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Evaluation of the Laboratory Comparison Exercise for SO_2, CO, O_3, NO and NO_2 19-23 October 2015, Ispra

European Commission harmonisation programme for Air Quality Measurements

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Abstract

Within the harmonisation programme of Air Quality monitoring in Europe the European Reference Laboratory of Air Pollution (ERLAP) is organizing Inter-Laboratory Comparison Exercises (IE) in the facility of Ispra (Italy).

From the 19 to the 23 October 2015 in Ispra (Italy), eight Laboratories of AQUILA (Network of European Air Quality Reference Laboratories) and one of French regional network (AIRPARIF) met for a comparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants. In order to cover the prescription of the European Directive 2008/50/EC [1] and its the recent amendment 2015/1480/EC [42] about air quality, the following pollutants were measured: sulphur dioxide (SO_2), nitrogen dioxide (NO_2), nitrogen monoxide (NO), carbon monoxide (CO) and ozone (O_3).

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on compliance with Data Quality Objectives (DQO) and measurement capabilities of the National Air Quality Laboratories to the European Commission (EC) and can be used by participants in their laboratory's quality system.

On the basis of criteria imposed by the EC, 75.6% of the results reported by the participants was satisfactory both in terms of measured values and reported uncertainties. Part of the results (18.1%) had acceptable measured values, but the reported uncertainties were either too high (10.8%) or too small (7.3%). Against the usual tendency during this IE a great number of results (2.2%) were unsatisfactory for both the value and the uncertainty.
Comparability of results among AQUILA participants at the highest concentration level, excluding outliers, is acceptable for almost all pollutants measurements. CO and NO_2 show a deviation from the objectives.

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Abbreviations

AQUILA	Network of National Reference Laboratories for Air Quality
BIPM	Bureau Intenational des Poids et Mesures
CCQM	Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology
CO	Carbon monoxide
CRMs	Certified Reference Materials
DQO	Data Quality Objective
ERLAP	European Reference Laboratory of Air Pollution
EC	European Commission
GPT	Gas Phase Titration
IE	Inter-laboratory Comparison Exercise
ISO	International Organisation for Standardization
JRC	Joint Research Centre
NIST	National Institute of Standards and Technology
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 Organisation Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin

Mathematical symbols

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

1. Introduction

The 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 [1] is that the ambient air quality shall be assessed on the basis of common methods and criteria. It concerns with the air pollutants SO_2, NO_2, NO, particulate matter, lead, benzene, CO and O_3. Among other things it specifies the reference methods for measurements and DQOs for the accuracy of measurements.
The 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 standardised by the International Organisation for Standardisation (ISO).
As foreseen in the Air Quality Directive, the European Reference Laboratory of Air Pollution (ERLAP) of the Directorate Energy, Transport & Climate the Joint Research Centre (JRC) regularly organises IEs to assess and improve the status of comparability of measurements of National Reference Laboratories (NRLs) of the Member States of the European Union.
The World Health Organisation Collaborating Centre for Air Quality Management and Air Pollution Control (WHO CC) in Berlin is carrying out similar activities since 1994 [9] [10], [24], [31], [33], [35], [38] and [43] but with a view to obtaining harmonized air quality data for health related studies. Their programme is integrated within the WHO EURO area, which includes public health institutes and other national institutes — especially from the Central and Eastern Europe, the Caucasus and countries in Central Asia.
In 2004, it was decided to bring together the efforts of both the JRC-ERLAP and the WHO CC and to coordinate activities as much as possible, with a view to optimizing resources and securing better international harmonisation.

The following report deals with the IE that took place from 19 to the 23 October 2015 in Ispra (Italy).

Since 1990 ERLAP has been organizing 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) [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 organisation of IEs was developed by ERLAP in collaboration with AQUILA and is described in a paper on the organisation of laboratory comparison exercises for gaseous air pollutants [12].
This evaluation scheme was adopted by AQUILA in December 2008 and has since been applied to all IEs. It contains common criteria to alert the EC of possible performance failures which do not rely solely on the uncertainty claimed by participants. The evaluation scheme implements the z' 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 above mentioned document, NRLs with an overall unsatisfactory performance in the z' 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/IEC 17025 [44], they are requested to include their measurement uncertainty. Hence, the results

of participants (measurement values and uncertainties) are compared to the assigned values applying the E_n scores method [13].
Beside the proficiency of participating laboratories, the repeatability (r) and reproducibility (R) of standardised measurement methods [14], [15] and [16] are evaluated as well. These group evaluations are useful indicators of trends in measurement quality over different IE.

2. Inter-laboratory organisation

The IE was announced in June 2015 to the members of the AQUILA network and the WHO CC representative. Registration was opened in September 2015 and closed at the beginning of October 2015.
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).

Participants were invited to arrive on Monday, 19th of October 2015, 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 either organisations dealing with the routine ambient air monitoring or institutions involved in environmental or public health protection. The national representatives came from Bulgaria, Republic of Lithuania, France, the Czech Republic, Cyprus, Republic of Serbia and Norway.

Country	Laboratory	Code
Bulgaria	Executive Environmental Agency (EEA)	A
Republic of Lithuania	Environmental Protection Agency (AAA)	B
France	AirParif (AIRPARIF)	C
Czech Republic	Czech Hydrometereological Institute (CHMI)	D
Cyprus	Dept. of Labour Inspection (DLI)	E
Spain	Instituto De Salud Carlos III (ISCIII)	F
European Commission	European Reference Laboratory for Air Pollution (ERLAP)	G
Republic of Serbia	Serbian Environmental Protection Agency (SEPA)	H
France	LCSQA – Mines de Douai (LCSQA)	I
Norway	Norwegian Institute for Air Research (NILU)	L

Table 1: list of participating organisations

Table 2 reports the manufacturer and model of the instrumentation used by each participant during the IE, included those used in the calculation of the assigned values.

As a whole, the instrumentation was manufactured by four different companies for all parameters analysed.
The list contains the information reported by participants and by no means can it be considered as an implicit or explicit endorsement of the organisers to any specific type of instrumentation.

Gas	Lab code	Instrument
SO_2	A	Horiba, 2009, APSA 370
	B	Horiba, Apsa 370, 2011
	C	SO2 analyzer: Thermo electron 43C (2001)
	D	Thermo Environmental Instruments, Inc., 1997, model 43C
	E	Ecotech, Year: 2005, EC9850B with an external pump
	F	THERMO 43i
	G	Thermo Scientific, 2009, 43i-TLE
	H	Teledyn API; 2011; T100
	I	API, 2008, UV fluorescence, model 100E
	L	Teledyne API, 2005, API 100E
NO_X	A	Horiba, 2009, analyzer NOx, APNA 370
	B	Horiba, Apna 370, 2011
	C	NO analyzer: Environnement SA AC32M (2002) / NO2 analyzer: Environnement SA AS32M (2015)
	D	Thermo Environmental Instruments, Inc., 1997, model 42C
	E	Ecotech, Year: 2005, EC 9841B with an external pump
	F	TELEDYNE API 200E
	G	Thermo Electrom Corporation, 1999, 42C
	H	Teledyn API; 2011; T200
	I	Thermo Environmental Instruments Inc., 2000, model 42C
	L	Teledyne API, 2005, API 200E
CO	A	Horiba, 2009, APMA 370
	B	Horiba, Apma 370, 2011
	C	CO analyzer: Thermo electron 48C (2001)
	D	Thermo Environmental Instruments, Inc., 1997, model 48C
	E	Ecotech, Year: 2005, EC9830B with an external pump
	F	TELEDYNE API T300
	G	Horiba Model APMA-370, 2010
	H	Teledyn API; 2011; T300
	I	HORIBA, 2013, non dispersive IR spectroscopy, APMA 370
	L	Teledyne API, 2005, API 300E
O_3	A	Horiba, 2008, APOA 370
	B	Horiba, Apoa 370, 2011
	C	O3 analyzer: Environnement SA O342e (2015)
	D	Thermo Environmental Instruments, Inc., 1997, model 49C
	E	Thermo Electron Corporation, Year: 2006, Model 49i Ozone Analyzer
	F	THERMO 49i
	G	Thermo Scientific 49-PS , 2014
	H	Teledyn API; 2011; T400
	I	Thermo Environmental Instruments Inc., 2000, model 49 C
	L	Teledyne API, 2005, API 400E

Table 2: list of instruments used by participants

2.2. Preparation of test mixtures

The ERLAP IE facility has been described in several reports [17] and [18]. 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 the European Air Quality Directive [1].

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 [8]. O_3 was added using an ozone generator and NO_2 was produced applying the gas phase titration (GPT) method [19] in a condition of NO excess.

The participants were required to report three 30-min mean measurements for each concentration level (run) in order to evaluate the repeatability of standardised measurement methods. Zero concentration levels were generated for 1 hour and one 30-min mean measurement was reported. The sequence programme 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	$NO-NO_2$				450	150			
2nd	16:00	2	O_3						150		
2nd	18:00	2	$NO-NO_2$				210				
2nd	20:00	2	$NO-NO_2$				100	110			
2nd	22:00	2	O_3						120		
3rd	0:00	2	$NO-NO_2$				80				
3rd	2:00	2	$NO-NO_2$				20	60			
3rd	4:00	2	O_3						55		
3rd	6:00	2	$NO-NO_2$				390				
3rd	8:00	2	$NO-NO_2$				300	90			
3rd	10:00	2	O_3						90		
3rd	12:00	2	$NO-NO_2$				50				
3rd	14:00	2	$NO-NO_2$				30	20			
3rd	16:00	2	O_3						15		
3rd	< 18:00	2	calibration		X						
3rd	20:00	1	$CO-SO_2$			0					
3rd	21:00	2	$CO-SO_2$							8.5	130
3rd	23:00	2	$CO-SO_2$							3.5	70
4th	1:00	1	$CO-SO_2$	Zero Air not reported						0	0
4th	2:00	2	$CO-SO_2$							1.0	5
4th	4:00	2	$CO-SO_2$							5.0	30
4th	6:00	2	$CO-SO_2$							2.0	10
4th	8:00	1				0					
4th	9:00	END									

Table 3: sequence programme 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 [13] was applied. It was agreed among the AQUILA members to consider the measurement results of ERLAP as the assigned/reference values for the whole IE [12].
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 [12], the proficiency of the participants was assessed by calculating two performance indicators.
The first performance indicator (z' scores) tests whether the difference between the participant's measured value and the assigned/reference value remains within the limits of a common criterion.
The second performance indicator (E_n scores) tests if the difference between the participant's measured values and assigned/reference value remains within the limits of a criterion, which 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' scores

The z' scores 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 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 [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 an 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 a 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.

	σ_p=a·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' 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 has occurred an anomaly that should be investigated and corrected. A list of questionable and unsatisfactory results is reported in the following table (Table 5).

Parameter	Lab. code	Lab. value	z' evaluation
NO2 _4	A	108.9	questionable
CO _1	B	9.64	unsatisfactory
CO _2	B	4.004	questionable
CO _4	B	5.7	questionable
NO2 _2	B	138.2	unsatisfactory
NO2 _8	B	82.67	unsatisfactory
NO2 _4	E	108.2	questionable
NO _2	F	489.3	questionable
NO _4	F	109.1	questionable
NO _6	F	23.08	questionable
CO _1	I	4.696	unsatisfactory
CO _2	I	2.014	unsatisfactory
CO _3	I	0.757	questionable
CO _4	I	2.882	unsatisfactory
CO _5	I	1.253	unsatisfactory
NO _10	I	24.91	questionable
NO _4	I	93.38	questionable
NO _5	I	71.99	questionable
NO _9	I	43.33	questionable
NO2 _6	I	55.53	questionable

Table 5: Questionable and unsatisfactory results according to z'

The results of the z' evaluation are presented in bar plots (Figure 1 to Figure 5) in which the z' of each participant are grouped together, and assessment criteria are presented as z'=±2 and z'=±3 lines.

Figure 1: z' scores 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 (70 nmol/mol), 3 (5 nmol/mol), 4 (30 nmol/mol), 5 (10 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.

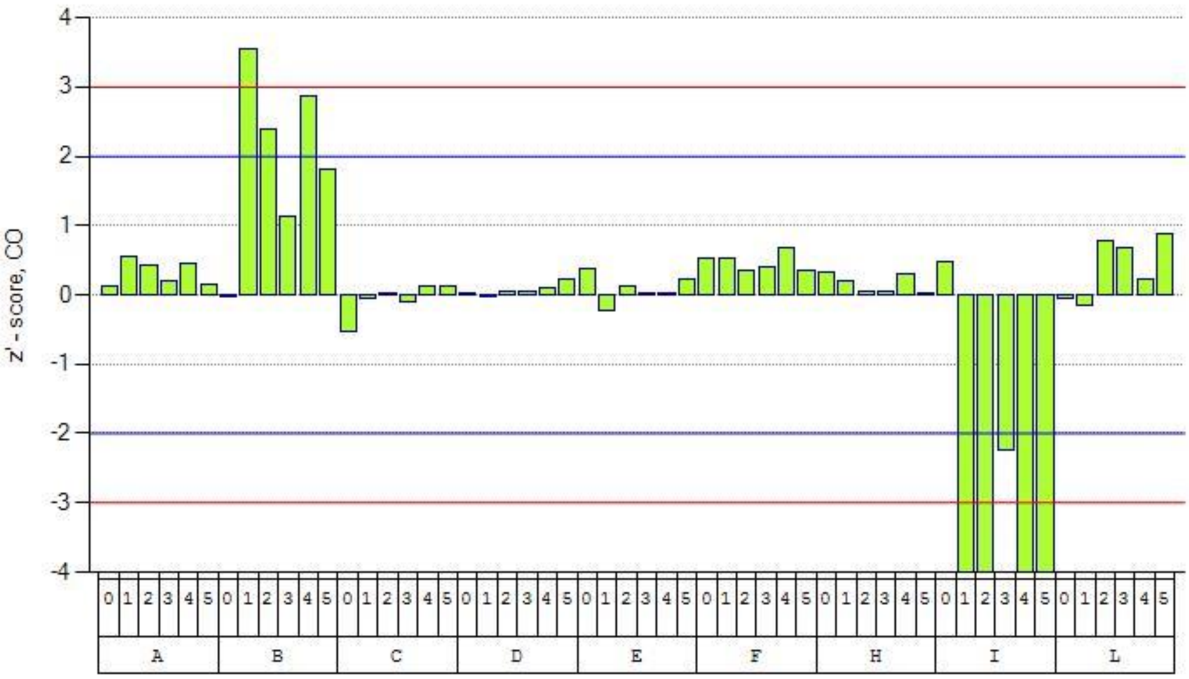

Figure 2: z' scores evaluations of CO measurements
Scores are given for each participant and each tested concentration level (run). Run number order (with nominal concentration) is: 0 (0 µmol/mol), 1 (8,5 µmol/mol), 2 (3,5 µmol/mol), 3 (1 µmol/mol), 4 (5 µmol/mol), 5 (2 µmol/mol). The assessment criteria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

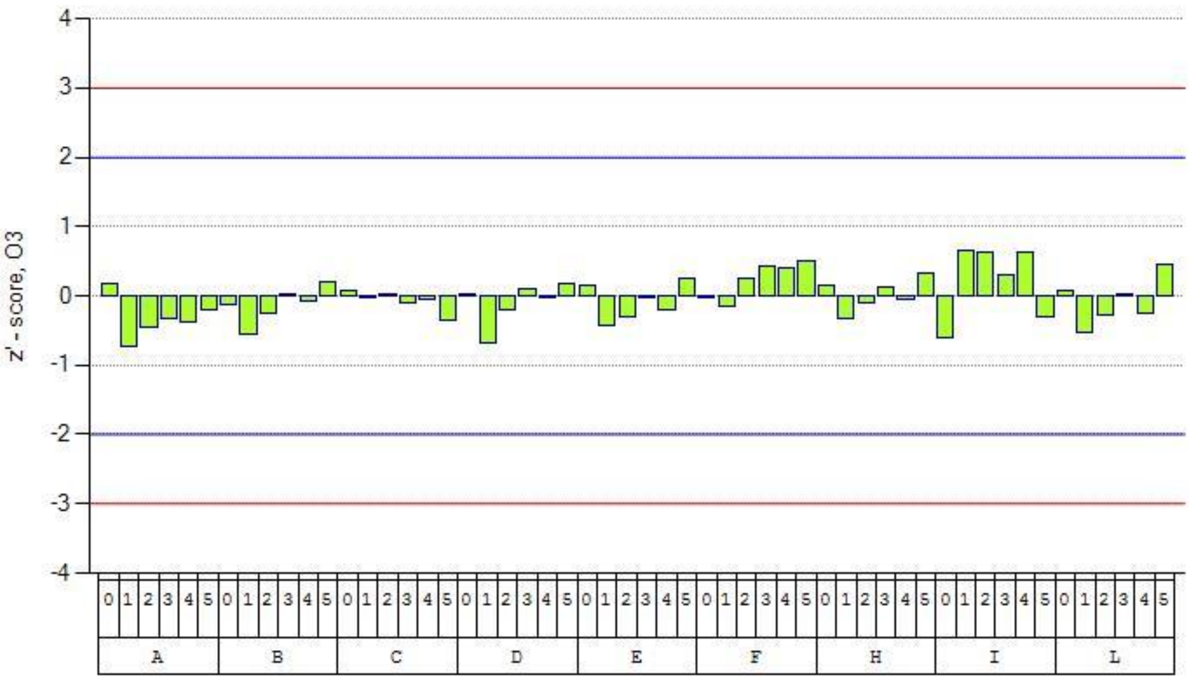

Figure 3: z' scores evaluations of O_3 measurements

Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (150 nmol/mol), 2 (120 nmol/mol), 3 (55 nmol/mol), 4 (90 nmol/mol), 5 (15 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.

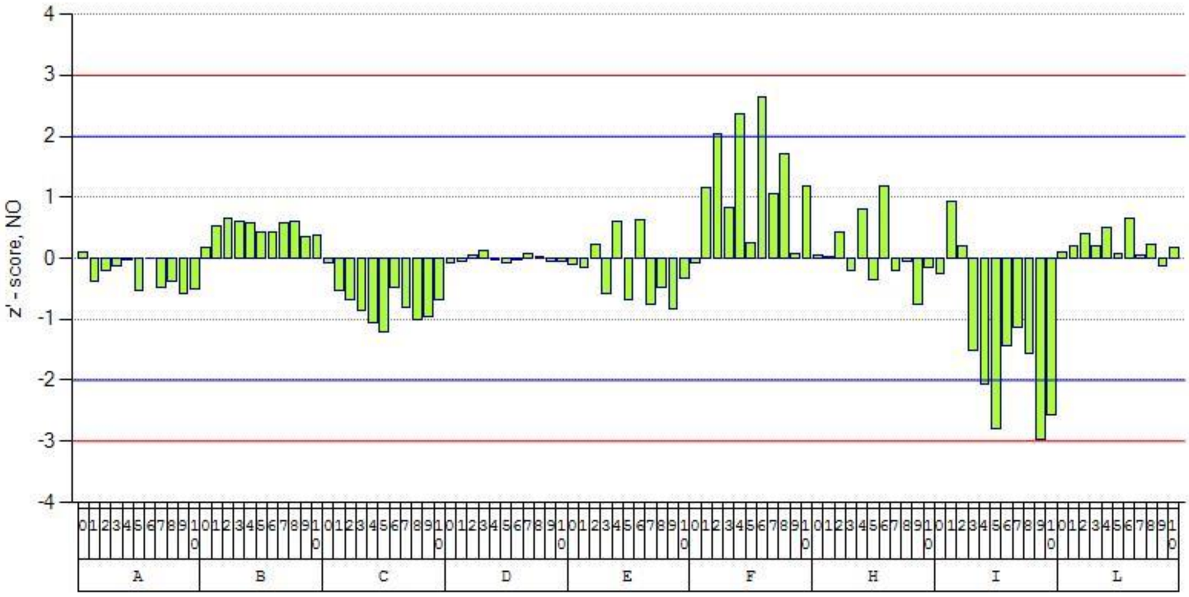

Figure 4: z' scores evaluations of NO measurements

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 (450 nmol/mol), 3 (210 nmol/mol), 4 (100 nmol/mol), 5 (80 nmol/mol), 6 (20 nmol/mol), 7 (390 nmol/mol), 8 (300 nmol/mol), 9 (50 nmol/mol), 10 (30 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.

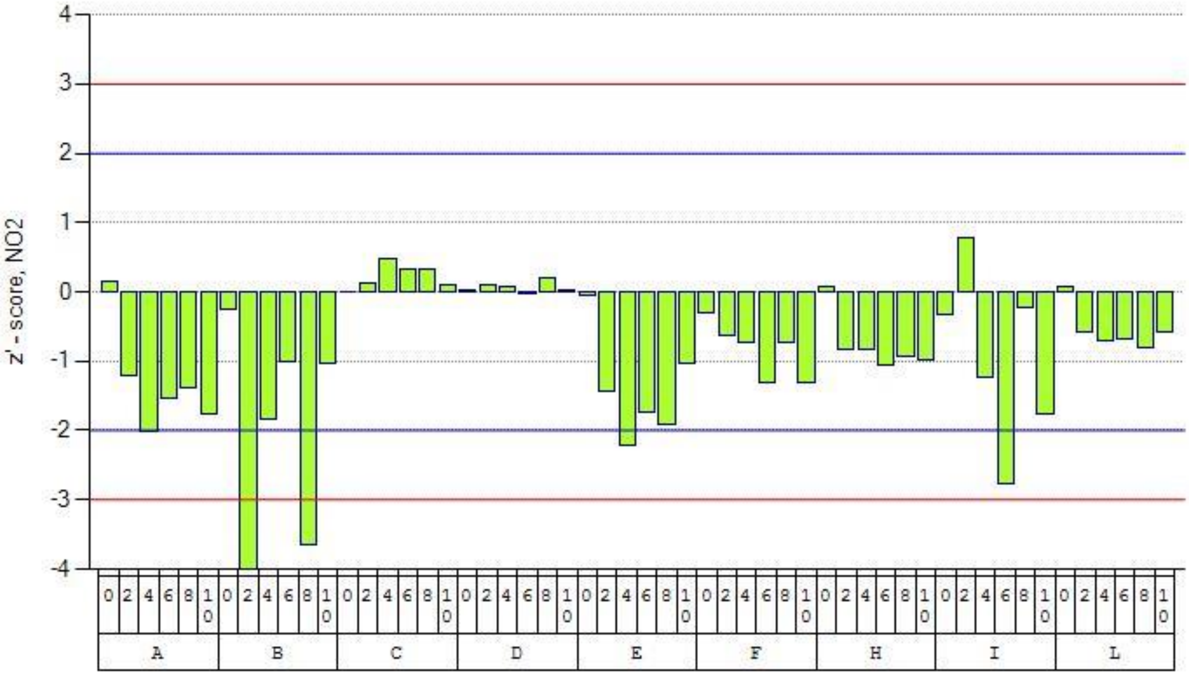

Figure 5: z' scores evaluations of NO_2 measurements
Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (150 nmol/mol), 2 (110 nmol/mol), 3 (60 nmol/mol), 4 (90 nmol/mol), 5 (20 nmol/mol). The assessment criteria 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 scores

The normalised deviations [13] (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}'. The values with $|E_n| \leq 1$ are satisfactory.

