STANDARD OPERATION PROCEDURE

FOR THE

IAGOS-CORE NOy INSTRUMENT (P2a)

P/N: IAG0S-PIIa-01

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Content:

1 Rationale

Nitrogen oxides play a key role in atmospheric photochemistry by catalysing the recycling of free radicals and the formation of ozone. The distribution and variability of nitrogen oxides is still not well known, in particularly in the upper troposphere and lower stratosphere (UT/LS). The existing data suggest a large variability and significant differences in the partitioning of NO_y into active compounds, i.e., NO_x ($NO+NO_2$) and reservoir species such as HNO_3, HNO_4, PAN and other organic nitrates. The different sources of NO_y to the upper troposphere include lightning and emissions by aircraft (in the form of NOx), uplifting of surface emissions (variable NO_x/NO_y ratio) and downward transport from the stratosphere (mainly HNO_3, cf., Neuman et al., 2001).

Measurements of the NO_y distribution in the UT/LS can help to gain a better understanding of the downward transport of O_3 from the stratosphere (cf., Murphy et al., 1993; Murphy and Fahey, 1994) and to discriminate the impact of aircraft emissions on the UT/LS from the influence of convective transport of surface emissions.

1.1 Measurement Objectives

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

- Climatology of NO_y in the UTLS
- Vertical profiles in the troposphere
- Frequency of pollution events
- Influence of lightning and biomass burning on the NO_y distribution
- Impact of air transportation

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

2 Description of method

2.1 Principle

The IAGOS-CORE NO_y instrument (P/N: IAGOS-PIIa-01 and IAGOS-PIIb-02, henceforth denoted Package 2a or P2a) is designed for the autonomous measurement of total odd nitrogen in the atmosphere, which is defined as the sum of nitrogen monoxide (NO) and its atmospheric oxidation products such as nitrogen dioxide (NO_2), nitric acid (HNO_3) and peroxyactetyl nitrate (PAN).

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 the oxidation products to NO is achieved by catalytic reduction with traces of hydrogen (H_2) on a hot gold surface (R2). The specific set-up of IAGOS P2a is very similar to the MOZAIC NOy instrument which is described in detail by *Volz-Thomas et al., (2005)* and *Pätz et al.,* (2006).

R1	$NO + O_3$	→	$NO_2 + O_2 + h\nu$	($600 < \lambda < 3000$ nm)
R2	$NO_y + H_2$	→	$NO + H_2O$	(T = 300°C)

2.2 *Description of Instrument*

IAGOS Package 2a 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.

