JRC TECHNICAL REPORT

Report of laboratory and in-situ validation of micro-sensor for monitoring ambient air pollution

NO2: AlphaSense NO2-B4

Spinelle, L., Gerboles, M. and Aleixandre, M

2020

This publication is a Technical report by the Joint Research Centre (JRC), the European Commission's science and knowledge service. It aims to provide evidence-based scientific support to the European policymaking process. The scientific output expressed does not imply a policy position of the European Commission. Neither the European Commission nor any person acting on behalf of the Commission is responsible for the use that might be made of this publication. For information on the methodology and quality underlying the data used in this publication for which the source is neither Eurostat nor other Commission services, users should contact the referenced source. The designations employed and the presentation of material on the maps do not imply the expression of any opinion whatsoever on the part of the European Union concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries.

ABSTRACT

The aim of this study, carried out within the frame of the MACPoll project, is to assess if the NO2-B4 AlphaSense sensor meets the data quality objective (DQO) set in the European Air Quality Directive for NO_2 indicative measurements. The report presents the evaluation of the performances and determination of the laboratory and field measurement uncertainty, compared to uncertainties fixed by the DQO, namely 25% at 100 nmol/mol, for hourly NO_2 indicative measurements.

The laboratory evaluation shows that the NO2-B4 sensor give a linear answer with changing NO_2 concentrations. However, the tested sensors were suffering from an important long-term drift and a huge hysteresis effect against humidity and temperature changes.

Among ozone (O_3), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen monoxide (NO), ammonia (NH_3) and sulphur dioxide (SO_2), the sensor showed a high sensitivity to ozone (about 120 %). Moreover, the NO2-B4 was found slightly sensitive to NH_3 while it was independent from the other species. The NO2-B4 sensor did suffer from short-term drift but did not show any hysteresis effect when NO_2 levels change.

The sensor appeared to be slightly influenced by wind velocity. Conversely, power supply (220 V) did not appear to have an effect on the sensor response likely because of the quality of the DC transformer used in laboratory. In our current laboratory set-up, it was not possible to test the effect of pressure.

A multi-linear equation model was established in laboratory based on the aging of calibration, O_3, temperature and relative humidity to estimate NO_2. Using this model, the measurement uncertainty of NO2-B4 sensors was found lower than the DQO provided that the O_3 contribution after correction was lower than 5%. Using a simple linear calibration did not allow reaching the DQO of the Directive.

The sensors used during the field tests were first calibrated in laboratory experiments against reference NO_2 gas mixtures. Unfortunately, the field campaign took place in late winter - summer period when NO_2 was lower than O_3 in ambient air. Additionally, since NO2-B4 sensor is sensitive to both species, NO_2 was obfuscated by O_3 that made impossible to evaluate the final field uncertainty. The noise was found to be high during the whole field campaign preventing from obtaining valid measurements. Therefore, the model established with the laboratory experiments could not be verified in field.

According to this study, the application of the sensor as indicative method for NO_2 measurement is not fully validated. In fact, the sensor is lacking field confirmation of the laboratory results which that suggest the need of sensor data correction for long term drift, O_3 cross-sensitivity, temperature and relative humidity.

Even though the NO2-B4 sensor is not fully selective, it produces repeatable values that can be useful provided that a correction algorithms is developed to correctly estimate NO_2 using influencing variables to solve the sensitivity, selectivity and stability drawback of sensor measurements.

ENV01- MACPoll Metrology for Chemical Pollutants in Air

Report of the laboratory and in-situ validation of micro-sensors and evaluation of suitability of model equations.

NO2: NO2-B4 of αSense

Deliverable number: MACPoll_WP4_D435_NO2_AlphaSense_V1

Version: 1.0 (Draft - Version to be sent to the manufacturer)

Date: Oct. 2013

JRC

JRC building 44 TP442

via E. Fermi 21027 - Ispra (VA)

Italy

Manuel Aleixandre (REG) - CSIC

Instituto de Física Aplicada,

Serrano 144 - 28006 Madrid

Spain

Reviewed by:

MACPoll Collaborator

1 Task 4.3: Testing protocol, procedures and testing of performances of sensors (JRC, MIKES, INRIM, REG-Researcher (CSIC))

The aim of this task was to validate NO_2 and O_3 cheap sensors under laboratory. Based on the recommendations of the review (Task 4.1), the graphene sensors and a limited number of sensor types and air pollutants were chosen. At the beginning of the validation a testing protocol was drafted, which was improved and refined during the process of validation experience. This task provided the information needed for estimating the measurement uncertainty of the tested sensors. Further, procedures for the calibration of sensors able to ensure full traceability of measurements of sensors to SI units were also drafted.

The laboratory work package endeavoured to find a solution to the current problem of validation of sensors. In general, the validation of sensors is either carried out in a laboratory using synthetic mixtures, or at an ambient air monitoring station with real ambient matrix. Generally, these results are not reproducible at other sites than the one used during validation. In fact, sensors are highly sensitive to matrix effects, meteorological conditions and gaseous interferences that change from site to site.

Commonly, the validation generally performed by sensor users consists in establishing the minimum parameter set of sensors to describe their selectivity, sensitivity and stability. Since, this features is generally not reproducible from site to site, it was proposed in this project to extend the validation procedure by establishing simplified model descriptions of the phenomena involved in the sensor detection process. Both laboratory experiment in exposure chambers and fine tuning of these models during field experiments were carried out in this project.

The sensors were exposed to controlled atmospheres of gaseous mixtures in exposure chambers. These laboratory controlled atmospheres consisted of a set of mixtures with several levels of NO_2/O_3 concentrations, under different conditions of temperature and relative humidity and including the main gaseous interfering compounds.

Description of work:

- The tested sensors were selected by CSIC and JRC. The development of the protocol for the evaluation of sensors was carried out by CSIC and JRC. INRIM and MIKES carried out the initial laboratory evaluations of the new NO_2 graphene sensors. JRC carried out the experimental test of the selected O_3 and NO_2 commercial sensors and JRC and the REG-Researcher (CSIC) performed the evaluation of their test results. After laboratory tests, the commercial O_3 and NO_2 sensors were tested at field sites under real conditions by JRC.

- Along the different step of the project, the protocol for evaluation of sensors was improved by CSIC and JRC based on the test results and the technical feasibility of the experiments.

- The controlled atmospheres of the INRIM and MIKES tests were designed to evaluate the linearity of graphene sensors at different NO_2 levels (5) and their stability with respect to temperature (3 levels) and/or relative humidity (3 levels) at constant NO_2 level.

- JRC performed laboratory tests to determine the parameters of the NO_2 and O_3 model equations (task 4.1) using full or partial experimental design of influencing variables (identified in task 4.1). In any case, the controlled atmosphere included at least 5 levels of air pollutants, 3 levels of air pollutants and 3 levels of relative humidity and 2 levels of the chemical interference evidenced in task 4.1.

- CSIC and JRC applied the protocol of evaluation to the commercial sensors with determination of their metrological characteristics: detection limits, response time, poisoning points, hysteresis, etc., measurement uncertainty in laboratory and field experiment.

Activity summary: (The text with yellow background shows the activity reported in this report)

1. Selection of suitable sensors for validation (at least 2 commercially available NO_2 sensors, 3 commercially available O_3 sensors and the INRIM and MIKES graphene sensors **(JRC, REG-Researcher (CSIC))**

2. Development of a validation protocol and procedures for calibration of micro-sensors **(CSIC)**

3. Laboratory evaluation of the INRIM and MIKES graphene sensors: lab tests of NO_2 level, temperature, humidity, response time and hysteresis **(INRIM)**

4. Laboratory evaluation of the INRIM and MIKES graphene sensors (lab tests of NO_2 concentration, response time, warming time and temperature or humidity effect) **(MIKES)**

5. Laboratory tests in exposure chamber and at one field site according to the validation protocol (JRC). The field site was of rural type consistent with the sampling sites in which NO_2 micro-sensors are likely to be used. The NO_2 sensors was tested at a suburban/rural site (at the JRC).

6. Improvement of graphene sensors based on the results of JRC laboratory tests **(INRIM, MIKES)**

7. Estimation of the effect of influencing variables based on laboratory and field tests and evaluation of the suitability of the model equations proposed in 4.1 **(REG-Researcher (CSIC), JRC)**

This task leads to deliverables 4.3.1 -4.3.5.

1.1 *"Laboratory and in-situ validation of micro-sensors"* and "Report of the laboratory and in-situ validation of micro-sensors (and uncertainty estimation) and evaluation of suitability of model equations"

1.2 Time schedule and activities

4.3.4	Laboratory and in-situ validation of micro-sensors	JRC	INRIM, MIKES	Data sets	Jul. 2013
4.3.5	Report of the laboratory and in-situ validation of micro-sensors (and uncertainty estimation) and evaluation of suitability of model equations	JRC	INRIM, MIKES, REG-Researcher (CSIC)	Report	Dec. 2013

1.3 Protocol of evaluation

This report presents the evaluation of the performances of the NO2-B4 sensors of AlphaSense according to the MACPoll Validation protocol [1]. The objective of this evaluation was to determine the laboratory and field measurement uncertainties and to compare these uncertainties with the Data Quality Objective (DQO) of the European Air Quality Directive [2] for indicative method. The DQOs correspond to a relative expanded uncertainty. A flow chart describing the procedure for the validation of sensors is given in Figure *1*.

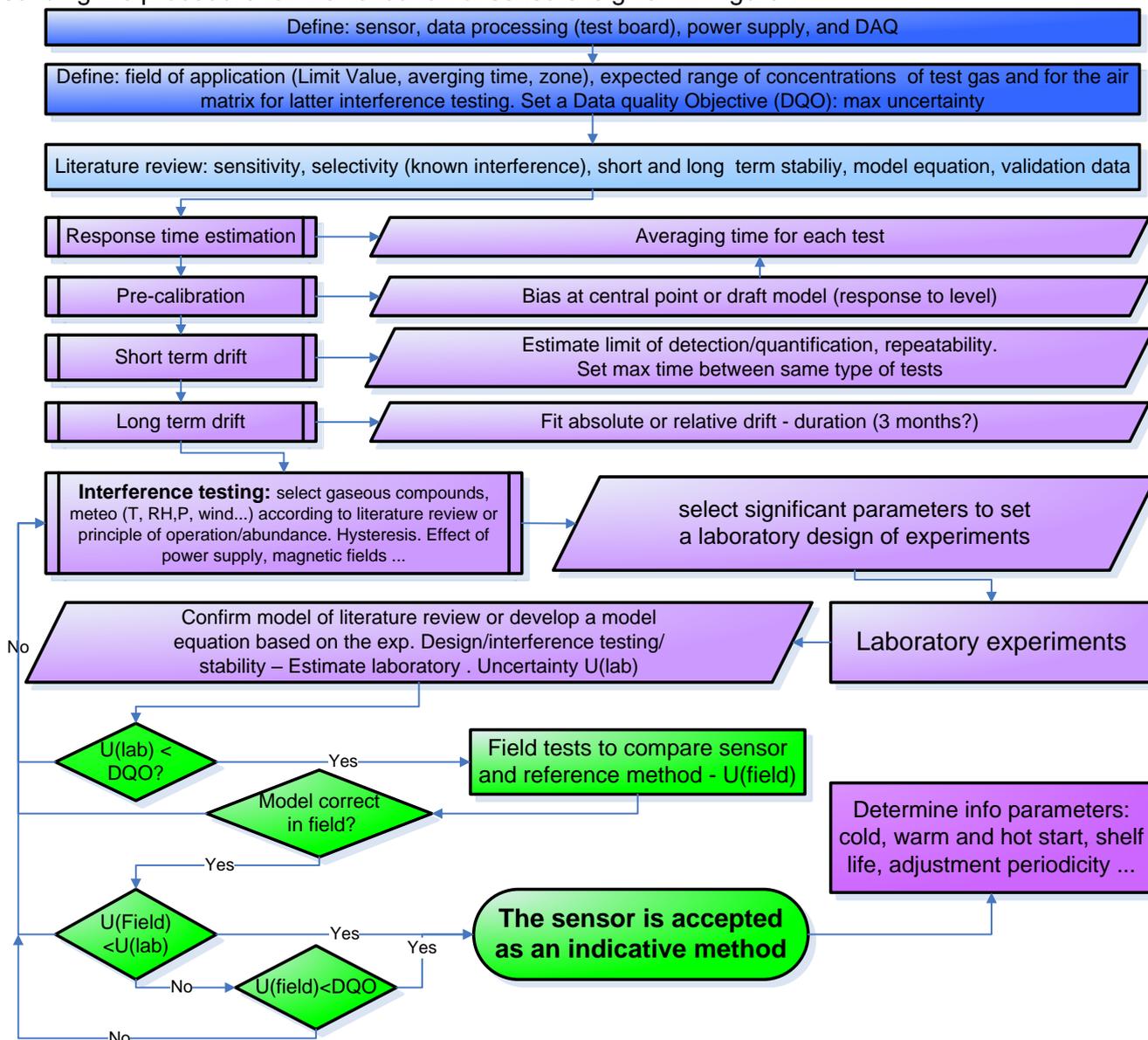*Figure* 1*: Protocol of evaluation of sensor*

[1] Spinelle L, Aleixandre M, Gerboles M. Protocol of evaluation and calibration of low-cost gas sensors for the monitoring of air pollution. EUR 26112. Luxembourg (Luxembourg): Publications Office of the European Union; 2013. JRC83791.

[2] Directive 2008/50/EC of the European Parliament and the Council of 21 May 2008 on ambient air quality and cleaner air for Europe

Table 1: Matrix of laboratory tests carried out in exposure chamber under controlled conditions

	Tests	Temperature, ºC	Relative humidity, %	Comment
1	Response Time	Middle value	Middle value	Three times: 0 to 80 % of FS and 80% of FS to 0
2	Pre-calibration	Middle value	Middle value	At least 3 levels including 0, LV, IT, AT, CL, LAT and UAT
3	Repeatability, short-long term drifts			
3-1	Repeatability	Middle value	Middle value	0 and 80 % of LV, 3 repetitions every averaging time
3-2	Short term drift	Middle value	Middle value	0, 50 % and 80 % of LV, 3 repetitions per day for 3 consecutive days
3-3	Long term drift	Middle value	Middle value	0, 50 % and 80 % of LV, repeated every 2 weeks during 3 months
4	Interference testing			
4-1	Gaseous interference	Middle value	Middle value	Interfering gaseous compound at 0 and middle value in ambient air, test gas at 0 and LV
4-2	Air matrix	Middle value	Middle value	Zero air, laboratory air and ambient air at 0 and LV
4-3	Temperature	From middle value-10 °C to middle value +10 °C by step of 5 °C	Middle value	At LV
4-4	Humidity	Middle value	From middle value-20% to middle value +20% by step of 10%	At LV
4-5	Hysteresis	Middle value	Middle value	Increasing-decreasing-increasing concentration cycles of the pre-calibration levels
4-6	Pressure	Middle value	Middle value	Overpressure 10 mbar and under pressure 5 mbar
4-7	Power supply effect	Middle value	Middle value	At LV test under 210, 220 and 230 V
4-8	Wind velocity	Middle value	Middle value	From 1 to 5 m/s
4	Validation/modelling			
4-1	Lab experiments (model)	Middle value ± 10°C, middle value, if significant	Middle value ±-20%, middle value, if significant	0, LV, AT for each significant parameter: temperature and humidity (levels) and interference (2 levels)
4-2	Field experiment			At an automatic station equipped with reference methods of measurement
5	Additional information			
5-1	Cold start, warm start, hot start	Middle value	Middle value	At LV

CL: Critical levels for the protection of the vegetation, FS: Full Scale, IT/AT: Information and alert thresholds, LAT/UAT: Lower and upper assessment threshold, LV: Limit values or target value, Middle value: average temperature or humidity typical in the field of application.

Table 1 gives a list of all the tests for the evaluation of micro-sensors included in the protocol in Figure 1. Even when the DQO cannot be met, the application of the protocol is still of interest as the method produces a full estimation of laboratory and field measurement uncertainty which demonstrates the performance of the sensor.

1.4   Gas sensor tested within MACPoll

Within MACPoll, Work Package 4, eleven models of nitrogen dioxide (NO_2) sensors were selected for evaluation (see Table 2). Hereafter, we report the results of the evaluation of the nitrogen dioxide sensor of AlphaSense (see yellow background on Table 2) which is an amperometric sensor with 4 electrodes plugged into a transmitter board.

Table 2: List of NO₂ sensors selected for the MACPoll validation programme.

N°	Manufacturer	Model	Type	Data acquisition
NO1	Unitec s.r.l	NO2 Sens 3000	Res.	Analogic voltage of transmitter board
NO2	AlphaSense	NO2 sensors NO2-B4	4 Elect.	Analogic Voltage of transmitter board
NO3	Citytech	Sensoric NO2 3E 50	3 Elect.	Analogic Voltage
NO4	Citytech	Sensoric NO 3E 100	3 Elect.	Analogic Voltage
NO5	Citytech	A3OZ EnviroceL	4 Elect.	No testing board existing?
NO6	e2V	MiCS-2710 sensor	Res.	Analogic Voltage
NO7	e2V	MiCS 4514 sensor	Res.	Analogic Voltage
NO8	Figaro	TGS 2201	Res.	No testing board existing?
NO9	Cairpol	CairClip NO2	3 Elect.	Analogic Voltage of transmitter board embedded in the sensor
NO10	MIKES	Graphene sensor	Res.	
NO11	INRIM	Graphene sensor	Res.	

3 Elect. and 4 Elect.: electrochemical sensor, 3 or 4 electrode sensor, Res.: resistive sensor

2 Sensor Identification

2.1 Manufacturer and supplier:

Alphasense Ltd, Sensor Technology House, 300 Avenue West, Skyline 120, Great Notley, Essex, CM77 7AA, Tel.: +44 (0)1376 556 700 (General), Fax: +44 (0)1376 335 899, www.alphasense.com, contact person: John Safell.

2.2 Sensor model and part number:

4 NO₂ sensors NO2-B4, 4 electrodes sensors, were received for test. It was requested by the manufacturer to also test 2 AlphaSense O₃ sensors model O3-B4

- 2 NO2-B4 for the laboratory tests with reference NO2B4_107 and NO2B4_113
- 2 NO2-B4 the field tests with reference NO2B4_109 and NO2B4_110
- 1 O3-B4 for the laboratory tests with reference O3_V011_20
- 1 O3-B4 the field tests with reference O3_V011_17

The sensors were not calibrated by the manufacturer.

2.3 Data processing of the sensor

Each sensor gives two signals, the first (named OP1) correspond to the electrode exposed to ambient air and the second (named OP2) is an auxiliary reference electrode. The 2nd one (OP2) being a background signal, it is subtracted to the raw response of the sensor (OP1).

It is thought that the sensor does not include any embedded data processing system that may change with other models of the sensor.

2.4 Auxiliary systems such as power supply, test board and data acquisition system.

NO₂ and O₃ sensors were sent mounted on test boards for evaluation. The test board consisted in the Alphasense 4-electrode Individual Sensor Board (ISB) Issue 4, s7n 085-2217, User Manual Issue 2 (see appendix).

The following auxiliary systems were used:

- Power supply: in the laboratory an accurate power supply to avoid electronic noise, model ISO-TECH IPS 303A was used while for the field tests a plug-in power supply 3-12V/800-1600 mA (rs-electronic 148 957) was used.
- Test board: no need for an external test board, Alphasense supplied the sensors mounted on their own test board.
- Data acquisition: we used a cheap DAQ 4 differential channel, PC powered. The board was a National Instrument USB 6009, 14 bits Analogic to digital converter. The periodicity of data acquisition was 100 Hz and measurements averaged every minute without filtering. No other data treatment was applied during data acquisition.

2.5 Protection box and/or sensor holder used with the material used for its preparation

During the laboratory in the exposure chamber, the sensors were used without any protection box. Figure 2 upper right, shows an example of a sensor installed in the exposure chamber. Each sensor was wrapped in a Teflon tape to avoid any reaction with gaseous compounds. For the field tests, the sensors were included into an aluminium box covered with a Teflon plate (see Figure 2 bottom right). The membrane of the sensor was put outside the Teflon plate (see Figure 2).
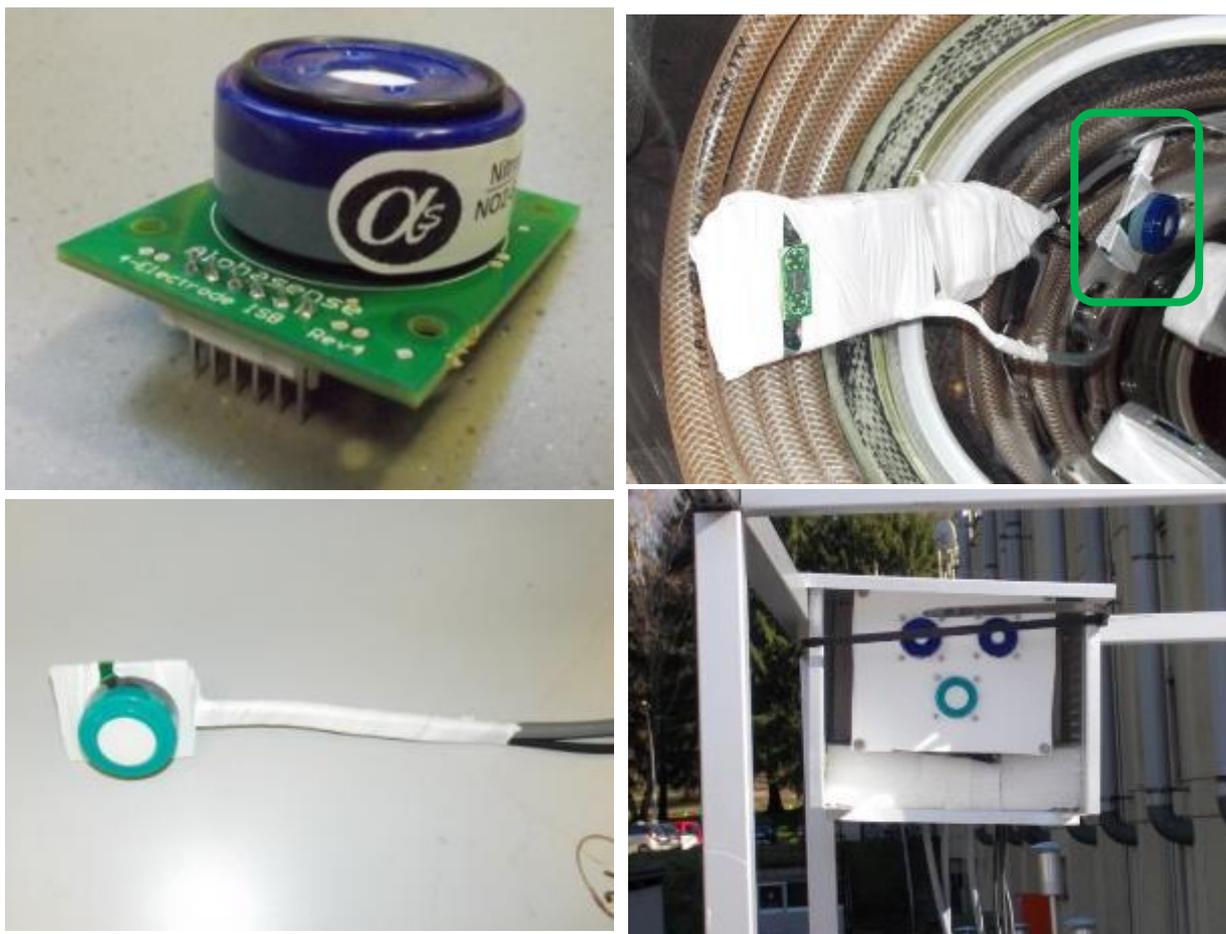
Figure 2: Top left: view of the sensor; top right: example of sensors in the exposure chamber (green square); bottom left: sensors protected with Teflon film; bottom right sensor box installed at the field monitoring site

3 Scope of validation

This validation report aims at demonstrating that the gas sensor satisfies the Data Quality Objective (DQO) of the European Directive for NO_2 Indicative Measurements at the limit value (LV).

- the DQO consists of a relative expanded uncertainty of 25 % in the region of the LV,
- the LV corresponds to 200 µg/m³ or about 100 nmol/mol at 20 °C and 1013 hPa,
- the LV is defined as an 1-hour mean. Consequently, an <u>averaging time of one hour</u> is mandatory for the sensor evaluation. Other important values defined in the Directive are the alert thresholds (AT): 400 µg/m³ (200 nmol/mol), the lower and upper assessment threshold (LAT/UAT): 100 µg/m³ (50 nmol/mol) and 140 µg/m³ (70 nmol/mol). The lowest value is the yearly average with 40 µg/m³ (20 nmol/mol)
- it was planned to validate the sensor in the following micro-environment: <u>traffic and background type of station in urban/suburban areas</u>.

Using several on-line databases and literature sources, the typical air composition given in Figure 3 was established, more details are given in [3]. Using this table, the full scale of the nitrogen dioxide gas sensor was set to 150 nmol/mol with main mode at 50 nmol/mol. Major gas molecules in urban/suburban areas appears to be O_3, CO, NO.
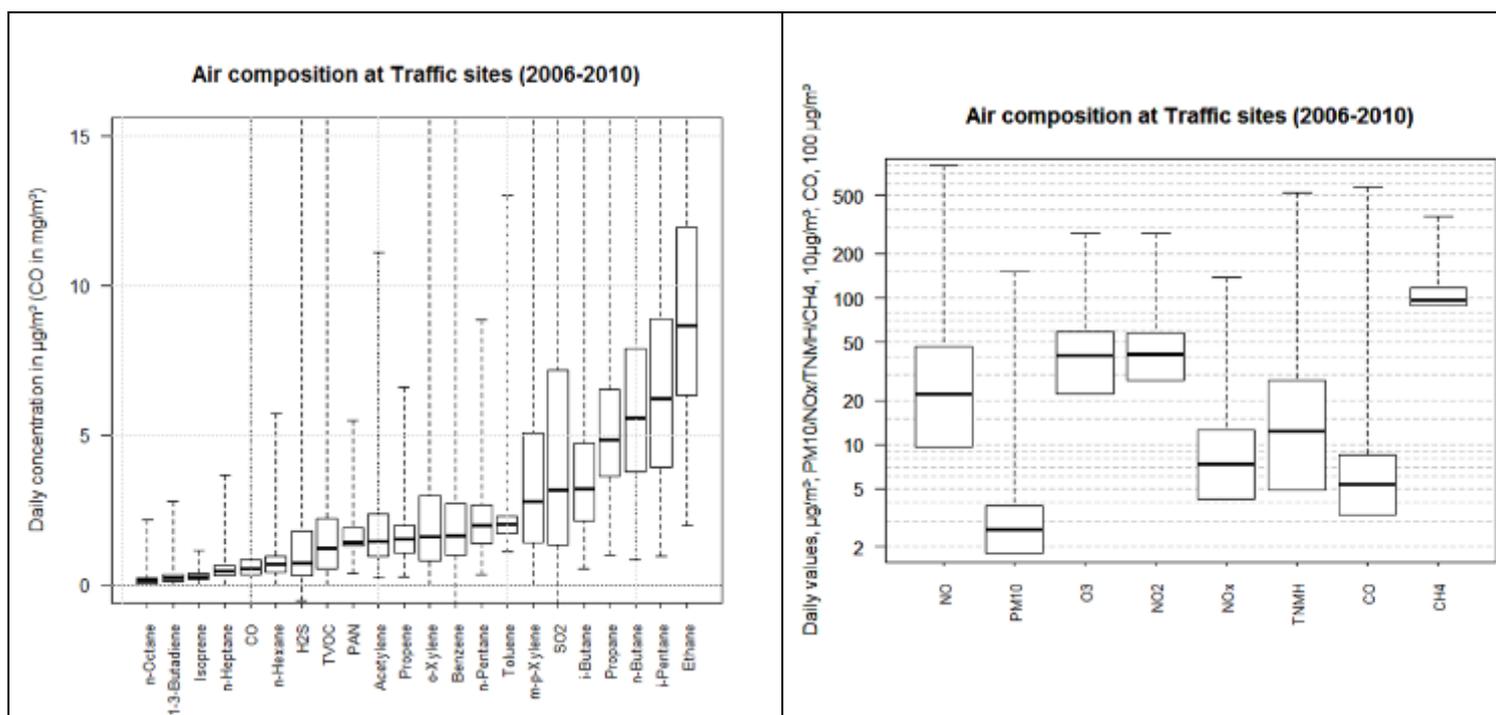
Figure 3: Box plots of ambient air composition for NO_2 and other gaseous compounds at traffic station, urban/suburban areas form the Airbase EUsar and TTorchs database. Daily data are reported. Compounds showing negative values are represented without whiskers

Further to this information it was decided to:

- Set the full scale to the alert threshold: 300 µg/m³ (about 150 nmol/mol) taking into consideration the distribution of NO_2 (see **Error! Reference source not found.**).
- The list of possible interferents of abundant compounds includes: O_3, NO, CO.
- The average temperature and relative humidity is set to 22 °C and 60 %, respectively.

It is worth reminding that before using the sensor based on the validation data included in this report, it should be ascertained that the sensor is applied in the same configuration in which it was tested here. This requires using the same data acquisition and processing, the same protection box and calibration type. The sensor shall be submitted to the same regime of QA/QC as during evaluation. In addition, it is strongly recommended that sensors results are periodically compared side-by-side using the reference method.

4 Literature review

Information about the performance of this sensor can be found in the Data sheet (see Annex1) with details on physical performances and cross sensitivities.

Moreover, a recent publication presents information of AlphaSense sensors performances for CO, NO and NO_2 [4]. In this publication, the results of NO2-A1 sensors are presented. The NO-A1 sensor is smaller than the NO2-B4 (20 mm instead of 32.3 mm for the NO2-B4).The NO2-A1 is slightly more sensitive than the NO2-B4 sensor (-400 to -700 nA/µmol/mol compared to -250 to -600 nA/µmol/mol, respectively). The NO2-A1 sensor is a 3 electrode cell, it does not have an auxiliary electrode as the NO2-B4 does, and consequently its zero baseline drift is higher (50 nmol/mol/year compared to 20 nmol/mol/year). Conversely, the sensitivity of the NO2-A1 remains within ±15 % for temperature between -30 and +50 °C while it changes by -60 % for the NO2-B4 sensor in the same temperature range. The cross-sensitivities of the NO2-A1 is similar or slightly lower than the ones of the NO2-B4 sensor apart for O_3 (30 to 55 % for NO2-B4 and 120 % for NO2-A1). However, in the following section, the results of the laboratory tests show that for the NO2-B4 sensor, the cross-sensitivity is also about 120 %.

The paper shows good linearity of the sensor responses versus ambient NO_2 levels, short response time (about 20 s) and good repeatability ($s \approx 0.3$ nmol/mol) in the concentration range 0 to 150 nmol/mol. The limit of detection was estimated to be about 1 nmol/mol. O_3 was reported to have an interference on the sensor responses of about 100 % and NO about 1 %. Temperature and humidity were shown to have an effect of the stability of the baseline of sensors while these parameters should not influence the sensor sensitivity. Correction for temperature and absolute humidity effect which consisted of scatterplot of partial derivatives of temperature and humidity versus sensor responses corrected using the minimum values obtained applying a low pass filter is presented for the NO-A1 sensor. The correction is meant to be applicable to the NO2-A1 sensor. After correction for temperature and humidity, the dependence of the NO sensor on temperature, humidity and pressure was found within the uncertainty of the determination of these effects while a significant effect of -13 %/m.s⁻¹ effect was evidenced for wind velocity. It was confirmed by field experiments that it is necessary to correct NO_2 sensor measurements for O_3 interference.

The information received from AlphaSense LTD consisted of the sensor sensitivity: between 0.350 and 0.450 mV/(nmol/mol) for the channel OP1 while the zero channel (OP2) was given at 200 mV. No other information was received about the relationship between sensor responses and other influencing parameters. The results of the tests in this study can be used to set up a model equation and to estimate the resulting measurement uncertainty. The

---

[4] M.I. Mead, O.A.M. Popoola, G.B. Stewart, P. Landshoff, M. Calleja, M. Hayes, et al., The use of electrochemical sensors for monitoring urban air quality in low-cost, high-density networks, Atmospheric Environment. 70 (2013) 186–203.

company did not supply information about any data treatment and processing and the model equation used for the transformation of the sensor responses into NO_2 values.

5 Laboratory experiments

5.1 Exposure chamber for test in laboratory

The gas sensors are evaluated in the JRC exposure chamber. This chamber allows the control of NO_2 and other gaseous interfering compounds, temperature, relative humidity and wind velocity (see Figure 4). The exposure chamber is an "O"-shaped ring-tube system, covered with dark insulation material. It can accommodate the NO_2 micro-sensors directly inside the "O"-shaped ring-tube system.
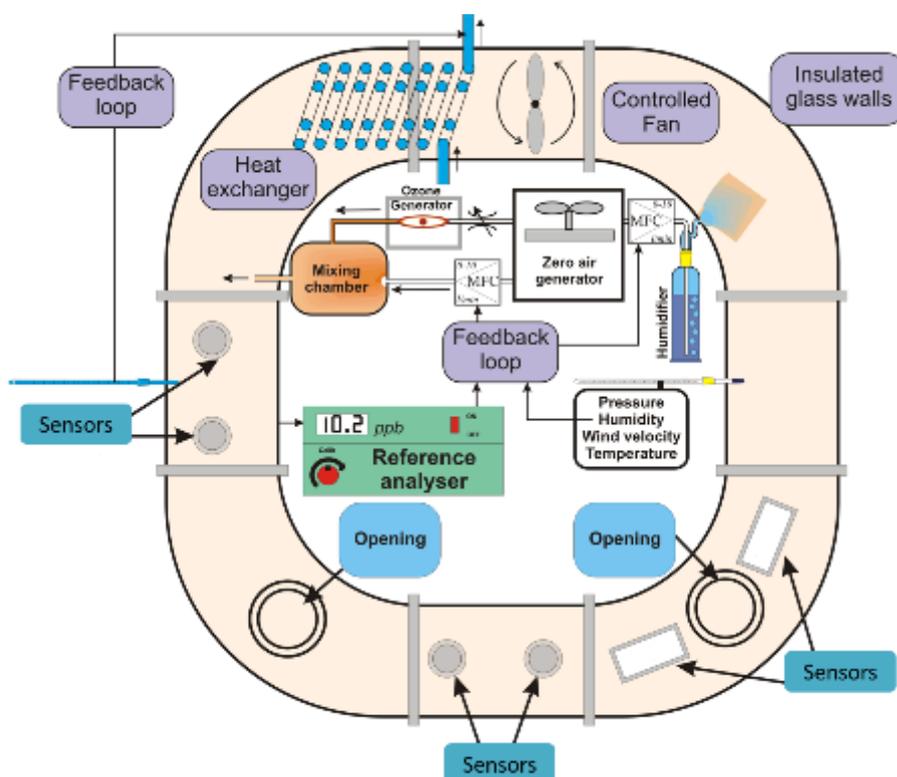
Figure 4: Exposure chamber for micro-sensors used in laboratory

A special LabView software was developed for controlling the exposure chamber and for easy programming of a set of experiments under different controlled conditions: temperature, humidity, wind velocity, NO_2 and gaseous interfering compounds. It allowed setting criteria for the stability of each parameter and for duration of each step (see Figure 5). The software was also able to manage data acquisition and all results (exposure conditions and sensors responses) were collected in Access databases for latter data treatment. The data acquisition system had a frequency of acquisition of 100 Hz and averages over one minute were stored.

