European Commission

JRC TECHNICAL REPORTS

Evaluation of the Laboratory Comparison Exercise for NO, NO_2, SO_2, CO and O_3 Langen (D) 1st – 6th September 2013

EC Harmonization Program for Air Quality Measurements

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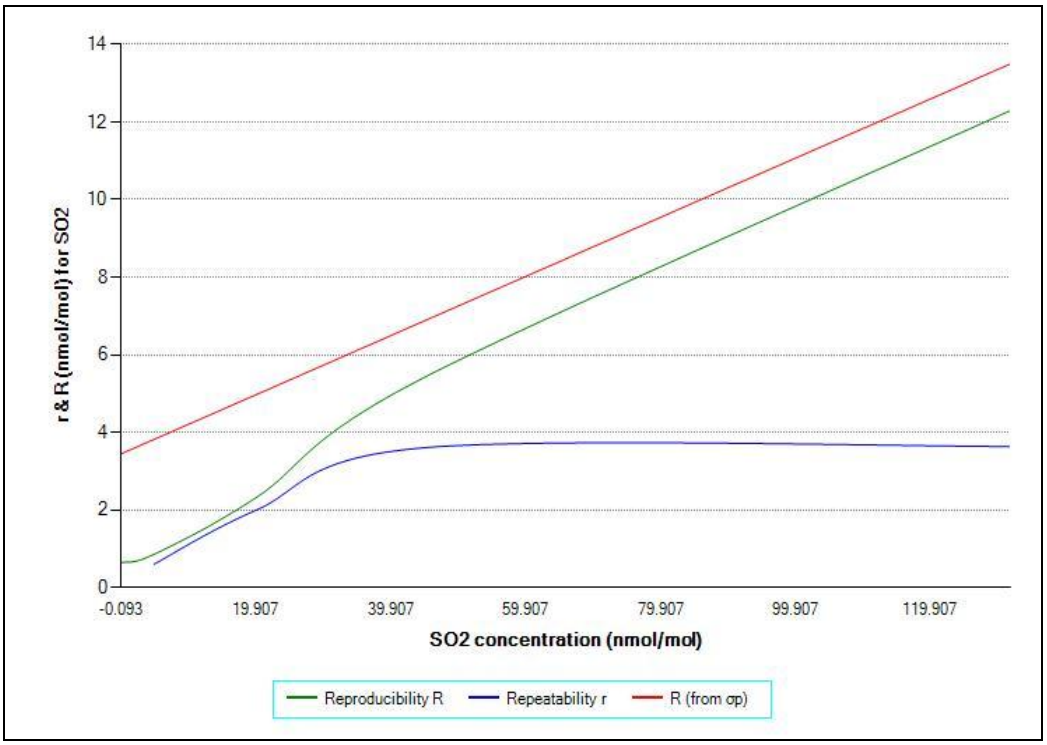
2013



Report EUR 26578 EN

Joint Research Centre

European Commission
Joint Research Centre
Institute for Environment and Sustainability

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JRC89315

EUR 26578 EN

ISBN 978-92-79-36781-6 (PDF)

ISSN 1831- 9424 (online)

DOI: 10.2788/43930

Luxembourg: Publications Office of the European Union, 2014

In collaboration with:
Kislova, O.; Karev, A. ; Beslic, I.; Sega, K.; Davila, S.; Mykhina, L.; Petruk, L.; Adasnki-Spasic, L.; Sostaric, A.; Grozdanovski, L.; Atanasov, I.; Lepri, P.; Premec, K.

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REVIEW	F. LAGLER	DRAFT 1.1	14/01/2014
REVIEW	A. BOROWIAK	DRAFT 1.2	15/01/2014
REVIEW	H.-G. MÜCKE	DRAFT 1.3	21/01/2014
REVIEW	V. STUMMER	DRAFT 1.4	22/01/2014
APPROVAL	N. JENSEN	2.0	27/01/2014

Executive Summary

From the 1st to the 6th of September 2013 seven Laboratories of the World Health Organization (WHO) European-Region met for another joint JRC-ERLAP/WHO inter-laboratory comparison exercise (IE). They met at the National Air Quality Reference laboratory at the German Federal Environment Agency in Langen, Germany, to evaluate their proficiency in the analysis of inorganic gaseous pollutants (NO, NO_2, SO_2, CO and O_3) covered by the European Air Quality Directive 2008/50/EC.

Most of the laboratories participating in the IE used automated instruments while one laboratory performed analysis using manual methods.

The proficiency evaluation, where each participant's bias was compared to two AQUILA based criteria, provides information on compliance with Data Quality Objectives and measurement capabilities of the National Air Quality Laboratories to the European Commission (AQUILA) and can be used by participants in their laboratory's quality system.
In terms of the criteria (σ_p) imposed by the European Directive (that are not mandatory for WHO laboratories which do not belong to EU), 75.7% of the results reported by WHO/AQUILA laboratories were considered good both in terms of measured values and evaluated uncertainties. Among the remaining results the majority presented satisfactory measured values but the evaluated uncertainties were either too high (20.9%) or too small (2.0%). Only two reported values (1.4% of all) were questionable for the z-score and "not OK" for the En-number.

The comparability of results among AQUILA participants at the highest generated concentration levels, excluding outliers, was acceptable for NO, SO_2 and O_3 measurements while CO and NO_2 measurements showed less satisfactory results.

Generally this proficiency evaluation confirmed the good performance of the previous one with a high percentage of valid measurement and uncertainties.
The evaluation of reproducibility shows an improvement for NO, O_3 and SO_2. It is confirmed the analytical difficulties for NO_2 measurements continue, and a performance decrease for CO is noticed.

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Abbreviations

AQUILA	Network of National Reference Laboratories for Air Quality http://ies.jrc.ec.europa.eu/aquila-homepage.html
CO	Carbon monoxide
DQO	Data Quality Objective
ERLAP	European Reference Laboratory of Air Pollution http://ies.jrc.ec.europa.eu/our-activities/support-for-member-states/erlap.html
EC	European Commission
GPT	Gas Phase Titration
IE	Inter-laboratory Comparison Exercise
IES	Institute for Environment and Sustainability
ISO	International Organization for Standardization
JRC	Joint Research Centre
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_X	the oxides of nitrogen, the sum of NO and NO_2
NRL	National Reference Laboratory
O_3	Ozone
SO_2	Sulphur dioxide
WHO-CC	World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin http://www.umweltbundesamt.de/en/topics/health/commissions-working-groups/who-collaborating-centre-for-air-quality-management

Mathematical Symbols

symbol	*explanation*
α	converter efficiency (EN 14211; [4])
E_n	E_n – number statistic (ISO 13528; [13])
r	repeatability limit (ISO 5725; [14])
R	reproducibility limit (ISO 5725; [14])
σ_p	standard deviation for proficiency assessment (ISO 13528; [13])
x*	robust average (Annex C ISO 13528; [13])
s*	robust standard deviation (Annex C ISO 13528; [13])
s_r	repeatability standard deviation (ISO 5725; [14])
s_R	reproducibility standard deviation (ISO 5725; [14])
$U_{X'}$	expanded uncertainty of the assigned/reference value (ISO 13528; [13])
U_{xi}	expanded uncertainty of the participant's value
$u_{X'}$	standard uncertainty of the assigned/reference value (ISO 13528; [13])
X	assigned/reference value (ISO 13528; [13])
x_i	average of three values reported by the participant *i* (for particular parameter and concentration level) (ISO 5725; [14])
$x_{i,j}$	j-the reported value of participant i (for particular parameter and concentration level) (ISO 5725; [14])
z'	z'-score statistic (ISO 13528; [13])

1. Introduction

Directive 2008/50/EC [1] on Ambient Air quality and Cleaner Air for Europe sets a framework for a harmonized air quality assessment in Europe. One important objective of the Directive is that the ambient air quality shall be assessed on the basis of common methods and criteria. It deals with the air pollutants sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and monoxide (NO), particulate matter, lead, benzene, carbon monoxide (CO) and ozone (O_3). Among others it specifies the reference methods for measurements and Data Quality Objectives (DQO) for the accuracy of measurements.
The European Commission (EC) has supported the development and publication of reference measurement methods for CO [2], SO_2 [3], NO-NO_2 [4] and O_3 [5] as European standards. Appropriate calibration methods [6], [7] and [8] have been standardized by the International Organization for Standardization (ISO).

As foreseen in the Air Quality Directive, the European Reference Laboratory of Air Pollution (ERLAP) of the Institute for Environment and Sustainability (IES) at the Joint Research Centre (JRC-Italy) organizes inter-laboratory comparison exercises (IE) to assess and improve the status of comparability of measurements of National Reference Laboratories (NRL) of each Member State of the European Union.
The World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin (WHO-CC) is carrying out similar activities since 1994 [9] [10] [31] [33], but with a view to obtaining harmonized air quality data for health related studies. Their program is an integrated quality assurance and control approach for Member States of the WHO European Region, which includes public health and other environmental institutes - particularly from countries of Central and Eastern Europe, Caucasus and Central Asia.

Starting in 2004, it has been decided to bring together the efforts of both the JRC-ERLAP and WHO-CC and to coordinate activities as far as possible, with a view to optimize resources and have better international harmonization.
The following report deals with the IE that took place from the 1st to the 6th of September 2013 at the National Reference laboratory for Air Pollution, German Federal Environment Agency (UBA) in Langen, Germany, in joint cooperation of EC/ JRC/IES/ERLAP and WHO-CC.

Since few decades in Europe IE are organized to evaluate the comparability of measurements carried out by NRLs and promoting information exchange among the expert laboratories.
Currently, a more systematic approach has been adopted, in accordance with the Network of National Reference Laboratories for Air Quality (AQUILA) [11], aiming both at providing an alert mechanism for the purposes of the EC legislation and at supporting the implementation of quality schemes by NRLs. The methodology for the organization of IE was developed by ERLAP in collaboration with AQUILA and is described in a paper on the organization of laboratory comparison exercises for gaseous air pollutants [12].
This evaluation scheme was adopted in December 2008 and is applied to all IE since then. It contains common criteria to alert the EC on possible performance failures which do not rely solely on the uncertainty claimed by participants. The evaluation scheme implements the z'-score method [13] with the uncertainty requirements for calibration gases stated in the European standards [2], [3], [4] and [5], which are consistent with the DQOs of European Directives.
According to the mentioned document, NRLs with an overall unsatisfactory performance in the z'-score evaluation (one unsatisfactory or two questionable results per parameter) ought to repeat their participation in the following IE in order to demonstrate remediation

measures [12]. In addition, considering that the evaluation scheme should be useful to participants for accreditation according to ISO 17025, they are requested to include their measurement uncertainty. Hence, participants' results (measurement values and uncertainties) are compared to the assigned values applying the E_n – number method [13].
Beside the proficiency of participating laboratories, the repeatability and reproducibility of standardized measurement methods [14], [15] and [16] are evaluated as well. These group evaluations are useful indicators of trends in measurement quality over different IE.

1.1 Communication and time schedule

The IE was announced at the beginning of April 2013 to the members of the AQUILA network and the WHO-CC representative. Registration was opened until the end of April 2013. A registration letter was sent by WHO-CC to interested parties and the registration was closed with the list of six participating laboratories.
The participants were required to bring their own measurement instruments, data acquisition equipment and travelling standards (to be used for calibrations or checks during the IE).
The participants were invited to arrive on the 1st of September 2013, for the installation of their equipment. On the following morning the gas generation program started at 9:00 with NO mixture. On the 3rd of September at 8:45 the zero air analysis for NO_2 measurement started. SO_2 and CO measurement was carried out on the following day starting at 8:45. O_3 was measured on Thursday the 4th of September from 8:45 am till 16:45 when the IE ended.

1.2 Participants

All participating laboratories belonged to institutions dealing with routine ambient air quality monitoring or to institutions involved in public health protection. The representatives came from following countries: Russian Federation, Croatia, Ukraine, Serbia, Former Yugoslav Republic of Macedonia and Germany and the description is shown in Table 1.

Country	Laboratory	Code	Network	Method
Russian Federation	State Environmental Institution 'Mosecommonitoring' (MOSECOM)	A	WHO	automatic
Croatia	Institute for Medical Research and Occupational Health (IMI)	B	AQUILA/WHO	automatic
Ukraine	State Institution 'O.M. Marzeev Institute of Hygiene and Medical Ecology, Academy of Medical Sciences of Ukraine' (IHME)	C	WHO	Semi-auto/manual
Serbia	Institute of Public Health (IPH_S)	D	AQUILA/WHO	automatic
Germany	Federal Environment Agency (UBA)	E	AQUILA	automatic
Macedonia	Ministry of Environment and Physical Planning (MOEPP)	F	WHO	automatic
Croatia	Meteorological and Hydrological Service (DHMZ)	G	AQUILA/WHO	automatic

Table 1: The list of participating institutions.

Table 2 reports the manufacturer and model of the instrumentation used by every participant during the inter-laboratory comparison exercise included those used in the calculation of the assigned values.
As a whole, the instrumentation belongs to five different manufacturers with the exception of SO_2 where four brands are present.
The list contains the information reported by participants and by no means can be considered as an implicit or explicit endorsement of the organizers to any specific type of instrumentation. All participants have used automatic analyzer beside the Ukraine laboratory (C) that used a semi-automatic method.

Gas	Lab Code	Instrument
CO	A	Environnement model CO 12M, # 1083
	B	HORIBA, APMA – 370, 2010
	C	-
	D	HORIBA, 2008, APMA-370
	E	HORIBA, 2008, APMA 370
	F	Thermo Environment, TEI 48C.
	G	HORIBA, 2011, APMA-370
NOX	A	HORIBA, APNA 370, # NEDJDB14
	B	HORIBA, APNA – 370, 2009
	C	-
	D	HORIBA, 2008, APNA-370
	E	HORIBA,2004. APNA 360
	F	Thermo Environment, TEI 42C.
	G	Horiba, 2011, APNA-370
O3	A	Environnement model O342M, # 978
	B	HORIBA APOA – 370, 2009
	C	-
	D	HORIBA, 2008, APOA-370
	E	Thermo Instruments,2009, TE 49i
	F	Thermo Environment, TEI 49C.
	G	Thermo scientific, 2012, 49i
SO2	A	HORIBA model APSA 370, # NWMMEJR5
	B	HORIBA, APSA – 370 , 2010
	C	-
	D	HORIBA, 2009, APSA-370
	E	HORIBA, 2004, APSA 360
	F	Thermo Environment, TEI 43C
	G	HORIBA, 2010, APSA-370

Table 2: The list of instruments used by participants.

Semi-automatic method adopted by laboratory C:

- The NO_2 method is based on the interaction of nitrogen dioxide and sulfanilic acid with a formation of diazo compound which sets off an azo dye in reaction with ȧ-naphthylamin. Diazo compound colors the solution from light rose to red-violet. The amount of nitrogen dioxide is determined by color intensity (manual, photocolorimetric method, wave length of 540 nm). Range of measurements and error: 0.02 to 0.64 mg/m3; e= ± 25 %
- NO method is based on the oxidation of nitrogen oxide of chromic acid till dioxide and on the catching of the dioxide with the help of potassium iodine. The diazo compound is formed during the interaction of nitrogen dioxide with sulfanilic acid. This diazo compound is colored from light rose to red-violet while reacting with ȧ-naphthylamin. The amount of nitrogen dioxide is determined by color intensity (manual, photocolorimetric method, wave length of 540 nm). Range of measurements and error: 0.013 to 0.28 mg/m3; e= ± 25 %
- O_3 method is based on the displacement of iodine with ozone while ozone is absorbed by potassium iodine with a buffer based on boric acid. Extracted iodine is determined with a spectrometric measurement, wave length of 325 nm (manual, photo-colorimetric method). Range of measurements and error: 0.01 to 1.0 mg/m3; e= ± 25 %

- SO_2 method is based on the oxidation of sulphurous gas in the process of its catching from the air with the solution of potassium chlorate or hydrogen peroxide with a further turbidimetric determination of forming sulphat-ion with barium chloride (manual, photocolorimetric method, wave length of 400 nm). Range of measurements and error: 0.01 – 0.8 mg/m3; e= ± 25 %.

1.3 The preparation of test mixtures

The facility of the UBA National Reference Laboratory is described in [9]. During this IE, gas mixtures were prepared for NO and NO_2, SO_2, CO and O_3 at concentration levels around limit values, critical levels and assessment thresholds set by European Air Quality Directive [1].

The test mixtures were prepared by the dilution of gases from cylinders containing high concentration of NO, NO_2, SO_2 or CO using thermal mass flow controllers [8]. O_3 was added using an ozone generator.
The participants were required to report three half-hour-mean measurements for each concentration level (run) in order to evaluate the repeatability of standardized measurement methods. Zero concentration levels were generated at least for one hour and one half-hour-mean measurement was reported. The sequence program of generated test gases is given in Table 3.

day	start time	duration	parameter	installation	calibration	Zero Air	NO	NO2	O3	CO	SO2
		h				nmol/mol	nmol/mol	nmol/mol	nmol/mol	µmol/mol	nmol/mol
01-Sep	15:00	3	/	X							
02-Sep	08:45	0.15	/		X						
02-Sep	09:00	2.5	NO			0					
02-Sep	11:45	1.5	NO				180-220				
02-Sep	13:30	1.5	NO				15-25				
03-Sep	08:45	1.00	NO2			0					
03-Sep	10:00	1.5	NO2					180-220			
03-Sep	11:45	1.5	NO2					80-120			
03-Sep	13:30	1.5	NO2					50-70			
03-Sep	15:15	1.5	NO2					15-25			
04-Sep	08:45	1	SO2			0					
04-Sep	10:00	1.5	SO2								120-140
04-Sep	11:45	1.5	SO2								40-50
04-Sep	13:30	1.5	SO2								15-25
04-Sep	15:15	1.5	SO2								4-7
04-Sep	17:00	1	CO			0					
04-Sep	18:00	2	CO							6-9	
04-Sep	20:00	2	CO							5-8	
04-Sep	22:00	2	CO							2-4	
05-Sep	00:00	2	CO							0.5-2	
05-Sep	02:00	2	CO							4-5	
05-Sep	08:45	1	O3			0					
05-Sep	10:00	1.5	O3						280-320		
05-Sep	11:45	1.5	O3						80-100		
05-Sep	13:30	1.5	O3						50-70		
05-Sep	15:15	1.5	O3						15-25		
06-Sep	08:45	0.15	evaluation								
06-Sep	09:00	3	dismantling								

Table 3: The sequence program of generated test gases

2. The evaluation of laboratory's measurement proficiency

To evaluate the participants measurement proficiency the methodology described in ISO 13528 [13] was applied. It has been agreed among the AQUILA members to take the measurement results of UBA as the assigned/reference values for the whole IE [12]. The traceability of UBA's measurement results and the method applied to validate them are presented in Annex A.
All data reported by participating laboratories are presented in Annex C.
As it is described in the AQUILA position paper [12], the proficiency of the participants was assessed by calculating two performance indicators. The first performance indicator (z'-score) tests whether the difference between the participants measured value and the assigned/reference value remains within the limits of a common criterion. The second performance indicator (E_n-number) tests if the difference between the participants measured values and assigned/reference value remains within the limits of a criterion, that is calculated individually for each participant, from the uncertainty of the participants measurement result and the uncertainty of the assigned/reference value.

