

STANDARD OPERATION PROCEDURE FOR THE IAGOS-CORE GREENHOUSE GASES (GHG) INSTRUMENT (P2D)

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Date	Revision	Reason	Affected chapter or pages
10. Jan. 2017	IR	Initial release Remark: Since the instrument is not yet flying and in operation, some of the given values are only based on laboratory tests and test flights on research aircraft. As soon as real IAGOS flight data are available, the SOP will be adapted	All

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1 Rationale

Atmospheric CO₂ and CH₄ play an important role in global climate change. Monitoring of the climate forcing by atmospheric CO₂ and CH₄ is key to improving our understanding of GHG budgets and their trends under a changing climate. The measurements made by IAGOS help to improve the predictive capabilities of global and regional climate models, which require a better understanding and a quantification of processes and feedbacks controlling the atmospheric abundance of GHGs.

IAGOS is providing high-quality in-situ data on a long-term perspective also from regions of the atmosphere which are most sensitive for climate change and which are not adequately observed by space-borne and ground-based instruments like the upper tropopause/lower stratosphere region.

Information about the vertical distribution of GHGs across the globe will provide the most direct way to validate and anchor remote sensing based measurements to the calibration scales used for in situ measurements, thus paving the way for a homogenized data basis to be used in inverse modelling of GHGs targeted at regional fluxes.

The atmospheric signature of the long-lived greenhouse gases CO₂ and CH₄ is closely related to the specifics of atmospheric transport, thus IAGOS GHG measurements provide essential data for validation and improvement of atmospheric tracer transport models.

Atmospheric CO has dominant sources from anthropogenic emissions, thus in combination with CO₂ these observations will provide additional constraints on the fossil fuel emission component of atmospheric CO₂. The additional measurement of CO by the IAGOS-core package 2 version d (GHG) in addition to those made by IAGOS core package 1 allows for additional quality control, and opens new possibilities for future IAGOS core system configurations.

2 Description of the Method

2.1 Equipment

The instrument is designed for but not limited to deployment aboard Airbus A340 and A330 aircraft as part of the IAGOS project (www.iagos.org). The IAGOS installation provides a mounting rack, installed in the avionics bay below the cockpit, with electrical and pneumatic provisions for installation and operation, as well as the central data acquisition system (DAS), which collects the aircraft position and other aircraft parameters that are relevant for geo referencing of the measurements. The data measured by IAGOS Package 2 version d (P2d) are transmitted via Ethernet to IAGOS Package 1, besides being stored on a solid-state drive (SSD). After each flight the data are sent by GSM to the central IAGOS-database. In future it is planned to send also near-real time data with the help of the Real time Transmission Unit (RTTU) using the AMDAR (Aircraft Meteorological DATA Relay) service.

The instrument is designed for the autonomous measurement of greenhouse gases in the atmosphere and measures simultaneously CO₂, CH₄, CO and water vapor at high precision. It is based on a commercial analyzer developed by PICARRO Inc. (US, model G2401-m), which was redesigned to meet the requirements regarding physical dimensions (size, weight), performance (long term stability, low maintenance, robustness, full automation), and safety aspects. The measurement principle is based on wavelength-scanned cavity ring-down spectroscopy technique (CRDS), using spectral lines in the infrared.

Package P2d consists of several units as listed in Table 1 and shown in Figure 1, 2 and 3. A schematic gas flow diagram is given in Figure 4.

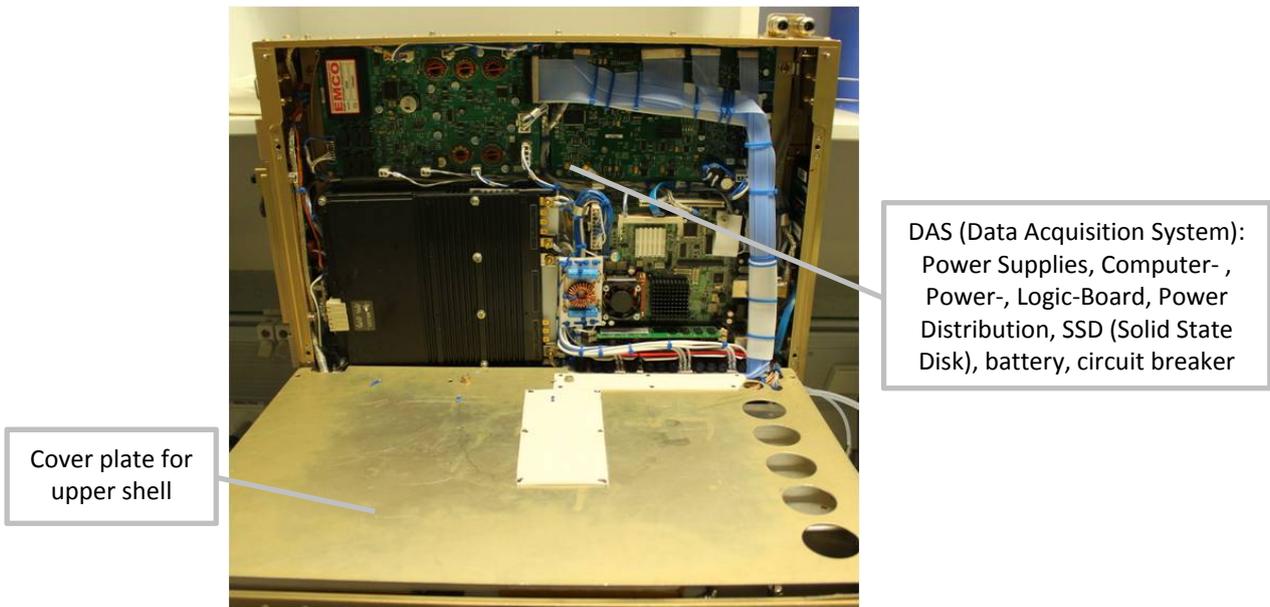


Figure 1: Photograph of IAGOS-P2d-01 with indication of sub-assemblies; upper shell

