Global Atmosphere Watch
World Calibration Centre
for Nitrous Oxide

WCC-N_2O REPORT 2008/11

Report to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT FOR NITROUS OXIDE

GLOBAL GAW STATION IZAÑA

TENERIFE, SPAIN, NOVEMBER 2008

Submitted by

H.E. Scheel

WMO World Calibration Centre for Nitrous Oxide

Karlsruhe Institute of Technology
IMK-IFU, Garmisch-Partenkirchen, Germany

under contract with

Umweltbundesamt (UBA)
QA/SAC Germany

WCC-N_2O Report 2008 / 11

November 2009

Contact information:

WCC-N_2O
c/o Karlsruhe Institute of Technology (KIT) [formerly Forschungszentrum Karlsruhe]
IMK-IFU
Kreuzeckbahnstr. 19
82467 Garmisch-Partenkirchen, Germany

Phone: +49 8821 183 257
Fax: +49 8821 73573
E-mail: hans-eckhart.scheel@kit.edu

Contents:

1 Summary and Recommendations

1.1 General

A system and performance audit for nitrous oxide (N_2O) was conducted at the Global Atmosphere Watch (GAW) station Izaña by the World Calibration Centre for N_2O (WCC-N_2O) on 11-12 November 2008. It was the first N_2O audit at the site and was conducted according to the WMO/GAW guidelines and SOPs for audits as existing in November 2008. The audit directly involved the project leader Greenhouse Gases and partly the manager of instrumentation and infrastructure of the station. This report is for distribution to the project manager, the GAW Country Contact, the WMO/GAW secretariat as well as QA/SAC-Germany.

1.2 System Audit of the Observatory

The global GAW station Izaña offers very good facilities for atmospheric monitoring and research. The installations for ambient air sampling and measurements of N_2O as well as other trace gases, notably CO_2, CH_4, CO and surface O_3, fulfil WMO/GAW requirements. All systems are operated with great care. The operator responsible for the measurements and data evaluation is well-experienced and highly motivated.

Due to its favourable clean-air location in the Atlantic Ocean and its instrumentation, the station is well suited for making measurements of background concentrations for a number of species. Izaña therefore forms an important part within the GAW network. It is noted that the station serves as a platform for other monitoring and research projects and forms part of the Izaña Atmospheric Research Centre with a wide scope of activities in atmospheric research.

1.3 Audit of the N_2O Measurements

The gas-chromatographic system with its peripheral devices represents state-of-the art instrumentation and is well suited for high-quality N_2O measurements. As part of the audit, the individual procedures from operation to data management were considered and generally found to comply well with WMO/GAW requirements.

As part of the audit, a comparison with five WCC-N_2O travelling standards was conducted. It has shown differences "IZO – WCC" [ppb] ranging between 0.12 ppb for the lowest mole fraction (295.89 ppb) and – 0.32 ppb for the highest (347.47 ppb).

The deviations show a small, but systematic dependence on mole fraction (Table 4 and Fig. 13). The smallest value is obtained for the test candidate (at 318.97 ppb) close to the ambient level of N_2O.

1.4 Recommendations

The following recommendations are listed according to their priority. Priorities from high to low are classified by star symbols, ranging from three to one, respectively.

1.4.1 Recommendation 1 (★★★)

The installation of metal frames or other constructions for securing the cylinders is an urgent matter of laboratory safety. This severe safety gap came to the fore during the audit, and is therefore mentioned here as a high-priority recommendation. However, it is noted that appropriate installations were made before this audit report was finalised.

1.4.2 Recommendation 2 (★★)

It is recommended to install a target gas with N_2O mole fraction close to ambient levels as a permanent quality control measure. Samples from it should be run once or twice daily.

1.4.3 Recommendation 3 (★★)

The submission of N_2O data together with respective meta-data to the WDCGG is strongly recommended after all N_2O data have been carefully reviewed.
Moreover, the entries for Izaña in the GAWSIS data base should be carefully reviewed on a regular basis and updated upon need.

1.4.4 Recommendation 4 (★★)

Based on the situation during the audit, the preparation of a web page is strongly encouraged. However, it is noted that a very comprehensive homepage of the station has been created in 2009, i.e. before this audit report was finalised (http://www.aemet.izana.org/index.php?lang=en).

1.4.5 Recommendation 5 (★)

Comparisons with NOAA results from flask samples taken at IZO are encouraged.

1.4.6 Recommendation 6 (★)

The preparation of time series plots of all relevant parameters for different periods, notably months and years, is recommended. In particular, a graphical visualisation of mole fractions on a routine basis should be implemented.

1.4.7 Recommendation 7 (★)

It is recommended to try improving the separation of SF_6 from N_2O in the chromatogram.

1.4.8 Recommendation 8 (★)

Since the ECD was operated in the fast response mode, it is recommended to perform tests of the slow response mode. Possibly this might improve the repeatability of the GC results. However, it is noted that such tests have been carried out during one month by the Izaña GHGs project leader before this audit report was finalised, obtaining no improvement in the repeatability of peak height when using the slow response mode.

1.5 Conclusions

The global GAW station Izaña (IZO) is an important part of the GAW network. Because of its location and its modern facilities, the station is well suited for providing data sets of representative concentrations for a number of species.

The station has passed its first N_2O audit well, and has achieved excellent results for the intercomparison with five WCC-N_2O travelling standards.

1.6 Summary Ranking of the N_2O Audit at the Station Izaña

Audit Aspect	Adequacy		Comment
	(0 = inadequate (□□□□□) through 5 = adequate (■■■■■))		
Access	■■■■■	(5)	
Facilities			
Laboratory and office space	■■■■■	(5)	
Air conditioning	■■■■■	(5)	
Power supply	■■■■■	(5)	
General management and operation	■■■■■	(5)	
Organisation	■■■■■	(5)	
Competence of staff	■■■■■	(5)	
Air inlet system	■■■■■	(5)	
Instrumentation			
Trace gases	■■■■■	(5)	
Instrumental performance N_2O	■■■■■	(5)	
Standards	■■■■■	(5)	Complete set of laboratory standards (NOAA-calibrated)
Data management			
Data acquisition	■■■■■	(5)	
Data processing	■■■■■	(5)	
Data submission	□□□□□	(0)	No N_2O data submitted yet
Documentation			
Log books and internal instructions	■■■■■	(5)	
Web site	■■■■■	(5)	No yet at the time of the audit, but excellent presentation thereafter.
GAWSIS	■■■■□	(4)	Should be checked for errors

WCC-N_2O, Garmisch-Partenkirchen, November 2009

2 Introduction

The Global GAW Station Izaña (IZO) is part of Spain's contribution to the World Meteorological Organization Global Atmosphere Watch (WMO/GAW) programme.

The German Environment Agency (Umweltbundesamt, UBA) was assigned by WMO to operate a Quality Assurance/Science Activity Centre (QA/SAC Germany), which – among others – takes over responsibilities for the operation of a GAW World Calibration Centre for Nitrous Oxide (WCC-N_2O). Under contract with UBA, the Institute for Meteorology and Climate Research, IMK-IFU of the Karlsruhe Institute of Technology (KIT), formerly Forschungszentrum Karlsruhe, was designated to operate the WCC-N_2O.

Preliminary Measurement Guidelines for N_2O (MG-N_2O) have been compiled within GAW, with the WCC-N_2O acting as lead author and editor. While the MG progressed, they were discussed within GAW at several occasions. The Data Quality Objectives (DQO) and quality control measures set out therein are used for audits performed by the WCC-N_2O as agreed upon by the GAW Scientific Advisory Group for Greenhouse Gases (SAG GG).

In agreement with the Izaña WMO/GAW greenhouse gas project manager, a system and performance audit was conducted at the station by the WCC-N_2O on 11-12 November 2008.

The audit under consideration was performed according to the procedure detailed in the preliminary documents. As a central part of the audit procedure, a N_2O intercomparison based on five travelling standards (TS) of the WCC-N_2O was conducted. Moreover, the whole measurement set-up as well as data processing and quality assurance measures were reviewed. Since this was the first WMO/GAW system and performance audit for N_2O at the station Izaña, the technical details of the N_2O measurements are described in this audit report in some detail.

In 2006 the Central Calibration Laboratory (CCL) for N_2O, operated by NOAA ESRL GMD (formerly NOAA CMDL), was developing an update of its NOAA-2000 scale. Moreover, the CCL conducted an intercomparison with the Scripps Institution of Oceanography (SIO), where the widely used SIO-98 scale for N_2O is maintained. Thereafter the new NOAA-2006 scale and the outcome of the intercomparison have been published by Hall et al. (2007). All N_2O mole fractions of the WCC-N_2O are now related to the NOAA-2006 scale.

3 System and Performance Audit for Nitrous Oxide (N_2O)

3.1 Description of the Site

The following brief description of the Izaña station is mainly taken from the detailed information provided under GAWSIS, www.empa.ch/gaw/gawsis/ and by the recently created web site of the observatory
http://www.aemet.izana.org/index.php?option=com_content&view=article&id=44&Itemid=45&lang=en.

Izaña (Tenerife, Spain)
Global fixed station in WMO RA I - Africa
28.309°N, 16.499°W, 2373 m a.s.l., Time zone: UT

The Izaña station is located on the Island of Tenerife, Spain, roughly 300 km west of the African coast (Fig. 1). The meteorological observatory is situated on a mountain platform (Fig. 2), 15 km north-east of the volcano Teide (3718 m a.s.l.). The local wind field is dominated by north-westerly winds. At the site, there is warm temperate climate with dry and warm summer.

