European
Commission

JRC TECHNICAL REPORTS

Protocol of evaluation and calibration of low-cost gas sensors for the monitoring of air pollution

MACPoll

L. Spinelle, M. Aleixandre and M. Gerboles

2013

Report EUR 26112 EN

Joint
Research
Centre

European Commission
Joint Research Centre
Institute for Environment and Sustainability

Contact information
Michel Gerboles
Address: Joint Research Centre, Via Enrico Fermi 2749, TP 442, 21027 Ispra (VA), Italy
E-mail: michel.gerboles@ec.europa.eu
Tel.: +39 0332 78 5652
Fax: +39 0332 78 9931

http://ies.jrc.ec.europa.eu/
http://www.jrc.ec.europa.eu/

JRC83791

EUR 26112 EN

ISBN 978-92-79-32691-2 (pdf)

ISSN 1831-9424 (online)

doi: 10.2788/9916 (online)

Luxembourg: Publications Office of the European Union, 20xx

Printed in 2013

Summary

Metrology for Chemical Pollutants in Air (MACPoll) is a joint research project of the European Metrology Research Programme of EURAMET that among other activities deals with low-cost gas sensors for air quality monitoring. Gas sensors are identified as emerging measuring devices for “indicative measurements” regulated in the Air Quality Directive. Compared to reference measurements, gas sensors would allow air pollution monitoring at a lower cost. The Directive allows using indicative measurements without restriction in the zones where the upper assessment threshold (UAT) is not exceeded while they permit a reduction of 50 % of the minimum reference measurements where the UAT is exceeded. The Directive does not specify any indicative method but it requires to demonstrate that they can meet a data quality objective (DQO) that is about twice less stringent than the one of reference methods. The DQO is defined as a relative expanded uncertainty. Since the Directive does not give any guidance for this demonstration, within MACPoll it has been decided to draft a protocol for the evaluation of gas sensors.

The protocol requires to identify the sensor, manufacturer and supplier, model, p/n, test board, power supply, data acquisition, treatment and processing and other relevant information like the heater and cycle temperature, the protection box and/or sensor holder. The evaluation of the sensor is carried out against a limit or target value (LV) defined in the Directive with a corresponding averaging time. The selection of the micro-environment (urban, rural or suburban areas for background, traffic or industrial monitoring sites) in which it is planned to use the sensor allows estimating the full scale of the sensor, the abundance of possible gaseous interferences, the average temperature and relative humidity of exposure. Existing information about the sensitivity, selectivity (known interference), stability and existing validation data shall be gathered including, if available, a model equation describing sensor responses according to influencing parameters.

The objective of this evaluation protocol may be different according to the knowledge of the model equation used for the sensors. One may distinguish:

- sensors behaving as a black box: the test results of this protocol can be used to directly estimate the measurement uncertainty induced by the variation of influencing parameters or after setting up a correction function to compensate for these effects.
- sensors for which only a model equation is given with which users shall compute sensor responses: the results of the tests are used to estimate uncertainty after adjusting the coefficients of the model equation.
- nothing is known about the relationship between sensor responses and the concentrations of the tested gas pollutant. In this case, the results of the tests are used to set up a model equation and to estimate the resulting measurement uncertainty.

A dynamic system for generating, known concentrations of a test gas is necessary. An exposure chamber of inert materials shall be used for the simultaneous test of several sensors. It must be possible to measure, control and change the rate of airflow through the chamber and the concentration of the test gas, temperature, relative humidity and any added gaseous interference. All parameters shall be controlled independently to avoid the effect of uncontrolled variables on sensor responses are attributed to controlled parameters. The evaluation of sensors shall only rely on the comparison between sensor responses and reference measurements excluding data calculated from the gas mixture generation system.

The response time of sensors is evaluated as 90% of the final stable value, when concentration changes from 0 to 80 % of the full scale. It is used to set the length of all tests of the protocol and to check if the sensor is able to reach stability within averaging time.

Then, a pre-calibration of the sensor is performed at several concentration levels over the full scale, at the average exposure conditions. The objective of this calibration is to eliminate any bias at the mean temperature and relative humidity and to establish a draft model equation if needed.

Then 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, three consecutive days and every 2 weeks during three months of use, respectively. Hysteresis is evaluated by repeating the pre-calibration experiment in an increasing ramp, a decreasing ramp and an increasing ramp of test gas, consecutively. Repeatability figures impose limits on the accuracy of the calibration. The short term stability is used to set the maximum time between similar tests. If a trend in the long term drift or significant hysteresis or interference (see below) effects are identified, they might be included into the model equation or treated as sources of uncertainty.

The next step is the identification of significant interferences. The tests are all performed one at time at the mean concentration of the test gas with all influencing variables kept constant. Temperature and humidity are tested between mean-10 °C and mean+10 °C by step of 10 °C and between mean-20% to mean+20% by step of 20 % respectively. The sensor response is also tested using filtered air, laboratory air and ambient air. Gaseous interferences are tested at two levels: at zero level and at the expected average values observed in the selected micro-environment. For some sensors, ambient pressure, power supply and wind velocity shall be tested.

Finally a design of experiments for validation/modeling is set up: the test levels of the pre-calibration experiment are tested at 3 temperatures (mean-10 °C, mean and mean+10 °C) under 3 relative humidity (mean-20 %, mean and mean+20%) and at 2 levels of any parameter found to be significant (0 level and its average value for the selected micro-environment). The laboratory measurement uncertainty is estimated with these test results either by evaluating the differences between the black-box sensor values and the reference measurements [4] or by application of the law of propagation of error if a model equation exists. A gas sensor is rejected when the laboratory uncertainty exceeds the DQO.

An appropriate test site of the intended field of application of the sensor is selected regarding its exposure conditions. A test of at least three months should be employed which shall include periods representative of the extremes likely to be encountered in the selected micro-environment of the sensor. The monitoring sites should be equipped with reference methods of measurements for the gaseous pollutants of interest and influencing variables. The field uncertainty is calculated by comparing the sensor results with the reference measurements using the methodology of the Guide for the Demonstation of Equivalence of methods of measurement. A gas sensor is accepted as indicative method if the field uncertainty does not exceed the DQO.

ENV01- MACPoll
Metrology for Chemical Pollutants in Air

Revision of the validation protocol and procedure for calibration

Deliverable number: (4.3.3)

Version: 1.0

Date: Jun 2013

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

MACPoll

European
Commission

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

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

1 MACPOLL, TASK 4.3: TESTING PROTOCOL, PROCEDURES AND TESTING OF PERFORMANCES OF SENSORS (JRC, MIKES, INRIM, REG-RESEARCHER (CSIC))

The aim of this task is to validate NO_2 and O_3 sensors in the laboratory, in the field under ambient/indoor air conditions, and when sensors are transported by human beings or vehicles in different micro-environments for the assessment of human exposure. Based on the recommendations of the review (Task 4.1), graphene sensors and a limited number of sensor types and air pollutants will be chosen. At the beginning of the validation a testing protocol will be drafted, which will be improved and refined during the process of validation experience. This task will provide the information needed to estimate the measurement uncertainty of the tested type of sensors. Further, procedures for the calibration of sensors able to ensure full traceability of measurements of sensors to SI units will be drafted.

Description of work:

- Sensors shall be exposed to controlled atmospheres of standard gas mixtures of the selected pollutant in exposure chambers. Lower detection limits, response time, poisoning points, hysteresis, etc., shall be evaluated according to the developed testing protocol. Based on the test results, the testing protocol may be improved while validating. After laboratory tests, the sensors shall be exposed and tested in real atmospheres and conditions.
- INRIM and MIKES will carry out the initial laboratory evaluations of the new graphene sensors. JRC and the REG-Researcher (CSIC) will carry out the validation. The laboratory validation will endeavour to find a solution to the current problem of validation of sensors. In general, the validation of sensors, which is carried out in a laboratory using synthetic mixtures, or at an ambient air monitoring station, are not applicable to other sites than the one used during validation. In fact, sensors are too sensitive to matrix effects, meteorological conditions and gaseous interferences that change from site to site. It is proposed to extend the common validation of sensors for which users only try to establish the minimum parameter set of sensors to describe their selectivity, sensitivity and stability. As this set of features is not reproducible from site to site, an attempt will be made to fit simplified model descriptions of the phenomena involved in the sensor detection process in exposure chambers and fine tuning these models during experiments with real air matrix in field experiments.
- The laboratory controlled atmospheres will consist of a set of mixtures with several levels of NO_2/O_3 concentrations, under different conditions of temperature and relative humidity and including potential gaseous interferences. The controlled atmospheres of the INRIM and MIKES tests will be 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 will run laboratory tests in order to determine the parameters of 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 will include at least 5 levels of air pollutants, 3 levels of temperature and 3 levels of relative humidity and 2 levels of the chemical interference evidenced in task 4.1.

Activity summary:

- 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))**

- Development of a validation protocol and procedures for calibration of micro-sensors **(CSIC)**
- Laboratory evaluation of the INRIM and MIKES graphene sensors: laboratory tests of NO_2 level, temperature, humidity, response time and hysteresis **(INRIM)**
- Laboratory evaluation of the INRIM and MIKES graphene sensors (laboratory tests of NO_2 concentration, response time, warming time and temperature or humidity effect) **(MIKES)**
- Laboratory tests in exposure chamber and at one field site according to the validation protocol **(JRC).** The site will be representative of the population exposure and should be consistent with the sampling sites in which micro-sensors are likely to be used in future. Unless the bibliographic review will suggest other locations for any reason, the O_3 sensors will be tested at a suburban/rural site (at the JRC). The sampling site for NO_2 will be representative for urban areas or traffic sites where high levels of NO_2 in conjunction with sufficient population density are expected. Nevertheless, the actual location of the field site will be confirmed after the bibliographic review.
- Improvement of graphene sensors based on the results of JRC laboratory tests **(INRIM, MIKES)**
- 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

4.3.3	Revision of the validation protocol and procedure for calibration	REG-Researcher (CSIC)	JRC	Data sets	Jun 2013

2 INTRODUCTION

Gas sensors are identified as emerging measuring devices for “indicative measurements” regulated in the Air Quality Directive [1], because they provide fast cheap results and allow good spatial coverage. Compared to reference measurements, gas sensors would allow air pollution monitoring at a lower cost [2]. The Directive allows using indicative measurements without restriction in the zones where the upper assessment threshold (UAT [1]) is not exceeded while they permit a reduction of 50 % of the minimum reference measurements where the UAT is exceeded. The Directive does not specify any indicative method but it requires to demonstrate that they can meet a data quality objective (DQO [1]) corresponding to a measurement uncertainty that is about twice less stringent than the one of reference methods. Since the Directive does not give any guidance for this demonstration, within MACPoll it has been decided to draft such a protocol using related literature (EN 13528-2:2002) and [3].

3 TERMS AND DEFINITIONS

For the purpose of this protocol of evaluation the following terms and definitions apply.

ambient air
outdoor air in the troposphere, excluding indoor air and workplaces.

averaging time
period of time for which a limit value is associated in the air quality Directive [1] which shall be equal or higher than four times the response time of the gas sensor.

bias
difference between the expectation of the test results and an accepted reference value [ISO 3534-1]. Estimate of a systematic measurement error [JCGM 200: 2008].

calibration
operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication [JCGM 200:2008, 2.39].

NOTE: A calibration may be expressed by a statement, calibration function, calibration diagram, calibration curve, or calibration table. In some cases, it may consist of an additive or multiplicative correction of the indication with associated measurement uncertainty. Calibration should not be confused with adjustment of a measuring system, often mistakenly called “self-calibration”, nor with verification of calibration.

cold start
cold starts tend to occur after a seasonal shutdown or a long maintenance. While the durations can vary, typically a cold start follows a shutdown of at least 48 hours (2 days or more).

combined standard measurement uncertainty

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[1] Directive 2008/50/EC of the European Parliament and the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, Official Journal of the European Union L 152/1 of 11.6.2008. Available at: http://eur-lex.europa.eu

[2] Guide for Local Authorities, Purchasing Air Quality Monitoring Equipment, AEAT/ENV/R/2088 Issue 2, August 2006, UK

[3] Guide to the demonstration of equivalence of ambient air monitoring methods, Report by an EC Working, Group on Guidance

standard measurement uncertainty that is obtained using the individual standard measurement uncertainties associated with the input quantities in a measurement model [JCGM 200:2008 2.31].

coverage factor
number larger than one by which a combined standard measurement uncertainty is multiplied to obtain an expanded measurement uncertainty [JCGM 200:2008, 2.38].

NOTE: A coverage factor is usually symbolized k.

detection limit or limit of detection
measured quantity value, obtained by a given measurement procedure, for which the probability of falsely claiming the absence of a component in a material is β, given a probability α of falsely claiming its presence [4.18 JCGM 200:2008].

NOTE: IUPAC recommends default values for α and β equal to 0.05. The abbreviation LOD is sometimes used. The term “sensitivity” is discouraged for ‘detection limit’.

expanded measurement uncertainty, expanded uncertainty
product of a combined standard measurement uncertainty and a factor larger than the number one [JCGM 200:2008, 2.35].

NOTE: The factor depends upon the type of probability distribution of the output quantity in a measurement model and on the selected coverage probability. The term “factor” in this definition refers to a coverage factor. Expanded measurement uncertainty is termed “overall uncertainty” in paragraph 5 of Recommendation INC-1 (1980) (see the GUM) and simply “uncertainty” in IEC documents.

hot start
while the duration can vary, typically a hot start occurs after a shut down period of a few minutes.

hysteresis
hysteresis is the dependence of a system not only on its current environment but also on its past environment. This dependence arises because the system can be in more than one internal state. To predict its future development, either its internal state or its history must be known. If a given input alternately increases and decreases, the output tends to form a loop [Wikipedia].

measurement repeatability, repeatability
measurement precision under a set of repeatability conditions of measurement [JCGM 200:2008, 2.21].

repeatability condition of measurement, repeatability condition
condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time [JCGM 200:2008, 2.20].

NOTE: A condition of measurement is a repeatability condition only with respect to a specified set of repeatability conditions. In chemistry, the term “intra-serial precision condition of measurement” is sometimes used to designate this concept.

measurement reproducibility, reproducibility
measurement precision under reproducibility conditions of measurement [JCGM 200:2008, 2.25].

NOTE: Relevant statistical terms are given in ISO 5725-1:1994 and ISO 5725-2:1994.

reproducibility condition of measurement, reproducibility condition

condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects [JCGM 200:2008, 2.24].

