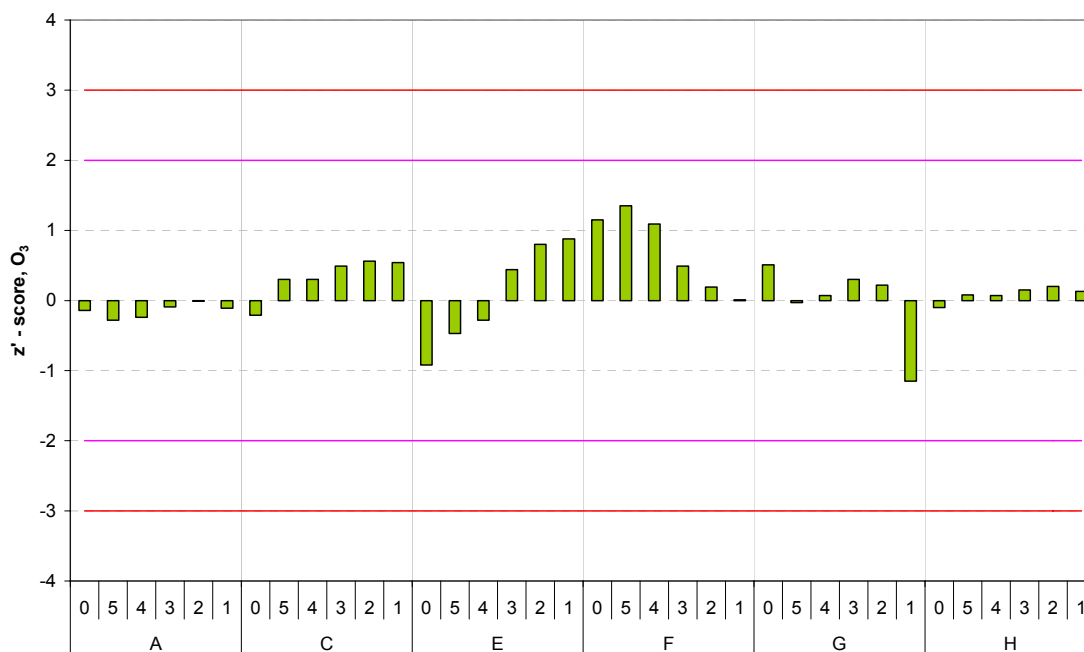


JRC Scientific and Technical Reports

EC Harmonization Programme for Air Quality Measurements:

The evaluation of the Intercomparison Exercise for SO₂, CO, O₃, NO and NO₂ - April 2008-

Matej Kapus Dukarić, Annette Borowiak and Fritz Lagler



EUR 23805 EN - 2009

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JRC 50587

EUR 23805 EN
ISBN 978-92-79-12169-2
ISSN 1018-5593

Luxembourg: Office for Official Publications of the European Communities

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Bilić, M.; Blazicko, R.; Borodkin, Y.; Bugmann, S.; Dell'Acqua, A.; Gabrysch, M.; Galan, D.;
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WHO COLLABORATING CENTRE FOR AIR QUALITY
MANAGEMENT AND AIR POLLUTION CONTROL

at the

FEDERAL ENVIRONMENTAL AGENCY



Executive Summary

In April 2008 in Ispra (IT), 8 AQUILA (Network of European Air Quality Reference Laboratories) laboratories met at an intercomparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO₂, CO, NO, NO₂ and O₃).

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system.

In terms of criteria imposed by the European Commission, 80% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 18% of the results had good measured values, but the reported uncertainties were either too small (7%) or too high (11%).

The comparability of results among AQUILA participants is satisfactory for all studied measurement methods.

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Abbreviations:

AQUILA	Network of National Reference Laboratories for Air Quality
CO	Carbon monoxide
DQO	Data Quality Objective
ERLAP	European Reference Laboratory of Air Pollution
EC	European Commission
GPT	Gas phase titration
IE	Intercomparison Exercise
IES	Institute for Environment and Sustainability
ISO	International Organization for Standardization
JRC	Joint Research Centre
NO	Nitrogen monoxide
NO ₂	Nitrogen dioxide
NO _X	the oxides of nitrogen, the sum of NO and NO ₂
NRL	National Reference Laboratory
O ₃	Ozone
SO ₂	Sulphur dioxide
WHO	World Health Organization Collaborating Centre for Air Quality
CC-EURO	Management and Air Pollution Control, Berlin

Mathematical Symbols:

<i>symbol</i>	<i>explanation</i>
α	converter efficiency (EN 14211; [9])
E_n	E_n – number statistic (ISO 13528; [18])
r	repeatability limit (ISO 5725; [19])
R	reproducibility limit (ISO 5725; [19])
σ_p	the standard deviation for proficiency assessment (ISO 13528; [18])
x^*	robust average (Annex C ISO 13528; [18])
s^*	robust standard deviation (Annex C ISO 13528; [18])
s_r	repeatability standard deviation (ISO 5725; [19])
s_R	reproducibility standard deviation (ISO 5725; [19])
U_X	The expanded uncertainty of the assigned/reference value (ISO 13528; [18])
U_{xi}	The expanded uncertainty of the participant's value
u_X	The standard uncertainty of the assigned/reference value (ISO 13528; [18])
X	Assigned/reference value (ISO 13528; [18])
x_i	the average of three values reported by the participant i (for particular parameter and concentration level) (ISO 5725; [19])
$x_{i,j}$	j -th reported value of participant i (for particular parameter and concentration level) (ISO 5725; [19])
z'	z' -score statistic (ISO 13528; [18])

1. Introduction

As the old “Framework Directive” [1] and its “Daughter Directives” [2], [3], [4] and [5], the new Directive 2008/50/EC [6] on ambient air quality and cleaner air for Europe sets a framework for a harmonized air quality assessment in Europe. One important objective of the Directive is that the ambient air quality shall be assessed on the basis of common methods and criteria. It deals with the air pollutants sulphur dioxide (SO₂), nitrogen dioxide (NO₂) and monoxide (NO), particulate matter, lead, benzene, carbon monoxide (CO) and ozone (O₃). Among others it specifies the reference methods for measurements and Data Quality Objectives (DQO) for the accuracy of measurements.

The European Commission (EC) has supported the development and publication of reference measurement methods [7], [8], [9] and [10] as European standards. Appropriate calibration methods [11], [12] and [13] have been standardised by the International Organization for Standardization (ISO).

As foreseen in the new Directive, the European Reference Laboratory of Air Pollution (ERLAP) of the Institute for Environment and Sustainability (IES) at the Joint Research Centre (JRC) organizes intercomparison exercises (IE) to assess and improve the status of comparability of measurements of National Reference Laboratories (NRL) of each Member State of the European Union.

The World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin (WHO CC) is carrying out similar activities since 1994 [14] [15], but with a view to obtaining harmonized air quality data for health related studies. Their program integrates within the WHO EURO region, which includes public health institutes and other national institutes - especially from the Central Eastern Europe, Caucasus and countries from Central Asia.

Starting in 2004, it has been decided to bring together the efforts of both the JRC-ERLAP and WHO CC and to coordinate activities as far as possible, with a view to optimize resources and have better international harmonization. The following report deals with the IE that took place from the 14th to the 17th of April 2008 in Ispra (IT) in joint cooperation of EC/ JRC/IES/ERLAP and WHO CC.

ERLAP has been organizing IEs since 1990 aiming at evaluating the comparability of measurements carried out by NRLs and promoting information exchange among the expert laboratories. Nowadays the main objective, in accordance with the Network of National Reference Laboratories for Air Quality (AQUILA) [16], comprises a more systematic approach that offers alert mechanism for the purposes of the EC and is also useful to NRLs in quality assurance of their implemented quality systems. The methodology of organization of IEs was developed by ERLAP and is described in a position paper on the organization of intercomparison exercises for gaseous air pollutants [17]. This position paper is currently a proposal to the AQUILA and the final agreement of position paper is foreseen to take place during 2008. Then it will be applied throughout all future IEs.

The evaluation scheme applied to this IE is described in detail in the position paper [17] and it reflects the inputs given by AQUILA. Firstly, it was acknowledged that the evaluation scheme should have common criteria, to alert the EC on the possible performance failure, and not to base these alerts on claimed uncertainty of participants. For that purpose the common criterion was proposed to AQUILA and the z'-score method [18] was implemented in to the evaluation scheme. The common criterion is derived from the uncertainty requirements for calibration gases stated in the European standards [7], [8], [9] and [10], which are consistent with the DQOs of European Directives. In view of AQUILA, NRLs with overall unsatisfactory results of the z'-score evaluation (one unsatisfactory or two questionable results per parameter) are required to repeat their participation to the next IE in order to demonstrate remediation measures [17]. Secondly, it was acknowledged that the evaluation scheme

should be useful to participants accredited according to ISO 17025 and thus should include measurement uncertainty of participants. For that purpose, participants measurement results (measurement values and uncertainties) are compared to assigned values applying the E_n – number method [18].

Beside the proficiency of participating laboratories the repeatability and reproducibility of standardized measurement methods [19], [20] and [21] are evaluated as well. These group evaluations will be used in a separate communication as the indicators of trends of quality of measurements over different IEs undertaken by ERLAP.

2. Communication and time schedule

The IE was announced in November 2007 to the members of the AQUILA network and the WHO CC representative. A registration letter was sent to interested parties and the registration was closed in January 2008 with the list of 9 participating laboratories. The participants were required to bring their own measurement instruments, data acquisition equipment and travelling standards (to be used for calibrations or checks during the IE).