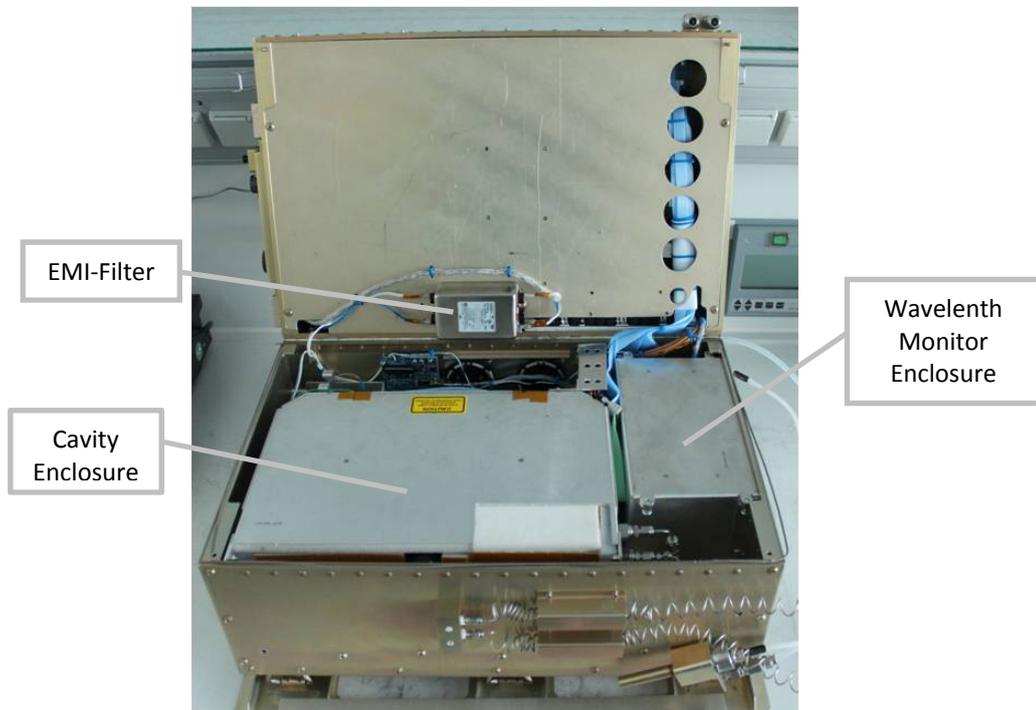


Figure 2: Photograph of IAGOS-P2d-01 with indication of sub-assemblies; lower shell.
EMI stands for electromagnetic interference.

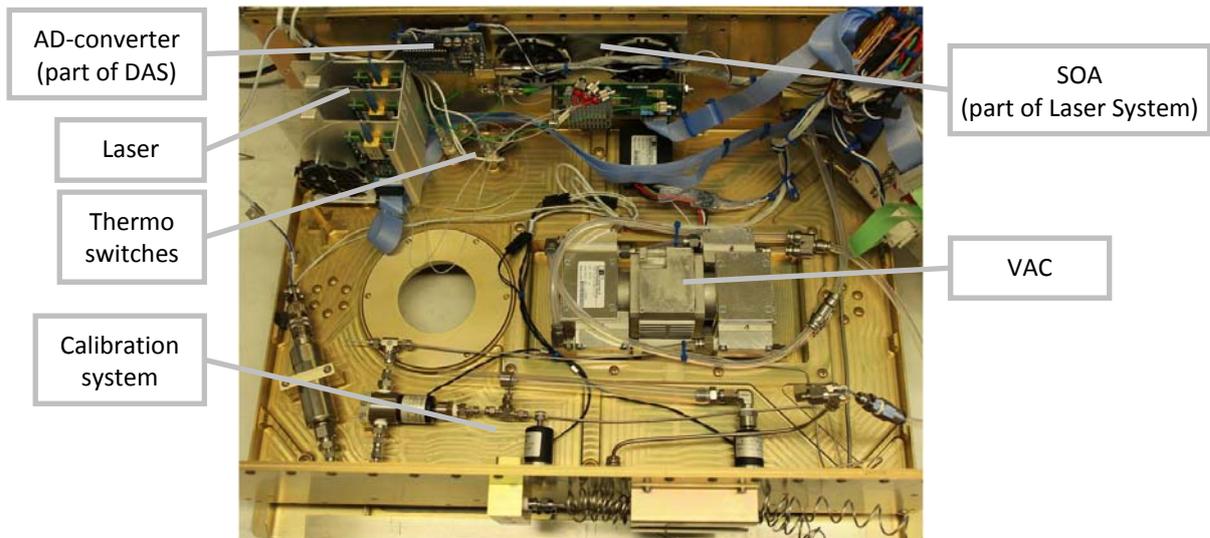


Figure 3: Photograph of IAGOS-PIId-01 with indication of sub-assemblies; floor section.
“AD” stands for analog-digital convertor, used specifically for the calibration gas pressure sensor.

Table 1: Description of sub-assemblies and auxiliary parts

Part or assembly	Abbr.	function / description
1.1 Frame	1.2 FRM	1.3 Aluminum box hosting all parts and providing the mechanical, electrical, and pneumatic interface to the installation structure and to the calibration gas cylinders
Functional parts:		
1.4 Cavity Enclosure	1.5 CE	1.6 The Cavity Enclosure contains the sample cell (cavity). The enclosure is temperature controlled and set to T=45°C.
1.7 Wavelength Monitor Enclosure	1.8 WME	1.9 The Wavelength Monitor Enclosure is the containment for the wavelength monitor. The enclosure is temperature controlled. Set point is 45 °C.
1.10 Vacuum Pump	1.11 VAC	1.12 Vacuum pump providing the airflow through the instrument
1.13 Laser System	1.14 LS	1.15 The four-channel analyzer uses 3 telecom-grade distributed feedback lasers, mounted on similar diode laser electronic boards. Laser light is carried by fiber optics. 1.16 A Semiconductor Optical Amplifier (SOA) amplifies the laser light before the measurement.
1.17 Calibration System	CS	1.18 The CS controls 3 valves to calibrate the instrument with standard gas provided by the two high-pressure cylinders.
1.19 Thermo Switches	1.20 TS	1.21 The thermo switches interrupt the electrical power provision to the whole instrument at temperatures above 70°C.
Auxiliary parts:		
1.22 Data Acquisition System and Power management	1.23 DAS	1.24 Circuit breaker; DC/DC converters for generation of 12V, -12V, 3.3V, 5V and 24V; Computer board to manage the data storage and handling the data transfer to the PI data interface; Power Board and Logic Board to control the subunits; SSD;

