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Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 Langen 23rd- 28th October 2011

EC Harmonization Program for Air Quality Measurements

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Executive Summary

From the 23rd to the 28th of October 2011 seven Laboratories of the World Health Organization (WHO) European-Region met for another joint JRC-ERLAP/WHO inter-laboratory comparison exercise (IE) 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 (SO_2, CO, NO, NO_2 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 criteria, provides information on compliance with Data Quality Objectives and measurement capabilities of the National Air Quality Laboratories to the European Commission and can be used by participants in their laboratory's quality system.

In terms of criteria imposed by the European Commission (that are not mandatory for WHO laboratories), 59.4% of the results reported by National Reference Laboratories (AQUILA network) were good both in terms of measured values and reported uncertainties. Another 39.9% of the results had good measured values, but the reported uncertainties were either too high. Only one reported value (0.7%) has been evaluated as questionable.
The comparability of results among AQUILA participants at the highest generated concentration levels, excluding outliers, is acceptable for CO and NO measurements while SO_2, O_3 and NO_2 measurements showed less satisfactory results.

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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

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) 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 integrates within the WHO European Region, which includes public health and other environmental institutes - especially 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 23rd to the 28th of October 2011 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 aiming at evaluating 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 said 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 in March 2011 to the members of the AQUILA network and the WHO-CC representative. Registration was opened on March 2011. A registration letter was sent by WHO-CC to interested parties and the registration was closed with the list of seven 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 Sunday, 23rd October 2011, for the installation of their equipment. On Monday (24/10/2011) morning the generation of NO gas mixtures started at 9:00. On Tuesday morning at 8:45 the zero air analysis for NO_2 measurement started. SO_2 and CO measurement was carried out on Wednesday 8:45. O_3 was measured on Thursday 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: Croatia, Macedonia, Lithuania, Russia, Serbia, Ukraine and Germany.

Country	Laboratory	Code	Network	Method
Croatia	Institute for Medical Research and Occupational Health (IMI)	B	WHO	automatic
Macedonia	Ministry of Environment and Physical Planning (MOEPP)	C	WHO	automatic
Lithuania	Environmental Protection Agency (AAA)	D	AQUILA	automatic
Russian Federation	State Environmental Institution 'Mosecommonitoring' (MOSECOM)	E	WHO	automatic
Serbia	Institute of Public Health (IPH_S)	F	AQUILA	automatic
Ukraine	State Institution 'O.M. Marzeev Institute of Hygiene and Medical Ecology, Academy of Medical Sciences of Ukraine' (IHME)	G	WHO	auto/manual
Germany	Federal Environment Agency (UBA)	H	AQUILA	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 Ukraine laboratory that used a semi-automatic method.

Gas	Lab Code	Instrument
CO	B	APMA-370, 2010
	C	Thermo Environment, TEI 48C
	D	Horiba Ltd., 2011, NDIR, APMA 370
	E	OPTEC, model K-100 (№58-1-04)
	F	HORIBA, 2008, APMA 370
	G	-
	H	HORIBA, 2009, APMA 370
NOX	B	Horiba APNA-370, 2008
	C	Thermo Environment, TEI 42C
	D	Horiba Ltd, 2011, cemiluminescense, APNA 370,
	E	Monitor Europe, ME-9841B (№ 09-1638)
	F	Horiba, 2008, APNA370
	G	-
	H	HORIBA, 2004, APNA 360
O3	B	HORIBA APOA – 370
	C	Thermo Environment, TEI 49C.
	D	Horiba Ltd, 2011, NDUV, APOA 370,
	E	Monitor Europe, ME-9810B (№ M1692-M343)
	F	HORRIBA, 2008, APOA 370
	G	-
	H	Thermo Scientific, 2009, 49i
SO2	B	APSA-370, 2009
	C	Thermo Environment, TEI 43C
	D	Horiba Ltd., 2011, UV fluorescence, APSA 370
	E	Monitor Europe, ME-9850B (№M1704-M654)
	F	HORIBA, 2009, APSA 370
	G	-
	H	HORIBA , 2005. APSA 360

Table 2: The list of instruments used by participants.

Semi-automatic method adopted by laboratory G:

- 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. 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; d= + 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. 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; d= + 25 %
- O_3 method is based on the displacement of iodine with ozone while ozone is adsorbed 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; d= + 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; d= + 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 SO_2, CO, O_3, NO and NO_2 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 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
23-Oct	13:00	3.5	/	X							
24-Oct	8:45	0.15	/		X						
24-Oct	9:00	2.5	NO			0					
24-Oct	11:45	1.5	NO				200				
24-Oct	13:30	1.5	NO				20				
25-Oct	8:45	0.30	NO2			0					
25-Oct	10:00	1.5	NO2					200			
25-Oct	11:45	1.5	NO2					100			
25-Oct	13:30	1.5	NO2					60			
25-Oct	15:15	1.5	NO2					20			
26-Oct	8:45	1	SO2			0					
26-Oct	10:00	1.5	SO2								130
26-Oct	11:45	1.5	SO2								45
26-Oct	13:30	1.5	SO2								20
26-Oct	15:15	1.5	SO2								5
26-Oct	17:00	1	CO			0					
26-Oct	18:00	2	CO							8	
26-Oct	20:00	2	CO							6	
26-Oct	22:00	2	CO							3	
27-Oct	0:00	2	CO							1	
27-Oct	2:00	2	CO							4.5	
27-Oct	8:45	1	O3			0					
27-Oct	10:00	1.5	O3						300		
27-Oct	11:45	1.5	O3						100		
27-Oct	13:30	1.5	O3						60		
27-Oct	15:15	1.5	O3						20		
28-Oct	8:45	0.15	evaluation								
28-Oct	9:00	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 said 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. For 'a' and 'b' see 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 1 to Figure 5) in which the z'-scores of each participant are grouped together, and assessment criteria are presented as z'=±2 and z'=±3 lines.

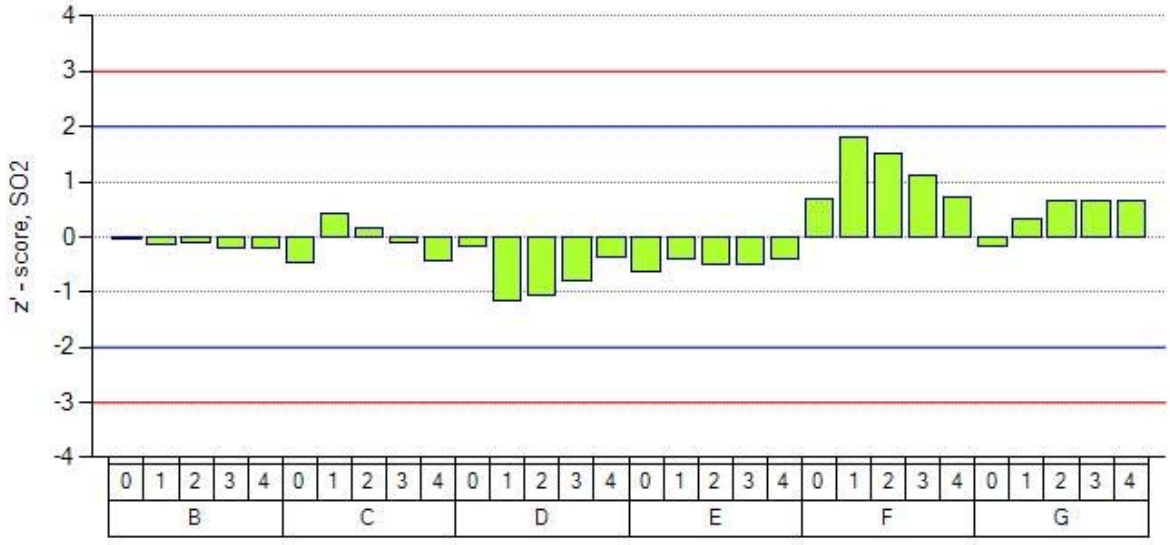

Figure 1: The z'-score evaluations of SO_2 measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (130 nmol/mol), 2 (45 nmol/mol), 3 (20 nmol/mol), 4 (5 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

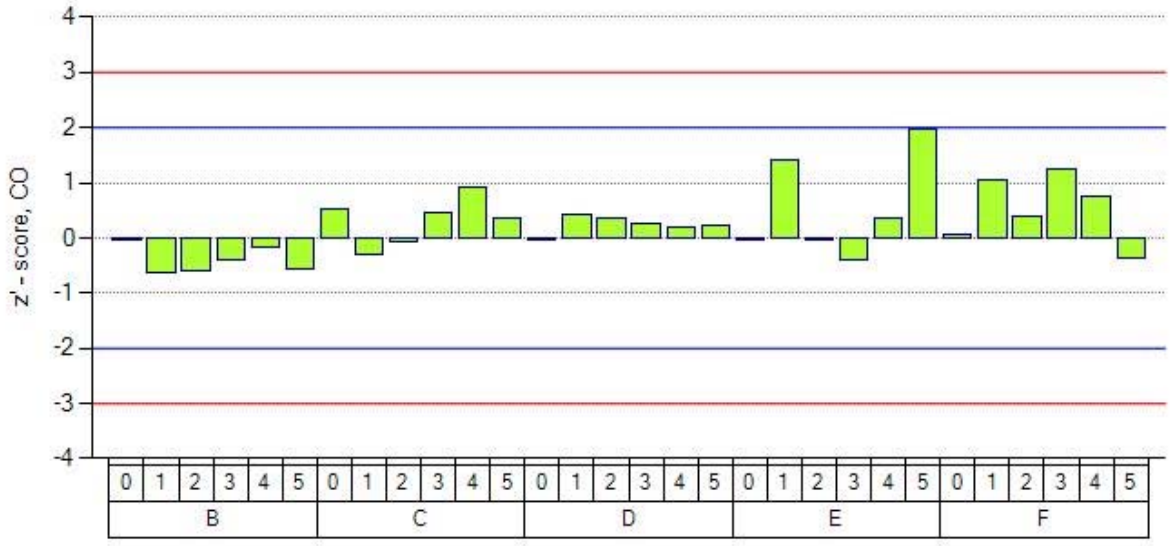

Figure 2: The z'-score evaluations of CO measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 µmol/mol), 1 (8 µmol/mol), 2 (6 µmol/mol), 3 (3 µmol/mol), 4 (1 µmol/mol), 5 (4.5 µmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

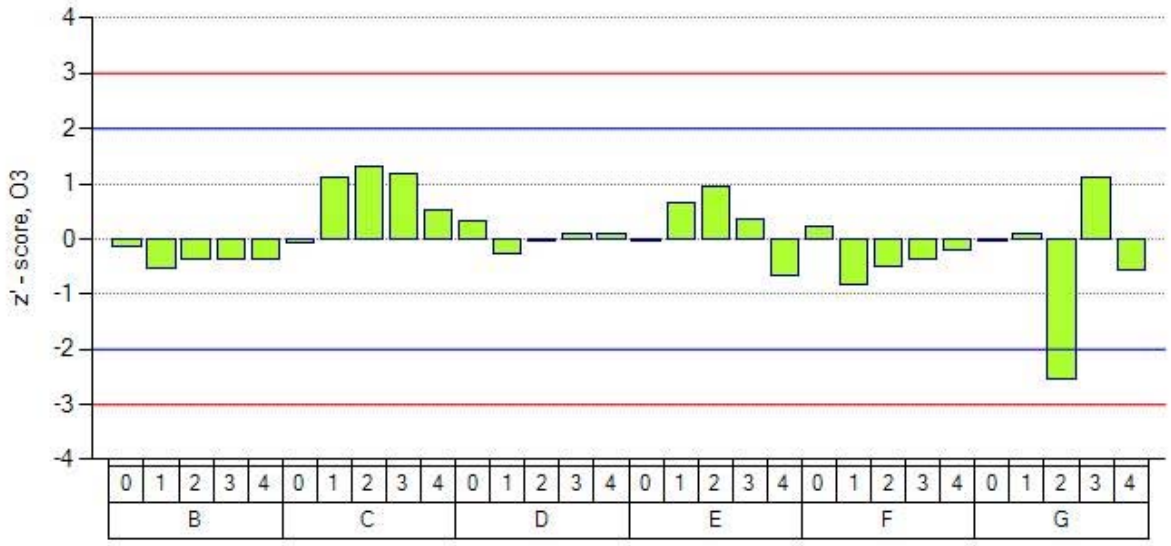

Figure 3: The z'-score evaluations of O_3 measurements
Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (300 nmol/mol), 2 (100 nmol/mol), 3 (60 nmol/mol), 4 (20 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

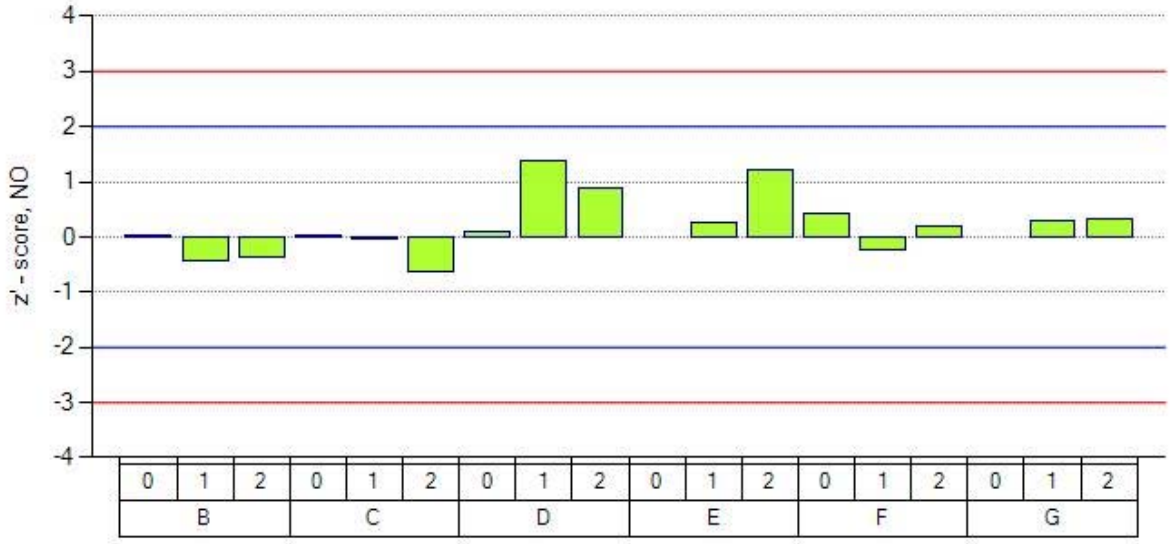

Figure 4: The z'-score evaluations of NO measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (200 nmol/mol), 2 (20 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

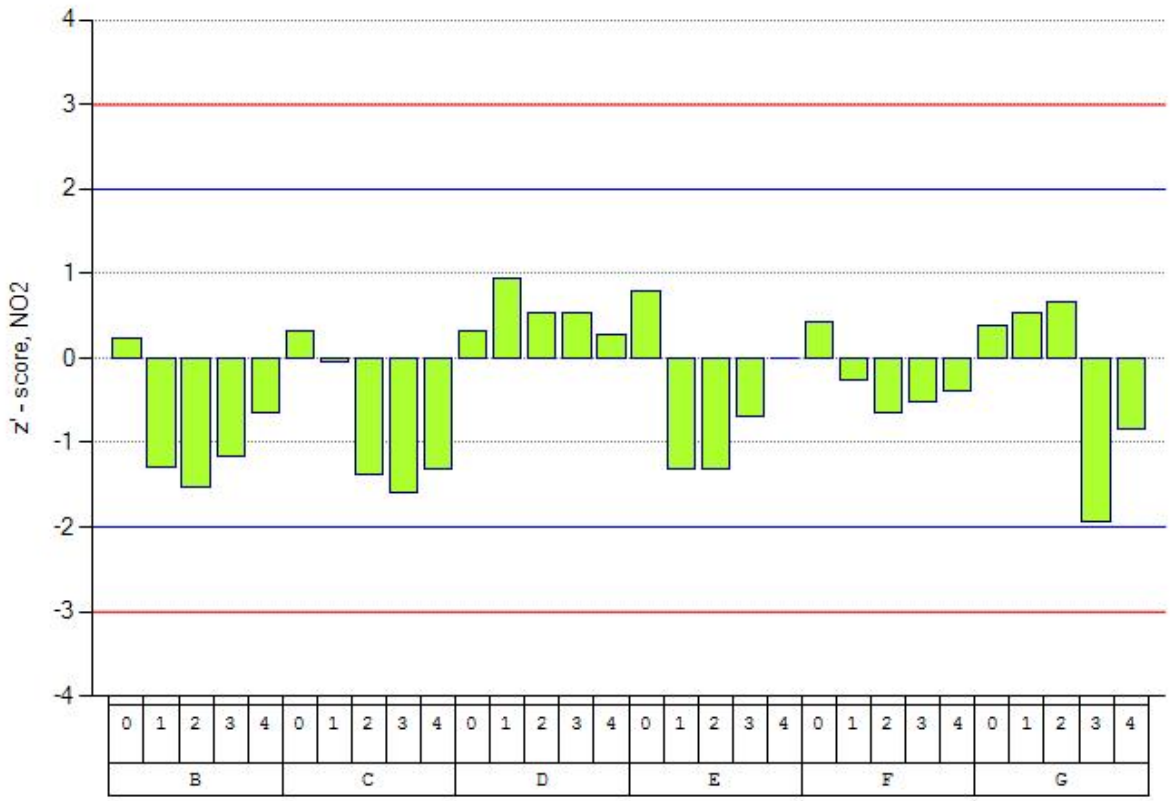

Figure 5: The z'-score evaluations of NO_2 measurements
Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (200 nmol/mol), 2 (100 nmol/mol), 3 (60 nmol/mol), 4 (20 nmol/mol). The assessment criteria are presented 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 $|E_n| \leq 1$.

In Figure 6 to Figure 10 the bias of each participant (x_i-X) are 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.

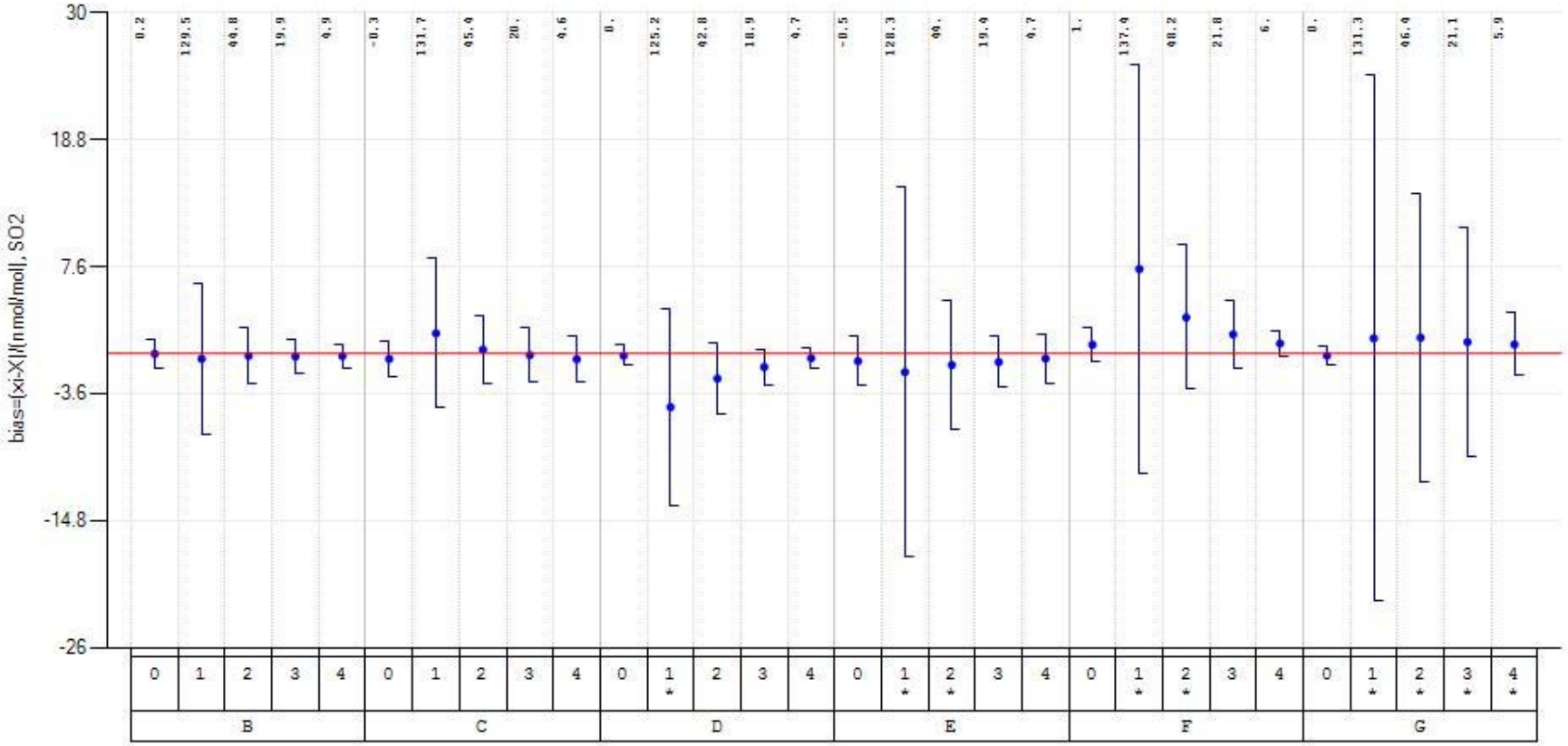

Figure 6: Bias of participant's SO_2 measurement results
Expanded uncertainty of bias for each run is presented as error bar. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 4) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

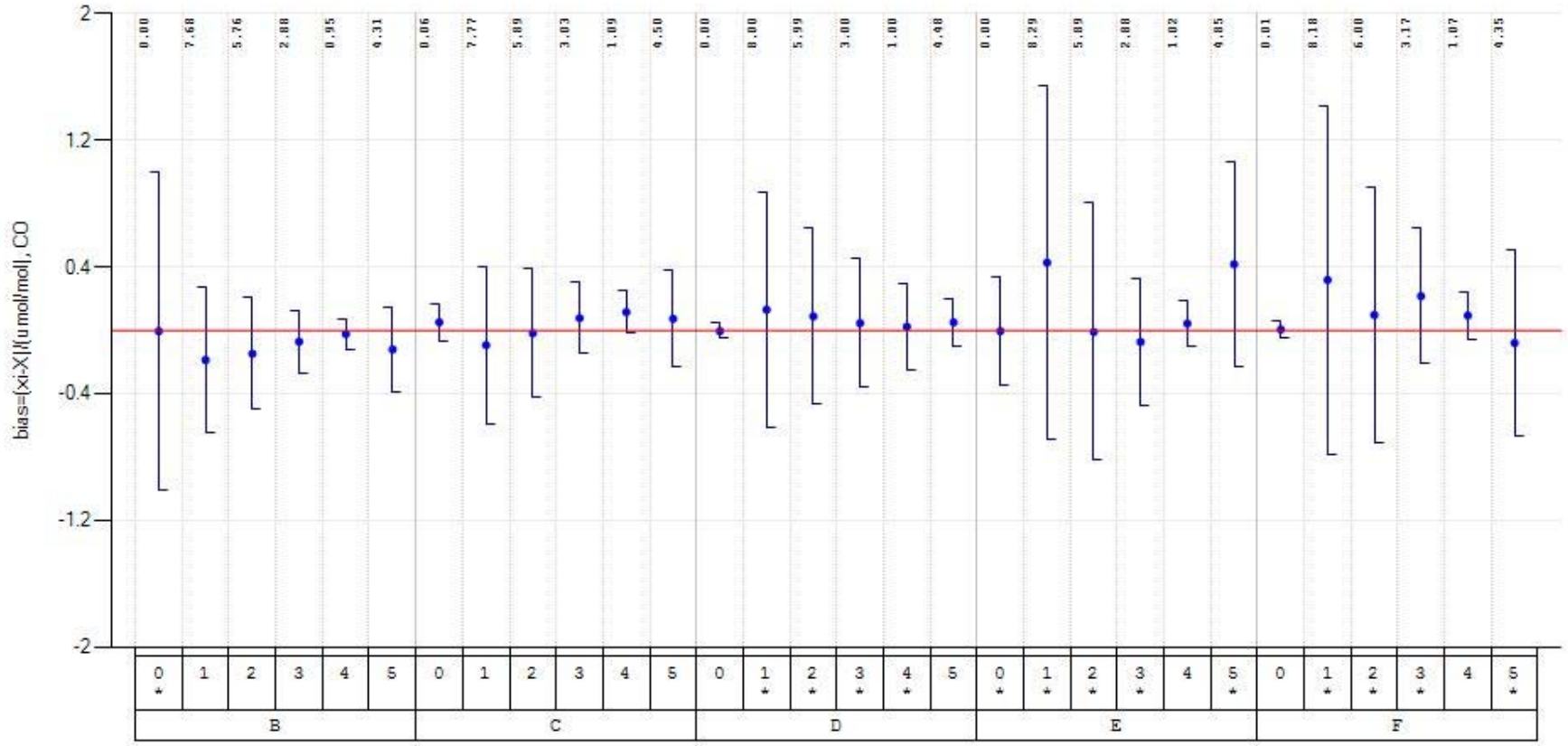

Figure 7: Bias of participant's CO measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (µmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

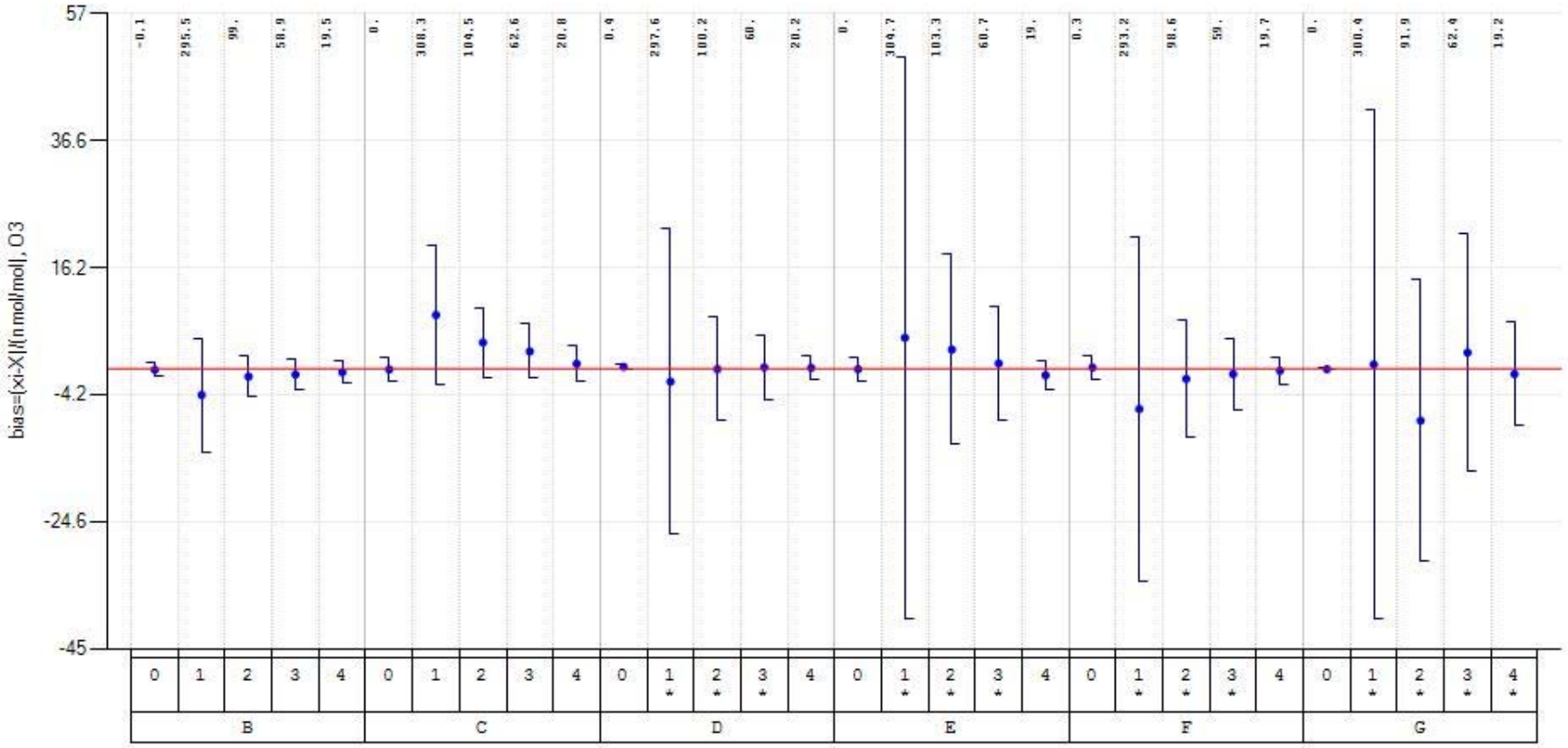

Figure 8: Bias of participant's O_3 measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 4) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

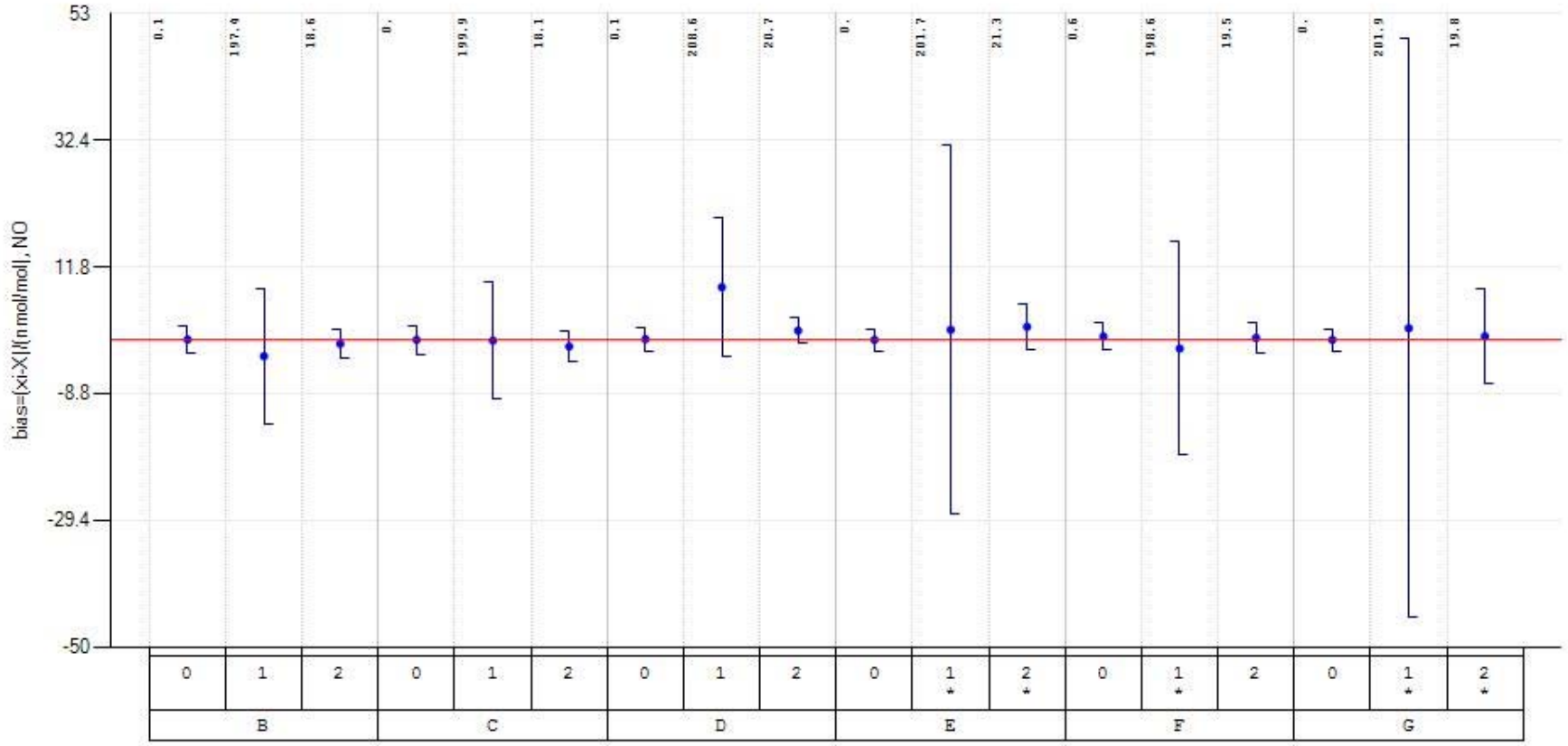

Figure 9: Bias of participant's NO measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 2) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

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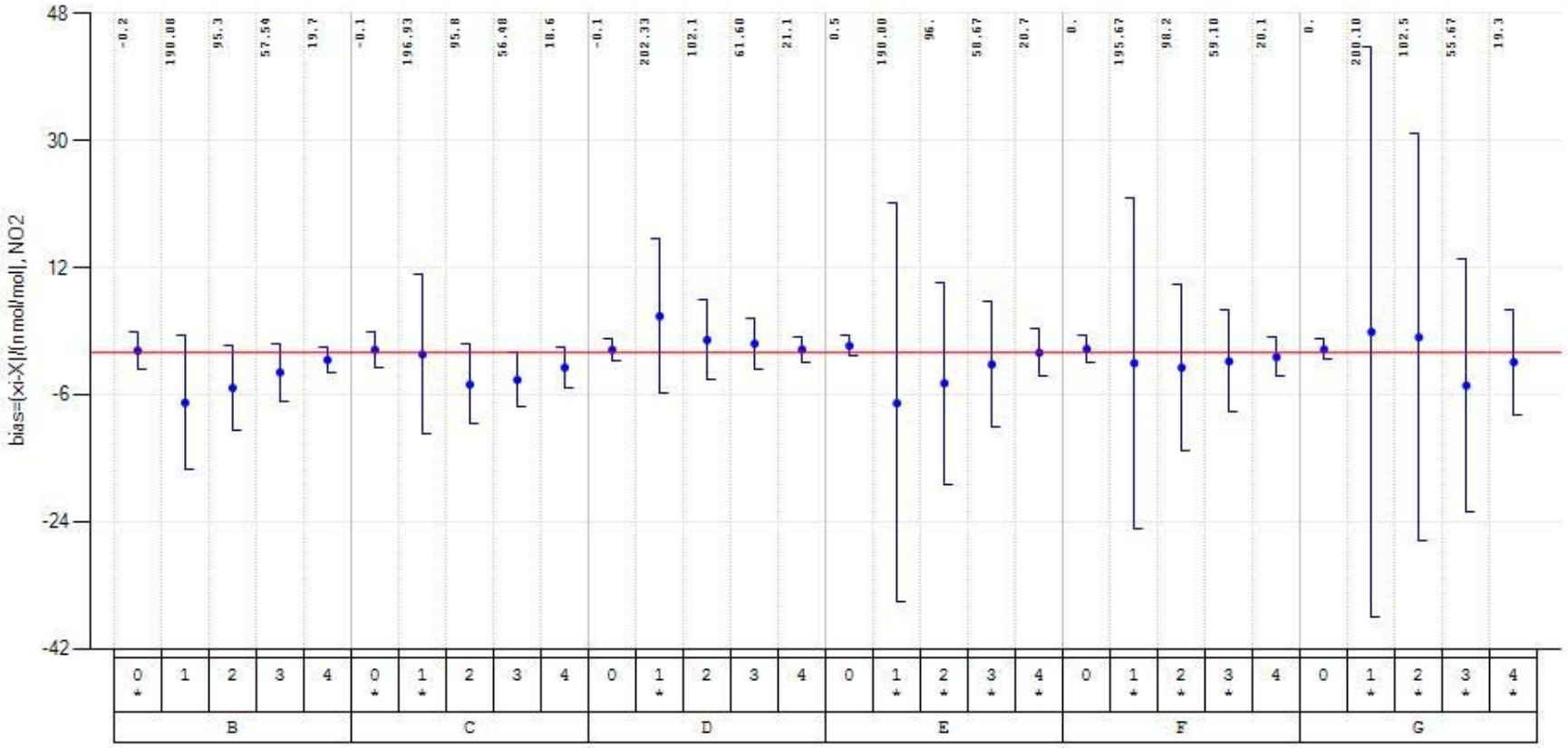

Figure 10: Bias of participant's NO_2 measurement results
Expanded uncertainty of bias is presented as error bar for NO_2 run numbers 0, 1, 2, 3 and 4. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

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)

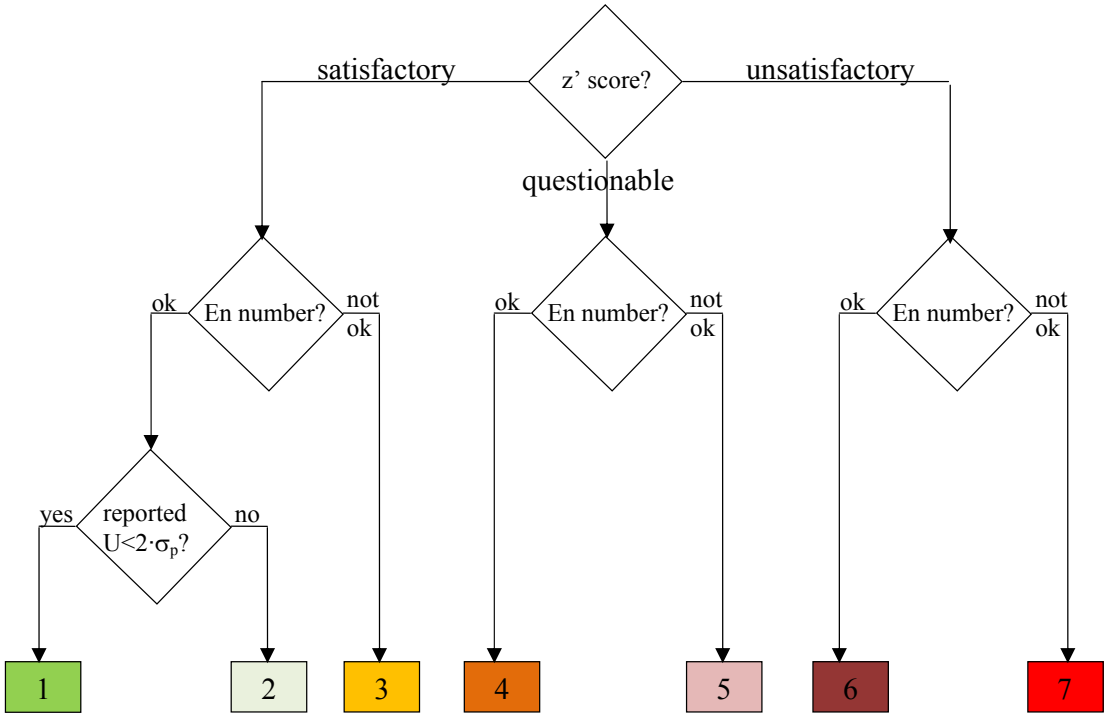

Figure 11: The decision diagram for general assessment of proficiency results.

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	IE code B	C	D	E	F	G
CO (µmol/mol)	0	0.003	2	1	1	2	1	nd
	1	7.864	1	1	2	2	2	nd
	2	5.901	1	1	2	2	2	nd
	3	2.951	1	1	2	2	2	nd
	4	0.976	1	1	2	1	1	nd
	5	4.428	1	1	1	2	2	nd
NO (nmol/mol)	0	0.00	1	1	1	1	1	1
	1	200.03	1	1	1	2	2	2
	2	19.21	1	1	1	2	1	2
NO_2 (nmol/mol)	0	-0.47	2	2	1	1	1	1
	1	197.16	1	2	2	2	2	2
	2	100.32	1	1	1	2	2	2
	3	60.33	1	1	1	2	2	2
	4	20.68	1	1	1	2	1	2
O_3 (nmol/mol)	0	0.04	1	1	1	1	1	1
	1	299.67	1	1	2	2	2	2
	2	100.23	1	1	2	2	2	4
	3	59.79	1	1	2	2	2	2
	4	20.02	1	1	1	1	1	2
SO_2 (nmol/mol)	0	0.20	1	1	1	1	1	1
	1	129.99	1	1	2	2	2	2
	2	45.05	1	1	1	2	2	2
	3	20.14	1	1	1	1	1	2
	4	5.17	1	1	1	1	1	2

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) 59.4% 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 39.9% presented good measured values but the evaluated uncertainties were too high (category '2') and 0.7% of results (category '4') were questionable compared to z-score and 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] 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].
In the present IE compared to the past (see Table 6) it has been found a low share of results in category '1'.
A relative high percentage of results falling in category '2' was found and it could be useful to investigate in detail the procedure to calculate the uncertainty used by the participants.

	Categories %						
IE	1	2	3	4	5	6	7
Apr-08	68.4	18.1	7.3	1.0	1.0	2.6	1.6
Oct-08 (I)	37.9	40.8	14.2	0.6	3.6	1.0	1.9
Oct-08 (II)	34.3	38.9	23.7	1.0	2.0	0.0	0.0
Sep-09	60.8	29.9	3.1	4.1	1.0	1.0	0.0
Oct-09	85.0	5.7	7.5	0.4	1.4	0.0	0.0
Jun-10	84.6	8.1	4.4	0.7	2.3	0.0	0.0
Sep-11	86.0	7.9	5.4	0.0	0.3	0.0	0.3
Oct-11 (I)	78.5	12.5	7.6	0.0	1.3	0.0	0.0
Oct-11 (II)	59.4	39.9	0.0	0.7	0.0	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 and CO measurements while NO_2 and O_3 and SO_2 one showed less satisfactory results.
The relative reproducibility limits, at the highest studied concentration levels, are 11.5% for SO_2, 11.0% for CO, 8.5% for O_3, 9.9% for NO and 10.3% for NO_2. Only NO and CO are within the objective derived from criteria imposed by the European Commission (σ_p).

During this IE the performance of all participants has been quite positive. Only two outliers have been identified at zero level for NO and CO (Annex D) and 1 straggler for NO.

In this exercise there were no unsatisfactory results in the z'-score evaluations. Laboratory G obtained one questionable result for O_3. The good performance of this IE is above the average of the last years 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%

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 two computer applications were used, the "GUM WORKBENCH" [20] and "ProControl®" [31].
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]:

$$\frac{\left|x^* - X\right|}{\sqrt{\frac{\left(1{,}25 \cdot s^*\right)^2}{p} + u_X^2}} < 2 \qquad \textbf{Equation 3}$$

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 expression **Error! Reference source not found.** 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.
NO2 _0	nmol/mol	-0.47	0.71	-0.061	0.179	7	OK
NO2 _1	nmol/mol	197.163	2.26	196.038	5.284	7	OK
NO2 _2	nmol/mol	100.32	1.3	98.606	3.457	7	OK
NO2 _3	nmol/mol	60.33	0.95	58.483	2.377	7	OK
NO2 _4	nmol/mol	20.677	0.74	20.033	0.971	7	OK
O3 _0	nmol/mol	0.04	0.05	0.013	0.074	7	OK
O3 _1	nmol/mol	299.667	3.52	299.912	5.91	7	OK
O3 _2	nmol/mol	100.23	1.29	100.256	2.852	7	OK
O3 _3	nmol/mol	59.79	0.92	60.444	1.659	7	OK
O3 _4	nmol/mol	20.017	0.6	19.758	0.681	7	OK
SO2 _0	nmol/mol	0.2	0.43	0.007	0.343	7	OK
SO2 _1	nmol/mol	129.987	1.42	130.118	2.728	7	OK
SO2 _2	nmol/mol	45.047	0.64	45.119	1.699	7	OK
SO2 _3	nmol/mol	20.143	0.48	20.111	1.003	7	OK
SO2 _4	nmol/mol	5.167	0.44	5.016	0.412	7	OK
CO _0	µmol/mol	0.003	0.022	0.002	0.003	6	OK
CO _1	µmol/mol	7.8637	0.086	7.964	0.271	6	OK
CO _2	µmol/mol	5.9013	0.066	5.908	0.092	6	OK
CO _3	µmol/mol	2.9513	0.038	2.98	0.112	6	OK
CO _4	µmol/mol	0.976	0.024	1.019	0.061	6	OK
CO _5	µmol/mol	4.428	0.057	4.449	0.129	6	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.

$$u_{X'}^2 = u_X^2 + \left(X \cdot u_{\text{hom ogeneity}}\right)^2 \qquad \text{Equation 4}$$

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 SO_2

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	0.15	-0.30	0.00	-0.50	0.95	0.00	0.20
u(xi) (nmol/mol)	0.51	0.68	0.15	0.98	0.60	0.00	0.43
U(xi) (nmol/mol)	1.01	1.37	0.30	1.96	1.20	0.00	0.86

Table 9: Reported values for SO_2 run 0.

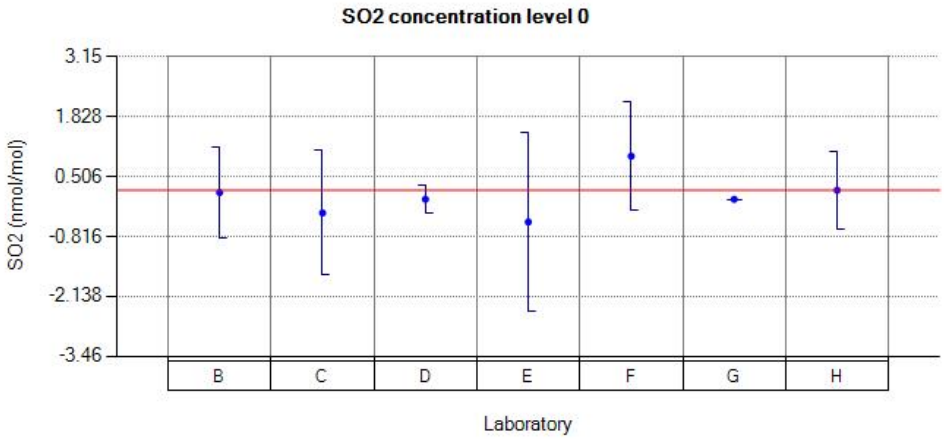

Figure 12: Reported values for SO_2 run 0.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	129.56	131.67	124.96	129.00	137.35	124.36	129.96
xi,2 (nmol/mol)	129.34	131.76	125.29	128.00	137.40	131.06	130.11
xi,3 (nmol/mol)	129.57	131.80	125.47	128.00	137.45	138.47	129.89
Xi (nmol/mol)	129.49	131.74	125.24	128.33	137.40	131.29	129.98
Si (nmol/mol)	0.13	0.06	0.25	0.57	0.05	7.05	0.11
u(xi) (nmol/mol)	3.00	2.95	4.09	8.02	8.86	7.22	1.37
U(xi) (nmol/mol)	6.00	5.90	8.18	16.04	17.72	22.98	2.74

Table 10: Reported values for SO_2 run 1.

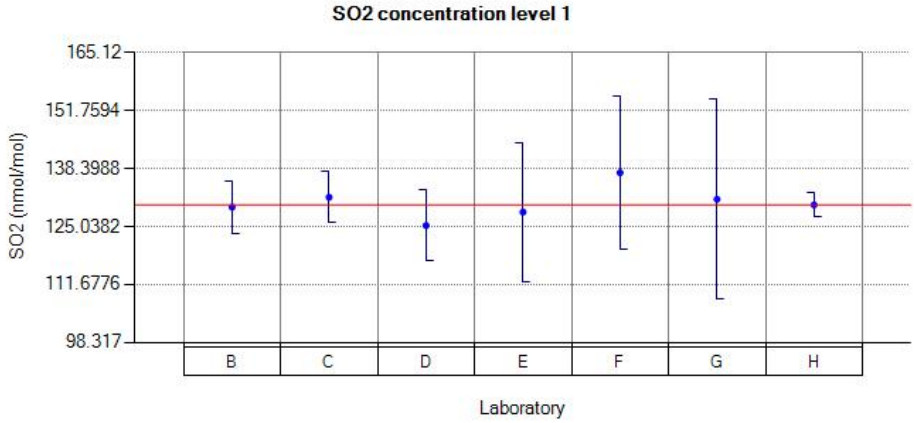

Figure 13: Reported values for SO_2 run 1.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	44.89	45.32	42.88	44.00	48.13	49.33	45.11
xi,2 (nmol/mol)	44.81	45.38	42.79	44.00	48.24	42.09	44.98
xi,3 (nmol/mol)	44.75	45.38	42.79	44.00	48.22	47.83	45.05
Xi (nmol/mol)	44.81	45.36	42.82	44.00	48.19	46.41	45.04
Si (nmol/mol)	0.07	0.03	0.05	0.00	0.05	3.82	0.06
u(xi) (nmol/mol)	1.04	1.35	1.40	2.75	3.11	3.97	0.62
U(xi) (nmol/mol)	2.08	2.70	2.80	5.50	6.22	12.64	1.25

Table 11: Reported values for SO_2 run 2.

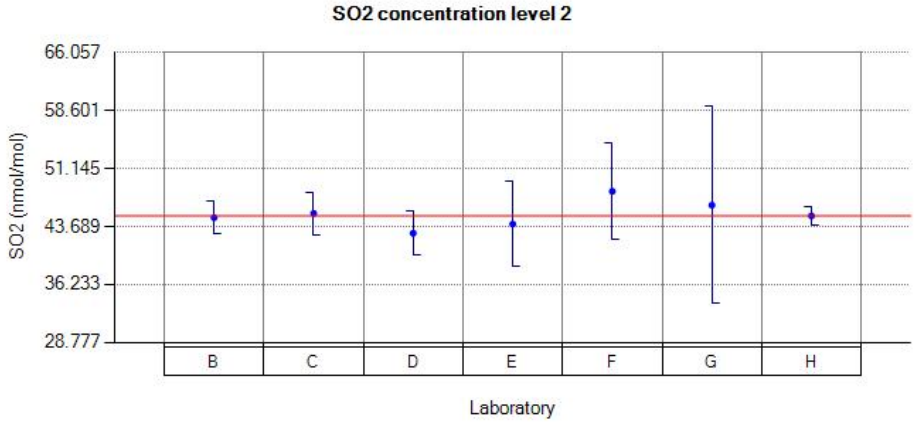

Figure 14: Reported values for SO_2 run 2.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	19.88	20.07	18.93	19.10	21.79	23.92	20.10
xi,2 (nmol/mol)	19.88	20.02	18.95	19.50	21.85	21.52	20.18
xi,3 (nmol/mol)	19.82	19.88	18.87	19.50	21.78	17.94	20.15
Xi (nmol/mol)	19.86	19.99	18.91	19.36	21.80	21.12	20.14
Si (nmol/mol)	0.03	0.09	0.04	0.23	0.03	3.00	0.04
u(xi) (nmol/mol)	0.61	1.09	0.62	1.01	1.41	3.17	0.47
U(xi) (nmol/mol)	1.22	2.18	1.24	2.03	2.81	10.09	0.95

Table 12: Reported values for SO_2 run 3.

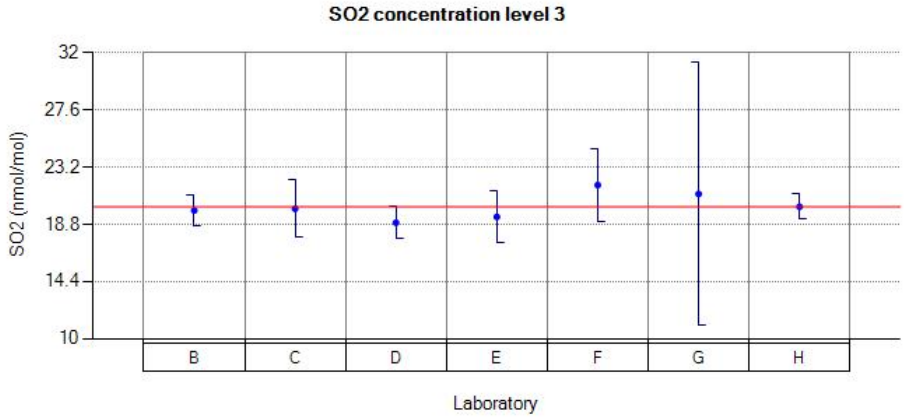

Figure 15: Reported values for SO_2 run 3.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	4.94	4.73	4.73	4.70	6.05	6.70	5.19
xi,2 (nmol/mol)	4.87	4.65	4.70	4.70	6.03	5.74	5.16
xi,3 (nmol/mol)	4.92	4.54	4.76	4.70	5.99	5.38	5.15
Xi (nmol/mol)	4.91	4.64	4.73	4.70	6.02	5.94	5.16
Si (nmol/mol)	0.03	0.09	0.03	0.00	0.03	0.68	0.02
u(xi) (nmol/mol)	0.32	0.93	0.15	0.98	0.39	0.83	0.43
U(xi) (nmol/mol)	0.64	1.87	0.31	1.96	0.78	2.63	0.87

Table 13: Reported values for SO_2 run 4.

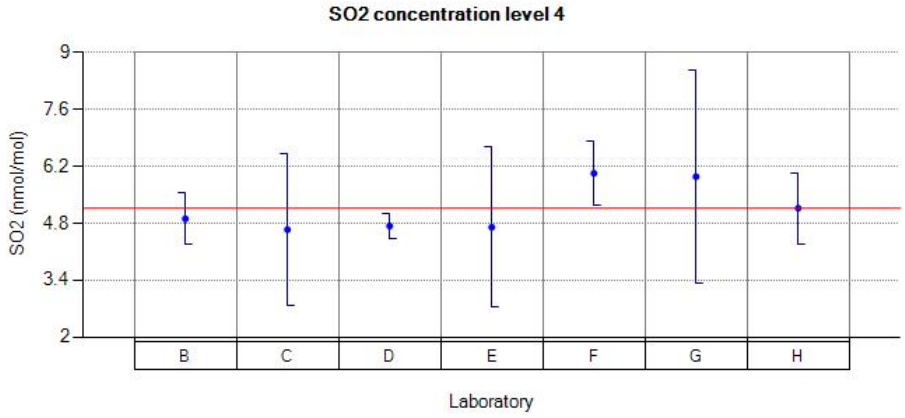

Figure 16: Reported values for SO_2 run 4.

Reported values for CO

	laboratories					
values	B	C	D	E	F	H
xi,1 (µmol/mol)	0.000	0.056	0.000	0.000	0.010	0.003
u(xi) (µmol/mol)	0.500	0.054	0.010	0.170	0.018	0.022
U(xi) (µmol/mol)	1.000	0.109	0.020	0.340	0.035	0.044

Table 14: Reported values for CO run 0.

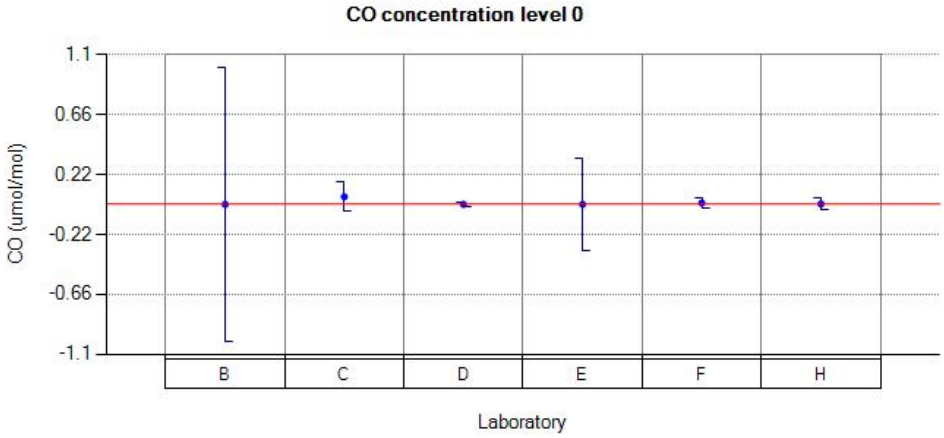

Figure 17 Reported values for CO run 0

	laboratories					
values	B	C	D	E	F	H
xi,1 (µmol/mol)	7.676	7.762	7.994	8.320	8.120	7.859
xi,2 (µmol/mol)	7.680	7.773	7.999	8.260	8.191	7.864
xi,3 (µmol/mol)	7.679	7.782	7.995	8.300	8.237	7.868
Xi (µmol/mol)	7.678	7.772	7.996	8.293	8.183	7.864
Si (µmol/mol)	0.002	0.010	0.003	0.031	0.059	0.005
u(xi) (µmol/mol)	0.212	0.233	0.360	0.550	0.543	0.083
U(xi) (µmol/mol)	0.424	0.466	0.720	1.100	1.086	0.166

Table 15: Reported values for CO run 1.

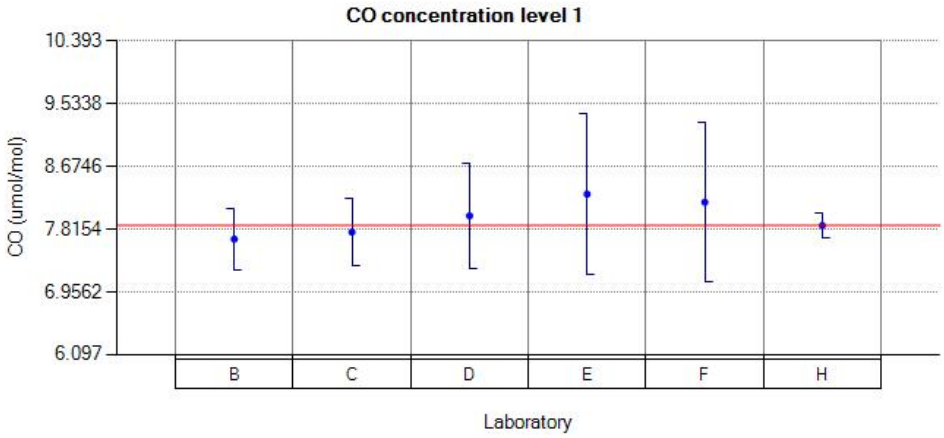

Figure 18: Reported values for CO run 1.

	laboratories					
values	B	C	D	E	F	H
xi,1 (µmol/mol)	5.758	5.878	5.995	5.860	5.991	5.901
xi,2 (µmol/mol)	5.756	5.888	5.990	5.920	5.999	5.901
xi,3 (µmol/mol)	5.751	5.890	5.989	5.900	6.011	5.902
Xi (µmol/mol)	5.755	5.885	5.991	5.893	6.000	5.901
Si (µmol/mol)	0.004	0.006	0.003	0.031	0.010	0.001
u(xi) (µmol/mol)	0.163	0.193	0.270	0.400	0.397	0.064
U(xi) (µmol/mol)	0.326	0.386	0.540	0.800	0.794	0.128

Table 16: Reported values for CO run 2.

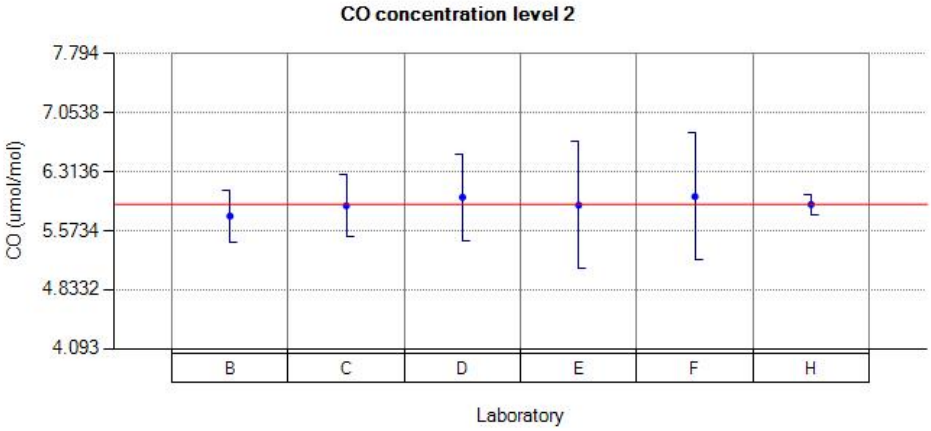

Figure 19: Reported values for CO run 2.

	laboratories					
values	B	C	D	E	F	H
xi,1 (µmol/mol)	2.884	3.029	3.000	2.880	3.166	2.952
xi,2 (µmol/mol)	2.881	3.025	2.995	2.880	3.168	2.951
xi,3 (µmol/mol)	2.881	3.035	2.998	2.880	3.172	2.951
Xi (µmol/mol)	2.882	3.030	2.998	2.880	3.169	2.951
Si (µmol/mol)	0.002	0.005	0.003	0.000	0.003	0.001
u(xi) (µmol/mol)	0.091	0.106	0.200	0.200	0.209	0.037
U(xi) (µmol/mol)	0.182	0.211	0.400	0.390	0.419	0.074

Table 17: Reported values for CO run 3.

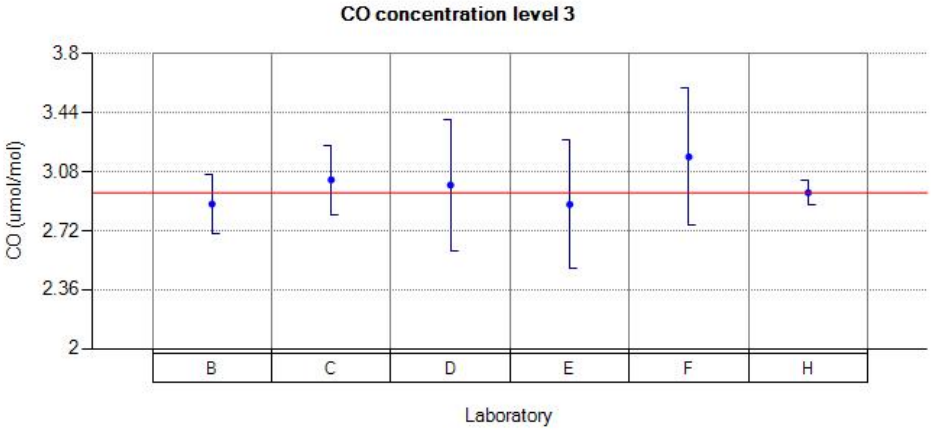

Figure 20: Reported values for CO run 3.

	laboratories					
values	B	C	D	E	F	H
xi,1 (µmol/mol)	0.956	1.091	1.003	0.980	1.069	0.976
xi,2 (µmol/mol)	0.952	1.093	1.000	1.040	1.072	0.976
xi,3 (µmol/mol)	0.953	1.094	1.000	1.040	1.073	0.976
Xi (µmol/mol)	0.954	1.093	1.001	1.020	1.071	0.976
Si (µmol/mol)	0.002	0.002	0.002	0.035	0.002	0.000
u(xi) (µmol/mol)	0.042	0.063	0.135	0.070	0.071	0.024
U(xi) (µmol/mol)	0.084	0.126	0.270	0.140	0.142	0.048

Table 18: Reported values for CO run 4.

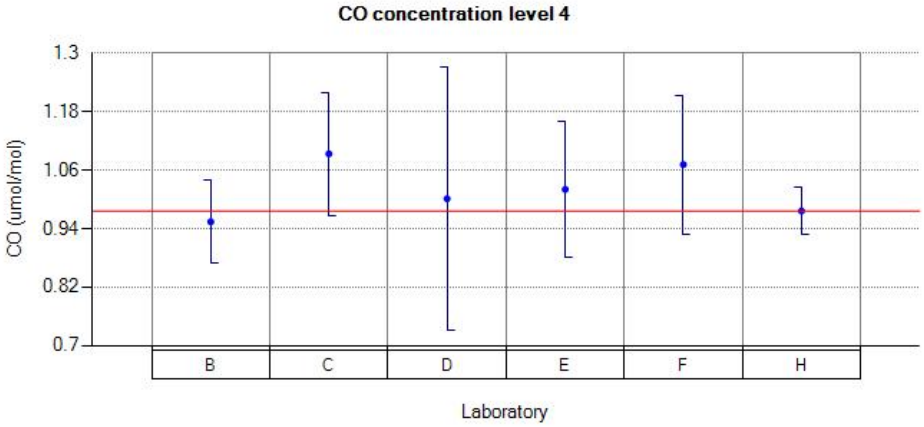

Figure 21: Reported values for CO run 4.

	laboratories					
values	B	C	D	E	F	H
xi,1 (µmol/mol)	4.310	4.496	4.478	4.800	4.340	4.427
xi,2 (µmol/mol)	4.309	4.505	4.481	4.880	4.352	4.428
xi,3 (µmol/mol)	4.309	4.509	4.480	4.860	4.359	4.429
Xi (µmol/mol)	4.309	4.503	4.480	4.847	4.350	4.428
Si (µmol/mol)	0.001	0.007	0.002	0.042	0.010	0.001
u(xi) (µmol/mol)	0.122	0.142	0.050	0.320	0.288	0.055
U(xi) (µmol/mol)	0.244	0.284	0.100	0.640	0.575	0.110

Table 19: Reported values for CO run 5.

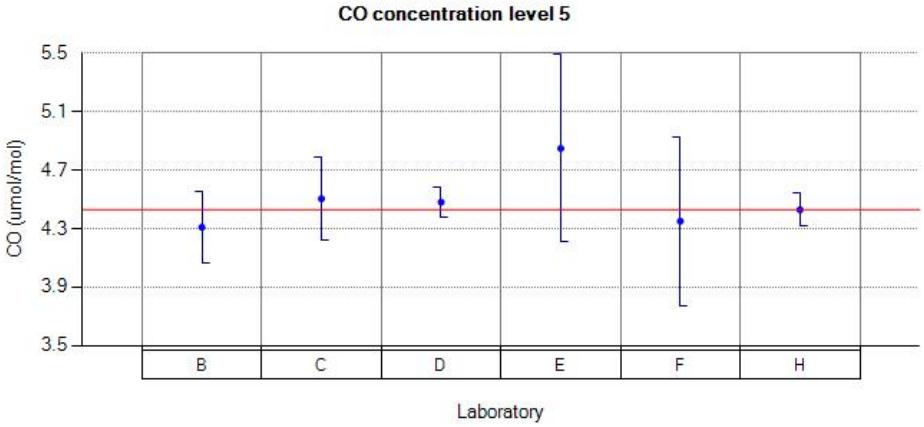

Figure 22: Reported values for CO run 5.

Reported values for O_3

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	-0.09	-0.04	0.37	0.00	0.26	0.00	0.04
u(xi) (nmol/mol)	0.54	1.00	0.25	0.93	1.00	0.00	0.55
U(xi) (nmol/mol)	1.09	2.00	0.50	1.86	2.00	0.00	0.10

Table 20: Reported values for O_3 run 0.

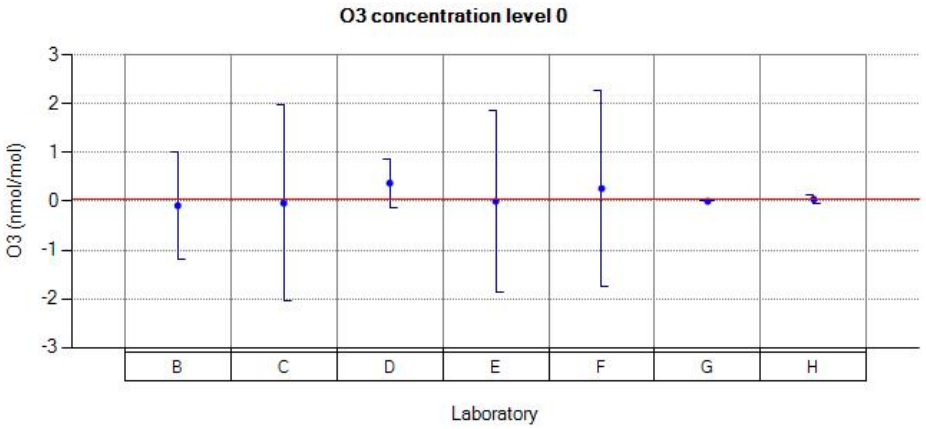

Figure 23: Reported values for O_3 run 0.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	291.70	302.18	293.96	297.00	289.68	288.53	297.57
xi,2 (nmol/mol)	296.40	309.75	298.38	304.00	294.50	299.16	300.11
xi,3 (nmol/mol)	298.38	313.04	300.53	313.00	295.53	313.43	301.32
Xi (nmol/mol)	295.49	308.32	297.62	304.66	293.23	300.37	299.66
Si (nmol/mol)	3.43	5.56	3.35	8.02	3.12	12.49	1.91
u(xi) (nmol/mol)	2.95	4.39	11.77	22.24	13.34	12.66	3.40
U(xi) (nmol/mol)	5.80	8.79	23.54	44.47	26.68	40.29	6.80

Table 21: Reported values for O_3 run 1

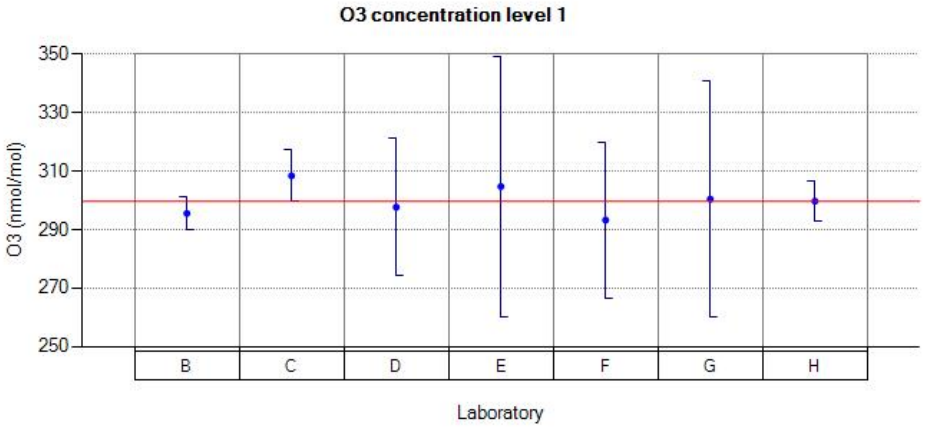

Figure 24: Reported values for O_3 run 1.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	99.51	104.85	100.67	104.00	99.14	99.89	100.67
xi,2 (nmol/mol)	98.78	104.37	100.04	103.00	98.45	87.36	100.07
xi,3 (nmol/mol)	98.74	104.19	99.88	103.00	98.30	88.54	99.95
Xi (nmol/mol)	99.01	104.47	100.19	103.33	98.63	91.93	100.23
Si (nmol/mol)	0.43	0.34	0.41	0.57	0.44	6.91	0.38
u(xi) (nmol/mol)	1.00	2.49	3.97	7.53	4.49	7.07	1.25
U(xi) (nmol/mol)	2.00	4.98	7.94	15.06	8.98	22.50	2.50

Table 22: Reported values for O_3 run 2.

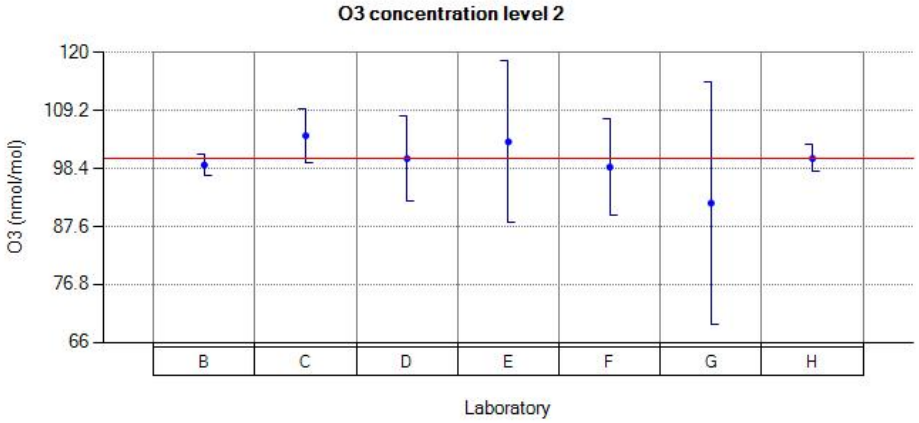

Figure 25: Reported values for O_3 run 2.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	59.15	62.58	60.09	61.00	59.07	68.66	59.97
xi,2 (nmol/mol)	58.90	62.55	60.05	61.00	58.99	57.22	59.73
xi,3 (nmol/mol)	58.62	62.64	59.93	60.00	58.82	61.35	59.67
Xi (nmol/mol)	58.89	62.59	60.02	60.66	58.96	62.41	59.79
Si (nmol/mol)	0.26	0.04	0.08	0.57	0.12	5.79	0.15
u(xi) (nmol/mol)	0.80	1.98	2.38	4.42	2.68	5.96	0.90
U(xi) (nmol/mol)	1.60	3.96	4.76	8.85	5.37	18.95	1.80

Table 23: Reported values for O_3 run 3.

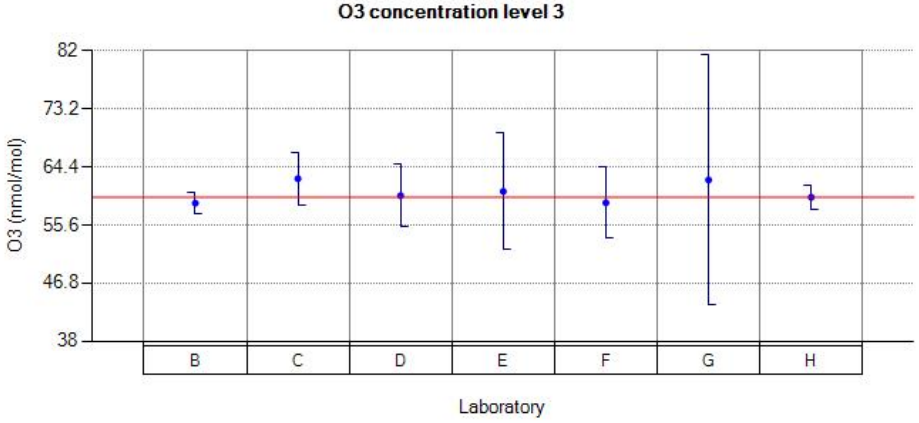

Figure 26: Reported values for O_3 run 3.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	19.30	20.85	20.13	19.00	19.68	21.53	19.99
xi,2 (nmol/mol)	19.56	20.90	20.20	19.00	19.76	19.32	20.03
xi,3 (nmol/mol)	19.58	20.74	20.20	19.00	19.75	16.68	20.03
Xi (nmol/mol)	19.48	20.83	20.17	19.00	19.73	19.17	20.01
Si (nmol/mol)	0.15	0.08	0.04	0.00	0.04	2.42	0.02
u(xi) (nmol/mol)	0.60	1.30	0.80	0.93	0.90	2.59	0.60
U(xi) (nmol/mol)	1.20	2.60	1.60	1.86	1.80	8.23	1.20

Table 24: Reported values for O_3 run 4.

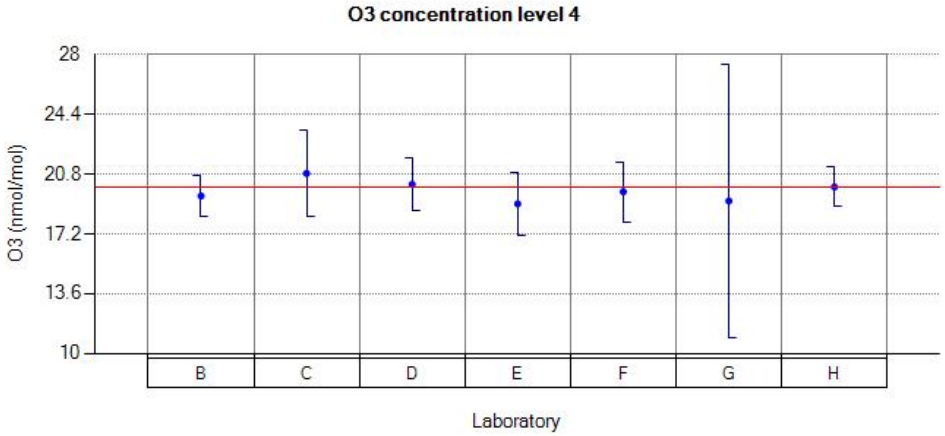

Figure 27: Reported values for O_3 run 4.

Reported values for NO

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	0.05	0.01	0.11	0.00	0.56	0.00	0.00
u(xi) (nmol/mol)	0.58	0.75	0.25	0.10	0.60	0.00	0.90
U(xi) (nmol/mol)	1.16	1.50	0.50	0.21	1.20	0.00	1.80

Table 25: Reported values for NO run 0.

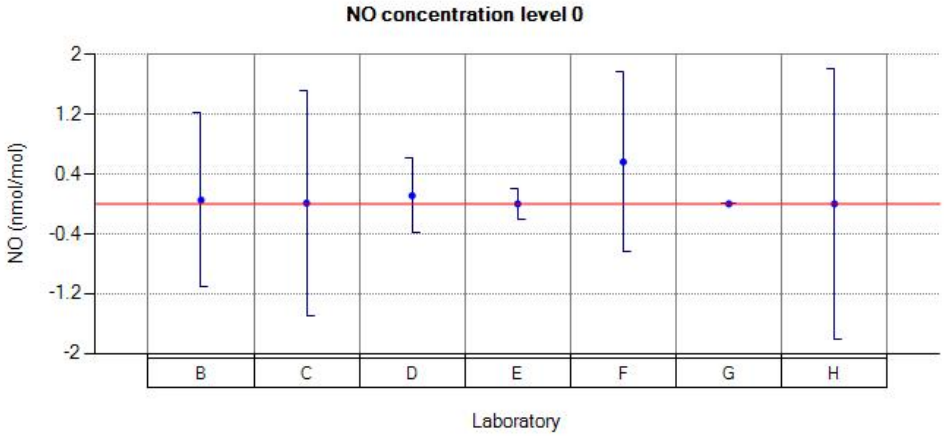

Figure 28: Reported values for NO run 0.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	197.42	199.88	208.22	202.00	198.58	216.77	199.91
xi,2 (nmol/mol)	197.32	199.78	208.70	201.00	198.65	187.69	200.06
xi,3 (nmol/mol)	197.36	200.07	208.81	202.00	198.64	201.29	200.11
Xi (nmol/mol)	197.36	199.91	208.57	201.66	198.62	201.91	200.02
Si (nmol/mol)	0.05	0.14	0.31	0.57	0.03	14.55	0.10
u(xi) (nmol/mol)	5.00	4.21	5.17	14.78	8.39	14.72	2.19
U(xi) (nmol/mol)	10.00	8.42	10.35	29.56	16.77	46.83	4.39

Table 26: Reported values for NO run 1.

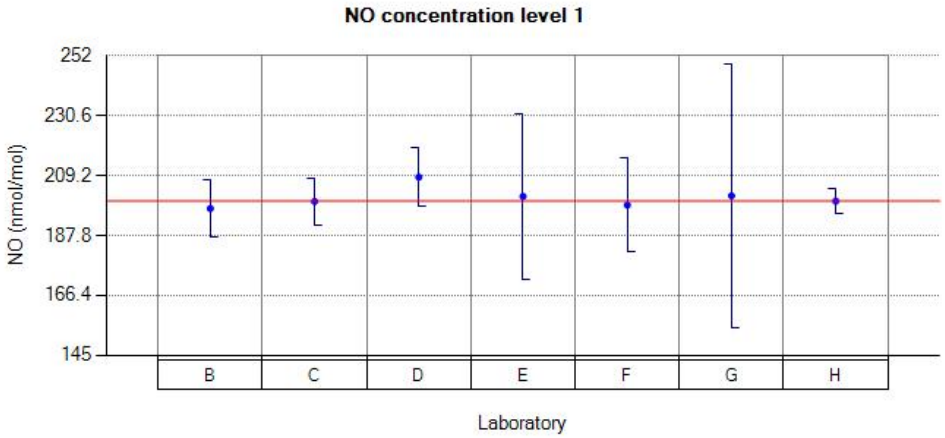

Figure 29: Reported values for NO run 1.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	18.65	18.23	20.90	21.00	19.52	19.37	19.26
xi,2 (nmol/mol)	18.53	18.12	20.75	21.00	19.51	17.83	19.21
xi,3 (nmol/mol)	18.57	18.04	20.49	22.00	19.57	22.13	19.16
Xi (nmol/mol)	18.58	18.13	20.71	21.33	19.53	19.77	19.21
Si (nmol/mol)	0.06	0.09	0.20	0.57	0.03	2.17	0.05
u(xi) (nmol/mol)	0.70	0.84	0.53	1.57	0.75	2.34	0.92
U(xi) (nmol/mol)	1.40	1.69	1.06	3.13	1.65	7.45	1.85

Table 27: Reported values for NO run 2.

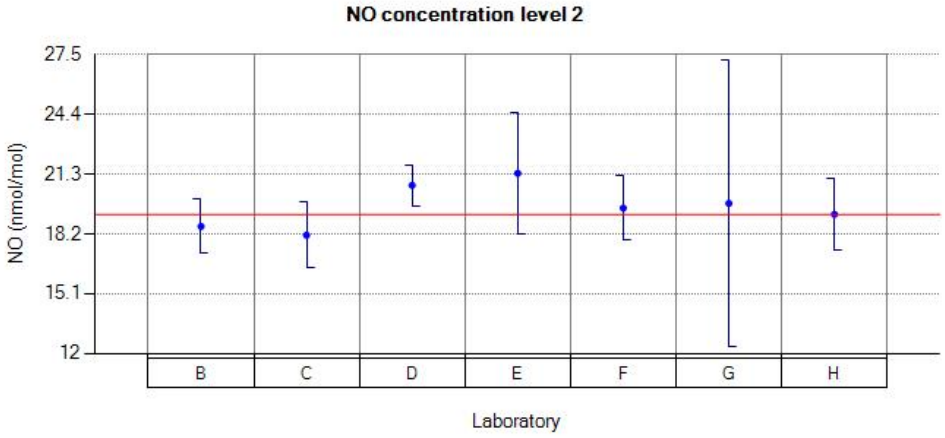

Figure 30: Reported values for NO run 2.

Reported values for NO_2

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	-0.18	-0.07	-0.08	0.50	0.04	0.00	-0.47
u(xi) (nmol/mol)	1.12	1.00	0.25	0.17	0.60	0.00	0.71
U(xi) (nmol/mol)	2.24	2.00	0.50	0.35	1.20	0.00	1.42

Table 28: Reported values for NO_2 run 0.

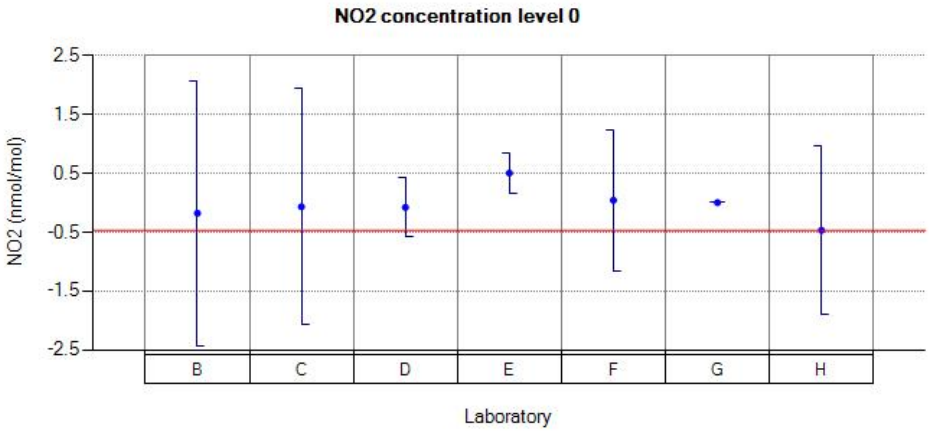

Figure 31: Reported values for NO_2 run 0.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	190.84	197.37	202.04	189.00	195.94	189.13	196.85
xi,2 (nmol/mol)	189.91	196.70	202.19	190.00	195.46	213.61	196.87
xi,3 (nmol/mol)	189.48	196.71	202.76	191.00	195.61	197.56	197.77
Xi (nmol/mol)	190.07	196.92	202.33	190.00	195.67	200.10	197.16
Si (nmol/mol)	0.69	0.38	0.38	1.00	0.24	12.43	0.52
u(xi) (nmol/mol)	4.18	5.17	5.02	13.93	11.46	12.60	2.18
U(xi) (nmol/mol)	8.36	10.34	10.04	27.85	22.91	40.09	4.36

Table 29: Reported values for NO_2 run 1.

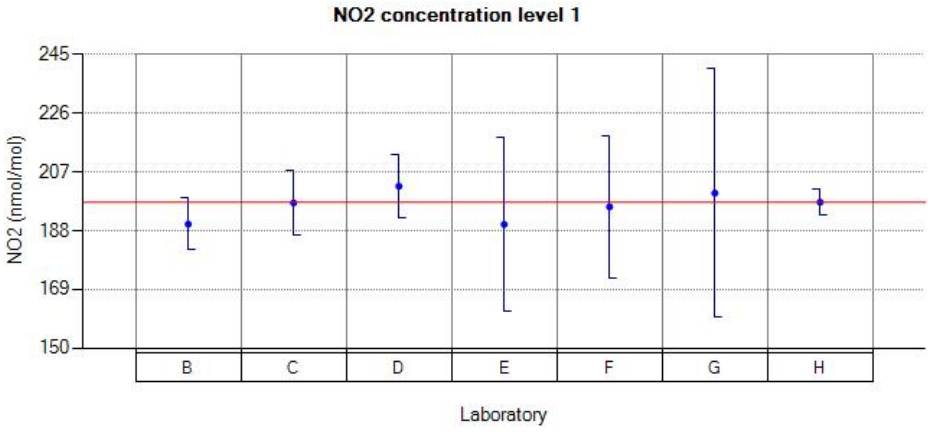

Figure 32: Reported values for NO_2 run 1.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	95.51	96.22	102.11	96.00	98.39	111.98	100.28
xi,2 (nmol/mol)	95.29	95.68	102.13	96.00	98.12	100.98	100.90
xi,3 (nmol/mol)	95.18	95.53	102.06	96.00	98.08	94.51	99.78
Xi (nmol/mol)	95.32	95.81	102.10	96.00	98.19	102.49	100.32
Si (nmol/mol)	0.16	0.36	0.03	0.00	0.16	8.83	0.56
u(xi) (nmol/mol)	2.70	2.50	2.53	7.04	5.75	9.00	1.26
U(xi) (nmol/mol)	5.40	5.00	5.07	14.07	11.50	28.63	2.52

Table 30: Reported values for NO_2 run 2.

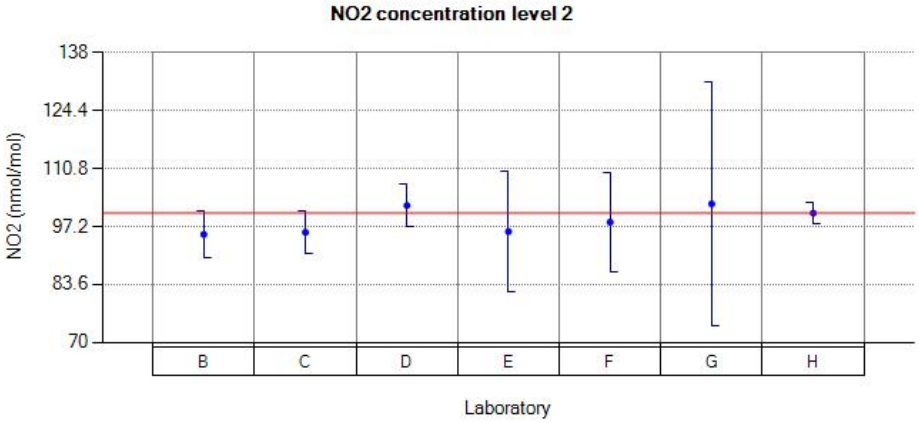

Figure 33: Reported values for NO_2 run 2.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	57.55	56.65	61.74	59.00	59.10	61.75	60.53
xi,2 (nmol/mol)	57.50	56.51	61.69	59.00	59.14	51.22	60.31
xi,3 (nmol/mol)	57.57	56.28	61.36	58.00	59.07	54.03	60.15
Xi (nmol/mol)	57.54	56.48	61.59	58.66	59.10	55.66	60.33
Si (nmol/mol)	0.03	0.18	0.20	0.57	0.03	5.45	0.19
u(xi) (nmol/mol)	1.80	1.63	1.53	4.30	3.46	5.61	0.93
U(xi) (nmol/mol)	3.60	3.26	3.07	8.60	6.92	17.85	1.86

Table 31: Reported values for NO_2 run 3.

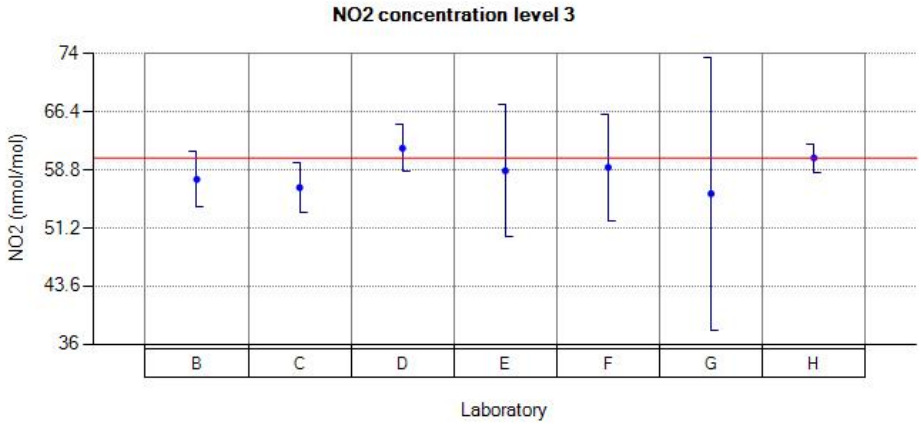

Figure 34: Reported values for NO_2 run 3.

	laboratories						
values	B	C	D	E	F	G	H
xi,1 (nmol/mol)	19.68	18.57	21.31	21.00	20.20	21.63	20.97
xi,2 (nmol/mol)	19.68	18.57	21.14	21.00	19.93	18.99	20.66
xi,3 (nmol/mol)	19.63	18.56	20.92	20.00	20.06	17.41	20.40
Xi (nmol/mol)	19.66	18.56	21.12	20.66	20.06	19.34	20.67
Si (nmol/mol)	0.02	0.00	0.19	0.57	0.13	2.13	0.28
u(xi) (nmol/mol)	0.44	1.21	0.53	1.52	1.17	2.29	0.74
U(xi) (nmol/mol)	0.88	2.42	1.07	3.03	2.35	7.29	1.48

Table 32: Reported values for NO_2 run 4.

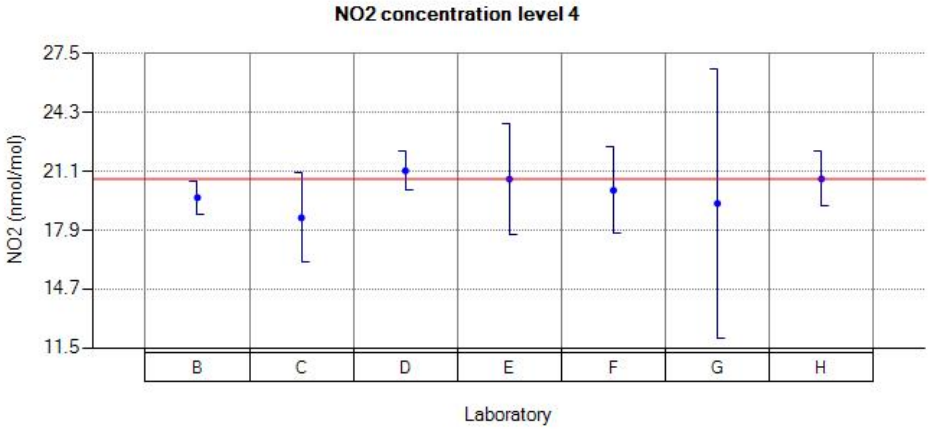

Figure 35: Reported values for NO_2 run 4.

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. 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 G 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.

SO_2 data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.1		1.6	
5.2	0.8	2.2	
20.2	3.5	4.7	
45.2	4.4	7.2	
130.5	8.1	15.0	11.5%

Table 34: The R and r of SO_2 standard measurement method.

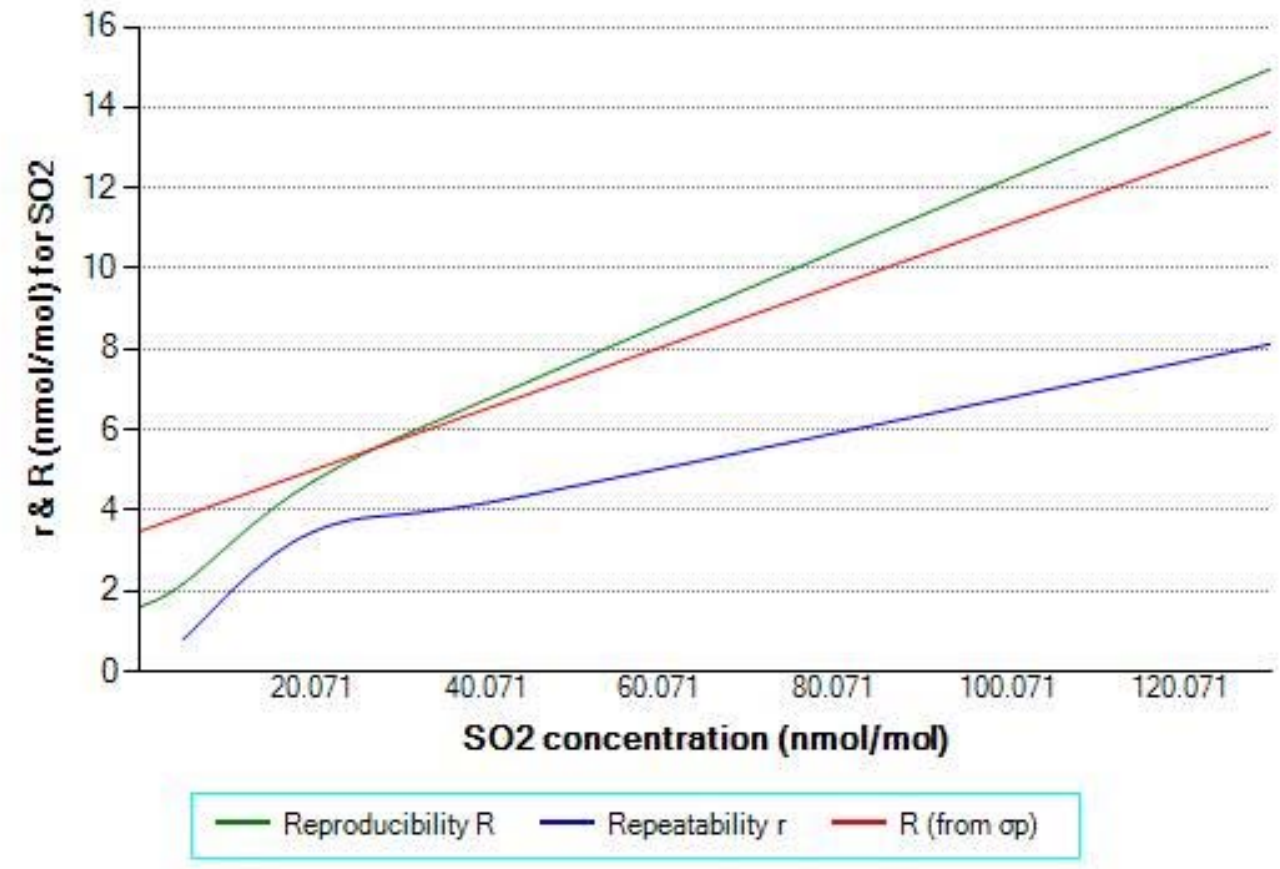

Figure 36: The R and r of SO_2 standard measurement method as a function of concentration.

CO data (µmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.012		0.081	
1.019	0.044	0.202	
2.985	0.009	0.395	
4.486	0.055	0.699	
5.904	0.042	0.326	
7.964	0.085	0.873	11.0%

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

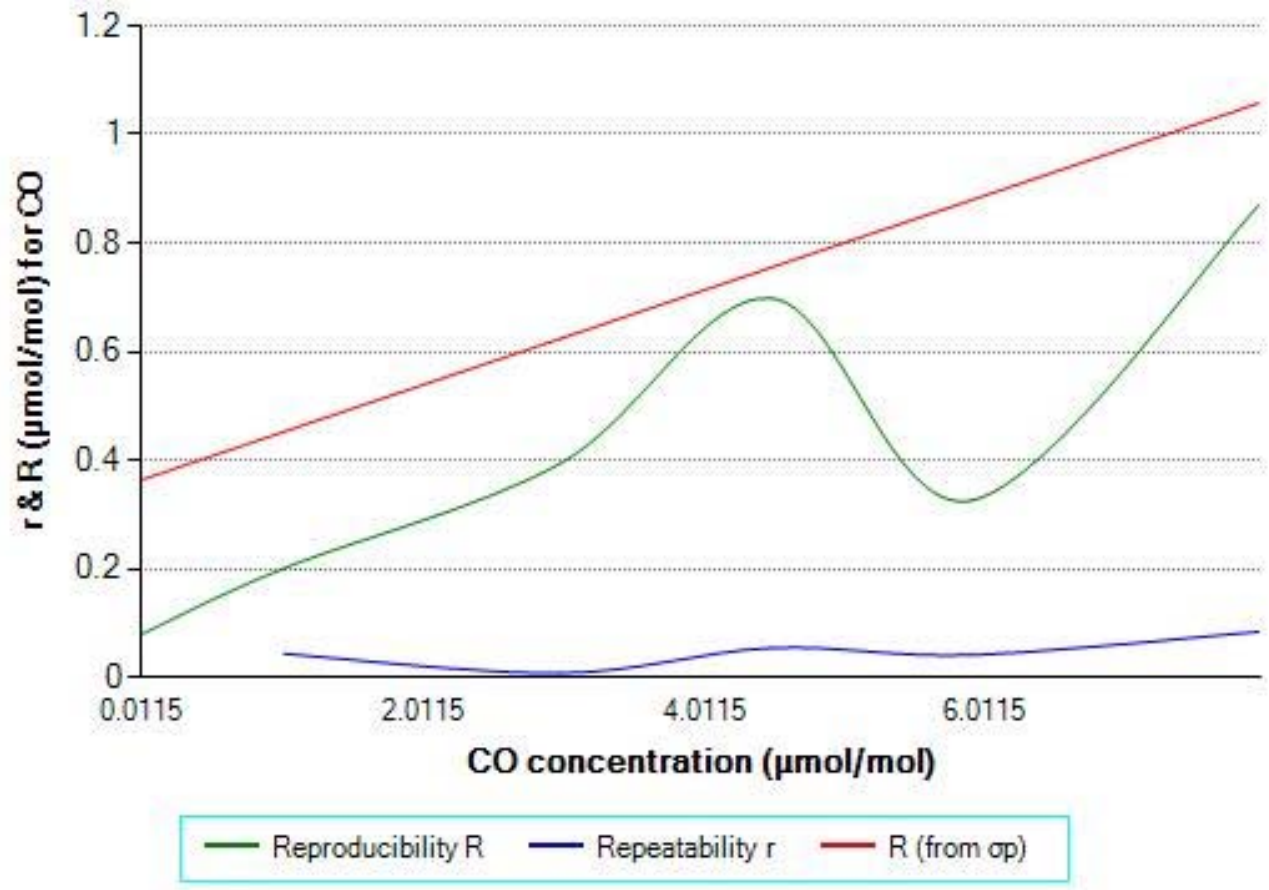

Figure 37: The R and r of CO standard measurement method as a function of concentration.

O_3 data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.1		0.6	
19.8	2.8	3.4	
60.5	6.7	8.1	
99.7	8.0	15.9	
299.9	19.5	25.6	8.5%

Table 36: The R and r of O_3 standard measurement method.

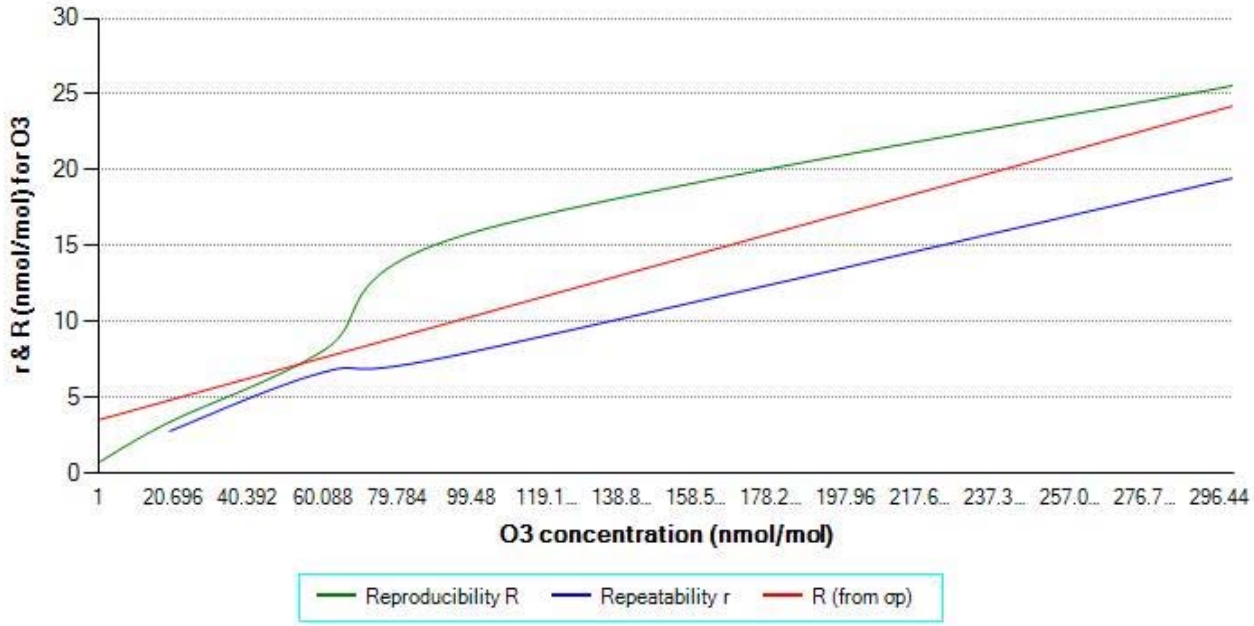

Figure 38: The R and r of O_3 standard measurement method as a function of concentration.

NO data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.1		0.7	
19.6	2.6	4.6	
201.2	16.7	20.0	9.9%

Table 37: The R and r of NO standard measurement method.

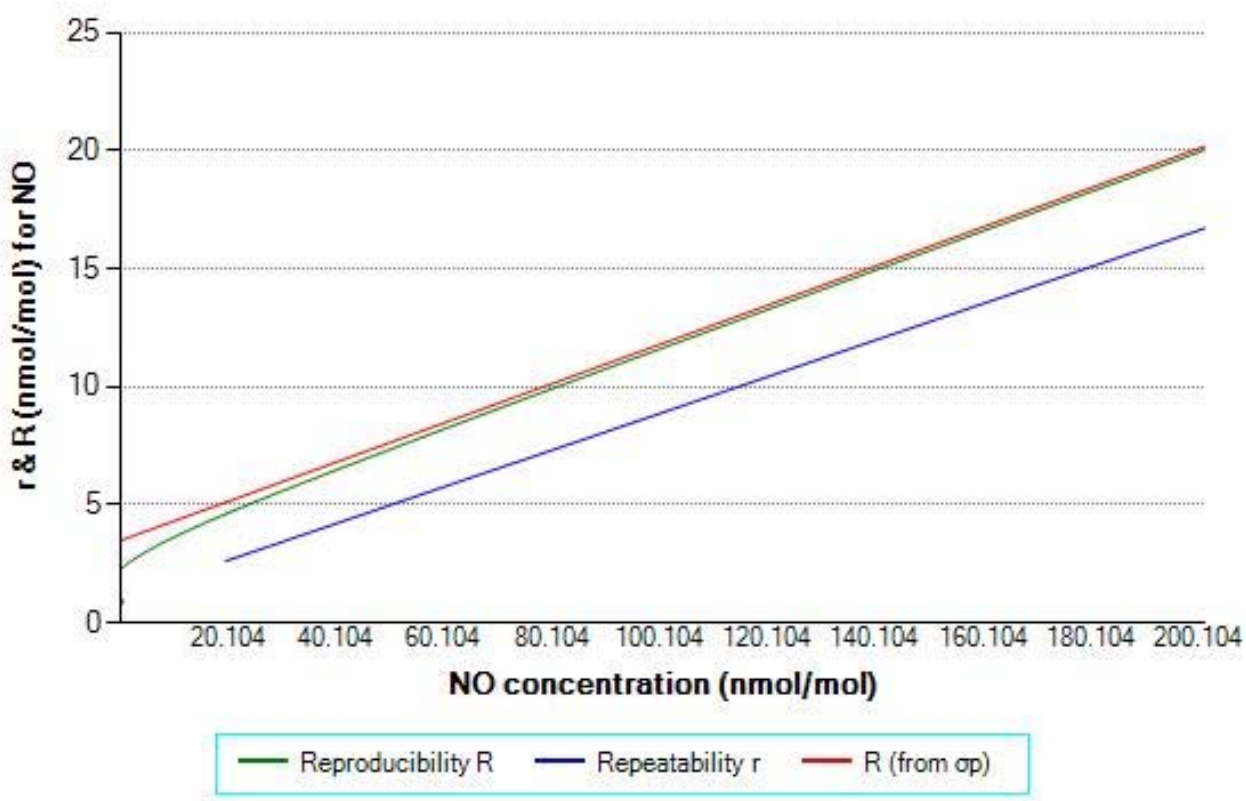

Figure 39: The R and r of NO standard measurement method as a function of concentration.

NO_2			
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	10.3%

Table 38: The R and r of NO_2 standard measurement method.

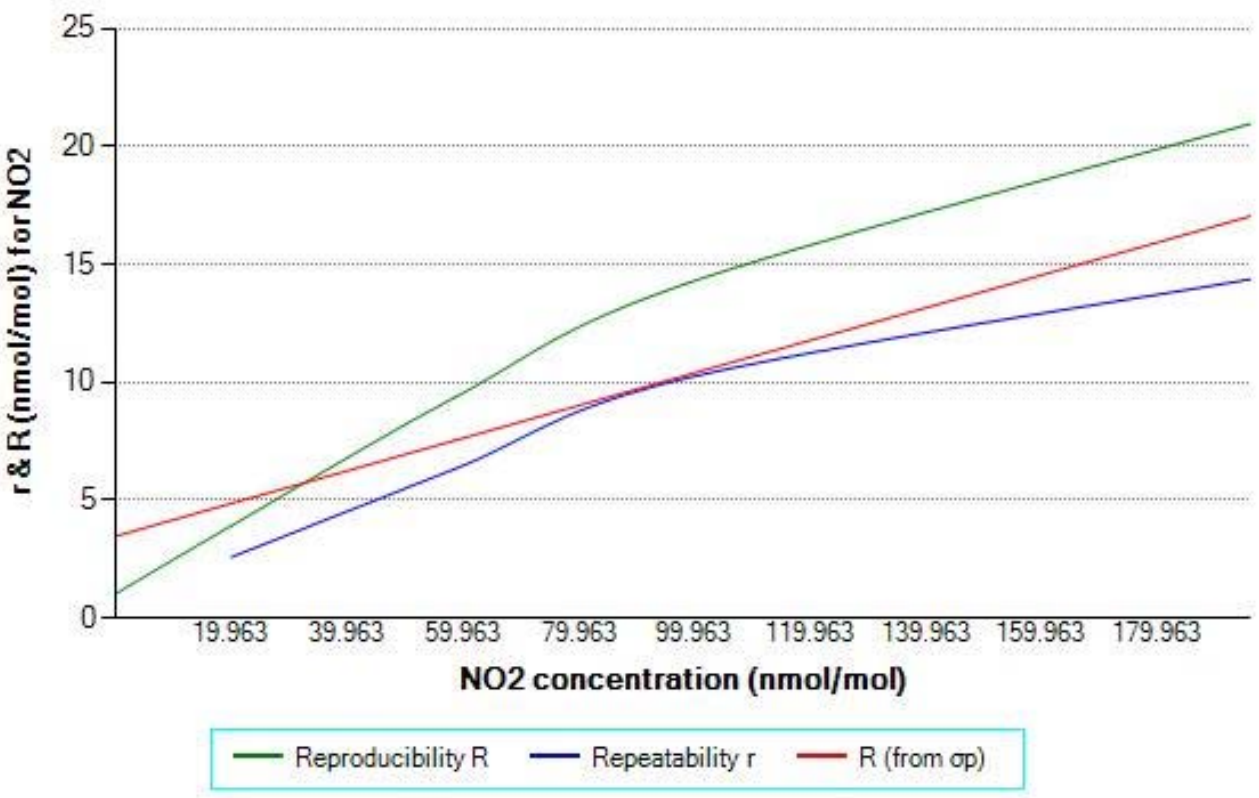

Figure 40: The R and r of NO_2 standard measurement method as a function of concentration.

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 outliers presented in the table below are related only to zero levels:

parameter	run	laboratory	measured value	failing test	confidence level
NO	0	F	0.56	G1 maximum	1%, 5%
CO	0	C	0.056	G1 maximum	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.

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Abstract

From the 23rd to the 28th of October 2011 in Langen (DE), 7 Laboratories of WHO/AQUILA (Network of European Air Quality Reference Laboratories) met at an laboratory comparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Directive about air quality (SO_2, CO, NO, NO_2 and O_3).

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, 59.4% of the results reported by the laboratories were good both in terms of measured values and reported uncertainties. Another 39.9% of the results had good measured values, but the reported uncertainties were too high and only 0.7% delivered questionable results.

Comparability of results among participants at the highest concentration level, excluding outliers, is acceptable for CO and NO measurements while SO_2, O_3 and NO_2 measurements showed less satisfactory results.

As the Commission's in-house science service, the Joint Research Centre's mission is to provide EU policies with independent, evidence-based scientific and technical support throughout the whole policy cycle.

Working in close cooperation with policy Directorates-General, the JRC addresses key societal challenges while stimulating innovation through developing new standards, methods and tools, and sharing and transferring its know-how to the Member States and international community.

Key policy areas include: environment and climate change; energy and transport; agriculture and food security; health and consumer protection; information society and digital agenda; safety and security including nuclear; all supported through a cross-cutting and multi-disciplinary approach.

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