2.1 z' - score

The z'- score statistic is calculated according to ISO 13528 [13] as:

$$z' = \frac{x_i - X}{\sqrt{\sigma_p^2 + u_X^2}} = \frac{x_i - X}{\sqrt{(a \cdot X + b)^2 + u_X^2}} \qquad \textbf{Equation 1}$$

where 'x_i' is a participant's run average value, 'X' is the assigned/reference value, 'σ_p' is the 'standard deviation for proficiency assessment' and '$u_{X'}$' is the standard uncertainty of assigned value. The values of 'a' and 'b' are reported in Table 4.

In the European standards [2], [3], [4] and [5] the uncertainties for calibration gases used in ongoing quality control are prescribed. In fact, it is stated that the maximum permitted expanded uncertainty for calibration gases is 5% and that 'zero gas' shall not give instrument reading higher than the detection limit. As one of the tasks of NRLs is to supply calibration gas mixtures, the 'standard deviation for proficiency assessment' (σ_p) [13] is calculated in fitness-for-purpose manner from requirements given in European standards.

Over the whole measurement range σ_p is calculated by linear interpolation between 2.5% at the calibration point (75% of calibration range) and the limit of detection at zero concentration level. The limits of detection of studied measurement methods were evaluated from the data of previous IE. The linear function parameters of σ_p are given in Table 4:

	$\sigma_p = a \cdot c + b$	
Gas	**a**	**b**
		nmol/mol
SO_2	0.022	1
CO	0.024	100
O_3	0.020	1
NO	0.024	1
NO_2	0.020	1

Table 4: The standard deviation for proficiency assessment (σ_p).

σ_p is a linear function of concentration (c) with parameters: slope (a) and intercept (b).

The assessment of results in the z`-score evaluation is made according to the following criteria:

- $|z'| \leq 2$ are considered satisfactory.
- $2 < |z'| \leq 3$ are considered questionable.
- $|z'| > 3$ are considered unsatisfactory. Scores falling in this range are very unusual and are taken as evidence that an anomaly has occurred that should be investigated and corrected.

The results of z'-score evaluation are presented in bar plots (Figure 3 to Figure 2) in which the z'-scores of each participant are grouped together, and assessment criteria are presented as z'=±2 and z'=±3 lines.

Figure 1: The z'-score evaluations of NO measurements

Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (180-220 nmol/mol), 2 (15-25 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

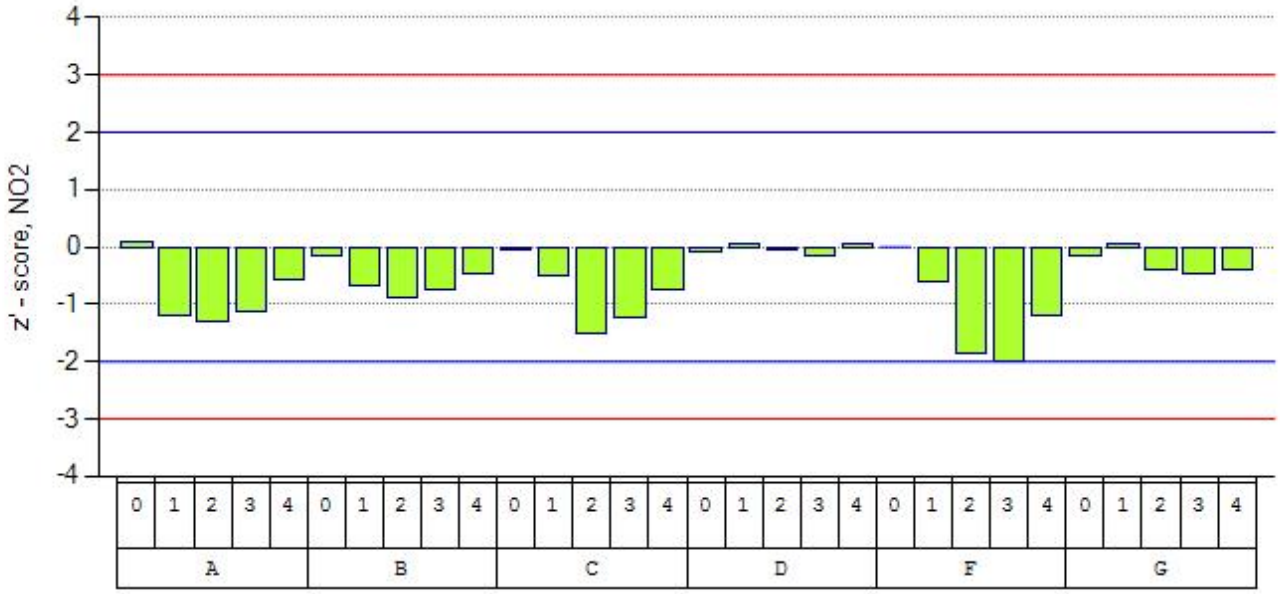

Figure 2: The z'-score evaluations of NO_2 measurements

Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (180-220 nmol/mol), 2 (80-120 nmol/mol), 3 (50-70 nmol/mol), 4 (15-25

nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

Figure 3: The z'-score evaluations of SO_2 measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (120-140 nmol/mol), 2 (40-50 nmol/mol), 3 (15-25 nmol/mol), 4 (4-7 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

Figure 4: The z'-score evaluations of CO measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 µmol/mol), 1 (6-9 µmol/mol), 2 (5-8 µmol/mol), 3 (2-4 µmol/mol), 4 (0.5-2 µmol/mol), 5 (4-5 µmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

Figure 5: The z'-score evaluations of O_3 measurements
Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (280-320 nmol/mol), 2 (80-100 nmol/mol), 3 (50-70 nmol/mol), 4 (15-25 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

2.2 E_n - number

The normalized deviations [13] (E_n) were calculated according to:

$$E_n = \frac{x_i - X}{\sqrt{U_{x_i}^2 + U_X^2}} \qquad \textbf{Equation 2}$$

where 'X' is the assigned/reference value with an expanded uncertainty 'U_X' and 'x_i' is the participant's average value with an expanded uncertainty 'U_{Xi}'. Satisfactory results are the ones for which $|E_n| \leq 1$.

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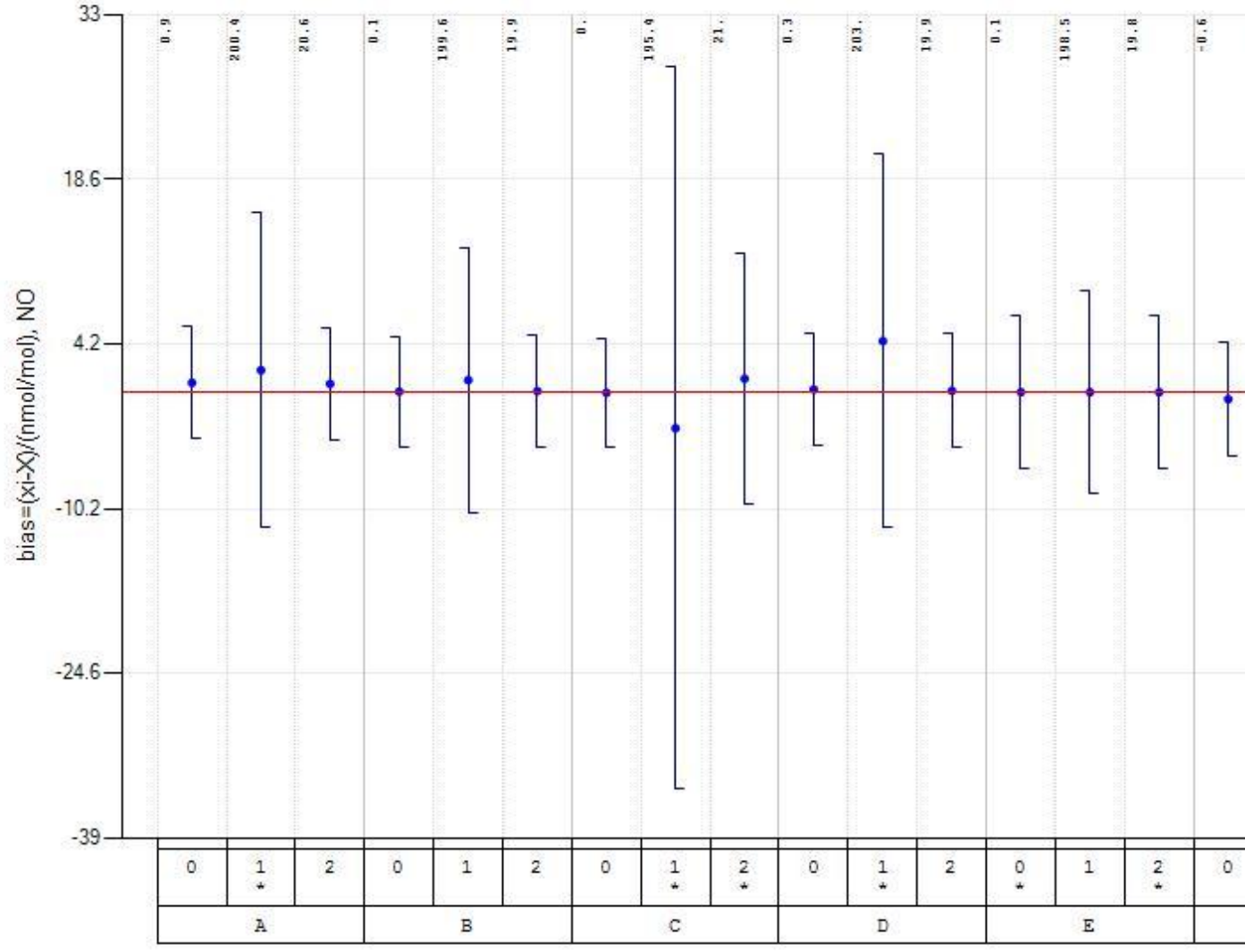

Figure 6: Bias of participant's NO measurement results

Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 2) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

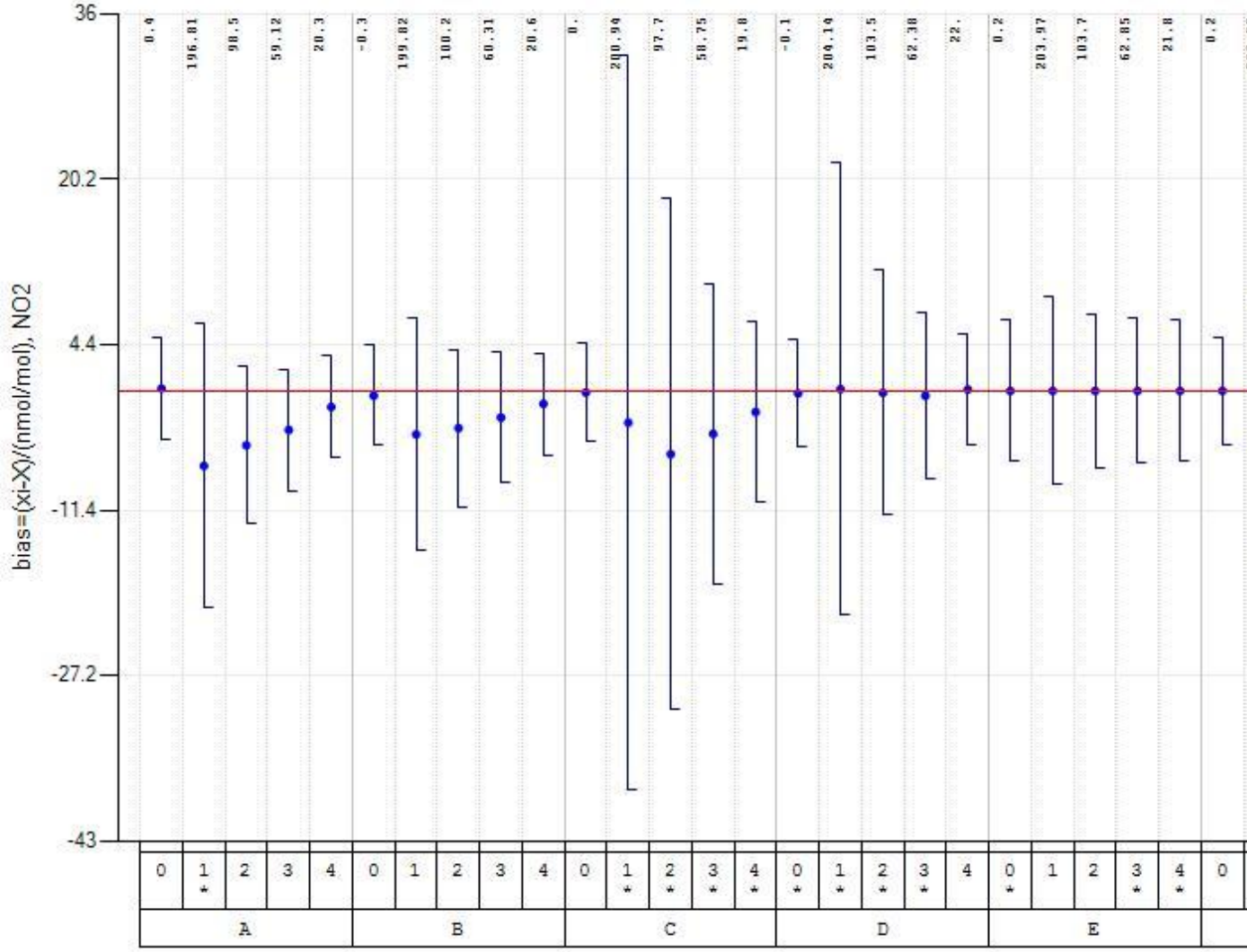

Figure 7: Bias of participant's NO_2 measurement results
Expanded uncertainty of bias is presented as error bar for NO_2 run numbers 0, 1, 2, 3 and 4. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

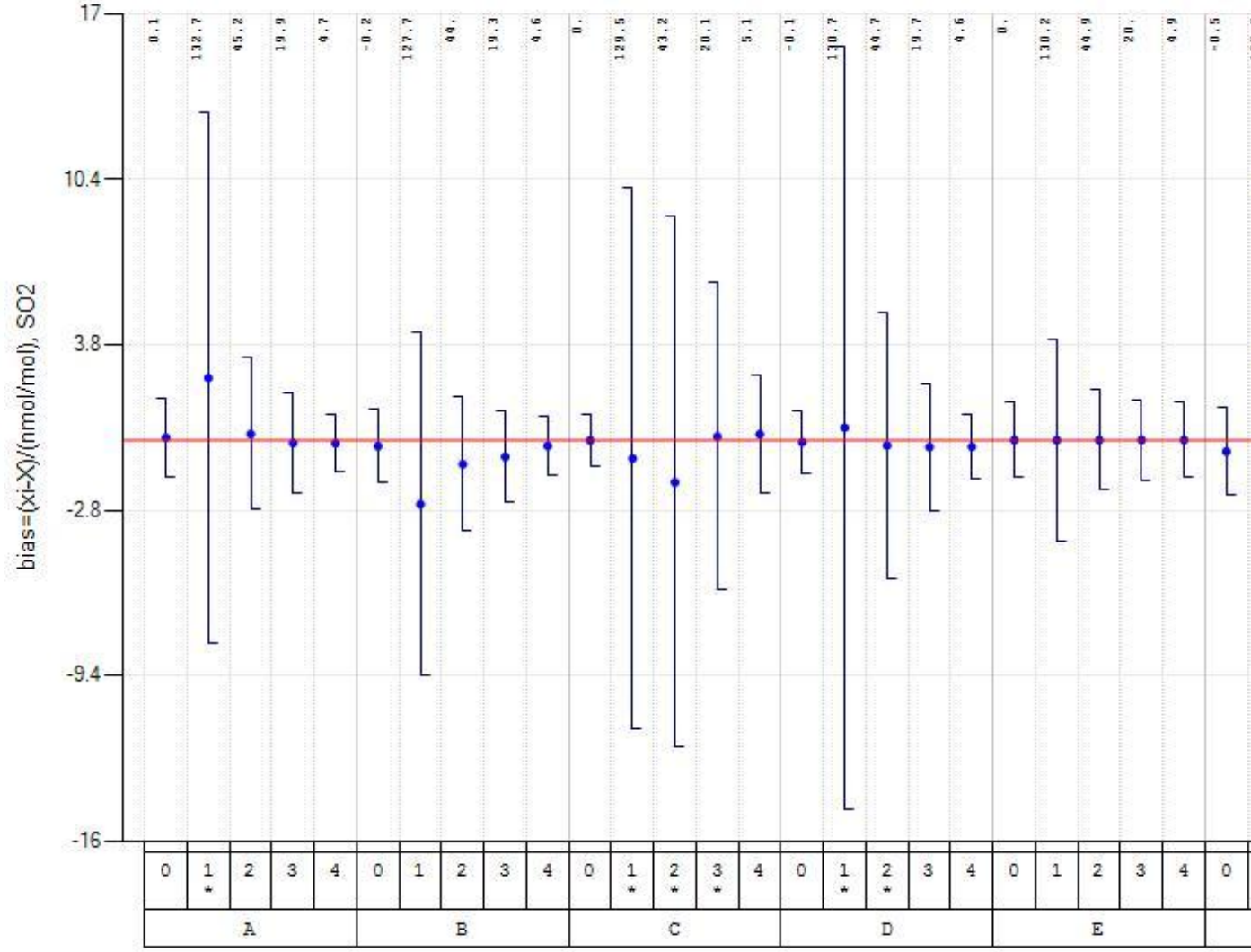

Figure 8 to Figure 7 the bias of each participant (x_i-X) is plotted and error bars are used to show the value of denominator of Equation 2$\left(\sqrt{U_{x_i}^2 + U_X^2}\right)$. These plots represent also the E_n-number evaluations where, considering the E_n criteria ($|E_n| \leq 1$), all results with error bars touching or crossing x-axis are satisfactory. Reported standard uncertainties (Annex B) that are bigger than "standard deviation for proficiency assessments" (σ_p, Table 4) are considered not fit-for-purpose and are denoted with "*" in the x-axis of each figure.