The participants were invited to arrive on Monday, 14th April 2008, for the installation of their equipment. The calibration of NO_x and O₃ analysers was carried out on Tuesday morning and the generation of NO_x and O₃ gas mixtures started at 11:00. The calibration of SO₂ and CO analysers was carried out on Wednesday 18:00 and the generation of CO and SO₂ gas mixtures started at 20:00. The test gases generation finished on Thursday at 7:00 a.m..

3. Participants

The majority of participants were organizations dealing with the routine ambient air monitoring. The national representatives came from EU member states, Austria, Estonia, Latvia, Malta and Spain, and from Croatia and Switzerland. One participant (EC/ JRC/IES/ 'Climate Change Unit') is responsible for the GAW EMEP station.

Table 1: The list of participating organizations.

Country	Name of Organization	IE code
Austria	Amt der Oö. Landesregierung	A
Croatia	Energy and Environmental Protection Institute	B
Estonia	Estonian Environmental Research Centre	C
European Commission	European reference laboratory of air pollution	D
European Commission	EC GAW EMEP station	E
Latvia	Latvia Environment Geology and Meteorology agency	F
Spain	Instituto de Salud Carlos III	G
Switzerland	Material Science & Technology Institute (EMPA)	H
Malta	Environment and Planning Authority	

The representative from Malta attended the IE in the quality of observer.

4. The preparation of test mixtures

The ERLAP IE facility has been described in several reports [22] and [23]. During this IE, gas mixtures were prepared for SO₂, CO, O₃, NO and NO₂ at concentration levels around European Air Quality limit values, critical levels and assessment thresholds.

The test mixtures were prepared by the dilution of gases from cylinders containing high concentration of NO, SO₂ or CO using thermal mass flow controllers [13]. O₃ was added using an ozone generator and NO₂ was produced applying the gas phase titration method [24] in the conditions of excess NO.

The participants were required to report three half-hour-mean measurements for each concentration level in order to evaluate the repeatabilities of standardized measurement methods. Zero concentration levels were generated for one hour and one half-hour-mean measurement was reported. The sequence program of generated test gases is given in Table 2.

Table 2: The sequence program of generated test gases.

day	start time	duration	operation or number run	zero air	NO	NO ₂	O ₃	CO	SO ₂
		(h)		(nmol/mol)	(nmol/mol)	(nmol/mol)	(nmol/mol)	(μmol/mol)	(nmol/mol)
14-Apr	12:00	6	installation						
15-Apr	08:00	3	calibration						
15-Apr	11:00	1	NO & NO ₂ & O ₃ run 0	0					
15-Apr	12:00	2	NO & NO ₂ run 1		500	0			
15-Apr	14:00	2	NO & NO ₂ run 2		380	120			
15-Apr	16:00	2	O ₃ run 1				120		
15-Apr	18:00	2	NO & NO ₂ run 3		250	0			
15-Apr	20:00	2	NO & NO ₂ run 4		146	104			
15-Apr	22:00	2	O ₃ run 2				104		
16-Apr	00:00	2	NO & NO ₂ run 5		150	0			
16-Apr	02:00	2	NO & NO ₂ run 6		90	60			
16-Apr	04:00	2	O ₃ run 3				60		
16-Apr	06:00	2	NO & NO ₂ run 7		50	0			
16-Apr	08:00	2	NO & NO ₂ run 8		29.1	20.9			
16-Apr	10:00	2	O ₃ run 4				20.9		
16-Apr	12:00	2	NO & NO ₂ run 9		15.7	0			
16-Apr	14:00	2	NO & NO ₂ run 10		2.1	13.6			
16-Apr	16:00	2	O ₃ run 5				13.6		
16-Apr	< 18:00	2	calibration						
16-Apr	20:00	1	CO & SO ₂ run 0	0					
16-Apr	21:00	2:30	CO & SO ₂ run 1					8.6	132
16-Apr	23:30	2	CO & SO ₂ run 2					6	47
17-Apr	01:30	2	CO & SO ₂ run 3					4.3	18.8
17-Apr	03:30	2	CO & SO ₂ run 4					2	7.5
17-Apr	05:30	2	CO & SO ₂ run 5					1	3
17-Apr	07:30	1		0					
17-Apr	08:30								

5. The evaluation of laboratory's measurement proficiency

To evaluate the participants measurement proficiency the methodology described in ISO 13528 [18] was applied. It has been agreed among the AQUILA members to take the measurement results of ERLAP as the assigned/reference values for the whole IE [17]. 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 [17], the proficiency of the participants was assessed by calculating two performance indicators. The first performance indicator (z'-score) tests if the difference between the participants measured value and the assigned/reference value remains within the limits of a common criterion, while the second performance indicator (E_n-number) tests if the difference between the participants measured values and assigned/reference value remains within the limits of a criterion, that is calculated individually for each participant, from the uncertainty of the participants measurement result and the uncertainty of assigned/reference value.

z' - score

The z' - score statistic is calculated according to ISO 13528 [18] as:

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

where 'x_i' is a participant's run average value, 'X' is the assigned/reference value, 'σ_p' is the 'standard deviation for proficiency assessment' and 'u_x' is the standard uncertainty of assigned value. For 'a' and 'b' see Table 3.

In the European standards [6], [8], [9] and [10] the uncertainties for calibration gases used in ongoing quality control are prescribed. In fact, it is stated that the maximum permitted expanded uncertainty for calibration gases is 5% and that 'zero gas' shall not give instrument reading higher than the detection limit. As one of the tasks of NRLs is to supply calibration gas mixtures, the 'standard deviation for proficiency assessment' (σ_p) [18] is calculated in fitness-for-purpose manner from requirements given in European standards.

Over the whole measurement range σ_p is calculated by linear interpolation between 2.5 % at the calibration point (75% of calibration range) and the limit of detection at zero concentration level. The limits of detection of studied measurement methods were evaluated from the data of previous IEs. The linear function parameters of σ_p are given in Table 3:

Table 3: The standard deviation for proficiency assessment as a linear function of concentration (c) with linear function parameters: slope (a) and intercept (b).

	σ _p =a·c+b	
	a	b
		nmol/mol
SO ₂	0.024	0.4
CO	0.023	100
O ₃	0.022	0.5
NO	0.025	0.35
NO ₂	0.023	0.46

During the November 2008 AQUILA meeting, σ_p was enlarged, to 1 ppb at zero concentration of SO₂, O₃, NO, NO₂, and approved. It has been agreed that this change is noted in all relevant and not yet published IE reports and applied to all future IEs.

The z'-score evaluation allows the following criteria to be used for the assessment of results:

- $|z'| \leq 2$ are designated satisfactory.
- $2 < |z'| \leq 3$ are designated questionable.
- $|z'| > 3$ are designated unsatisfactory. Scores falling in this range are very unusual and are taken to indicate that the cause of the event should be investigated and remedied.

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

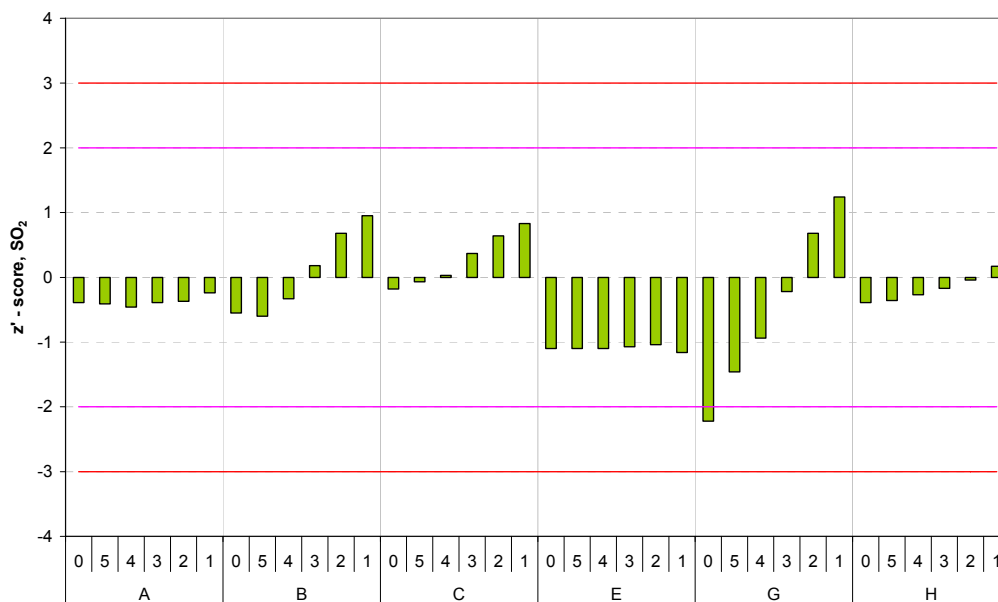


Figure 1: The z'-score evaluations of SO₂ measurements are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 5 (3 nmol/mol), 4 (7 nmol/mol), 3 (19 nmol/mol), 2 (47 nmol/mol), 1 (132 nmol/mol)). The assessment criteria are presented as $z'=\pm 2$ and $z'=\pm 3$ lines. They represent the limits for the questionable and unsatisfactory results.