The location is normally above a temperature inversion layer, generally well established over the island, and so free of local anthropogenic influences. Clean air and clear sky conditions are prevailing around the year.

There is easy access via public roads, with the last few kilometres on a private road that is closed for public traffic.

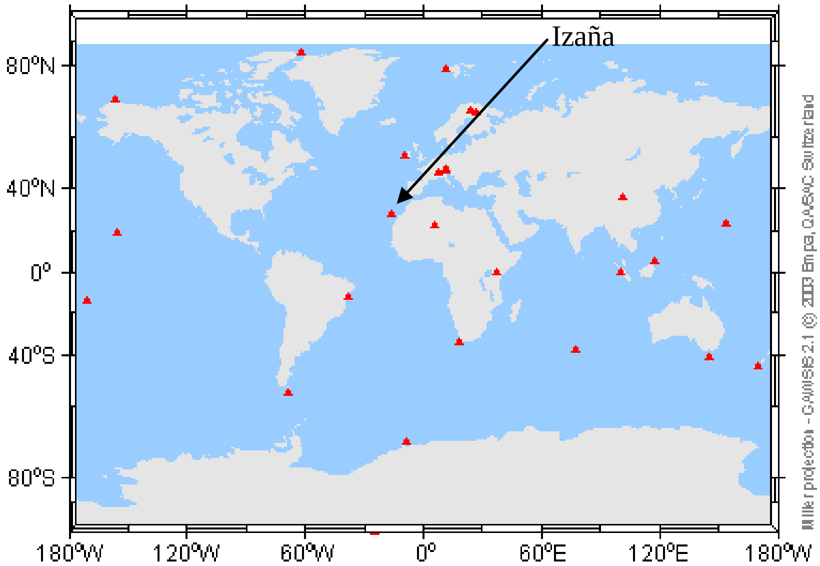

Fig. 1 : Map of the global GAW stations (source: GAWSIS, www.empa.ch/gaw/gawsis/).

3.2 Description of the Observatory

The Izaña Atmospheric Research Centre (Fig. 3), which is part of AEMET (Meteorological State Agency of Spain), forms the platform for the WMO/GAW global station Izaña (WMO abbreviation IZO). First atmospheric observations date back to the beginning of the 20^{th} century. In 1984 the governments of Germany and Spain signed an agreement by which the observatory became a station of the WMO BAPMoN programme under joint co-operation. In 1989 BAPMoN and GO3OS

(Global Ozone Observing System) merged in the current GAW programme (Global Atmosphere Watch) of which Izaña is one of the principal stations.
The GAW measurements are conducted in the newest building of the observatory. The laboratories for greenhouse gas measurements are installed on the 3rd floor of the tower building. The laboratories are air-conditioned and offer sufficient space for the instrumentation.

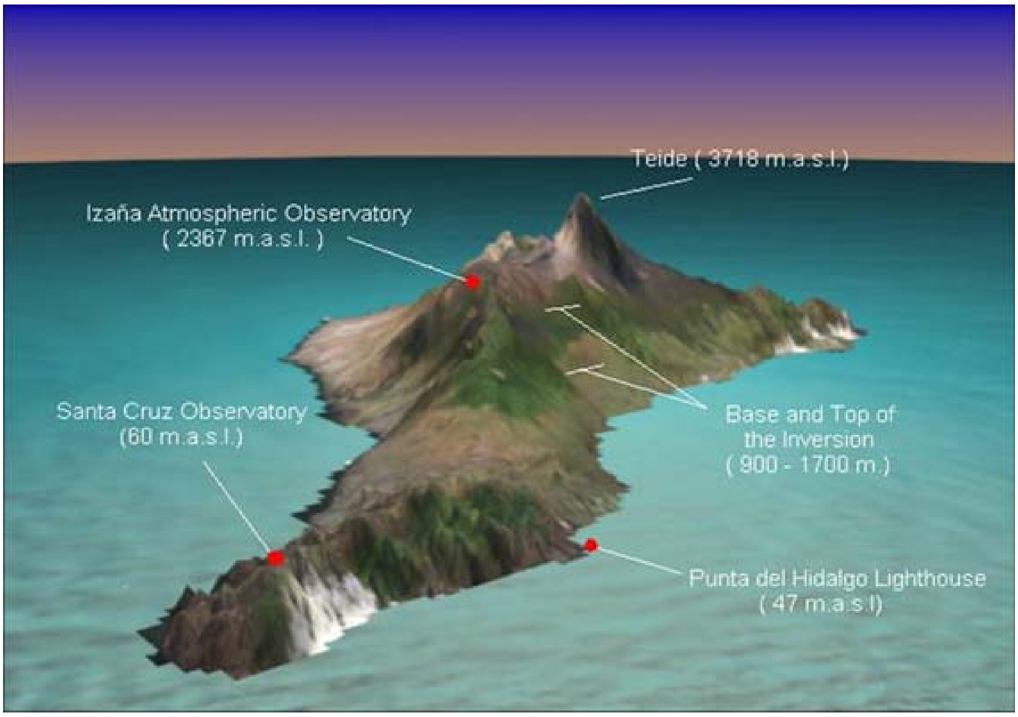

Fig. 2 : 3-D simulation of the island of Tenerife showing the location of the Izaña observatory. View from northeast to southwest (picture provided by AEMET).

Fig. 3 : Overview on the Izaña observatory buildings. The GAW-related laboratories are located in the upper floors of the tall building. Installations for air intake and meteorological measurements are located on the roof.

3.2.1.1 Comment

The Izaña facilities fulfil the infrastructural requirements needed for a global GAW station. The GAW laboratory and the adjacent rooms are clean, orderly and in good shape. They provide ample space for the instruments and related infrastructure. All support devices, such as clean air generators and gas cylinders, are kept in the same environment. There is currently no need for suggesting modifications.

3.3 Staff / Operators

The responsibility for the trace gas monitoring programme at the Izaña GAW station lies with the Meteorological State Agency of Spain (AEMET). The station director is Dr. Emilio Cuevas. Mr. Ramon Ramos, as the deputy station manager, is responsible for the scientific instrumentation and infrastructure. The greenhouse gas measurements at the site are under the responsibility of the programme leader Mr. Angel J. Gomez-Pelaez. He is responsible for the entire chain from the operation of the analytical systems to the final data products. He has gained professional experience through his work at the station, by participation in a GAWTEC course in 2005 and by contacts with other scientists.

Table 1: Staff responsible for the trace gas measurements at the GAW station Izaña.

Name	Position and duty	E-mail
Emilio Cuevas	Izaña Atmospheric Research Centre: Director	ecuevas@inm.es
Angel J. Gomez-Pelaez	Greenhouse gases and carbon cycle programme: Head	ajgomez@inm.es
Ramon Ramos	Scientific instrumentation and infrastructure: Head	rramos@inm.es
Julian Perez-delaPuerta	Technician	

Staff involved in the audit on 11-12 November 2008

Izaña	Angel J. Gomez-Pelaez	Programme leader
	Ramon Ramos	Field manager
	Julian Perez-delaPuerta	Technician
WCC-N_2O	Hans-Eckhart Scheel	Auditor

3.4 Monitoring Set-up and Procedures

3.4.1 Air Inlet System for N_2O

The air intake for N_2O analysis and other systems is located at the eastern corner of the laboratory on the 3rd floor of the station building, about 5 m away from the N_2O instrumentation. The main tube consists of stainless steel 316, the height above the 3rd floor is 18 m, while the total length of the vertical tube is 30 m, measured from the ground floor. The entire air intake tube (80 mm i.d.) is flushed using an aluminium pump (Blowers) installed on the ground floor (thus, the pump is located downstream of all the bifurcations for the dedicated instrument pipes). The flow rate is about 1600 L min^{-1}.

From a manifold in the laboratory of the 3rd floor (Figs. 4 and 5), sample air is conducted to the systems for N_2O and CO (2 analysers) through 1/4" PFA tubing using a KNF membrane pump (same type as used in Thermo Electron ozone instruments), capable of a maximum flow of about 1

L min[-1]. The air flow through the N_2O sample loop is about 150 mL min^{-1}. With this set-up, the overall residence time of the sample air is sufficiently low. Note that in the case of N_2O, the residence time of sample air in the inlet line is not a crucial parameter, in contrast to reactive gaseous species.

There is no particle filter installed for the GC sample air. The sample air is dried in a glass tube kept at -32 °C. After the audit and before this audit report was finalised, the refrigerating machine was replaced, and the glass tube is kept at -70 ºC. The cooling traps are exchanged every 2 days. Changes are documented in a logbook of the station operator and a Varian GC check list in place, which is filled in twice daily.

Fig. 4 : Sample air inlet for trace gas analysers with manifold in the laboratory of the 3rd floor of the Izaña station building. The picture also shows the set of laboratory standards for N_2O (see 3.6.2).