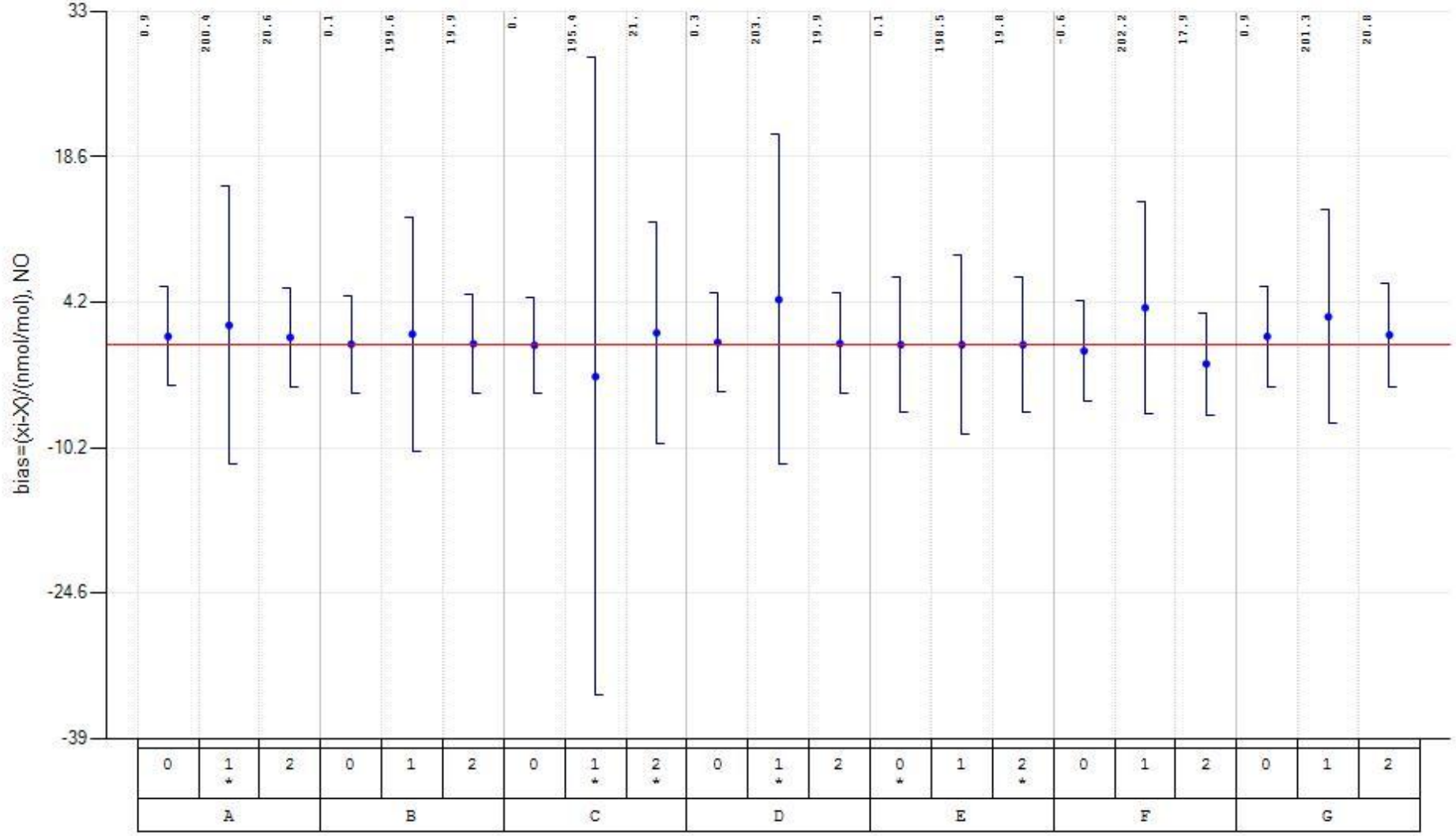

Figure 6: Bias of participant's NO measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 2) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

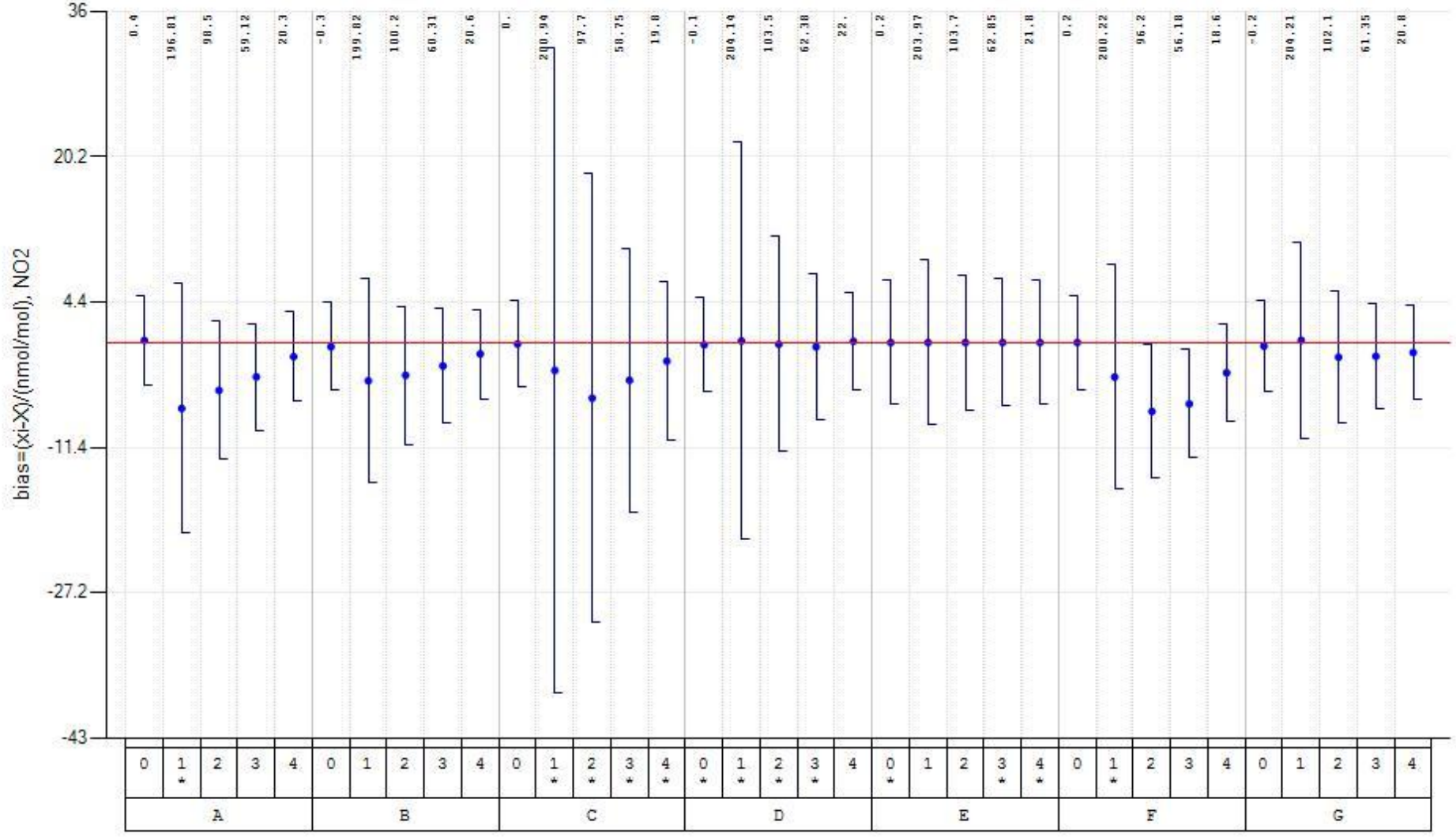

Figure 7: Bias of participant's NO_2 measurement results
Expanded uncertainty of bias is presented as error bar for NO_2 run numbers 0, 1, 2, 3 and 4. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

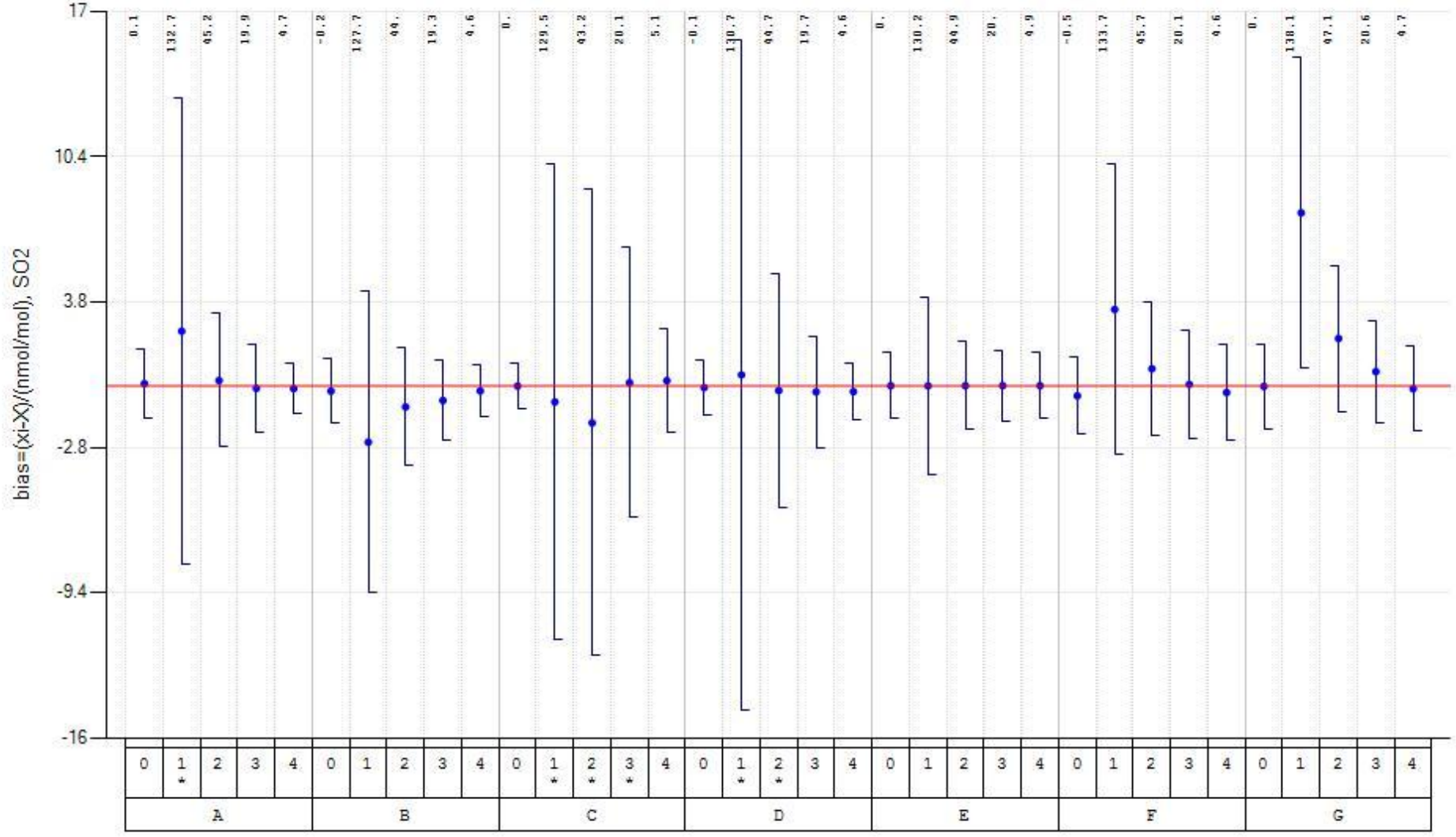

Figure 8: Bias of participant's SO_2 measurement results

Expanded uncertainty of bias for each run is presented as error bar. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 4) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

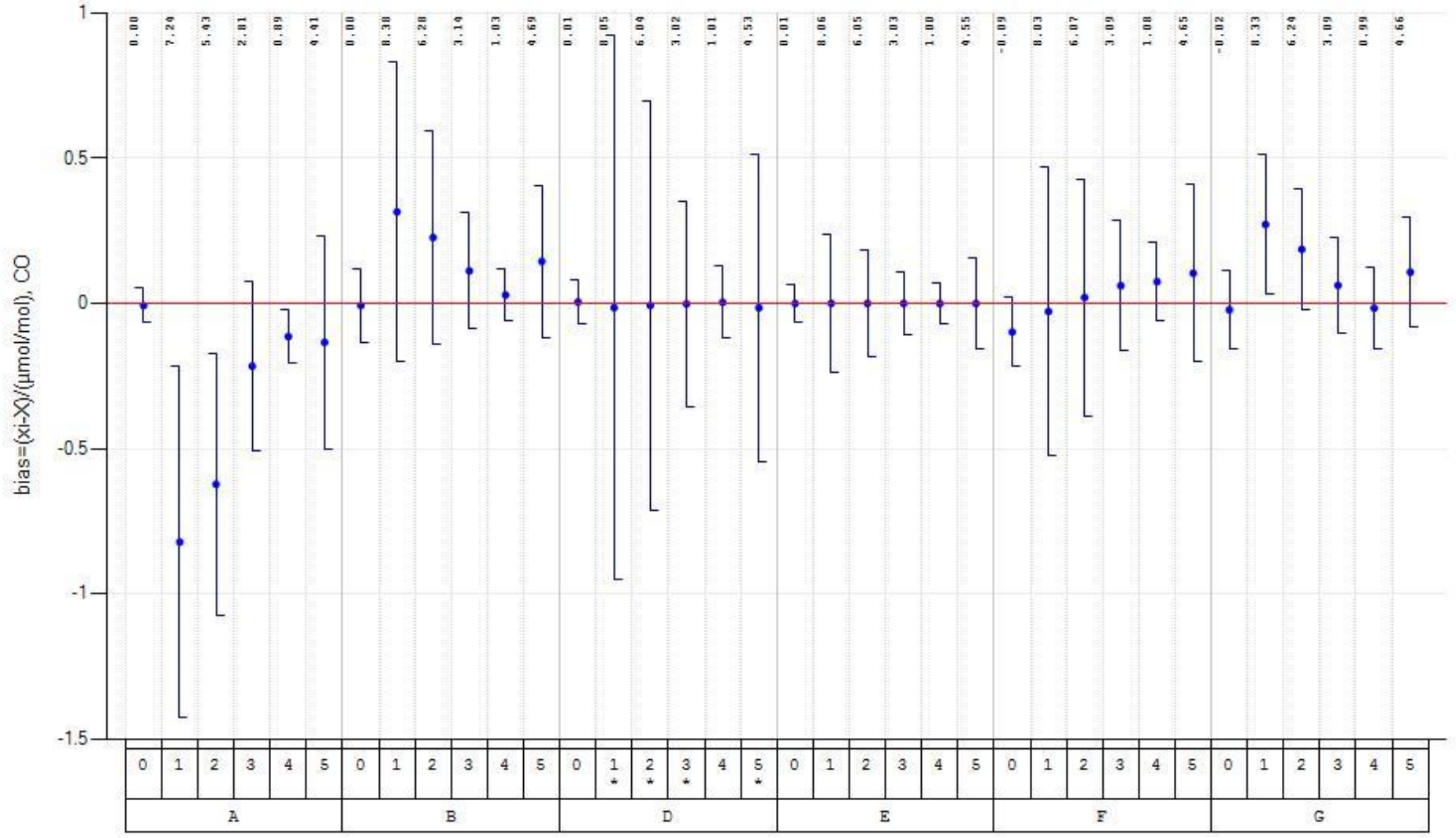

Figure 9: Bias of participant's CO measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (µmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

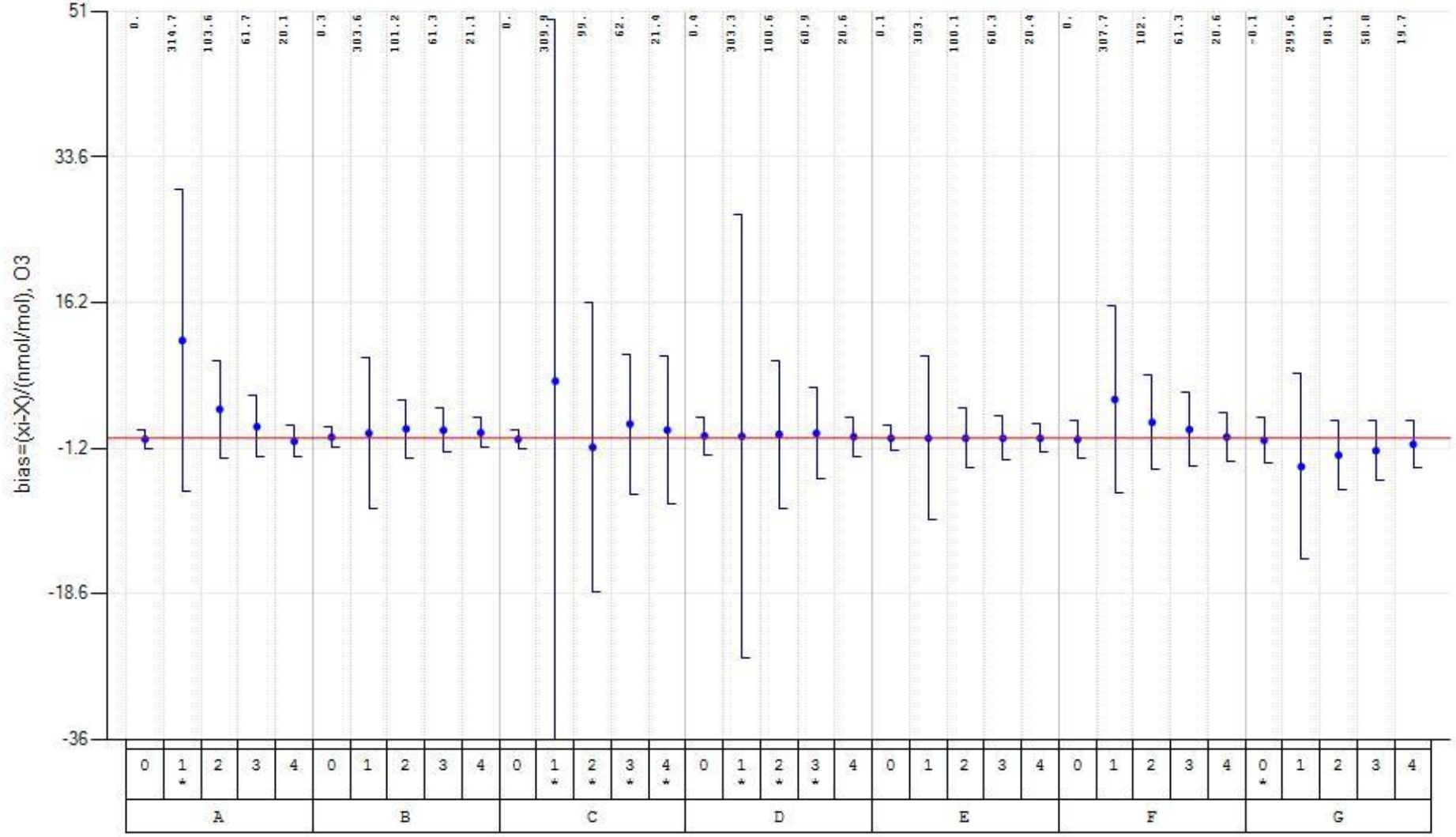

Figure 10: Bias of participant's O_3 measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 4) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

3. Discussion

For a general assessment of the quality of each result a decision diagram was developed (Figure 11) that results in seven categories (1 to 7). The general comments for each category are:

- **1**: measurement result is completely satisfactory
- **2**: measurement result is satisfactory (z'-score satisfactory and En-number ok) but the reported uncertainty is too high
- **3**: measured value is satisfactory (z'-score satisfactory) but the reported uncertainty is underestimated (En-number not ok)
- **4**: measurement result is questionable (z'-score questionable) but due to a high reported uncertainty can be considered valid (En-number ok)
- **5**: measurement result is questionable (z'-score questionable and En-number not ok)
- **6**: measurement result is unsatisfactory (z'-score unsatisfactory) but due to a high reported uncertainty can be considered valid (En-number ok)
- **7**: measurement result is unsatisfactory (z'-score unsatisfactory and En-number not ok).