The software was able to set initial values for all parameters controlling the generation of gaseous compounds (NO_2 as main gas and interfering compounds), temperature, humidity and wind velocity according to the targets set in the programming worksheet (see Figure 5). During experiments, an automatic system (feed-back loop) used the reference measurements of gaseous compounds, temperature, humidity and wind speed to auto-correct the gas mixture

generation system, temperature controlling cryostat and wind velocity to reach the target conditions (see the logical graph in Figure 5 and Figure 6).
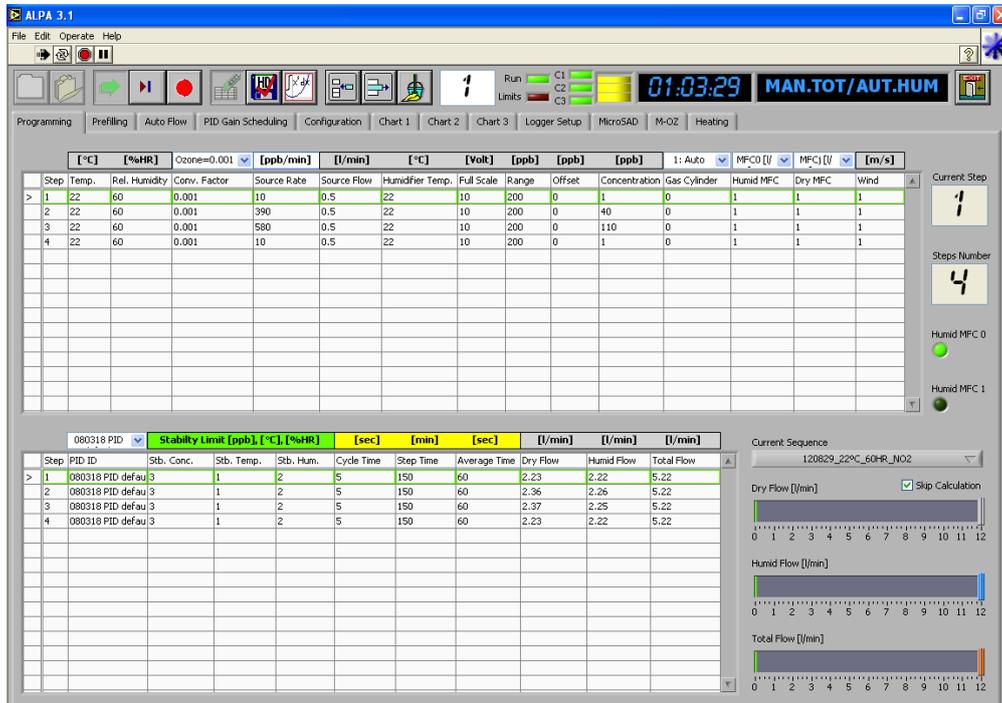
Figure 5: Example of programming of conditions
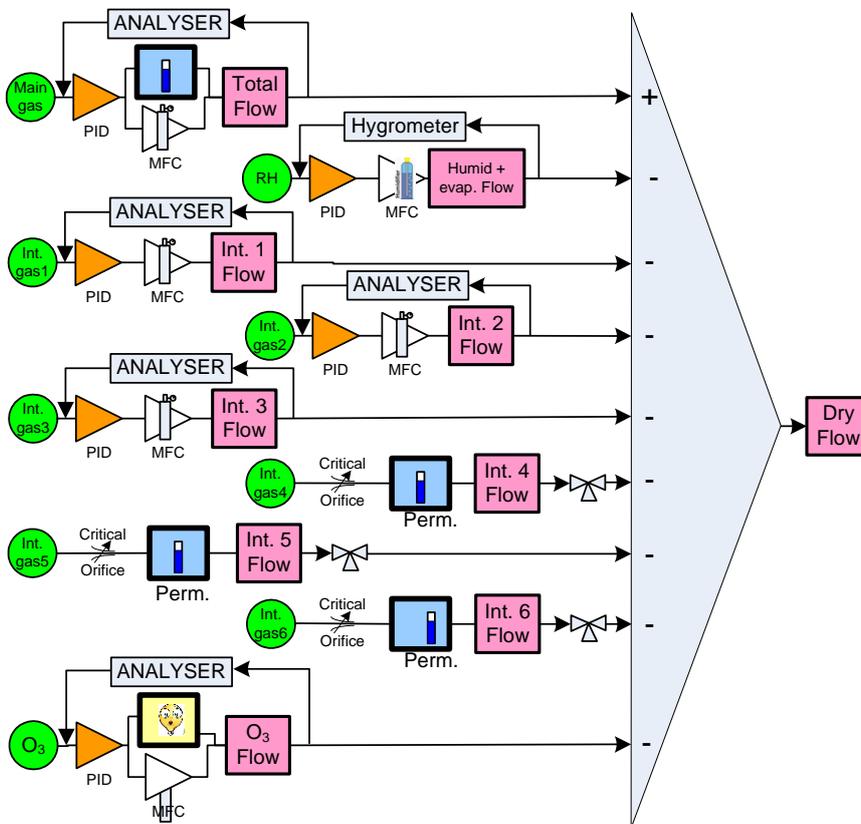
Figure 6: Feedback loops of the exposure chamber control system

5.2 Gas mixture generation system

NO_2 was produced by two different methods:

- Using NO_2 permeation tubes manufactured by KinTec (G) and Calibrage (F) in the range 500 to 2000 ng/min and diluted with zero air,
- and using a NO_2 certified highly concentrated cylinder (Air Liquide, about 60 µmol/mol of NO_2) with dilution using thermal mass flow controllers of both the cylinder and zero air. To modify the NO_2 concentration in the exposure chamber, the software used a Proportional Integrative Derivative (PID) feed-back loop able to modify the total flow inside the exposure chamber. Conversely to permeation tubes, which depend on the total dilution flow, the gas cylinder was used as an adjustable source of NO_2 to reach high concentration in fast way.

Mixtures of gaseous interference were generated with an in-house designed permeation system, using NH_3, SO_2, HNO_3 permeation tubes from AeroLaser (DE), Calibrage (FR) and KinTec. They were weighed every 3 weeks. CO mixtures were generated by dynamic dilution from highly concentrated cylinders from Air Liquide at 2000 ppm. For generating O_3, two MicroCal 5000 Umwelttechnik MCZ Gmbh (G) generators were used. These generators are equipped with a UV lamp that dissociates O_2 molecules into reactive O^* atoms that later combine with O_2 molecules to form O_3. The quantity of O_3 directly depends on the intensity of the current applied to the UV lamp and the total flow of zero air of the generator which is adjusted by a mass flow controller.

For the response time experiment, the controlled conditions in the exposure chamber shall be established as fast as possible at least within a few minutes. Because of the large internal volume of the exposure chamber (about 120 L), we used the automatic bench that the European Reference Laboratory for Air Pollution (ERLAP) operates for the European intercomparison exercises of the National Reference Laboratories of Air Pollution [5] that can generated mixture with a flow of about 100 L/min.

5.3 Reference methods of measurements

5.3.1 Methods

$NO/NOx/NO_2$ was monitored using Thermo Environment 42 C chemiluminescence analyser, calibrated against certified gas cylinder from Air Liquide. The analyser was calibrated against a permeation system for NO_2 and a NO working standard consisting of a gas cylinder at low concentration (down to 80 nmol/mol) certified by ERLAP against Primary Reference Material of NMI-VSL – NL. Other gaseous compounds were recorded to ease understanding sensors results:

- O_3: Thermo Environment Instrument (TEI), model TEI 49C UV-photometer, calibrated against an O_3 primary standard (multi-point calibration between 0 and 200 nmol/mol using a TEI Model 49 C, Thermo Environmental Instruments) that was cross-checked against a long-path UV photometer (National Institute of Standards and Technology, NIST reference photometer n° 42, USA).
- SO_2: Environment SA, model AF 21 M, calibrated with a working standard consisting of gas cylinder (Air Liquide, 50 nmol/mol) certified by ERLAP against a Primary Reference Material of NMI VSL - NL. The calibration of the analyser was confirmed by cross-checking with a permeation method.
- CO: TEI analyser, model 48i-TLE NDIR, calibrated with a CO working standard consisting of a gas cylinder at low concentration (down to 1 µmol/mol) certified against a Primary Reference Material of NMI VSL - NL.

---

5 For example: M. Barbiere and F. Lagler, Evaluation of the Laboratory Comparison Exercise for SO2 , CO, O3 , NO and NO2, 11th–14th June 2012, EUR 25536, ISBN 978-92-79-26844-1, ISSN 1831-9424, doi:10.2788/52649 ftp://ftp_erlap_ro:3rlapsyst3m@s-jrciprvm-ftp-ext.jrc.it/ERLAPDownload.htm

- CO$_2$: an infra-Red sensor, Gascard NG 0-1000 µmol/mol (Edinburg Sensors – UK) was used. This sensor includes pressure correction and temperature compensation. The sensor was calibrated with a CO$_2$ cylinder (prepared and certified by Air Liquide, 369 µmol/mol) and zero air obtained from an ultra-pure Nitrogen cylinder (Alphagaz B50 grade).

The NO, NO$_2$, O$_3$, CO and SO$_2$ working standards used for routine calibration of the analysers were all certified by ERLAP. ERLAP, as reference laboratory for air pollution of the European Comission is accredited against the ISO 17025 for these analyses (see 5.3.2).

The Teflon PFE or PTFE sampling line of each gas analyser was equipped with a nafion dryer to avoid interference from water vapour on O$_3$, NO$_x$, SO$_2$ and CO analyser.

In addition, some other parameters were recorded and/or controlled using:

- Three refrigerated/Heating Circulators were used to regulate the temperature of the exposure chamber. One cryostat (Julabo (G) Model SP-FP50) was used to control the temperature inside the exposure chamber, another one (Julabo (G) Model HE-FP50) for the surface of the O-shaped glass tube and the last one (Julabo (G) Model HE-FP50) was devoted to the control of temperature of the humid and dry air flows. These cryostats used a laboratory calibrated pt-100 probe placed inside the exposure chamber.

- Two KZC 2/5 sensors from TERSID-It (one with ISO 17025 certificate) were used to control temperature and relative humidity. One sensor was used to monitor in real-time using our LabView software, the second one was used to register these parameters.

- One Testo 445 sensor (Testoterm – G) with a temperature and relative humidity probe was used as a control interface to check values inside the chamber.

- One Testo 452 sensor (Testoterm – G) with a temperature and relative humidity probe was used as a reference sensor and to monitor temperature and relative humidity.

- One wind velocity probe based on hot-wire technology was used to monitor wind velocity during tests.

- One pressure gauge DPI 261 from Druck (G) was used to monitor pressure inside the exposure chamber

- Fan ventilator placed in the chamber, Papst (G) model, DV6224, 540 m³/hr.

- An in-house developed permeation system able to accommodate 8 permeation cells with carrier flows about 200 ml/min with critical orifices (Calibrage SA, (F)). Each permeation cells were dipped in a water bath (Haake (G) W26 Thermostatic Circulating Water Bath with Haake E8 Controller). The temperature of each cell was set at 40 °C. The permeation tubes were weighed every three weeks. The permeation cells were filled with NO$_2$, SO$_2$, NH$_3$ and HNO$_3$ permeation tubes manufactured by KinTec (G) and Calibrage (F).

5.3.2 Quality control

During the experiments, the analysers were monthly checked using a certified gas cylinder from Air Liquide. The O$_3$ analyser was monthly checked using a portable O$_3$ generator SYCOS KTO 3 (Ansyco, GmbH - G) certified against the laboratory primary standard (NIST n°42). The NO$_2$, SO$_2$ and CO analysers were calibrated once a month using cylinders certified by the ERLAP laboratory. ERLAP is ISO-17025 accredited (ACCREDIA-IT, n°1362) for the

measurement of O_3, NO_2, SO_2 and CO according to EN 14625:2012, EN 14211:2012, EN 14212:2012 and EN 14626:2012, respectively.

5.3.3 Homogeneity

The homogeneity of exposure conditions in the chamber was investigated during several tests. The influence of humidity on the Thermo Environment 42 C was eliminated by using a nafion dryer.

6 Metrological parameters

6.1 Response time

The response time of sensors was estimated by t_{0-90} and t_{90-0} (the time needed by the sensor to reach 90 % of the final stable value), after a sharp change of test gas level from 0 to 80 % of the full scale (FS) (rise time) and from 80 % of FS to 0 (fall time). Four determinations of rise and fall t_{90} were performed, see Table 3. The averaging time of the NO_2 TE42C analyser was set to 60 sec.

Table 3: Response time measurements

Step	Test gas	RH	T	Interference	Notes
1	0 nmol/mol	60 %	22 °C	none	Until stable response
2	100 nmol/mol	60 %	22 °C	none	Until stable response
3	0 nmol/mol	60 %	22 °C	none	Until stable response
4	100 nmol/mol	60 %	22 °C	none	Until stable response
5	0 nmol/mol	60 %	22 °C	none	Until stable response
6	100 nmol/mol	60 %	22 °C	none	Until stable response
7	0 nmol/mol	60 %	22 °C	none	Until stable response
8	100 nmol/mol	60 %	22 °C	none	Until stable response
9	0 nmol/mol	60 %	22 °C	none	Until stable response

Any change of all influencing variables of influence (see the list of the monitored variables in Table 4) would result in overestimation of the response time of sensors. Therefore these parameters were kept as stable as possible. Table 4 shows that the Relative Standard Deviations (RSD) of temperature, relative humidity, pressure and O_3 were within 1% at 80 % of FS and less than 0.5 nmol/mol at zero. The only imaginable influencing variable that could not be regulated while measured were ambient pressure and a small concentration of NO due to the use of high volume NO_2 gas cylinder.

Table 5 shows the response times of the sensor (with the response time of the analyser already subtracted) compared to the ones of the reference measurements. The analyser's response time was subtracted because it mainly corresponds to the time needed for establishing stable NO_2 levels in the exposure chamber by dilution.

Table 4: Response time experiment, stability of physical parameters during experiments. Temperature is in degree Celsius, relative humidity is in %, pressure is in hPa, O_3, NO_2 and NO are in nmol/mol.

	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9
NO_2, nmol/mol	2.0 ± 0.2	100.0 ± 0.6	1.9 ± 0.3	100.0 ± 0.7	2.0 ± 0.4	100.0 ± 0.5	2.0 ± 0.3	100.0 ± 0.8	2.0 ± 0.2
NO, nmol/mol	5.8 ± 0.1	8.6 ± 0.1	6.4 ± 0.2	9.3 ± 0.2	6.2 ± 0.1	8.2 ± 0.1	5.9 ± 0.1	8.1 ± 0.1	5.7 ± 0.1
Temperature, °C	22.0 ± 0.1	21.9 ± 0.1	22.0 ± 0.1	21.9 ± 0.1	22.0 ± 0.1	22.0 ± 0.1	22.0 ± 0.1	22.0 ± 0.1	22.0 ±0.1
Humidity, %	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1	60.0 ± 0.1
Pressure, kPa	970.3 ± 0.1	983.5 ± 0.2	984.9 ± 0.2	991.5 ± 0.3	970.8 ± 0.3	969.7 ± 0.2	977.9 ± 0.2	979.1 ± 0.1	984.0 ± 0.1
O_3, nmol/mol	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.2	0.0 ± 0.1	0.0 ± 0.1	0.0 ± 0.1
Time length, in min	273	118	339	2565	1418	357	955	389	1181

Table 5: Sensor's response time (t_{90}) in minutes compared to the chemiluminescence analyser response time(t_{90}) in the exposure chamber.

t_{0-90} or t_{90-0}	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9
	Rise	Fall	Rise	Fall	Rise	Fall	Rise	Fall
NO₂, chemiluminescence	11	5	4	5	4	6	3	6
NO2B4_107*	NA	Na	3	2	3	0	0	0
NO2B4_113*	NA	NA	NA	NA	NA	NA	NA	NA
O3_V011_20*	0	1	0	0	1	0	0	0

*The analyser response time is subtracted from the sensor response time.

The estimated response times in this experiment were likely slightly underestimated because the response time of the chemiluminescence analyser was subtracted while the sensors started responding to the concentration change before the end of the analyser response time.

NO2B4_113 was not working during the test (see Appendix B, Figure 4). However, its response seems to be similar as NO2B4_107. The response times of both NO2B4_107 and O3_V011_20 were in the same range as the NO₂ analyser, taking into account that the analyser's response time was subtracted. Step 2 should not be considered representative since the flow of the generation system was not sufficient to ensure a fast change in concentration. In fact, the response time of step 2 was higher, compared to the rest of the experiment and it was discarded. For NO2B4_107, response time of step 2 and step 3 correspond to the response of the sensible electrode OP1 as the second electrode shows jump in tension that alter the sensor's response. Both NO2B4_107 and O3_V011_20 showed a stable response after few minutes (Figure 7).

In average and excluding step 2 from the calculation, the response time of NO2B4_107 was about 1'30''and O3_V011_20 was 1'. For both sensors it was not observed differences between fall and rise conditions. Consequently, the sensor t_{90} was less than ¼ of the required averaging time of one hour. It makes no doubt that the sensors were able to reach stability within the averaging time.
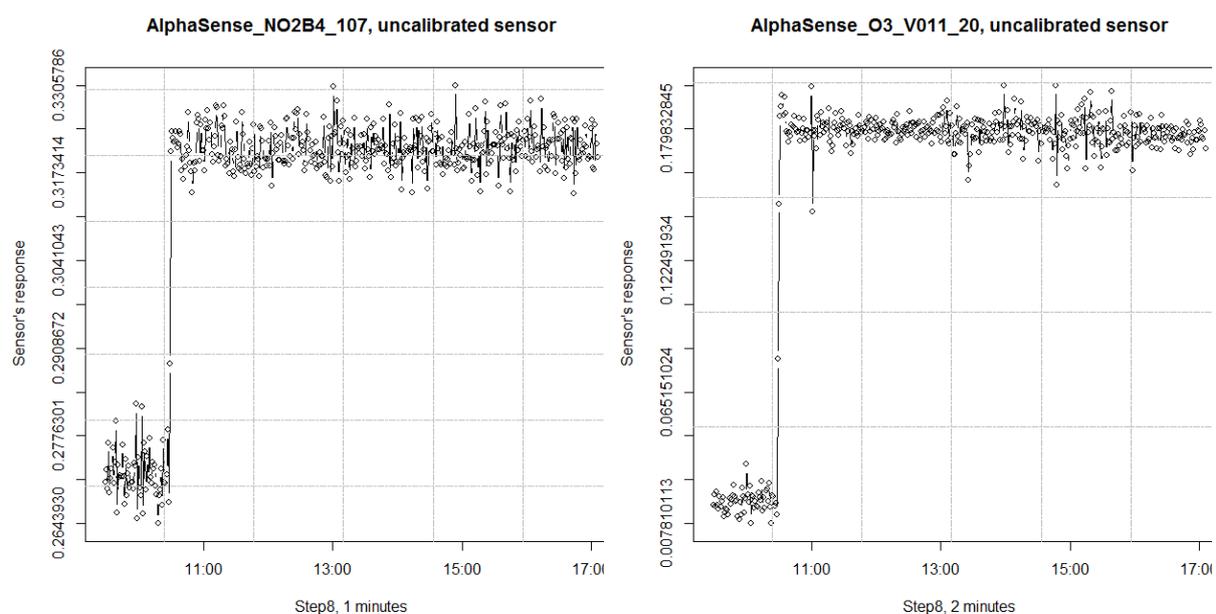

Figure 7: AlphaSense_NO2B4_107 (left) and AlphaSense_O3_V011_20 (right) response to 100 nmol/mol of NO₂ during the step 8 of the response time evaluation.

The NO$_2$ EN standard states that individual measurements [6, 3.16] are not influenced by previous individual measurements provided that two individual measurements are separated by at least four response times. Applying the same idea to sensors, tests should last for at least 1.50 x 4 = 6.00 minutes plus the stabilisation time of the exposure chamber. However, because of other slower sensors, it was decided to have each lasting for 150 minutes, well longer that the response time of the AlphaSense's sensors.

With a response time of less than 2 minutes, AlphaSense sensors were found rather suitable for mobile monitoring, a type of monitoring for which NO$_2$ levels may changes very fast when moving.

6.2 Pre-calibration

The objective of this experiment was to check if the conversion of sensor responses into air pollutant concentration does not include any bias at the mean temperature and relative humidity. The full scale of the sensor was previously defined at 150 nmol/mol. More test levels were used the following pattern 80, 40, 60, 0, 50, 20, 100% of the full scale (see levels in Table 6). The order of the tests was randomised to take into account possible hysteresis effect for the sensor (see Table 6).

The level of monitored conditions (NO$_2$, NO, O$_3$, estimated NH$_3$, T, RH and P) and sensor responses were averaged over the last hour of test in the exposure chamber. The experiment went on for 150 minutes once stabilisation of exposure conditions was reached. Temperature and humidity, which were suspected to affect the sensor response, were kept under control with relative standard deviation (RSD) of about 2 % while it is not possible to control atmospheric pressure (and less than 0.5 nmol/mol at 0 nmol/mol). The temperature and relative humidity of the test were set at 22°c and 60 %. NO$_2$ was generated both from gas cylinder and permeation tubes. Some NO$_2$ reaction occurs resulting in a small conversion into NO (in the report we will show that there is no effect of NO on the sensor response, 7.1.2).

Table 6: Experimental conditions for pre-calibration experiments of the AlphaSense's sensors

NO$_2$ Test levels, nmol/mol	NO, nmol/mol	T, °C	RH, %	Pressure, hPa	Interference	Comments
125.0 ± 0.6	10.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	980.9 ± 0.2	None	
50.0 ± 0.4	11.5 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	979.9 ± 0.1	None	LAT
100.0 ± 0.5	8.2 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	982.4 ± 0.2	None	LV
1.8 ± 0.3	4.7 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	985.2 ± 0.1	None	
75.0 ± 0.6	9.1 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	985.1 ± 0.1	None	~ UAT
25.0 ± 0.3	5.8 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	985.1 ± 0.2	None	~ DQO
150.0 ± 0.8	10.5 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	983.6 ± 0.1	None	

Apart from sensitivity and baseline value, the manufacturer did not give more information about calibration. The results of this experiment were used to calibrate the sensor (see Figure 8) and we did not use the manufacturer sensitivity and baseline in the following tests.

Figure 8 shows that both NO$_2$ and O$_3$ sensors had a linear response in the range 0 to 150 nmol/mol. The pre-calibration functions were established by plotting sensors responses (OP1 – OP2, valid for all experimental results) versus reference values measured by the Thermo Environment 42 C analyser at stable conditions 22 °C and 60 % of relative humidity. Each step lasted for 150 minutes once the condition of NO$_2$ concentrations, temperature and humidity were reached. The averages of the last 60 minutes are plotted. For NO2B4_107, NO2B4_113 and O3_V011_20 it has been decided to use a linear regression as the parabolic function did not change the distribution of residuals. For NO2B4_113, the calibration function

---

[6] EN 14625:2005 'Ambient air quality - Standard method for the measurement of the concentration of ozone by ultraviolet photometry'

was based on an experiment did after 200 days of exposure because during the initial calibration the reference electrode did not work properly.
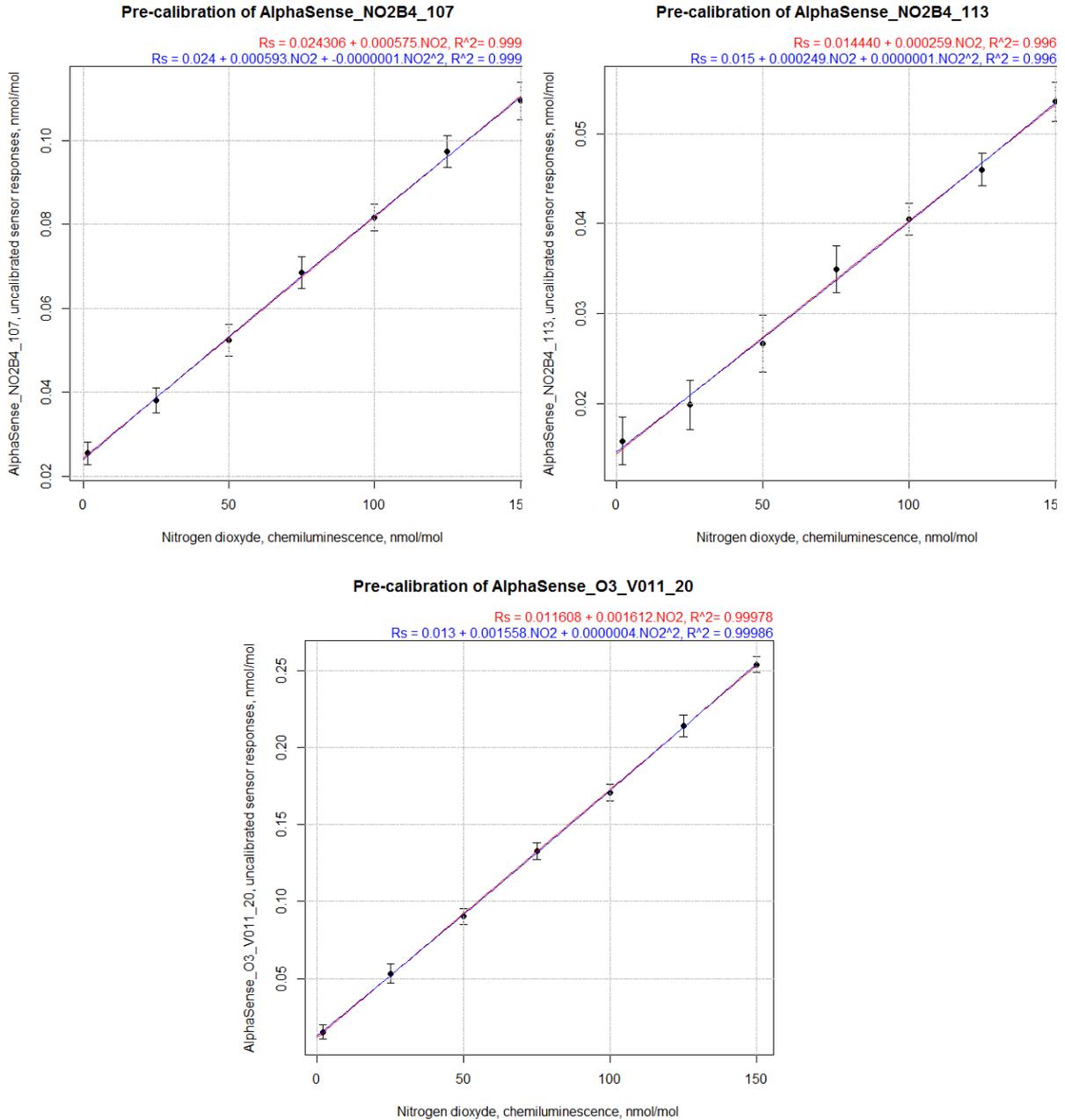
Figure 8: Initial calibration of *AlphaSense*'s sensors at 22ºC and 60 % of relative humidity.

A standard uncertainty for the lack of fit of the calibration function, u(lof), was estimated using Eq. 1 where $\rho_{max,LV}$ is the maximum residual of the model or the residual at the Limit Value (LV).

$$u^2(lof) = \rho_{max,LV}{}^2/3 \qquad\qquad\qquad \textbf{Eq. 1}$$

Table 7 gives the model, the maximum residual and the u(lof) for the 3 sensors.

Table 7: Model, maximum residual and u(lof) of AlphaSense's sensors

		Model	max residual (nmol/mol)	u(lof) (nmol/mol)
NO2B4_107	linear	$R_s = 2.43\ 10^{-2} + 5.75\ 10^{-4}.[NO_2]$	2.1	1.2
	quadratic	$R_s = 2.39\ 10^{-2} + 5.93\ 10^{-4}.[NO_2] - 1.17\ 10^{-7}.[NO_2]^2$	-	-
NO2B4_113	linear	$R_s = 1.44\ 10^{-2} + 2.59\ 10^{-4}.[NO_2]$	4.2	2.4
	quadratic	$R_s = 1.47\ 10^{-2} + 2.49\ 10^{-4}.[NO_2] + 6.47\ 10^{-8}.[NO_2]^2$	-	-
O3_V011_20	linear	$R_s = 1.16\ 10^{-2} + 1.61\ 10^{-3}.[NO_2]$	1.2	0.7
	quadratic	$R_s = 1.28\ 10^{-2} + 1.56\ 10^{-3}.[NO_2] + 3.57\ 10^{-7}.[NO_2]^2$	-	-

u(lof) was always small enough to be consistent with the DQO. u(lof) will not be included into the estimation of the laboratory uncertainty since the standard uncertainty of lack of fit of the experimental design/modelling (see 8.2) will already include the standard uncertainty of the lack of fit of the calibration function. In all the following tests the pre-calibration will be applied on request on the manufacturer unless mentioned. Eq. 2 should be used to correct the R_s to a calibrated value.

$$\text{NO2B4\_107} \qquad R_{s,cal} = \frac{R_s - 2.43\ 10^{-2}}{5.75\ 10^{-4}}$$

$$\text{NO2B4\_113} \qquad R_{s,cal} = \frac{R_s - 1.44\ 10^{-2}}{2.59\ 10^{-4}} \qquad \text{Eq. 2}$$

$$\text{O3\_V011\_20} \qquad R_{s,cal} = \frac{R_s - 1.16\ 10^{-2}}{1.61\ 10^{-3}}$$

6.3 Repeatability, short-term and long-term drift

The repeatability, short- and long-term drifts of the sensor are determined by calculating the standard deviation of sensor values for 3 consecutive averaging time periods, 3 consecutive days and every 2 weeks during three months of use, respectively.

The repeatability value imposes limits on the accuracy of the calibration and allows estimating the limit of detection and limit of quantification of the sensor. The short-term stability is used to set the maximum time between similar tests and/or the contribution of the short-term stability to the measurement uncertainty. The long-term stability is used to set the periodicity of recalibration and maximum time between similar tests. If a trend in the long-term drift is identified, it might be included into the model equation or later treated as sources of uncertainty.

6.3.1 Repeatability

The repeatability of the sensor's response was determined by calculating the standard deviation of sensor values for 3 consecutive averaging time periods (one hour) when the sensor was measuring at 0 and 100 nmol/mol under repeatability conditions. All parameters suspected to have an effect on the sensor response (test gas, O_3, temperature and humidity) were kept under control with relative standard deviation of about 2 %. Each measurement lasted for 150 minutes (6.1). The standard deviation of repeatability is calculated using the following equation:

$$s_r = \sqrt{\frac{\sum(R_i - \bar{R})^2}{N-1}} \qquad \text{Eq. 3}$$

Where R_i is each measurement, $\bar{R}$ is the mean sensor response and N the number of measurements.

Some calculations are carried out for minute-measurements. In this case, N corresponds to 60 consecutive measurements.

	NO_2 (nmol/mol)	NO (nmol/mol)	O_3 (nmol/mol)	T (°C)	Rel. Hum (%).	P (hPa)	NO2B4_107 (nmol/mol)	NO2B4_113 (nmol/mol)	O3_V011_20 (nmol/mol)
Mean ± s (N=23)	2.0 ± 0.1	6.1 ± 0.8	0.0 ± 0.2	21.9 ± 0.1	60.0 ± 0.2	983 ± 7	10.6 ± 1.1	245.6 ± 9.9	-0.6 ± 2.9
Mean ± s (N=42)	100.0 ± 0.1	8.7 ± 0.5	0.0 ± 0.5	21.9 ± 0.1	60.0 ± 0.1	993 ± 2	109.5 ± 2.4	195.3 ± 3.4	93.0 ± 4.1

The standard deviations of all parameters during experiments are given in Table 8. The repeatability of sensor measurements, the likely difference between two measurements made under repeatability conditions, was computed as $2\sqrt{2}s_r$ where s_r is the standard deviation of repeatability at 100 nmol/mol of NO₂. The limit of detection and limit of quantification are estimated as $3s_r$ and $10s_r$ where s_r is the standard deviation at 0 nmol/mol of NO₂. For mobile measurement, it may be useful to consider minute values. Table 9 gives the s_r and both hourly and minute repeatability at 100 nmol/mol, the limit of detection and the limit of quantification for the 3 sensors. All values are given in nmol/mol.

	s_r, hourly	Repeatability at 100 nmol/mol		Limit of detection	Limit of quantification
		hourly	minute		
NO2B4_107	2.4	4.3	7.8	7.1	23.6
NO2B4_113	3.4	5.2	13.2	10.1	33.5
O3_V011_20	4.1	5.7	5.9	12.3	41.1

6.3.2 Short term drift

For the short term drift, sensor responses were evaluated at 0, 50, 100 and 150 nmol/mol were calculated with stable conditions of NO₂, temperature and relative humidity on 3 consecutive days each of them being separated by a period of time between 12 and 36 hours. The averages of sensor responses were calculated over the last hour of stable conditions of NO₂, temperature and relative humidity while each steps lasted for 150 min long after stabilisation. The full experiment was repeated twice. Stabilisation was defined by the difference between the objective levels and actual measurements of less than 2 nmol/mol for NO₂, 1°C and 1% of relative humidity (this is valid throughout this report). The short-term stability was estimated using Eq. 4.

$$D_{ss} = \frac{\sum_1^N |R_{s,after} - R_{s,before}|}{N}$$ **Eq. 4**

where R_s are the sensor responses (calibrated as in 6.2) at 0, 50, 100 and 150 nmol/nmol at t_0 (before) and 24 hours after (after); N is the number of pairs of measurements.

During the experiment all parameters suspected to have an effect on the sensor response (test gas, temperature, humidity test values and other possible influencing) were kept under control. In particular, the experiments for which O₃ was higher than 5 nmol/mol were not considered in this evaluation. The standard deviation of NO₂, NO, temperature and humidity are given in Figure 9 which shows that the maximum standard deviation were found at 0 nmol/mol with 0.8 nmol/mol for NO₂, 0.2 °C for temperature and 0.2 % for relative humidity. NO shows a higher

standard deviation, especially at 150 nmol/mol of NO_2 with 2.9 nmol/mol due to an internal reactivity of our source of NO_2.

Figure 9: Stability of NO₂, temperature and relative humidity in the exposure chamber during the short-term drift experiments

The stability of NO_2, temperature and humidity were found low enough to use simple standard deviations of *Dss* as an indication of the contribution of the short-term drift to the measurement uncertainty Eq. 5.

$$u^2(D_{ss}) = \frac{\sum_{i=1}^{k}(n_i-1)s_i^2}{\sum_{i=1}^{k}(n_i-1)} \qquad \text{Eq. 5}$$

The results of these tests for the AlphaSense's sensors are given in Figure 10 which gives the number of replicate estimations of *Dss* at each concentration level (n).
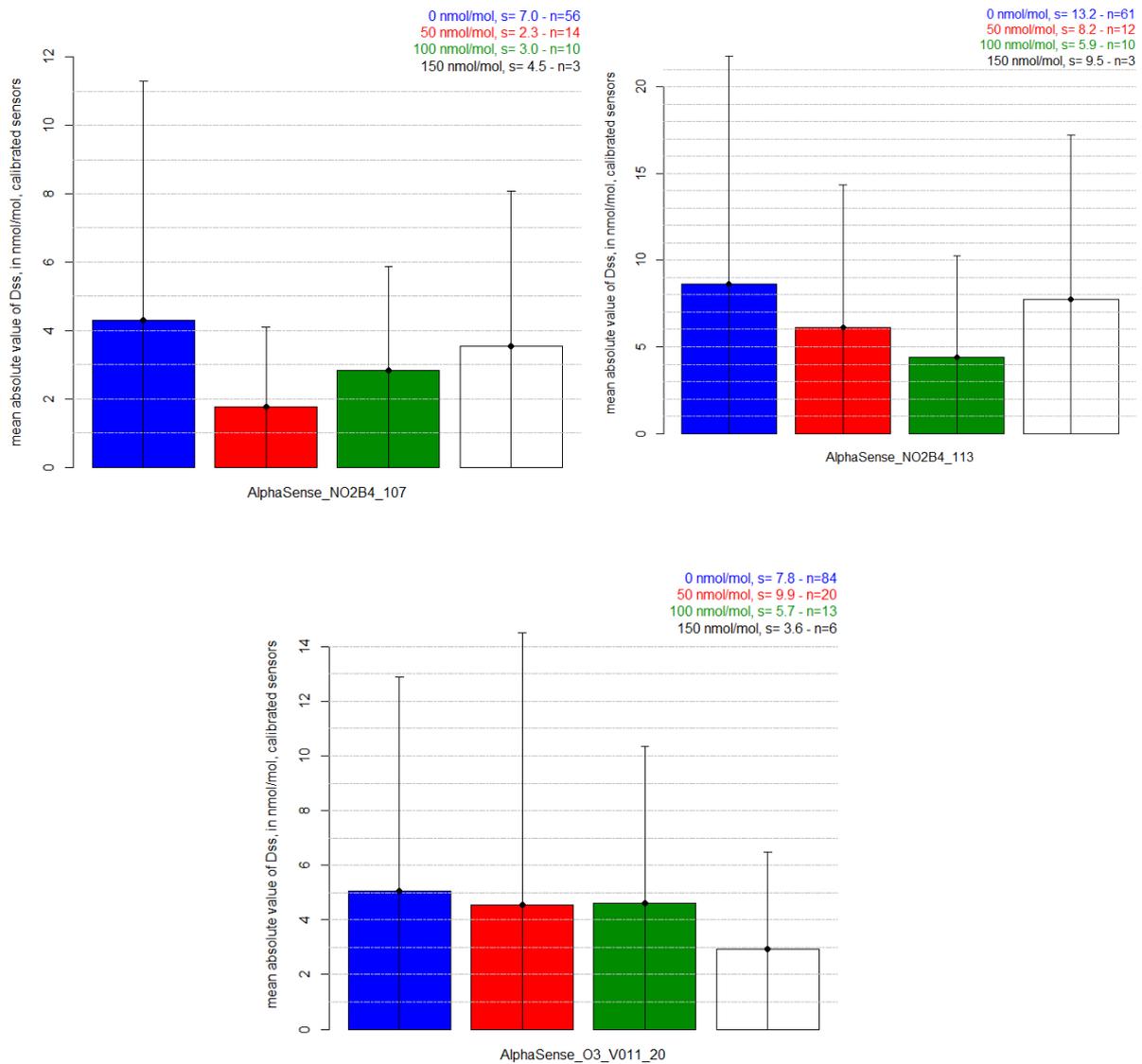
Figure 10: Short term drift for AlphaSense's sensors at 4 NO₂ levels. Each bar represents the absolute mean differences between Dss at t and t + 24 hours, the errors bars corresponds to the standard deviation of Dss

Since D_{ss} looks similar for the 4 levels, the best estimation of the short term drift consists in the average of D_{ss} at 0, 50, 100 and 150 nmol/mol with uncertainty calculated using Eq. 5 where s_i represents the standard deviation of the absolute difference between the sensor responses $\left|R_{s,after} - R_{s,berfore}\right|$:

- Dss = 3.1 nmol/mol and u(Dss) = 6.0 nmol/mol for NO2B4_107

- Dss = 6.7 nmol/mol and u(Dss) = 11.9 nmol/mol for NO2B4_113

- Dss = 4.3 nmol/mol and u(Dss) = 7.9 nmol/mol for O3_V011_20

Apart for NO2B4_107, the Dss was in the same range than the repeatability of each sensor response (see 6.3.1). The Dss of NO2B4_107 was twice as the repeatability (Dss = 3.1 nmol/mol/ for s_r = 1.7 nmol/mol). Nevertheless, the maximum duration of experiments can be set last for 48 hours.