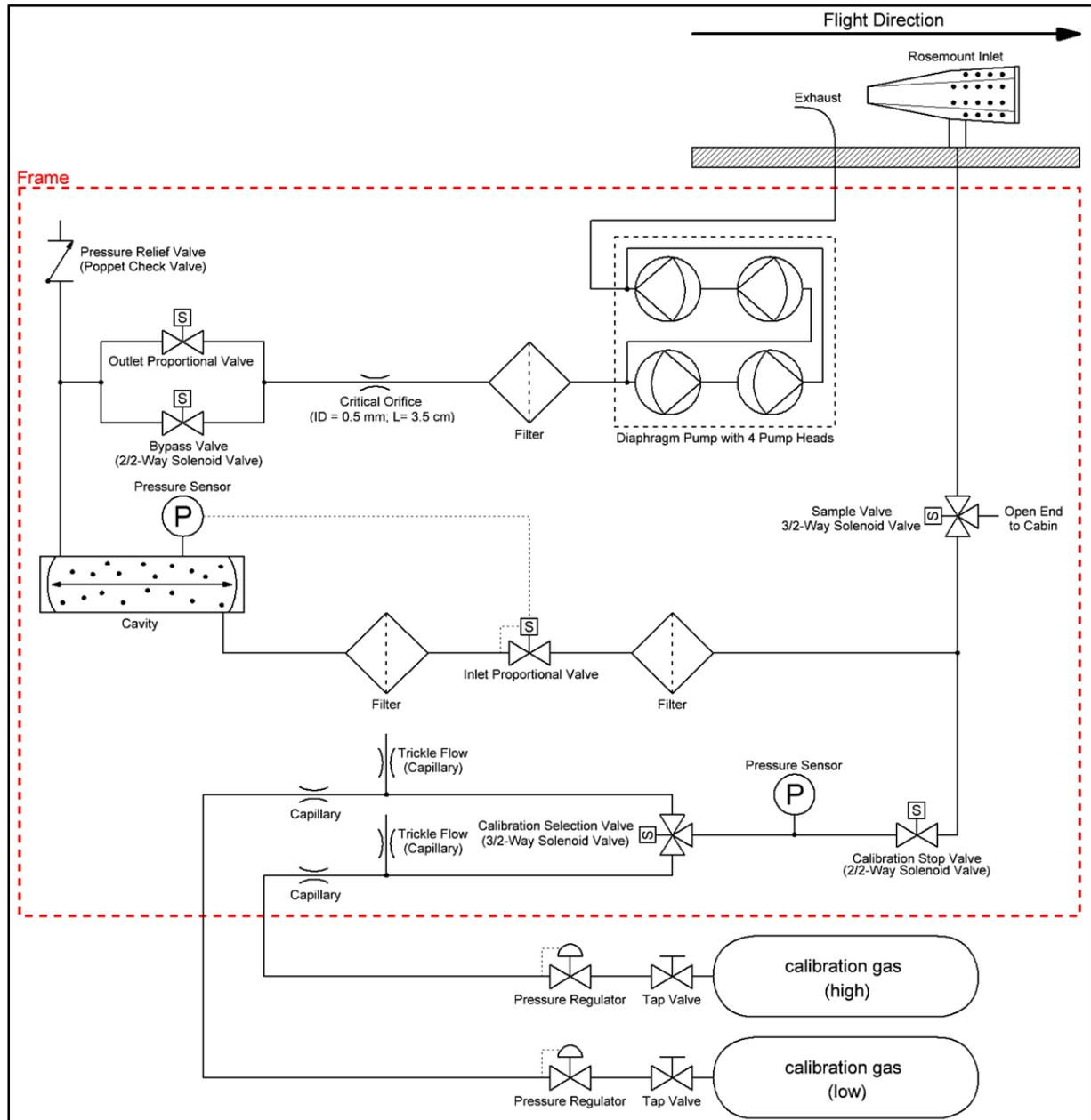


Figure 4: schematic flow diagram of IAGOS P2d

The cavity (35 scc; standard conditions for all given flows and volumes here and in the following: $T = 20\text{ }^{\circ}\text{C}$, $p = 101\text{ kPa}$) inside the Cavity Enclosure, equipped with three high-reflectivity mirrors (>99,995%), is constantly flushed with the sample gas during operation. The sample cell (cavity) pressure is controlled to 140 Torr (variations of less 0.1 Torr) with a proportional valve (inlet valve) upstream of the cell. The gas flow through the cavity is controlled at 100 sccm by a fixed flow restrictor (capillary) downstream of the cavity and upstream of the pump (VAC). This capillary acts as critical orifice, as the pressure drops by more than a factor two between cavity and pump. This makes the flow rate independent on ambient or cabin pressure. Temperature in the cavity is kept at $45\text{ }^{\circ}\text{C}$ (variations of less than 20 mK). Constant pressure and temperature in the sample cell minimize impact on gas density and spectroscopy. A pressure relief valve (set point 1 PSIG) protects the cavity from accidental excess pressure during all stages (in flight, on ground, during laboratory maintenance).

For a measurement laser light of a specific wavelength is injected into the cavity through a partially reflecting mirror. It gets reflected between the three mirrors (path length 15-20 km). The light intensity inside the cavity builds up over time and is monitored through a second partially reflecting mirror using a photo-detector located outside the cavity. When the light intensity reaches a threshold the laser is turned off. The following exponential decay ("ring-down") is modulated by absorption of the sample gas, and from the decay time ("ring-down time") the absorption coefficient is calculated. By tuning the wavelength of the laser a whole specific spectral line of a species can be scanned. Mathematical analysis of this absorption line provides a quantity, which at constant pressure and temperature is proportional to the mole fraction of the species.

The analyzer uses spectral lines in the infrared for its measurements: at 1603 nm for $^{12}\text{C}^{16}\text{O}_2$, 1651 nm for $^{12}\text{CH}_4$ and H_2^{16}O and 1567 nm for $^{12}\text{C}^{16}\text{O}$. Three telecom-grade distributed feedback (DFB) lasers provide light of the appropriate wavelengths.

Each species is measured once every 2.3 seconds. The physical exchange time of the sample cell is 3.6 seconds (volume = 35 ccm, sample flow = 100 sccm, pressure = 140 torr), ensuring that the ambient air is continuously sampled given the shorter measurement interval of 2.3 seconds.

2.2 Instrument Operation

The instrument operates fully automatically and without interrupt as long as the aircraft has power. The functions of the instrument are controlled by a single board PC using Picarro Inc. measurement software.

Two operation modes are implemented to fulfill the different measurement requirements while the aircraft is in air (about 12 hours per day, depending on the exact flight schedule) or on ground (about 8 hours per day):

1. When the a/c is on the ground the instrument measures air from inside the frame (cabin air, i.e. outside air filtered by the air conditioning system) to protect the analyzer from highly polluted air. In this mode the sample valve is off (see Table 2 and Figure 4). High frequency of calibrations.
2. When the a/c is flying ambient air is measured and the calibration frequency is lower than on the ground. Exact calibration frequencies will be worked out as soon as the measurements have started (scheduled for 2015).

The instrument uses the Weight-on-Wheel (WoW) signal from the aircraft to switch between ground and flight mode (in air). In the laboratory the instrument can be operated in ground mode as well as in flight mode and also in manual mode, where all valves and I/O functions can be switched individually.

The instrument is calibrated at regular intervals by measuring calibration gas provided by two fiber-wrapped aluminum cylinders. Each cylinder contains dried ambient air, but with different CO_2 , CH_4 and CO concentrations. With the help of three valves (sample valve, calibration stop valve, calibration selection valve) (GEMS Sensors Inc., G- & GH-Series) the gas flow through the measurement cell can be switched between calibration gas and air from the inlet as can be seen in Figure 4 and Table 2.