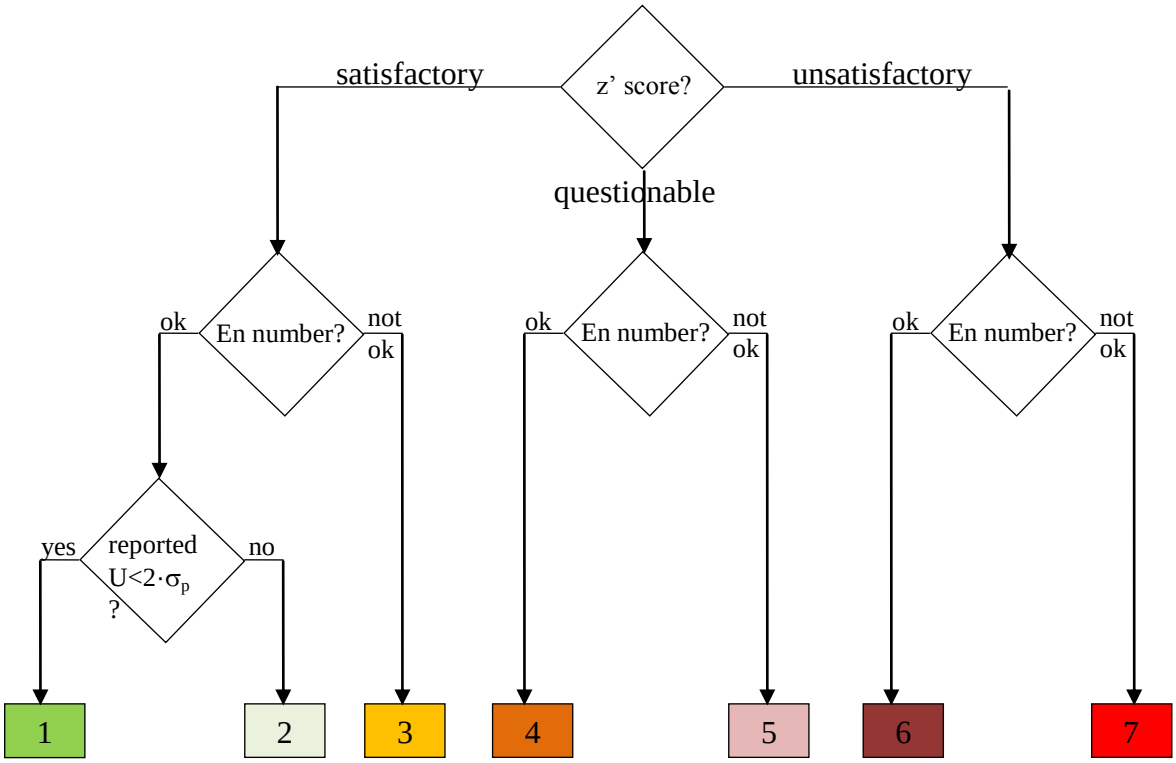

Figure 11: The decision diagram for general assessment of proficiency results.

The results of the IE were assigned to categories according to the diagram given in Figure 11 and are presented in Table 5.

	run number	Ref. conc. level	Unit	IE code						
				A	B	C	D	E	F	G
CO (µmol/mol)	0	0.007	µmol/mol	1	1	nd	1	1	1	1
	1	8.062	µmol/mol	5	1	nd	2	1	1	3
	2	6.050	µmol/mol	5	1	nd	2	1	1	1
	3	3.026	µmol/mol	1	1	nd	2	1	1	1
	4	1.001	µmol/mol	3	1	nd	1	1	1	1
	5	4.547	µmol/mol	1	1	nd	2	1	1	1
NO (nmol/mol)	0	0.05	nmol/mol	1	1	1	1	2	1	1
	1	198.51	nmol/mol	2	1	2	2	1	1	1
	2	19.82	nmol/mol	1	1	2	1	2	1	1
NO_2 (nmol/mol)	0	0.15	nmol/mol	1	1	1	2	2	1	1
	2	103.73	nmol/mol	1	1	2	2	1	1	1
	4	21.84	nmol/mol	1	1	2	1	2	1	1
O_3 (nmol/mol)	0	0.13	nmol/mol	1	1	1	1	1	1	2
	1	303.04	nmol/mol	2	1	2	2	1	1	1
	2	100.10	nmol/mol	1	1	2	2	1	1	1
	3	60.29	nmol/mol	1	1	2	2	1	1	1
	4	20.43	nmol/mol	1	1	2	1	1	1	1
SO_2 (nmol/mol)	0	0.01	nmol/mol	1	1	1	1	1	1	1
	1	130.22	nmol/mol	2	1	2	2	1	1	3
	2	44.93	nmol/mol	1	1	2	2	1	1	1
	3	19.99	nmol/mol	1	1	2	1	1	1	1
	4	4.87	nmol/mol	1	1	1	1	1	1	1

Table 5: The general assessment of proficiency results, "nd" is referring to values not reported.

4. Conclusions

The proficiency evaluation scheme has provided an assessment of the participants measured values and their evaluated uncertainties.
In terms of the criteria imposed by the European Directive (σ_p) 75.7% of the results reported by WHO/AQUILA laboratories fall into category '1' and are good both in terms of measured values and evaluated uncertainties. Among the remaining results the majority presented satisfactory measured values but the evaluated uncertainties were either too high, category '2' (20.9%), or too small category '3' (2.0%). Only 1.4% of results (category '5') were questionable for the z-score and "not OK" for the En-number.
As in previous IE, the adopted criteria for high concentrations were the standard deviations for proficiency assessment, deriving from the European Standards' uncertainty requirements. The reproducibility standard deviations obtained at this IE (Annex C) and previous IE [20], [21], [22], [23], [24], [25], [33], [35], [36], [37], [38] and [39] are comparable to the mentioned criteria. On the other hand, the uncertainty criteria for zero levels were those set in AQUILA's position paper [12].
This IE is confirming a good performance compared to the previous one in 2011 with a high share of results in category '1'(see Table 6).

IE	Site	Categories %						
		1	2	3	4	5	6	7
Apr-08	Ispra (IT)	68.4	18.1	7.3	1.0	1.0	2.6	1.6
Oct-08 (I)	Ispra (IT)	37.9	40.8	14.2	0.6	3.6	1.0	1.9
Oct-08 (II)	Ispra (IT)	34.3	38.9	23.7	1.0	2.0	0.0	0.0
Sep-09	Langen (DE)	60.8	29.9	3.1	4.1	1.0	1.0	0.0
Oct-09	Ispra (IT)	85.0	5.7	7.5	0.4	1.4	0.0	0.0
Jun-10	Ispra (IT)	84.6	8.1	4.4	0.7	2.3	0.0	0.0
Sep-11	Ispra (IT)	86.1	7.9	5.4	0.0	0.3	0.0	0.3
Oct-11 (I)	Ispra (IT)	78.6	12.5	7.6	0.0	1.3	0.0	0.0
Oct-11 (II)	Langen (DE)	59.4	39.9	0.0	0.7	0.0	0.0	0.0
Jun-12	Ispra (IT)	92.2	0.5	7.3	0.0	0.0	0.0	0.0
Sep-13	Langen (DE)	75.7	20.9	2.0	0.0	1.4	0.0	0.0

Table 6: history of the results in the last IE

Comparability of results among participants at the highest concentration level (from Figure 36 to Figure 40), excluding outliers, is acceptable for NO, SO_2 and O_3 measurements while for NO_2 and CO the results are less satisfactory.
The relative reproducibility limits, at the highest studied concentration levels, are 6.80% for NO, 10.26 for NO_2, 9.30% for SO_2, 18.60% for CO and 7.80 for O_3. Only NO_2 and CO are not within the objectives derived from criteria imposed by the European Commission (σ_p). More in details NO_2 is out of EC criteria from 25 to 150 nmol/mol (see Figure 37: The R and r of NO2 standard measurement method as a function of concentration.) and CO is out of EC criteria for values above 6 μmol/mol (see Figure 39: The R and r of CO standard measurement method as a function of concentration.).

During this IE the performance of all participants has been quite positive. Only one outlier has been identified at zero level for CO (Annex D), 1 struggler for NO and 4 strugglers for CO.

In this exercise there were no unsatisfactory results in the z'-score evaluations. Laboratory A obtained two questionable results for CO and in general it was confirmed the good performance of last IE as shown in Table 7.

IE	*Site*	*Questionable*	*Unsatisfactory*	*Satisfactory*
June-05	Ispra (IT)	2.3%	2.3%	95.5%
June-07	Ispra (IT)	1.9%	0.3%	97.8%
October-07	Essen (DE)	4.6%	2.2%	93.2%
April-08	Ispra (IT)	2.1%	4.1%	93.8%
October-2008_1	Ispra (IT)	4.2%	2.9%	92.9%
October-2008_2	Ispra (IT)	3.0%	0.0%	97.0%
September-09	Langen (DE)	4.7%	0.9%	94.3%
October-09	Ispra (IT)	1.8%	0.0%	98.2%
June-10	Ispra (IT)	3.0%	0.0%	97.0%
September-11	Ispra (IT)	0.3%	0.3%	99.4%
October-11	Ispra (IT)	1.3%	0.0%	98.7%
October-11	Langen (DE)	0.7%	0.0%	99.3%
June-12	Ispra (IT)	0.0%	0.0%	100.0%
September-13	Langen (DE)	1.4%	0.0%	98.6%

Table 7: z'-score summary

5. References

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Annex A. Assigned values

The assigned values of tested concentration levels (run) were derived from UBA measurements which are calibrated against the certified reference values of CRMs and are traceable to international standards. In this perspective the assigned values are reference values as defined in the ISO 13528 [13].

UBA's SO_2, CO and NO analysers were calibrated according to the methodology described in the ISO 6143 [6]. The procedure and the device for generating primary calibration gases is described elsewhere [31]. Gas mixtures for the calibration experiment were produced from the reference mixtures by static volumetric dilution method ISO 6144 [34].
SO_2, CO and NO gas mixtures manufactured by Air Liquide and certified by UBA (U≤ 2%) were used as internal standards.
For the reference gas mixture composition evaluation and for the calibration experiment evaluation the computer application "GUM WORKBENCH" [20] was used.
For O_3 measurements, the primary standard NIST photometer SRP 29 was used.

UBA's measurement results were validated by comparison to the group statistics (x* and s*) for every parameter and concentration level of the IE. These statistics are calculated from participants, applying the robust method described in the Annex C of the ISO 13528 [13]. The validation is taking into account UBA's measurement result (X) and its standard uncertainty (u_X) as given in Equation 3[13]:

$$\frac{\left|x^* - X\right|}{\sqrt{\frac{\left(1{,}25 \cdot s^*\right)^2}{p} + u_X^2}} < 2$$

Equation 3

Where 'x*' and 's*' represent robust average and robust standard deviation respectively and 'p' is the number of participants.

In Table 8 all inputs for Equation 3 are given and all UBA's measurement results are confirmed to be valid.

As a group evaluation robust average (x*) and robust standard deviation (s*) were calculated (applying the procedure described in Annex C of ISO 13528 for each run) and are presented in the following Table 8.

run	unit	X	uX'	x*	s*	p	val.
NO _0	nmol/mol	0.05	2.37	0.162	0.328	7	OK
NO _1	nmol/mol	198.513	3.16	200.213	2.514	7	OK
NO _2	nmol/mol	19.823	2.38	20.133	0.8	7	OK
NO2 _0	nmol/mol	0.15	2.37	0.005	0.266	7	OK
NO2 _1	nmol/mol	203.967	3.2	201.443	3.179	7	OK
NO2 _2	nmol/mol	103.727	2.61	100.29	3.34	7	OK
NO2 _3	nmol/mol	62.847	2.45	60.228	2.435	7	OK
NO2 _4	nmol/mol	21.843	2.38	20.598	1.242	7	OK
SO2 _0	nmol/mol	0.01	0.53	-0.036	0.091	7	OK
SO2 _1	nmol/mol	130.223	1.45	131.371	2.937	7	OK
SO2 _2	nmol/mol	44.93	0.71	44.908	1.261	7	OK
SO2 _3	nmol/mol	19.987	0.57	19.96	0.262	7	OK
SO2 _4	nmol/mol	4.867	0.53	4.731	0.18	7	OK
CO _0	μmol/mol	0.007	0.022	-0.003	0.014	6	OK
CO _1	μmol/mol	8.0617	0.086	8.096	0.27	6	OK
CO _2	μmol/mol	6.0497	0.066	6.087	0.175	6	OK
CO _3	μmol/mol	3.0257	0.038	3.056	0.06	6	OK
CO _4	μmol/mol	1.001	0.024	1.005	0.039	6	OK
CO _5	μmol/mol	4.547	0.057	4.59	0.101	6	OK
O3 _0	nmol/mol	0.13	0.55	0.066	0.143	7	OK
O3 _1	nmol/mol	303.037	3.52	305.655	5.102	7	OK
O3 _2	nmol/mol	100.10	1.29	100.65	2.08	7	OK
O3 _3	nmol/mol	60.29	0.92	61.11	0.72	7	OK
O3 _4	nmol/mol	20.43	0.60	20.55	0.65	7	OK

Table 8: The validation of assigned values (X)
by comparison to the robust averages (x*) with taking into account the standard uncertainties of assigned values (uX'), and robust standard deviations (s*) as denoted by Equation 3.

The homogeneity of test gas was evaluated from measurements at the beginning and end of the distribution line. From the relative differences between beginning and end measurements, average and standard deviation were calculated, and the uncertainty of test gas due to lack of homogeneity was calculated as the sum of squares of these average and standard deviation. The upper and lower limits of bias due to homogeneity was evaluated to be smaller than 0.5% which constitutes the relative standard uncertainty of 0.3% of each concentration level. The standard uncertainties of assigned/reference values ($u_{X'}$) were calculated with Equation 4 and used in the proficiency evaluations of chapter 2.

$$u_{X'}^2 = u_X^2 + \left(X \cdot u_{\mathrm{homogeneity}}\right)^2 \qquad \textbf{Equation 4}$$

Annex B. The results of the IE

In this annex are reported participant's results, presented both in tables and graphs. For each run, participants were asked to report 3 results representing 30 minutes measurement each (x_{ij}). In this annex are presented the reported data and their uncertainty $u(x_i)$ and $U(x_i)$ expressed in mol/mol units.
For all the runs except concentration levels 0, also average (x_i) and standard deviation (s_i) of each participant are presented.
The assigned value is indicated on the graphs with the red line and the individual laboratories expanded uncertainties (Ux_i) are indicated with error bars.

Reported values for NO

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	0.87	0.10	0.00	0.28	0.05	-0.57	0.87
u(xi)	0.58	0.41	0.00	0.70	2.37	0.75	0.80
U(xi)	1.16	0.82	0.00	1.40	4.74	1.50	1.60

Table 9: Reported values for NO run 0.

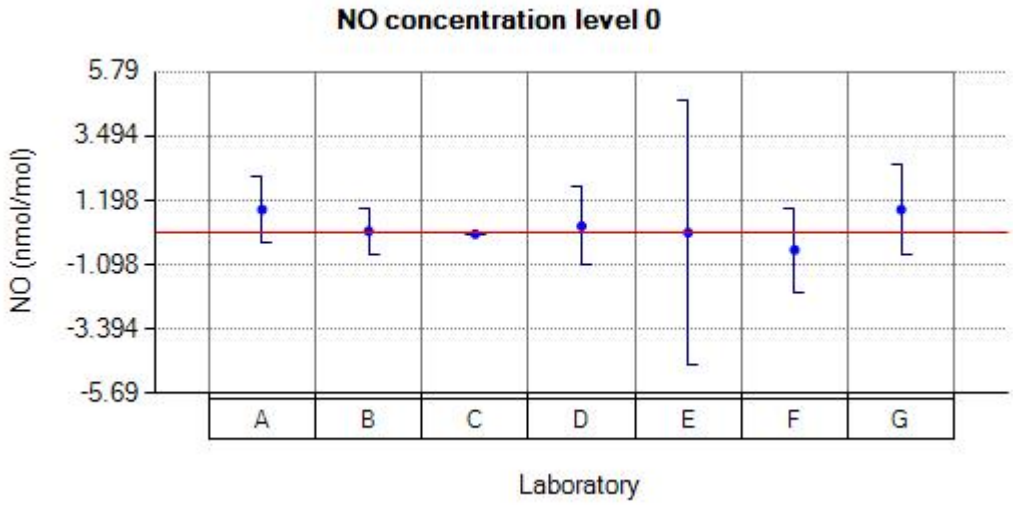

Figure 12: Reported values for NO run 0.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	200.53	199.61	185.70	202.74	198.29	203.00	201.16
xi, 2	200.48	199.47	195.57	203.02	198.48	202.10	201.21
xi, 3	200.29	199.62	204.82	203.17	198.77	201.45	201.46
xi	200.43	199.56	195.36	202.97	198.51	202.18	201.27
si	0.12	0.08	9.56	0.21	0.24	0.77	0.16
u(xi)	6.09	4.85	9.73	7.55	3.16	4.21	4.25
U(xi)	12.18	9.70	30.95	15.10	6.31	8.42	8.50

Table 10: Reported values for NO run 1.

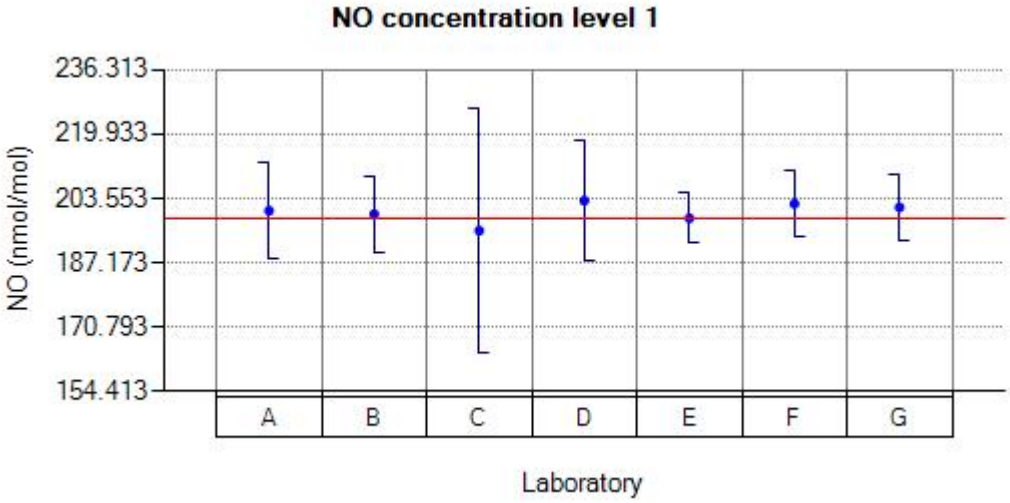

Figure 13: Reported values for NO run 1.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	20.59	20.04	18.53	19.94	19.85	18.06	20.87
xi, 2	20.51	19.91	24.25	19.90	19.85	17.92	20.65
xi, 3	20.54	19.78	20.22	19.95	19.77	17.81	20.84
xi	20.54	19.91	21.00	19.93	19.82	17.93	20.78
si	0.04	0.13	2.93	0.02	0.04	0.12	0.11
u(xi)	0.53	0.65	3.10	0.74	2.38	0.84	1.00
U(xi)	1.25	1.30	9.85	1.48	4.76	1.69	2.00

Table 11: Reported values for NO run 2.

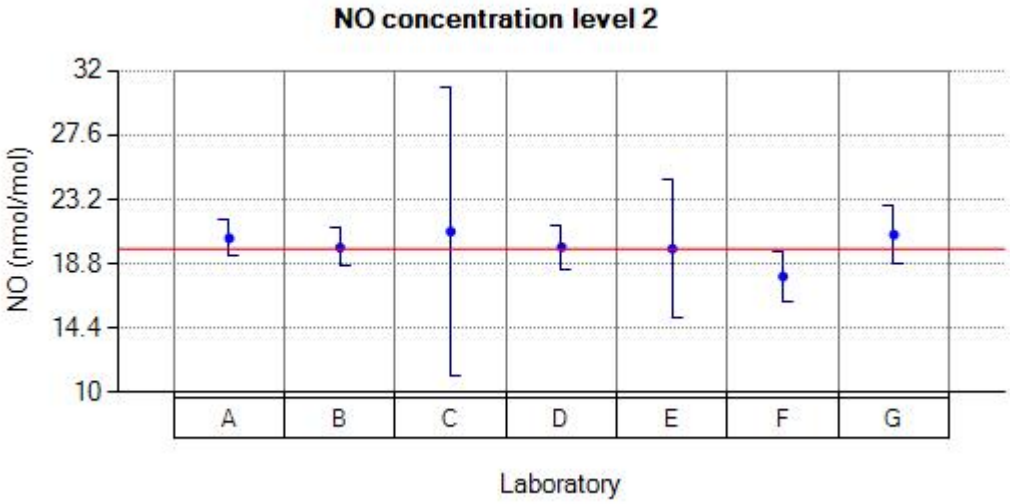

Figure 14: Reported values for NO run 2.