6.3.3 Long term drift

For the long-term drift, a similar approached was carried out over a longer time span, measuring about once a week. The long-term drift stability was estimated with the same method as the short-term stability except that the differences were estimated between t_0 and the end of all laboratory experiment (268 days).

During the experiment all parameters suspected to have an effect on the sensor response (test gas, temperature, humidity, test values and other possible influencing) were kept under control. Dss for NO_2, temperature and humidity were calculated using Eq. 4. They are given in Figure 11 which shows that the maximum Dss were found at 0 nmol/mol with 0.8 nmol/mol for NO_2 and 0.3 % for relative humidity. The temperature shows a stable Dss around 0.2 ºC for all steps.
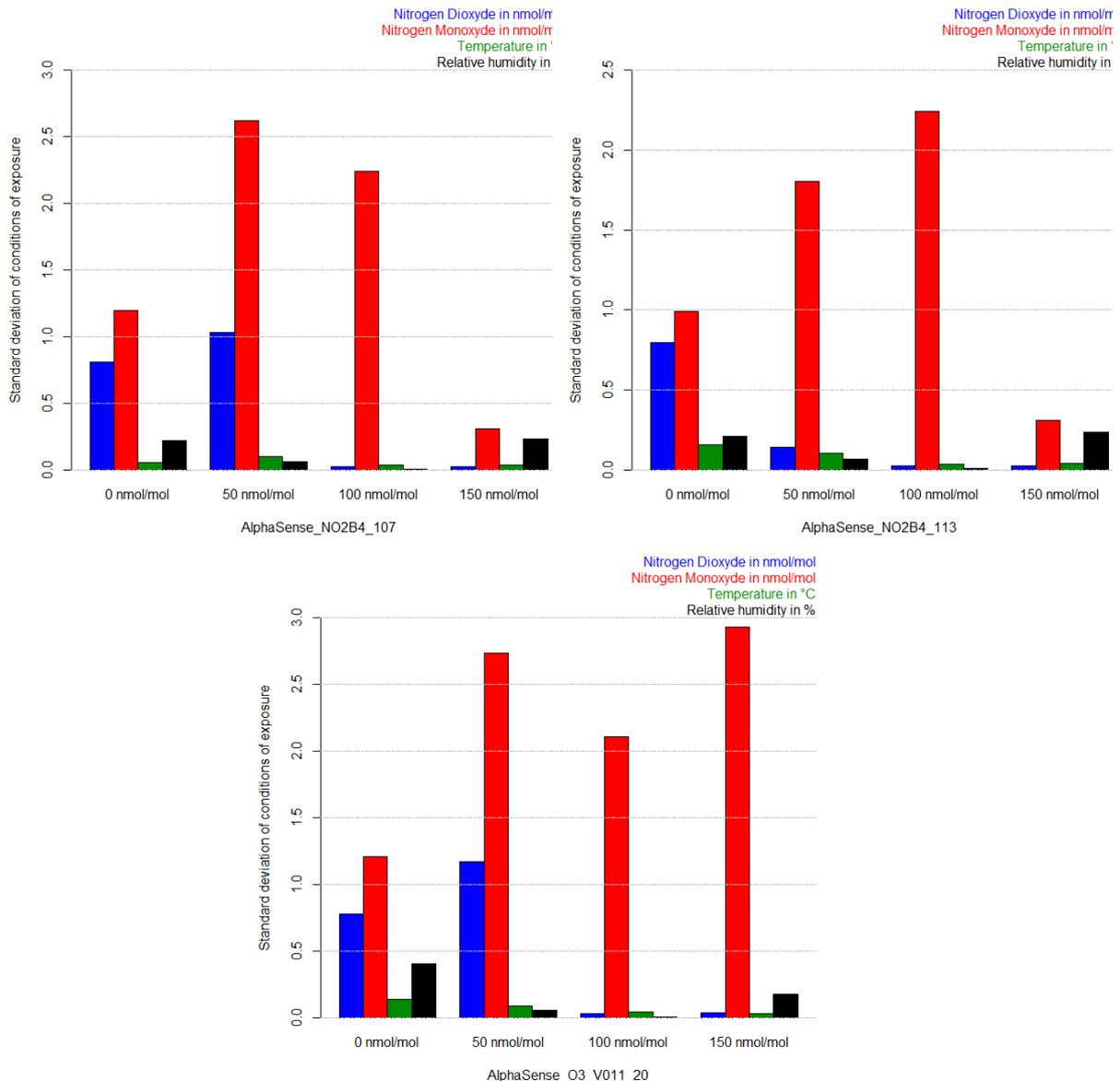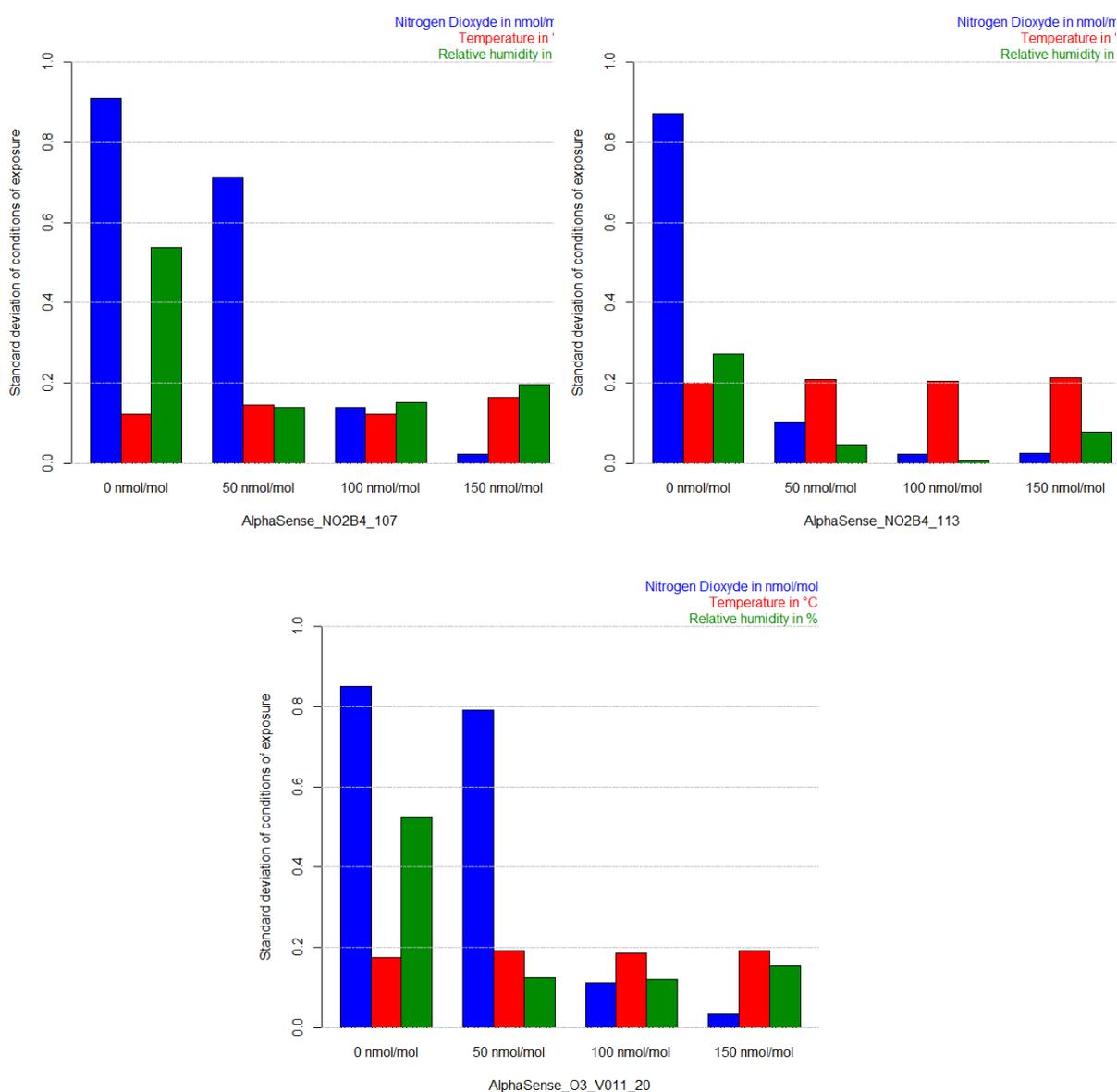

Figure 11: Stability of NO₂, temperature and relative humidity in the exposure chamber during the long-term drift experiments

For the AlphaSense's sensors, long term drifts are given in Figure 12.
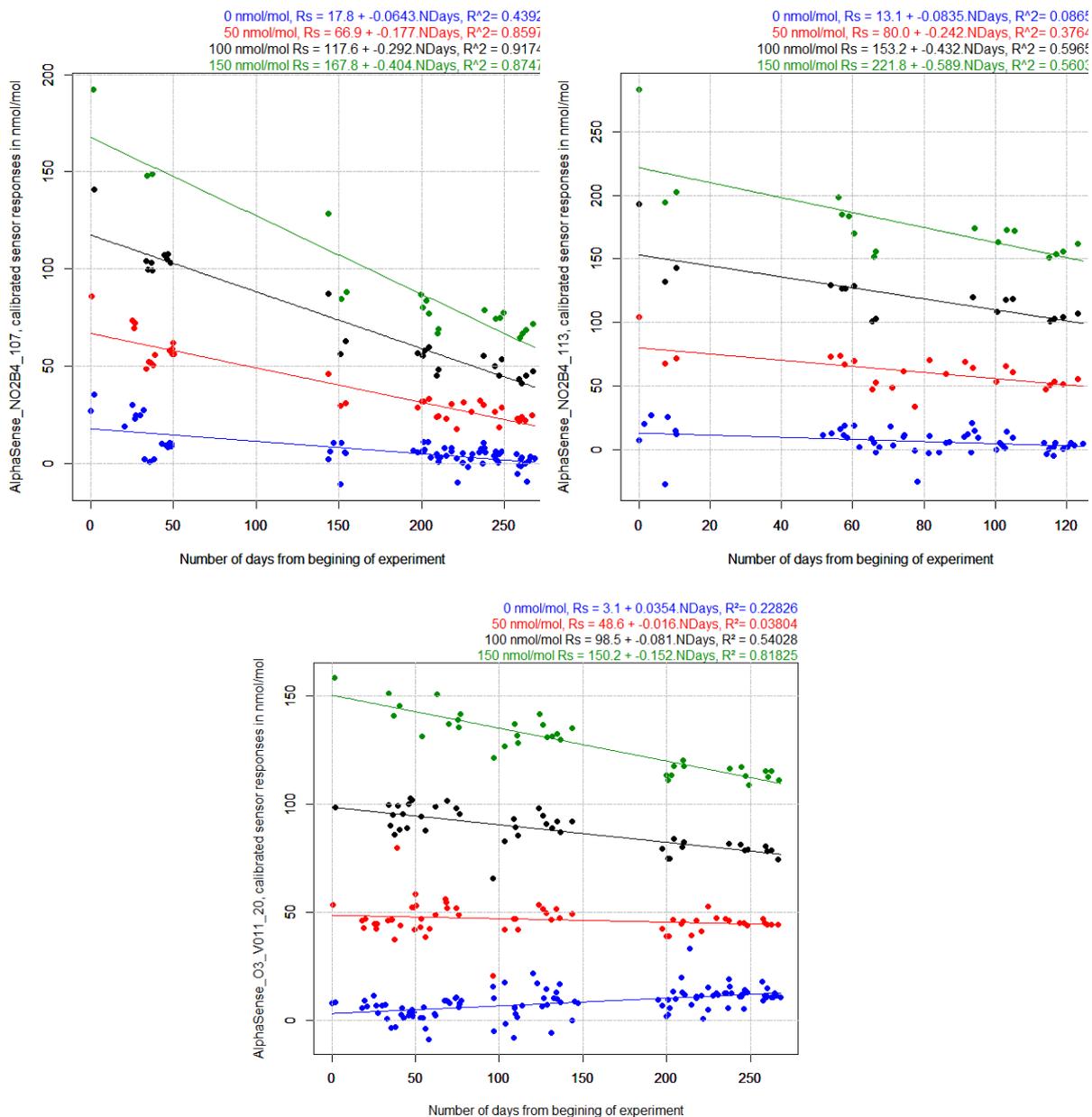
Figure 12: Long term stability of AlphaSense's sensors

For NO2B4_113 the time scale was not the same as for the two other sensors because the pre-calibration was not done at the same date. Thus the 0 for NO2B4_113 correspond to the day 145 for the two other sensors.

For the two NO2B4 sensors, the lack of values corresponds as invalidated data due to an error on the reference electrode (OP2). For the 3 other levels, the slope increases with the concentration. For the O3_V011_20, the drift at 0 nmol/mol show a positive slope, meaning that the response of the sensor under zero air tend to increase in time. For the 3 other levels the slope has the same behaviour as the NO2B4 sensors. It was therefore necessary to add the influence of the long-term drift in the final design of experiment. The contribution of the long-term stability to the sensor measurement can be characterised using a linear model, as shown on Figure 13.

AlphaSense_NO2B4_107
Intercept = 17.37 + 1.0018.NO2, R^2 = 0.99996
Slope = -0.064461 + -0.002268.NO2, R^2 = 0.99997

AlphaSense_NO2B4_113
Intercept = 12.12 + 1.3988.NO2, R^2 = 0.99974
Slope = -0.080526 + -0.003413.NO2, R^2 = 0.99855

AlphaSense_O3_V011_20
Intercept = 1.44 + 0.9821.NO2, R² = 0.99916
Slope = 0.040608 + -0.001254.NO2, R² = 0.99509
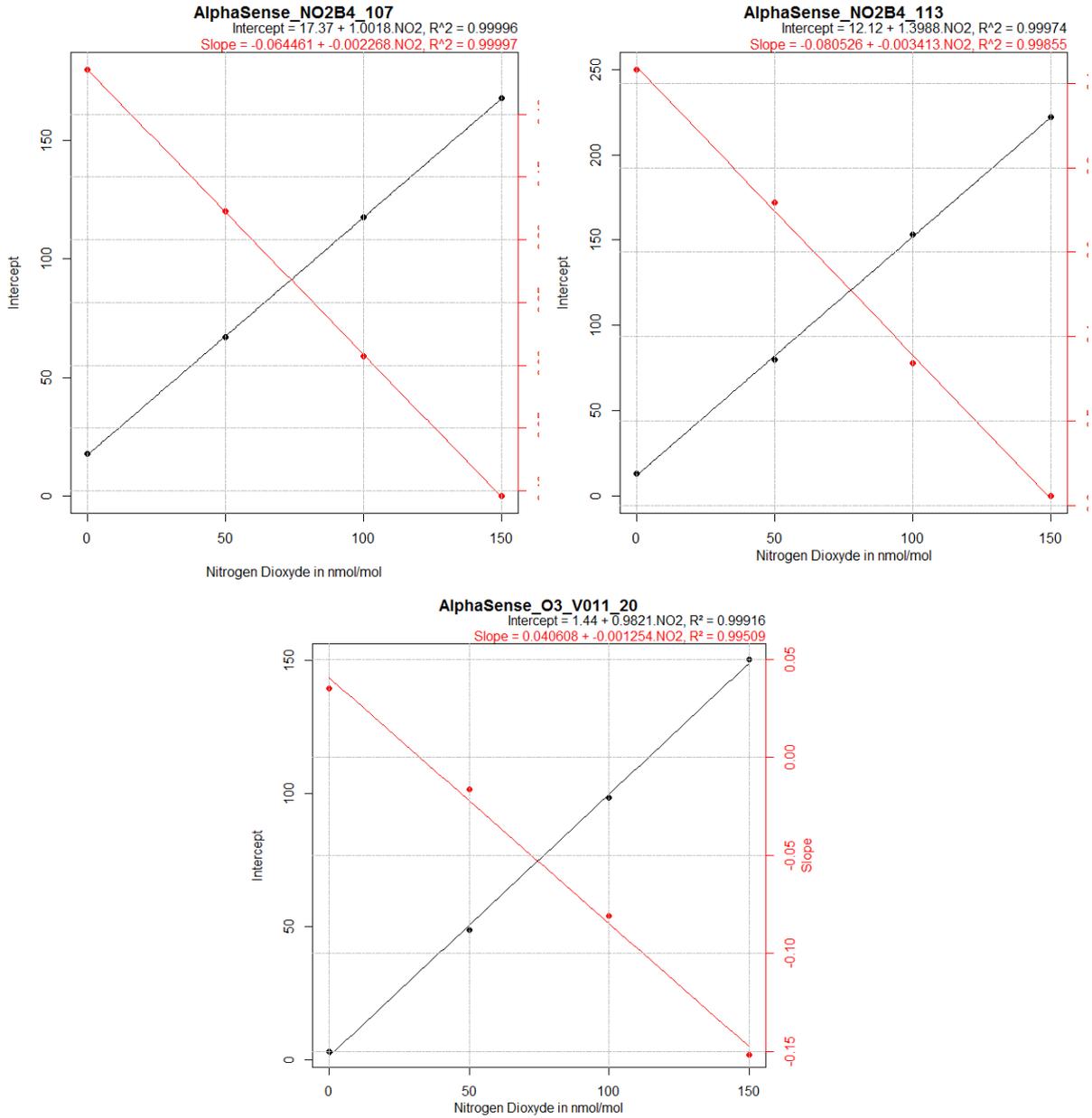
Figure 13: Contribution of the long-term stability to the sensor measurement over the levels

To the selected data will be applied a correction function depending of the NO$_2$ level and the number of days after the beginning of the experiment (Eq. 6):

NO2B4_107
$$R_{s,corr} = R_s - (-6.4 \ 10^{-2} - 2.3 \ 10^{-3} \ NO_2)NDays$$

NO2B4_113
$$R_{s,corr} = R_s - (-8.1 \ 10^{-2} - 3.4 \ 10^{-3} \ NO_2)NDays$$ Eq. 6

O3_V011_20
$$R_{s,corr} = R_s - (4.1 \ 10^{-2} - 1.3 \ 10^{-4} \ NO_2)NDays$$

Where $R_{s,corr}$ is the sensor response corrected in long term drift, R_s was the sensor's response, NO_2 was the level of NO$_2$ and $NDays$ was the time difference from the beginning of the exposition in days.

Assuming a rectangular distribution of the sensor response between the initial value and the final value, the contribution of the long term drift to the measurement uncertainty can be estimated using Eq. 7 with which $u(D_{ls})$ was found equal to 20.0 nmol/mol, 69.8 nmol/mol and 10.8 nmol/mol for NO2B4_107, NO2B4_113 and O3B4_20 respectively. Eq. 7, where a correspond to the slope of the linear regression show in Figure 13, can be used to set a periodicity of re-calibration based on the contribution of the total drift and the residuals of models ε. If the model equation is applied, the uncertainty only consists of the residuals of the regression lines.

$$u^2(D_{ls}) = \frac{(a\ NO_2\ NDays)^2}{12} + \varepsilon^2 \qquad\qquad \text{Eq. 7}$$

7 Interference testing

7.1 Gaseous compounds

Sensors generally suffer from cross sensibility to other gaseous species that may have a positive of negative effect on the sensor response. Further to the literature review of all NO_2 sensors, and the technical feasibility of testing such gas, the compounds presented in Table 10 were selected for the interference testing. The level of the interfering compounds were selected taking into account either the average level of the gaseous interference in the selected micro-environment (see deliverable D4.3.1 of MACPoll project, "Selection of suitable micro-sensors for validation"), its maximum value or another more convenient level, which are to be expected to be present in rural ambient air at background sites.

Table 10: Interference testing conditions

	O_3, nmol/mol		NO, nmol/mol		SO_2, nmol/mol		CO, μmol/mol		CO_2, μmol/mol		NH_3, nmol/mol	
Level	Low	High(int)	Low	High(int)	Low	High(int)	Low	High(int)	Low	High(int)	Low	High(int)
Interfering compound	0	50	0	100	0	~ 25	0	~ 8000	Purified air	400	0	± 85
Level	Low	High(c_t)	Low	High(c_t)	Low	High(c_t)	Low	High(c_t)	Low	High(c_t)	Low	High(c_t)
NO_2, nmol/mol	0	50	0	50	0	50	0	50	0	50	0	50
Temperature, ºC	22		22		22		22		22		22	
Relative humidity, %	60		60		60		60		60		60	

The influence of each gaseous interfering compound was determined separately with all influencing variables kept constant during tests. The tests were carried out at the mean temperature and relative humidity and in absence of other interference. After adjustment of the analyser (NO_2 and one for interfering compound apart for NH_3 for which we relied on gravimetric values), the full procedure including four steps was carried out:

- the sensor was exposed to a low level of NO_2 followed by a high level either with or without interfering compound: sensor's responses will be named Y_0 and c_t respectively. The level of NO_2 was taken equal to 50 nmol/mol, corresponding to the lower assessment threshold (LAT);
- this scheme was then repeated at a high level of interfering compound (int), first without NO_2 and finally with a mixture of NO_2 and interferent gas: sensor's responses will be named Y_z and Y_{ct} respectively.

The mixtures were supplied for a time period equal to one independent measurement, and, following this, three individual measurements will then be taken of the sensor responses. The level of the mixtures of the test gas and gaseous interfering compounds were measured using

reference methods of measurement with a low uncertainty of measurements (uncertainty of less than 5 %) traceable to (inter)nationally accepted standards (see 5.3).

The influence quantity of an interfering compound at zero ($Y_{int,z}$) and at level ct ($Y_{int,ct}$) are calculated using Eq. 8 and Eq. 9. Eq. 10 gives the influence quantity of the interferent $Y_{int,LAT}$.

$$Y_{int,z} = Y_z - Y_0 \qquad\qquad \text{Eq. 8}$$

$$Y_{int,ct} = Y_{ct} - c_t \qquad\qquad \text{Eq. 9}$$

$$Y_{int,LAT} = \left(Y_{int,ct} - Y_{int,z}\right)\frac{LAT}{c_t} + Y_{int,z} \qquad\qquad \text{Eq. 10}$$

Usually air pollutants distributions approach a log normal distribution, with the exception of O_3 distribution. The distribution for O_3 can be approximated using a rectangular distribution. The standard uncertainty associated to the interferent, $u(int)$, can be calculated according to Eq. 10 where C_{imax} is the maximum concentration of interfering compound present in the micro environment, C_{imin} is its minimum value, M is the population median and DoE is the level of the gaseous interfering compound during the laboratory experiments used to establish a sensor model. In this equation it is supposed that M, the mode of the distribution is never corrected and it is accounted as a bias in the equation.

$$u(int) = \left|\frac{Y_{int,LAT}}{int}\right| \cdot \sqrt{(M - DoE)^2 + \frac{(C_{imax} - C_{imin})^2}{12}} \qquad\qquad \text{Eq. 11}$$

$$u(int) = \left|\frac{Y_{int,z}}{int}\right| \cdot \sqrt{(M - DoE)^2 + \frac{C_{imax}^2}{12}} \ or$$

$$u(int) = \left|\frac{Y_{int,ct}}{int}\right| \cdot \sqrt{(M - DoE)^2 + \frac{C_{imax}^2}{12}} \qquad\qquad \text{Eq. 12}$$

When it is not possible to estimate $Y_{int,z}$ and/or $Y_{int,ct}$, for example the interference of NO on O_3 cannot be estimated because of the oxidation of NO in NO_2 or $Y_{int,z}$ was sometimes doubtful because of the higher variability of the sensor at 0 nmol/mol of O_3 level. In this case, the simple approach given in paragraph 8.5.6 of ISO 14956:2002 based on the determination of the sensitivity coefficient b (difference of sensor responses divided by the extent of the interfering compound level at one level) was applied.

The tables (Table 11, Table 12 and Table 13) hereafter give a summary of the effect of all tested interfering compounds. The units are the one of the interfering compounds except for the sensitivity coefficient (b) which was in nmol/mol per nmol/mol (or µmol/mol for CO). It shows that O_3 has the main significant effect on the AlphaSense's sensors. CO_2 and NH_3 can also be considered as interferents but they will not been used in the design of experiment as it's not the case for the major number of sensors. The uncertainty for the rest of the compounds was found within the repeatability of the measurements. For Table 12, Table 13 (NO2B4_113) and Table 14 (O3_V011_20) the units are the one of the interfering compounds except for the sensitivity coefficient (b) which is in nmol/mol per nmol/mol (or µmol/mol for CO) of the interfering compounds.

Table 11: Summary of results of interference testing for NO2B4_107.

Interfering compounds	Y_0	Y_z	c_t	Y_{ct}	int	$Y_{int,z}$	$Y_{int,ct}$	$Y_{int,LAT}$	C_{imin}	C_{imax}	b	$u(int)$
O₃, nmol/mol	2.3	54.7	17.7	82.2	50.9	52.4	64.6	76.8	0	60	1.268	41.1
NO, nmol/mol	3.8	4.5	22.9	21.7	100.0	0.7	-1.3	-3.2	0	80	-0.012	0.29
CO, μmol/mol	7.7	3.8	30.4	23.1	8167.5	-4.0	-7.4	-10.8	0	2	-0.001	0.52
CO₂, μmol/mol	-5.5	-0.3	23.0	17.9	20.7	5.2	-5.1	-15.5	350	450	-0.248	7.15
SO₂, nmol/mol	4.9	-1.6	26.5	24.3	22.7	-6.5	-2.2	2.2	0	10	0.097	0.28
NH₃, nmol/mol	5.6	0.4	32.1	25.7	85.0	-5.2	-6.4	-7.6	0	90	-0.075	1.95

Table 12: Summary of results of interference testing for NO2B4_113

Interfering compounds	Y_0	Y_z	c_t	Y_{ct}	int	$Y_{int,z}$	$Y_{int,ct}$	$Y_{int,LAT}$	C_{imin}	C_{imax}	b	$u(int)$
O₃, nmol/mol	-0.9	118.5	33.8	179.8	50.9	119.5	146.0	172.6	0	60	2.867	93.01
NO, nmol/mol	3.4	5.3	48.8	46.1	100.0	1.9	-2.7	-7.3	0	80	-0.027	0.63
CO, μmol/mol	11.1	4.4	61.6	45.0	8167.5	-6.7	-16.6	-26.5	0	2	-0.002	1.17
CO₂, μmol/mol	-3.8	-3.4	47.1	49.8	20.7	0.4	2.6	4.9	350	450	0.127	3.67
SO₂, nmol/mol	5.8	-6.2	59.8	51.8	22.7	-12.0	-8.0	-4.0	0	10	-0.352	1.02
NH₃, nmol/mol	10.0	-3.0	69.2	55.8	85.0	-13.0	-13.5	-13.9	0	90	-0.164	4.26

Table 13: Summary of results of interference testing for O3_V011_20

Interfering compounds	Y_0	Y_z	c_t	Y_{ct}	int	$Y_{int,z}$	$Y_{int,ct}$	$Y_{int,LAT}$	C_{imin}	C_{imax}	b	$u(int)$
O₃, nmol/mol	11.3	79.0	41.2	119.7	50.9	67.7	78.5	89.3	0	60	1.541	50.00
NO, nmol/mol	7.1	10.4	39.3	36.6	100.0	3.3	-2.7	-8.7	0	80	-0.027	0.628
CO, μmol/mol	10.2	6.1	46.0	42.5	8167.5	-4.1	-3.5	-3.0	0	2	0.001	0.250
CO₂, μmol/mol	9.2	8.9	47.0	45.3	20.7	-0.3	-1.7	-3.0	350	450	-0.080	2.32
SO₂, nmol/mol	11.9	5.3	47.3	39.3	22.7	-6.6	-7.9	-9.2	0	10	-0.349	1.01
NH₃, nmol/mol	12.4	5.2	46.9	41.0	85.0	-7.2	-6.0	-4.7	0	90	-0.070	1.82

7.1.1 Ozone – O_3

In this interference test, O_3 was generated using two UV generators (see 5.2). The results of the tests are given in Table 14. The responses of the AlphaSense's sensors had been transformed using the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO_2, NO, O_3, T, RH and P) were averaged over the last hour of experiment. The interference effect and contribution to the measurement uncertainty are given in Table 11 together with the maximum value and C_{imax} and C_{imin} the maximum and minimum values of the interferences present in the ambient gas in the selected micro-environment.

Table 14: Test conditions for the O_3 interference testing conditions and sensors responses for the AlphaSense's sensors

	NO2B4_107, mol/mol	NO2B4_113, mol/mol	O3_V011_20, mol/mol	NO_2, nmol/mol	NO, nmol/mol	O_3, nmol/mol	T, °C	RH, %	P, hPa
Y_0	2.3 ± 3.4	-0.9 ± 8.1	11.3 ± 2.6	1.2 ± 0.2	1.9 ± 0.1	0.5 ± 0.2	21.9 ± 0.1	60.0 ± 0.1	993 ± 1
c_t	17.7 ± 1.9	33.8 ± 5.5	41.2 ± 2.2	50.0 ± 0.4	6.1 ± 0.2	0.4 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	990 ± 1
Y_z	54.8 ± 3.5	118.5 ± 8.8	79.0 ± 3.4	1.2 ± 0.2	1.5 ± 0.1	50.9 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	993 ± 1
Y_{ct}	82.2 ± 5.0	179.8 ± 12.0	119.7 ± 4.6	50.0 ± 0.3	1.9 ± 0.1	51.0 ± 0.4	22.0 ± 0.1	60.0 ± 0.1	991 ± 1

O_3 was the gaseous components with the higher cross-sensitivity for the AlphaSense's sensors. It is important to remember that in ambient air, NO_2 and O_3 are correlated and therefore all values have distinct probabilities. In fact, Figure 14 shows the scatter plot between hourly NO_2 and O_3 for all traffic sites in urban/suburban areas between 2007-2010, for the following countries: BG, CH, CY, DE, DK, ES, FR, GB, GR, HU, IE, IT, LU, PL, RO, SE, SI. This graph show a correlation coefficient of $r = -0.52$.

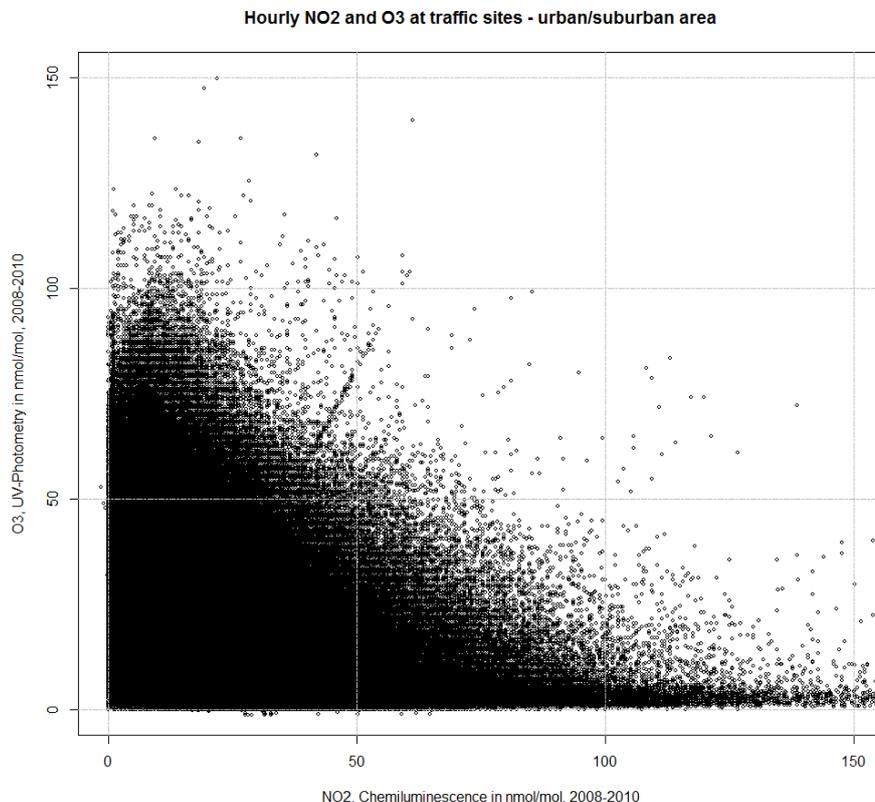Hourly NO2 and O3 at traffic sites - urban/suburban area

Figure 14: Relationship between hourly NO_2 and O_3, all traffic sites – urban/suburban areas in 2007-2010, for the following countries BG, CH, CY, DE, DK, ES, FR, GB, GR, HU, IE, IT, LU, PL, RO, SE, SI

7.1.2 Nitrogen monoxide − NO

In this interference test, NO was generated using a highly concentrated NO cylinders (Air Liquide 9468D 62.3 ± 1.2 µmol/mol) diluted with the zero air generator of the exposure chamber and controlled by MFC (0-100 mL/min). The results of the tests are given in Table 15. The responses of the AlphaSense's sensors had been transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO$_2$, NO, O$_3$, T, RH and P) are averaged over the last hour of test in the exposure chamber. The interference effect and contribution to the measurement uncertainty are given in Table 11, Table 12 and Table 13 together with the maximum value and C$_{imax}$ and C$_{imin}$ of the selected micro-environment.

Table 15: Test conditions for the NO interference testing conditions and sensors responses for the AlphaSense's sensors

	NO2B4_107, mol/mol	NO2B4_113, mol/mol	O3_V011_20, mol/mol	NO$_2$, nmol/mol	NO, nmol/mol	O$_3$, nmol/mol	T, °C	RH, %	P, hPa
Y_0	3.9 ± 3.0	3.4 ± 6.0	7.1 ± 1.7	3.2 ± 0.2	2.8 ± 0.1	0.5 ± 0.2	21.9 ± 0.1	60.0 ± 0.1	1001 ± 1
c_t	22.9 ± 5.4	48.8 ± 10.7	39.3 ± 5.0	50.0 ± 0.3	4.1 ± 0.1	0.5 ± 0.2	21.9 ± 0.1	60.0 ± 0.1	1001 ± 1
Y_z	4.5 ± 2.6	5.3 ± 6.6	10.4 ± 3.1	6.0 ± 0.5	100.0 ± 0.3	0.2 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	998 ± 1
Y_{ct}	21.7 ± 2.2	46.1 ± 5.3	36.6 ± 3.3	50.0 ± 0.5	100.0 ± 0.4	0.1 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	993 ± 1

The results of this experiment showed that NO had no significant influence on AlphaSense's sensors.