NOTE: The different measuring systems may use different measurement procedures. A specification should give the conditions changed and unchanged, to the extent practical.

selectivity of a measuring system, selectivity
property of a measuring system, used with a specified measurement procedure, whereby it provides measured quantity values for one or more measurands such that the values of each measurand are independent of other measurands or other quantities in the phenomenon, body, or substance being investigated [JCGM 200:2008, 4.13].

NOTE: In chemistry, the measured quantities often involve different components in the system undergoing measurement and these quantities are not necessarily of the same kind. In chemistry, selectivity of a measuring system is usually obtained for quantities with selected components in concentrations within stated intervals.

sensitivity of a measuring system, sensitivity
quotient of the change in an indication of a measuring system and the corresponding change in a value of a quantity being measured [JCGM 200: 2008, 4.12].

NOTE: Sensitivity of a measuring system can depend on the value of the quantity being measured. The change considered in a value of a quantity being measured must be large compared with the resolution.

stability of a measuring instrument, stability
property of a measuring instrument, whereby its metrological properties remain constant in time [JCGM 200:2008, 4.19]

NOTE: Stability may be quantified in several ways. In terms of the duration of a time interval over which a metrological property changes by a stated amount. In terms of the change of a property over a stated time interval.

shelf life
a time period so that at the end of the shelf life the results obtained in accordance with the long-term stability experiments (7.4.5.3) shall not differ by more than 10 % from the original [based on EN 13528-2, 5.5].

measurement uncertainty, uncertainty of measurement, uncertainty
non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used [JCGM 200:2008, 2.26].

NOTE 1: Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated.

NOTE 2: The parameter may be, for example, a standard deviation called standard measurement uncertainty (or a specified multiple of it), or the half-width of an interval, having a stated coverage probability.

NOTE 3: Measurement uncertainty comprises, in general, many components. Some of these may be evaluated by Type A evaluation of measurement uncertainty from the statistical distribution of the quantity values from series of measurements and can be characterized by standard deviations. The other components, which may be evaluated by Type B evaluation of measurement uncertainty, can also be characterized by standard deviations, evaluated from probability density functions based on experience or other information.

NOTE 4: In general, for a given set of information, it is understood that the measurement uncertainty is associated with a stated quantity value attributed to the measurand. A modification of this value results in a modification of the associated uncertainty.

warm start
while the durations can vary, typically a warm start occurs after a short maintenance period of typically 1 hour.

zero gas
gas or gas mixture used to produce the zero response of a given analytical procedure or measuring device for a given range of content [ISO 7504:2001, 4.6].

NOTE: Zero gas is used to establish the “zero point” of a calibration curve (see Note 1 of 7.4.1) or to verify the zero indication of a measuring system. The gas or the gas mixture used as zero gas shall contain the calibration component only at a level of content that is insignificant for the application.

Attention is drawn to the fact that the terms Assessment, Limit Value and Pollutant are defined in the Air Quality Directive [1].

4 LIST OF SYMBOLS

$\overline{R}$	Mean sensor response
a, b, n, m, c	Parameters
C	Concentration
C_{imax}, C_{imin}	Maximum and minimum value of the interferences present in the ambient gas
CL	Critical levels for the protection of the vegetation
C_r	Concentration calculated from the linear regression
C_t	Gas concentration of the target gas measured
C_{X1}, C_{X2}	Sensor responses when a tested parameter is in condition X_1 or X_2
D_{ls}	Long term drift
D_{matrix}	Variability of the sensors due to air matrix influence
DQO	Data quality objective
D_{ss}	Short term drift
D_t	Sensor response difference after cold, warm and hot start
e_{s0}	Reference saturation vapour pressure
FS	Full Scale
G	Conductivity
GUM	Guide to the Expression of Uncertainty in Measurement
IT/AT	Information and alert thresholds
k	Boltzmann constant
LAT	Lower assessment threshold
l_v	Latent heat of vaporisation
LV	Limit values or target value
M	Molar mass (of water)
N	Number of measurements
P	Pressure
q	Electron charge
R	Individual measurement
R_a	Resistance of the sensor without the humidity and temperature corrections
R_{air}	Resistance of the sensor in air
RH	Relative humidity
RSD	Relative standard deviation
RSS	Sum of square of the relative residuals

R_T	Resistance of the sensor without the humidity correction
Rv	Gas constant (for water vapour)
s(a), s(b),…	Standard deviation of parameter a, b,…
Rs	Sensor response
S_r	Standard deviation of repeatability
T	Temperature
t_0	Time of the initial measurement
t_{90}	Time needed by the sensor to reach 90 % of the final stable value
u	Standard uncertainty
$u(D_{ls})$	Standard uncertainty due to long term drift
$u(D_{ss})$	Standard uncertainty due to short term drift
$u_{r,h}$	Relative combined uncertainty due to the hysteresis of sensors
u(int)	Standard uncertainty associated to a gaseous interference
u(lof)	Standard uncertainty of lack of fit
u(ref)	Standard uncertainty of the reference measurements of the test gas
$u(x_i)$	Standard uncertainty of the reference measurements
$u(X_P)$	Standard uncertainty associated to pressure
$u(X_{RH})$	Standard uncertainty associated to humidity
$u(X_T)$	Standard uncertainty associated to temperature
$u(Y_i)$	Standard uncertainty of the black box model
UAT	Upper assessment threshold
$u_c(f)$	Combined uncertainty calculated according to the GUM
V	Schotty barrier voltage
X	Reference measurements
X_1, X_2	Parameter in condition 1 or 2
$Y_{int,ct}$	Influence of the interference gas at level ct on the sensor response
X_{max}, X_{min}	Maximum and minimum values of parameter X
$Y_{int,z}$	Influence of the interference gas at zero level on the sensor response
Y	Sensors values
ρ	Residuals
$\rho_{max,LV}$	Maximum residual of the model at LV

5 REFERENCES

EN 13528-2:2002, Ambient air quality. Diffusive samplers for the determination of concentrations of gases and vapours. Requirements and test methods. Specific requirements and test methods

ISO 14956:2002, Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty

ISO 3534-1:2006, Statistics -- Vocabulary and symbols -- Part 1: General statistical terms and terms used in probability

ISO 5725-1:1994, Accuracy (trueness and precision) of measurement methods and results - Part 1: General principles and definitions

ISO 5725-2:1994, Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method

ISO 6145-1:2003 Gas analysis - Preparation of calibration gas mixtures using dynamic volumetric methods - Part 1: Methods of calibration

ISO 6145-2:2001 - Part 2: Volumetric pumps

ISO 6145-4:2004 - Part 4: Continuous syringe injection method

ISO 6145-5:2009 - Part 5: Capillary calibration devices

ISO 6145-6:2003- Part 6: Critical orifices

ISO 6145-7:2009 - Part 7: Thermal mass-flow controllers

ISO 6145-8:2005 - Part 8: Diffusion method

ISO 6145-9:2009 - Part 9: Saturation method

ISO 6145-10:2002 - Part 10: Permeation method

ISO 6145-11:2005 - Part 11: Electrochemical generation

ISO 7504:2001, Gas analysis -- Vocabulary

JCGM, 100:2008. Evaluation of measurement data — Guide to the expression of uncertainty in measurement

JCGM 200:2012, International Vocabulary of Metrology – Basic and General Concepts and Associated Terms (JCGM 200:2008 with minor corrections)

6 PROTOCOL OF VALIDATION OF SENSORS FOR MONITORING AMBIENT AIR POLLUTION AS AN INDICATIVE METHOD

The objective of the evaluation is to determine the laboratory and field measurement uncertainties of the sensor values and to compare theses uncertainties with the DQO of the European Air Quality Directive [1] for indicative method. The DQOs correspond to a relative expanded uncertainty of 30 % for ozone and benzene, 25 % for nitrogen dioxide, nitrogen oxides, sulphur dioxide and carbon monoxide and 50 % for particulate matter (see Annex A). A flow chart depicting the procedure for the validation of sensors is given in Figure 1.

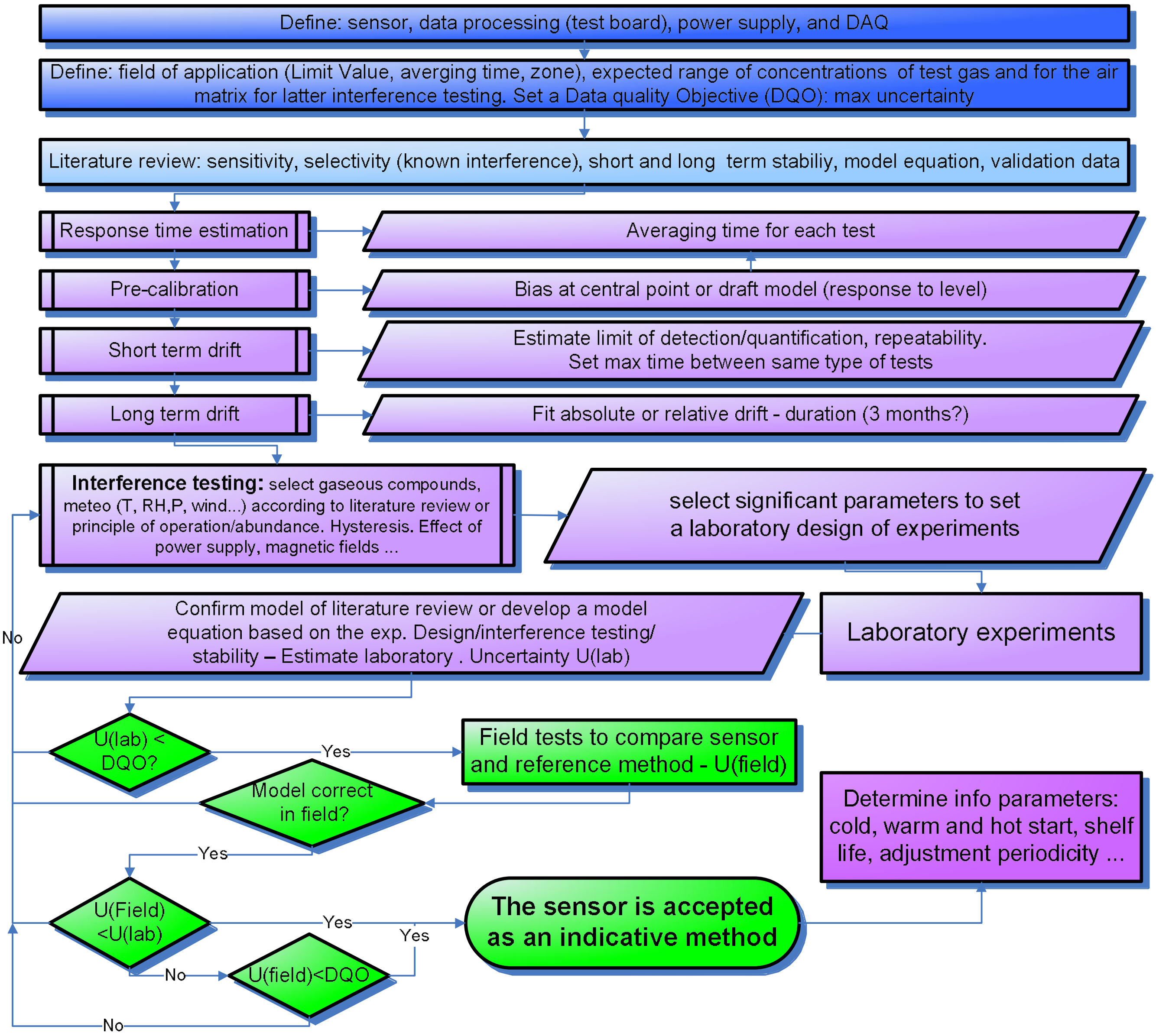

Figure 1: Protocol of evaluation of sensor

Table 1 gives an example of all the tests that shall be performed for the evaluation of micro-sensors following the protocol of evaluation.

The DQO of the European Air Quality Directive shall be evaluated at the limit values or target value (LV) defined in the European Directive and other legislative thresholds including information and alert thresholds (IT/AT), critical levels for the protection of the vegetation (CL), upper assessment threshold (UAT) and lower assessment threshold (LAT). These levels are listed Annex A.

When the DQO cannot be met, the application of the protocol is still of interest since the method produces a full estimation of laboratory and field uncertainties that can be used to assess the performance of sensors.

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

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

Mean represents the average temperature or humidity observed in the field of application.

7 EXPERIMENTS WITHIN THE PROTOCOL OF VALIDATION OF SENSORS

7.1 SENSOR IDENTIFICATION

Clearly define the sensor including:

- manufacturer and supplier.
- sensor model and part number if relevant.
- if relevant data treatment and processing, e.g. zero correction, pre-calibration.
- power supply, test board used and data acquisition.

The supplied information must be sufficient to repeat the experiment under the same conditions so that other information may be necessary for example:

- if relevant, the heater temperature or electrical power applied to the sensor.
- specify if heater temperature is constant or if the sensor is warmed with temperature cycling.
- details of the protection box and/or sensor holder used with the material used for construction.

This information must be given both for the laboratory and field experiments.

7.2 SCOPE OF VALIDATION

The field of application of the sensor in the evaluation must be defined in particular the LV and corresponding averaging time against which the sensor will be evaluated. The LV and averaging time stated in the Air Pollution Directive are given in Annex A. The Directive sets that annual average are computed by averaging hourly values. Therefore for LV based on annual average, the averaging time remains equal to one hour.

Furthermore the micro-environment (urban, rural or suburban areas for background, traffic or industrial monitoring sites...) in which it is planned to use the sensor must be defined. With the selection of microenvironment, one will estimate the expected range of pollutant (full scale, FS) to be monitored and the likely gaseous interference as well as the average temperature and relative humidity under the selected micro-environment. The quantitative description of air composition given in the Annex 3 of D4.3.1 [4] can be used for helping performing these tasks.

Additionally, before using the sensor validation data, it should be ascertained that the sensor is applied in the same configuration in which it has been tested, using the same data acquisition and processing, the same heating wave, protection box and calibration. 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 with the reference method.

7.3 LITERATURE REVIEW

The existing information about the sensitivity, selectivity (known interference), stability of sensors shall be gathered including if available a model equation describing the change of sensor responses according to influencing parameters and laboratory/field validation data against reference measurements.

The objective of this evaluation protocol may be different according to the knowledge of the model equation used for the sensors.