The calibration gas flow is maintained by capillaries acting as flow restrictors with an upstream pressure regulated to 5.7-6.7 bar (depending on cylinder pressure and cabin pressure) with pressure regulators. This pressure is monitored with a pressure sensor in the calibration gas line (GCT-225 model, Synotech GmbH). Calibration gas flow is kept above 110 sccm (ranging up to 165 sccm with nearly empty cylinders and at lowest cabin pressure (800 hPa)) and thus higher than the normal sample flow (100 sccm). During calibration the overflow of at least 10 sccm leaves the system backwards through the inlet to ensure that no air from outside is entering the system.

To eliminate back-diffusion and minimize the impact of permeation and surface interaction effects in the regulator (in the following: "regulator effects") a trickle flow of 2.8 sccm is applied to constantly flush the regulators.

Table 2: Valve selection for different instrument modes

Instrument Mode	Sample Valve (off = cabin air)	Calibration stop valve	Calibration selection valve
Ground mode	Off	Off	Off
Calibration tank I (at ground)	Off	On	Off
Calibration tank II (at ground)	Off	On	On
Flight mode	On	Off	Off
Calibration tank I (during flight)	On	On	Off
Calibration tank II (during flight)	On	On	On

2.3 System Layout

Externally required provisions for instrument operation are 28 V power supply and the Weight-on-Wheel (WoW) signal from the aircraft.

The instrument has provisions to be connected to two calibration gas cylinders (“flight cylinders”). The connection to the outlets of the cylinder regulators is made via coiled 1/16” OD stainless steel tubes equipped with quick connectors (Stäubli Tec-Systems GmbH, model RBE03, sealing: fluoroc rubber (FPM)). The quick connectors are sealed when not connected.

In order to provide uncontaminated ambient air to the instrument, it is equipped with an inlet line (1/8” OD FEP tube, 60cm) which connects package P2d with a Rosemount Total Air Temperature (TAT) housing (model 102B; Stickney et al., 1994) mounted on the inlet plate at the fuselage of the aircraft. The Rosemount probe offers several advantages: it acts as a virtual impactor since the inlet line is pointed orthogonal to the airflow through the housing, and thus prevents from sampling larger aerosols (larger than about 2 μm), ice particles, and water droplets; due to the strong speed reduction of the air it provides positive ram-pressure; and as standard housing for temperature and humidity sensors onboard civil aircraft it already possesses the required certifications (Volz-Thomas et al., 2005; Fahey et al., 2001). The additional positive ram-pressure, together with a low sample gas flow of 100 sccm and the relatively short inlet line ensures operation of the instrument throughout an aircraft altitude operating range up to 12.5 km without an upstream sampling pump. The inlet line material (FEP) is a compromise with respect to the impacts on the different measured species. As the IAGOS GHG system can be fully interchanged with the IAGOS core NO/NO_x and NO/NO_y system, the choice for FEP was made. Given the short residence time of sample gas, the small inner surface area, the small mole fraction differences between ambient and cabin air, and the low permeability of FEP, any impact from diffusion of CO₂, CH₄, and CO is minimal. The sample flow is exhausted through an exhaust line (1/4” OD FEP tube, 60 cm) connected to the dedicated exhaust duct included in the inlet plate.

The connection between Calibration Stop Valve and the tee-connector (see Figure 4), which connects ambient air, calibration gas and the sample cell, is kept small (2.5 cm long 3.18 mm (1/8”) OD tube, 2mm ID) to minimize the dead volume when measuring ambient/cabin air. Diffusion flow from the dead volume into the sample gas is <0.1 % of the sample flow 30 seconds after switching from calibration to ambient/cabin sampling, and can thus be neglected.

To protect the sample cell from contamination, filters (Wafergard II F Micro In-Line Gas Filters, Entegris Inc.) are implemented. They also ensure thermal equilibration of the sample gas, as they are kept at the same temperature as the sample cell.

3 Maintenance and Calibration

3.1 Test Procedure

Before and after each deployment, the following checks are mandatory:

- (1) Visual inspection for loose, broken or overheated parts
- (2) Verification of electrical load during start up and operation
- (3) Functional Test of instrument (check if the measurement and housekeeping data are within their regular limits, verification of inlet and outlet flow, etc.) and all sub-assemblies/parts (valves, sensors, pump, ...)
- (4) Verification of total mass (only before deployment)

Each step is documented following a detailed checklist. From the results of the inspection after deployment the required maintenance tasks, such as cleaning or replacement of components, are determined.

3.2 Maintenance Procedure

The following parts are exchanged regularly during each maintenance (i.e. every six months):

- pump diaphragms
- inlet filter (“F1” in Figure 4)

All other parts are exchanged based on necessity (i.e. if broken or damaged).

3.3 Calibration Methodology and Standards

3.3.1 CO_2 , CH_4 and CO

Traceability of the IAGOS-CORE GHG measurements to the WMO primary scales (currently WMO X2007 scale for CO_2 , WMO X2004 scale for CH_4 , WMO X2014 scale for CO) is ensured in a multi-step-procedure (see also Fig. 5):

During the six month deployment of the instrument aboard aircraft regular calibration take place by measuring pressurized ambient air from two “flight cylinders” (mole fractions for CO_2 , CH_4 and CO of 375 ppm, 1700 ppb, and 70 ppb, and of 400 ppm, 1900 ppb, and 150 ppb for the low and high cylinders, respectively) about every 3 hours (“In-flight calibrations”). With such a schedule the calibrations will be performed at all altitudes encountered during the flights so that potential pressure effects can be detected. Since the analyzer detects only the most abundant isotopologue of each trace gas, standards were prepared with similar isotopic composition to that found in ambient background air.