7.1.3 Carbon monoxide − CO

In this interference testing, CO was generated using a highly concentrated CO cylinder (1998±40 µmol/mol, Air Liquide-Messer Grieshiem 1898G) diluted with zero air of the exposure chamber and controlled by the MFC (0-100 mL/min). These tests were carried out at a high level of CO corresponding to the CO limit value of the European air quality directive (8 µmol/mol).

The results of the tests are given in Table 16. The responses of the AlphaSense's sensors had been transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO$_2$, NO, O$_3$, CO, T, RH and P) are averaged over the last hour of test in the exposure chamber. The interference effect and contribution to the measurement uncertainty are given in Table 11, Table 12 and Table 13 together with the maximum value and C$_{imax}$ and C$_{imin}$ of the selected micro-environment.

Table 16: Test conditions for the CO interference testing conditions and sensors responses for the AlphaSense's sensors

	NO2B4_107, mol/mol	NO2B4_113, mol/mol	O3_V011_20, mol/mol	NO$_2$, nmol/mol	O$_3$, nmol/mol	CO, nmol/mol	T, °C	RH, %	P, hPa
Y_0	7.7 ± 2.5	11.1 ± 5.4	10.2 ± 3.0	1.5 ± 0.1	0.5 ± 0.2	2961.2 ± 9.7	22.0 ± 0.1	59.8 ± 0.1	993 ± 1
c_t	30.5 ± 2.4	61.6 ± 4.8	46.0 ± 3.0	50.0 ± 0.4	0.7 ± 0.4	2967.8 ± 6.1	21.9 ± 0.1	60.0 ± 0.1	991 ± 1
Y_z	3.8 ± 2.4	4.4 ± 4.1	6.1 ± 2.7	0.7 ± 0.2	0.1 ± 0.2	8153.4 ± 13.2	22.0 ± 0.1	60.0 ± 0.1	994 ± 1
Y_{ct}	23.1 ± 4.1	45.0 ± 6.6	42.5 ± 4.2	50.0 ± 0.3	0.3 ± 0.2	8181.5 ± 85.1	21.9 ± 0.1	60.0 ± 0.1	992 ± 1

The results of this experiment showed that CO had no influence on AlphaSense's sensors, even if the sensor responses tend to diminish. It is likely that this effect is caused by a decrease of NO$_2$ (0.8 nmol/mol) or by a sensor drift at zero level rather that a CO effect. But $u(int)$, showed in Table 11, Table 12 and Table 13, were smaller than the repeatability so it will not be taking into account as interfering parameters in the full factorial design of experiment.

7.1.4 Carbon dioxide − CO₂

The interference tests were carried out at the mean temperature and relative humidity and in the absence of any other variation from other known interfering compounds. In this interference testing, two experiments were carried out: one with air dilution of the zero air of the exposure chamber including of the CO_2 and one using zero air filtered for CO_2. A FTIR Purge Gas Generator (85 lpm, Parker-Balston, USA) was used to filter CO_2 down to less than 1 µmol/mol). The differences of sensor response during the two tests were then observed.

The results of the tests are given in Table 17. The responses of the AlphaSense's sensors had been transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO_2, NO, O_3, CO_2, T, RH and P) were averaged over the last hour of test in the exposure chamber. The interference effect and contribution to the measurement uncertainty are given in Table 11, Table 12 and Table 13 together with the maximum value and C_{imax} and C_{imin} of the micro-environment.

Table 17: Test conditions for the CO₂ interference testing conditions and sensors responses for the AlphaSense's sensors

	NO2B4_107, mol/mol	NO2B4_113, mol/mol	O3_V011_20, mol/mol	NO₂, nmol/mol	O₃, nmol/mol	CO₂, nmol/mol	T, °C	RH, %	P, hPa
Y_0	-5.5 ± 5.6	-3.8 ± 9.3	9.2 ± 3.1	1.6 ± 0.1	1.0 ± 0.3	398.9 ± 3.9	22.0 ± 0.1	60.0 ± 0.1	989 ± 1
c_t	23.7 ± 3.7	47.1 ± 7.5	47.0 ± 4.1	50.0 ± 0.3	1.0 ± 0.2	396.5 ± 3.6	22.0 ± 0.1	60.0 ± 0.1	989 ± 1
Y_z	-0.3 ± 6.6	-3.4 ± 12.2	8.9 ± 4.5	1.3 ± 0.1	1.0 ± 0.2	16.8 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	989 ± 1
Y_{ct}	17.9 ± 5.7	49.8 ± 10.3	45.3 ± 3.0	50.0 ± 0.2	1.0 ± 0.2	24.7 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	989 ± 1

The results of this experiment showed that CO_2 had a small influence only on NO2B4_107 as the sensor response tends to diminish. Table 11, Table 12 and Table 13 also show that $u(int)$ of the NO2B4_107 was the only to be higher than the repeatability with 7.15 nmol/mol. For NO2B4_113 and O3_V011_20, the $u(int)$ were in the range of the repeatability thus CO_2 will not be taking into account as a main interfering parameter in the full factorial design of experiment.

7.1.5 Sulphur dioxide − SO₂

In this interference testing, SO_2 was generated using permeation tubes from Calibrage (FR). These tests were carried out at a low level of SO_2 higher than the maximum value observed in traffic station and urban/suburban areas. To assure the maximum stability of SO_2 level, the total flow inside the exposition chamber was fixed during all experiment.

The results of the tests are given in Table 18. The responses of the AlphaSense's sensors had been transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO_2, NO, O_3, SO_2, T, RH and P) were averaged over the last hour of test in the exposure chamber. The interference effect and contribution to the measurement uncertainty are given in Table 11, Table 12 and Table 13 together with the maximum value and C_{imax} and C_{imin} of micro-environment.

Table 18: Test conditions for the SO₂ interference testing conditions and sensors responses for the AlphaSense's sensors

	NO2B4_107, mol/mol	NO2B4_113, mol/mol	O3_V011_20, mol/mol	NO₂, nmol/mol	O₃, nmol/mol	SO₂, nmol/mol	T, °C	RH, %	P, hPa
Y_0	4.9 ± 2.8	5.8 ± 6.0	11.9 ± 3.0	1.0 ± 0.1	1.0 ± 0.3	0.0 ± 0.5	22.0 ± 0.1	60.0 ± 0.1	9987 ± 1
c_t	26.5 ± 2.9	59.8 ± 5.1	47.3 ± 2.9	50.0 ± 0.2	1.0 ± 0.4	0.0 ± 0.5	21.9 ± 0.1	60.0 ± 0.1	984 ± 1
Y_z	-1.6 ± 2.3	-6.2 ± 5.1	5.3 ± 3.5	1.9 ± 0.5	0.0 ± 0.2	17.5 ± 1.6	21.9 ± 0.1	60.0 ± 0.1	987 ± 1
Y_{ct}	24.3 ± 3.0	51.8 ± 6.5	39.3 ± 2.8	50.0 ± 0.4	0.0 ± 0.3	28.0 ± 0.6	22.0 ± 0.1	60.0 ± 0.1	1003 ± 1

The results of this experiment showed that SO_2 had no significant influence on AlphaSense's sensors.

7.1.6 Ammonia – NH₃

In this interference test, NH₃ was generated using permeation tubes from AeroLaser (DE). To assure the maximum stability of NH₃ level and as we cannot measure the NH₃ concentration during the all experiment, the total flow inside the exposition chamber was kept constant. NH₃ was later estimated based on gravimetric values and flow measurements.

The tests were carried out at the mean temperature and relative humidity and in absence of other interfering compounds. Two steps of experiment were carried out: first, the sensor was exposed to a mixture of zero air and NO₂ and second, adding a constant concentration of NH₃.

The results of the tests are given in Table 19. The responses of the AlphaSense's sensors had been transformed following the calibration function established in the pre-calibration experiment (see 6.2). The controlled conditions (NO₂, NO, O₃, estimated NH₃, T, RH and P) were averaged over the last hour of test in the exposure chamber. The interference effect and contribution to the measurement uncertainty are given in Table 11, Table 12 and Table 13 together with the maximum value and C_{imax} and C_{imin} of the selected micro-environment.

Table 19: Test conditions for the NH₃ interference testing conditions and sensors responses for the AlphaSense's sensors

	NO2B4_107, mol/mol	NO2B4_113, mol/mol	O3_V011_20, mol/mol	NO₂, nmol/mol	O₃, nmol/mol	NH3, nmol/mol	T, °C	RH, %	P, hPa
Y_0	5.6 ± 2.3	10.0 ± 5.5	12.4 ± 2.6	2.0 ± 0.1	1.0 ± 0.2	0	22.0 ± 0.1	60.0 ± 0.1	1000 ± 1
c_t	32.1 ± 2.1	69.2 ± 5.6	46.9 ± 2.4	50.0 ± 0.1	1.0 ± 0.2	0	22.0 ± 0.1	60.0 ± 0.1	997 ± 1
Y_z	0.4 ± 3.1	-3.0 ± 6.0	5.2 ± 3.3	0.9 ± 0.1	0.0 ± 0.2	~ 85	22.0 ± 0.1	60.0 ± 0.1	994 ± 1
Y_{ct}	24.7 ± 2.6	55.8 ± 4.8	41.0 ± 2.8	50.0 ± 0.1	0.0 ± 0.2	~ 85	22.0 ± 0.1	60.0 ± 0.1	993 ± 1

The results of this experiment showed that NH₃ had a little influence on AlphaSense's sensors, as the sensor response tend to diminish. Table 11, Table 12 and Table 13 show that $u(int)$ was high in particular for NO2B4_113 with 4.26 nmol/mol. Nevertheless it will not be taking into account as a main interfering parameter in the full factorial design of experiment because NH₃ was not one of the main gaseous compounds present in the selected micro-environment.

7.2 Air Matrix

To evaluate the influence of the air matrix on the sensor values, tests were performed at pre-calibration levels using 3 different air matrixes: zero air (filtered air), a mixture of zero air and ambient air and a mixture of zero air and indoor air. For the ambient air and indoor air experiments a constant air flow of outside and inside our building was injected in the exposure chamber. The air was sampled using a low volume samplers (LVS, Derenda 3.1 samplers - G) also used to filter the bulk air from particulate matter with a European PM₁₀ sampling head. The air was sampled just outside our laboratory (near a small parking lot) for the ambient air experiment and inside our laboratory for the indoor air experiment. The LVS sampling inlets was cleaned before sampling. The flow of the LVS was adjusted to 1 m³/hr (around 16 l/min) and regulated to 12 l/min using a cross pattern needle valve. All parameters suspected to have an effect on the sensor response (test gas, O₃, temperature and humidity) were kept under control with relative standard deviation of about 2 % (see Table 20).

Table 20 : Experiments conditions for Air Matrix interference experiments

NO$_2$ Test levels, nmol/mol	NO, nmol/mol	T, °C	RH, %	Pressure, hPa	Zero Air, l/min	Comments
125.0 ± 0.4	3.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.2 ± 0.1	9.4	Filtered air
50.0 ± 0.3	3.2 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.4 ± 0.1	8.8	
100.0 ± 0.4	3.7 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	933.6 ± 0.1	9.3	
3.2 ± 0.2	2.5 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	997.1 ± 0.1	11.1	
75.0 ± 0.4	3.1 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	995.8 ± 0.2	12.9	
25.0 ± 0.2	2.6 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.2 ± 0.2	11.8	
150.0 ± 0.5	4.1 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.6 ± 0.1	9.1	
125.0 ± 0.5	3.4 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	996.8 ± 0.1	2.4	Ambient air ~ 12 l/min
50.0 ± 0.3	4.3 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	997.6 ± 0.1	2.8	
100.0 ± 0.4	5.0 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	996.9 ± 0.1	2.4	
2.1 ± 0.2	2.7 ± 0.2	21.9 ± 0.1	58.8 ± 0..3	1001.8 ± 0.1	19.8	
75.0 ± 0.4	4.1 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	996. ± 0.17	6.4	
25.0 ± 0.3	3.4 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	997.2 ± 0.1	6.6	
150.0 ± 0.6	4.0 ± 0.1	22.0 ± 0.1	60.5 ± 0.2	994.9 ± 0.3	3.0	
125.0 ± 0.5	5.2 ± 0.2	21.9 ± 0.1	60.0 ± 0.1	1001.1 ± 0.1	2.6	Indoor air ~ 12 l/min
49.3 ± 0.5	4.6 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	1000.8 ± 0.1	2.7	
100.0 ± 0.5	5.1 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	1000.9 ± 0.1	3.4	
2.3 ± 0.2	2.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.3	1002.7 ± 0.4	17.0	
75.0 ± 0.3	4.3 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	997.7 ± 0.1	4.9	
25.0 ± 0.2	3.6 ± 0.1	21.9 ± 0.1	60.0 ± 0.1	998.3 ± 0.1	5.3	
150.0 ± 0.5	5.4 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	997.3 ± 0.1	3.2	

The Zero Air was monitored/regulated by our automatic system to reach the stability conditions. For more information we had the flow monitored in the table. For ambient and indoor the LVS should be added to obtain the total flow in the exposition chamber. For the ambient and indoor air matrix the total was in average slightly higher than for the zero air matrix. Only for step at 0 nmol/mol the total flow was higher than 20 l/min leading to a higher pressure. Figure 15 presents the sensor responses to the 7 levels under the 3 air matrix. Each sensor's response can be fitted using a linear model so it can be assumed that the increase of pressure doesn't affect the sensor's response. Air matrix different form filtered air had an effect on the sensor's response as shown for NO2B4_107 and NO2B4_113, especially for the high NO$_2$ levels. O3_V011_20 doesn't show significant variation between the 3 air matrix.
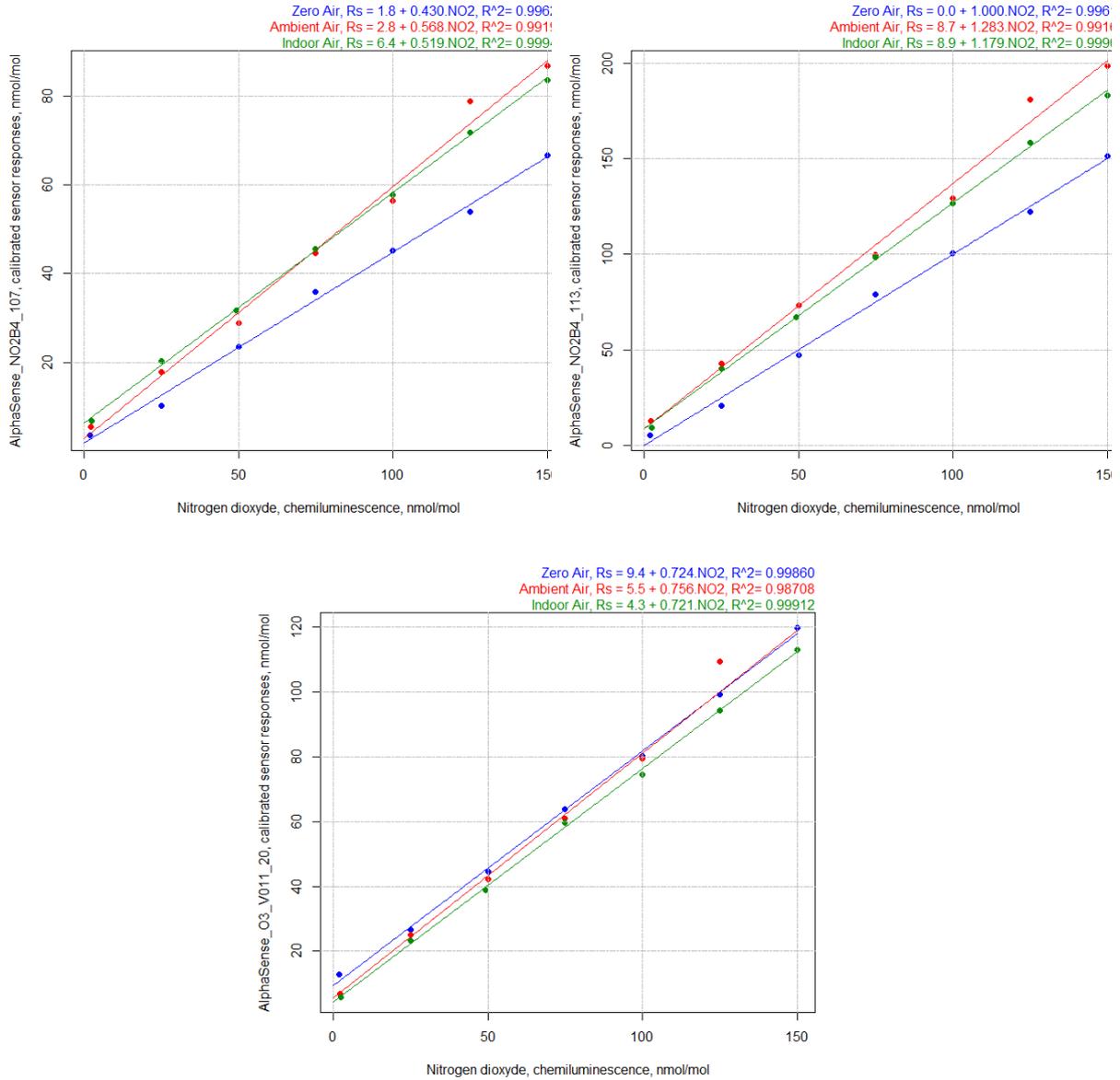
Figure 15: Effect of air matrix on AlphaSense's sensors

The uncertainty contribution $u(D_{matrix})$ was calculated based on a linear model (Eq. 13) for each type of dilution air: zero air, ambient air and indoor air (see Figure 15). In the equations, Rs was the response of the sensor, calibrated according to the pre-calibration equation Eq. 2), a and b are the parameters of the linear model and c_c the reference measurements of the test gas.

$$Rs = a + b.c_c \qquad \text{Eq. 13}$$

Then Eq. 14 allows determining c_r, the corrected sensor response calculated from Eq. 13.

$$C_r = \frac{Rs - a}{b} \qquad \text{Eq. 14}$$

Eq. 15 gives $u_{r,Matrix}$, the relative combined uncertainty due to the air matrix effect where S_r is the repeatability of the sensor response and s denotes the standard deviation of the parameters between parentheses determined using their scattering in the three linear models for zero air, ambient air and indoor air dilution.

$$u_{r,Matrix}^2 = \frac{u(c_r)^2}{c_r^2} = \frac{S_r^2 + s^2(a) + s^2(b).c_r^2}{b^2.c_r^2}$$ Eq. 15

$$u_{r,Matrix}^2 = \frac{2.36^2 + 2.40^2 + 0.07^2.c_r^2}{0.51^2.c_r^2}$$ NO2B4_107

$$u_{r,Matrix}^2 = \frac{3.35^2 + 5.08^2 + 0.14^2.c_r^2}{1.15^2.c_r^2}$$ NO2B4_113

$$u_{r,Matrix}^2 = \frac{4.11^2 + 2.66^2 + 0.02^2.c_r^2}{0.73^2.c_r^2}$$ O3_V011_20

The variability of the sensor's response can be represented using D_{matrix} given by Eq. 16. Rs represents the sensor's response to the different air matrixes: filtered, indoor and ambient air matrix.

$$D_{matrix} = \frac{\sum_1^N |R_{s,matrix} - R_{s,filtered}|}{N}$$ Eq. 16

	NO2B4_107	NO2B4_113	O3_V011_20	
$D_{matrix,Amb} =$	11.38 nmol/mol	30.06 nmol/mol	4.31 nmol/mol	Ambient Air
$D_{matrix,Ind} =$	11.24 nmol/mol	22.36 nmol/mol	5.33 nmol/mol	Indoor Air
$D_{matrix} =$	11.31 nmol/mol	26.21 nmol/mol	4.82 nmol/mol	Average ambient and indoor air

Figure 16 shows $u_{r,Matrix}$ as a function of c_r, the sensor corrected NO_2 level. The red line shows the standard uncertainty as a function of the NO_2 level. Table 21 gives $u_{r,Matrix}$ and u_{Matrix} at the limit value (100 nmol/mol) and shows that for the three sensors Even if this value is higher than the repeatability, the influence of the air matrix on the sensor values will not be consider in the final model as it is already included in each single gaseous interfering compounds.

Table 21: $u_{r,Matrix}$ and u_{Matrix} at the limit value (100 nmol/mol)

	$u_{r,Matrix}$	u_{Matrix}	s_r
NO2B4_107	15.23 %	15.23 nmol/mol	2.36
NO2B4_113	13.27 %	13.27 nmol/mol	3.35
O3_V011_20	7.24 %	7.24 nmol/mol	4.11
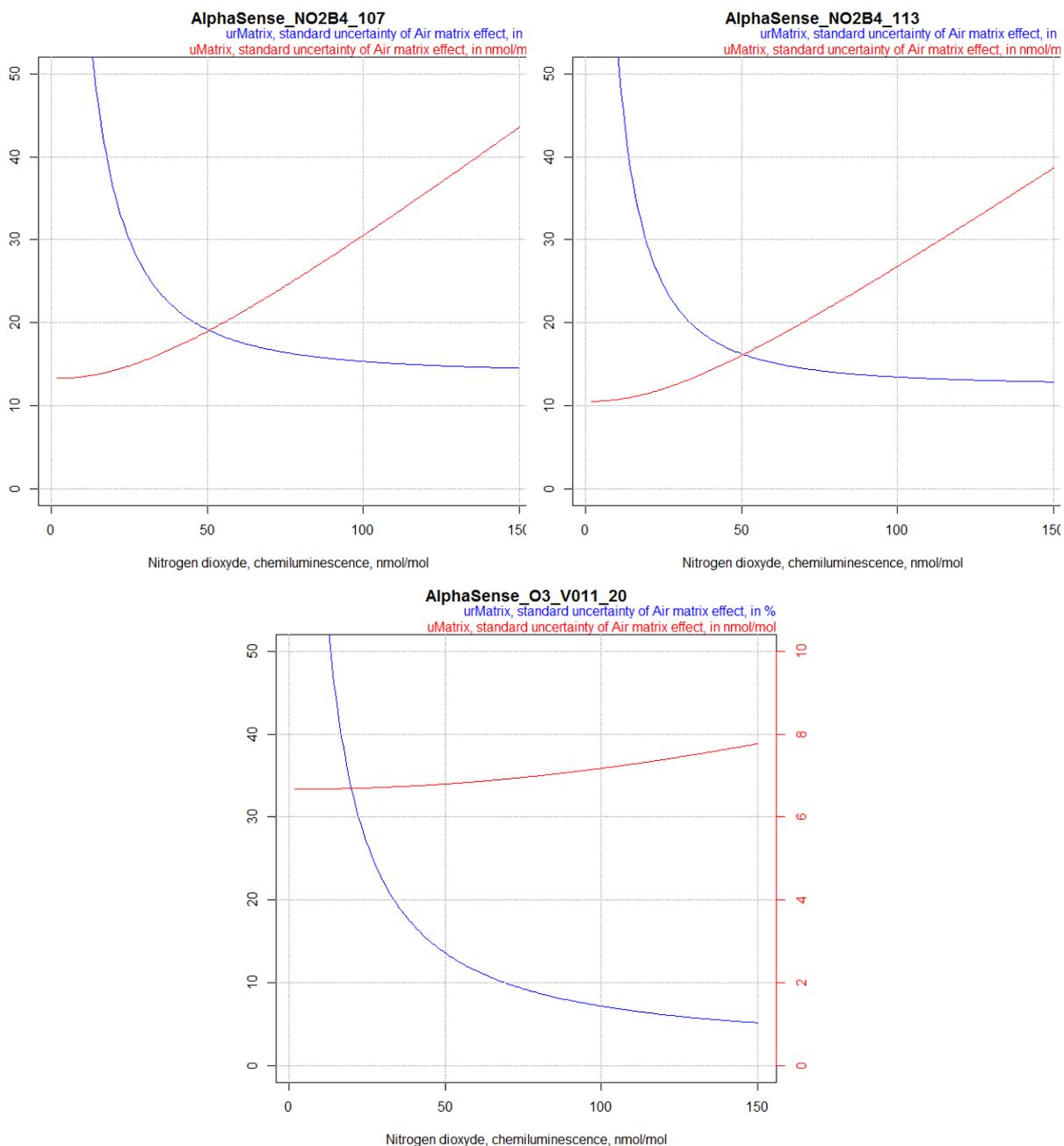
Figure 16: Evolution of $u_{r,Matrix}$ and u_{Matrix} as a function of the concentration of NO₂

7.3 Hysteresis

The sensors can present some hysteresis as the order of the measurements can influence the responses. To evaluate this hysteresis effect, we realised an exposure of the all sensor set respecting experimental conditions resume in Table 22. All parameters suspected to have an effect on the sensor response (test gas, O_3, temperature and humidity) were kept under control with relative standard deviation of about 2 %.

Table 22 : Experiments conditions for Hysteresis experiment

NO$_2$ Test levels, nmol/mol	NO, nmol/mol	T, °C	RH, %	Pressure, hPa	Interference	Comments
1.0 ± 0.1	1.6 ± 0.1	22.0 ± 0.1	58.3 ± 0.1	994.4 ± 0.1	None	
25.5 ± 0.2	2.3 ± 0.1	22.0 ± 0.1	58.6 ± 0.2	996.6 ± 0.1	None	
50.0 ± 0.3	2.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	996.3 ± 0.1	None	
75.0 ± 0.4	3.1 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	995.8 ± 0.2	None	1st cycle, rising
100.0 ± 0.4	3.7 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.6 ± 0.1	None	
125.0 ± 0.4	3.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.2 ± 0.1	None	
150.0 ± 0.5	4.1 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.6 ± 0.1	None	
125.0 ± 0.5	4.0 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.6 ± 0.2	None	
100.0 ± 0.3	3.9 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.0 ± 0.1	None	
75.0 ± 0.4	3.3 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.9 ± 0.1	None	2nd cycle, falling
50.0 ± 0.3	3.2 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.4 ± 0.1	None	
25.0 ± 0.2	2.6 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	993.2 ± 0.2	None	
2.8 ± 0.1	2.4 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	991.3 ± 0.1	None	
25.0 ± 0.2	2.5 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	991.3 ± 0.1	None	
50.0 ± 0.3	3.0 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	991.4 ± 0.1	None	
75.0 ± 0.5	3.2 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	992.9 ± 0.1	None	3rd cycle, rising
100.0 ± 0.4	3.7 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	991.9 ± 0.1	None	
125.0 ± 0.5	4.0 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	992.8 ± 0.1	None	
150.0 ± 0.6	4.2 ± 0.1	22.0 ± 0.1	60.0 ± 0.1	994.9 ± 0.3	None	

Using Eq. 13 to Eq. 15, we can calculate the uncertainty by first fitting a model to each part of the hysteresis cycle. Eq. 17 gives $u_{r,h}$, the relative combined uncertainty due to the hysteresis effect where $u(Rs)$ was the repeatability of the sensor response and s denotes the standard deviation of the parameters between parentheses determined using their scattering in the three linear models for the 3 part of the hysteresis cycle.

$$u_{r,h}^2 = \frac{u(c_r)^2}{c_r^2} = \frac{S_r^2 + s^2(a) + s^2(b).c_r^2}{b^2.c_r^2} \qquad \textbf{Eq. 17}$$

$$u_{r,h}^2 = \frac{2.36^2 + 0.78^2 + 0.01^2.c_r^2}{0.53^2.c_r^2} \qquad \textbf{NO2B4\_107}$$

$$u_{r,h}^2 = \frac{3.35^2 + 1.66^2 + 0.02^2.c_r^2}{1.21^2.c_r^2} \qquad \textbf{NO2B4\_113}$$

$$u_{r,h}^2 = \frac{4.11^2 + 0.82^2 + 0.002^2.c_r^2}{0.74^2.c_r^2} \qquad \textbf{O3\_V011\_20}$$

1st cycle, rising, Rs = -21.2 + 0.540.NO2, R^2= 0.998
2nd cycle, falling, Rs = -19.6 + 0.524.NO2, R^2= 0.999
3rd cycle, rising, Rs = -20.1 + 0.535.NO2, R^2= 0.999

1st cycle, rising, Rs = -47.0 + 1.218.NO2, R^2= 0.999
2nd cycle, falling, Rs = -44.0 + 1.191.NO2, R^2= 0.999
3rd cycle, rising, Rs = -44.4 + 1.217.NO2, R^2= 0.999

1st cycle, rising, Rs = 2.3 + 0.744.NO2, R^2= 0.99977
2nd cycle, falling, Rs = 0.8 + 0.741.NO2, R^2= 0.99953
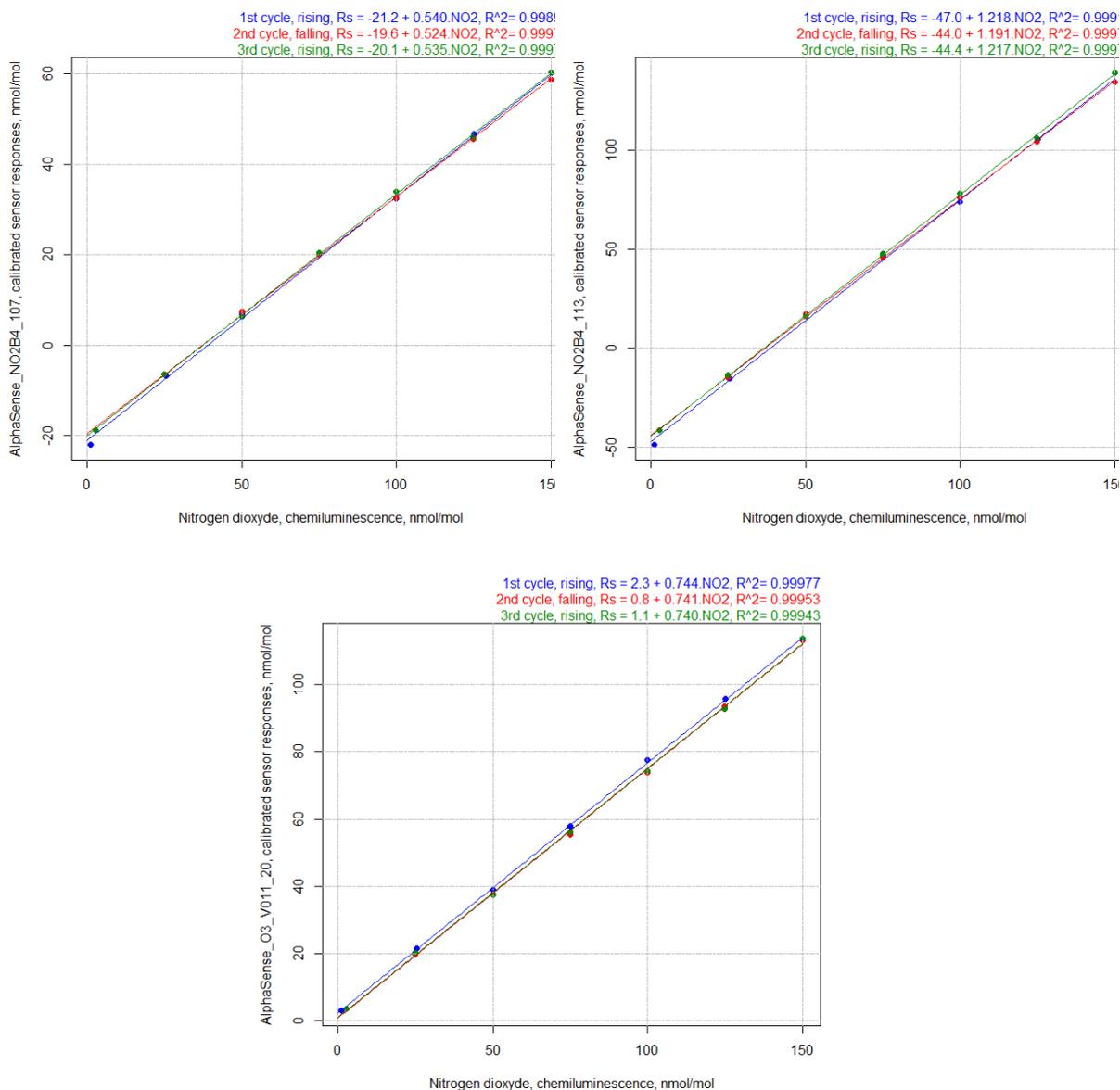3rd cycle, rising, Rs = 1.1 + 0.740.NO2, R^2= 0.99943

Figure 17: Effect of hysteresis on AlphaSense's sensors

Figure 17 shows the sensor responses when exposed to the hysteresis experiment. Both NO2-B4 sensors showed a linear response in each part of the hysteresis test without variation between rise and fall and between the two rises. O3_V011_20 had shown the same type of response and the same insensitivity towards hysteresis variation of concentration.
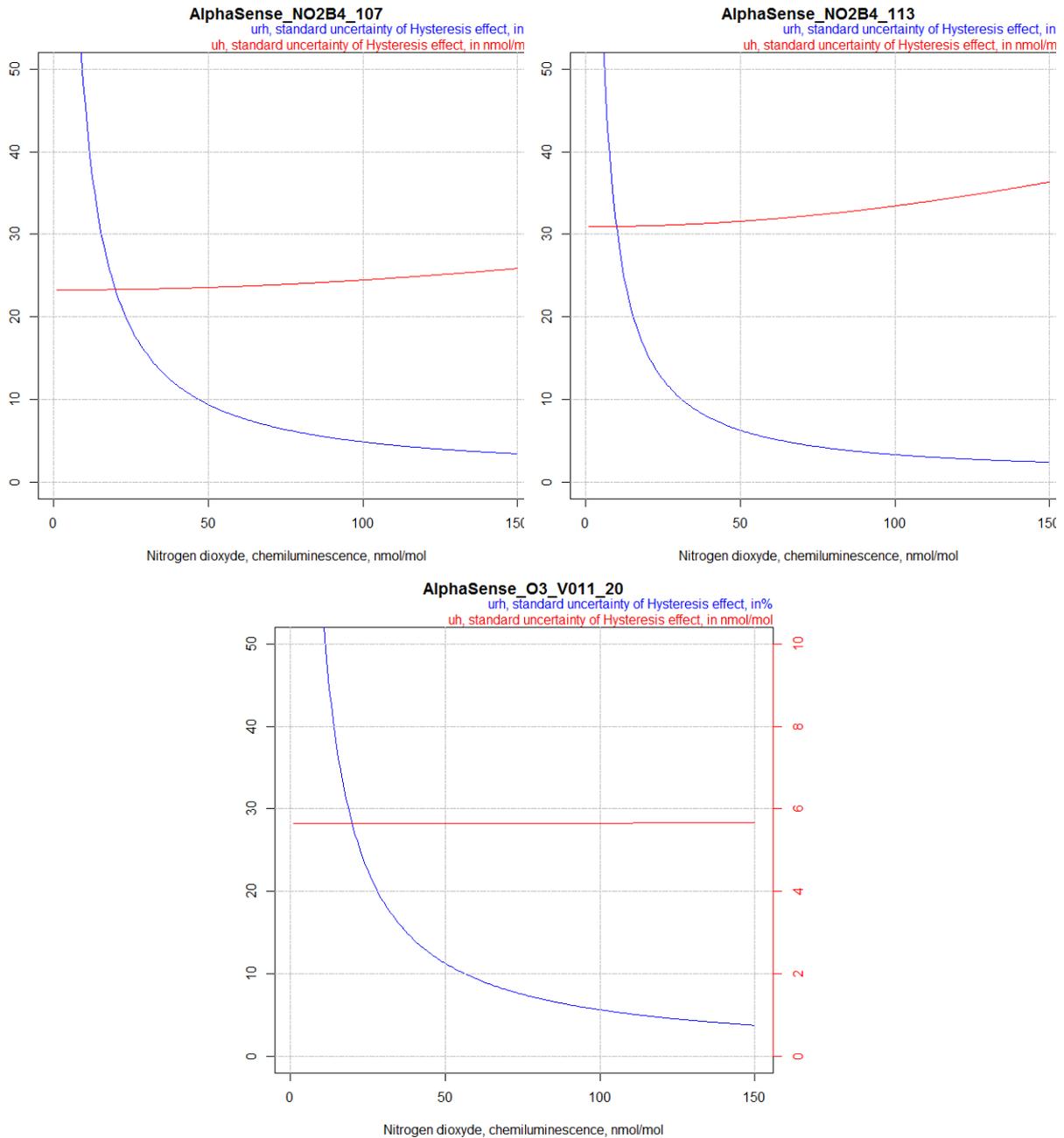
AlphaSense_NO2B4_107

AlphaSense_NO2B4_113

AlphaSense_O3_V011_20

Figure 18: Evolution of $u_{r,h}$ and u_h as a function of the concentration of NO_2

Figure 18 shows $u_{r,h}$ as a function of c_r, the NO_2 level. For the whole range of concentration, u_h stay rather stable. Table 23 gives $u_{r,h}$ and u_h at the limit value (100 nmol/mol) and shows that for the three sensors, u_h were in the range of the repeatability. The sensor does not suffer from hysteresis effect so that hysteresis effect will not be considered in the final model.

