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Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 7th - 10th October 2013 Ispra

EC Harmonization Program for Air Quality Measurements

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Abstract

Within the harmonization program of Air Quality monitoring in Europe ERLAP Laboratories are organizing Inter-Laboratory Comparison in the facility of Ispra (Italy). From the 7th to the 10th of October 2013 in Ispra (IT), nine Laboratories of AQUILA (Network of European Air Quality Reference Laboratories) met for a laboratory comparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants. In order to cover the prescription of the European Directive about air quality these pollutants were measured: 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, 86.8% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Part of the results (12.5%) had good measured values, but the reported uncertainties were either too high (8.9%) or too small (3.6%).Only two values (0.8%) were found with unsatisfactory En number.
Comparability of results among AQUILA participants at the highest concentration level, excluding outliers, is acceptable for all pollutants measurements.

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Executive Summary

Within the harmonization program of Air Quality monitoring in Europe the ERLAP Laboratory is organizing Inter-Laboratory Comparison in its facility of Ispra (Italy).
From the 7th to the 10th of October 2013 nine laboratories of AQUILA (Network of European Air Quality Reference Laboratories) met for a laboratory comparison exercise in Ispra (IT) 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.
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.
On the basis of criteria imposed by the European Directive, 86.8% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Some results (12.5%) had good measured values, but the reported uncertainties were either too high (8.9%) or too small (3.6%). Two results were found questionable according to the z'-score and between them one was 'satisfactory' and the other 'unsatisfactory' through the En number evaluation.
The majority of the values were satisfactory (99.3%) for the z-score and only 0.7% was questionable. Only 3.4% of the values were found "not ok" regarding the En-number.
The comparability of results among AQUILA participants at the highest generated concentration levels, excluding outliers, is satisfactory for measurements of all pollutants.

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Abbreviations

AQUILA	Network of National Reference Laboratories for Air Quality
CO	Carbon monoxide
DQO	Data Quality Objective
ERLAP	European Reference Laboratory of Air Pollution
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; 0)
E_n	E_n – number statistic (ISO 13528; 0)
r	repeatability limit (ISO 5725; 0)
R	reproducibility limit (ISO 5725; 0)
σ_p	standard deviation for proficiency assessment (ISO 13528; 0)
x*	robust average (Annex C ISO 13528; 0)
s*	robust standard deviation (Annex C ISO 13528; 0)
s_r	repeatability standard deviation (ISO 5725; 0)
s_R	reproducibility standard deviation (ISO 5725; 0)
$U_{X'}$	expanded uncertainty of the assigned/reference value (ISO 13528; 0)
U_{xi}	expanded uncertainty of the participant's value
$u_{X'}$	standard uncertainty of the assigned/reference value (ISO 13528; 0)
X	assigned/reference value (ISO 13528; 0)
x_i	average of three values reported by the participant *i* (for particular parameter and concentration level) (ISO 5725; 0)
$x_{i,j}$	j-the reported value of participant i (for particular parameter and concentration level) (ISO 5725; 0)
z'	z'-score statistic (ISO 13528; 0)

1. Introduction

The Directive 2008/50/EC 0 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 (DQOs) for the accuracy of measurements.
The European Commission (EC) has supported the development and publication of reference measurement methods for CO 0, SO_2 0, NO-NO_2 0 and O_3 0 as European standards. Appropriate calibration methods 0, 0 and 0 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 the Member States 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 0 0, [31] Mücke H-G, et al. (1996). European Intercomparison Workshops on Air Quality Monitoring. Vol. 2 – Measuring of CO, NO, NO_2 and O_3 – Air Hygiene Report 9. Berlin, Germany: WHO Collaborating Centre for Air Quality Management and Air Pollution Control; ISSN 0938-9822., [33] Belis C. A., Lagler F., Barbiere M., Mücke H.G., Wirtz K. and Stummer V. (2009) The evaluation of the Interlaboratory Comparison Exercise for SO2, O3, NO and NO2 Langen 20th-25th September 2009., [37] Barbiere M. et al. (2012) Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2, Langen 23rd-28th October 2011. [40] Barbiere M., Lagler F., Mücke H.G., Wirtz K. and Stummer V. (2014) Evaluation of the Laboratory Comparison Exercise for NO, NO2, SO2, CO, and O3 Langen (D) 1st-6th September 2013.] but with a view to obtaining harmonized air quality data for health related studies. Their program integrates within the WHO EURO region, which includes public health institutes and other national institutes - especially from the Central Eastern Europe, Caucasus and countries from 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 7th to the 10th of October 2013 in Ispra (IT) in joint cooperation of EC-JRC and WHO CC.

Since 1990 ERLAP organizes IEs 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) 0, 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 IEs 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 0.

This evaluation scheme was adopted by AQUILA in December 2008 and is applied to all IEs 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 0 with the uncertainty requirements for calibration gases stated in the European standards 0, 0, 0 and 0, which are consistent with the DQOs of European Directives.
According to the above 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 0. 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 0.
Beside the proficiency of participating laboratories, the repeatability and reproducibility of standardized measurement methods 0, 0 and 0 are evaluated as well. These group evaluations are useful indicators of trends in measurement quality over different IE.

2. Inter-laboratory organization

The IE was announced in February 2013 to the members of the AQUILA network and the WHO CC representative. Registration was opened in February 2013 and closed at the end of June 2013.
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 Monday, 7th of October 2013, for the installation of their equipment. The calibration of NO_x and O_3 analysers was carried out on Tuesday morning and the generation of NO_x and O_3 gas mixtures started at 11:00.
The calibration of SO_2 and CO analysers was carried out on Wednesday afternoon and the generation of CO and SO_2 gas mixtures started at 20:00.
The test gases generation and measurements finished on Thursday at 9:00.

2.1. Participants

All participants were organizations dealing with the routine ambient air monitoring or institutions involved in environmental or public health protection. The national representatives came from United Kingdom, Italy, Hungary, Norway, Belgium, Switzerland, Denmark and Spain.

Country	Laboratory	Code
United Kingdom	RICARDO-AEA (AEA)	A
Italy	Institute of Atmospheric Pollution Research (CNR)	B
Hungary	Hungarian Meteorological Service (HMS)	C
Norway	Norwegian Institute for Air Research (NILU)	D
Belgium	Flemish Environmental Agency (VMM)	E
Switzerland	Swiss Federal Laboratories for Materials and Science Technology (EMPA)	F
European Commission	European Reference Laboratory for Air Pollution (ERLAP)	G
Denmark	National Environmental Research Institute (NERI)	H
Spain	Instituto De Salud Carlos III (ISCIII)	I

Table 1: The list of participating organizations.

In

Table 2 are reported 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 was manufactured by 4 different companies for all parameters analyzed.

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.

Gas	Lab Code	Instrument
SO_2	A	Thermo 43i, 2011
	B	API, 2008, 100
	C	
	D	SO2 analyzer, TAPI 100E
	E	Thermo Scientific, 2010, 43i
	F	Thermo Scientific Model 43i TLE (2012)
	G	Thermo Electrom Corporation, 2005, 43C
	H	Teledyne-API, 2003, 100A
	I	THERMO 43i
NO_X	A	Thermo 42i, 2008
	B	API, 2008, 200E
	C	Teledyne model 200E
	D	NOx analyzer, TAPI 200E
	E	Thermo Scientific, 2011, 42i
	F	Horiba Model APNA-360 (2005)
	G	Thermo Electrom Corporation, 1999, 42C
	H	Teledyne-API, 2012, T200
	I	THERMO ENVIRONEMNTAL 42i. 2008
CO	A	API M300E, 2007
	B	API, 2008, 300
	C	TEI 48C
	D	CO analyzer, TAPI 300E
	E	API, 2012, API T300
	F	Picarro Model G1302 CO/CO2/H2O Analyzer (2010)
	G	Horiba Model APMA-370, 2010
	H	Teledyne-API, 2002, 300A
	I	API 300E
O_3	A	Thermo 49i, 2007
	B	API, 2008, 400
	C	TEI 49 C
	D	O3 analyzer, TAPI T400
	E	Thermo Scientific, 2009, 49i
	F	Thermo Scientific Model 49i (2012)
	G	Thermo Electronic Corporation, 1996, 49CPS
	H	Teledyne-API, 2012, T400
	I	API 400E, 2009

Table 2: The list of instruments used by participants.

2.2. Preparation of test mixtures

The ERLAP IE facility has been described in several reports 0 and 0. 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 0.
The test mixtures were prepared by the dilution of gases from cylinders containing high concentrations of NO, SO_2 or CO using thermal mass flow controllers 0. O_3 was added using an ozone generator and NO_2 was produced applying the gas phase titration method 0 in a condition of NO excess.
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	NO_2	O_3	CO	SO_2
		h				nmol/mol	nmol/mol	nmol/mol	nmol/mol	mmol/mol	nmol/mol
1st	9:00	5	/	X							
2nd	8:00	3	/		X						
2nd	11:00	1	NO-NO_2-O_3			0					
2nd	12:00	2	NO-NO_2				600				
2nd	14:00	2	NO-NO_2				470	130			
2nd	16:00	2	O_3						125		
2nd	18:00	2	NO-NO_2				190				
2nd	20:00	2	NO-NO_2				130	60			
2nd	22:00	2	O_3						60		
3rd	0:00	2	NO-NO_2				350				
3rd	2:00	2	NO-NO_2				250	100			
3rd	4:00	2	O_3						90		
3rd	6:00	2	NO-NO_2				18				
3rd	8:00	2	NO-NO_2				6	12			
3rd	10:00	2	O_3						10		
3rd	12:00	2	NO-NO_2				60				
3rd	14:00	2	NO-NO_2				40	20			
3rd	16:00	2	O_3						20		
3rd	< 18:00	2	calibration		X						
3rd	20:00	1	CO-SO_2			0					
3rd	21:00	2	CO-SO_2							2.5	125
3rd	23:00	2	CO-SO_2							8	4
4th	1:00	1	CO-SO_2	Zero Air not reported						0	0
4th	2:00	2	CO-SO_2							4	48
4th	4:00	2	CO-SO_2							5.5	15
4th	6:00	2	CO-SO_2							0.8	8
4th	8:00	1				0					
4th	9:00	END									

Table 3: The sequence program of generated test gases with indicative pollutant concentrations

3. The evaluation of laboratory's measurement proficiency

To evaluate the participants measurement proficiency the methodology described in ISO 13528 0 was applied. It has been agreed among the AQUILA members to take the measurement results of ERLAP as the assigned/reference values for the whole IE 0.
The traceability of ERLAP's measurement results and the method applied to validate them are presented in Annex A. In the following proficiency evaluations, the uncertainty of test gas homogeneity (Annex A) was added to the uncertainties of ERLAP's measurement results.

All data reported by participating laboratories are presented in Annex B.
As it is described in the position paper 0, 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.

3.1. z' – score

The z'- score statistic is calculated according to ISO 13528 0 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 average value for each run, 'X' is the assigned/reference value, 'σ_p' is the 'standard deviation for proficiency assessment' and 'u_X' is the standard uncertainty of the assigned value. For 'a' and 'b' see Table 4.

In the European standards 0, 0, 0 and 0 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) 0 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:

Gas	σ_p=a·c+b 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.

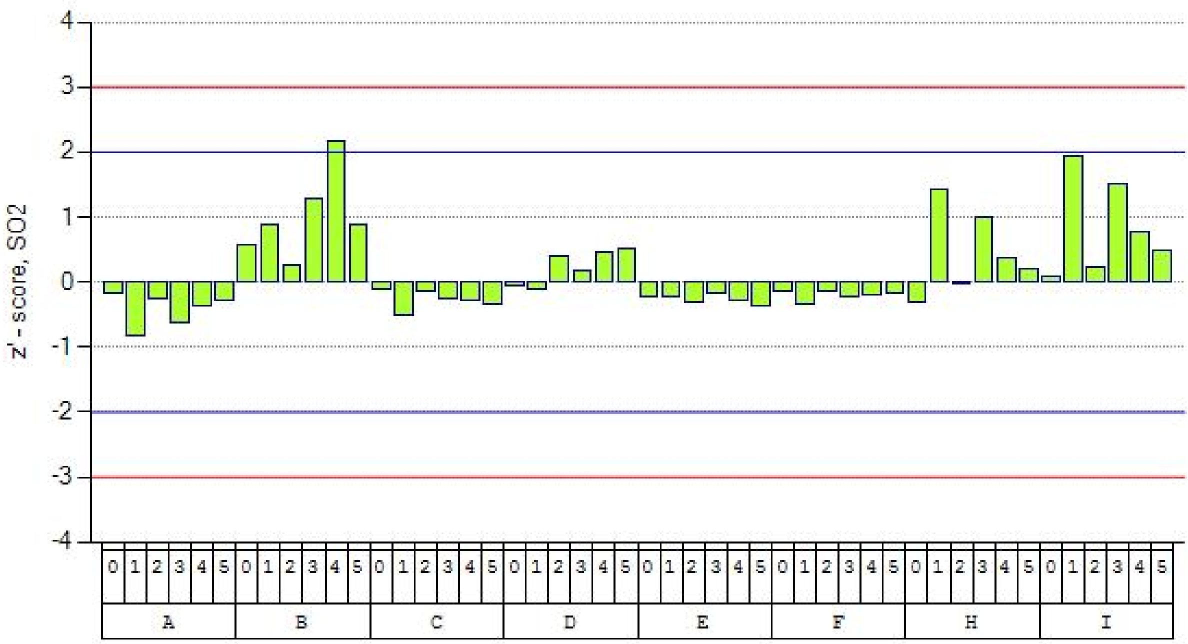

Figure 1: The z′-score evaluations of SO_2 measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (125 nmol/mol), 2 (4 nmol/mol), 3 (48 nmol/mol), 4 (15 nmol/mol), 5 (8 nmol/mol). The assessment criteria are presented as z′=±2 (blue line) and z′=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

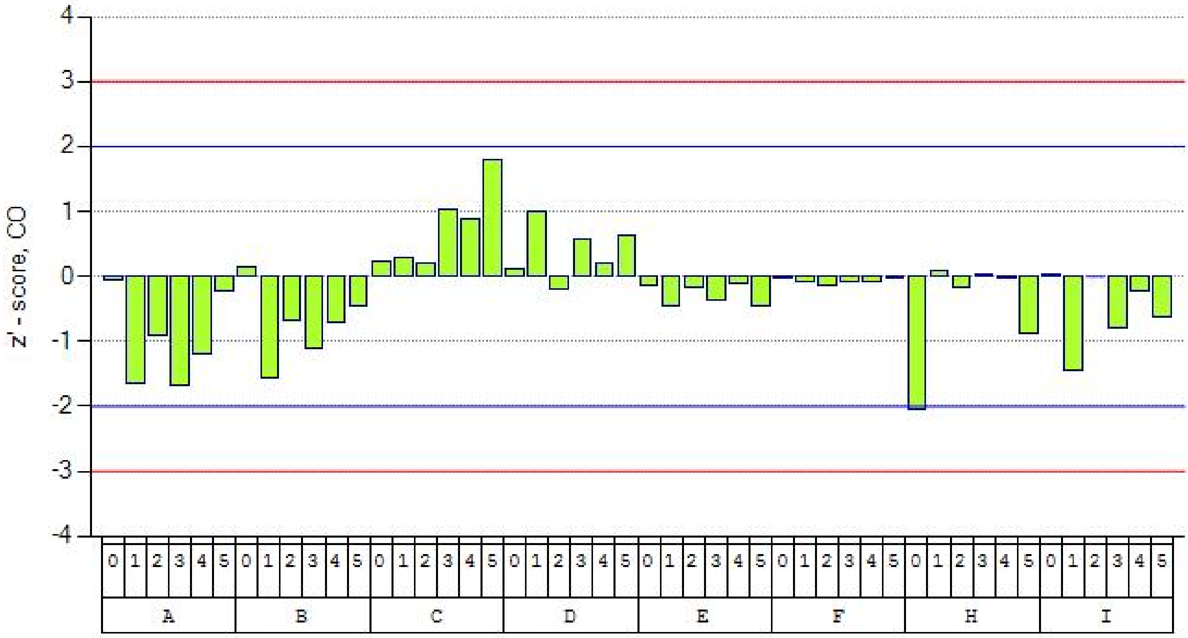

Figure 2: The z'-score evaluations of CO measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 µmol/mol), 1 (2.5 µmol/mol), 2 (8 µmol/mol), 3 (4 µmol/mol), 4 (5.5 µmol/mol), 5 (0.8 µmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

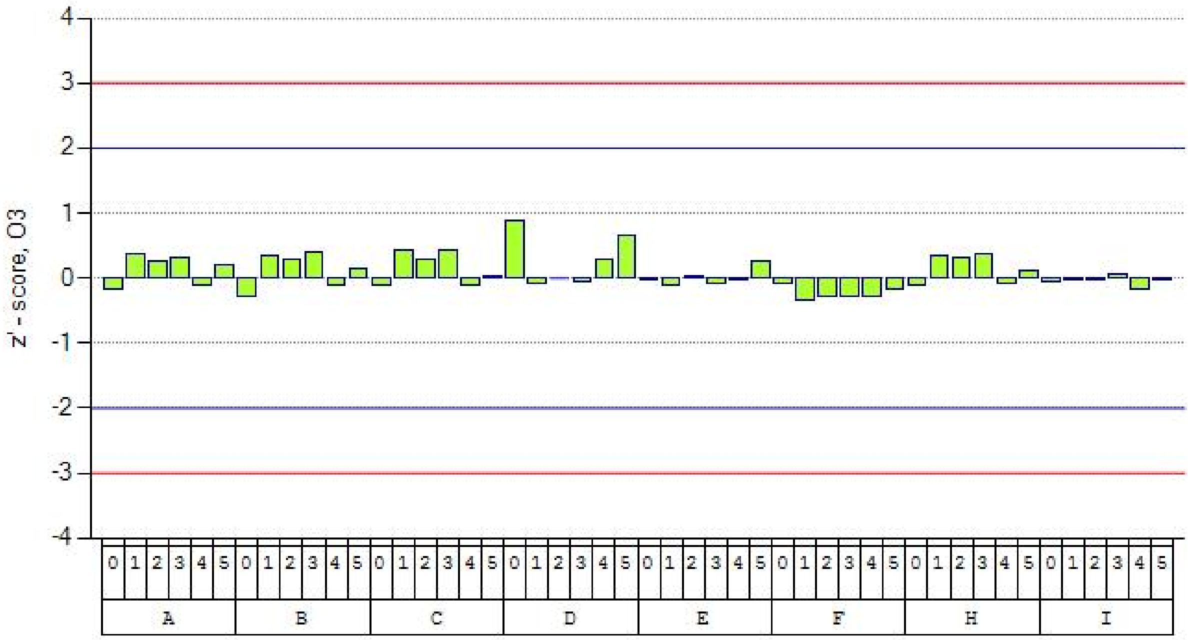

Figure 3: The z'-score evaluations of O_3 measurements
Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (125 nmol/mol), 2 (60 nmol/mol), 3 (90 nmol/mol), 4 (10 nmol/mol), 5 (20 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

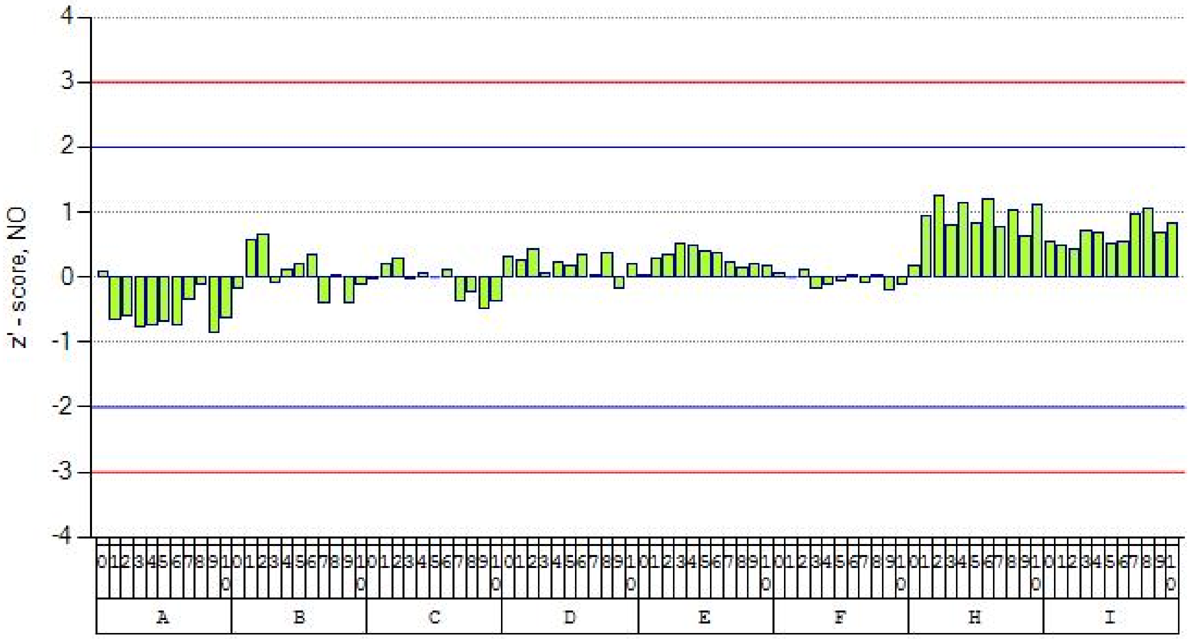

Figure 4: The z'-score evaluations of NO measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (600 nmol/mol), 2 (470 nmol/mol), 3 (190 nmol/mol), 4 (130 nmol/mol), 5 (350 nmol/mol), 6 (250 nmol/mol), 7 (18 nmol/mol), 8 (6 nmol/mol), 9 (60 nmol/mol), 10 (40 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.

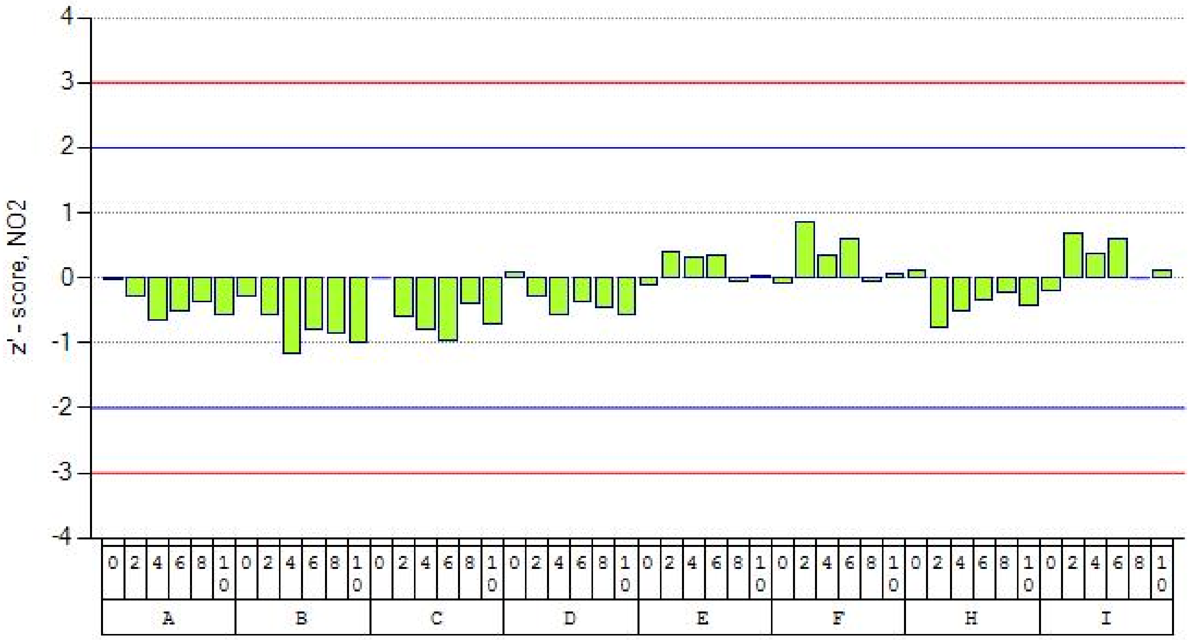

Figure 5: The z'-score evaluations of NO_2 measurements
Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (130 nmol/mol), 2 (60 nmol/mol), 3 (100 nmol/mol), 4 (12 nmol/mol), 5 (20 nmol/mol). The assessment criteria are presented as z'=±2 (blue line) and z'=±3 (red line). They represent the limits for the questionable and unsatisfactory results.

3.2. E_n - number

The normalized deviations 0 (E_n) were calculated according to:

$$E_n = \frac{x_i - X}{\sqrt{U_{x_i}^2 + U_X^2}}$$ **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 the 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.

Parameter	Lab Code	Value	Run	En	En unsatisfactory?
CO	**A**	5.27	CO _4	-1.6	unsatisfactory
CO	**A**	3.72	CO _3	-1.9	unsatisfactory
CO	**A**	7.79	CO _2	-1.4	unsatisfactory
CO	**A**	2.28	CO _1	-1.5	unsatisfactory
SO2	**B**	18.50	SO2 _4	1.4	unsatisfactory
CO	**C**	1.04	CO _5	1.2	unsatisfactory
CO	**D**	2.70	CO _1	1.4	unsatisfactory
SO2	**I**	52.90	SO2 _3	1.3	unsatisfactory
SO2	**I**	136.30	SO2 _1	1.3	unsatisfactory
CO	**I**	0.75	CO _5	-1.7	unsatisfactory
CO	**I**	2.31	CO _1	-1.9	unsatisfactory

Table 5: Unsatisfactory results according to En number.

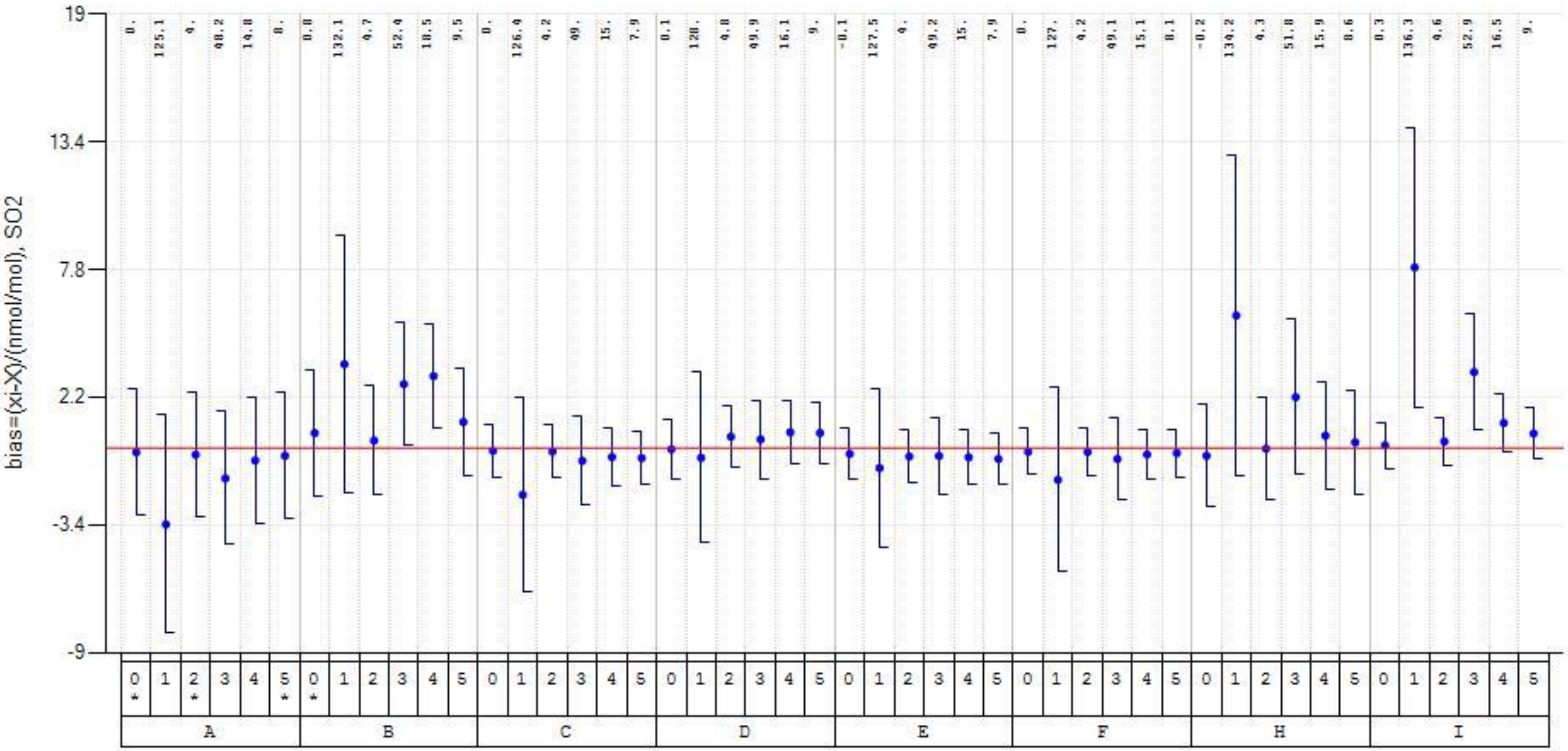

Figure 6: Bias of participant's SO_2 measurement results

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 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

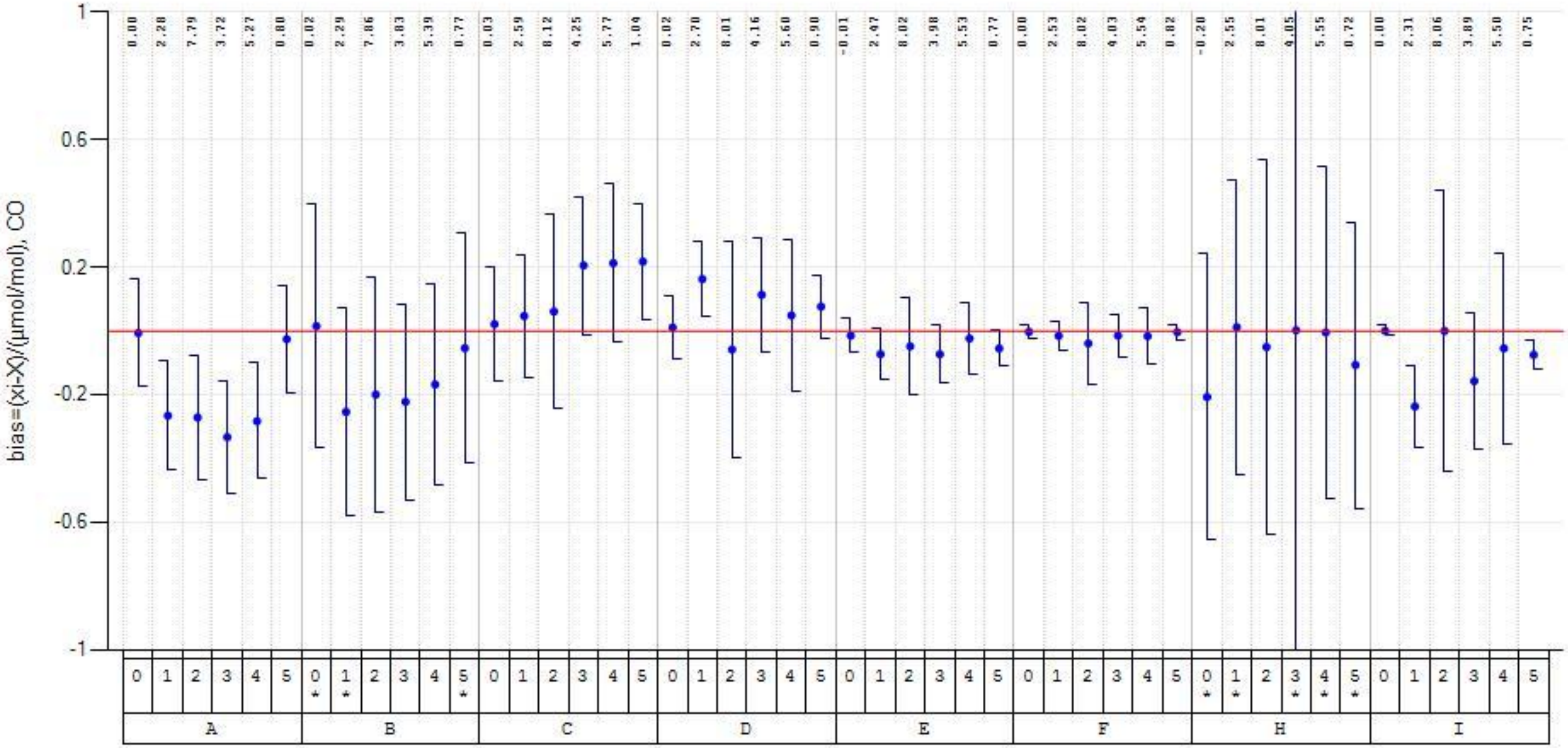

Figure 7: Bias of participant's CO measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average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

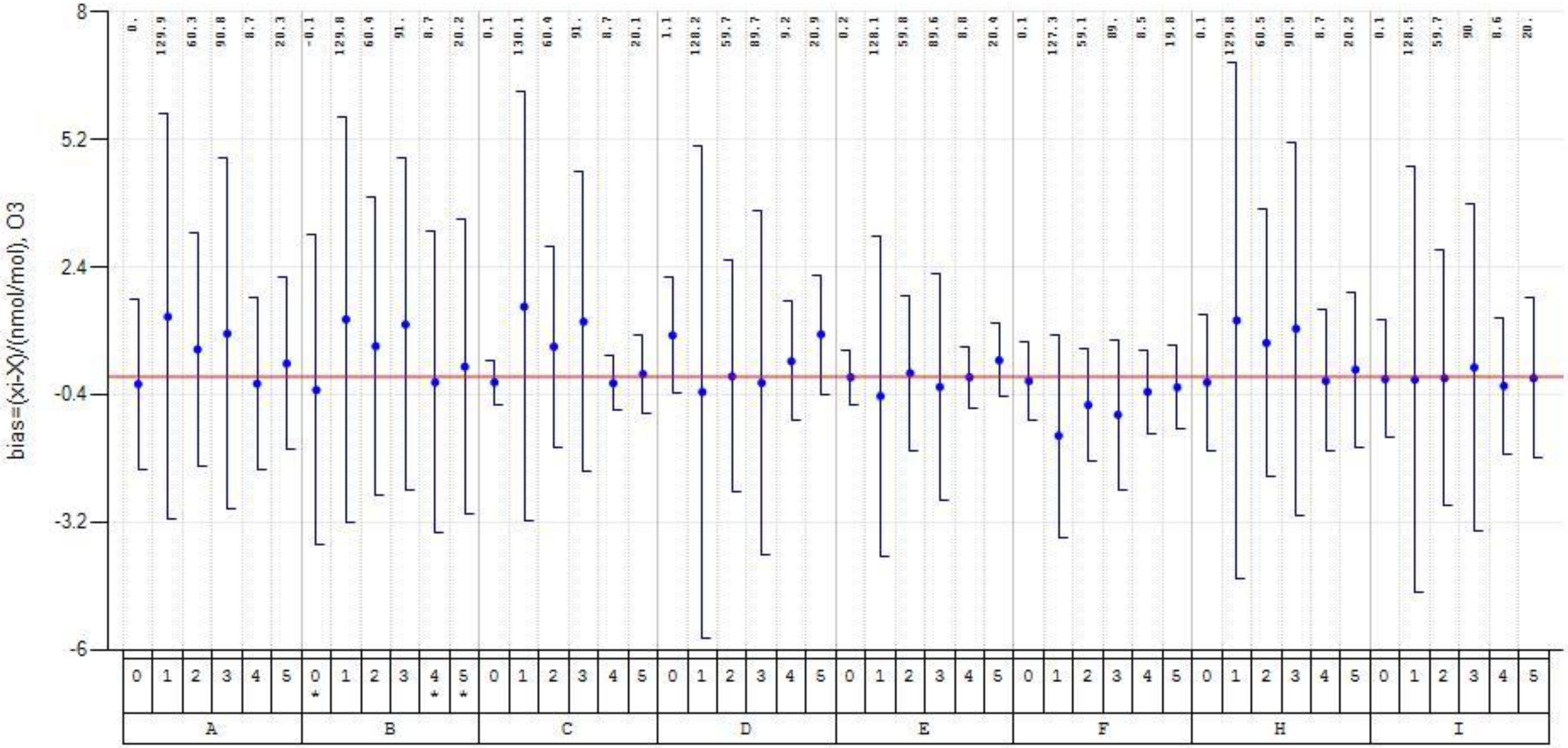

Figure 8: Bias of participant's O_3 measurement results

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 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

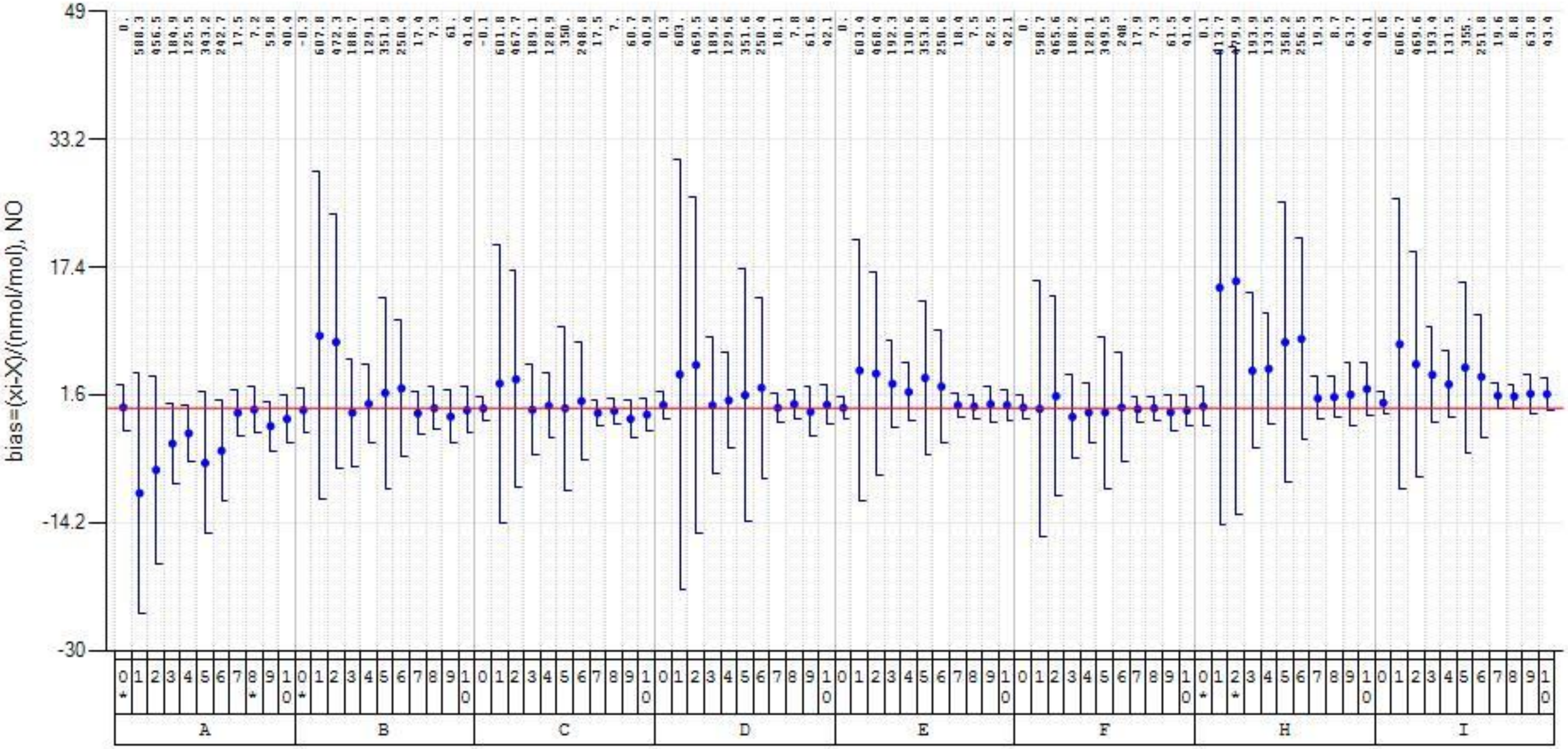

Figure 9: Bias of participant's NO measurement results
Expanded uncertainty of bias for each run is presented as error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 10) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σp.

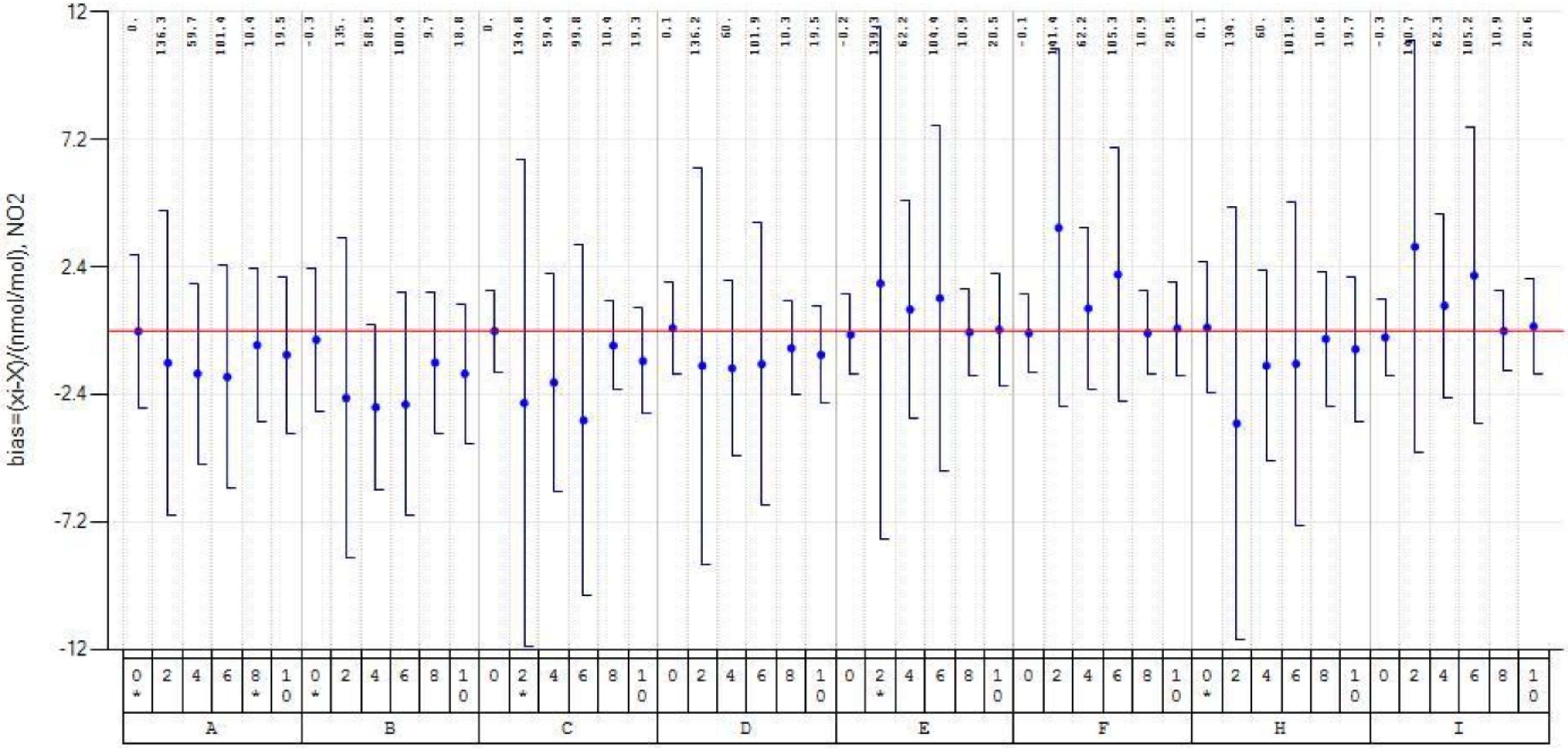

Figure 10: Bias of participant's NO_2 measurement results
Expanded uncertainty of bias is presented as error bar for NO_2 run numbers 0, 2, 4, 6, 8 and 10 (see Table 3). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

4. Performance characteristics of individual laboratories

Individual participants' bias were evaluated and are presented in chapter 2 (Figure 6-Figure 10). Since the results of NO_2 runs 1, 3, 5, 7 and 9 were not treated in proficiency evaluation the bias of these runs are presented in Figure 11.

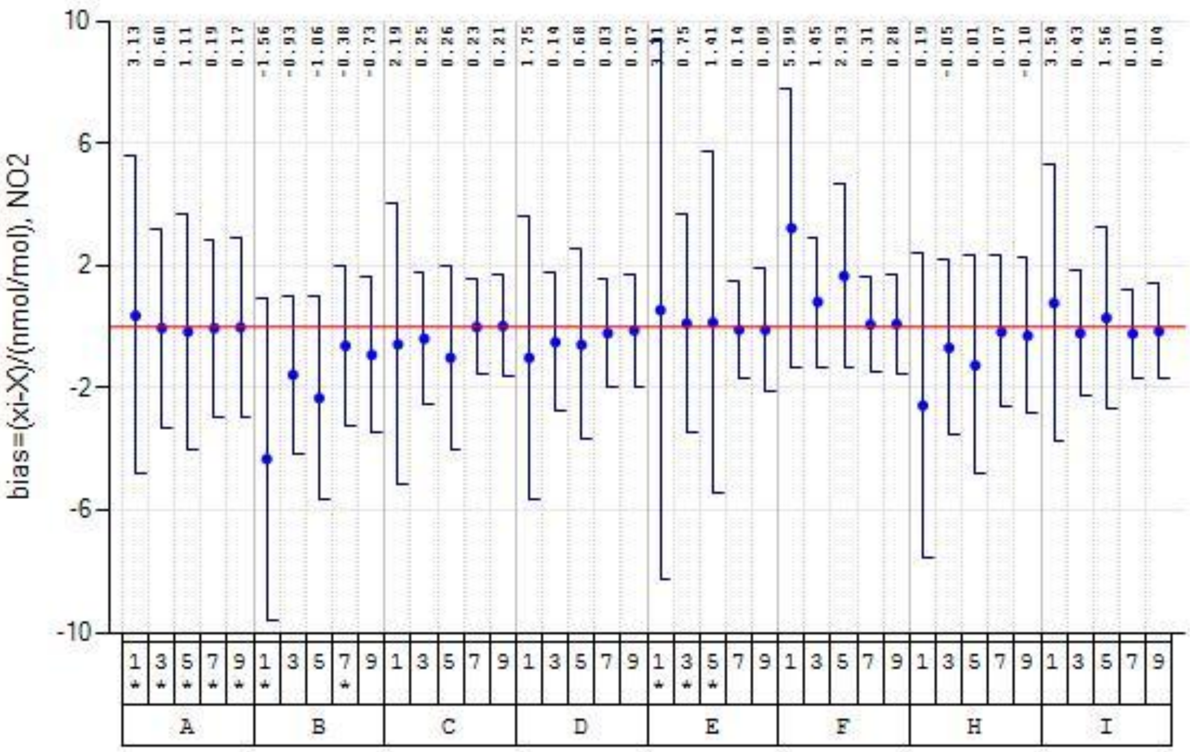

Figure 11: Bias of participant's NO_2 measurements for run numbers 1, 3, 5, 7 and 9
Within these test gas mixtures there is no gas phase titration to produce NO_2 (see Table 3). For each evaluation the run number together with the participants rounded run average (nmol/mol) is given.

4.1. Converter efficiencies of NO_2-to-NO for NO_X analyzers

Since NO and NO_2 test gases were produced by gas phase titration it is possible to evaluate the efficiency of the NO_2-to-NO converter of each participant's NO_X analyser. The evaluation takes each participant's NO and NO_2 measurements before and after oxidation by O_3. However, possible minor instabilities in the preparation of the test gas mixtures were not taken into account. The converter efficiency (α) is calculated using Equation 3 [4] EN 14211:2012, Ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence:

$$\alpha = \frac{[NO2]_i - [NO2]_{i-1}}{[NO]_{i-1} - [NO]_i} \cdot 100\% \qquad \textbf{Equation 3}$$

Ideal value for α is 100%.

Lab code	NO_2 (nmol/mol)	α (%)
A	20	99.6
A	12	98.6
A	100	99.7
A	60	99.6
A	130	101.1
B	20	99.9
B	12	100.3
B	100	99.9
B	60	99.7
B	130	100.8
C	20	96.3
C	12	96.9
C	100	98.3
C	60	98.3
C	130	98.9
D	20	99.9
D	12	99.6
D	100	100.0
D	60	99.6
D	130	100.7
E	20	99.7
E	12	98.6
E	100	99.8
E	60	99.5
E	130	100.7
F	20	100.7
F	12	99.4
F	100	100.8
F	60	101.0
F	130	101.8
G	20	99.50
G	12	99.6
G	100	99.8
G	60	100.1
G	130	100.1
H	20	100.9
H	12	100.0
H	100	100.2
H	60	99.5
H	130	100.0
I	20	100.9
I	12	100.8
I	100	100.4
I	60	100.0
I	130	100.0

Table 6: The efficiency of NO_2-to-NO converters.

The evaluation of equation 3 for each participant at different concentration levels are given in
Table 6.

5. Discussion

For a general assessment of the quality of each result a decision diagram was developed (Figure 12) 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)

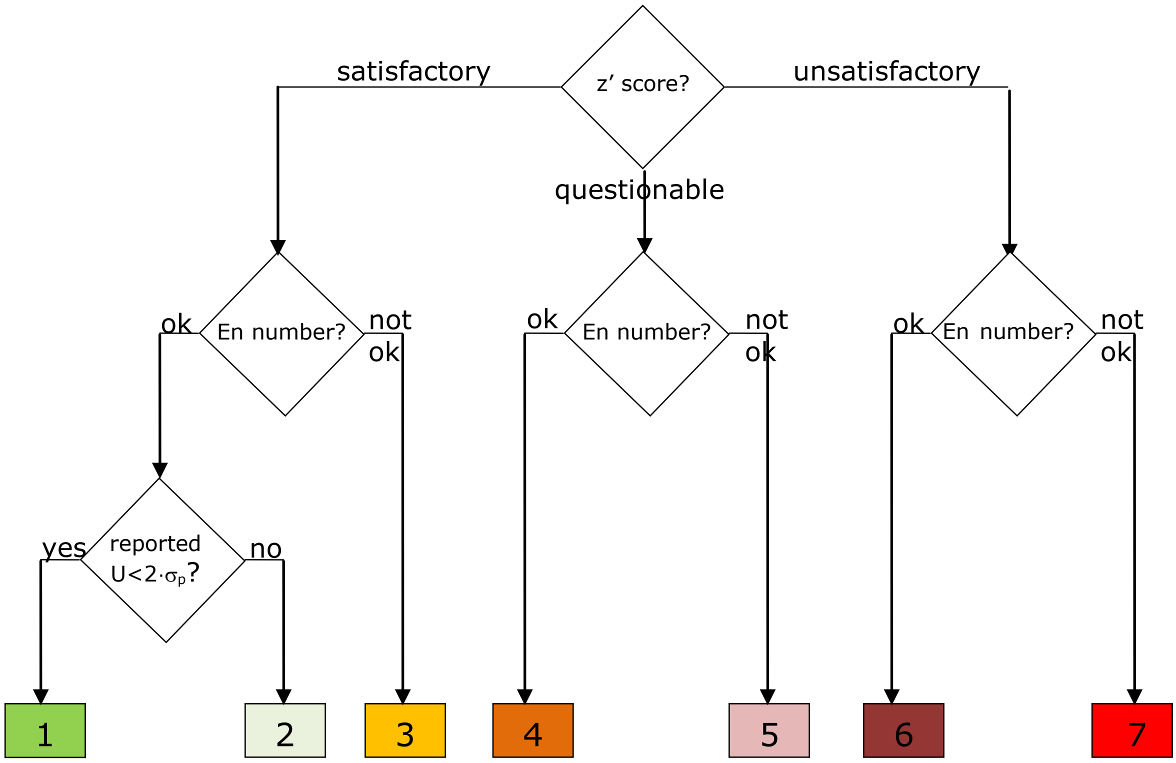

Figure 12: The decision diagram for general assessment of proficiency results.

The results of the IE were assigned to categories according to the diagram given in Figure 12 and are presented in the following
Table 7.

	run numb	Ref. conc. level	IE code							
			A	B	C	D	E	F	H	I
CO (µmol/mol)	0	0.003	1	2	1	1	1	1	4	1
	1	2.541	3	2	1	3	1	1	2	3
	2	8.062	3	1	1	1	1	1	1	1
	3	4.048	3	1	1	1	1	1	2	1
	4	5.555	3	1	1	1	1	1	2	1
	5	0.826	1	2	3	1	1	1	2	3
NO (nmol/mol)	0	-0.09	2	2	1	1	1	1	2	1
	1	598.77	1	1	1	1	1	1	1	1
	2	464.14	1	1	1	1	1	1	2	1
	3	189.25	1	1	1	1	1	1	1	1
	4	128.57	1	1	1	1	1	1	1	1
	5	349.99	1	1	1	1	1	1	1	1
	6	247.89	1	1	1	1	1	1	1	1
	7	18.05	1	1	1	1	1	1	1	1
	8	7.31	2	1	1	1	1	1	1	1
	9	62.00	1	1	1	1	1	1	1	1
	10	41.68	1	1	1	1	1	1	1	1
NO2 (nmol/mol)	0	-0.01	2	2	1	1	1	1	2	1
	2	137.50	1	1	2	1	2	1	1	1
	4	61.35	1	1	1	1	1	1	1	1
	6	103.12	1	1	1	1	1	1	1	1
	8	10.93	2	1	1	1	1	1	1	1
	10	20.41	1	1	1	1	1	1	1	1
O3 (nmol/mol)	0	0.19	1	2	1	1	1	1	1	1
	1	128.56	1	1	1	1	1	1	1	1
	2	59.72	1	1	1	1	1	1	1	1
	3	89.80	1	1	1	1	1	1	1	1
	4	8.83	1	2	1	1	1	1	1	1
	5	20.00	1	2	1	1	1	1	1	1
SO2 (nmol/mol)	0	0.16	2	2	1	1	1	1	1	1
	1	128.40	1	1	1	1	1	1	1	3
	2	4.34	2	1	1	1	1	1	1	1
	3	49.56	1	1	1	1	1	1	1	3
	4	15.39	1	5	1	1	1	1	1	1
	5	8.35	2	1	1	1	1	1	1	1

Table 7: The general assessment of proficiency results.

6. 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) 86.8% of the results reported (see Table 8) by AQUILA laboratories fall into category '1' and are satisfactory 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' (8.9%), or too small, category '3' (3.6%). Two results were found questionable for the z'-score but one was ok for the En number (category '4') and the other was not ok for the En number (category '5').

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
Sep-13	Ispra (IT)	89.4	7.3	3.3	0.0	0.0	0.0	0.0
Oct-13	Ispra (IT)	86.8	8.9	3.6	0.4	0.4	0.0	0.0

Table 8: Flags summary

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 deviation obtained at this (Annex C) and previous IE 0, [21] Kapus M. et al. (2009)The evaluation of the Intercomparison Exercise for SO2, CO, O3, NO and NO2 - April 2008. JRC scientific and technical reports. EUR 23805., 0, 0, 0, 0, [32], [32], [32], [32], [32], [32] and [40] Barbiere M., Lagler F., Mücke H.G., Wirtz K. and Stummer V. (2014) Evaluation of the Laboratory Comparison Exercise for NO, NO2, SO2, CO, and O3 Langen (D) 1st-6th September 2013. is comparable to the mentioned criteria. On the other hand, the uncertainty criteria for zero levels were those set in AQUILA's position paper [0 below].

In the present IE a high share of '1' results can be observed confirming the good performance of the most recent IEs.

In this exercise 99.3% of the results in the z'-score evaluations (Table 9) were satisfactory and only 2 results were found questionable.

IE	Site	Satisfactory (%)	Questionable (%)	Unsatisfactory (%)
June/05	Ispra (IT)	94.7	2.3	3.0
June/07	Ispra (IT)	97.8	1.9	0.3
October/07	Essen (DE)	93.2	4.6	2.2
April/08	Ispra (IT)	93.8	2.1	4.1
October 2008_1	Ispra (IT)	92.9	4.2	2.9
October 2008_2	Ispra (IT)	97.0	3.0	0.0
September/09	Langen (DE)	94.3	4.7	0.9
October/09	Ispra (IT)	98.2	1.8	0.0
June/10	Ispra (IT)	97.0	3.0	0.0
September/11	Ispra (IT)	99.4	0.3	0.3
October/11	Ispra (IT)	98.7	1.3	0.0
October/11	Langen (DE)	99.3	0.7	0.0
June/12	Ispra (IT)	100.0	0.0	0.0
September/13	Langen (DE)	98.6	1.4	0.0
September/13	Ispra (IT)	100.0	0.0	0.0
October/13	Ispra (IT)	99.3	0.7	0.0

Table 9: Z'-score summary

Comparability of results among AQUILA participants at the highest concentration level, excluding outliers, is acceptable for all pollutants measurements.

The relative reproducibility limits, at the highest studied concentration levels, are 4.8% for SO_2, 9.7% for CO, 2.6% for O_3, for NO 3.9% and for NO_2 6.3% all within the objective derived from criteria imposed by the European Commission (σ_p see Table 4).

During this IE the performance of all NRL has been satisfactory. Only two outliers were identified: at level 0 for CO and level 0 for O_3 (**Error! Reference source not found.**).

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Annex A. Assigned values

The assigned values of tested concentration levels (run) were derived from ERLAPs 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 0.

To foster its reference function ERLAP is participating regularly to key comparisons of the Gas Analysis Working Group within the framework of BIPM's CCQM.

During this IE ERLAP's SO_2, CO and NO analysers were calibrated according to the methodology described in the ISO 6143 0. Reference gas mixtures were produced from the primary reference materials (produced and certified by NMi Van Swinden Laboratorium) by dynamic dilution method using mass flow controllers 0. All flows were measured with a certified molbloc/molbox1 system. For O_3 measurements, the analyzers were calibrated using the JRC SRP42 primary standard (constructed by NIST) which has been compared to BIPM primary standard 0. The photometer absorption cross section uncertainty (1.06%) was included in the uncertainty budget 0 0.

The reference gas mixture and the calibration experiment evaluation were carried out using two computer applications, the "GUM WORKBENCH" 0 and "B-least" 0 respectively. For extending calibration from the NO to NO_2 channel of NO_X analyser the GPT test was performed to establish the efficiency of NO_2-converter.
ERLAP'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 0. The validation is taking into account ERLAP's measurement result (X) and its standard uncertainty (u_X) as given in Equation 4 0:

$$\frac{\left|x^* - X\right|}{\sqrt{\frac{\left(1{,}25 \cdot s^*\right)^2}{p} + u_X^2}} < 2 \qquad \textbf{Equation 4}$$

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

In Table 10 all inputs for Equation 4 are given and all ERLAP'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 tables.

run	unit	X	uX'	x*	s*	p	val.
NO _0	nmol/mol	-0.09	0.72	0.02	0.19	9	OK
NO _1	nmol/mol	598.77	4.25	602.90	6.31	9	OK
NO _2	nmol/mol	464.14	3.34	468.24	4.40	9	OK
NO _3	nmol/mol	189.25	1.52	189.61	1.89	9	OK
NO _4	nmol/mol	128.57	1.16	129.40	1.82	9	OK
NO _5	nmol/mol	349.99	2.56	351.66	3.36	9	OK
NO _6	nmol/mol	247.89	1.89	249.77	2.35	9	OK
NO _7	nmol/mol	18.05	0.73	18.16	0.81	9	OK
NO _8	nmol/mol	7.31	0.72	7.44	0.33	9	OK
NO _9	nmol/mol	62.00	0.85	61.79	1.41	9	OK
NO _10	nmol/mol	41.68	0.78	41.74	0.80	9	OK
NO2 _0	nmol/mol	-0.01	0.71	-0.07	0.16	9	OK
NO2 _1	nmol/mol	2.76	2.27	2.58	1.34	9	OK
NO2 _2	nmol/mol	137.50	2.50	136.93	2.49	9	OK
NO2 _3	nmol/mol	0.63	1.03	0.40	0.47	9	OK
NO2 _4	nmol/mol	61.35	1.13	60.63	1.60	9	OK
NO2 _5	nmol/mol	1.26	1.48	0.96	0.80	9	OK
NO2 _6	nmol/mol	103.12	1.68	102.58	2.30	9	OK
NO2 _7	nmol/mol	0.23	0.72	0.13	0.14	9	OK
NO2 _8	nmol/mol	10.93	0.73	10.59	0.37	9	OK
NO2 _9	nmol/mol	0.18	0.78	0.09	0.15	9	OK
NO2 _10	nmol/mol	20.41	0.78	19.86	0.73	9	OK

run	unit	X	uX'	x*	s*	p	val.
CO _0	μmol/mol	0.003	0.008	0.003	0.017	9	OK
CO _1	μmol/mol	2.541	0.017	2.501	0.112	9	OK
CO _2	μmol/mol	8.062	0.048	8.014	0.079	9	OK
CO _3	μmol/mol	4.048	0.025	3.999	0.180	9	OK
CO _4	μmol/mol	5.555	0.034	5.535	0.066	9	OK
CO _5	μmol/mol	0.826	0.009	0.802	0.053	9	OK
O3 _0	nmol/mol	0.19	0.23	0.11	0.11	9	OK
O3 _1	nmol/mol	128.56	0.90	128.92	1.14	9	OK
O3 _2	nmol/mol	59.72	0.43	59.97	0.48	9	OK
O3 _3	nmol/mol	89.80	0.63	90.18	0.84	9	OK
O3 _4	nmol/mol	8.83	0.26	8.72	0.12	9	OK
O3 _5	nmol/mol	20.00	0.26	20.15	0.25	9	OK
SO2 _0	nmol/mol	0.16	0.50	0.06	0.19	9	OK
SO2 _1	nmol/mol	128.40	1.36	128.55	2.78	9	OK
SO2 _2	nmol/mol	4.34	0.51	4.34	0.34	9	OK
SO2 _3	nmol/mol	49.56	0.71	49.72	1.06	9	OK
SO2 _4	nmol/mol	15.39	0.53	15.59	0.77	9	OK
SO2 _5	nmol/mol	8.35	0.51	8.46	0.62	9	OK

Table 10: 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 4.

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.

$$u_{X'}^2 = u_X^2 + \left(X \cdot u_{\mathrm{homogeneity}}\right)^2$$ **Equation 5**

The upper and lower limits of bias due to homogeneity were 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 5 and used in the proficiency evaluations of chapter 2.

Annex B. The results of the IE

In this annex are reported participant's results, presented both in tables and graphs. For all mixture concentration generated (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	A	B	C	D	E	F	G	H	I
xi, 1	-0.03	0.81	0.03	0.10	-0.10	-0.01	0.16	-0.19	0.27
u(xi)	1.26	1.28	0.29	0.43	0.26	0.04	0.50	1.00	0.01
U(xi)	2.55	2.57	0.57	0.86	0.51	0.07	1.01	2.00	0.02

Table 11: Reported values for SO_2 run 0.

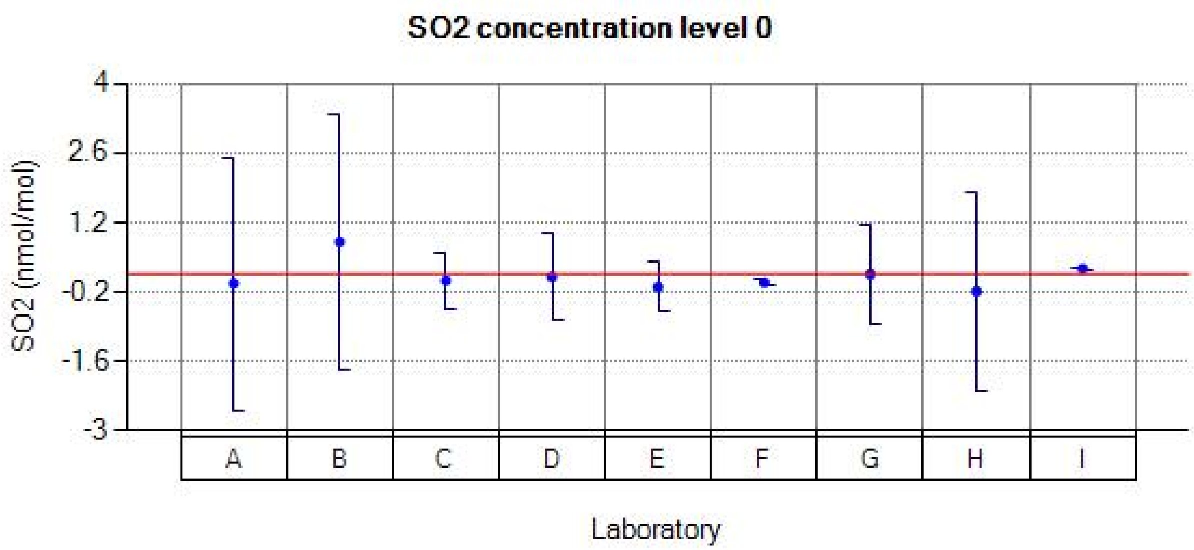

Figure 13: Reported values for SO_2 run 0.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	124.46	131.40	126.08	127.57	126.93	126.54	127.95	133.78	135.71
xi, 2	125.36	133.38	126.36	127.97	127.81	127.14	128.65	134.28	136.63
xi, 3	125.33	131.42	126.62	128.36	127.82	127.31	128.61	134.53	136.59
xi	125.05	132.06	126.35	127.96	127.52	126.99	128.40	134.19	136.31
si	0.51	1.13	0.27	0.39	0.51	0.40	0.39	0.38	0.52
u(xi)	1.97	2.45	1.62	1.28	1.08	1.49	1.36	3.22	2.74
U(xi)	3.93	4.91	3.24	2.56	2.17	2.98	2.72	6.44	5.48

Table 12: Reported values for SO_2 run 1.

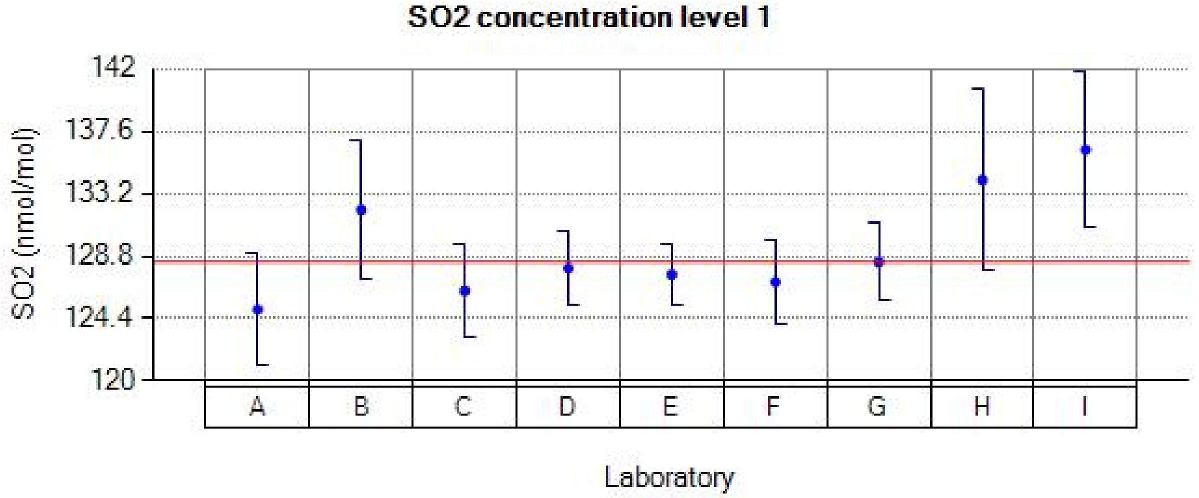

Figure 14: Reported values for SO_2 run 1.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	4.05	4.55	4.25	4.76	3.97	4.20	4.36	4.34	4.65
xi, 2	4.03	4.64	4.18	4.76	3.97	4.14	4.34	4.27	4.63
xi, 3	4.04	4.78	4.11	4.96	3.93	4.15	4.32	4.30	4.57
xi	4.04	4.65	4.18	4.82	3.95	4.16	4.34	4.30	4.61
si	0.01	0.11	0.07	0.11	0.02	0.03	0.02	0.03	0.04
u(xi)	1.26	1.08	0.29	0.43	0.26	0.06	0.51	1.00	0.10
U(xi)	2.55	2.17	0.58	0.86	0.52	0.12	1.01	2.00	0.20

Table 13: Reported values for SO_2 run 2.

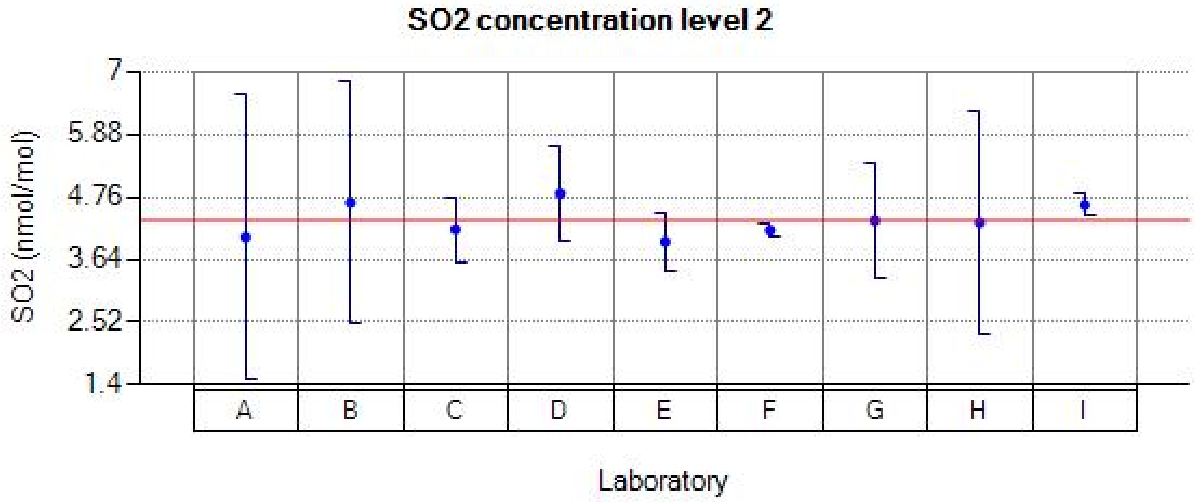

Figure 15: Reported values for SO_2 run 2.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	48.17	52.15	49.00	50.10	49.07	49.02	49.56	51.68	52.65
xi, 2	48.14	52.22	49.00	50.00	49.19	49.08	49.52	51.81	52.80
xi, 3	48.36	52.68	48.97	49.70	49.34	49.10	49.59	51.86	53.19
xi	48.22	52.35	48.99	49.93	49.20	49.06	49.55	51.78	52.88
si	0.11	0.28	0.01	0.20	0.13	0.04	0.03	0.09	0.27
u(xi)	1.26	1.13	0.68	0.49	0.47	0.58	0.71	1.55	1.07
U(xi)	2.55	2.27	1.36	0.98	0.95	1.15	1.41	3.10	2.14

Table 14: Reported values for SO_2 run 3.

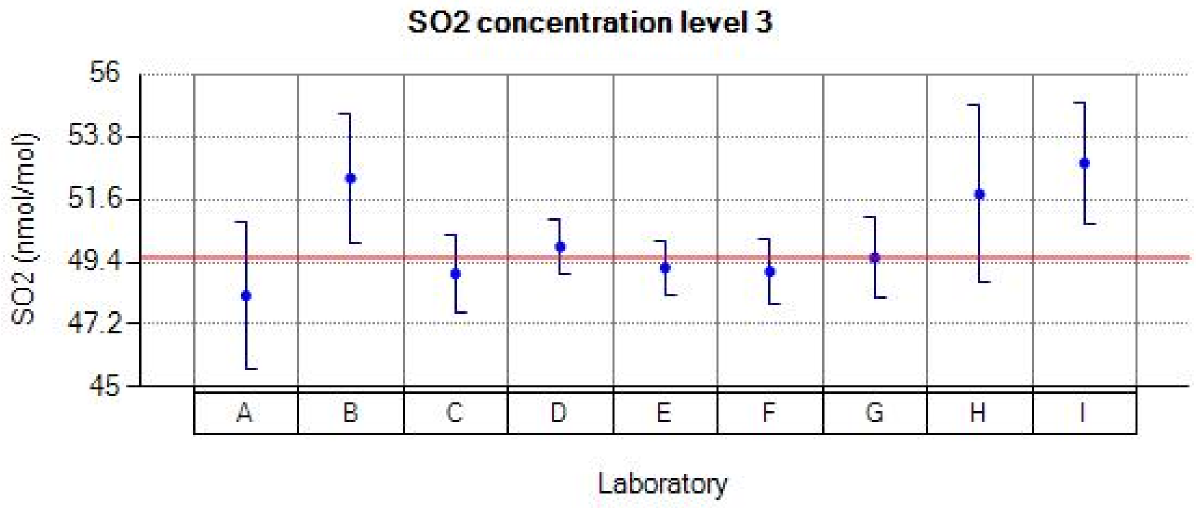

Figure 16: Reported values for SO_2 run 3.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	14.87	18.56	14.99	16.17	15.02	15.08	15.35	15.96	16.47
xi, 2	14.77	18.50	14.98	16.07	14.93	15.11	15.41	15.95	16.51
xi, 3	14.89		15.00	15.97	15.00	15.12	15.41	15.85	16.46
xi	14.84	18.53	14.99	16.07	14.98	15.10	15.39	15.92	16.48
si	0.06	0.04	0.01	0.10	0.04	0.02	0.03	0.06	0.02
u(xi)	1.26	1.00	0.34	0.43	0.28	0.18	0.53	1.06	0.33
U(xi)	2.55	2.00	0.69	0.86	0.52	0.36	1.05	2.12	0.66

Table 15: Reported values for SO_2 run 4.

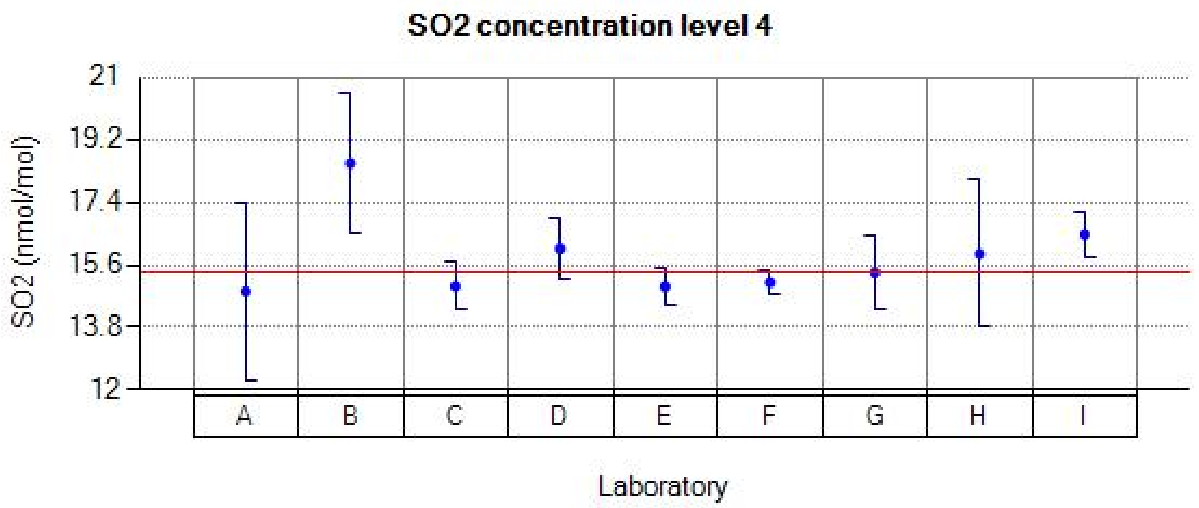

Figure 17: Reported values for SO_2 run 4.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	7.99	8.67	7.92	8.83	7.85	8.11	8.33	8.60	8.99
xi, 2	7.97	9.32	7.88	9.03	7.91	8.15	8.35	8.61	9.11
xi, 3	8.03	10.46	7.89	9.13	7.83	8.09	8.36	8.55	8.84
xi	7.99	9.48	7.89	8.99	7.86	8.11	8.34	8.58	8.98
si	0.03	0.90	0.02	0.15	0.04	0.03	0.01	0.03	0.13
u(xi)	1.26	1.05	0.30	0.43	0.27	0.10	0.51	1.02	0.20
U(xi)	2.55	2.11	0.61	0.86	0.53	0.20	1.02	2.04	0.40

Table 16: Reported values for SO_2 run 5.

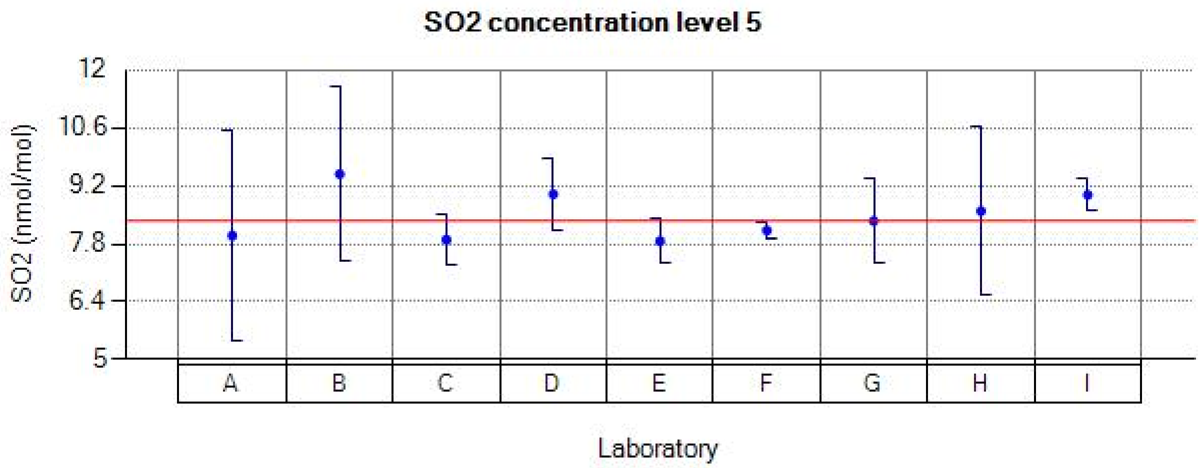

Figure 18: Reported values for SO_2 run 5.

Reported values for CO

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	-0.003	0.019	0.025	0.015	-0.011	0.001	0.003	-0.203	0.004
u(xi)	0.084	0.192	0.090	0.049	0.025	0.006	0.008	0.224	0.000
U(xi)	0.168	0.383	0.180	0.098	0.051	0.012	0.016	0.448	0.000

Table 17: Reported values for CO run 0.

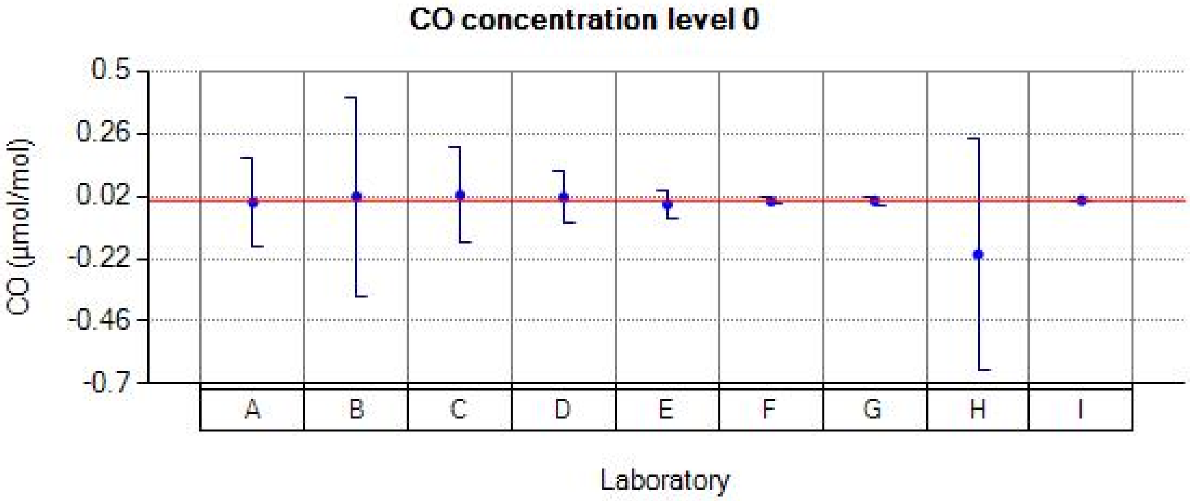

Figure 19: Reported values for CO run 0.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	2.309	2.288	2.576	2.705	2.473	2.524	2.539	2.556	2.301
xi, 2	2.309	2.286	2.590	2.705	2.464	2.526	2.541	2.545	2.306
xi, 3	2.209	2.289	2.598	2.703	2.469	2.527	2.542	2.558	2.307
xi	2.276	2.288	2.588	2.704	2.469	2.526	2.541	2.553	2.305
si	0.058	0.002	0.011	0.001	0.005	0.002	0.002	0.007	0.003
u(xi)	0.084	0.161	0.100	0.055	0.036	0.014	0.017	0.231	0.061
U(xi)	0.168	0.322	0.190	0.110	0.073	0.028	0.034	0.462	0.122

Table 18: Reported values for CO run 1.

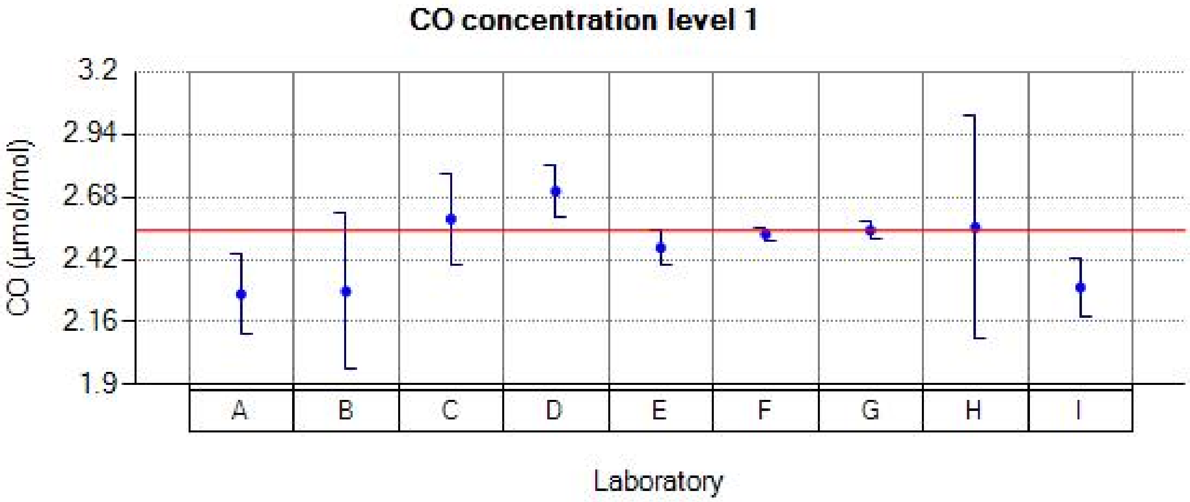

Figure 20: Reported values for CO run 1.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	7.786	7.858	8.117	8.007	8.018	8.023	8.063	8.014	8.063
xi, 2	7.803	7.875	8.125	8.004	8.011	8.025	8.063	8.016	8.061
xi, 3	7.786	7.859	8.131	8.005	8.015	8.023	8.061	8.009	8.066
xi	7.792	7.864	8.124	8.005	8.015	8.024	8.062	8.013	8.063
si	0.010	0.010	0.007	0.002	0.004	0.001	0.001	0.004	0.003
u(xi)	0.084	0.178	0.150	0.163	0.060	0.041	0.048	0.289	0.214
U(xi)	0.168	0.357	0.290	0.326	0.121	0.082	0.096	0.578	0.428

Table 19: Reported values for CO run 2.

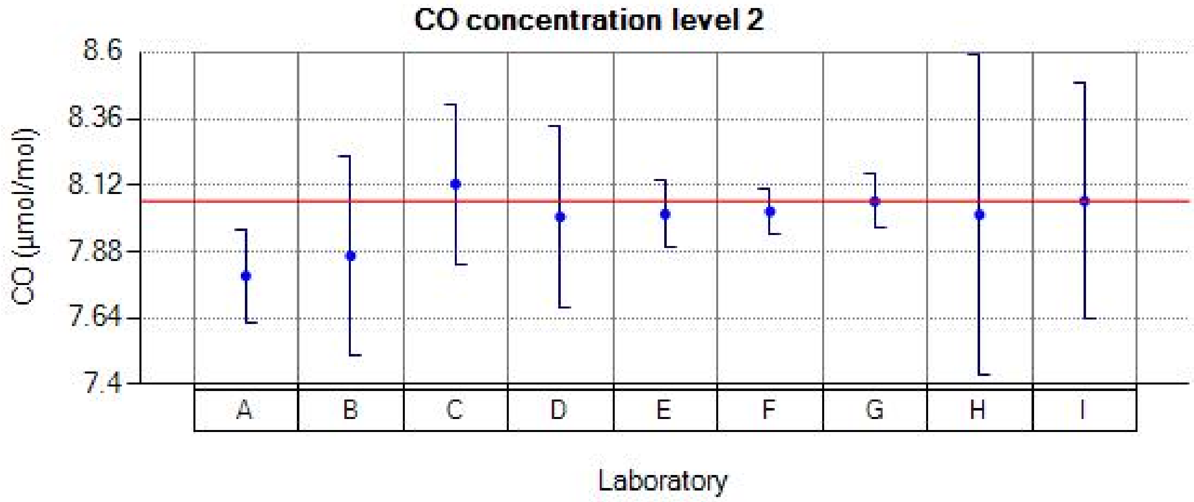

Figure 21: Reported values for CO run 2.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	3.716	3.830	4.249	4.163	3.976	4.032	4.047	4.047	3.890
xi, 2	3.716	3.825	4.254	4.161	3.976	4.034	4.049	4.049	3.897
xi, 3	3.716	3.825	4.258	4.163	3.977	4.035	4.048	4.057	3.888
xi	3.716	3.827	4.254	4.162	3.976	4.034	4.048	4.051	3.892
si	0.000	0.003	0.005	0.001	0.001	0.002	0.001	0.005	0.005
u(xi)	0.084	0.151	0.110	0.085	0.037	0.021	0.025	0.242	0.103
U(xi)	0.168	0.303	0.210	0.170	0.075	0.043	0.050	2.484	0.206

Table 20: Reported values for CO run 3.

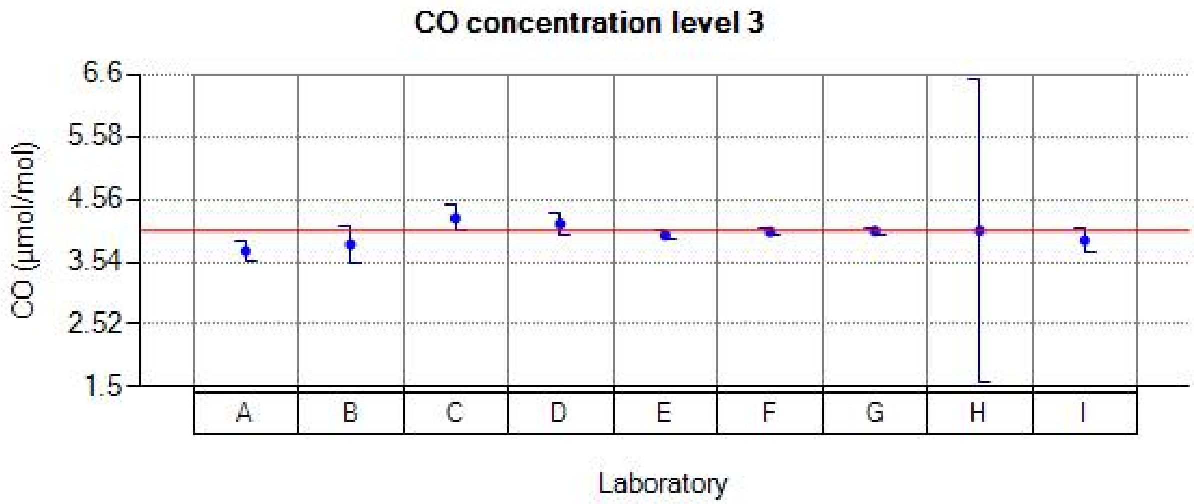

Figure 22: Reported values for CO run 3.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	5.273	5.387	5.765	5.603	5.535	5.538	5.556	5.551	5.501
xi, 2	5.273	5.383	5.767	5.606	5.531	5.539	5.556	5.558	5.502
xi, 3	5.273	5.393	5.772	5.603	5.529	5.539	5.552	5.543	5.499
xi	5.273	5.388	5.768	5.604	5.532	5.539	5.555	5.551	5.501
si	0.000	0.005	0.004	0.002	0.003	0.001	0.002	0.008	0.002
u(xi)	0.084	0.153	0.120	0.114	0.045	0.029	0.034	0.257	0.146
U(xi)	0.168	0.306	0.240	0.228	0.091	0.057	0.068	0.514	0.292

Table 21: Reported values for CO run 4.

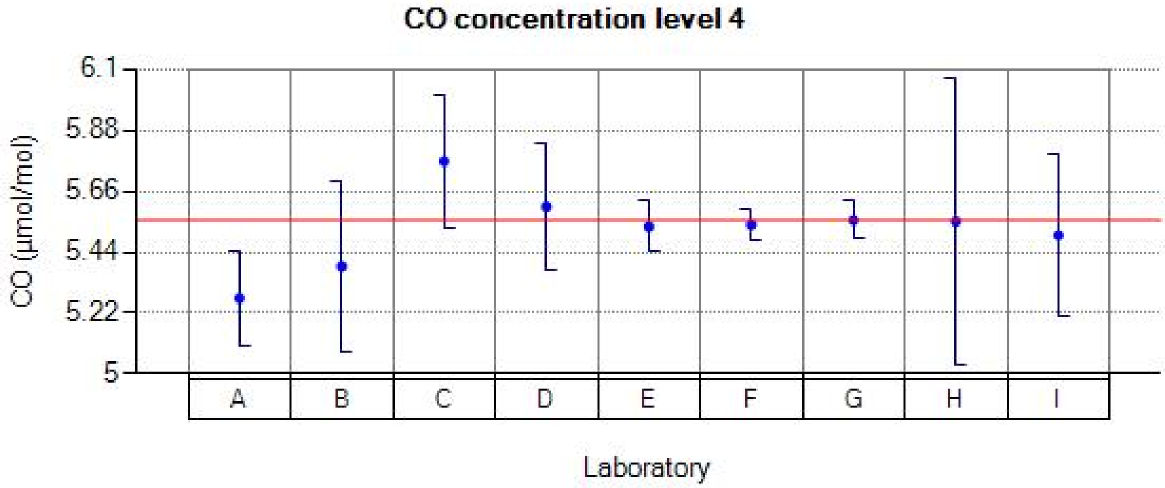

Figure 23: Reported values for CO run 4.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	0.801	0.778	1.041	0.904	0.768	0.823	0.826	0.727	0.751
xi, 2	0.801	0.770	1.045	0.902	0.772	0.823	0.826	0.712	0.752
xi, 3	0.801	0.770	1.045	0.903	0.775	0.823	0.826	0.722	0.752
xi	0.801	0.773	1.044	0.903	0.772	0.823	0.826	0.720	0.752
si	0.000	0.005	0.002	0.001	0.004	0.000	0.000	0.008	0.001
u(xi)	0.084	0.180	0.090	0.049	0.026	0.007	0.009	0.224	0.020
U(xi)	0.168	0.360	0.180	0.098	0.052	0.014	0.019	0.448	0.040

Table 22: Reported values for CO run 5.

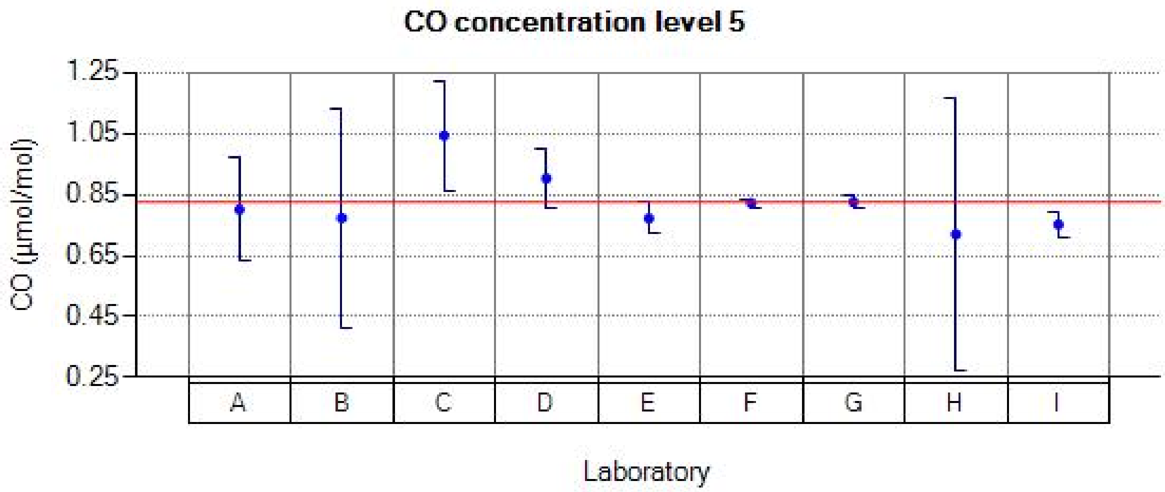

Figure 24: Reported values for CO run 5.

Reported values for O_3

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	0.03	-0.10	0.07	1.10	0.18	0.10	0.19	0.07	0.14
u(xi)	0.91	1.68	0.08	0.60	0.20	0.37	0.23	0.71	0.60
U(xi)	1.81	3.37	0.15	1.20	0.39	0.74	0.46	1.42	1.20

Table 23: Reported values for O_3 run 0.

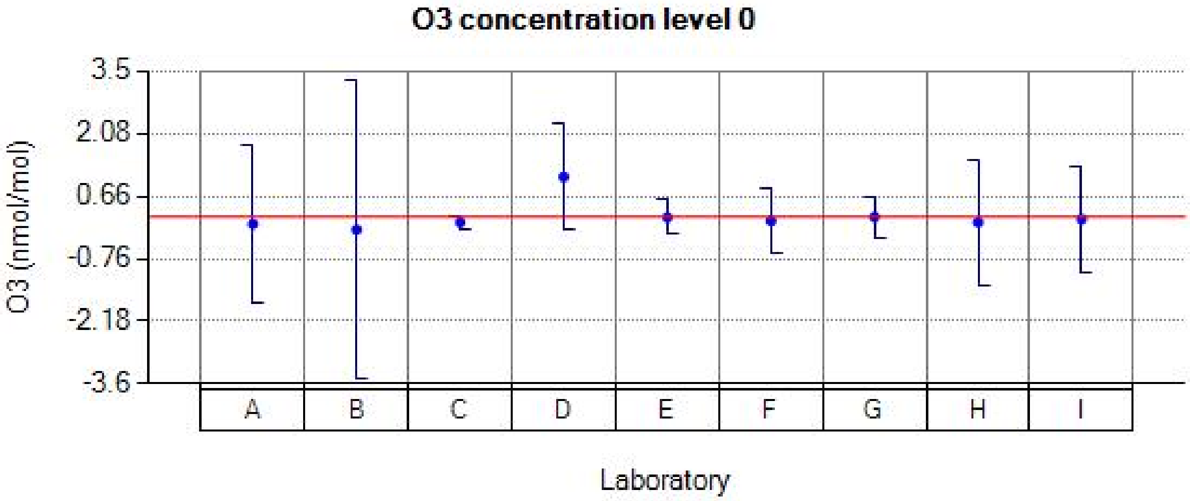

Figure 25: Reported values for O_3 run 0.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	129.70	129.39	129.97	128.10	127.97	127.00	128.41	129.27	128.21
xi, 2	129.96	129.90	130.16	128.20	128.14	127.30	128.61	129.98	128.52
xi, 3	129.99	130.16	130.17	128.40	128.30	127.50	128.67	130.14	128.77
xi	129.88	129.81	130.10	128.23	128.13	127.26	128.56	129.79	128.50
si	0.15	0.39	0.11	0.15	0.16	0.25	0.13	0.46	0.28
u(xi)	2.03	2.04	2.18	2.55	1.52	0.66	0.90	2.69	2.15
U(xi)	4.06	4.07	4.36	5.10	3.03	1.32	1.79	5.38	4.30

Table 24: Reported values for O_3 run 1

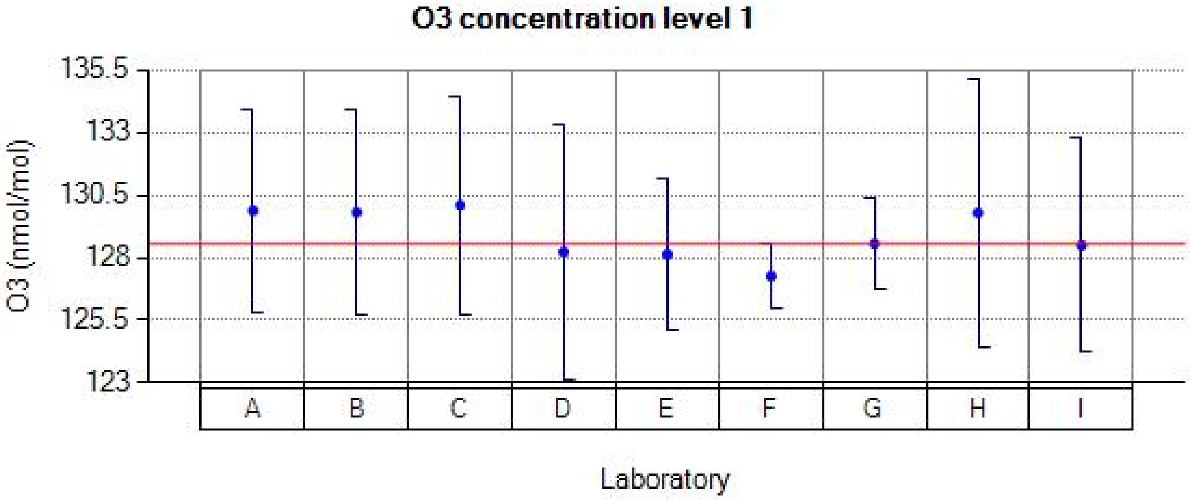

Figure 26: Reported values for O_3 run 1.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	60.41	60.40	60.52	59.80	59.91	59.20	59.82	60.44	59.95
xi, 2	60.33	60.46	60.37	59.70	59.79	59.10	59.72	60.53	59.78
xi, 3	60.22	60.30	60.24	59.70	59.71	59.00	59.62	60.42	59.34
xi	60.32	60.38	60.37	59.73	59.80	59.10	59.72	60.46	59.69
si	0.09	0.08	0.14	0.05	0.10	0.10	0.10	0.05	0.31
u(xi)	1.21	1.57	1.01	1.19	0.73	0.45	0.43	1.40	1.33
U(xi)	2.41	3.15	2.03	2.38	1.46	0.90	0.86	2.80	2.66

Table 25: Reported values for O_3 run 2.

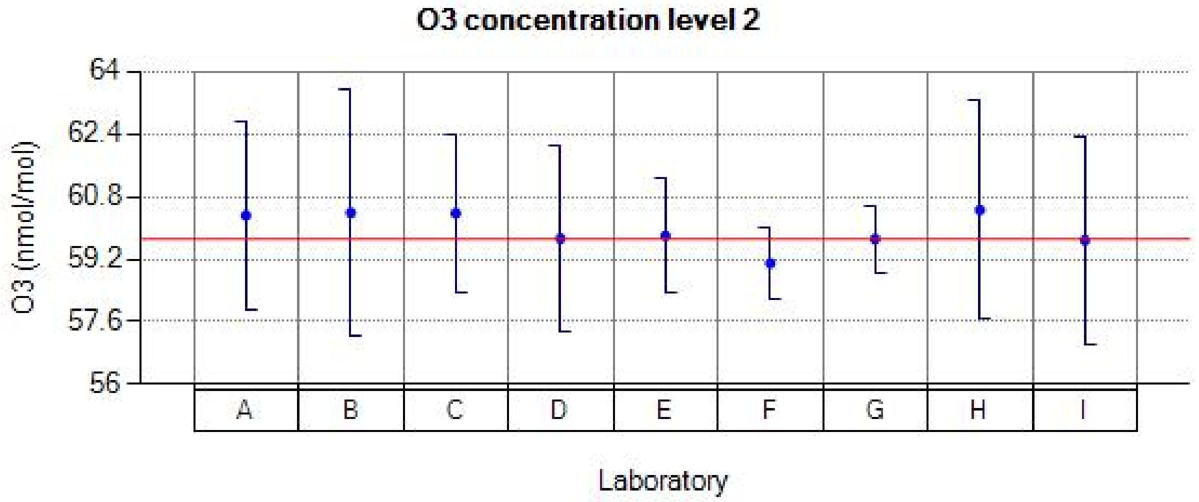

Figure 27: Reported values for O_3 run 2.

values	A	B	C	D	E	F	G	H	I
	laboratories								
xi, 1	90.63	90.80	90.98	89.60	89.49	88.80	89.72	90.70	89.88
xi, 2	90.78	90.94	91.02	89.70	89.62	89.00	89.85	90.85	90.14
xi, 3	90.83	91.12	91.04	89.70	89.63	89.10	89.84	91.03	90.00
xi	90.74	90.95	91.01	89.66	89.58	88.96	89.80	90.86	90.00
si	0.10	0.16	0.03	0.05	0.07	0.15	0.07	0.16	0.13
u(xi)	1.81	1.71	1.53	1.78	1.07	0.53	0.63	1.95	1.68
U(xi)	3.63	3.41	3.05	3.56	2.15	1.06	1.25	3.90	3.36

Table 26: Reported values for O_3 run 3.

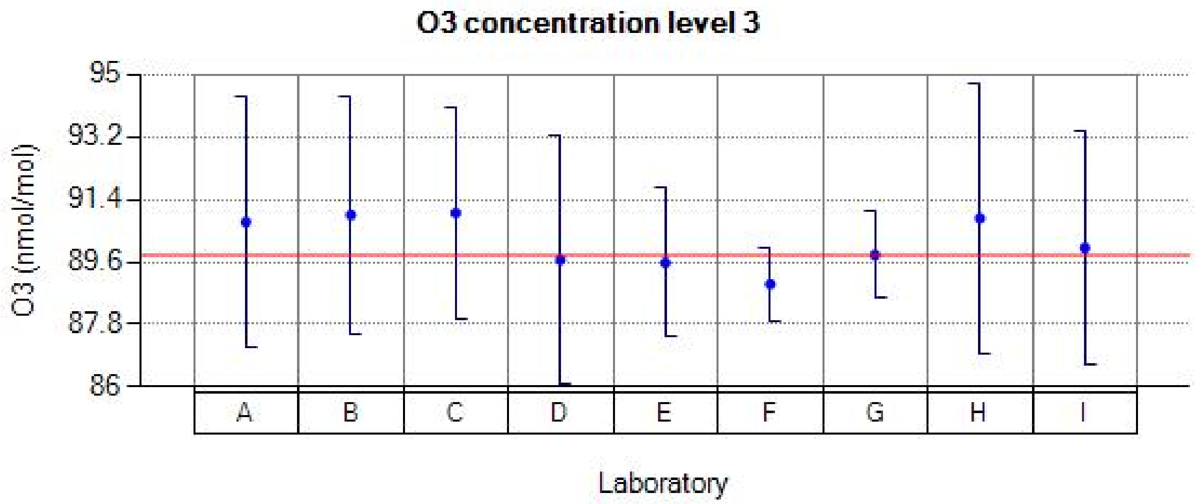

Figure 28: Reported values for O_3 run 3.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	8.63	8.66	8.67	9.10	8.84	8.50	8.79	8.65	8.61
xi, 2	8.71	8.80	8.70	9.10	8.85	8.50	8.82	8.78	8.63
xi, 3	8.69	8.67	8.70	9.30	8.76	8.50	8.88	8.78	8.65
xi	8.67	8.71	8.69	9.16	8.81	8.50	8.83	8.73	8.63
si	0.04	0.07	0.01	0.11	0.04	0.00	0.04	0.07	0.02
u(xi)	0.91	1.63	0.16	0.60	0.22	0.37	0.26	0.73	0.70
U(xi)	1.81	3.26	0.33	1.20	0.44	0.75	0.51	1.46	1.40

Table 27: Reported values for O_3 run 4.

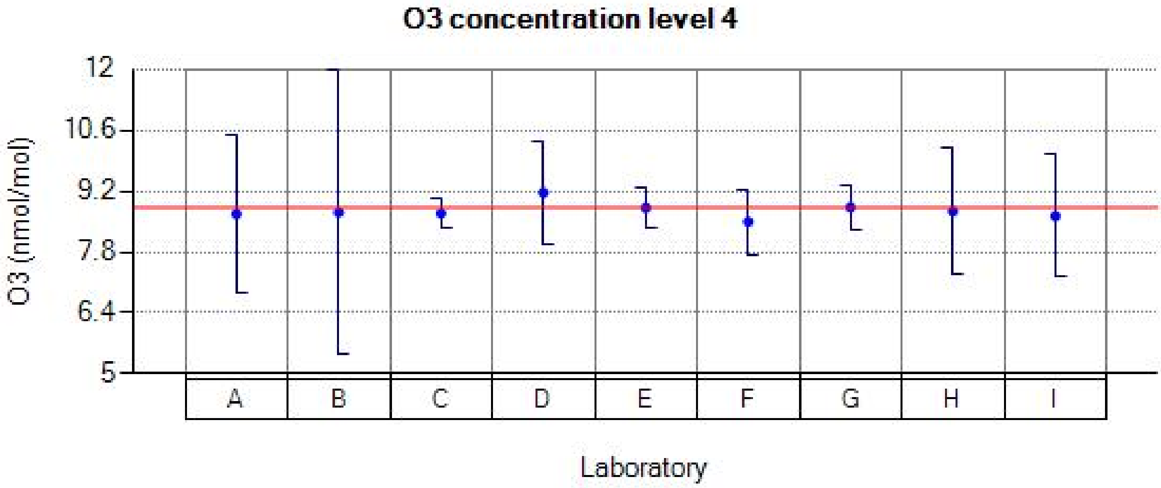

Figure 29: Reported values for O_3 run 4.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	20.25	20.24	20.10	20.90	20.39	19.80	19.98	20.26	20.06
xi, 2	20.36	20.42	20.03	21.00	20.46	19.80	20.05	20.21	20.00
xi, 3	20.25	20.00	20.05	20.90	20.23	19.70	19.97	20.02	19.86
xi	20.28	20.22	20.06	20.93	20.36	19.76	20.00	20.16	19.97
si	0.06	0.21	0.03	0.05	0.11	0.05	0.04	0.12	0.10
u(xi)	0.91	1.59	0.34	0.60	0.31	0.38	0.26	0.81	0.84
U(xi)	1.81	3.18	0.69	1.20	0.61	0.76	0.52	1.62	1.68

Table 28: Reported values for O_3 run 5.

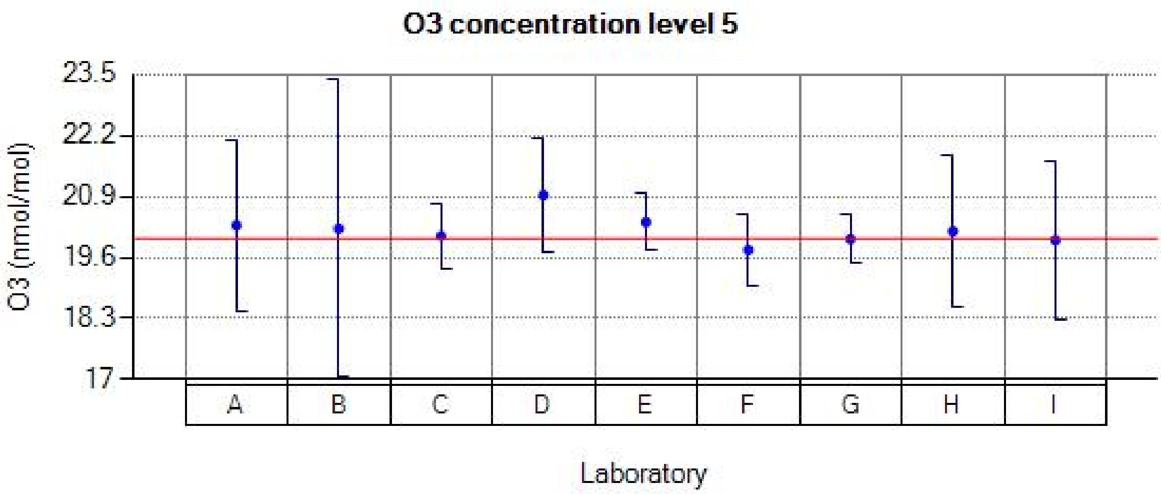

Figure 30: Reported values for O_3 run 5.

Reported values for NO

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	0.02	-0.31	-0.11	0.31	-0.04	0.00	-0.09	0.12	0.57
u(xi)	1.25	1.13	0.29	0.49	0.07	0.17	0.72	1.00	0.02
U(xi)	2.51	2.27	0.57	0.98	0.14	0.34	1.43	2.00	0.04

Table 29: Reported values for NO run 0.

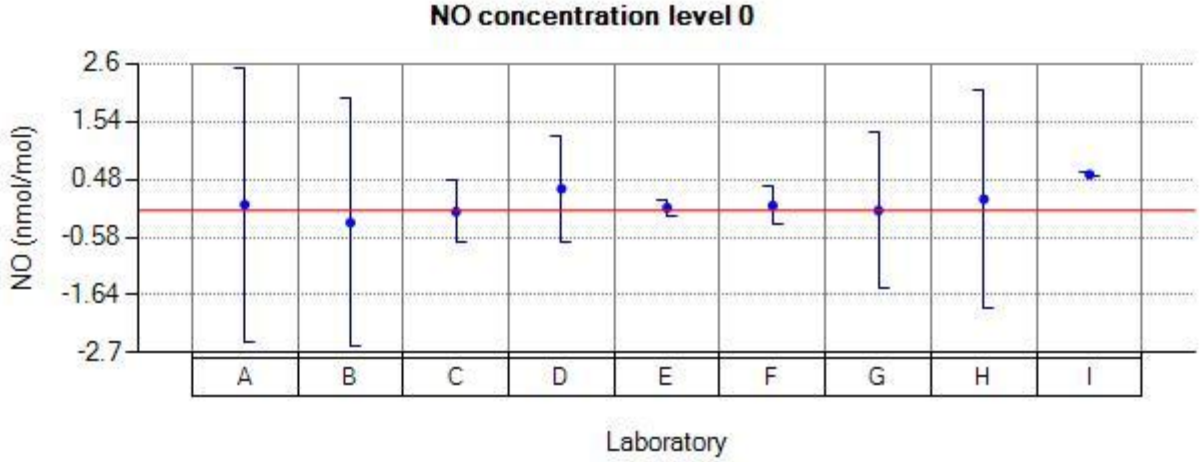

Figure 31: Reported values for NO run 0.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	587.27	607.29	601.29	601.96	602.08	598.17	598.63	614.33	606.14
xi, 2	588.14	608.11	601.84	603.30	603.53	598.76	598.87	613.53	607.00
xi, 3	589.43	607.86	602.40	603.61	604.69	599.16	598.81	613.22	606.92
xi	588.28	607.75	601.84	602.95	603.43	598.69	598.77	613.69	606.68
si	1.08	0.42	0.55	0.87	1.30	0.49	0.12	0.57	0.47
u(xi)	6.09	9.15	7.46	12.60	6.87	6.71	4.25	14.03	7.89
U(xi)	12.18	18.30	14.91	25.20	13.74	13.42	8.50	28.06	15.78

Table 30: Reported values for NO run 1.

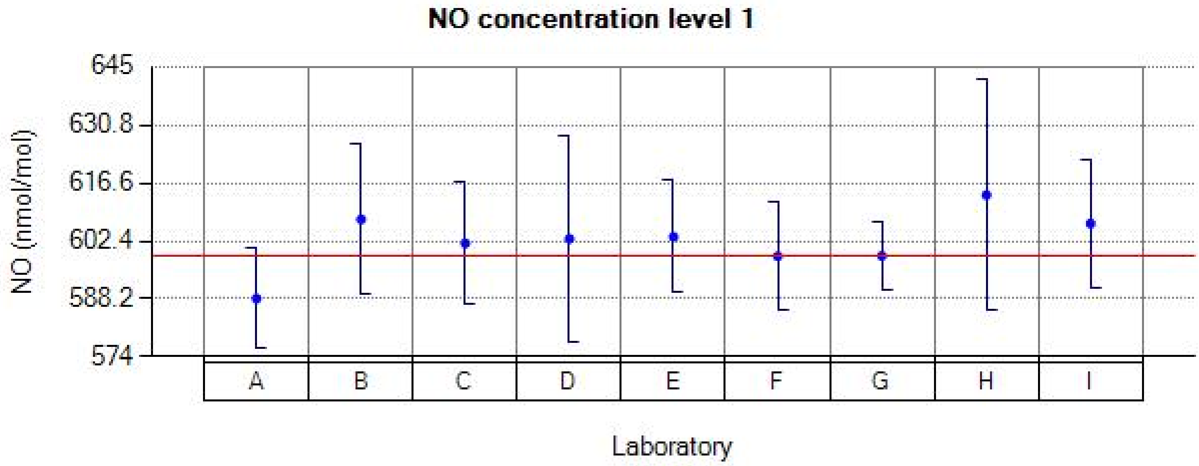

Figure 32: Reported values for NO run 1.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	456.41	471.80	468.08	469.22	468.39	467.71	464.14	480.25	469.36
xi, 2	456.55	472.62	467.77	469.63	468.27	464.61	464.30	479.42	469.38
xi, 3	456.60	472.53	467.32	469.63	468.61	464.61	463.97	479.87	470.04
xi	456.52	472.31	467.72	469.49	468.42	465.64	464.13	479.84	469.59
si	0.09	0.45	0.38	0.23	0.17	1.79	0.16	0.41	0.38
u(xi)	4.73	7.11	5.80	9.81	5.33	5.21	3.34	14.04	6.11
U(xi)	9.45	14.21	11.60	19.62	10.67	10.41	6.68	28.08	12.22

Table 31: Reported values for NO run 2.

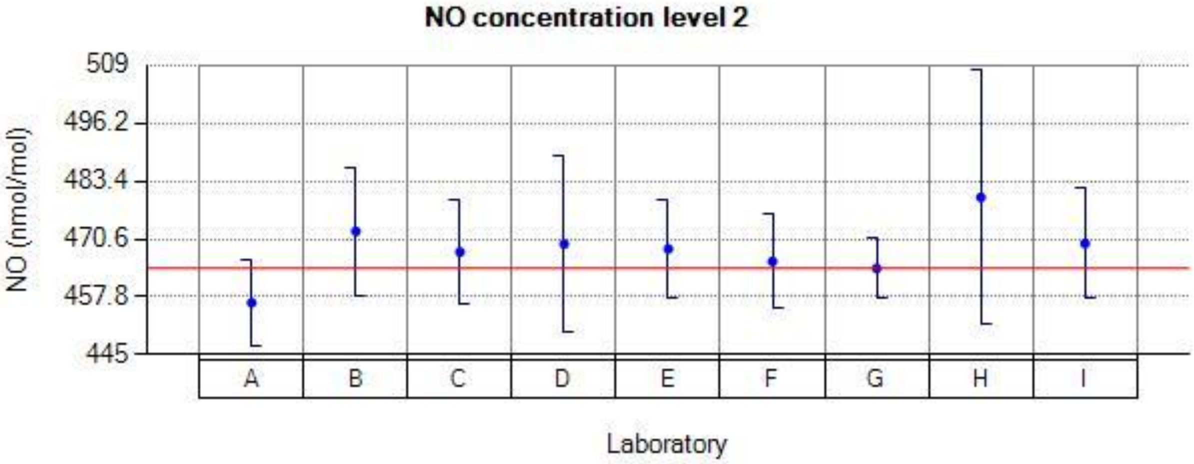

Figure 33: Reported values for NO run 2.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	184.63	188.39	188.88	189.54	191.98	188.07	189.11	193.95	193.32
xi, 2	184.94	188.97	189.16	189.64	192.31	188.17	189.23	194.09	193.32
xi, 3	185.06	188.78	189.17	189.64	192.55	188.36	189.41	193.57	193.52
xi	184.87	188.71	189.07	189.60	192.28	188.20	189.25	193.87	193.38
si	0.22	0.29	0.16	0.05	0.28	0.14	0.15	0.26	0.11
u(xi)	1.91	2.92	2.36	3.96	2.19	2.11	1.52	4.53	2.52
U(xi)	3.83	5.84	4.72	7.92	4.38	4.23	3.04	9.06	5.04

Table 32: Reported values for NO run 3.

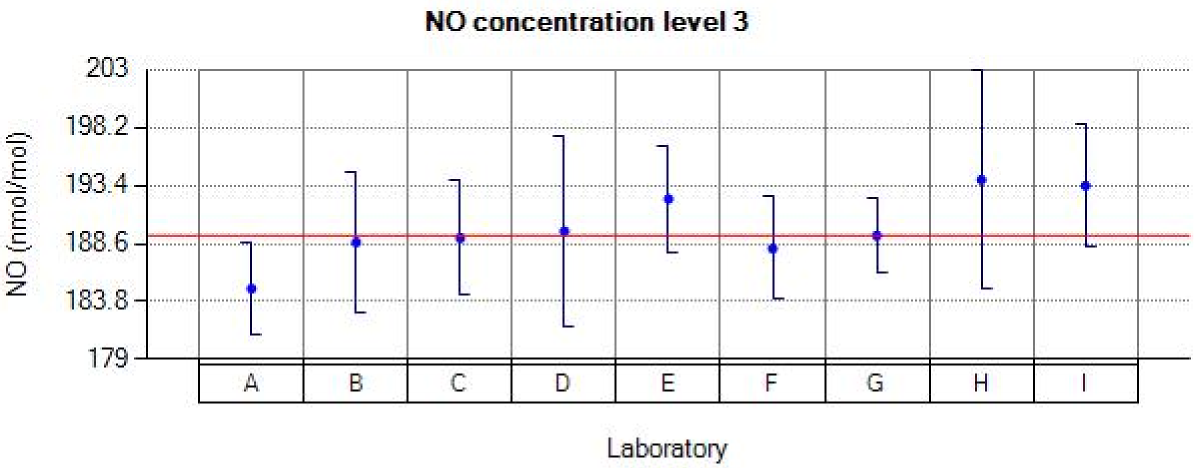

Figure 34: Reported values for NO run 3.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	125.67	128.97	129.09	129.65	130.72	128.12	128.67	133.64	131.68
xi, 2	125.44	129.25	128.88	129.55	130.58	128.12	128.55	133.35	131.57
xi, 3	125.34	129.18	128.68	129.45	130.46	127.92	128.49	133.35	131.36
xi	125.48	129.13	128.88	129.55	130.58	128.05	128.57	133.44	131.53
si	0.16	0.14	0.20	0.10	0.13	0.11	0.09	0.16	0.16
u(xi)	1.30	2.11	1.62	2.71	1.40	1.44	1.16	3.21	1.71
U(xi)	2.60	4.22	3.24	5.42	2.81	2.89	2.32	6.42	3.42

Table 33: Reported values for NO run 4.

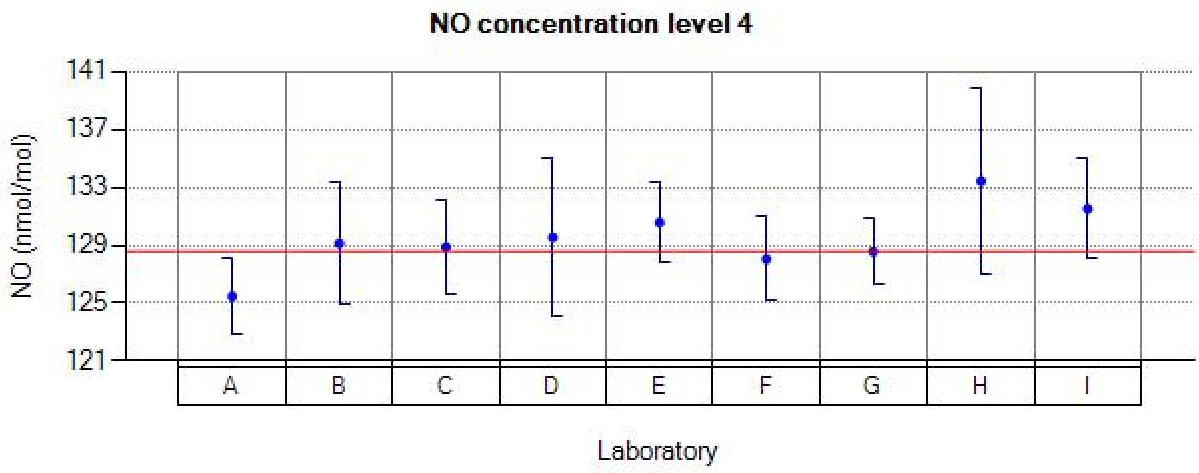

Figure 35: Reported values for NO run 4.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	343.17	351.19	349.54	351.30	353.63	349.39	349.89	357.93	354.94
xi, 2	343.09	351.70	350.13	351.81	353.92	349.59	349.99	358.00	355.14
xi, 3	343.44	352.78	350.30	351.71	353.70	349.49	350.09	358.54	355.01
xi	343.23	351.89	349.99	351.60	353.75	349.49	349.99	358.15	355.03
si	0.18	0.81	0.39	0.27	0.15	0.10	0.10	0.33	0.10
u(xi)	3.55	5.31	4.34	7.34	4.03	3.92	2.56	8.23	4.62
U(xi)	7.11	10.60	8.69	14.68	8.07	7.84	5.12	16.46	9.24

Table 34: Reported values for NO run 5.

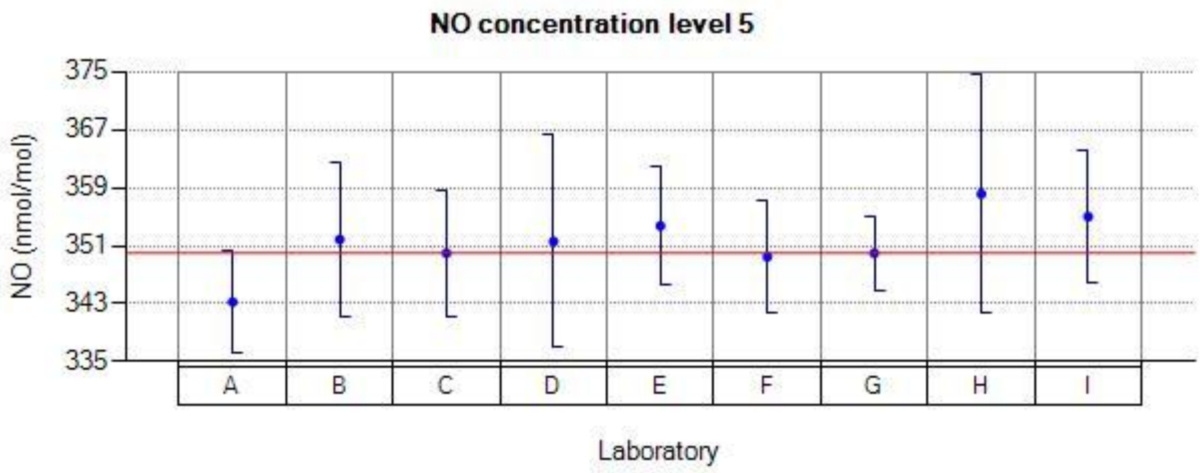

Figure 36: Reported values for NO run 5.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	242.56	250.44	248.90	250.15	250.51	247.92	247.89	256.33	251.98
xi, 2	242.64	250.33	248.75	250.46	250.55	248.02	247.86	256.41	251.59
xi, 3	242.74	250.32	248.67	250.66	250.68	248.02	247.92	256.66	251.81
xi	242.64	250.36	248.77	250.42	250.58	247.98	247.89	256.46	251.79
si	0.09	0.06	0.11	0.25	0.08	0.05	0.03	0.17	0.19
u(xi)	2.51	3.81	3.09	5.23	2.86	2.78	1.89	5.93	3.28
U(xi)	5.03	7.61	6.19	10.46	5.72	5.57	3.79	11.86	6.56

Table 35: Reported values for NO run 6.

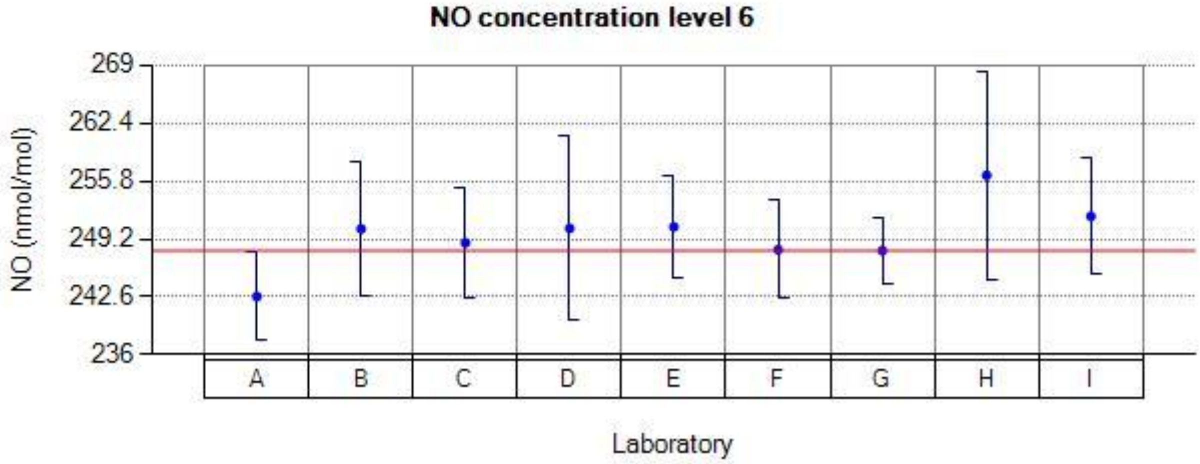

Figure 37: Reported values for NO run 6.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	17.48	17.39	17.48	17.90	18.38	17.94	18.02	19.10	19.56
xi, 2	17.51	17.39	17.42	18.32	18.42	17.94	18.08	19.38	19.57
xi, 3	17.51	17.50	17.48	18.11	18.47	17.94	18.05	19.37	19.70
xi	17.50	17.42	17.46	18.11	18.42	17.94	18.05	19.28	19.61
si	0.01	0.06	0.03	0.21	0.04	0.00	0.03	0.15	0.07
u(xi)	1.25	1.12	0.36	0.49	0.22	0.26	0.73	1.09	0.26
U(xi)	2.51	2.24	0.72	0.98	0.43	0.53	1.46	2.18	0.52

Table 36: Reported values for NO run 7.

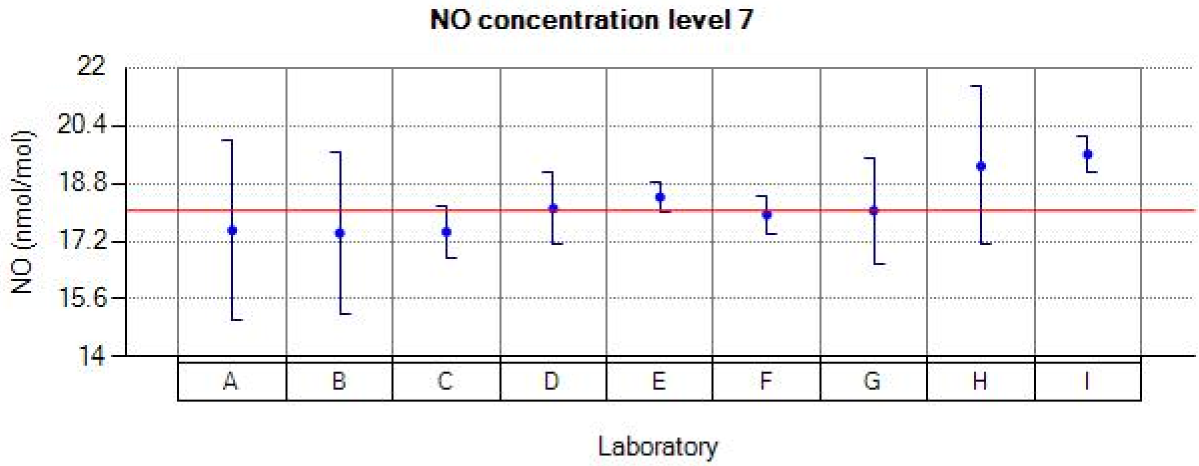

Figure 38: Reported values for NO run 7.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	7.19	7.33	7.00	7.92	7.56	7.33	7.33	8.53	8.81
xi, 2	7.14	7.41	7.02	7.82	7.53	7.33	7.34	8.83	8.69
xi, 3	7.13	7.26	6.94	7.72	7.50	7.33	7.26	8.78	8.84
xi	7.15	7.33	6.98	7.82	7.53	7.33	7.31	8.71	8.78
si	0.03	0.07	0.04	0.10	0.03	0.00	0.04	0.16	0.07
u(xi)	1.25	1.12	0.30	0.49	0.12	0.19	0.72	1.02	0.12
U(xi)	2.51	2.24	0.60	0.98	0.23	0.38	1.43	2.04	0.24

Table 37: Reported values for NO run 8.

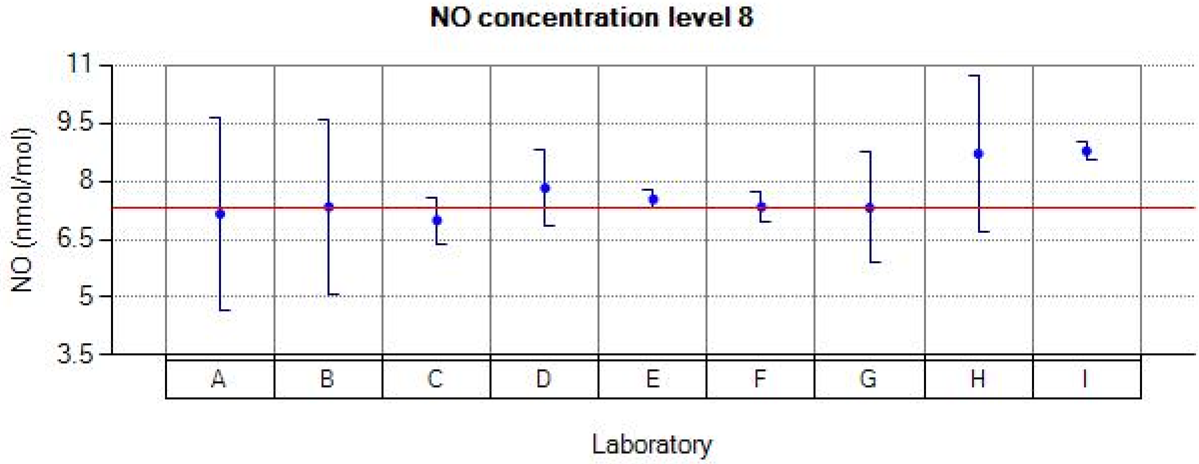

Figure 39: Reported values for NO run 8.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	59.74	60.90	60.61	61.43	62.42	61.54	62.01	63.78	63.37
xi, 2	59.83	61.18	60.75	61.64	62.52	61.54	61.98	63.80	63.91
xi, 3	59.83	60.86	60.74	61.64	62.59	61.44	62.01	63.48	64.09
xi	59.80	60.98	60.70	61.57	62.51	61.50	62.00	63.68	63.79
si	0.05	0.17	0.07	0.12	0.08	0.05	0.01	0.17	0.37
u(xi)	1.25	1.34	0.81	1.29	0.72	0.71	0.85	1.76	0.84
U(xi)	2.51	2.69	1.62	2.58	1.44	1.42	1.69	3.53	1.68

Table 38: Reported values for NO run 9.