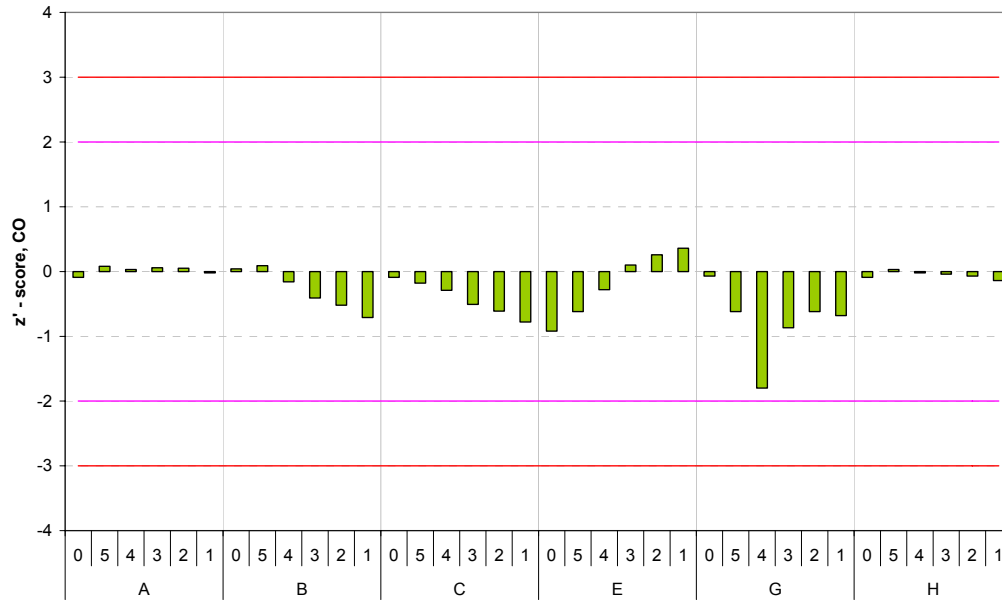


Figure 2: The z'-score evaluations of CO measurements are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 µmol/mol), 5 (1 µmol/mol), 4 (2 µmol/mol), 3 (4 µmol/mol), 2 (6 µmol/mol), 1 (9 µmol/mol)). The assessment criteria are presented as $z'=\pm 2$ and $z'=\pm 3$ lines. They represent the limits for the questionable and unsatisfactory results.

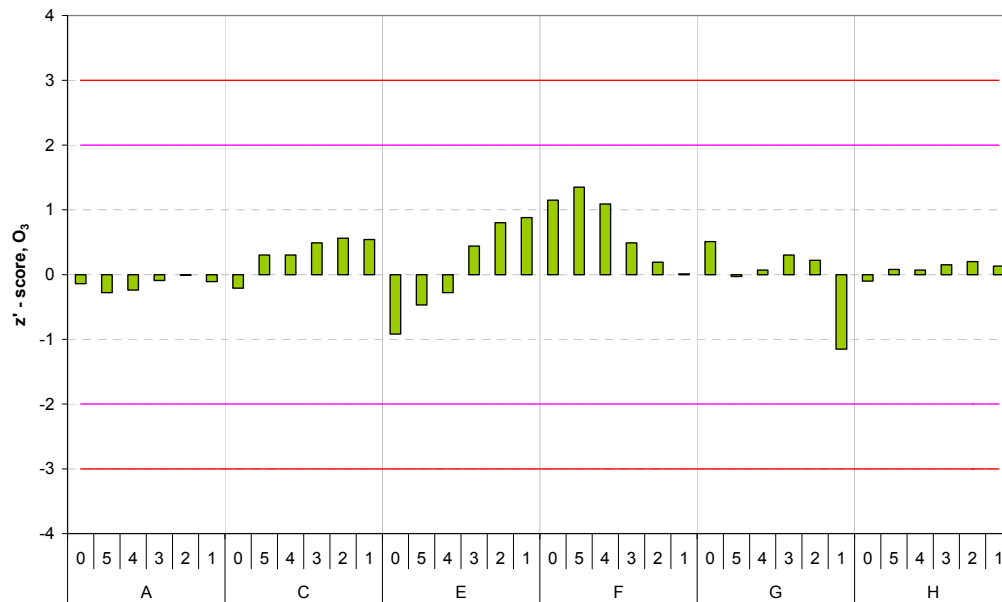


Figure 3: The z'-score evaluations of O₃ measurements are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 5 (14 nmol/mol), 4 (21 nmol/mol), 3 (60 nmol/mol), 2 (104 nmol/mol), 1 (120 nmol/mol)). The assessment criteria are presented as $z'=\pm 2$ and $z'=\pm 3$ lines. They represent the limits for the questionable and unsatisfactory results.

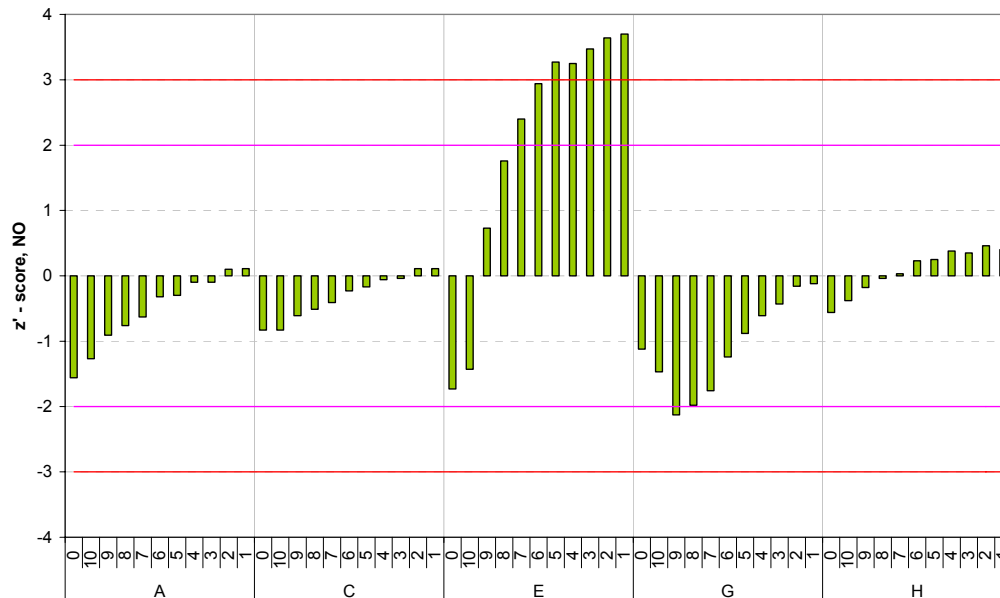


Figure 4: The z'-score evaluations of NO measurements are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (2 nmol/mol), 9 (16 nmol/mol), 8 (30 nmol/mol), 7 (50 nmol/mol) , 6 (90 nmol/mol) , 5 (150 nmol/mol) , 4 (150 nmol/mol) , 3 (250 nmol/mol) , 2 (380 nmol/mol), 1 (500 nmol/mol)). The assessment criteria are presented as $z'=\pm 2$ and $z'=\pm 3$ lines. They represent the limits for the questionable and unsatisfactory results.

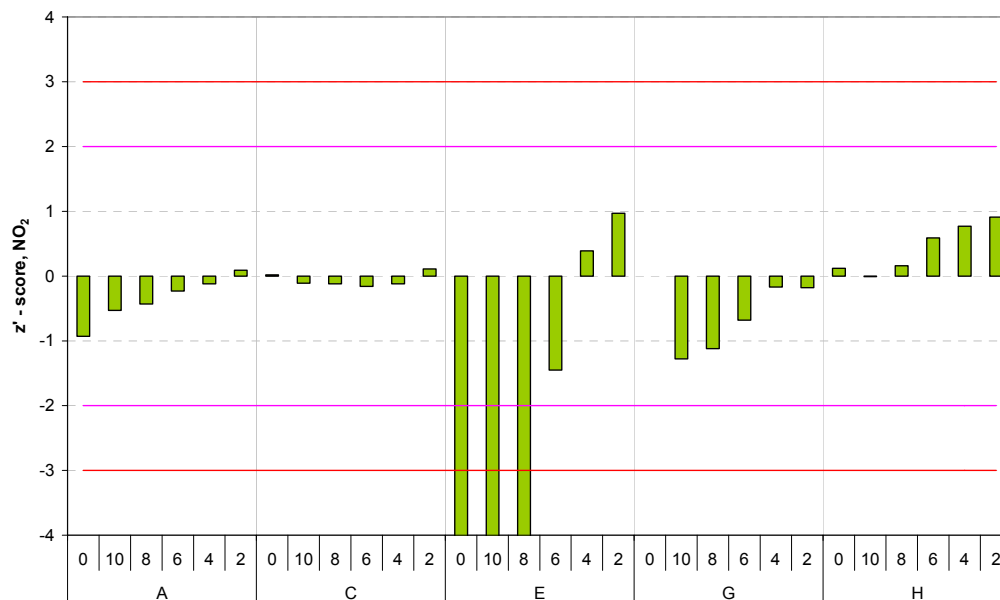


Figure 5: The z'-score evaluations of NO₂ measurements are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (14 nmol/mol), 8 (21 nmol/mol), 6 (60 nmol/mol), 4 (104 nmol/mol), 2 (120 nmol/mol)). The assessment criteria are presented as $z'=\pm 2$ and $z'=\pm 3$ lines. They represent the limits for the questionable and unsatisfactory results.

E_n - number

The normalised deviations [18] (E_n) were calculated according to:

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

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 $|E_n| \leq 1$.

In Figure 6 to Figure 10 the biases of each participant (x_i-X) are plotted and error bars are used to denote the value of denominator of equation 2 ($\sqrt{U_{x_i}^2 + U_X^2}$). These plots represent also the E_n-number evaluations where, considering the E_n criteria ($|E_n| \leq 1$), all results with error bars touching or crossing x-axis are satisfactory. Reported standard uncertainties (Annex B) that are bigger than "standard deviation for proficiency assessments" (σ_p, Table 3) are considered not fit-for-purpose and are denoted with "*" in the x-axis of each figure.