Table 23: $u_{r,h}$ and u_h at the limit value (100 nmol/mol)

	$u_{r,h}$	u_h	s_r
NO2B4_107	4.89 %	4.89 nmol/mol	2.36
NO2B4_113	3.35 %	3.35 nmol/mol	3.35
O3_V011_20	5.65 %	5.65 nmol/mol	4.11

7.4 Meteorological parameters

7.4.1 Relative Humidity and Temperature

To determine the influence of temperature and humidity on the sensor's response, we carried out a cycle exposure to 5 levels of each parameter according to Figure 19.
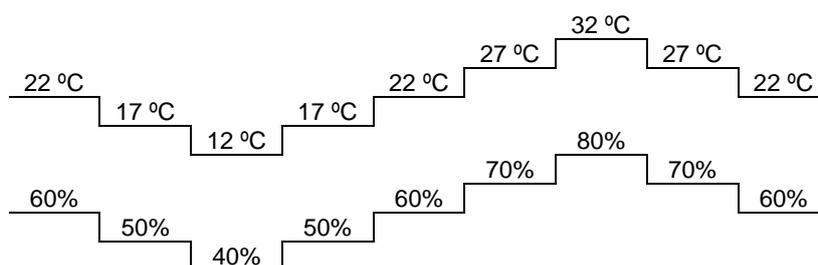

Figure 19: Testing of temperature and humidity effect

All other parameters suspected to have an effect on the sensor response (test gas, O_3, temperature or humidity) were kept under control with relative standard deviation of about 2 %, as shown on Figure 20.
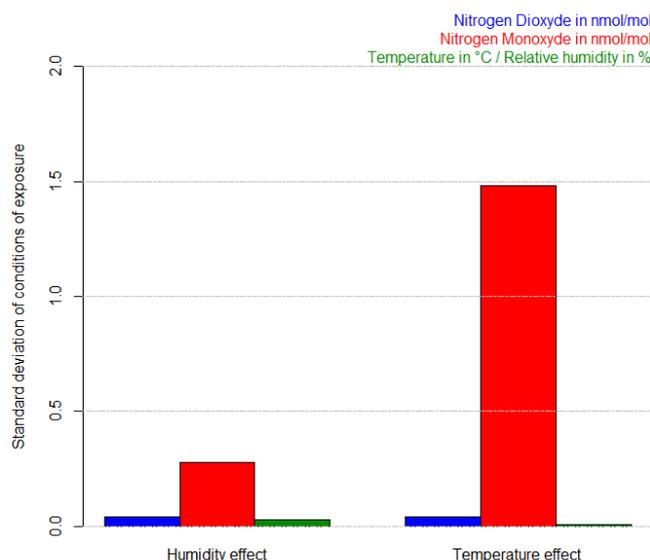

Figure 20: Stability of NO2, NO and temperature or relative humidity during Humidity and Temperature effect experiment

Figure 21 shows the evolution of the sensor's response over the relative humidity and temperature effect exposure. Both NO2-B4 sensors show the same ratio of sensitivity towards relative humidity and temperature: the sensor response tends to follow the shape of the changes of relative humidity or temperature. O3_V011_20 show a higher sensitivity compared to the NO_2 sensors.

45

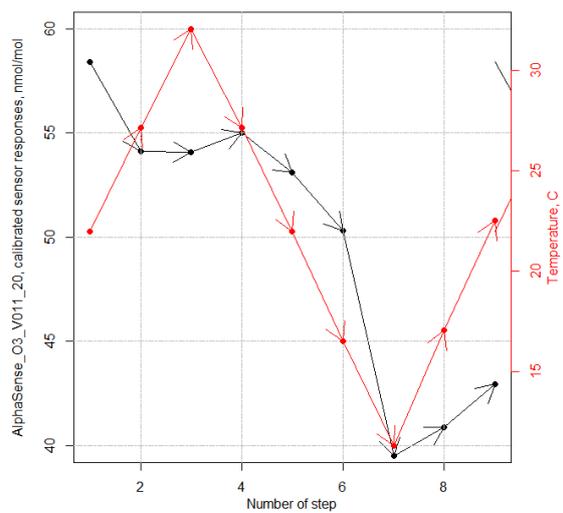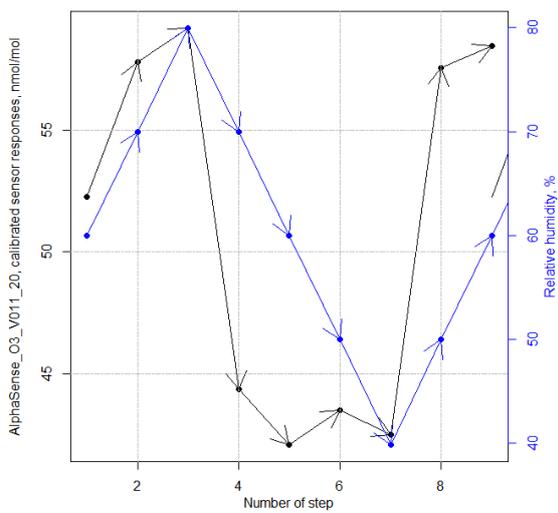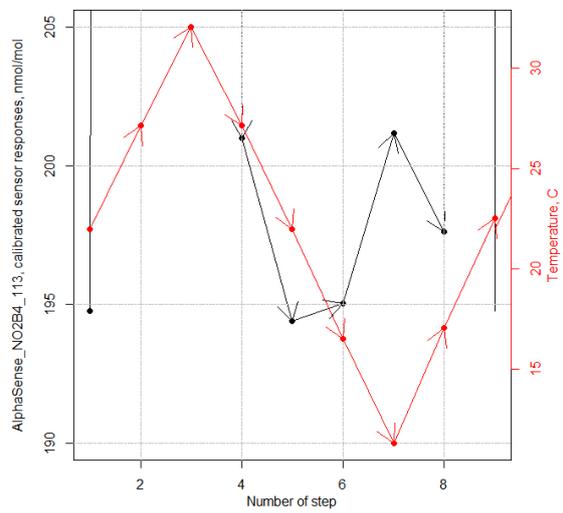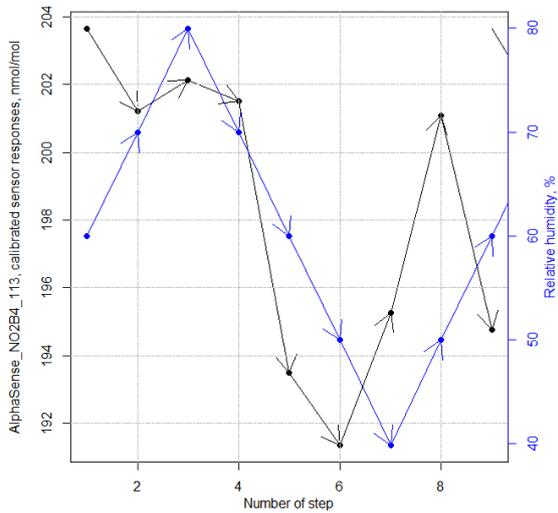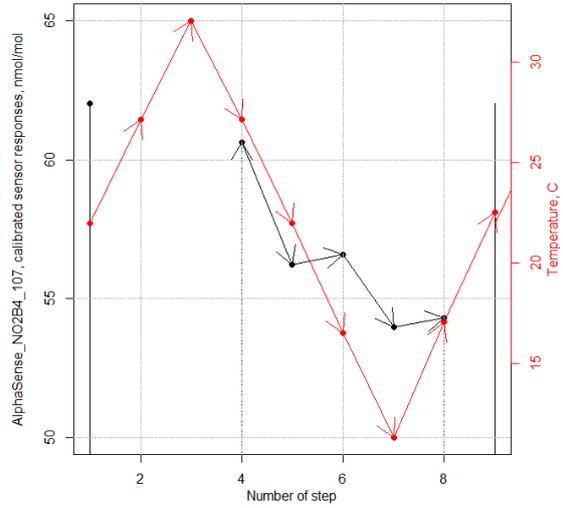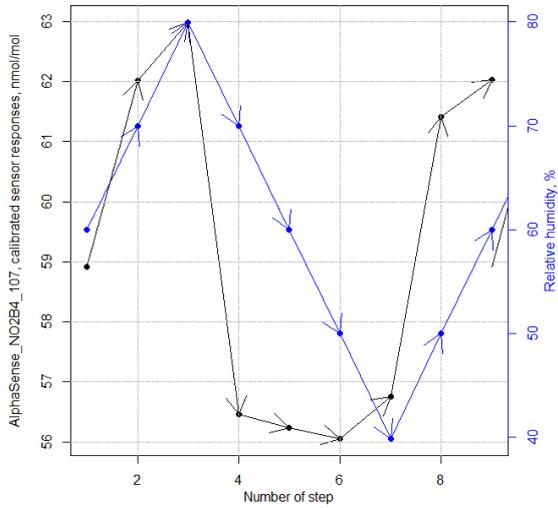*Figure 21: Temporal evolution of the sensor's response toward relative humidity (left) and temperature (right) over the different exposure step.*
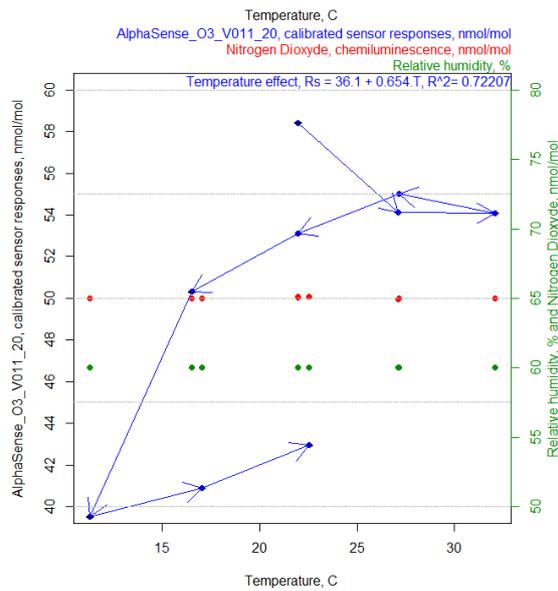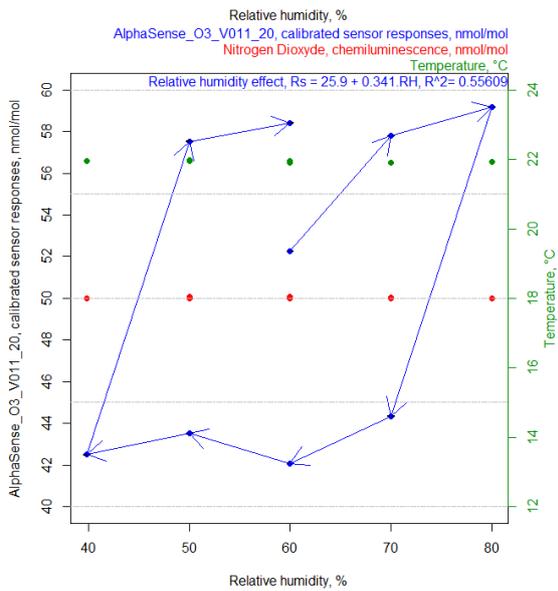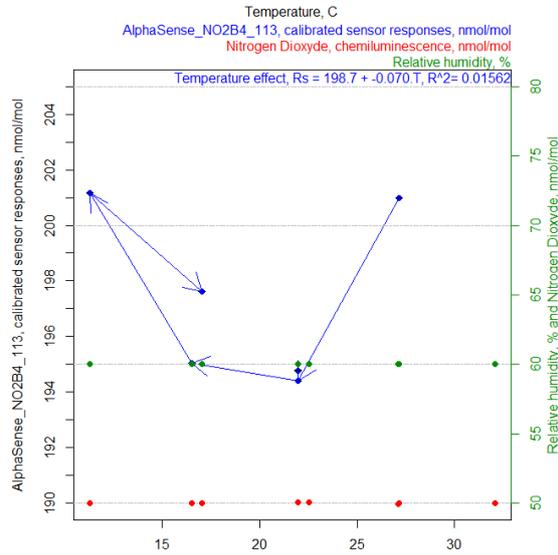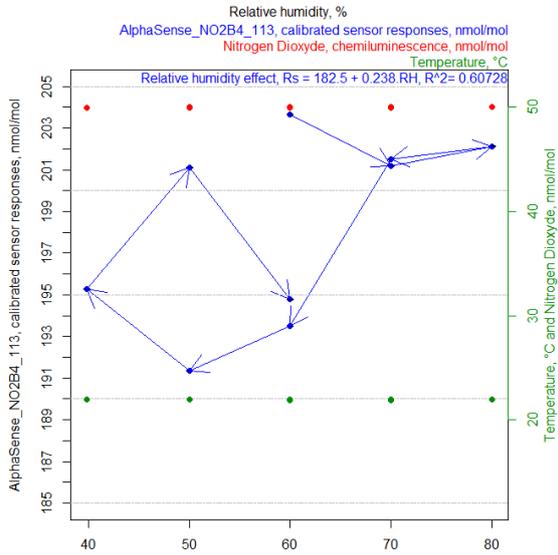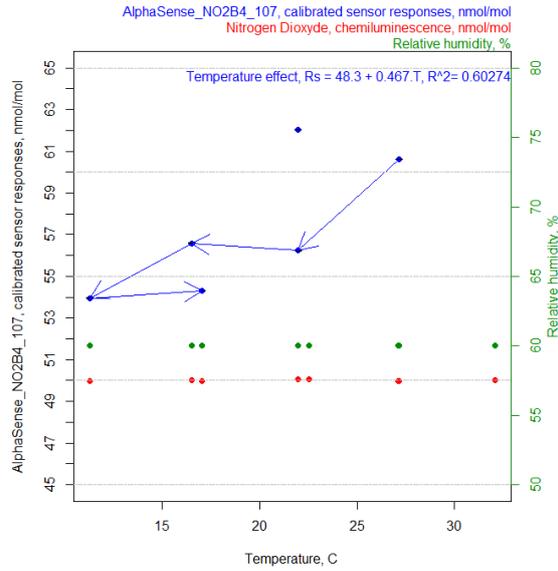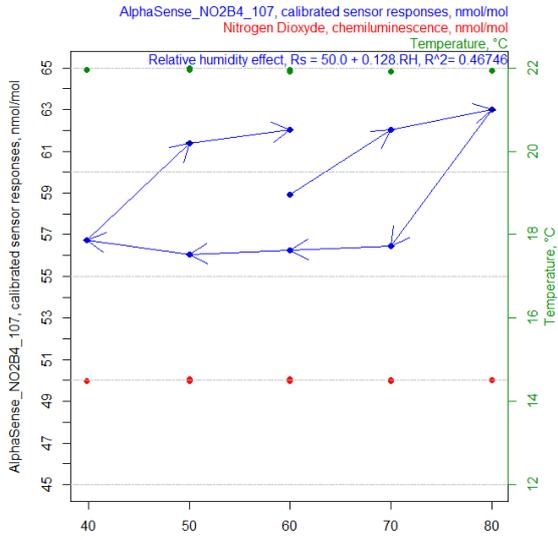
Figure 22: Sensitivity of AlphaSense's sensors toward relative humidity (left) and temperature (right).

Figure 22 shows the influences evaluated during these two tests. The effects seen in Figure 21 are confirmed in these graphs on which we have had a linear fit to the rise in humidity or temperature. It was also shown that NO$_2$ concentration and temperature or humidity were kept stable during all the test.

AlphaSense's sensors had shown an effective sensibility toward both temperature and humidity. The sensor's response tends to increase with the augmentation of relative humidity and temperature. Moreover, the sensors sensitivity against humidity was characterised by a clear hysteresis loop. Linear regression alone cannot correct the humidity effect because of this loop behaviour. More sophisticated model would be necessary

Variation of the sensor response against temperature and relative humidity was estimated using the sensitivity coefficient (the slope of the regression lines) for the influencing variable to estimate its standard uncertainty $u(x)$ and adding a contribution from the hysteresis of temperature and humidity corresponding to the maximum deviation to the regression lines or preferably the one at the LV (Eq. 18).

$$u(x) = \left(b^2 \frac{(X_{max} - X_{min})^2}{3} + \frac{\rho^2_{max,LV}}{3} \right)^{1/2} \qquad \textbf{Eq. 18}$$

Where X was the tested parameter, b was the slope of the regression line of the sensor responses versus temperature and humidity, X_{max} and X_{min} the maximum and minimum values encountered in real ambient for parameter x and ρ was the maximum residuals between the regression line and the sensor responses or the one at the LV.

Assuming a relative humidity range between 30 and 95 %, the maximum residual of the linear fit at the LAT, the contribution of the relative humidity effect was $u(RH)$ with and without correction for the relative humidity effect are given in Table 24.

Table 24: Effect of relative humidity on AlphaSense's sensors

	Maximum residual	$u(RH)$ corrected in humidity	$u(RH) =$ not corrected
NO2B4_107	2.7 nmol/mol	4.8 nmol/mol	5.1 nmol/mol
NO2B4_113	3.3 nmol/mol	8.9 nmol/mol	9.1 nmol/mol
O3_V011_20	6.0 nmol/mol	12.8 nmol/mol	13.3 nmol/mol

Assuming a temperature range between 15 and 45 °C, the maximum residual of the linear fit at the LAT, the contribution of the temperature effect $u(T)$ with and without correction for the temperature effect are given in Table 25.

Table 25: Effect of temperature on AlphaSense's sensors

	Maximum residual	$u(T) =$ corrected in temperature	$u(T) =$ not corrected
NO2B4_107	3.5 nmol/mol	8.1 nmol/mol	8.3 nmol/mol
NO2B4_113	4.2 nmol/mol	1.2 nmol/mol	2.7 nmol/mol
O3_V011_20	4.0 nmol/mol	11.3 nmol/mol	11.6 nmol/mol

Both relative humidity and temperature have a significant effect on the sensor's response. The influence of these two parameters must be add in the final design of experiment.

7.4.2 Wind velocity effect

Wind velocity should also be taken into account as a meteorological interferent. To determine the influence of wind velocity on the sensor's response, we carried out a 4 levels exposure

between 1 m/s to 4 m/s with step of 1 m/s. The NO_2 level chosen for this test was equal to 100 nmol/mol instead of 50 nmol/mol as previously. All other parameters suspected to have an effect on the sensor response (test gas, O_3, temperature or humidity) were kept under control with relative standard deviation of about 2 %, as shown on Figure 23.
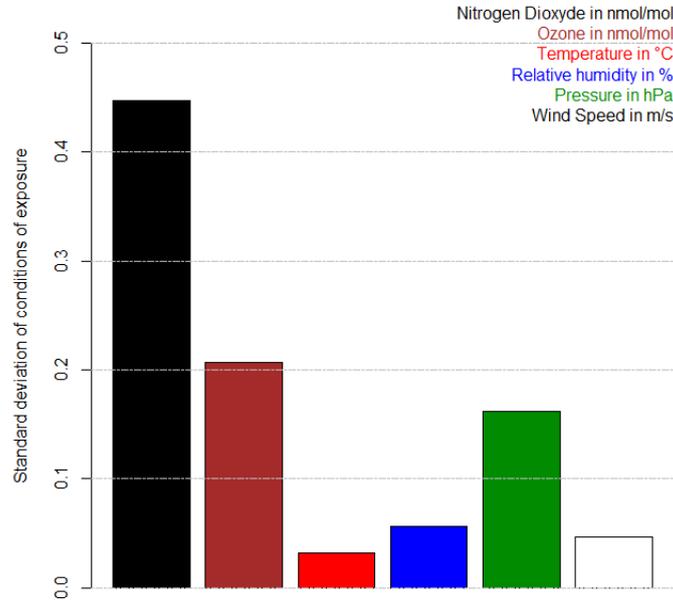
Figure 23: Stability of NO₂, temperature and relative humidity in the exposure chamber during the wind velocity experiments

Figure 24 shows the effect of wind velocity on the sensor's responses. The sensor responses increased with wind velocity and the maximum difference are given in Table 26.

Table 26: Maximum difference, sensitivity coefficient and uncertainty

	Maximum difference nmol/mol	$\Delta C / \Delta WV$ (nmol/mol)/(m/s)	$u(X_{WV})$ nmol/mol
NO2B4_107	6.0	2.4	6.3
NO2B4_113	10.8	3.6	9.3
O3_V011_20	6.4	2.1	5.4

For the 3 sensors we used a linear model to estimate the uncertainty resulting from wind velocity changes. Eq. 19 and Eq. 20 were applied to estimate the sensitivity coefficient of the sensors to changes in the wind velocity and the contribution of this parameter to the measurement uncertainty of the sensor, u(WV), with sensor response C_{Xn} at X_n, X_{max} and X_{min} the max and min values of the tested velocities.

$$\frac{\Delta C}{\Delta X} = \left| \frac{C_{X2} - C_{X1}}{X_2 - X_1} \right| \qquad \text{Eq. 19}$$

$$u(X_p) = \sqrt{ \left| \frac{C_{X2} - C_{X1}}{X_2 - X_1} \right|^2 \cdot \frac{(X_{max} - X_{min})^2}{3} } \qquad \text{Eq. 20}$$

The sensitivity coefficient $\Delta C / \Delta WV$ and the standard uncertainty $u(X_{WV})$ were calculated assuming a change of wind velocity in the range 0.5 to 5 m/s and are given in Table 26.
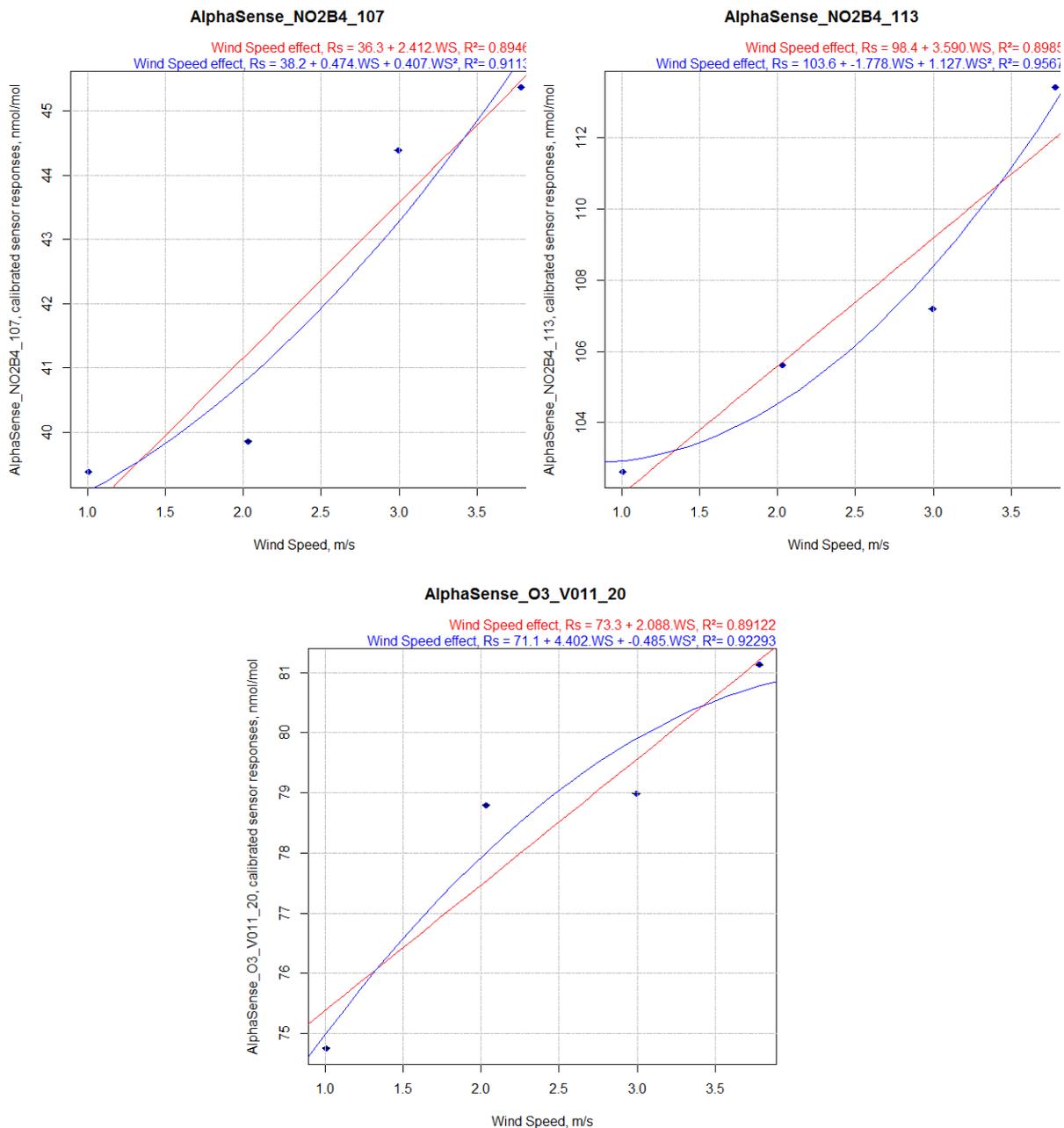
Figure 24: Effect of Wind speed on the sensor responses at 100 nmol/mol

With the Reynolds formula, it is possible to estimate the type of flow inside the exposure chamber against wind velocity. Figure 25 shows the value of the estimated Reynolds coefficient during the wind velocity test. Below 2 m/s, the flow in the exposure chamber can be considerate as laminar. Above this speed, the flow is turbulent and it's not possible to determine the real wind velocity around the sensor.

It is likely that the sensitivity coefficient and the standard uncertainty are overestimated because turbulent flows are more likely than laminar ones both reducing the sensitivity coefficient and the range of possible wind velocity.
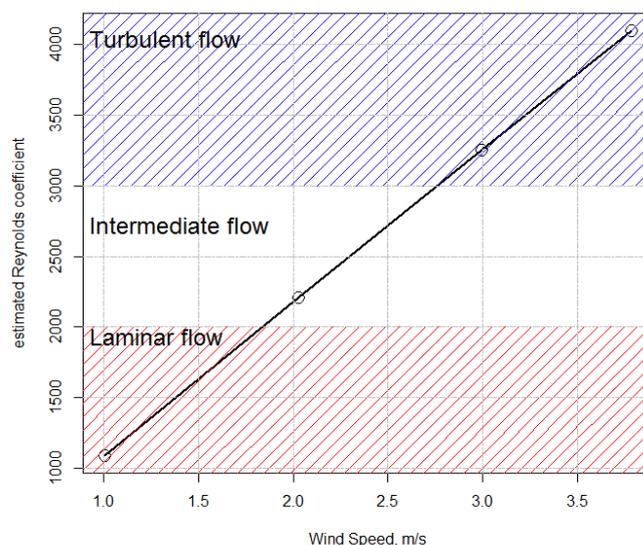
Figure 25: Flow type depending on the wind speed

It was shown that below 2 m/s, the flow in the exposure chamber can be considerate as laminar. Above those speed, the flow was turbulent and it's not possible to determine if the wind velocity was equal or not to this value at the sensor. Taking into account that in field conditions the flow was mainly turbulent and to ensure an efficient flow inside the exposure chamber we will fix the wind velocity at around 3.2 m/s for the design of experiment.

7.4.3 Ambient pressure effect

During the first experiment we observe that the level of NO_2 and NO were strongly affected by ambient air coming into our exposition chamber and by a cycling increase of concentration during daytime. To avoid this dependence, we chose to seal all possible leaks to maintain a constant but slight overpressure. That way all experiments were carried out in overpressure, even if the mean pressure was still dependant from the ambient pressure.

7.5 Effect of power supply

The effect of power supply on the sensor responses was tested at 3 levels of tension (210, 220 and 230 V) while all other parameters suspected to have an effect on the sensor response (test gas, O_3, temperature or humidity) were kept under control. In this experiment, the power supply of the sensor was changed using a variable generator (rheostat) model Rheothor ADB. The results of the test are given in Table 27.

Table 27: Effect of change of power supply on the AlphaSense's sensor responses and conditions of exposure with average and standard deviation for each parameter during the experiments

Tension V	NO2B4_107, mol/mol	NO2B4_113, mol/mol	O3_V011_20, mol/mol	NO_2, nmol/mol	O_3, nmol/mol	T, °C	RH, %	P, hPa
210	55.0 ± 5.6	116.7 ± 11.2	79.9 ± 4.1	100.0 ± 0.6	1.0 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	1006 ± 0.2
220	55.9 ± 5.6	116.8 ± 12.0	80.6 ± 3.9	100.0 ± 0.6	1.0 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	1007 ± 0.1
230	55.0 ± 5.6	115.2 ± 12.8	77.8 ± 2.7	100.0 ± 0.5	1.0 ± 0.2	22.0 ± 0.1	60.0 ± 0.1	1005 ± 0.1

Eq. 21 and Eq. 22 were applied to estimate the sensitivity coefficient of the sensors to change in the power supply and the contribution of this parameter to the measurement uncertainty of the sensor, $u(X_V)$, where X_V was the tested tension, with sensor response C_{XV} at X_V, X_{Vmax} and X_{Vmin} the max and min values.

$$\frac{\Delta C}{\Delta X} = \left| \frac{C_{X2} - C_{X1}}{X_2 - X_1} \right| \qquad \text{Eq. 21}$$

$$u(X_V) = \left| \frac{C_{X2} - C_{X1}}{X_2 - X_1} \right| \times \frac{X_{Vmax} - X_{Vmin}}{\sqrt{3}} \qquad \text{Eq. 22}$$

The sensitivity coefficient for AlphaSense's sensors $\Delta C / \Delta V$ and the standard uncertainty $u(X_V)$ were calculated assuming a change of tension in the range of 20 Volts are given in Table 28.

Table 28: Effect of variation of tension on AlphaSense's sensors

	$\Delta C / \Delta V$	$u(X_V)$
NO2B4_107	0.04 nmol/mol/V	0.50 nmol/mol
NO2B4_113	0.04 nmol/mol/V	0.46 nmol/mol
O3_V011_20	0.09 nmol/mol/V	0.99 nmol/mol

NO2-B4 sensors and O3_V011_20 do not show sensitivity towards variations of tension.

7.6 Choice of tested interfering parameters in full factorial design

The major cross sensitivities showed by the AlphaSense's sensors were in order of magnitude: O_3, long-term drift, relative humidity and temperature. All the results are resumed in Table 29, Table 30 and Table 31. The experimental design will include tests based on the effect of O_3, temperature and humidity which were found significant for the majority of the other sensors tested within MACPoll.

Among the remaining factors:

- the effect of CO_2 and NH_3 were found very significant. Nevertheless it was not the case for the majority of the other sensors tested within MACPoll. Therefore the uncertainty will be only taken into account when estimating the laboratory uncertainty of the sensor results.
- the effect of wind velocity was found significant especially at velocity below 2 m/s. Nevertheless it was unlikely that during field measurement wind velocity would be measured and latter corrected. Consequently, wind velocity can only be estimated and taken into account when estimating the measurement uncertainty of the sensor results.
- the estimation of the hysteresis effect of humidity can only be done during field experiment since the real speed and profile of change of humidity must be tested and is not possible to simulate in exposure chamber.
- finally the long term drift was found very significant and depending on NO_2 concentration and elapsed time since the first calibration. Eq. 6 will be used in the model equation of the sensor response as well as the pre-calibration curve.

Table 29: Summary of effect of all tested parameters on NO2B4_107

Parameters	Can be controlled?	Can be corrected?	$\Delta C/(\Delta X)$ (µ or n) mol/mol/Xunit	Standard uncertainty at LV
Laboratory calibration, nmol/mol	No	Yes	$f(NO_2)$	1.20
Repeatability	No	Not needed	-	2.36
Short term drift, after 1 day	No	Not needed	-	6.0
Long term drift, per days	Periodic calibration?	Yes	$-6.4\ 10^{-2}$-$2.3\ 10^{-3}$ NO_2	$< sqrt(4.0^2 + s(E)^2)$ or $s(E)\ f(NO2)$
O_3, nmol/mol	No, filter?	O_3 sensor needed	1.268	$41.1 + 2.u(O3).u(NO2)$
NO, nmol/mol	No	Not needed	-0.012	0.29
CO, µmol/mol	No	Not needed	-0.001	0.52
CO_2, µmol/mol	No	Not needed	-0.248	7.15
NH_3, nmol/mol	No	Not needed	-0.075	1.95
SO_2, nmol/mol	No	Not needed	-0.097	0.28
Matrix effect	No	Within the results of the single interfering compounds	0.51	15.23
Hysteresis of concentration	No	Not needed	0.53	4.89
Relative Humidity in %	Yes	A HR sensor is needed	0.13 (uncorrected)	5.1 (uncorrected), 4.8 (linear correction)
Temperature, °C	Yes	A T sensor is needed	0.47 (uncorrected)	8.3 (uncorrected), 8.1 (linear correction)
Wind, m/s	No	No: wind velocity sensor too expensive	2.4	6.3
Pressure, hpa	Test not carried out.			
Power supply, Volt	No	Not needed	0.04	0.5

Table 30: Summary of effect of all tested parameters on NO2B4_113

Parameters	Can be controlled?	Can be corrected?	$\Delta C/(\Delta X)$ (μ or n) mol/mol/Xunit	Standard uncertainty at LV
Laboratory calibration, nmol/mol	No	Yes	$f(NO_2)$	2.40
Repeatability	No	Not needed	-	3.35
Short term drift, after 1 day	No	Not needed	-	11.9
Long term drift, per days	Periodic calibration?	Yes	$-8.1 \cdot 10^{-2} - 3.4 \cdot 10^{-3}$ NO_2	$< \sqrt{4.0^2 + s(E)^2}$ or $s(E)$ $f(NO2)$
O_3, nmol/mol	No, filter?	O_3 sensor needed	2.867	$93.01 + 2.u(O3).u(NO_2)$
NO, nmol/mol	No	Not needed	-0.027	0.63
CO, µmol/mol	No	Not needed	-0.002	1.17
CO_2, µmol/mol	No	Not needed	0.127	3.67
NH_3, nmol/mol	No	Not needed	-0.164	4.26
SO_2, nmol/mol	No	Not needed	-0.352	1.02
Matrix effect	No	Within the results of the single interfering compounds	1.15	13.27
Hysteresis of concentration	No	Not needed	1.21	3.35
Relative Humidity in %	Yes	A HR sensor is needed	0.24 (uncorrected)	9.0 (uncorrected), 8.9 (linear correction)
Temperature, °C	Yes	A T sensor is needed	0.07 (uncorrected)	2.7 (uncorrected), 1.2 (linear correction)
Wind, m/s	No	No: wind velocity sensor too expensive	3.6	9.3
Pressure, hpa	Test not carried out.			
Power supply, Volt	No	Not needed	0.04	0.5

54

Table 31: Summary of effect of all tested parameters on O3_V011_20

Parameters	Can be controlled?	Can be corrected?	$\Delta C/(\Delta X)$ (μ or n) mol/mol/Xunit	Standard uncertainty at LV
Laboratory calibration, nmol/mol	No	Yes	$f(NO_2)$	0.68
Repeatability	No	Not needed	-	4.11
Short term drift, after 1 day	No	Not needed	-	7.9
Long term drift, per days	Periodic calibration?	Yes	$-4.1\ 10^{-2}$–$1.3\ 10^{-4}$ NO_2	$< \sqrt{4.0^2 + s(E)^2}$ or $s(E)$ $f(NO2)$
O_3, nmol/mol	No, filter?	O_3 sensor needed	1.541	$50.00 + 2.u(O3).u(NO_2)$
NO, nmol/mol	No	Not needed	-0.027	0.628
CO, μmol/mol	No	Not needed	0.001	0.250
CO_2, μmol/mol	No	Not needed	-0.080	2.32
NH_3, nmol/mol	No	Not needed	-0.070	1.82
SO_2, nmol/mol	No	Not needed	-0.349	1.01
Matrix effect	No	Within the results of the single interfering compounds	0.73	7.24
Hysteresis of concentration	No	Not needed	0.74	5.65
Relative Humidity in %	Yes	A HR sensor is needed	0.34 (uncorrected)	13.3 (uncorrected), 12.8 (linear correction)
Temperature, °C	Yes	A T sensor is needed	0.65 (uncorrected)	11.6 (uncorrected), 11.3 (linear correction)
Wind, m/s	No	No: wind velocity sensor too expensive	2.1	5.4
Pressure, hpa	Test not carried out.			
Power supply, Volt	No	Not needed	0.09	1.0

8   Experimental design

8.1   Data and model

A full factorial design of experiments was set up including the 7 levels of NO_2 of the pre-calibration experiment, 3 temperatures (12, 22 and 32 °C) under 3 relative humilities (40, 60 and 80%) and at 2 levels of O_3 (0 and 60 nmol/mol). Table 32 presents the full factorial design of experiments with NO2-B4 AlphaSense's sensors responses and Table 33 the same dataset O3-B4 AlphaSense's sensors responses. In order to save time, the order of experiments was randomized only for NO_2 and not for temperature and humidity.

