STANDARD OPERATION PROCEDURE

FOR THE

IAGOS-CORE NOx INSTRUMENT (P2b)

P/N: IAG0S-PIIb-01

Andreas Volz-Thomas

Institut für Energie und Klimaforschung 8 (IEK-8)

Forschungszentrum Jülich GmbH

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Content:

1 Rationale

Nitrogen oxides (NO_x, sum of NO and NO_2) play an important role in atmospheric chemistry related to ozone and oxidation capacity (OH and NO_3 radicals). They are observed at mixing ratios ranging from a few ppt in the remote marine boundary layer to a few ppb in continental background and up to several hundreds of ppb in urban environments (c.f. *Emmonds et al., 1997, 2000*). Sources of NO_x are combustion processes (power generation, transportation, biomass burning, wild fires), soil emissions, lightning and photochemical production from N_2O in the stratosphere. The most important sources of NO_x to the upper troposphere are lightning, transport from the boundary layer and aircraft emissions.

Measurements of NO_x in the free troposphere and lower stratosphere are important for understanding the local photochemistry and for assessment of the impact of aircraft on the budgets of greenhouse gases such as ozone and methane. Because of the strong influence of UV radiation on the ratio between NO and NO_2, it is important to measure both species or at least the sum of both. Remote sensing is so far only capable of providing information on NO_2 (vertical column and limited information on vertical profile).

1.1 Measurement Objectives

Objectives for the measurements of NO_x made in IAGOS-CORE are to generate basic information on the distribution of NO_x in regions not well covered by other monitoring activities. Specifically, the measurements shall contribute to produce information on the:

- Climatology of NO_x in the UTLS
- Vertical profiles in the troposphere
- Frequency of pollution events
- Influence of lightning and biomass burning on the NO_x distribution

The analysis of long-term trends is not an objective for the NO_x measurements made in IAGOS-CORE, because of the large expected variability of high NO_x concentrations and the respectively large uncertainty of background concentrations.

2 Description of method

2.1 Principle

The IAGOS-CORE NO_x instrument (P/N: IAGOS-PIIb-01 and IAGOS-PIIb-02, henceforth denoted Package 2b or P2b) is designed for the autonomous measurement of nitrogen oxides in the atmosphere. The measurement principle is based on the well-established technique of chemiluminescence, i.e., the photoelectric detection of the photons (hv) produced in a chemical reaction (R1) between atmospheric NO and ozone (*Clough and Thrush, 1967; Drummond et al., 1985*). Conversion of NO_2 to NO is achieved by photolysis at wavelengths of 395 ± 5 nm (R2). The specific set-up of IAGOS P2b is described in detail by *Volz-Thomas et al.,* (2015).

R1 $NO + O_3 \rightarrow NO_2 + O_2 + h\nu$ $(600 < \lambda < 3000\ \mathrm{nm})$

R2 $NO_2 + O_2 + h\nu \rightarrow NO + O_3$ $\lambda = 395 \pm 5\ \mathrm{nm}$

2.2 *Description of Instrument*

IAGOS Package 2b is designed for but not limited to deployment aboard Airbus A340 and A330 as part of the IAGOS-CORE installation, which is located in on the port side of the avionics compartment (see **Figure 1**). This installation provides a mounting rack with all electrical and pneumatic provisions required for installation and operation, including a plate on the fuselage of the aircraft with appropriate probes for connecting the instruments to ambient air. The IAGOS-CORE installation consists of two packages: Package 1, which is installed on all aircraft, contains monitors for ozone, carbon monoxide, relative humidity and cloud particles, as well as the central data acquisition system which collects the aircraft position and other aircraft parameters that are relevant for geo-referencing of the measurements. For Package 2, several options are foreseen, of which only one can be installed on a given aircraft. They are denoted Package 2a (NO_y), Package 2b (NO_x), Package 2c (Aerosol), and Package 2d (Greenhouse Gases).

The data measured by Package 2 are transmitted via Ethernet to IAGOS Package 1, besides being stored on hard disk. Package 1 contains a modem for transmission of the collected data after each flight.

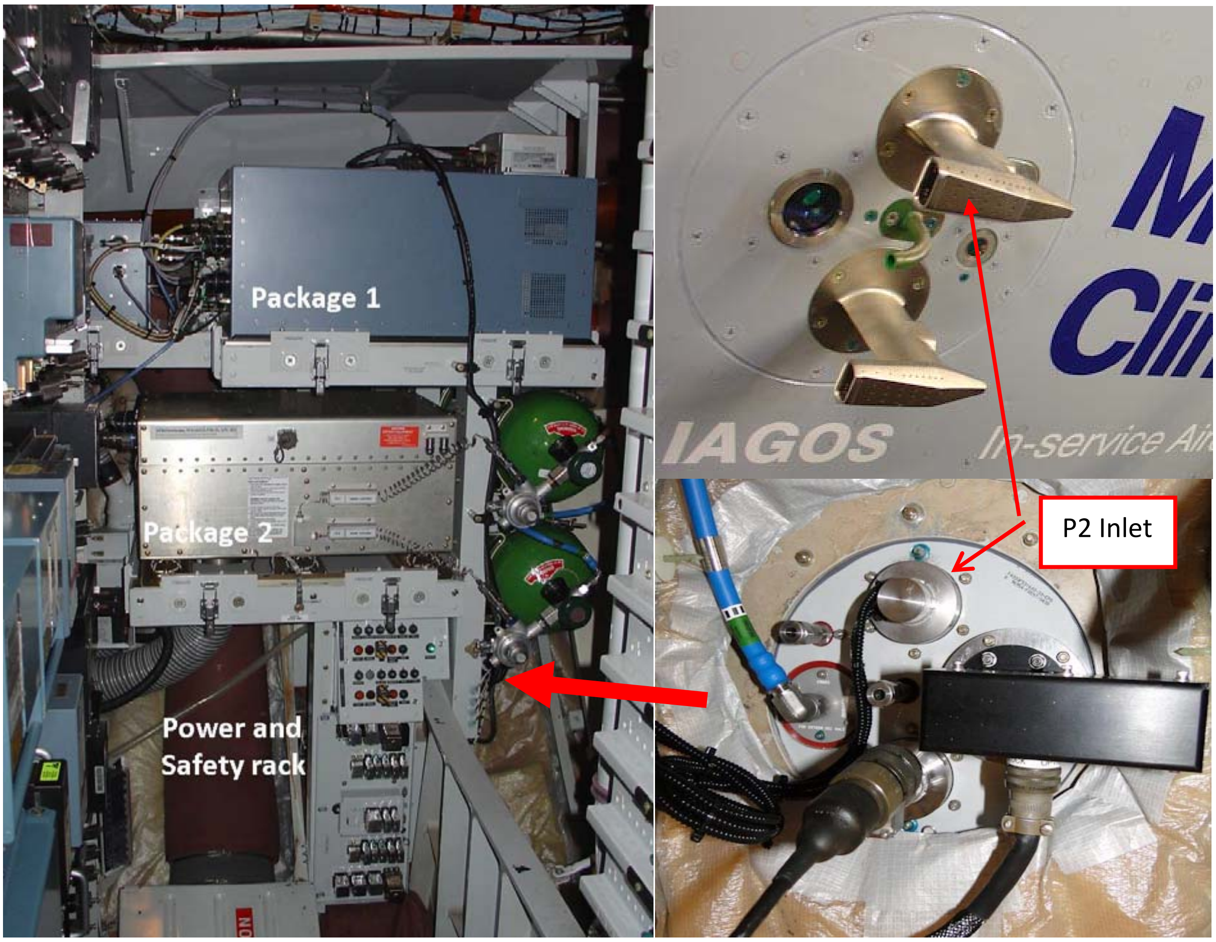

Figure 1: IAGOS rack installed in an Airbus A340 of Lufthansa AG (left) and IAGOS Inlet Plate (upper right: outside view, lower right: inside view).

