



**Global Atmosphere Watch
World Calibration Centre for Surface Ozone
WCC-O₃**



**Swiss Federal Laboratories for Materials Testing
and Research (EMPA)**

REPORT

**Submitted to the
World Meteorological Organisation**

**SYSTEM AND PERFORMANCE AUDIT
FOR SURFACE OZONE
GLOBAL GAW STATION MACE HEAD
IRELAND, OCTOBER 1996**

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1. Abstract

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

Air Inlet System:

The inlet system, concerning construction materials as well as residence time, is adequate for gas analysis. No loss of ozone could be detected.

Instrumentation:

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

To help improve the stability of the analyser, moving it into the fully air-conditioned laboratory, in the same building, downstairs, is suggested. If this proves to be unsatisfactory, then extensive servicing would be necessary.

Data Handling:

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, could still be improved. Concerning the zero point correction a data treatment that deviates from the actual practice is recommended. For further details see Appendix I and II.

Operation and Maintenance:

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 ozone analysers. The synergies resulting from the affiliation to the UK ozone network have created a high standard of implemented quality assurance.

Documentation:

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.

Competence:

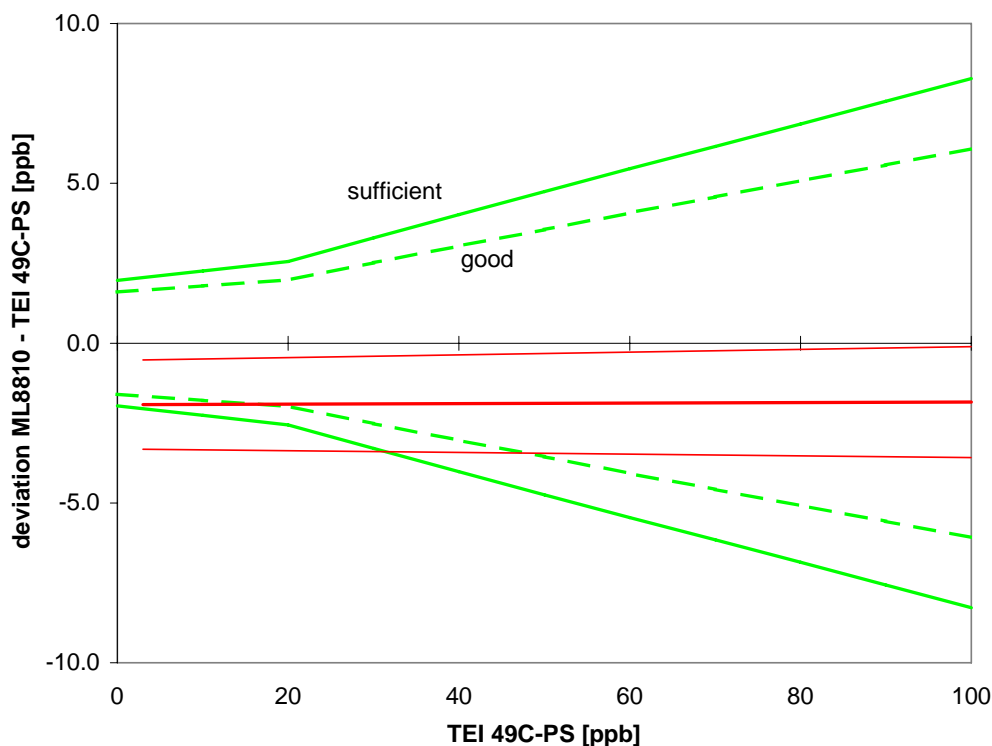
All persons associated directly or indirectly with the operation of the station are highly motivated and experts in their fields. Obviously, due to long-standing experience and adequate education, the operator was very familiar with the techniques and problems connected with ozone measurements.

Instrument Intercomparisons:

The ozone concentration observed at Mace Head (1994) usually ranged between 23 and 47 ppb (5- and 95-percentile of hourly mean values). Considering the range relevant to the site, the field instrument fulfils the assessment criteria as "sufficient", but only partly satisfies them lower than 30 ppb (figure 1). This is due to a substantial offset and a relatively wide precision interval. The reason for the broad precision interval, in particular in the low ppb range, is the large discrepancy of the three intercomparisons (see Fig. 7). This is an indication of the poor stability of the instrument. Possible improvements are discussed in chapter 4.2.

However, deviating from the actual practice of data treatment, we suggest another method, as can be seen in Appendix I and II. In this case, despite a low precision of the instrument, fulfilment of the assessment criteria as "good" could be achieved.

Figure 1: Intercomparison of instrument ML 8810



Dübendorf, 5. November 2007

EMPA Dübendorf, WCC-O₃

Project engineer

Project manager

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2. Introduction

In establishing a co-ordinated 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 Center for Surface Ozone for Europe and Africa (WCC-O₃). At the beginning of 1996 our work started within the GAW programme. The detailed goals and tasks of the WCC-O₃ are described in WMO-GAW Report No. 104.

In agreement with the responsible persons in charge of ozone measurements at the Atmospheric Research Station, Mace Head, Ireland, a 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 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 October 21 to 24 in 1996 was confined to the surface ozone measurements. The entire process, beginning with the inlet system and continuing up to the data processing, and also the supporting measures of quality assurance, were inspected during the audit. The audit at Mace Head 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 intercomparison have been developed by EMPA and are based on WMO Report No. 97 ("Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements" by P. Hofer, B. Buchmann and A. Herzog, 1996, available on request from the authors at: EMPA, 134, Ueberlandstr. 129, CH-8600 Dübendorf).