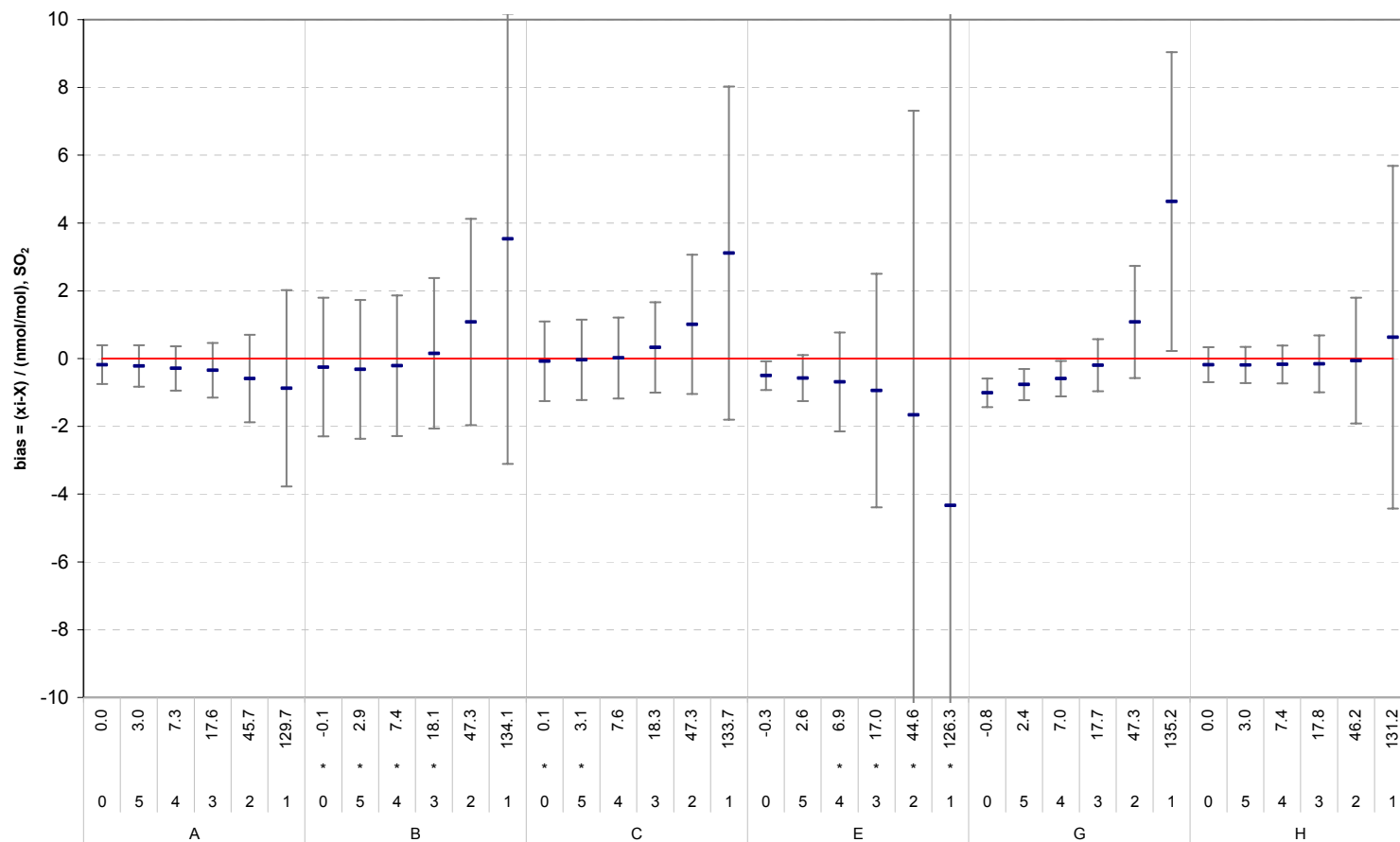


Figure 6: Bias of participant's SO₂ measurement results together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p .

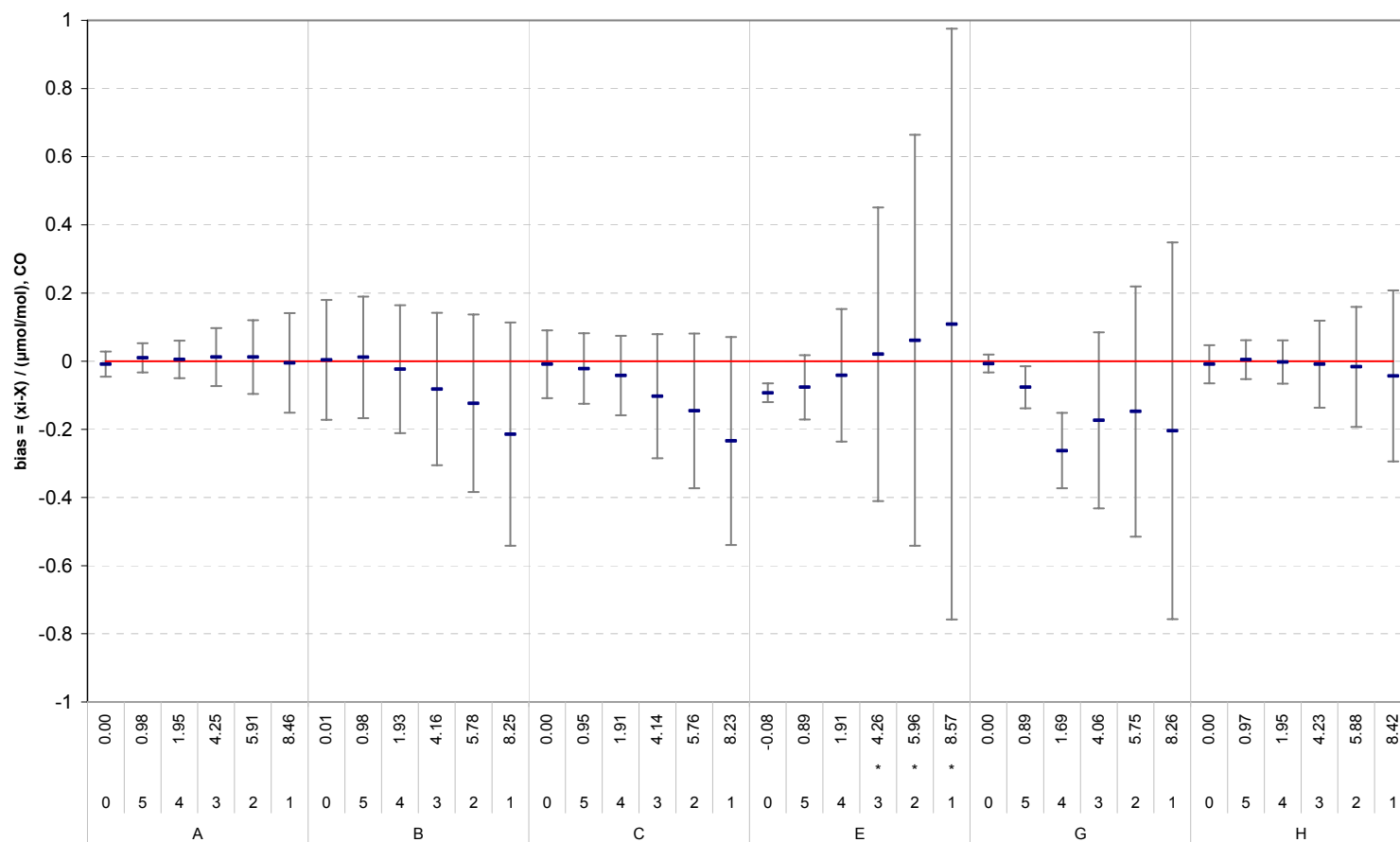


Figure 7: Bias of participant's CO measurement results together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together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