From Figure 6 to Figure 10 the bias of each participant (x_i-X) is plotted and error bars are used to show the value of the denominator of Equation 2. These plots represent also the E_n 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. The E_n evaluation showed some unsatisfactory results as reported in Table 6.
This high number of results with an E_n value above 1 (unsatisfactory) could be explained observing the uncertainties submitted by the participants that are rather small. It could be interesting to check the calculation form used by the participants to calculate the uncertainty.

Parameter	Lab. code	Lab. value	Lab. U	Unit	E_n evaluation
NO2 _4	A	108.9	3.9	nmol/mol	unsatisfactory
NO2 _6	A	58.52	2.1	nmol/mol	unsatisfactory
NO2 _10	A	18	0.64	nmol/mol	unsatisfactory
SO2 _4	A	29.43	1.06	nmol/mol	unsatisfactory
CO _1	B	9.64	1	µmol/mol	unsatisfactory
NO2 _2	B	138.2	16.1	nmol/mol	unsatisfactory
NO2 _8	B	82.67	9.72	nmol/mol	unsatisfactory
NO _2	C	455.8	4.94	nmol/mol	unsatisfactory
NO _7	C	393.5	4.86	nmol/mol	unsatisfactory
NO2 _4	E	108.2	5.02	nmol/mol	unsatisfactory
NO2 _6	E	58.08	2.76	nmol/mol	unsatisfactory
NO2 _8	E	88.46	4.1	nmol/mol	unsatisfactory
CO _3	F	1.088	0.03	µmol/mol	unsatisfactory
CO _4	F	5.213	0.12	µmol/mol	unsatisfactory
NO _1	F	637.4	12.8	nmol/mol	unsatisfactory
NO _2	F	489.3	9.82	nmol/mol	unsatisfactory
NO _4	F	109.1	2.2	nmol/mol	unsatisfactory
NO _6	F	23.08	0.64	nmol/mol	unsatisfactory
NO _7	F	413.8	8.3	nmol/mol	unsatisfactory
NO _8	F	324.4	6.5	nmol/mol	unsatisfactory
NO _10	F	31.87	0.68	nmol/mol	unsatisfactory
NO2 _6	F	59.1	1.92	nmol/mol	unsatisfactory
NO2 _10	F	18.71	0.66	nmol/mol	unsatisfactory
SO2 _1	F	137.4	2.3	nmol/mol	unsatisfactory
SO2 _2	F	74.45	1.2	nmol/mol	unsatisfactory
SO2 _1	H	126.3	5.69	nmol/mol	unsatisfactory
CO _1	I	4.696	0.3	µmol/mol	unsatisfactory
CO _2	I	2.014	0.33	µmol/mol	unsatisfactory
CO _3	I	0.757	0.22	µmol/mol	unsatisfactory
CO _4	I	2.882	0.25	µmol/mol	unsatisfactory
CO _5	I	1.253	0.18	µmol/mol	unsatisfactory
NO _3	I	206.1	6.6	nmol/mol	unsatisfactory
NO _4	I	93.38	3.2	nmol/mol	unsatisfactory
NO _5	I	71.99	2.7	nmol/mol	unsatisfactory
NO _6	I	16.45	1.4	nmol/mol	unsatisfactory
NO _8	I	296	9.4	nmol/mol	unsatisfactory
NO _9	I	43.33	2.1	nmol/mol	unsatisfactory
NO _10	I	24.91	1.5	nmol/mol	unsatisfactory
NO2 _6	I	55.53	2.2	nmol/mol	unsatisfactory
CO _5	L	2.171	0.1	µmol/mol	unsatisfactory

Table 6: Unsatisfactory results according to the E_n

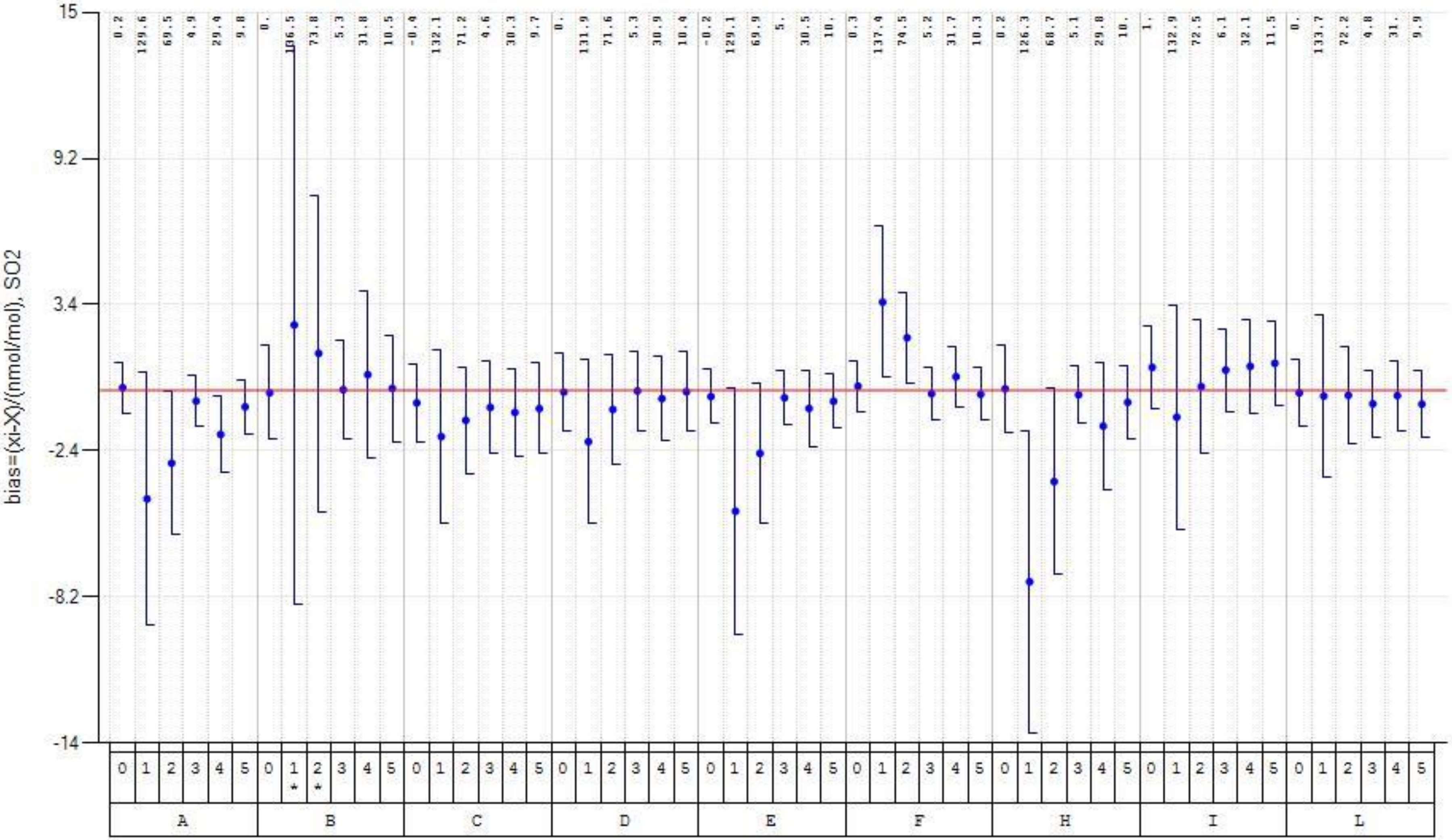

Figure 6: Bias of participant's SO_2 measurement results
Expanded uncertainty of bias for each run is presented as an error bar. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

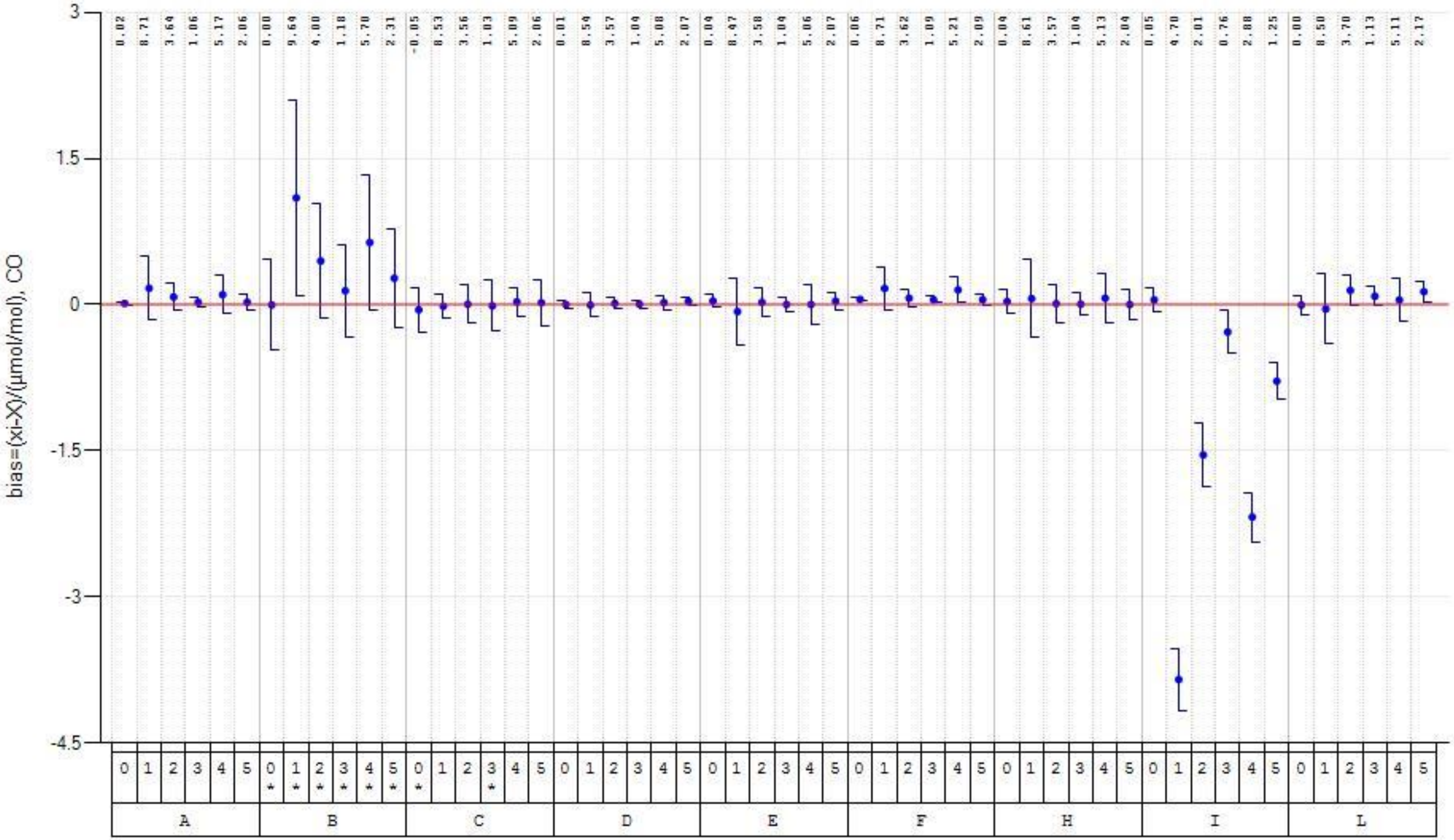

Figure 7: Bias of participant's CO measurement results
Expanded uncertainty of bias for each run is presented as an error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average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

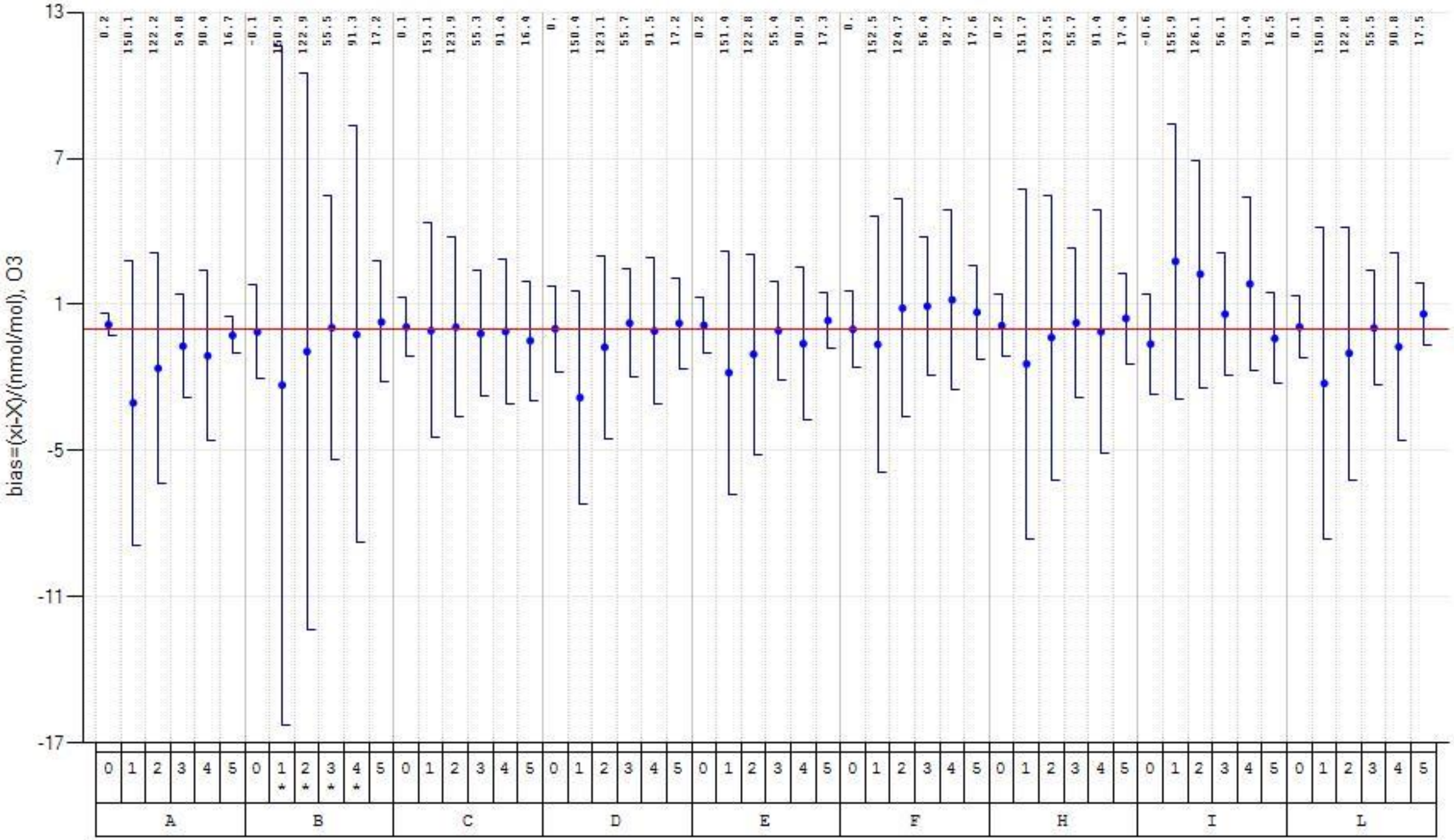

Figure 8: Bias of participant's O_3 measurement results
Expanded uncertainty of bias for each run is presented as an error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p.

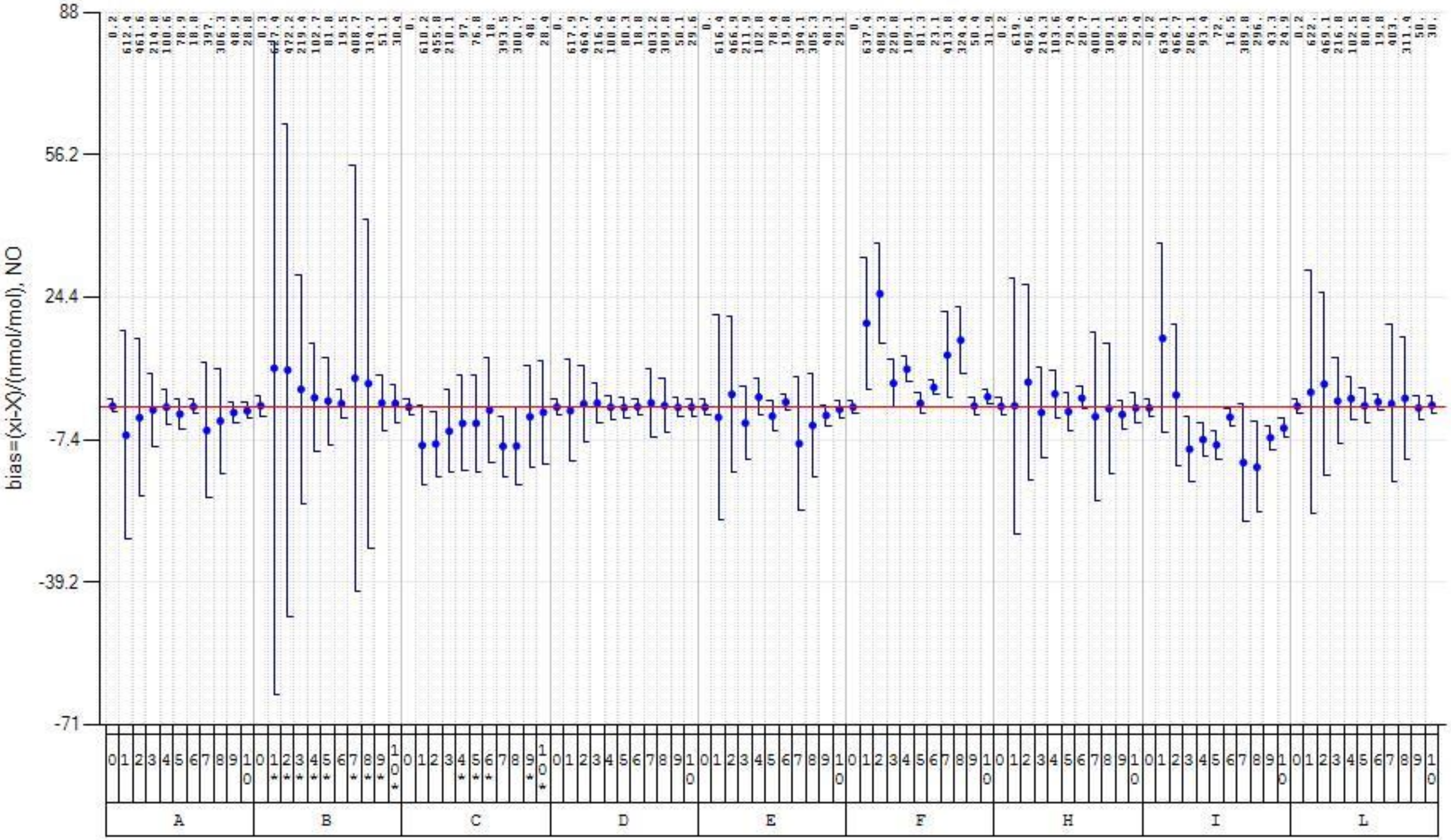

Figure 9: Bias of participant's NO measurement results
Expanded uncertainty of bias for each run is presented as an error bar. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 10) together with the participants rounded run average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

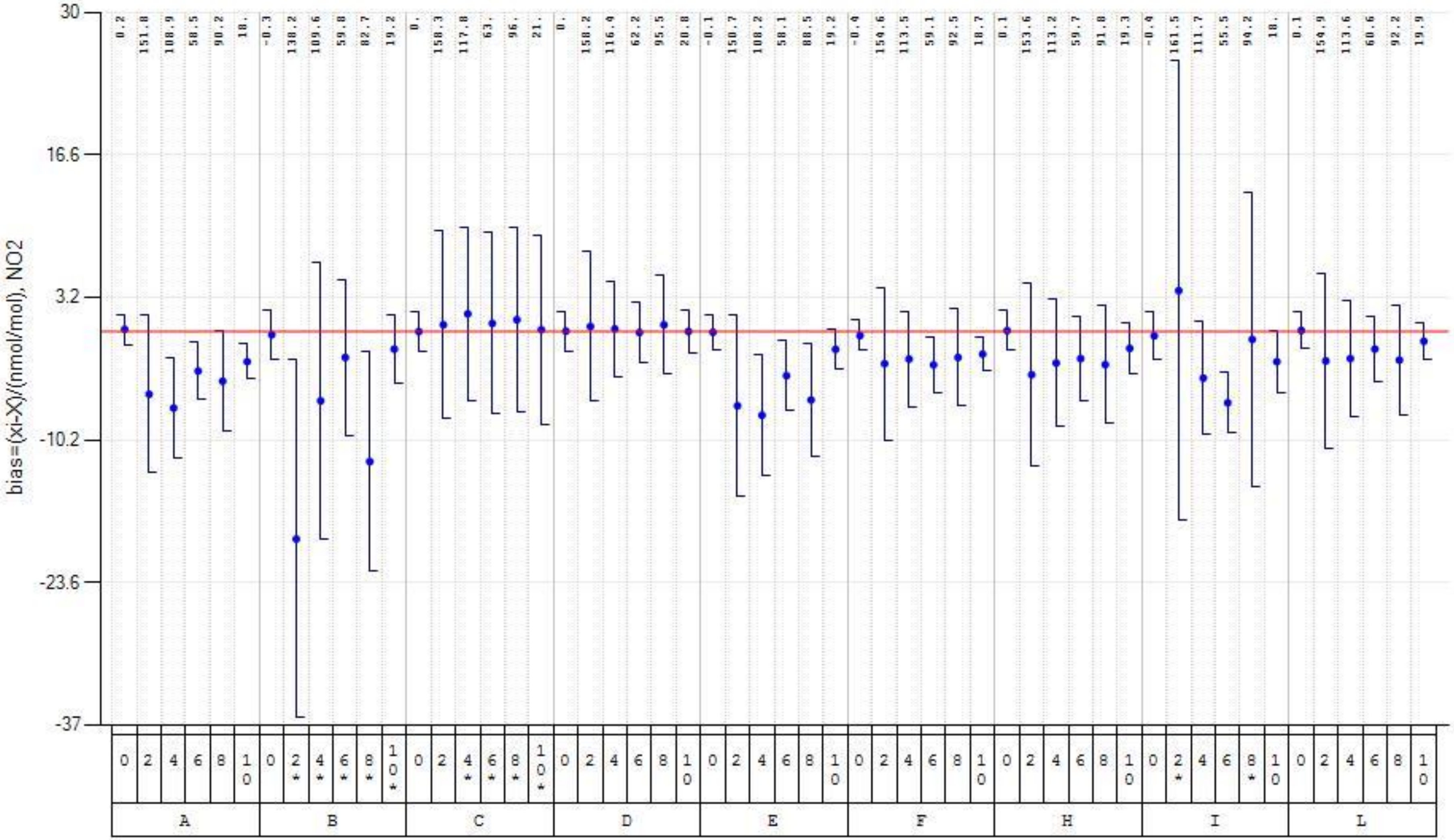

Figure 10: Bias of participant's NO_2 measurement results
Expanded uncertainty of bias is presented as an error bar for NO_2 run numbers 0, 2, 4, 6, 8 and 10 (see Table 3). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants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

4. Performance characteristics of individual laboratories

Individual participant's bias was evaluated and is presented in Chapter 3.2 (Figure 6 to 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.