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

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 3). 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 95'000 inhabitants.

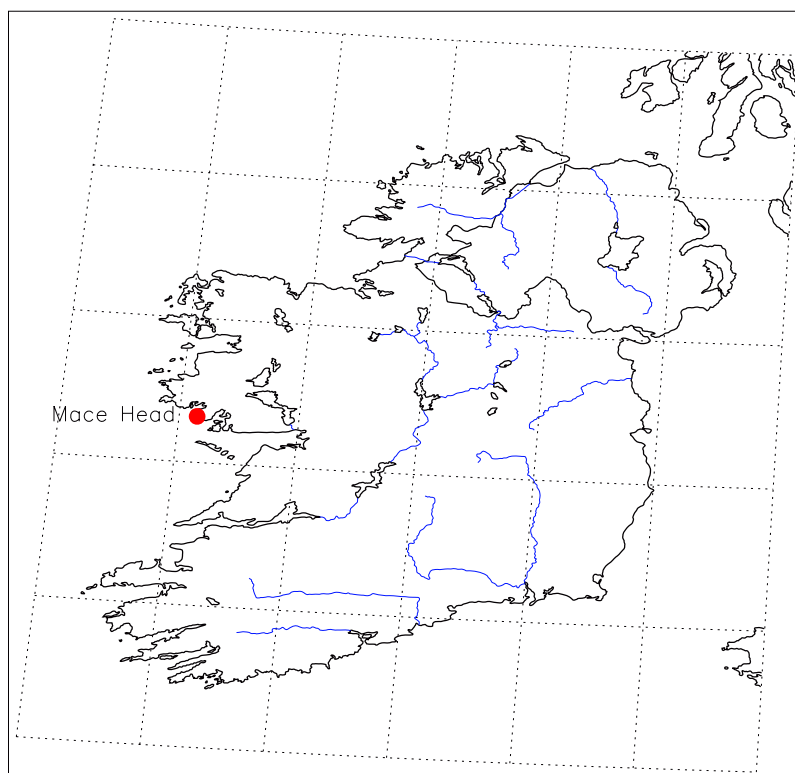
The hilly area around Mace Head is wet and boggy with a lot of exposed rocks and vegetation which consists mainly of grasses and sedges. There are three small islands offshore which are within the clean air sector, and are uninhabited.

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 double story buildings, near the shore, the ozone analyser is installed in the upper floor. The air inlet system for the ozone measurements is mounted on the outside wall at the same level and exposed to the sea.

Figure 2: Picture of the station Mace Head:



Figure 3: Map of Ireland:

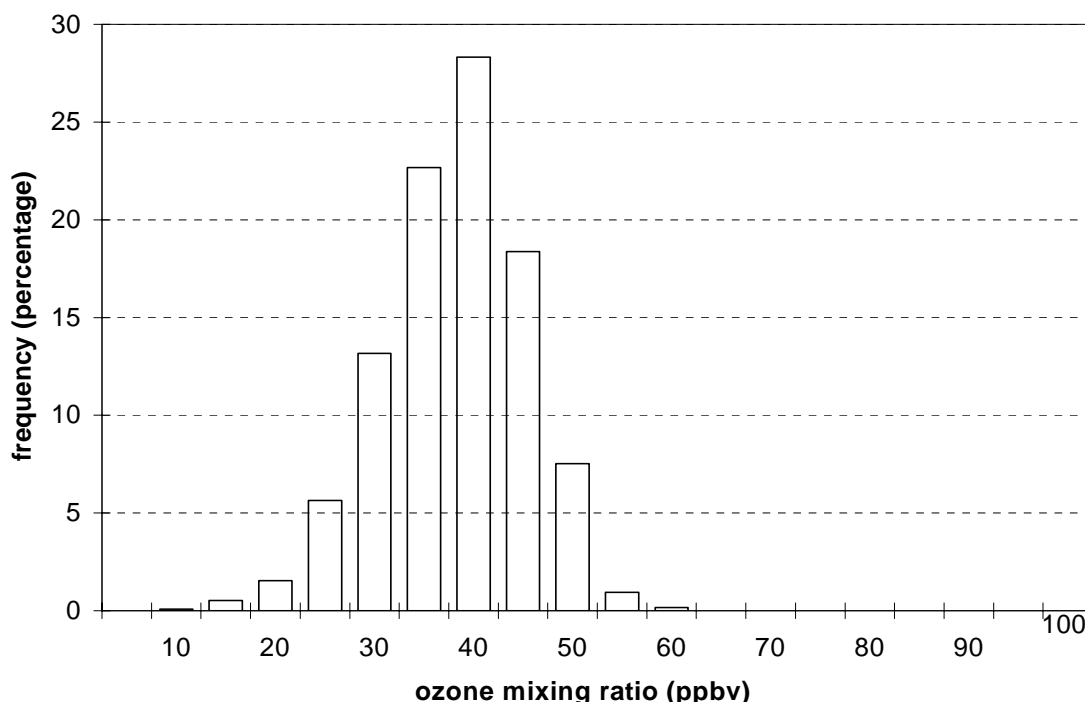


3.2. Ozone Level

The site characteristics and the relevant ozone concentration range can be well defined by the frequency distribution. In figure 4 the frequency distribution of the hourly mean values of the year 1994 is shown. The relevant ozone concentrations were calculated ranging between 23 and 47 ppb according the 5- and 95-percentile of the hourly mean values.