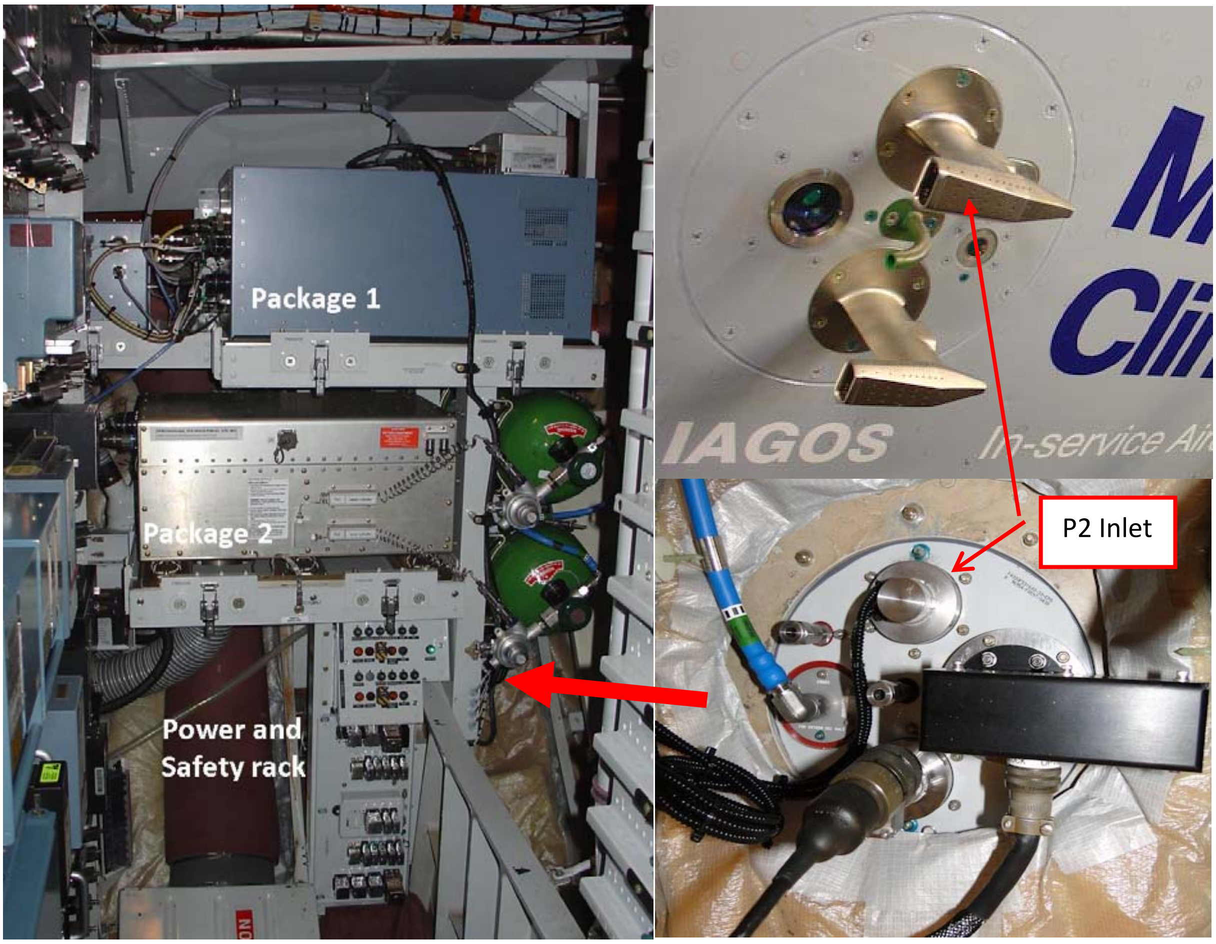

Figure 1: IAGOS rack installed in an Airbus A340 of Lufthansa AG (left) and IAGOS Inlet Plate (upper right: outside view, lower right: inside view).

Note: 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 P2a (NO_y), which is subject of this SOP, consists of several units as listed in **Table 1** and 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)*.

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 gold converter for transforming NO_y 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

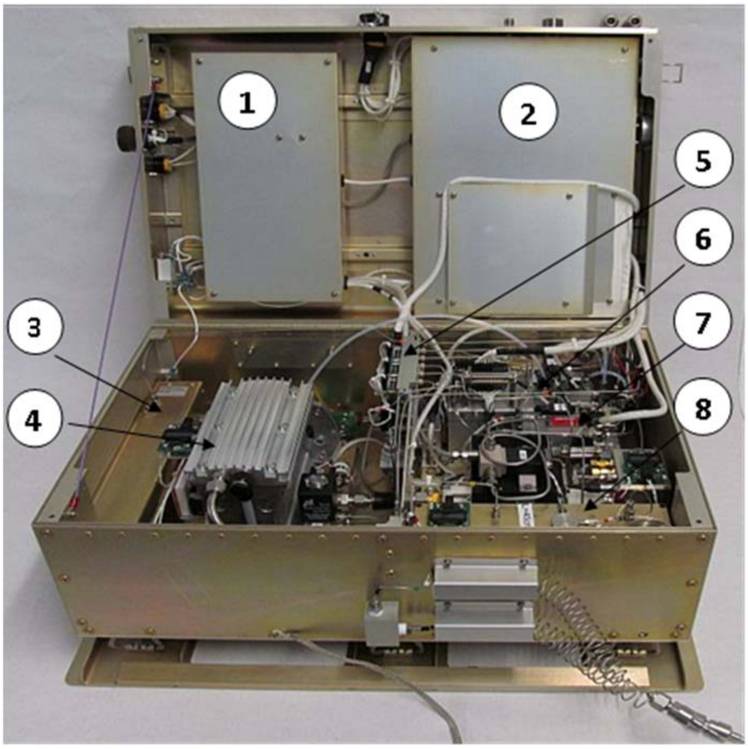

Figure 2: Photograph of IAGOS-PIIa-02 with indication of sub-assemblies:
(1, 2): DAS; (3): Hydrogen supply; (4): VAC; (5): O2D; (6): ICC; (7): NOD; (8): O3G

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 70-90 sccm is drawn from the inlet manifold through the converter (AuC), a flow controller and the NO detector by means of a membrane pump. 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 10 sccm of O_2.