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[4] MACPoll, WP4, Selection of suitable micro-sensors for validation, D4.3.1 , vs 1, Mar 2012

One may distinguish:

- Sensors behaving as a black box: the test results of this protocol can be directly used for validation by estimating the measurement uncertainty resulting of the variation of influencing parameters or after setting up a correction function to compensate for these effects.
- Sensors for which only a model equation is given with which users shall compute sensor responses: the results of the tests are used to estimate uncertainty after adjusting the coefficients of the model equation.
- Sensors for which nothing is known about the relationship between sensor responses and the concentrations of the tested gas pollutant: the results of the tests are used to set up a model equation and to estimate the resulting measurement uncertainty.

7.4 LABORATORY EXPERIMENTS

7.4.1 Generation of gas mixtures

A dynamic system for generating, pre-mixing and delivering a known concentration of a test gas or vapour in air is necessary. Information on suitable procedures for the generation of gas mixtures are given in ISO-6145 series and in [5]. The concentration of the generated calibration gas mixture in the exposure chamber shall be traceable to national standards or shall be verified by a reference method described in a CEN or ISO standard or by any other method which can be demonstrated to give results equivalent to the reference method [3]. Dilution shall be performed using complementary gas coming from synthetic air or filtered air in order to eliminate gaseous interference with a level of purity that does not affect reference measurements and sensor values (see on-going Purity analysis Project, ISO/TC 158/WG 3 N133).

7.4.2 Exposure chamber for test in laboratory

An exposure chamber shall be used for the test of sensors, through which the generated atmosphere is passed and of sufficient capacity to accommodate simultaneously several sensors. It shall be constructed of inert materials such as glass, polytetrafluoroethylene (PTFE) or stainless steel, depending on the substance to be measured. The exposure chamber shall be equipped with systems able to measure, control and change the rate of airflow through the chamber and the concentration, temperature and relative humidity of the test gas and of any added interferent. It must be possible to control all these parameters independently to avoid the effect of uncontrolled variable on sensor responses are attributed to controlled parameters. It can also be necessary to control ambient pressure and wind velocity in the exposure chamber. An example of an exposure chamber is given in Figure 2.

The exposure chamber system shall allow the measurement of gas mixtures using the reference method of measurements (see Annex B of the current protocol) or by any other method which can be demonstrated to give results equivalent to the reference method [3]. The sampling of gas mixture to be measured with the reference method shall be positioned in such a manner that no sampling differences exist between each sensor and the reference method.

The evaluation of sensors shall only rely on the comparison between sensor responses and reference measurements excluding data calculated from the gas mixture generation system. (i.e. from the dilution of certified standards with complementary gas) since absorption on the wall of the exposure chamber or reactions between species can take place and may significantly modify the real concentration level to which sensors are exposed.

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[5] G.O. Nelson. Gas Mixtures: Preparation and Control. Lewis Publishers, US, 1992. ISBN 0-87371-298-6

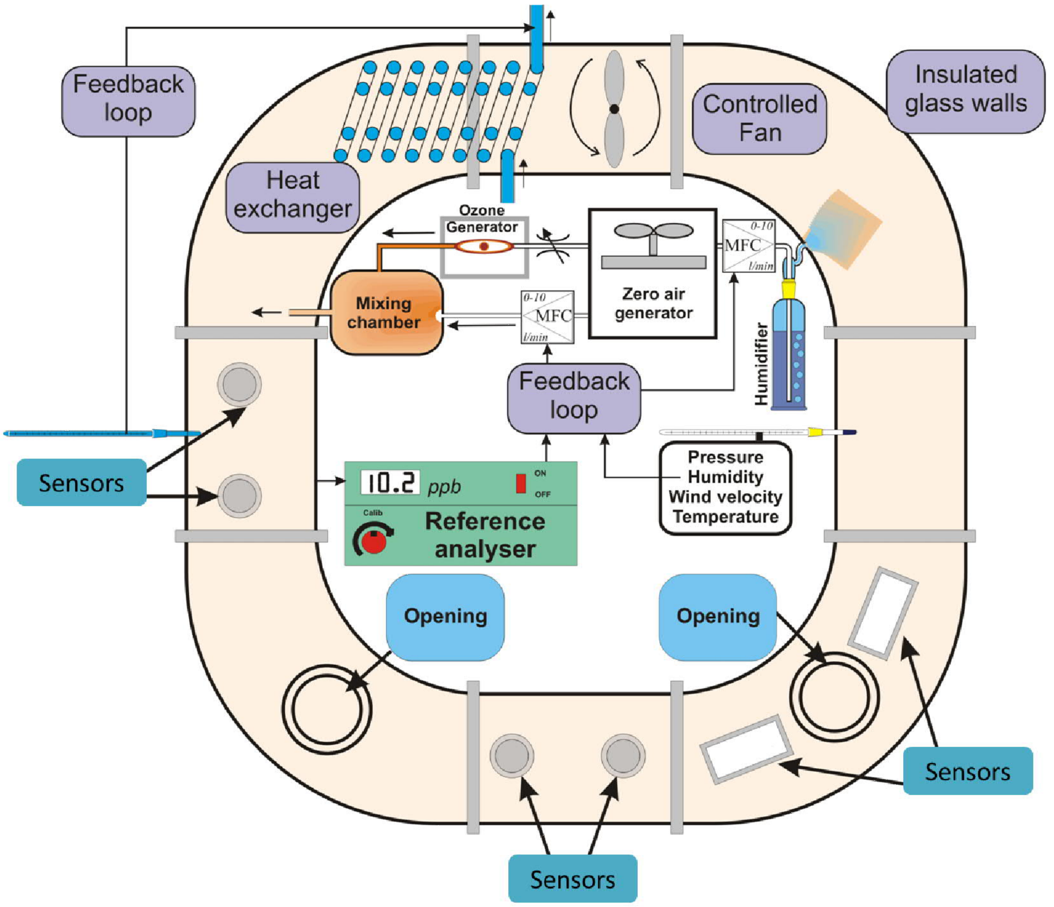

Figure 2: Example of exposure chamber for ozone micro-sensors used in laboratory

Note: Seen the number of tests to be performed, it is suggested to computerize the control of the exposure chamber with a system able to program sets of experiments under different controlled conditions of temperature, humidity, wind velocity, concentration of gas pollutant and interference, criteria for the stability of each parameter and for duration of each step. The computerized system should also be able to merge in databases sensor responses with reference data including gaseous pollutant of interest, interference, meteorological parameters and physical parameters (temperature, humidity etc) with the averaging time of interest.

7.4.3 Response time

The response time of sensors is estimated by t_{90} (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). The full scale of the sensor is determined in 7.2. Three determinations of rise and fall t_{90} are performed. It may be time consuming to wait for a stable response of the sensor at each test so that only 3 repetitions are performed. The response time of the sensors is determined to assess:

- the necessary duration of all following tests of the protocol.
- if the sensor is able to reach stability within the averaging time (defined in 7.2). It is required that the mean t_{90} is less than ¼ of the required averaging time and that t_{90} for increasing and decreasing concentration levels do not differ for more than 10 %.
- if the sensor is suitable for mobile monitoring in micro-environment where air pollutants rapidly change either in time or space, e. g. near local emission or for mobile monitoring.

Normally, the Directive sets that annual average are computed by averaging hourly values. Therefore for LV base on annual average, the averaging time remains equal to one hour.

Note: Sensors with a long response time are still likely to be useful for fixed monitoring in areas where changes in gas pollutant levels are expected to be slow like fixed rural stations. If sensors don't reach a stable response faster than the periodicity of ambient concentration variation, sensor responses can still be representative of an averaged dose.

Table 2 shows the tests to be performed, where the mean relative humidity (RH) and temperature (T) are determined in 7.2. With the 7 experiments, 3 determinations of rise and fall time, t_{90}, are performed. It is important that during experiments all parameters suspected to have an effect on the sensor response are kept under control with relative standard deviation (RSD) of about 2 % at 80 % FS and about 0 for zero gas[6] (e. g. < 0.5 nmol/mol). The same RSD will be applied on all parameters suspected to have an effect during the whole validation protocol. Sensors do not need previous calibration for this experiment. The response time of the reference measurements, is subtracted to the response time of the gas sensor to take into account the stabilisation time in the exposure chamber. An example of response time determination is given in Figure 3.

Table 2: Response time experiments

Test gas levels	RH	T	Interference	Notes
Zero gas	Mean	Mean	none	Until stable response
80% FS	Mean	Mean	none	Until stable response
Zero gas	Mean	Mean	none	Until stable response
80% FS	Mean	Mean	none	Until stable response
Zero FS	Mean	Mean	none	Until stable response
80% max	Mean	Mean	none	Until stable response
Zero FS	Mean	Mean	none	Until stable response

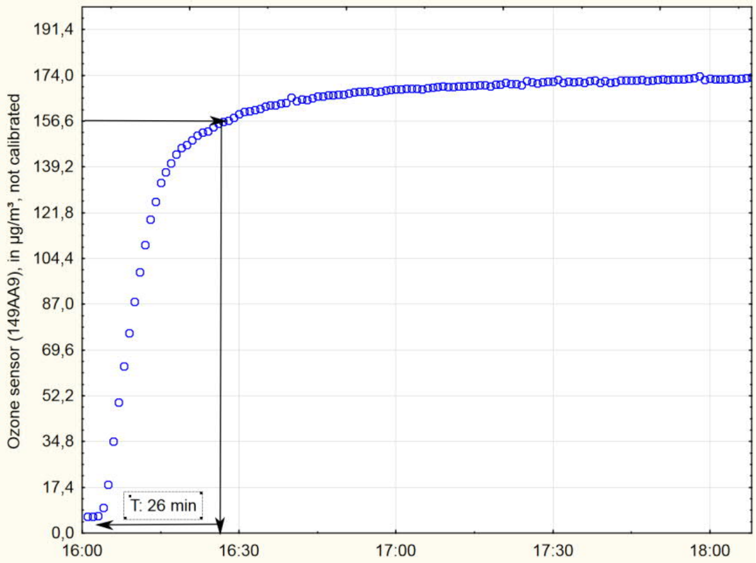

Figure 3: Example of determination of response time: 26 minutes for an ozone sensor with concentration rising from zero to 80 % of full scale

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[6] The zero condition will not be repeated in the rest of the document even though it is meant when mentioning a RSD of 2% at high concentration levels.

7.4.4 Pre-calibration

The objective of this experiment is to make sure that the transformation of sensor responses into air pollutant concentration does not include any bias at the mean temperature and relative humidity. The use of the results of this test may be different according to the available information about sensors. One may distinguish:

- Sensor behaving like a black box: in this case the results of the experiment can be used to confirm the sensors black-box measurement, to ask the manufacturer to correct the sensor calibration if needed or to create a calibration correction function.
- The manufacturer supplies a model equation to compute the sensors results. The model equation may only consist in the sole sensitivity of the sensor or a more sophisticated model including correction for temperature and humidity etc. The results of the experiment are used to adjust the coefficients of the calibration function.
- Nothing is known about the relationship between sensor responses and the concentration of gas pollutant. In this case, the regression analysis is applied, with the sensor responses versus the reference data to create a calibration function.

At least 3 levels of test gas shall be used including the LV and among the IT/AT, CL, UAT or LAT (see Annex A). More test levels are necessary if the calibration function is shown not to be linear for example using the following pattern: about 80, 40, 0, 60, 20, 95% of the full scale defined for the sensor. The order of the concentration levels shall be randomised in this experiment to be representative of sensor suffering hysteresis. An example of test levels is given in Table 3 for a calibration of ozone at background site in rural areas.

Table 3: Measurements for pre-calibration experiments, example for ozone sensors with a full scale of 120 nmol/mol

Test levels, nmol/mol	RH	T	Interference	Directive Thresholds	% of FS
90	Mean	Mean	None	IT	~ 80 %
40	Mean	Mean	None		~ 40 %
0	Mean	Mean	None		0 %
60	Mean	Mean	None	LV	~ 60 %
20	Mean	Mean	None	AOT40	~ 20 %
110	Mean	Mean	None	AT	~ 95 %

It is important that during the determination all parameters suspected to have an effect on the sensor response is kept under control with relative standard deviation of about 2 %. This would include the variation of temperature, humidity and other interference gases that should be set to the mean temperature, relative humidity and interference gas level of the selected micro-environment.

The pre-calibration function of the sensor under evaluation is determined by plotting the sensor's responses versus the reference values (see Figure 4). The most straightforward approach for the calibration would be a linear or a more general (like splines) adjustment to the data. Other method would be to use a physical model and adjust the model parameters with the measurement data. Eq. 1 shows one of such models of the response in which the different rates of absorption and desorption are taken into account [7]. G is the sensor conductivity, C the gas concentration and n,

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[7] Wenli Liu, Wencai Ma, Lei Li, Jianming Li, The temperature change in SnO2-based gas sensors during sensing reaction, Sensors and Actuators B: Chemical, Volume 66, Issues 1–3, 25 July 2000, Pages 222-224, ISSN 0925-4005, http://dx.doi.org/10.1016/S0925-4005(00)00367-1

m, a and b are parameters to be adjusted. Other guidance can be found in [8] and in 7.4.7 or for electrochemical sensors in [10].

$$\boldsymbol{G} = \frac{\boldsymbol{a} \cdot \boldsymbol{C}^{\boldsymbol{n}}}{\boldsymbol{1} + \boldsymbol{b} \cdot \boldsymbol{C}^{\boldsymbol{m}}} \qquad \text{Eq. 1}$$

$$\boldsymbol{u}^{2}(\boldsymbol{lof}) = \boldsymbol{\rho}^{2}_{\boldsymbol{max,LV}}/\boldsymbol{3} + \boldsymbol{u}^{2}(\boldsymbol{ref}) \qquad \text{Eq. 2}$$

A standard uncertainty $u(lof)$ shall be estimated for the lack of fit of the calibration function of the sensor. The maximum residual (fitting error) of the model can be used to determine $u(lof)$ according to Eq. 2 where $\rho_{\text{max,LV}}$ is the maximum residual of the model and $u(ref)$ is the uncertainty of the reference measurements of the test gas. More accurate estimations are possible by studying the relationship between residuals and reference measurements.

$u(lof)$ 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 7.4.8) will be used instead. All sensor responses of the next tests of the protocol shall be transformed into gaseous concentration using the pre-calibration function established in this experiment if the sensor does not provide concentration of the test gas or if it has been decided not to use them in the evaluation of the sensor.