Source of data: Climate and Monitoring and Diagnostics Laboratory (CMDL), NOAA, Boulder, CO
downloaded from the internet: <http://www.cmdl.noaa.gov/surfoz/>

Figure 4: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Mace Head of the year 1994. Data capture higher 96 per cent



3.3. Operators

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

Table 1: Operators

<p style="text-align: center;">Co-ordination and management</p> <p>Dr. Peter Simmonds, consultant Administration and database management</p>
<p style="text-align: center;">Station operator and observer</p> <p>Mr Gerard Spain, physician, University of County Galway (UCG) Station maintenance, data processing, research projects Mr Duncan Brown, deputy</p>
<p style="text-align: center;">QA by National Physical Laboratory (NPL)</p> <p>Mr Brian Sweeney and Mr David Butterfield QA and ozone intercalibrations for the UK network</p>

4. Measurement Technique

4.1. Air Inlet System

The air inlet system for the ozone measurements is mounted approximately one meter outside the wall of the two story building on the upper floor at same level as the ozone analyser and exposed to the sea. 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 hole in the wall to the instrument, which is protected from dust and particles with a teflon inlet filter. The residence time of the ambient air in the inlet line lies between 2 to 3 seconds.

The inlet line was checked with regard to loss of ozone in the third run of the 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 relevant 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 consequence.

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.

4.2. Instrumentation

The instrument is installed on a bench on the upper floor (attic story) in one of the laboratory buildings which is near the shore. The room temperature condition is insufficiently controlled by a low performance mobile air-conditioner so the temperature upstairs can easily rise to 30°C in summer. In such an environment diurnal cycles can hardly be equalised and could be an explanation for the relatively poor stability of the instrument.

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: 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 - flow rate around 1.5 l / min
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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 consequently interference of the detector may occur. This problem is known by the operators and there are plans to move the ozone instrument to the fully air-conditioned laboratory in the same building downstairs, to help improve its stability. We recommend taking this step and if this proves to be unsatisfactory, then extensive servicing would be necessary.

The above mentioned non-linearity of the analyser is acceptable for Mace Head, since ozone concentrations below 5 ppb rarely occur.

4.3. Data Handling

Because of a break down of the regular data acquisition system, an Enviro data logger for averaging the analog output signal of the analyser to hourly mean values was installed at the time of the audit. In parallel, the means were transferred to a printer. The reinstallation of an ADC circuit board to store the data automatically on the computer is planned. The data would then be sent via up to date connection to the station manager.

Data processing consists of a daily or alternate day visual inspection of the raw data. Every few days a data set is prepared and recalculated. This is processed by subtracting the daily zero offset from the obtained data. The daily zero offset is determined by zero check around midnight and is applied to the past day. Together with the instrument logbook, the data set is then revised for errors in connection with special events like circuit-breaks, for example. Diagrams for plausibility control are plotted from the final data set. The checked data are then transferred to the station manager and reviewed again. Until the moment of going to press it was not yet cleared whether the station manager would apply an additional modification to the data and to what databases they will be distributed.

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, could still be improved.

Concerning the zero point correction a data treatment that deviates from the actual practice is recommended. For further details see Appendix I and II.

4.4. Operation and Maintenance

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. The charcoal cartridge of the analyser's zero air supply is renewed every 6 month. For the monthly maintenance a separate checklist is filled in and sent to the station manager.

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, span and zero checks and noise recording.

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 zero and span (100 ppb) checks are 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 ozone analysers. The synergies resulting from the affiliation to the UK ozone network have created a high standard of implemented quality assurance.

4.5. 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" 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 manager 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.

4.6. Competence

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

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 night, in deviation to GAW Report No. 97 which recommends only one hour of warm-up. During this stabilisation time the standard and the PFA tubing connections to the instruments were conditioned with 200 ppb ozone. During the next two days, three comparison runs between the field instrument and the EMPA transfer standard were performed. In the meantime the inlet system and the station documentation were inspected. Table 3 shows the experimental details and Figure 5 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. As an additional check, the EMPA data acquisition and the data logger on site were compared but showed no discrepancy. Finally, the observed results were discussed in an informal review with the person involved.

