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

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

**EMPA-WCC REPORT 98/3**

**Submitted to the**

**World Meteorological Organization**

# SYSTEM AND PERFORMANCE AUDIT

# SURFACE OZONE and CARBON MONOXIDE

# GLOBAL GAW STATION MACE HEAD

# IRELAND, MAY 1998

**Submitted by**

**A. Herzog, B. Buchmann, P. Hofer**

**WMO World Calibration Centre for Surface Ozone and Carbon Monoxide**

**EMPA Dübendorf, Switzerland**

# Contents:

Figures:



Tables:

# 1. Abstract

A system and performance audit was conducted by the World Calibration Centre for Surface Ozone and Carbon Monoxide at the global GAW station Mace Head, Ireland. Below, the findings, comments and recommendations are summarised:

**Air Inlet System:**
Ozone: The air coming from a westerly direction (seaward direction, clean air sector) may come into contact with the wall of the building. However, in view of the prevailing strong winds, this disadvantage seems to be of no or minor consequence. Neither is the shift of the air intake part regarded as critical.
The teflon tube and the rain protection at the inlet were clean and free of dust. The inlet system, concerning construction materials as well as residence time, is adequate for gas analysis. No loss of ozone could be detected.
CO: The inlet system installed (same as for CFC's, $CH_4$ and $N_2O$) is adequate for analysing CO concerning construction materials as well as residence time.

**Instrumentation:**
Ozone: The measurement technique used is the UV-method which is the preferred method in the GAW programme.
Ozone analysers are relatively sensitive to abrupt temperature deviations of the environment (i.e. diurnal cycles of higher than +/- 5 °C) and shocks. This problem was reduced by moving the ozone instrument to the fully air-conditioned laboratory on the ground floor with a concrete base. Considering its age, the analysers ML 8810 is in reasonable condition.
The detected instrument non-linearity for the very low ppb range is acceptable for Mace Head, since ozone concentrations below 5 ppb rarely occur and certainly never refer to unpolluted air masses.
CO and gas standards: The gas chromatography technique followed by mercury reduction detection, as operated at Mace Head, is a widely-used method. Applied with care it is characterised by excellent specificity, very low detection limits and high precision (WMO-GAW report No. 98). The analyser RGA-3, although in operation for around 10 years, is in good condition.
The alternating calibration of the system with the certified working standard (within the relevant range provided by SIO, see 3.4.) validates the measurements. The variety of additional CO gases at the site is welcomed. The samples range from synthetic to real air (CSIRO Australia), from low ppb to ppm, even one counter-checked with the NDIR method. This reflects the active role of the station regarding networking, although a direct treaceability to CMDL standards is not given.

**Operation and Maintenance:**
The appearance of the station is clean and functional.
Ozone: The schedule of regular daily checks and routine preventive maintenance is well established and adhered to in order to facilitate the operation of the analysers. The synergies resulting from the affiliation to the UK ozone network have created a high standard of implemented quality assurance.
CO: Because of the operators' experience with gas chromatography some of the maintenance is carried out according to a schedule and some on a case by case basis. Daily check of some test points of the analyser and examining chromatograms gives the person in charge enough information about the state of the instrument to determine if maintenance is necessary.

**Data Handling:**
Ozone: Review of the final data set by two persons is welcome, since this action increases the reliability of the data. The transparency of data flux, in view of distribution to databases, was improved.
As recommended in the last audit report, the zero point correction of the raw data was adopted accordingly (for further details see Ozone Appendix I). However, this is just carried out for the

dataset relevant for the GAW programme. The fact that differently recalculated data sets are distributed is regarded as very confusing for the user of such data and has to be avoided if possible.
CO: Data treatment at different geographical locations has made necessary to provide sophisticated GC software to allow access to required information anytime for all partners involved. Transparency is assured to a maximum extent with the implemented electronic log files which are very carefully written and up-to-date. Review process of the data set is regarded as reliable and optimised for resources.
The available data should be sent to the WDC for greenhouse gases as soon as possible.

**Documentation:**
Ozone: The documentation of the ozone measurement meets all the requirements of the GAW guidelines and can be taken as a perfect example of practice orientated implementation.
CO: The way of presenting the field log books in an electronic format instead of on paper is regarded as a very user-friendly and powerful method. This is beneficial since several persons located at different institutes are working with the data and thus need to have access to the necessary documents. By logging all the information in log files, i.e. special events or conditions, calibrations, maintenance or malfunctions, the process of data treatment is certainly simplified.
The log files were kept up-to-date and clearly structured containing all the necessary information.

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

**Ozone Intercomparisons:**
The ozone concentration observed at Mace Head (1997) usually ranged between 17 and 48 ppb (5- and 95-percentile of hourly mean values). The instrument fulfils the assessment criteria as "good" over the tested and relevant range up to 100 ppb (figure 8). The stability of the instrument has improved likely due to moving it to the air conditionend laboratory at the ground floor (less shocks).

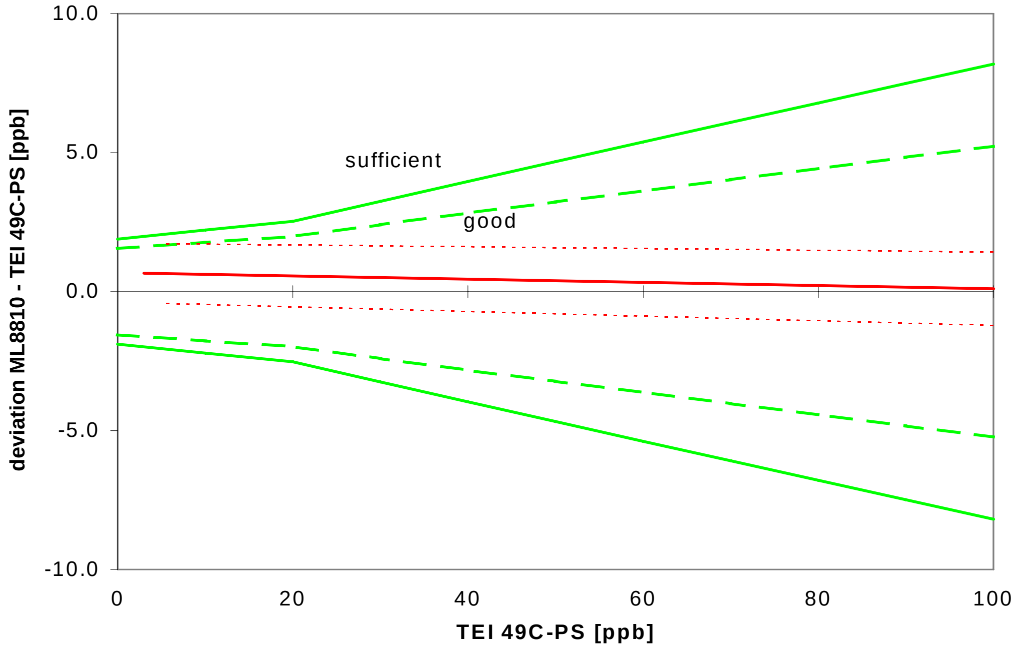


Figure 1: Intercomparison of ozone instrument ML 8810

**Carbon Monoxide Intercomparisons:**
The results of the CO intercomparison measurements (figure 13) deviate only by about 1 to 3% from the conventional true value with a certified uncertainty of the CMDL transfer standards of approximately 1% until 200 ppb and 3% for 300 ppb. Regarding the relevant range (79 and 214 ppb, 5- and 95-percentile respectivley), this is a good result but could be improved considering the nonlinearity of the CO analyser system and applying the results of the regular multipoint calibrations.

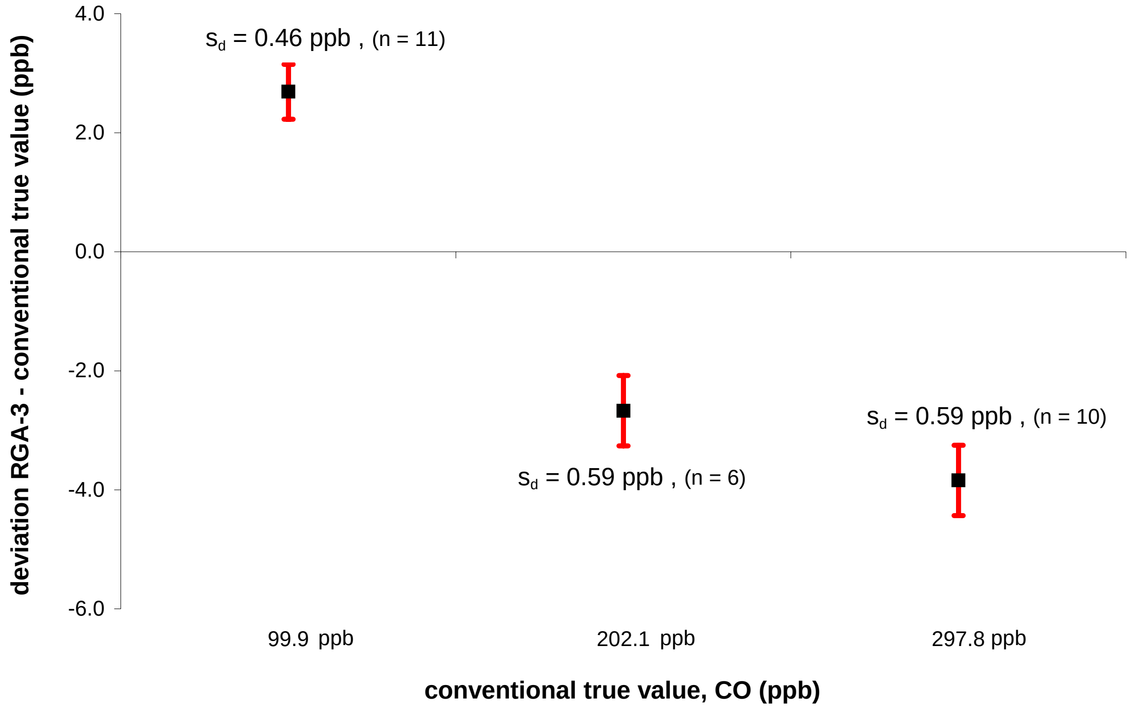


Figure 2: Intercomparison of CO gas chromatograph RGA-3

---

Dübendorf, 5. November 2007

Dübendorf, EMPA-WCC

Project engineer

Project manager

A. Herzog

B. Buchmann

Technical assistant and VOC / CFC expert: S. Reimann

# 2. Introduction

In establishing a coordinated quality assurance programme for the WMO Global Atmosphere Watch programme, the air pollution and environmental technology section of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) was assigned by the WMO to operate the WMO-GAW World Calibration Centre (WCC) for Surface Ozone and Carbon Monoxide. At the beginning of 1996 our work had started within the GAW programme with the parameter surface ozone. The activities were extended to carbon monoxide in the middle of the year 1997. The detailed goals and tasks of the WCC concerning surface ozone are described in the WMO-GAW report No. 104.