<u>Note:</u> Installation of the instrument on aircraft, which are not equipped with IAGOS Package 1, requires appropriate provisions for installation and operation, including a central data acquisition system, a supply of high purity (> 99.999 %) oxygen and provisions at the fuselage for connecting inlet and exhaust line (equivalent to that shown in **Figure 1**).

Package P2b (NO_x), which is subject of this SOP, consists of several units as listed in Table 1and shown in **Figure 2**. Because of the limitations provided by the physical boundary conditions for installation in the IAGOS rack and long deployment periods the instrument employs only one chemiluminescence channel and much lower flow rates than instruments flown on research aircraft, similar to the instrument used in MOZAIC for measurements of NO_Y described in *Volz-Thomas et al., (2005)*. Hence, measurements of NO and NO_x are made sequentially.

Table 1: Description of sub-assemblies and auxiliary parts

Functional parts:	**Abbr.**	**function / description**
Oxygen Distribution Unit	O2D	Assembly with magnetic valves and capillaries for distribution of oxygen to the different functional parts at controlled flow rates (5 - 250 sccm).
NO Detector Unit	NOD	Detector for nitrogen monoxide (NO), based on the detection of photons produced in the chemical reaction between atmospheric NO with ozone (from O3G). Usually named CLD = chemiluminescence detector
Ozone Generator Unit	O3G	Assembly for the generation of ozone (electrical discharge in a small oxygen flow) needed for the measurement of NO
Vacuum Unit	VAC	Assembly containing two membrane pumps and a shut-off valve (MV4)
Converter and Calibration Unit	ICC	Unit containing provisions for internal calibration check of the instrument, the photolytic converter (PLC) for transforming NO_2 to NO, and a flow controller (FC).
Auxiliary parts:		
Data Acquisition System and Electrical parts	DAS	Single board PC with interfaces for analog and digital I/Os, interface for aircraft status (WoW); line filter, circuit breaker, DC/DC converter for generation of 24V; cable assemblies
Pneumatic parts		Internal pressure regulator, tubing , fittings
Mechanical parts		Mounting and fixation material

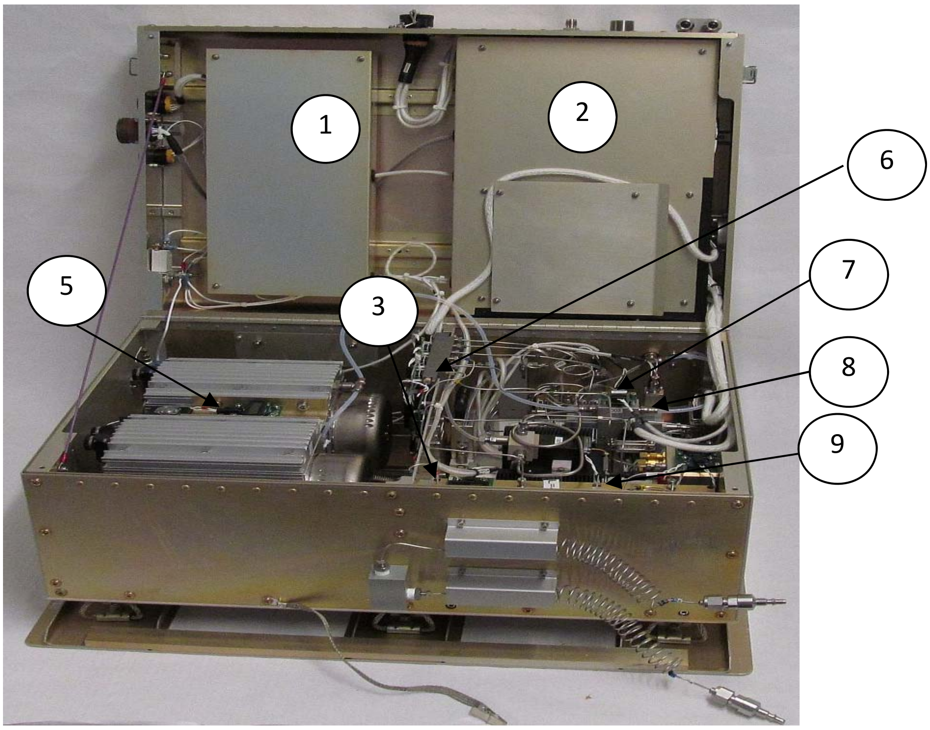

Figure 2: Photograph of IAGOS-PIIb-02 with indication of sub-assemblies:
(1, 2): DAS; (3): Power supply; (5): VAC; (6): O2D; (7): ICC; (8): NOD; (9): O3G

A schematic gas flow diagram is given in **Figure 3**. Ambient air is drawn from a Rosemount TAT housing mounted on the fuselage of the aircraft (see **Figure 1**) through a 1 m 1/8” PFA tube at a flow rate of > 1 SLM to the inlet manifold. Most of the sample flow is exhausted through a dedicated outlet on the fuselage. A flow of 150 sccm is drawn from the inlet manifold through the converter (PLC), a flow controller and the NO detector by means of two membrane pumps. In the reaction chamber of the detector (NOD), the sample air is mixed with O_3 generated in unit O3G by a silent discharge through a flow of 20 sccm of O_2.