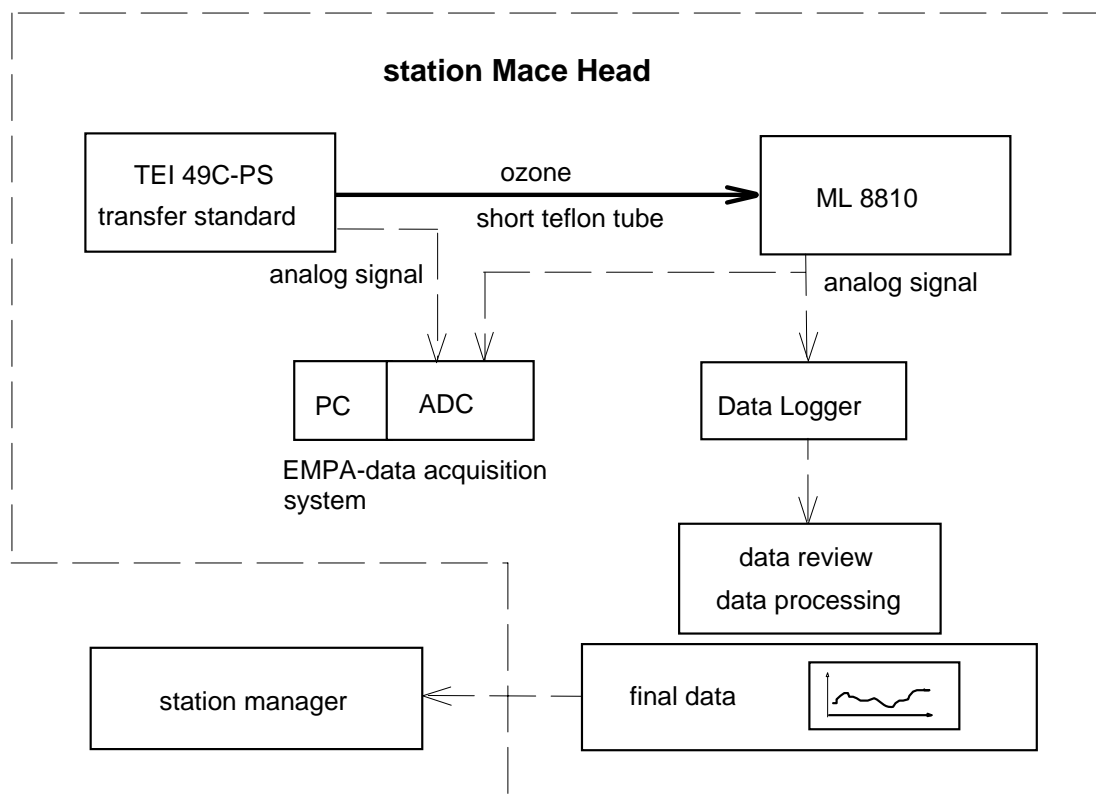
The audit procedure included a direct intercomparison of the TEI 49C-PS transfer standard with the Standard Reference Photometer SRP#15 (NIST UV photometer) before and after the audit in the calibration laboratory at EMPA. The results are shown in the Appendix IV.

Table 3: Experimental details

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 μ m - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 μ m
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 to 15 minutes
number of runs:	1 x on October 22, 1996 2 x on October 23, 1996

connection between instruments:	1. / 2. run: less than 1 meter of 1/4" PFA tubing 3. run: total inlet line, 4.5 m, 1/4" PFA tubing
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Figure 5: Experimental set up



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 October 22/23, 1996.

In the following tables the resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty to thirty 30-second-means (10 to 15 min) 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 the field instrument compared with the EMPA transfer standard. The results of the three runs are then summarised to the mean regression equation and presented with the assessment criteria for GAW field instruments (Figure 8).

The data used for the evaluation were recorded by the EMPA data acquisition system. These raw data were treated according to the station SOP "Local site operator manual" for ambient air measurements. Corresponding to this procedure the daily zero offset was determined by zero check around midnight and was applied to the data of the intercomparison of the past day (see 4.3.). In table 4 to 6 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 4: 1. Intercomparison

No.	TE 49C-PS		ML 8810 #437			
	conc.	S _d	conc. (-3.5 ppb) *	S _d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.5	0.12	0.7	0.42	0.2	
2	49.8	0.11	48.3	1.33	-1.6	-3.2%
3	9.9	0.16	8.2	1.19	-1.8	-17.8%
4	29.8	0.14	27.8	1.12	-2.0	-6.8%
5	89.8	0.10	87.1	0.81	-2.6	-2.9%
6	19.9	0.18	17.7	1.05	-2.2	-11.0%
7	0.4	0.12	-0.3	0.70	-0.8	

Table 5: 2. Intercomparison

No.	TE 49C-PS		ML 8810 #437			
	conc.	S _d	conc. (-3.5 ppb) *	S _d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.5	0.14	1.3	0.14	0.8	
2	19.7	0.14	19.0	2.10	-0.8	-3.9%
3	49.7	0.13	47.5	3.50	-2.2	-4.5%
4	10.1	0.17	8.6	1.15	-1.5	-14.5%
5	89.6	0.14	88.2	2.54	-1.4	-1.6%
6	29.8	0.14	26.5	1.31	-3.3	-11.1%
7	0.4	0.09	0.1	0.99	-0.2	

Table 6: 3. Intercomparison

No.	TE 49C-PS		ML 8810 #437			
	conc.	S _d	conc. (-3.5 ppb) *	S _d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.2	0.15	0.4	0.75	0.2	
2	49.8	0.12	48.2	1.93	-1.6	-3.2%
3	19.8	0.14	16.9	1.13	-2.9	-14.8%
4	89.7	0.13	88.4	1.58	-1.3	-1.4%
5	10.0	0.13	8.4	1.38	-1.7	-16.4%
6	29.8	0.12	28.3	1.20	-1.5	-5.0%
7	0.1	0.16	0.4	0.84	0.3	

★ data treatment regarding the station SOP "Local site operator manual"