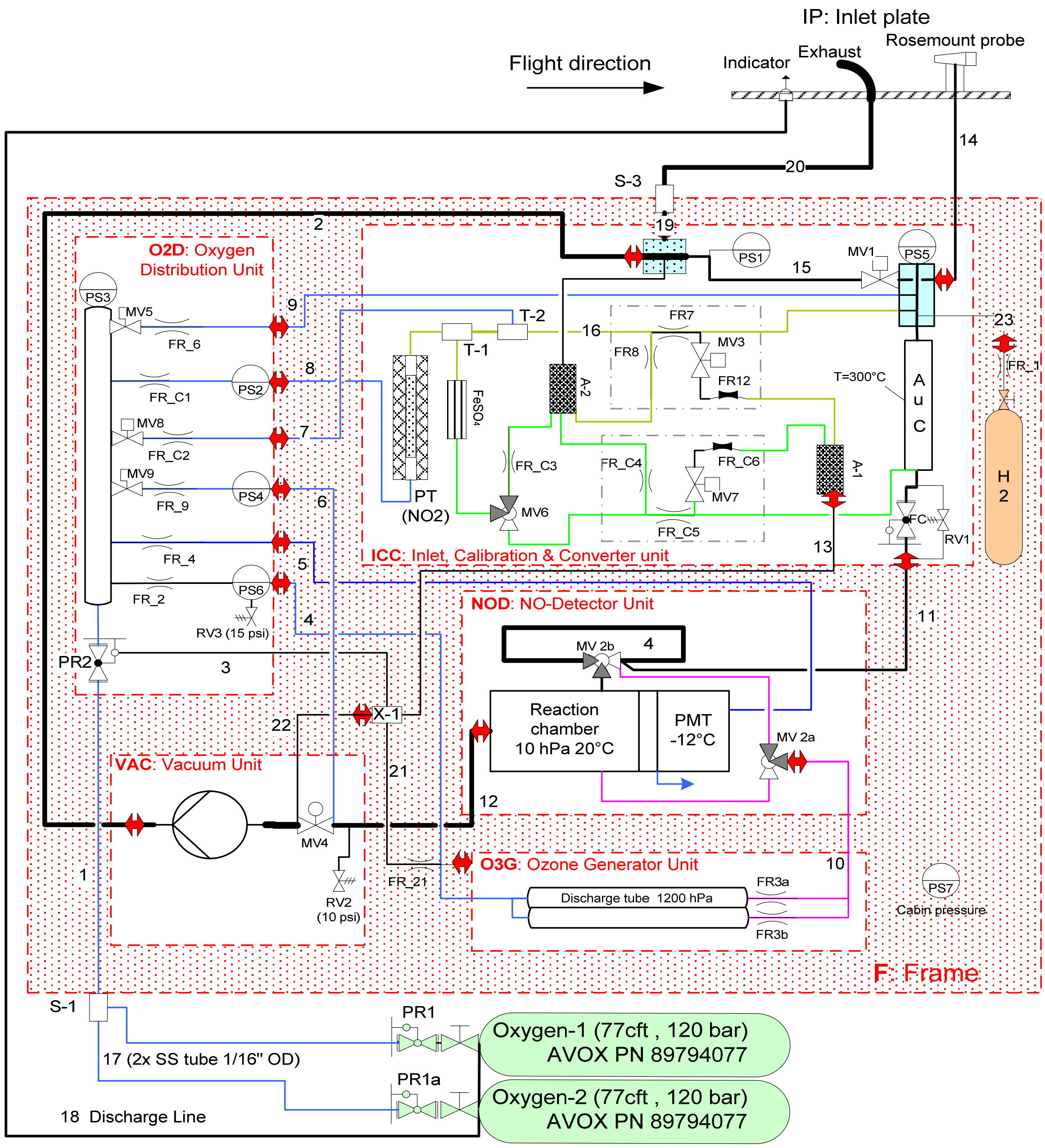

Figure 3: Flow diagram of IAGOS P2a (NOy instrument), showing all pneumatic connections. The red arrows refer to pneumatic junctions that are disconnected for servicing of the units. A: Absorber (NO_x scrubber); MV: Magnetic Valve; RV: Relief Valve, PR: Pressure regulator; PS: Pressure Sensor; FR: Flow Restrictor (capillary or orifice); AuC: Gold Converter; PMT: photomultiplier; PT: Permeation Tube; T: Tee; S: Bulkhead; X: Cross;

The instrument always measures NO_y as it has no provision for by-passing the AuC for measurement of NO (except by manual manipulation in the laboratory during maintenance).