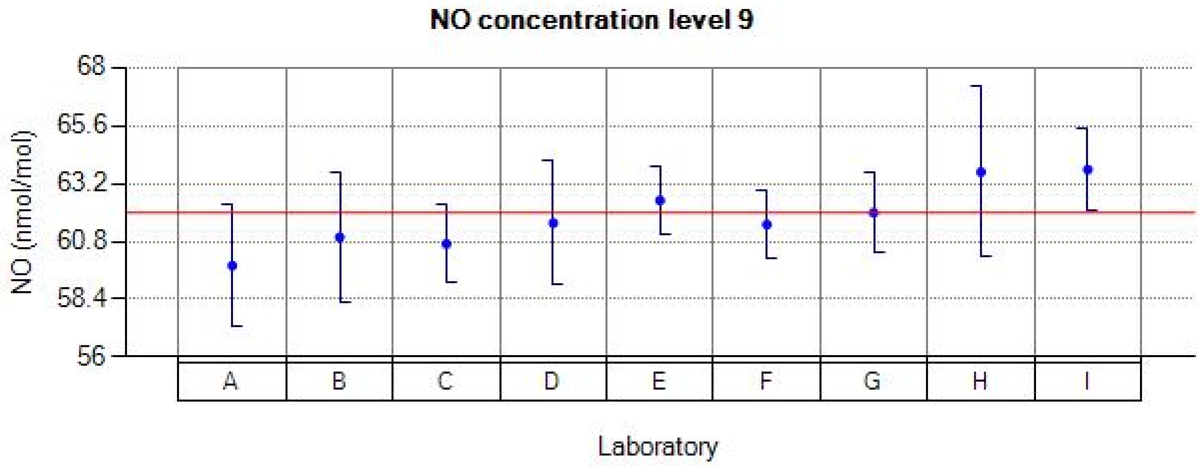

Figure 40: Reported values for NO run 9.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	40.41	41.60	40.96	41.98	42.08	41.32	41.71	44.13	43.40
xi, 2	40.37	41.40	40.88	42.19	42.08	41.52	41.69	43.80	43.52
xi, 3	40.37	41.31	40.85	42.19	42.04	41.42	41.64	44.24	43.37
xi	40.38	41.43	40.89	42.12	42.06	41.42	41.68	44.05	43.43
si	0.02	0.14	0.05	0.12	0.02	0.10	0.03	0.22	0.07
u(xi)	1.25	1.21	0.58	0.88	0.48	0.49	0.78	1.42	0.57
U(xi)	2.51	2.41	1.16	1.76	0.97	0.99	1.56	2.84	1.14

Table 39: Reported values for NO run 10.

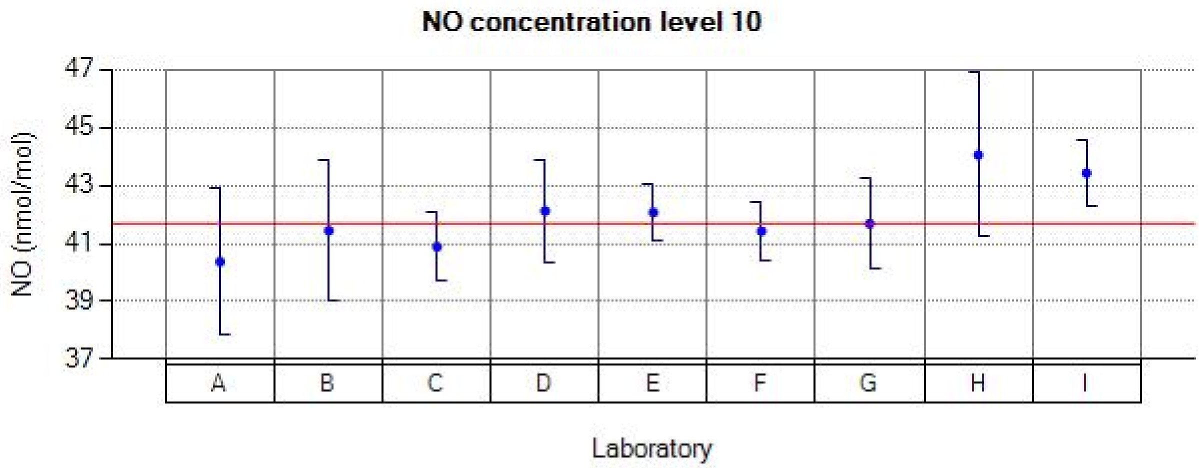

Figure 41: Reported values for NO run 10.

Reported values for NO_2

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	-0.02	-0.34	-0.01	0.10	-0.15	-0.09	-0.01	0.12	-0.25
u(xi)	1.25	1.13	0.29	0.49	0.26	0.24	0.71	1.00	0.01
U(xi)	2.51	2.27	0.57	0.98	0.52	0.48	1.42	2.00	0.02

Table 40: Reported values for NO_2 run 0.

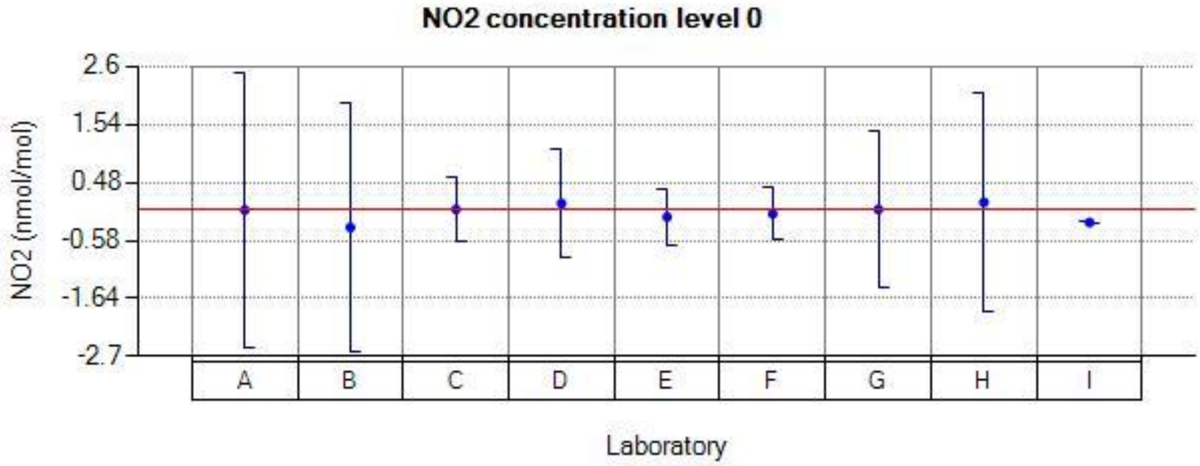

Figure 42: Reported values for NO_2 run 0.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	136.35	135.17	134.59	136.98	139.32	141.51	137.87	133.34	140.78
xi, 2	136.28	135.05	134.70	136.05	139.33	141.41	137.32	134.60	140.52
xi, 3	136.26	134.72	135.07	135.54	139.23	141.21	137.31	134.13	140.71
xi	136.29	134.98	134.78	136.19	139.29	141.37	137.50	134.02	140.67
si	0.04	0.23	0.25	0.73	0.05	0.15	0.32	0.63	0.13
u(xi)	1.42	1.67	3.83	2.77	4.12	2.25	2.50	3.22	2.96
U(xi)	2.83	3.34	7.66	5.54	8.23	4.51	5.00	6.44	5.91

Table 41: Reported values for NO_2 run 2.

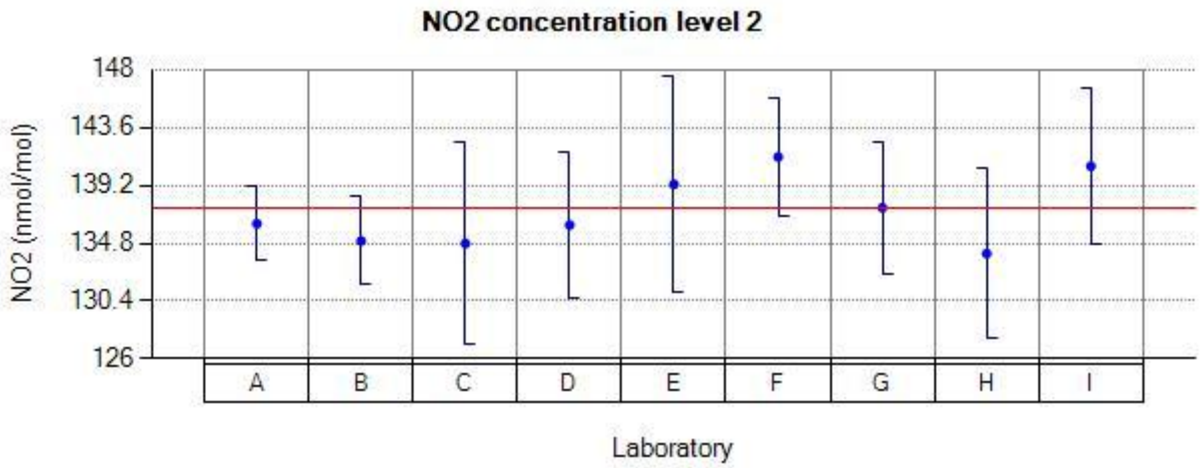

Figure 43: Reported values for NO_2 run 2.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	59.78	58.78	59.24	59.85	62.15	62.20	61.30	59.53	62.29
xi, 2	59.76	58.17	59.50	60.16	62.11	62.20	61.34	60.17	62.28
xi, 3	59.69	58.48	59.48	59.85	62.23	62.20	61.41	60.42	62.34
xi	59.74	58.47	59.40	59.95	62.16	62.20	61.35	60.04	62.30
si	0.04	0.30	0.14	0.17	0.06	0.00	0.05	0.45	0.03
u(xi)	1.25	1.04	1.71	1.22	1.70	1.01	1.13	1.40	1.31
U(xi)	2.51	2.09	3.42	2.44	3.40	2.03	2.26	2.80	2.62

Table 42: Reported values for NO_2 run 4.

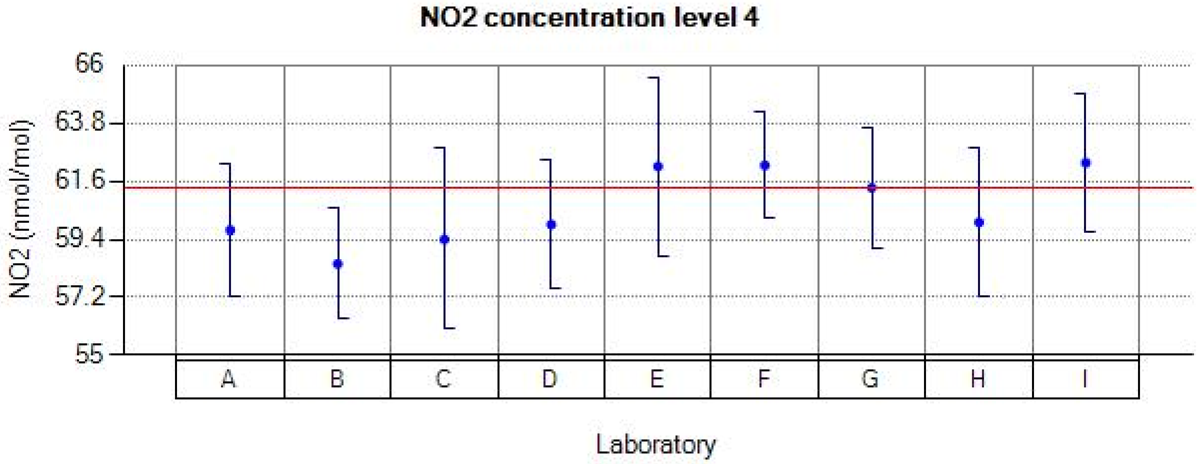

Figure 44: Reported values for NO_2 run 4.

	laboratories								
values	A	B	C	D	E	F	G	H	I
xi, 1	101.48	100.36	99.76	102.53	104.36	105.42	103.28	101.88	105.10
xi, 2	101.45	100.36	99.79	101.60	104.32	105.22	103.12	101.67	105.37
xi, 3	101.23	100.37	99.72	101.50	104.37	105.12	102.97	102.13	105.16
xi	101.38	100.36	99.75	101.87	104.35	105.25	103.12	101.89	105.21
si	0.13	0.00	0.03	0.56	0.02	0.15	0.15	0.23	0.14
u(xi)	1.25	1.25	2.84	2.07	2.77	1.68	1.68	2.53	2.21
U(xi)	2.51	2.50	5.68	4.14	5.54	3.37	3.37	5.06	4.42

Table 43: Reported values for NO_2 run 6.

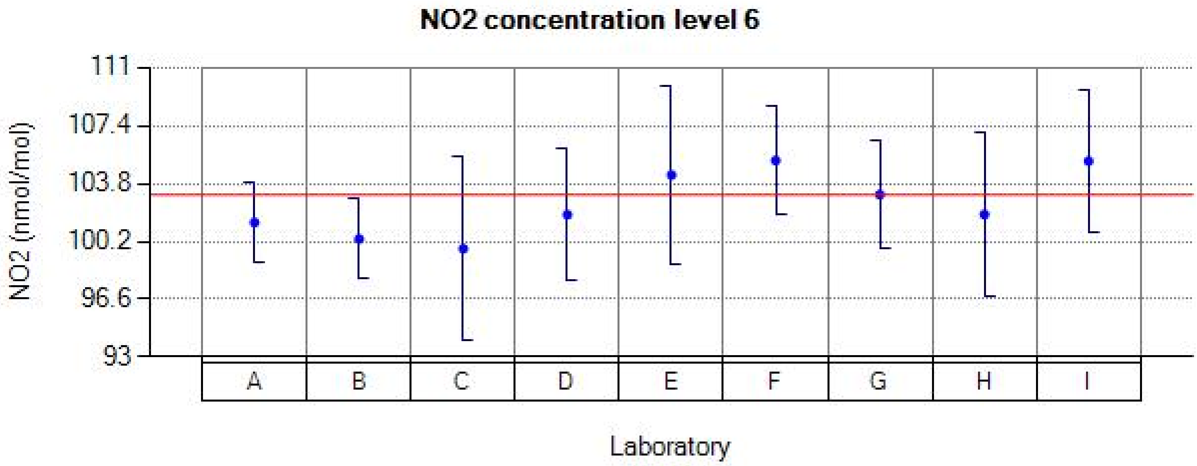

Figure 45: Reported values for NO_2 run 6.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	10.37	9.64	10.36	10.28	10.90	10.85	10.89	10.76	10.88
xi, 2	10.41	9.92	10.41	10.28	10.86	10.85	10.90	10.56	10.96
xi, 3	10.41	9.67	10.36	10.28	10.88	10.85	11.00	10.58	10.94
xi	10.39	9.74	10.37	10.28	10.88	10.85	10.93	10.63	10.92
si	0.02	0.15	0.02	0.00	0.02	0.00	0.06	0.11	0.04
u(xi)	1.25	1.12	0.41	0.49	0.38	0.30	0.73	1.03	0.23
U(xi)	2.51	2.24	0.82	0.98	0.76	0.59	1.45	2.06	0.46

Table 44: Reported values for NO_2 run 8.

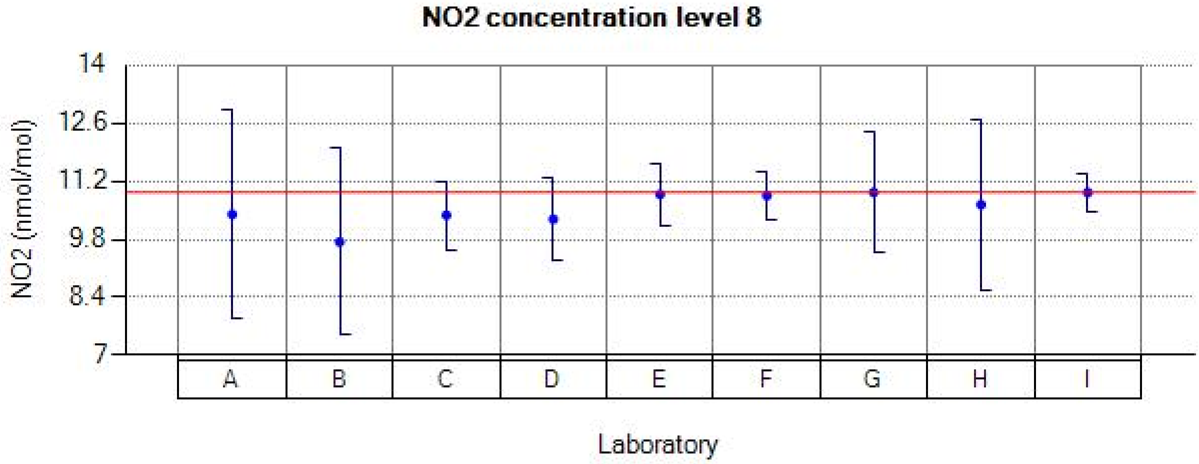

Figure 46: Reported values for NO_2 run 8.

values	laboratories								
	A	B	C	D	E	F	G	H	I
xi, 1	19.51	18.73	19.23	19.64	20.42	20.56	20.39	19.63	20.53
xi, 2	19.56	18.67	19.37	19.44	20.52	20.47	20.41	19.69	20.62
xi, 3	19.46	18.99	19.25	19.44	20.45	20.47	20.42	19.83	20.58
xi	19.51	18.79	19.28	19.50	20.46	20.50	20.40	19.71	20.57
si	0.05	0.17	0.07	0.11	0.05	0.05	0.01	0.10	0.04
u(xi)	1.25	1.05	0.62	0.49	0.72	0.40	0.78	1.10	0.43
U(xi)	2.51	2.11	1.24	0.98	1.44	0.81	1.56	2.20	0.86

Table 45: Reported values for NO_2 run 10.

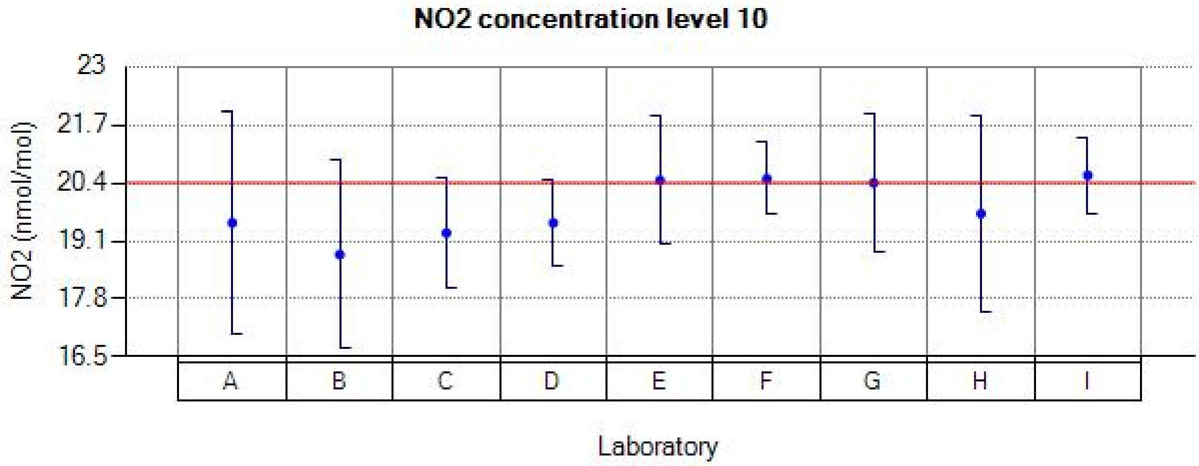

Figure 47: Reported values for NO_2 run 10.

Annex C. The precision of standardized measurement methods

For the main purpose of monitoring trends between different IE undertaken by ERLAP the precision of standardized SO_2, CO, O_3 and NO_X measurement methods 0, 0, 0 and 0 as implemented by NRLs was evaluated.
Applied methodology is described in ISO 5725-1, -2 and -6 0, 0 and 0. The precision experiment has involved a total of seven laboratories, the actual number of labs (p_j) varying from run to run (Table 46). Six concentration levels (for run 0 is requested only one value so repeatability cannot be evaluated) were tested for O_3, CO, SO_2 and NO_2, and eleven 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 5725-6 as the square root of average within-laboratory variance. The repeatability limit (r) is calculated using Equation 6 0. 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.

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

The reproducibility standard deviation (s_R) was calculated in accordance with ISO 5725-6 as the square root of sum of repeatability and between-laboratory variance. The reproducibility limit (R) is calculated using Equation 7 0. 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.

$$R = t_{95\%,\nu} \cdot \sqrt{2} \cdot s_R \qquad \textbf{Equation 7}$$

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 46.

parameter	run	p_j	t critical value 95% for r	t critical value 95% for R
CO	1,2,3,4,5	9	2.101	2.306
NO	1,2,3,4,5,6,7,8,9,10	9	2.101	2.306
NO_2	2,4,6,8,10	9	2.101	2.306
O_3	1,2,3,4,5	9	2.101	2.306
SO_2	1,2,3,4,5	9	2.101	2.306

Table 46: 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 47 to Table 51 and from Figure 48 to Figure 52. It is also reported the 'reproducibility from common criteria (R (from σ_p))' calculated by substituting s_R in Equation 7 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 (0 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		1.0	
4.3	0.2	1.0	
8.5	0.9	2.0	
15.5	0.2	2.0	
50.2	0.5	5.5	
129.4	1.7	12.6	9.7%

Table 47: The R and r of SO_2 standard measurement method.