The dataset of measurement of the experimental design included the results of the AlphaSense's sensors and reference values for NO_2, O_3, temperature and relative humidity. Only one data was excluded from our modelisation, the one highlighted in yellow, because the O_3 concentration was too high: 39.3 nmol/mol instead of 0.0 nmol/mol as required.

Table 32: Laboratory experimental design for the NO2-B4 AlphaSense's sensors in nmol/mol

T	RH	O₃	NO₂	NO2B4_107	NO2B4_113	T	RH	O₃	NO₂	NO2B4_107	NO2B4_113
°C	%	nmol/mol		nmol/mol		°C	%	nmol/mol		nmol/mol	
11.4	40.0	-3.5	125.0	56.6	128.8	11.4	40.0	61.1	125.0	118.5	255.8
11.4	39.9	-3.6	50.0	7.8	13.1	11.4	40.0	61.1	50.0	75.6	155.6
11.8	40.0	-3.5	100.0	60.9	90.2	11.4	40.0	61.1	100.0	101.9	217.0
11.4	40.0	-3.4	2.2	-1.4	-62.5	11.4	40.0	61.2	2.7	48.0	90.6
11.4	40.0	-3.3	75.0	44.0	44.0	11.4	40.0	61.1	75.0	17.3	172.8
11.4	40.0	-3.4	25.0	92.6	-29.2	11.4	40.0	61.1	25.0	-27.6	116.1
11.4	40.0	-3.6	150.0	104.7	171.8	11.4	40.0	61.1	150.0	121.0	272.0
11.4	60.0	-3.5	125.0	121.6	146.8	11.7	60.0	61.1	125.0	137.4	296.8
11.4	59.4	-3.8	50.0	29.7	8.3	11.4	60.0	61.1	50.0	83.0	174.4
11.5	60.0	-3.8	100.0	65.7	102.5	11.4	60.0	61.1	100.0	115.2	246.9
11.4	60.0	-3.6	1.6	38.5	-66.9	11.4	60.0	61.1	2.0	53.1	102.7
11.4	60.0	-3.5	75.0	10.4	52.5	11.4	60.0	61.1	75.0	99.8	210.4
11.4	58.9	-3.8	25.0	68.5	-27.1	11.4	60.0	61.2	25.0	60.6	132.4
11.4	60.0	-3.4	150.0	200.1	194.2	11.4	60.0	61.1	150.0	138.0	313.7
11.5	80.0	-3.7	125.0	107.7	144.2	11.4	80.0	61.1	125.0	129.7	279.4
11.4	80.0	-3.6	50.0	94.1	17.2	11.5	80.0	61.2	50.0	80.4	162.3
11.4	80.0	-3.5	100.0	69.8	98.6	11.5	80.0	61.1	100.0	115.7	243.5
11.4	80.0	-3.6	1.7	-38.1	-80.4	11.4	80.0	61.2	2.0	23.0	88.9
11.4	80.0	-3.6	75.0	62.6	56.8	11.4	80.0	61.1	75.0	80.1	202.3
11.4	80.0	-3.5	25.0	29.4	-25.7	11.4	80.0	61.2	25.0	51.9	123.1
11.4	80.0	-3.8	150.0	147.8	205.5	11.5	80.0	61.2	150.0	140.1	329.2
21.9	40.2	-3.8	125.0	117.2	224.0	22.0	40.0	61.1	125.0	115.0	255.5
21.9	39.9	-4.1	50.0	41.7	208.4	22.0	40.0	61.2	50.0	72.8	154.6
21.9	40.0	-3.8	100.0	87.0	271.2	22.0	40.0	61.1	100.0	97.6	214.7
21.9	39.9	-4.2	1.9	12.2	168.3	21.9	40.0	61.1	2.1	45.9	90.4
21.9	40.2	-4.1	75.0	52.5	254.7	21.9	40.0	61.2	75.0	83.8	182.2
21.9	39.9	-3.7	25.0	45.0	197.2	22.0	40.0	61.1	25.2	57.9	120.7
22.0	40.0	-3.6	150.0	147.9	304.5	22.0	40.0	61.1	150.0	121.6	273.4
21.9	60.0	-3.4	125.0	80.7	302.0	22.0	60.0	61.1	125.1	154.8	355.2
21.9	60.0	-3.4	50.0	49.4	259.1	22.0	60.0	61.1	50.0	106.4	241.0
21.9	60.0	-3.7	100.0	112.8	239.8	21.9	60.0	61.1	100.0	139.3	317.4
21.9	60.0	-3.7	1.9	57.9	119.7	21.9	60.0	61.1	4.2	75.8	168.0
21.9	60.0	-3.9	75.0	93.6	238.3	21.9	60.0	61.1	75.0	121.9	276.9
21.9	60.0	-4.0	25.0	15.4	241.3	21.9	60.0	61.1	25.0	90.0	204.0
21.9	60.0	-4.0	150.1	118.9	320.5	21.9	60.0	61.1	150.0	170.0	389.8
21.9	80.0	-3.3	125.0	79.3	282.6	22.0	80.0	61.1	125.0	142.6	319.8
21.9	80.0	-3.7	50.0	50.7	187.5	22.0	80.0	61.2	50.0	87.7	193.3
21.9	80.0	-3.7	100.0	136.7	160.4	22.0	80.0	61.1	100.0	127.4	283.8
21.9	80.0	-3.6	1.8	51.0	45.6	22.0	80.0	61.1	2.3	45.7	97.1
21.9	80.0	-3.7	75.0	36.7	278.8	22.0	79.3	61.2	75.0	102.3	226.2
21.9	80.0	-3.7	25.0	44.0	134.4	22.0	80.0	61.1	25.0	60.5	151.6
21.9	80.0	-3.6	148.7	155.8	239.9	21.9	80.0	61.1	150.0	152.3	378.4
32.0	39.9	-3.9	125.0	120.0	300.6	32.1	40.0	61.1	125.0	136.5	337.3
32.0	40.0	-3.8	50.0	74.5	138.3	32.1	40.0	61.1	50.0	81.3	210.3
32.0	40.0	-4.1	100.0	35.8	235.6	32.1	40.0	61.2	100.0	109.3	281.0
32.0	40.0	-3.7	1.9	45.5	36.2	32.1	40.0	61.2	4.6	42.6	122.7
32.0	40.0	-3.7	75.0	62.9	178.5	32.1	40.0	61.2	75.0	84.5	230.6
32.0	40.0	-3.8	25.0	35.9	74.5	32.1	40.0	61.1	25.0	51.5	152.2
32.0	40.0	-4.0	150.0	95.2	328.3	32.1	40.0	61.1	150.0	136.0	339.3
32.0	60.0	-4.0	125.0	84.0	317.8	32.1	60.0	61.1	125.0	126.9	291.3
32.0	60.0	-3.9	50.0	94.3	146.6	32.1	60.0	61.2	50.0	53.4	179.2

32.0	60.0	-3.9	100.0	64.5	256.7	32.1	60.0	61.1	100.0	85.5	264.1
32.0	60.0	-3.6	2.3	98.5	29.3	32.1	60.0	61.2	4.3	47.4	104.2
32.0	60.0	-3.7	75.0	66.9	192.3	32.1	60.0	61.1	75.0	99.2	226.5
32.0	60.0	-4.0	25.0	65.9	80.1	32.1	60.0	61.2	25.0	39.3	147.1
32.0	60.0	-4.1	150.0	42.6	370.2	32.1	60.0	61.1	150.0	143.0	365.4
32.0	80.0	-4.1	125.7	139.2	306.9	32.1	80.0	61.1	125.0	155.1	350.6
32.0	80.0	39.3	49.8			32.1	80.0	61.1	50.0	92.7	205.0
32.0	80.0	-4.0	100.0	120.3	263.7	32.1	80.0	61.1	100.0	139.9	313.9
32.0	80.0	-3.7	1.2	15.6	41.8	32.1	80.0	61.3	4.7	58.3	136.7
32.0	79.4	-3.6	75.0	90.7	203.7	32.1	80.0	61.2	75.0	114.5	264.9
32.0	80.0	-3.7	25.1	36.2	80.7	32.1	80.0	61.1	25.0	69.8	163.8
32.0	80.0	-4.3	150.4	174.3	390.4	32.1	80.0	61.1	150.0	170.0	430.5

Table 33: Laboratory experimental design for the O3-B4 AlphaSense's sensor in nmol/mol.

T	RH	O₃	NO₂	O3_V011_20	T	RH	O₃	NO₂	O3_V011_20
°C	%	nmol/mol		nmol/mol	°C	%	nmol/mol		nmol/mol
11.4	40.0	-3.5	125.0	112.7	11.4	40.0	61.1	125.0	158.0
11.4	39.9	-3.6	50.0	46.6	11.4	40.0	61.1	50.0	95.6
11.8	40.0	-3.5	100.0	88.4	11.4	40.0	61.1	100.0	134.2
11.4	40.0	-3.4	2.2	3.2	11.4	40.0	61.2	2.7	59.6
11.4	40.0	-3.3	75.0	66.0	11.4	40.0	61.1	75.0	113.8
11.4	40.0	-3.4	25.0	24.0	11.4	40.0	61.1	25.0	77.2
11.4	40.0	-3.6	150.0	127.5	11.4	40.0	61.1	150.0	174.6
11.4	60.0	-3.5	125.0	118.9	11.7	60.0	61.1	125.0	184.5
11.4	59.4	-3.8	50.0	47.1	11.4	60.0	61.1	50.0	107.5
11.5	60.0	-3.8	100.0	98.1	11.4	60.0	61.1	100.0	151.0
11.4	60.0	-3.6	1.6	3.8	11.4	60.0	61.1	2.0	63.9
11.4	60.0	-3.5	75.0	72.1	11.4	60.0	61.1	75.0	126.6
11.4	58.9	-3.8	25.0	25.1	11.4	60.0	61.2	25.0	79.7
11.4	60.0	-3.4	150.0	142.6	11.4	60.0	61.1	150.0	186.9
11.5	80.0	-3.7	125.0	120.0	11.4	80.0	61.1	125.0	177.1
11.4	80.0	-3.6	50.0	46.4	11.5	80.0	61.2	50.0	107.3
11.4	80.0	-3.5	100.0	92.4	11.5	80.0	61.1	100.0	153.7
11.4	80.0	-3.6	1.7	-0.7	11.4	80.0	61.2	2.0	61.5
11.4	80.0	-3.6	75.0	68.0	11.4	80.0	61.1	75.0	128.8
11.4	80.0	-3.5	25.0	28.2	11.4	80.0	61.2	25.0	79.0
11.4	80.0	-3.8	150.0	142.7	11.5	80.0	61.2	150.0	205.5
21.9	40.2	-3.8	125.0	91.0	22.0	40.0	61.1	125.0	183.3
21.9	39.9	-4.1	50.0	44.3	22.0	40.0	61.2	50.0	114.4
21.9	40.0	-3.8	100.0	85.5	22.0	40.0	61.1	100.0	158.3
21.9	39.9	-4.2	1.9	3.3	21.9	40.0	61.1	2.1	72.1
21.9	40.2	-4.1	75.0	67.1	21.9	40.0	61.2	75.0	135.9
21.9	39.9	-3.7	25.0	22.3	22.0	40.0	61.1	25.2	90.8
22.0	40.0	-3.6	150.0	132.3	22.0	40.0	61.1	150.0	197.7
21.9	60.0	-3.4	125.0	126.1	22.0	60.0	61.1	125.1	187.7
21.9	60.0	-3.4	50.0	49.4	22.0	60.0	61.1	50.0	116.1
21.9	60.0	-3.7	100.0	98.5	21.9	60.0	61.1	100.0	162.0
21.9	60.0	-3.7	1.9	-1.1	21.9	60.0	61.1	4.2	76.1
21.9	60.0	-3.9	75.0	72.3	21.9	60.0	61.1	75.0	144.6
21.9	60.0	-4.0	25.0	21.6	21.9	60.0	61.1	25.0	94.7
21.9	60.0	-4.0	150.1	147.7	21.9	60.0	61.1	150.0	208.8
21.9	80.0	-3.3	125.0	126.1	22.0	80.0	61.1	125.0	200.0
21.9	80.0	-3.7	50.0	60.2	22.0	80.0	61.2	50.0	118.0
21.9	80.0	-3.7	100.0	103.6	22.0	80.0	61.1	100.0	170.2
21.9	80.0	-3.6	1.8	2.6	22.0	80.0	61.1	2.3	66.6
21.9	80.0	-3.7	75.0	77.6	22.0	79.3	61.2	75.0	142.8
21.9	80.0	-3.7	25.0	37.9	22.0	80.0	61.1	25.0	92.8
21.9	80.0	-3.6	148.7	141.7	21.9	80.0	61.1	150.0	222.4
32.0	39.9	-3.9	125.0	132.2	32.1	40.0	61.1	125.0	206.7

32.0	40.0	-3.8	50.0	58.1	32.1	40.0	61.1	50.0	129.6
32.0	40.0	-4.1	100.0	106.2	32.1	40.0	61.2	100.0	179.2
32.0	40.0	-3.7	1.9	10.1	32.1	40.0	61.2	4.6	82.9
32.0	40.0	-3.7	75.0	81.0	32.1	40.0	61.2	75.0	154.6
32.0	40.0	-3.8	25.0	31.9	32.1	40.0	61.1	25.0	104.8
32.0	40.0	-4.0	150.0	153.8	32.1	40.0	61.1	150.0	225.9
32.0	60.0	-4.0	125.0	138.0	32.1	60.0	61.1	125.0	191.0
32.0	60.0	-3.9	50.0	63.2	32.1	60.0	61.2	50.0	122.4
32.0	60.0	-3.9	100.0	111.0	32.1	60.0	61.1	100.0	176.4
32.0	60.0	-3.6	2.3	6.7	32.1	60.0	61.2	4.3	75.2
32.0	60.0	-3.7	75.0	83.9	32.1	60.0	61.1	75.0	153.6
32.0	60.0	-4.0	25.0	35.7	32.1	60.0	61.2	25.0	106.2
32.0	60.0	-4.1	150.0	165.8	32.1	60.0	61.1	150.0	242.4
32.0	80.0	-4.1	125.7	141.1	32.1	80.0	61.1	125.0	226.2
32.0	80.0	39.3	49.8		32.1	80.0	61.1	50.0	134.9
32.0	80.0	-4.0	100.0	113.9	32.1	80.0	61.1	100.0	196.4
32.0	80.0	-3.7	1.2	15.7	32.1	80.0	61.3	4.7	96.2
32.0	79.4	-3.6	75.0	89.9	32.1	80.0	61.2	75.0	167.2
32.0	80.0	-3.7	25.1	32.7	32.1	80.0	61.1	25.0	105.6
32.0	80.0	-4.3	150.4	164.1	32.1	80.0	61.1	150.0	250.9

As shows in Figure 26, significant co-linearities were observed between NO and O_3, between O_3 and CO, between temperature and absolute humidity and between temperature/absolute humidity and wind speed.

The relation between O_3 and NO can be explained by the fact that O_3 and NO are the two reactant of a chemical equilibrium that produces NO_2. The co-linearity between CO and O_3 can also be explained by a chemical reaction involving those two molecules to form CO_2. During the selection process of interferent compounds, CO was found rather significant for AlphaSense's sensors but not for the majority of MACPoll sensors. The relation between temperature and absolute humidity was due to the fact that absolute humidity was calculated based on temperature and relative humidity values using the Clausius-Clapeyron equation. Finally, wind velocity and temperature/absolute humidity co-linearity (the biggest one) was mainly due to the measurement method of wind velocity and can therefore explain the effect of wind velocity on the sensor which was likely an effect of temperature. Since it was chosen to design an experiment with orthogonal factors NO_2, O_3, temperature and relative humidity do not present any correlations.

During the experiments the reference sensor of both NO2-B4 has given wrong value. To correct this issue, it has been decided to estimate an average value based on the other experiments taking into consideration different levels of temperature and humidity.
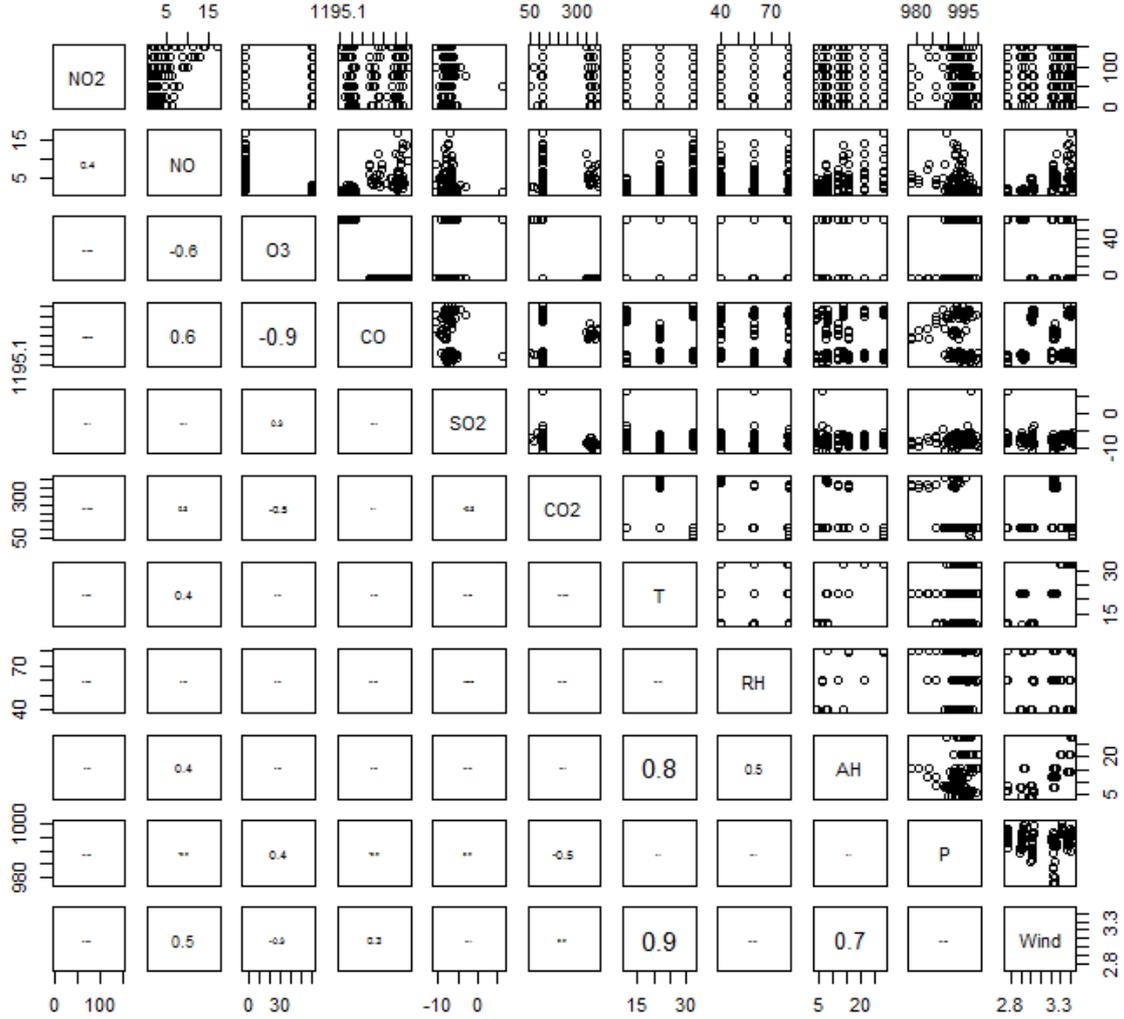
Figure 26: Co-linearities of covariates within the dataset of the experimental design

Multi Linear Regresssion (MLR) was used to model the sensor responses according to the available covariates within our dataset. Initially, all main effects were included in the MLR and only NO_2, O_3, temperature and relative humidity were found significant. This was consistent with the results of the single interference testing which show a strong effect of O_3 on the sensor response. Equations giving the sensor responses according to NO_2, O_3, temperature and relative humidity are given in Eq. 23 with $R_{s,corr}$ being the sensor response after pre-calibration and corrected in long term drift, NO_2 the concentration of nitrogen dioxide, O_3 the ozone concentration, T the temperature and RH the relative humidity.

$$R_{s,corr} = a + b\,NO_2 + c\,O_3 + d\,T + e\,RH \qquad \text{Eq. 23}$$

$$R_{s,corr} = -19.53 + 0.88\,NO_2 + 0.47\,O_3 + 0.68\,T + 0.47\,RH \qquad \text{NO2B4\_107}$$

$$R_{s,corr} = -85.25 + 1.82\,NO_2 + 1.18\,O_3 + 4.57\,T + 0.38\,RH \qquad \text{NO2B4\_113}$$

$$R_{s,corr} = -37.85 + 0.96\,NO_2 + 1.07\,O_3 + 1.19\,T + 0.26\,RH \qquad \text{O3\_V011\_20}$$

Table 34 gives the multiple analysis of variance which shows that all the effects and the interaction were highly significant (smallest probability that these factors were fainted was < 0.04 %).

Table 34: Analysis of variance of the model for NO2B4_107

Coefficients	Estimate	Standard Error	t-value	Probability (Pr(>|t|)
Intercept	-19.53	11.60	-1.68	9.48E-02
NO$_2$	0.88	0.05	18.67	< 2e-16
O$_3$	0.47	0.08	6.10	1.36E-08
Temperature	0.68	0.28	2.45	1.60E-02
Relative humidity	0.47	0.14	3.27	1.39E-03

Table 35: Analysis of variance of the model for NO2B4_113

Coefficients	Estimate	Standard Error	t-value	Probability (Pr(>|t|)
Intercept	-85.25	22.32	-3.82	2.13E-04
NO$_2$	1.82	0.09	20.06	< 2e-16
O$_3$	1.18	0.15	8.00	8.91E-13
Temperature	4.57	0.54	8.52	5.51E-14
Relative humidity	0.38	0.28	1.37	1.72E-01

Table 36: Analysis of variance of the model for O3_V011_20

Coefficients	Estimate	Standard Error	t-value	Probability (Pr(>|t|)
Intercept	-37.85	3.34	-11.32	< 2e-16
NO$_2$	0.96	0.01	70.21	< 2e-16
O$_3$	1.07	0.02	48.24	< 2e-16
Temperature	1.19	0.08	14.81	< 2e-16
Relative humidity	0.26	0.04	6.3	4.80E-09
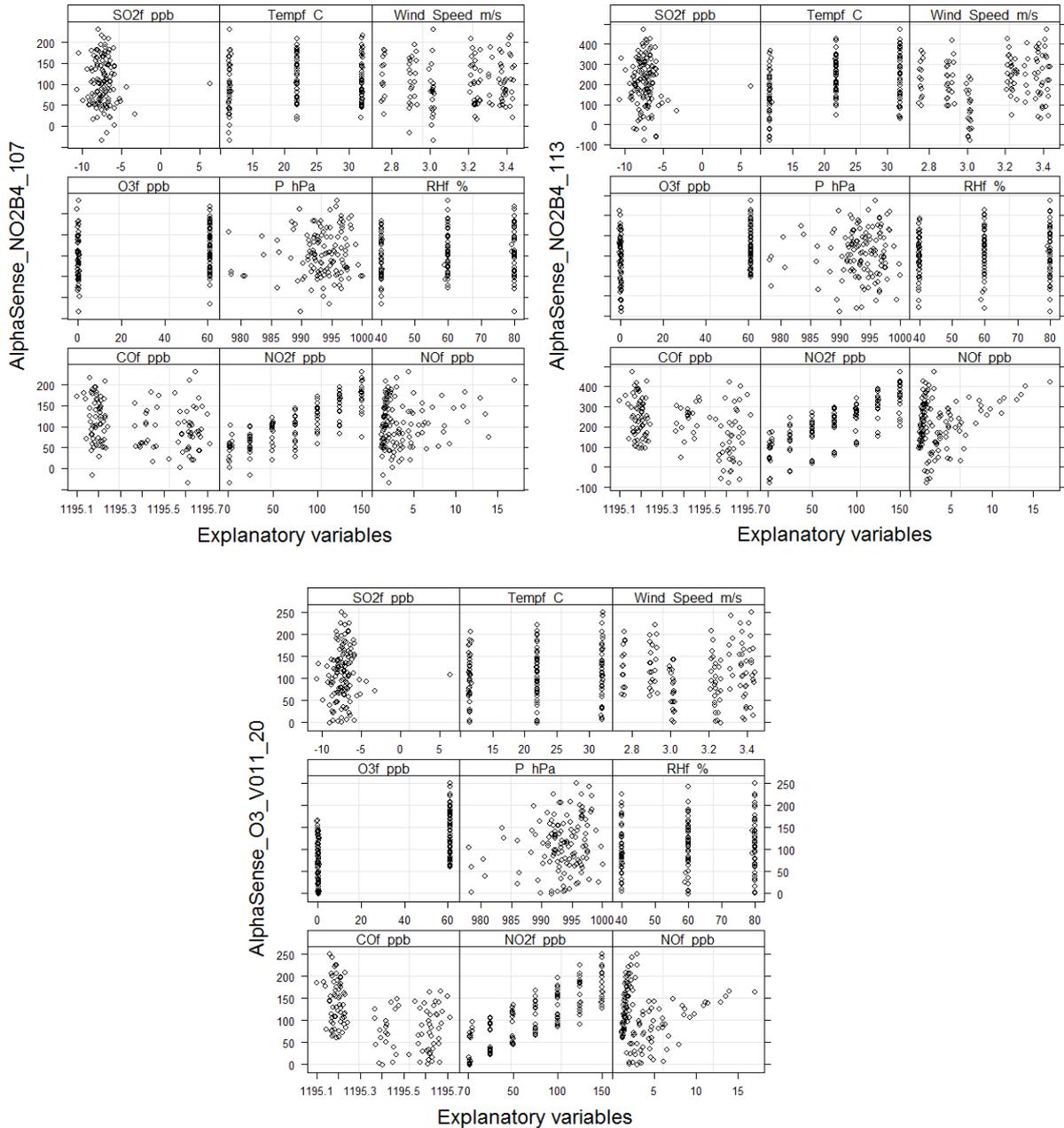
Figure 27: Relationships between variables and all possible covariates

It was checked that the residuals of the model equation were independent of all available covariates (Figure 28): references values of NO_2, temperature, relative humidity, O_3, NO, CO, SO_2, ambient pressure and wind velocity.
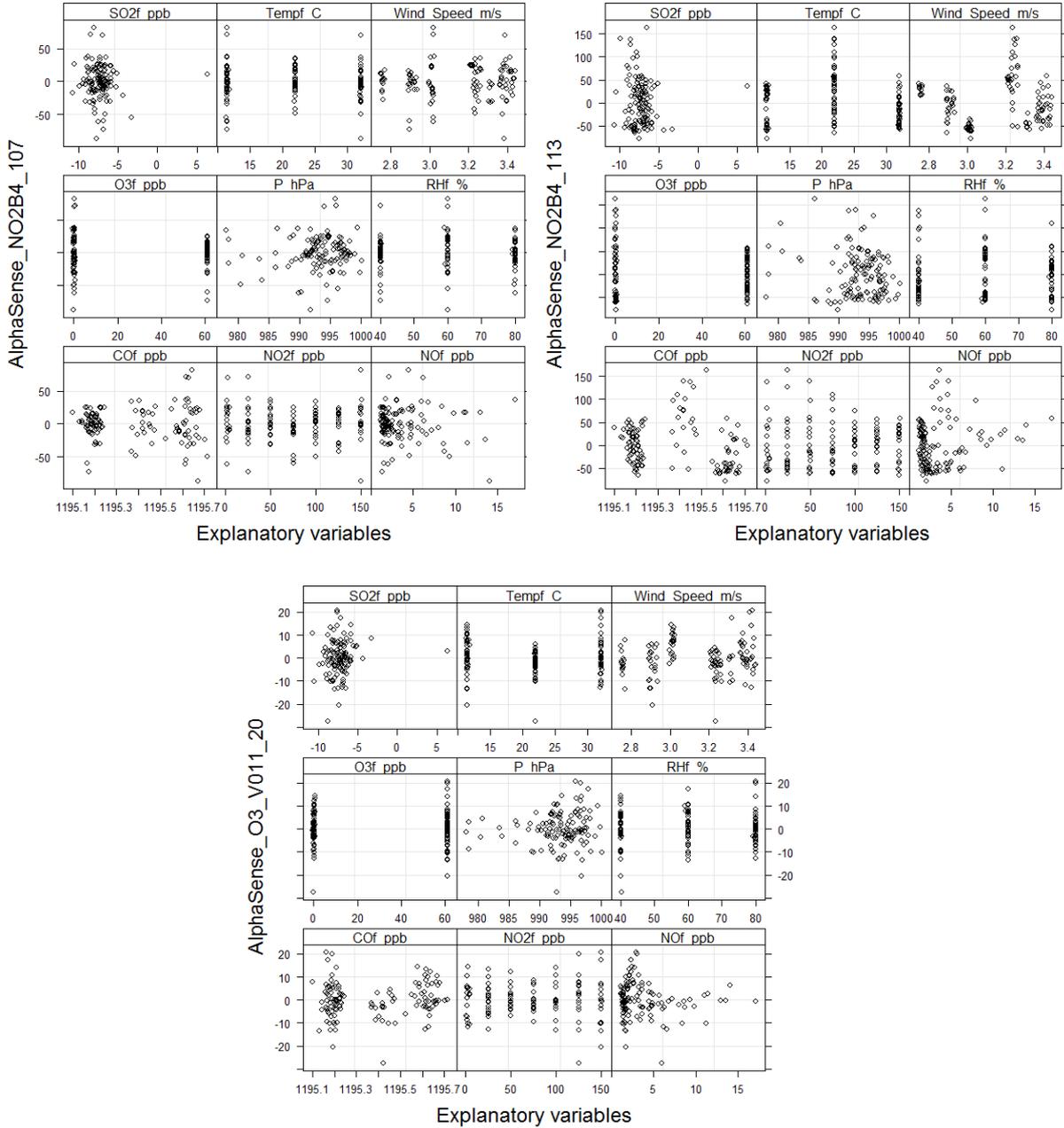
Figure 28: Relationships between residuals of the model equation and all possible covariates

Finally Eq. 25 can used to estimate NO₂ from the sensor response. However, the sensor response Rs first need to be pre-calibrated. Obviously, the drawback of this equation was that it uses temperature T, relative humidity RH, the elapsed time $NDays$ and ozone O_3.

$$NO_2 = \frac{f(NO_{2,pre-cal}) - (a\,NDays + b + c\,O_3 + d\,T + e\,RH)}{f\,NDays + g}$$

Eq. 24

$$NO_2 = \frac{Rs - (-6.4\,10^{-2}\,NDays - 19.53 + 0.47\,O_3 + 0.68\,T + 0.47\,RH)}{0.88 - 2.3\,10^{-3}\,NDays}$$

NO2B4_107

$$NO_2 = \frac{Rs - (-8.1\ 10^{-2}\ NDays - 85.25 + 1.18\ O_3 + 4.57\ T + 0.38\ RH)}{1.82 - 3.4\ 10^{-3}\ NDays}$$ NO2B4_113

$$NO_2 = \frac{Rs - (-4.1\ 10^{-2}\ NDays - 37.85 + 1.07\ O_3 + 1.19\ T + 0.26\ RH)}{0.96 - 1.3\ 10^{-4}\ NDays}$$ O3_V011_20

8.2   Uncertainty estimation

To estimate the measurement uncertainty it should be possible to use the GUM method (see Eq. 25).

$$u_c^2(O3) = \sum \left(\frac{\partial O3}{\partial X_i}\right)^2 u^2(X_i)\ and\ U = k \times u_c\ with\ k = 2$$ **Eq. 25**

Even if with our model was not complicated (4 variables), it was decided to use the "variance approach". We will assume that the variance of the measurement was the sum of the variance of individual random variables including the contributions of the lack of fit of the model equation, O_3 interference and temperature and humidity effects for the main effect. As decided in 7.6 and according to Table 29, Table 30 and Table 31, we will add the effect of short term drift, NH_3 and wind velocity after having subtracted the repeatability contribution as it was already included in the lack of fit.

Table 37: Uncertainty after laboratory experiment at the NO₂ limit value (100 nmol/mol) for NO2B4_107

	Parameters	Model applied + corrections/adjustments		Model not applied without corrections and adjustments
		Correction	Variance½	Variance½
1	Rs, lack of fit of model	yes	26.2	
2	O_3 in nmol/mol	yes	4.7*	$(41.1^2 + 2.u(O3).u(NO_2))^{1/2}$
3	Long term drift in nmol/mol	yes	8.4	27.4
4	Relative Humidity in %	no	$(4.8^2 - 1.0^2)^{1/2}$	$(4.8^2 - 1.0^2)^{1/2}$
5	Temperature in ºC	no	$(8.1^2 - 1.0^2)^{1/2}$	$(8.1^2 - 1.0^2)^{1/2}$
6	Short term drift in nmol/mol	no	$(6.0^2 - 1.0^2)^{1/2}$	$(6.0^2 - 1.0^2)^{1/2}$
7	NH_3 in nmol/mol	no	$(2.0^2 - 1.0^2)^{1/2}$	$(2.0^2 - 1.0^2)^{1/2}$
8	Wind in nmol/mol	no	$(6.3^2 - 1.0^2)^{1/2}$	$(6.3^2 - 1.0^2)^{1/2}$
$U = 2 \times u_c$ (see Eq. 25)		$u_c = 12.5\ (DQO = 25)$		$U = 2 \times 16.9 > DQO$

*: obtained by difference between the DQO and the other contributions

Table 38: Uncertainty after laboratory experiment at the NO₂ limit value (100 nmol/mol) for NO2B4_113

	Parameters	Model applied + corrections/adjustments		Model not applied without corrections and adjustments
		Correction	Variance$^{1/2}$	Variance$^{1/2}$
1	Rs, lack of fit of model	yes	50.4	
2	O_3 in nmol/mol	yes	1.9*	$(93.0^2 + 2.u(O3).u(NO2))^{1/2}$
3	Long term drift in nmol/mol	yes	33.0	34.9
4	Relative Humidity in %	no	$(8.9^2 - 1.0^2)^{1/2}$	$(8.9^2 - 1.0^2)^{1/2}$
5	Temperature in ºC	no	$(1.2^2 - 1.0^2)^{1/2}$	$(1.2^2 - 1.0^2)^{1/2}$
6	Short term drift in nmol/mol	no	$(11.9^2 - 1.0^2)^{1/2}$	$(11.9^2 - 1.0^2)^{1/2}$
7	NH_3 in nmol/mol	no	$(4.3^2 - 1.0^2)^{1/2}$	$(4.3^2 - 1.0^2)^{1/2}$
8	Wind in nmol/mol	no	$(3.6^2 - 1.0^2)^{1/2}$	$(3.6^2 - 1.0^2)^{1/2}$
$U = 2 \times u_c$ (see Eq. 25)		$u_c = 12.5$ $(DQO = 25)$		$U = 2 \times 16.9 > DQO$

*: obtained by difference between the DQO and the other contributions

Table 39: Uncertainty after laboratory experiment at the NO₂ limit value (100 nmol/mol) for O3B4_20

	Parameters	Model applied + corrections/adjustments		Model not applied without corrections and adjustments
		Correction	Variance$^{1/2}$	Variance$^{1/2}$
1	Rs, lack of fit of model	yes	7.55	
2	O_3 in nmol/mol	yes	5.0*	$(50.0^2 + 2.u(O3).u(NO2))^{1/2}$
3	Long term drift in nmol/mol	yes	9.7	8.0
4	Relative Humidity in %	no	$(12.8^2 - 1.0^2)^{1/2}$	$(12.8^2 - 1.0^2)^{1/2}$
5	Temperature in ºC	no	$(11.3^2 - 1.0^2)^{1/2}$	$(11.3^2 - 1.0^2)^{1/2}$
6	Short term drift in nmol/mol	no	$(7.9^2 - 1.0^2)^{1/2}$	$(7.9^2 - 1.0^2)^{1/2}$
7	NH_3 in nmol/mol	no	$(1.9^2 - 1.0^2)^{1/2}$	$(1.9^2 - 1.0^2)^{1/2}$
8	Wind in nmol/mol	no	$(5.4^2 - 1.0^2)^{1/2}$	$(5.4^2 - 1.0^2)^{1/2}$
$U = 2 \times u_c$ (see Eq. 25)		$u_c = 12.5$ $(DQO = 25)$		$U = 2 \times 16.9 > DQO$

*: obtained by difference between the DQO and the other contributions

1. The variance of the lack of fit of the model equation was estimated using the residuals of the MLR. This parameter already includes contribution from the lack of fit of the calibration, the repeatability of sensor responses and hence these parameters are not repeated in the table.