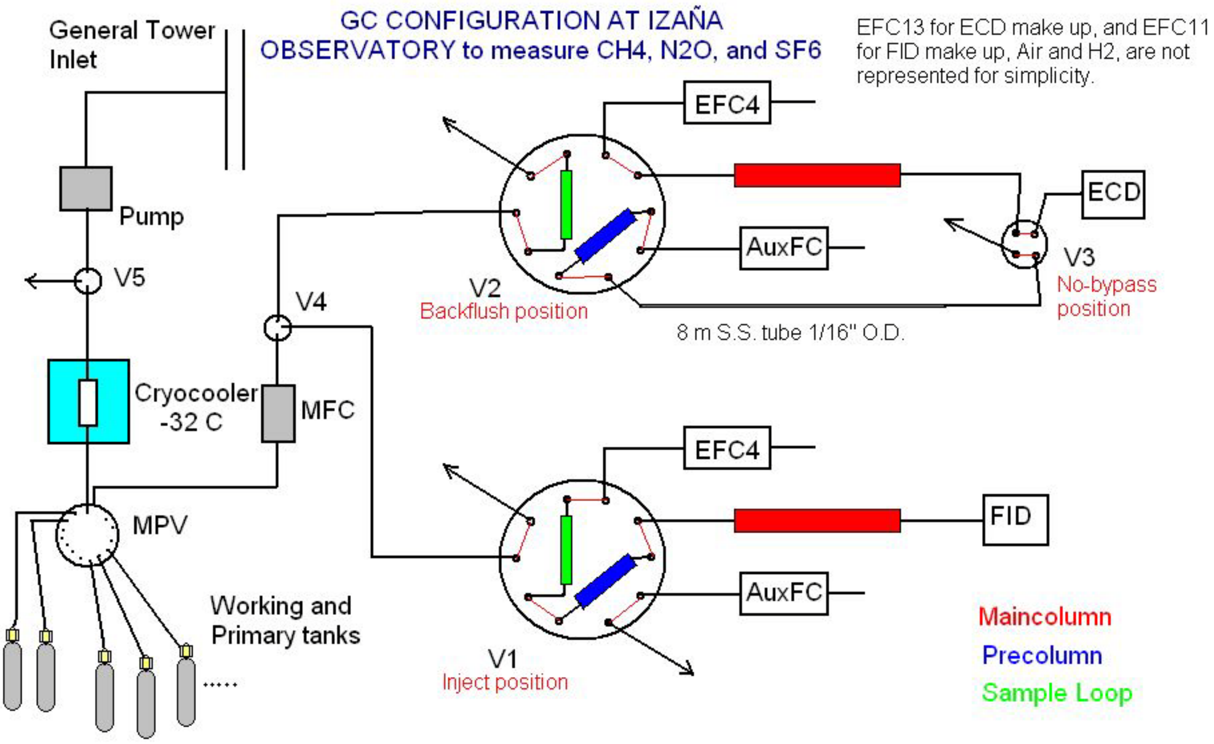

Fig. 5 : Schematic of the airflow from the ambient air intake to the analytical devices (taken from: Gomez-Pelaez and Ramos, in: WMO/GAW Report No. 186, 55-59).

3.4.1.1 Comment

With respect to material and total set-up, the inlet system is adequate for N_2O measurements. The entire installation was found to be in good conditions.

3.4.2 Gas-chromatographic System

The gas-chromatographic system for N_2O is based on a VARIAN GC 3800 instrument (Fig. 6). It was acquired in 2002 and set in operation for tests of N_2O analysis in 2005 (the year in which the ECD was acquired). Since June 2007 the GC has been in operation for regular N_2O monitoring. The GC has two channels (detectors): an ECD for N_2O and SF_6, and an FID for the detection of CH_4. For the near future, a methaniser for the additional measurement of CO_2 was foreseen. Both detectors were manufactured by VARIAN. The ECD is a model 02-001972-01, S/N: A14637, installed on 10 August 2005.

The plumbing is shown in the schematic of Fig. 5. The gas sampling valve (GSV) is a Valco 10-port valve with pneumatic actuator. All tubing is made of stainless steel, 1/16" outer diameter. The sample loop consists of stainless steel tubing (1/4"o.d.) and has a volume of 10 mL. Backflush is configured for routine operation.

For the separation of N_2O, two packed columns are installed in the GC oven and operated at 80 °C.
(i) Precolumn: Porapak Q 80-100 mesh, length = 2 m; o.d. = 1/8"; i.d. = 2.0 mm
(ii) Main column: Hayesep Q 80-100 mesh, length = 3 m; o.d. = 1/8"; i.d. = 2.0 mm

As carrier gas, the widely used mixture of Ar/CH_4 (95% / 5%) is employed. The gas is of ECD quality with traces of H_2O and O_2 specified as being less than 5 ppm. For the removal of oxygen and moisture, a trap is installed in the carrier gas line between the pressure regulator at the cylinder and the GC. It is an Agilent OXYGEN TRAP OT3, which uses metal oxides on aluminium support and also removes water vapour (for details see Agilent on the web).

The ECD is operated at 395 °C without additional make-up gas. The direct carrier flow is about 31 mL min^{-1}, while the backflow is set to about 32 mL min^{-1}.

The peripheral devices comprise one bypass valve and a stream selection valve (SSV). The latter is a Valco 16-port valve with port 2 being closed.

Switching of the valves is actuated via the VARIAN build-in switching valve outlets, except for the external SSV, which is controlled with self-developed software. Synchronisation with the GC operation is achieved by the sample list. A time server is run for the synchronisation of the PC that serves for controlling the entire GC operation.

For the operation of the ECD a special security system has been constructed in order to guarantee an uninterrupted carrier gas flow through the hot ECD if power should fail. Therefore a mechanical flow controller is employed for the auxiliary carrier gas (used for backflush), supplemented with a bypass valve (powered via UPS) that returns to the right position (bypass) in case of power failure.

As part of the documentation, a flow diagram, GC manual as well as a SOP for operators and safety instructions were available near the instrument.

Fig. 6 : Pictures showing the N_2O gas chromatographic system in the Izaña station laboratory.

3.4.2.1 Comment

The GC system with its peripheral devices represents state-of-the art instrumentation and is well suited for high-quality N_2O measurements. The availability of detailed documentation, including safety instructions, is acknowledged.

3.5 Operation and Maintenance

3.5.1 General

Since the GAW station Izaña is operated in parallel to a meteorological observatory at the site, a meteorological observer is present during seven days a week from 9:00 to 17:30. The GAW station is usually visited by technicians and Ramon Ramos (head of scientific instrumentation and infra-structure) on two or three days per week. If necessary, also the responsible scientist travels up to the station.

The entire analytical system for N_2O is fully automated with the possibility for remote control of the gas chromatograph PC from the office by way of the software Radmin Viewer.

The calibration standards employed for the operation and quality control of the N_2O system consist of high-pressure cylinders from different manufacturers and of different size. They are kept in the same laboratory as the GC itself. Unfortunately they were not appropriately fixed (see Fig. 4). During the audit the staff promised to close this safety gap soon.

3.5.1.1 Comment

It is very risky to keep high-pressure cylinders with pressure regulators in an upright position without fixing them in any way. The installation of metal frames or other con-structions for securing the cylinders is an urgent matter of laboratory safety.

3.5.2 Sampling and Calibration

The gas cylinder lines are leak-tested every two weeks. Other tubings and fittings are checked only upon need, for example, if problems are encountered with column fittings. In 2008, a leak check of the GSV had been performed using carrier gas as sample.

3.5.2.1 Sequence of Injections

The usual sequence of working standard (W) and ambient air (A) is one injection of the working standard followed by one ambient sample: … W / A / W / A ... Working standards and ambient air samples are analysed every 15 minutes, i.e. 8 analysis runs per hour, from which 4 ones are ambients. For routine operation 1-level calibration is configured.

3.5.2.2 Response Curve Based on Laboratory Standards

The response curve of the ECD is determined using five levels delivered by NOAA-calibrated laboratory standards, which were covering the range 257.3 – 356.8 ppb (see 3.6.2). This is usually performed every 2 weeks. The working standard is tied to the response curve. In detail, the response curve used has the shape:

$$\frac{h}{h_{ws}} = a_0 + a_1 r + a_2 r^2 \quad ,$$

where h is peak height, h_{ws} is the peak height of the working standard, r is mixing ratio, and a_0 , a_1 , and a_2 , are parameters to determine in the calibrations (through least squares fitting). When solving such response curve for the mixing ratio, there are two solutions, the appropriate one is that obtained using the plus sign before the square root.

Abundance range tests of the ECD go in line with the regular determination of the response curve (every two weeks) using five levels of N_2O. The last check of this kind prior to the audit was performed on 10 November 2008. Results from five injections per level were: relative standard deviation of 0.14 % for the relative height (h/h_{ws}), with the best value at 0.08 % (h_{ws} is obtained by interpolation of the directly preceding and following working standard injections. Note that injections of the same level are separated 1.25 hours in time). The RMS (root mean squares) value of the average residuals (one residual per level) from the curve fit was 0.25 ppb (where the number of degrees of freedom was taken into account, i.e. there are only two degrees of freedom because there are three parameters to fit in the response curve). All such data are generally stored in a file managed by the responsible scientist.

In practice, the five laboratory standards employed for the above procedures are permanently connected to the SSV with their valves and pressure regulators being closed. As part of the preparation of calibration sequences, each valve/regulator is opened/closed four times (filling and emptying the high pressure side of the regulator each time), and then, flow is allowed for two minutes, for flushing the system.