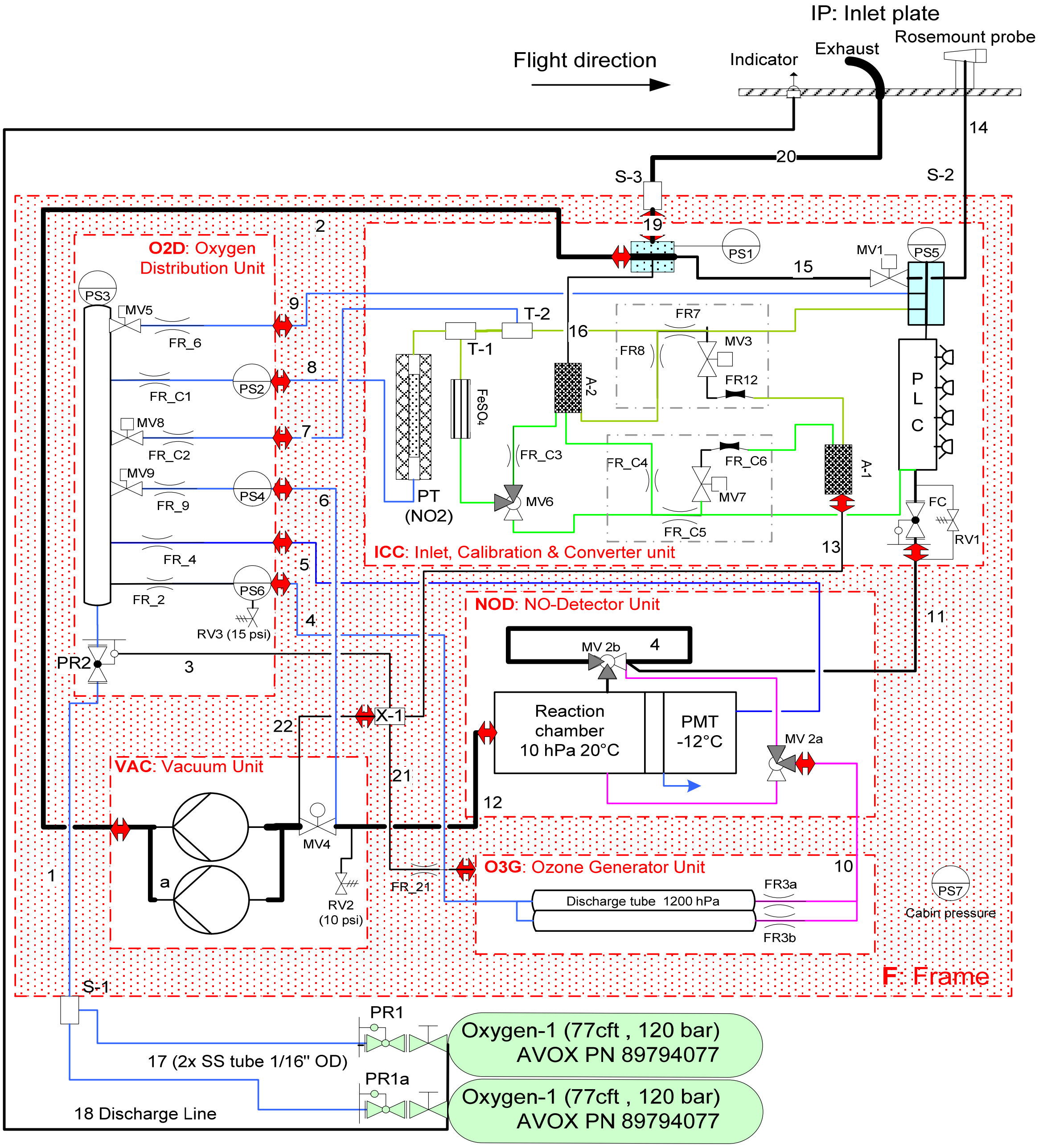

Figure 3: Flow diagram of IAGOS P2b (NOx instrument), showing all pneumatic connections. The red arrows refer to pneumatic junctions that are disconnected for servicing of the units. A: Absorber (NO_x scrubber); MV: Magnetic Valve; RV: Relief Valve, PR: Pressure regulator; PS: Pressure Sensor; FR: Flow Restrictor (capillary or orifice); PLC: Photolytic Converter; PMT: photomultiplier; PT: Permeation Tube; T: Tee; S: Bulkhead; X: Cross;

The oxygen (purity > 99.999%) is supplied to the instrument from two avionic cylinders (AVOX P/N 89794077), each with a capacity of 2m^3 (STP), which are mounted at the IAGOS rack.

The NO mixing ratio is determined by counting the photons produced in R1 by means of a photomultiplier (PMT; in unit NOD), which is cooled to < -12°C. The NO-detector employs chemical zeroing by passing the sample air together with the O_3 through a pre-reaction volume (no. 4 in **Figure 3**), where > 95% of the ambient NO is oxidised before entering the reaction chamber. The remaining signal, the so-called zero mode, thus contains the PMT background plus chemiluminescence from contaminants in the O_3 and from atmospheric species, such as olefins, which react much more slowly with O_3 than NO (*cf. Drummond et al., 1985*). The NO-detector has a sensitivity of typically 0.8 counts/s (cps) for a NO mixing ratio of 1 ppt (henceforth denoted as 0.5 cps/ppt).

The photolytic converter (PLC) used for conversion of NO_2 to NO consists of a 25 ml glass tube which is illuminated by 4 UV LEDs (395 ± 5 nm). The LEDs are regularly switched on and off in order to determine NOx and NO, respectively. In the absence of ambient ozone, the conversion efficiency is typically 75% at cruise altitude (250 mbar) and 85% at ground.

The sample flow rate is controlled by a thermal mass flow controller located between PLC and NOD. All other flows are controlled by capillaries or critical orifices (denoted FR_*x* in **Figure 3**).

The instrument contains provisions for in-flight checks of sensitivity and instrument background. For sensitivity check, a small flow (5 sccm) of O_2 is continuously passed through a NO_2 permeation tube (PT), which operates at constant pressure and temperature when the instrument is powered.

Behind the PT, the gas flow is split in two branches, one half going through a bed of $FeSO_4$, in which the NO_2 is converted to NO for calibration of the NOD and the other half going to the inlet manifold for calibration of the PLC. In both calibration branches, another split of approx. 10:1 is installed. Thereby, 95% of the calibration gas flow is wasted through an absorber into the exhaust and only a small fraction (0.2 sccm) of the flow is used for calibration. The split is necessary in order to (i) have a sufficient gas flow through the system for avoiding long transient times and (ii) to obtain NO_2 concentrations within the dynamic range of the system with commercially available PTs. During operation, the calibration gas flows to the inlet manifold, where it is pumped away. For calibration, the valve MV3 (see **Figure 3**) is closed and the calibration gas is allowed to flow into the sample air upstream of the PLC. The valves MV8 (n.o.) and MV6 (normally grey position) serve the purpose to avoid contamination of the inlet by NO_2 or NO from the calibration system during stand-by, while maintaining the operational conditions of the PT. Both valves are always activated during normal operation. In stand-by or when the instrument has no power (MV8 open), the additional flow of O_2 through FR_C2 flows via FR_7 to the inlet manifold, whilst the calibration gas is ventilated through MV6, FR_C3 and absorber A2 to the exhaust port.

<u>Note:</u> The NO mixing ratio produced in the branch going through the $FeSO_4$ was found less stable than the conversion efficiency of the PLC. Therefore, only the NO_2 branch is used for internal calibration checks during flight, whereas the PLC conversion efficiency is only checked in the laboratory during maintenance.

3 Instrument Operation

The instrument is designed for autonomous deployment over periods of up to 6 months. The actual deployment period depends largely on the performance of the instrument, which may be deteriorated by, e.g., contamination of the converter.

In flight mode, the instrument operates fully automatically. All functions are controlled by a single-board PC using dedicated software. Measurement cycles and calibration data are stored in initialisation files, which are specific for each serial number and must be updated with actual calibration data before each deployment (see **Table B.2**).

The instrument utilises the Weight on Wheels (WoW) signal of the aircraft to switch between standby (on ground) and normal operation (in air).

When the aircraft is on ground, the instrument is in standby (O3G off, MV4 and MV1 closed (see **Figure 3**)). O_2 flows through O3G, NOD and inlet manifold backwards through the inlet line in order to avoid contamination. The flow from the PT is directed away from the inlet (MV6, MV8 deactivated) and is purged via charcoal absorbers to the exhaust (see **Figure 3**).

When WoW disappears, the pump valve (MV4) is opened, the calibration gas flow is set to normal (MV6, MV8, MV3, MV7 activated), the ozone generator is turned on, and a new data file is opened. The following internal calibration checks are made automatically:

Instrument background is determined several times during each flight by overflowing the inlet manifold with O_2. Laboratory tests have shown no significant difference in the background when using high purity O_2 instead of high purity synthetic air (*Volz-Thomas et al., 2005*).