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_y 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 0.5 counts/s (cps) for a NO mixing ratio of 1 ppt (henceforth denoted as 0.5 cps/ppt).

The converter (AuC) used for conversion of NO_y to NO consists of a gold tube (2 mm I.D., 110 mm long), which is placed inside an oven. The oven is constructed from stainless steel, with mineral wool for insulation. The temperature of the gold tube is controlled at 300°C by a temperature controller. The oven is mounted inside a thermal shielding which is ventilated by ambient air. The hydrogen required for the catalytic reaction of NO_y to NO is supplied from a metal hydride storage cylinder. The H_2-flow (< 0.1 sccm at 20 °C) is restricted by a capillary (FR_1). The conversion efficiency is typically >95%, independent of pressure. A potentially important interference is HCN, which is converted as well as NO_y.

The sample flow rate is controlled by a thermal mass flow controller located between AuC 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 AuC. 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 AuC. The addition of NO calibration gas occurs in exactly the same way as for NO_2, but behind the AUC. 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.

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 from a permeation tube to the sample flow behind the AUC (see above). The conversion efficiency of the AUC is checked with NO_2 added to the inlet manifold. The conversion efficiency for HNO_3 was found to be equal or better than that for NO_2 (*Volz-Thomas et al., 2005*) and is hence only checked sporadically in the laboratory.

The NO and NO_2 mixing ratios in the sample air during internal calibration checks is:

$$\mathbf{\mu\_NO = F\_NO_2 / (FR\_C1*(P\_O_2^2 - P\_PT^2)) * FR\_C5* (P\_PT^2 - P\_Inlet^2) / F\_Inlet}$$

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

with:

μ_NO:	NO mixing ratio in the sample air (in addition to the ambient mixing ratio)
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 AuC (in sccm)
FR_C1, FR_7, FR_C5:	Capillary coefficients (in sccm/bar^2)
P_*x*:	Pressures controlling the flows (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, AuC, 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	Not available in-flight		
NOc Mode	NOc	By design always on		
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 AuC	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

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/NOy Mode	n.a.				
NO Calibration	MV7	6600	300	5400	1-5 times per flight
NO_2 Calibration	MV3	6000	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 AuC, 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_Y concentrations, but contain information on zero mode, and calibrations.

Table 4: Definition of the (sequential) data modes of the NO_Y instrument and the electrical status of the different magnetic valves (see Figure 3). 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*
Ambient-NOc-Zero Mode	AA_NOc_ZM	●	○	●	●	○	●	●	●	○
Ambient-NOc-Measure Mode	AA_NOc_MM	●	●	●	●	○	●	●	●	○
Background-NOc-Zero Mode	BG_NOc_ZM	●	○	●	●	●	●	●	●	○
Background-NOc-Measure Mode	BG_NOc_MM	●	●	●	●	●	●	●	●	○
NOcal-NOc-Zero Mode	I1_NOc_ZM	●	○	●	●	○	●	○	●	○
NOcal-NOc-Measure Mode	I1_NOc_MM	●	●	●	●	○	●	○	●	○
NO2cal-NOc-Zero Mode	I2_NOc_ZM	●	○	○	●	○	●	●	●	○
NO2cal-NOc-Measure Mode	I2_NOc_MM	●	●	○	●	○	●	●	●	○
ExternalNOcal-NOc- Zero Mode	E1_NOc_ZM	●	○	●	●	○	●	●	●	○
ExternalNOcal-NOc- Measure Mode	E1_NOc_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		○	○	○	○	○	○	○	○	○

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_Y 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_Y)
- 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_NO_Y < 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 for blocking the UV flux, 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.
- Suitable provision for connecting the calibration gas mixture behind the AUC and purging the gold tube without changing the sample flow of P2a.
- 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 NO_Y-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 or flight mode sufficiently long for the NO_Y signal to stabilize (>1h). Analyse the data in the same way as for ambient measurements.

Calculate the net NO_C signal (**AA_NOc_DM**) obtained in zero air.

AA_NOc_DM = AA_NOc_MM – AA_NOc_ZM

Compare the signal to those obtained during the internal background procedure (MV5 activated; BG_NOc_DM). The difference should be < 25 cps.

Apply the zero air behind the AUC and apply a purge flow of zero air (ca. 100 sccm) to the gold tube in order to keep it clean (requires opening of the connection behind the gold tube and special provision, see above).

Calculate the net NO signal (AA_NO_DM) obtained in zero air.