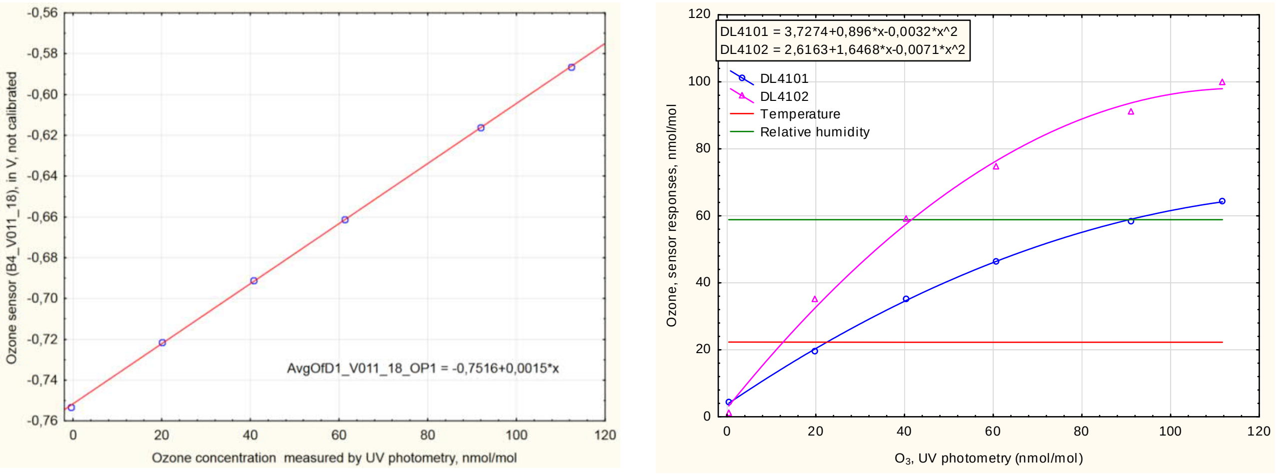

Figure 4: Example of pre-calibration of two types of ozone sensors in the range 0 to 120 nmol/mol, one with a linear response and one with a quadratic response. Setting up of the calibration functions

7.4.5 Repeatability, short and long term drifts

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 3 months of use, respectively. The repeatability figure 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 or the contribution of the short term stability to the measurement uncertainty. The long term stability is used to set the periodicity of recalibration. 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.

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[8] Bibliographic review of commercially available NO/NO2/NOx, SO2, O3, CO, benzene and NH3 sensors excluding graphene sensors. MACPoll project, Deliverable number: 4.1.2 Version: 1 Date: Dec 2011

[10] Fernando H. Garzon, Rangachary Mukundan, Eric L. Brosha, “Solid-state mixed potential gas sensors: theory, experiments and challenges”, Solid State Ionics 136–137 (2000) 633–638

7.4.5.1 Repeatability

The repeatability of the sensor's response shall be evaluated by calculating the standard deviation of sensor values for 3 consecutive averaging time periods when the sensor is exposed to zero gas and 80 % of LV under repeatability conditions. It is important that during the experiment all parameters suspected to have an effect on the sensor response (test gas, temperature, humidity test values and other possible influencing) are kept under control with relative standard deviation (RSD) of about 2 %. Each measurement shall last for the averaging period determined in the response time experiment (7.2). To avoid hysteresis effect, the order of the tests shown in Table 4**Error! Reference source not found.** will be respected.

Table 4 : Measurements for short and long term drift

Gas Concentration	RH	T	Interference	Notes
Zero gas	Mean	Mean	None	t_0
Zero gas	Mean	Mean	None	t_0 + 1 averaging time
Zero gas	Mean	Mean	None	t_0 + 2 averaging time
50% max	Mean	Mean	None	t_0 + 3 averaging time
50% max	Mean	Mean	None	t_0 + 4 averaging time
50% max	Mean	Mean	None	t_0 + 5 averaging time
80% max	Mean	Mean	None	t_0 + 6 averaging time
80% max	Mean	Mean	None	t_0 + 7 averaging time
80% max	Mean	Mean	None	t_0 + 8 averaging time

The calculation of the standard deviation of repeatability is carried out using the Eq. 3 where R_i are individual measurements, $\bar{R}$ is the mean sensor response and N the number of measurements. A higher number of experiments should be carried out in order to get better estimates for repeatability provided that the duration of the experiment does not drastically increase.

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

Repeatability, the likely difference between two measurements made under repeatability conditions, is computed as $2\sqrt{2}s_r$ where s_r is the standard deviation of repeatability for 50 and 80 % of LV. The limit of detection and limit of quantification are expressed as 3 s_r and $10s_r$ where s_r is the standard deviation of repeatability for the blank value. It is necessary to isolate the real variation of the sensor from the one of the influencing parameters. The variance of the sensor would increase with the variation of each influencing variable (e. g. temperature, relative humidity and other gaseous interference...). This justifies the need of the RSD lower than 2 % for the influencing variables.

7.4.5.2 Short term drift

For the short term drift, 3 measurements are carried out at zero, 50 % and 80 % of the LV at least on 3 consecutive days, see Table 5. Each measurement shall last for the averaging time determined within the response time experiment (7.2). It is important that during the experiment all parameters suspected to have an effect on the sensor response (test gas, temperature, humidity test values and other possible influencing) are kept under control with relative standard deviation of about 2 %. To avoid hysteresis effect, the order of the tests shown in Table 5 will be respected.

Table 5 : Measurements for short-term drift

Gas Concentration	RH	T	Interference	Notes
Zero gas	Mean	Mean	None	t_0
Zero gas	Mean	Mean	None	
Zero gas	Mean	Mean	None	
50% max	Mean	Mean	None	
50% max	Mean	Mean	None	
50% max	Mean	Mean	None	
80% max	Mean	Mean	None	
80% max	Mean	Mean	None	
80% max	Mean	Mean	None	
Zero gas	Mean	Mean	None	t_0 + 24 hours
Zero gas	Mean	Mean	None	
Zero gas	Mean	Mean	None	
50% max	Mean	Mean	None	
50% max	Mean	Mean	None	
50% max	Mean	Mean	None	
80% max	Mean	Mean	None	
80% max	Mean	Mean	None	
80% max	Mean	Mean	None	
Zero gas	Mean	Mean	None	t_0 + 48 hours
Zero gas	Mean	Mean	None	
Zero gas	Mean	Mean	None	
50% max	Mean	Mean	None	
50% max	Mean	Mean	None	
50% max	Mean	Mean	None	
80% max	Mean	Mean	None	
80% max	Mean	Mean	None	
80% max	Mean	Mean	None	

The average short term stability is estimated by two differences between sensor responses with 24 hours delay using Eq. 4.

$$\boldsymbol{D_{ss}} = \frac{\sum_{1}^{N-9}\left|\boldsymbol{R_{s,after}} - \boldsymbol{R_{s,berfore}}\right|}{\boldsymbol{N-9}} \qquad \text{Eq. 4}$$

where R_s are the sensor responses at zero, 50 and 80% of the full scale either at t_0 (Before) and 24 hours after (After), N is the number of repeated measurements for all test levels (N=27). D_{ss} are estimated at zero, 50 and 80% of the full scale.

Provided that D_{ss} at zero, 50 and 80% of the full scale are independent between each others, the mean D_{ss} can be used to estimate the contribution of the short term drift to the measurement uncertainty of sensors. For example if a rectangular distribution of D_{ss} is observed, its standard uncertainty $u(D_{ss})$ would be calculated using Eq. 5. Other distribution of D_{ss} would lead to other standard uncertainty according to the methodology given in the Guide for the Expression of Uncertainty GUM. For example if a normal distribution is assumed, then Eq. 6, can be applied with N = 27. If D_{ss} significantly depends on the concentration level of the test gas, the stability should be computed for each level separately or relative stability $\left(R_{s,after} - R_{s,before}\right)/R_{s,before}$ should be computed if a linear relationship can be established.

$$\boldsymbol{u(D_{ss})^2 = s^2 = D_{ss}^2/3} \qquad \text{Eq. 5}$$

$$u(D_{ss})^2 = s^2 = \frac{\sum_1^{N-9}\left(R_{S,after} - R_{S,before}\right)^2}{(N-9)-1} \qquad \text{Eq. 6}$$

The contribution of $u(D_{ss})$ will not be included in the laboratory uncertainty since this uncertainty is included in the uncertainty caused by the long-term stability, see 7.4.5.3.

The maximum time between similar tests is set to 48 hours like in the current experiment (Figure 5) unless $u(D_{ss})$ is found to be too high compared to the DQO. In this case the maximum time between similar tests is reduced until $u(D_{ss})$ is comparable to the repeatability figures (Eq. 3) and can be neglected compared to the long term drift (Eq. 8 to Eq. 10).

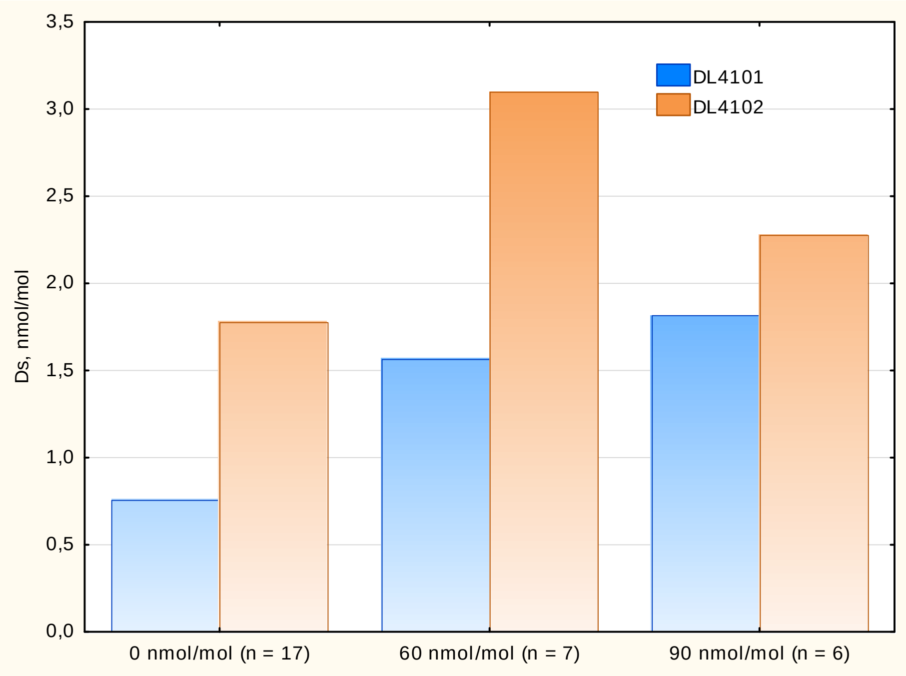

Figure 5: Example of short term drift for two ozone sensors at three O_3 levels. Each bar represents the mean differences between two hourly averages at t and t + 24 hours

7.4.5.3 Long term drift

For the long term drift, the same approach as for the short term stability is carried out on a longer time basis (at least 3 months) measuring every half a month, but without repetition. 3 measurements are carried out at zero, 50 % and 80 % of the LV, see Table 6. Each measurement shall last for the period determined within the response time experiment (7.2). It is important that during the experiment all parameters suspected to have an effect on the sensor response (test gas, temperature, humidity test values and other possible influencing) are kept under control with relative standard deviation of about 2 %. To avoid hysteresis effect, the order of the tests shown in Table 6 will be respected.

Table 6: Measurements for long-term drift

Gas Concentration	RH	T	Interference	Notes
Zero gas	Mean	Mean	None	t_0
50% max	Mean	Mean	None	
80% max	Mean	Mean	None	
Zero gas	Mean	Mean	None	t_0 + ½ month
50% max	Mean	Mean	None	
80% max	Mean	Mean	None	
Zero gas	Mean	Mean	None	t_0 + 1 month
50% max	Mean	Mean	None	
80% max	Mean	Mean	None	
Zero gas	Mean	Mean	None	t_0 + 1 and ½ month
50% max	Mean	Mean	None	
80% max	Mean	Mean	None	
Zero gas	Mean	Mean	None	t_0 + 2 months
50% max	Mean	Mean	None	
80% max	Mean	Mean	None	
Zero gas	Mean	Mean	None	t_0 + 2 and ½ months
50% max	Mean	Mean	None	
80% max	Mean	Mean	None	
Zero gas	Mean	Mean	None	t_0 + 3 months
50% max	Mean	Mean	None	
80% max	Mean	Mean	None	

The average long-term drift stability can be estimated using Eq. 7 where the differences are estimated between t_0 and the end of the series (at least 3 months from the beginning of experiment with N=6) if a trend is evidenced in sensor responses. If no trend is detected (see Figure 6), the average long-term drift stability can be estimated using whatever differences between all consecutive 15-day test results (Eq. 7, N=18). The contribution of the long term stability to the uncertainty of sensor measurement $u(D_{sl})$ is estimated using Eq. 8 if a rectangular distribution can be assumed. Eq. 9 is applied if a normal distribution is observed. Eq. 10 is used if the stability is different at different test gas levels.

$$\boldsymbol{D_{ls}} = \frac{\sum_1^{N-3}\left|\boldsymbol{R_{s,after}} - \boldsymbol{R_{s,berfore}}\right|}{\boldsymbol{N-3}} \qquad \text{Eq. 7}$$

$$\boldsymbol{u(D_{ls})^2 = s^2 = D_{ls}^2/3} \qquad \text{Eq. 8}$$

$$\boldsymbol{u(D_{ls})^2 = s^2} = \frac{\sum_1^{N-9}\left(\boldsymbol{R_{S,after} - R_{S,before}}\right)^2}{\boldsymbol{(N-9)-1}} \qquad \text{Eq. 9}$$

$$\boldsymbol{u(D_{ls})^2} = \frac{\sum_{i=1}^{k}\boldsymbol{(n_i-1)u(D_{ls})_i^2}}{\sum_{i=1}^{k}\boldsymbol{(n_i-1)}} \qquad \text{Eq. 10}$$

If an obvious trend of the sensor's responses can be observed, either a resulting uncertainty, $u(D_{ls})$, can be estimated or the trend can be modelled (e.g. by regression analysis or by studying the trend of the sensor responses at 0, 50 and 80 % of LV over time. The long term stability effect can be included into the model equation of the sensor in order to diminish $u(D_{ls})$. One should not forget to add a contribution for the lack of fit of modelled trend evaluated using the residuals of the trend model. As a long term drift model, one can add a constant term depending on the time for example as in Eq. 11, where c is the slope of the sensor change over time t. Another possibility to compensate for the long term drift is to model R/R_0 over time where R is the sensor's response ($\neq$ 0) and R_0 is the sensor's response at 0 nmol/mol.

$$\boldsymbol{R = a + bC + ct} \qquad \text{Eq. 11}$$

The contribution of $u(D_s)$ to the laboratory uncertainty can be decreased if too high compared to the DQO by setting a periodicity of re-calibration of the sensor to a time length lower than 3 months. This allows applying Eq. 8 to Eq. 10 on a short time period resulting in a smaller $u(D_s)$. Otherwise the periodicity of re-calibration is set to the total duration of the long-term stability experiment that is at least 3 months.