Reported values for NO_2

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	0.38	-0.30	0.00	-0.09	0.15	0.16	-0.24
u(xi)	0.56	0.31	0.00	1.02	2.37	1.00	0.80
U(xi)	1.12	0.62	0.00	2.04	4.74	2.00	1.60

Table 12: Reported values for NO_2 run 0.

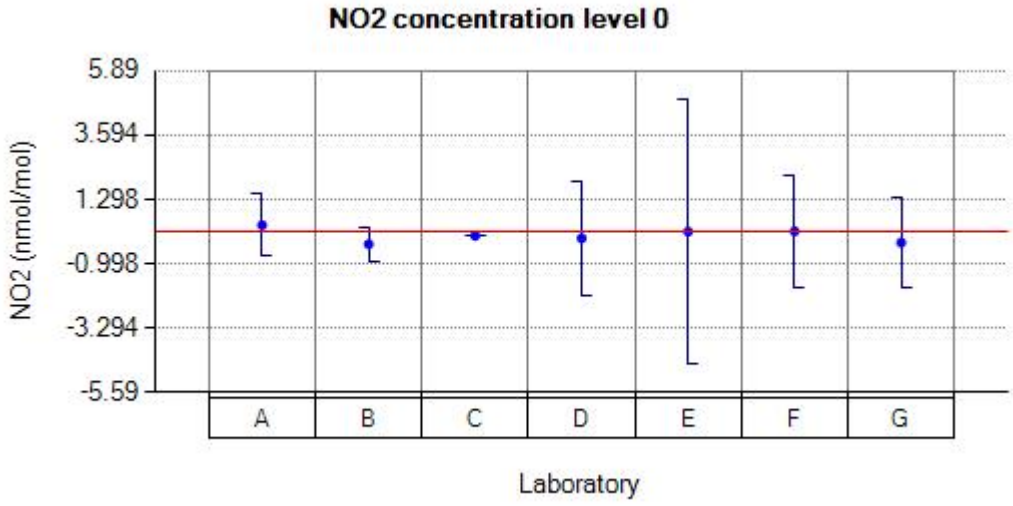

Figure 15: Reported values for NO_2 run 0.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	196.51	200.81	210.35	204.15	203.82	200.75	204.12
xi, 2	196.90	199.52	189.37	204.10	203.59	200.26	204.23
xi, 3	197.01	199.14	203.11	204.16	204.49	199.64	204.27
xi	196.80	199.82	200.94	204.13	203.96	200.21	204.20
si	0.26	0.87	10.65	0.03	0.46	0.55	0.07
u(xi)	5.96	4.50	10.82	10.33	3.20	5.17	4.25
U(xi)	11.92	9.00	34.43	20.66	6.40	10.34	8.50

Table 13: Reported values for NO_2 run 1.

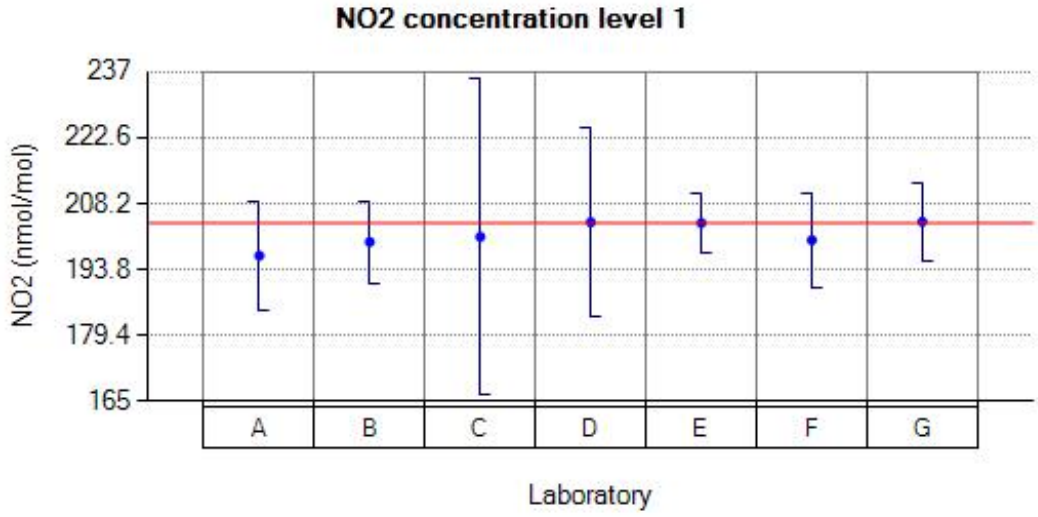

Figure 16: Reported values for NO_2 run 1.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	98.62	100.39	104.87	103.66	103.93	96.60	102.36
xi, 2	98.56	100.18	90.23	103.59	103.65	96.36	102.13
xi, 3	98.42	99.94	97.97	103.38	103.60	95.76	101.90
xi	98.53	100.17	97.69	103.54	103.72	96.24	102.13
si	0.10	0.22	7.32	0.14	0.17	0.43	0.23
u(xi)	2.72	2.70	7.49	5.24	2.61	2.50	2.50
U(xi)	5.45	5.40	23.83	10.48	5.22	5.00	5.00

Table 14: Reported values for NO_2 run 2.

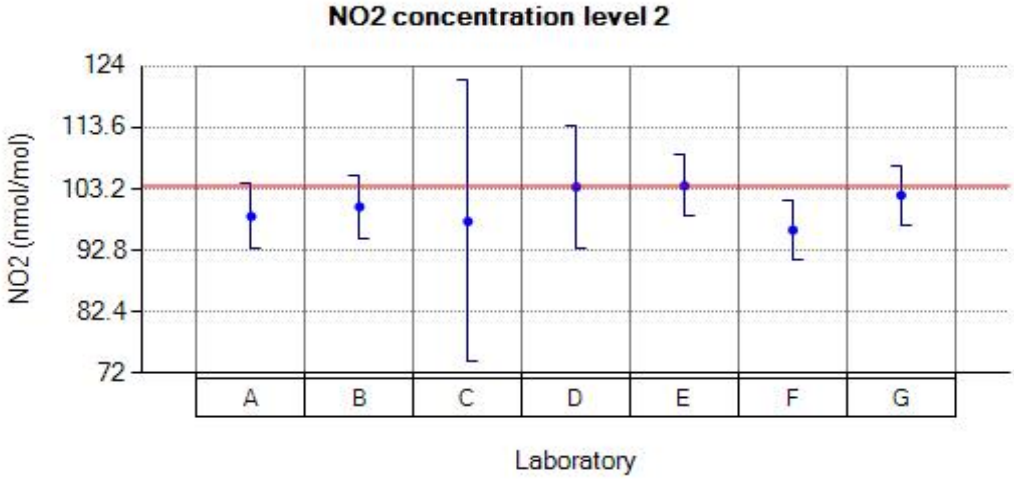

Figure 17 Reported values for NO_2 run 2.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	59.19	60.33	59.91	62.53	63.07	56.32	61.43
xi, 2	59.15	60.37	62.11	62.32	62.75	56.19	61.33
xi, 3	59.01	60.23	54.23	62.29	62.72	56.02	61.30
xi	59.11	60.31	58.75	62.38	62.84	56.17	61.35
si	0.09	0.07	4.06	0.13	0.19	0.15	0.06
u(xi)	1.57	1.90	4.22	3.16	2.45	1.63	1.50
U(xi)	3.14	3.80	13.44	6.31	4.89	3.26	3.00

Table 15: Reported values for NO_2 run 3.

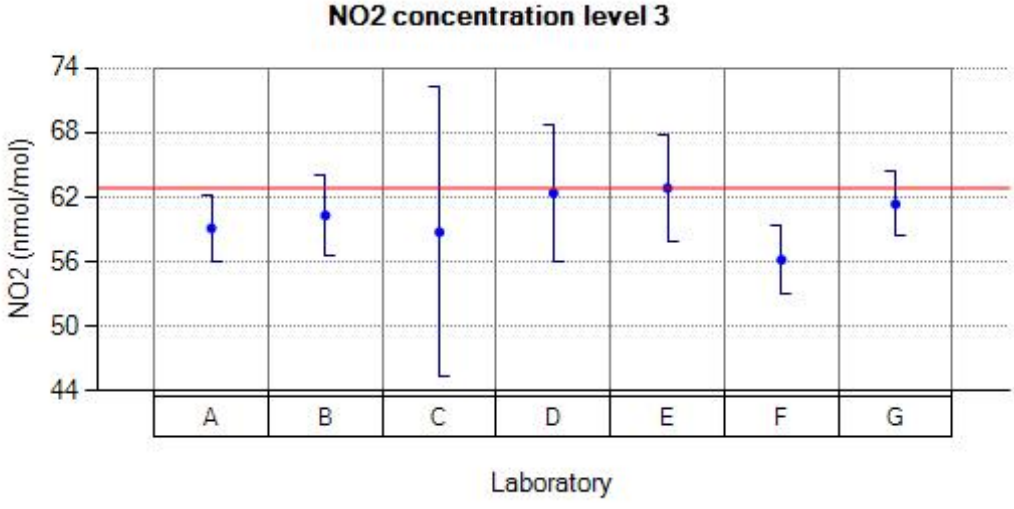

Figure 18: Reported values for NO_2 run 3.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	20.35	20.80	17.89	22.07	22.35	18.64	20.94
xi, 2	20.31	20.59	22.08	21.93	21.76	18.53	20.70
xi, 3	20.23	20.41	19.50	21.98	21.42	18.47	20.63
xi	20.29	20.60	19.82	21.99	21.84	18.54	20.75
si	0.06	0.19	2.11	0.07	0.47	0.08	0.16
u(xi)	0.52	0.52	2.27	1.11	2.38	1.21	1.00
U(xi)	1.04	1.04	7.23	2.23	4.76	2.42	2.00

Table 16: Reported values for NO_2 run 4.

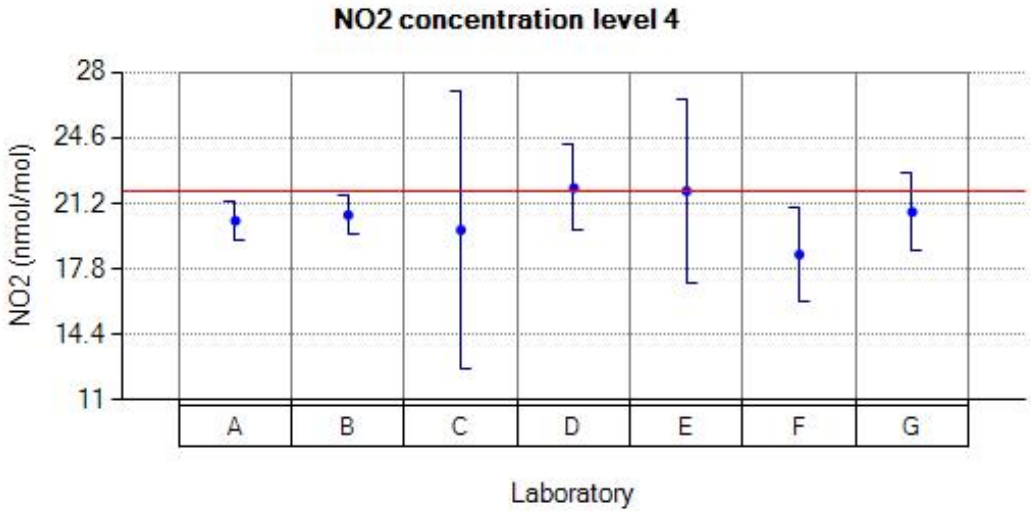

Figure 19: Reported values for NO_2 run 4.

Reported values for SO_2

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	0.11	-0.23	0.00	-0.07	0.01	-0.45	-0.02
u(xi)	0.57	0.52	0.00	0.34	0.53	0.68	0.80
U(xi)	1.14	1.04	0.00	0.68	1.06	1.37	1.60

Table 17: Reported values for SO_2 run 0.

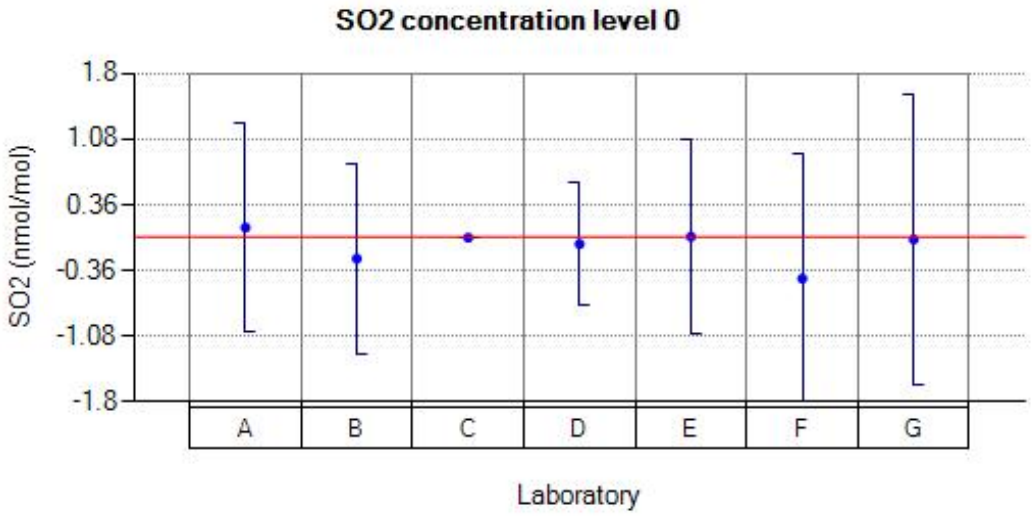

Figure 20: Reported values for SO_2 run 0.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	132.60	127.76	126.63	131.06	129.98	134.00	138.34
xi, 2	132.48	127.84	132.80	130.48	130.25	133.52	137.94
xi, 3	133.02	127.38	129.03	130.63	130.44	133.54	137.96
xi	132.70	127.66	129.48	130.72	130.22	133.68	138.08
si	0.28	0.24	3.11	0.30	0.23	0.27	0.22
u(xi)	5.07	3.10	3.27	7.47	1.45	2.95	3.20
U(xi)	10.15	6.20	10.41	14.94	2.91	5.90	6.40

Table 18: Reported values for SO_2 run 1.

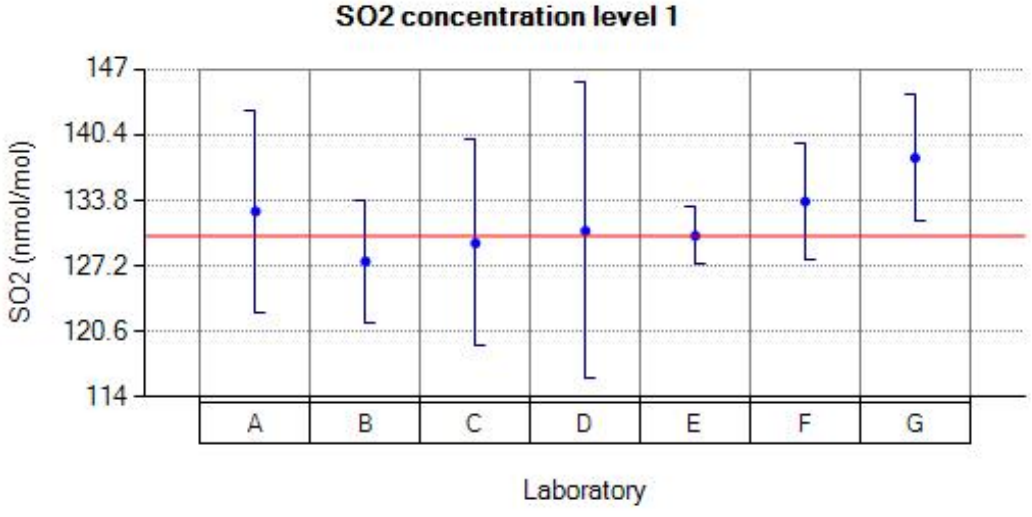

Figure 21: Reported values for SO_2 run 1.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	45.33	44.09	43.71	44.75	45.07	45.84	47.13
xi, 2	45.08	43.92	46.11	44.72	44.88	45.65	47.07
xi, 3	45.10	43.89	39.89	44.65	44.84	45.61	47.05
xi	45.17	43.96	43.23	44.70	44.93	45.70	47.08
si	0.13	0.10	3.13	0.05	0.12	0.12	0.04
u(xi)	1.34	1.12	3.30	2.56	0.71	1.35	1.50
U(xi)	2.67	2.24	10.49	5.11	1.43	2.70	3.00

Table 19: Reported values for SO_2 run 2.

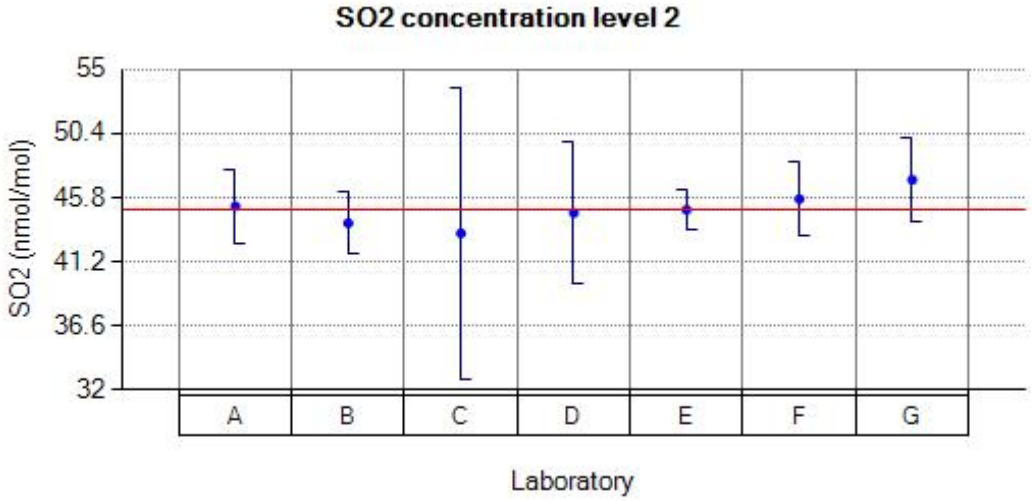

Figure 22: Reported values for SO_2 run 2.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	20.00	19.45	19.90	19.84	20.08	20.10	20.73
xi, 2	19.78	19.25	18.53	19.58	19.91	20.03	20.55
xi, 3	19.82	19.25	21.97	19.72	19.97	20.01	20.60
xi	19.86	19.31	20.13	19.71	19.98	20.04	20.62
si	0.11	0.11	1.73	0.13	0.08	0.04	0.09
u(xi)	0.80	0.71	1.89	1.12	0.57	1.09	1.00
U(xi)	1.60	1.42	6.01	2.25	1.15	2.18	2.00

Table 20: Reported values for SO_2 run 3.