AA_NO_DM = AA_NO_MM – AA_NO_ZM

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:

μ_NO = μ_NO-Std * F_NO / (F_SL + F_O2 + F_NO)

Note: Apply the calibration mixture in each mode for sufficient time (> 30 min) to observe stable signals.

First apply the calibration mixture behind the AUC (see section 4.2.2) with the shutter of the GPT closed (no ozone produced => full NO concentration => E1_NO). Repeat with GPT-shutter open. Ensure that the remaining NO signal (E2_NO) recorded by P2a is >10% and <30% of E1_NO. If not, adjust the slit of the GPT and repeat.

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

Reconnect the AUC to the flow controller of P2a and apply the calibration mixture to the inlet of P2a instrument with GPT shutter open (E2_NOc) and closed (E1_NOc).

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 NOc signal obtained with external calibration gas applied with GPT off (E1) and with GPT on (E2).

E1_NOc_DM = E1_NOc_MM – E1_NOc_ZM
E2_NOc_DM = E2_NOc_MM – E2_NOc_ZM

Subtract the NOc signal obtained with external zero air from those obtained during calibration to obtain E1 and E2.

E1_NOc = (E1_NOc_DM – AA_NOc_DM)
E2_NOc = (E2_NOc_DM – AA_NOc_DM)

Calculate the sensitivity of the NOD (**S_NOD**), the conversion efficiency of the AuC (**E_AuC**), and their uncertainties.

S_NOD = E1_NO / μ_NO
E_AUC = (E2_NOc– E2_NO) / (E1_NO – E2_NO)

4.2.4 Calibration of capillaries and pressure transducers

The capillaries used for control of 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 effective permeation rate (F_NO2) for the branch connected to the inlet manifold is determined indirectly from the signal obtained during internal calibration check using the actual sensitivity and conversion efficiency obtained from a concurrent external calibration.

F_NO2 = F_Inlet*(FR_C1*(P_O$_2$^{2} - P_PT^2))/(FR_7 * (P_PT^2 - P_Inlet^2))*(I2_NOc)/(S_NOD* E_AUC)

With:

FR_*x*:	Capillary constants
P_x:	Pressures
I2_NOc:	Net signal obtained during internal NO_2 cal through AUC
S_NOD:	Sensitivity of the CLD
E_AUC:	Conversion efficiency of the AUC

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

Similarly the effective permeation rate of NO generated from NO2 through the bed of FeSO4 (see Figure 3) is calculated from the NO signal obtained during internal calibration (I1_NOc) and the actual sensitivity obtained from the concurrent external calibration.

F_NO = F_Inlet*(FR_C1*(P_O$_2$^{2} - P_PT^2))/(FR_C5 * (P_PT^2 - P_Inlet^2))*(I1_NOc)/(S_NOD)

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*
H_2 Reservoir	6 months	Replace and refill
O_2 cylinders	4 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
AUC	6 months	Clean gold 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. 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.

5. Subtraction of ambient signals from internal calibrations.

6. Interpolation of the calibration coefficients (S_NOD and E_AuC) over the past deployment period from the laboratory calibrations (S_NOD_pre, S_NOD_post, E_AuC_pre, E_AuC_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 E_AuC. The latter require knowledge on calibration coefficients of capillaries, flow controller and pressure sensors.

7. Calculation of atmospheric mixing ratios and uncertainties for NO_y (MR_NOy) by application of S_NOD and E_AuC to the ambient signals.

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_y mixing ratios arise from

1. Precision of PMT signal ($\Delta MM = \pm (MM)^{0.5}$) calculated from the counting statistics (depends on integration time).
2. Variance of Instrument Background over a flight (Δ_BG typically ±(25-50) ppt)
3. Uncertainty of the conversion efficiency of the AuC (ΔE_AuC/E_AUC typically ±3%; larger if conversion efficiency decreases severely during deployment)
4. Uncertainty of the sensitivity of the NOD over the deployment period (ΔS_NOD/E_NOD typically < 5%, but sometimes larger in case of excessive drift during a deployment period)
5. Uncertainty in the calibration of the secondary standard (ΔNOCal: < 5%, if standard is checked once per year against a primary standard provided by , i.e., WMO-GAW)

The total uncertainty of the measured NOy 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.