In agreement with the responsible persons in charge of $O_3$ and CO measurements at the Atmospheric Research Station, Mace Head, Ireland, the second system and performance audit was conducted. The site is part of a number of international research and monitoring networks including the GAW programme (global GAW station), the UK ozone network, the AGAGE network and the CMDL / NOAA co-operative flask sampling network. The station is an established site for long-term measurements of several chemical compounds and physical and meteorological parameters. Located on the west coast of Ireland, the site offers excellent exposure to the North Atlantic (clean air sector, 180° through west to 300°).

The scope of the audit, which took place from May 22 to 28, 1998, was confined to the surface ozone and carbon monoxide measurements. The entire process, beginning with the inlet system and continuing up to the data processing, and also the supporting measures of quality assurance, were inspected during the audit. The audit concerning ozone was performed according to the "Standard Operating Procedure (SOP) for performance auditing ozone analysers at global and regional WMO-GAW sites", WMO-GAW Report No. 97. No Standard Operation Procedures (SOP) have been established for CO measurements by QA/SAC until now. For this reason, the ozone SOP was adapted for carbon monoxide. The assessment criteria for the ozone intercomparison have been developed by EMPA and are based on WMO-GAW Report No. 97 (EMPA-WCC report 98/5 "Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements" by P. Hofer, B. Buchmann and A. Herzog, September 1998, available on request from the authors at: EMPA, 134, Ueberlandstr. 129, CH-8600 Dübendorf).

The present audit report is submitted to the station manager and involved persons, the World Meteorological Organization in Geneva and the Quality Assurance and Scientific Activity Centre (QA / SAC) for Europe and Africa.

The last audit at Mace Head had been performed in October 1996. System and performance audits at global GAW stations will be regularly conducted on mutual arrangement.

# 3. Global GAW Site Mace Head

## 3.1. Site Characteristics

The Atmospheric Research Station at Mace Head is located on the west coast of Ireland, County Galway (see map figure 4). The site offers excellent exposure to the North Atlantic (clean air sector, 180° through west to 300°). The nearest major conurbation which is 90 km east of Mace Head is Galway, a city with a population of approximately 52'000 inhabitants.

The hilly area around Mace Head is wet and boggy with a lot of exposed rocks and vegetation which consists mainly of grasses and sedges. There are three small islands offshore which are within the clean air sector, and are uninhabited.

The facilities at the site (coordinates: 53°19' N, 9°51' W; elevation: 5m above sea level) consist of three laboratory buildings, one 300m and two ~90m from the shore, a 23 m aluminium walk-up tower and a converted 20 ft cargo container office (see picture figure 2). In one of the two two-story buildings, near the shore, the ozone analyser is installed in a air-conditionend room at the ground level. The air inlet system for the ozone measurements is mounted on the outside wall at about 3 m height, 1.2 m from the wall and exposed to the sea.

Since the last audit, the environment near the site has not changed in a way that could have influenced the ozone or carbon monoxide measurements significantly.

Figure 3: Picture of the station Mace Head

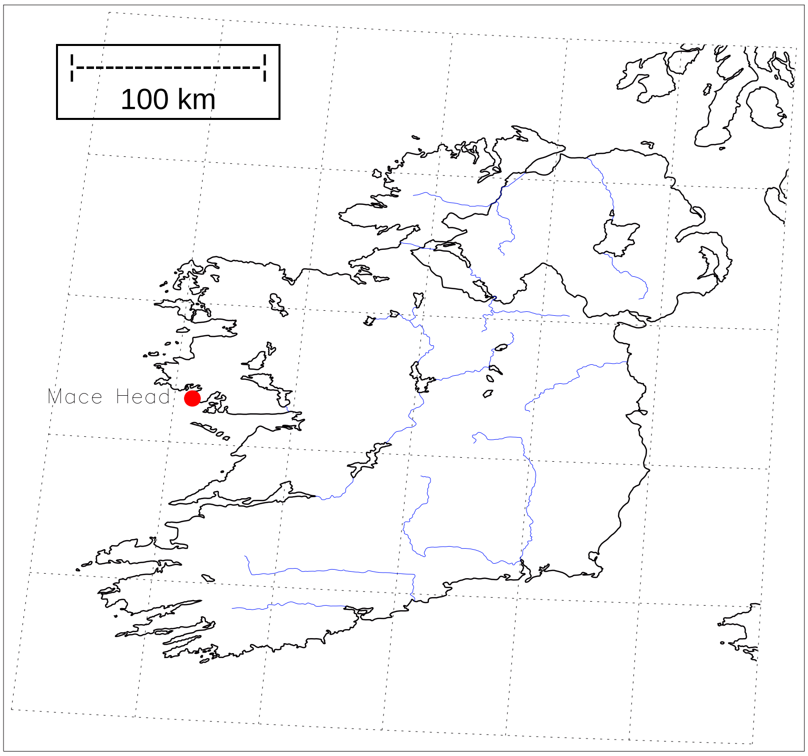


Figure 4: Map of Ireland

## 3.2. Operators

The internationally well-known Atmospheric Research Station at Mace Head is owned and operated by the National University of Ireland, Galway (NUI). The financial support of the station and its measurement activities are granted by the University, several institutes and national and international projects. The ozone and AGAGE programs are co-ordinated and managed by Dr P. Simmonds. The structure of the management of these programs at Mace Head is shown in Table 1.

Table 1: Operators

| |
|---|
| Co-ordination and management<br>Peter Simmonds, consultant<br>Administration and management |
| Station manager<br>Gerard Spain, scientist, National University of Ireland, Galway<br>Duncan Brown, backup operator |
| QA by National Physical Laboratory (NPL)<br>Brian Sweeney and Mr David Butterfield<br>QA and ozone intercalibrations for the UK network |

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

## 3.3. Ozone Level

The site characteristics and the relevant ozone concentration range can be well described by the frequency distribution. In figure 5 the frequency distribution of the hourly mean values of the year 1997 is shown. The relevant ozone concentrations were calculated ranging between 17 and 48 ppb according the 5- and 95-percentile of the hourly mean values. The annual mean is 33 ppb

Source of data: Gerry Spain, preliminary results

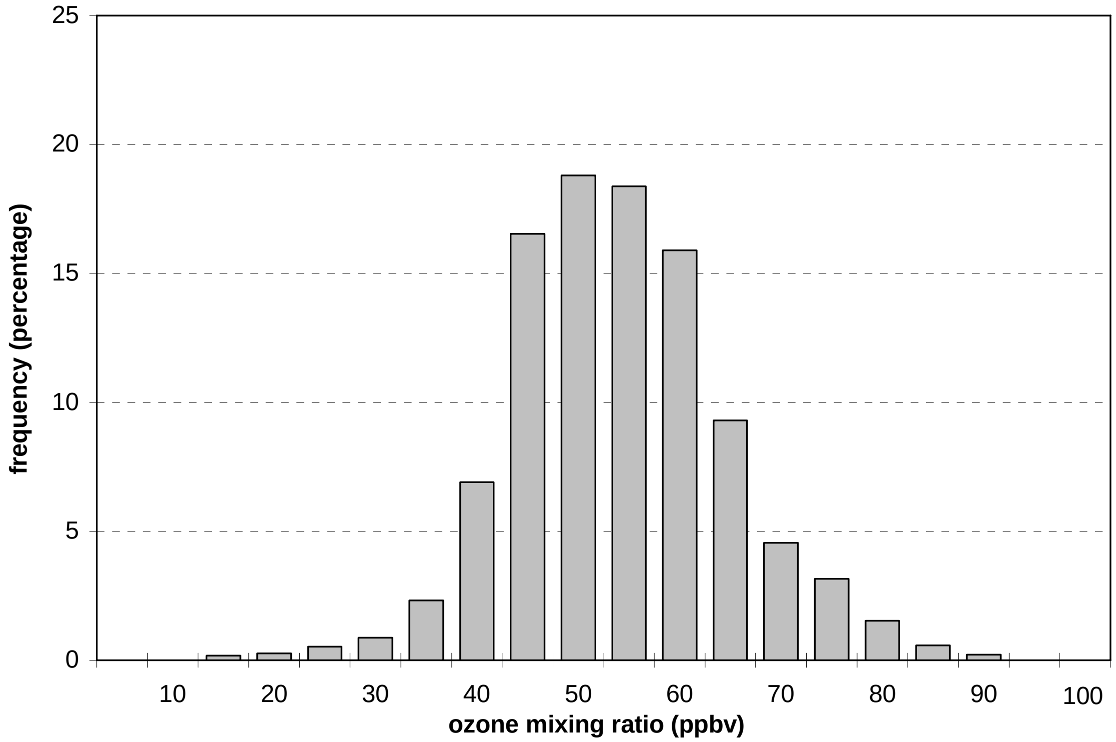


Figure 5: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Mace Head of the year 1997. Data capture higher 97 per cent

## 3.4. Carbon Monoxide Level

The relevant carbon monoxide concentration range can be well defined by the frequency distribution. In figure 6 the frequency distribution of the hourly mean values from the year 1997 is shown. The relevant carbon monoxide concentrations were calculated, ranging between 79 and 214 ppb according the 5 and 95 percentile values. The annual data capture of carbon monoxide was about 83 %. The annual mean is 137 ppb.