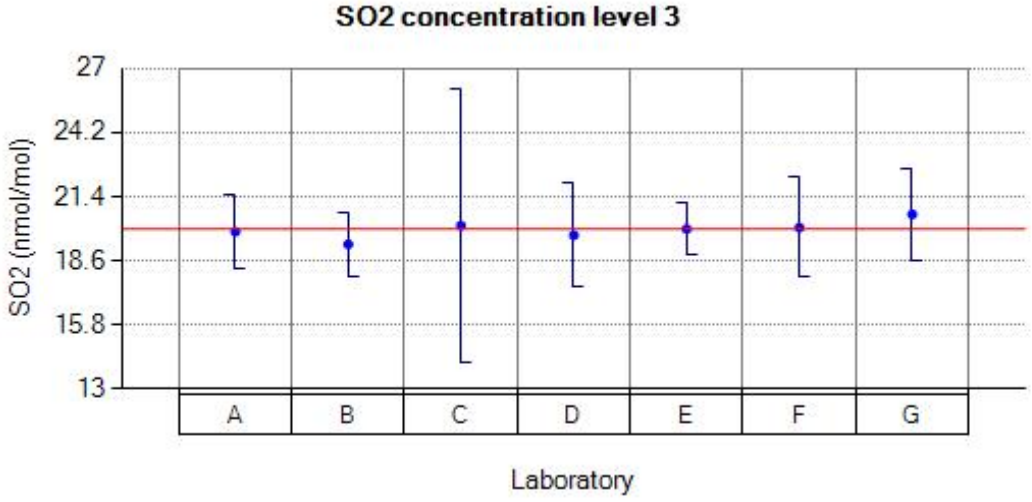

Figure 23: Reported values for SO_2 run 3.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	4.77	4.65	5.23	4.62	4.88	4.62	4.79
xi, 2	4.72	4.63	5.54	4.60	4.87	4.50	4.72
xi, 3	4.72	4.60	4.52	4.57	4.85	4.55	4.68
xi	4.73	4.62	5.09	4.59	4.86	4.55	4.73
si	0.02	0.02	0.52	0.02	0.01	0.06	0.05
u(xi)	0.19	0.28	0.67	0.35	0.53	0.93	0.80
U(xi)	0.38	0.56	2.12	0.71	1.06	1.87	1.60

Table 21: Reported values for SO_2 run 4.

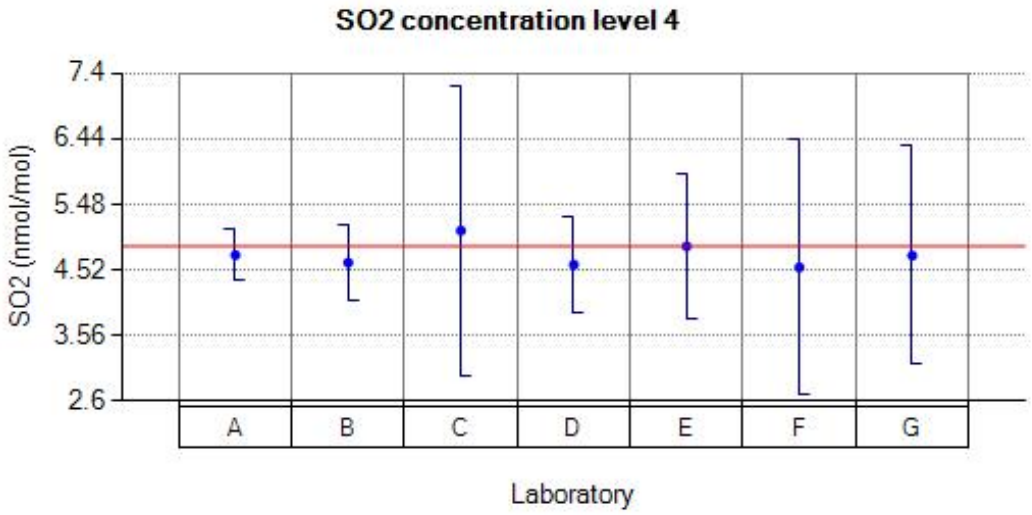

Figure 24: Reported values for SO_2 run 4.

Reported values for CO

	laboratories					
values	A	B	D	E	F	G
xi, 1	0.000	0.000	0.012	0.007	-0.091	-0.015
u(xi)	0.020	0.060	0.030	0.022	0.054	0.065
U(xi)	0.040	0.120	0.060	0.044	0.109	0.130

Table 22: Reported values for CO run 0.

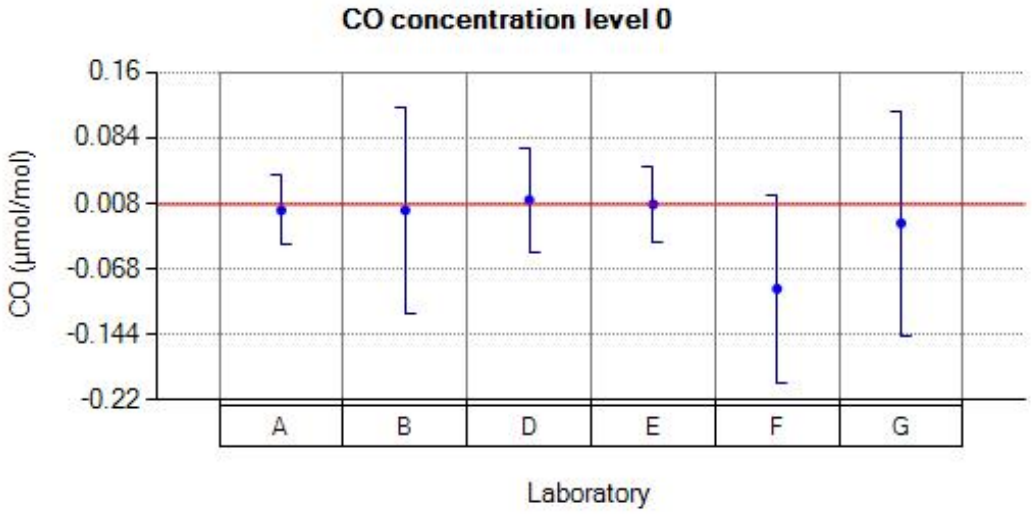

Figure 25: Reported values for CO run 0.

	laboratories					
values	A	B	D	E	F	G
xi, 1	7.200	8.382	8.049	8.059	8.015	8.337
xi, 2	7.260	8.377	8.047	8.065	8.040	8.334
xi, 3	7.260	8.371	8.045	8.061	8.048	8.332
xi	7.240	8.377	8.047	8.062	8.034	8.334
si	0.035	0.006	0.002	0.003	0.017	0.003
u(xi)	0.290	0.243	0.460	0.086	0.233	0.084
U(xi)	0.580	0.486	0.921	0.173	0.466	0.168

Table 23: Reported values for CO run 1.

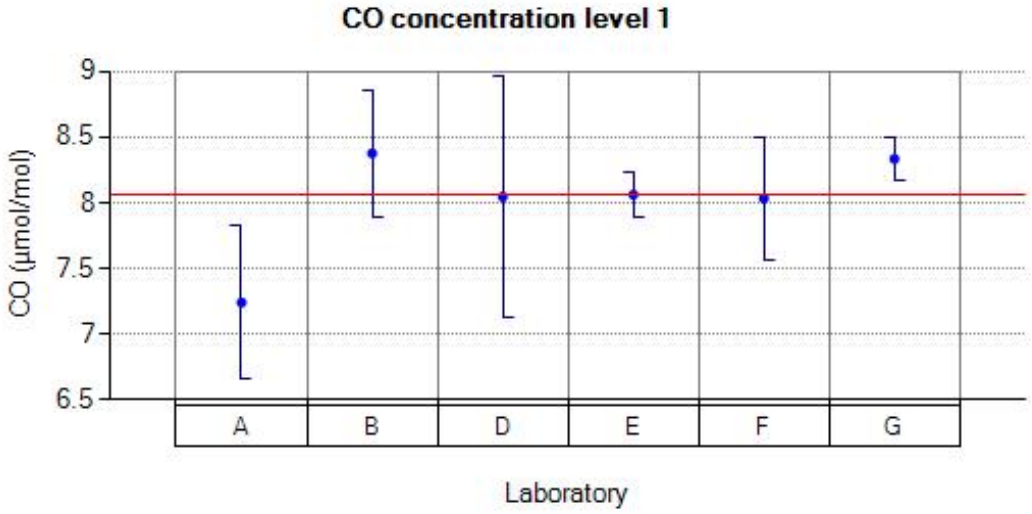

Figure 26: Reported values for CO run 1.

	laboratories					
values	A	B	D	E	F	G
xi, 1	5.430	6.280	6.041	6.049	6.074	6.241
xi, 2	5.420	6.276	6.042	6.049	6.054	6.235
xi, 3	5.430	6.276	6.046	6.051	6.082	6.231
xi	5.427	6.277	6.043	6.050	6.070	6.236
si	0.006	0.002	0.003	0.001	0.014	0.005
u(xi)	0.220	0.171	0.346	0.066	0.193	0.079
U(xi)	0.430	0.342	0.691	0.133	0.386	0.158

Table 24: Reported values for CO run 2.

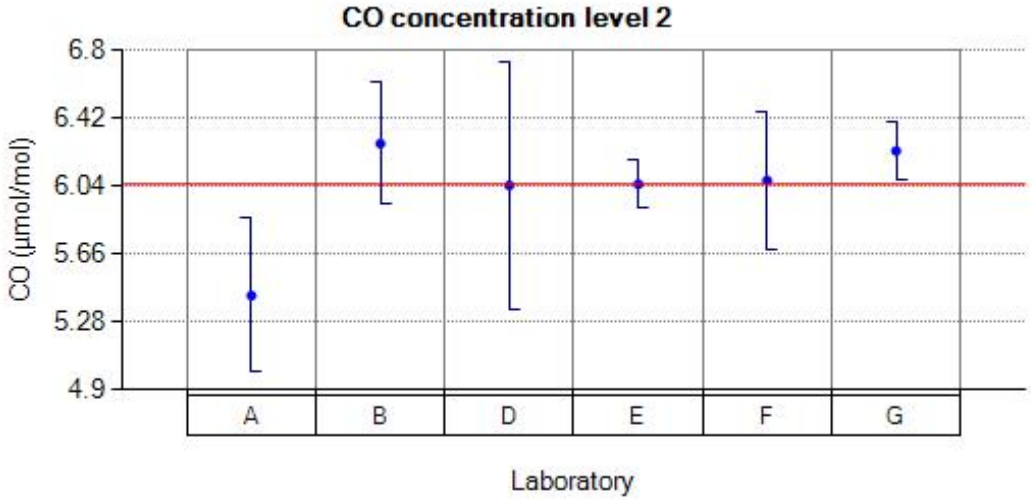

Figure 27: Reported values for CO run 2.

	laboratories					
values	A	B	D	E	F	G
xi, 1	2.740	3.139	3.024	3.026	3.085	3.088
xi, 2	2.870	3.138	3.024	3.025	3.083	3.087
xi, 3	2.820	3.137	3.025	3.026	3.093	3.090
xi	2.810	3.138	3.024	3.026	3.087	3.088
si	0.066	0.001	0.001	0.001	0.005	0.002
u(xi)	0.140	0.092	0.173	0.038	0.106	0.072
U(xi)	0.280	0.184	0.346	0.076	0.211	0.144

Table 25: Reported values for CO run 3.

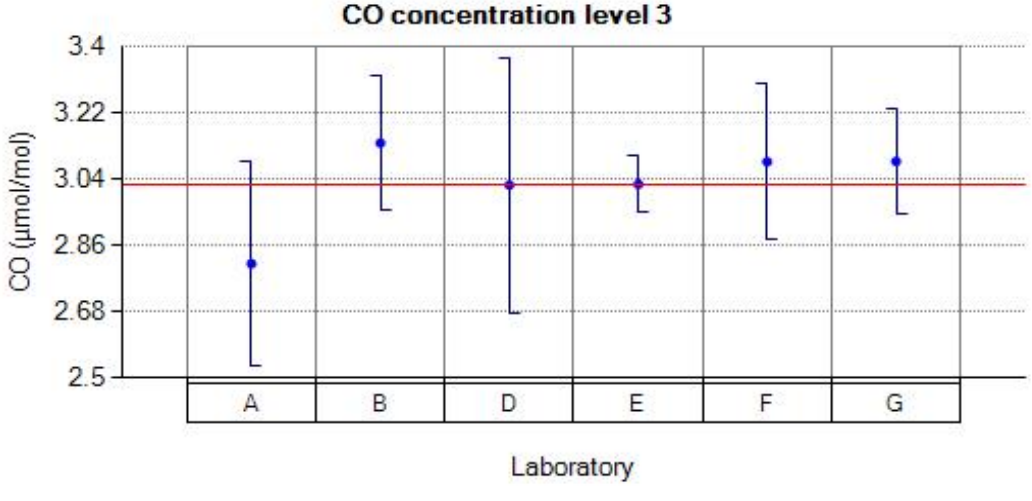

Figure 28: Reported values for CO run 3.

	laboratories					
values	A	B	D	E	F	G
xi, 1	0.860	1.030	1.006	1.001	1.072	0.985
xi, 2	0.900	1.030	1.005	1.000	1.078	0.985
xi, 3	0.900	1.030	1.005	1.002	1.078	0.986
xi	0.887	1.030	1.005	1.001	1.076	0.985
si	0.023	0.000	0.001	0.001	0.003	0.001
u(xi)	0.040	0.038	0.057	0.024	0.063	0.067
U(xi)	0.080	0.076	0.115	0.048	0.126	0.134

Table 26: Reported values for CO run 4.

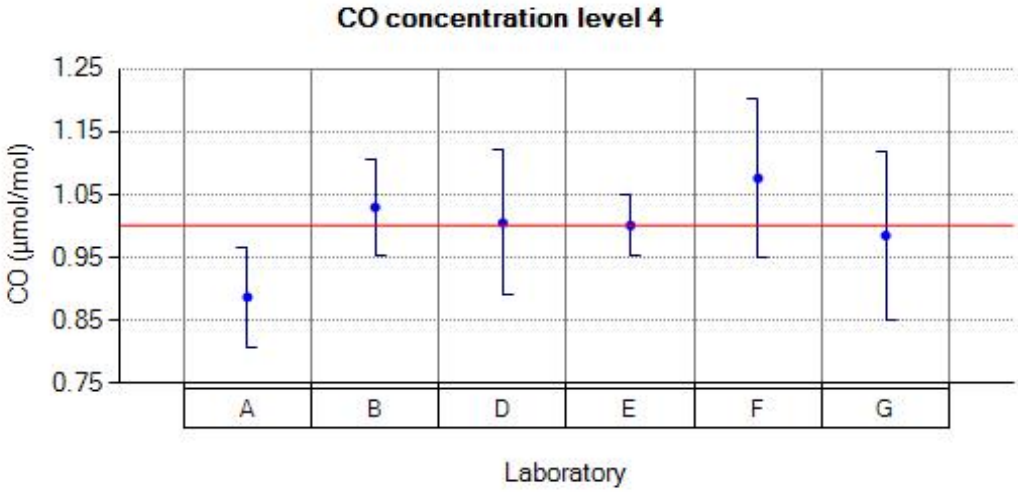

Figure 29: Reported values for CO run 4.

	laboratories					
values	A	B	D	E	F	G
xi, 1	4.400	4.691	4.533	4.548	4.647	4.653
xi, 2	4.420	4.693	4.531	4.547	4.651	4.655
xi, 3	4.420	4.691	4.531	4.546	4.656	4.656
xi	4.413	4.692	4.532	4.547	4.651	4.655
si	0.012	0.001	0.001	0.001	0.005	0.002
u(xi)	0.180	0.118	0.259	0.057	0.142	0.076
U(xi)	0.350	0.236	0.518	0.113	0.284	0.152

Table 27: Reported values for CO run 5.

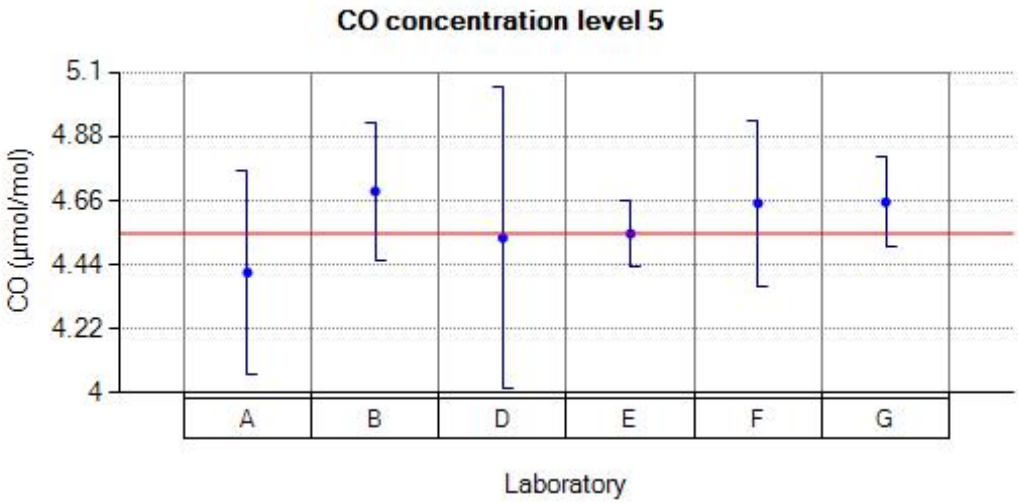

Figure 30: Reported values for CO run 5.

Reported values for O_3

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	0.00	0.25	0.00	0.40	0.13	-0.01	-0.10
u(xi)	0.14	0.28	0.00	1.00	0.55	1.00	1.25
U(xi)	0.28	0.56	0.00	2.00	1.10	2.00	2.50

Table 28: Reported values for O_3 run 0.

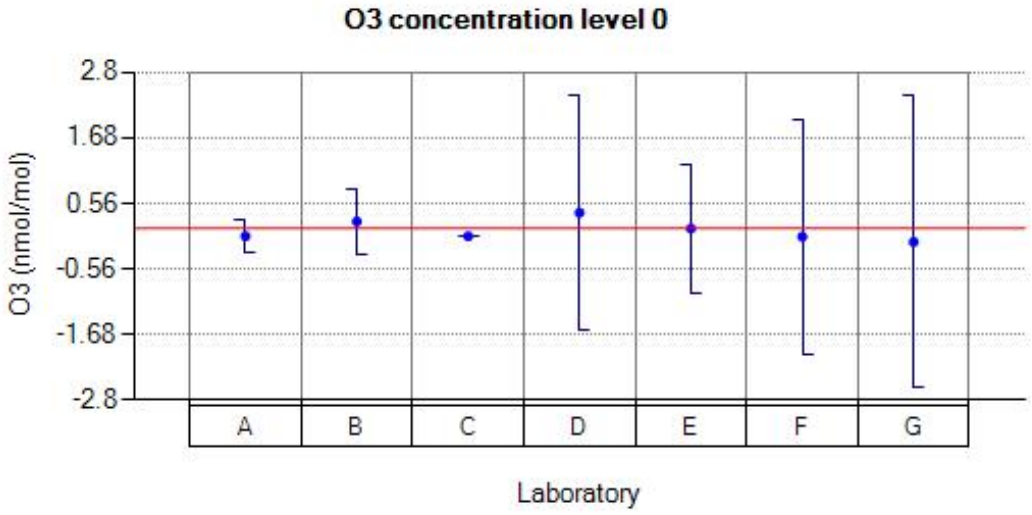

Figure 31: Reported values for O_3 run 0.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	310.00	300.21	321.21	301.80	301.02	303.39	297.79
xi, 2	315.50	303.81	295.33	303.18	303.41	308.54	300.11
xi, 3	318.67	306.86	313.04	304.77	304.68	311.09	301.02
xi	314.72	303.62	309.86	303.25	303.03	307.67	299.64
si	4.38	3.32	13.23	1.48	1.85	3.92	1.66
u(xi)	8.27	2.84	13.39	12.77	3.52	4.39	4.30
U(xi)	16.53	5.68	42.61	25.53	7.04	8.79	8.60

Table 29: Reported values for O_3 run 1.