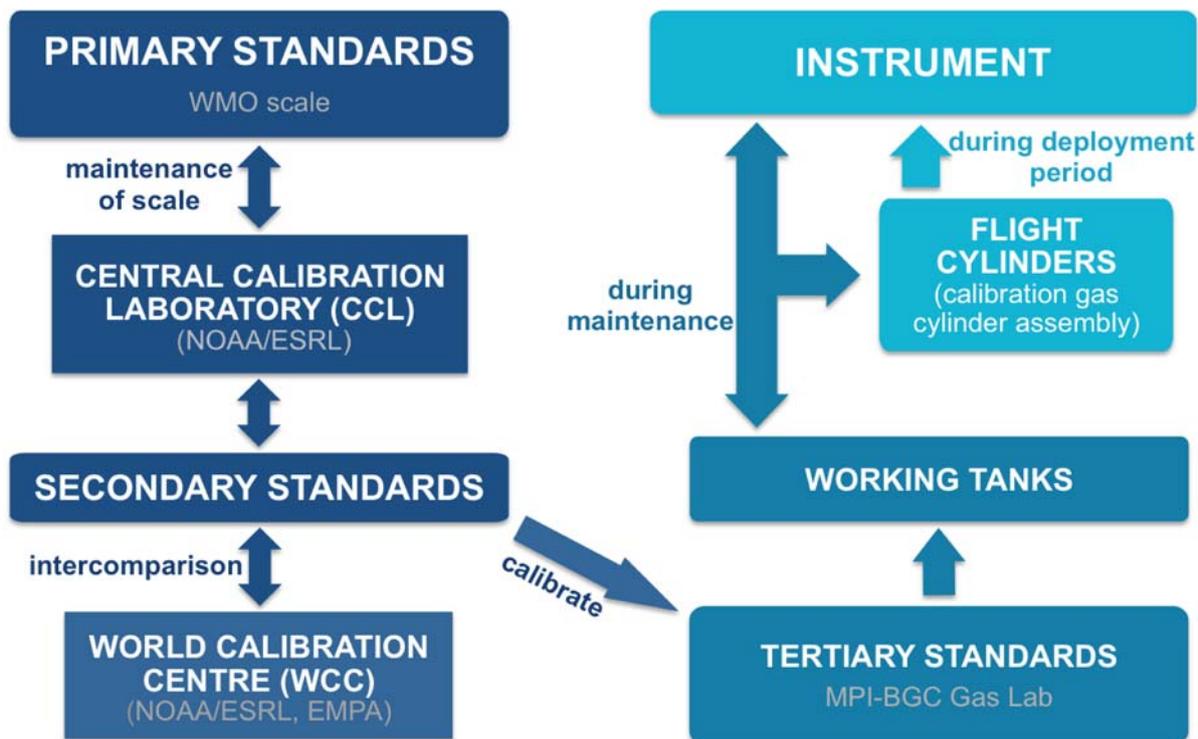


Figure 5: diagram showing the calibration chain from WMO primary standards to the IAGOS P2d instrument deployed in the aircraft

After the deployment period the flight cylinder assembly (cylinders, pressure regulators, tubing) and the instrument get calibrated at MPI-BGC with the help of three working tanks traceable to the respective primary scales. This “post-deployment calibration” is achieved with the following detailed steps:

- (1) Connect P2d with the two flight cylinders and open the cylinder valves
- (2) Connect P2d with power, a/c-signal and data cable and switch on P2d
- (3) Connect one of the three working standards at the inlet of P2d (Connect a needle valve between the pressure regulator and the inlet; Set the pressure regulator to about 2.5 bar at the low pressure side and use an open split in front of the instruments inlet; Adjust the excess flow at the open split to 40-60 sccm with the needle valve)
- (4) Measure the concentrations of CO₂, CH₄, CO and H₂O of the two flight cylinders
- (5) Measure the first working tank
- (6) Disconnect the first working tank
- (7) Connect the second working tank and measure it
- (8) Continue with the third tank
- (9) Finally, measure the two flight cylinders again

The working tanks are filled with pressurized ambient air at the Gas Lab of the MPI-BGC and are measured against the calibrated reference gas mixtures (tertiary standards) provided by the WMO Central Calibration Laboratory (CCL) that maintain the primary standard. The in-house tertiary standards are regularly (every 3-5 years) recalibrated by the CCL. CCL for all three species (CO₂, CH₄, CO) is NOAA/ESRL and World Calibration Centre (WCC) is EMPA.

After the post-deployment calibration and maintenance the flight cylinders are refilled, and the flight cylinders together with the instrument are calibrated again with the help of three calibrated laboratory tanks (“pre-deployment calibration”). Afterwards instrument and flight cylinders are shipped for a new deployment period.

A settling time of two weeks between filling and measuring the flight cylinders ensures that a representative measurement of the gas can be made, as experience with the first set of flight

cylinders indicated. Hence, the cylinders might be replaced by a different set for the next flight period depending on the time-schedule.

During both, post- and pre-deployment calibrations the same pressure regulators for the flight cylinders are used as during flight operation. This minimizes impact from potentially different effects on CO₂ from different regulators (i.e. with a different serial number). To ensure minimal impact from wall-effects in the flight cylinders (release of CO₂ bound to the cylinder walls), the final pressure (at the end of the post-deployment calibration) is kept above 30 bar.

The role of the in-flight calibrations in the data processing will be assessed as soon as first data are available. Possible options are: fully rely on each individual in-flight calibration; fully rely on the linear drift of the instrument between the pre- and post-deployment calibrations in the laboratory; or a mixture of both options, e.g. only a temporal average of the in-flight calibrations is used for the correction.

The data management system allows for easy reprocessing and propagation of scale changes from the secondary standards to the final measurements.

3.3.2 Water vapor

Currently the water vapor measurements are not calibrated against a reference standard that is traceable to the primary scale. For the initial water calibration of the instrument, a calibration of a similar instrument (EnviroSense 3000i, Picarro Inc.) performed at MPI-BGC Jena against a dew point mirror (Dewmet, Cooled Mirror Dewpointmeter, Michell Instruments Ltd., UK, referenced to National Institute of Standards and Technology (NIST)) in the range from 0.7 to 3.0% was transferred to all subsequently manufactured CRDS instruments by Picarro Inc.. A procedure to ensure proper traceability is under development.

4 Data Flow and Uncertainty Analysis

4.1 Data Flow

The measurements (wet air mole fractions) are recorded at a sample rate of around 3.2 seconds. Housekeeping data, as well as the status of the valves of the calibration system are measured and stored at intervals of 1Hz. An EventLog-file containing the status of the instrument and possible problems is also recorded.

The data are stored locally as text files.

At the IAGOS/MOZAIC Data Base near real-time data as well as final data are stored. Final data include individual uncertainty components (e.g. from calibrations, wet-to-dry correction, isotopic effects) for every observation. These time dependent uncertainty estimates will for CO₂, CH₄, and CO include effects from varying water vapor content, varying mole fractions (relative to the calibration range set by the low-span and high-span gases), and possibly effects rising from different ambient pressure. In section 4.3 we discuss conservatively estimated uncertainties, but for mole fractions within the calibration range.

4.2 Calculation of Results

- (1) Check of the housekeeping data (especially cavity pressure, cavity temperature, pressure of the calibration cylinders and sample flow; see Table 3) to identify periods where the instrument was not working properly. Apply possible corrections for e.g. small deviations in cavity pressure.

Table 3: Important Housekeeping Data and their acceptable limits

	Regular value	Acceptable limit
Cavity Pressure	186.6 hPa	± 0.13 hPa
Cavity Temperature	45 °C	± 0.05 °C
Pressure in the calibration gas line	5.5-6.2 x10 ⁵ Pa	± 0.35 x10 ⁵ Pa
Sample flow	100 sccm	± 20 sccm

Although small variations in sample flow have no impact on the measurements, it is important to monitor the flow as it affects the exchange rate of the sample gas. When the instrument switches between ambient air, cabin air or calibration gas measurement, time passes until the change in signal occurs. The flow is inversely proportional to this lag time and can be calculated if the inner volume of the flushed tubing is known. To allow a regular determination of the sample flow, the “open end to cabin” in Figure 4 is realized as a 0.5” ID tube with a length of about 22 cm. This causes a lag time when switching from calibration gas to cabin air during ground operation is extended, as the tube is first filled with calibration gas, but the volume is flushed by cabin air. Determining this lag time combined with the information about the inner volume of the 0.5” ID tube and the cabin pressure allows monitoring the sample flow with ~5 % accuracy.