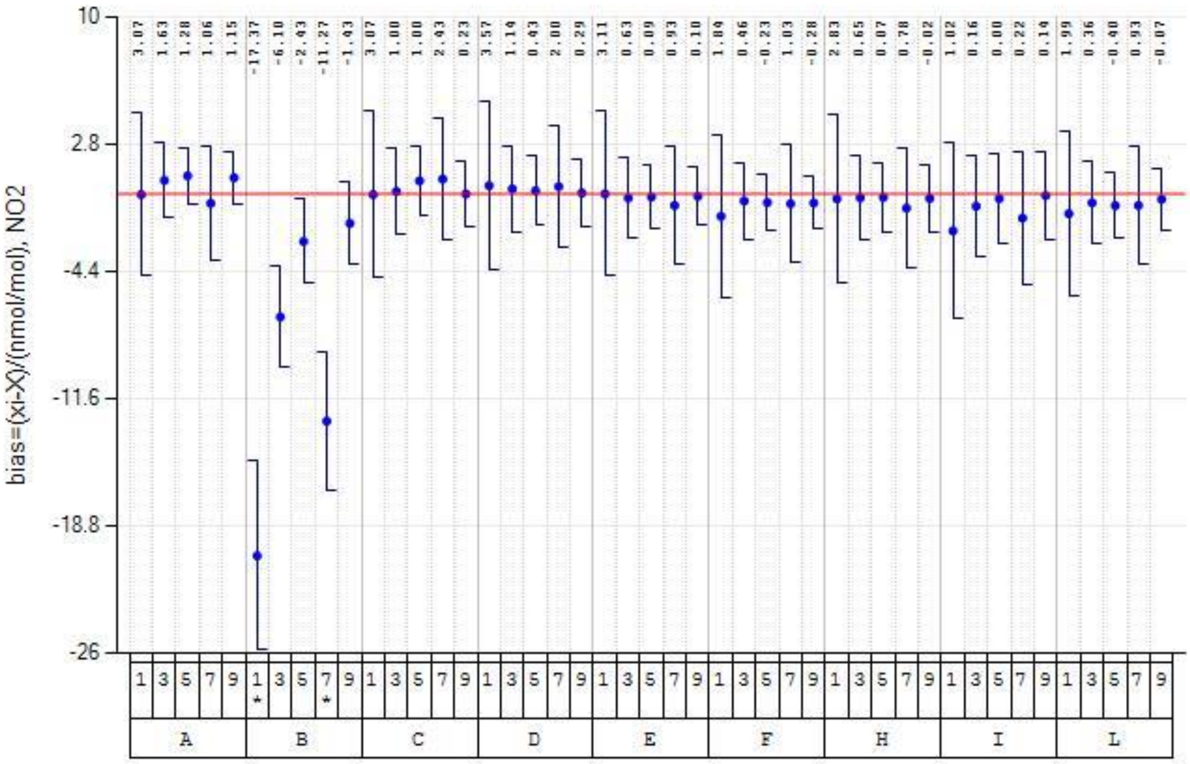

Figure 11: Bias of participant's NO_2 measurements for run numbers 1, 3, 5, 7 and 9
Within these test gas mixtures there is no GPT to produce NO_2 (see Table 3). For each evaluation the run number together with the participants rounded run average (nmol/mol) is given.

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

Since NO and NO_2 test gases were produced by GPT 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]:

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

Ideal value for α is 100%.

Lab code	NO_2 nmol/mol	α %
A	150	98.3
A	110	93.9
A	60	95.2
A	90	98.0
A	20	83.8
B	150	100.2
B	110	99.0
B	60	100.2
B	90	99.9
B	20	100.0
C	150	99.6
C	110	103.2
C	60	105.1
C	90	100.3
C	20	103.8
D	150	100.7
D	110	100.0
D	60	100.4
D	90	100.1
D	20	100.2
E	150	99.4
E	110	99.2
E	60	99.0
E	90	98.3
E	20	99.7
F	150	103.2
F	110	102.0
F	60	102.1
F	90	101.4
F	20	104.0

IE code	NO_2 nmol/mol	α %
G	150	99.5
G	110	100.6
G	60	100.0
G	90	100.5
G	20	100.2
H	150	100.9
H	110	101.4
H	60	101.2
H	90	99.3
H	20	100.6
I	150	95.6
I	110	98.6
I	60	100.1
I	90	99.6
I	20	95.5
L	150	101.0
L	110	99.0
L	60	100.2
L	90	99.1
L	20	100.3

Table 7: efficiency of NO_2-to-NO converters

The evaluation of Equation 3 for each participant at different concentration levels is given in Table 7.

5. Discussion

A decision diagram was developed for a general assessment of the quality of each result (Figure 12). It results in seven categories (1 to 7). The general comments for each category are the following:

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

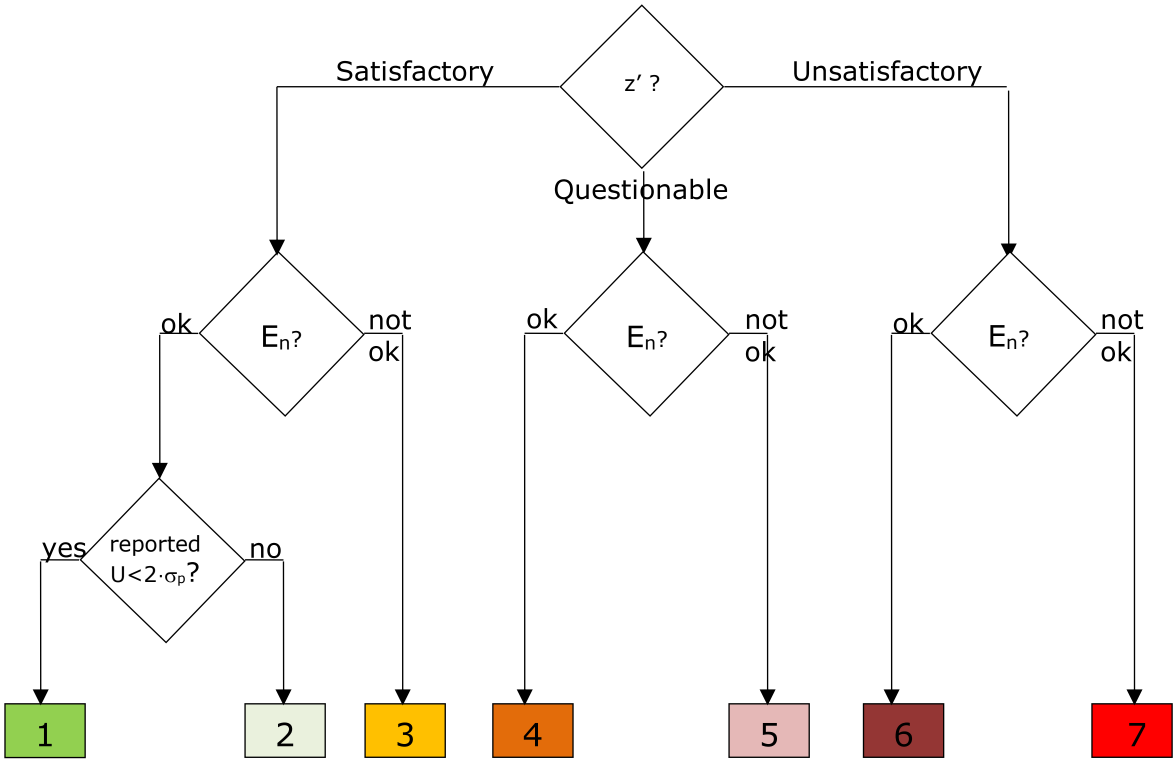

Figure 12: The decision diagram for general assessment of proficiency results.

The results of the IE were assigned to categories according to the diagram given in Figure 12 and are presented in the following Table 8.

	run num	Ref. conc. level	IE code								
			A	B	C	D	E	F	H	I	L
CO (µmol/mol)	0	0.003	1	2	2	1	1	3	1	1	1
	1	8.544	1	7	1	1	1	1	1	7	1
	2	3.556	1	4	1	1	1	1	1	7	1
	3	1.038	1	2	2	1	1	3	1	5	1
	4	5.062	1	4	1	1	1	3	1	7	1
	5	2.039	1	2	1	1	1	1	1	7	3
NO (nmol/mol)	0	0.09	1	1	1	1	1	1	1	1	1
	1	618.80	1	2	1	1	1	3	1	1	1
	2	464.08	1	2	3	1	1	5	1	1	1
	3	215.56	1	2	1	1	1	1	1	3	1
	4	100.72	1	2	2	1	1	5	1	5	1
	5	80.53	1	2	2	1	1	1	1	5	1
	6	18.78	1	1	2	1	1	5	1	3	1
	7	402.30	1	2	3	1	1	3	1	1	1
	8	309.51	1	2	1	1	1	3	1	3	1
	9	50.24	1	2	2	1	1	1	1	5	1
	10	29.67	1	2	2	1	1	3	1	5	1
NO2 (nmol/mol)	0	0.00	1	1	1	1	1	1	1	1	1
	2	157.66	1	7	1	1	1	1	1	2	1
	4	116.11	5	2	2	1	5	1	1	1	1
	6	62.23	3	2	2	1	3	3	1	5	1
	8	94.89	1	7	2	1	3	1	1	2	1
	10	20.83	3	2	2	1	1	3	1	1	1
O3 (nmol/mol)	0	0.02	1	1	1	1	1	1	1	1	1
	1	153.17	1	2	1	1	1	1	1	1	1
	2	123.80	1	2	1	1	1	1	1	1	1
	3	55.46	1	2	1	1	1	1	1	1	1
	4	91.53	1	2	1	1	1	1	1	1	1
	5	16.91	1	1	1	1	1	1	1	1	1
SO2 (nmol/mol)	0	0.10	1	1	1	1	1	1	1	1	1
	1	133.94	1	2	1	1	1	3	3	1	1
	2	72.36	1	2	1	1	1	3	1	1	1
	3	5.31	1	1	1	1	1	1	1	1	1
	4	31.18	3	1	1	1	1	1	1	1	1
	5	10.43	1	1	1	1	1	1	1	1	1

Table 8: 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) 75.6% of the results reported (see Table 9) by AQUILA laboratories fall into category '1' and are satisfactory both in terms of measured values and of evaluated uncertainties. Among the remaining results the majority presented satisfactory measured values, but the evaluated uncertainties were either too high, category '2' (10.8%), or too small, category '3' (7.3%). Two results were found to be questionable for the z' and valid for the E_n (0.6% in category '4'). Eleven results were found questionable for the z' and not valid for the E_n (3.5% in category '5'). Seven results were found to be unsatisfactory for both indicators (2.2% in category '7').

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
May-14	Ispra (IT)	81.8	15.2	1.1	0.0	0.7	0.0	1.1
Oct-15	Langen (DE)	73.2	23.9	0.7	1.4	0.0	0.7	0.0
Oct-15-(I)	Ispra (IT)	89.2	7.6	1.9	0.3	0.6	0.0	0.3
Oct-15-(II)	Ispra (IT)	75.6	10.8	7.3	0.6	3.5	0.0	2.2

Table 9: 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 (s_R) obtained at this (0) and previous IE, [20], [21], [22], [23], [24], [25], [33], [34], [35], [36], [37], [38], [39], [40], [41] and [43] is 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 the results in category '1' are lower than the last few years of exercises in Ispra. The increased number of values in category '5' and the highest number ever obtained of poor quality results in category '7' has to be underlined.

In this IE, 93.7% of the results in the z' evaluations (Table 10) were satisfactory, 13 results were found to be questionable (4.1%) and 7 unsatisfactory (2.2%).

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
May/14	Ispra (IT)	98.1	0.7	1.1
October/15	Langen (DE)	97.9	1.4	0.7
October/15_I	Ispra (IT)	98.8	0.9	0.3
October/15_II	Ispra (IT)	93.7	4.1	2.2

Table 10: z' scores summary

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

The relative reproducibility (R) limits, at the highest studied concentration levels, are 8.8% for SO_2, 14.8% for CO, 3.9% for O_3, for NO 4.9% and for NO_2 14.2% almost all within the objective derived from criteria imposed by the EC (σ_p see Table 4). NO_2 shows a deviation from the objectives already at the level of 50 ppb while CO deviates at 5.5ppm.
During this IE the performance of all NRL was generally satisfactory. Only laboratory I had an unsatisfactory performance for CO due to instrument problem occurred during the calibration.

7. References

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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 [13].

To foster its reference function ERLAP is regularly participating in key comparisons of the Gas Analysis Working Group within the framework of the 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 [6]. Reference gas mixtures were produced from the primary reference materials (produced and certified by NMi Van Swinden Laboratorium) by a dynamic dilution method using mass flow controllers [8]. 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 [26]. The photometer absorption cross section uncertainty (1.06%) was included in the uncertainty budget [27], [28].

The reference gas mixture and the calibration experiment evaluation were carried out using two computer applications, the "GUM WORKBENCH" [29] and "B-least" [30] 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 the NO_2-converter.
ERLAP's measurement results were validated in 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 takes into account ERLAP's measurement result (X) and its standard uncertainty (u_X) as given in Equation 4 [13].

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

Equation 4

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

In Table 11 all inputs for Equation 4 are given and all of ERLAP's measurement results are confirmed to be valid.

As a group evaluation, x* and 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	0.71	0.07	0.14	10	OK
NO _1	nmol/mol	618.80	3.54	620.33	7.69	10	OK
NO _2	nmol/mol	464.08	2.70	466.84	4.71	10	OK
NO _3	nmol/mol	215.56	1.41	214.96	4.13	10	OK
NO _4	nmol/mol	100.72	0.92	101.58	2.09	10	OK
NO _5	nmol/mol	80.53	0.85	79.58	1.84	10	OK
NO _6	nmol/mol	18.78	0.73	19.24	1.19	10	OK
NO _7	nmol/mol	402.30	2.37	400.38	7.92	10	OK
NO _8	nmol/mol	309.51	1.88	308.62	5.78	10	OK
NO _9	nmol/mol	50.24	0.77	49.27	1.41	10	OK
NO _10	nmol/mol	29.67	0.74	29.42	0.99	10	OK
NO2 _0	nmol/mol	0.00	0.71	-0.03	0.16	10	OK
NO2 _1	nmol/mol	3.10	2.30	2.70	0.65	10	OK
NO2 _2	nmol/mol	157.66	2.50	154.92	4.65	10	OK
NO2 _3	nmol/mol	0.85	1.05	0.65	0.50	10	OK
NO2 _4	nmol/mol	116.11	1.29	112.90	3.72	10	OK
NO2 _5	nmol/mol	0.25	0.78	0.12	0.54	10	OK
NO2 _6	nmol/mol	62.23	0.87	59.97	2.32	10	OK
NO2 _7	nmol/mol	1.58	1.60	1.04	0.69	10	OK
NO2 _8	nmol/mol	94.89	1.70	92.29	3.36	10	OK
NO2 _9	nmol/mol	0.23	0.74	0.09	0.25	10	OK
NO2 _10	nmol/mol	20.83	0.75	19.49	1.28	10	OK
CO _0	µmol/mol	0.00	0.01	0.02	0.03	10	OK
CO _1	µmol/mol	8.54	0.04	8.57	0.12	10	OK
CO _2	µmol/mol	3.56	0.02	3.59	0.05	10	OK
CO _3	µmol/mol	1.04	0.01	1.05	0.03	10	OK
CO _4	µmol/mol	5.06	0.03	5.11	0.06	10	OK
CO _5	µmol/mol	2.04	0.01	2.07	0.04	10	OK
O3 _0	nmol/mol	0.02	0.22	0.06	0.12	10	OK
O3 _1	nmol/mol	153.17	1.10	151.82	1.49	10	OK
O3 _2	nmol/mol	123.80	0.89	123.36	0.85	10	OK
O3 _3	nmol/mol	55.46	0.40	55.55	0.32	10	OK
O3 _4	nmol/mol	91.53	0.66	91.39	0.55	10	OK
O3 _5	nmol/mol	16.91	0.23	17.07	0.46	10	OK
SO2 _0	nmol/mol	0.10	0.50	0.07	0.19	10	OK
SO2 _1	nmol/mol	133.94	0.96	132.48	3.50	10	OK
SO2 _2	nmol/mol	72.36	0.67	71.63	2.06	10	OK
SO2 _3	nmol/mol	5.31	0.51	5.12	0.29	10	OK
SO2 _4	nmol/mol	31.18	0.54	30.86	1.00	10	OK
SO2 _5	nmol/mol	10.43	0.51	10.16	0.40	10	OK

Table 11: validation of assigned values (X)
In 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 these measurements, average and standard deviation were calculated. The uncertainty of test gas, due to lack of homogeneity, was also calculated as the sum of the squares of these average and standard deviations.