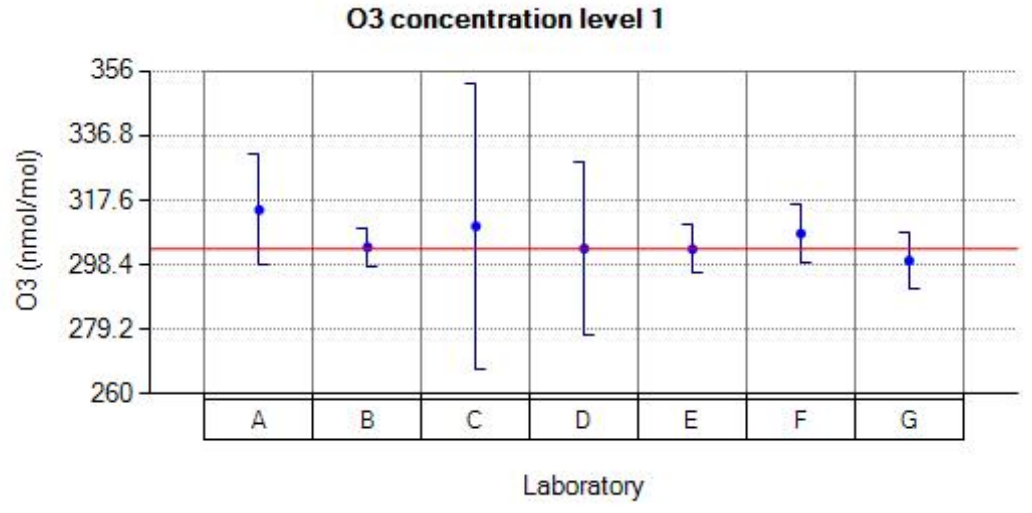

Figure 32: Reported values for O_3 run 1.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	104.17	101.62	104.67	100.70	100.68	102.63	98.65
xi, 2	103.33	101.05	98.00	100.50	99.97	101.81	97.93
xi, 3	103.17	100.99	94.38	100.50	99.66	101.55	97.62
xi	103.55	101.22	99.01	100.56	100.10	101.99	98.06
si	0.53	0.34	5.22	0.11	0.52	0.56	0.52
u(xi)	2.61	1.20	5.38	4.22	1.29	2.49	1.65
U(xi)	5.21	2.40	17.12	8.44	2.57	4.98	3.30

Table 30: Reported values for O_3 run 2.

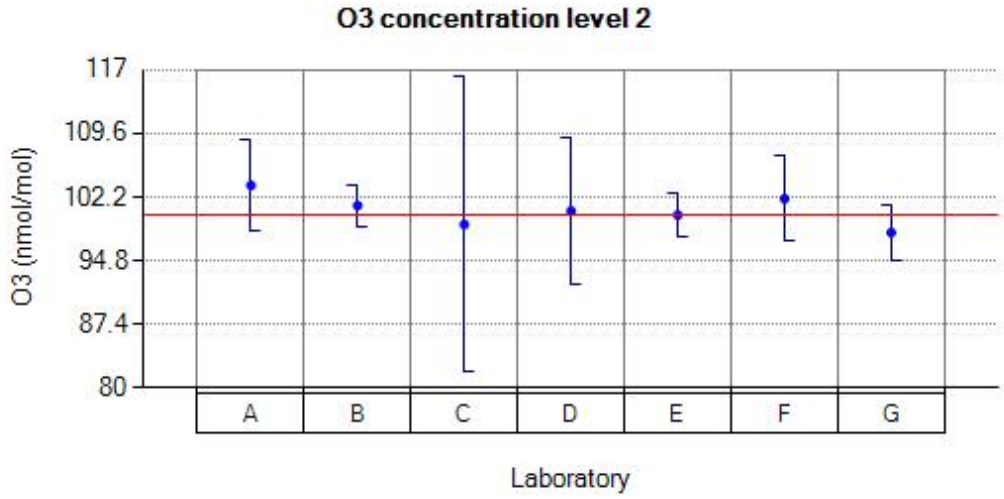

Figure 33: Reported values for O_3 run 2.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	62.00	61.29	62.93	60.59	60.36	61.39	58.85
xi, 2	62.00	61.20	63.79	60.79	60.30	61.30	58.78
xi, 3	61.00	61.27	59.24	61.29	60.22	61.30	58.77
xi	61.66	61.25	61.98	60.89	60.29	61.33	58.80
si	0.57	0.04	2.41	0.36	0.07	0.05	0.04
u(xi)	1.58	0.92	2.57	2.56	0.92	1.98	1.50
U(xi)	3.15	1.84	8.18	5.13	1.84	3.96	3.00

Table 31: Reported values for O_3 run 3.

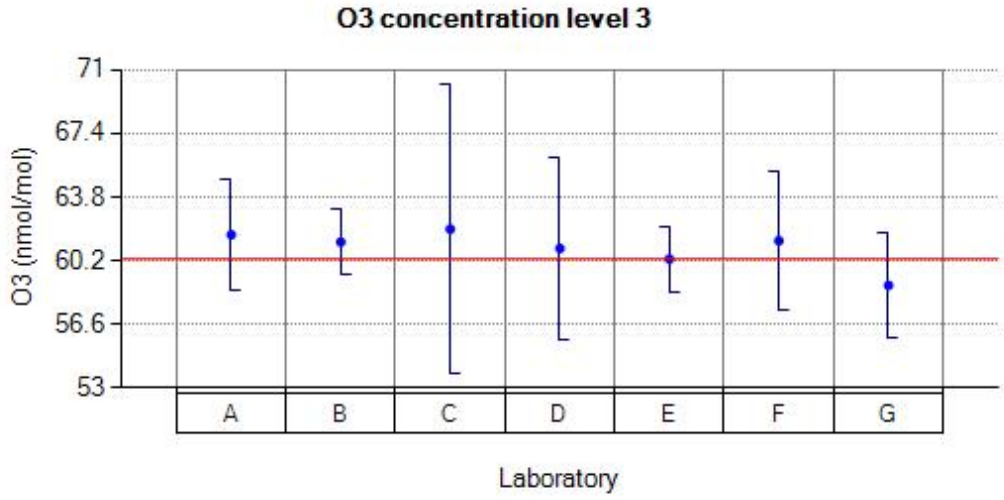

Figure 34: Reported values for O_3 run 3.

	laboratories						
values	A	B	C	D	E	F	G
xi, 1	20.17	21.11	20.56	20.94	20.48	20.65	19.77
xi, 2	20.00	21.06	19.30	20.66	20.41	20.56	19.69
xi, 3	20.00	21.06	24.33	20.19	20.41	20.50	19.68
xi	20.05	21.07	21.39	20.59	20.43	20.57	19.71
si	0.09	0.02	2.61	0.37	0.04	0.07	0.04
u(xi)	0.75	0.64	2.77	1.01	0.60	1.30	1.30
U(xi)	1.50	1.28	8.82	2.02	1.21	2.60	2.60

Table 32: Reported values for O_3 run 4.

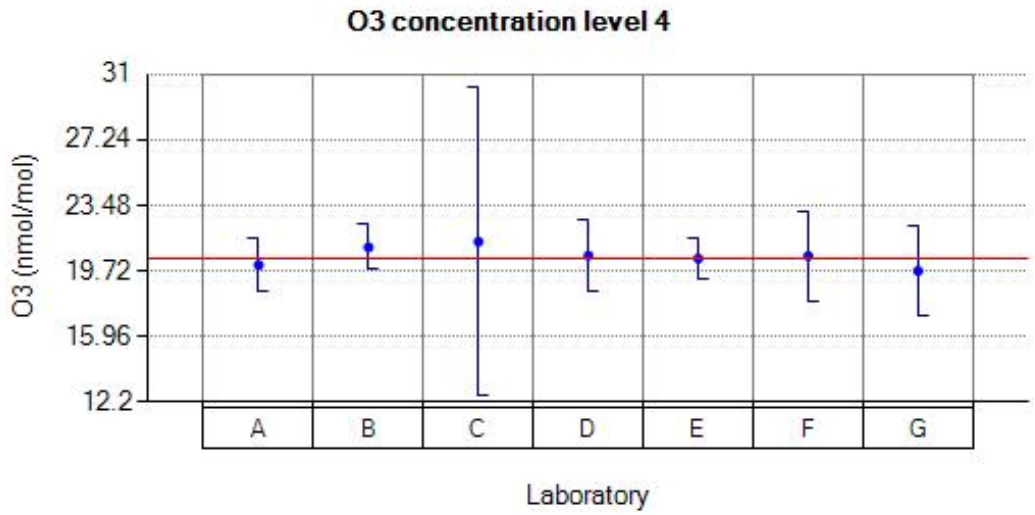

Figure 35: Reported values for O_3 run 4.

Annex C. The precision of standardized measurement methods

For the main purpose of monitoring trends between different IE the precision of standardized SO_2, CO, O_3 and NO_X measurement methods [2], [3], [4] and [5] as implemented by NRLs was evaluated. The applied methodology is described in ISO 5725-1, -2 and -6 [14], [15] and [16].

The precision experiment has involved a total of 7 laboratories the actual number of labs (p_j) varying from run to run (Table 33). Laboratory C didn't reported results for CO. For run 0 was requested only one value so repeatability cannot be evaluated. Five concentration levels were tested for CO, four levels for O_3, SO_2 and NO_2, and two for NO. Outlier tests were performed and results are reported in Annex D.

The repeatability standard deviation (s_r) was calculated in accordance with ISO 5725-2 as the square root of average within laboratory variance. The repeatability limit (r) is calculated using Equation 5 [16]. It represents the biggest difference between two test results found on an identical test gas by one laboratory using the same apparatus within the shortest feasible time interval, that should not been exceeded on average more than once in 20 cases in the normal and correct operation of method.

$$r = t_{95\%,\nu} \cdot \sqrt{2} \cdot s_r \qquad \textbf{Equation 5}$$

The reproducibility standard deviation (s_R) was calculated in accordance with ISO 5725-2 as the square root of sum of repeatability and between laboratory variance. The reproducibility limit (R) is calculated using Equation 6 [16]. It represents the biggest difference between two measurements on an identical test gas reported by two laboratories, which should not occur on average more than once in 20 cases in the normal and correct operation of method.

$$R = t_{95\%,\nu} \cdot \sqrt{2} \cdot s_R \qquad \textbf{Equation 6}$$

The repeatability standard deviation was evaluated with (p_j*(3-1)) degrees of freedom (ν) and reproducibility standard deviation with (p_j-1) degrees of freedom. The critical range student factors ($t_{\alpha,\nu}$) are reported in Table 33.

parameter	run	p_j	t critical value 95% for r	t critical value 95% for R
CO	1,2,3,4,5	6	2.179	2.571
NO	1,2	7	2.145	2.447
NO_2	1,2,3,4	7	2.145	2.447
O_3	1,2,3,4	7	2.145	2.447
SO_2	1,2,3,4	7	2.145	2.447

Table 33: Critical values of t used in the repeatability (r) and reproducibility (R) evaluation.

The repeatability (r) and reproducibility (R) limits of measurement methods are presented from Table 34 to
Table 38 and from Figure 36 to Figure 40. It is also reported the 'reproducibility from common criteria (R (from σ_p))' calculated by substituting s_R in Equation 6 with a 'standard deviation for proficiency assessment' (Table 4). Comparison between R and R (from σ_p) serves to indicate that σ_p is realistic ([13] par. 6.3.1) or from the other point of view, that the general methodology implemented by NRLs is appropriate for σ_p.

NO data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.2		1.8	
20.0	3.4	4.7	
200.0	11.0	13.6	6.8%

Table 34: The R and r of NO standard measurement method.

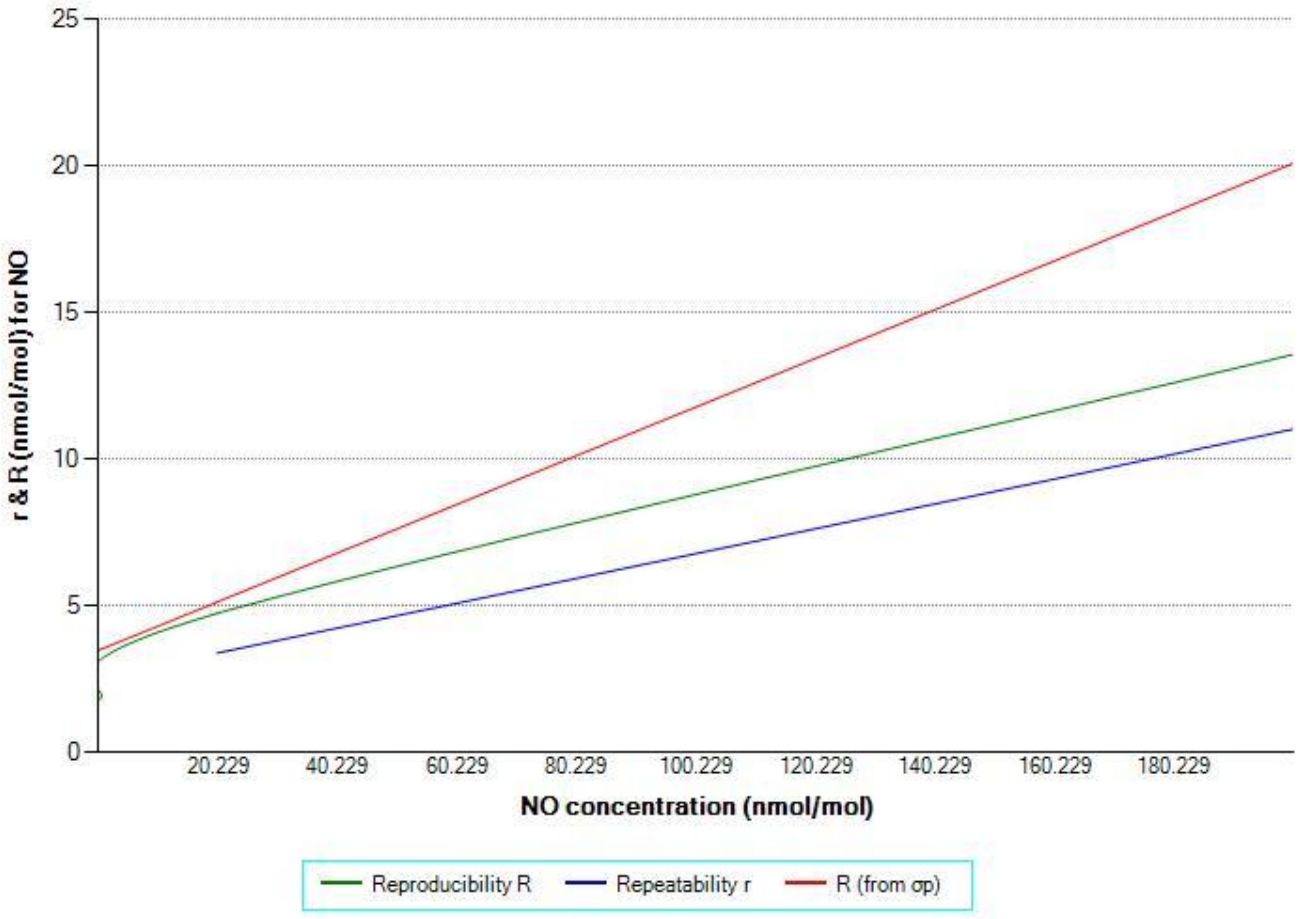

Figure 36: The R and r of NO standard measurement method as a function of concentration.

NO_2 data (nmol/mol) without outlier			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.02		0.94	
13.41	0.22	2.13	
20.22	0.16	2.51	
58.96	0.29	6.36	
99.78	0.61	11.60	
119.43	0.87	12.25	10.26%

Table 35: The R and r of NO_2 standard measurement method.

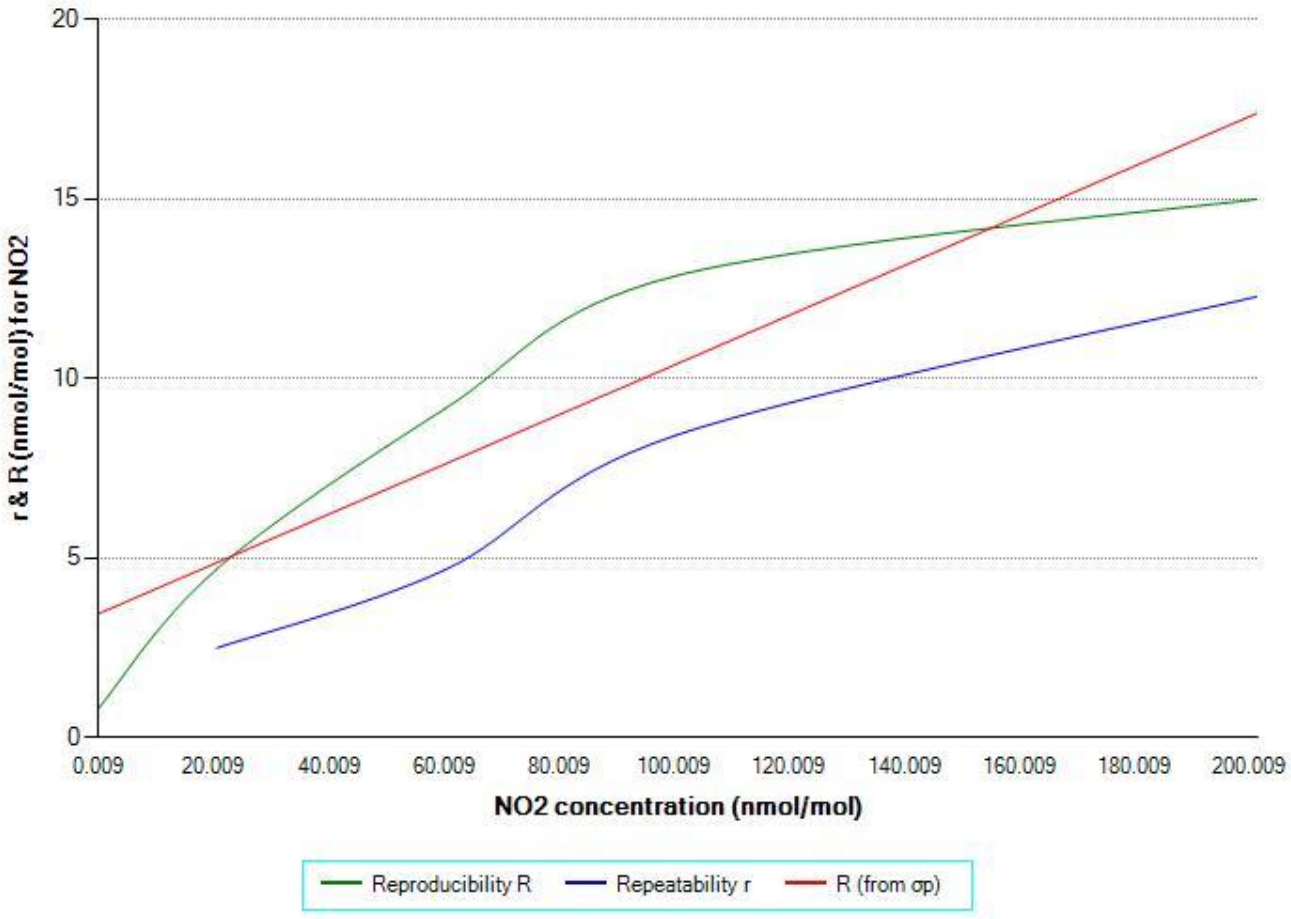

Figure 37: The R and r of NO_2 standard measurement method as a function of concentration.