During the audit the sequences configured for the 5-level calibration tests (L1 … L5) were discussed in detail.
It is noted that the CCL usually runs the following sequence: W / L1.1 / W / L1.2 / W / L1.3 / W /L1.4 / W / L1.5 / W / W / L2.1 / W /L2.2 …

In an earlier set-up at Izaña a sequence as follows was used: L1.1 / L2.1 / L3.1 / L4.1 / L5.1 / W1 / W2 / W1 / L1.2 / L2.2 …

This was replaced by the configuration used at the time of the audit: W / L1.1 / W / L2.1 / W / L3.1 …

3.5.3 Zero and Repeatability Checks, Target Gas

Two types of zero checks are performed manually using carrier gas. The first type uses carrier gas via a special 3-way connection ("T") in the line. This set-up is installed upstream of the oxygen trap and equipped with needle valve and nut for complete closing. The main purpose of this type of zero checks is checking that there is no oxygen in the carrier gas, in case of doubt. The second type uses carrier gas as follows. When the GSV is in inject position, carrier gas is flowing through the sample loop. Then the GSV is commuted to load position and there is no flushing of the sample loop. Finally, the GSV is commuted to inject position (injecting the carrier gas content of the sample loop). This second type of zero checks has the purpose of leak checking.

Two types of repeatability checks are performed. The first type of repeatability checks concerns the analysis results for relative height (h/h_{ws}), which are performed every two weeks as part of the comparisons between working standard and laboratory standards. The last repeatability check before the audit had yielded a relative standard deviation of ≈ 0.14 % for relative height (≈ 0.5 ppb for ambient level), with n = 25 (indeed 5 injections per laboratory standard). The second type of repeatability checks concerns peak height for the working standard (h_{ws}), which is continuously injected every 15 minutes. To estimate the magnitude of the random fluctuations superposed to smooth drifts in response, a 3-hour running mean is applied to the series h_{ws}, and then, the residuals are computed. Finally, the RMS residual is computed for each day. The typical relative RMS residual value is 0.12%.

So far no target gas (gas of known N_2O mole fraction stored in a dedicated cylinder) was run. The suggested N_2O mole fraction would be ± 5 ppb around the ambient level.

3.5.3.1 Comment

It is recommended injecting a target gas once or twice daily.

3.5.3.2 Comment

The repeatability for single injections of ≈ 0.44 ppb (≈ 0.12 % in peak height) obtained here with the GC system is less good than should be achievable with a GC system of this kind. However, taking into account that the repeatability for the average of several injections (e.g. 4 injections for hourly means, 96 injections for daily means) will be better (due to cancellation of random errors), and given the frequent comparisons between working standard and laboratory standards, this performance will still be suited to provide precise average results for the ambient measurements. Nonetheless, it is noted that the target value within GAW, as driven by scientific requirements, is 0.1 ppb (0.03 %) at ambient levels (see e.g. WMO/GAW Report No. 168).

3.5.4 Maintenance

Maintenance of the N_2O system is conducted primarily upon need only. Regular maintenance comprises the change of the glass flasks of the cooling trap every two days - as the most frequent action – and the change of carrier gas cylinders.

3.5.5 Corrective Actions

No general procedure can be described for the case of instrumental drift or instability as well as for problems such as excessive baseline noise or peak shape degradation.

After instrumental malfunction or repair, the routine operation is continued after additional calibration procedures. Depending on the problems, decisions are made about corrections to be applied.

3.6 Standards

3.6.1 Regulators and Connections

The pressure regulators used on the high-pressure cylinders are of the type Scott Specialty, two-stage, brass (Fig. 7) or Air Gas Y12-C144B CGA. The tubing from the cylinders to the valves is made out of stainless steel, 1/16" o.d.

Fig. 7 : Picture showing Izaña N_2O laboratory standards equipped with two-stage brass pressure regulators, manufacturer Scott Specialty.

3.6.2 Laboratory Standards

Nominally six laboratory standards (standards of the highest rank at the site) were available in the laboratory and were stored adjacent to the N_2O GC. These comprised five ones acquired in 2006 plus a cylinder from 2008. Since one of the six standards has a N_2O mole fraction of ≈ 410 ppb, it was discarded so that practically only five standards were suited for the 5-level calibrations within the recommended range of 290 – 350 ppb.

The cylinders of the standards are 30-l aluminium tanks filled by Scott-Marrin (USA; www.scottmarrin.com) with gas mixtures balanced with ultrapure air. The cylinders were calibrated by NOAA.

Table 2 lists the N_2O and SF_6 mole fractions of the standards together with the standard deviation reported by the Central Calibration Laboratory. The originally assigned N_2O values of 2006 were given in the NOAA-2000 scale and converted to the NOAA-2006 scale, while the mole fraction of the cylinder from 2008 was directly given in the NOAA-2006 scale.

Table 2: Laboratory standards for N_2O and SF_6 at the station. Cylinder numbers, year of purchase and mole fractions with standard deviation as reported by the Central Calibration Laboratory. N_2O expressed in NOAA-2006 scale.

	Cylinder ID	Year	Pressure	N_2O	Std.	SF_6	Std.
			[psi]	[ppb]	[ppb]	[ppt]	[ppt]
1	CA06739	2006	1900	257.31	0.16	4.13	0.03
2	CA06996	2006	1930	305.89	0.12	5.15	0.04
3	CA06970	2006	1910	330.14	0.16	7.08	0.04
4	CA06964	2006	1860	356.81	0.15	8.03	0.04
5	CA08203	2008	1930	321.58	0.07	7.55	0.03

3.6.2.1 Comment

The suite of N_2O laboratory standards kept at the Izaña station fulfils the requirements of the DQOs with respect to the range of mole fractions to be tested. Through calibration by the Central Calibration Laboratory for N_2O (NOAA ESRL GMD) a direct link to the GAW N_2O scale is established. This is in fulfilment of the GAW recommendation that each laboratory should maintain the shortest possible direct link to the respective WMO Primary Standard (WMO/GAW Report No. 168).

During the audit it was suggested to use the cylinder with $N_2O \approx 410$ ppb for the spiking of cylinders when filling with ambient air by way of a RIX compressor at the station.

3.6.3 Working Standards

One working standard was in place in the laboratory for the routine determination of ambient mole fractions. The cylinder itself is a 20-L type aluminium high-pressure cylinder provided by Air Liquide. The tank contained pressurised ambient air. It had been filled at the station using a dedicated set-up with an oil-free RIX compressor (www.rixindustries.com), which is permanently installed at the ground level of the building (Fig. 8).

The N_2O mole fraction (NOAA-2006 scale) of the cylinder in use during the audit (S/N 99660) was determined from comparisons with the laboratory standards. The assigned value was 322.17 ppb N_2O. In addition, the SF_6 content had been quantified, yielding a value of 6.55 ppt. The uncertainty of the mean value as obtained from the comparisons at the site was estimated to 0.1 ppb. The absolute uncertainty was estimated to be not less than 0.2 ppb. Comparisons of the working standard with the laboratory standards are performed every two weeks. The last of such comparisons was conducted on 10 November 2008.

3.6.3.1 Comment

It is appreciated that the comparisons between working standard and laboratory standards are made much more frequently than twice a year, which is the minimum frequency recommended by GAW.

Fig. 8 : Picture showing the set-up for filling high-pressure cylinders using an oil-free RIX compressor.

3.6.4 Target Gases

Until the date of the audit no target gas (sometimes also denoted surveillance cylinder) was in operation for the N_2O analysis at Izaña.

3.6.4.1 Comment

As a permanent quality control measure, the installation of a target gas is recommended. It should be run like an unknown sample once or twice a day.

3.7 Data Acquisition and Processing

3.7.1 General

Data acquisition of the gas chromatographic signals and parameters is made via the VARIAN software "Star". All data acquired are on UT, which is also the local time. Remote access to the PC is possible from the office in Santa Cruz. Further processing of the data is done using self-developed Fortran routines.

The quality of the measurements is first assessed by checking the calibration results and the calculated mole fractions. The instrument logbook is considered as part of the data validation procedure. In the case of gas chromatographic outliers, the associated chromatogram is inspected. For the routine data processing no special data filtering techniques are applied, which is mainly due to the clean-air location of the station. The flagging of outliers was not yet implemented, but was foreseen for the future. During the audit no separate time series plots (covering months or years) were available. All data processing and final data validation is within the responsibility of the project manager, Mr. Angel Gomez-Pelaez.

The calculation of the final mole fraction results takes into account the dilution effect due to the presence of a tiny amount of water vapour in the injected dried ambient air (sampled ambient air is dried cooling it to -32 ºC) , which typically yields a correction of about 0.1 ppb. Comparisons with results from flask sampling (NOAA) had not yet been made, but were envisaged for the future.

3.7.1.1 Comment

The preparation of time series plots of all relevant parameters for different periods, notably months and years, is recommended. In particular, a graphical visualisation of mole fractions on a routine basis should be implemented.

Comparisons with NOAA results from flask samples taken at IZO are encouraged.

3.7.2 Chromatogram Characteristics

The sequence of peaks in the chromatogram is (i) CO_2, ii) N_2O and (iii) SF_6. O_2 peak cut-off is implemented by specific valve switching. A typical chromatogram is shown in Fig. 9. Good separation of the N_2O from the CO_2 and SF_6 signals is achieved, with full return to baseline of the ECD signal (Fig. 10).