Figure 6: Individual linear regressions of intercomparisons 1 to 3, ML 8810

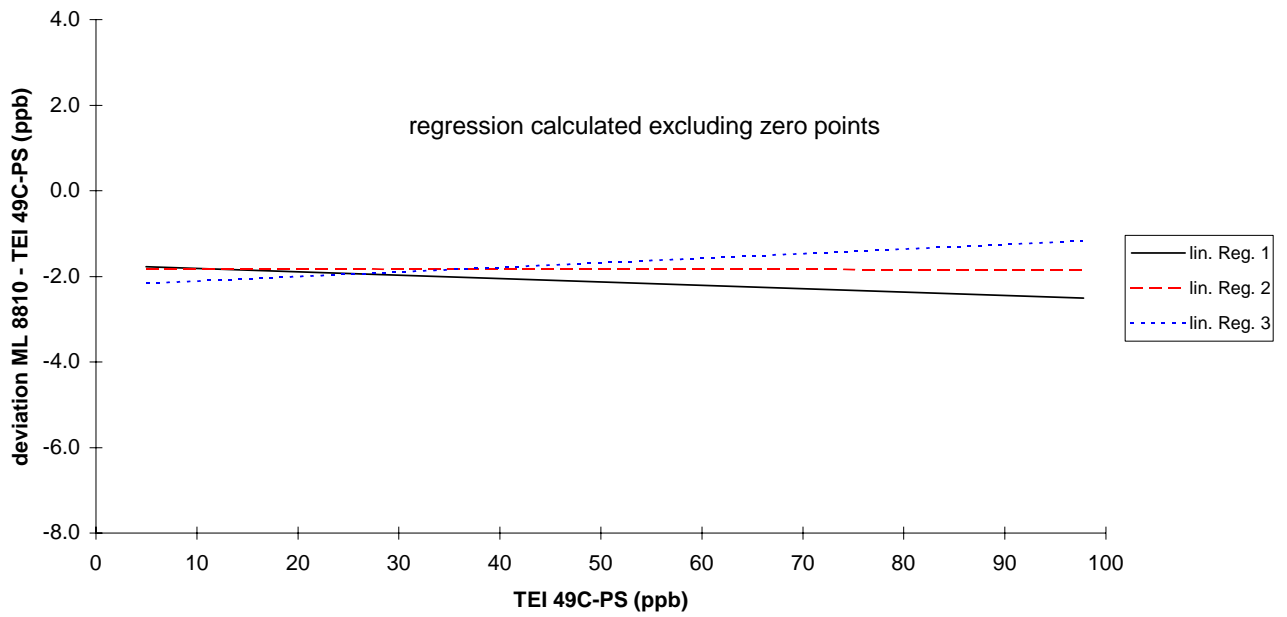
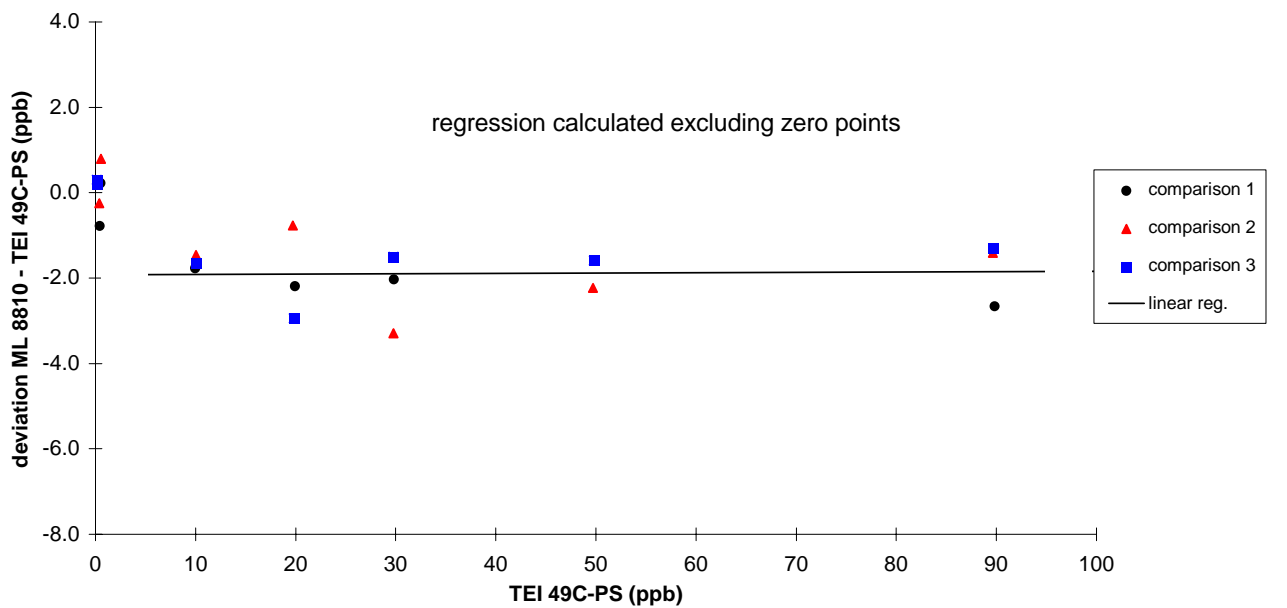


Figure 7: Mean linear regression of intercomparisons 1 to 3, ML 8810



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:

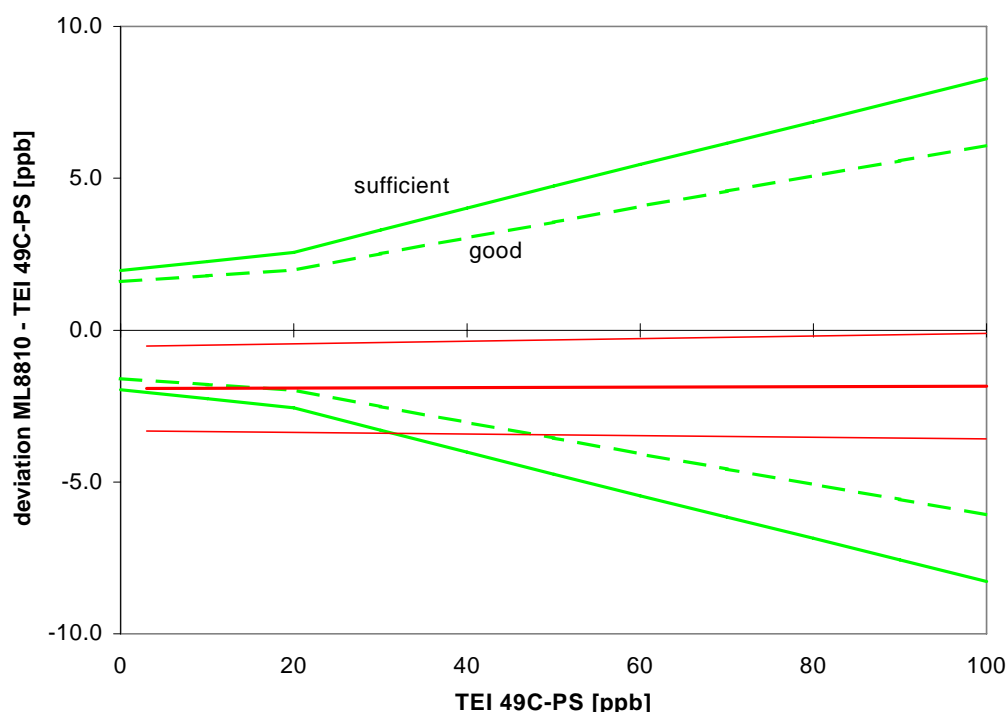
$$\text{ML 8810} = 1.001 \times \text{TEI 49C-PS} - 1.93 \text{ ppb}$$

ML 8810 = O₃ mixing ratio in ppb, determined for ML 8810 #437

TEI 49C-PS = O₃ mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of: - slope s_m	0.0064 (f = 3) <small>f=degree of freedom</small>
- offset S_b in ppb	0.31 (f = 3)
- residuals in ppb	0.95 (f = 13)

Figure 8: Intercomparison of instrument ML 8810



Comments

In Figure 6 of the linear regressions no clear trend could be observed during the two days when the intercalibration took place. Such a drift could indicate insufficient warm up time (stability) or pollution in the measurement cell of the instrument.

The ozone concentration observed at Mace Head (1994) usually ranged between 23 and 47 ppb (5- and 95-percentile of hourly mean values). Considering the range relevant to the site, the field instrument fulfils the assessment criteria as "sufficient", but only partly satisfies them lower than 30 ppb (figure 8). This is due to a substantial offset and a relatively wide precision interval. The reason for the broad precision interval, in particular in the low ppb range, is the large discrepancy of the three intercomparisons (see Fig. 7). This is an indication of the poor stability of the instrument. Possible improvements are discussed in chapter 4.2.

However, deviating from the actual practice of data treatment, we suggest another method, as can be seen in Appendix I and II. In this case, despite a low precision of the instrument, fulfilment of the assessment criteria as "good" could be achieved.

Appendix

I National Physical Laboratory (NPL) Intercalibration, Results Extract

In the course of the regular QA measures by NPL on 17. October '96 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's service by Enviro Technology. In this report only a brief extract of the NPL report is quoted (table 7). 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 of about 1 to 3 ppb. Therefore, in deviation to the NPL evaluation of the intercomparison, we propose considering this non-linearity to calculate the linear regression excluding the zero point. The results of the regression would be then a slope of 1.006 and an intercept of 1.61 ppb as shown below.

Table 7: NPL intercomparison on 17. October '96 at Mace Head

No.	NPL transfer standard ppb	ML 8810 #437 raw data ppb
1	200.0	203.3
2	150.0	151.4
3	100.0	101.6
4	60.0	64.9
5	34.0	34.0
6	0.6	6.0

$$\text{ML 8810} = 0.994 \times \text{TS NPL} + 3.36 \quad \text{including zero points}$$

$$\text{ML 8810} = 1.006 \times \text{TS NPL} + 1.61 \quad \text{excluding zero points}$$

ML 8810 = O₃ mixing ratio in ppb, determined for ML 8810 #437

TS NPL = O₃ mixing ratio in ppb, related to the transfer standard used by the NPL