- (2) The measurement data of CO₂, CH₄ and CO are converted from wet air mole fractions to dry air mole fractions using the H₂O measurements made by the instrument. This water correction is based on laboratory experiments made with each IAGOS-CORE P2d instrument during each maintenance cycle, i.e. every 6 months, as this method has been shown to result in the lowest uncertainty in the water vapor correction (Rella et al., 2013, Chen et.al, 2013).
- (3) Measurement and calibration data get separated.
- (4) With the help of the calibrations during the deployment period, together with the pre- and post-deployment calibrations, the instrument calibration factors for this deployment period are determined.

To reduce the impact from non-equilibrium calibration gas measurements during the relatively short in-flight calibrations, i.e. the fact that CO₂ values might not yet have reached the final value at the end of the calibration cycle, a fit procedure is applied to each calibration to estimate the equilibrium values for dry air mole fraction for each calibration gas. This procedure will be regularly re-assessed during maintenance.

- (5) The measurement data get calibrated using the calibration factors.
- (6) Adjustment of delays and transient times to account for residence times in tubing and for memory after switching. Transient times are determined using a step change in mixing ratio provided to the inlet.

4.3 Uncertainty Budget

An overview of the measurement precision and overall uncertainties can be seen in Table 4. Note that the WMO GAW compatibility goals should actually represent most upper limits, as individual measurement programs should strive for significantly smaller uncertainties. However, the fact that those are likely not met for CO₂ and CO indicate that this is hard to achieve with aircraft measurement programs.

Table 4: Repeatability and overall uncertainties (1-sigma values)

Species	Repeatability (at 3.2 second time resolution)*	WMO-GAW compatibility goal	Achieved Overall Uncertainty
CO ₂	<0.039 ppm	0.1 ppm/0.05 ppm	<0.13 ppm

		(northern/southern hemisphere)	
CH ₄	<0.4 ppb	2 ppb	<1.3 ppb
CO	<15 ppb	2 ppb	<4 ppb
H ₂ O	<4 ppm		<15 ppm @ below 100 ppm <25% @ 100 – 300 ppm <11% @ 300 – 200 ppm <6% @ 1000-10000 ppm <4% at above 10000 ppm

* Random errors are uncorrelated, such that with sufficient temporal integration the precision will be small compared to the overall uncertainty (For example for CO at minimum a 100 second integration time is needed to achieve the uncertainty of 2 ppb).

4.3.1 CO₂

Overall uncertainty for CO₂ includes referencing of the inflight calibration gases to WMO primary standards, isotopic effects, measurement repeatability, and uncertainty in the applied H₂O-correction. Instrument response drift is compensated by regular calibrations. As the steps in calibration transfer are independent from each other, and independent of the uncertainty introduced by the wet-to-dry correction, propagation of uncertainties is made assuming that all contributions are independent (Gaussian error propagation assuming independent variables). Only the bias for isotopic effects is added linearly.

1. Uncertainty of the NOAA secondary standards: 0.014 ppm (Zhao and Tans, 2006)
Uncertainty of the NOAA tertiary standards: 0.014 ppm (the MPI-BGC GasLab has 7 tertiary standards available)

-> uncertainty of the BGC-GasLab implementation of the WMO primary scale:

$$\sqrt{(0.014\text{ppm})^2 + (0.014\text{ppm}/\sqrt{7})^2} = 0.015\text{ppm}$$

2. CO₂ calibration of the laboratory working tanks is made at the MPI-BGC GasLab using a CRDS analyzer (G1301, Picarro Inc.) which is calibrated daily using three GasLab working standards (spanning the atmospheric range of CO₂) that are assigned relative to the above mentioned suite of WMO tertiary standards. The reproducibility of assignments of these standards for multiple calibration episodes relative to the WMO tertiary standard suite (ca. 10 episodes per working standard) is 0.01 ppm for CO₂. Within this series of re-calibrations drifts of CO₂ mole fractions of 0.01-0.015 ppm/year have been detected in several working standards. A linear drift function is applied in these cases. The overall uncertainty of the CO₂ scale transfer is approximated as 0.01 ppm.

The accuracy of the GasLab assignments of IAGOS working tanks is assessed based on the time series of daily target standard measurements. The standard deviation of these daily mean values is 0.015-0.02 ppm for CO₂ for a 20 min measurement period. These long-term quality control records do not only represent the analyzers precision but also additional disturbances apparent in the laboratory operation (e.g. temporary small leakages). Combining the uncertainty of the GasLab working standard assignment (including its stability over time) and the general reproducibility of the analytical method yields a total MPI-BGC GasLab scale transfer uncertainty of 0.02 ppm.

Uncertainty of calibration transfer to the laboratory working tanks: 0.02 ppm

-> Uncertainty of the working tanks compared to the primary scale:

$$\sqrt{(0.015\text{ppm})^2 + (0.02\text{ppm})^2} = 0.025\text{ppm}$$

- The last step of the calibration chain is the calibration of the IAGOS-core GHG instrument with the help of the working tanks and the flight cylinders. Here, the repeatability of the instrument for the measurements of the working tank calibration gases and the flight cylinders is deduced from laboratory experiments as 0.015 ppm for CO₂. For the in-flight calibrations the uncertainty of the fit procedure (applied to each calibration to estimate the equilibrium value) has to be added to the measurement uncertainty. In the worst case instrument drift needs to be compensated for by three-hourly calibrations. In the best case the instrument does not drift significantly, and all calibrations (pre-, post-, and all in-flight calibrations) can be statistically combined, which reduces the uncertainty significantly. For now, without flight experience, the worst-case scenario is considered for the calculations to give an upper limit of the uncertainty, which leads to an uncertainty of the fit procedure of 0.07 ppm for CO₂. By combining the repeatability of the working tank measurements and the in-flight calibration gas measurements with the uncertainty of the fitting procedure, the overall uncertainty of this calibration transfer step is determined as 0.07 ppm.