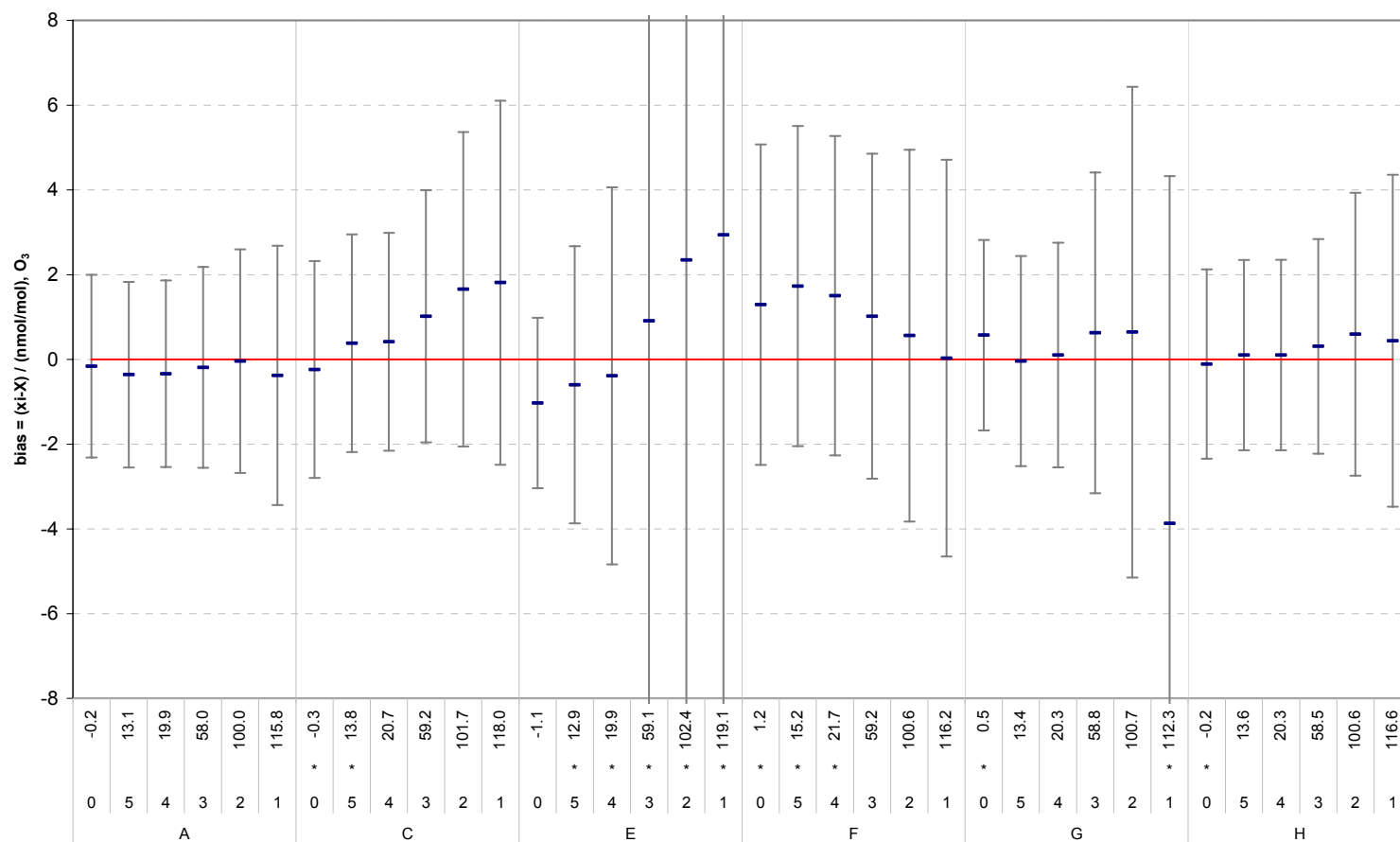


Figure 8: Bias of participant's O₃ measurement results together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p .

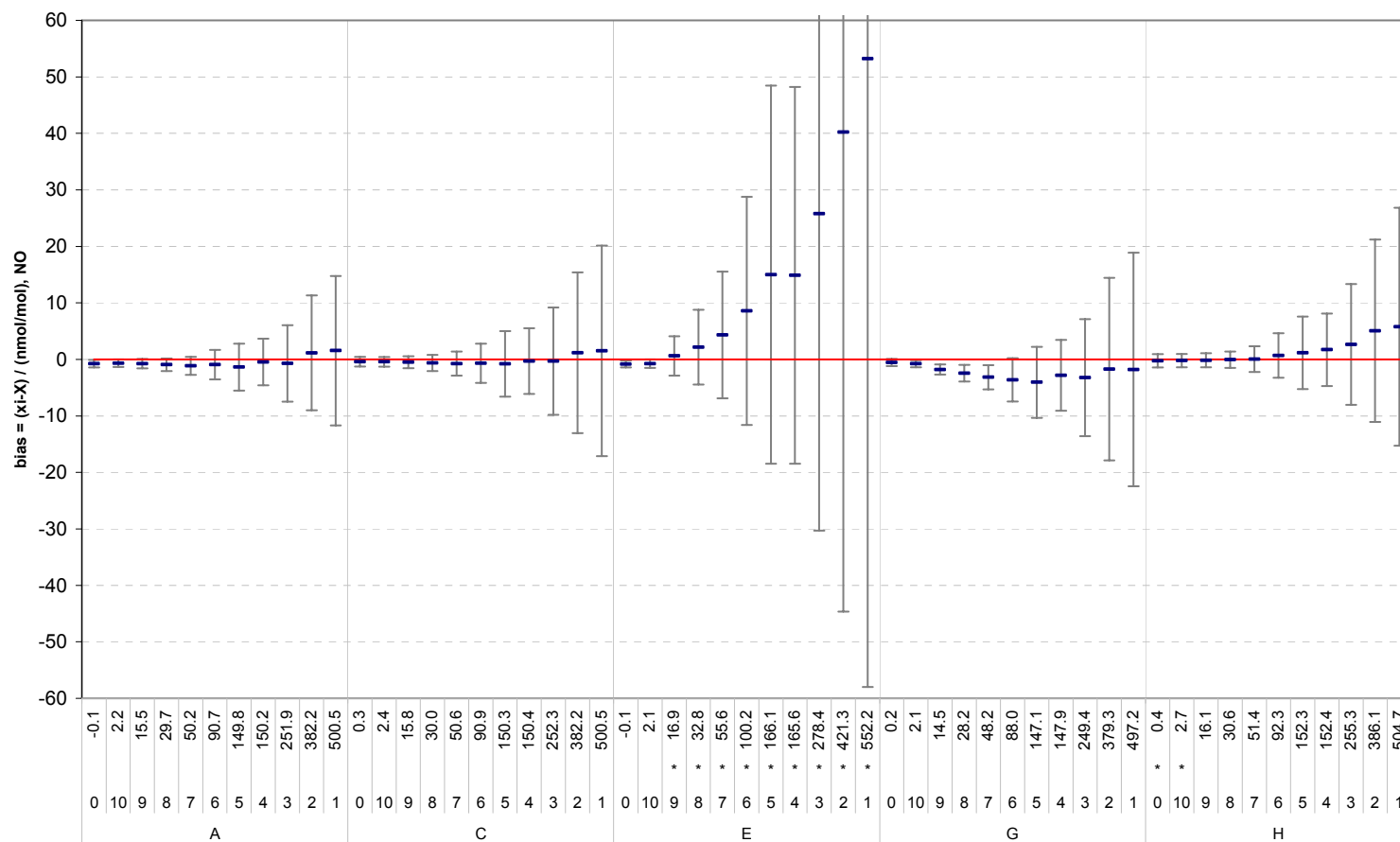


Figure 9: Bias of participant's NO measurement results together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 10)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

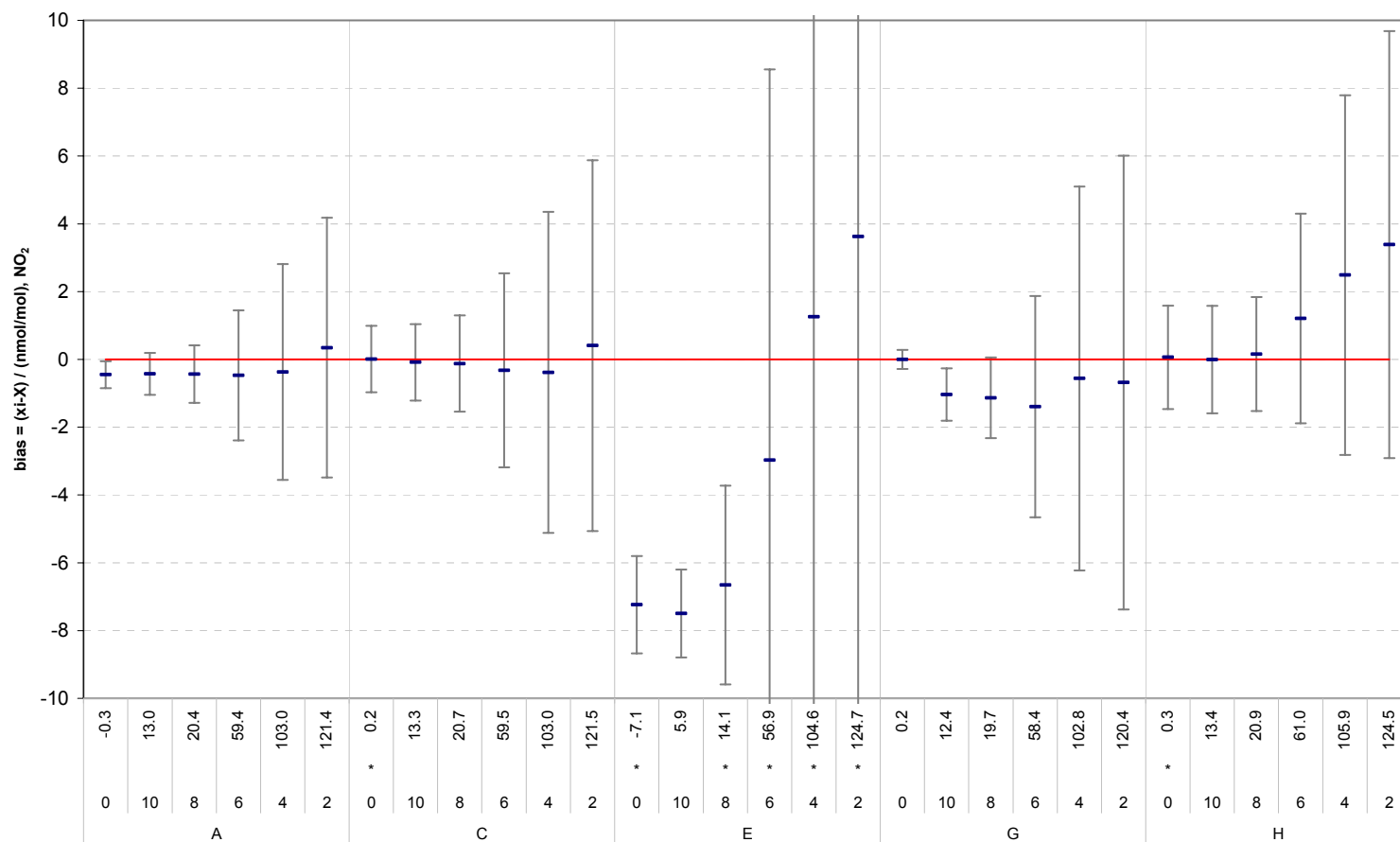


Figure 10: Bias of participant's NO₂ measurement results together with the expanded uncertainty of bias presented with error bar are given for tested concentration level with NO₂ run numbers 0, 2, 4, 6, 8 and 10 (see Table 2). Results with error bars touching or crossing the x-axis are satisfactory. 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 .