2. In the "Model applied + corrections/adjustments" column the contribution arising from O_3 becomes null. However this implies that O_3 shall be measured to be included in the model equation of the sensor and hence an uncertainty for O_3 measurements cannot be excluded. The standard uncertainty was set by difference between the DQO and the rest of the parameter contribution. Conversely, if the sensor values are not corrected for O_3 then the interference estimated in 7.1 is taken into account subtracting the correlation between O_3 and NO_2 observed in field.

3. For the long term drift, the uncertainty showed into the column "Model applied + corrections/adjustments" correspond to the residual standard error of the linear

regression at the limit value whereas in the "Model not applied" column it correspond to its standard deviation.

4. It was shown in 7.4.1 that relative humidity and temperature only affect the sensor by a kind of hysteresis effect to which the repeatability shall be subtracted rather than a systematic effect with a sensitivity coefficient.

5. As decided in 7.6 and according to Table 29, contribution of Short term drift, NH_3 and Wind will be included after having subtracted the repeatability.

9 Field experiments

9.1 Monitoring stations

The JRC station for atmospheric research (45°48.881'N, 8°38.165'E, 209 m asl) was located by the Northern fence of the JRC-Ispra site, situated in a semi-rural area at the NW edge of the Po valley. The station was several tens of km away from large emission sources like intense road traffic or big factories. The main cities around are Varese, 20 km east, Novara, 40 km south, Gallarate - Busto Arsizio, about 20 km south-east and the Milan conurbation, 60 km to the south-east. Busy roads and highways link these urban centers. Four industrial large source points (CO emissions > 1000 tons / yr) are located between 20 and 50 km E to SE of Ispra. The closest (20 km SSE) emits also > 2000 tons of NOx per year. The aim of the JRC-Ispra station was to monitor the concentration of pollutants in the gas phase, the particulate phase and precipitations, as well as aerosol optical parameters, which can be used for assessing the impact of European policies on air pollution and climate change. Measurements are performed in the framework of international monitoring programs like the Co-operative program for monitoring and evaluation of the long range transmission of air pollutants in Europe (EMEP) of the UN-ECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) and the Global Atmosphere Watch (GAW) Program of the World Meteorological Organization (WMO).

Test were carried out with the collaboration of ERLAP Laboratory at an air conditioned mobile laboratory that has been installed at the station in replacement of the routine analysers normally installed in the containers of the EMEP station. Gases were sampled using a sampling line (see Figure 29) placed at the top of the roof of the van at about 3.5 m above the ground and on the roof of the mobile laboratory. The sampling line consists in a stainless steel gas inlet with grid protection for rain, insects and dust wh. The stainless steel inlet tube of 4 cm internal diameter with internal PTFE tube that ends with a Teflon manifold of 8 PTFE ports to connect the gas analysers. The sampling line was flushed with ambient air with about 2 second resident time of samples in the sampling line. Each instrument samples from the glass tube with its own pump through a ¼" PTFE/PFE tube and a 1 µm pore size 47 mm diameter Teflon filter to eliminate particles from the sampled air.

The mobile laboratory was equipped with meteorological sensors and gas analysers which were calibrated in laboratory before the in-situ measurements and then checked every month. Field checks were carried out using zero air in gas cylinders and a span value (internally certified gas cylinders at low concentration for NO/NOx and SO2, highly concentrated cylinders for CO and ozone generator do O_3). The highest observed drift of calibration was 3 %, consistent with the uncertainty of the working standards used on field. Therefore, no correction of measurements was undergone apart from the discarding values during maintenance and calibration checks.

- Meteorological parameters (ambient temperature, ambient relative humidity, ambient pressure, 10m mast for wind speed and wind direction) a mobile. The mobile laboratory was equipped with:

- Gaseous pollutants: for O_3 an UV Photometric Analyzer Thermo Environment 49C; for NO2/NO/NOx a Chemiluminescent Nitrogen Oxides Analyzer Thermo 42C; for CO a non-Dispersive Infrared Gas-Filter Correlation Spectroscopy Thermo 48C-TL, for SO_2 and UV Fluorescent Analyser Thermo 43C TL
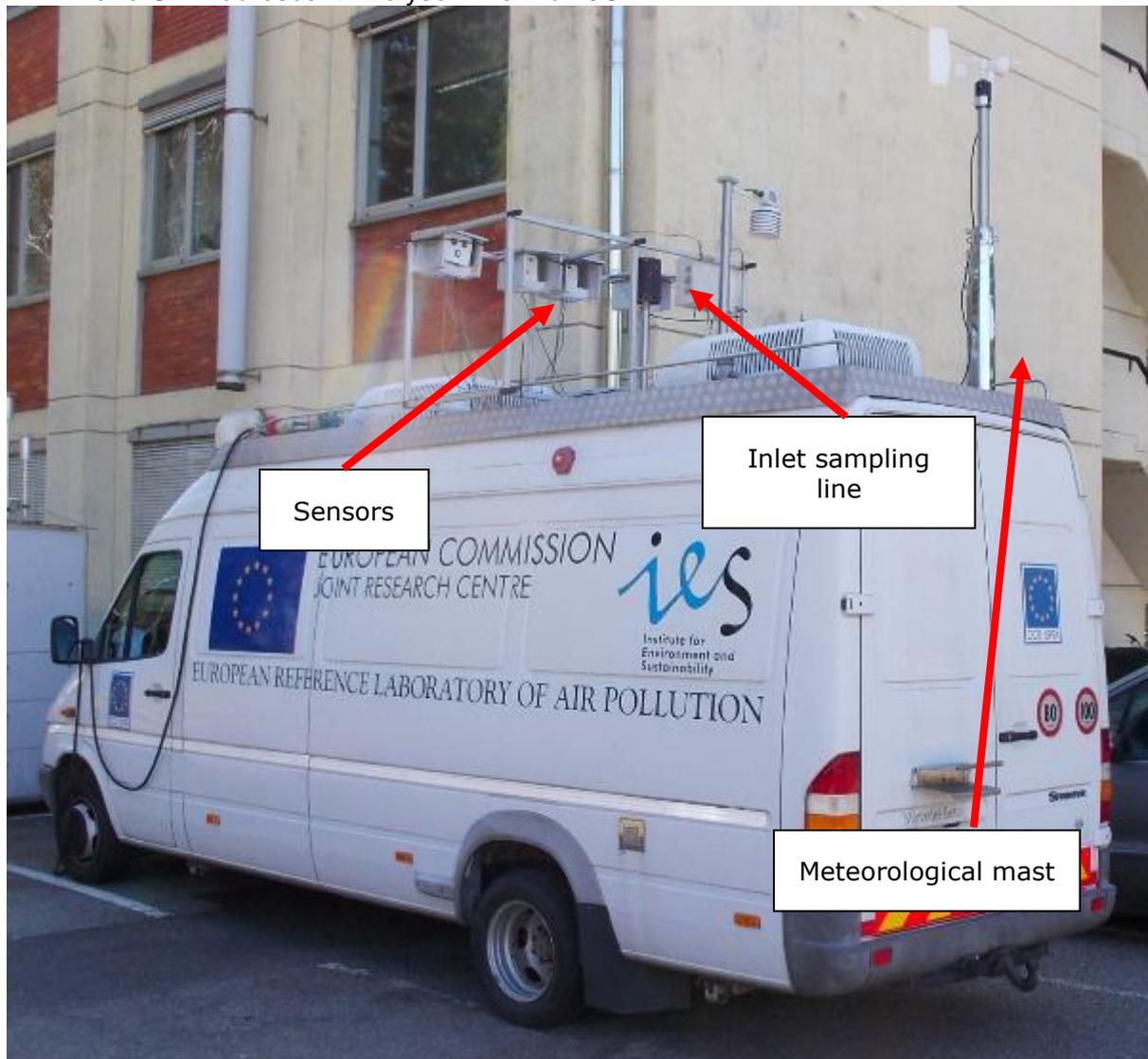

Figure 29: Mobile laboratory used in front of the building and after in the provisory EMEP Station at JRC Ispra.

To avoid interference, we made sure that the flow air coming out of the air condition system was blowing far enough from the sensor to avoid any effect on the sensor responses.

9.2   Sensor equipment

2 NO_2 sensors NO2-B4 and 1 O_3 sensors O3-B4 were installed on the field:

- NO2-B4 reference NO2B4_109 and NO2B4_110
- O3-B4 reference O3_V011_17

The same equipment as the one used in laboratory was used:

- Power supply: a plug-in power supply 3-12V/800-1600 mA (RS-electronic 148 957) was used

- Test board used: no need for an external test board, AlphaSense supplied the sensors mounted on their own test board.
- Data acquisition: the data acquisition was performed by means of special Labview software developed to manage data acquisition synchronously with the gaseous and other parameters such as temperature, humidity (see 2.5.1). It consisted of a NI USB-6009 acquisition system from National Instrument with a periodicity of data acquisition of 100Hz and an average data acquisition every minute without filtering.

9.3 Check of the sensor in laboratory

In a first step all the sensors were installed inside the exposure chamber in order to verify their proper functioning and to create a pre-calibration curve before the installation on the field. As for all the experiments of the laboratory study, temperature, relative humidity and other gaseous compounds which were suspected to affect the sensor response, were kept under control with relative standard deviation (RSD) of about 2 %. The temperature and relative humidity of the test were set at 22°c and 60 %.

The pre-calibration functions were established by plotting sensors responses versus reference values measured by the Thermo Environment 42 C analyser at stable conditions 22 °C and 60 % of relative humidity (see Figure 30). Each step lasted for 150 minutes once the condition of NO_2 concentrations, temperature and humidity were reached. The average of the last 60 minutes is plotted. For NO2B4_109, NO2B4_110 and O3_V011_17 it has been decided to use a linear regression as the parabolic function does not change the distribution of residuals. Eq. 26 should be used to correct the R_s to a calibrated value.

NO2B4_109 $\qquad R_{s,cal} = \dfrac{R_s - 1.71\ 10^{-2}}{5.75\ 10^{-4}}$

NO2B4_110 $\qquad R_{s,cal} = \dfrac{R_s - 3.38\ 10^{-2}}{5.07\ 10^{-4}} \qquad$ Eq. 26

O3_V011_17 $\qquad R_{s,cal} = \dfrac{R_s - 6.00\ 10^{-2}}{6.13\ 10^{-4}}$

Pre-calibration of AlphaSense_NO2B4_109

Rs = -0.017053 + 0.000575.NO2, R^2= 0.9989
Rs = -0.018 + 0.000606.NO2 + -0.0000002.NO2^2, R^2 = 0.9992

Pre-calibration of AlphaSense_NO2B4_110

Rs = -0.003375 + 0.000507.NO2, R^2= 0.9987
Rs = -0.004 + 0.000522.NO2 + -0.0000001.NO2^2, R^2 = 0.9988

Pre-calibration of AlphaSense_O3B4_V011_17

Rs = -0.060020 + 0.000613.NO2, R^2= 0.99548
Rs = -0.061 + 0.000643.NO2 + -0.0000002.NO2^2, R^2 = 0.99568
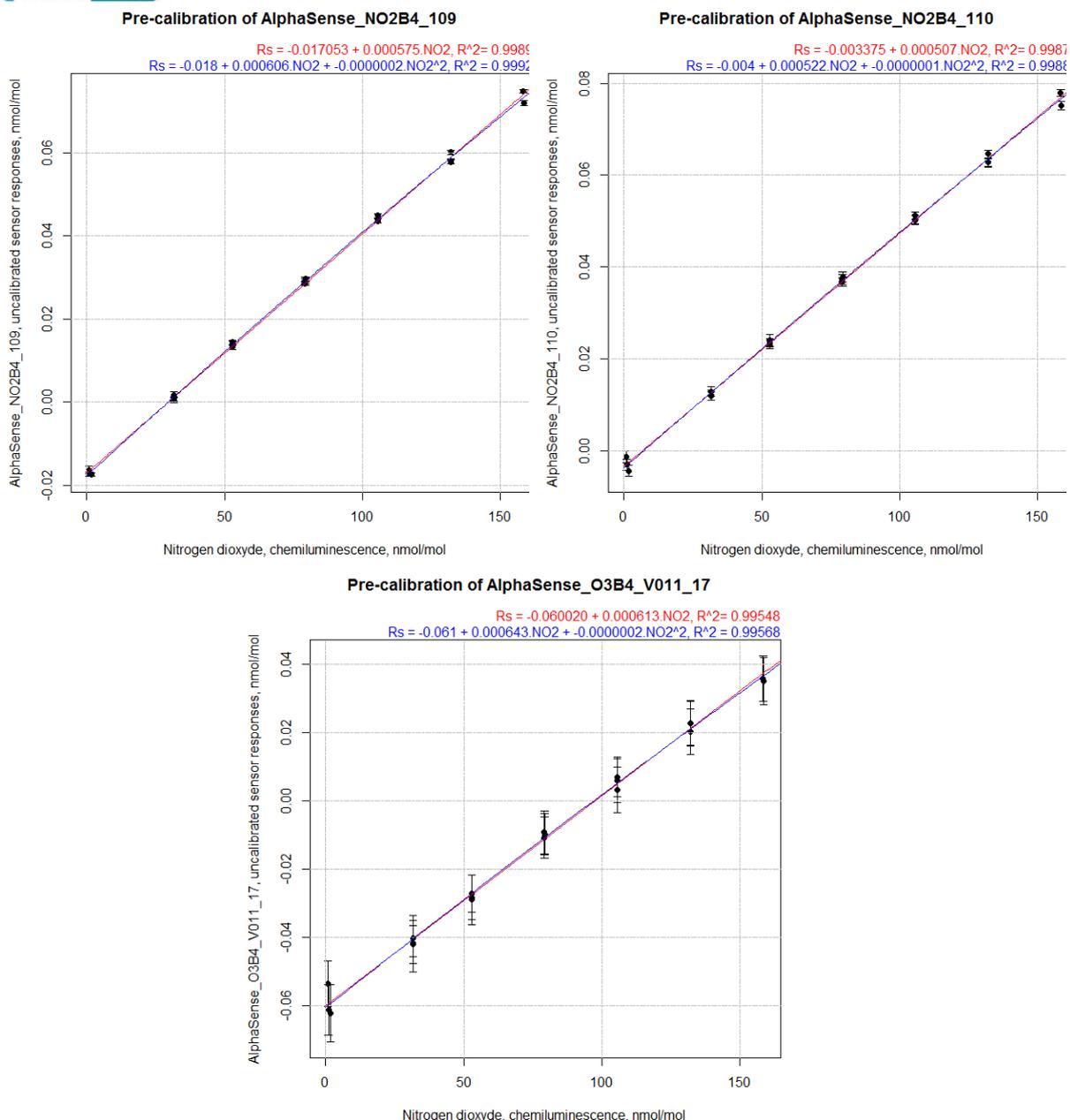
Figure 30: Laboratory pre-calibration of field sensors

9.4   Field Results

The sensors were installed between 20 March and 21 October 2013. From the beginning to 09 July, the mobile laboratory was placed near our laboratory, in a parking place, to simulate in the best way our micro environment. From the 09 July to the 21 of October, a new location was decided for the mobile laboratory and it was placed in a field inside the Research Centre as far as possible from traffic and building to be representative for a rural area.

Apart from sensors, reference values were registered for O_3, NO_2 and NO, SO_2, CO, PM_{10}, temperature, relative humidity while absolute humidity was calculated. However, the time series for PM_{10} being incomplete it had to be dropped.

Figure 31 and Figure 32 show the co-linearities in the field data set with scatterplots between pairs of parameters (upper matrix plots) and their correlation (lower matrix values) for hourly values of O_3, NO_2, NO, and SO_2 in nmol/mol, CO in µmol/mol, temperature in °C (T), relative humidity in % (RH), absolute humidity in mg/m³ (H2O), wind direction in ° (WD), wind velocity in m/s (WV) and pressure in hPa (P). Sens correspond to the uncalibrated CairClip NO_2 values.

Being in field where factors cannot be controlled, collinearities between each other is unavoidable. Figure 31 shows the co-linearities during the first period of the campaign, from 30 March to 09 July 2013. There are strong correlations between O_3, temperature and relative humidity as expected, making it impossible to include all of these parameters into a regression model. A lower level of correlation can be also observed between O_3 and wind velocity. Unfortunately, during this time period, NO_2 was not the main gaseous compounds in the ambient air; ozone was present at least as the same levels. NO_2 concentration stays under 45nmol/mol with a mean concentration equal to 6 nmol/mol whereas the mean concentration of ozone is equal to 35 nmol/mol.
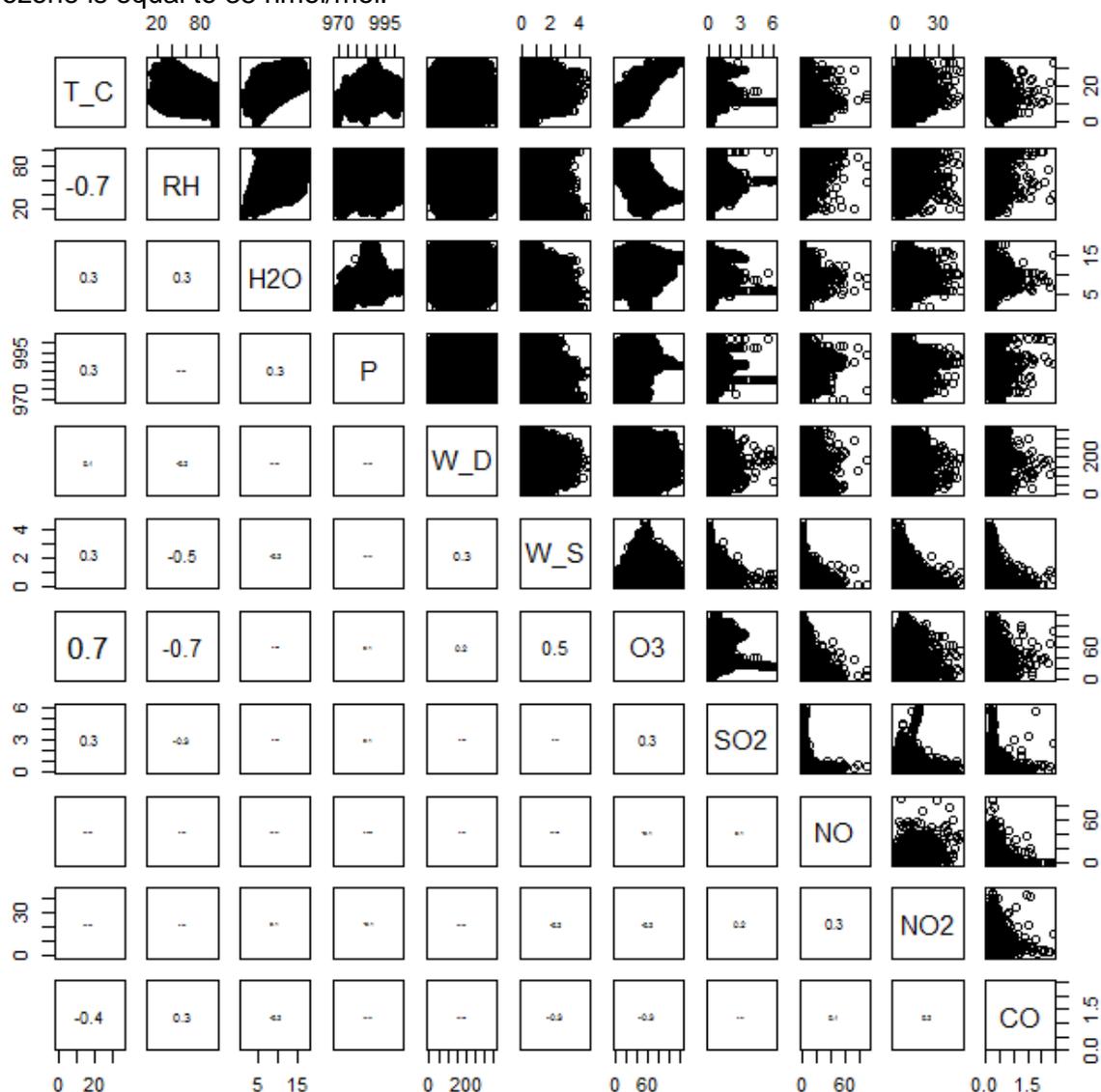
Figure 31: Co-linearities in the field data set during the first half of the filed campaign: building parking place

Figure 32 shows the co-linearities during the second period of the campaign, from 05 March to 09 July 2013. We observe the same correlation as the one in Figure 31 with in average a higher coefficient. There are strong correlation between O_3, temperature and relative humidity as expected, making it impossible to include all of these parameters into a regression model. A lower level of correlation can be also observed between O_3 and wind velocity. Unfortunately, during this time period, NO_2 was not the main gaseous compounds in the ambient air; ozone was present at least as the same levels.
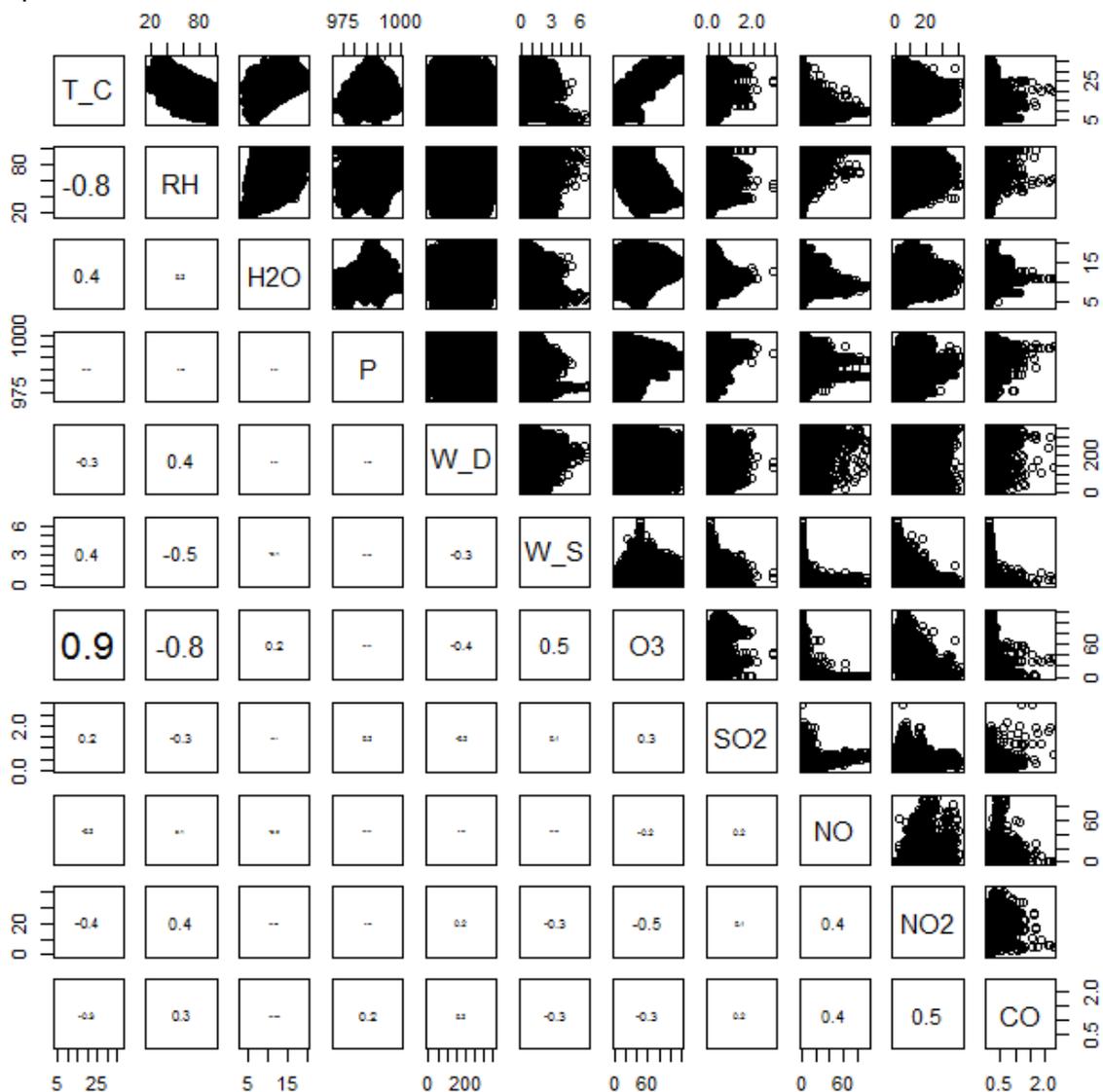
Figure 32: Co-linearities in the field data set during the second half of the filed campaign: rural area

It was decided for the next part of the evaluation to focus on the first time period as it's the one which can better represent our micro-environment.

Figure 33 shows the relationship between sensor response and reference measurement of NO_2, NO, O_3, CO, SO_2, temperature, relative humidity, pressure, wind (both direction and velocity) and absolute humidity. By comparing the sensor response toward NO_2 and O_3 it's clearly shows that:

1. O_3 was most of the time present in higher concentration than NO_2 during the field campaign (mean concentration of ozone is equal to 35 nmol/mol whereas NO_2 concentration stays under 45nmol/mol with a mean concentration equal to 6 nmol/mol).

2. All sensors showed a high noise. This can be linked to the acquisition system, a NI USB 6009 or to the sensors themselves that generated a high noise in the measurements and valid measurements could not be obtained. Consequently, we were not able to find good relationship with NO_2. Only O3B4_V011_17 sensor showed a light correlation with O_3
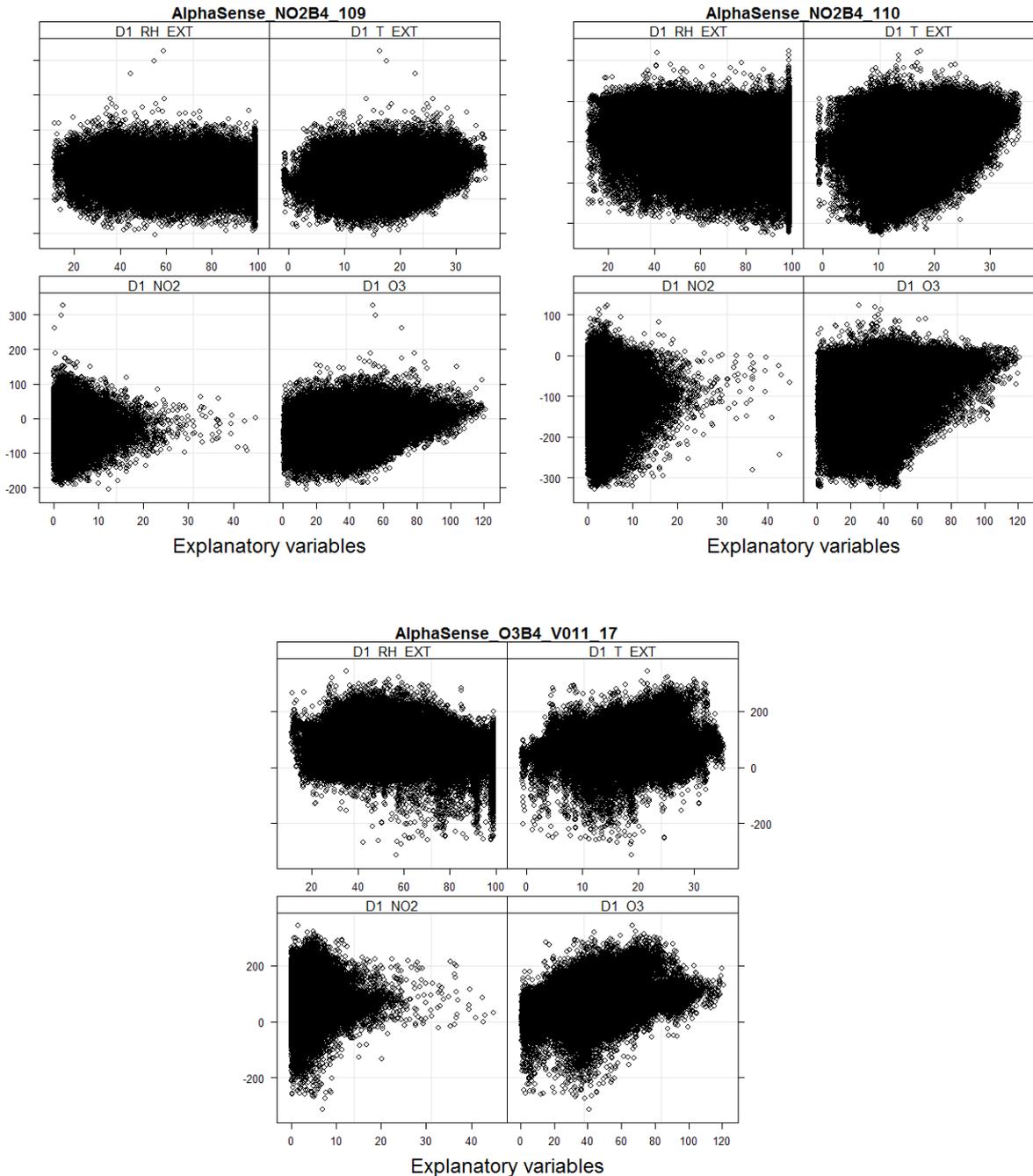
Figure 33: Relationship between sensors response and reference measurements values

9.5 Estimation of field uncertainty and calibration procedure

It was not possible to estimate neither the field uncertainty nor the efficiency of the calibration procedure because of the electronic noise within the data.

10 Conclusion

The purpose of this study was to assess if the NO2-B4 AlphaSense sensor meets the data quality objective (25% of uncertainty at 100 nmol/mol) for indicative methods of hourly NO_2 measurements.

The laboratory evaluation shows that the NO2-B4 sensor was found highly linear. However the tested sensors were suffering from an important long term drift, a huge hysteresis effect against humidity and temperature.

Regarding gaseous interfering compounds, the laboratory experiments showed a high sensitivity to ozone. Among CO, CO_2, NO, NH_3 and SO_2, the sensor was found slightly sensitive to NH_3 but it was independent from the other species. They did suffer from short term drift but did not present hysteresis effect with increasing/decreasing ramps of NO_2 levels.

The sensor appeared to be slightly influenced by wind velocity while power supply (220 V) did not have an effect on the sensor likely because of the quality of the DC transformer used in laboratory. It was not possible to conclude on the effect of pressure as the experiment was not feasible in the current laboratory exposure chamber.

A correction model equation was established in laboratory based on the number of exposure days, ozone concentration, temperature and relative humidity to estimate NO_2. Using this model the measurement uncertainty was found lower than the Data Quality Objective of the European Directive only for very low O_3 levels while DQOs would not be met without the correction model.

The field deployed sensors were first calibrated in laboratory and showed the same high linearity of response and lack of hysteresis effect.

Unfortunately, the field campaign was realised in late winter - summer period during which the NO_2 was lowest than O_3 in ambient air that made impossible to evaluate the final field uncertainty. Moreover, the noise was found too high during the whole field campaign preventing from obtaining valid measurements. Therefore, the models established with the laboratory experiments could not be verified in field experiment.

Further to this study, the application of the sensor as indicative method for NO_2 fixed measurement at traffic and background type of station with urban/suburban areas is not validated. In fact, it is lacking field confirmation of the laboratory results that gave satisfaction provided that a correction model based on, long term drift, O_3, temperature and relative humidity was used.

Even though the NO2-B4 sensor is not fully selective, it produces repeatable sensor values that may be used with correction algorithms with data from multi-sensor (e.g. NO, NO_2, O_3) to solve the sensitivity, selectivity and stability shortcoming of sensors.
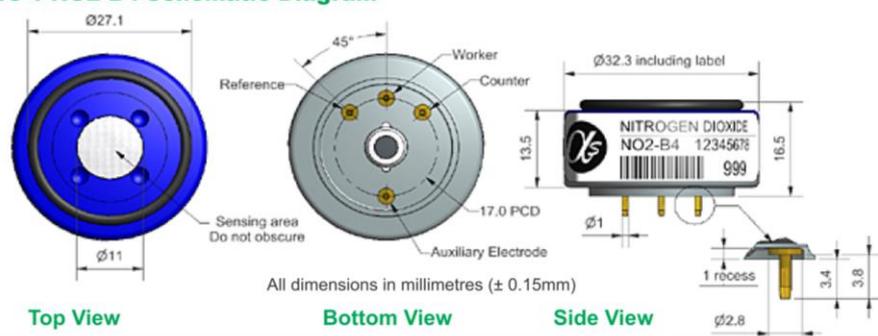
11 Appendix A: Technical Data Sheet AlphaSense's NO2-B4/O3-B4 and Individual Sensor Board (ISB) Issue 4, 085-2217 User Manual Issue 2

NO2-B4 Nitrogen Dioxide Sensor
4-Electrode

Figure 1 NO2-B4 Schematic Diagram

All dimensions in millimetres (± 0.15mm)

Top View　　　　**Bottom View**　　　　**Side View**

PERFORMANCE

Sensitivity	nA/ppm at 2ppm NO_2	-250 to -600
Response time	t_{90} (s) from zero to 2ppm NO_2	< 25
Zero current	nA in zero air at 20°C	-15 to 20
Noise*	±2 standard deviations (ppb equivalent)	12
Range	ppm NO_2 limit of performance warranty	20
Linearity	ppb error at full scale, linear at zero and 5ppm NO_2	< ±1
Overgas limit	maximum ppm for stable response to gas pulse	50

* Tested with Alphasense ISB low noise circuit

LIFETIME

Zero drift	ppb equivalent change/year in lab air	0 to 20
Sensitivity drift	% change/year in lab air, monthly test	-20 to -40
Operating life	months until 50% original signal (12 month warranted)	> 18

ENVIRONMENTAL

Sensitivity @ -20°C	(% output @ -20°C/output @ 20°C) @ 2ppm NO_2	40 to 70
Sensitivity @ 50°C	(% output @ 50°C/output @ 20°C) @ 2ppm NO_2	120 to 135
Zero @ -20°C	nA change from 20°C	±10
Zero @ 50°C	nA change from 20°C	60 to 380

CROSS SENSITIVITY

H_2S	sensitivity % measured gas @ 5ppm	H_2S		< -130
NO	sensitivity % measured gas @ 5ppm	NO		< 4
Cl_2	sensitivity % measured gas @ 5ppm	Cl_2		< 100
SO_2	sensitivity % measured gas @ 5ppm	SO_2		< -20
CO	sensitivity % measured gas @ 5ppm	CO		< 0.1
H_2	sensitivity % measured gas @ 100ppm	H_2		< 0.1
C_2H_4	sensitivity % measured gas @ 100ppm	C_2H_4		< 0.1
NH_3	sensitivity % measured gas @ 20ppm	NH_3		< 0.1
CO_2	sensitivity % measured gas @ 5% Vol	CO_2		< 0.1
O_3	sensitivity % measured gas @ 100ppb	O_3		30 to 65
Halothane	sensitivity % measured gas @ 100ppm	Halothane		< 0.1

KEY SPECIFICATIONS

Temperature range	°C	-30 to 50
Pressure range	kPa	80 to 120
Humidity range	% rh continuous	15 to 85
Storage period	months @ 3 to 20°C (stored in sealed pot)	6
Load resistor	Ω (ISB circuit is recommended)	33 to 100
Weight	g	< 13

At the end of the product's life, do not dispose of any electronic sensor, component or instrument in the domestic waste, but contact the instrument manufacturer, Alphasense or its distributor for disposal instructions.