Uncertainty of calibration transfer from the in-flight cylinders and the working tanks to the instrument: 0.07 ppm

-> uncertainty of the instrument measurements compared to the primary scale:

$$\sqrt{(0.025\text{ppm})^2 + (0.07\text{ppm})^2} = 0.074\text{ppm}$$

- Uncertainty due to drift correction of the flight cylinders, and due to regulator effects (for now roughly estimated, will later be based on experience from QA/QC cycles): 0.05 ppm

-> uncertainty of the instrument measurements compared to the primary scale:

$$\sqrt{(0.074\text{ppm})^2 + (0.05\text{ppm})^2} = 0.089\text{ppm}$$

- Uncertainty of the water correction: 0.05 ppm (Rella et al., 2013; Chen et.al., 2010)

-> uncertainty of the instrument measurements compared to the primary scale:

$$\sqrt{(0.089\text{ppm})^2 + (0.05\text{ppm})^2} = 0.102\text{ppm}$$

- Measurement repeatability: 0.039 ppm

-> uncertainty of the instrument measurements compared to the primary scale:

$$\sqrt{(0.102\text{ppm})^2 + (0.039\text{ppm})^2} = 0.109\text{ppm}$$

- Measurement bias due to differences in the isotopic signature of CO₂ between the tertiary standards calibrated by the CCL and the laboratory working tanks (filled with the calibration gases): 0.019 ppm

=> overall uncertainty for CO₂ (1-sigma):

$$0.109\text{ppm} + 0.019\text{ppm} = \underline{\underline{0.128\text{ppm}}}$$

4.3.2 CH₄

Overall uncertainty for CH₄ includes referencing of the flight cylinders to WMO primary standards, measurement repeatability, and uncertainty in the applied H₂O correction. Instrument response drift is compensated by regular calibrations. Measurement errors caused by deviations of the calibration gases in the isotopic composition of CH₄ were found to be negligible as the fraction of these deviations to total methane is small; in addition the measured biases due to ¹³C and deuterium compensate each other. As the steps in calibration transfer are independent from each other, and independent of the uncertainty introduced by the wet-to-dry correction, propagation of uncertainties is made assuming that all contributions are independent (Gaussian error propagation assuming independent variables).

- Uncertainty of the NOAA tertiary standards: 0.7 ppb (Dlugokencky et al., 2013)

-> the MPI-BGC GasLab has 7 tertiary standards available, which would lead to an uncertainty of the BGC-GasLab implementation of the WMO primary scale of

$$\sqrt{(0.7 \text{ ppb} / \sqrt{7})^2} = 0.26 \text{ ppm}$$

-> however, experience has shown that it is more realistic to assume an uncertainty of 0.7 ppb

2. CH₄ calibration of the laboratory working tanks is made at the MPI-BGC GasLab using a CRDS analyzer (G1301, Picarro Inc.), which is calibrated daily using three GasLab working standards (spanning the atmospheric range of CH₄) that are assigned relative to the above mentioned suite of WMO tertiary standards. The reproducibility of assignments of these standards for multiple calibration episodes relative to the WMO tertiary standard suite (ca. 10 episodes per working standard) is 0.1 ppb for CH₄. Within this series of re-calibrations all working standards have been stable in their CH₄ mole fraction. Thus, the uncertainty of the CH₄ scale transfer to the GasLab working standards is corresponding to the standard error of 0.03 ppb (0.1 ppb / \sqrt{n}).

The accuracy of the GasLab assignments of IAGOS working tanks is assessed based on the time series of daily target standard measurements. The standard deviation of these daily mean values is 0.1-0.2 ppb for CH₄ for a 20 min measurement period. These long-term quality control records do not only represent the analyzers precision but also additional disturbances apparent in the laboratory operation (e.g. temporary small leakages). Combining the uncertainty of the GasLab working standard assignment (including its stability over time) and the general reproducibility of the analytical method yields a total MPI-BGC GasLab scale transfer uncertainty of 0.15 ppb.

Uncertainty of calibration transfer to the laboratory working tanks: 0.15 ppb

-> Uncertainty of the working tanks compared to the primary scale:

$$\sqrt{(0.7 \text{ ppb})^2 + (0.15 \text{ ppb})^2} = 0.71 \text{ ppb}$$

3. The last step of the calibration chain is the calibration of the IAGOS-core GHG instrument with the help of the working tanks and the flight cylinders. Here, the repeatability of the instrument for the measurements of the working tank calibration gases and the flight cylinders is deduced from laboratory experiments as 0.15 ppb for CH₄. For the in-flight calibrations the uncertainty of the fit procedure (applied to each calibration to estimate the equilibrium value) has to be added to the measurement uncertainty. In the worst case instrument drift needs to be compensated for by three-hourly calibrations. In the best case the instrument does not drift significantly, and all calibrations (pre-, post, and all in-flight calibrations) can be statistically combined, which reduces the uncertainty significantly. For now, without flight experience, the worst-case scenario is considered for the calculations to give an upper limit of the uncertainty, which leads to an uncertainty of the fit procedure of 0.19 ppb for CH₄. By combining the repeatability of the working tank measurements and the in-flight calibration gas measurements with the uncertainty of the fitting procedure, the overall uncertainty of this calibration transfer step is determined as 0.28 ppb.

Uncertainty of calibration transfer from the in-flight cylinders and the working tanks to the instrument: 0.28 ppb

-> uncertainty of the instrument measurements compared to the primary scale:

$$\sqrt{(0.71 \text{ ppb})^2 + (0.28 \text{ ppb})^2} = 0.76 \text{ ppb}$$

4. Uncertainty of the water correction: 1 ppb (Rella et al., 2013)

-> uncertainty of the instrument measurements compared to the primary scale:

$$\sqrt{(0.76 \text{ ppb})^2 + (1 \text{ ppb})^2} = 1.26 \text{ ppb}$$

5. Measurement repeatability: 0.4 ppb

=> overall uncertainty for CH₄ (1-sigma):

$$\sqrt{(1.26\text{ppb})^2 + (0.4\text{ppb})^2} = \underline{\underline{1.32\text{ppb}}}$$

4.3.3 CO

Overall uncertainty for CO includes referencing of the flight cylinders to WMO primary standards, measurement repeatability, and uncertainty in the applied H₂O correction. Instrument response drift is compensated by regular calibrations. The isotopic composition for CO is not known, but estimations based on similar values as for CO₂ are insignificant compared to the measurement repeatability. As the steps in calibration transfer are independent from each other, and independent of the uncertainty introduced by the wet-to-dry correction, propagation of uncertainties is made assuming that all contributions are independent (Gaussian error propagation assuming independent variables).