The shelf life of the sensor in its original package shall be equal to the duration of the long term stability allowing that the results obtained does not differ by more than 10 % from the initial results.

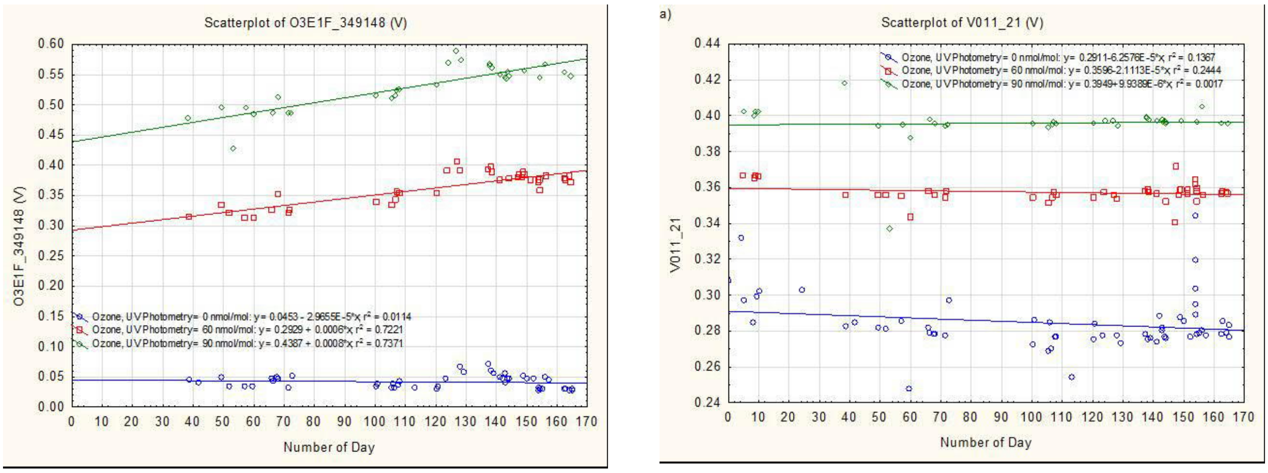

Figure 6: Example of long term drift for ozone sensor: on the left the sensor response increase as a function of the number of days, on the right the sensor does not show any variation over the whole experimental period

7.4.6 Interference

It shall be ensured that the reference measurements are not invalidated by the effect of the interfering covariates being tested.

7.4.6.1 Air Matrix

The air matrix effect can have an important influence on the sensor values. This effect may be different at zero level, which represents the base line of the sensor's response and at a higher level of the test gas. In order to evaluate the effect of air matrix, sensors are exposed to pre-calibration levels using 3 different air matrixes for the dilution of the gas generation system (see 7.4.1): filtered air, laboratory air and outdoor air with all other influencing variables kept at their average values (see Table 7). It is important that during the experiment, all parameters suspected to have an effect on the sensor response (test gas, temperature, humidity test values and other possible influencing) are kept under still control with relative standard deviation of about 2 %.

Table 7 : Experiments for determining the effect of air matrix

Test level	RH	T	Interference	Notes
90	Mean	Mean	None	Filtered air
40	Mean	Mean	None	
0	Mean	Mean	None	
60	Mean	Mean	None	
20	Mean	Mean	None	
110	Mean	Mean	None	
90	Mean	Mean	None	Indoor air
40	Mean	Mean	None	
0	Mean	Mean	None	
60	Mean	Mean	None	
20	Mean	Mean	None	
110	Mean	Mean	None	
90	Mean	Mean	None	Outdoor air
40	Mean	Mean	None	
0	Mean	Mean	None	
60	Mean	Mean	None	
20	Mean	Mean	None	
110	Mean	Mean	None	

The uncertainty contribution $u(D_{matrix})$ is calculated by first fitting a linear model (Eq. 12) for each type of dilution air: zero air, ambient air and indoor air (see Figure 7). In the 3 equations, Rs is the response of the sensor, calibrated according to the pre-calibration equation (7.4.4), a and b are the parameters of the linear model and c_c the reference measurements of the test gas. Then Eq. 13 allows determining c_r, the corrected sensor response calculated from Eq. 12. Eq. 14 gives $u_{r,\mathrm{Matrix}}$, the relative combined uncertainty due to the air matrix effect where u(Rs) 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.

$$Rs = a + b \cdot c_c \qquad \text{Eq. 12}$$

$$c_r = \frac{Rs - a}{b} \qquad \text{Eq. 13}$$

$$u_{r,Matrix}^2 = \frac{u(c_r)^2}{c_r^2} = \frac{u^2(Rs) + s^2(a) + s^2(b) \cdot c_r^2}{b^2 \cdot c_r^2} \qquad \text{Eq. 14}$$

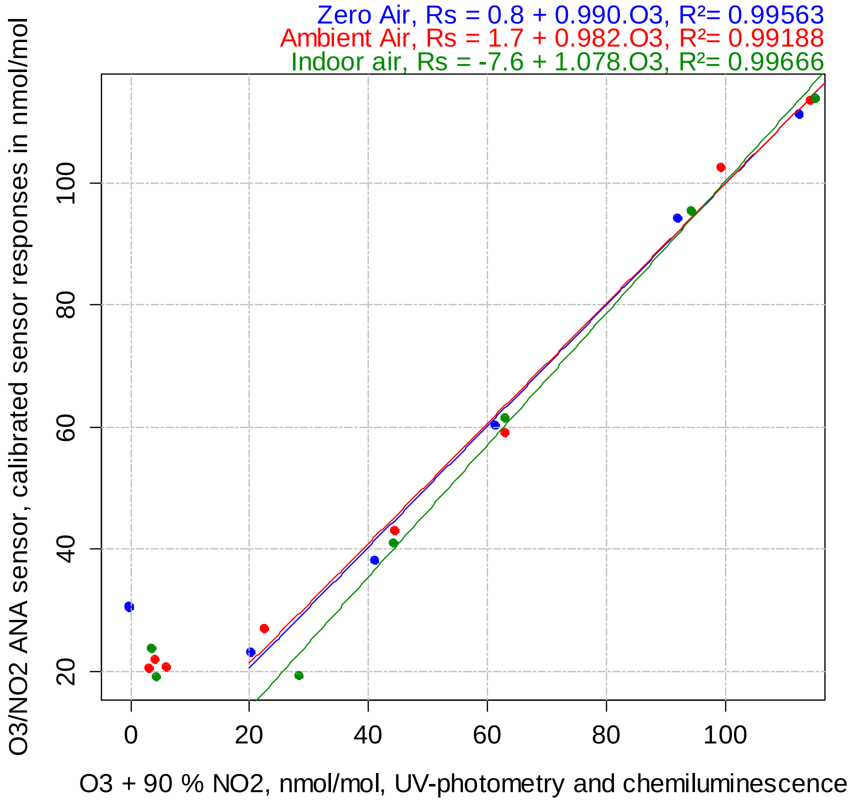

Figure 7: Example of the matrix effect on the response of gas sensor

A simpler approach with only two levels of the test gas (0 and LV) can be used if the quantity of tests to be performed in the full approach (with all the test levels of the pre-calibration experiment) is not sustainable. In this case, Eq. 15 gives the variability of the sensors, D_{matrix}. Rs represents the sensor responses to the different air matrixes, summed over filtered, indoor and ambient air matrix.

$$\boldsymbol{D_{matrix}} = \frac{\sum_1^N |\boldsymbol{R_{s,matrix}} - \boldsymbol{R_{s,filtered}}|}{\boldsymbol{N}} \qquad \text{Eq. 15}$$

If the effect of the matrix cannot be corrected in the model equation of the sensor, the contribution of the matrix effect to the uncertainty of sensor measurement $u(D_{matrix})$ is estimated using Eq. 16 where a rectangular distribution is assumed or using other transformation as mentioned in 7.4.5.2.

$$\boldsymbol{u(D_{matrixls})^2 = s^2 = D_{matrix}^2/3} \qquad \text{Eq. 16}$$

7.4.6.2 Gaseous compounds

Sensors normally suffer from cross sensibility, either positive or negative, to other gaseous species especially for the ones which are abundant in the selected micro-environment. Where possible, the level of the test gas and gaseous interferents shall be measured using reference methods of measurement with a low uncertainty of measurements (uncertainty of less than 5 %) and they should be traceable to (inter)nationally accepted standards (see 7.4.1).

The influence of each interferent shall be determined separately with all influencing variables kept constant during tests. The tests are carried out at the mean temperature and relative humidity and in absence of other interference. After adjustment, the analyser shall be fed with a mixture of first zero gas and second the interferent to be investigated. The level of the interferent should correspond to the average level of the gaseous interference in the selected micro-environment (see D4.3.1 [4]), its maximum value or another more convenient level. This procedure shall be repeated with a mixture of the test gas at concentration called ct (e.g. the LV) and the interferent to be investigated. The mixtures shall be supplied for a time period equal to one independent measurement, and, following this, 3 individual measurements will then be taken of the sensor responses.

The influence quantity of the interferent at zero ($Y_{\text{int,z}}$) and at concentration ct ($Y_{\text{int,ct}}$) are calculated using Eq. 17 and Eq. 18 where

- Y_z is the sensor measurements at 0 nmol/mol of test gas with interferent while Y_0 is the average of the measurements at 0 nmol/mol of test gas without interferent compound,
- Y_{ct} is the average of the measurements of a mixture made of the test gas at concentration ct with interferent while ct represents the average of the sensor measurements at concentration ct of the test gas without interferent compounds.

The influence quantity of the interferent, Yint, at the LV of the test gas is estimated using Eq. 19. The standard uncertainty associated to the interferent, u(int), at the maximum concentration of interfering compound, $c_{i,max}$ is calculated according to Eq. 20 where C_{imin} is the minimum value of the interferences present in the ambient gas.

$$Y_{\text{int},z} = Y_z - Y_0 \tag{Eq. 17}$$

$$Y_{\text{int},ct} = Y_{ct} - c_t \tag{Eq. 18}$$

$$Y_{\text{int}} = \frac{\left(Y_{\text{int},ct} - Y_{\text{int},z}\right) LV}{C_t} + Y_{\text{int},z} \tag{Eq. 19}$$

$$u(\text{int}) = \left| \frac{Y_{\text{int}}}{C_{i\max}} \right| \cdot \sqrt{\frac{C_{i\max}^2 + C_{i\max} C_{i\min} + C_{i\min}^2}{3}} \tag{Eq. 20}$$

When it is not possible to estimate $Y_{\text{int,z}}$ and/or $Y_{\text{int,ct}}$ (for example the interference of NO on O_3 sensor cannot be estimated because of the oxidation of NO in NO_2), the simple approach given in paragraph 8.5.6 of ISO 14956:2002 based on the determination of the sensitivity coefficient of the sensor response to the interferent can be applied.

The interference gases to be measured depend on the target gas and the reported cross sensitivities from the manufacturers. The selected micro-environment also constrains the interference compounds to be tested. For example Table 8 presents the gaseous interference for an ozone sensor at a background site and at rural area. The results of this table show that CO and NO_2 would be the major interference that should be included into the validation experiment (see 7.4.7).

Table 8: Interference gases, experimental conditions and difference of sensibility for an ozone sensor

Interference gases	Interference Concentration	Ozone Concentration	RH	T	Response to interference (nmol/mol)
NO_2	100 nmol/mol	60 nmol/mol	60 %	22 ºC	- 6.51 ± 1.03
NO	100 nmol/mol	0 nmol/mol	60 %	22 ºC	1.55 ± 0.08
CO_2	Purified air	60 nmol/mol	60 %	22 ºC	- 0.6 ± 0.03
CO	8 µmol/mol	60 nmol/mol	60 %	22 ºC	5.11 ± 0.03
NH_3	± 85 nmol/mol	60 nmol/mol	60 %	22 ºC	- 2.00 ± 0.36

7.4.6.3 Temperature effect and Humidity effect

Temperature is tested between mean-10 °C and mean+10 °C by step of 10 °C while humidity is set at his mean value and the test gas is set at the LV. It is important that during the experiment all parameters including test gas and humidity that are suspected to have an effect on the sensor response are kept under strict control with relative standard deviation of about 2 %. Subsequently the same experiment is performed for relative humidity changing between mean-20% to mean+20% by step of 20% respectively while temperature is set at his mean value and the test gas is set at the LV.

It may be that resistive sensors depend on absolute humidity $[H_2O]$ rather than on relative humidity (an index of number of molecules that may be adsorbed on the sensing material) and that electrochemical sensors depend on relative humidity (which is an index of a change of state of water vapour). Knowing temperature and humidity, the concentration of water vapour can be expressed according to Eq. 21 using the Clausius-Clapeyron relation where $[H_2O]$ is the concentration of water vapour in g m^{-3}, e_{s0} is the reference saturation vapour pressure (6.11 hPa at T_0 equal to 273.15 K), RH is the relative humidity, l_v is the latent heat of vaporisation ($2.5\ 10^6$ J), T is the temperature in K, M is the molar mass of water in g, Rv is the gas constant for water vapour (461.5 J K kg^{-1}).

$$[H_2O] = RH\, e_{s_0}\, \exp\left(\frac{l_v}{Rv}\left(1/T_0 - 1/T\right)\right)\frac{M}{R\,T} \qquad \text{Eq. 21}$$

The use of $[H_2O]$ as a covariate allows avoiding the highly anti-correlated temperature and relative humidity parameters. Their high correlation in field tests obfuscates their specific effect on sensor responses. Figure 8 gives an example of two black box sensors that are successful in correcting the ozone concentration while the sensor resistance is both affected by temperature and relative humidity.