Instrument sensitivity is checked several times during flight by adding a small flow of O_2 with NO_2 from a permeation tube to the inlet manifold (see above). Using NO_2 instead of NO for internal calibration checks is possible because of the extremely stable conversion efficiency of the PLC (<< 5% drift during a deployment period). The conversion efficiency is only determined in the laboratory before and after deployment (see next chapter).

The NO_2 mixing ratio in the sample air during internal calibration check is:

$$\mathbf{\mu\_NO_2 = F\_NO_2 / (FR\_C1*(P\_O_2{}^2 - P\_PT^2)) * FR\_7* (P\_PT^2 - P\_Inlet^2) / F\_Inlet}$$

With:

μ_NO_2:	NO_2 mixing ratio in the sample air (in addition to the ambient mixing ratio)
F_NO_2:	Permeation rate of NO_2 (in ppb*sccm), as determined prior to deployment
F_Inlet:	Sample flow through the PLC (in sccm)
FR_C1, FR_7:	Capillary coefficients (in sccm/bar^2)
P_*x*:	Pressures controlling the flows through FR_C1 and FR_7 (see Figure 3 for P-sensors; P_PT: PS2; P_O2: PS3; P_inlet: PS5)

In the laboratory, the instrument can be operated either in automatic mode (like in flight) or in manual mode, where all valves and I/O functions can be switched individually.

3.1 Data acquisition and storage

The PMT signal (counts) of the NO detector is recorded at a sample rate of 10 Hz. Pressures and temperatures which are critical for instrument performance are measured at intervals of 1 Hz and stored as 1 min averages together with the standard deviation. The status of the different digital I/Os used to drive the different functions of the instrument is recorded at 1 s intervals and stored with the data.

The different modes of the instrument are defined in **Table 2**. They are generated by instrument functions on three hierarchical levels (NOD, PLC, ICC) and, in the laboratory, from external calibrations, i.e., by feeding the inlet line with calibration gas mixtures of known NO and NO_2 concentrations.

Timing of the different modes of operation is defined in an initialisation file used by the data acquisition program. Typical values are listed in **Table 3**.

Table 2: Definition and explanation of the different functions/modes of the instrument. For position of all valves in **Figure 3**, see **Table 4**.

Name of Mode	*Short*	*How achieved*	*Origin*	*Valve*
Measure Mode	MM	O_3 and air mixed in reaction chamber	NOD	MV2a,b
Zero Mode	ZM	O_3 and air mixed before pre-reaction chamber	NOD	Not MV2a,b
NO Mode	NO	LEDs off	PLC	
NOc Mode	NOc	LEDs on	PLC	SSR 10
Ambient	AA	Ambient air (no cal, no background)	ICC	MV3, MV7, not MV5
Instrument Background	BG	Excess O_2 flow added to inlet	O2D	MV5
NO calibration internal*	I1	NO_2 from PT via $FeSO_4$ added to sample air behind PLC	ICC	not MV7
NO_2 calibration internal	I2	NO_2 from PT added to sample air at inlet manifold	ICC	not MV3
NO calibration external	E1	NO calibration gas mixed with zero air	Ext.	GPT off
NOx calibration external	E2	NO calibration gas mixed with zero air via a GPT unit which converts 70-90% of the NO to NO_2	Ext.	GPT on

* *internal NO calibration not used anymore in P2b instrument*

Table 3: Typical timing of the different modes of operation. Lead time defines the period after take-off before the first cycle starts.

Mode	*Function*	*Lead time*	*On time*	*Cycle*	*Explanation*
Measure/Zero Mode	MV2 a,b	0	120	150	30 s zero mode, 120 s measure mode
NO/NOx Mode (PLC on/off)	LEDs	0	50	100	50 s NOc, 50 s NO
NO_2 Calibration	MV3	6600	300	5400	1-5 times per flight
Zero Air	MV5	0	300	5400	1-5times per flight

The raw data are stored locally as binary files with one file per flight, one minute per record. Each data record contains a time stamp, 600 values of the PMT counts, 16 ADC values (pressures, temperatures, sample flow rate); 60 integers stating the status of the instrument (valve positions), and finally data from Package 1 (O_3 mixing ratio, latitude, longitude, and altitude; all at 4s resolution). Each section in the record is preceded by a descriptor (see **Table A.1 - Table A.3**).

The first record (header) provides information on instrument P/N, S/N and deployment cycle, and contains the relevant parameters derived from the last valid calibration (i.e., sensitivity of the NOD, conversion efficiency of the PLC, and calibration data of capillaries used for internal calibration checks). Calibration data of the pressure transducers, temperature sensors and flow controller are stored in separate files used by the data acquisition programme.

Due to combinations of the different modes in **Table 2**, the data stream contains the modes listed in **Table 4**, which are strictly sequential, since the instrument contains only one NOD channel. Therefore, not all intervals contain valid data on ambient NO or NO_x concentrations, but contain information on zero mode, and calibrations.

Table 4: Definition of the (sequential) data modes of the NO_x instrument and the electrical status of the different magnetic valves (see Figure 3) and the PLC. Note that MV8 is normally open. Also included are data modes during external calibrations in the laboratory, which do not occur during flight. Stand-by mode and power off are shown for valve status only.

Description of Data Mode	**Variable**	**MV*i* (active: ●; not act.: ○)**									
		1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*P*
Ambient-NO-Zero Mode	AA_NO_ZM	●	○	●	●	○	●	●	●	○	○
Ambient-NO-Measure Mode	AA_NO_MM	●	●	●	●	○	●	●	●	○	○
Ambient-NOc-Zero Mode	AA_NOc_ZM	●	○	●	●	○	●	●	●	○	●
Ambient-NOc-Measure Mode	AA_NOc_MM	●	●	●	●	○	●	●	●	○	●
Background-NO-Zero Mode	BG_NO_ZM	●	○	●	●	●	●	●	●	○	○
Background-NO-Measure Mode	BG_NO_MM	●	●	●	●	●	●	●	●	○	○
Background-NOc-Zero Mode	BG_NOc_ZM	●	○	●	●	●	●	●	●	○	●
Background-NOc-Measure Mode	BG_NOc_MM	●	●	●	●	●	●	●	●	○	●
NOcal-NO-Zero Mode*	I1_NO_ZM	●	○	●	●	○	●	○	●	○	○
NOcal-NO-Measure Mode*	I1_NO_MM	●	●	●	●	○	●	○	●	○	○
NOcal-NOc-Zero Mode*	I1_NOc_ZM	●	○	●	●	○	●	○	●	○	●
NOcal-NOc-Measure Mode*	I1_NOc_MM	●	●	●	●	○	●	○	●	○	●
NO2cal-NO-Zero Mode	I2_NO_ZM	●	○	○	●	○	●	●	●	○	○
NO2cal-NO-Measure Mode	I2_NO_MM	●	●	○	●	○	●	●	●	○	○
NO2cal-NOc-Zero Mode	I2_NOc_ZM	●	○	○	●	○	●	●	●	○	●
NO2cal-NOc-Measure Mode	I2_NOc_MM	●	●	○	●	○	●	●	●	○	●
ExternalNOcal-NO- Zero Mode	E1_NO_ZM	●	○	●	●	○	●	●	●	○	○
ExternalNOcal-NO- Measure Mode	E1_NO_MM	●	●	●	●	○	●	●	●	○	○
ExternalNOcal-NOc- Zero Mode	E1_NOc_ZM	●	○	●	●	○	●	●	●	○	●
ExternalNOcal-NOc- Measure Mode	E1_NOc_MM	●	●	●	●	○	●	●	●	○	●
ExternalNOxcal-NO- Zero Mode	E2_NO_ZM	○	○	●	●	○	●	●	●	○	○
ExternalNOxcal-NO- Measure Mode	E2_NO_MM	●	●	●	●	○	●	●	●	○	○
ExternalNOxcal-NOc- Zero Mode	E2_NOc_ZM	○	○	●	●	○	●	●	●	○	●
ExternalNOxcal-NOc- Measure Mode	E2_NOc_MM	●	●	●	●	○	●	●	●	○	●
Stand-by (MV9 on for 5s before standby)		○	○	○	○	○	○	○	○	(●	○
Power off		○	○	○	○	○	○	○	○	○	○