II Recommendation for Data Treatment at Mace Head

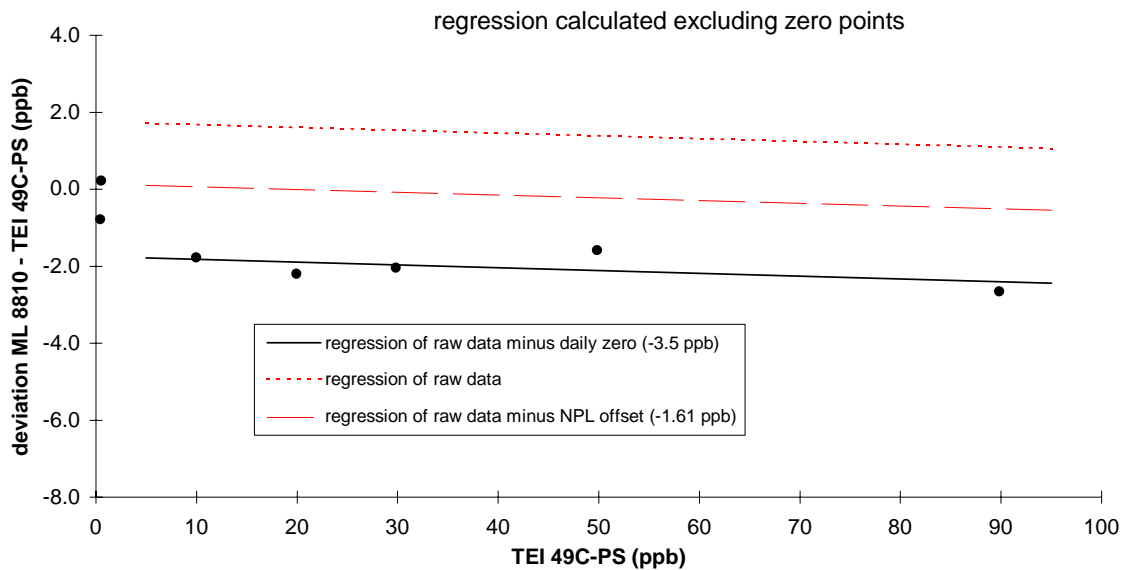
The following recommendation takes into consideration the discussed non-linearity of the ozone analyser in the report and the results of the intercomparison by NPL above. It suggests applying a constant offset factor to the obtained data set for the time between two intercomparisons. This factor can be defined by NPL's intercalibrations by excluding zero. This proposal is made because it is believed that it comprises the experimental findings of the practise better than the actual data treatment.

As an example, in the following table 8 and figure 9 the NPL offset correction was applied on the results of the first run of the intercalibration. Obviously, the zero points were again neglected for the linear regression.

Table 8: Example: Results of intercomparison 1

No.	TEI 49C-PS	raw data	ML 8810	
	transfer standard		- 3.5 ppb daily zero check	- 1.61 ppb NPL calibration offset
	ppb	ppb	ppb	ppb
1	0.5	4.2	0.7	2.6
2	49.8	51.8	48.3	50.2
3	9.9	11.7	8.2	10.1
4	29.8	31.3	27.8	29.7
5	89.8	90.6	87.1	89.0
6	19.9	21.2	17.7	19.6
7	0.4	3.2	-0.3	1.6

Figure 9: Example: Linear regressions of intercomparison 1, ML 8810



Using the NPL intercept of the regression equation (excluding zero) the results of the audit, including now all three runs, would be the following:

$$ML\ 8810 = 1.001 \times TEI\ 49C-PS - 0.32\ ppb$$

ML 8810 = O₃ mixing ratio in ppb, determined for ML 8810 #437

TEI 49C-PS = O₃ mixing ratio in ppb, related to TEI 49C-PS #54509-300

It is noted that treating the data in the recommended way would result in fulfilling the assessment criteria as "good".

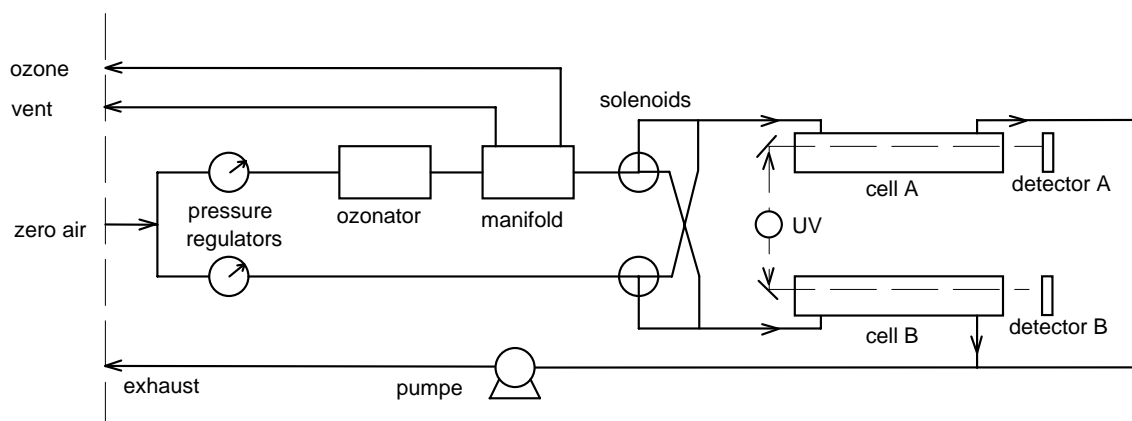
III EMPA Transfer Standard TEI 49C-PS

The Model 49C-PS is based on the principle that ozone molecules absorb UV light at a wavelength of 254 nm. The 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 10. 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 10: Flow schematic of TEI 49C-PS