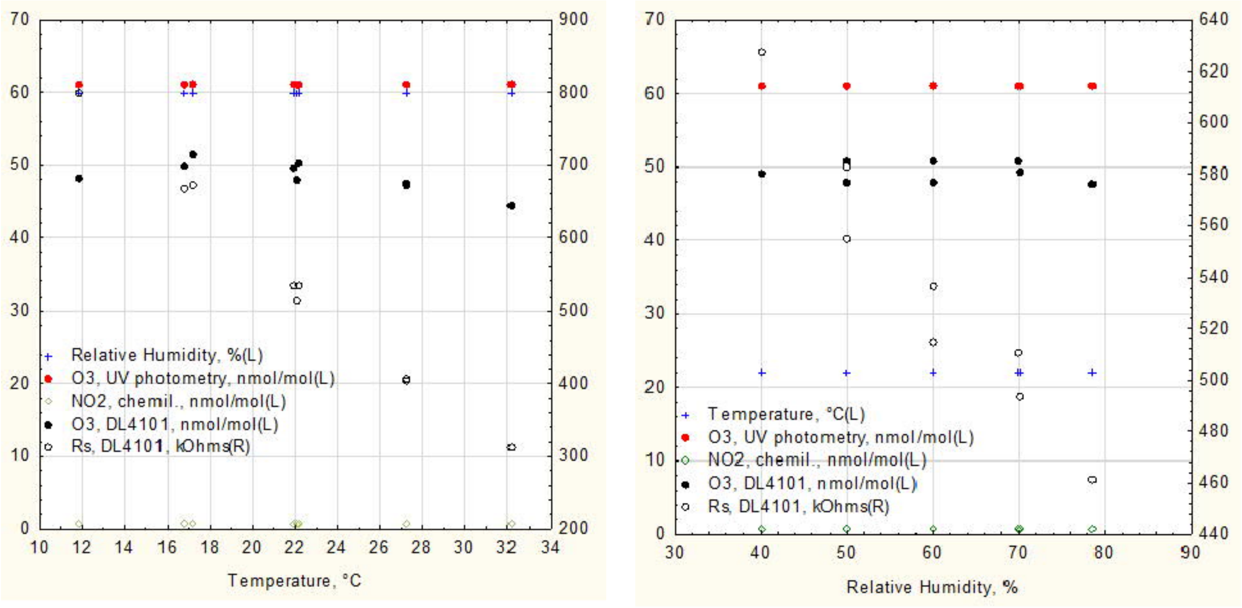

Figure 8: Sensitivity of ozone sensors (DL4101) toward temperature (left) and relative humidity (right)

Typically, a linear model of the variation of the sensor response (Rs) against temperature and humidity can be assumed as in Figure 8. Eq. 22 gives the sensitivity coefficient for the influencing variable, Eq. 23 gives the standard uncertainty u_x to estimate the effect of temperature and humidity on the sensor response.

$$\hat{b} = \frac{n\sum_{i=1}^{n} X_i C_i - \sum_{i=1}^{n} X_i \sum_{i=1}^{n} C_i}{n\sum_{i=1}^{n} X_i^2 - (\sum_{i=1}^{n} X_i)^2} \qquad \text{Eq. 22}$$

$$u_x = \left|\hat{b}\right| \cdot \frac{X_{\max} - X_{\min}}{\sqrt{3}} \qquad \text{Eq. 23}$$

Where X is the tested parameter with sensor responses C_i at level X_i, C_t the test gas level at which the parameter is tested, X_{max} and X_{min} the max and min values encountered in real ambient for parameter X.

If a lack of linearity of the sensor responses versus temperature or humidity is observed, the experiment shall be repeated with a temperature step of 5 °C instead or 10 °c and a humidity step of 10 % instead of 20 % in a hysteresis cycle (see Figure 9). This will add two test points allowing better understanding the type of effect of these parameters. In this case the possible hysteresis effect of these parameters should be studied using the method presented in 7.4.6.5.

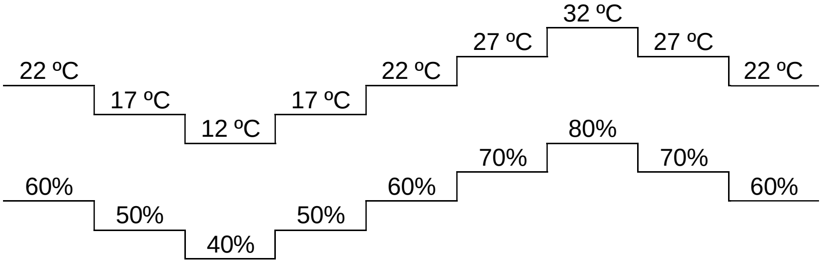

Figure 9: Testing of temperature and humidity effect

7.4.6.4 Pressure effect

Pressure is tested at 2 levels: ambient pressure ± 10 hPa at the LV of the test gas. It is important that during the experiment all parameters that are suspected to have an effect on the sensor response are kept under strict control with relative standard deviation of about 2 %. 3 repetitions of each test shall be performed. Possible effect of pressure changes on the reference measurements shall be studied and corrected if needed, in particular for the chemiluminescence and UV photometry methods that are the reference method for NO_2 and O_3, respectively. Eq. 24 and Eq. 25 are applied to estimate the effect of pressure and its standard uncertainty, $u(X_P)$ that contributes to the laboratory uncertainty.

$$\frac{\Delta C}{\Delta X} = \left| \frac{C_{X_2} - C_{X_1}}{X_2 - X_1} \right|$$

Eq. 24

$$u_x = \left| \frac{C_{X_2} - C_{X_1}}{X_2 - X_1} \right| \cdot \frac{X_{\max} - X_{\min}}{\sqrt{3}}$$

Eq. 25

Where X_n is the tested parameter, with sensor response C_{Xn} at X_n, C_t the test gas level at which the sensor is tested, X_{max} and X_{min} the max and min values encountered in real ambient for parameter Xn giving sensor responses C_{X1} and C_{X2}, respectively.

7.4.6.5 Hysteresis

The estimation of the dependence of sensors toward hysteresis shall be carried out. Each plot corresponds to the hourly average for one O_3 concentration at the mean temperature and mean relative humidity.

Table 9: Measurements for hysteresis

Test gas	RH	T	Interference	Notes
Zero gas	Mean	Mean	None	
20% Full Scale	Mean	Mean	None	
40% Full Scale	Mean	Mean	None	
60% Full Scale	Mean	Mean	None	
80% Full Scale	Mean	Mean	None	
95 %Full Scale	Mean	Mean	None	
80% Full Scale	Mean	Mean	None	
60% Full Scale	Mean	Mean	None	
40% Full Scale	Mean	Mean	None	
20% Full Scale	Mean	Mean	None	
Zero gas	Mean	Mean	None	
20% Full Scale	Mean	Mean	None	
40% Full Scale	Mean	Mean	None	
60% Full Scale	Mean	Mean	None	
80% Full Scale	Mean	Mean	None	
95% Full Scale	Mean	Mean	None	

Sensors can present some hysteresis as the order of the measurements can influence their responses. A hysteresis exposure of the all sensor shall be carried out respecting the following experimental conditions:

- order and concentrations: fixed scales up and down: 0, 20, 40, 60, 80, 95% of the full scale
- 3 repetitions of each concentration
- mean conditions of all influencing variables.

The relative uncertainty contribution on the sensor response $u_{r,h}$ is calculated using the same method as the one described in 7.4.6.1. It is calculated by first fitting a linear model as given in Eq. 12 to each concentration scale (rise, fall and rise again, see Eq. 12). In the 3 equations, Rs is the response of the sensor, calibrated according to the pre-calibration equation (7.4.4), a and b are the parameters of the linear model and c_c the reference measurements of the test gas. Then Eq. 13 allows determining c_r, the corrected sensor response. Eq. 26 gives $u_{r,h}$, the relative combined uncertainty due to hysteresis where u(Rs) is the repeatability of the response and s denotes the standard deviation of the parameters between parentheses determined using their scattering in the three linear models for concentration rise, fall and rise again.

$$u_{r,h}^2 = \frac{u(c_r)^2}{c_r^2} = \frac{u^2(Rs) + s^2(a) + s^2(b) \cdot c_r^2}{b^2 \cdot c_r^2} \qquad \text{Eq. 26}$$

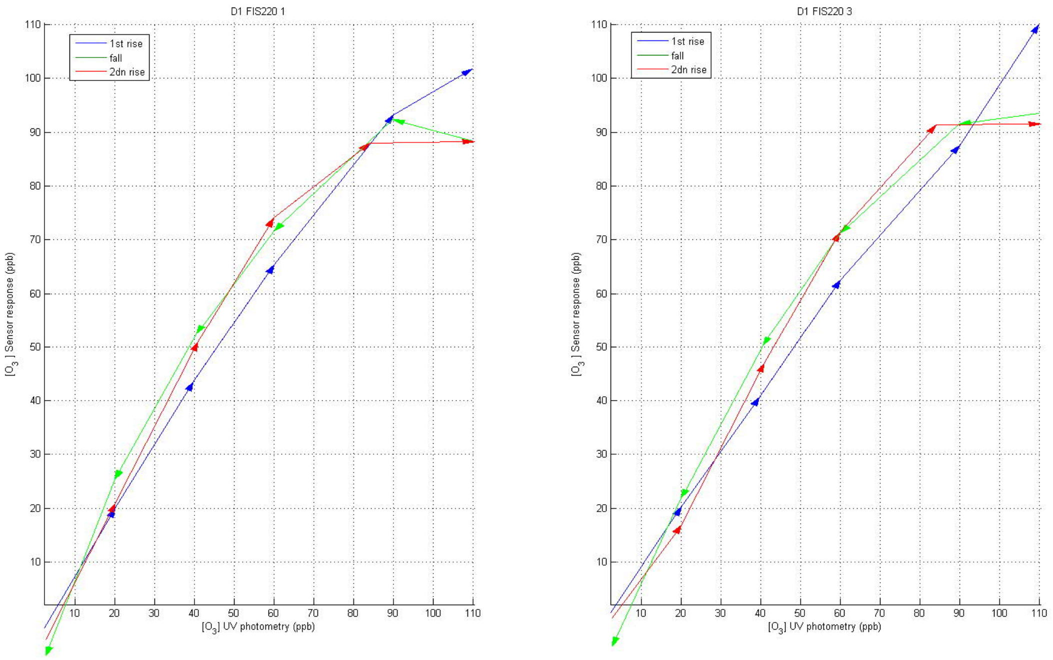

Figure 10: Response of the two ozone sensors during the hysteresis test

The same method (Eq. 12 to Eq. 14 and Eq. 26) could be applied to investigate the possible hysteresis of the sensor responses to temperature and humidity cycles (using data of 7.4.6.3).

7.4.7 Design of experiments for validation/modelling of sensor values

For inorganic gas sensors, temperature and humidity are usually two significant covariates. A design of experiments for validation/modelling is set up: the test levels of the pre-calibration experiment are tested at 3 temperatures (mean-10 °C, mean and mean+10 °C) under 3 relative humidities (mean-20 %, mean and mean+20%) and at 2 levels of any parameter found to be significant (0 level and its average value for the selected micro-environment). The interferences that were found to be significant in 7.4.6 should also be included in the experimental design provided that it will be possible to measure and correct during field tests or if one wants to know interactions between interferences and other covariates. A full or partial factorial design of experiments shall be developed taking into consideration selected significant parameters.

Table 10 gives an example of a full factorial design for an ozone sensor with the following variables: temperature, humidity, NO_2 and obviously O_3. No repetition of tests at the same level is performed (during one averaging time equal to 4 response times) while experiments should be carried out in a randomized order.

Preferably, a physical model, given in the review of the sensors [4], should be fitted to the experimental design results. It is suggested to use the model with the Schotty expression for the conductivity of the thick porous layers of SnO_2 (see Eq. 27, [9-10]), where the exponential term is the temperature correction to the conductivity. A similar approach can be followed with pressure, adding it to the temperature correction (see Eq. 28). A model for the humidity influence can be obtained from Eq. 29 and Eq. 31 in which the resistance is corrected by a constant that will depend on the humidity and temperature.

$$G = const \cdot e^{(-\frac{q \cdot V}{k \cdot T})} \qquad \text{Eq. 27}$$

$$G = const \cdot e^{(-\frac{q \cdot V . P}{k \cdot T})} \qquad \text{Eq. 28}$$

$$R_{air} = C \cdot R_T \cdot H_d \qquad \text{Eq. 29}$$

$$R_T = R_a \cdot e^{(b \cdot T)} \qquad \text{Eq. 30}$$

$$\boldsymbol{Sr} = \boldsymbol{a_0} + \sum \boldsymbol{a_i X_i} + \sum \sum \boldsymbol{a_{i,j} X_i X_j} \qquad \text{Eq. 31}$$

If a physical model cannot be fitted to the experimental design results, a parametric model should be used to compensate for the influence of the temperature humidity and pressure. With a full or fractional design, it is possible to estimate the a_i of main terms of the model and the $a_{i,j}$ of interaction effects with confounded effects in the case of fractional design [11] according to Eq. 31 where Sr is the sensor's response in nmol/mol.

For the same example given in

Table 10, the ozone concentration estimated with the sensor response is calculated using the reverse equation, Eq. 32 , considering only the main effects of the experimental design.

$$\boldsymbol{O_3} = \frac{\boldsymbol{Rs - (a_1 + a_3\, T + a_4\, RH + a_5\, NO_2)}}{\boldsymbol{a_2}} \qquad \text{Eq. 32}$$

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[9] N. Barsan, R. Ionescu, y A. Vancu, «Calibration curve for SnO2-based gas sensors», Sensors and Actuators B: Chemical 19, no. 1-3 (April 1994): 466-469

[10] N. Bârsan y A. Tomescu, «Calibration procedure for SnO2-based gas sensors», Thin Solid Films 259, no. 1 (April 1, 1995): 91-95.

[11] Design and analysis of experiments, Douglas C. Montgomery, John Wiley and Sons, Inc, ISBN 0-471-48735-X

Table 10: Laboratory experimental design for the in nmol/mol.