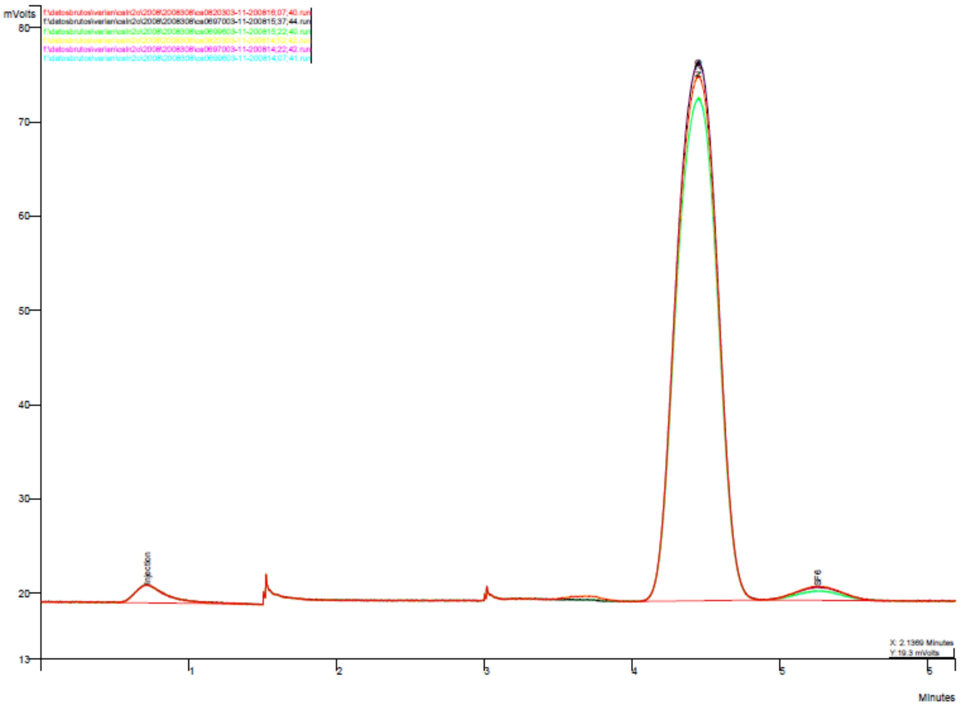

Fig. 9 : Overlay of a series of chromatograms obtained with the ECD channel of the GC system. The O_2 peak is cut off. The N_2O peak is followed by SF_6. Figure provided by A.J. Gomez-Pelaez (AEMET).

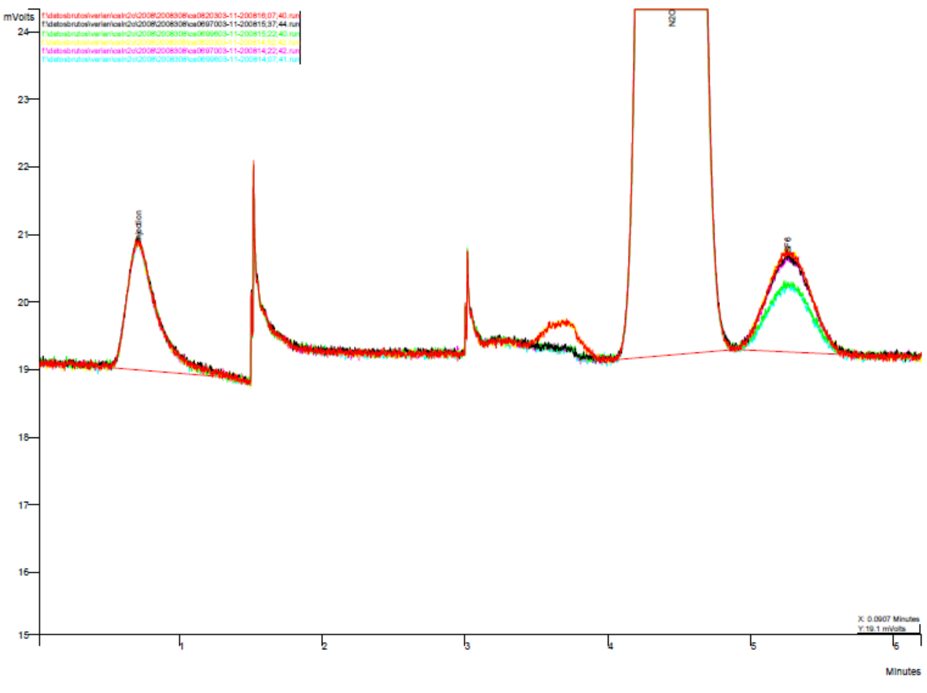

Fig. 10 : Overlay of a series of chromatograms obtained with the ECD channel of the GC system. Here: zoom into the lower part of Fig. 9. The N_2O peak is fully separated from the preceding CO_2 signal, and sufficiently separated from the subsequent SF_6 peak. Only one of the laboratory standards contains traces of CO_2.

3.7.2.1 Comment

With respect to the zoom of the chromatogram in Fig. 10 it is suggested to perform tests with the aim of improving the separation between N_2O and SF_6.

3.7.3 Chromatogram Evaluation

Peak integration is performed automatically. From the GC data of each analysis run, the chromatogram, the analysis report and a summary report are stored. The chromatographic parameters comprise peak height, retention time as well as half width (the typical value is 19 s), ambient pressure at injection, baseline level, and baseline noise. Chromatograms can be reintegrated (e.g. using a different method) whenever desired.

All these parameters are routinely used for data quality control.
Typical values are: Height of ambient N_2O peak ≈ 56 mV, baseline peak-to-peak noise level ≈ 0.18 mV. The typical signal-to-noise ratio (peak-to-peak) amounts to 309. These values refer to the fast response mode of the ECD.

Peak height is used for the calculation of mole fractions. The calculation is based on the comparison with the working standard and the regularly determined response curve of the ECD. Calculations via peak area will be tested, after reintegrating chromatograms to obtain peak area (Varian Star integration software provides height or area, but not both simultaneously). From the automatically processed chromatograms, particular ones are routinely inspected by the operator. The ambient N_2O mole fractions are averaged to yield hourly, daily and monthly mean values.

The absolute values of the detector signal are recorded and are available for visualisation, or reintegration if necessary. No automatic baseline reset to zero is configured. Column regeneration is made upon need only.

3.7.3.1 Comment

Acquisition and processing of the chromatograms were found to be adequate. Nonetheless, it is noted that the ECD was operated in the fast response mode, which is primarily for fast peaks from capillary columns. Since packed columns are used here, it is recommended to try the slow response mode.

However, it is noted that such tests have been carried out during one month by the Izaña GHGs project leader after the audit, but before this audit report was finalised. There was reduction in the baseline peak-to-peak noise, but no improvement in the repeatability of peak height, when using the slow response mode. This is probably due to the fact that Varian Star integration software applies some kind of smoothing to the chromatograms when integrating, so the resulting smoothed chromatogram is probably the same, independent of the response time mode.

3.8 Data Management and Submission

There are provisions for redundant, off-site data storage, which is run every two weeks. In total, the backup procedure comprises (i) a hard disk at the station, (ii) copy to an office PC, and (iii) storage on CD-ROM every 6 months.

A Data Base Management System (DBMS) is in use, which is based on self-developed Fortran routines. Data in LINUX directories are classified by type, year, month, day, and graphical representations of the raw data are available.

At the time of the audit, N_2O data and meta data had not yet been submitted to the WDCGG. Submission by the responsible scientist was planned for 2009, but later postponed to the beginning of 2010. The structure of the meta data was foreseen to be similar to the ones for CO_2 and CH_4. Auxiliary data to be submitted comprise meteorological parameters.

Detailed information about the complex measurement programme at IZO, including N_2O, is provided by GAWSIS. As a minor detail, it is noted that the time zone given there needs to be corrected.

3.8.1.1 Comment

The use of a DBMS, which is in line with GAW recommendations, is acknowledged.
The submission of data to the WDCGG is strongly encouraged. It is noted that N_2O data were not yet submitted when this audit report was edited in 2009.
The entries for Izaña in the GAWSIS data base should be carefully reviewed on a regular basis and updated upon need.

3.9 Documentation

3.9.1 Technical and QA/QC

As part of the system audit, the documentation was reviewed. Instrument manuals were available at the station. Field logbooks were kept at the site and in the office, partly with complementary information, and kept in an orderly manner. They are mainly hand-written, but calibrations are documented electronically. At the time of the audit, they were found to be up-to-date.

Instrument logbooks are maintained at the site. In particular, there is a dedicated logbook for the VARIAN gas chromatograph. Other logbooks consist of forms that are filled out regularly by meteorological observers and technicians. The information compiled there comprises instrument malfunction and repair, changes of an instrument or components of it, date and reasons of last data loss as well as periods of questionable data and reasons therefore. Moreover, the staff has prepared a SOP for the N_2O instrumentation including daily check lists for routine inspection.

QC control forms were available for calibrations and data quality objectives defined for the station's measurements. It is noted that WMO/GAW Measurement Guidelines for N_2O, including DQOs, were not yet officially released by GAW at the time of the audit, but already approved by GAW through the SAG GG during its meeting in September 2007. A draft version of the Guidelines was available to the programme manager.

3.9.1.1 Comment

The technical documentation was comprehensive. The use of detailed logbooks and daily check lists is particularly acknowledged.

3.9.2 Station Information

At the time of the audit in November 2008 a web page of the station did not yet exist.

3.9.2.1 Comment

Based on the audit, the preparation of a web page is strongly encouraged.
It is noted that a very comprehensive homepage of the station has been created in 2009, i.e. before this audit report was finalised (http://www.aemet.izana.org/index.php?lang=en). The presentation of the station in the internet is a good example of a very valuable homepage. It offers a wealth of information to the reader.

3.9.3 Reports of Results

Some details of the greenhouse gas measurements conducted at Izaña have been published in the WMO/GAW Report No. 186 (2009), 55-64.