6. Performance characteristics of individual laboratories

Individual participants' biases were evaluated and are presented in chapter 5 (Figure 6-Figure 10). Since the results of NO₂ runs 1,3,5,7 and 9 were not treated in the proficiency evaluation the biases of these runs are presented in Figure 11.

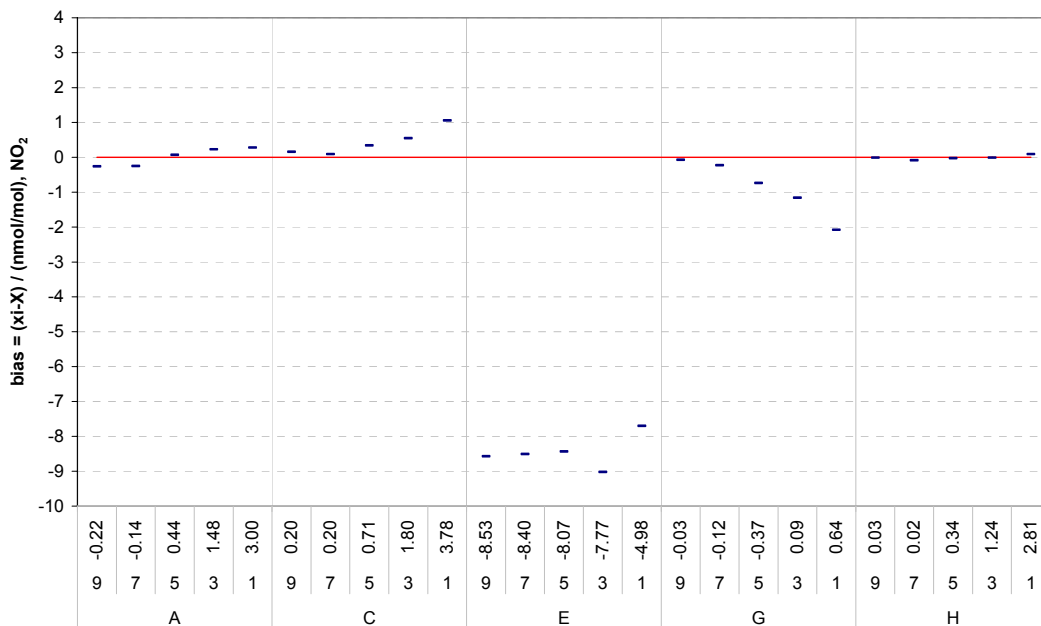


Figure 11: Bias of participant's NO₂ measurements for run numbers 1, 3, 5, 7 and 9
 At these test gas mixtures the concentration levels of NO₂ were zero and the concentration levels of NO were not zero (see Table 2). In that perspective the figure shows the effect of NO concentration on NO₂ measurements. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given.

The efficiency of NO₂-to-NO converters of NO_x analyzers

Since NO and NO₂ test gases were produced by gas phase titration it is possible to evaluate the efficiency of NO₂-to-NO converter of each participant's NO_x analyser. The evaluation takes each participants NO and NO₂ measurements before and after oxidation by O₃. The converter efficiency (α) is calculated using equation 3 [9]:

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

The O₃ measurements of each participant can also be compared to NO₂ measurements by calculating Δ using equation 4:

$$\Delta = [O_3]_{i+1} - ([NO_2]_i - [NO_2]_{i-1}) \quad (4)$$

Ideal values for α and Δ are 100% and 0 nmol/mol respectively.

The evaluation of equation 4 can not be made for the fifth GPT test (at 14 ppb of NO₂), because O₃ was not completely reduced due to insufficient excess of NO. The remaining evaluations of equations 3 and 4 for each participant at different concentration levels are given in Table 4.

Table 4: The efficiency of NO₂-to-NO converters.

IE code	NO ₂ (nmol/mol)	α (%)	Δ (nmol/mol)	IE code	NO ₂ (nmol/mol)	α (%)	Δ (nmol/mol)
A	14	99.3		E	14	97.8	
A	22	100.0	-0.6	E	22	98.6	-2.7
A	60	99.7	-1.0	E	60	98.4	-5.9
A	100	99.8	-1.6	E	100	99.6	-10.1
A	120	100.1	-2.6	E	120	99.0	-10.5
C	14	98.5		G	14	100.4	
C	22	99.4	0.2	G	22	99.0	0.6
C	60	98.9	0.4	G	60	99.5	0.0
C	100	99.3	0.5	G	100	101.2	-2.1
C	120	99.5	0.3	G	120	101.6	-7.4
D	14	99.8		H	14	99.5	
D	22	99.9	-0.4	H	22	100.6	-0.6
D	60	99.9	-1.3	H	60	101.1	-2.2
D	100	100.2	-2.1	H	100	101.7	-4.0
D	120	100.4	-2.2	H	120	102.5	-5.0

The uncertainty of converter efficiency evaluation at higher NO₂ concentration is smaller than at lower NO₂ concentration. For the general feeling, the average standard uncertainty of the converter efficiency is calculated, by taking standard deviations of repeatable measurements of quantities in equation 3, and is evaluated to approximately 0.5%, at 120 nmol/mol of NO₂, and 1%, at 14 nmol/mol of NO₂.

7. Discussion

For a general assessment of the quality of each result a decision diagram was developed (Figure 12) that categorises results in seven categories (a1 to a7). The general comments for each category are:

- a1: measurement result is completely satisfactory
- a2: measurement result is satisfactory (z'-score satisfactory and En-number ok) but the reported uncertainty is too high
- a3: measured value is satisfactory (z'-score satisfactory) but the reported uncertainty is underestimated (En-number not ok)
- a4: measurement result is questionable (z'-score questionable) but due to a high reported uncertainty can be considered valid (En-number ok)
- a5: measurement result is questionable (z'-score questionable and En-number not ok)
- a6: measurement result is unsatisfactory (z'-score unsatisfactory) but due to a high reported uncertainty can be considered valid (En-number ok)
- a7: measurement result is unsatisfactory (z'-score unsatisfactory and En-number not ok)

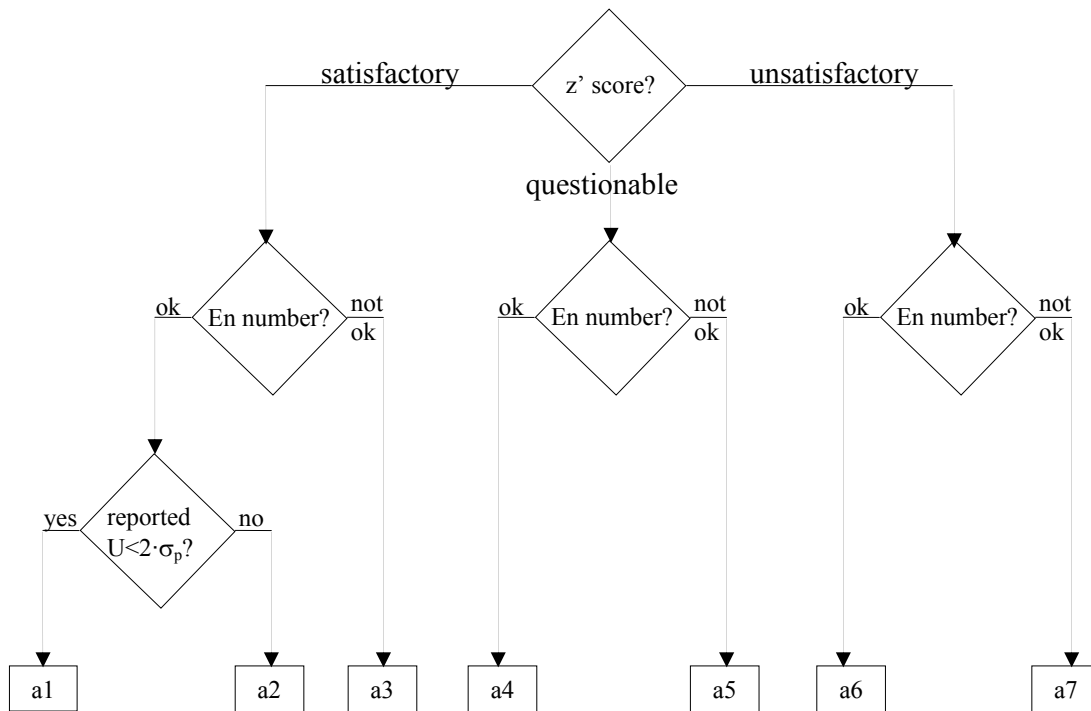


Figure 12: The decision diagram for general assessment of proficiency results.

The results of the IE were assigned to categories according to the diagram given in Figure 12 and are presented in Table 5. For clarity reasons, notation 'a1' is not inserted in Table 5 and all empty spaces represent 'a1' results.