Source of data: P. Simmonds

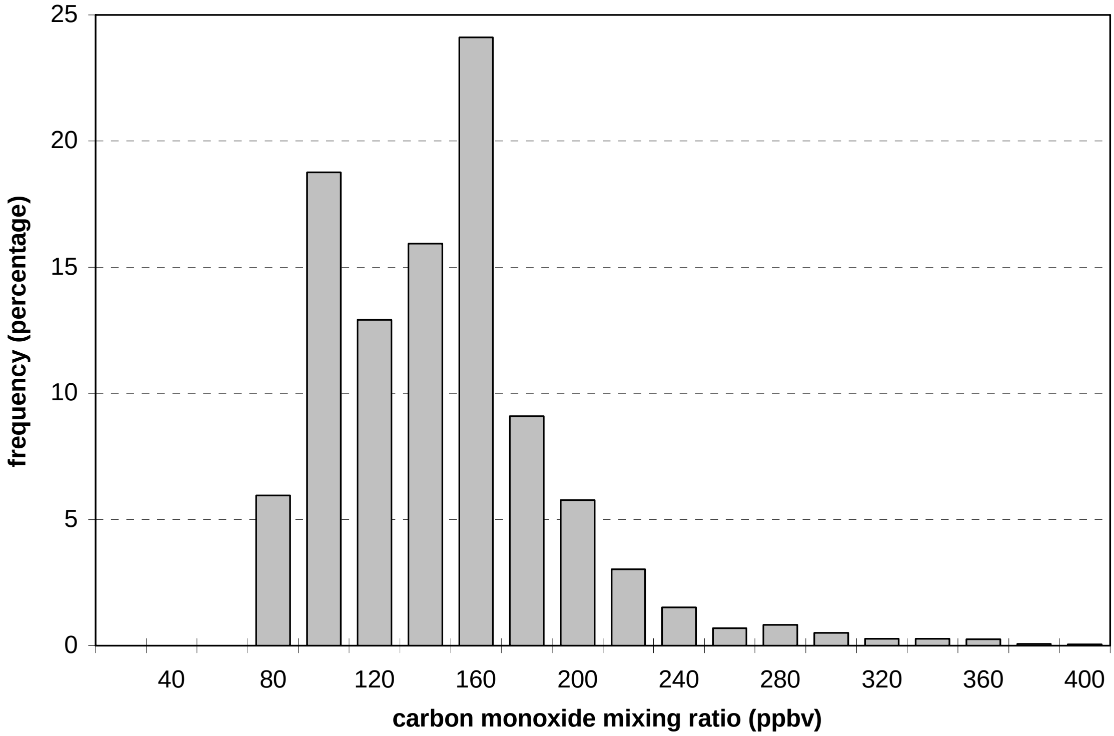


Figure 6: Frequency distribution of the hourly mean values of the carbon monoxide mixing ratio (ppb) at Mace Head of the year 1997. Data capture is around 83 per cent.

# 4. Measurement Techniques

## 4.1. Surface Ozone

## 4.1.1. Air Inlet System for Ozone

The air inlet system for the ozone measurements is mounted approximately 3m above the ground and 1.2 meters from the wall on the seaward side of a two story laboratory building. It consists of a small, inverse teflon-bucket which shields a 1/4" teflon tube from rain and snow. The 4.5 m long tube leads directly through a sampling port in the wall to the air-conditionend room at the ground level where the instrument is installed. A teflon inlet filter protectes the analyser from dust and particles. The residence time of the ambient air in the inlet line lies between 2 to 3 seconds.

As a consequence of moving the analyser downstairs, in order to use the same inlet line, the position of the air intake part had to be shifted by about 3 m keeping it positioned on the same wall and level above ground.

The inlet line was checked with regard to loss of ozone in an additional intercomparison. For this experiment the short connection tube (less than 1m) between the ozone producing transfer standard and the analyser was replaced by the 4.5 m inlet line. No significant difference between measurements with the dust-free short tube and the relatively long inlet line was found.

### Comments

The air coming from a westerly direction (seaward direction, clean air sector) may come into contact with the wall. However, in view of the prevailing strong winds, this disadvantage seems to be of no or minor consequence. Neither is the shift of the air intake part regarded as critical.

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

## 4.1.2. Instrumentation, Ozone Analyser

The instrument is installed in an environmentally controlled room (about 21 ±1°C). In the same room is the CO system.

The instrumentation used for measuring ozone at Mace Head during this second audit was identical with the configuration during the last audit in October 1996 and is shown below in table 2.

The instrument is installed on a bench on the ground floor in one of the laboratory buildings which is near the shore. Since the last audit it had been moved from the upper floor (attic story) to the fully air conditioned room downstairs. The instrument is also now powered via an uninterruptible power supply (UPS).

Specifically, elderly Monitor Labs instruments of the type 8810 show a non linearity in the very low ppb range (0-5 ppb) which leads to an instrument dependent offset of about 1 to up to 4 ppb. This observation is based on experience from laboratory and field tests.

Table 2: Ozone field instrument

| | |
|---|---|
| Type | Monitor Labs 8810#437 |
| Method | UV absorption |

| | |
|---|---|
| at Mace Head | since 1987 |
| Range | 0-500 ppb |
| analog output | 0-1 V |
| instrument's specials | - internal ozone source and zero air unit integrated |

The zero air unit, which is integrated in the instrument, consists of an activated charcoal cartridge and a particulate filter. It is used to determine the analyser's daily zero and span readings.

**Comments**

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

Ozone analysers are relatively sensitive to abrupt temperature deviations of the environment (i.e. diurnal cycles of higher than +/- 5 °C) and shocks. This problem was reduced by moving the ozone instrument to the fully air-conditioned laboratory downstairs with a concrete base. Considering its age, the analysers ML 8810 is in reasonable condition.

The above mentioned non-linearity of the analyser is acceptable for Mace Head, since ozone concentrations below 5 ppb rarely occur and certainly never refer to unpolluted air masses.

### 4.1.3. Operation and Maintenance, Ozone

A regular schedule of routine preventive maintenance has been established. Under this monthly service checking the flow, the p / T readings, the flow and the lamp voltage, replacement of filters and performance of span and zero checks are included. For the monthly maintenance a separate checklist is filled in and sent to the NPL.

Any further maintenance of the analyser is conducted twice a year by Enviro Technology according to a service contract within the UK network. It incorporates cleaning of the sample line and the instrument cell as well as leak testing, replacement of spare parts, renewing the charcoal cartridge of the analyser's zero air supply, span and zero checks and noise recording. They also carry out a multipoint calibration which is just used for diagnostic purposes.

Before and after every such a general service, the UK's National Physical Laboratory (NPL) carries out an intercalibration using a transfer standard which is in turn checked with the national primary standard for ozone at NPL. The intercalibration consists of a multipoint calibration procedure similar to the one performed during the audit. A brief extract of the latest NPL report is quoted in Appendix I.

At midnight a zero (10 min) and a span (10 min) check at 100 ppb is made as a routine check of the ozone analyser.

**Comments**

The appearance of the station is clean and functional.

The schedule of regular daily checks and routine preventive maintenance is well established and adhered to in order to facilitate the operation of the analysers. The synergies resulting from the affiliation to the UK ozone network have created a high standard of implemented quality assurance.

### 4.1.4. Data Handling

The acquisition system installed at the site consists of an ADC circuit board and a computer to store the one-minute-mean values and the hourly means automatically in data files.
Data processing consists of a daily or alternate day visual inspection of the raw data. Every few months a data set is prepared and recalculated after a certain procedure, see table 3. Together with the instrument logbook, the data set is then revised for errors in connection with special events like power cuts, for example. Data for plausibility control are plotted from the final data set.

Table 3: Ozone data treatment

| | Treatment of raw data at the station before distribution | data transfer by the station | |
|---|---|---|---|
| | | Tool | interval |
| <u>Data receivers:</u><br><br>P. Simmonds (station co-ordinator) | Subtracting the zero offset obtained from the NPL calibrations (excluding zero for lin. regression calculation) made by the station manager<br>the submitted data is reviewed again | internet (hourly data) | every 3 month |
| NPL (UK ozone network) | none | internet (hourly data) | every 3 months |
| Irish EPA | none | internet (hourly data) | every 3 hours |
| CMDL / NOAA | none | diskette | monthly |

**Comments**

Review of the final data set by two persons is welcome, since this action increases the reliability of the data. The transparency of data flux, in view of distribution to databases, was improved.
As recommended in the last audit report, the zero point correction of the raw data was adopted accordingly (for further details see Ozone Appendix I). However, this is just carried out for the dataset relevant for the GAW programme. The fact that a number of data sets which are calculated differently are distributed is regarded as very confusing for the user of such data and has to be avoided if possible. It is strongly recommended to work towards harmonisation.

### 4.1.5. Documentation

Within the GAW guidelines for documentation, the transparency and the access to the station documents are required. During the audit the documentation was reviewed for availability and usefulness.

In the scope of quality assurance the UK ozone network established a specific system operating procedure (SOP) for each station. The documentation called "Local site operator manual", Bryan Sweeney, describes the maintenance, the operation and the data treatment for ozone measurements. The SOP is structured in a very detailed and practically oriented form. Its content is consistent with the more general SOP of WMO-GAW Report No. 97. Furthermore, a station instrument/maintenance logbook (bound copy) was kept in an organised manner and contained all necessary information about special investigations, maintenance or unusual events. For the monthly maintenance a separate checklist is filled in sent to the station co-ordinator and stored in a file.

**Comment**

The documentation of the ozone measurement meets all the requirements of the GAW guidelines and can be taken as a perfect example of practice orientated implementation.

## 4.2. Carbon Monoxide (in situ)

### 4.2.1. Air Inlet System for CO

The air inlet system for the CO measurements is mounted at the 10 meter level of the aluminium walk-up tower between the two cottages near the sea. It consists of a small, inverse stainless steel cup which shields a 1/4" stainless steel tube from rain and snow. The tube leads down along the tower through a sampling port in the wall to the air-conditioned room at the ground level where the RGA-3 CO analyser is installed. The ambient air is sucked through that outside line by a metal bellows pump (6 l / min). For most of the time the air is vented after the pump but 90 seconds before injection a solenoid valve is activated, so that approximately 110 ml / min (corresponding 50 mbar overpressure in the sample loop) flows through a 7 μm SS-fritte, a nafion dryer, the 1ml sample loop and a flow regulator valve to the RGA-3 instrument. The residence time of the ambient air in the inlet line lies around 2 seconds. The inlet lines are not regularly cleaned but replaced after a few years instead.

**Comments**

The inlet system installed (same as for CFC's, $CH_4$ and $N_2O$) is adequate for analysing CO concerning construction materials as well as residence time.

### 4.2.2. Instrumentation, CO Analyser

The in situ CO analyser, a RGA-3 GC-system, is installed in an environmentally controlled room (about 21 ±1°C) in one of the laboratory buildings which is near the shore.