NOTE: all sensors are tested at ambient environmental conditions, with 47 ohm load resistor, unless otherwise stated. As applications of use are outside our control, the information provided is given without legal responsibility. Customers should test under their own conditions, to ensure that the sensors are suitable for their own requirements.

NO2-B4 Performance Data

Technical Specification

Figure 2 Sensitivity Temperature Dependence
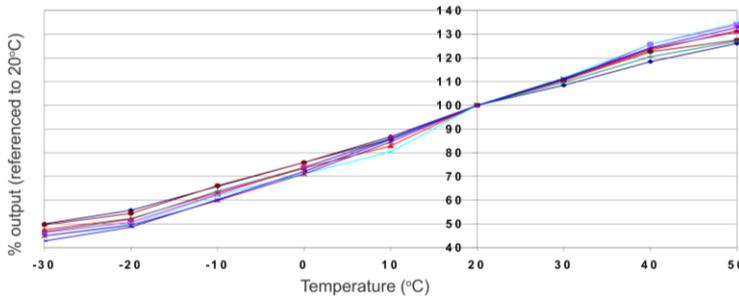
Figure 2 shows the temperature dependence of sensitivity at 2ppm NO_2.

This data is taken from a typical batch of sensors.

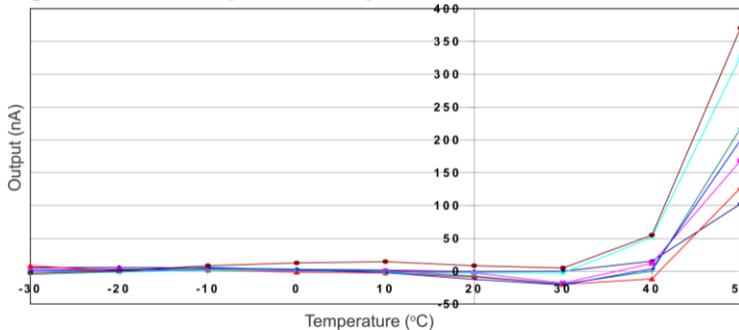## Figure 3 Zero Temperature Dependence

Figure 3 shows the variation in zero output of the working electrode caused by changes in temperature, expressed as nA.

This data is taken from a typical batch of sensors.

Contact Alphasense for futher information on zero current correction.

Figure 4 Response to 20 ppb NO_2 using ISB circuit
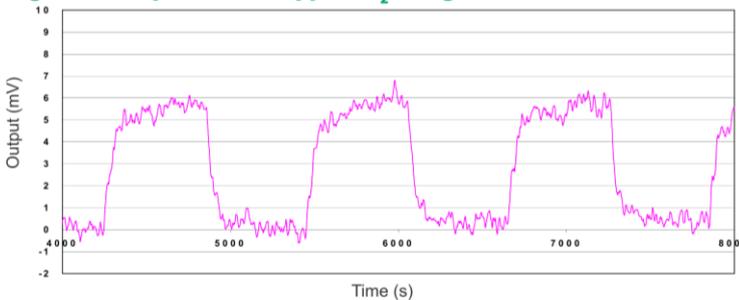
Figure 4 shows response to 20ppb NO_2.

Use of Alphasense ISB circuit reduces noise to 12ppb, with the opportunity of digital smooting to reduce noise even further

Figure 5 Response to 200 ppb NO_2
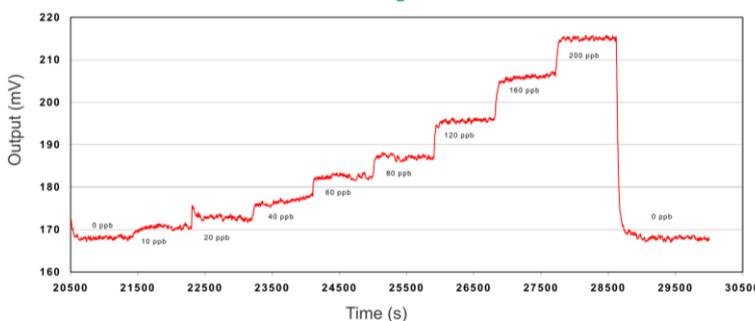
With a 33 Ω load resistor, the NO2-B4 shows excellent resolution, even at the ppb level: ideal for outdoor air environmental testing.

This raw data can be digitally smoothed.

For further information on the performance of this sensor, on other sensors in the range or any other subject, please contact Alphasense Ltd. For Application Notes visit "www.alphasense.com".

Individual Sensor Board (ISB) Issue 4, 085-2217 User Manual Issue 2 (copyright AlphaSense Ltd)

The purpose of this manual is to explain how the circuit operates, how to connect power and take readings, mount the circuit board and correct the data in Excel.

1 How the circuit operates

Figure 1 below shows the circuit for the ISB, issue 4. This circuit is designed for use only with AlphaSense B4 family of four-electrode gas sensors. The ISB uses low noise components and in order to achieve good resolution, best practice for grounding and screening is necessary. Take time to optimise your EMC environment to a low level to achieve low ppb resolution.

The ISB includes a low noise bandgap to provide a bias voltage for NO sensors and can measure both oxidising (CO, H_2S, NO) and reducing (O_3, NO_2) gas sensors. The ISB is configured as four versions for specific sensors: NO, NO_2, O_3 and CO/ H_2S/ SO_2:

Part number	Sensor
810-016-00	CO-B4, SO2-B4, H2S-B4
810-016-01	NO-B4
810-016-02	NO2-B4
810-016-03	O3-B4

Table 1. Part numbers for the four types of ISBs

Ensure your ISB is configured correctly for your B4 sensor if the ISB has been supplied separate from the sensor.

The circuit uses a single op amp to provide balance current into the counter electrode. In addition, both the working electrode (*WE*) and auxiliary electrode (*Aux-* used to compensate for zero current) have equivalent two stage amplifiers: the first stage is a high gain transimpedance amplifier and the second buffer stage allows for inverting sensor signals for NO_2 and O_3 sensors. Both signals are available on the 6-way Molex socket as separate pairs, but note that the power and output ground (-) pins are connected together.

There are no adjustments on the ISB. The offset voltages for both channels have been measured and are marked on the label attached to the packing sleeve for the ISB. If the ISB was shipped with a B4 sensor, the label will include both the zero voltage (expressed as mV) and sensitivity (expressed as mV/ppm) for the sensor with ISB. If you swap the sensor and ISB then the offset voltage will change but the sensitivity will be the same ($\pm1\%$) since sensitivity is dependent on the sensor, not the ISB.
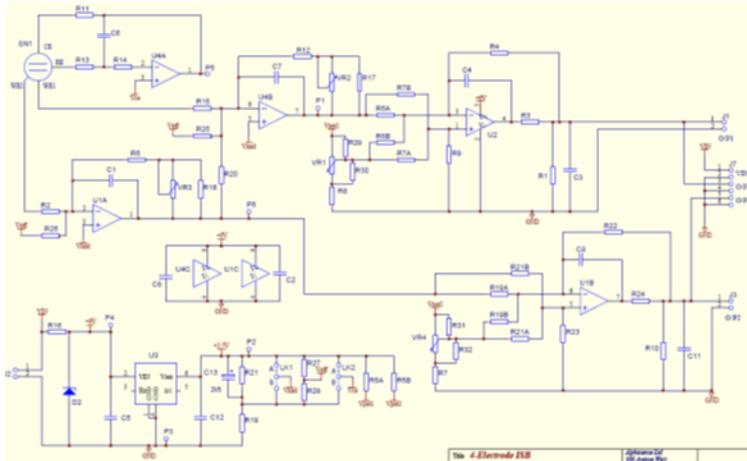
Figure 1. Schematic of Issue 3 ISB

2   Connecting power and taking readings

The socket for power and signals is shown in figure 2 below.
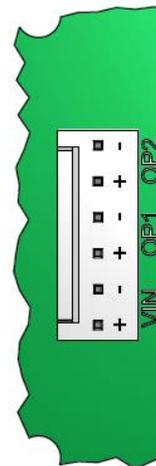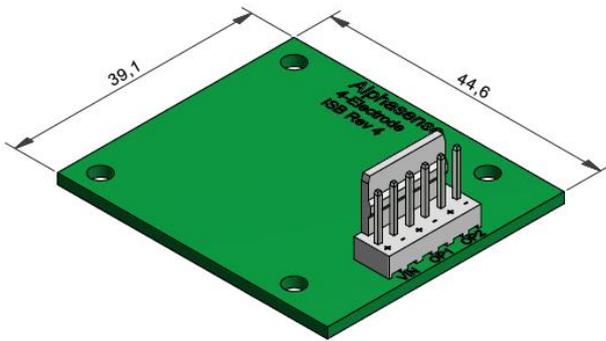
The Molex socket is polarised.

Figure 2. ISB socket for power and signals

DC power is required: 6.0 ±0.2 VDC. Ensure your power supply is low noise and decoupled, or its noise component will be added to the measured signal.

OP1 is the signal from the Working Electrode and OP2 is the signal from the Auxiliary Electrode.

The –ve pins are connected so you can use either 6-way or 4-way cable to connect to the ISB. OP1 and OP2 are buffered DC signals so a normal A/D converter will be fine, so long as it does not inject noise back into the ISB. If you are concerned about noise injection, then decouple using 10nF plus 100nF capacitors close to the Molex connector.

Table 2 below lists expected outputs from ISB with a typical B4 sensor.

Gas	Zero offset mV (WE / Aux)	sensitivity mV/ppm	Min/ max sensitivity mV/ppm	Full scale ppm	Gain mV/nA
CO	270/ 340	320	230/ 550	15	1.76
H$_2$S	350/ 350	1650	1600/ 1700	3	1.76
SO$_2$	355/ 345	450	370/ 520	10	1.76
NO	545/ 510	800	550/ 930	5	2.53
NO$_2$	225/ 245	430	340/ 520	10	1.24
O$_3$	260/ 300	1150	1000/1200	5	1.01

Table 2. Offset, sensitivity and full scale for typical B4 sensors with ISB

Noise

1   These gas sensors are very sensitive to gas and are also very susceptible to EMC pickup. Ideally the sensors would be housed in a Faraday cage, but this is not normally practicable, so shield and ground as best you can. Nearby digital circuits can also disrupt the signal quality.

2   Typical noise at AlphaSense, when calibrating on a bench without additional shielding, but with good power supply is 3 mV (p-p). Digital averaging can reduce this to less than one mV, equivalent to typically 2 ppb. Further reduction of noise can be achieved by shielding.

3   It is important to decouple your power supply and A/D converter from the ISB. Since the 0V line is shared by the power supply and output, any noise injected by your power supply or reading circuit will appear on the measured signal. We recommend using two decoupling capacitors close to the Molex socket: 10nF and 100nF.

3   Mounting the circuit board

The mounting hole locations and diameters are shown in figure 3 below.

MOUNTING HOLE DIAMETER Ø3.2mm
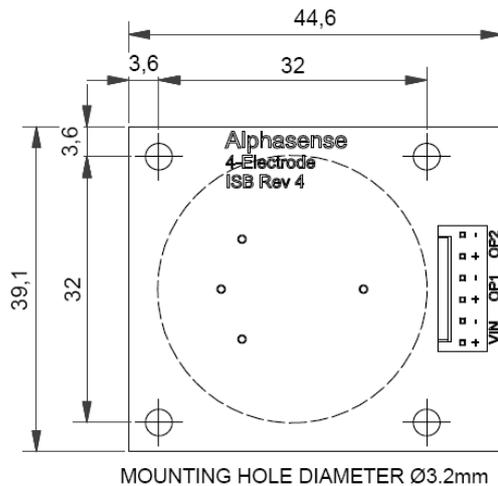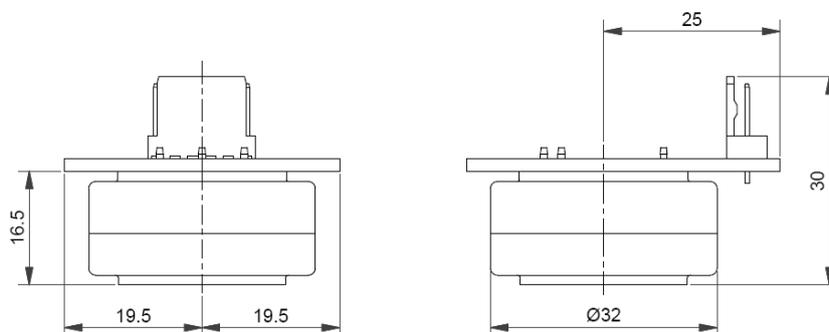
Figure 3. ISB dimensions and mounting hole locations

An optional **ISB Fitting Kit** can be purchased.

Order part number **000- 0ISB-KIT**. The kit includes:

4x pillars	16.0 mm length, M3 tapped
4x washers	M3: fits between pillar and ISB to achieve 16.5 mm pillar height
4x screws	M3 x 6
1x header	Molex 22-23-2061, 6-way, Series KK6373
	Other Molex part references:
	Housing: Molex 22-01-2065, Series KK6471
	Crimp: Molex 08-50-0032

4   Correcting the data using a spreadsheet

The two DC signals can be measured at any desired interval. It is normal to measure frequently and apply a smoothing algorithm to digitally filter noise.

The method for determining the concentration depends on whether you have purchased sensor with ISB or sensor and ISB separately. AlphaSense recommends purchasing the ISB and sensor together- this allows us to measure accurately the zero gas voltage before shipping.

4.1   Measuring when the ISB and sensor were shipped together

Create a spreadsheet similar to the layout below:

	Vo (OP1)		Vo(OP2)		mV/ppm		
Time	**WE (OP1) WE- Vo**		**Aux Aux-Vo (OP2)**		**ppm**	**We-Aux**	**ppm**

Each column is specified as:

Column	Label	Cell data	Comments
A	Time	From your data acquisition system	Sampling faster than 1 second is rarely useful unless it reduces noise.
B	WE (OP1)	mV from ISB channel 1	0.1 mV resolution is ideal
C	WE-Vo	Column B- Vo (constant specified on ISB bag label)	Subtract the WE offset voltage- typical values are the second column in table 2.
D	Aux (OP2)	mV from ISB channel 2	0.1 mV resolution is ideal.
E	Aux-Vo	Column D- Vo (constant specified on ISB bag label)	Calculates the Aux offset voltage shift- typical Vo are the second column in table 2.This difference is a few mV.
F	ppm	Column C * sensitivity (specified on ISB bag label)	ppm calculated from the sensitivity constant (mV/ppm), corrected for offset voltage but not the auxiliary electrode.
G	WE-Aux	Column C – Column E	Correction for any drift in the auxiliary and WE (as mV)
H	ppm	Column G * sensitivity (specified on ISB bag label)	ppm, corrected for offset drift

Table 3. Typical data spreadsheet layout and cell assignment

4.2 Measuring when the ISB and sensor were shipped separately

If the ISB and sensor were shipped separately then set up the same spreadsheet as above, but the zero voltage will be for the ISB only and does not include the sensor. You must measure the zero voltage with the sensor connected to the ISB:

Plug sensor into ISB and apply 6 VDC to power the sensor/ISB pair.

1   Allow to stabilise in clean air for at least 6 hours.
2   Apply zero air (synthetic air or scrubbed/ cleaned zero air) for 20 minutes.
3   Record Vo for both WE (OP1) and Aux (OP2). Enter these values in cells C1 and
     E1.

Additionally, the sensor is calibrated as nA/ ppm but this must be converted to mV/ppm. The last column in Table 2 lists the scaling constant which must be applied for your sensor type. The ISBs have a gain that is repeatable ±1.2% (95% confidence interval) so this conversion constant is the same for all ISBs for a specific sensor/ gas.

4.3 Recalibration

The ISB with sensor calibration has been measured before leaving the factory, but environmental conditions and sensor drift mean that periodic checking of the calibration may be required.

Also, at low ppb concentrations both temperature and humidity will affect the offset voltage of both the WE and Auxiliary electrodes. Previously it was thought that simple subtraction of the Auxiliary would correct for ambient changes but this is not true. Contact AlphaSense for assistance in use of the correct method for compensation in your application.

4.3.1 Zero correction

 Follow the procedure in 4.2 above and modify the Vo mV in your spreadsheet after zero calibration. Be careful that the zero air you use is very clean: ambient or lab air is not sufficiently clean to be used as a zero calibration air source.

4.3.2 Gain/ sensitivity correction

Unless you have access to an accurate 1 ppm or less gas supply, it is advised to return

(sensor + ISB) to AlphaSense for gain recalibration.

End of User Manual

12 Appendix B: Response time steps
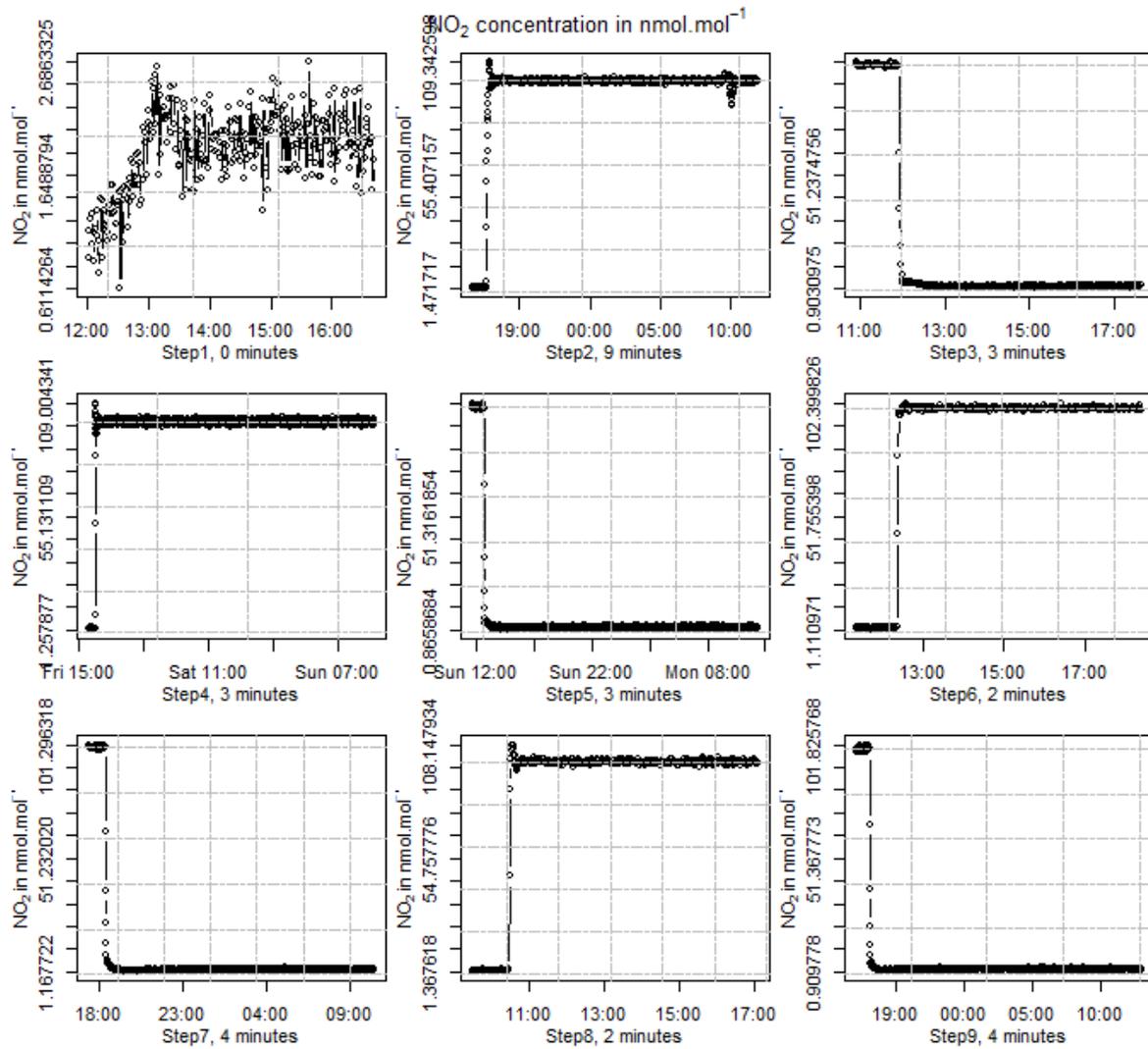
Appendix C, Figure 1: Response time of the whole exposure chamber
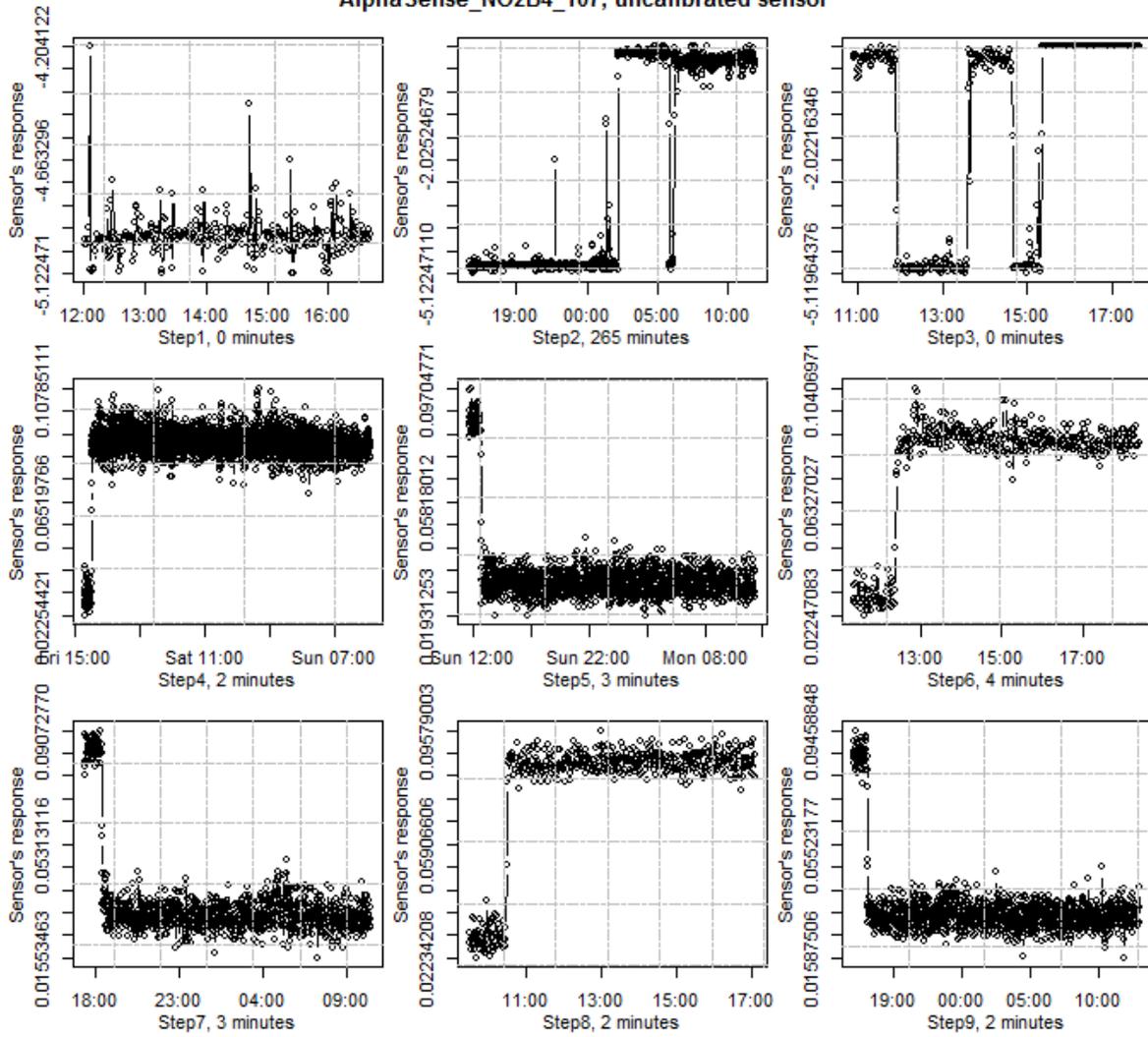
Appendix C, Figure 2: Response time of B4_107
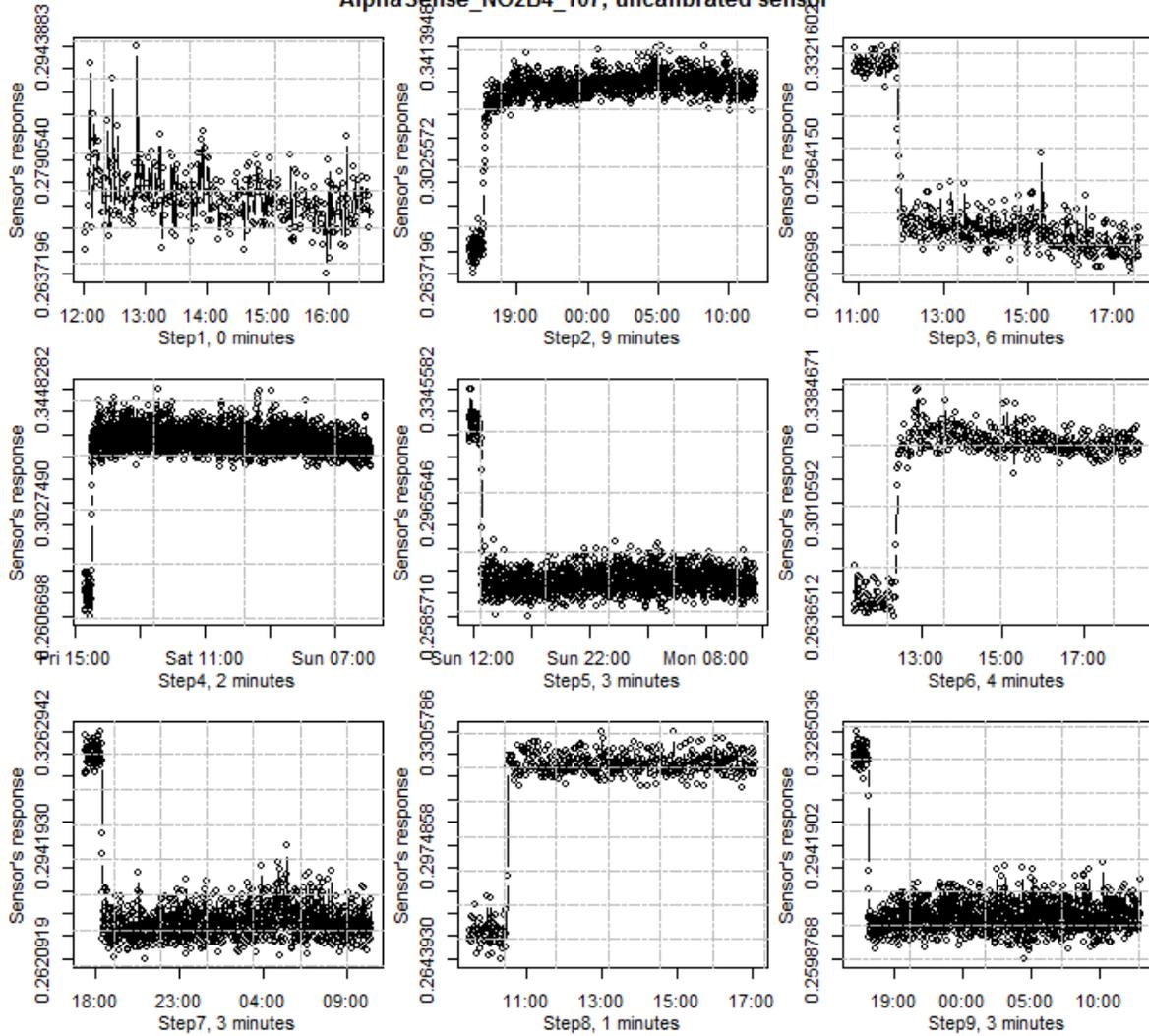
Appendix C, Figure 3: Response time of B4_107_OP1
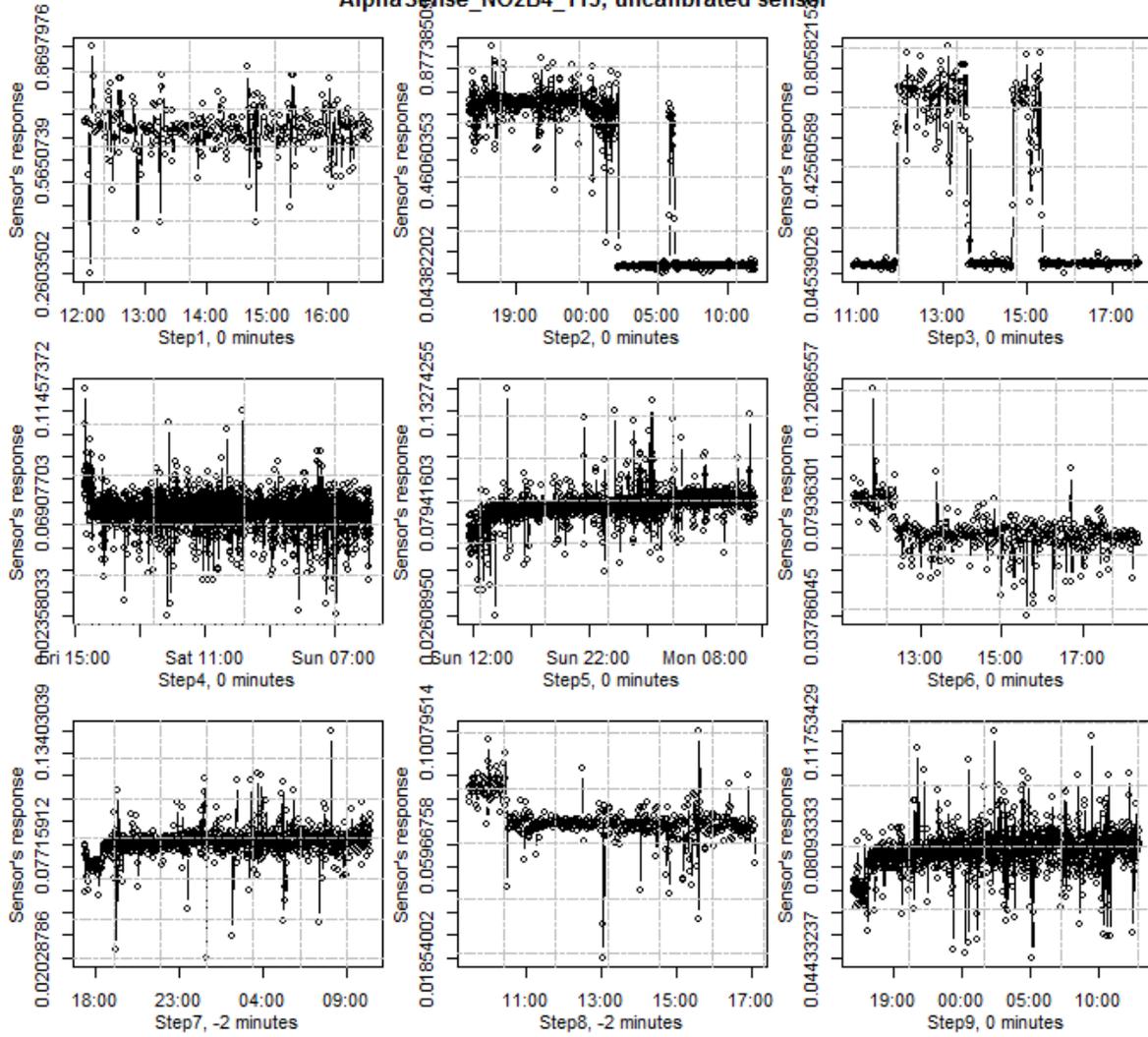
Appendix C, Figure 4: Response time of B4_113
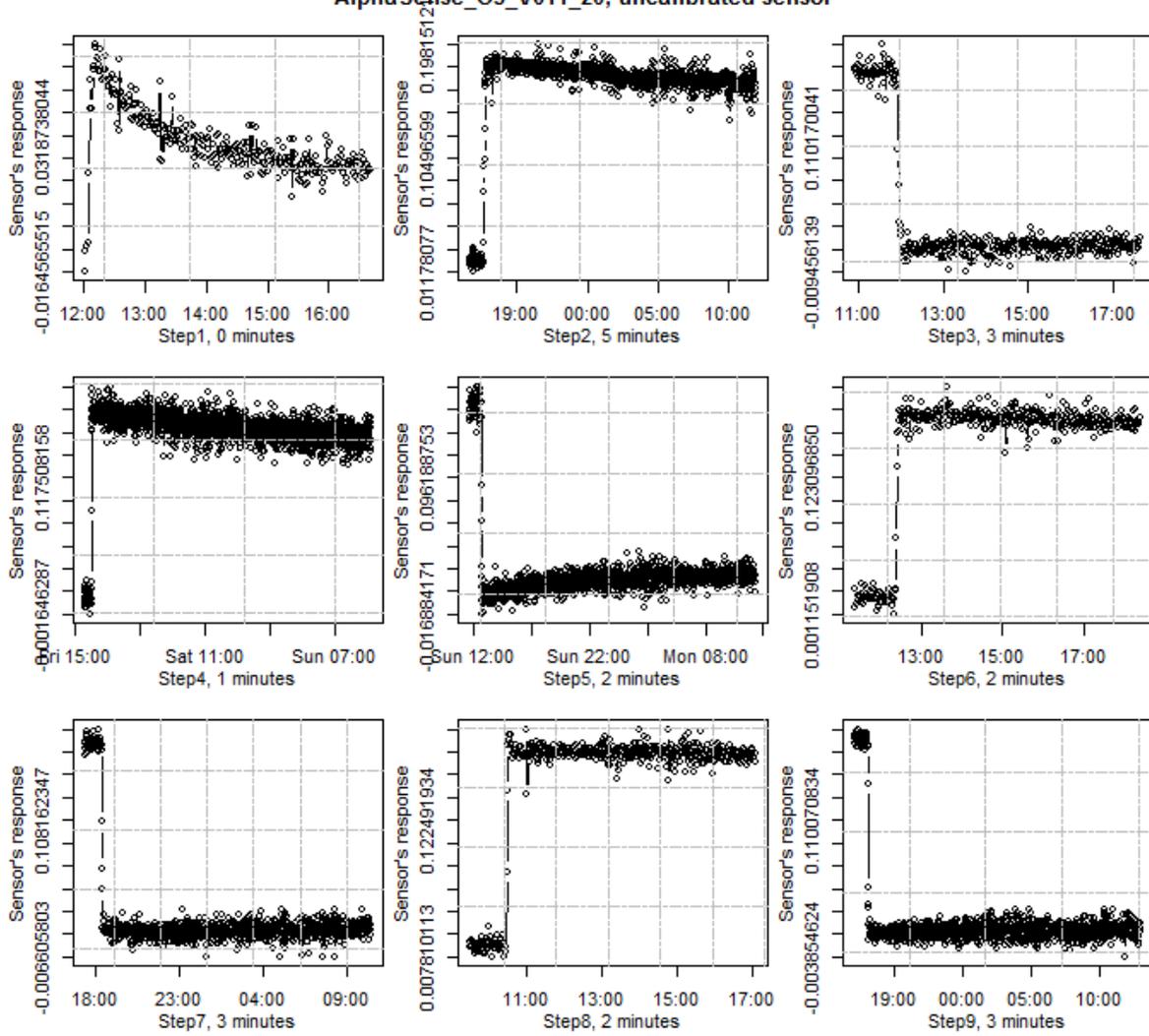
Appendix C, Figure 5: Response time of O3_V011_20

The European Commission's science and knowledge service
Joint Research Centre

JRC Mission

As the science and knowledge service of the European Commission, the Joint Research Centre's mission is to support EU policies with independent evidence throughout the whole policy cycle.

EU Science Hub
ec.europa.eu/jrc

@EU_ScienceHub

EU Science Hub - Joint Research Centre

EU Science, Research and Innovation

EU Science Hub

Publications Office
of the European Union