Table 5: The general assessment of proficiency results.
 Empty spaces represent 'a1' results while results not reported are represented by 'nv' (no value).

	run number	conc. level	IE code							
			A	B	C	E	F	G	H	
SO ₂ (nmol/mol)	0	0.2		a2	a2	a3	nv	a5		
	5	3.2		a2	a2		nv	a3		
	4	7.6		a2		a2	nv	a3		
	3	17.9		a2		a2	nv			
	2	46.3				a2	nv			
	1	130.6				a2	nv	a3		
CO (µmol/mol)	0	0.009				a3	nv			
	5	0.970					nv	a3		
	4	1.948					nv	a3		
	3	4.238				a2	nv			
	2	5.901				a2	nv			
	1	8.465				a2	nv			
O ₃ (nmol/mol)	0	-0.1		nv	a2		a2	a2	a2	
	5	13.5		nv	a2	a2	a2			
	4	20.2		nv		a2	a2			
	3	58.2		nv		a2				
	2	100.0		nv		a2				
	1	116.2		nv		a2		a2		
NO (nmol/mol)	0	0.7	a3	nv		a3	nv		a2	
	10	2.9		nv			nv	a3	a2	
	9	16.3		nv		a2	nv	a5		
	8	30.6		nv		a2	nv	a3		
	7	51.3		nv		a4	nv	a3		
	6	91.6		nv		a4	nv			
	5	150.7		nv		a6	nv			
	4	151.1		nv		a6	nv			
	3	252.6		nv		a6	nv			
	2	381.0		nv		a6	nv			
1	499.0		nv		a6	nv				
NO ₂ (nmol/mol)	0	0.2	a3	nv	a2	a7	nv		a2	
	10	13.4		nv		a7	nv	a3		
	8	20.8		nv		a7	nv			
	6	59.8		nv		a2	nv			
	4	103.4		nv		a2	nv			
	2	121.1		nv		a2	nv			

Comparability of NO₂ and ozone measurements via GPT was investigated in studies [26] [27], where O₃ was traceable to international standards implementing ultraviolet photometry method and NO₂ was traceable to NO international standards and GPT method was applied, and a significant difference of about 2% was confirmed. At this IE, this difference can not be confirmed by individual participants, due to significant uncertainties attributed to O₃ and NO₂ measurements, but in the general evaluation a difference of 3% is observed between group average NO₂ and average O₃.

8. 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 Commission (σ) 80% of the results reported by AQUILA laboratories fall into 'a1' category and are good both in terms of measured values and evaluated uncertainties. In residual 18% of the results have good measured values but the evaluated uncertainties were either too high, category 'a2' (11%), or too small, category 'a3' (7%). The relative high number of 'a2' cases, where participant's evaluated uncertainty is higher than the common IE criterion, needs further investigation. The common IE criterion is confirmed to be realistic by comparison to reproducibility standard deviation obtained at this (Annex C) and other IEs [25], and is derived from the European standards' uncertainty requirements, which are explicit at high concentrations. Since the uncertainty requirements at zero concentration are not quantitatively stated in the European standards, the IE criteria at zero concentration had to be set within AQUILA. The initially proposed values were in use for IEs since June 2007 to October 2008 but at the November 2008 AQUILA meeting the IE criteria at zero concentration were enlarged and approved. The final values were also communicated to relevant CEN working group for potential future amendments of European standards. With that in mind especially 'a2' results at high concentration levels should be further investigated by the NRLs.

None of the NRLs had overall unsatisfactory results of the z'-score evaluation (one unsatisfactory, categories 'a6' or 'a7', or two questionable, categories 'a4' or 'a5', result per parameter) which would in the view of AQUILA require participation to the next IE in order to demonstrate remediation measures.

The comparability of results among AQUILA participants is best for NO and worst for SO₂ measurement method. The relative reproducibility limits, at the highest studied concentration levels, are 6.1% for SO₂, 4.9% for CO, 3.3% for O₃, 2.2% for NO, and 5.1% for NO₂ which are all below the objective derived from criteria imposed by the European Commission (σ).

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Annex A. Assigned values

The assigned values of tested concentration levels 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 [18].

ERLAPs SO₂, CO and NO analysers were calibrated according to the methodology described in the ISO 6143 [11]. A different number (4 for SO₂, 7 for CO and 5 for NO) of 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 [13]. All flows were measured with a certified volumeter. For the reference gas mixture composition evaluation and for the calibration experiment evaluation two computer applications were used, the “GUM WORKBENCH” [26] and “B-least” [29] respectively. For extending calibration from the NO to NO₂ channel of NO_x analyser the GPT test was performed to establish the efficiency of NO₂-converter. For O₃ measurements, the primary standard was used.

ERLAP’s measurement results were validated by comparison to the group statistics (x* and s*) for every parameter and concentration level of the IE. These statistics are calculated from participants, applying the robust method described in the Annex C of the ISO 13528 [18]. The validation is taking in account ERLAP’s measurement result (X) and its standard uncertainty (u_X) as given in expression 5 [18]:

$$\frac{|x^* - X|}{\sqrt{\frac{(1,25 \cdot s^*)^2}{p} + u_X^2}} < 2 \quad (5)$$

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

In Table 6 all inputs for expression 5 are given and all ERLAP’s measurement results are confirmed to be valid.

Table 6: The validation of assigned values (X) by comparison to the robust averages (x*) with taking into the account the standard uncertainties of assigned values (uX'), and robust standard deviations (s*) as denoted by expression 5.

run	unit	X	uX'	x*	s*	val.	run	unit	X	uX'	x*	s*	val.
CO_0	µmol/mol	0.009	0.013	0.001	0.003	OK	NO_0	nmol/mol	0.7	0.3	0.2	0.4	OK
CO_1	µmol/mol	8.465	0.061	8.381	0.151	OK	NO_1	nmol/mol	499.0	6.5	501.3	3.8	OK
CO_2	µmol/mol	5.901	0.043	5.849	0.097	OK	NO_2	nmol/mol	381.0	5.0	382.9	3.3	OK
CO_3	µmol/mol	4.238	0.032	4.210	0.049	OK	NO_3	nmol/mol	252.6	3.3	253.0	2.8	OK
CO_4	µmol/mol	1.948	0.019	1.923	0.032	OK	NO_4	nmol/mol	150.7	2.0	150.8	2.0	OK
CO_5	µmol/mol	0.970	0.014	0.963	0.019	OK	NO_5	nmol/mol	151.1	2.0	150.8	2.2	OK
O3_0	nmol/mol	-0.1	1.0	-0.1	0.2	OK	NO_6	nmol/mol	91.6	1.3	91.3	1.4	OK
O3_1	nmol/mol	116.2	1.4	116.3	0.8	OK	NO_7	nmol/mol	51.3	0.8	50.9	1.1	OK
O3_2	nmol/mol	100.0	1.2	100.8	0.9	OK	NO_8	nmol/mol	30.6	0.5	30.2	0.8	OK
O3_3	nmol/mol	58.2	1.1	58.7	0.6	OK	NO_9	nmol/mol	16.3	0.4	15.9	0.7	OK
O3_4	nmol/mol	20.2	1.0	20.3	0.5	OK	NO_10	nmol/mol	2.9	0.3	2.4	0.3	OK
O3_5	nmol/mol	13.5	1.0	13.5	0.5	OK	NO2_0	nmol/mol	0.2	0.1	0.2	0.1	OK
SO2_0	nmol/mol	0.2	0.2	0.0	0.2	OK	NO2_1	nmol/mol	2.7	0.9	2.5	1.1	OK
SO2_1	nmol/mol	130.6	1.2	131.6	3.5	OK	NO2_2	nmol/mol	121.1	1.9	121.7	1.2	OK
SO2_2	nmol/mol	46.3	0.5	46.4	1.1	OK	NO2_3	nmol/mol	1.3	0.6	1.1	0.7	OK
SO2_3	nmol/mol	17.9	0.3	17.8	0.3	OK	NO2_4	nmol/mol	103.4	1.5	103.3	0.5	OK
SO2_4	nmol/mol	7.6	0.2	7.3	0.3	OK	NO2_5	nmol/mol	0.4	0.5	0.3	0.4	OK
SO2_5	nmol/mol	3.2	0.2	2.9	0.3	OK	NO2_6	nmol/mol	59.8	0.9	59.3	1.2	OK
							NO2_7	nmol/mol	0.1	0.3	0.0	0.2	OK
							NO2_8	nmol/mol	20.8	0.4	20.4	0.6	OK
							NO2_9	nmol/mol	0.0	0.2	0.0	0.2	OK
							NO2_10	nmol/mol	13.4	0.3	13.1	0.4	OK

The homogeneity of test gas was evaluated from measurements at the beginning and end of the distribution line. From the relative differences between beginning and end measurements, average and standard deviation were calculated, and the uncertainty of test gas due to lack of homogeneity was calculated as the sum of squares of these average and standard deviation. The upper and lower limits of bias due to homogeneity was evaluated to be smaller than 1% which constitutes the relative standard uncertainty of 0,6% of tested concentration level. The standard uncertainties of assigned/reference values (u_X) were calculated with equation 6 and used in the proficiency evaluations of chapter 5.

$$u_X^2 = u_{X'}^2 + (X \cdot u_{\text{homogeneity}})^2 \quad (6)$$

Annex B. The results of the IE

The reported values, presented also in graphs, are given in this annex. The participants were asked to report results (x_{ij} , $u(x_i)$ 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. 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. The assigned value is indicated on the graphs with the red line and the individual laboratories expanded uncertainties ($U(x_i)$) are indicated with error bars.