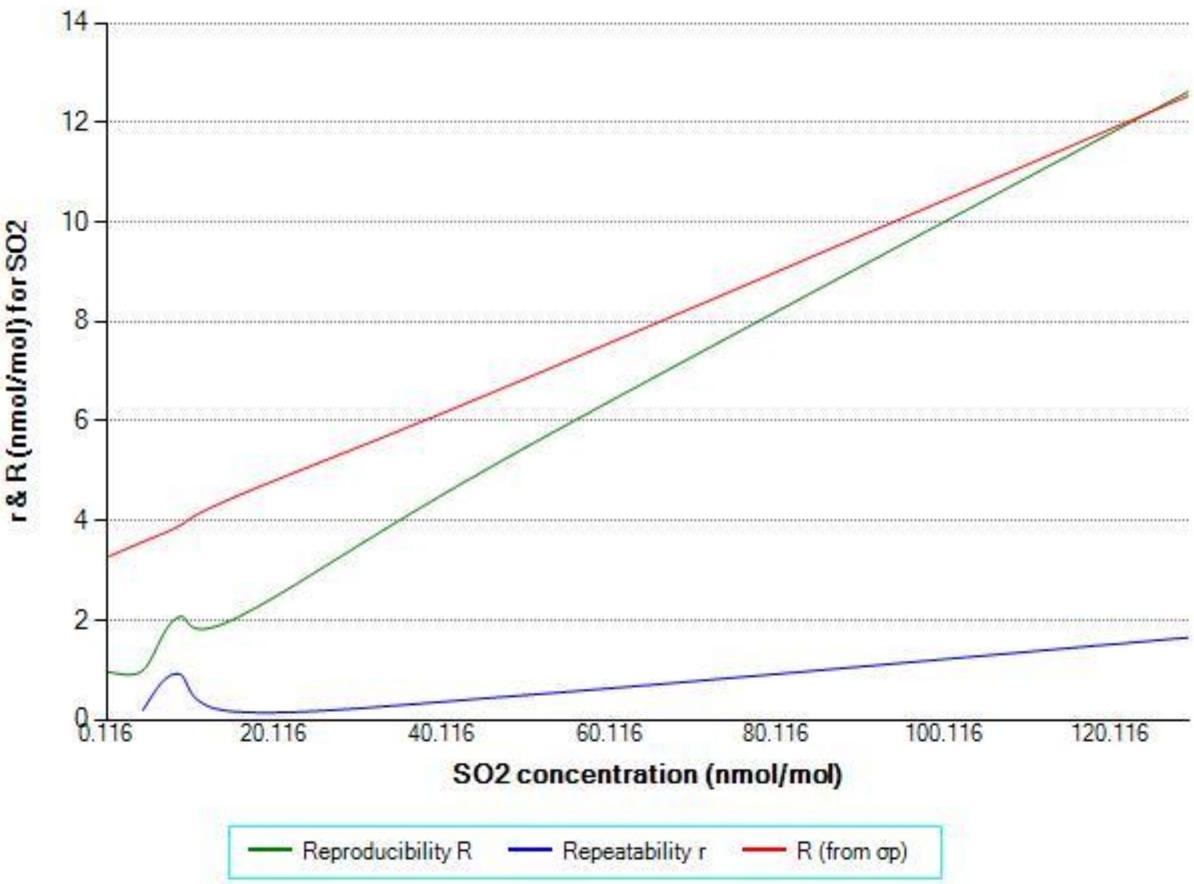

Figure 48: The R and r of SO_2 standard measurement method as a function of concentration.

CO data (µmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
-0.017		0.231	
0.824	0.01	0.319	
2.472	0.059	0.495	
3.996	0.01	0.541	
5.523	0.011	0.447	
7.996	0.017	0.339	4.2%

Table 48: The R and r of CO standard measurement method.

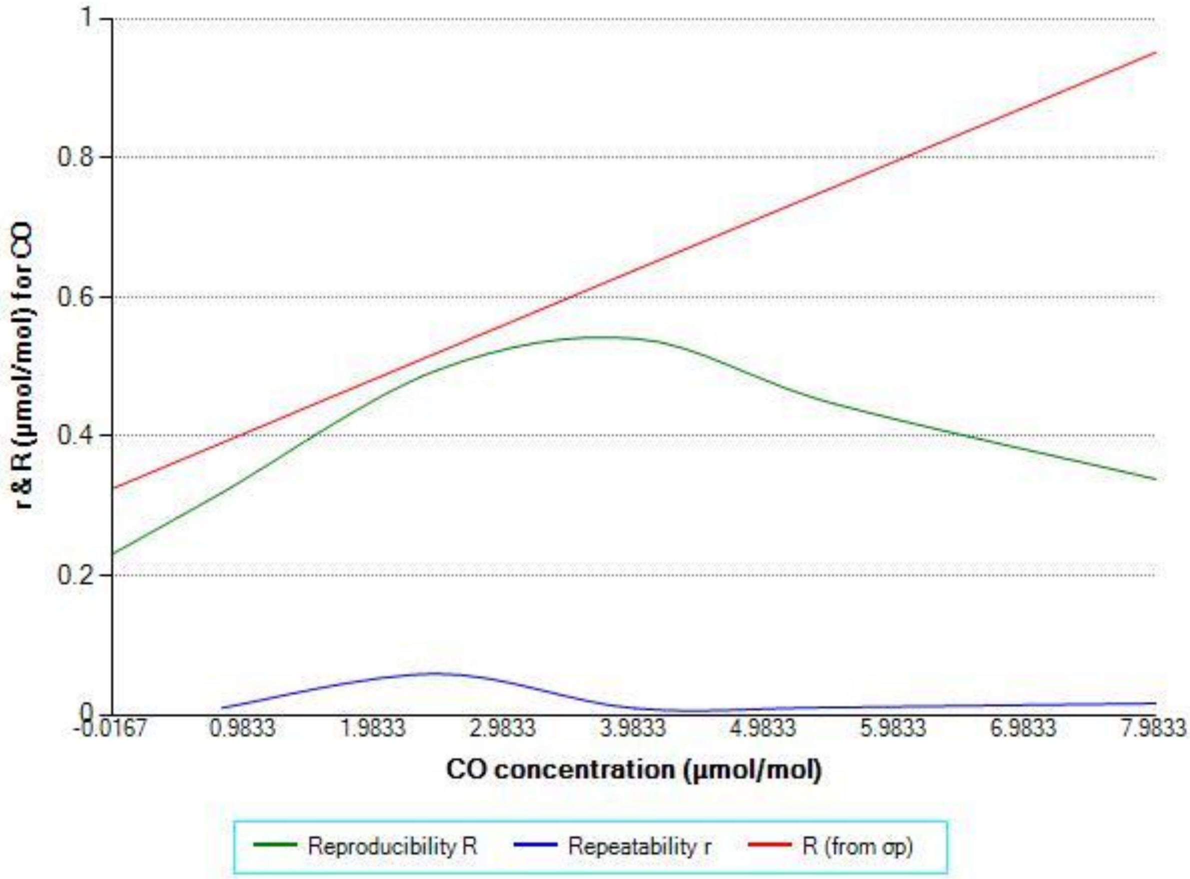

Figure 49: The R and r of CO standard measurement method as a function of concentration.

O_3 data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
0.2		1.1	
8.8	0.2	0.6	
20.2	0.3	1.1	
60.0	0.4	1.5	
90.2	0.3	2.4	
128.9	0.8	3.3	2.6%

Table 49: The R and r of O_3 standard measurement method.

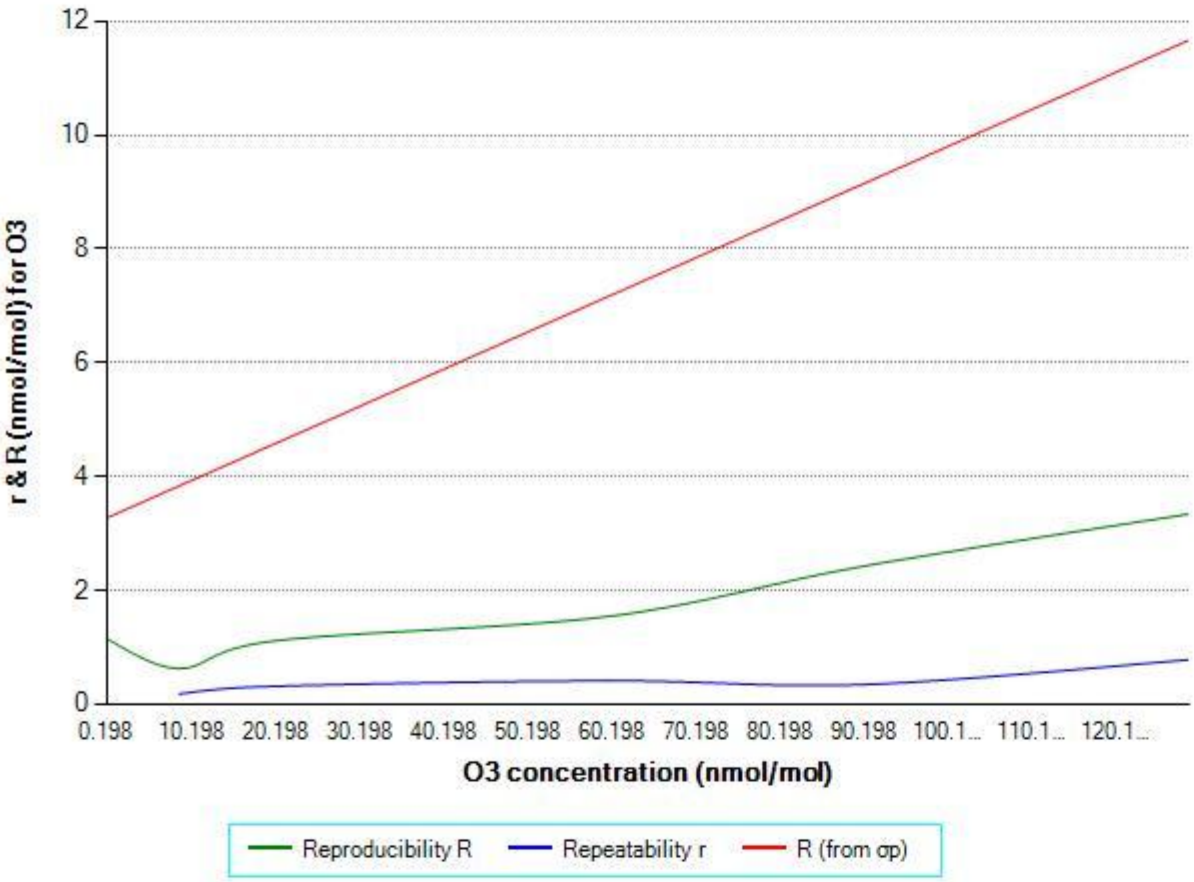

Figure 50: The R and r of O_3 standard measurement method as a function of concentration.

NO data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
0.1		0.8	
7.7	0.2	2.2	
18.2	0.3	2.6	
41.9	0.3	3.8	
61.8	0.5	4.3	
129.5	0.4	7.4	
189.9	0.6	9.3	
249.7	0.4	12.0	
351.5	1.0	13.6	
468.2	2.0	20.6	
602.5	2.2	23.2	3.9%

Table 50: The R and r of NO standard measurement method.

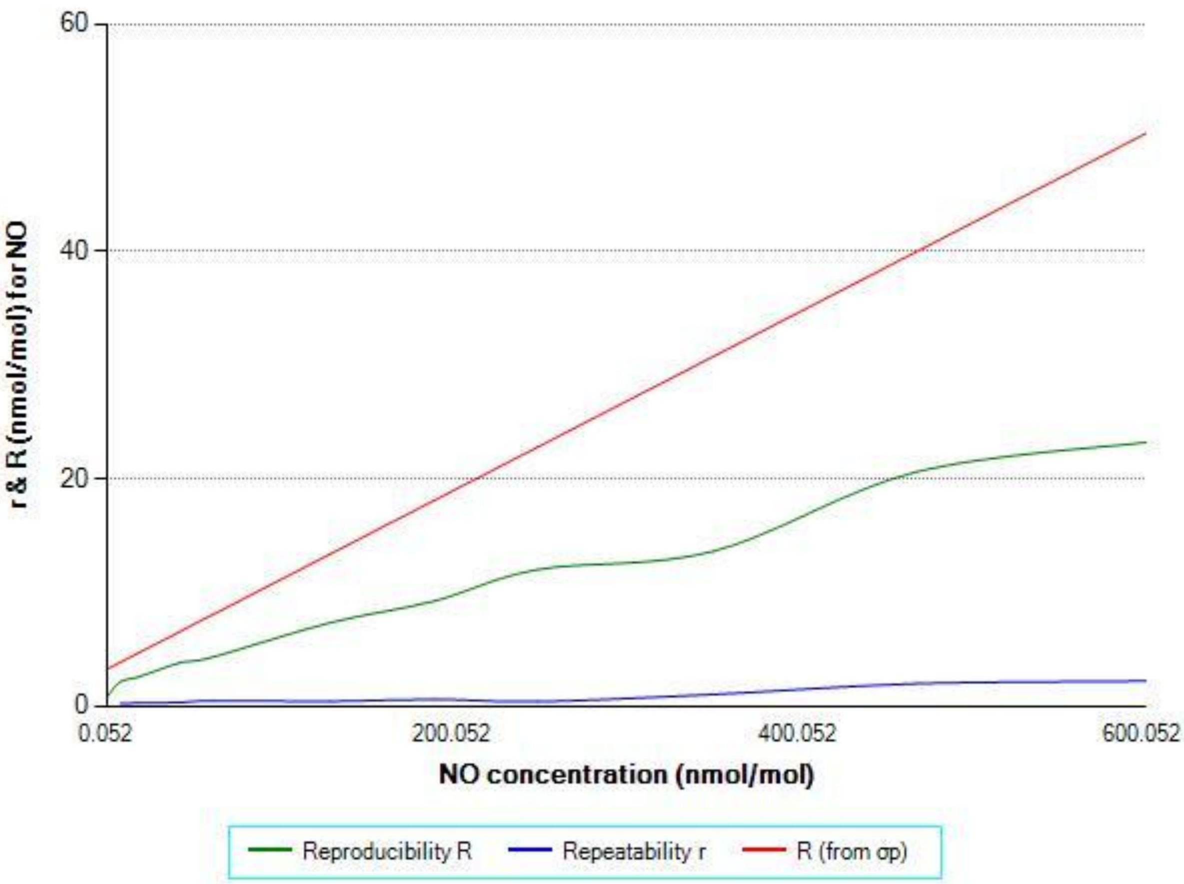

Figure 51: The R and r of NO standard measurement method as a function of concentration.

NO_2 data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
-0.1		0.5	
10.6	0.2	1.3	
19.9	0.3	2.1	
60.6	0.6	4.6	
102.6	0.7	6.6	
137.2	1.1	8.7	6.3%

Table 51: The R and r of NO_2 standard measurement method.

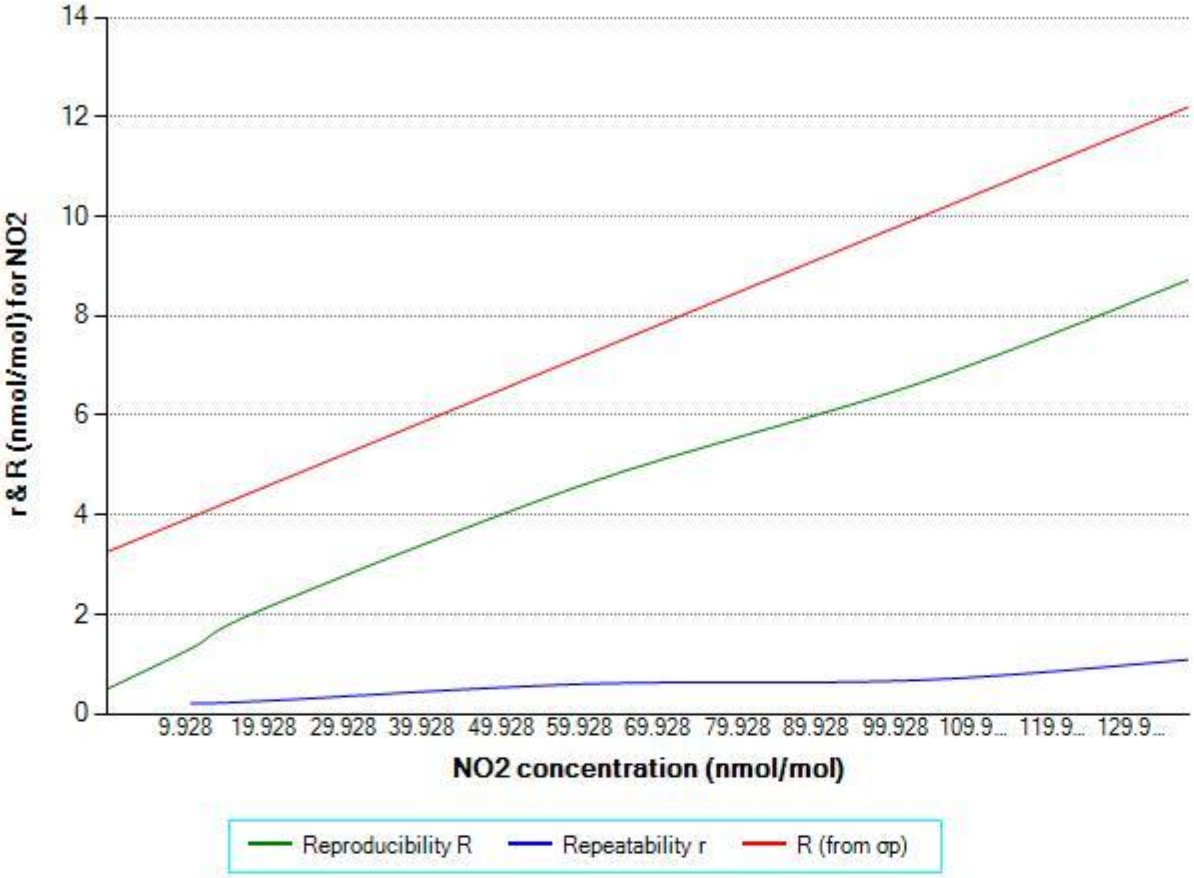

Figure 52: The R and r of NO_2 standard measurement method as a function of concentration.

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.
For runs where outliers were detected, outliers were removed and "Grubb's one outlying observation test" was repeated until no more outliers were observed. Statistical outliers obtained at this stage are not considered as due to extraordinary errors but due to significant difference in participant's standard operating procedure.

In the table below are reported the outliers identified during this Inter-comparison exercise. They are related to zero level of CO and O_3.

parameter	run	laboratory	measured value	failing test	confidence level
CO	0	H	-0.203	G1 minimum	1%, 5%
O_3	0	D	1.1	G1 maximm	1%, 5%

Table 52: "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.

According to Grubb's test results between a confidence level of 1 and 5% are considered straggler and they deserve a specific check.
In order to give useful information to the participants for judging their performance also the stragglers are reported in the following table:

Laboratory	parameter	run	value	Gmin_5%	Gmax_5%
B	SO2	0	0.12	OK	straggler
C	CO	5	0.82	OK	straggler
D	O3	5	20.20	OK	straggler
D	O3	4	8.75	OK	straggler

Table 53: Stragglers according to Grubb's one observation test.

Annex E. Accreditation certificate

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CERTIFICATO DI ACCREDITAMENTO
Accreditation Certificate

Accreditamento n° / *Accreditation n°* **1362** Rev. **0**

Si dichiara che / *We declare that*

European Reference Laboratory for Air Pollution (ERLAP) Air and Climate Unit - Institute for Environment and Sustainability - Joint Research Centre - European Commission
Sede:
Via E. Fermi 2749 - 21027 Ispra VA

è conforme ai requisiti della norma: UNI CEI EN ISO/IEC 17025:2005 "Requisiti generali per la competenza dei Laboratori di prova e taratura"

meets the reqirements of the standard: EN ISO/IEC 17025:2005 "General Requirements for the Competence of Testing and Calibration Laboratories" standard

quale **Laboratorio di Prova**

as ***Testing Laboratory***

L'accreditamento attesta la competenza tecnica del Laboratorio relativamente allo scopo riportato nelle schede allegate al presente certificato. Le schede possono variare nel tempo. I requisiti gestionali della ISO/IEC 17025:2005 (sezione 4) sono scritti in un linguaggio idoneo all'attività dei Laboratori di Prova, sono conformi ai principi della ISO 9001:2008 ed allineati con i suoi requisiti applicabili.
Il presente certificato non è da ritenersi valido se non accompagnato dalle schede allegate e può essere sospeso o revocato in qualsiasi momento nel caso di inadempienza accertata da parte di ACCREDIA.
La vigenza dell'accreditamento può essere verificata sul sito WEB (www.accredia.it) o richiesta direttamente ai singoli Dipartimenti .

The accreditation certifies the technical competence of the laboratory limited to the scope detailed in the attached Enclosure. The scope may vary in the time. The management system requirements in ISO/IEC 17025:2005 (Section 4) are written in a language relevant to Testing Laboratories operations and meet the principles of ISO 9001:2008 and are aligned with its pertinent requirements.
The present certificate is valid only if associated to the annexed schedule, and can be suspended or withdrawn at any time in the event of non fulfilment as ascertained by ACCREDIA.
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ELENCO PROVE ACCREDITATE - CATEGORIA: 0

Synthetic mixture gas

Denominazione della prova / Campi di prova	*Metodo di prova*
carbon monoxide (0-86 mmol/mol)	EN 14626:2012
nitrogen oxides (NO: 0-962 nmol/mol; NO2: 0-261 nmol/mol)	EN 14211:2012
ozone (0-250 nmol/mol)	EN 14625:2012
sulphur dioxide (0-376 nmol/mol)	EN 14212:2012

Legenda
En= norma europea

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Il Direttore del Dipartimento
(*Dr. Paolo Bianco*)

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