** Internal NO calibration not used anymore in P2b instrument*

4 Maintenance and calibration

This chapter describes the procedures to be performed in the laboratory between deployments of the instrument. They serve two purposes: (i) assessment and assurance of the data quality and (ii) technical maintenance required for ensuring continued airworthiness of the instrument in compliance with aeronautic legislation.

Note: In order to receive a release to service certificate (EASA Form 1) after maintenance, all tasks must be performed and documented in compliance with predefined procedures set out in the contract between the scientific institution acting as Extended Workbench (EW) and the Maintenance Organisation (MO) responsible for continued airworthiness of the equipment.

4.1 Test Procedures

Mandatory checks for continued airworthiness:

When: Before and after each deployment

- Visual inspection for loose, broken or overheated parts
- Verification of electrical load during start up and operation
- Verification of total mass (only before deployment)

Checks for data quality assurance:

When: Before and after each deployment

- Determination of sensitivity for NO and conversion efficiency for NO_2 with an external NO/NO_2 calibration gas
- Determination of instrument background with an external supply of zero air (i.e., synthetic air without traces of NO or NO_2)
- Determination of the internal instrument background
- Determination of the NO conversion in the pre-reaction volume of the NOD
- Determination of the permeation rate of the internal permeation tube
- Calibration of capillaries and pressure sensors, if deviations are encountered

The required maintenance tasks, such as cleaning or replacement of components, are determined on the basis of the results of the inspection and calibration after deployment, in addition to the planned tasks which are based on the lifetime of consumables and critical parts (see Table 5).

The relevant calibration and performance data as well as the replaced components must be recorded in the data base. After maintenance and final calibration, the instrument is released to the MO with a Certificate of Conformity (CoC), a signed service protocol, and a list of replaced parts.

Note: If calibration after deployment shows that instrument performance has changed by < 10% during deployment and no maintenance is required, there is no need to perform an additional calibration before deployment.

4.2 Calibration Methodology and Standards

4.2.1 Equipment:

- Secondary NO standard (mixture of 10 ppm NO in high purity N_2 contained in a spectra seal cylinder and referenced to a primary standard); High purity pressure regulator, 10 sccm flow controller (or pressure gauge and capillary).
- Constant supply of zero air (μ_NOx < 10 ppt), capacity > 2 SLM
- Supply of high purity O_2 (> 4.7), capacity > 20 sccm;
- Gas-phase titration (GPT) unit for converting a known amount of the NO calibration gas into NO_2. (A GPT unit usually consists of a O_2 supply, a photolysis cell, a Hg-lamp equipped with adjustable slit and mechanical shutter, and a relaxation volume of sufficient size to allow for > 5 e-foldings of the NO + O_3 reaction.)
- Manifold with provisions for connection of inlet and exhaust lines of the instrument and capable to simulate in-flight conditions (P_Inlet 1-0.25 bar; P_Exhaust 1-0.15 bar) while maintaining the excess flow of the zero air /calibration mixture.
- Calibrated volumetric flow meters (accuracy > 98% of measured value; e.g., Gillibrator, Drycal, Definer)

4.2.2 Determination of instrument background:

Connect the inlet of the instrument to an excess flow (> 2 SLM) of NOx-free zero air and the exhaust to a vacuum manifold. The provisions must ensure that the pressures in the inlet manifold and exhaust manifold can be adjusted for in-flight conditions, and that the flow of zero air remains constant (e.g. by using a thermal mass flow controller).

Apply the zero air to the instrument operating in automatic measuring mode sufficiently long for the NO and NO_2 signals to stabilize (>1h). Analyse the data in the same way as for ambient measurements.

1. Calculate the net NO and NOc signals (**AA_NO_DM; AA_NOc_DM**) obtained in zero air.

   AA_NO_DM = AA_NO_MM – AA_NO_ZM
   AA_NOc_DM = AA_NOc_MM – AA_NOc_ZM

Compare the signals to those obtained during the internal background procedure (MV5 activated; BG_NO_DM; BG_NOc_DM). The difference should be < 20 cps.

4.2.3 Determination of sensitivity and conversion efficiency:

Mix a known and constant flow (2-5 sccm) of the secondary calibration standard (nominally 2-10 ppm NO in high purity N_2; actual value (**μ_NO-std**) derived from calibration against primary standard) and a constant flow (a few sccm) of oxygen through the GPT system to the zero air flow. At the start of each calibration procedure, purge the pressure regulator of the NO standard and tubing at least 3 times. Turn the Hg-lamp of the GPT on and allow to stabilize (> 1h).

Measure the flow rates of the NO standard (**F_NO**), oxygen (**F_O2**) and zero air (**F_SL**) using volumetric flow meters. The theoretical uncertainty of the flow measurements should be < 2% and the resulting NO mixing ratio should be in the range of 1 to 20 ppb.

Calculate the amount of NO (**μ_NO**) present in the calibration gas:

$$\mu\_\text{NO} = \mu\_\text{NO-Std} * \text{F\_NO} / (\text{F\_SL} + \text{F\_O2} + \text{F\_NO})$$

Apply the calibration mixture with GPT shutter closed to the NO_x instrument operating in automatic mode for sufficient time (> 30 min) to observe stable signals.

Repeat with GPT-shutter open. Ensure that the remaining NO signal recorded by P2b is >10% and <30% of the NO signal with GPT-shutter closed. If not, adjust the slit of the GPT.

<u>Note:</u> Smaller amounts of NO_2 influence the precision of the calibration. Overtitration leads to erroneous results and must be avoided!

Measure the flow rates again after completion of calibration. If not within 2% of the measurement before, repeat the procedure (after the source of the problem has been fixed).

Analyse the data in the same way as described for ambient measurements (see Chapter 5.1).