3.10 Intercomparison of N_2O Standards

3.10.1 Experimental Procedure

Prior to the audit, five travelling standards of the WCC-N_2O and dedicated pressure regulators were sent to the the station. They were available at IZO before the audit. Flushing and leak checks were performed by the technician indicated in Table 1 and the greenhouse gas programme manager, who conducted the intercomparison. First analyses took place on 4 November 2008 and were continued until 19 November.

No modifications of the GC system itself were made for the intercomparisons. The gas from the actually selected travelling standard was directed to a dedicated inlet of the stream selection valve.

The intercomparison experiment involved the working standard of the station and five of the WCC-N_2O travelling standards listed in Table A2 of the Appendix. All data processing was performed by the programme manager. Raw data were submitted to the WCC-N_2O together with the mole fractions determined for the individual analysis runs (see Appendix 5.1). N_2O mole fractions were reported on the basis of the NOAA-2006 scale.

Table 3: Experimental details of the N_2O intercomparison

Instrument at the site	GC system as described above
Travelling standards	5 10-L cylinders of the WCC containing N_2O in synthetic air
Data acquisition system	the routinely used PC-based software
N_2O levels for audit	5 levels, approx. 295, 305, 320, 330, and 350 ppb
Time per analysis run	15 min
Total number of injections per level	16 – 31 (Table 4)

3.10.2 Results of the N_2O Intercomparisons

The individual analyses of the 5 travelling standards were evaluated using a single working standard, i.e. 1-level calibration, and the detector response curve as separately determined with the laboratory standards of the station. Results are listed in Table 4.

The mole fraction relative standard deviations obtained for the audit comparisons vary between between 0.135 and 0.176 %. It is noted that these values are higher than would be expected from modern N_2O GC instrumentation.

In Table 5 the final mole fractions reported for the travelling standards are compared with those assigned by the WCC-N_2O (cf. Table A2 of the Appendix). The last column of Table 5 shows the outcome of the intercomparison in terms of differences between IZO and WCC-N_2O. Fig. 11 gives an overview on the mole fractions of the cylinders involved, while Fig. 12 displays the N_2O differences between IZO and WCC-N_2O. Fig. 13 represents the differences as a function of mole fractions.

Table 4: Summary of results for the intercomparison as reported by the IZO station.

Cylinder No.	Short name	N_2O [ppb]	Standard dev. [ppb]	Rel. std. dev. [%]	N
6061	DS11	296.01	0.52	0.176	16
4616	DS14	306.05	0.43	0.140	31
4586	DS15	318.89	0.46	0.144	24
4563	DS13	332.53	0.45	0.135	16
4594	DS10	347.15	0.59	0.170	24

Table 5: Comparison of the N_2O mole fractions reported by the IZO station with the mole fractions assigned by the WCC-N_2O. For details on the WCC-assigned values see the Appendix. All mole fractions expressed in NOAA-2006 scale.

Cylinder No.	Short name	WCC, NOAA-2006	N_2O (IZO)	Diff. IZO – WCC
		[ppb]		
6061	DS11	295.89	296.01	0.12
4616	DS14	305.95	306.05	0.10
4586	DS15	318.97	318.89	-0.08
4563	DS13	332.65	332.53	-0.12
4594	DS10	347.47	347.15	-0.32

The differences "IZO – WCC" [ppb] range between -0.32 and +0.12 ppb. The deviations show a small, but systematic dependence on mole fraction (Table 5 and Fig. 13). The greatest differences show up at the higher mole fractions. In any case, the deviations within the typical range of ambient mole fractions are around 0.1 ppb only. This means excellent agreement. It is concluded these results already meet the target for the network comparability of 0.1 ppb set out by GAW.

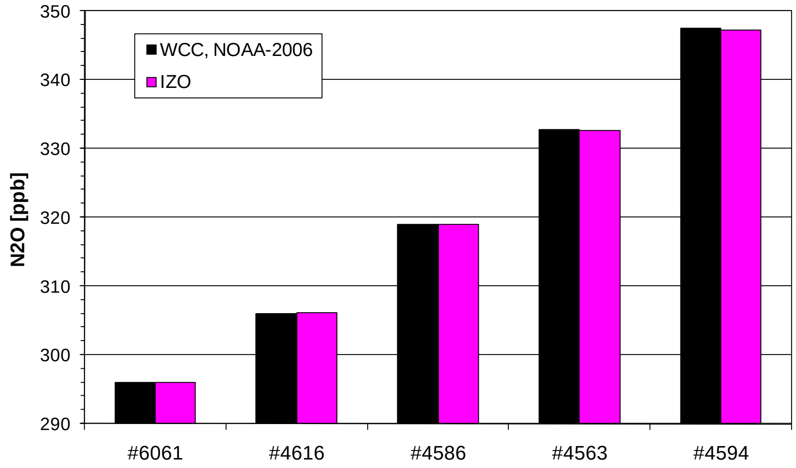

Fig. 11. N_2O levels of the five travelling standards employed during the audit (NOAA-2006 scale): Mole fractions assigned by the WCC-N_2O and values obtained during the intercomparison at Izaña.

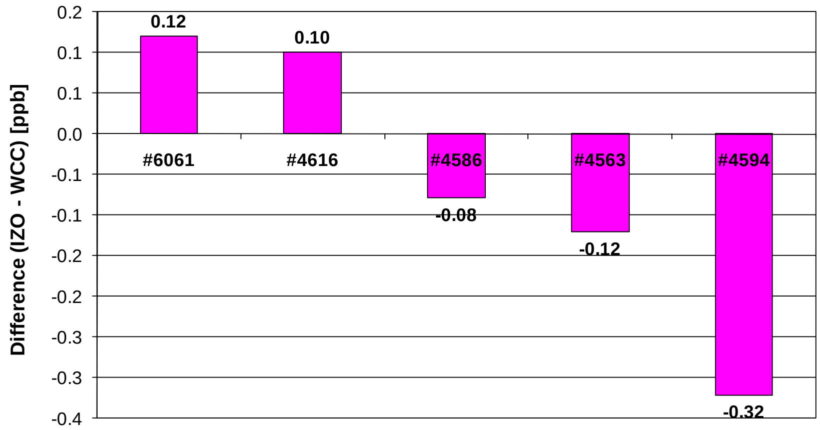

Fig. 12. Differences between the values reported by the Izaña station for the five travelling standards and mole fractions assigned by the WCC-N_2O (NOAA-2006 scale).

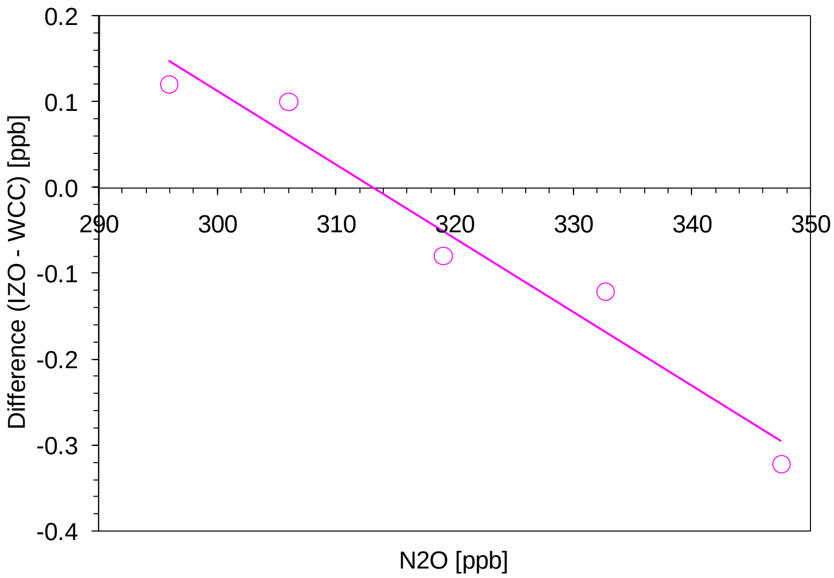

Fig. 13. Differences between the reported and assigned values as a function of N_2O mole fractions of the travelling standards (NOAA-2006 scale).

3.10.2.1 Comment

The outcome of the audit intercomparison shows differences < 0.1 ppb for ambient levels of N_2O. This means very good agreement and already meets the respective DQO set out for N_2O within GAW.

3.10.3 Response Curve of the ECD

As part of the data processing for the audit intercomparisons, the station has also reported normalised average peak heights for the travelling standards. These values were calculated relative to the working standard. The data enable the construction of the detector (ECD) response curve for the interval between 296 and 347 ppb. Fig. 14 displays a plot of the WCC-assigned mole fractions vs. normalised peak area. Both 2nd order polynomial and linear fit are shown, which are in good agreement. In Fig. 15 both types of fit are extrapolated towards zero. The respective behaviour of the fit gives a qualitative impression of the closeness to linearity of the detector response.

The excellent agreement between data points and fitting curve is quantitatively presented in Table 6, where the residuals are listed for the 2nd order polynomial fit. Over the entire range that was tested, the residuals are within a range ≤ 0.05 ppb around the fit. Residuals obtained for the linear fit and the 2nd order polynomial are compared in Fig. 16.