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

The upper and lower limits of bias due to homogeneity were evaluated as being 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

This annex reports the participant's results, presented both in tables and in graphs. For all mixture concentration that is generated (run), participants were asked to report three results each representing 30 minutes measurement (x_{ij}).
This annex presents the reported data and their combined uncertainty $u(x_i)$ and expanded uncertainty $U(x_i)$) expressed in mol/mol units.
For all of the runs except concentration levels 0, the average (x_i) and the standard deviation (s_i) of each participant are also presented.
The assigned value is indicated in 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	L
xi, 1	0.20	0.00	-0.40	0.03	-0.15	0.26	0.10	0.16	1.01	0.00
u(xi)	0.02	0.78	0.58	0.58	0.18	0.00	0.50	0.70	0.65	0.43
U(xi)	0.04	1.56	1.15	1.20	0.36	0.01	1.01	1.40	1.30	0.86

Table 12: Reported values for SO2 run 0

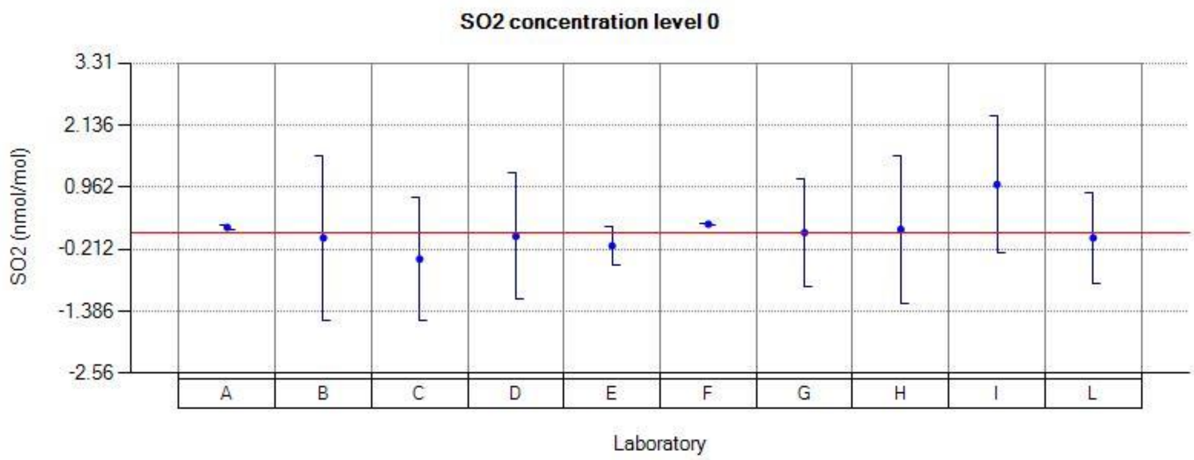

Figure 13: Reported values for SO_2 run 0

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	129.50	136.30	131.60	131.20	128.85	136.87	133.77	125.77	132.60	133.14
xi, 2	129.60	136.60	132.30	132.60	129.21	137.44	134.00	126.22	133.10	133.95
xi, 3	129.80	136.70	132.40		129.36	138.02	134.05	127.04	132.90	134.05
xi	129.63	136.53	132.10	131.90	129.14	137.44	133.94	126.34	132.86	133.71
si	0.15	0.20	0.43	0.99	0.26	0.57	0.14	0.64	0.25	0.49
u(xi)	2.33	5.46	1.41	1.28	2.24	1.15	0.87	2.85	2.00	1.31
U(xi)	4.66	10.92	2.82	2.60	4.48	2.30	1.75	5.69	4.00	2.62

Table 13: Reported values for SO_2 run 1

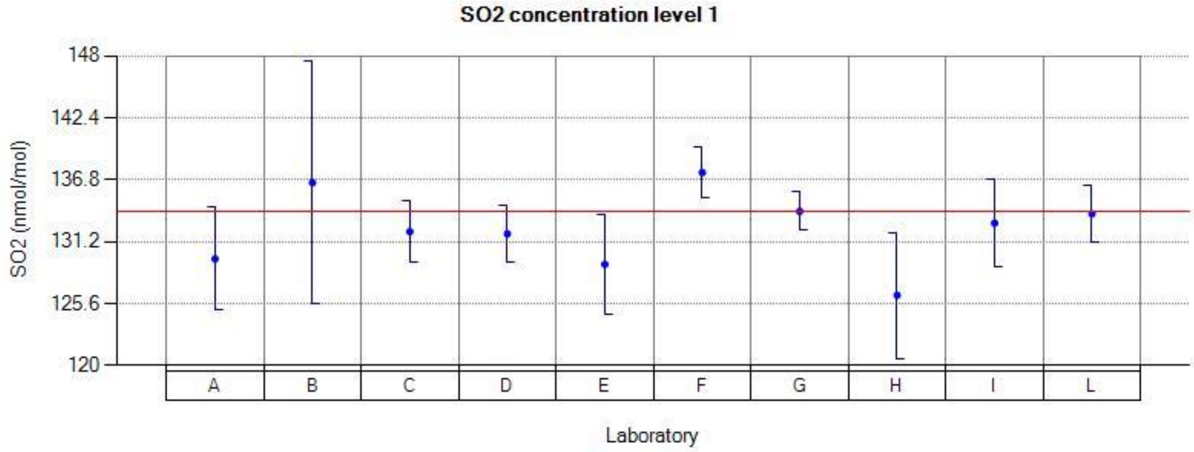

Figure 14: Reported values for SO_2 run 1

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	68.50	73.80	71.10	71.60	69.75	74.59	72.33	68.70	72.85	72.16
xi, 2	69.70	73.80	71.20	71.60	69.83	74.32	72.39	68.74	72.77	72.37
xi, 3	70.20	73.90	71.20		70.00	74.45	72.37	68.79	71.90	71.96
xi	69.46	73.83	71.16	71.60	69.86	74.45	72.36	68.74	72.50	72.16
si	0.87	0.05	0.05	0.00	0.12	0.13	0.03	0.04	0.52	0.20
u(xi)	1.25	3.07	0.81	0.85	1.21	0.60	0.64	1.71	1.15	0.71
U(xi)	2.50	6.14	1.62	1.70	2.43	1.20	1.27	3.43	2.30	1.42

Table 14: Reported values for SO_2 run 2

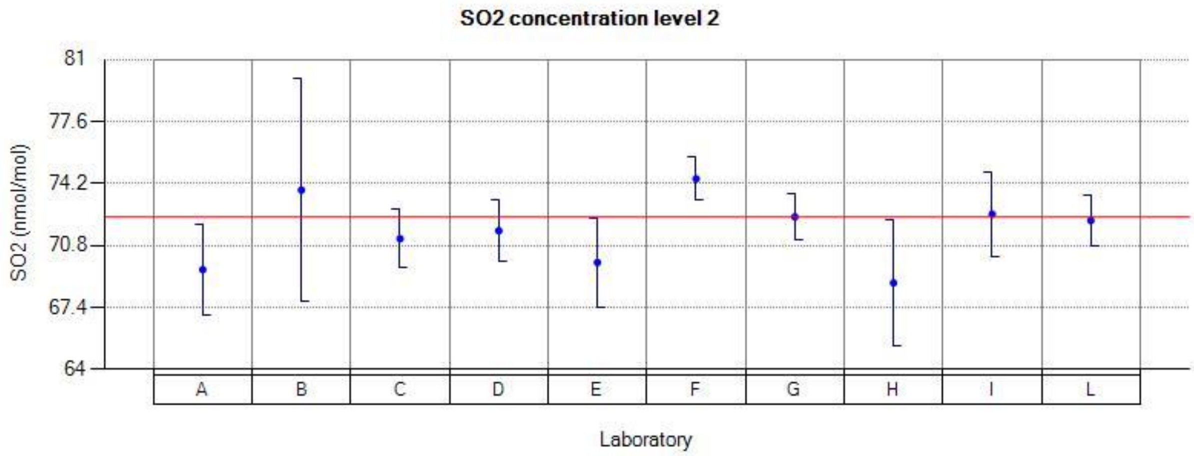

Figure 15: Reported values for SO_2 run 2

values	A	B	C	D	E	F	G	H	I	L
	laboratories									
xi, 1	4.85	5.30	4.70	5.32	5.02	5.12	5.31	5.16	6.31	4.94
xi, 2	4.90	5.40	4.60	5.23	5.00	5.21	5.31	5.15	6.03	4.74
xi, 3	4.90	5.30	4.60		5.00	5.19	5.30	5.09	5.99	4.64
xi	4.88	5.33	4.63	5.27	5.00	5.17	5.30	5.13	6.11	4.77
si	0.02	0.05	0.05	0.06	0.01	0.04	0.00	0.03	0.17	0.15
u(xi)	0.11	0.84	0.77	0.58	0.18	0.05	0.51	0.28	0.65	0.43
U(xi)	0.22	1.68	1.54	1.20	0.36	0.10	1.01	0.56	1.30	0.86

Table 15: Reported values for SO_2 run 3

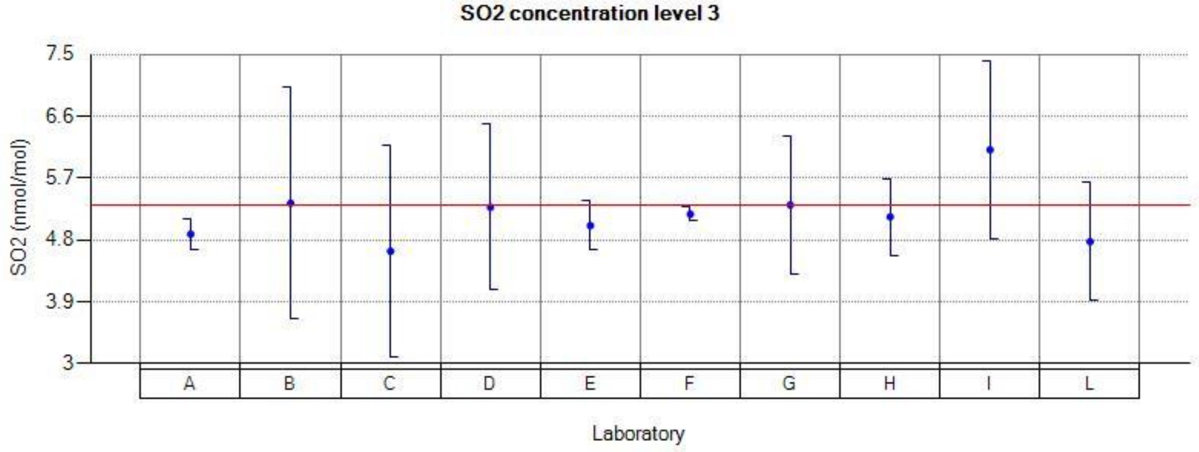

Figure 16: Reported values for SO_2 run 3

values	A	B	C	D	E	F	G	H	I	L
	laboratories									
xi, 1	29.30	31.80	30.30	30.80	30.46	31.74	31.15	29.73	32.13	30.84
xi, 2	29.50	31.80	30.30	30.90	30.46	31.64	31.19	29.78	31.80	30.94
xi, 3	29.50	31.80	30.30		30.45	31.77	31.20	29.77	32.45	31.14
xi	29.43	31.80	30.30	30.85	30.45	31.71	31.18	29.76	32.12	30.97
si	0.11	0.00	0.00	0.07	0.00	0.06	0.02	0.02	0.32	0.15
u(xi)	0.53	1.55	0.67	0.64	0.53	0.26	0.53	1.13	0.75	0.43
U(xi)	1.06	3.10	1.34	1.30	1.06	0.52	1.07	2.26	1.50	0.86

Table 16: Reported values for SO_2 run 4

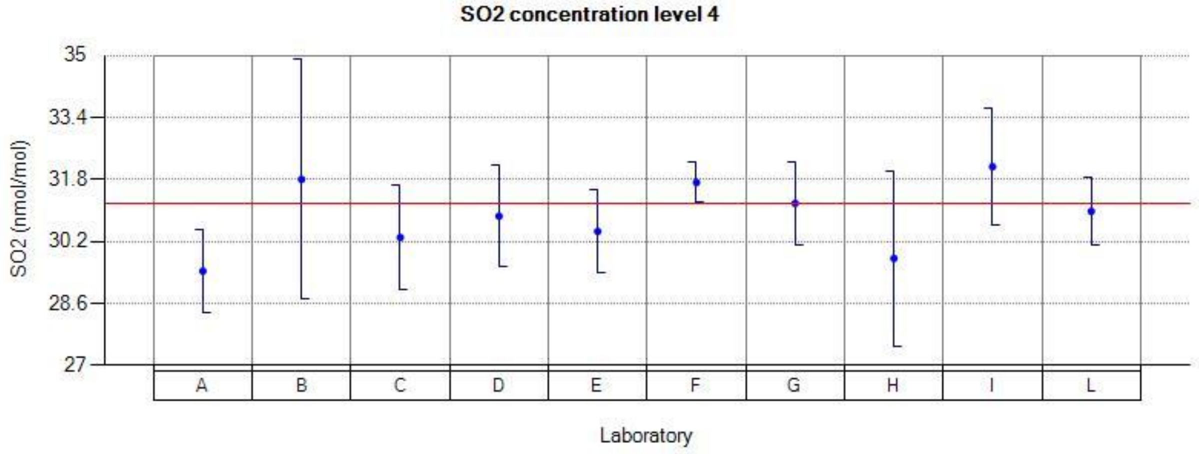

Figure 17: Reported values for SO_2 run 4

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	9.70	10.50	9.70	10.40	9.99	10.31	10.46	9.97	11.70	9.98
xi, 2	9.75	10.50	9.70	10.34	10.02	10.26	10.43	9.93	11.49	9.98
xi, 3	9.85	10.50	9.70		9.96	10.25	10.39	9.94	11.30	9.68
xi	9.76	10.50	9.70	10.37	9.99	10.27	10.42	9.94	11.49	9.88
si	0.07	0.00	0.00	0.04	0.03	0.03	0.03	0.02	0.20	0.17
u(xi)	0.16	0.93	0.74	0.59	0.18	0.08	0.51	0.51	0.65	0.43
U(xi)	0.32	1.86	1.48	1.20	0.37	0.16	1.02	1.01	1.30	0.86

Table 17: Reported values for SO2 run 5

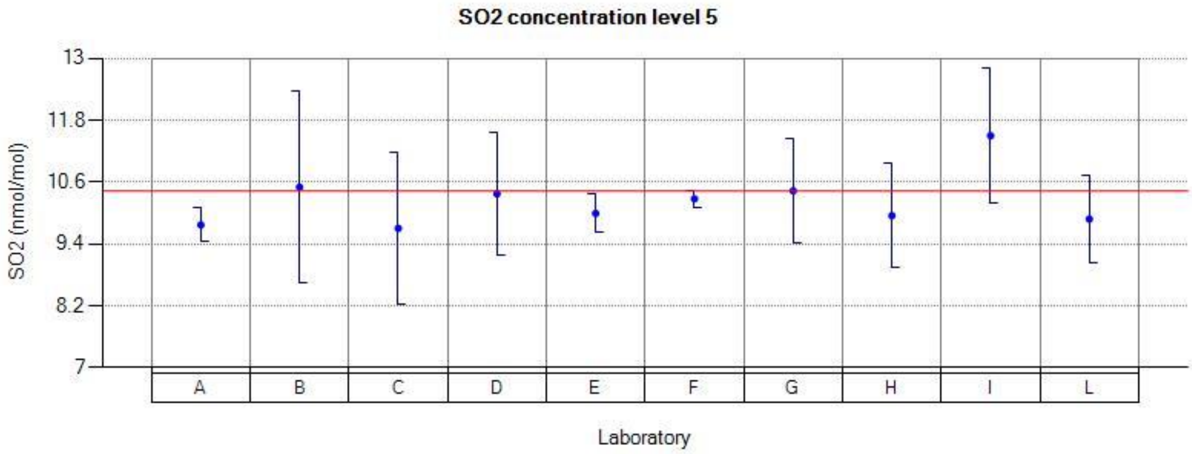

Figure 18: Reported values for SO_2 run 5

Reported values for CO

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	0.015	0.000	-0.050	0.005	0.041	0.057	0.003	0.035	0.052	-0.001
u(xi)	0.001	0.234	0.120	0.017	0.030	0.001	0.009	0.061	0.060	0.049
U(xi)	0.002	0.468	0.230	0.035	0.060	0.002	0.017	0.122	0.120	0.098

Table 18: Reported values for CO run 0

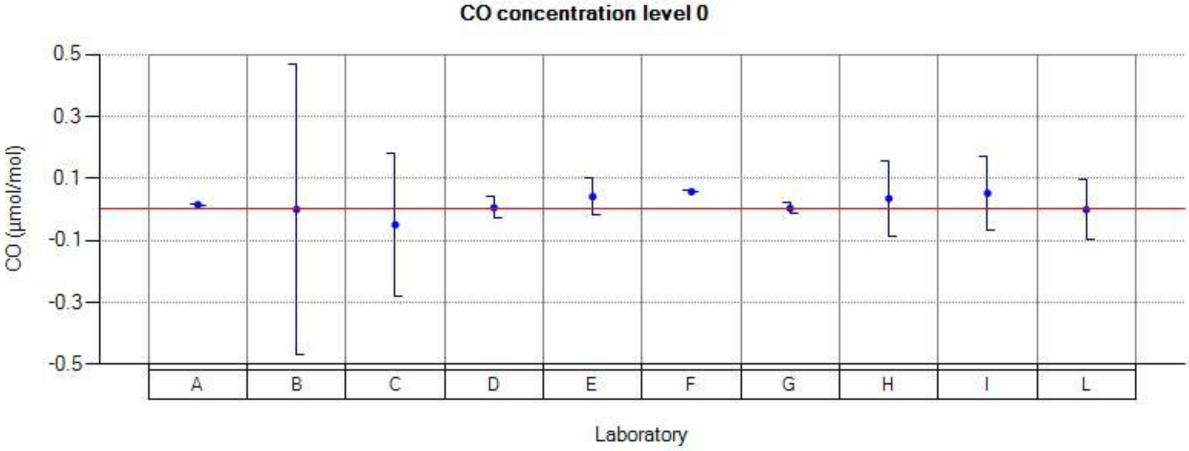

Figure 19: Reported values for CO run 0

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	8.680	9.640	8.500	8.515	8.476	8.700	8.533	8.605	4.695	8.502
xi, 2	8.705	9.640	8.530	8.565	8.473	8.717	8.546	8.605	4.704	8.496
xi, 3	8.755	9.640	8.550		8.469	8.717	8.554	8.607	4.689	8.503
xi	8.713	9.640	8.527	8.540	8.473	8.711	8.544	8.606	4.696	8.500
si	0.038	0.000	0.025	0.035	0.004	0.010	0.011	0.001	0.008	0.004
u(xi)	0.157	0.500	0.040	0.041	0.166	0.100	0.034	0.197	0.152	0.173
U(xi)	0.314	1.000	0.090	0.082	0.332	0.200	0.069	0.394	0.304	0.347

Table 19: Reported values for CO run 1

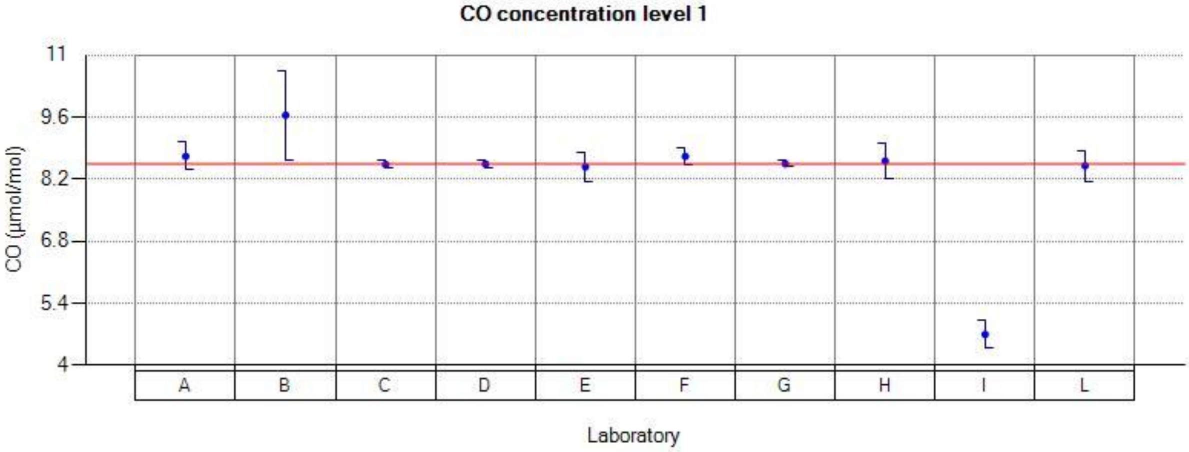

Figure 20: Reported values for CO run 1

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	3.625	4.010	3.560	3.565	3.581	3.613	3.556	3.567	2.008	3.704
xi, 2	3.635	4.001	3.560	3.570	3.577	3.633	3.556	3.567	2.012	3.701
xi, 3	3.645	4.001	3.560		3.575	3.620	3.556	3.565	2.023	3.702
xi	3.635	4.004	3.560	3.568	3.578	3.622	3.556	3.566	2.014	3.702
si	0.010	0.005	0.000	0.004	0.003	0.010	0.000	0.001	0.008	0.002
u(xi)	0.066	0.294	0.090	0.023	0.070	0.042	0.016	0.097	0.164	0.075
U(xi)	0.132	0.588	0.190	0.046	0.141	0.084	0.032	0.194	0.328	0.151

Table 20: Reported values for CO run 2

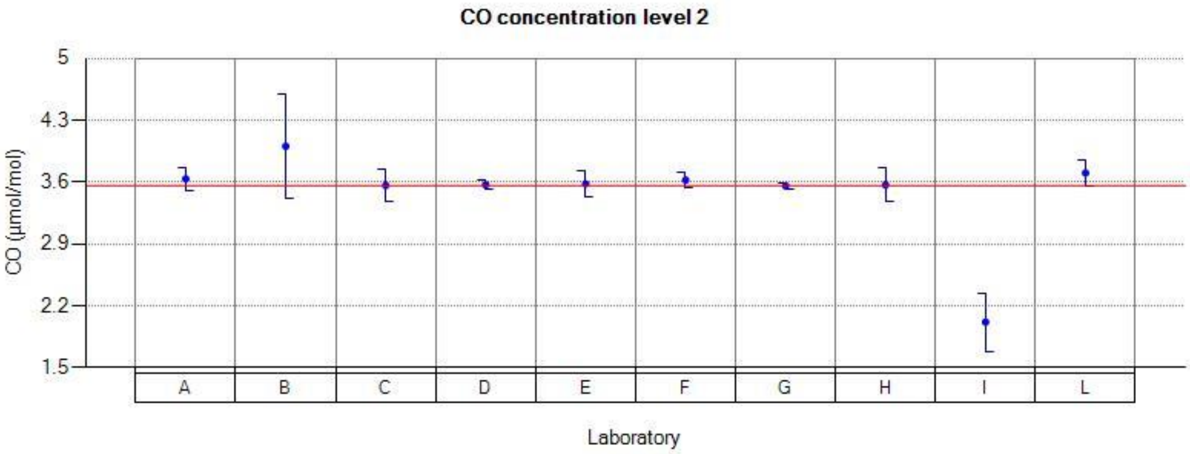

Figure 21: Reported values for CO run 2

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	1.055	1.180	1.030	1.043	1.039	1.083	1.039	1.043	0.761	1.125
xi, 2	1.058	1.180	1.030	1.044	1.042	1.087	1.038	1.042	0.757	1.125
xi, 3	1.075	1.180	1.020		1.039	1.093	1.037	1.045	0.752	1.126
xi	1.063	1.180	1.027	1.043	1.040	1.088	1.038	1.043	0.757	1.125
si	0.011	0.000	0.006	0.001	0.002	0.005	0.001	0.002	0.005	0.001
u(xi)	0.019	0.238	0.130	0.018	0.035	0.013	0.009	0.058	0.110	0.049
U(xi)	0.038	0.476	0.260	0.036	0.070	0.026	0.018	0.116	0.220	0.098

Table 21: Reported values for CO run 3

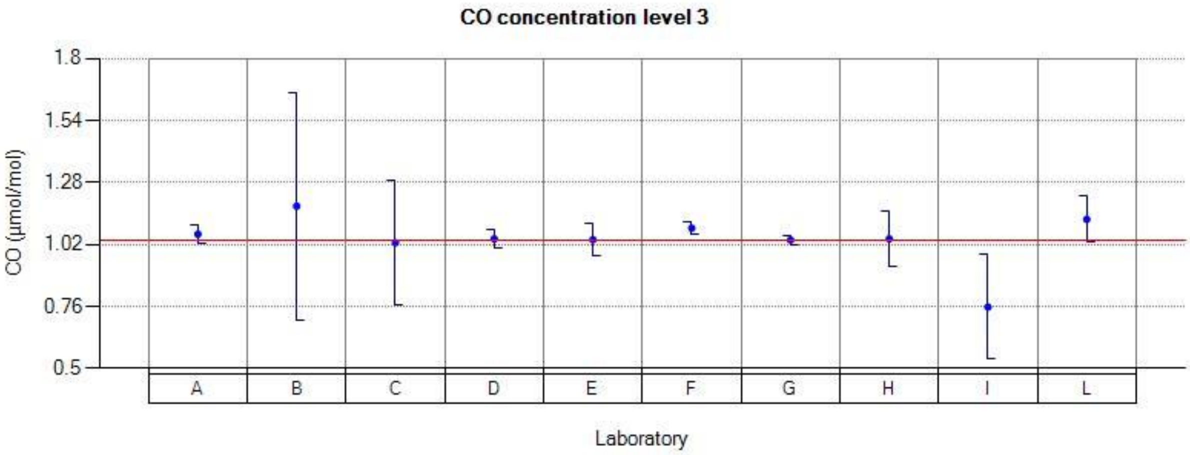

Figure 22: Reported values for CO run 3

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	5.155	5.700	5.090	5.078	5.060	5.200	5.061	5.129	2.884	5.119
xi, 2	5.165	5.700	5.090	5.088	5.064	5.213	5.063	5.128	2.882	5.113
xi, 3	5.175	5.700	5.090		5.069	5.227	5.062	5.128	2.879	5.097
xi	5.165	5.700	5.090	5.083	5.064	5.213	5.062	5.128	2.882	5.110
si	0.010	0.000	0.000	0.007	0.005	0.014	0.001	0.001	0.003	0.011
u(xi)	0.093	0.348	0.070	0.028	0.099	0.060	0.021	0.124	0.124	0.104
U(xi)	0.186	0.696	0.140	0.056	0.199	0.120	0.043	0.248	0.248	0.208