Calculate the net NO and NO_2 signals obtained with external calibration gas applied with GPT off (E1) and with GPT on (E2).

$$\begin{aligned}
\text{E1\_NO\_DM} &= \text{E1\_NO\_MM} - \text{E1\_NO\_ZM}\\
\text{E1\_NOc\_DM} &= \text{E1\_NOc\_MM} - \text{E1\_NOc\_ZM}\\
\text{E2\_NO\_DM} &= \text{E2\_NO\_MM} - \text{E2\_NO\_ZM}\\
\text{E2\_NOc\_DM} &= \text{E2\_NOc\_MM} - \text{E2\_NOc\_ZM}
\end{aligned}$$

Subtract the NO and NO_c signals obtained with external zero air from those obtained during calibration to obtain E1 and E2.

$$\begin{aligned}
\text{E1\_NO} &= (\text{E1\_NO\_DM} - \text{AA\_NO\_DM})\\
\text{E1\_NOc} &= (\text{E1\_NOc\_DM} - \text{AA\_NOc\_DM})\\
\text{E2\_NO} &= (\text{E2\_NO\_DM} - \text{AA\_NO\_DM})\\
\text{E2\_NOc} &= (\text{E2\_NOc\_DM} - \text{AA\_NOc\_DM})
\end{aligned}$$

Calculate the sensitivity of the NOD (**S_NOD**), the conversion efficiency of the PLC (**E_PLC**) and the photolysis rate coefficient of the PLC (**J_PLC**), and their uncertainties.

$$\begin{aligned}
\text{S\_NOD} &= \text{E1\_NO} / \mu\_\text{NO}\\
\text{E\_PLC} &= (\text{E2\_NOc} - \text{E2\_NO}) / (\text{E1\_NO} - \text{E2\_NO})\\
\text{J\_PLC} &= -\ln(1-\text{E\_PLC}) / \text{t\_PLC}
\end{aligned}$$

With **t_PLC** being the residence time of the sample air in the PLC (t_PLC = V_PLC ▪ F_Inlet/P_Inlet).

<u>Note:</u> J_PLC is required for calculation of NO_2 from the NO_c signal if ozone is present in the sample air (see section on Data Analysis). E_PLC can be used only in the absence of ozone.

4.2.4 Calibration of capillaries and pressure transducers

The capillaries used for control of internal calibration gas flows must be calibrated in regular intervals. This requires an oxygen supply at constant pressure, a calibrated pressure gauge and a calibrated volumetric flow meter (e.g., Drycal, Definer, or Gillibrator for flows > 5 sccm, and micropipette or special equipment for smaller flows). Some capillaries are difficult to remove and should therefore be calibrated inside the instrument.

The pressure transducers in the instrument must be calibrated against calibrated pressure gauges. The calibration must at least comprise zero offset and two points around the actual operating pressure.

The calibration data (and their uncertainties) must be stored in the data base and included in the data analysis.

4.2.5 Calibration of the permeation tube (PT)

Because the PT is contained inside a double housing, the inner part of which is connected to the instruments pneumatics, it is difficult to remove the PT for calibration of the permeation rate by weight loss. Therefore, the permeation rate (F_NO2) is determined indirectly from the signal obtained during internal calibration check using the actual sensitivity and conversion efficiency obtained from a concurrent external calibration.

$$\mathbf{F\_NO2 = F\_Inlet*(FR\_C1*(P\_O_2^2 - P\_PT^2))/(FR\_7 * (P\_PT^2 - P\_Inlet^2))*(I2\_NOc - I2\_NO)/(S\_NOD* E\_PLC)}$$

With:
FR_*x*: Capillary constants
P_x: Pressures
I2_NOc: Net signal obtained during internal NO_2 cal with PLC on
I2_NO: Net signal obtained during internal NO_2 cal with PLC off
S_NOD: Sensitivity of the CLD
E_PLC: Conversion efficiency of the PLC

Calculate the uncertainty of F_NO2 from the uncertainties of S_NOD, E_PLC, FR-values and pressures.

4.3 Regular Maintenance tasks

The schedule for replacement of consumables and service of components, if not indicated earlier by malfunction or reduced performance, is listed in Table 5.

Note that the regular replacement of the oxygen cylinders is only listed for completeness. It is not part of this SOP, because it has to be performed by authorised personnel at the aircraft. The oxygen cylinders are filled at Research Centre Jülich with O_2 of grade 5.0 under supervision of enviscope GmbH, who are authorised by EASA for this process.

Table 5: Schedule for regular replacement of consumables and service of components

Component	*Interval*	*Action*
O_2 cylinders	3 months	Replace and refill
NO_2-PT	5 years	Replace
Absorbers	5 years	Refill
Vacuum pumps	1 year	Replace membranes and valves
Ozone generator	1 year	Clean discharge tube
NO Detector	1 year	Clean, replace valves
Inlet line	6 months	clean
PLC	6 months	Clean tube

5 Analysis

5.1 Data Analysis

Data analysis comprises the following steps:

1. Adjustment of instrument time to that of Package 1, if necessary. Verification by comparison of inlet pressure to static air pressure of aircraft during transients.

2. Adjustment of delays to account for residence times in tubing after switching between different modes and of transient times to discard ambiguous data influenced by transients or memory.

3. Interpolation of the zero modes by a non-linear fit over one entire data file and subtraction from all measure modes (both, for NO and NO_C mode). The zero mode of the NOD is composed of two components, (i) a slowly varying contribution (A) composed of the dark signal of the PMT and chemiluminescence from impurities and slowly reacting atmospheric compounds and (ii) the chemiluminescence from the fraction of NO remaining behind the relaxation volume (B usually < 0.05), i.e.:

   ZM(t) = A(t) + B*MM(t)

   B = (ZM(t)-A(t))/MM(t) is calculated from the ratio between ZM and MM during calibrations, i.e., where MM(t)>>ZM(t), and A(t) is obtained from a non-linear fit to the ZM data from an entire flight. Fitting of B and A has to be iterated until stable results are obtained (usually 2-3 times).

4. Interpolation of the instrument background signal over an entire flight and subtraction from ambient data (separately for NO and NO_C modes).

5. Subtraction of ambient signals from internal calibrations (separately for NO and NO_C modes).

6. Interpolation of the calibration coefficients (S_NOD and J_PLC) over the past deployment period from the laboratory calibrations (S_NOD_pre, S_NOD_post, J_PLC_pre, J_PLC_post). Normally, averages of the values obtained before and after deployment are used. Only if the values before and after differ significantly, the in-flight calibration checks are used in order to improve the uncertainty of S_NOD and J_PLC. The latter require knowledge on calibration coefficients of capillaries, flow controller and pressure sensors.

7. Calculation of atmospheric mixing ratios and uncertainties for NO (MR_NO) and NO_x (MR_NOx) by application of S_NOD and J_PLC to the ambient signals.

   a) For NO, a (pressure dependent) correction must be applied in order to account for losses of NO in the PLC by reaction with ambient ozone (R1).

   b) For NO_x, instead of applying a constant conversion efficiency (E_PLC), a time dependent chemical model of the PLC is best employed, which solves reactions R2 (photolysis of NO_2) and R1 (back reaction of NO with ambient O_3). The calculation requires knowledge of J_PLC (see point 5.) and of the ambient O_3 concentration (from Package 1). As the differential equation cannot be solved analytically, the model is run in forward mode and the initial concentrations of NO and NO_2 are iterated until the difference between measured and calculated NO_C behind the converter converges.

The data analysis is accomplished by dedicated software, which can be employed in automatic or manual mode. In automatic mode, information on excessive errors which point to potential problems in the analysis is generated. This information is to be used by the operator for decision if manual analysis is required in order to improve data quality.