Temp. °C	Rel. hum. %	O_3	NO_2	Temp. °C	Rel. hum. %	O_3	NO_2
12	40	0	0	12	40	0	95
12	40	20	0	12	40	20	95
12	40	40	0	12	40	40	95
12	40	60	0	12	40	60	95
12	40	90	0	12	40	90	95
12	40	110	0	12	40	110	95
12	60	0	0	12	60	0	95
12	60	20	0	12	60	20	95
12	60	40	0	12	60	40	95
12	60	60	0	12	60	60	95
12	60	90	0	12	60	90	95
12	60	110	0	12	60	110	95
12	80	0	0	12	80	0	95
12	80	20	0	12	80	20	95
12	80	40	0	12	80	40	95
12	80	60	0	12	80	60	95
12	80	90	0	12	80	90	95
12	80	110	0	12	80	110	95
22	40	0	0	22	40	0	95
22	40	20	0	22	40	20	95
22	40	40	0	22	40	40	95
22	40	60	0	22	40	60	95
22	40	90	0	22	40	90	95
22	40	110	0	22	40	110	95
22	60	0	0	22	60	0	95
22	60	20	0	22	60	20	95
22	60	40	0	22	60	40	95
22	60	60	0	22	60	60	95
22	60	90	0	22	60	90	95
22	60	110	0	22	60	110	95
22	80	0	0	22	80	0	95
22	80	20	0	22	80	20	95
22	80	40	0	22	80	40	95
22	80	60	0	22	80	60	95
22	80	90	0	22	80	90	95
22	80	110	0	22	80	110	95
32	40	0	0	32	40	0	95
32	40	20	0	32	40	20	95
32	40	40	0	32	40	40	95
32	40	60	0	32	40	60	95
32	40	90	0	32	40	90	95
32	40	110	0	32	40	110	95
32	60	0	0	32	60	0	95
32	60	20	0	32	60	20	95
32	60	40	0	32	60	40	95
32	60	60	0	32	60	60	95
32	60	90	0	32	60	90	95
32	60	110	0	32	60	110	95
32	80	0	0	32	80	0	95
32	80	20	0	32	80	20	95
32	80	40	0	32	80	40	95
32	80	60	0	32	80	60	95
32	80	90	0	32	80	90	95
32	80	110	0	32	80	110	95

Where a_1 is a constant, a_2 is the relative variation of the response sensor Rs due to change in ozone concentration, a_3T is the variation due to the temperature, a_4RH is the variation due to the relative humidity, a_5NO2 is the variation due to the NO_2 cross sensitivity with O_3, T the temperature, RH the relative humidity and NO_2 the concentration of nitrogen dioxide. When the interaction between the interference gases and the gas being measured is not linear the full factorization of the response should be used according to the general equation: Rs= $a_1 + a_2O_3 + a_3T + a_4RH + a_5\,NO_2 + a_{2,3}O_3.NO_2$.

Figure 11 gives an example of the main effects on a black box sensor using the experimental design given in

Table 10. The developed model does not show dispersion, either physical or parametric is found to be valid only if the residuals between model values and reference measurements are found independent of any of the covariates.

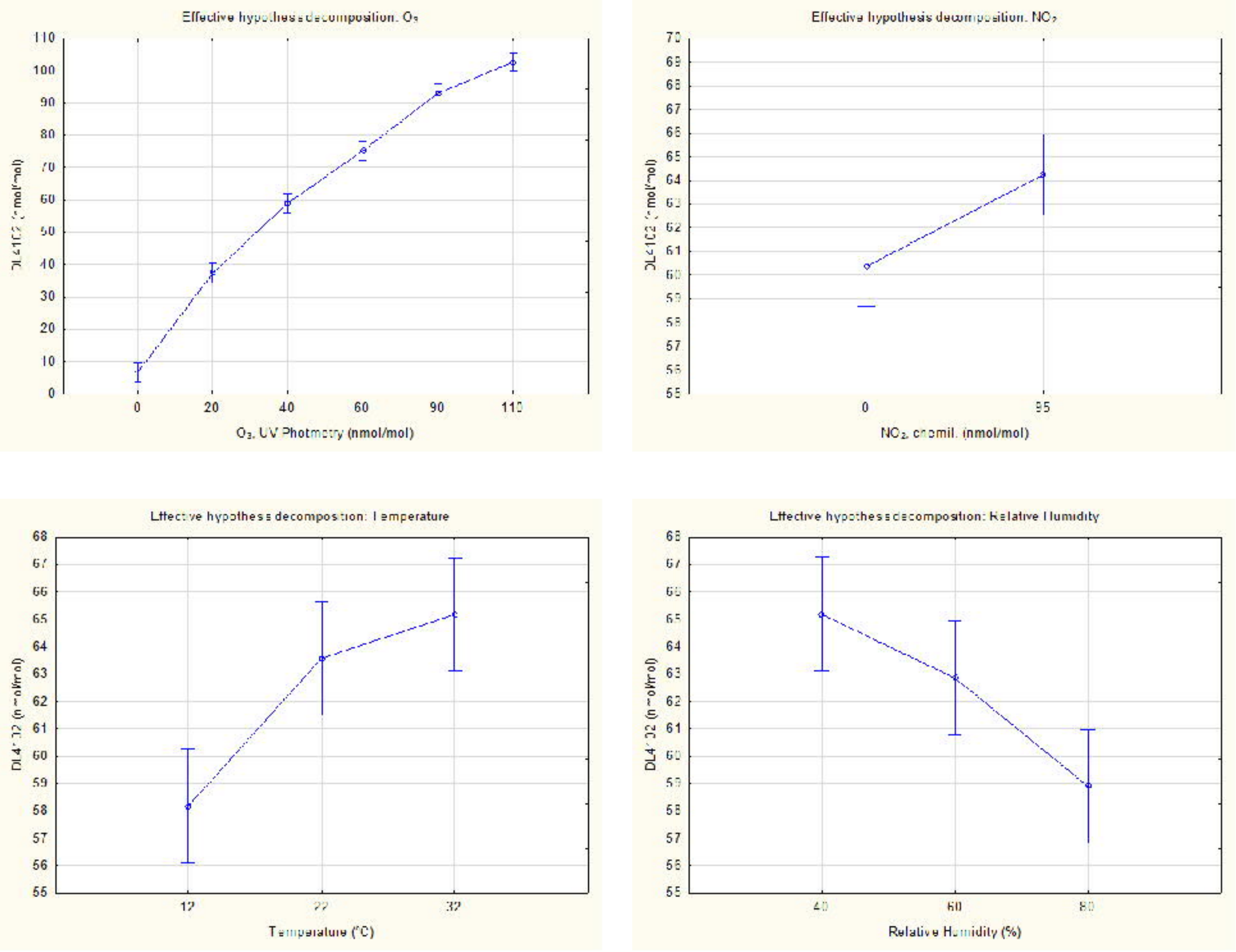

Figure 11: *Example of dependence of ozone sensor response on the tested main effects*

7.4.8 Uncertainty determined under Laboratory conditions

The laboratory uncertainty is calculated as a quadratic sum of the standard uncertainty of long term drift (see 7.4.5.3), interference that were not included in the experimental design or that cannot be corrected in field tests and the standard uncertainty resulting from the lack of fit of the model developed during the experimental design (see 7.4.7) or for the lack of such model for black-box sensor. The uncertainty resulting from the experimental design is assessed in the two following paragraphs. First it is estimated with the test results of the experimental design either by evaluating the differences between the black-box sensor values and the reference measurements [3] and second by application of the law of propagation of error [GUM] if a model equation exists. A gas sensor is rejected when the laboratory uncertainty exceeds the DQO.

7.4.8.1 *Uncertainty when a Black-box sensor is validated*

In order to validate a black-box sensor, the results of the experimental design are used to calculate the uncertainty due to the lack of fit of the sensor results using. Eq. 33 gives the underlying linear model between reference measurements (x) and sensors values (Y). Eq. 34 gives the uncertainty of the sensor values where RSS is the sum of the relative residuals resulting from the orthogonal regression of the sensor values versus reference measurements according to Eq. 35 or Eq. 36, $u^2(x_i)$ is the random uncertainty of the reference measurements (that shall be estimated according to the CEN standards of the reference methods, see Annex B) and a and b are the parameters of the orthogonal regression (see [3]). The last term in Eq. 34 gives the bias of the gas sensor at the limit value/target value x_i .The algorithm to estimate the values for a and b together with their uncertainty is given in the Guide for the demonstration of equivalence.

$$Y_i = a + bx_i \qquad \text{Eq. 33}$$

$$u(Y_i) = \frac{RSS}{(n-2)} - u^2(x_i) + [a + (b-1) \cdot x_i]^2 \qquad \text{Eq. 34}$$

$$RSS = \sum \left(y_i - b_0 - b_1 x_i\right)^2 \text{ if } \left(y_i - b_0 - b_1 x_i\right)^2 \text{ is constant} \qquad \text{Eq. 35}$$

$$RSS = \sum \left(\frac{y_i}{a - b x_i} - 1\right)^2 \text{ if } \left(\frac{y_i}{a - b x_i} - 1\right)^2 \text{ is constant} \qquad \text{Eq. 36}$$

7.4.8.2 *Laboratory uncertainty when a model is established*

When a model equation is available, the law of propagation of error, allowing for correlated quantities Xi, is used to estimate the standard uncertainty u_c(f) for a sensor measuring a gas compound f where r(Xi, Xj) is the correlation between two main effects or interactions of the model equation of the sensor with standard deviation u(Xi) and u(Xj). The correlation between effects allows decreasing the combined uncertainty according to the coefficient of correlation between main effects or interactions. For example, O_3/NO_2 and temperature/humidity are highly anti-correlated. The measurement of uncertainty is estimated at the LV (60 nmol/mol for ozone) using the model equation developed in the experimental design by application of the GUM method.

$$u_c^2(Y) = \sum \left(\frac{\partial Y}{\partial X_i}\right)^2 u^2(X_i) + 2 \sum \sum \frac{\partial Y}{\partial X_i} \frac{\partial Y}{\partial X_j} r(X_i, X_j) u(X_i) u(X_j) \qquad \text{Eq. 37}$$

7.5 FIELD EXPERIMENTS

The field tests are designed to identify additional errors arising from the use of the sensor in the field that are not adequately covered by the laboratory tests.

An appropriate test site of the intended field of application of the sensor is selected regarding its exposure conditions. A test of at least three months should be carried out which shall include periods representative of the extremes likely to be encountered in the selected micro-environment of the sensor. The monitoring sites should be equipped with reference methods of measurements for the gaseous pollutants of interest and influencing variables.

Consideration should be given to location (urban, rural, background), topography (soil covering), environmental conditions (temperature, humidity, wind speed) and likely chemical interferences. For each test, expose at least 2 sensors in an area such that they sample from the same atmosphere as the reference measurements.

7.5.1 Monitoring stations

Describe the monitoring site:

- station type and type area
- geographical location
- reference measurement methods
- authority managing the monitoring site
- description of main emission source, meteorological situation
- give details of typical air pollution levels
- quality control figures
- details of position of sensors and the sampling line of the monitoring station
- information about sensor holder, protection box, auxiliary systems ...

7.5.2 Estimation of field uncertainty

The field uncertainty is calculated by comparing the sensor results with the reference measurements using the methodology described in the guide for the demonstration of equivalence [3], see Eq. 33 to Eq. 36. Initially, if a model equation as being developed in the laboratory experiment, it shall be applied to get the sensor responses during the field test. A gas sensor is accepted as indicative method if the field uncertainty does not exceed the DQO. If the intercept and slope of the linear orthogonal regression line (sensor values versus reference measurements) are not significantly different from 0 and 1, respectively, the laboratory model equation is demonstrated to be valid. Conversely, some more guidance is given in 7.5.3 for field calibration. Figure 12 gives an example of field test for an ozone sensor.

RAW DATA		
Regression	**0,95y + 3,012**	
Regression (i=0)	**0,98y**	
N	2098	n
Outliers	60	n
Outliers	3%	%
Mean CM	62,9	µg/m^3
Mean RM	62,8	µg/m^3
Number of RM > 0.5LV	964	n
Number of RM > LV	299	n
REGRESSION RESULTS (RAW)		
Slope b	**1,053**	**significant**
Uncertainty of b	0,007	
Intercept a	**-3,171**	**significant**
Uncertainty of a	0,545	
r^2	0,909	
Slope b forced trough origin	**1,020**	**significant**
Uncertainty of b (forced)	0,0042	
EQUIVALENCE TEST (RAW)		
Uncertainty of calibration	0,99	µg/m^3
Uncertainty of calibration (forced)	0,50	µg/m^3
Random term	15,07	µg/m^3
Additional uncertainty (optional)	0,00	µg/m^3
Bias at LV	3,14	µg/m^3
Combined uncertainty	15,39	µg/m^3
Expanded relative uncertainty	**25,7%**	***pass***
Ref sampler uncertainty	2,00	µg/m^3
Limit value	120	µg/m^3

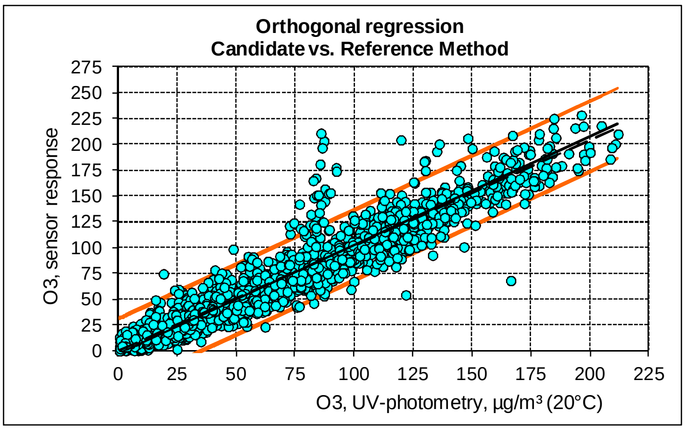

Figure 12: Example of results of field experiment for an ozone sensor

Field tests have to be performed in such a way that the gas sensor and the Reference Method are compared side-by-side. A minimum of 3 months or the shelf life defined in 7.4.5.3 – each one carried out with one or more replicates over a specified period of time – have to be collected with the sensor during the field tests. However, the value of the parameters important to characterise the exposure conditions (test gas, temperature, humidity, interference ...) shall encompass all their expected values during the later use of the sensor. Moreover, at least 20% of the results should be greater than or equal to the upper assessment threshold specified in the Air Quality Directive.

7.5.3 Procedure of calibration

If the laboratory model was demonstrated to be valid in the field test (see 7.5.2), the laboratory calibration is acceptable. The calibration of the sensor can be carried out in laboratory according to the experiments described in 7.4.4 and/or 7.4.7. Calibration is not necessary for black-box sensors.