Instrumental details for the carbon monoxide analyser on site are listed in table 4.

Table 4: Field CO analyser

| | |
|---|---|
| instrument | Trace Analytical GC |
| model, S/N | RGA3, - 090189-010 ANE 294 |
| at Mace Head | since 1989 |
| configuration (model) | E-001 (Trace Analytical terminology) |
| method | GC / HgO Detector |
| interval of sample injection | 20 min (alternatingly standard and ambient air) |
| loop | 1 ml, flushed for 90s at 110 ml/min |

| | |
|---|---|
| columns | pre-column: Unibeads 1S 60/80<br>analytical column: Mole sieve 5A 60/80 |
| carrier gas | ambient air – AADCO - Sofnocat - Mole sieve - Dryrite - GC, 20 ml/min |
| operating temperatures | Detector: 265 °C, Columns: 105 °C |
| analog output | 0-1 V |
| calibration interval | every 40 min |
| instrument's specials | - the flow through the loop is verified by adjusting the flow so that the pressure in the loop is about 50 mbar above ambient pressure (accuarate manometer)<br>- a few seconds before injection, the flow through the loop is stopped (solenoid valve) to equalise the pressure inside the loop |

Two kinds of zero air are available at the site. One consists of a synthetic air cylinder in combination with a Sofnocat cartridge, the other one is a AADCO system. They are sporadically used to check the analyser's zero readings.

**Comments**

The gas chromatography technique followed by mercury reduction detection, as operated at Mace Head, is a widely-used method. Applied with care it is characterised by excellent specificity, very low detection limits and high precision (WMO-GAW report No. 98).

The analyser RGA-3, although in operation for around 10 years, is in good condition.

### 4.2.3. Gas Standards

The following gas standard are used at the site for verificating the measurements. While the working standard is analysed alternatingly with ambient air some others are just used less frequently. Further a linearity check is performed occasionally using two MFCs for dynamic dilution.

Table 5: Station CO cylinders

| | Gas cylinders | filling | Conc. |
|---|---|---|---|
| 1 | working standard provided by SIO, calibrated against CSIRO Australia standards | real air | 174.85 ppb * |
| 2 | CSIRO Australia, Cape Grim, G-050 | real air | 59 ppb |
| 3 | CSIRO Australia, Cape Grim, G-055 | real air | 134 ppb |
| 4 | certified BOC at 0.56 ppm, No. 49177, verified with NDIR (365 ppb) and CSIRO (364 ppb) | synthetic air | 365 ppb |

| | | | |
|---|---|---|---|
| 5 | certified BOC, No. 55604, used for dilution purpose – linearity check, verified with NDIR (600 ppb) | synthetic air | 0.60 ppm |
| 6 | Scott Specialty Gases, CLM 005557, NIST SRM certified, verified with NDIR (1003.6 ppb) | synthetic air | 1.003 ppm |

* is verified at the end of usage

**Comments**

The alternating calibration of the system with the certified working standard (within the relevant range provided by SIO, see 3.4.) validates the measurements. The variety of additional CO gases at the site is welcomed and also essential for linearity checks. The samples range from synthetic to real air (CSIRO Australia), from low ppb to ppm, even one counter-checked with the NDIR method. This reflects the active role of the station regarding networking, although a direct traceability to CMDL standards is not given.

## 4.2.4. Operation and Maintenance, CO

Most of the maintenance works for the RGA-3 CO analyser are performed on a case by case basis, i.e. cleaning the optical filters every few month, exchanging the lamp and reset the electronic baseline.

Daily, the station manager inspects the CO measurements for a quick check of general operation of the analysers. This includes checking of the test points 1 and 2 of the RGA-3 and examination of chromatograms. As preventative maintenance, the Sofnocat® cartridge of the zero air supply on site is replaced semi-annually to annually (the Sofnocat® is regenerated). Furthermore, every six months the Hg-scrubber is renewed.

The system is calibrated with a CO working standard (around 170 ppb) which is injected alternately with ambient air. Occasionally some other real air samples from Cape Grim ranging from 60 to 135 ppb CO are used to verify the linearity of the RGA-3 analyser. About once a year or on demand the zero air is checked.

**Comments**

The appearance of the station is clean and functional.

Because of the operators experience with gas chromatography some of the maintenance is carried out according to a schedule and some on a case by case basis. Daily check of some test points of the analyser and examining chromatograms gives the person in charge enough information about the state of the instrument and to determine if any action is necessary.

## 4.2.5. Data Handling

The data acquisition facility consists of a workstation and the "AGAGE GC control" software package developped at Scripps Institution of Oceanography (SIO). All the chromatograms are stored and automatically transferred twice daily via modem/internet to the main database at SIO. Peak integrations are carried out both for area and height but peak height is used for the final dataset.

The responsibility of data reviewing and data management is split between the station operator, the data reviewer in the University of Bristol, England and the SIO in the U.S. In a first step, the station operator plots the data daily and examines the chromatograms. Comments and notes are made in electronic log files. These comments contain e.g. calibration notes or remarks on events that might influence the data. After this practically oriented pre-selection the data reviewer applies flags to the data, based mainly on the station operators logs but also flagging data which appears suspect. To get the final results, the raw data (every single chromatogram) is recalculated by applying the appropriate calibration factor. This parameter is evaluated from the pre- and post-analysis of the working standard cylinder at SIO. During 6-monthly meetings of the AGAGE members the data is further discussed regarding scientific aspects and is finalised.

To date only a few monthly mean values (until 1993) are distributed to the GAW WDC for greenhouse gases, Tokyo.

**Comments**

Data treatment at different geographical locations has made it necessary to provide ~~a~~ sophisticated GC software to allow access to required information anytime for all partners involved. Transparency is assured to a maximum extent with the implemented electronic log files which are very carefully written and up-to-date. Review process of the data set is regarded as reliable and optimised for resources.

The available data should be sent to the WDC for greenhouse gases as soon as possible.

### 4.2.6. Documentation

Within the GAW guidelines for documentation the transparency and the access to the station documents are required. During the audit the documentation was reviewed for availability and usefulness.

For the CO measurements which are an integrated part of the AGAGE programme all information is documented in the form of electronic log files. These files are organised within the relational database in use. The content of the log files is chronologically listed for example calibration notes or remarks of events that influence the data. Other log files are structured like a list containing information, e.g. reference cylinder values.

The instrument manuals were available at the site.

**Comments**

The way of presenting the field log books in an electronic format instead of on paper is regarded as a very user-friendly and powerful method. This is beneficial since several persons located at different institutes are working with the data and thus need to have access to the necessary documents. By logging all the information in log files, i.e. special events or conditions, calibrations, maintenance or malfunctions, the process of data treatment is certainly simplified.

The log files were kept up-to-date and clearly structured containing all the necessary information.

# 5. Intercomparison of Ozone Instrument

## 5.1. Experimental Procedure

At the site, the transfer standard (detailed description see Appendix III) was hooked up to power for warming up over the weekend, in deviation from the GAW Report No. 97 which recommends only one hour of warm-up. In the morning, before the intercomparison was started the transfer standard, the PFA tubing connections to the instrument and the instrument itself were conditioned with about 250 ppb ozone for 40 min. During the next two days, three comparison runs between the field instrument and the EMPA transfer standard were performed. The inlet line was checked with regard to loss of ozone in an additional intercomparison. In the meantime the inlet system and the station documentation were inspected. Table 6 shows the experimental details and Figure 7 the experimental set up of the audit. In general, no modifications of the ozone analyser which could influence the measurements were made for the intercomparison.

The EMPA acquisition system which was used for the audit consisted of a 16-channel ADC circuit board and a PC with the corresponding software. Hooked up to the analog output of the field instrument and of the transfer standard, the data were collected. The EMPA data acquisition and the data logger on site were compared but showed no discrepancy. For data interpretation the EMPA data is used.

Finally, the observed results were discussed in an informal review with the person involved.

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

Table 6: Experimental details, ozone

| | |
|---|---|
| reference: | EMPA: TEI 49C-PS #54509-300 transfer standard |
| field instrument: | Monitor Labs 8810 #437 |
| ozone source: | EMPA: TEI 49C-PS, internal generator |
| zero air supply: | EMPA: silica gel - inlet filter 5 μm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 μm |
| data acquisition system: | EMPA: 16-channel ADC circuit board, software |
| pressure transducers reading: | readings of both instruments agreed within 1 mbar |
| concentration range | 0 - 100 ppb |
| number of concentrations: | 5 + 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: | 1 x on May 25, 1998<br>2 x on May 26, 1998<br>+ inlet line check on May 27 |
| connection between instruments: | less than 1 meter of 1/4" PFA tubing<br>additional run: inlet line, 4.5 m, 1/4" PFA tubing |

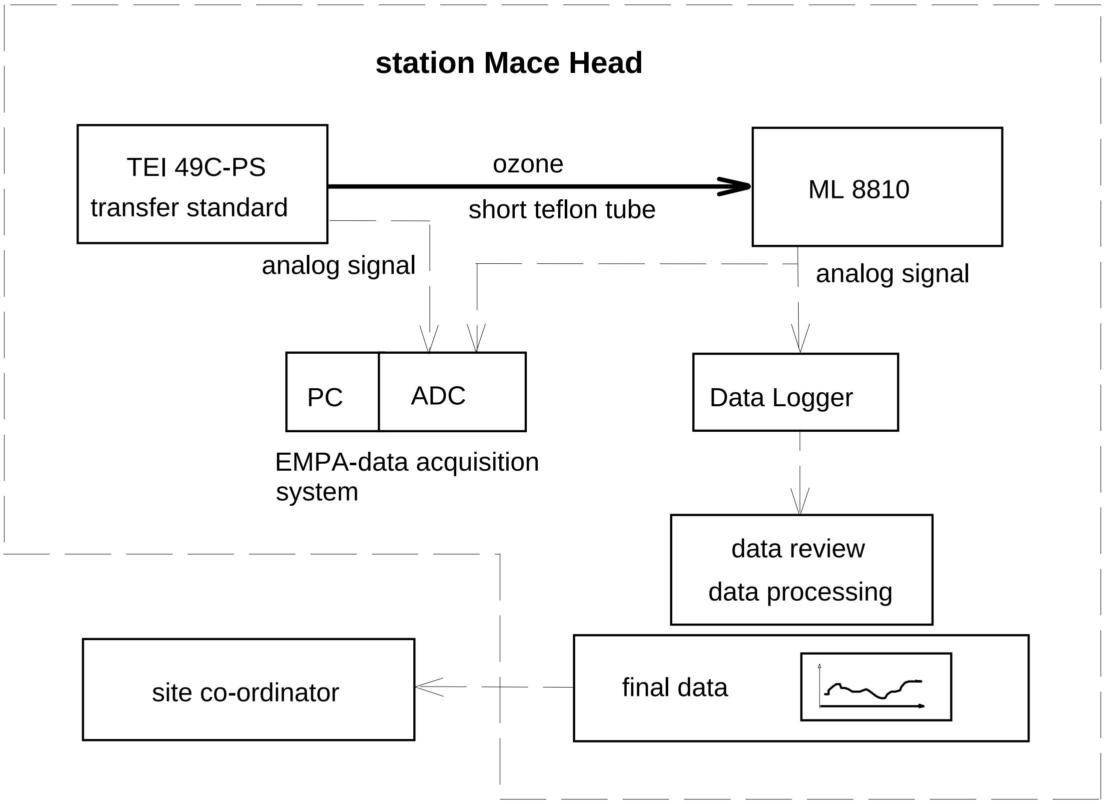


Figure 7: Experimental set up, ozone

## 5.2. Results

The results comprise the three runs of the intercomparisons between the field instrument Monitor Labs 8810 and the transfer standard TEI 49C-PS, carried out on May 25/26, 1998.