1. Uncertainty of the BGC-GasLab implementation of the WMO primary scale (1-sigma):
0.5 ppb or 0.25% (whichever is greater) (taken from the GAW Report No. 206)
2. CO calibration of the laboratory working tanks is made at the MPI-BGC GasLab using a vacuum ultraviolet resonance fluorescence (VURF) analyzer (Aerolaser AL 5002), which is calibrated by working standards that are assigned relative to the above mentioned suite of WMO tertiary standards. A one-point calibration using a single working standard and a zero gas analyzed each for six minutes is made every 30 minutes. The relative reproducibility of working standard assignments relative to the WMO tertiary standard suite (6 episodes per working standard) is 0.2 % (0.4 ppb and 0.8 ppb for two working standards at 246 ppb and 426 ppb, respectively). The first working standard showed a steady increase of CO mole fractions at a drift rate of 0.6 ppb/year that was accounted for using a linear interpolation. Likewise, one of the standards in the GasLab CO WMO tertiary standard set showed a CO growth of 1 ppb/year and therefore has not been used for calibration. This points to a potential bias of the tertiary set due to a similar drift of the entire set as it has been reported by the WMO-CCL for CO in some primary standards at a rate of 0.3 ppb/year (see http://www.esrl.noaa.gov/gmd/ccl/co_scale.html). Recent re-calibrations at the WMO-CCL of two tertiary standards, however, did not indicate any CO growth over a period of nine years. Absolute values of the residuals of the seven tertiaries with CCL assignments obtained in different years since 2005 are below 0.5 ppb with no systematic trend in the time-series of residuals of any single standard. Based on this evidence, it is assumed to be unlikely that the MPI-BGC GasLab tertiary standard suite comprises any bias due to instabilities in the standards CO mole fractions. This is consistent with the absence of any significant drift in the time series of target standards. However, despite the absence of a clear indicator for drift of the GasLab tertiaries an upper limit of 0.5 ppb for the stability of the set is taken as conservative estimate for the uncertainty of the tertiary assignments considering the known problems with CO growth and the associated challenge of detecting small drifts. Accounting for this uncertainty a relative calibration transfer uncertainty of the GasLab working standards of 0.3 % is derived for the working standard containing 246 ppb CO. Target standards are analyzed daily in the same way as the IAGOS working tanks (15 min measurement period divided by a calibration). The record of these target standards measurements documents a long-term relative reproducibility of the VURF CO analysis of 0.25 %. By combining the uncertainty of the MPI-BGC GasLab working standard assignment and the reproducibility of the analytical method the MPI-BGC GasLab scale transfer uncertainty for CO is estimated as 0.4 % relative or 0.7 ppb absolute (whichever is greater).

Uncertainty of calibration transfer to the laboratory working tanks:

0.7 ppb or 0.4 % (whichever is greater)

-> Uncertainty of the working tanks compared to the primary scale:

$$\sqrt{(0.5 \text{ ppb})^2 + (0.7 \text{ ppb})^2} = 0.86 \text{ ppb}$$

- The last step of the calibration chain is the calibration of the IAGOS-core GHG instrument with the help of the working tanks and the flight cylinders. Here, the repeatability of the instrument for the measurements of the working tank calibration gases and the flight cylinders is deduced from laboratory experiments as 2 ppb for CO. By combining these two uncertainties the overall uncertainty of this calibration transfer step is determined as 2.8 ppb.

Uncertainty of calibration transfer from the in-flight cylinders and the working tanks to the instrument: 2.8 ppb

-> uncertainty of the instrument measurements compared to the primary scale:

$$\sqrt{(0.86 \text{ ppb})^2 + (2.8 \text{ ppb})^2} = 2.93 \text{ ppb}$$

- Uncertainty of the water correction: 2 ppb (Chen et al., 2013)

-> uncertainty of the instrument measurements compared to the primary scale:

$$\sqrt{(2.93 \text{ ppb})^2 + (2 \text{ ppb})^2} = 3.55 \text{ ppb}$$

- Measurement repeatability (3 minutes time resolution): 1.7 ppb

=> overall uncertainty for CO (1-sigma):

$$\sqrt{(3.55 \text{ ppb})^2 + (1.7 \text{ ppb})^2} = \underline{\underline{3.94 \text{ ppb}}}$$

4.3.4 Water vapor

For H₂O the overall uncertainty includes instrument response drift and traceability to the NIST scale:

- Instruments response drift over 6 months:
<100 ppm or <0.5 % (whichever is greater)
- uncertainty of calibration transfer from NIST scale to the instrument:
0.2 °C dewpoint at 20 °C dewpoint (corresponding to 1.2% relative uncertainty at 2.3% vmr),
linearly increasing to 0.4 °C dewpoint at -60 °C dewpoint (corresponding to 5.5% relative uncertainty at 11 ppm vmr)

5 Flagging of data

To clearly identify the state of validation and reliability of the measurement a two separate index numbering flag scheme is defined:

- Flag Index Number FI1: State of Data Processing/Validation
- Flag Index Number FI2: Reliability of Data

The Data Flag Scheme for the first flag index FI1 is IAGOS specific and gives the state of processing of the measured data. The second flag index FI2 is compatible with WMO flagging code scheme 0-33-020 (WMO Report 306) that most likely will become the standard within WMO/GAW in the next future (2016-2017).

Table 5: Data Flag Scheme for the two flag indexes

Flag Index FI1	IAGOS-State of Processing (e.g. validation)	Comments
0	Raw	

1	Preliminary (=Delayed Mode)	NRT data has same level of validation
2	Final (Validated)	
7	n/a	
Flag Index FI2	IAGOS State of Reliability of Data	WMO Code 0 33 020
0	Good (i.e. acceptable)	Good
1	n/a	Inconsistent
2	Limited (i.e. Questionable)	Doubtful
3	Erroneous	Wrong
4	Not Validated	Not Checked
5	n/a	Has Been Changed
6	n/a	Estimated
7	Missing Value	Missing Value

The numerical value for missing values is 999999, which is larger than the largest expected measured value for all gases measured with the IAGOS-CORE GHG system.

6 Specifications

Table 6: Specifications of the IAGOS-Core GHG instrument

Quantity	Value Units	Explanations/Comments
Dimensions	560x400x296.5 mm ³	LxWxH (envelope)
Mounting		Mounting base plate with shock mounts for vibration dampened fixation of instrument box.
Mass	30 kg	Box with base plate and pneumatic lines
Connectors	MS3470 W 14-5 P MS3470 W 16-26 PRJFTV 2 1RA G ABS0607B53-260	Power in Aircraft control signals Ethernet Bonding
Electrical Load Voltage: Average Current: Start up (1 min): Warming phase:	28 V DC 4.5 A 4 A max. 12.5 A	
Ventilation	20 L/s	External fan and matching adapter required
Ambient Temperature	10°C to 35°C -10°C to 45°C -10°C to 50°C	Measurement specification Save Operation Storage
Inlet line DIA, Length	FEP tube 1/8" OD, <1m	Front part fitted with an adapter to fit to external inlet (Goodrich, P/N 102XB)
Exhaust line	FEP tube ¼" OD	No important limitations
Sample flow rate	100 sccm	
Measured quantity	CO ₂ , CH ₄ , CO, H ₂ O	
Method of detection	Cavity ring-down spectroscopy	Absorption of IR laser light
Precision	CO ₂ : 0.1 ppm CH ₄ : 1 ppb CO: <15 ppb H ₂ O: 4 ppm	
Time resolution	4 s	
Calibration	Automatic	Calibration Gas: Pressurized ambient air
Data acquisition and control system (DAS)		Among others: Computer Board, SSD, interfaces, and Ethernet port to external DAS, no provision to acquire aircraft position
Control signals	2x 28V DC, <50mA	a/c signals (WOW) required for automatic operation

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