Table 22: Reported values for CO run 4

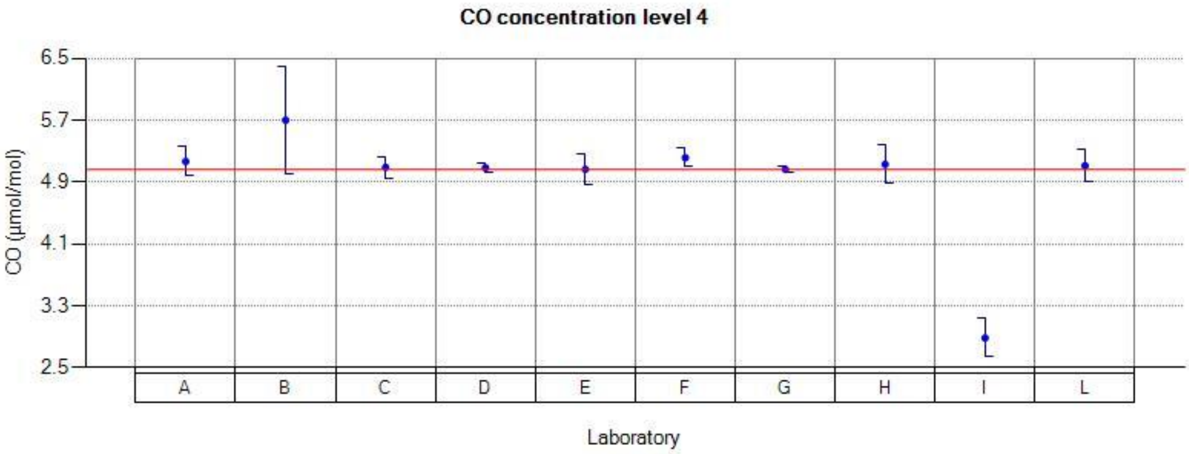

Figure 23: Reported values for CO run 4

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	2.055	2.310	2.060	2.070	2.074	2.097	2.039	2.042	1.253	2.168
xi, 2	2.065	2.310	2.060	2.074	2.071	2.100	2.039	2.038	1.251	2.166
xi, 3	2.070	2.310	2.050		2.073	2.073	2.038	2.040	1.254	2.180
xi	2.063	2.310	2.057	2.072	2.073	2.090	2.039	2.040	1.253	2.171
si	0.008	0.000	0.006	0.003	0.002	0.015	0.001	0.002	0.002	0.008
u(xi)	0.037	0.254	0.120	0.020	0.041	0.025	0.011	0.076	0.092	0.049
U(xi)	0.074	0.508	0.230	0.040	0.083	0.050	0.023	0.152	0.184	0.098

Table 23: Reported values for CO run 5

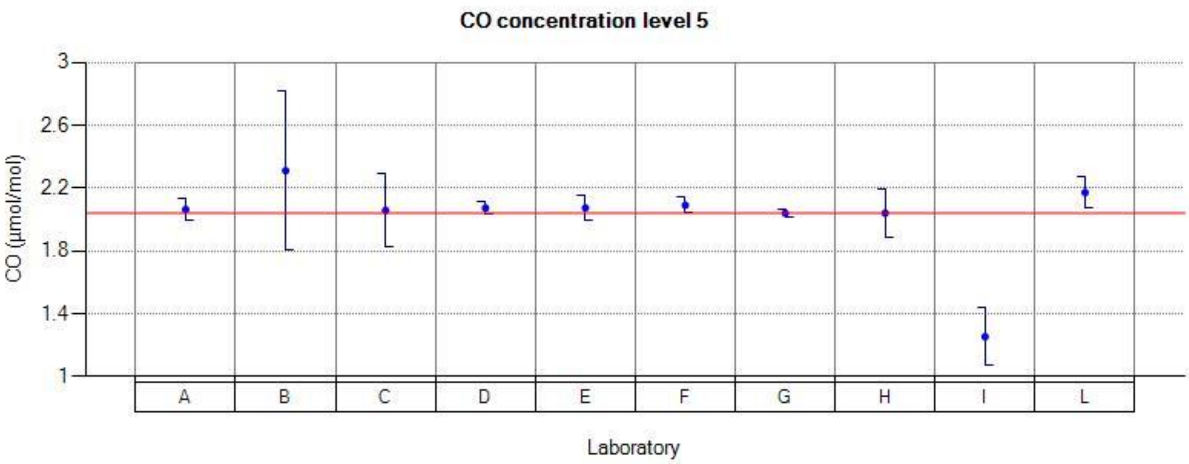

Figure 24: Reported values for CO run 5

Reported values for O_3

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	0.20	-0.10	0.10	0.03	0.17	0.01	0.02	0.16	-0.60	0.10
u(xi)	0.02	0.94	0.58	0.85	0.51	0.75	0.22	0.60	1.00	0.60
U(xi)	0.04	1.88	1.15	1.70	1.02	1.50	0.44	1.21	2.00	1.20

Table 24: Reported values for O_3 run 0

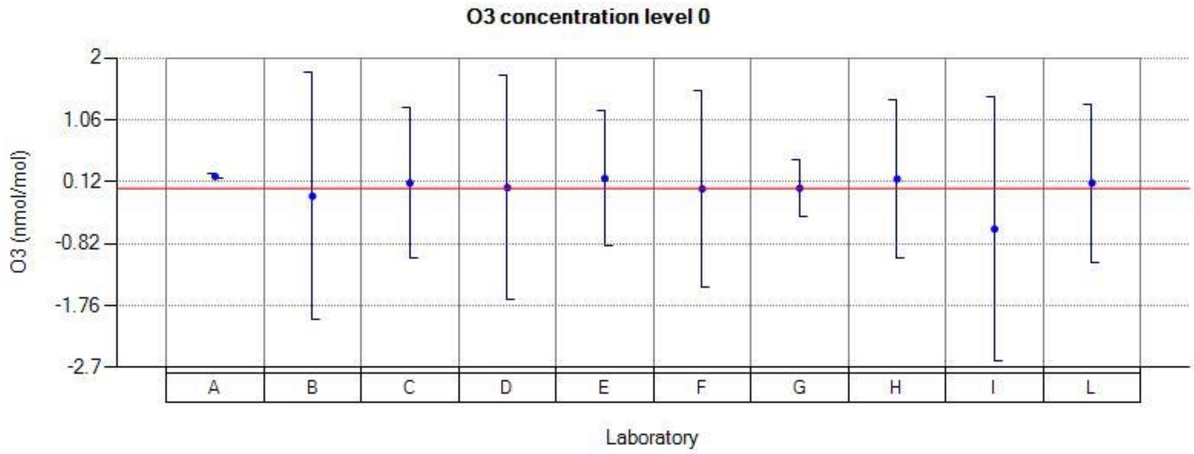

Figure 25: Reported values for O_3 run 0

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	149.40	150.12	152.30	149.10	150.96	151.78	152.80	151.26	155.63	150.00
xi, 2	150.25	151.08	153.40	151.60	151.48	153.04	153.27	151.98	155.93	151.20
xi, 3	150.75	151.39	153.60		151.66	152.77	153.43	151.95	156.27	151.60
xi	150.13	150.86	153.10	150.35	151.36	152.53	153.16	151.73	155.94	150.93
si	0.68	0.66	0.70	1.76	0.36	0.66	0.32	0.40	0.32	0.83
u(xi)	2.71	6.88	1.91	1.92	2.26	2.38	1.00	3.42	2.60	3.00
U(xi)	5.42	13.76	3.83	3.80	4.51	4.76	1.99	6.83	5.20	6.00

Table 25: Reported values for O_3 run 1

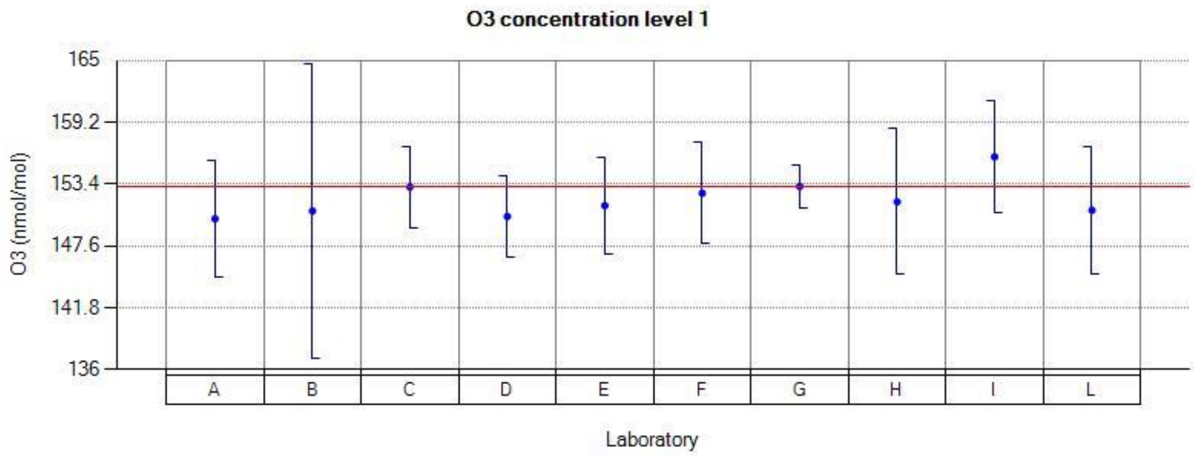

Figure 26: Reported values for O_3 run 1

values	laboratories									
	A	B	C	D	E	F	G	H	I	L
xi, 1	121.80	122.62	123.30	122.60	122.56	124.53	123.66	123.20	125.63	122.40
xi, 2	122.20	122.94	124.10	123.50	122.83	124.85	123.83	123.56	126.26	122.90
xi, 3	122.55	123.04	124.20		122.88	124.58	123.90	123.60	126.26	123.10
xi	122.18	122.86	123.86	123.05	122.75	124.65	123.79	123.45	126.05	122.80
si	0.37	0.21	0.49	0.63	0.17	0.17	0.12	0.22	0.36	0.36
u(xi)	2.20	5.63	1.62	1.64	1.85	2.06	0.80	2.78	2.15	2.44
U(xi)	4.40	11.26	3.24	3.30	3.70	4.12	1.61	5.57	4.30	4.88

Table 26: Reported values for O_3 run 2

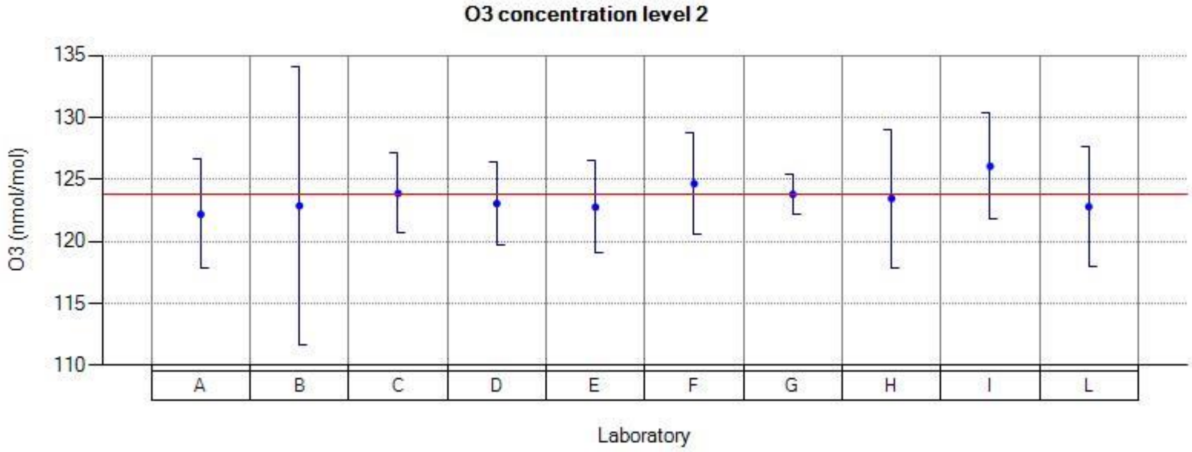

Figure 27: Reported values for O_3 run 2

values	laboratories									
	A	B	C	D	E	F	G	H	I	L
xi, 1	54.50	55.33	55.00	55.60	55.28	56.17	55.37	55.55	55.93	55.40
xi, 2	54.75	55.54	55.30	55.80	55.39	56.45	55.46	55.79	56.19	55.60
xi, 3	55.00	55.65	55.50		55.50	56.56	55.54	55.78	56.08	55.50
xi	54.75	55.50	55.26	55.70	55.39	56.39	55.45	55.70	56.06	55.50
si	0.25	0.16	0.25	0.14	0.11	0.20	0.08	0.13	0.13	0.10
u(xi)	0.98	2.68	1.23	1.06	0.94	1.35	0.37	1.48	1.20	1.10
U(xi)	1.96	5.36	2.45	2.10	1.88	2.70	0.73	2.96	2.40	2.20

Table 27: Reported values for O_3 run 3

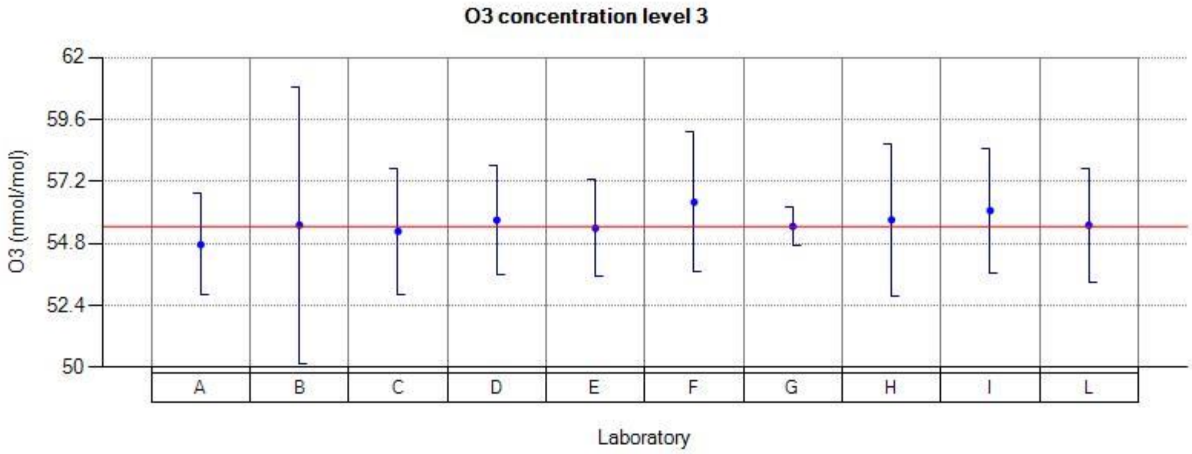

Figure 28: Reported values for O_3 run 3

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	90.25	91.09	90.80	91.00	90.69	92.54	91.42	91.15	93.23	90.50
xi, 2	90.50	91.30	91.70	91.90	91.01	92.73	91.57	91.55	93.37	91.00
xi, 3	90.55	91.51	91.80		91.10	92.91	91.61	91.57	93.53	90.90
xi	90.43	91.30	91.43	91.45	90.93	92.72	91.53	91.42	93.37	90.80
si	0.16	0.21	0.55	0.63	0.21	0.18	0.10	0.23	0.15	0.26
u(xi)	1.63	4.23	1.32	1.34	1.41	1.73	0.60	2.41	1.65	1.80
U(xi)	3.26	8.46	2.64	2.70	2.83	3.46	1.19	4.82	3.30	3.60

Table 28: Reported values for O_3 run 4

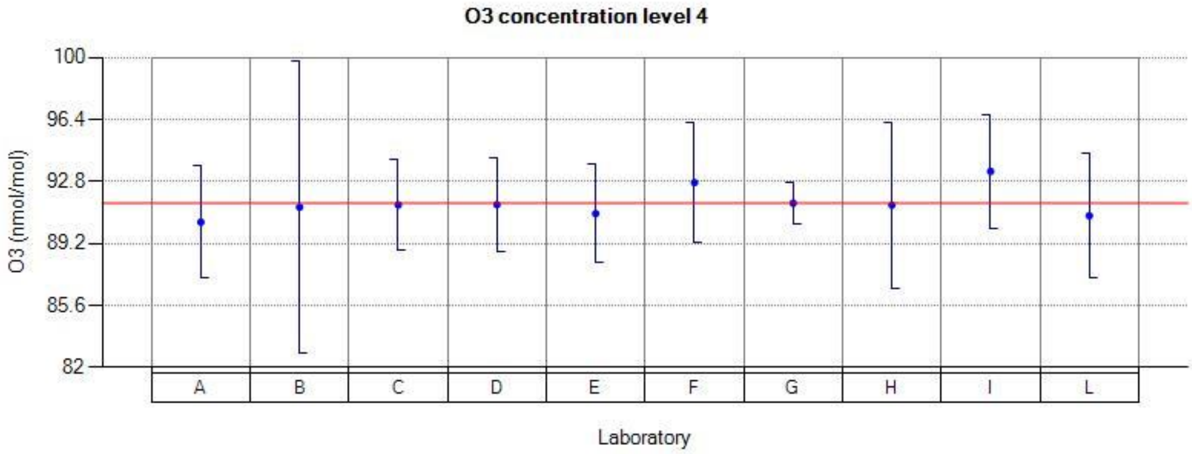

Figure 29: Reported values for O_3 run 4

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	16.50	17.13	16.30	17.10	17.28	17.59	16.93	17.33	16.43	17.50
xi, 2	16.65	17.24	16.50	17.20	17.25	17.65	16.92	17.37	16.66	17.60
xi, 3	16.80	17.24	16.50		17.26	17.57	16.89	17.36	16.46	17.50
xi	16.65	17.20	16.43	17.15	17.26	17.60	16.91	17.35	16.51	17.53
si	0.15	0.06	0.11	0.07	0.01	0.04	0.02	0.02	0.12	0.05
u(xi)	0.30	1.22	1.20	0.87	0.51	0.94	0.22	0.90	0.90	0.60
U(xi)	0.60	2.44	2.40	1.80	1.02	1.87	0.44	1.81	1.80	1.20

Table 29: Reported values for O_3 run 5.