IV Stability of the Transfer Standard TEI 49C-PS

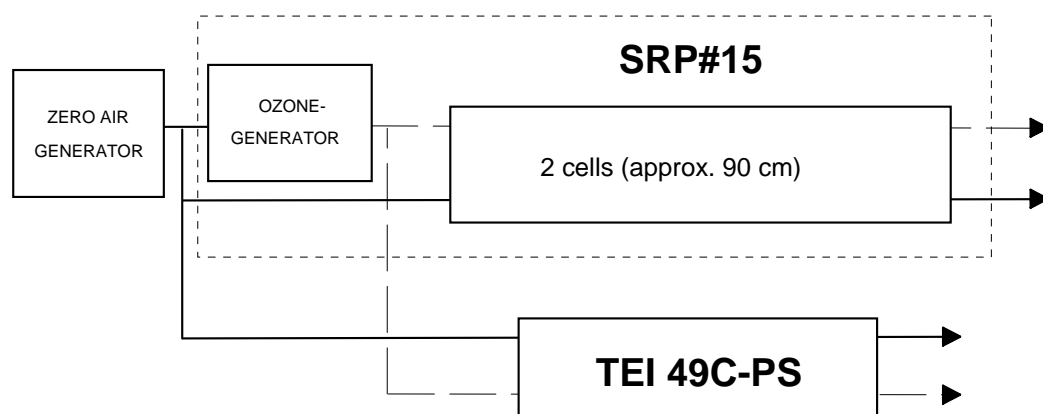
To exclude errors which might occur through transportation of the transfer standard, the TEI 49C-PS #54509-300 has to be compared with the SRP#15 before and after the field audit.

The procedure and the instruments set up of this intercomparison in the calibration laboratory at EMPA are summarised in Table 9 and Figure 11.

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 - 250 ppb
number of concentrations:	6 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 120 / 180 / 240 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	2 before and 2 after audit
zero air supply:	Pressurised air - activated charcoal - zero air generator (AADCO)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

Figure 11: Instruments set up SRP - TEI 49C-PS



The stability of the transfer standard is thoroughly examined with respect to the uncertainties of the different components (systematic error and precision). For the GAW transfer standard of the WCC-O₃ (TEI 49C-PS) the assessment criteria, taking into account the uncertainty of the SRP, are defined to $\pm(1 \text{ ppb} + 0.7\%)$.

Figures 12 and 13 show the resulting linear regression and the corresponding 95% precision interval for the comparisons of TEI 49C-PS vs. SRP#15. Clearly, the results show that the EMPA transfer standard fulfilled the recommended criterias for the periode of the audit, including transportation.

Figure 12: Transfer standard before audit

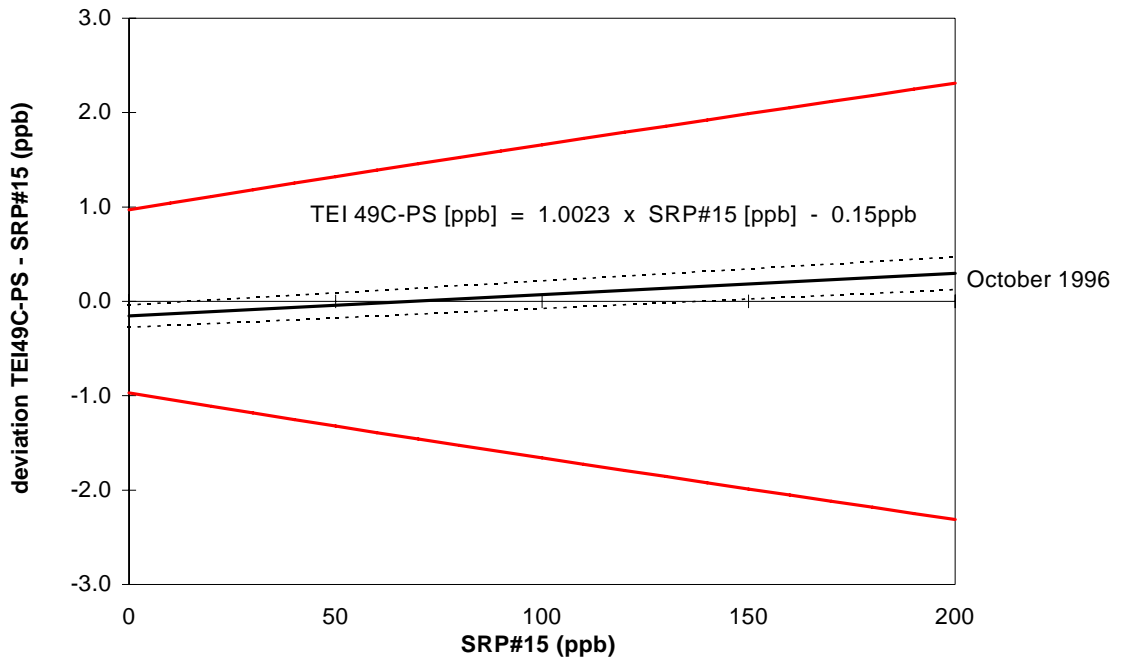


Figure 13: Transfer standard after audit