SO_2 data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
-0.1		0.7	
4.7	0.6	0.9	
20.0	2.0	2.3	
45.0	3.6	5.4	
131.8	3.6	12.3	9.3%

Table 36: The R and r of SO_2 standard measurement method.

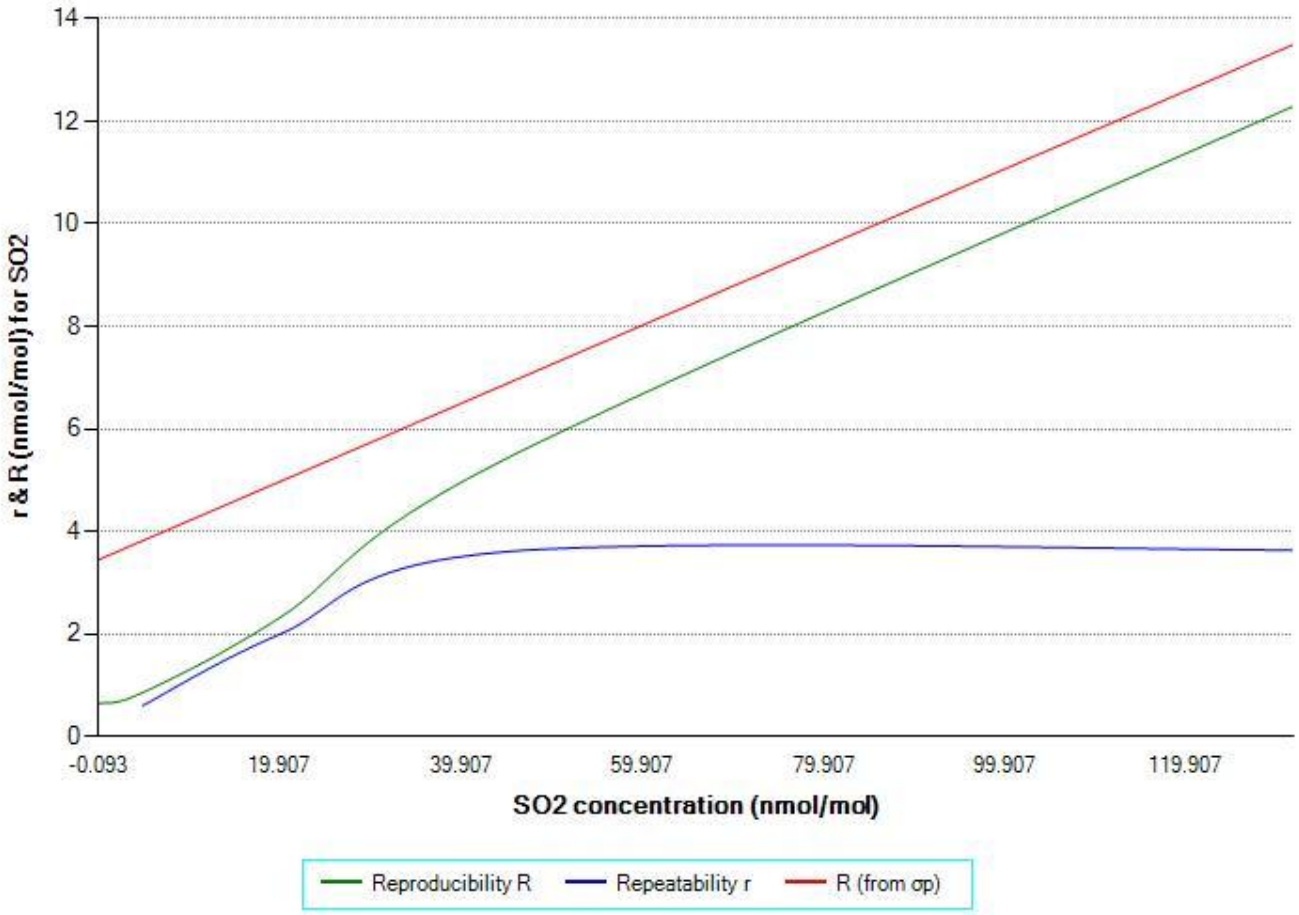

Figure 38: The R and r of SO_2 standard measurement method as a function of concentration.

CO data (µmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
-0.015		0.141	
0.997	0.03	0.231	
3.029	0.083	0.428	
4.582	0.016	0.38	
6.017	0.021	1.114	
8.016	0.05	1.489	18.6%

Table 37: The R and r of CO standard measurement method.

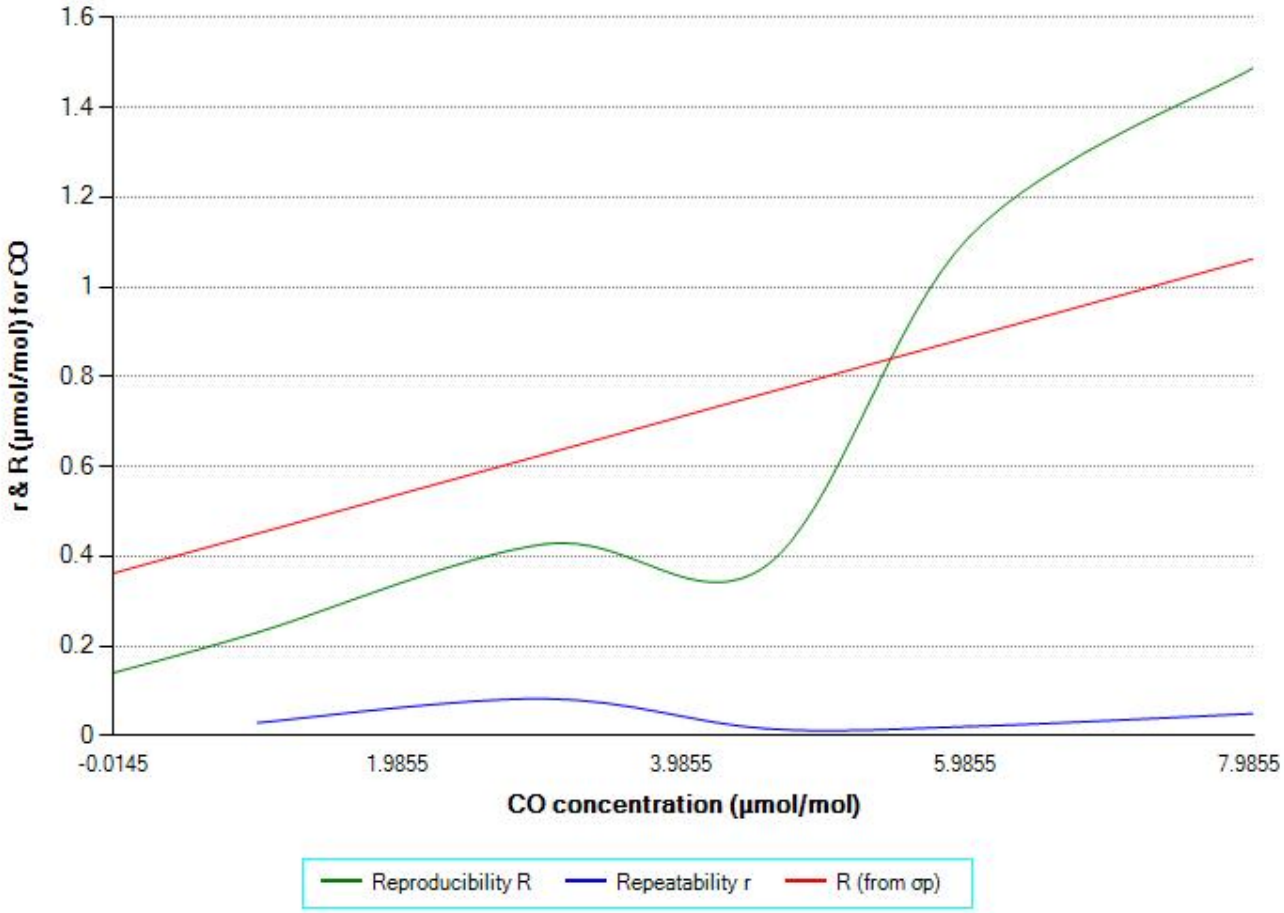

Figure 39: The R and r of CO standard measurement method as a function of concentration.

O_3 data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.1		0.6	
20.5	3.0	3.5	
60.9	2.9	4.6	
100.6	6.1	8.5	
306.0	17.4	23.9	7.8%

Table 38: The R and r of O_3 standard measurement method.

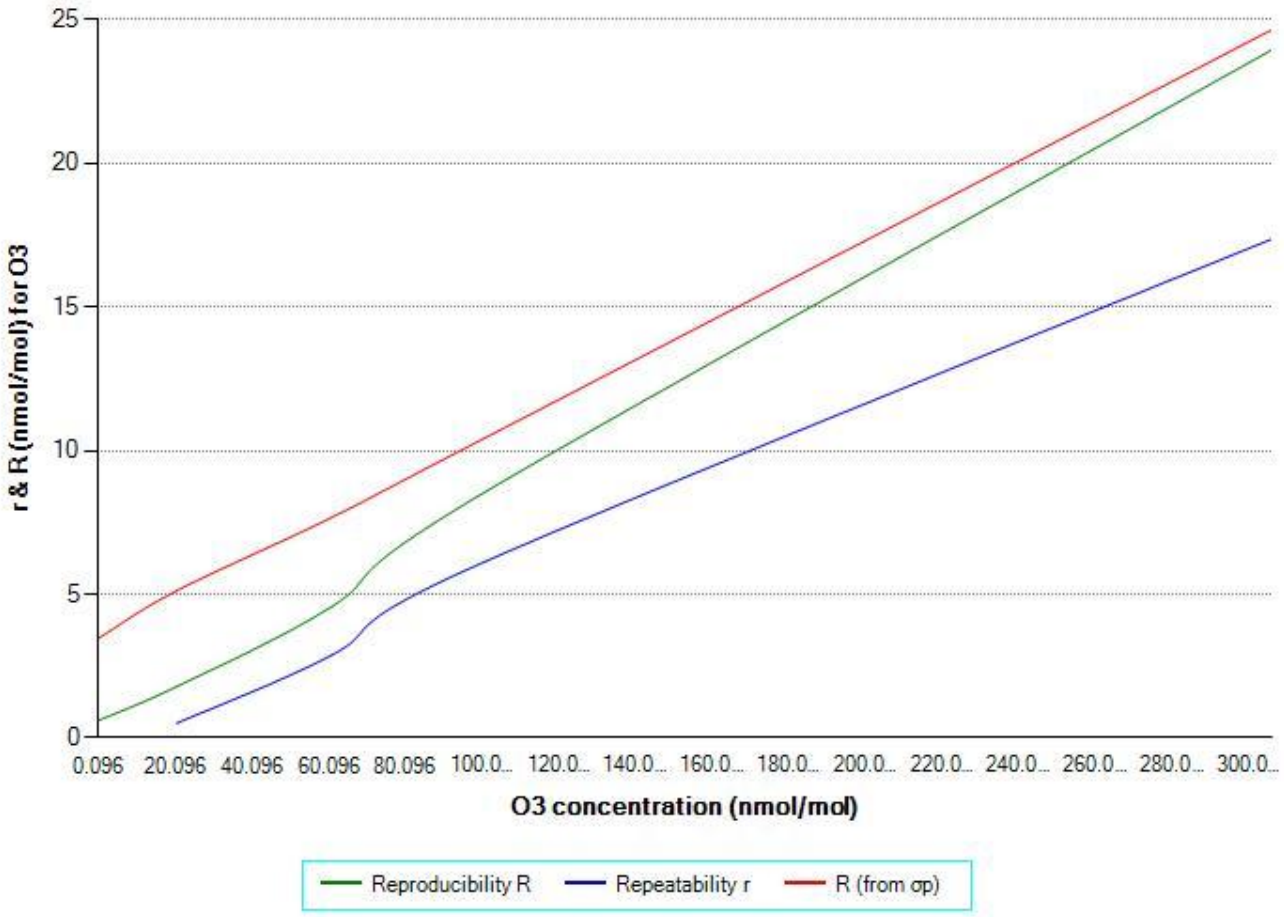

Figure 40: The R and r of O_3 standard measurement method as a function of concentration.

Annex D. The scrutiny of results for consistency and outlier test

The precision evaluation (Annex C) focuses on data that are as much as possible the reflection of every day work of NRLs and thus represents the comparability of participant's standard operating procedures.
For that reason a procedure for the detection of exceptional errors (error during typing, slip in performing the measurement or the calculation, wrong averaging interval, malfunction of instrumentation, etc.) was applied.
In this procedure were carried out tests for data consistency and statistical outliers as described in ISO 5725-2.
Laboratories showing some form of statistical inconsistency were requested to investigate the cause of discrepancies. Laboratories were allowed to correct their results in case of identification of exceptional errors. Subsequently, data were considered definitive and "Grubb's one outlying observation test" was performed. If detected, outliers were removed and "Grubb's one outlying observation test" was repeated until no more outliers were observed.

During this IE the statistical outlier presented in the table below is related only to zero level:

parameter	run	laboratory	measured value	failing test	confidence level
CO	0	F	-0.09	G1 minimum	1%, 5%

Table 39: "Genuine" statistical outliers according to Grubb's one outlying observation test.

The precision of standardized measurement methods reported in Annex C are calculated using the database without outliers.

Annex E. Laboratory accreditation certificate

In this annex is shown the accreditation certificate of the laboratory who organized this Inter-laboratory comparison.

Deutsche Gesellschaft für Akkreditierung mbH

Unterzeichner der Multilateralen Abkommen von
EA und ILAC zur gegenseitigen Anerkennung

vertreten im

Deutschen AkkreditierungsRat

Akkreditierung

Die **DGA Deutsche Gesellschaft für Akkreditierung mbH** bestätigt hiermit, dass das Prüflaboratorium

Umweltbundesamt
Fachgebiet II 4.4
Nationales EU-Referenzlabor für Luftqualität
Paul-Ehrlich-Str. 29
63225 Langen

die Kompetenz nach DIN EN ISO/IEC 17025:2005 besitzt, Prüfungen im folgenden Geltungsbereich auszuführen:

Prüfgebiet:	**Chemie**
Prüfverfahren:	Gaschromatographie, UV/VIS-Spektroskopie, Photometrie
Prüfgegenstände:	synthetische Prüfgase

Die Anlage ist Bestandteil der Urkunde und besteht aus 2 Seiten.
Die Akkreditierung ist gültig vom **23.12.2009** bis **22.12.2014**.
DAR-Registriernummer: **DGA-PL-6673.09**

Deutsche Gesellschaft für Akkreditierung mbH EA IAF ILAC MITGLIED

Frankfurt am Main, 23.12.2009

Dr. A. Steinhorst

Siehe Hinweise auf der Rückseite

DGA Deutsche Gesellschaft für Akkreditierung mbH

Anlage zur Akkreditierungsurkunde DGA-PL-6673.09 (23.12.2009)

Die Akkreditierung nach DIN EN ISO/IEC 17025:2005 ist gültig bis: 22.12.2014

Urkundeninhaber:

Umweltbundesamt

Fachgebiet II 4.4

Nationales EU-Referenzlabor für Luftqualität

Paul-Ehrlich-Str. 29

63225 Langen

Prüfungen im Bereich

- Chemie

Einzelne Prüfverfahren der

- Gaschromatographie
- UV/VIS-Spektroskopie
- Photometrie

Seite 1 von 2

Einzelne Prüfverfahren der Gaschromatographie

Norm/Ausgabedatum Hausmethode/Version	Analyt – Titel der Norm Angabe zu Probenvorbehandlung/Prüftechnik	Prüfgegenstand
DIN EN 14662-3 2005-08	Luftbeschaffenheit - Standardverfahren zur Bestimmung von Benzolkonzentrationen - Teil 3: Automatische Probenahme mit einer Pumpe mit gaschromatographischer In-situ-Bestimmung	synthetische Prüfgase

Einzelne Prüfverfahren der UV/VIS-Spektroskopie

Norm/Ausgabedatum Hausmethode/Version	Analyt – Titel der Norm Angabe zu Probenvorbehandlung/Prüftechnik	Prüfgegenstand
DIN EN 14211 2005-06	Luftqualität - Messverfahren zur Bestimmung der Konzentration von Stickstoffdioxid und Stickstoffmonoxid mit Chemilumineszenz	synthetische Prüfgase
DIN EN 14212 2005-06	Luftqualität - Messverfahren zur Bestimmung der Konzentration von Schwefeldioxid mit Ultraviolett-Fluoreszenz	

Einzelne Prüfverfahren der Photometrie

Norm/Ausgabedatum Hausmethode/Version	Analyt – Titel der Norm Angabe zu Probenvorbehandlung/Prüftechnik	Prüfgegenstand
DIN EN 14626 2005-07	Luftqualität - Messverfahren zur Bestimmung der Konzentration von Kohlenmonoxid mit nicht-dispersiver Infrarot-Photometrie	synthetische Prüfgase
DIN EN 14625 2005-07	Luftqualität - Messverfahren zur Bestimmung der Konzentration von Ozon mit Ultraviolett-Photometrie	

European Commission
EUR 26578 – Joint Research Centre – Institute for Environment and Sustainability

Title: Evaluation of the Laboratory Comparison Exercise for SO2, CO, O3, NO and NO2, Langen (D) 1st-6th September 2013

Author(s): Maurizio Barbiere, Volker Stummer, Friedrich Lagler, Hans-Guido Muecke

Luxembourg: Publications Office of the European Union

2013 – 58 pp. – 21.0 x 29.7 cm

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

ISBN 978-92-79-36781-6

DOI: 10.2788/43930

Abstract

From the 1st to the 6th of September 2013 in Langen (D), 7 Laboratories of WHO/AQUILA (Network of European Air Quality Reference Laboratories) met at a laboratory comparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Directive about air quality (SO2, CO, NO, NO2 and O3).
The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system.
On the basis of criteria imposed by the European Commission, 75.7% of the results reported by the laboratories were good both in terms of measured values and reported uncertainties. Another 20.9% of the results had good measured values, but the reported uncertainties were too high and for 2.0% values the uncertainty was underestimated. 1.4% values were questionable.
Comparability of results among participants at the highest concentration level, excluding outliers, is acceptable for NO, SO2 and O3 measurements while NO2 and CO one showed less satisfactory results.

LB-NA-26578-EN-N

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Serving society
Stimulating innovation
Supporting legislation

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ISBN 978-92-79-36781-6

Publications Office