If the intercept and the slope of the field sensor's responses versus reference measurements (see 7.5.2) were different from 0 and 1 or if the residuals of the orthogonal regression line were found either not normally distributed or dependent on any covariates of the model, then the laboratory model is also invalid. In this case, calibration of the sensor can only be carried out using the field data by comparison to reference measurements to set up a physical or statistical modeling whose validity will be limited to the monitoring site of the field experiment. The duration of the field calibration shall be such that the variations of influencing parameters are the same range than during the later implementation of the sensor.

The re-calibration periodicity defined in the long term-drift should be applied (see 7.4.5.3) unless the field experiment gives evidence of a drift over a shorter period that would result in the measurement uncertainty sensor exceeding the DQO.

7.6 ADDITIONAL INFORMATION: COLD START, WARM START AND HOT START

The sensors may show different response when they are switched on and after a few cycles of measurements are carried out. 3 types of regime shall be studied: cold start, warm start and hot start (see 3) with 3 repetitions for the 2 latter ones. The tests to be performed are listed in Table 11. 2 types of information will be obtained with these experiments:

- the time needed by the sensor to reach a stable response (response time).
- the extent of the possible differences between the sensor responses before and after being shut-down

The response time shall be estimated as explained in 7.4.3. Sensors will have to be warmed up for longer times before producing valid measurements implemented following in order to avoid that sensors are used before they reaches stable response signals.

Eq. 38 is used to calculate the differences between the sensor responses before and after being shut-down D_t are similar what the determination of short drift (see 7.4.5.2). D_t, if not null, will result in a contribution to the uncertainty of measurement of sensors that can be estimated with Eq. 39.

$$D_t = \left| \frac{\sum_{stable} \left(Rs_{stable} - Rs_{start} \right)}{N} \right| \qquad \text{Eq. 38}$$

$$\boldsymbol{u(D_t)^2 = D_{ls}^2/12} \qquad \text{Eq. 39}$$

If D_t is not null for any of the three regimes then $u(D_t)$ shall be added to the field uncertainty with possible exceedance of the DQO. Any shutdown regime resulting in a field uncertainty exceeding the DQO shall be either prohibited or it shall trigger a new calibration of the sensor (see 7.5.3). If any D_t is not null then it is necessary to tracks the date of every switching on and off of the sensor during use.

Table 11 : Experiments for cold, warm and hot starts

Gas Concentration	RH	T	Interference	Rs	Notes
80% Full Scale	Mean	Mean	None	Rs_{start}	Cold start- after 48 hours
80% Full Scale	Mean	Mean	None	Rs_{stable}	
80% Full Scale	Mean	Mean	None	Rs_{start}	Warm start after 1 hour, 3 repetitions
80% Full Scale	Mean	Mean	None	Rs_{stable}	
80% Full Scale	Mean	Mean	None	Rs_{start}	Hot Start after a few minutes, 3 repetitions
80% Full Scale	Mean	Mean	None	Rs_{stable}	

8 TEST REPORT

The test report shall include a reference to this freely available protocol of sensor evaluation. The report shall include the following information:

8.1 SENSOR IDENTIFICATION

- manufacturer and supplier
- sensor model and part number if relevant
- if available, data pre-processing, e.g. zero correction, temperature and humidity correction or pre-calibration
- auxiliary systems such as power supply, test board and data acquisition system.
- if relevant, include information about technical points such as the electrical power applied to the sensor, the heater temperature and whether it works at constant or alternated temperature
- describe the protection box and/or sensor holder, e.g. the shape and material used to protect the sensor

8.2 SCOPE OF VALIDATION

- the type of micro-environment (urban, rural or suburban areas for background, traffic or industrial monitoring sites...) in which it is intended to use the sensor
- the air composition of the selected micro environment with the range of expected levels (Full scale, average temperature and humidity …)
- the limit value (LV) that the sensor shall be able to monitor with the DQO for indicative methods
- its averaging time defined in the European Air Pollution Directive (see Annex A)

8.3 LITERATURE REVIEW

The category under which the sensor falls shall be described according to the following scheme:

- evaluation of a gas sensor behaving as a black box directly providing measurement values in gas concentration with or without a correction function established using the test results of the evaluation protocol
- evaluation of a gas sensor relying on a previously known model equation with or without adjustment of the coefficients of the model equation using the test results of the evaluation protocol
- evaluation of a gas sensor relying on a model equation established with the test results of the evaluation protocol

According to the type of gas sensor and availability of information, the report will list:

- a model equation or a sensitivity figure
- field implementation and comparison with reference method
- known interference and selectivity on the sensor
- short/long term stability and other metrological parameters (repeatability, limit of detection, hysteresis, temperature/humidity effect …)

8.4 LABORATORY EXPERIMENTS

- description of the exposure chamber for test in laboratory
- description of the gas mixture generation system
- a list of the reference analysers used to measure the gas concentration in the exposure chamber with the calibration method and uncertainties

8.4.1 Response time

- the average value of t_{90} in fall and rise in concentrations conditions

- the average of all t_{90}
- the stability of the influencing parameters during test
- the duration of all following tests of the protocol which is defined as 3 times t_{90}
- whether the mean t_{90} is less than ¼ of the required averaging time or not. If this objective is not met, the sensor will have to be discarded. Moreover, the following information will be given:
    - if the sensor is able to reach stability within the averaging time (defined in 2.2)
    - if the difference of t_{90} for the fall and rise time less than 10% (of the longest time)

8.4.2 Pre calibration

- the selected test levels
- a plot of the sensor responses against the test levels at the mean temperature and relative humidity; include the regression equation, its slope and intercept
- the stability of the influencing parameters during test
- the uncertainty of the lack of fit of the pre-calibration experiments u(lof) (see below)
- if the slope and intercept of the regression line is different from 1 and 0, respectively or if the uncertainty of the lack of fit u(lof) is not consistent with the DQO proceed with the following scheme:
    - for black-box type sensor contact the manufacturer for re-calibration or set-up a correction function.
    - for sensor with a known model equation, adjust the coefficients of the model equation to get a slope of 1 and an intercept of 0 and the lowest u(lof)
    - for sensor relying on a model equation to be established, change the equation to reach a better agreement and the lowest u(lof)
- If it is not possible to reach a slope and intercept of the regression line equal to 1 and 0, respectively or if u(lof) remains in consistent with the DQO, the validation study should be stopped.

8.4.3 Repeatability, short and long term drifts

- the repeatability (0, 50 and 80 % FS), s_r and $2\sqrt{2}s_r$
- the corresponding limit of detection and limit of quantification
- the short term stability D_{ss} and its uncertainty contribution $u(D_{ss})$
- the minimum time between similar tests
- the long term stability D_{ls}
- the stability of the influencing parameters during all the tests
- if relevant a model for the long term drift of the sensor response
- the uncertainty contribution resulting from the long term drift $u(D_{ls})$, indicating whether the trend was included into the model equation of the sensor or not
- the periodicity of re-calibration
- if relevant shelf life of the sampler

8.4.4 Interference

- the variability of the sensor D_{matrix} for filtered air, indoor air and outdoor air with its uncertainty contribution $u(D_{matrix})$
- the list of tested gaseous interference, their concentration level, the effect of the interference on the sensor and their uncertainty contribution $u(int)$;
- the scatter plot of the sensor response against temperature, humidity (relative and/or absolute) and pressure; give their main effect $\frac{\Delta C}{\Delta X}$ and their uncertainty u_x

- the presence of hysteresis of the sensor response by a cycling exposure to the different concentration levels of the test gas; give the equations fitted to the rise and fall ramps and the relative uncertainty contribution $u_{r,h}$
- if a lack of linearity of the sensor responses when changing temperature and humidity is observed study the hysteresis of the sensor response by a cycling exposure to the temperature and humidity; give the equations fitted to the rise and fall ramps and the relative uncertainty contribution (calculated as $u_{r,h}$)

All those information will determine the contribution of all parameters in the sensor response and its uncertainty that will be compared to the general requirements.

8.4.5 Experimental design for validation/modelling of sensor values

- list the parameters included in the experimental design
- for each parameter, the levels included in the experimental design
- a table of the experimental design with all trials, the level of each parameter and sensor responses
- fitted physical model or parametric model
- plot residuals between model values and reference measurements against all covariates
- homogeneity, independence of the residuals

8.4.6 Uncertainty determined under Laboratory conditions

- calculate the uncertainties of the sensor measurements for the laboratory experiments according to the following scheme:
  - for a black box sensor, give the lack of fit of the predicted concentrations and the one measured by the reference methods
  - if a physical model or a parametric adjustment is supplied, use the law of propagation of error
- determine if the sensor can meet or not the DQO.

8.5 FIELD EXPERIMENTS

8.5.1 Monitoring stations

- geographical location
- authority managing the monitoring site
- reference measurement methods
- calibration method and quality control
- station type (background, traffic and industrial)
- area type (urban, rural, background)
- topography (soil covering)
- likely chemical interferences
- description of main emission source, meteorological situation
- details of typical air pollution levels
- environmental conditions (temperature, humidity, wind speed)
- details of position of sensors and the sampling line of the monitoring station
- sensor holder, protection box, auxiliary systems ...

8.5.2 Estimation of field uncertainty

- plot the results of experiments:
  - trend over time of sensor responses and covariates of the model
  - scatter plot of the sensor responses versus the reference measurements of the test gas, with the regression line

- indicate if the intercept and the slope are not significantly different from 0 and 1 and if the residual of the orthogonal regression line are independent of the test gas level, laboratory model is found valid. In such a case
    - calculate the field uncertainty
    - evaluate if the uncertainty exceed the DQO (in this case declare that the sensor is a suitable indicative method when use under the same condition as in the evaluation study)
- if the intercept and the slope are different from 0 and 1 or if the residual of the orthogonal regression line depends on the test gas level, then the laboratory model is found invalid
    - either reject the sensor
    - or give a new model equation developed with the field data together with
    - trend over time of sensor responses and covariates of the model
    - scatter plot of the sensor response versus the reference measurements of the test gas, with the regression line

8.5.3 Calibration of Sensor

- black-box sensor should not need calibration!
- indicate if the laboratory model is valid allowing calibration in laboratory
- indicate if a field calibration is possible and allows meeting the DQO
- periodicity of re-calibration

8.6 ADDITIONAL INFORMATION

- response time, D_t and $u(D_t)$ D_t and $u(D_t)$ for cold start
- response time, D_t and $u(D_t)$ D_t and $u(D_t)$ for warm start
- response time, D_t and $u(D_t)$ D_t and $u(D_t)$ for hot start
- indicates if any of these shutdown regimes results in the field measurement uncertainties exceeding the DQO or would need re-calibration

9 ANNEX A

Limit and target values (LV), Data quality objectives (DQO), information and alert thresholds (IT/AT), critical levels for the protection of the vegetation (CL), upper assessment threshold (UAT) and lower assessment threshold (LAT).

Pollutant	Averaging period	DQO	LV, µg/m^3	IT	AT	CL	LAT	UAT
Ozone	Eight hour mean	30 %	120	180	240			
Nitrogen dioxide	One hour	25 %	200		400	30 (NOx)	100	140
	Calendar year	25 %	40				32	26
Carbon monoxide	Eight hour mean	25 %	10 mg/m^3				7	5
Sulphur dioxide	One hour	25 %	350		500	20		
	One day	25 %	125				50	75
Benzene	Calendar year	50 %	5				3.5	2
PM$_{10}$	One hour	50 %	50				35	25
PM$_{10}$	Calendar year	50 %	40				28	20
PM$_{2.5}$	Calendar year	50 %	25					

10 ANNEX B

Reference measurement methods [1]:

The reference method for the measurement of sulphur dioxide is that described in EN 14212:2005 ‘Ambient air quality — Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence’.

The reference method for the measurement of nitrogen dioxide and oxides of nitrogen is that described in EN14211:2005 ‘Ambient air quality — Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence’.

The reference method for the sampling of lead is that described in Section A(4) of this Annex. The reference method for the measurement of lead is that described in EN 14902:2005 ‘Standard method for measurement of Pb/Cd/As/Ni in the PM 10 fraction of suspended particulate matter’.

The reference method for the sampling and measurement of PM 10 is that described in EN 12341:1999 ‘Air Quality —Determination of the PM 10 fraction of suspended particulate matter — Reference method and field test procedure to demonstrate reference equivalence of measurement methods’.

The reference method for the sampling and measurement of PM 2,5 is that described in EN 14907:2005 ‘Standard gravimetric measurement method for the determination of the PM 2,5 mass fraction of suspended particulate matter’.

The reference method for the measurement of benzene is that described in EN 14662:2005, parts 1, 2 and 3 ‘Ambient air quality — Standard method for measurement of benzene concentrations’.

The reference method for the measurement of carbon monoxide is that described in EN 14626:2005 ‘Ambient air quality — Standard method for the measurement of the concentration of carbon monoxide by non-dispersive infrared spectroscopy’.

The reference method for the measurement of ozone is that described in EN 14625:2005 ‘Ambient air quality - Standard method for the measurement of the concentration of ozone by ultraviolet photometry’.

European Commission
EUR 26112 – Joint Research Centre – Institute for Environment and Sustainability

Title: Protocol of evaluation and calibration of low-cost gas sensors for the monitoring of air pollution

Author(s): L. Spinelle, M. Aleixandre and, M. Gerboles

Luxembourg: Publications Office of the European Union

2013 – 44 pp. – 21.0 x 29.7 cm

EUR – Scientific and Technical Research series – ISSN 1831-9424 (online)

ISBN 978-92-79-32691-2 (pdf)

doi: 10.2788/9916 (online)

Abstract

Metrology for Chemical Pollutants in Air (MACPoll) is a joint research project of the European Metrology Research Programme of EURAMET that among other activities deals with low-cost gas sensors for air quality monitoring. Gas sensors are identified as emerging measuring devices for “indicative measurements” regulated in the Air Quality Directive. Compared to reference measurements, gas sensors would allow air pollution monitoring at a lower cost. The Directive allows using indicative measurements without restriction in the zones where the upper assessment threshold (UAT) is not exceeded while they permit a reduction of 50 % of the minimum reference measurements where the UAT is exceeded. The Directive does not specify any indicative method but it requires to demonstrate that they can meet a data quality objective (DQO) that is about twice less stringent than the one of reference methods. The DQO is defined as a relative expanded uncertainty. Since the Directive does not give any guidance for this demonstration, within MACPoll it has been decided to draft a protocol for the evaluation of gas sensors.

LB-NA-26112-EN-N

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Publications Office

ISBN 978-92-79-32691-2

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