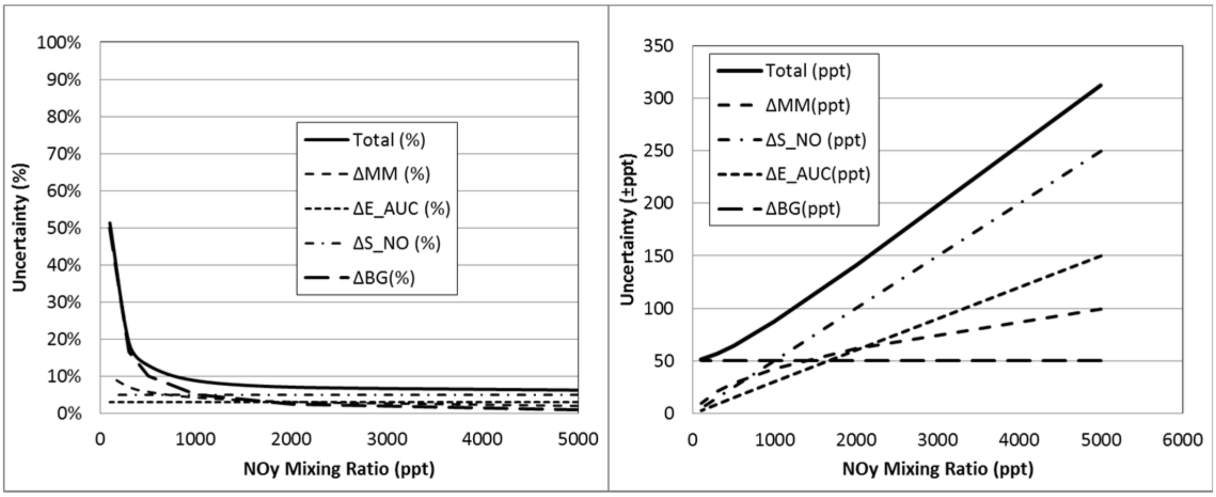

Figure 4: Individual contributions to uncertainty and total uncertainty of the NOy measurement calculated from error propagation for nominal conditions as outlined under points 1-5 above (left panel: relative error in % of measured value; right panel: absolute error in ppt).

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 NOy mixing ratios. Note that trend analysis is not a key objective of the IAGOS-CORE NO_y measurements.

6 References

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7 Glossary

ADC	Analog to Digital Converter
AuC	Gold 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_Au	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 (A*npp*.ini) 'A' for P2a, *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=A301`	Filename for flight data
`LabName=Lab`	Filename for Lab data
`MsgFileName=A301`	Filename for message files
`TimerFileName=A301_TR.csv`	Filename of timer routines (see **Table B.2**)
`ADCFileName=A301_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 = 850`	Time in seconds for heating of AuC at beginning of the flight
`[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=TRUE`	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=1`	NO_2 permeation rate in ppb*sccm
`F_Inlet=145`	Inlet flow in sccm
`SN_FR_C5=003`	Serial number of capillary FR_C5
`FR_C5=0.0266991`	Capillary constant of FR_C5 in sccm/bar^2
`SN_FR_7=006`	Serial number of capillary FR_7
`FR_7=0.0240468`	Capillary constant of FR_7 in sccm/bar^2
`SN_FR_C1=003`	Serial number of capillary FR_C1
`FR_C1=0.9447749`	Capillary constant of FR_C1 in sccm/bar^2
`S_NO=800`	Sensitivity of NO detector in cps/ppb
`W_AuC=0.97`	Conversion efficiency of gold converter
`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 (A*npp*_TR.csv)

"Name"	"First Start"	"Cycle"	"Duration"	"Setting"	"SetValue"
"Meas/Zero-Mode"	**0**	**150**	**120**	**"A1"**	**1**
"Nox/NO-Mode"	**0**	**60000**	**0**	**"B2"**	**1**
"NO_Calibration"	**6600**	**5400**	**300**	**"A6"**	**0**
"NO2_Calibration"	**6000**	**5400**	**300**	**"A2"**	**0**
"ZeroAir"	**0**	**5400**	**300**	**"A4"**	**1**
"Flush"	**0**	**9999**	**10**	**"B0"**	**1**

Table B.3: Calibration coefficients for housekeeping data (A*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	-0.13	301.01	60	200	0	"A02"
"p_cell"	0	4.49	0	-125.70	1002.02	5	20	0	"A03"
"p_inlet"	0	4.49	0	-115.46	1006.29	100	1000	0	"A04"
"p_exhaust"	0	4.49	0	-124.26	1001.18	100	1000	0	"A05"
"p_O2"	0	4.49	0	-661.06	4989.29	3800	4500	0	"A06"
"p_permT"	0	4.49	0	-614.38	5031.17	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	-383.88	1997.45	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"