zero air pump

IV CO Checklist (3-montly)

Date:

Operator:

1. Fill in **weekly checklist**
2. Check **inlet filter** during SPAN check; exchange when polluted
3. **Span Calibration** (only if instrument was running for more than 24 hours)
   not between 1:00 to 1:30, 3:00 to 3:30, 5:00 to 5:30 etc (automatic zero checks)
   A. Press RUN until ZERO and wait until zero concentration has stabilised
   B. Calibrate ZERO (Menu Calibration)
   C. Switch calibration selection valve to position 2
   D. Open cal gas valve (1.06 ppm)
   E. Adjust flow rate to 1.1 LPM
   F. Press RUN until SPAN and wait until span has stabilised
   G. SPAN ..... ppb (Expected 1.06 ppm, OK if 1.00 to 1.06)
   H. If span outside limits calibrate CO (Menu CALIBRATION)
   I. Press RUN until SAMPLE
   J. Close cal gas