5.2 *Error Analysis*

Uncertainties in the calculated NO or NO_x mixing ratios arise from

1. Precision of PMT signal ($\Delta MM0 = \pm (MM)^{0.5}$) calculated from the counting statistics (depends on integration time).
   (ZM not influenced by averaging as it is determined from fit to all data)

2. Variance of Instrument Background over a flight (Δ_BG typically < 15ppt for NO and < 30 ppt for NO_C, independent of averaging interval)

3. Uncertainty of the conversion efficiency of the PLC (ΔE_PLC/E_PLC < 10%, if correction for ambient O_3 is applied)

4. Uncertainty of the sensitivity of the NOD over the deployment period (ΔS_NOD/S_NOD typically 5%, but larger in case of excessive drift during a deployment period)

5. Uncertainty in the calibration of the secondary standard (to be included in the uncertainty of S_NOD; contribution < 5%, if standard is checked once per year against a primary standard provided by , i.e., WMO-GAW)

The total uncertainty of the measured NOx mixing ratio is calculated by error propagation from the individual contributions. An example of the total relative and absolute uncertainty and the individual sources of uncertainty is shown in **Figure 4**, for typical values. It is seen that points 1 and 2 comprise the largest contribution to the overall uncertainty of a 1 min average value.

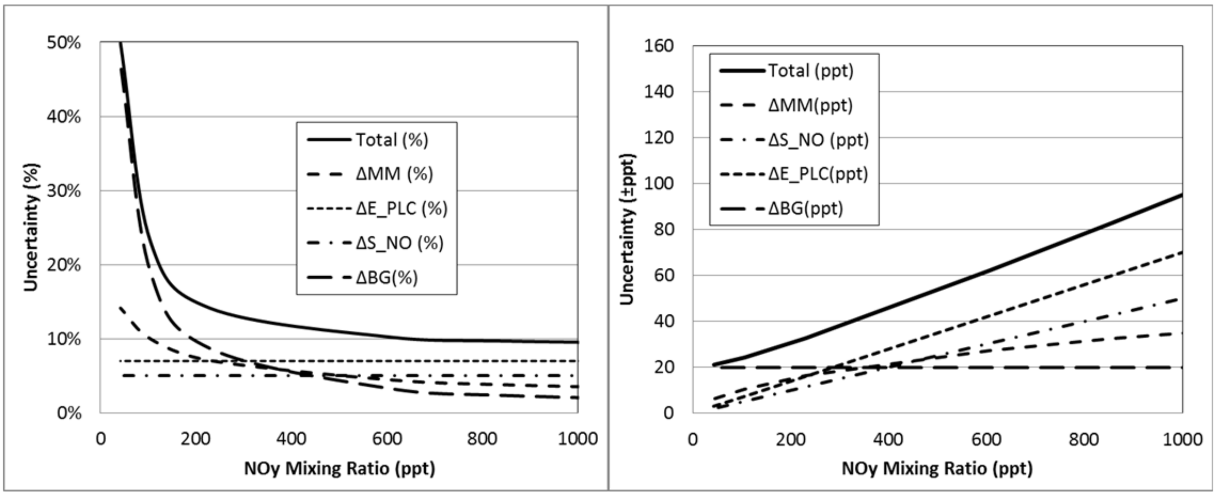

Figure 4: Individual contributions to uncertainty and total uncertainty of the NOx measurement calculated from error propagation for nominal conditions as outlined under points 1-5 above (left panel: relative error in % of measured value; right panel: absolute error in ppt).

Points 3 and 4 can make larger contributions in case of a strong drift of the conversion efficiency or sensitivity during deployment. A potential drift in the calibration of the secondary standard (point 5) is of minor importance,except for very large NOx mixing ratios. Note that trend analysis is not a key objective of the IAGOS-CORE NO_x measurements, because the atmospheric NO_x concentrations (< 100 ppt) encountered in the free troposphere and UTLS are either close to the detection limit of the instrument or are influenced by relatively local sources.

6 References

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7 Glossary

ADC	Analog to Digital Converter
CLD	Chemiluminescence Detector
CoC	Certificate of Conformity
DAS	Data Acquisition System
EASA	European Aviation Safety Agency
EW	Extended Workbench
FC	Flow Controller
GPT	Gas-Phase Titration
IAGOS	In-service Aircraft for a Global Observing System
ICC	Converter and Calibration Unit
LED	Light-Emitting Diode
MO	Maintenance Organisation
MOZAIC	Measurements of Ozone, Water Vapour, Carbon Monoxide and Nitrogen Oxides with In-service Airbus Aircraft
NOD	NO Detector Unit
NOx	$NO + NO_2$
NOy	Total Odd Nitrogen (NO + its atmospheric oxidation products)
O2D	Oxygen Distribution Unit
O3G	Ozone Generator Unit
PC	Personal Computer
PFA	Perfluoroalkoxy
PLC	Photolytic Converter
PMT	Photomultiplier
PT	Permeation Tube
P/N	Part Number
SOP	Standard Operation Procedure
STP	Standard Temperature and Pressure
S/N	Serial Number
TAT	Total Air Temperature
UTLS	Upper Troposphere/Lower Stratosphere
UV	Ultraviolet
VAC	Vacuum Unit
WoW	Weight on Wheels

Annex A: Data structure

The first record (header) provides information on calibration coefficients. The following records contain the data according to the structure in **Table A. 1**.

Table A. 1: Binary data record structure

No	Parameter	Description	Data Type	Bytes
1	Time	s since flight start	uint16	2 Byte
2	ArraySize	Array size = 600 (Counts)	uint32	4 Byte
3	Data (Counts)	Count rate every 0.1 s	600 * uint16 [1 … 600]	1200 Byte
4	ArraySize	Array size = 16 (AnalogData)	uint32	4 Byte
5	AnalogData	Mean per minute in bits for 16 ADC Channel (-32768 … 32767)	16 * int16 [1 … 16]	32 Byte
6	ArraySize	Array size = 16 (AnalogStdDev)	uint32	4 Byte
7	AnalogStdDev	Standard deviation per minute in bits for 16 ADC Channel (-32768..32767)	16 * int16 [1 … 16]	32 Byte
8	ArraySize	Array size = 5 (AnalogDev)	uint32	4 Byte
9	ArraySize	Array Size = 60 (AnalogDev)	uint32	4 Byte
10	AnalogDev	Deviation from mean in bits every s for 5 ADC channel (-128 … 127)	5 * 60 int8 [1 … 5] [1 … 60]	300 Byte
11	ArraySize	Array Size = 60 (Ports)	uint32	4 Byte
12	Ports	Status every s	60 * uint32 [1 … 60]	240 Byte
13	ArraySize	Array size = 60 (4 x 15) (P1Data)	uint32	4 Byte
14	P1Data	Package 1 data (lon, lat, alt, O_3) in physical units every 4s	4 * 15 single [1 … 4][1 … 15]	240 Byte

Table A. 2: Assignment of Ports

No	I/O No		Description	Value
0	A0	MV1	Exhaust	
1	A1	MV2a,b	Measure Mode/Zero Mode	0 = Zero Mode
2	A2	MV3	NO_2 Calibration on/off	0 = on
3	A3	MV4	Pump on/off	1 = on
4	A4	MV5	Zero Air on/off	1 = on
5	A5		NO/NO_y Mode	1 = NO; not used (no NO mode) (P2a)
6	A6	MV7	NO Calibration on/off	0 = on
7	A7	MV8a	Permeation Tube Bypass on/off	1 = off
8	B0	MV9	Flush instrument before landing	1 = yes
9	B1		O3 Generator	
10	B2		BLC on/off:	1 =NO_x (P2b)