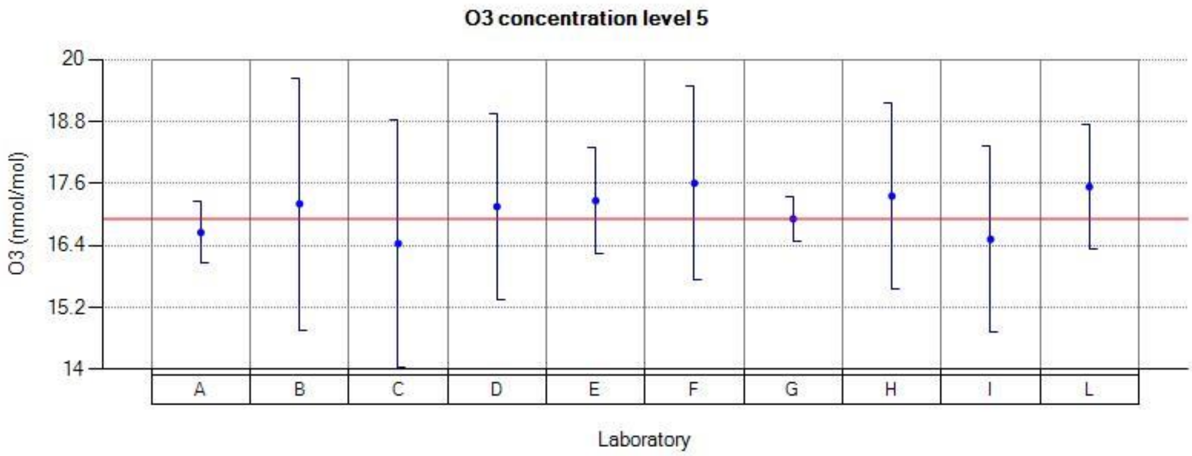

Figure 30: Reported values for O_3 run 5

Reported values for NO

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	0.20	0.30	0.00	0.01	-0.03	0.00	0.09	0.15	-0.20	0.20
u(xi)	0.02	0.90	0.58	0.58	0.45	0.01	0.71	0.60	0.61	0.40
U(xi)	0.04	1.80	1.15	1.20	0.91	0.02	1.42	1.20	1.30	0.80

Table 30: Reported values for NO run 0

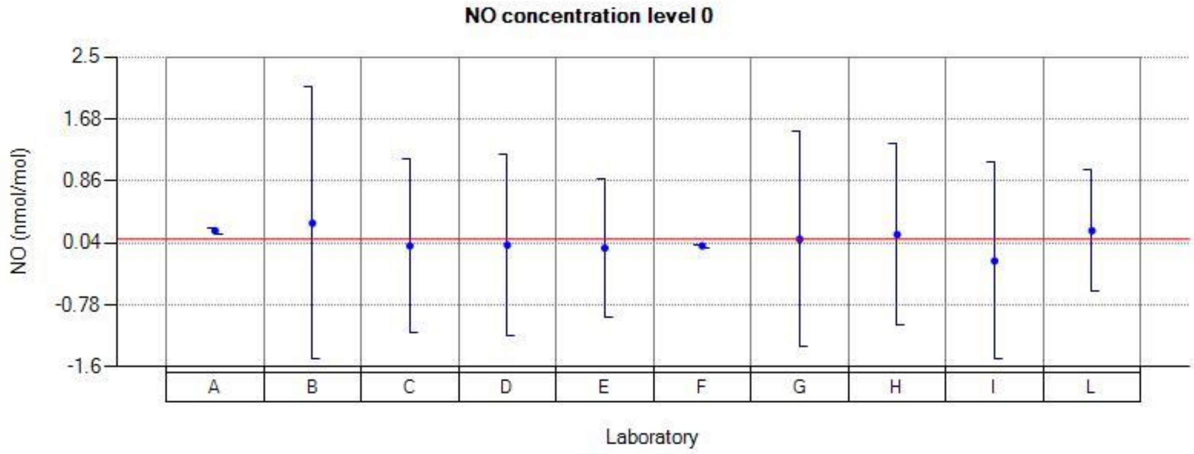

Figure 31: Reported values for NO run 0

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	611.50	626.80	609.20	616.90	615.86	636.35	618.65	619.03	633.82	621.29
xi, 2	612.60	627.40	610.50	618.90	616.55	637.23	618.95	618.53	634.21	621.99
xi, 3	613.20	627.90	610.80		616.88	638.71	618.81	619.45	634.11	622.78
xi	612.43	627.36	610.16	617.90	616.43	637.43	618.80	619.00	634.04	622.02
si	0.86	0.55	0.85	1.41	0.52	1.19	0.15	0.46	0.20	0.74
u(xi)	11.03	36.32	2.71	4.40	10.96	6.41	3.02	13.84	9.95	13.05
U(xi)	22.06	72.64	5.42	8.80	21.92	12.82	6.03	27.67	19.90	26.10

Table 31: Reported values for NO run 1

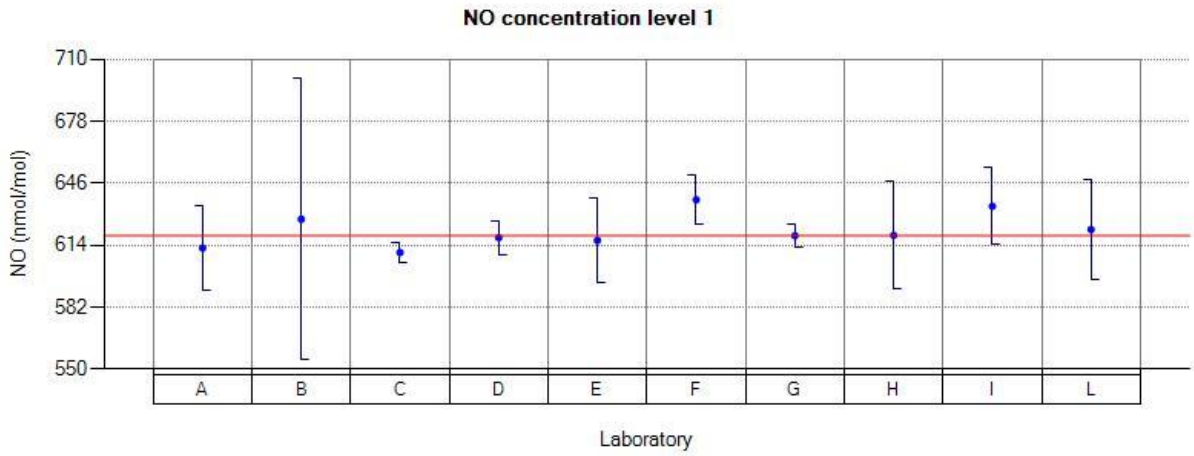

Figure 32: Reported values for NO run 1

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	462.20	472.70	457.00	465.40	467.42	489.93	464.73	470.08	468.60	469.95
xi, 2	461.90	472.20	455.30	464.00	466.20	489.23	464.00	469.43	466.39	468.86
xi, 3	460.80	471.80	455.00		466.96	488.65	463.52	469.16	465.01	468.56
xi	461.63	472.23	455.76	464.70	466.86	489.27	464.08	469.55	466.66	469.12
si	0.73	0.45	1.07	0.99	0.61	0.64	0.60	0.47	1.81	0.73
u(xi)	8.30	27.34	2.47	3.33	8.31	4.91	2.32	10.59	7.40	9.84
U(xi)	16.60	54.68	4.94	6.70	16.61	9.82	4.64	21.18	14.80	19.69

Table 32: Reported values for NO run 2

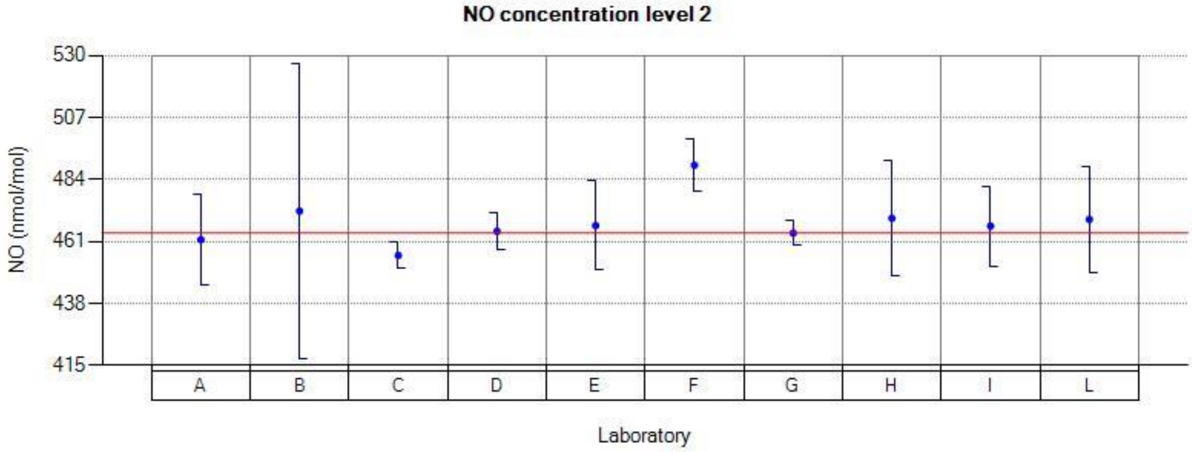

Figure 33: Reported values for NO run 2

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	214.60	219.30	209.80	216.10	211.29	219.80	215.24	214.05	206.05	216.85
xi, 2	214.90	219.50	210.50	216.60	212.11	221.10	215.52	214.05	206.15	216.75
xi, 3	215.00	219.50	210.00		212.26	221.48	215.92	214.68	206.06	216.85
xi	214.83	219.43	210.10	216.35	211.88	220.79	215.56	214.26	206.08	216.81
si	0.20	0.11	0.36	0.35	0.52	0.88	0.34	0.36	0.05	0.05
u(xi)	3.86	12.73	4.45	1.64	3.78	2.27	1.25	4.84	3.30	4.55
U(xi)	7.72	25.46	8.90	3.30	7.56	4.54	2.51	9.68	6.60	9.10

Table 33: Reported values for NO run 3

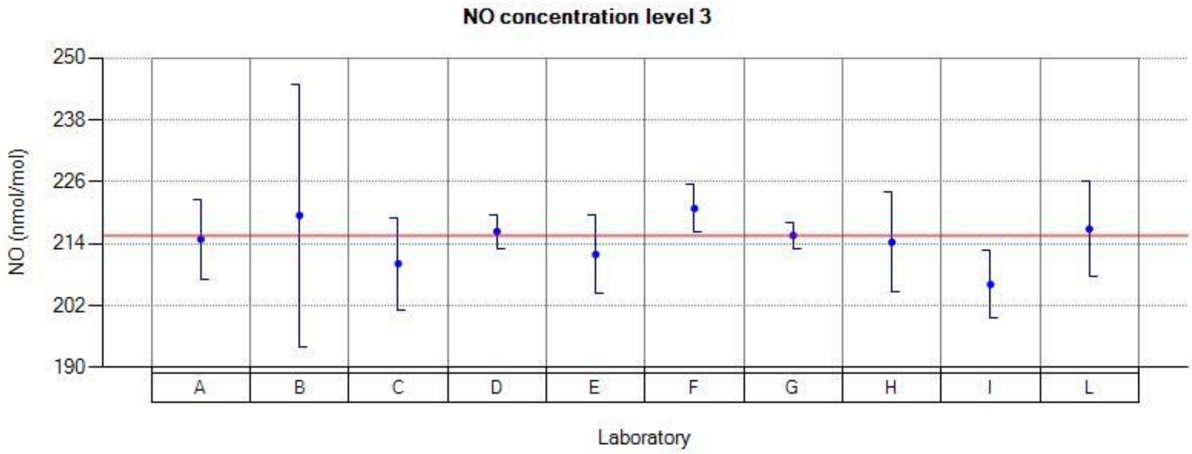

Figure 34: Reported values for NO run 3

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	100.80	102.90	97.30	100.90	103.02	108.96	100.89	103.68	94.15	102.95
xi, 2	100.70	102.70	97.00	100.30	102.84	109.45	100.71	103.60	93.11	102.45
xi, 3	100.35	102.60	96.70		102.66	108.89	100.55	103.37	92.89	102.15
xi	100.61	102.73	97.00	100.60	102.84	109.10	100.71	103.55	93.38	102.51
si	0.23	0.15	0.30	0.42	0.18	0.30	0.17	0.16	0.67	0.40
u(xi)	1.80	6.00	5.22	0.92	1.85	1.10	0.88	2.47	1.60	2.15
U(xi)	3.60	12.00	10.43	1.90	3.70	2.20	1.75	4.93	3.20	4.30

Table 34: Reported values for NO run 4

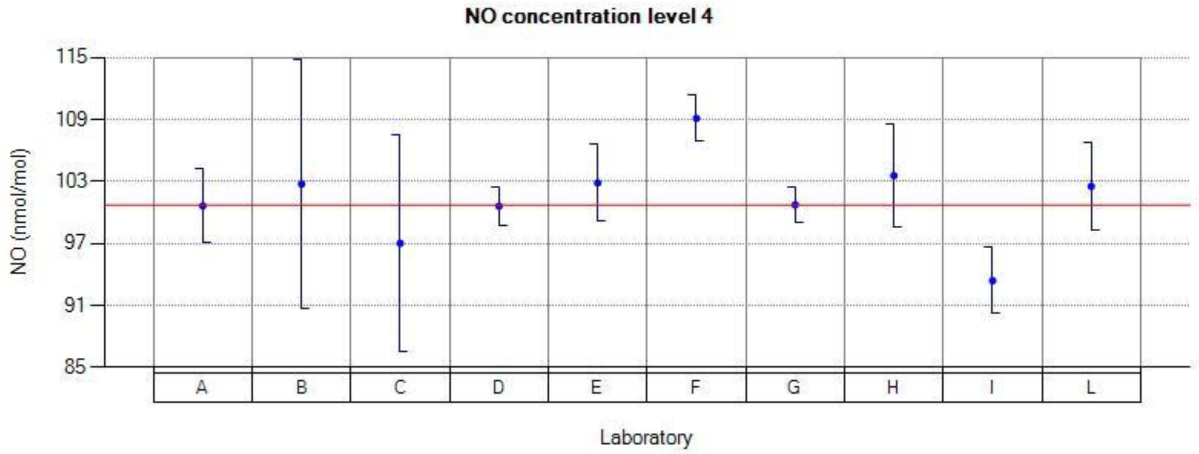

Figure 35: Reported values for NO run 4

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	78.70	81.50	76.50	80.15	78.21	80.81	80.22	79.18	71.82	80.35
xi, 2	78.95	81.90	77.00	80.50	78.47	81.26	80.63	79.51	72.01	80.75
xi, 3	79.00	82.00	77.00		78.54	81.76	80.73	79.59	72.13	81.15
xi	78.88	81.80	76.83	80.32	78.40	81.27	80.52	79.42	71.98	80.75
si	0.16	0.26	0.28	0.24	0.17	0.47	0.27	0.21	0.15	0.40
u(xi)	1.41	4.81	5.36	0.81	1.42	0.86	0.81	1.89	1.35	1.69
U(xi)	2.82	9.62	10.72	1.60	2.85	1.72	1.63	3.78	2.70	3.39

Table 35: Reported values for NO run 5

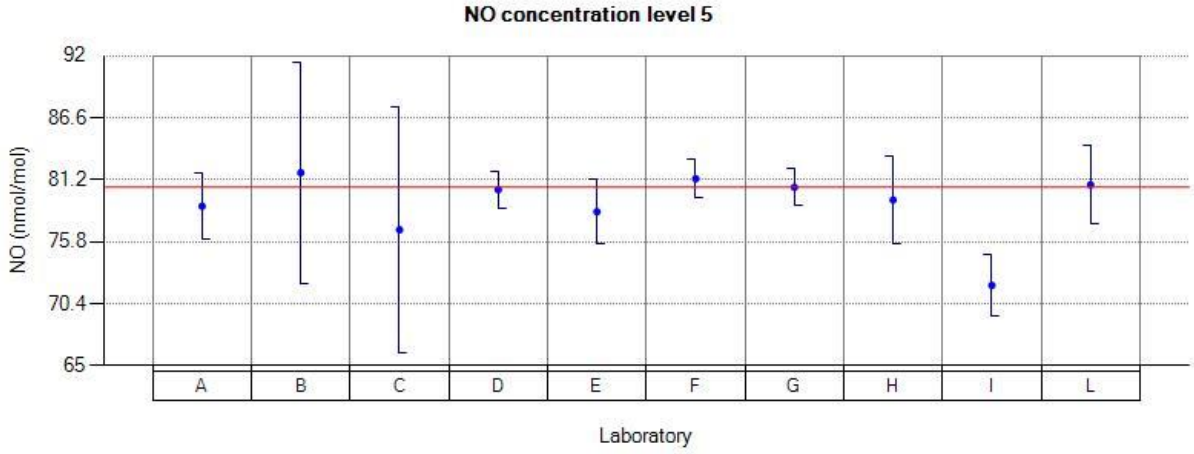

Figure 36: Reported values for NO run 5

values	laboratories									
	A	B	C	D	E	F	G	H	I	L
xi, 1	18.90	19.60	18.00	18.86	19.77	22.72	18.88	20.77	16.54	19.91
xi, 2	18.75	19.40	18.00	18.65	19.97	23.01	18.73	20.58	16.46	19.71
xi, 3	18.65	19.40	18.00		19.68	23.50	18.72	20.71	16.34	19.91
xi	18.76	19.46	18.00	18.75	19.80	23.07	18.77	20.68	16.44	19.84
si	0.12	0.11	0.00	0.14	0.14	0.39	0.09	0.09	0.10	0.11
u(xi)	0.34	1.43	5.79	0.59	0.58	0.32	0.72	1.02	0.70	0.42
U(xi)	0.68	2.86	11.57	1.20	1.17	0.64	1.45	2.03	1.40	0.84

Table 36: Reported values for NO run 6

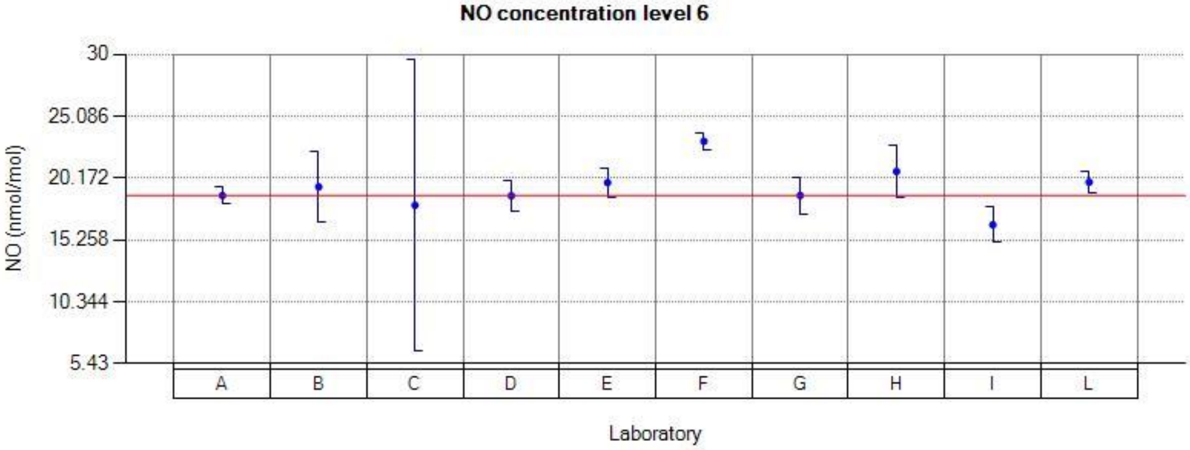

Figure 37: Reported values for NO run 6

values	laboratories									
	A	B	C	D	E	F	G	H	I	L
xi, 1	396.50	408.40	392.70	403.10	393.84	413.24	402.01	399.60	389.00	402.84
xi, 2	397.00	408.70	393.70	403.20	394.25	413.87	402.44	400.54	390.13	402.74
xi, 3	397.50	408.90	394.00		394.08	414.31	402.45	400.09	390.29	403.34
xi	397.00	408.66	393.46	403.15	394.05	413.80	402.30	400.07	389.80	402.97
si	0.50	0.25	0.68	0.07	0.20	0.53	0.25	0.47	0.70	0.32
u(xi)	7.15	23.66	2.43	2.90	7.01	4.15	2.04	9.02	6.20	8.45
U(xi)	14.30	47.32	4.86	5.80	14.02	8.30	4.09	18.04	12.40	16.91

Table 37: Reported values for NO run 7

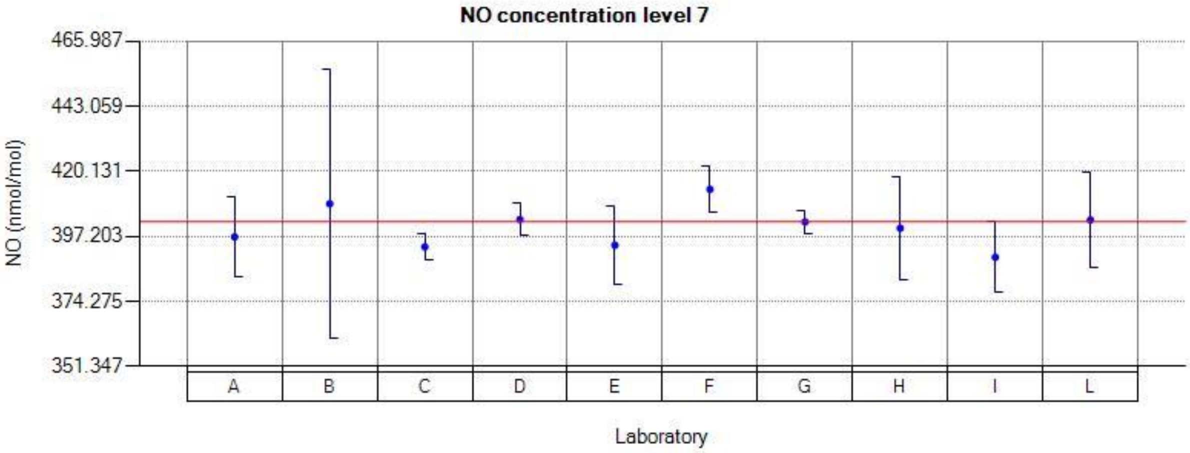

Figure 38: Reported values for NO run 7

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	305.50	314.70	301.00	309.70	305.17	324.12	309.39	309.56	296.49	311.74
xi, 2	306.55	314.70	300.50	309.80	305.18	324.12	309.57	308.83	295.68	311.14
xi, 3	306.90	314.60	300.70		305.58	324.84	309.57	308.88	295.82	311.24
xi	306.31	314.66	300.73	309.75	305.31	324.36	309.51	309.09	295.99	311.37
si	0.72	0.05	0.25	0.07	0.23	0.41	0.10	0.40	0.43	0.32
u(xi)	5.50	18.23	3.97	2.26	5.44	3.25	1.64	6.97	4.70	6.53
U(xi)	11.00	36.46	7.94	4.60	10.87	6.50	3.27	13.94	9.40	13.07

Table 38: Reported values for NO run 8

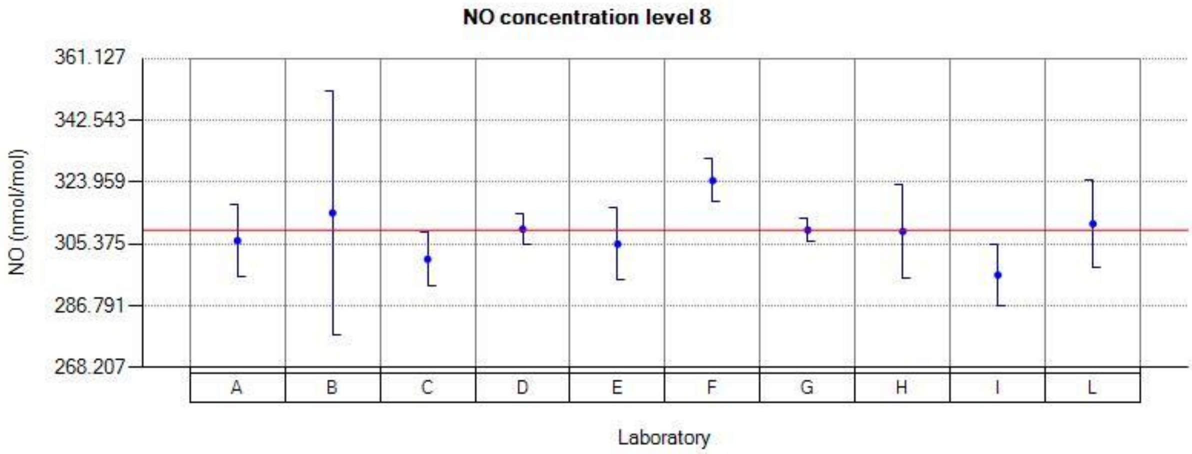

Figure 39: Reported values for NO run 8

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	48.85	51.10	47.30	50.10	48.32	50.33	50.22	48.50	43.16	49.68
xi, 2	48.90	51.00	48.00	50.10	48.22	50.50	50.26	48.44	43.61	49.98
xi, 3	49.00	51.10	48.70		48.34	50.38	50.25	48.50	43.23	50.18
xi	48.91	51.06	48.00	50.10	48.29	50.40	50.24	48.48	43.33	49.94
si	0.07	0.05	0.70	0.00	0.06	0.08	0.02	0.03	0.24	0.25
u(xi)	0.87	3.08	5.57	0.68	0.91	0.51	0.75	1.42	1.05	1.05
U(xi)	1.74	6.16	11.13	1.40	1.81	1.02	1.51	2.85	2.10	2.10

Table 39: Reported values for NO run 9

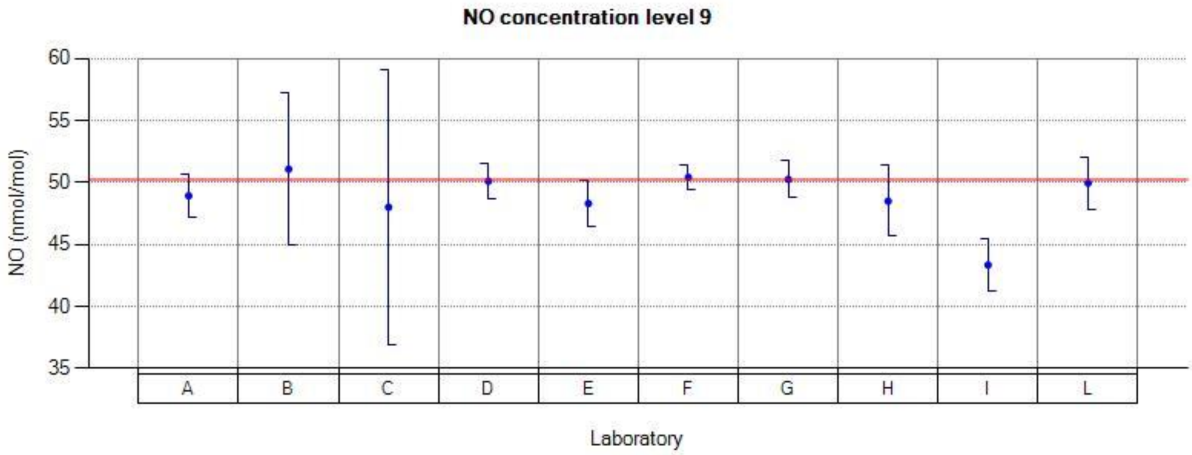

Figure 40: Reported values for NO run 9

values	laboratories									
	A	B	C	D	E	F	G	H	I	L
xi, 1	28.50	30.40	28.20	29.56	29.08	31.66	29.67	29.34	24.91	29.87
xi, 2	28.75	30.40	28.30	29.59	29.01	31.87	29.67	29.43	24.91	29.87
xi, 3	29.00	30.30	28.70		29.10	32.07	29.68	29.41	24.91	30.27
xi	28.75	30.36	28.40	29.57	29.06	31.86	29.67	29.39	24.91	30.00
si	0.25	0.05	0.26	0.02	0.04	0.20	0.00	0.04	0.00	0.23
u(xi)	0.51	1.96	5.71	0.62	0.70	0.34	0.73	1.44	0.75	0.63
U(xi)	1.02	3.92	11.42	1.30	1.40	0.68	1.46	2.88	1.50	1.26

Table 40: Reported values for NO run 10

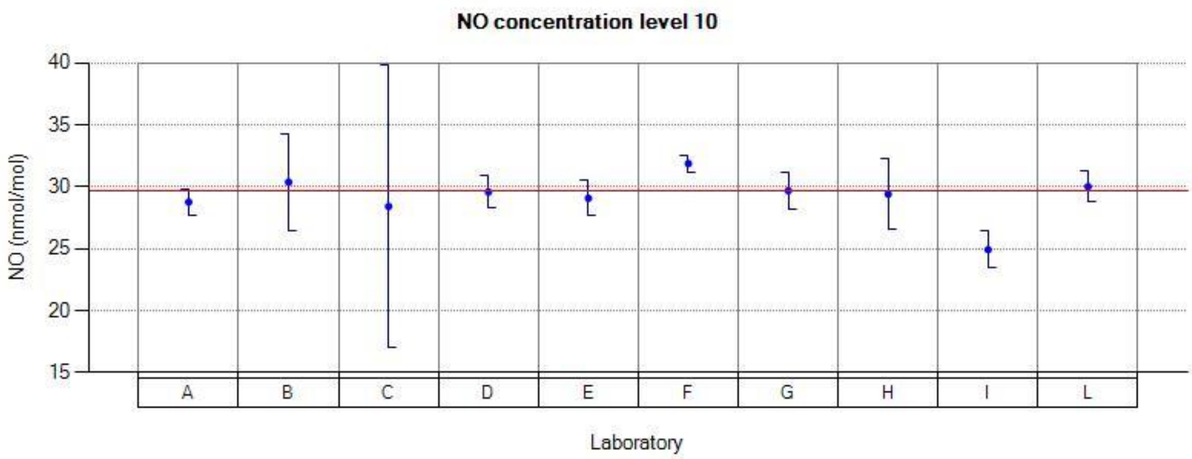

Figure 41: Reported values for NO run 10

Reported values for NO_2

values	A	B	C	D	E	F	G	H	I	L
	laboratories									
xi, 1	0.20	-0.30	0.00	0.04	-0.07	-0.38	0.00	0.08	-0.40	0.10
u(xi)	0.02	0.90	0.58	0.58	0.40	0.01	0.71	0.60	0.90	0.49
U(xi)	0.04	1.80	1.15	1.20	0.80	0.02	1.42	1.20	1.80	0.98

Table 41: Reported values for NO_2 run 0

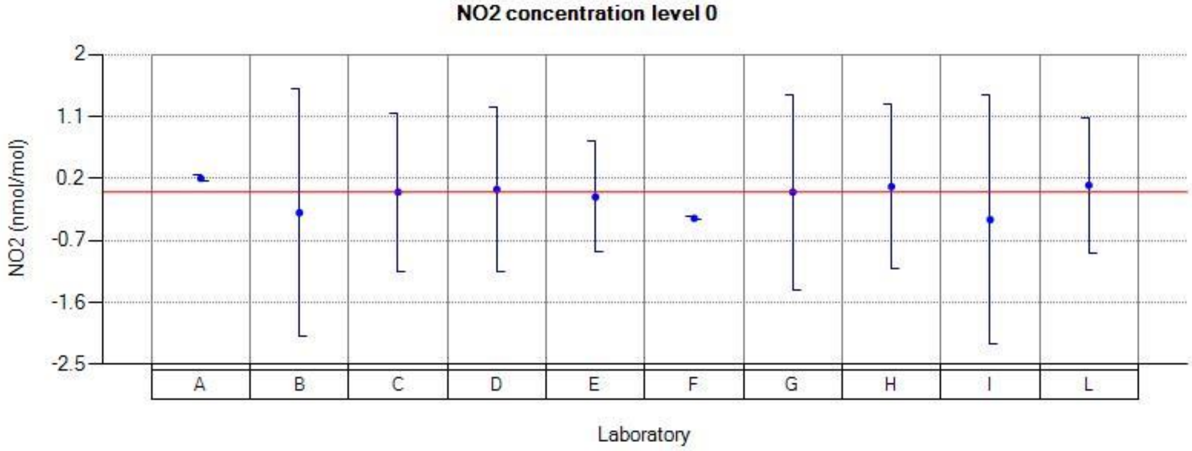

Figure 42: Reported values for NO_2 run 0

values	A	B	C	D	E	F	G	H	I	L
	laboratories									
xi, 1	151.50	137.50	157.20	157.48	150.79	153.47	157.20	153.31	160.27	154.74
xi, 2	151.80	138.20	158.70	158.82	150.65	154.53	157.66	153.99	161.85	155.24
xi, 3	152.00	138.80	159.00		150.59	155.92	158.13	153.54	162.40	154.74
xi	151.76	138.16	158.30	158.15	150.67	154.64	157.66	153.61	161.50	154.90
si	0.25	0.65	0.96	0.94	0.10	1.22	0.46	0.34	1.10	0.28
u(xi)	2.73	8.04	3.66	2.46	3.46	2.57	2.45	3.48	10.50	3.26
U(xi)	5.46	16.08	7.32	4.90	6.93	5.14	4.90	6.96	21.00	6.51

Table 42: Reported values for NO_2 run 2

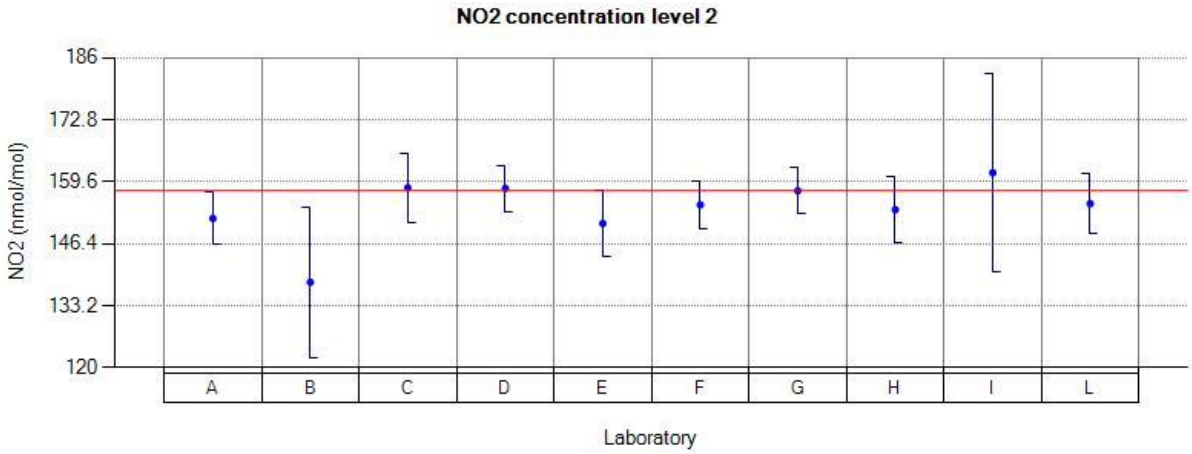

Figure 43: Reported values for NO_2 run 2

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	108.50	109.50	117.30	116.36	108.35	113.49	115.92	112.97	111.30	113.10
xi, 2	109.00	109.60	118.00	116.36	108.33	113.09	116.07	113.10	111.95	113.90
xi, 3	109.25	109.70	118.00		108.05	113.98	116.34	113.40	111.98	113.70
xi	108.91	109.60	117.76	116.36	108.24	113.52	116.11	113.15	111.74	113.56
si	0.38	0.10	0.40	0.00	0.16	0.44	0.21	0.22	0.38	0.41
u(xi)	1.95	6.39	3.87	1.85	2.51	1.83	1.24	2.70	2.30	2.39
U(xi)	3.90	12.78	7.74	3.70	5.02	3.66	2.48	5.39	4.60	4.77

Table 43: Reported values for NO_2 run 4

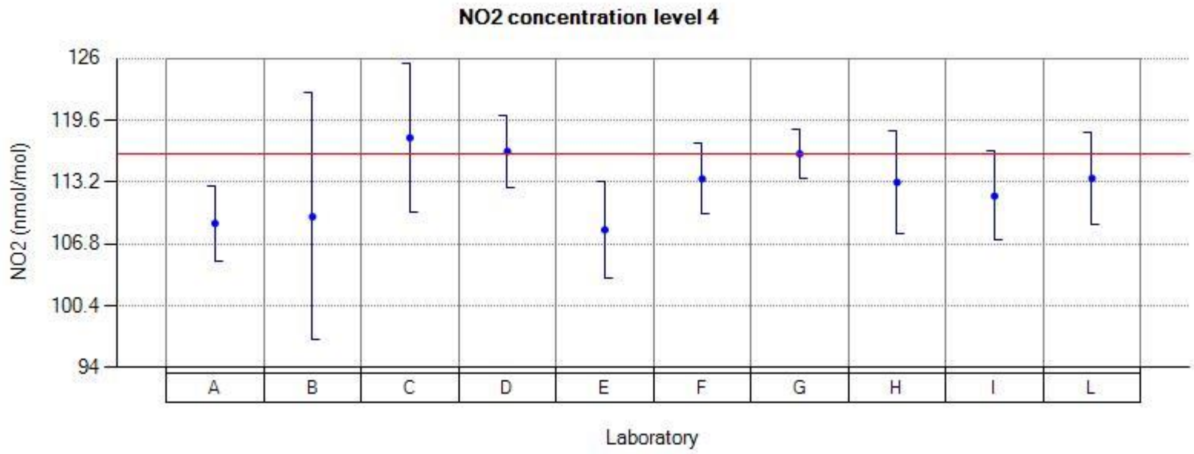

Figure 44: Reported values for NO_2 run 4

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	58.25	59.60	63.00	62.01	58.20	58.95	62.16	59.55	55.47	60.53
xi, 2	58.55	59.90	63.00	62.29	57.98	59.40	62.27	59.73	55.55	60.72
xi, 3	58.75	59.90	63.00		58.06	58.94	62.27	59.80	55.58	60.53
xi	58.51	59.80	63.00	62.15	58.08	59.09	62.23	59.69	55.53	60.59
si	0.25	0.17	0.00	0.19	0.11	0.26	0.06	0.12	0.05	0.11
u(xi)	1.05	3.56	4.17	1.11	1.38	0.96	0.85	1.75	1.10	1.27
U(xi)	2.10	7.12	8.33	2.20	2.76	1.92	1.70	3.51	2.20	2.55

Table 44: Reported values for NO_2 run 6

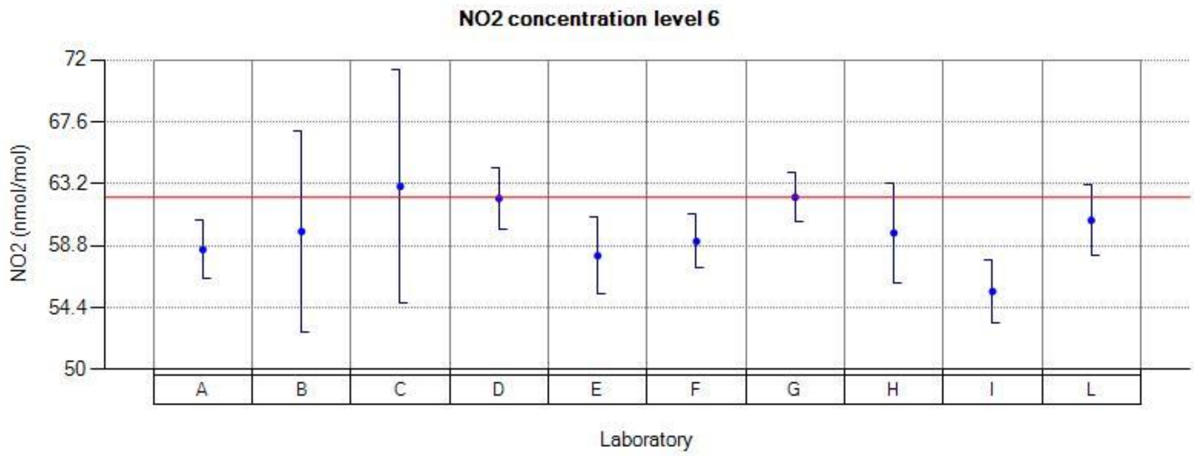

Figure 45: Reported values for NO_2 run 6

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	90.00	82.50	96.00	95.18	88.49	92.09	94.67	91.93	93.63	91.93
xi, 2	90.15	82.70	96.00	95.87	88.52	92.84	95.01	91.82	94.15	92.53
xi, 3	90.50	82.80	96.00		88.38	92.41	94.98	91.59	94.67	92.13
xi	90.21	82.66	96.00	95.52	88.46	92.44	94.88	91.78	94.15	92.19
si	0.25	0.15	0.00	0.48	0.07	0.37	0.18	0.17	0.52	0.30
u(xi)	1.63	4.86	3.98	1.57	2.05	1.49	1.68	2.19	6.70	1.94
U(xi)	3.26	9.72	7.97	3.20	4.10	2.98	3.35	4.37	13.40	3.88

Table 45: Reported values for NO_2 run 8

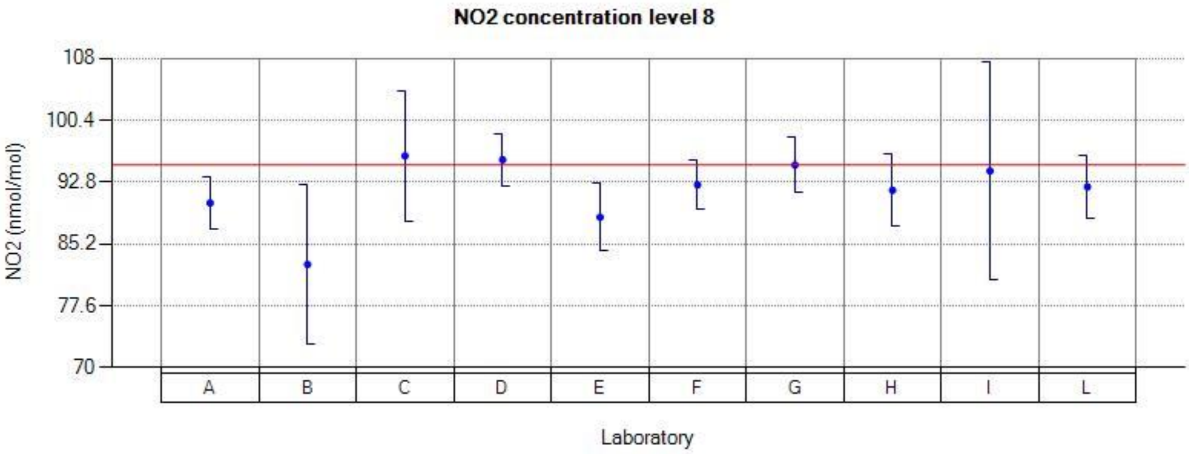

Figure 46: Reported values for NO_2 run 8

	laboratories									
values	A	B	C	D	E	F	G	H	I	L
xi, 1	18.00	19.20	21.00	20.81	19.07	18.96	20.81	19.36	18.11	20.17
xi, 2	18.00	19.20	21.00	20.87	19.26	18.57	20.85	19.12	17.99	19.78
xi, 3	18.00	19.10	21.00		19.14	18.60	20.83	19.27	17.91	19.78
xi	18.00	19.16	21.00	20.84	19.15	18.71	20.83	19.25	18.00	19.91
si	0.00	0.05	0.00	0.04	0.09	0.21	0.02	0.12	0.10	0.22
u(xi)	0.32	1.42	4.40	0.66	0.57	0.33	0.74	0.94	1.25	0.49
U(xi)	0.64	2.84	8.80	1.40	1.15	0.66	1.49	1.89	2.50	0.98

Table 46: Reported values for NO_2 run 10

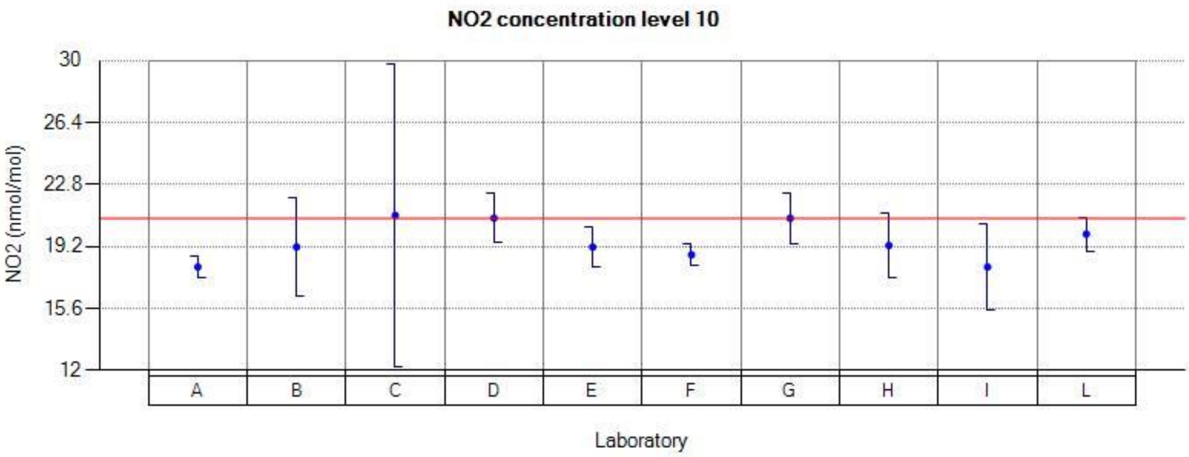

Figure 47: Reported values for NO_2 run 10

Annex C: The precision of standardised measurement methods

For the main purpose of monitoring trends between different IE undertaken by ERLAP the precision of standardised SO_2, CO, O_3 and NO_X measurement methods [2], [3], [4] and [5] as implemented by NRLs was evaluated.
The applied methodology is described in ISO 5725-Part 1 [14], Part 2 [15] and Part 6 [16]. The precision experiment has involved a total of seven laboratories, the actual number of labs (p_j) varying from run to run (Table 47). Six concentration levels (for run 0 only one value is requested 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 the 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 (r) limit is calculated using Equation 6 [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, which should not have been exceeded on average more than once in 20 cases in the normal and correct operation of method.

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

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

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

The 'S_r' was evaluated with (p_j *(3-1)) degrees of freedom (ν) and r 'S_R' with (p_j-1) degrees of freedom. The critical range student factors ($t_{\alpha,\nu}$) are reported in Table 47.

parameter	run	p_j	t critical value 95% for r	t critical value 95% for R
CO	1,2,3,4,5	10	2.086	2.262
NO	1,2,3,4,5,6,7,8,9,10	10	2.086	2.262
NO_2	2,4,6,8,10	10	2.086	2.262
O_3	1,2,3,4,5	10	2.086	2.262
SO_2	1,2,3,4,5	10	2.086	2.262

Table 47: Critical values of t used in the repeatability r and R evaluation

The r and R limits of measurement methods are presented from Table 48 to Table 52 and from Figure 48 to Figure 52. The R from common criteria (R (from σ_p) calculated by substituting S_R in Equation 7 with a 'standard deviation for proficiency assessment' (Table 4) is also reported. Comparison between R and R (from σ_p) serves to indicate that σ_p is realistic ([13] 6.3.1) or from another point of view, that the general methodology implemented by NRLs is appropriate for σ_p. The green (R) and blue (r) lines are representing a good performance if they run below the red line which represents the data quality objective of the IE.