Table 6: Results of 2nd order fit of mole fraction vs. normalised peak height

Peak height, normalised	N_2O [ppb] NOAA-2006	Fitting curve (2nd order) [ppb]	Residuals [ppb]
0.92717	295.89	295.88	0.01
0.95523	305.95	305.98	-0.03
0.99093	318.97	318.92	0.05
1.02860	332.65	332.68	-0.03
1.06871	347.47	347.46	0.01

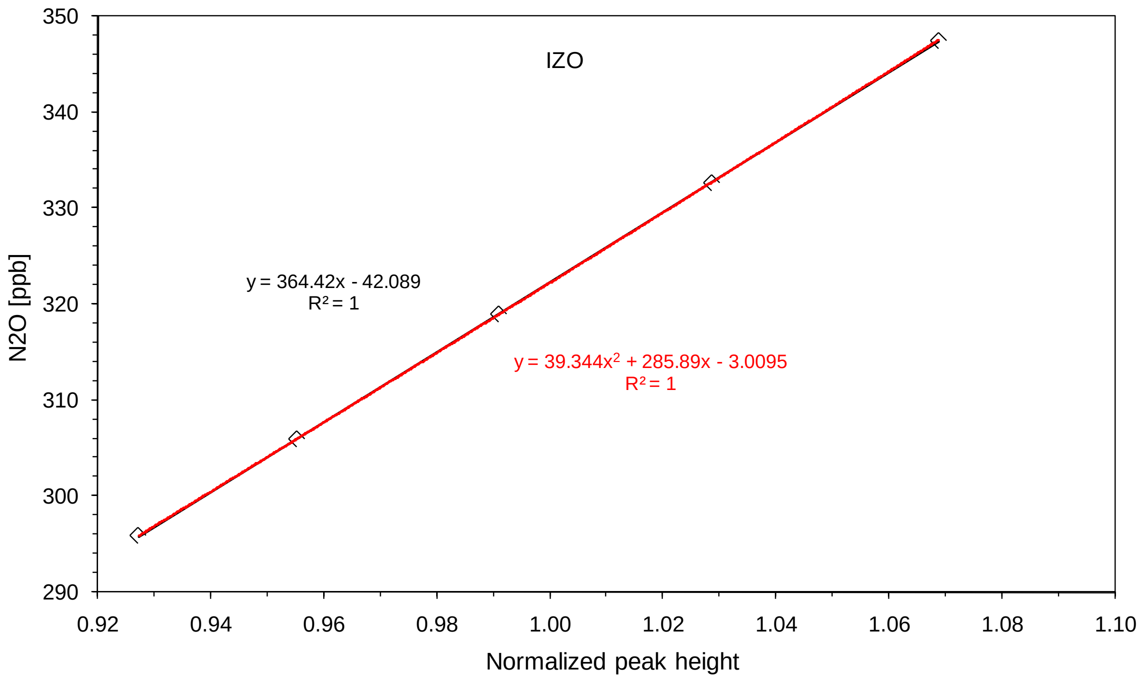

Fig. 14. N_2O mole fractions as assigned by the WCC-N_2O to the five travelling standards plotted vs. normalized peak height determined with the IZO GC system (relative to the station's working standard). The 2[nd] order polynomial practically coincides with the linear fit.

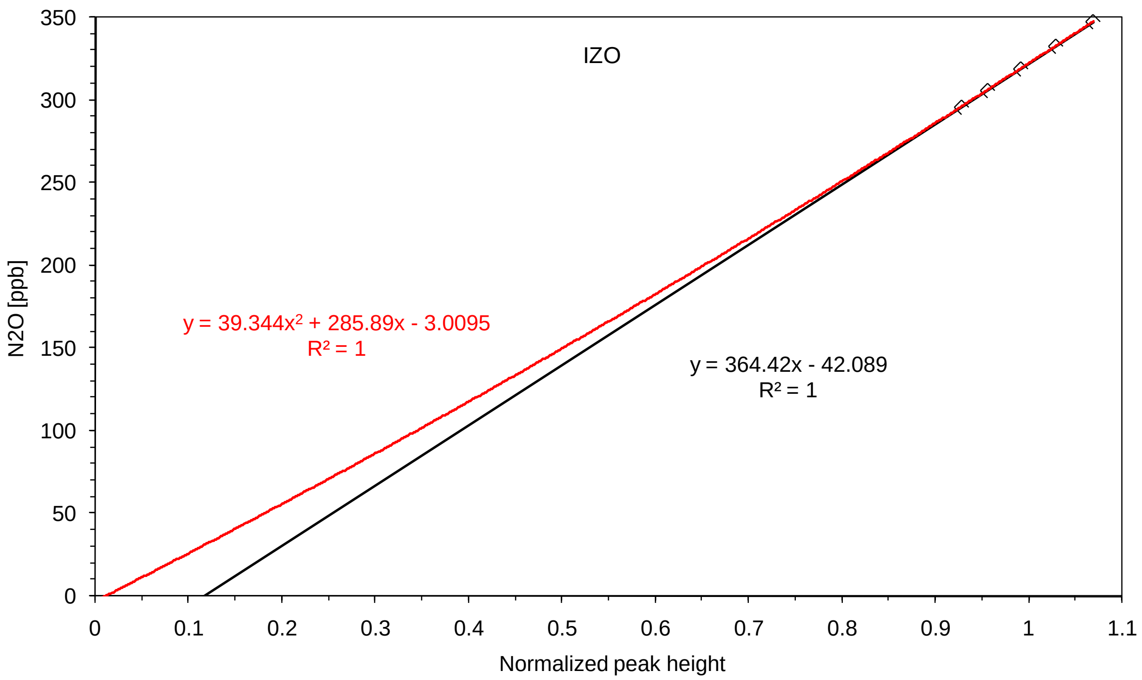

Fig. 15. Same as Fig. 14, but with linear and 2[nd] order fit extrapolated to near-zero.

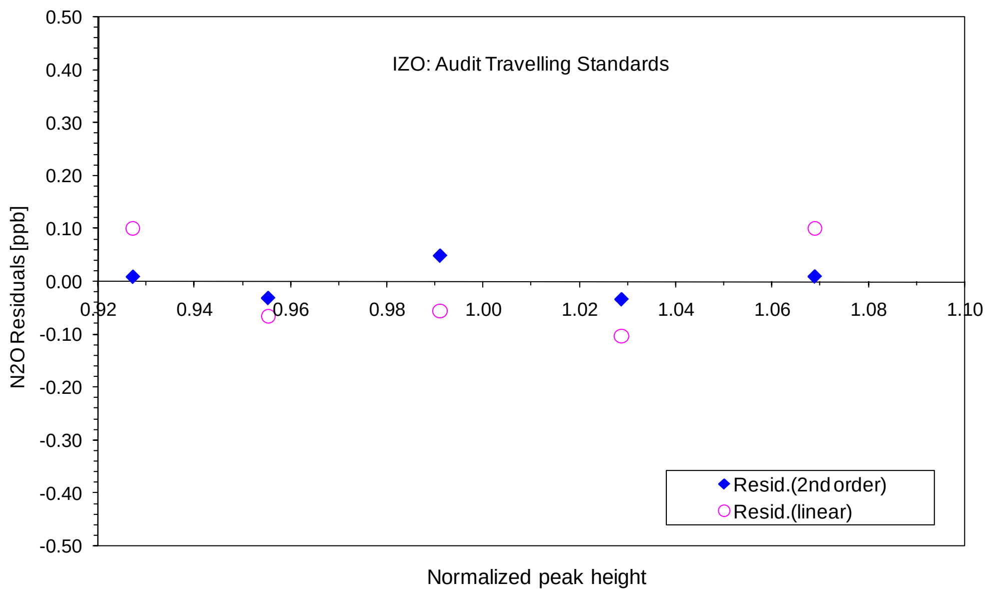

Fig. 16. N_2O residuals for the least squares fits shown in Fig. 14

3.10.3.1 Comment

The determination of the ECD response curve on the basis of the WCC-N_2O–assigned mole fractions has yielded very small residuals of 0.05 ppb or less. It thus documents a very good performance of the GC system.

4 References

Gomez-Pelaez, A.J., Ramos, R. (2009), Installation of a new gas chromatograph at Izaña GAW Station (Spain) to measure CH_4, N_2O and SF_6, in: World Meteorological Organization, Global Atmosphere Watch, Report No 186, "14th WMO/IAEA Meeting of Expert on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques", Helsinki, Finland, 10-13 September 2007, WMO TD No.1487, 55-59.

Hall, B.D., Dutton, G.S., Elkins, J.W. (2007), The NOAA nitrous oxide standard scale for atmospheric observations, J. Geophys. Res., 112, D09305, doi: 10.1029/2006JD007954.

World Meteorological Organization, Global Atmosphere Watch, Report No 161, "12th WMO/IAEA Meeting of Expert on Carbon Dioxide Concentration and Related Tracers Measurements Techniques", Toronto, Canada, 15-18 September 2003, WMO TD No.1275.

World Meteorological Organization, Global Atmosphere Watch, Report No.168, "13th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques", Boulder, Colorado, USA, 19-22 September 2005, WMO TD No. 1359.

World Meteorological Organization, Global Atmosphere Watch (2007), "WMO/GAW Glossary of QA/QC-Related Terminology", http://www.empa.ch/gaw/glossary.html

World Meteorological Organization, Global Atmosphere Watch (2007), "Audit Questionnaire for System and Performance Audits of Atmospheric Trace Gas Measurements at WMO/GAW Sites", http://www.empa.ch/plugin/template/empa/*/7571.

World Meteorological Organization, Global Atmosphere Watch (2007), "Standard Operating Procedure (SOP) for System and Performance Audits of Atmospheric Trace Gas Measurements at WMO/GAW Sites", http://www.empa.ch/plugin/template/empa/*/7571.