In the following tables the resulting mean values of each ozone concentration and the standard deviations (sd) of twenty 30-second-means (10min) are presented. For each mean value the differences between the tested instrument and the transfer standard are calculated in ppb and in %. Further, the diagrams show the results of the linear regression analysis of both field instruments compared to the EMPA transfer standard.

The data used for the evaluation were recorded by the EMPA data acquisition system. From these raw data the zero offset, which was determined at the last NPL multipoint calibrations, was subtracted from the data of the intercomparison. In table 7 to 9 the recalculated data are listed.

Considering the non-linearity of the Monitor Labs analysers of this type (see 4.2) the zero points were not included for calculating the regression lines.

Table 7: 1. Intercomparison, ozone

| No. | transfer standard TEI 49C-PS conc. ppb | transfer standard $S_d$ ppb | ML 8810 #437 conc. (-1.67 ppb) ppb | ML 8810 #437 $S_d$ ppb | deviation from reference ppb | deviation from reference % |
|---|---|---|---|---|---|---|
| 1 | 0.3 | 0.19 | 2.6 | 0.49 | 2.3 | |
| 2 | 29.9 | 0.13 | 30.0 | 0.79 | 0.1 | 0.3% |
| 3 | 49.9 | 0.13 | 50.4 | 0.58 | 0.5 | 0.9% |
| 4 | 10.0 | 0.12 | 11.0 | 0.56 | 1.1 | 10.8% |
| 5 | 19.9 | 0.13 | 19.9 | 0.93 | 0.0 | 0.0% |
| 6 | 89.9 | 0.08 | 90.2 | 0.81 | 0.3 | 0.3% |
| 7 | 0.2 | 0.16 | 2.5 | 0.53 | 2.3 | |

Table 8: 2. Intercomparison, ozone

| No. | transfer standard TEI 49C-PS conc. ppb | transfer standard $S_d$ ppb | ML 8810 #437 conc. (-1.67 ppb) ppb | ML 8810 #437 $S_d$ ppb | deviation from reference ppb | deviation from reference % |
|---|---|---|---|---|---|---|
| 1 | 0.4 | 0.16 | 2.8 | 0.77 | 2.4 | |
| 2 | 19.9 | 0.13 | 20.4 | 0.49 | 0.5 | 2.6% |
| 3 | 49.9 | 0.16 | 50.7 | 1.66 | 0.8 | 1.6% |
| 4 | 89.9 | 0.17 | 89.8 | 0.85 | -0.2 | -0.2% |
| 5 | 30.0 | 0.11 | 30.1 | 0.87 | 0.1 | 0.2% |
| 6 | 10.0 | 0.16 | 10.9 | 0.86 | 0.9 | 9.3% |
| 7 | 0.2 | 0.15 | 2.8 | 0.82 | 2.6 | |

Table 9: 3. Intercomparison, ozone

| No. | transfer standard TEI 49C-PS conc. ppb | transfer standard $S_d$ ppb | ML 8810 #437 conc. (-1.67 ppb) ppb | ML 8810 #437 $S_d$ ppb | deviation from reference ppb | deviation from reference % |
|---|---|---|---|---|---|---|
| 1 | 0.2 | 0.15 | 2.8 | 0.82 | 2.6 | |
| 2 | 49.9 | 0.10 | 51.9 | 1.44 | 2.0 | 3.9% |
| 3 | 20.0 | 0.14 | 20.2 | 1.53 | 0.2 | 1.0% |
| 4 | 30.0 | 0.13 | 31.0 | 1.19 | 1.0 | 3.3% |
| 5 | 90.0 | 0.17 | 89.6 | 0.62 | -0.4 | -0.5% |
| 6 | 10.0 | 0.14 | 10.0 | 1.95 | 0.1 | -0.3% |
| 7 | 0.2 | 0.16 | 2.4 | 0.49 | 2.2 | |

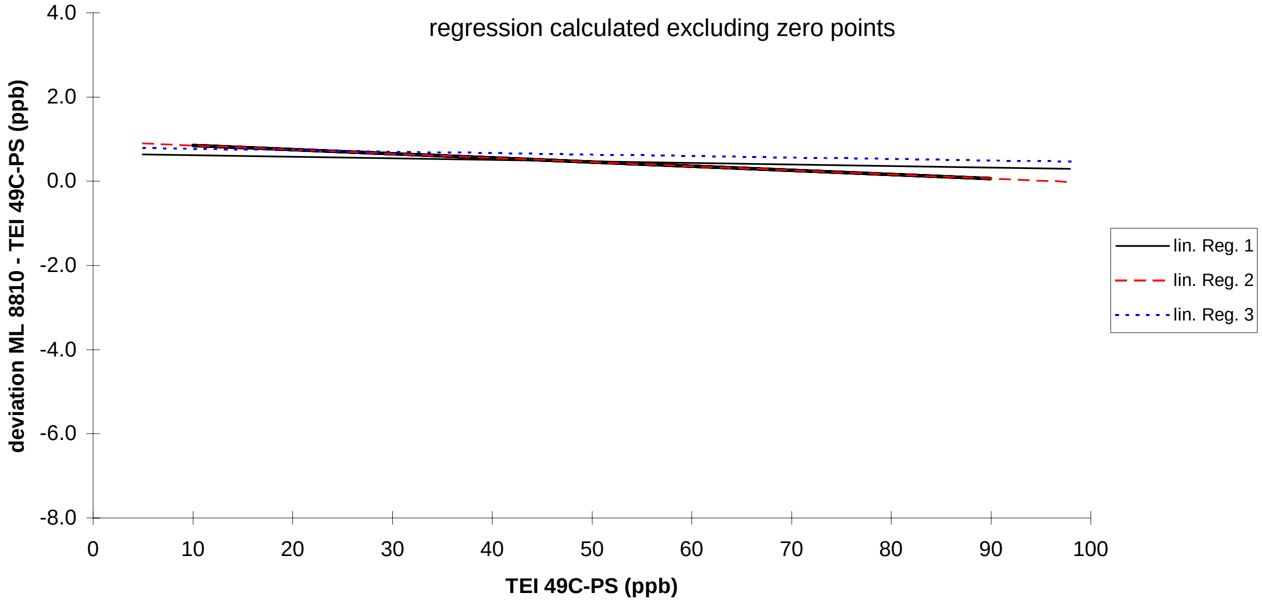


Figure 8: Individual linear regressions of intercomparisons 1 to 3, ML 8810

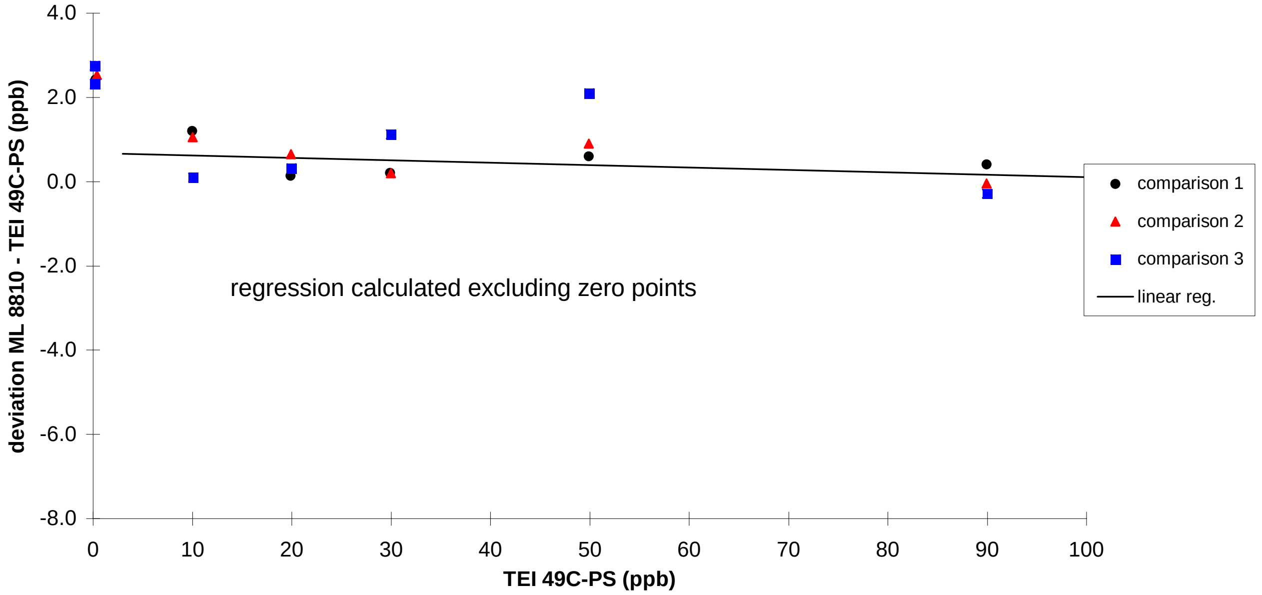


Figure 9: Mean linear regression of intercomparisons 1 to 3, ML 8810

From the intercomparisons of the Monitor Labs instrument ML 8810 #437 with the TEI 49C-PS transfer standard from EMPA the following equation (for the range of 5-100 ppb ozone) results:

$$\text{ML 8810} = 0.994 \times \text{TEI 49C-PS} + 0.7 \text{ ppb}$$

ML 8810 = $O_3$ mixing ratio in ppb, determined for ML 8810 #437

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

| | | | |
|---|---|---|---|
| Standard deviation of: | - slope sm | 0.0056 | (f = 3) f=degree of freedom |
| | - offset Sb in ppb | 0.27 | (f = 3) |
| | - residuals in ppb | 0.83 | (f = 13) |

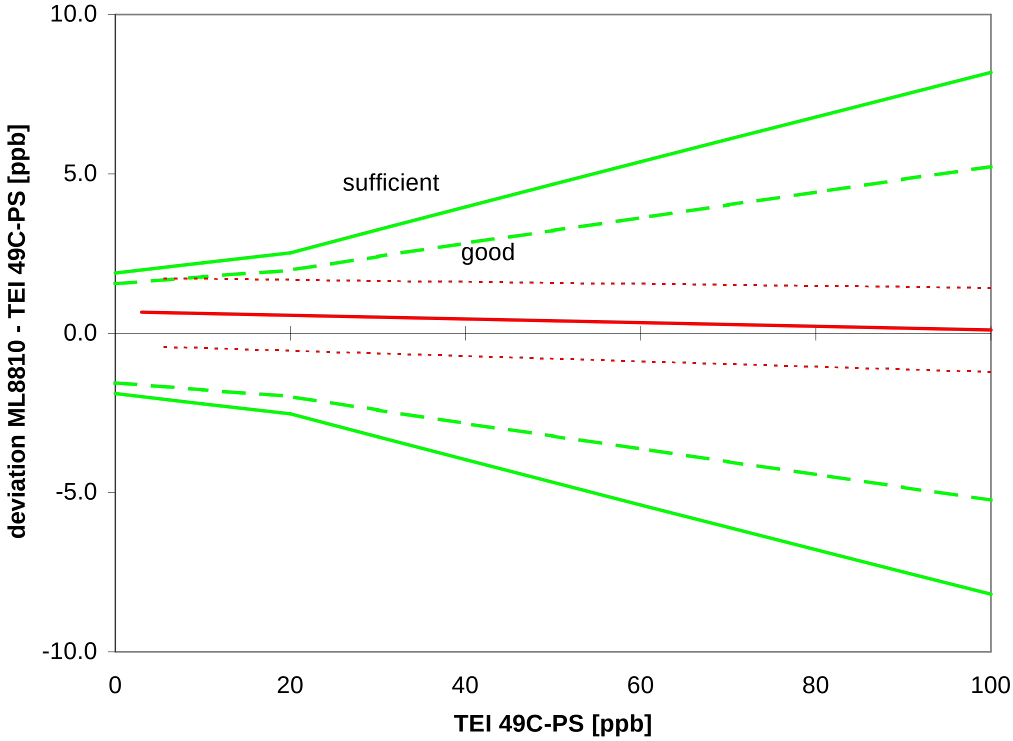


Figure 10: Intercomparison of instrument ML 8810

### Comments

In Figure 8 of the linear regressions no clear trend could be observed during the two days when the intercalibration took place.

The ozone concentration observed at Mace Head (1997) usually ranged between 17 and 48 ppb (5- and 95-percentile of hourly mean values). The instrument fulfils the assessment criteria as "good" over the tested and relevant range up to 100 ppb (figure 10). The stability of the instrument has improved likely due to moving it to the air conditioned laboratory at the ground floor (less shocks).

# 6. Intercomparison of in situ Carbon Monoxide Analyser

## 6.1. Experimental Procedure

No Standard Operation Procedure (SOP) has been established for CO measurements by QA/SAC until now. For this reason, the "SOP for performance auditing ozone analysers at global and regional WMO-GAW sites" (WMO-GAW Report No 97), was adapted for CO accordingly.

At the site the three CMDL CO transfer standards (100, 200 and 300 ppb CO) were stored in the same room as the CO measurement system to equilibrate over the weekend. The cylinders were connected to the measurement system as can be seen in figure 11. The pressure regulators and stainless steel tubings were flushed extensively and leak checked (no drop of pressure for half an hour with main cylinder valve closed). Between 25. – 28. May, each transfer standard was injected and analysed 6 to 11 times. The automated analysis procedure with an injection every 20 minutes was performed in the sequence cycle: ambient air – station working standard – CMDL transfer standard of the WCC. In general, no modification of the carbon monoxide analyser RGA-3 was made for the intercomparison. The chromatograms were acquired by the station "AGAGE GC control" software. The data (mean values and standard deviations) was reprocessed from the station manager and delivered to the WCC.

Finally, the observed results were discussed in an informal review with the person involved.

The audit procedure included a direct intercomparison of the three CMDL transfer standards with the CMDL Laboratory Standard before and after the audit in the WCC calibration laboratory at EMPA.

The station zero air (synthetic air and Sofnocat) was tested after the audit by the station operator. It was found that the treated synthetic air still contains around 5 ppb of CO. The problem with the zero air does not influence the measurements, however, according to the station operator, they will try to solve it.

Table 10: Experimental details, carbon monoxide

| | |
|---|---|
| audit team, WCC | A. Herzog, S. Reimann |
| reference: | CMDL Transfer standards (ppb): FAO1469; FAO1467; FAO1477 |
| field instrument: | RGA-3 #090189-010 |
| zero air supply: | station: synthetic air – Sofnocat |
| data acquisition system: | workstation "AGAGE GC control" software |
| surrounding conditions: | p: 1009 hPa ± 2 hPa and $T_{indoor}$: approx. 21°C |
| number of concentrations: | 3 + zero air of station |
| approx. concentration levels: | 100 / 200 / 300 ppb |
| number of injection per concentration: | 6 to 11 times |
| Sequence | ambient air – working standard – CMDL transfer |

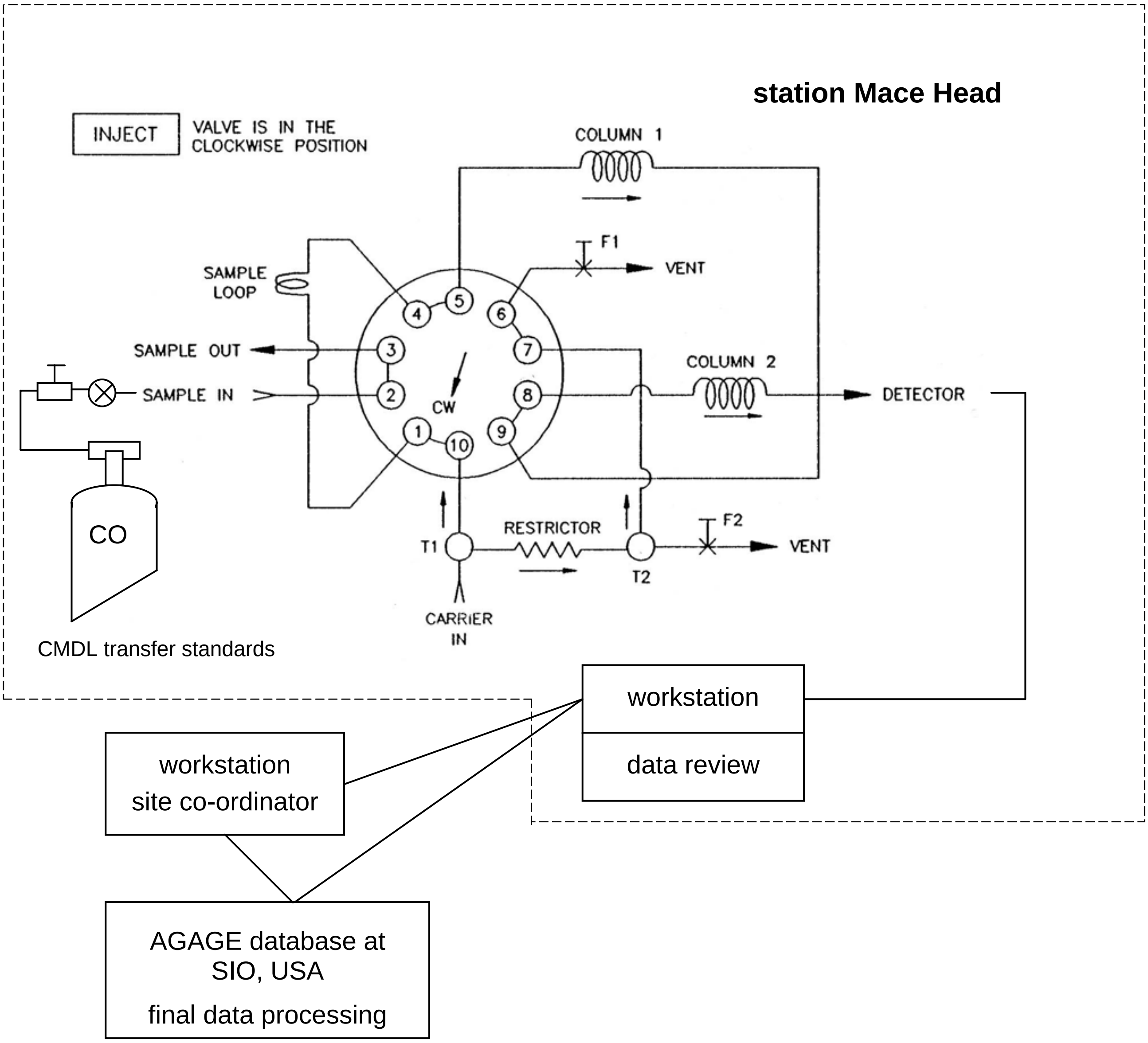


Figure 11: Experimental set up, carbon monoxide

## 6.2. Results

The results consist of the intercomparisons between the field instrument RGA-3 and the three CMDL transfer standards of the WCC, carried out between 25 - 28 May, 1998. The values from the RGA-3 field instrument had been delivered by the station operator and are based on the preliminary CO concentration (174.85) applied to the actual field standard J-025.

In the following table the resulting mean values of each carbon monoxide concentration and the standard deviations are presented. For each mean value the difference between the tested instrument and the transfer standards is calculated in ppb and in %. Further figures 12 and 13 show the results of the linear regression analysis of the field instrument compared to the WCC transfer standards.

Table 11: Intercomparisons, CO

| No. | CMDL standards | RGA-3 #090189-010 | | | | |
|---|---|---|---|---|---|---|
| | conc. | conc. | $s_d$ | No. of | deviation from reference | |
| | ppb | ppb | ppb | injections | Ppb | % |
| 1 | 99.9 | 102.6 | 0.46 | 11 | 2.7 | 2.7 |
| 2 | 202.1 | 199.4 | 0.59 | 6 | -2.7 | -1.3 |
| 3 | 297.8 | 294.0 | 0.59 | 10 | -3.8 | -1.3 |

The summary of the CO comparisons (for the CO range 80 - 320 ppb) of the RGA-3 CO analyser with the WCC transfer standards (CMDL cylinders) is the following linear regression equation:

$$\text{RGA-3} = 0.968 \times \text{CMDL scale} + 5.2 \text{ ppb}$$

RGA-3 = CO mixing ratio in ppb, determined for RGA-3 #090189-010
CMDL scale = CO mixing ratio in ppb from the three CMDL transfer standards of the WCC

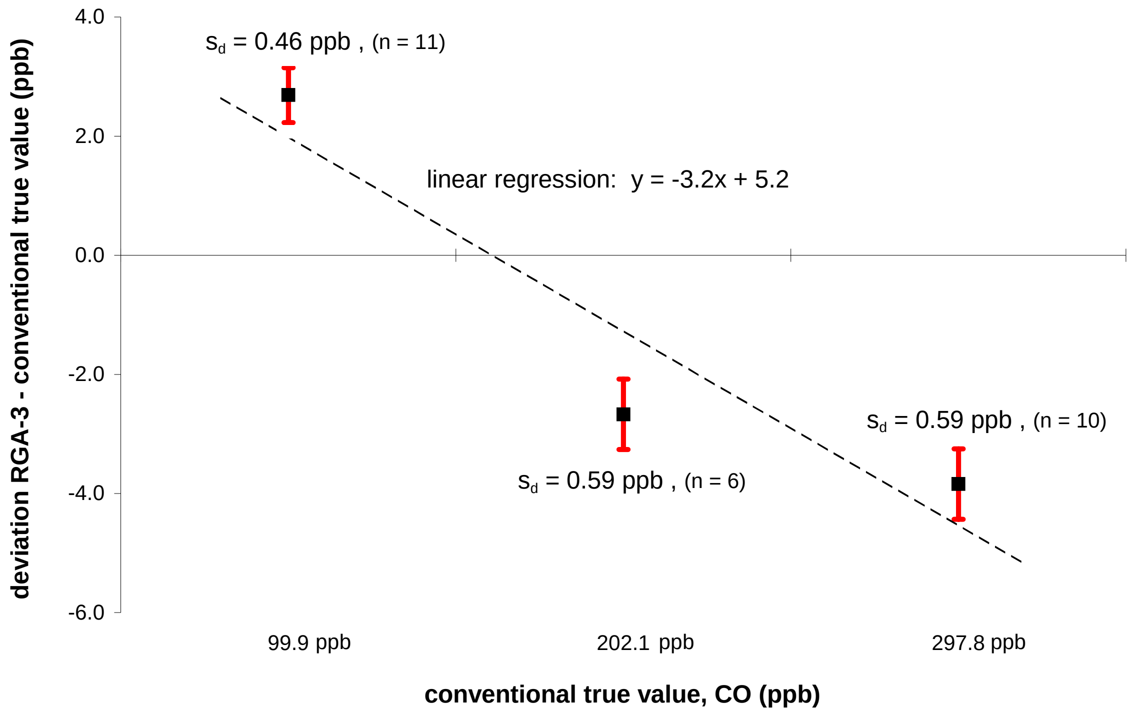


Figure 12: Deviations (ppb) between RGA-3 and CMDL transfer standards (conventional true value)

Figure 12 shows the absolute differences (ppb) between RGA-3 and the CMDL transfer standards (conventional true value). The dotted line is the linear regression line and the red error bars represent the standard deviation of n injections of the same type.

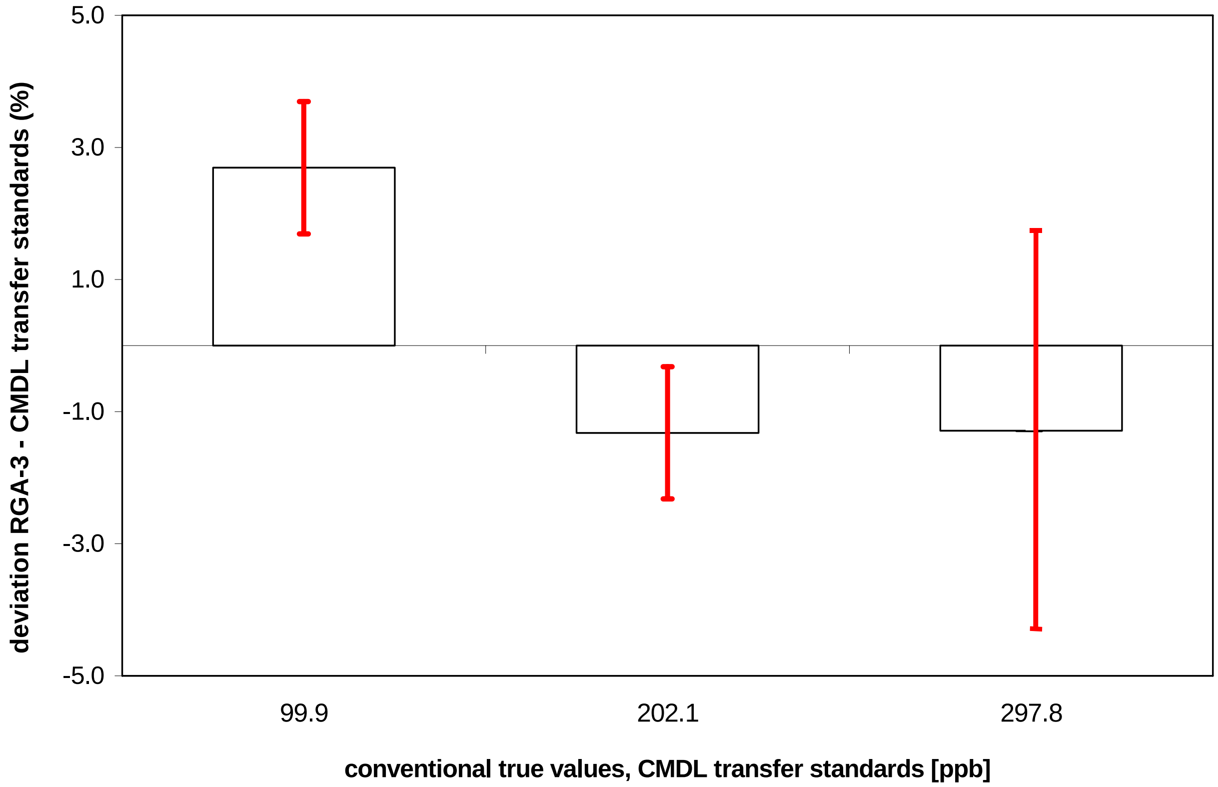


Figure 13: Differences (%) between the RGA-3 and the CMDL transfer standard (the red error bars show the given uncertainty of the CMDL gas cylinders)

### Comment

The results of the CO intercomparison measurements (figure 13) deviate only by about 1 to 3% from the conventional true value with a certified uncertainty of the CMDL transfer standards of approximately 1% until 200 ppb and 3% for 300 ppb. Regarding the relevant range (79 and 214 ppb, 5- and 95-percentile respectively) this is a good result but could be improved considering the nonlinearity of the CO analyser system and applying the results of the regular multipoint calibrations.

# Appendix Ozone

## I National Physical Laboratory (NPL) Intercalibration, Results Extract

In the course of the regular QA measures by NPL on 14. May '98 a back-intercomparison was performed (see 4.4 Operation and Maintenance). This took place a week before this audit and a few days after an instrument service by Enviro Technology. In this report only a brief extract of the NPL report is quoted (table 12). Based on the experience made in the laboratory and field tests for Monitor Labs instruments of the type 8810, non-linearity in the low ppb range (0-5 ppb) could be observed which leads to an instrument dependent offset ranging beween 1 to 3 ppb. Therefore, as recommended by the WCC but in deviation to the NPL evaluation of the intercomparison, the operators are considering this non-linearity and calculate the linear regression by excluding the zero point for the GAW data set. The results of the regression is then: slope 1.0135 and intercept 1.67 ppb as shown below.

Table 12: NPL intercomparison on 14. May '98 at Mace Head, ozone

| No. | NPL transfer standard ppb | ML 8810 #437 raw data ppb |
|---|---|---|
| 1 | 200.0 | 204.2 |
| 2 | 150.0 | 154.0 |
| 3 | 100.0 | 102.5 |
| 4 | 60.0 | 63.5 |
| 5 | 34.8 | 36.3 |
| 6 | 0.6 | 4.8 |

| | | | | | |
|---|---|---|---|---|---|
| ML 8810 | = | 1.0135 x | TS NPL | + 1.67 | excluding zero points |
| ML 8810 | = | 1.0053 x | TS NPL | + 2.84 | including zero points |

ML 8810 = $O_3$ mixing ratio in ppb, determined for ML 8810 #437
TS NPL = $O_3$ mixing ratio in ppb, related to the transfer standard used by the NPL

## II EMPA Transfer Standard TEI 49C-PS

The Model 49C-PS is based on the principle that ozone molecules absorb UV light at a wavelength of 254 nm. The degree to which the UV light is absorbed is directly related to the concentration as described by the Lambert-Beer Law.

Zero air is supplied to the Model 49C-PS through the zero air bulkhead and is split into two gas streams, as shown in Figure 14. One gas stream flows through a pressure regulator to the reference solenoid valve to become the reference gas. The second zero air stream flows through a pressure regulator, ozonator, manifold and the sample solenoid valve to become the sample gas. Ozone from the manifold is delivered to the ozone bulkhead. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa.

The UV light intensities of each cell are measured by detectors A and B. When the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The Model 49C-PS calculates the ozone concentration for each cell and outputs the average concentration.

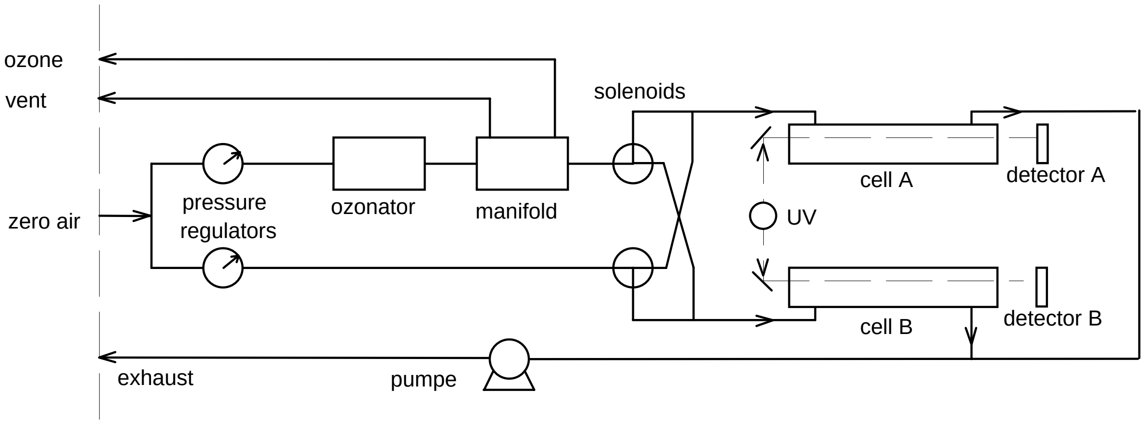


Figure 14: Flow schematic of TEI 49C-PS

## III Stability of the Transfer Standard TEI 49C-PS

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

The procedure and the instruments set up of this intercomparison in the calibration laboratory at EMPA are summarised in Table 13 and Figure 15.

Table 13: Intercomparison procedure SRP - TEI 49C-PS

| | |
|---|---|
| Pressure transducer: | zero and span check (calibrated barometer) at start and end of procedure |
| Concentration range: | 0 - 200 ppb |
| Number of concentrations: | 5 + zero air at start and end |
| Approx. concentration levels: | 30 / 60 / 90 / 125 / 185 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 |
|---|---|

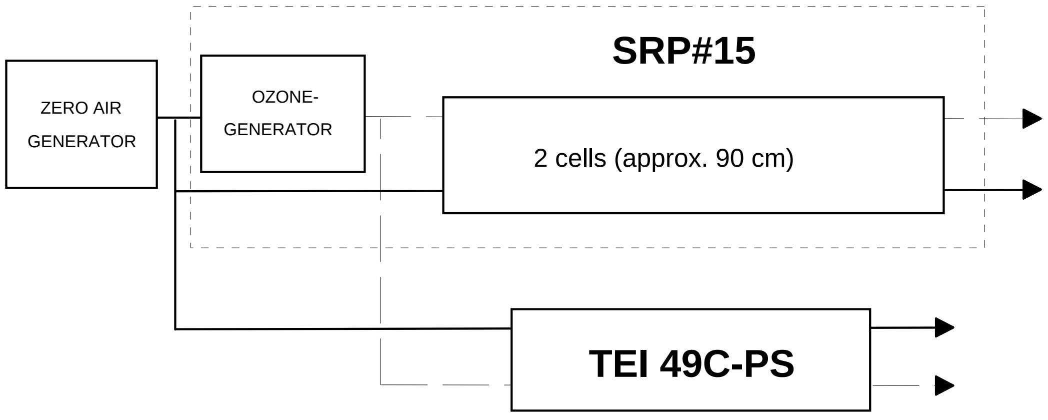


Figure 15: Instrument set up SRP - TEI 49C-PS

The stability of the transfer standard is thoroughly examined with respect to the uncertainties of the different components (systematic error and precision). For the GAW transfer standard of the EMPA-WCC (TEI 49C-PS) the assessment criteria, taking into account the uncertainty of the SRP, are defined to ±(1 ppb + 0.7%).

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

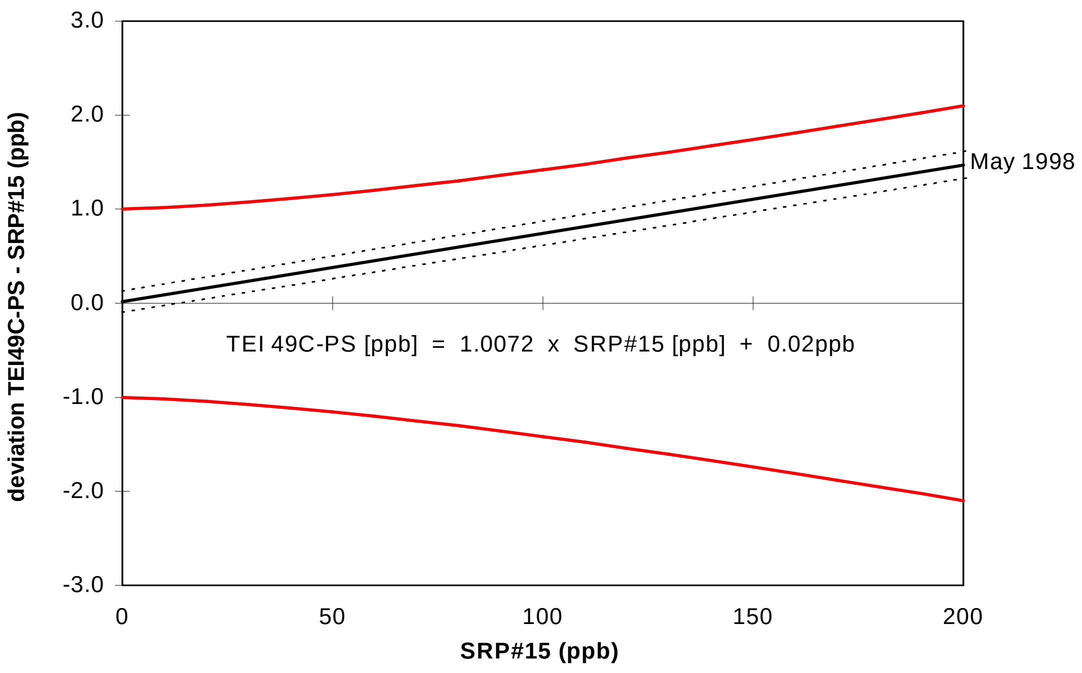


Figure 16: Transfer standard pre-audit check, ozone

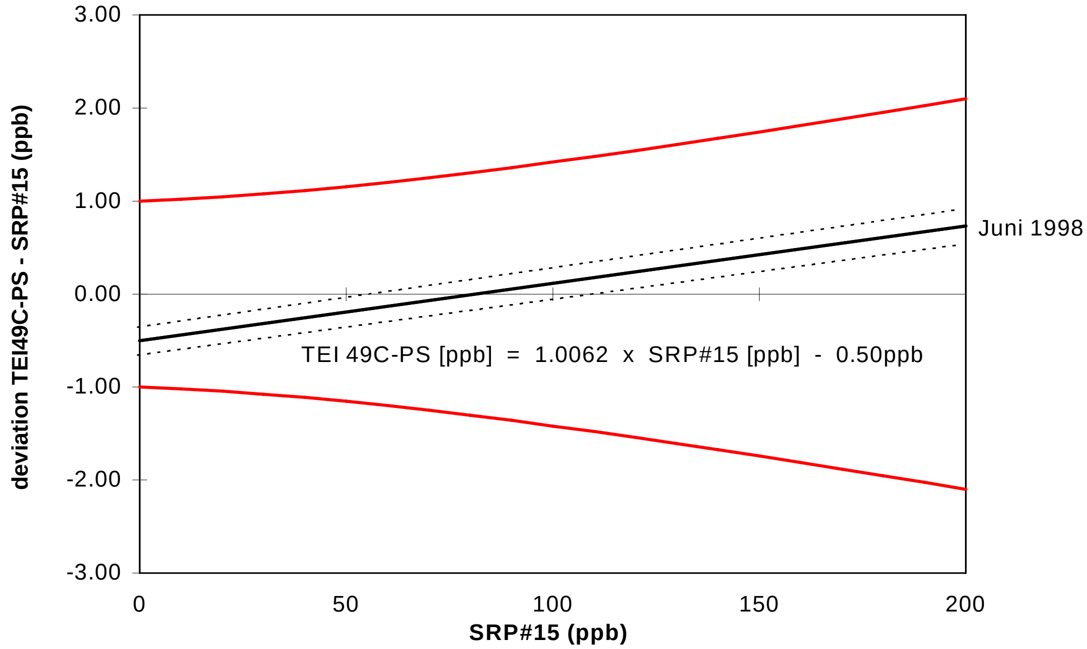


Figure 17: Transfer standard post-audit check, ozone

# Appendix Carbon Monoxide

## WCC CO Standards

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is 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 within the GAW programme. At the WCC we use the following standards:

Table 14: CO Standards at the WCC

| Standard (Gas Cylinders) | CO | Cylinder |
|---|---|---|
| CMDL Laboratory Standard (basis for WCC) | 44.0 ± 1.0 nmole/mole | CA03209 |
| CMDL Laboratory Standard ( " ) | 97.6 ± 1.0 nmole/mole | CA02803 |
| CMDL Laboratory Standard ( " ) | 144.3 ± 1.4 nmole/mole | CA03295 |
| CMDL Laboratory Standard ( " ) | 189.3 ± 1.9 nmole/mole | CA02859 |
| CMDL Laboratory Standard ( " ) | 287.5 ± 8.6 nmole/mole | CA02854 |
| CMDL Transfer Standard (6 l cylinder) | 99.9 ± 1.0 nmole/mole | FAO1469 |
| CMDL Transfer Standard (6 l cylinder) | 202.1 ± 2.0 nmole/mole | FAO1467 |
| CMDL Transfer Standard (6 l cylinder) | 297.8 ± 9.1 nmole/mole | FAO1477 |

| | | |
|---|---|---|
| NIST Reference Standard | 9.8 ± 0.05 μmol/mol | CLM006694 |
| NMI Reference Standard | 10.01 ± 0.04 μmol/mol | 316511 |

The absolute accuracy of the NOAA/CMDL CO scale has not been rigorously determined, but based on the uncertainties of the gravimetric and analytical procedures, and comparisons to the NIST CO scale, the NOAA/CMDL scale is probably accurate to within 3%.

The listed μmol/mol standards from NIST and NMI are checked against the CMDL standards by using dynamic dilution and analysis on an RGA-3 system.