11	B3		Au-Converter Heater (P2a)	
12	B4		Rosemount Heater	
13	B5		Permeation Tube Heater	
14	B6		aux	
15	B7		Aux	
16	C0		aux	
17	C1		aux	
18	C2		aux	
19	C3		aux	
20	C4		aux	
21	C5		aux	
22	C6		aux	
23	C7		aux	
24	D0		a/c Weight on Wheels (not transmitted)	
25	D1		a/c Gear locked (not transmitted)	
26	D2		a/c Cabin Door (not transmitted)	
27	D3		Not used	
28	D4		Not used	
29	D5		Not used	
30	D6		Not used	
31	D7		Not used	

Table A. 3: Analog Data

No	Parameter	Description
0	T_PMT	Temperature of the photomultiplier
1	T_Cell	Temperature of the reaction cell
2	F_Inlet	Inlet Flow
3	P_Cell	Pressure of the reaction cell
4	P_Inlet	Pressure at the inlet manifold
5	P_Exhaust	Pressure at the exhaust manifold
6	P_O2D	Pressure of O2D
7	P_PT	Pressure before the NO_2 permeation tube
8	P_Ambient	Pressure Ambient
9	T_PT	Temperature NO_2 Permeation Tube
10	P_O3G	Pressure O3G
11	T_AuC	Temperature of the gold converter (P2b)
12	T_Instrument	Temperature of the temperature safety switch (DAS-2 inside cover)
13		Not used
14		Not used
15		Not used

***Blue highlighted**: 5 channel for which deviation from mean every s is available*

Annex B: Files used for Instrument Control

Files used by the software for control of the instrument and calibration coefficients of the sensors used for housekeeping data (pressures, temperatures, flows)

Table B.1: Configuration File (B*npp*.ini) 'B' for P2b, *n* = S/N, *pp* = deployment period
Content: Filename, capillary coefficients, sensitivity, conversion efficiency etc.

[allgemein]	
AutoStart=1	1: Data acquisition starts at start of program, 0: No data acquisition
AutoCalib=1	1: Calibration as defined in Bnpp_TR.csv (see **Table B.2),** 0: no internal calibrations
FlightMode=1	1: Automatic Mode
ShowGraph=1	1: Show graphics on Screen
CheckStart=0	Not used anymore
InAirSignal=1	1: Start data aquisition with InAir signal
DataPath=D:\Data	Data path
Filename=B301	Filename for flight data
LabName=Lab	Filename for Lab data
MsgFileName=B301	Filename for message files
TimerFileName=B301_TR.csv	Filename of timer routines (see **Table B.2**)
ADCFileName=B301_ADC.csv	Filename of conversion data for ADCs (see **Table B.3**)
PWMDutyCycle=90	Duty cycle for counter in percent
ErrorTime=30	Error if AD value x seconds out of limits
AuCTime=0	Time in seconds for heating of AuC at beginning of the flight (n.a. for NOx instrument)
;For NOx Instrument AuCTime must be 0.	
[IP configuration]	
IAGOSRemoteHost=192.168.0.221	Remote host address for communication with P1
IAGOSRemotePort=32999	Remote port number for communication with P1
IAGOSConnectionType=UDP	Connection type with P 1
IAGOSTransferSize=1024	Transfer size in byte
[Regler1]	PID regulator 1 (software)
Name=AuC	Name of the regulator (gold converter)
Sollwert1=300	Setpoint in °C of gold converter (normal operation)
Sollwert2=450	Setpoint in °C of gold converter (heating)
Kc=1.0000	Regulator constant
Ti=0.010	Integral part
Td=0.000	Differential part
AI_Channel=11	Number of ADC channel for temperature
Active=False	Activated if true; deactivated if false
[Regler2]	PID regulator 2 (software)
Name=PT	Name of the regulator (permeation tube)
Sollwert1=40	Setpoint 1 in °C of permeation tube
Sollwert2=40	Setpoint 2 in °C of permeation tube (should be equal to setpoint 1)

`Kc=1.0000`	Regulator constant
`Ti=0.010`	Integral part
`Td=0.000`	Differential part
`AI_Channel=9`	Number of ADC channel for temperature
`Active=True`	Activated if true

`[Auswertung]`	Coefficients for data analysis
`F_NO2=2.13`	NO_2 permeation rate in ppb*sccm
`F_Inlet=140`	Inlet flow in sccm
`SN_FR_C5=004`	Serial number of capillary FR_C5
`FR_C5=0.026100468`	Capillary constant of FR_C5 in sccm/bar^2
`SN_FR_7=004`	Serial number of capillary FR_7
`FR_7=0.024026991`	Capillary constant of FR_7 in sccm/bar^2
`SN_FR_C1=008`	Serial number of capillary FR_C1
`FR_C1=0.8386952`	Capillary constant of FR_C1 in sccm/bar^2
`S_NO=850`	Sensitivity of NO detector in cps/ppb
`J_PLC=0.65`	Photolytic rate of photolysis converter in 1/s
`V_PLC=25`	Volume of photolysis converter in cm^3
`SN_FR_6=008`	Serial number of capillary FR_6
`FR_6=9.0989272`	Capillary constant of FR_6 in sccm/bar^2

Table B.2: Typical timing of instrument functions (B*npp*_TR.csv)

"Name"	"First Start"	"Cycle"	"Duration"	"Setting"	"SetValue"
"Meas/Zero-Mode"	0	150	120	"A1"	1
"Noy/NO-Mode"	n.a.	n.a.	n.a.	n.a.	n.a.
"Nox/NO-Mode"	0	100	50	"B2"	1
"NO_Calibration"	0	60000	0	"A6"	0
"NO2_Calibration"	6600	5400	300	"A2"	0
"ZeroAir"	0	5400	300	"A4"	1
"Flush"	0	60000	10	"B0"	1

Table B.3: Calibration coefficients for housekeeping data (B*npp*_ADC.csv)
Content: Calibration coefficients for housekeeping data

"Name"	"RangeLow"	"RangeHigh"	"BitOffset"	"ScaleLow"	"ScaleHigh"	"Limit_Low"	"Limit_High"	"Error"	"Port"
"T_PMT"	0	4.70	0	-57.35	40.00	-15	10	0	"A00"
"T_cell"	0	4.43	0	-0.70	90.00	0	25	0	"A01"
"Flow"	0	3.97	0	-1.13	305.28	60	200	0	"A02"
"p_cell"	0	4.49	0	-123.01	1000.00	5	20	0	"A03"
"p_inlet"	0	4.49	0	-121.01	1018.46	100	1000	0	"A04"
"p_exhaust"	0	4.49	0	-120.19	1018.28	100	1000	0	"A05"
"p_O2"	0	4.49	0	-683.64	5024.10	3800	4500	0	"A06"
"p_permT"	0	4.49	0	-617.57	5026.73	3800	4500	0	"A07"
"p_amb"	0	4.50	0	-124.00	1000.00	700	1000	0	"A08"
"T_permT"	0	4.53	0	-2.74	90.00	39.5	40.5	0	"A09"
"p_O3g"	0	4.49	0	-420.90	2043.63	900	1300	0	"A10"
"T_AUC"	0	4.48	0	-13.24	450.00	295	305	0	"A11"
"T_instr"	0	4.47	0	-1.56	90.00	15	25	0	"A12"
"aux"	0	5.00	0	0.00	5.00	0	100	0	"A13"
"aux"	0	5.00	0	0.00	5.00	0	100	0	"A14"
"aux"	0	5.00	0	0.00	5.00	0	100	0	"A15"