World Meteorological Organization, Global Atmosphere Watch, Report No 174,"World Data Centre for Greenhouse Gases, Data Submission and Dissemination Guide", WMO TD No. 1416.

5 Appendix

5.1 Individual Analysis Results

Table A1: Results of the individual analysis runs conducted for the comparison with the audit cylinders (data file provided by A.J. Gomez-Pelaez, AEMET).

	Normalised peak height	N_2O [ppb]	Year	Day	hour	min.
ta4563d	ta4563d					
1	1.028078	332.34	2008	309	10	15
2	1.029038	332.69				
3	1.027329	332.07				
4	1.03074	333.31				
5	1.030207	333.11				
6	1.027564	332.15				
7	1.028241	332.40				
8	1.027966	332.30				
1	1.029582	332.88	2008	310	13	45
2	1.028212	332.39				
3	1.029207	332.75				
4	1.028719	332.57				
5	1.026711	331.84				
6	1.02677	331.86				
7	1.030366	333.17				
8	1.028902	332.64				
Mean:	1.028602	332.53				
Sigma:	0.001224	0.45				
ta4594d	ta4594d					
1	1.071479	348.16	2008	309	12	30
2	1.070621	347.85				
3	1.069192	347.33				
4	1.067567	346.73				
5	1.068673	347.14				
6	1.070799	347.91				
7	1.070476	347.80				
8	1.06545	345.96				
1	1.069672	347.50	2008	312	13	0
2	1.06813	346.94				
3	1.070329	347.74				
4	1.067791	346.81				
5	1.070323	347.74				
6	1.068607	347.11				
7	1.066964	346.51				
8	1.067478	346.70				
1	1.067521	346.71	2008	319	14	45
2	1.067437	346.68				
3	1.068518	347.08				
4	1.071169	348.05				
5	1.067213	346.60				
6	1.069037	347.27				
7	1.067782	346.81				
8	1.066789	346.45				

Mean:	1.068709	347.15				
Sigma:	0.0016	0.59				

ta06061	ta06061					
1	0.92422	294.96	2008	309	14	45
2	0.926906	295.92				
3	0.928714	296.56				
4	0.92717	296.01				
5	0.926308	295.70				
6	0.929094	296.70				
7	0.927796	296.23				
8	0.928196	296.38				
1	0.927262	296.04	2008	312	10	45
2	0.926055	295.61				
3	0.92443	295.03				
4	0.927499	296.13				
5	0.929035	296.68				
6	0.926245	295.68				
7	0.928062	296.33				
8	0.927672	296.19				
Mean:	0.927167	296.01				
Sigma:	0.001444	0.52				

ta4586d	ta4586d					
1	0.990019	318.56	2008	309	17	0
2	0.991637	319.15				
3	0.991709	319.17				
4	0.992686	319.52				
5	0.990353	318.68				
6	0.989043	318.21				
7	0.989767	318.47				
8	0.991798	319.20				
1	0.991009	318.92	2008	316	10	30
2	0.993489	319.81				
3	0.992282	319.38				
4	0.990931	318.89				
5	0.992151	319.33				
6	0.98841	317.98				
7	0.990579	318.76				
8	0.991961	319.26				
1	0.989572	318.40	2008	324	14	45
2	0.990472	318.73				
3	0.991852	319.22				
4	0.990862	318.87				
5	0.989233	318.28				
6	0.99022	318.63				
7	0.992281	319.38				
8	0.989995	318.55				
Mean:	0.99093	318.89				
Sigma:	0.001276	0.46				

ta4616d	ta4616d					
1	0.9542	305.68	2008	310	11	30
2	0.954863	305.92				
3	0.95637	306.46				
4	0.957078	306.71				
5	0.955093	306.00				
6	0.957276	306.78				
7	0.956189	306.39				
8	0.955355	306.09				
1	0.954964	305.95	2008	316	13	0
2	0.952624	305.11				
3	0.954764	305.88				
4	0.95583	306.26				
5	0.955485	306.14				
6	0.953681	305.49				
7	0.95616	306.38				
8	0.956199	306.40				
9	0.955082	306.00				
10	0.956043	306.34				
11	0.95519	306.03				
12	0.956848	306.63				
13	0.954593	305.82				
1	0.954228	305.69	2008	319	12	0
2	0.952366	305.02				
3	0.955314	306.08				
4	0.95683	306.62				
5	0.955424	306.12				
6	0.954645	305.84				
7	0.953407	305.40				
8	0.956184	306.39				
9	0.955074	305.99				
10	0.954807	305.90				
Mean:	0.955231	306.05				
Sigma:	0.001198	0.43				

5.2 WCC N_2O Reference

The N_2O calibration scale maintained by the National Oceanic and Atmospheric Administration (NOAA) in its division ESRL GMD (formerly NOAA CMDL) has been designated by WMO as the reference scale for the GAW programme. NOAA acts as Central Calibration Laboratory (CCL). Therefore the laboratory standards used by the WCC-N_2O are gas mixtures with N_2O mole fractions assigned by the CCL. The most recent N_2O scale is the NOAA-2006 scale (Hall et al., 2007). The previous 2000 scale can be converted to the 2006 scale using the following polynomial:
Y = -2.20205•10-7*X3 + 1.20704•10-4*X2 + 0.98343*X, where Y is mole fraction (ppb) on the 2006 scale and X is mole fraction on the 2000 scale (www.esrl.noaa.gov/gmd/hats/standard/N2O_-scale.html).

Table A1: NOAA-certified N_2O laboratory standards at the WCC-N_2O. The cylinders contain N_2O in purified natural air. The consistency for the propagation of the scale is assumed to be ± 0.3 ppb or better. Mole fractions are shown for both NOAA-2000 and NOAA-2006 scale.

Cylinder No.	N_2O [ppb] NOAA-2000	N_2O [ppb] NOAA-2006
CA-04787	253.77	253.74
CA-04785	312.63	312.42
CA-04800	326.15	325.95
CA-04743	333.50	333.23
CA-04752	358.68	358.10
CA-6234	293.60	293.57
CA-6246	320.83	320.67

The travelling standards (TS) of the WCC-N_2O used for the Izaña audit were calibrated by comparisons with these laboratory standards. The values assigned to the travelling standards by the WCC-N_2O are shown in Table A2. All five travelling standards employed for the audit at Izaña were directly intercompared with the CCL at the beginning of 2007. The values determined by the CCL were directly reported in the new NOAA-2006 scale. Mean values are shown in Table A2. The related standard deviations were ≤ 0.15 ppb, number of data = 32. According to Hall et al. (2007), the NOAA scale can now be maintained to within 0.2 ppb. For four out of the five standards, the agreement between CCL and WCC-N_2O is within 0.1 ppb. This comparison defines the uncertainty associated with the mole fractions assigned to the travelling standards

For cylinder # 6061 the difference between WCC and CCL amounts to nearly 0.4 ppb. This is due to the value assigned to laboratory standard CA-6234. For some time already it has been known to the WCC-N_2O that this value (as provided by the CCL) did not match the overall response curve as close as the other standards, thus giving evidence that the actual mole fraction would be about 0.3 ppb lower. With respect to the above details, for cylinder #6061 the CCL-assigned value is used for the evaluations in this report, while for the other travelling standards the mole fractions determined by the WCC are used.

Table A2: Gas mixtures in 10-L cylinders serving as Travelling Standards of the WCC-N_2O. Cylinders employed for the audit at Izaña in November 2008 are underlined.

Cylinder		Additional gases in mixture		N_2O [ppb] as assigned by WCC-N_2O		CCL results (intercomparison 2007) [ppb]	Diff.: WCC – CCL [ppb]
Number	Short name	CO_2	SF_6	Based on NOAA-2000 scale	Converted to NOAA-2006 scale	NOAA-2006 scale	
4600D	DS 6	+		253.40	253.37		
4556D	DS 7	+		305.56	305.49		
4585D	DS 8	+		315.29	315.16		
4588D	DS 9	+		330.45	330.21		
4594D	DS 10	+		347.90	347.47	347.35	0.12
6061	DS 11	+	+	296.30	296.26	295.89	0.37
4618D	DS 12	+	+	326.59	326.38		
4563D	DS 13	+	+	332.91	332.65	332.77	-0.12
4616D	DS 14	+	+	306.03	305.95	305.89	0.06
4586D	DS 15	+	+	319.12	318.97	318.90	0.07
4590D	DS 16	+	+	332.59	332.33		

5.3 List of Abbreviations and Acronyms

CCL	Central Calibration Laboratory
DQO	Data Quality Objectives
ECD	Electron Capture Detector
EMPA	Swiss Federal Laboratories for Materials Testing and Research
ESRL	Earth System Research Laboratory, NOAA
FID	Flame Ionisation Detector
GAW	Global Atmosphere Watch (WMO Programme)
GC	Gas chromatograph
GG or GHG	Greenhouse Gas(es)
GMD	Global Monitoring Division (as part of NOAA ESRL)
GSV	Gas Sampling Valve (part of the GC system)
i.d.	inner diameter
MG	Measurement Guidelines
NOAA	National Oceanic and Atmospheric Administration (USA)
o.d.	outer diameter
QA	Quality Assurance
QC	Quality Control
QA/SAC	Quality Assurance/Science Activity Centre
SAG	Scientific Advisory Group
SIO	Scripps Institution of Oceanography
SOP	Standard Operating Procedure
SSV	Stream Selection Valve
WCC	World Calibration Centre
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization