

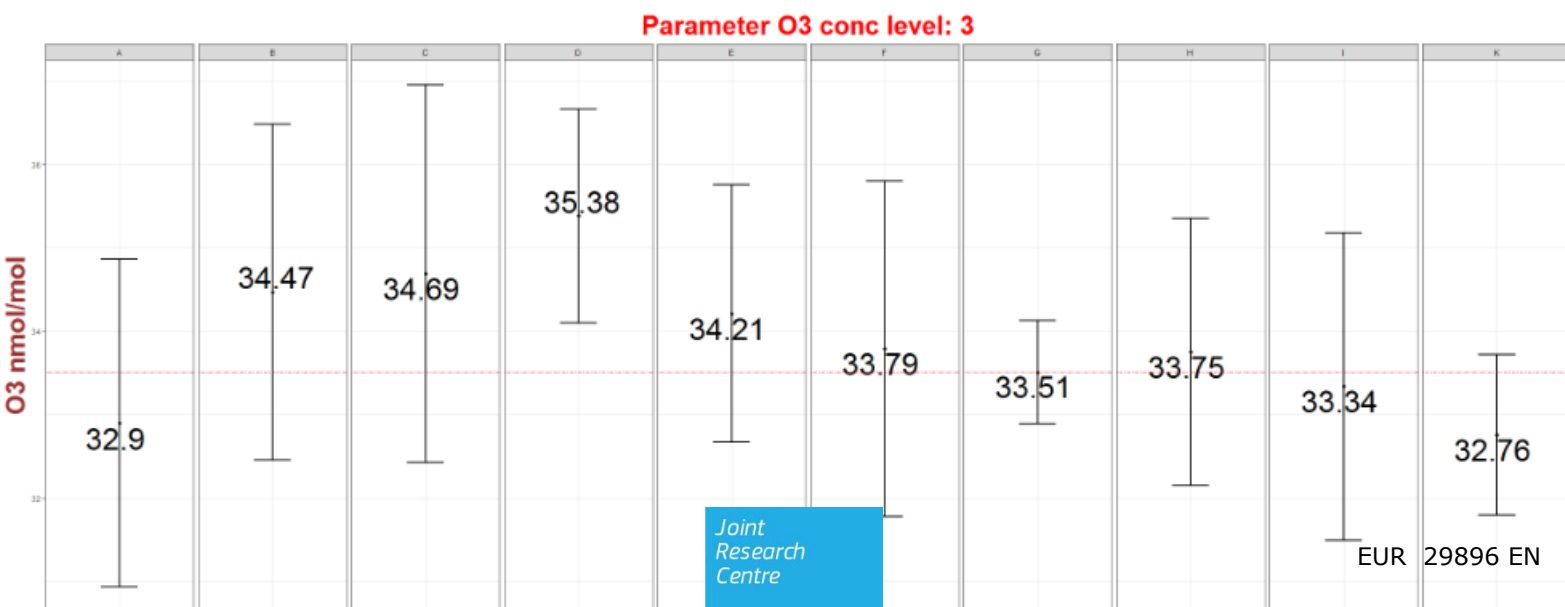
## JRC TECHNICAL REPORTS

# Evaluation of the Inter-Laboratory Comparison exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> (20-23 May 2019, Ispra)

*European Commission  
harmonisation  
programme for air  
quality measurements*

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## **2. Abstract**

Within the harmonisation programme of Air Quality monitoring in Europe the European Reference Laboratory of Air Pollution (ERLAP) organises Inter-Laboratory Comparison Exercises (ILC).

From the 20<sup>th</sup> to the 23<sup>rd</sup> of May 2019, including ERLAP, eight 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 air pollutants (NO, NO<sub>2</sub>, SO<sub>2</sub>, CO and O<sub>3</sub>) covered by the European Air Quality Directive 2008/50 EC [1] and its recent amendments 2015/1480/EC [42].

Two laboratories didn't report values for SO<sub>2</sub>.

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 adopted criteria, 82% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. The rest of the results had good measured values, but the reported uncertainties were either too high (11%) or too small (4%). Based on the z'-score evaluation, six values were found to be questionable (3%) and none of the values were unsatisfactory. Comparability of results among AQUILA participants at the highest generated concentration levels is satisfactory for measurements of all pollutants.

### 3. Introduction

The Directive 2008/50/EC [1] on ambient air quality and cleaner air for Europe sets a framework for a harmonised 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 deals with the air pollutants sulphur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>) and nitrogen monoxide (NO), particulate matter, lead, benzene, carbon monoxide (CO) and ozone (O<sub>3</sub>). 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 [2], SO<sub>2</sub> [3], NO-NO<sub>2</sub> [4] and O<sub>3</sub> [5] as European standards. Appropriate calibration methods [6], [7] and [8] have been standardised by the International Organization for Standardization (ISO).

As foreseen in the Air Quality Directive [1, 42], the European Reference Laboratory of Air Pollution (ERLAP) of the Directorate for Energy, Transport and Climate at the Joint Research Centre (JRC) organises inter-laboratory comparison exercises (ILC) 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 [9] [10], [24], [31], [35], [38] and [45], but with a view to obtaining harmonised air quality data for health related studies. Their programme 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 optimise resources and improve international harmonisation.

The following report deals with the ILC that took place from 20<sup>th</sup> to the 23<sup>rd</sup> of May 2019 in Ispra (IT).

Since 1990 ERLAP has organised ILC in order to evaluate the comparability of measurements carried out by NRLs and promote information exchange among the expert laboratories. Recently, a more systematic approach has been adopted, in agreement with the Network of National Reference Laboratories for Air Quality (AQUILA) [11], aiming to both provide an alert mechanism for the purposes of the EC legislation and support the implementation of quality schemes by NRLs.

The methodology for the organisation of ILC 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 is applied to all ILC since then. It contains common criteria to alert the EC on possible performance failures, which do not rely solely on the uncertainty claimed by participants. The evaluation scheme implements the z'-score method [13] with the uncertainty requirements for calibration gases stated in the European standards [2], [3], [4] and [5], which are consistent with the DQOs of European Directives.

According to the above-mentioned document [12], 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 ILC in order to demonstrate remediation measures [12]. In addition, considering that the evaluation scheme should be useful to participants for accreditation according to ISO 17025, they are requested to include their measurement uncertainty. Hence, participants' results (measurement values

and uncertainties) are compared to the assigned values applying the  $E_n$ -score method [13].

Beside the proficiency of participating laboratories, the repeatability and reproducibility 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 ILC.

## 4. Inter-laboratory organisation

The ILC was announced in February 2019 to the members of the AQUILA network and the WHO CC representative. Registration was opened in April 2019 and closed at the beginning of May 2019.

Every participants, together with the registration confirm received a detailed protocol with all the necessary information about the ILC. Each laboratory was required to bring their own measurement instruments, data acquisition equipment and travelling standards (to be used for calibrations or checks during the ILC).

The participants were invited to arrive on Monday, 20<sup>th</sup> of May 2019, for the installation of their equipment. The calibration of NO<sub>x</sub> and O<sub>3</sub> analysers was carried out next day on Tuesday morning and the generation of NO<sub>x</sub> and O<sub>3</sub> gas mixtures started at 11:00.

The calibration of SO<sub>2</sub> and CO analysers was carried out on Wednesday afternoon and the generation of CO and SO<sub>2</sub> gas mixtures started at 20:00.

The test gases generation and measurements finished on Thursday at 9:00.

### 4.1 Participants

All participants were organisations dealing with the routine ambient air monitoring or institutions involved in environmental or public health protection. The national representatives came from Croatia, France, United Kingdom, Bulgaria, and Czech Republic.

**Table 1:** List of participating organizations.

Acronym	Institute	Country	code
EKONERG	Energy and Environmental Protection Institute	Croatia	A
INERIS	Institut National de l'Environnement Industriel et des Risques	France	B
AEA	RICARDO-AEA Technology	United Kingdom	C
EEA	Executive Environmental Agency	Bulgaria	D
CHMI	Czech Hydrometereological Institute	Czech Republic	E
DHZ-CAL	Meteorological and Hydrological Service - CALIBRATION	Croatia	F
ERLAP	European Reference Laboratory for Air Pollution	Italy	G
DHZ-TES	Meteorological and Hydrological Service - TEST	Croatia	H

Table 2 reports the manufacturer and model of the instrumentation used by every participant during the inter-laboratory comparison exercise, including those used in the calculation of the assigned values.

The list contains the information reported by participants and cannot be considered as an implicit or explicit endorsement by the organisers of any specific instrumentation.



**Table 2:** List of instruments used by participants.

code	parameter	analyser
A	SO <sub>2</sub>	Horiba APSA 370. 2010
B		API, 2010, 100E
C		Thermo 43i
D		Horiba, 2009, APSA 370
E		Thermo Scientific 2018 model 43i
F		Teledyne API, 2019, T100U
G		Thermo 43C TLE, 2005
H		EAS ENVIMET, 2009, M100E
A	NO <sub>x</sub>	Horiba APNNA 370. 2015
B		Horiba , 2014, APNA 370
C		Thermo 42i
D		Horiba 2009, analyzer NO <sub>x</sub> , APNA 370
E		Thermo Scientific 2018 model 42i
F		Teledyne API, 2018, T200
G		Thermo, TE42iTL, 2015
H		EAS ENVIMET, 2009, M200E
A	CO	Horiba APMA 370. 2015
B		TEI, 2017, 48i
C		Horiba APMA 370
D		
E		Thermo Scientific 2018 model 48i
F		Teledyne API, 2019, T300U
G		Horiba, APMA-370, 2010
H		EAS ENVIMET, 2009,M 300E
A	O <sub>3</sub>	Horiba APOA 370. 2008
B		API, 2010, 400E
C		Thermo 49i
D		Horiba 2008, APOA 370
E		Thermo Scientific 2018 model 49i
F		Teledyne API, 2019, T400
G		Thermo, 49-iPS , 2015
H		EAS ENVIMET, 2009, M400E

## 4.2 Preparation of test mixtures

The ERLAP ILC facility has been described in several reports [17], [18]. During this ILC, gas mixtures were prepared for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> at concentration levels around limit values, critical levels and assessment thresholds set by the European Air Quality Directive [1].

**Table 3:** Sequence program of generated test gases with indicative pollutant concentrations

day	start time	duration	parameter	installation	calibration	Zero Air	NO	NO <sub>2</sub>	O <sub>3</sub>	CO	SO <sub>2</sub>
		h				nmol/mol	nmol/mol	nmol/mol	nmol/mol	mmol/mol	nmol/mol
1st	09:00		/	X							
2nd	08:00	3	/		X						
2nd	11:00	1	NO-NO <sub>2</sub> -O <sub>3</sub>			X					
2nd	12:00	2	NO-NO <sub>2</sub>				135				
2nd	14:00	2	NO-NO <sub>2</sub>				70	65			
2nd	16:00	2	O <sub>3</sub>						65		
2nd	18:00	2	NO-NO <sub>2</sub>				35				
2nd	20:00	2	NO-NO <sub>2</sub>				15	20			
2nd	22:00	2	O <sub>3</sub>						20		
3rd	00:00	2	NO-NO <sub>2</sub>				65				
3rd	02:00	2	NO-NO <sub>2</sub>				25	40			
3rd	04:00	2	O <sub>3</sub>						35		
3rd	06:00	2	NO-NO <sub>2</sub>				490				
3rd	08:00	2	NO-NO <sub>2</sub>				380	110			
3rd	10:00	2	O <sub>3</sub>						115		
3rd	12:00	2	NO-NO <sub>2</sub>				300				
3rd	14:00	2	NO-NO <sub>2</sub>				200	100			
3rd	16:00	2	O <sub>3</sub>						90		
3rd	18:00	2	/		X						
3rd	20:00	1	CO-SO <sub>2</sub>			X					
3rd	21:00	2	CO-SO <sub>2</sub>							2.8	115
3rd	23:00	2	CO-SO <sub>2</sub>							8.5	60
4th	01:00	1	CO-SO <sub>2</sub>			X	not to be reported				
4th	02:00	2	CO-SO <sub>2</sub>							5	35
4th	04:00	2	CO-SO <sub>2</sub>							2	18
4th	06:00	2	CO-SO <sub>2</sub>							0.9	10
4th	08:00	1	/								
4th	09:00	END									

The test mixtures were prepared by the dilution of gases from cylinders containing high concentrations of NO, SO<sub>2</sub> or CO using thermal mass flow controllers [8]. O<sub>3</sub> was added using an ozone generator and NO<sub>2</sub> was produced applying the gas phase titration method [19] 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 standardised measurement methods. Zero value concentration levels were generated for one hour and one half-hour-mean measurement was reported. The sequence programme of generated test gases is given in Table 3.

## 5. The evaluation of laboratory's measurement proficiency

To evaluate the participant's measurement proficiency, the methodology described in ISO 13528 [13] was applied. It has been agreed among the AQUILA members to take the measurement results of ERLAP as the assigned/reference values for the whole ILC [12].

The traceability of ERLAP's measurement results and the method applied to validate them are presented in paragraph 8. In the following proficiency evaluations, the uncertainty of test gas homogeneity (paragraph 8) was added to the uncertainties of ERLAP's measurement results.

All data reported by participating laboratories are presented in Annex A.

As described in the AQUILA document 37 [12], the proficiency of the participants was assessed by calculating two performance indicators.

The first performance indicator (z'-score) tests whether the difference between the participants measured value and the assigned/reference value remains within the limits of a common criterion.

The second performance indicator (E<sub>n</sub>-score) 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.

### 5.1 z'-score

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

$$z' = \frac{x_i - X}{\sqrt{\sigma_p^2 + u_x^2}} = \frac{x_i - X}{\sqrt{(a \cdot X + b)^2 + u_x^2}} \quad \text{Equation 1}$$

where  $x_i$  is a participant's average value for each run,  $X$  is the assigned/reference value,  $\sigma_p$  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 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' ( $\sigma_p$ ) [13] is calculated in fitness-for-purpose manner from requirements given in European standards.

Over the whole measurement range  $\sigma_p$  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 ILC. The linear function parameters of  $\sigma_p$  are given in Table 4.

**Table 4:** Standard deviation for proficiency assessment ( $\sigma_p$ ).

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

Gas	$\sigma_p = a \cdot c + b$	
	a	b nmol/mol
SO <sub>2</sub>	0.022	1
CO	0.024	100
O <sub>3</sub>	0.020	1
NO	0.024	1
NO <sub>2</sub>	0.020	1

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

- $|z'| \leq 2$  are considered satisfactory.
- $2 < |z'| < 3$  are considered questionable.
- $|z'| \geq 3$  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 5) in which the z'-scores of each participant are grouped together. The assessment criteria are presented as  $z' = \pm 2$  (blue line) and  $z' = \pm 3$  (red line). They represent the limits for the questionable and unsatisfactory results.

**Figure 1:** Z'-score evaluations of SO<sub>2</sub> 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 (115 nmol/mol), 2 (60 nmol/mol), 3 (35 nmol/mol), 4 (18 nmol/mol), 5 (10 nmol/mol). Laboratory B and D didn't reported results for this pollutant



**Figure 2: 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  $\mu\text{mol/mol}$ ), 1 (2.8  $\mu\text{mol/mol}$ ), 2 (8.5  $\mu\text{mol/mol}$ ), 3 (5  $\mu\text{mol/mol}$ ), 4 (2  $\mu\text{mol/mol}$ ), 5 (0.9  $\mu\text{mol/mol}$ ). The assessment criteria are presented as  $z'=\pm 2$  (blue line) and  $z'=\pm 3$  (red line).



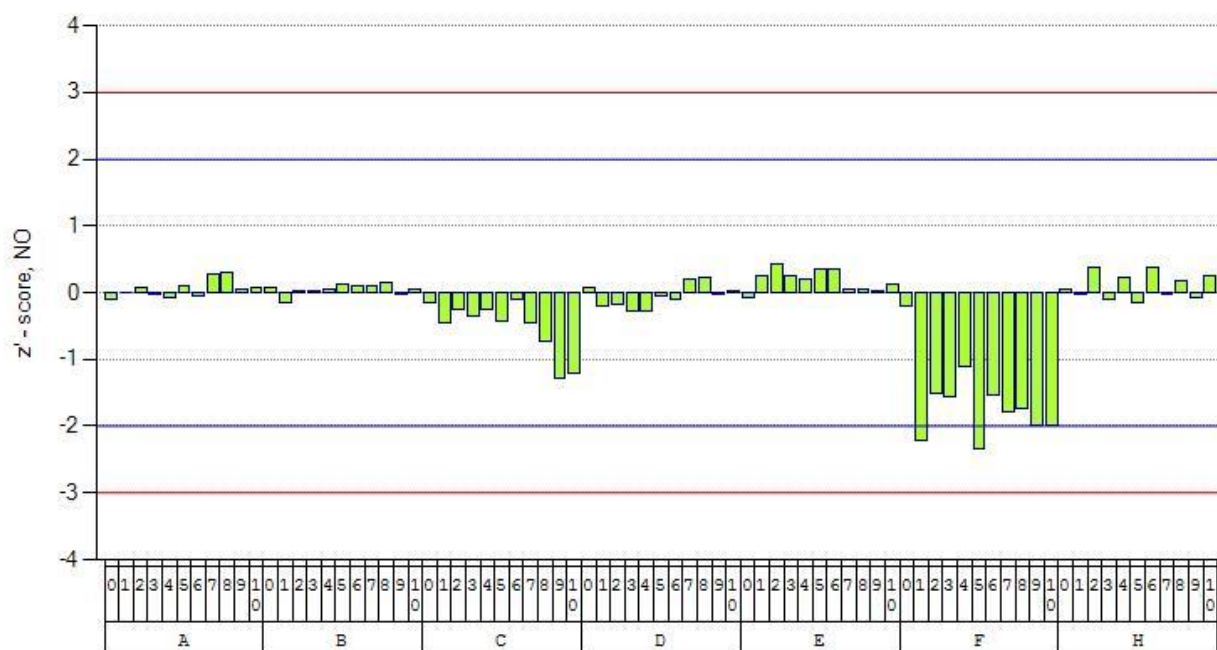
**Figure 3: Z'-score evaluations of O<sub>3</sub> measurements**

Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (65 nmol/mol), 2 (20 nmol/mol), 3 (35 nmol/mol), 4 (115 nmol/mol), 5 (90 nmol/mol).



**Figure 4: 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 (135 nmol/mol), 2 (70 nmol/mol), 3 (35 nmol/mol), 4 (15 nmol/mol), 5 (65 nmol/mol), 6 (25 nmol/mol), 7 (490 nmol/mol), 8 (380 nmol/mol), 9 (300 nmol/mol), 10 (200 nmol/mol).



**Figure 5: Z'-score evaluations of NO<sub>2</sub> measurements**

Scores are given for each participant and each concentration level (run). Run number order (with nominal concentration) is: 0 (0 nmol/mol), 1 (65 nmol/mol), 2 (20 nmol/mol), 3 (40 nmol/mol), 4 (110 nmol/mol), 5 (100 nmol/mol). The assessment criteria are presented as  $z'=\pm 2$  (blue line) and  $z'=\pm 3$  (red line).



## 5.2 E<sub>n</sub>-score

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

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

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  $U_{x_i}$ . Satisfactory results are the ones for which  $|E_n| < 1$ .

In 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 denominator of equation 2 ( $\sqrt{U_{x_i}^2 + U_X^2}$ ). These plots represent also the  $E_n$ -score evaluations where, considering the  $E_n$  criterion ( $|E_n| < 1$ ), all results with error bars crossing the x-axis are satisfactory. Reported standard uncertainties (Annex A) that are larger than the "standard deviation for proficiency assessments" ( $\sigma_p$ , Table 4) are considered not fit-for-purpose and are denoted with "\*" in the x-axis of each figure. The  $E_n$  evaluation showed few unsatisfactory results for different parameters and concentrations, as reported in table 5.

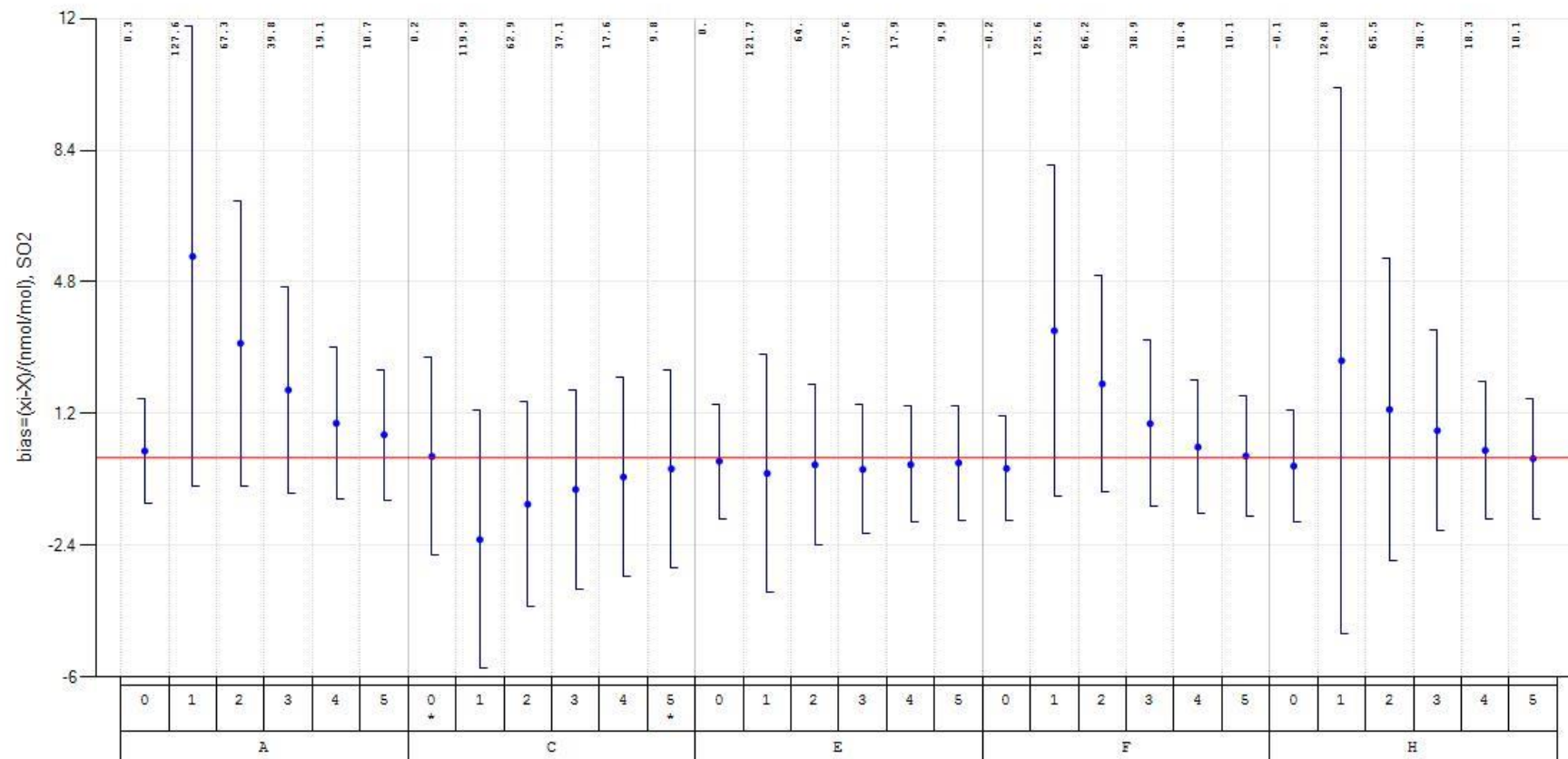
**Table 5:** Unsatisfactory results according to  $E_n$ -score.

Parameter	Lab Code	Value	Run	En	En evaluation
NO	C	291,43	NO_9	-1,1	unsatisfactory
NO	C	193,93	NO_10	-1,1	unsatisfactory
NO	F	67,58	NO_2	-1,4	unsatisfactory
NO	F	32,71	NO_3	-1,3	unsatisfactory
NO	F	59,73	NO_5	-2,2	unsatisfactory
NO	F	24	NO_6	-1,3	unsatisfactory
NO	F	469,45	NO_7	-1,8	unsatisfactory
NO	F	365,37	NO_8	-1,7	unsatisfactory
NO	F	285,44	NO_9	-2	unsatisfactory
NO	F	127,79	NO_1	-2,2	unsatisfactory



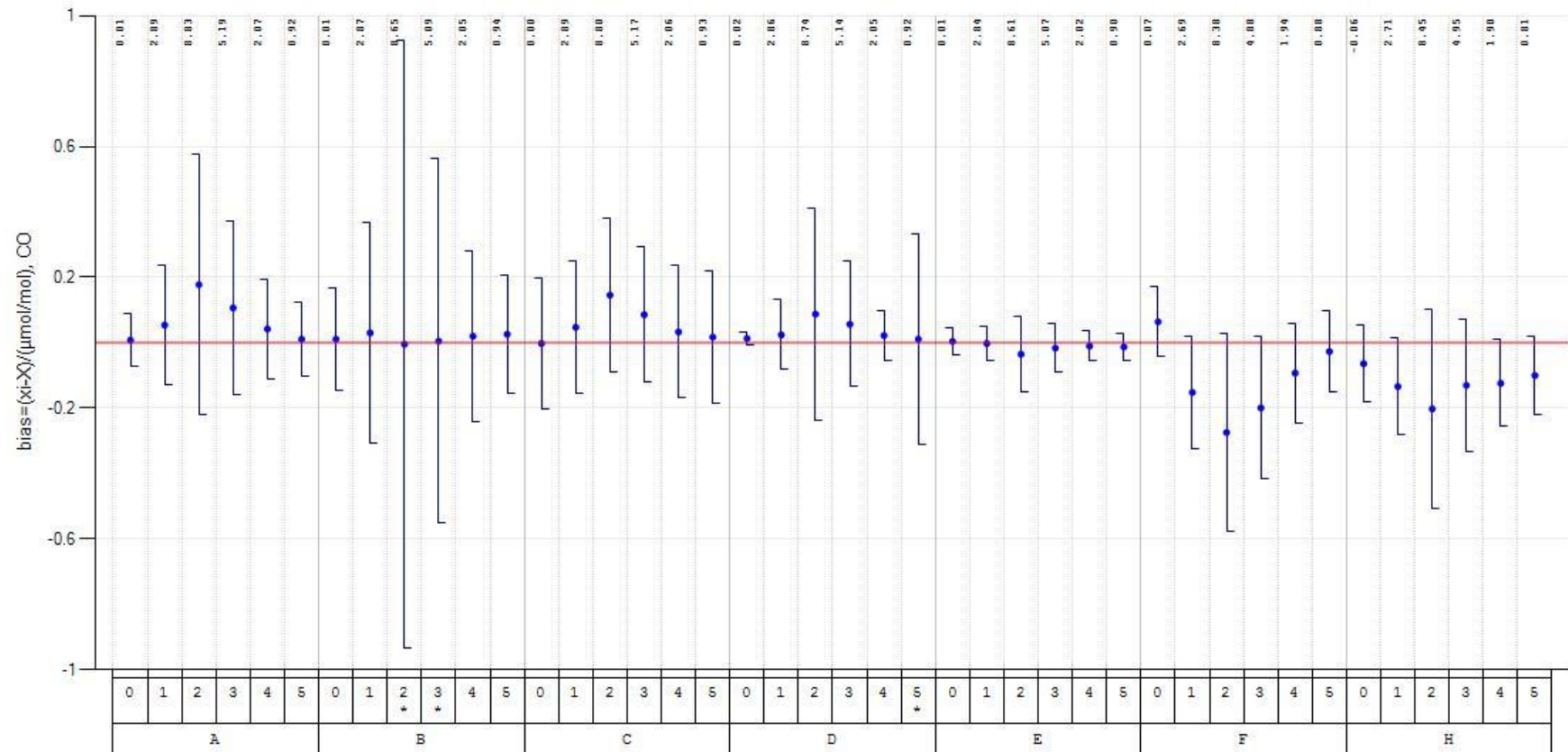
**Figure 6:** Bias of participant's SO<sub>2</sub> measurement results.

Expanded uncertainty of bias for each run is presented as error bar. For each evaluation is given the run number (from 0 to 5) and the participants rounded run average (nmol/mol). The '\*' mark indicates reported standard uncertainties bigger than  $\sigma_p$ . Laboratory B and D didn't reported results for this pollutant.



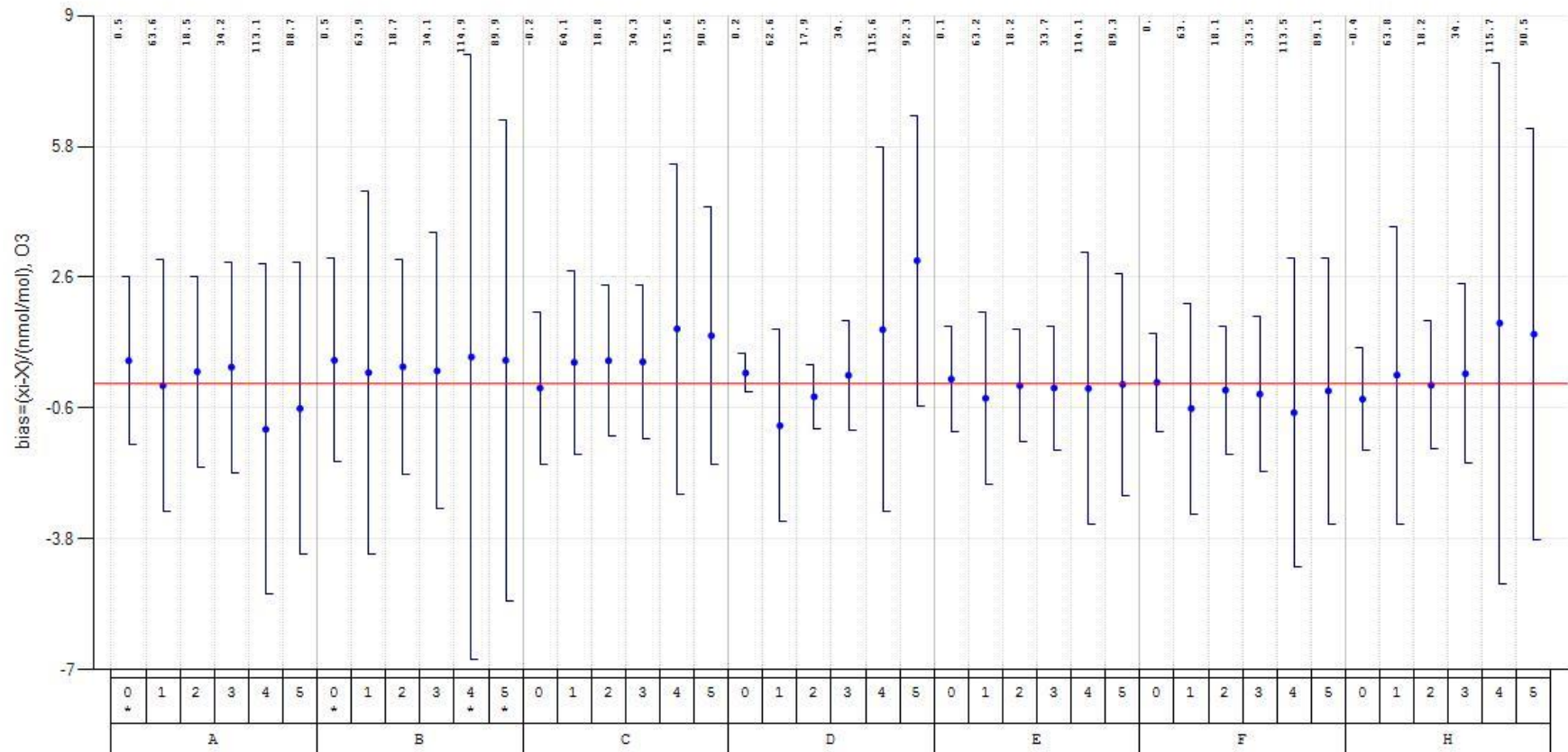
**Figure 7: Bias of participant's CO measurement results**

Expanded uncertainty of bias for each run is presented as error bar. For each evaluation is given the run number (from 0 to 5) and the participants rounded run average ( $\mu\text{mol/mol}$ ). The '\*' mark indicates reported standard uncertainties bigger than  $\sigma_p$ .



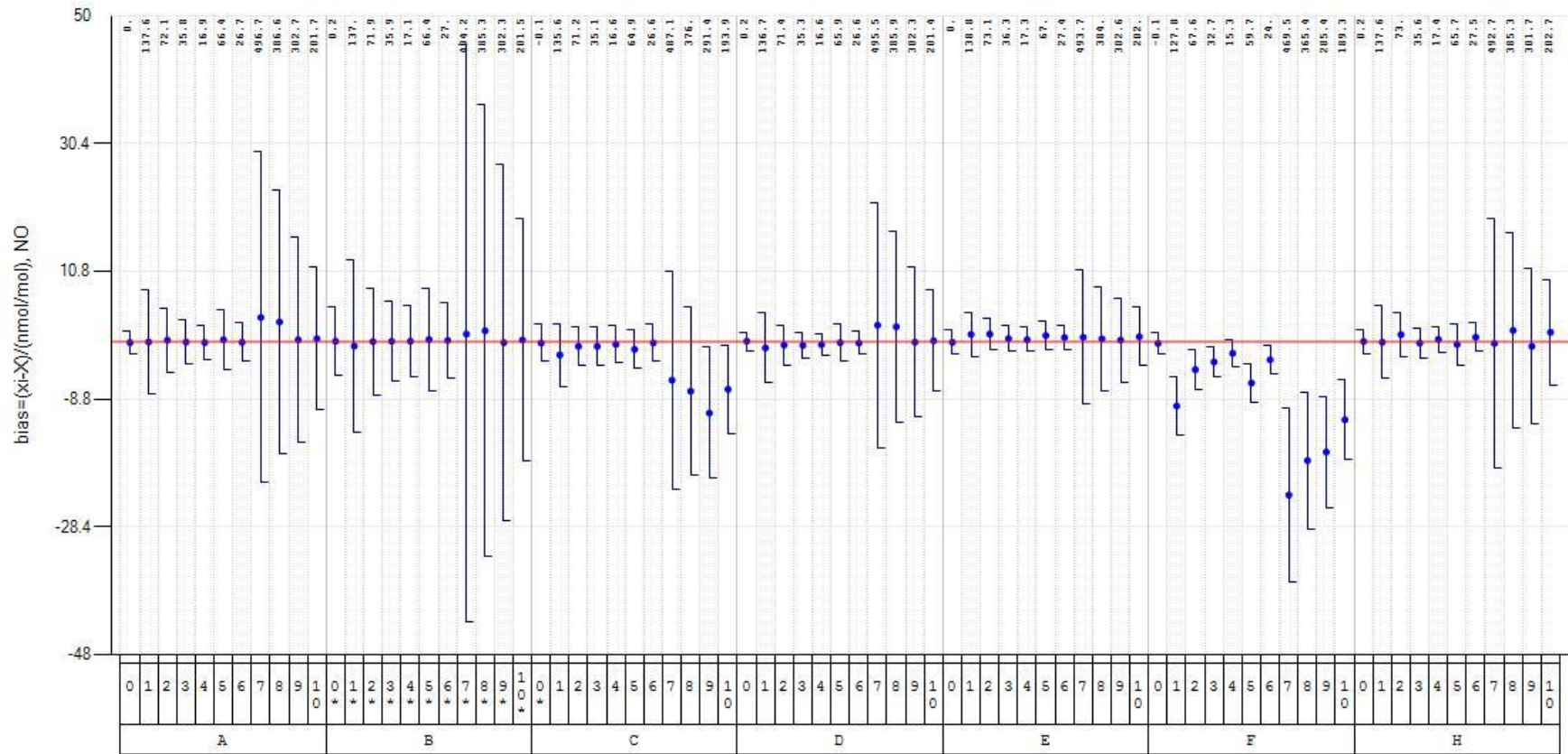
**Figure 8:** Bias of participant's O<sub>3</sub> measurement results

Expanded uncertainty of bias for each run is presented as error bar. For each evaluation is given the run number (from 0 to 5) and the participants rounded run average (nmol/mol). The '\*' mark indicates reported standard uncertainties bigger than  $\sigma_p$ .



**Figure 9: Bias of participant's NO measurement results**

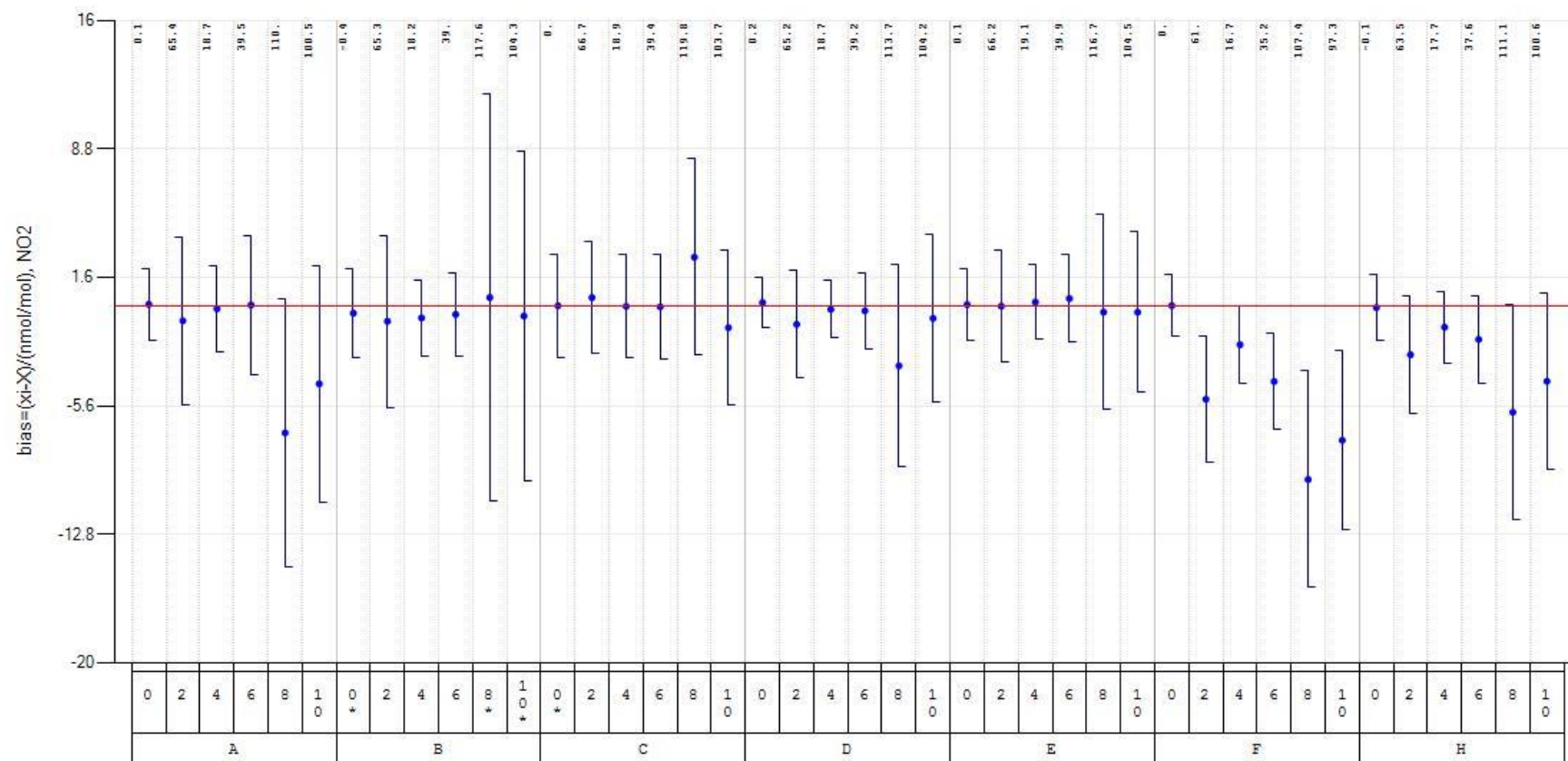
Expanded uncertainty of bias for each run is presented as error bar. For each evaluation is given the run number (from 0 to 10) and the participants rounded run average (nmol/mol). The '\*' mark indicates reported standard uncertainties bigger than  $\sigma_p$ .





**Figure 10:** Bias of participant's NO<sub>2</sub> measurement results

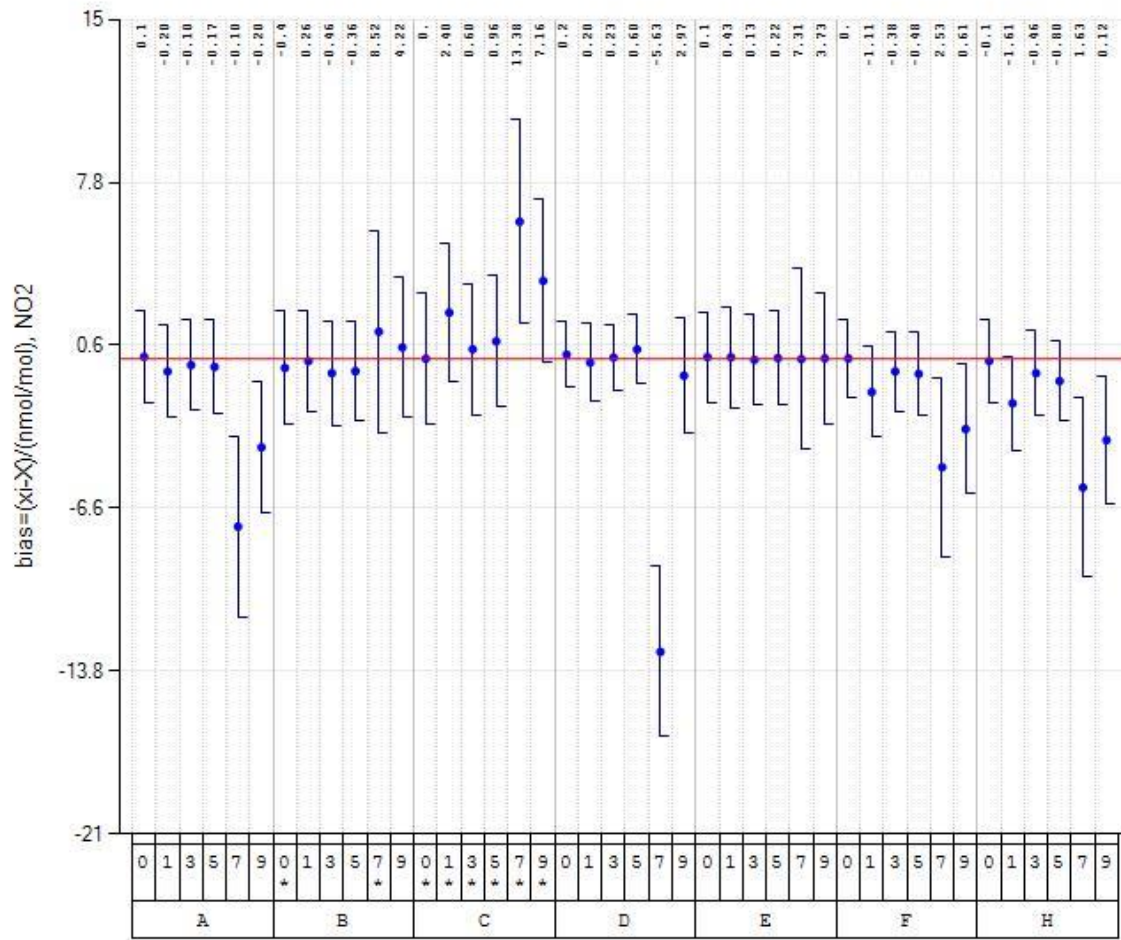
Expanded uncertainty of bias is presented as error bar for NO<sub>2</sub> run numbers 0, 2, 4, 6, 8 and 10 (see Table 3). For each evaluation is given the run number and the participants rounded run average (nmol/mol). The '\*' mark indicates reported standard uncertainties bigger than  $\sigma_p$ .



## 6. Performance characteristics of individual laboratories

Individual participants' biases were evaluated and are presented in chapter 5.2 (Figure 6 - 10). Since the results of NO<sub>2</sub> runs 0, 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<sub>2</sub> measurements with error bars representing expanded uncertainty for run numbers 0, 1, 3, 5, 7 and 9. Within these test gas mixtures there is no gas phase titration to produce NO<sub>2</sub> (see table 3). For each evaluation is given the run number and the participants rounded run average (nmol/mol).



### 6.1 Converter efficiencies of NO<sub>2</sub>-to-NO for NO<sub>x</sub> analysers

Since NO and NO<sub>2</sub> test gases were produced by gas phase titration, it is possible to evaluate the efficiency of the NO<sub>2</sub>-to-NO converter of each participant's NO<sub>x</sub> analyser. The evaluation takes each participant's NO and NO<sub>2</sub> measurements before and after oxidation by O<sub>3</sub>. However, possible minor instabilities in the preparation of the test gas mixtures were not taken into account. The converter efficiency ( $\alpha$ ) is calculated using Equation 3 [4]:

$$\alpha = \frac{[NO_2]_i - [NO_2]_{i-1}}{[NO]_{i-1} - [NO]_i} \cdot 100\% \quad \text{Equation 3}$$

Ideal value for  $\alpha$  is 100%. The evaluation of equation 3 for each participant at different concentration levels are given in Table 6. The results are all acceptable.

**Table 6:** Efficiency of NO<sub>2</sub>-to-NO converters.

Lab code	NO <sub>2</sub> nmol/mol	$\alpha$ (%)
A	65	100,1
	20	99,8
	40	100,0
	110	100,0
	100	99,7
B	65	100,0
	20	99,5
	40	99,7
	110	100,2
	100	99,3
C	65	99,7
	20	98,7
	40	100,4
	110	95,8
	100	99,0
D	65	100,7
	20	98,1
	40	99,6
	110	100,1
	100	100,7

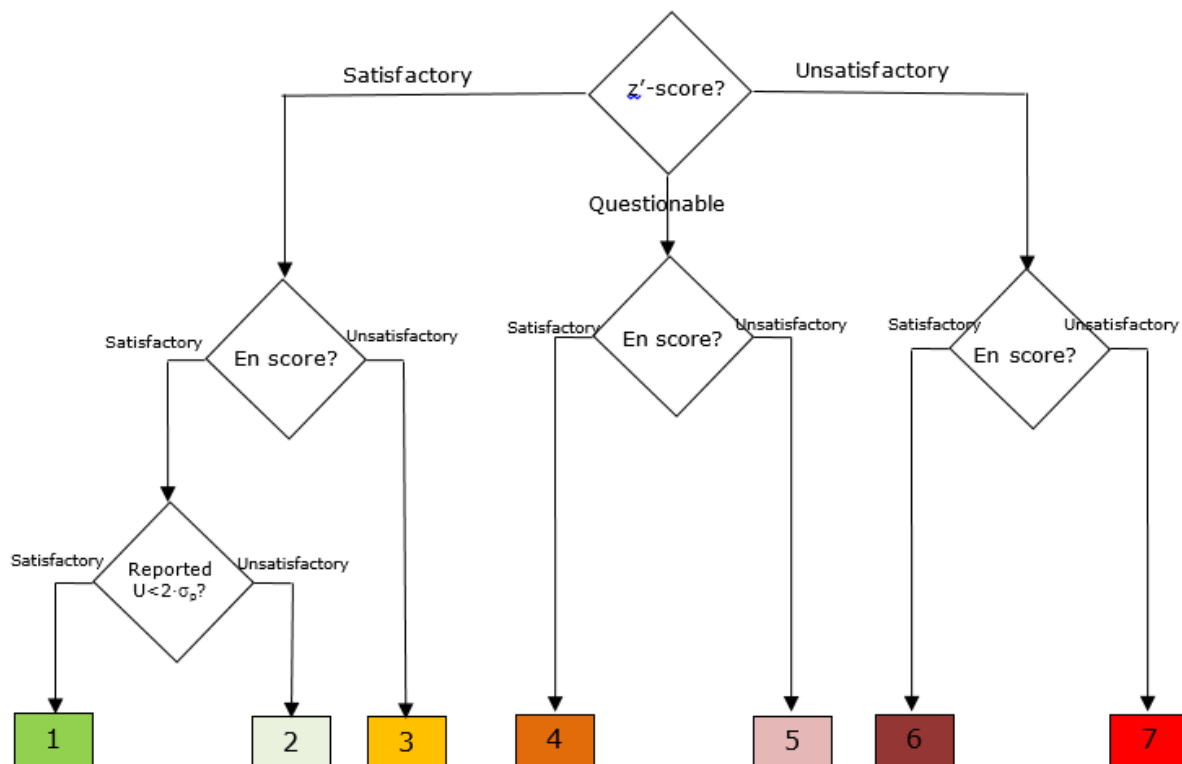
Lab code	NO <sub>2</sub> nmol/mol	$\alpha$ (%)
E	65	100,0
	20	100,0
	40	100,1
	110	99,8
	100	100,2
F	65	103,1
	20	97,9
	40	99,9
	110	100,7
	100	100,6
G	65	100,1
	20	99,5
	40	99,9
	110	100,4
	100	100,0
H	65	100,7
	20	99,6
	40	100,5
	110	102,0
	100	101,6

## 7. 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-score satisfactory), but the reported uncertainty is too high
- **3:** measured value is satisfactory (z'-score satisfactory) but the reported uncertainty is underestimated (En-score unsatisfactory)
- **4:** measurement result is questionable (z'-score questionable), but due to a high reported uncertainty can be considered valid (En-score satisfactory)
- **5:** measurement result is questionable (z'-score questionable and En-score unsatisfactory)
- **6:** measurement result is unsatisfactory (z'-score unsatisfactory) but due to a high reported uncertainty can be considered valid (En-score satisfactory)
- **7:** measurement result is unsatisfactory (z'-score unsatisfactory and En-score unsatisfactory)

**Figure 12:** Decision diagram for general assessment of proficiency results.





The results of the ILC were assigned to categories according to the diagram given in Figure 12 and are presented in the following Table 7. All the results are explained in paragraph 9.

**Table 7:** General assessment of proficiency results.

"n.r." is referring to values not reported.

	run numb	Ref. conc. level	ILC code						
			A	B	C	D	E	F	H
CO (μmol/mol)	0	0,002	1	1	1	1	1	1	1
	1	2,839	1	1	1	1	1	1	1
	2	8,649	1	2	1	1	1	1	1
	3	5,083	1	2	1	1	1	1	1
	4	2,028	1	1	1	1	1	1	1
	5	0,909	1	1	1	2	1	1	1
NO (nmol/mol)	0	0,12	1	2	2	1	1	1	1
	1	137,65	1	2	1	1	1	5	1
	2	71,87	1	2	1	1	1	3	1
	3	35,82	1	2	1	1	1	3	1
	4	17,01	1	2	1	1	1	1	1
	5	66,06	1	2	1	1	1	5	1
	6	26,77	1	2	1	1	1	3	1
	7	492,97	1	2	1	1	1	3	1
	8	383,60	1	2	1	1	1	3	1
	9	302,36	1	2	3	1	1	3	1
	10	201,22	1	2	3	1	1	3	1
NO <sub>2</sub> (nmol/mol)	0	0,01	1	2	2	1	1	1	1
	2	66,20	1	1	1	1	1	5	1
	4	18,89	1	1	1	1	1	1	1
	6	39,44	1	1	1	1	1	5	1
	8	117,08	1	2	1	1	1	5	1
	10	104,86	1	2	1	1	1	5	1
O <sub>3</sub> (nmol/mol)	0	-0,06	2	2	1	1	1	1	1
	1	63,60	1	1	1	1	1	1	1
	2	18,25	1	1	1	1	1	1	1
	3	33,80	1	1	1	1	1	1	1
	4	114,25	1	2	1	1	1	1	1
	5	89,29	1	2	1	1	1	1	1
SO <sub>2</sub> (nmol/mol)	0	0,12	1	n.r.	2	n.r.	1	1	1
	1	122,10	1	n.r.	1	n.r.	1	1	1
	2	64,21	1	n.r.	1	n.r.	1	1	1
	3	37,92	1	n.r.	1	n.r.	1	1	1
	4	18,13	1	n.r.	1	n.r.	1	1	1
	5	10,08	1	n.r.	2	n.r.	1	1	1

## 8. Assigned values

The assigned values of tested concentration levels (run) were derived from ERLAP's 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 participating regularly to key comparisons of the Gas Analysis Working Group within the framework of BIPM's CCQM.

During this ILC ERLAP's SO<sub>2</sub>, 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 dynamic dilution method using mass flow controllers [8]. All flows were measured with a certified molbloc/molbox1 system. For O<sub>3</sub> measurements, the analysers 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<sub>2</sub> channel of NO<sub>x</sub> analyser the GPT test was performed to establish the efficiency of NO<sub>2</sub>-converter.

ERLAP's measurement results were verified by comparison to the group statistics ( $x^*$  and  $s^*$ ) for every parameter and concentration level of the ILC. These statistics are calculated from participants, applying the robust method described in the Annex C of the ISO 13528 [13]. The verification is taking into account ERLAP's measurement result ( $X$ ) and its standard uncertainty ( $u_X$ ) as given in Equation 4 [13]:

$$\frac{|x^* - X|}{\sqrt{\frac{(1.25 s^*)^2}{p} + u_X^2}} \leq 2 \quad \text{Equation 4}$$

Where  $x^*$  and  $s^*$  represent robust average and robust standard deviation respectively and  $p$  is the number of participants. In **table 8** all inputs for Equation 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.

**Table 8:** Verification of assigned values (X)

run	unit	X	uX	x*	s*	p
CO_0	μmol/mol	0,00	0,01	0,01	0,01	8
CO_1	μmol/mol	2,84	0,02	2,85	0,04	8
CO_2	μmol/mol	8,65	0,04	8,64	0,18	8
CO_3	μmol/mol	5,08	0,03	5,08	0,11	8
CO_4	μmol/mol	2,03	0,01	2,03	0,03	8
CO_5	μmol/mol	0,91	0,01	0,91	0,02	8
NO_0	nmol/mol	0,12	0,71	0,07	0,14	8
NO_1	nmol/mol	137,65	1,06	137,17	0,86	8
NO_2	nmol/mol	71,87	0,82	71,87	0,98	8
NO_3	nmol/mol	35,82	0,74	35,60	0,50	8
NO_4	nmol/mol	17,01	0,72	16,89	0,46	8
NO_5	nmol/mol	66,06	0,81	65,94	0,69	8
NO_6	nmol/mol	26,77	0,73	26,78	0,36	8
NO_7	nmol/mol	492,97	2,92	493,20	2,71	8
NO_8	nmol/mol	383,60	2,31	384,38	1,93	8
NO_9	nmol/mol	302,36	1,88	302,10	0,55	8
NO_10	nmol/mol	201,22	1,36	201,39	0,75	8
NO2_0	nmol/mol	0,01	0,72	0,03	0,11	8
NO2_1	nmol/mol	0,36	0,86	0,13	0,55	8
NO2_2	nmol/mol	66,20	0,94	65,24	1,36	8
NO2_3	nmol/mol	0,17	0,72	-0,03	0,44	8
NO2_4	nmol/mol	18,89	0,73	18,59	0,45	8
NO2_5	nmol/mol	0,18	0,76	0,02	0,66	8
NO2_6	nmol/mol	39,44	0,78	39,22	0,47	8
NO2_7	nmol/mol	7,32	1,88	4,63	5,80	8
NO2_8	nmol/mol	117,08	1,98	114,27	4,74	8
NO2_9	nmol/mol	3,71	1,29	2,76	2,76	8
NO2_10	nmol/mol	104,86	1,40	103,50	1,31	8
O3_0	nmol/mol	-0,06	0,24	0,05	0,32	8
O3_1	nmol/mol	63,60	0,47	63,51	0,50	8
O3_2	nmol/mol	18,25	0,23	18,32	0,32	8
O3_3	nmol/mol	33,80	0,29	33,97	0,30	8
O3_4	nmol/mol	114,25	0,81	114,61	1,13	8
O3_5	nmol/mol	114,25	0,81	114,61	1,13	8
SO2_0	nmol/mol	0,12	0,50	0,05	0,15	6
SO2_1	nmol/mol	122,10	0,82	123,59	3,25	6
SO2_2	nmol/mol	64,21	0,62	65,04	1,83	6
SO2_3	nmol/mol	37,92	0,54	38,30	1,08	6
SO2_4	nmol/mol	18,13	0,52	18,21	0,42	6
SO2_5	nmol/mol	10,08	0,51	10,05	0,17	6

By comparison to the robust averages ( $\bar{x}^*$ ) with taking into account the standard uncertainties of assigned values ( $u_X$ ), 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. The relative differences between beginning and end measurements are calculated.

$$u_X^2 = u_{X'}^2 + (X \cdot u_{\text{homogeneity}})^2 \quad \text{Equation 5}$$

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 assuming a rectangular distribution of the bias. The standard uncertainties of assigned/reference values ( $u_X$ ) were calculated with Equation 5 and used in the proficiency evaluations of chapter 3.

All calculations about the homogeneity testing data are retained by ERLAP, they are not published in this ILC report, but are available on request.

## 9. 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 ( $\sigma_p$ ) 82% of the results reported during this ILC (see Table 7) by AQUILA laboratories fall into category '1' and are satisfactory both in terms of measured values and evaluated uncertainties. Among the remaining all results presented satisfactory measured values, but the evaluated uncertainties were either too high, category '2' (11%), or too small, category '3' (4%). Six values were found to be questionable for z'-score and unsatisfactory for En-score (category '5', 3% of total values). No values were found unsatisfactory for both value and uncertainty (category '6' and '7').

**Table 9:** Flags summary

<i>ILC</i>	<i>Site</i>	<i>Categories %</i>						
		<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>
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)	90.2	7.6	1.6	0.3	0.3	0.0	0.0
Oct-15 (II)	Ispra (IT)	75.6	10.8	7.3	0.6	3.5	0.0	2.2
Jun-16	Ispra (IT)	79.3	17.8	2.9	0.0	0.0	0.0	0.0
Jun-17 (I)	Ispra (IT)	92.8	4.3	1.8	0.0	0.7	0.0	0.4
Jun-17 (II)	Ispra (IT)	78.1	11.5	6.5	0.0	1.9	0.0	1.9
Jun-18	Ispra (IT)	95.6	1.3	3.1	0.0	0.0	0.0	0.0
Sep-18	Langen (DE)	59.6	40.4	0.0	0.0	0.0	0.0	0.0
May-19(I)	Ispra (IT)	86.0	8.0	4.0	1.0	1.0	0.0	0.0
May-19(II)	Ispra (IT)	82.0	11.0	4.0	0.0	3.0	0.0	0.0

As in previous ILC, 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 B) and previous ILC [20], [21], [22], [23], [24], [25], [33], [34], [35], [36], [37], [38], [39], [40], [41], [43], [44], [45], [46], [47] and [48] 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 this exercise 97.5% of the results in the z'-score evaluations were satisfactory and 2.5% questionable. The results of this ILC is in line with the performances of previous years as shown by the following table 10.

**Table 10:** Z'-score summary

<b>ILC</b>	<b>Site</b>	<b>Satisfactory (%)</b>	<b>Questionable (%)</b>	<b>Unsatisfactory (%)</b>
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/08_1	Ispra (IT)	92.9	4.2	2.9
October/08_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_1	Ispra (IT)	99.4	0.6	0.0
October/15_2	Ispra (IT)	93.7	4.1	2.2
June/16	Ispra (IT)	100	0.0	0.0
June/17_1	Ispra (IT)	98.9	0.7	0.4
June/17_2	Ispra (IT)	96.2	1.9	1.9
June/18	Ispra (IT)	100	0.0	0.0
Sep/18	Langen (DE)	100	0.0	0.0
May/19_1	Ispra (IT)	99.0	1.0	0.0
May/19_2	Ispra (IT)	97.5	2.5	0.0

Comparability of results among AQUILA participants at the highest concentration level is acceptable for all pollutant measurements.

The relative reproducibility limits, at the highest studied concentration levels, are 8.5% for SO<sub>2</sub>, 6.2% for CO, 3.0% for O<sub>3</sub>, for NO 6.1% and for NO<sub>2</sub> 12.8% all within the objective derived from criteria imposed by the European Commission ( $\sigma_p$  see Table 4).

During this ILC the performance of all NRL was generally satisfactory. No values were identified as outliers.

## 10. References

- [1] EC Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, L 152, 11.06.2008
- [2] CEN, EN 14626:2012, *ambient air quality - Standard method for the measurement of the concentration of carbon monoxide by non-dispersive infrared spectroscopy*
- [3] CEN, EN 14212:2012, *ambient air quality - Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence*
- [4] CEN, EN 14211:2012, *ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence*
- [5] CEN, EN 14625:2012, *ambient air quality - Standard method for the measurement of the concentration of ozone by ultraviolet photometry*
- [6] ISO 6143:2001, *Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures*
- [7] ISO 6144:2003, *Gas analysis - Preparation of calibration gas mixtures - Static volumetric method*
- [8] ISO 6145-7:2001, *Gas analysis - Preparation of calibration gas mixtures using dynamic volumetric methods - Part 7: Thermal mass-flow controllers*
- [9] Mücke H.-G., *Air quality management in the WHO European Region – Results of a quality assurance and control programme on air quality monitoring (1994-2004)*, Environment International, EI-01718. 2008
- [10] Mücke H.-G. et al., *European Intercomparison workshop on air quality monitoring vol.4 – Measuring NO, NO<sub>2</sub>, O<sub>3</sub> and SO<sub>2</sub> – Air Hygiene Report 13*, WHO Collaboration Centre for Air Quality Management and Air Pollution Control, ISSN 0938 – 9822. 2000
- [11] AQUILA Network of the National Reference Laboratories of the Member States [online]: Info available: <https://ec.europa.eu/jrc/en/aquila>.
- [12] AQUILA POSITION PAPER N. 37, *Protocol for intercomparison exercise. Organisation of intercomparison exercises for gaseous air pollution for EU national air quality reference laboratories and laboratories of the WHO EURO region*, 2008 Available: [https://ec.europa.eu/jrc/sites/jrcsh/files/aquila-n\\_37-intercomparison-exercise-protocol-2008.pdf](https://ec.europa.eu/jrc/sites/jrcsh/files/aquila-n_37-intercomparison-exercise-protocol-2008.pdf)
- [13] ISO 13528:2015, *Statistical methods for use in proficiency testing by inter-laboratory comparisons*
- [14] ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions*
- [15] ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*
- [16] ISO 5725-6:1994, *Accuracy (trueness and precision) of measurement methods and results - Part 6: Use in practice of accuracy values*
- [17] De Saeger E. et al., *Harmonisation of Directive 92/72/EEC on air pollution by ozone*, EUR 17662, 1997
- [18] De Saeger E. et al., *European comparison of Nitrogen Dioxide calibration methods*, EUR 17661, 1997
- [19] ISO 15337:2009, *Ambient air - Gas phase titration - Calibration of analysers for ozone*



- [20] Kapus M. et al. *The evaluation of the Intercomparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> carried out in June 2007 in Ispra*. JRC scientific and technical reports. EUR 23804. 2009
- [21] Kapus M. et al. *The evaluation of the Intercomparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> - April 2008*. JRC scientific and technical reports. EUR 23805. 2009
- [22] Kapus M. et al. *The evaluation of the Intercomparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 6-9 October 2008*. JRC scientific and technical reports. EUR 23806. 2009
- [23] Kapus M. et al. *The evaluation of the Intercomparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 13-16 October 2008*. JRC scientific and technical reports. EUR 23807. 2009
- [24] Belis C. A. et al. *The evaluation of the Interlaboratory comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> Langen 20-25 September 2009*. EUR 24376. 2010
- [25] Belis C. A. et al. *The evaluation of the Interlaboratory comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 19-22 October 2009*. EUR 24476. 2010
- [26] Viallon J. et al. *Final report, on-going key comparison BIPM.QM-K1: Ozone at ambient level, comparison with JRC, 2008*. Metrologia 46 08017, 2009. doi: 10.1088/0026-1394/46/1A/08017
- [27] Viallon, J., et al. *International comparison CCQM-P28: Ozone at ambient level*, Metrologia 43, Tech. Suppl., 08010, 2006. doi:10.1088/0026-1394/43/1A/08010
- [28] Tanimoto, H., et al. *Intercomparison of ultraviolet photometry and gas-phase titration techniques for ozone reference standards at ambient levels*, Journal of Geophysical Research, vol. 111, D16313, 2006. doi:10.1029/2005JD006983
- [29] ISO, *Guide to the expression of uncertainty in measurements*, Geneva, 1995, ISBN 92-67-10188-9
- [30] VDI 2449 Part3: 2001, *Measurement methods test criteria- General method for the determination of the uncertainty of calibratable measurement methods*.
- [31] Mücke H-G, et al. *European Intercomparison Workshops on Air Quality Monitoring. Vol. 2 – Measuring of CO, NO, NO<sub>2</sub> and O<sub>3</sub> – Air Hygiene Report 9*. Berlin, Germany: WHO Collaborating Centre for Air Quality Management and Air Pollution Control; 1996. ISSN 0938-9822.
- [32] ISO 17043:2010, *Conformity assessment - General requirements for proficiency testing*
- [33] Barbieri M. et al. *The evaluation of the Interlaboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> Ispra 14-17 June 2010*. EUR 24943. 2011
- [34] Barbieri M. et al. *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub>, 11<sup>th</sup>-14<sup>th</sup> June 2012 Ispra*. EUR 25536. 2012
- [35] Barbieri M. et al. *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub>, Langen 23<sup>rd</sup>-28<sup>th</sup> October 2011*. EUR 25387. 2012
- [36] Barbieri M. et al. *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub>, 03<sup>rd</sup>-06<sup>th</sup> October 2011 Ispra*. EUR 25386. 2012
- [37] Barbieri M. et al. *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub>, 26<sup>th</sup>-29<sup>th</sup> September 2011 Ispra*. EUR 25385. 2012
- [38] Barbieri M., Lagler F., Mücke H.G., Wirtz K. and Stummer V. *Evaluation of the Laboratory Comparison Exercise for NO, NO<sub>2</sub>, SO<sub>2</sub>, CO, and O<sub>3</sub> Langen (D) 1st-6th September 2013*. EUR 26578. 2014
- [39] Barbieri M., Lagler F., *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 30<sup>st</sup> September-3<sup>rd</sup> October 2013 Ispra*. EUR 26604. 2014

- [40] Barbieri M., Lagler F., *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 7<sup>st</sup>-10<sup>th</sup> October 2013 Ispra*. EUR 26639. 2014
- [41] Barbieri M., Lagler F., *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 19<sup>th</sup>-22<sup>nd</sup> May 2014 Ispra*. EUR 27199. 2014
- [42] EC COMMISSION DIRECTIVE (EU) 2015/1480 of 28 August 2015 (L226/4) amending several annexes to Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council laying down the rules concerning reference methods, data validation and location of sampling points for the assessment of ambient air quality
- [43] Lagler F., Barbieri M., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 12<sup>th</sup>-15<sup>th</sup> October 2015 Ispra*. EUR 28097. 2016
- [44] Barbieri M., Lagler F., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 19<sup>th</sup>-23<sup>rd</sup> October 2015 Ispra*. EUR 28047. 2016
- [45] Barbieri M., Lagler F., Mücke H.G., Wirtz K. and Stummer V. *Evaluation of the Laboratory Comparison Exercise for NO, NO<sub>2</sub>, SO<sub>2</sub>, CO, and O<sub>3</sub> Langen (D) 4<sup>th</sup>-9<sup>th</sup> October 2015*. EUR 27918. 2016
- [46] Barbieri M., Lagler F., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 13-16 June 2016, Ispra*. EUR 28610. 2017
- [47] Barbieri M., Lagler F., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 19-22 June 2017, Ispra*. EUR 29268. 2017
- [48] Barbieri M., Lagler F., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 26-29 June 2017, Ispra*. EUR 29271. 2017
- [49] Barbieri M., Lagler F., Borowiak A. *Evaluation of the Laboratory Comparison Exercise for SO<sub>2</sub>, CO, O<sub>3</sub>, NO and NO<sub>2</sub> 4-7 June 2018, Ispra*. EUR 29671. 2018
- [50] Barbieri M., Lagler F., Mücke H.G., Wirtz K. and Stummer V. *Evaluation of the Laboratory Comparison Exercise for NO, NO<sub>2</sub>, SO<sub>2</sub>, CO, and O<sub>3</sub> Langen (D) 2-7 September 2018*. EUR 29694. 2018

## List of abbreviations

AQUILA	Network of National Reference Laboratories for Air Quality
CEN	European Committee for Standardization
CO	Carbon monoxide
CRM	Certified Reference Material
DQO	Data Quality Objective
ERLAP	European Reference Laboratory for Air Pollution
EC	European Commission
GPT	Gas Phase Titration
ILC	Inter-Laboratory Comparison Exercise
ISO	International Organization for Standardization
JRC	Joint Research Centre
NO	Nitrogen monoxide
NO <sub>2</sub>	Nitrogen dioxide
NO <sub>x</sub>	The oxides of nitrogen, the sum of NO and NO <sub>2</sub>
NRL	National Reference Laboratory
O <sub>3</sub>	Ozone
SO <sub>2</sub>	Sulphur dioxide
VDI	Verein Deutscher Ingenieure
WHO-CC	World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin

### **Mathematical Symbols**

$\alpha$	converter efficiency (EN 14211)
$E_n$	$E_n$ -score statistic (ISO 13528)
$r$	repeatability limit (ISO 5725)
$R$	reproducibility limit (ISO 5725)
$\sigma_p$	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 (ISO 13528)
$u_X$	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)
$x_{i,j}$	$j$ -the reported value of participant $i$ (for particular parameter and concentration level) (ISO 5725)
$z'$	$z'$ -score statistic (ISO 13528)

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## Annex A: The results of the ILC

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 ( $x_i$ ).

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 ( $\bar{x}_i$ ) and standard deviation ( $s_i$ ) of each participant are presented.

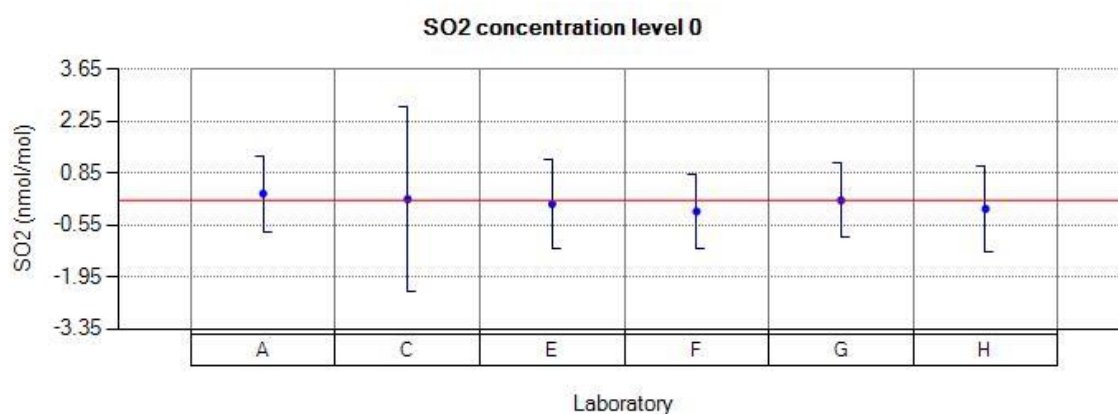
The assigned value is indicated on the graphs with the red line and the individual laboratories expanded uncertainties ( $Ux_i$ ) are indicated with error bars.

### Reported values for SO<sub>2</sub>

**Table 11:** Reported values for SO<sub>2</sub> run 0.

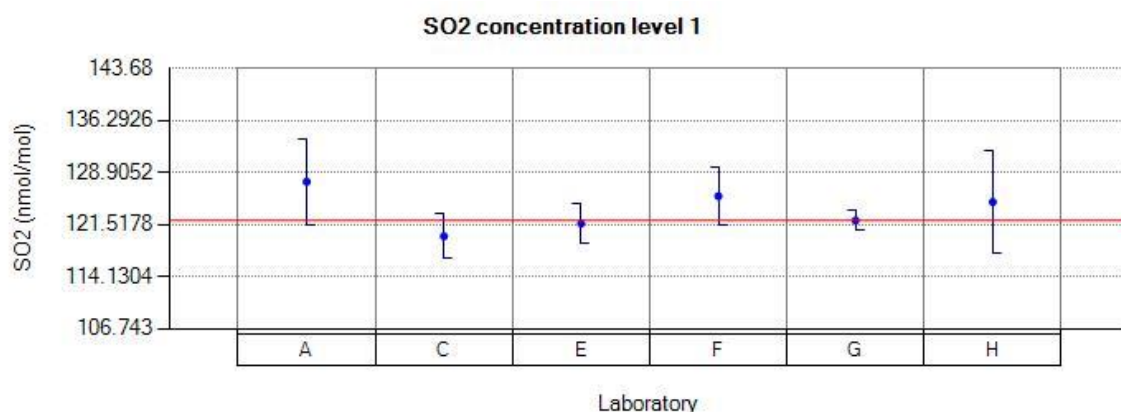
values	laboratories					
	A	C	E	F	G	H
$x_i, 1$	0.30	0.15	0.02	-0.18	0.12	-0.11
$u(x_i)$	0.51	1.25	0.58	0.50	0.51	0.58
$U(x_i)$	1.02	2.50	1.20	1.00	1.01	1.16

**Figure 13:** Reported values for SO<sub>2</sub> run 0.

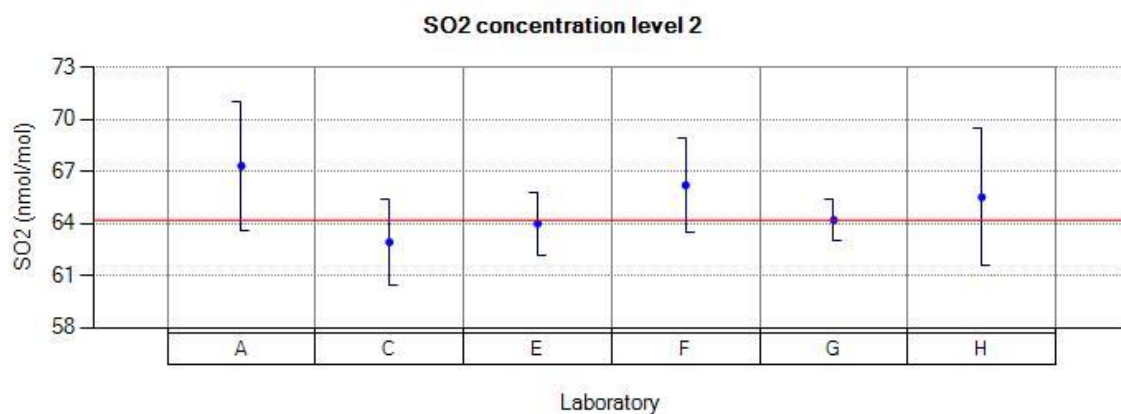


**Table 12:** Reported values for SO<sub>2</sub> run 1

values	laboratories					
	A	C	E	F	G	H
xi, 1	127.40	119.88	121.42	125.06	122.00	124.56
xi, 2	127.60	119.89	121.67	125.74	122.08	124.92
xi, 3	127.80	119.82	121.92	125.90	122.23	124.76
xi	127.60	119.86	121.67	125.56	122.10	124.74
si	0.20	0.03	0.25	0.44	0.11	0.18
u(xi)	3.04	1.56	1.38	2.10	0.73	3.64
U(xi)	6.08	3.12	2.80	4.20	1.46	7.28

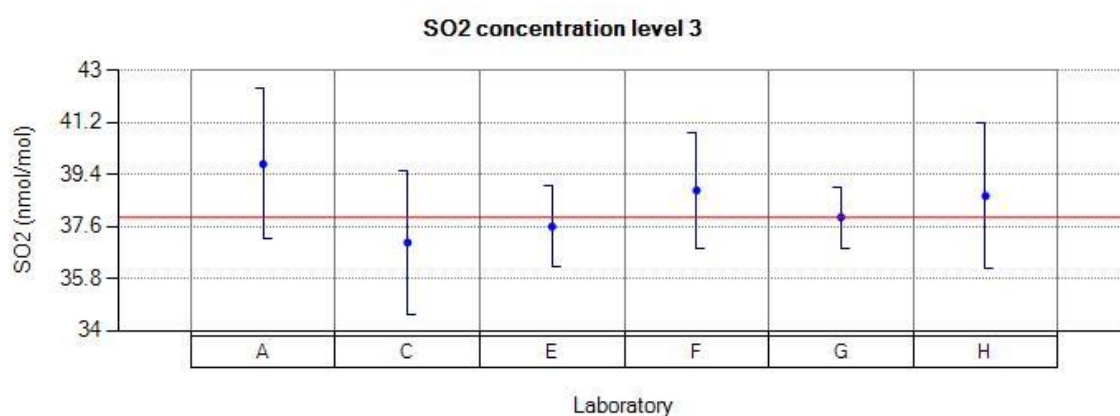
**Figure 14:** Reported values for SO<sub>2</sub> run 1.**Table 13:** Reported values for SO<sub>2</sub> run 2.

values	laboratories					
	A	C	E	F	G	H
xi, 1	67.30	63.03	63.91	66.21	64.17	65.52
xi, 2	67.30	63.06	64.04	66.23	64.17	65.37
xi, 3	67.40	62.71	64.07	66.21	64.28	65.68
xi	67.33	62.93	64.00	66.21	64.20	65.52
si	0.05	0.19	0.08	0.01	0.06	0.15
u(xi)	1.85	1.25	0.88	1.35	0.59	1.97
U(xi)	3.70	2.50	1.80	2.70	1.17	3.94

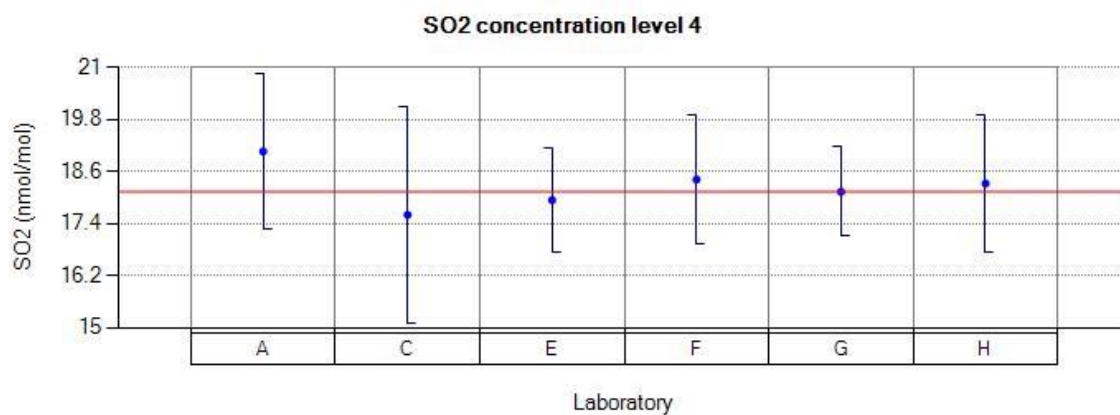
**Figure 15:** Reported values for SO<sub>2</sub> run 2.

**Table 14:** Reported values for SO<sub>2</sub> run 3.

values	laboratories					
	A	C	E	F	G	H
$x_i, 1$	39.80	37.09	37.57	38.81	37.87	38.68
$x_i, 2$	39.70	37.08	37.62	38.83	37.92	38.59
$x_i, 3$	39.80	36.97	37.62	38.92	37.98	38.72
$\bar{x}_i$	39.76	37.04	37.60	38.85	37.92	38.66
$s_i$	0.05	0.06	0.02	0.05	0.05	0.06
$u(\bar{x}_i)$	1.30	1.25	0.69	1.00	0.53	1.26
$U(\bar{x}_i)$	2.61	2.50	1.40	2.00	1.06	2.52

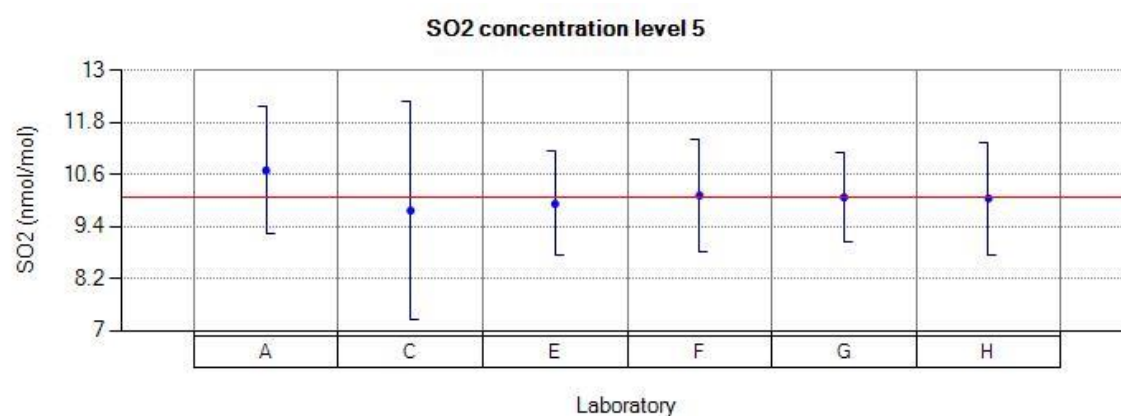
**Figure 16:** Reported values for SO<sub>2</sub> run 3.**Table 15:** Reported values for SO<sub>2</sub> run 4.

values	laboratories					
	A	C	E	F	G	H
$x_i, 1$	19.00	17.54	17.94	18.44	18.13	18.44
$x_i, 2$	19.10	17.63	17.94	18.42	18.14	18.29
$x_i, 3$	19.10	17.64	17.95	18.39	18.13	18.25
$\bar{x}_i$	19.06	17.60	17.94	18.41	18.13	18.32
$s_i$	0.05	0.05	0.00	0.02	0.00	0.10
$u(\bar{x}_i)$	0.90	1.25	0.61	0.75	0.52	0.79
$U(\bar{x}_i)$	1.79	2.50	1.20	1.50	1.03	1.58

**Figure 17:** Reported values for SO<sub>2</sub> run 4.

**Table 16:** Reported values for SO<sub>2</sub> run 5.

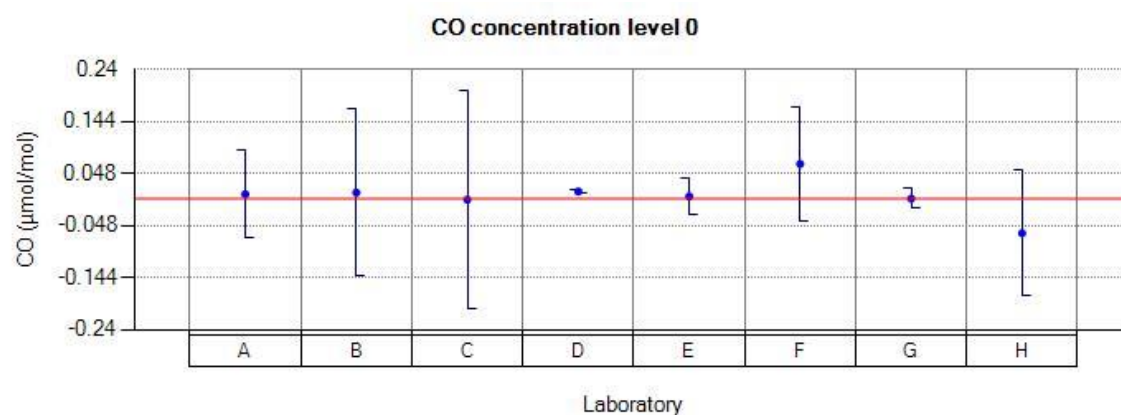
values	laboratories					
	A	C	E	F	G	H
xi, 1	10.70	9.78	9.92	10.12	10.06	10.00
xi, 2	10.70	9.77	9.91	10.12	10.08	10.04
xi, 3	10.70	9.76	9.95	10.12	10.09	10.12
xi	10.70	9.77	9.92	10.12	10.07	10.05
si	0.00	0.01	0.02	0.00	0.01	0.06
u(xi)	0.73	1.25	0.59	0.65	0.51	0.65
U(xi)	1.46	2.50	1.20	1.30	1.02	1.30

**Figure 18:** Reported values for SO<sub>2</sub> run 5.

## Reported values for CO

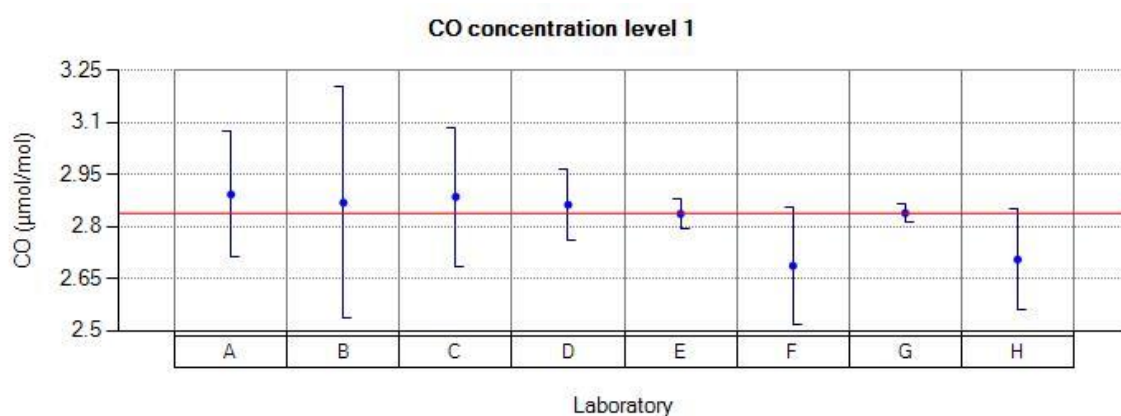
**Table 17:** Reported values for CO run 0.

values	laboratories							
	A	B	C	D	E	F	G	H
xi, 1	0.010	0.013	0.000	0.015	0.006	0.066	0.002	-0.062
u(xi)	0.038	0.077	0.100	0.001	0.017	0.052	0.009	0.058
U(xi)	0.080	0.154	0.200	0.002	0.035	0.105	0.018	0.116

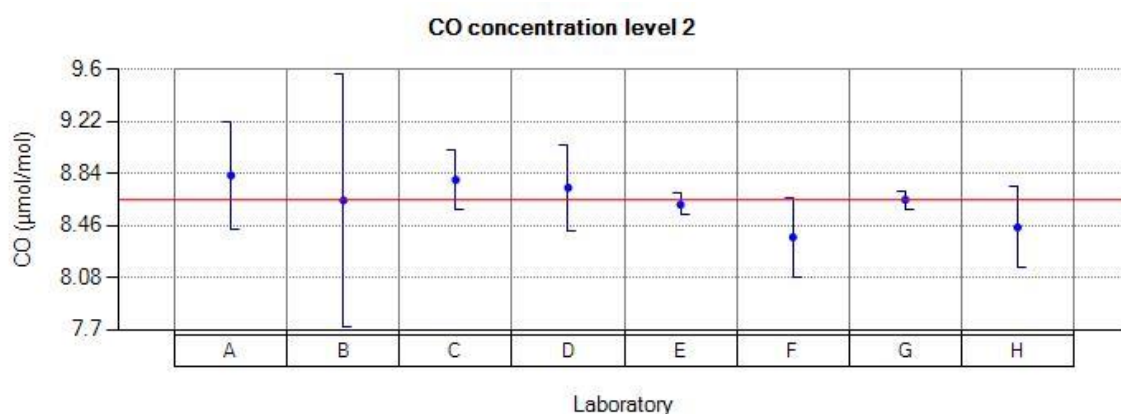
**Figure 19:** Reported values for CO run 0.

**Table 18:** Reported values for CO run 1.

values	laboratories							
	A	B	C	D	E	F	G	H
xi, 1	2.890	2.867	2.882	2.860	2.836	2.691	2.837	2.704
xi, 2	2.890	2.869	2.885	2.860	2.838	2.686	2.838	2.708
xi, 3	2.900	2.872	2.891	2.870	2.837	2.683	2.842	2.704
xi	2.893	2.869	2.886	2.863	2.837	2.687	2.839	2.705
si	0.006	0.003	0.005	0.006	0.001	0.004	0.003	0.002
u(xi)	0.090	0.167	0.100	0.051	0.021	0.085	0.013	0.072
U(xi)	0.180	0.334	0.200	0.102	0.042	0.170	0.027	0.144

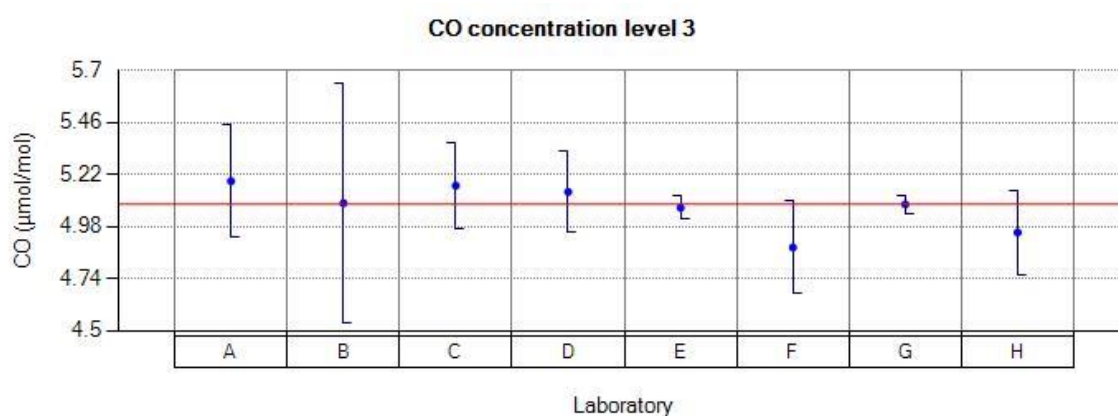
**Figure 20:** Reported values for CO run 1.**Table 19:** Reported values for CO run 2

values	laboratories							
	A	B	C	D	E	F	G	H
xi, 1	8.820	8.653	8.791	8.730	8.613	8.374	8.648	8.452
xi, 2	8.830	8.644	8.797	8.740	8.615	8.373	8.650	8.444
xi, 3	8.830	8.637	8.798	8.740	8.613	8.378	8.650	8.446
xi	8.827	8.645	8.795	8.737	8.614	8.375	8.649	8.447
si	0.006	0.008	0.004	0.006	0.001	0.003	0.001	0.004
u(xi)	0.197	0.462	0.110	0.157	0.039	0.145	0.034	0.147
U(xi)	0.390	0.924	0.220	0.314	0.079	0.290	0.067	0.294

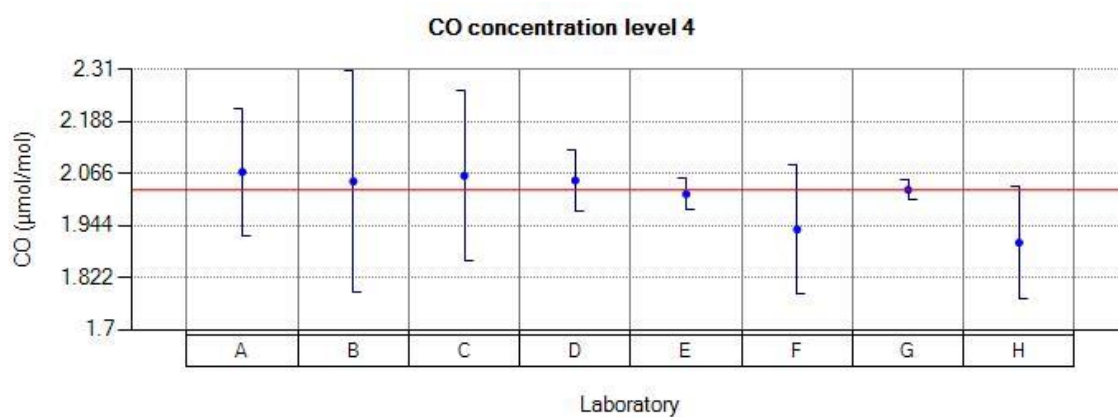
**Figure 21:** Reported values for CO run 2.

**Table 20:** Reported values for CO run 3.

values	laboratories							
	A	B	C	D	E	F	G	H
xi, 1	5.190	5.085	5.166	5.140	5.064	4.881	5.081	4.955
xi, 2	5.190	5.089	5.167	5.140	5.067	4.883	5.084	4.948
xi, 3	5.190	5.089	5.174	5.140	5.071	4.889	5.085	4.956
xi	5.190	5.088	5.169	5.140	5.067	4.884	5.083	4.953
si	0.000	0.002	0.004	0.000	0.004	0.004	0.002	0.004
u(xi)	0.132	0.277	0.100	0.092	0.027	0.106	0.021	0.098
U(xi)	0.260	0.555	0.200	0.185	0.054	0.212	0.041	0.196

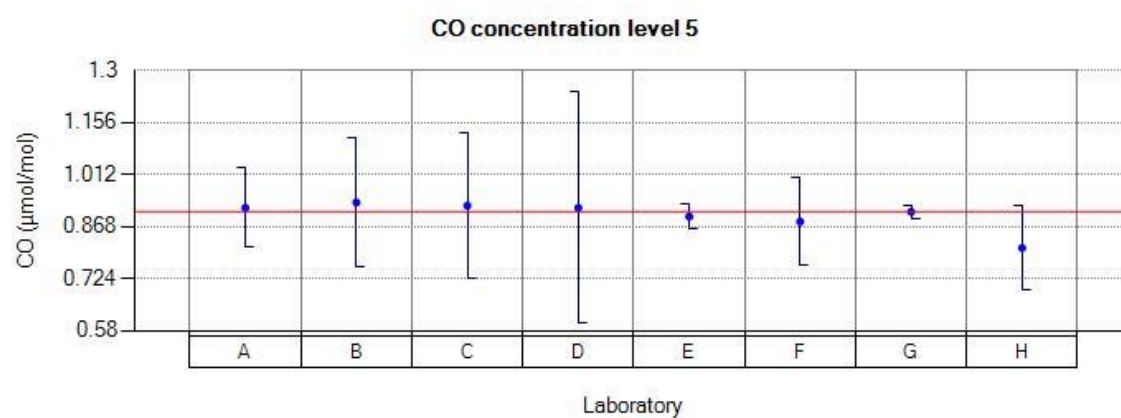
**Figure 22:** Reported values for CO run 3.**Table 21:** Reported values for CO run 4.

values	laboratories							
	A	B	C	D	E	F	G	H
xi, 1	2.070	2.046	2.063	2.050	2.019	1.935	2.030	1.903
xi, 2	2.070	2.047	2.061	2.050	2.018	1.934	2.028	1.909
xi, 3	2.070	2.050	2.058	2.050	2.018	1.935	2.026	1.901
xi	2.070	2.048	2.061	2.050	2.018	1.935	2.028	1.904
si	0.000	0.002	0.003	0.000	0.001	0.001	0.002	0.004
u(xi)	0.075	0.130	0.100	0.036	0.019	0.075	0.011	0.065
U(xi)	0.150	0.260	0.200	0.073	0.038	0.150	0.023	0.130

**Figure 23:** Reported values for CO run 4.

**Table 22:** Reported values for CO run 5.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i,1}$	0.920	0.933	0.926	0.920	0.896	0.881	0.909	0.810
$x_{i,2}$	0.920	0.934	0.926	0.920	0.896	0.879	0.909	0.808
$x_{i,3}$	0.920	0.939	0.925	0.920	0.895	0.885	0.909	0.808
$\bar{x}_i$	0.920	0.935	0.926	0.920	0.896	0.882	0.909	0.809
$s_i$	0.000	0.003	0.001	0.000	0.001	0.003	0.000	0.001
$u(x_i)$	0.055	0.090	0.100	0.160	0.018	0.061	0.010	0.059
$U(x_i)$	0.110	0.179	0.200	0.320	0.036	0.122	0.019	0.118

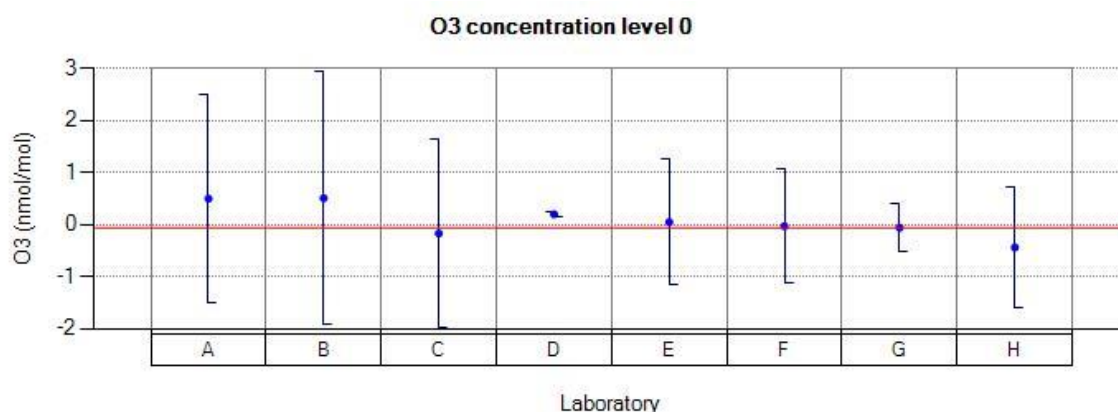
**Figure 24:** Reported values for CO run 5.

## Reported values for O<sub>3</sub>

**Table 23:** Reported values for O<sub>3</sub> run 0.

	laboratories							
values	A	B	C	D	E	F	G	H
$\bar{x}_i, 1$	0.50	0.51	-0.17	0.20	0.05	-0.03	-0.06	-0.44
$u(\bar{x}_i)$	1.00	1.22	0.90	0.02	0.61	0.55	0.24	0.58
$U(\bar{x}_i)$	2.00	2.44	1.80	0.04	1.20	1.10	0.47	1.16

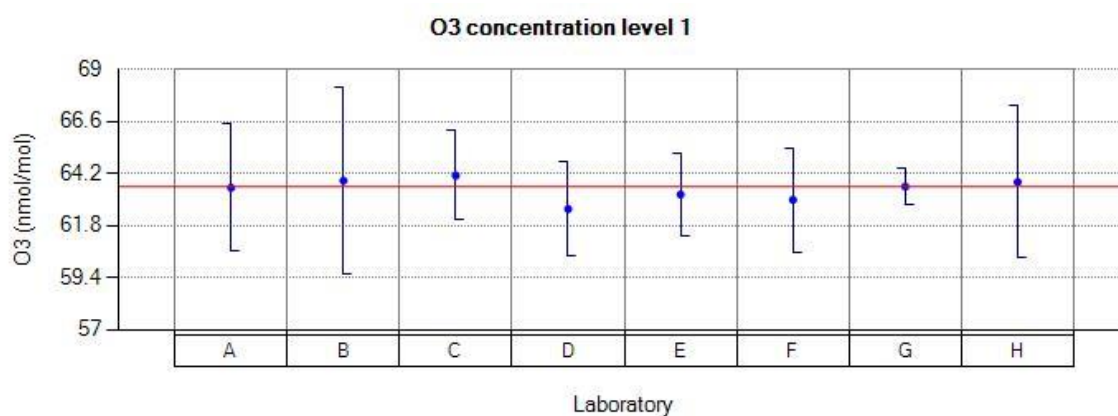
**Figure 25:** Reported values for O<sub>3</sub> run 0.



**Table 24:** Reported values for O<sub>3</sub> run 1.

	laboratories							
values	A	B	C	D	E	F	G	H
$\bar{x}_i, 1$	63.45	63.86	64.16	61.60	63.24	62.97	63.66	63.72
$\bar{x}_i, 2$	63.65	63.93	64.14	62.70	63.23	63.03	63.59	63.84
$\bar{x}_i, 3$	63.55	63.83	64.05	63.40	63.25	62.97	63.55	63.88
$\bar{x}_i$	63.55	63.87	64.11	62.56	63.24	62.99	63.60	63.81
$s_i$	0.10	0.05	0.05	0.90	0.01	0.03	0.05	0.08
$u(\bar{x}_i)$	1.48	2.17	1.03	1.08	0.94	1.20	0.42	1.76
$U(\bar{x}_i)$	2.95	4.34	2.05	2.16	1.90	2.40	0.85	3.52

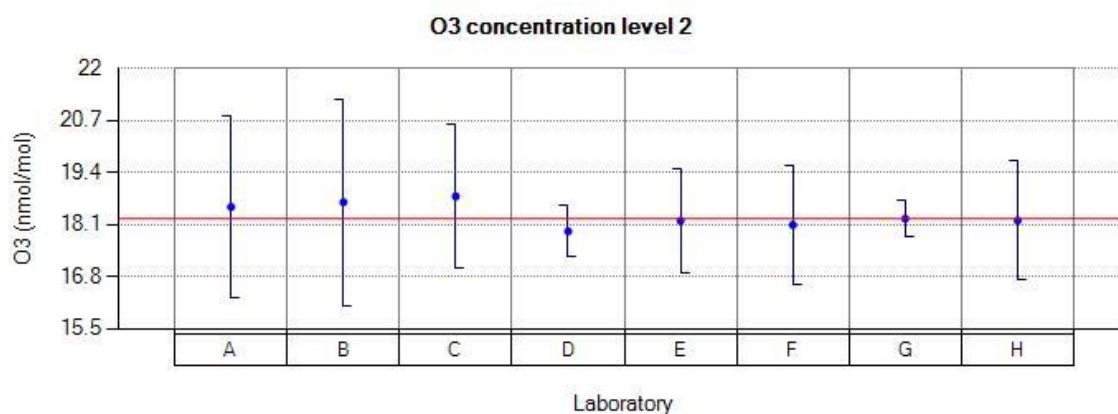
**Figure 26:** Reported values for O<sub>3</sub> run 1.



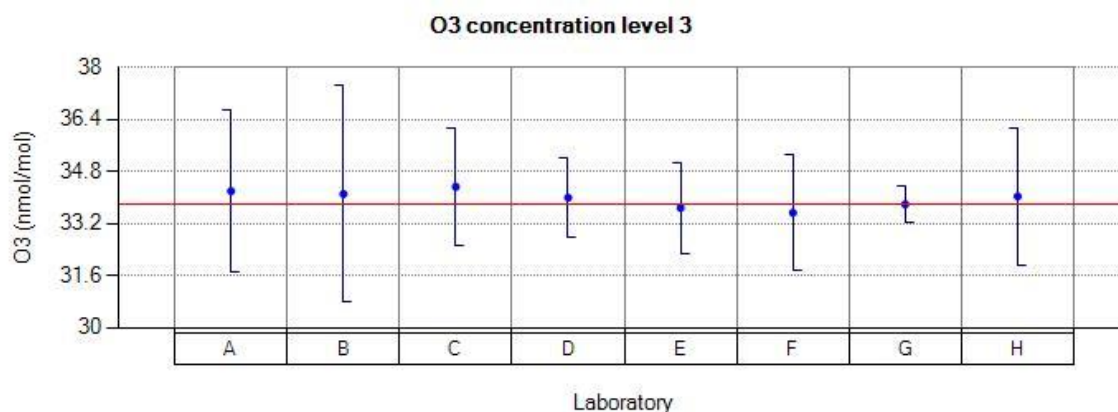


**Table 25:** Reported values for O<sub>3</sub> run 2.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i, 1}$	18.54	18.68	18.81	17.80	18.24	18.15	18.31	18.23
$x_{i, 2}$	18.54	18.67	18.86	18.00	18.19	18.12	18.23	18.20
$x_{i, 3}$	18.54	18.64	18.75	18.00	18.16	18.01	18.21	18.19
$\bar{x}_i$	18.54	18.66	18.80	17.93	18.19	18.09	18.25	18.20
$s_i$	0.00	0.02	0.05	0.11	0.04	0.07	0.05	0.02
$u(\bar{x}_i)$	1.14	1.29	0.90	0.32	0.64	0.75	0.23	0.75
$U(\bar{x}_i)$	2.28	2.58	1.80	0.64	1.30	1.50	0.45	1.50

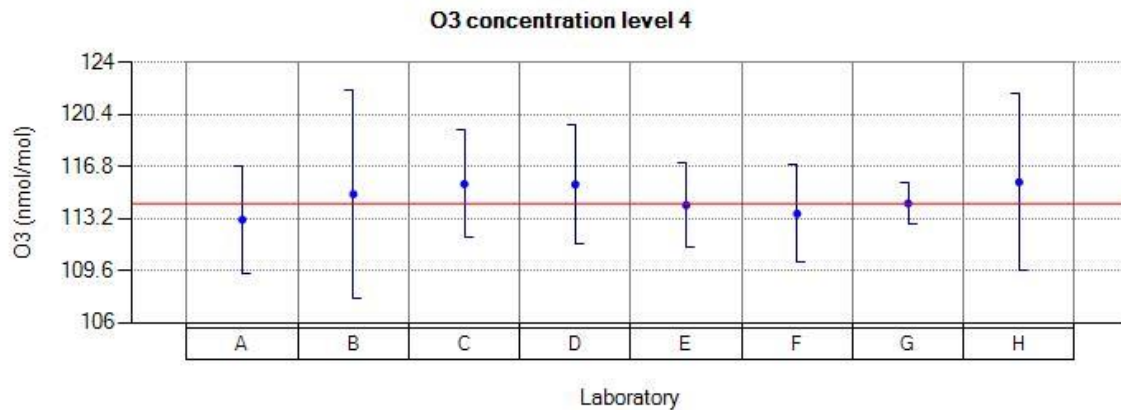
**Figure 27:** Reported values for O<sub>3</sub> run 2.**Table 26:** Reported values for O<sub>3</sub> run 3.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i, 1}$	34.20	34.08	34.37	33.90	33.71	33.46	33.81	34.02
$x_{i, 2}$	34.20	34.16	34.39	34.00	33.69	33.55	33.80	34.09
$x_{i, 3}$	34.20	34.10	34.24	34.10	33.66	33.60	33.78	34.01
$\bar{x}_i$	34.20	34.11	34.33	34.00	33.68	33.53	33.79	34.04
$s_i$	0.00	0.04	0.08	0.10	0.02	0.07	0.01	0.04
$u(\bar{x}_i)$	1.26	1.66	0.90	0.61	0.72	0.90	0.27	1.06
$U(\bar{x}_i)$	2.51	3.32	1.80	1.22	1.40	1.80	0.54	2.12

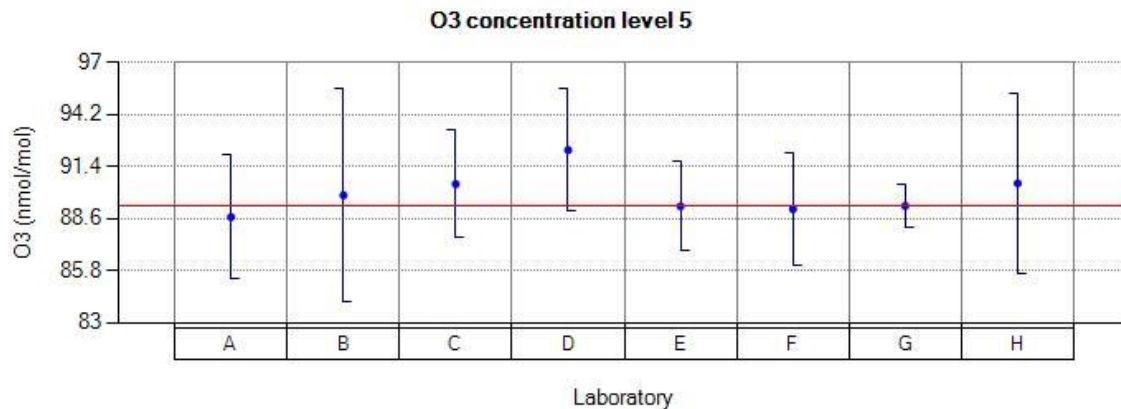
**Figure 28:** Reported values for O<sub>3</sub> run 3.

**Table 27:** Reported values for O<sub>3</sub> run 4.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i, 1}$	113.30	114.80	115.60	115.20	114.00	113.32	114.09	115.63
$x_{i, 2}$	112.99	114.88	115.77	115.50	114.10	113.61	114.25	115.62
$x_{i, 3}$	113.09	115.01	115.41	116.00	114.30	113.69	114.41	115.94
$\bar{x}_i$	113.12	114.89	115.59	115.56	114.13	113.54	114.25	115.73
$s_i$	0.15	0.10	0.18	0.40	0.15	0.19	0.16	0.18
$u(\bar{x}_i)$	1.85	3.60	1.85	2.07	1.44	1.70	0.74	3.08
$U(\bar{x}_i)$	3.70	7.21	3.70	4.15	2.90	3.40	1.47	6.16

**Figure 29:** Reported values for O<sub>3</sub> run 4.**Table 28:** Reported values for O<sub>3</sub> run 5.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i, 1}$	88.79	89.80	90.44	92.10	89.20	88.91	89.26	90.40
$x_{i, 2}$	88.68	89.93	90.51	92.30	89.30	89.28	89.28	90.47
$x_{i, 3}$	88.58	89.84	90.43	92.50	89.30	89.15	89.33	90.63
$\bar{x}_i$	88.68	89.85	90.46	92.30	89.26	89.11	89.29	90.50
$s_i$	0.10	0.06	0.04	0.20	0.05	0.18	0.03	0.11
$u(\bar{x}_i)$	1.67	2.87	1.45	1.66	1.19	1.50	0.58	2.43
$U(\bar{x}_i)$	3.33	5.74	2.89	3.32	2.40	3.00	1.16	4.86

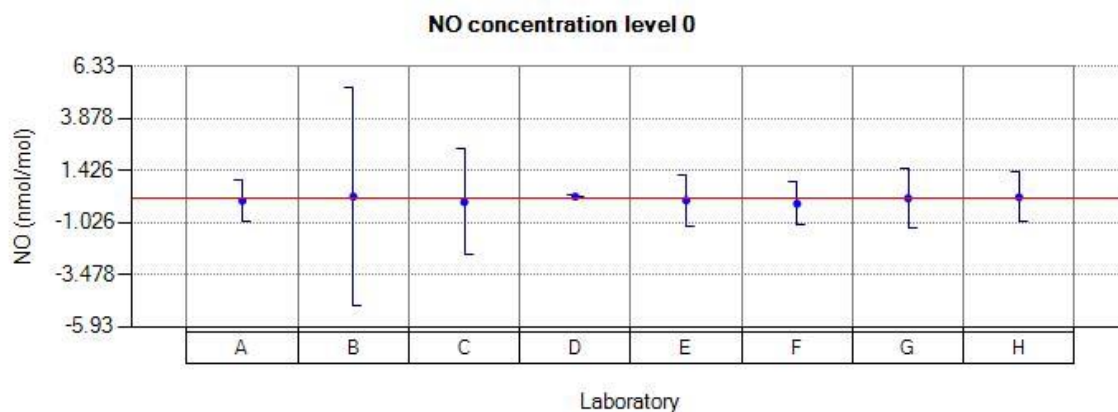
**Figure 30:** Reported values for O<sub>3</sub> run 5.

## Reported values for NO

**Table 29:** Reported values for NO run 0.

	laboratories							
values	A	B	C	D	E	F	G	H
$x_i, 1$	0.00	0.20	-0.06	0.20	0.03	-0.13	0.12	0.17
$u(x_i)$	0.50	2.56	1.25	0.02	0.58	0.50	0.71	0.58
$U(x_i)$	1.00	5.13	2.50	0.04	1.20	1.00	1.42	1.16

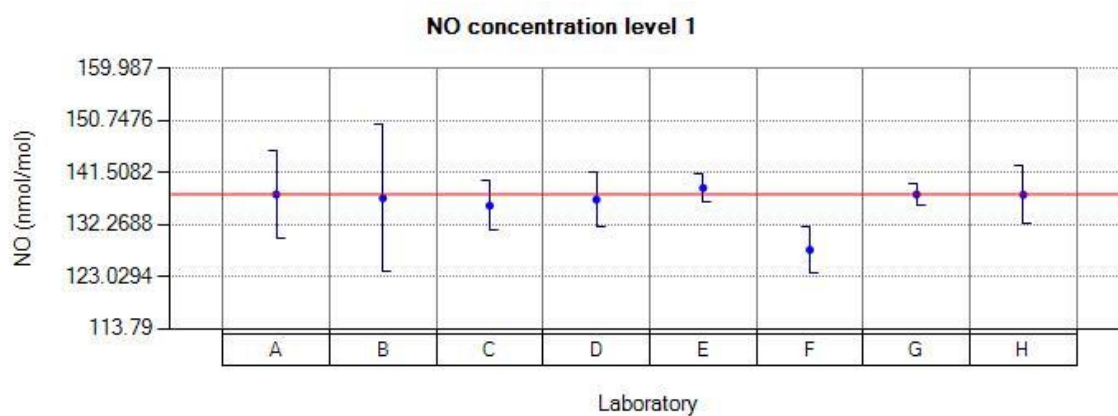
**Figure 31:** Reported values for NO run 0.



**Table 30:** Reported values for NO run 1.

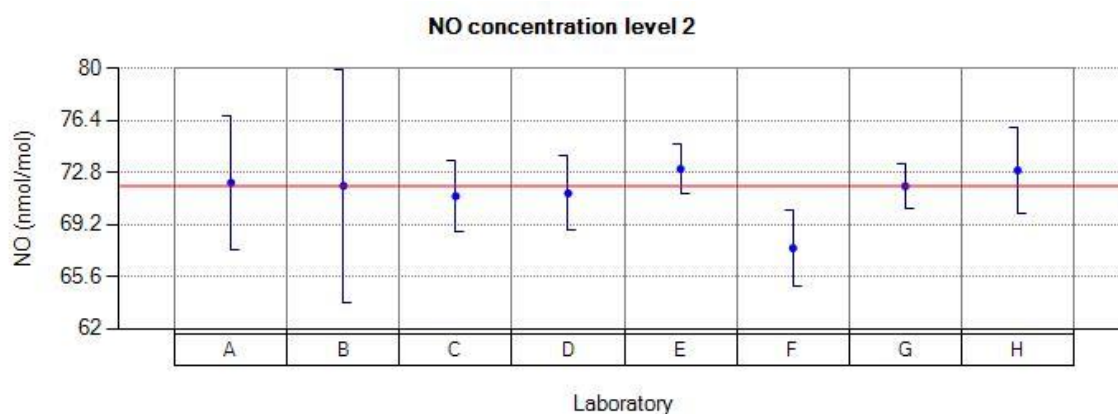
	laboratories							
values	A	B	C	D	E	F	G	H
$x_i, 1$	137.50	136.99	134.75	136.30	138.72	127.66	137.61	137.37
$x_i, 2$	137.60	136.91	135.96	136.90	138.82	127.85	137.61	137.63
$x_i, 3$	137.80	137.06	136.19	136.90	138.81	127.86	137.73	137.74
$\bar{x}_i$	137.63	136.98	135.63	136.70	138.78	127.79	137.65	137.58
$s_i$	0.15	0.07	0.77	0.34	0.05	0.11	0.06	0.19
$u(x_i)$	3.84	6.50	2.17	2.46	1.31	2.00	0.98	2.61
$U(x_i)$	7.69	13.00	4.34	4.92	2.60	4.00	1.96	5.22

**Figure 32:** Reported values for NO run 1.

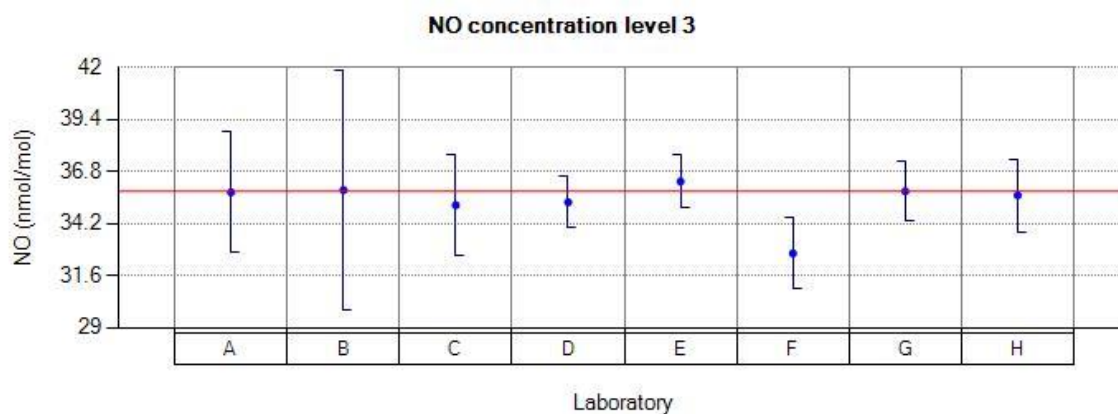


**Table 31:** Reported values for NO run 2.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i, 1}$	72.10	71.88	71.14	71.20	72.95	67.28	71.74	72.82
$x_{i, 2}$	72.10	71.80	71.25	71.40	73.02	67.52	71.84	72.97
$x_{i, 3}$	72.10	71.99	71.13	71.50	73.19	67.93	72.02	73.10
$\bar{x}_i$	72.10	71.89	71.17	71.36	73.05	67.57	71.86	72.96
$s_i$	0.00	0.09	0.06	0.15	0.12	0.32	0.14	0.14
$u(\bar{x}_i)$	2.34	4.03	1.25	1.29	0.85	1.30	0.79	1.49
$U(\bar{x}_i)$	4.67	8.07	2.50	2.58	1.70	2.60	1.59	2.98

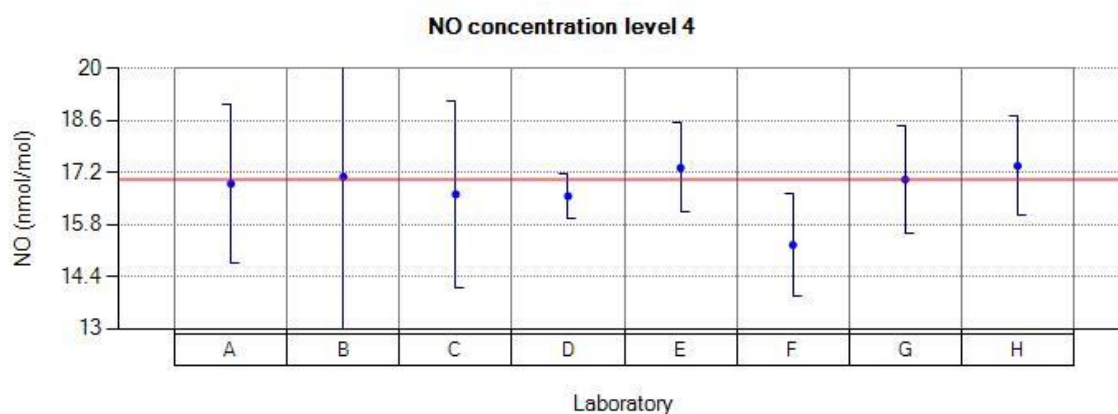
**Figure 33:** Reported values for NO run 2.**Table 32:** Reported values for NO run 3.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i, 1}$	35.70	35.93	35.06	35.20	36.31	32.80	35.82	35.59
$x_{i, 2}$	35.80	35.77	35.10	35.30	36.28	32.63	35.84	35.61
$x_{i, 3}$	35.80	35.94	35.21	35.30	36.34	32.71	35.80	35.65
$\bar{x}_i$	35.76	35.88	35.12	35.26	36.31	32.71	35.82	35.61
$s_i$	0.05	0.09	0.07	0.05	0.03	0.08	0.02	0.03
$u(\bar{x}_i)$	1.50	2.99	1.25	0.64	0.66	0.90	0.73	0.91
$U(\bar{x}_i)$	3.00	5.97	2.50	1.28	1.30	1.80	1.47	1.82

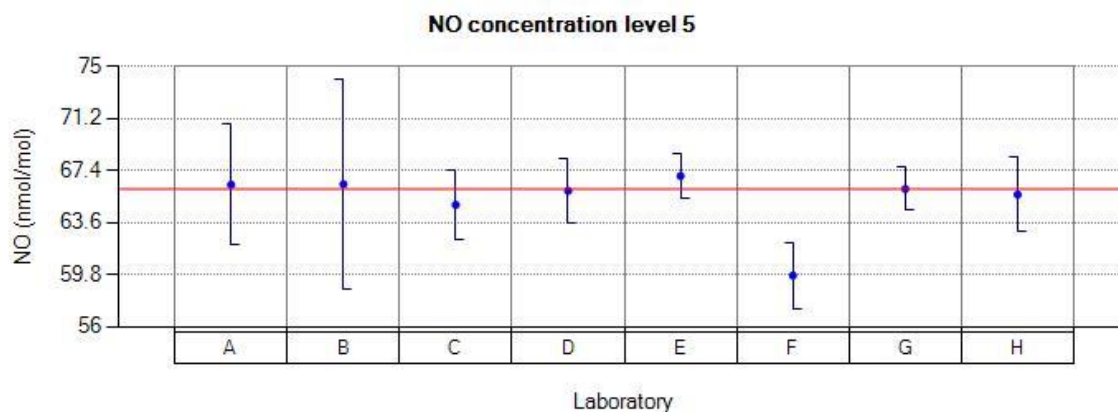
**Figure 34:** Reported values for NO run 3.

**Table 33:** Reported values for NO run 4.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i,1}$	16.90	17.08	16.65	16.50	17.31	15.20	17.02	17.33
$x_{i,2}$	16.90	17.11	16.62	16.70	17.32	15.22	17.02	17.39
$x_{i,3}$	16.90	17.08	16.58	16.50	17.36	15.34	17.00	17.42
$\bar{x}_i$	16.90	17.09	16.61	16.56	17.33	15.25	17.01	17.38
$s_i$	0.00	0.01	0.03	0.11	0.02	0.07	0.01	0.04
$u(\bar{x}_i)$	1.07	2.66	1.25	0.30	0.60	0.70	0.72	0.67
$U(\bar{x}_i)$	2.14	5.32	2.50	0.60	1.20	1.40	1.43	1.34

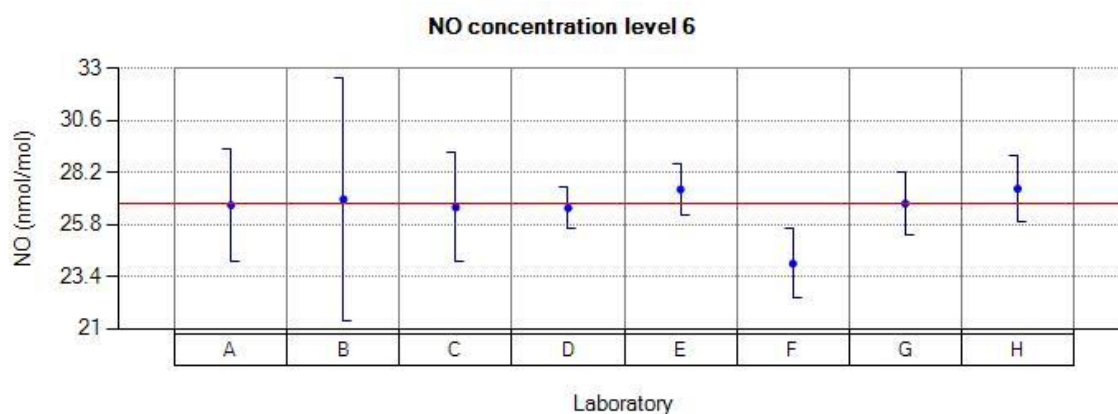
**Figure 35:** Reported values for NO run 4.**Table 34:** Reported values for NO run 5.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i,1}$	66.40	66.39	64.94	66.00	66.97	59.84	66.05	65.47
$x_{i,2}$	66.30	66.36	64.91	66.00	67.04	59.71	66.07	65.77
$x_{i,3}$	66.40	66.46	64.86	65.80	67.03	59.65	66.07	65.72
$\bar{x}_i$	66.36	66.40	64.90	65.93	67.01	59.73	66.06	65.65
$s_i$	0.05	0.05	0.04	0.11	0.03	0.09	0.01	0.16
$u(\bar{x}_i)$	2.21	3.85	1.25	1.19	0.82	1.20	0.78	1.35
$U(\bar{x}_i)$	4.41	7.70	2.50	2.38	1.60	2.40	1.56	2.70

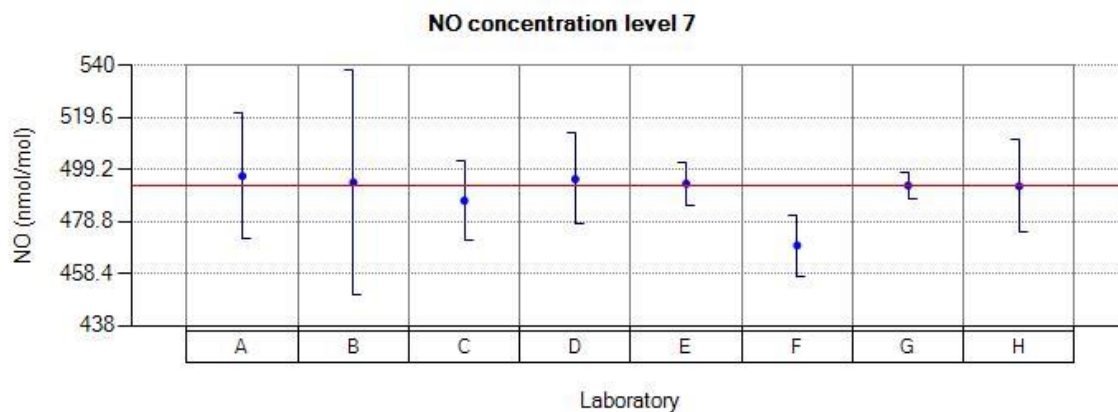
**Figure 36:** Reported values for NO run 5.

**Table 35:** Reported values for NO run 6.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i,1}$	26.50	26.76	26.45	26.50	27.25	23.92	26.59	27.40
$x_{i,2}$	26.70	26.96	26.73	26.60	27.46	24.00	26.81	27.57
$x_{i,3}$	26.90	27.19	26.62	26.60	27.56	24.07	26.91	27.41
$\bar{x}_i$	26.70	26.97	26.60	26.56	27.42	23.99	26.77	27.46
$s_i$	0.20	0.21	0.14	0.05	0.15	0.07	0.16	0.09
$u(\bar{x}_i)$	1.29	2.81	1.25	0.48	0.62	0.80	0.73	0.78
$U(\bar{x}_i)$	2.59	5.63	2.50	0.96	1.20	1.60	1.45	1.56

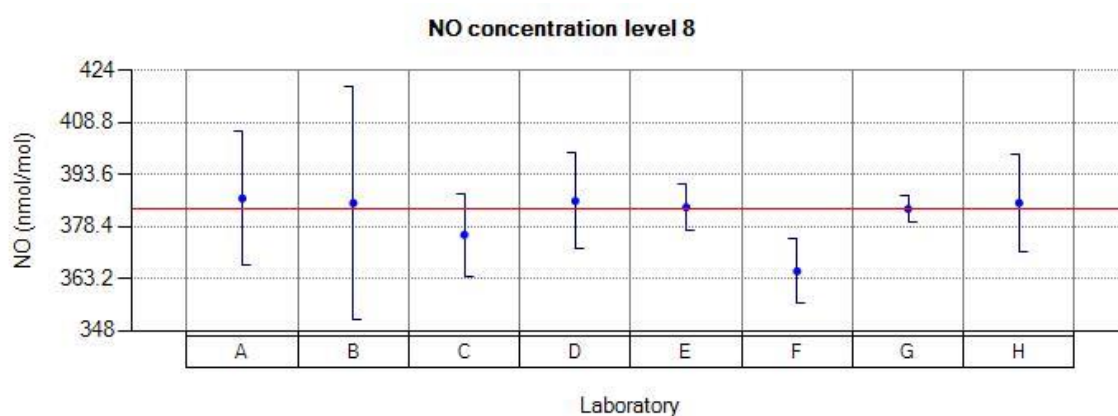
**Figure 37:** Reported values for NO run 6.**Table 36:** Reported values for NO run 7.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i,1}$	496.30	493.74	488.05	495.30	493.44	469.01	492.73	491.97
$x_{i,2}$	496.70	494.21	487.95	495.50	493.74	469.31	492.94	492.27
$x_{i,3}$	497.10	494.49	485.21	495.70	493.78	470.04	493.24	493.92
$\bar{x}_i$	496.70	494.14	487.07	495.50	493.65	469.45	492.97	492.72
$s_i$	0.40	0.37	1.61	0.20	0.18	0.53	0.25	1.05
$u(\bar{x}_i)$	12.32	21.94	7.79	8.92	4.23	6.00	2.52	9.12
$U(\bar{x}_i)$	24.65	43.88	15.59	17.84	8.50	12.00	5.04	18.24

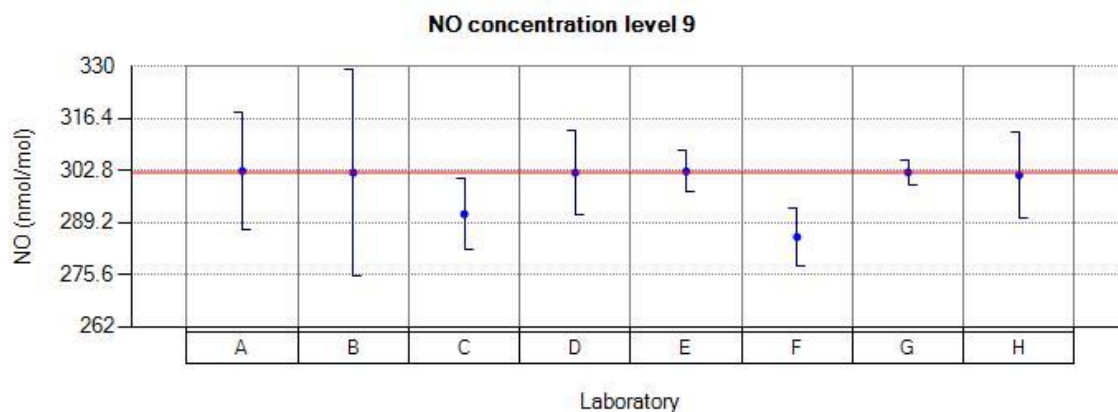
**Figure 38:** Reported values for NO run 7.

**Table 37:** Reported values for NO run 8.

values	laboratories							
	A	B	C	D	E	F	G	H
xi, 1	386.90	385.62	378.83	386.10	384.54	365.92	383.59	384.85
xi, 2	386.70	385.24	375.46	385.90	383.82	365.21	383.36	385.96
xi, 3	386.30	385.01	373.73	385.70	383.76	364.97	383.84	385.21
xi	386.63	385.29	376.00	385.90	384.04	365.36	383.59	385.34
si	0.30	0.30	2.59	0.20	0.43	0.49	0.24	0.56
u(xi)	9.79	17.13	6.02	6.94	3.30	4.70	2.01	7.15
U(xi)	19.59	34.27	12.03	13.88	6.60	9.40	4.01	14.30

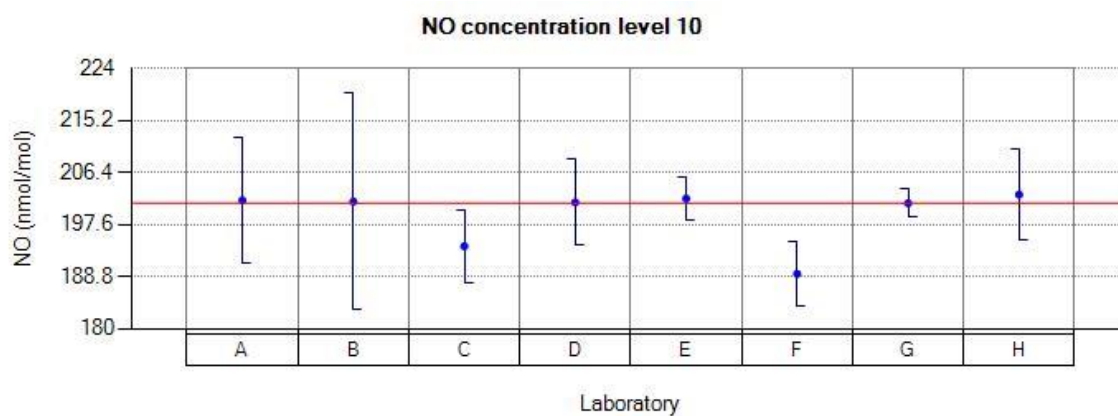
**Figure 39:** Reported values for NO run 8.**Table 38:** Reported values for NO run 9.

values	laboratories							
	A	B	C	D	E	F	G	H
xi, 1	302.60	301.87	292.13	301.90	302.37	284.87	302.21	301.16
xi, 2	302.60	302.28	291.64	302.90	302.58	285.60	302.47	302.20
xi, 3	302.80	302.59	290.51	302.10	302.84	285.86	302.41	301.63
xi	302.66	302.24	291.42	302.30	302.59	285.44	302.36	301.66
si	0.11	0.36	0.83	0.52	0.23	0.51	0.13	0.52
u(xi)	7.64	13.51	4.66	5.44	2.63	3.80	1.64	5.61
U(xi)	15.28	27.02	9.33	10.88	5.30	7.60	3.29	11.22

**Figure 40:** Reported values for NO run 9.

**Table 39:** Reported values for NO run 10.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i,1}$	202.10	201.96	194.50	201.80	202.41	189.81	201.56	202.81
$x_{i,2}$	201.60	201.26	193.57	201.30	201.90	189.00	201.12	202.79
$x_{i,3}$	201.40	201.26	193.73	201.00	201.70	189.00	200.99	202.45
$\bar{x}_i$	201.70	201.49	193.93	201.36	202.00	189.27	201.22	202.68
$s_i$	0.36	0.40	0.49	0.40	0.36	0.46	0.29	0.20
$u(x_i)$	5.32	9.19	3.10	3.62	1.81	2.70	1.22	3.79
$U(x_i)$	10.64	18.37	6.21	7.25	3.60	5.40	2.44	7.58

**Figure 41:** Reported values for NO run 10.

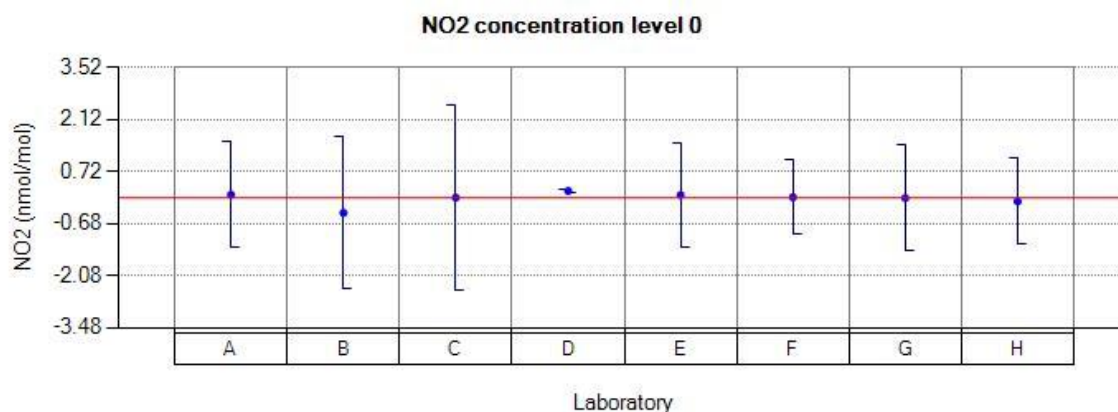


## Reported values for NO<sub>2</sub>

**Table 40:** Reported values for NO<sub>2</sub> run 0.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_i, 1$	0.10	-0.39	0.02	0.20	0.09	0.03	0.01	-0.08
$u(x_i)$	0.71	1.02	1.25	0.02	0.69	0.50	0.71	0.58
$U(x_i)$	1.42	2.04	2.50	0.04	1.40	1.00	1.43	1.16

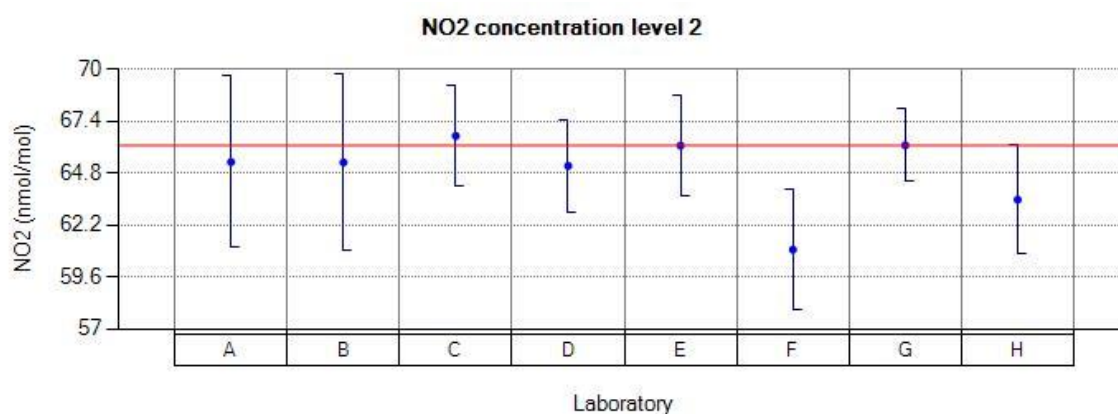
**Figure 42:** Reported values for NO<sub>2</sub> run 0.



**Table 41:** Reported values for NO<sub>2</sub> run 2.

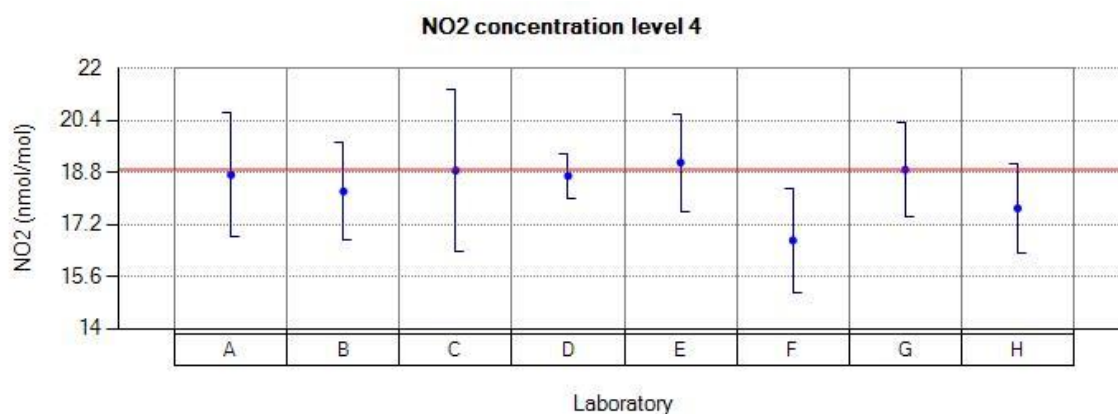
values	laboratories							
	A	B	C	D	E	F	G	H
$x_i, 1$	65.30	65.32	66.79	65.20	66.21	61.26	66.31	63.91
$x_i, 2$	65.30	65.44	66.70	65.10	66.25	60.68	66.22	63.39
$x_i, 3$	65.50	65.27	66.53	65.20	66.10	60.97	66.07	63.12
$\bar{x}_i$	65.36	65.34	66.67	65.16	66.18	60.97	66.20	63.47
$s_i$	0.11	0.08	0.13	0.05	0.07	0.29	0.12	0.40
$u(x_i)$	2.15	2.22	1.25	1.17	1.23	1.50	0.91	1.36
$U(x_i)$	4.30	4.44	2.50	2.34	2.50	3.00	1.83	2.72

**Figure 43:** Reported values for NO<sub>2</sub> run 2.

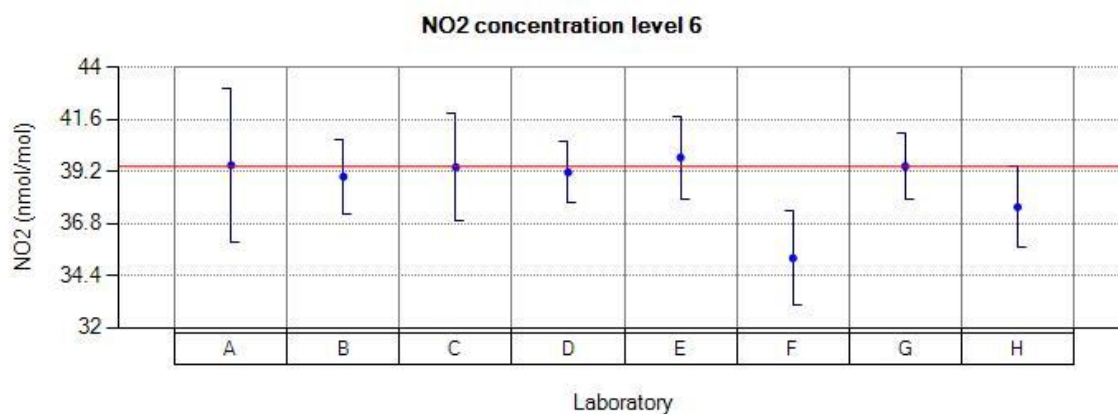


**Table 42:** Reported values for NO<sub>2</sub> run 4.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i,1}$	18.80	18.32	18.93	18.80	19.14	16.85	18.92	17.67
$x_{i,2}$	18.70	18.22	18.85	18.60	19.12	16.74	18.90	17.77
$x_{i,3}$	18.70	18.13	18.82	18.70	19.08	16.56	18.85	17.66
$\bar{x}_i$	18.73	18.22	18.86	18.70	19.11	16.71	18.89	17.70
$s_i$	0.05	0.09	0.05	0.10	0.03	0.14	0.03	0.06
$u(\bar{x}_i)$	0.94	0.76	1.25	0.34	0.76	0.80	0.73	0.68
$U(\bar{x}_i)$	1.89	1.52	2.50	0.68	1.50	1.60	1.46	1.36

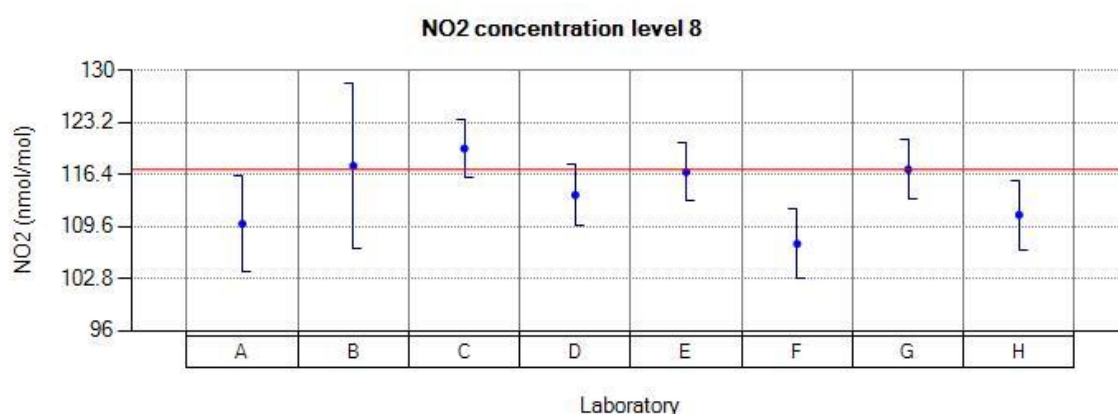
**Figure 44:** Reported values for NO<sub>2</sub> run 4.**Table 43:** Reported values for NO<sub>2</sub> run 6.

values	laboratories							
	A	B	C	D	E	F	G	H
$x_{i,1}$	39.70	39.27	39.52	39.40	40.02	35.29	39.63	37.41
$x_{i,2}$	39.50	38.97	39.48	39.10	39.82	35.22	39.40	37.60
$x_{i,3}$	39.30	38.67	39.21	39.00	39.73	35.11	39.30	37.69
$\bar{x}_i$	39.50	38.97	39.40	39.16	39.85	35.20	39.44	37.56
$s_i$	0.20	0.30	0.16	0.20	0.14	0.09	0.16	0.14
$u(\bar{x}_i)$	1.78	0.85	1.25	0.70	0.93	1.10	0.77	0.93
$U(\bar{x}_i)$	3.56	1.71	2.50	1.40	1.90	2.20	1.55	1.86

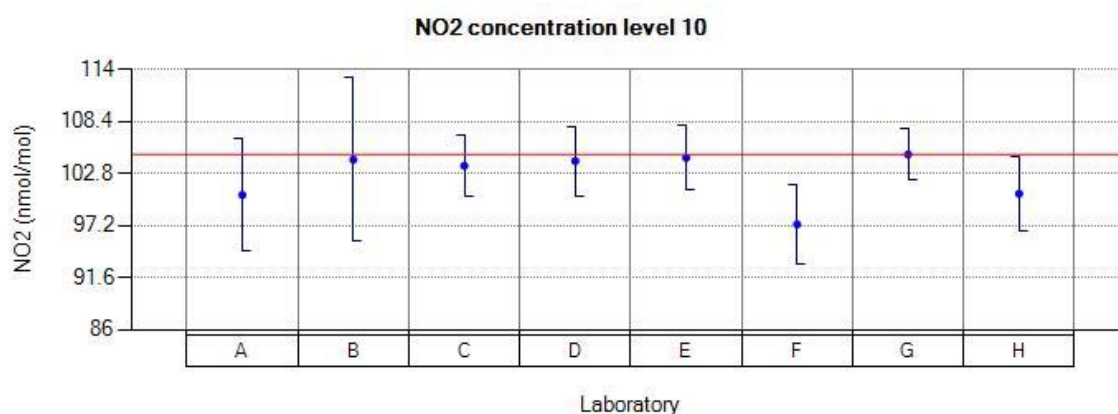
**Figure 45:** Reported values for NO<sub>2</sub> run 6.

**Table 44:** Reported values for NO<sub>2</sub> run 8.

values	laboratories							
	A	B	C	D	E	F	G	H
xi, 1	109.60	117.24	120.17	113.60	116.20	106.70	116.73	111.29
xi, 2	110.00	117.56	119.72	113.80	117.11	107.44	117.06	111.10
xi, 3	110.30	117.87	119.56	113.80	116.92	107.93	117.46	111.01
xi	109.96	117.55	119.81	113.73	116.74	107.35	117.08	111.13
si	0.35	0.31	0.31	0.11	0.48	0.61	0.36	0.14
u(xi)	3.18	5.37	1.92	2.04	1.90	2.30	1.95	2.28
U(xi)	6.36	10.73	3.83	4.08	3.80	4.60	3.89	4.56

**Figure 46:** Reported values for NO<sub>2</sub> run 8.**Table 45:** Reported values for NO<sub>2</sub> run 10.

values	laboratories							
	A	B	C	D	E	F	G	H
xi, 1	100.20	103.96	103.40	104.00	104.11	97.06	104.56	100.34
xi, 2	100.60	104.40	103.69	104.10	104.67	97.39	104.96	101.17
xi, 3	100.70	104.55	103.85	104.40	104.76	97.56	105.07	100.41
xi	100.50	104.30	103.64	104.16	104.51	97.33	104.86	100.64
si	0.26	0.30	0.22	0.20	0.35	0.25	0.26	0.46
u(xi)	3.00	4.39	1.66	1.87	1.74	2.10	1.36	2.01
U(xi)	6.00	8.78	3.32	3.74	3.50	4.20	2.73	4.02

**Figure 47:** Reported values for NO<sub>2</sub> run 10.

## Annex B: precision of standardised measurement methods

For the main purpose of monitoring trends between different ILC undertaken by ERLAP, the precision of standardized SO<sub>2</sub>, CO, O<sub>3</sub> and NO<sub>x</sub> measurement methods [2], [3], [4] and [5] as implemented by NRLs, was evaluated.

Applied methodology is described in ISO 5725-1, 5725-2 and 5725-6 [14], [15] and [16]. The precision experiment has involved a total of nine laboratories, the actual number of labs ( $p_j$ ) is reported in Table 46. Six concentration levels (for run 0 only one value is requested so repeatability cannot be evaluated) were tested for O<sub>3</sub>, CO, SO<sub>2</sub> and NO<sub>2</sub>, 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 [16]. It represents the biggest difference between two test results found on an identical test gas by one laboratory using the same apparatus within the shortest feasible time interval that should not be exceeded on average more than once in 20 cases in the normal and correct operation of method.

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

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 [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.

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

The repeatability standard deviation was evaluated with ( $p_j \cdot (3-1)$ ) degrees of freedom ( $\nu$ ) and reproducibility standard deviation with ( $p_j - 1$ ) degrees of freedom. The corresponding critical range student factors ( $t_{\alpha,\nu}$ ) are reported in Table 46.

**Table 46:** Critical values of t used in the repeatability (r) and reproducibility (R) evaluation.

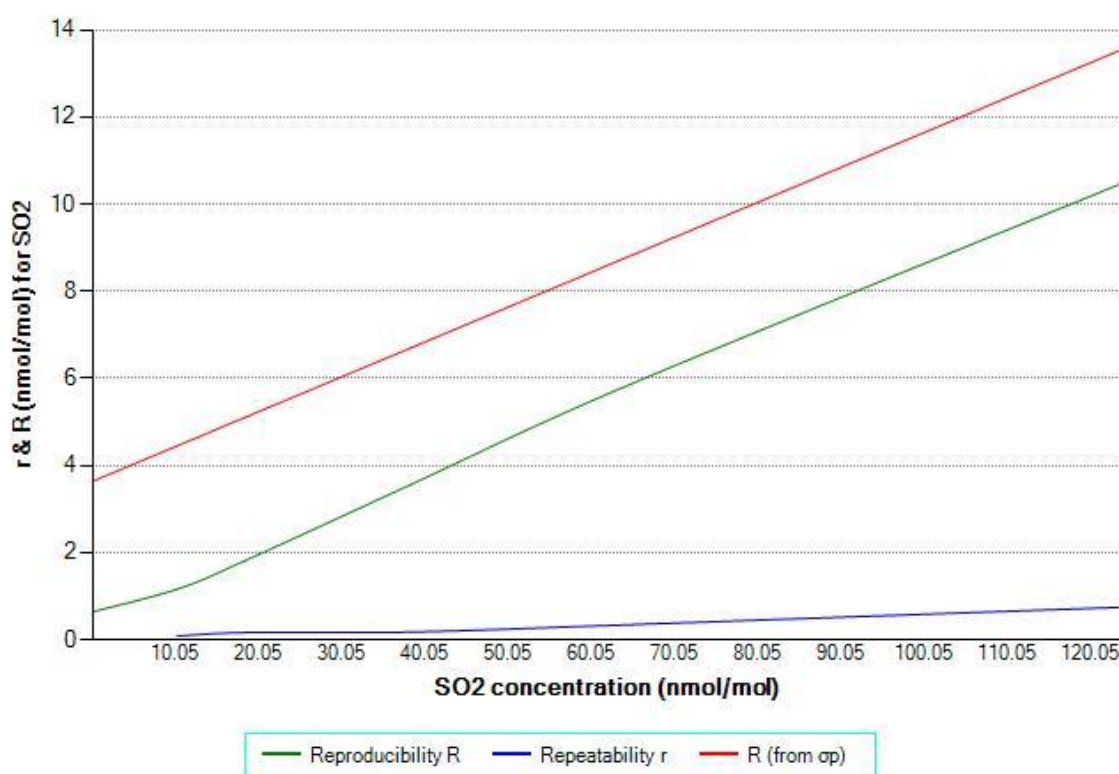
parameter	run	$p_j$	t critical value 95% for r	t critical value 95% for R
CO	1,2,3,4,5	8	2,120	2,365
NO	1,2,3,4,5,6,7,8,9,10	8	2,120	2,365
NO <sub>2</sub>	2,4,6,8,10	8	2,120	2,365
O <sub>3</sub>	1,2,3,4,5	8	2,120	2,365
SO <sub>2</sub>	1,2,3,4,5	6	2,179	2,571

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. Also reported is the 'reproducibility from common criteria ( $R$  (from  $\sigma_p$ ))' calculated by substituting  $s_R$  in Equation 7 with a 'standard deviation for proficiency assessment' (see Table 4). Comparison between  $R$  and  $R$  (from  $\sigma_p$ ) serves to indicate that  $\sigma_p$  is realistic [13] or from the other point of view, that the general methodology implemented by NRLs is appropriate for  $\sigma_p$ .

**Table 47:** The  $R$  and  $r$  of  $\text{SO}_2$  standard measurement method.

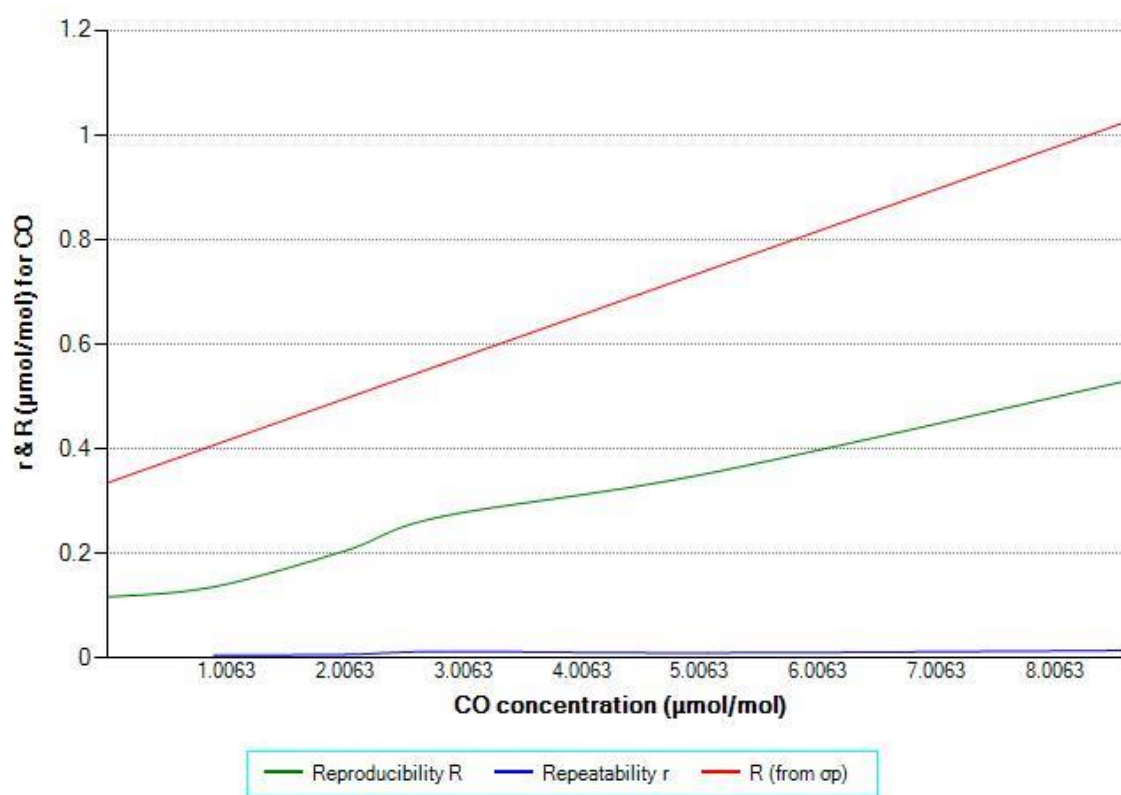
SO <sub>2</sub> data (nmol/mol) without outlier			
group average	repeatability limit : $r$	reproducibility limit : $R$	reproducibility limit (relative)
0,1		0,6	
10,1	0,1	1,2	
18,2	0,2	1,8	
38,3	0,2	3,6	
65,0	0,3	5,9	
123,6	0,7	10,5	8,5%

**Figure 48:** The  $R$  and  $r$  of  $\text{SO}_2$  standard measurement method as a function of concentration.



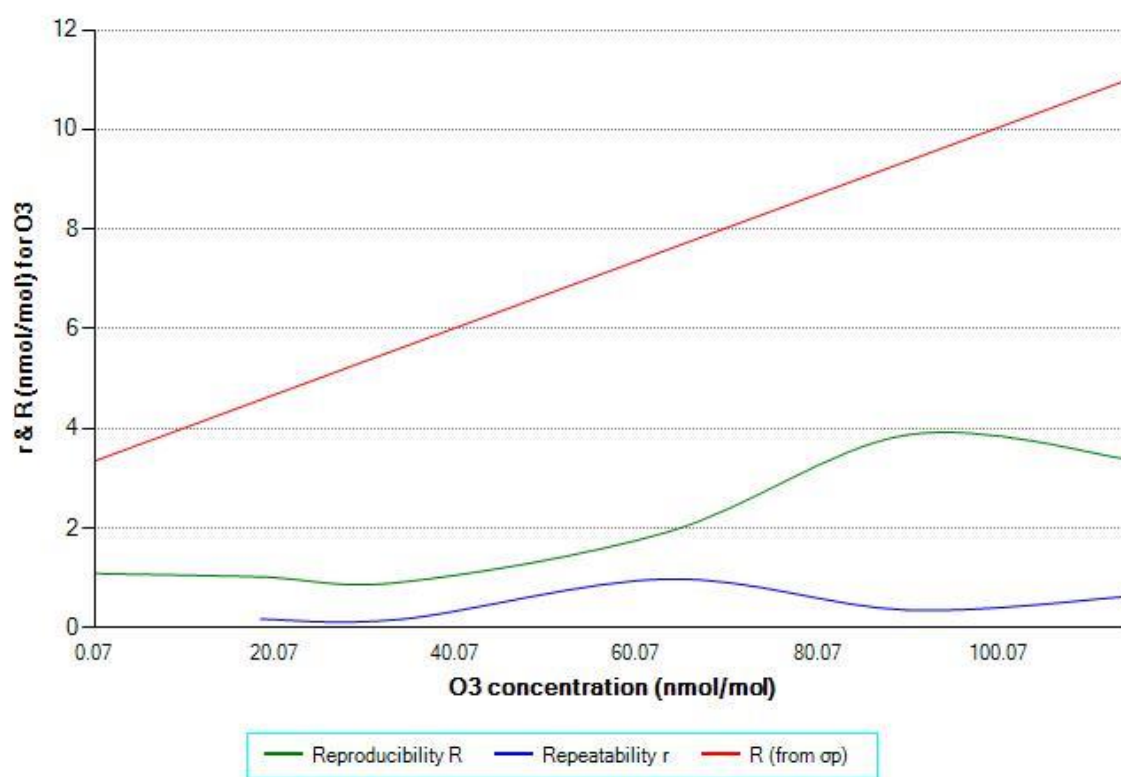
**Table 48:** The R and r of CO standard measurement method.

CO data ( $\mu\text{mol/mol}$ ) without outlier			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0,006		0,117	
0,900	0,005	0,136	
2,014	0,006	0,205	
2,823	0,012	0,27	
5,072	0,01	0,353	
8,636	0,014	0,532	6,2%

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

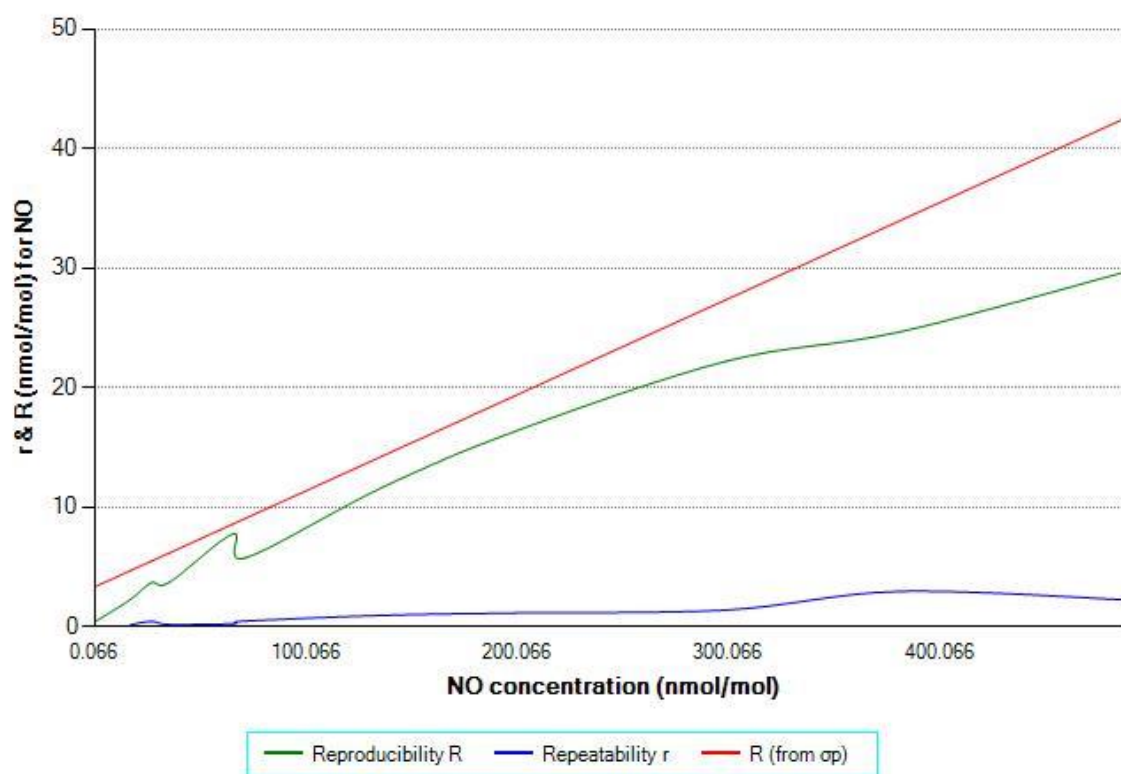
**Table 49:** The R and r of O<sub>3</sub> standard measurement method.

O <sub>3</sub> data (nmol/mol) without outlier			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0,1		1,1	
18,3	0,2	1,0	
34,0	0,2	0,9	
63,5	1,0	1,9	
89,9	0,4	3,9	
114,6	0,6	3,4	3,0%

**Figure 50:** The R and r of O<sub>3</sub> standard measurement method as a function of concentration.

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

NO data (nmol/mol) without outlier			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0,1		0,4	
16,8	0,2	2,3	
26,6	0,4	3,7	
35,3	0,2	3,7	
65,3	0,3	7,7	
71,5	0,5	5,8	
136,1	1,0	11,7	
199,2	1,2	16,4	
298,8	1,4	22,2	
381,5	3,0	24,7	
490,3	2,2	29,8	
			6,1%

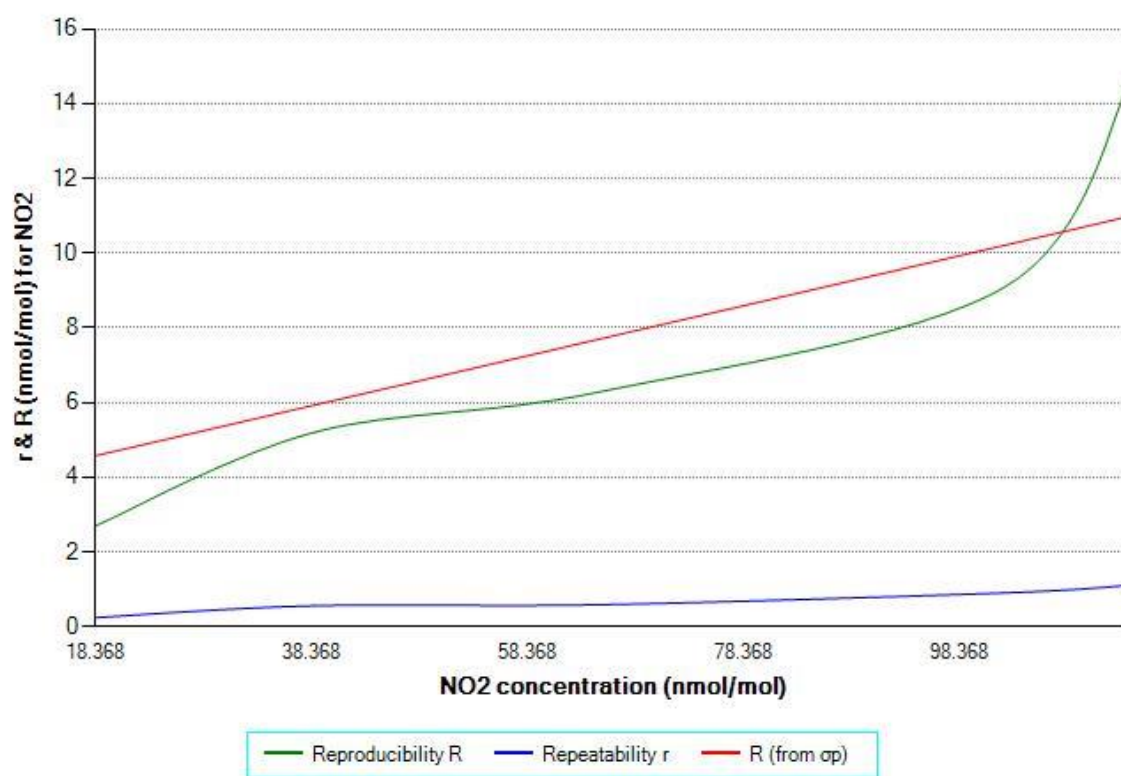
**Figure 51:** The R and r of NO standard measurement method as a function of concentration.



**Table 51:** The R and r of NO<sub>2</sub> standard measurement method.

NO <sub>2</sub> data (nmol/mol) without outlier			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0,0		0,6	
18,4	0,2	2,7	
38,6	0,6	5,2	
64,9	0,6	6,3	
102,5	0,9	9,1	
114,2	1,1	14,6	12,8%

**Figure 52:** The R and r of NO<sub>2</sub> standard measurement method as a function of concentration.



## Annex C: 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 z'-scores calculation was performed to estimate outliers.

Statistical outliers obtained at this stage are not considered as extraordinary errors but due to significant difference in participant's standard operating procedure.

During this ILC, no statistical outlier was identified.

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

According to z'-score calculation, z'-score values between |2| and |3| are considered stragglers and they deserve a specific check. Five values were evaluated as stragglers: level 1 and 5 of NO and level 2, 6, 8 and 10 of NO<sub>2</sub> for Laboratory F. (see Table 52)

**Table 52:** z'-score evaluation summary.

Code	Run	z'-score value	z'-score evaluation
F	NO _1	-2.23	questionable
F	NO _5	-2.34	questionable
F	NO <sub>2</sub> _2	-2.09	questionable
F	NO <sub>2</sub> _6	-2.17	questionable
F	NO <sub>2</sub> _8	-2.50	questionable
F	NO <sub>2</sub> _10	-2.21	questionable

## **Annex D: Confidentiality**

Results of the ILC are published according to the agreements included in the document AQUILA-N37 [12] approved by all NRL.

In order to ensure confidentiality of the laboratories information, ERLAP guarantees the submitted data as follows:

- Any administrative information provided by the laboratory is confidential and cannot be communicated to a third party.
- Access to ERLAP facilities is allowed only to members of the Unit JRC-C5 and authorized persons (cleaning staff, maintenance staff, safety and security staff etc.)
- Confidential passwords to access the web application for data submission are sent once the registration to ILC is completed. Confidential passwords allow access to the WEB interface and to on-line questionnaire. Passwords are valid until the ILC is closed. Laboratories can change their password online.
- The form LAB-REC-2000 (Confidentiality involvement form) is asked to be signed by the participants during their first participation to an ILC organized by ERLAP.

## Annex E: Accreditation certificates



### CERTIFICATO DI ACCREDITAMENTO Accreditation Certificate

ACCREDITAMENTO N.  
ACCREDITATION N. **0018P REV. 00**

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ISSUED BY **DIPARTIMENTO LABORATORI DI PROVA**

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È CONFORME AI REQUISITI  
DELLA NORMA **UNI CEI EN ISO/IEC 17043:2010**

MEETS THE REQUIREMENTS  
OF THE STANDARD **ISO/IEC 17043:2010**

QUALE **Organizzatori di prove valutative interlaboratorio**  
AS **Proficiency Testing Provider**

Data di 1<sup>a</sup> emissione  
1st issue date  
**17-01-2019**

Data di modifica  
Modification date  
**17-01-2019**

Data di scadenza  
Expiring date  
**16-01-2023**

Dott.ssa Silvia Tramontin  
Il Direttore di Dipartimento  
The Department Director

Dott. Filippo Trifiletti  
Il Direttore Generale  
The General Director

Ing. Giuseppe Rossi  
Il Presidente  
The President

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<b>European Reference Laboratory for air Pollution (ERLAP)</b>  Via E. Fermi 2749 21027 Ispra VA	Numero di accreditamento: <b>0018 P Sede A</b>	
	Revisione: <b>0</b>	Data: <b>17/01/2019</b>
	pag. <b>1</b> di <b>1</b>	UNI CEI EN ISO/IEC 17043:2010

#### ELENCO SCHEMI ACCREDITATI - CATEGORIA: 0

<i>Codice identificativo</i>	<i>Settore</i>	<i>Oggetto /Materiale/ Prodotto/Matrice</i>	<i>Misurando/ Proprietà misurata/ Grandezza</i>	<i>Tipologia</i>
	ambientale	purified ambient air	carbon monoxide	schema quantitativo
	ambientale	purified ambient air	nitrogen oxides	schema quantitativo
	ambientale	purified ambient air	ozone	schema quantitativo
	ambientale	purified ambient air	sulphur dioxide	schema quantitativo

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Accreditamento n°  
Accreditation n°

**1362**

Rev. 1

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Directorate C.Energy, Transport and Climate  
Joint Research Centre -European Commission**

Sede/Headquarters:  
- 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 requirements  
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**

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*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 the Laboratory of Proof 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. The in force status of the accreditation may be checked in the WEB site ([www.accredia.it](http://www.accredia.it)) or on direct request to appointed Department.*

Data di 1ª emissione  
1st issue date  
**2013-06-19**

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Modification date  
**2017-05-24**

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Expiring date  
**2021-06-17**

Il Direttore di Dipartimento  
The Department Director  
(Dott.ssa Silvia Tramontin)

Il Direttore Generale  
The General Director  
(Dr. Filippo Trifiletti)

Il Presidente  
The President  
(Ing. Giuseppe Rossi)

<b>European Reference Laboratory for Air Pollution (ERLAP) Air and Climate Unit</b> <b>Directorate C.Energy,Transport and Climate</b> <b>Joint Research Centre -European Commission</b>  Via E. Fermi 2749 21027 Ispra VA	Numero di accreditamento: <b>1362 Sede A</b>
	Revisione: <b>2</b> Data: <b>24/05/2017</b>
	Scheda <b>1 di 1</b> PA1779AR2.pdf

## ELENCO PROVE ACCREDITATE - CATEGORIA: 0

### Ambient Air

<i>Denominazione della prova / Campi di prova</i>	<i>Metodo di prova</i>
Particulate Elemental Carbon (EC) (0.2 to 16 µg/m³)	EN16909:2017
Particulate Matter <10 micrometers (PM10) (3.85 to 150 µg/m³)	EN 12341:2014
Particulate Matter <2.5 micrometers (PM2.5) (3.48 to 120 µg/m³)	EN 12341:2014
Particulate Organic Carbon (OC) (1.8 to 45 µg/m³)	EN16909:2017

### Synthetic mixture gas

<i>Denominazione della prova / Campi di prova</i>	<i>Metodo di prova</i>
carbon monoxide (0.015-86 mmol/mol)	EN 14626:2012
nitrogen oxides (NO: 1-962 nmol/mol; NO2: 1-261 nmol/mol)	EN 14211:2012
ozone (1-250 nmol/mol)	EN 14625:2012
sulphur dioxide (1-376 nmol/mol)	EN 14212:2012

### Legenda

En= norma europea

ACCREDIA  
Il Direttore del Laboratorio  
Firmato digitalmente da Alessandra Silvia Tramontin  
Data: 26/05/2017 23:09:46

La decorrenza del presente elenco delle prove accreditate, coincide con la data di revisione del documento, posta in alto a destra.  
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**End of report**



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