SO_2 data (nmol/mol) without outliers			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.1		1.2	
5.2	0.3	1.4	
10.2	0.3	1.8	
30.9	0.4	3.1	
71.6	1.1	6.5	
132.4	1.2	11.7	8.8%

Table 48: The R and r of SO_2 standard measurement method

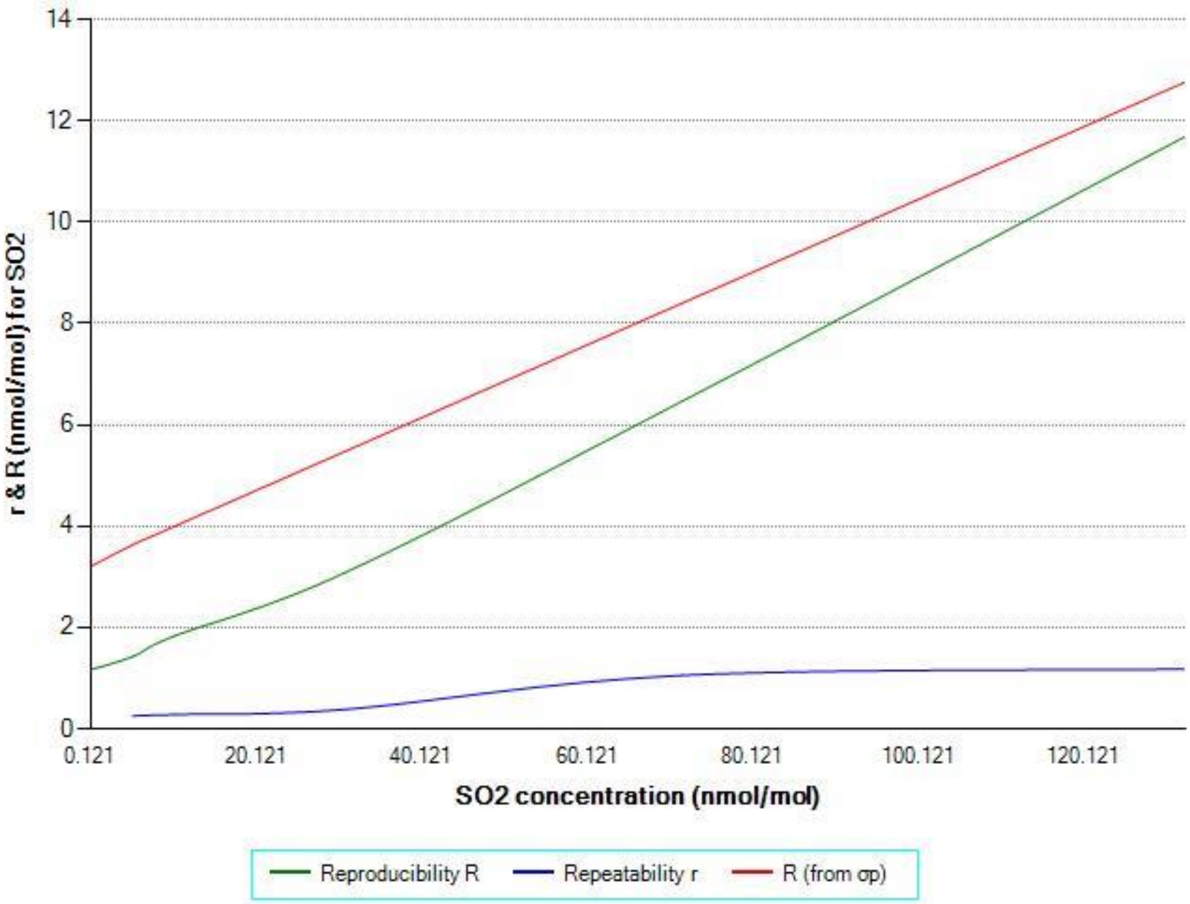

Figure 48: The R and r of SO_2 standard measurement method as a function of concentration

CO data (µmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
0.016		0.102	
1.076	0.015	0.179	
2.105	0.021	0.311	
3.653	0.017	0.503	
5.192	0.023	0.709	
8.714	0.052	1.288	14.8%

Table 49: The R and r of CO standard measurement method

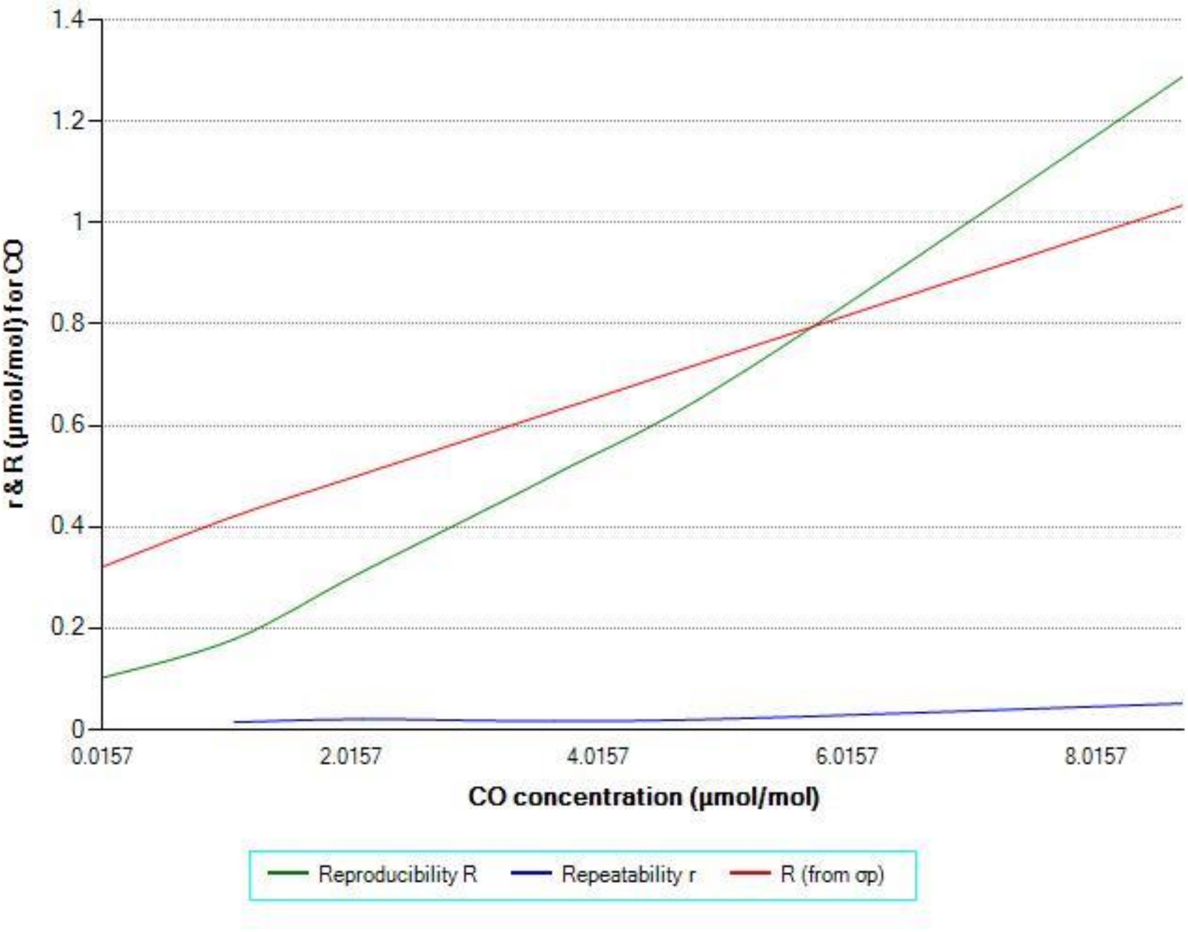

Figure 49: The R and r of CO standard measurement method as a function of concentration

O_3 data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
0.0		0.7	
17.1	0.2	1.4	
55.6	0.5	1.6	
91.6	0.8	3.1	
123.6	0.9	3.9	
152.2	1.7	5.9	3.9%

Table 50: The R and r of O_3 standard measurement method

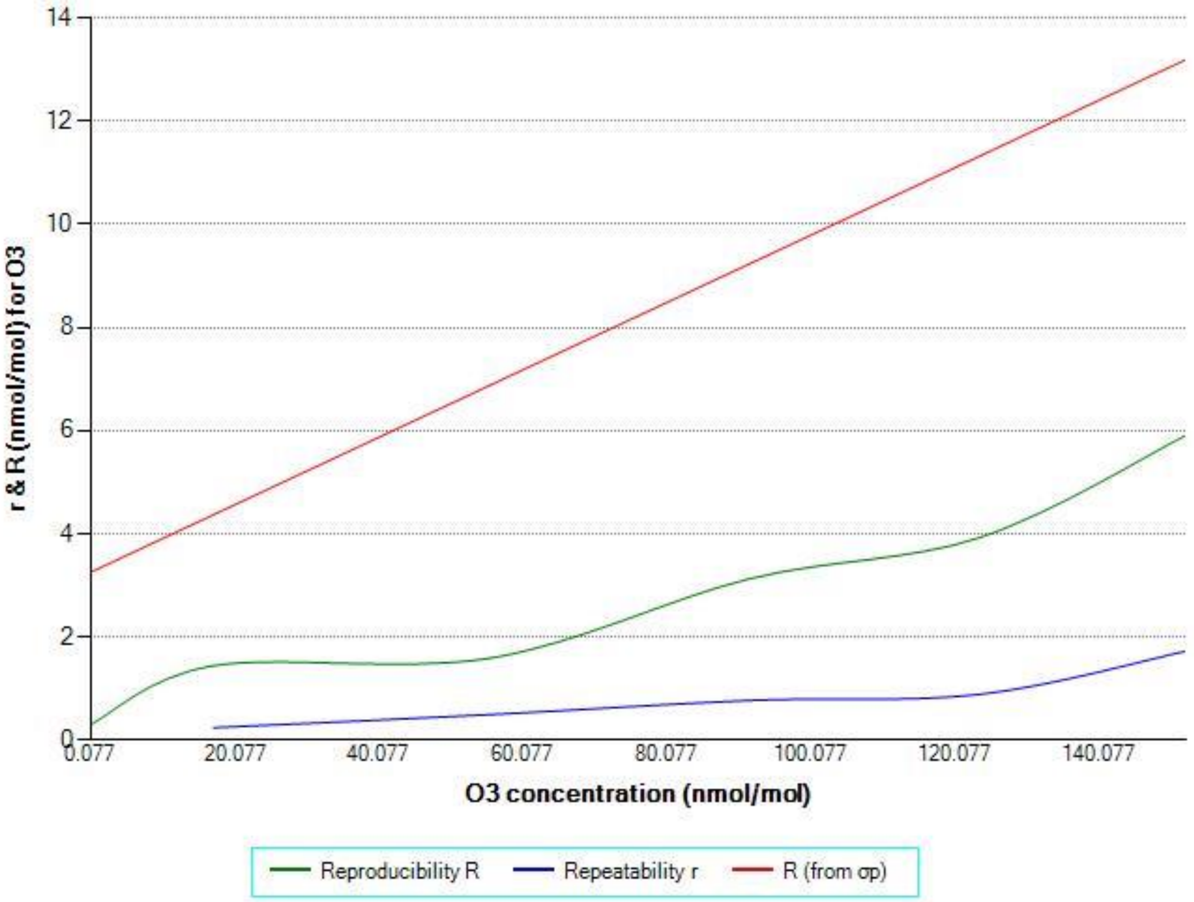

Figure 50: The R and r of O_3 standard measurement method as a function of concentration

NO data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
0.1		0.5	
19.4	0.5	6.0	
29.2	0.5	6.2	
48.7	0.8	7.5	
78.9	0.9	9.9	
101.4	1.0	14.3	
214.4	1.2	15.0	
308.6	1.1	26.6	
400.2	1.4	25.0	
468.4	2.6	30.2	
622.0	2.1	30.4	4.9%

Table 51: The R and r of NO standard measurement method

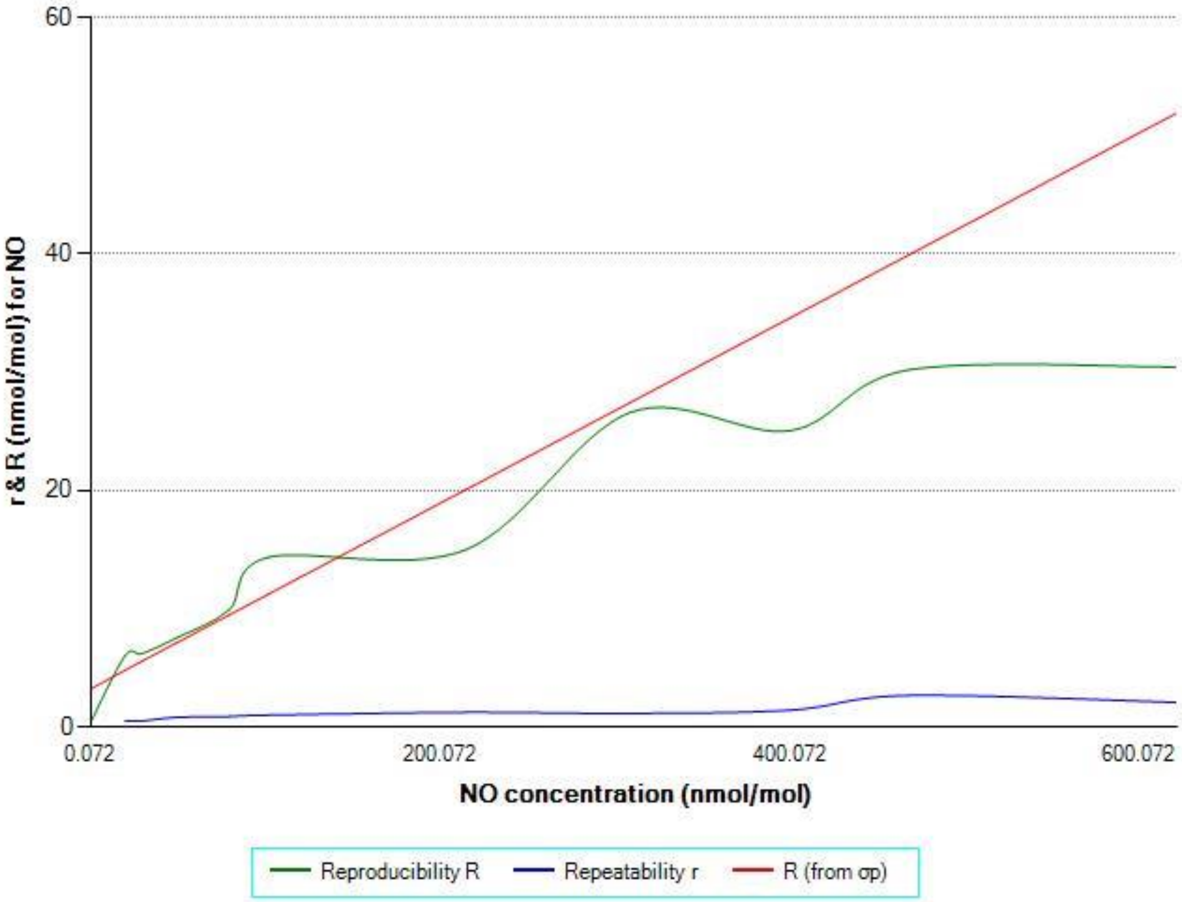

Figure 51: The R and r of NO standard measurement method as a function of concentration

NO_2 data (nmol/mol) without outliers			
group average	repeatability limit: r	reproducibility limit: R	reproducibility limit (relative)
-0.1		0.7	
19.3	0.4	3.5	
59.6	0.5	7.3	
91.4	0.8	13.1	
112.5	1.0	10.6	
153.5	2.1	21.8	14.2%

Table 52: The R and r of NO_2 standard measurement method

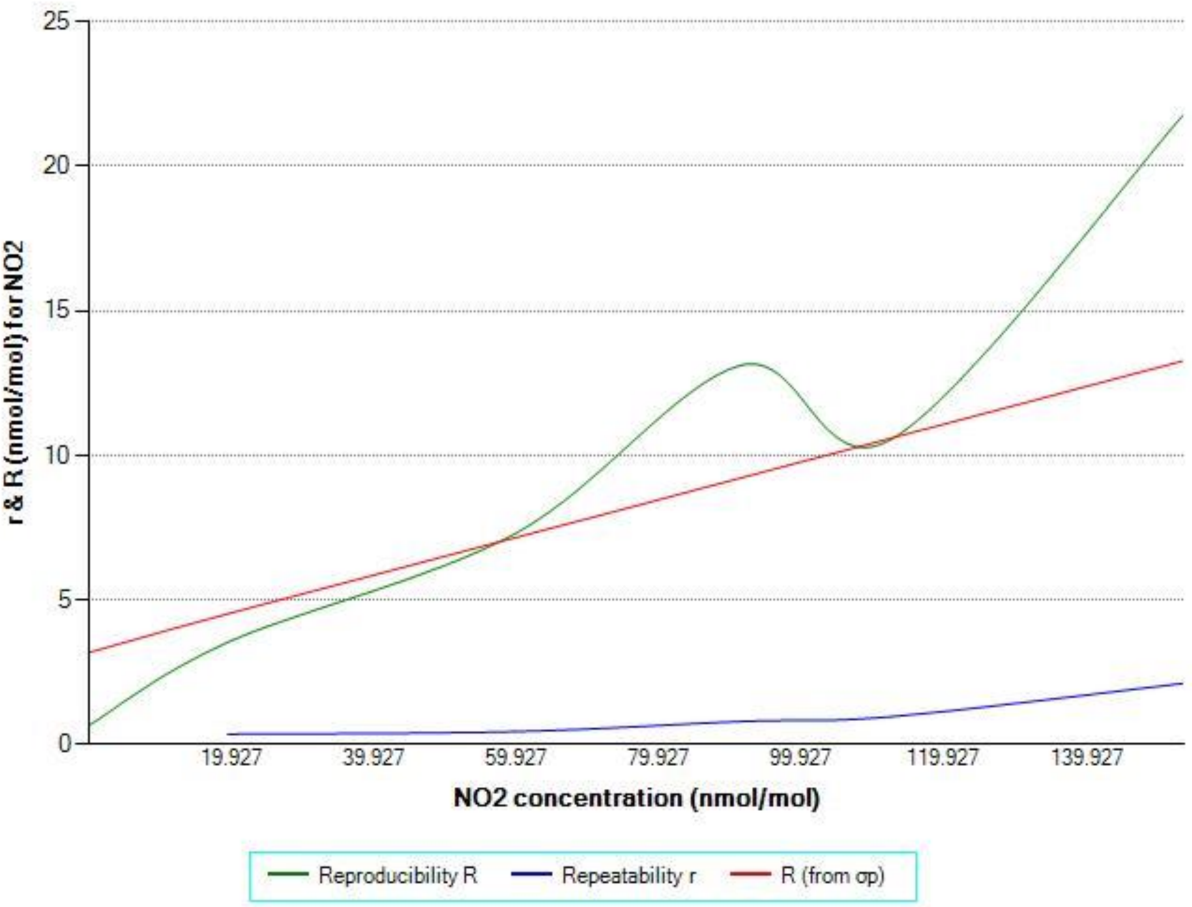

Figure 52: The R and r of NO_2 standard measurement method as a function of concentration

Annex C. Results evaluation for consistency and outlier test

The precision evaluation (Annex C) focuses on data that are as much as possible the reflection of the everyday 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. This procedure 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 if they identified of exceptional errors. Subsequently, data were considered definitive and "Grubb's one outlying observation test" was performed.
For runs where outliers were detected, these 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 to be due to extraordinary errors but to a significant difference in each participant's standard operating procedure.

During this IE the statistical process analysis has identified some outliers that are presented in the table below (Table 53). Laboratory "I" had problem with the calibration process of CO with the consequence of underestimation during the IE.

Laboratory	Parameter	Run	Value	Failing test	Confidence level
I	CO	1	4.696	G1 min	1%, 5%
I	CO	2	2.014	G1 min	1%, 5%
I	CO	3	0.756	G1 min	1%, 5%
I	CO	4	2.881	G1 min	1%, 5%
I	CO	5	1.252	G1 min	1%, 5%
I	O3	0	-0.6	G1 min	1%, 5%

Table 53: "Genuine" statistical outliers according to Grubb's one outlying observation test

The precision of standardised measurement methods reported in 0 are calculated using the database without outliers.

According to Grubb's test, results that have a confidence level between 1 and 5% are considered straggler and should be specifically checked.
In order to provide the participants with useful information for judging their performance, the stragglers are reported in the following table.

Laboratory	parameter	run	value	G1min_5%	G1max_5%
B	NO2	2	138.16	Straggler	OK
F	NO	2	489.27	OK	straggler
I	NO	5	71.98	Straggler	OK
I	NO	9	43.33	Straggler	OK
I	NO	10	24.91	Straggler	OK
I	SO2	0	1.01	OK	straggler
I	SO2	3	6.11	OK	straggler
I	SO2	5	11.49	OK	straggler

Table 54: Stragglers according to Grubb's one observation test

Annex D. Accreditation certificate

This annex provides the accreditation certificate for ISO/CEI 17025 [44] of ERLAP, who organised this inter-laboratory comparison and delivered the assigned value.

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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.
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Data di 1ª emissione *1st issue date* **2013-06-19**	Data di modifica *Modification date* **2013-06-19**	Data di scadenza *Expiring date* **2017-06-18**
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	Revisione: **0** Data: **22/07/2013**
Via E. Fermi 2749 21027 Ispra VA	Scheda **1** di **1** PA1779AR0.pdf

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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