Reported values for SO₂

Table 7: Reported values for SO₂ concentration level 0.

parameter: SO2 all units are nmol/mol							
level: 0 $x^* : -0.02$ $s^* : 0.17$							
	A	B	C	D	E	G	H
$x_{i,1}$	0.01	-0.06	0.11	0.19	-0.31	-0.82	0.01
$u(x_i)$	0.19	1.00	0.55	0.21	0.04	0.02	0.15
$U(x_i)$	0.39	2.00	1.10	0.42	0.07	0.03	0.30

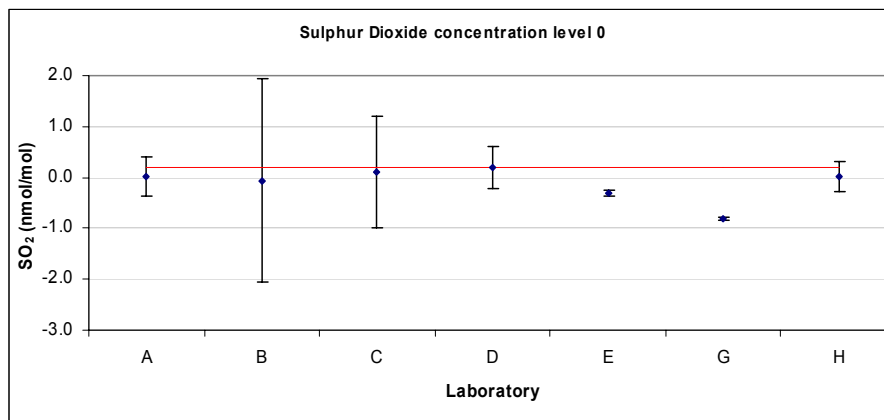


Figure 13: Reported values for SO₂ concentration level 0.

Table 8: Reported values for SO₂ concentration level 1.

parameter: SO2		all units are nmol/mol					
level: 1		x*: 131.57			s*: 3.47		
	A	B	C	D	E	G	H
xi,1	129.72	133.98	133.82	130.52	125.93	135.12	131.02
xi,2	129.76	134.08	133.60	130.63	126.23	135.30	131.38
xi,3	129.68	134.32	133.71	130.64	126.62	135.27	131.29
xi	129.720	134.127	133.710	130.597	126.260	135.230	131.230
si	0.040	0.175	0.110	0.067	0.346	0.096	0.187
u(xi)	0.82	3.10	2.15	0.92	12.63	1.86	2.23
U(xi)	1.65	6.20	4.30	1.84	25.26	3.71	4.46

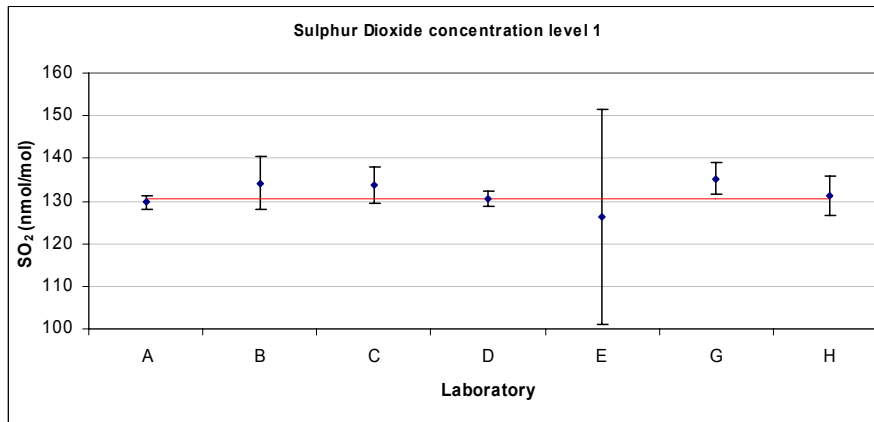


Figure 14: Reported values for SO₂ concentration level 1.

Table 9: Reported values for SO₂ concentration level 2.

parameter: SO2		all units are nmol/mol					
level: 2		x*: 46.40			s*: 1.14		
	A	B	C	D	E	G	H
xi,1	45.71	47.40	47.31	46.27	44.56	47.38	46.22
xi,2	45.64	47.30	47.31	46.26	44.62	47.37	46.27
xi,3	45.65	47.31	47.20	46.25	44.62	47.28	46.12
xi	45.667	47.337	47.273	46.260	44.600	47.343	46.203
si	0.038	0.055	0.064	0.010	0.035	0.055	0.076
u(xi)	0.42	1.44	0.90	0.42	4.46	0.67	0.79
U(xi)	0.83	2.88	1.80	0.84	8.92	1.33	1.57

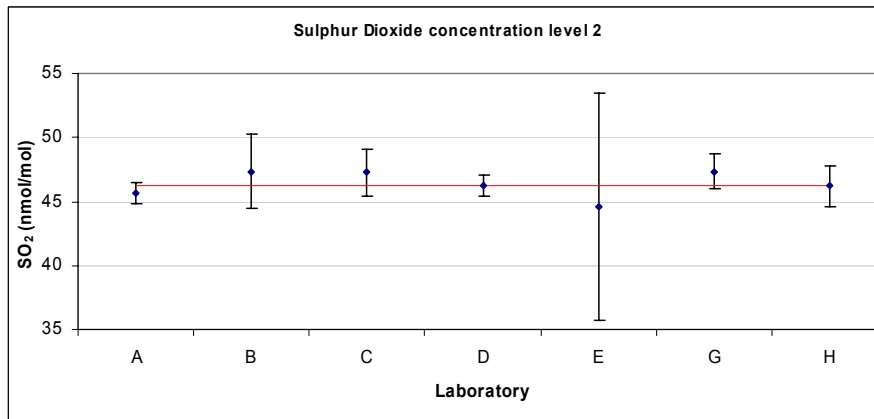


Figure 15: Reported values for SO₂ concentration level 2.

Table 10: Reported values for SO₂ concentration level 3.

parameter: SO ₂		all units are nmol/mol					
level: 3		x*: 17.80		s*: 0.33			
	A	B	C	D	E	G	H
xi,1	17.55	18.10	18.25	17.95	16.95	17.71	17.76
xi,2	17.59	18.07	18.25	17.90	16.99	17.73	17.78
xi,3	17.60	18.06	18.25	17.92	17.00	17.75	17.77
xi	17.580	18.077	18.250	17.923	16.980	17.730	17.770
si	0.026	0.021	0.000	0.025	0.026	0.020	0.010
u(xi)	0.28	1.07	0.60	0.27	1.70	0.25	0.31
U(xi)	0.56	2.14	1.20	0.54	3.40	0.50	0.61

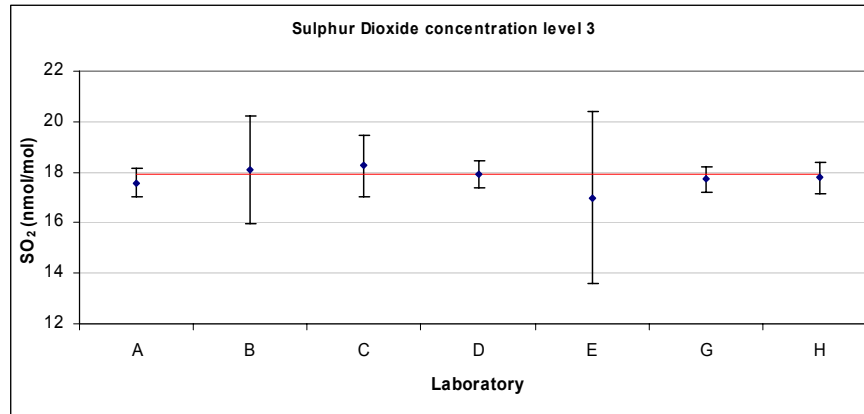


Figure 16: Reported values for SO₂ concentration level 3.

Table 11: Reported values for SO₂ concentration level 4.

parameter: SO ₂		all units are nmol/mol					
level: 4		x*: 7.31		s*: 0.30			
	A	B	C	D	E	G	H
xi,1	7.31	7.38	7.67	7.58	6.89	6.96	7.40
xi,2	7.29	7.38	7.56	7.58	6.89	7.01	7.40
xi,3	7.27	7.36	7.56	7.58	6.90	6.99	7.42
xi	7.290	7.373	7.597	7.580	6.893	6.987	7.407
si	0.020	0.012	0.064	0.000	0.006	0.025	0.012
u(xi)	0.23	1.01	0.55	0.23	0.69	0.12	0.15
U(xi)	0.46	2.02	1.10	0.46	1.38	0.23	0.30

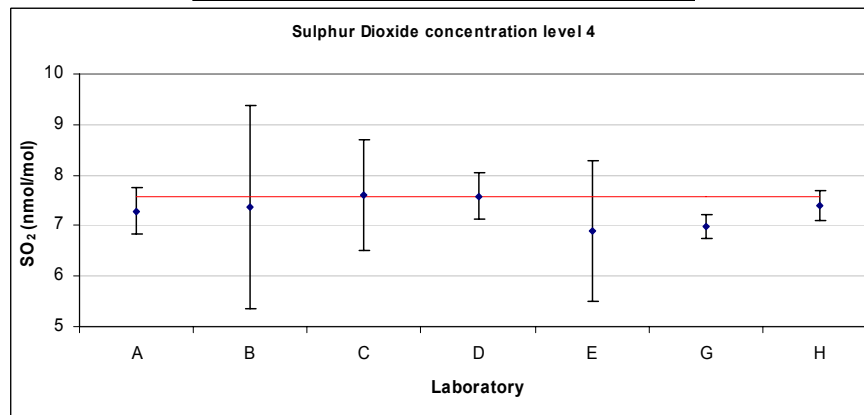


Figure 17: Reported values for SO₂ concentration level 4.

Table 12: Reported values for SO₂ concentration level 5.

parameter: SO ₂		all units are nmol/mol					
level: 5		x*: 2.89		s*: 0.28			
	A	B	C	D	E	G	H
xi,1	2.93	2.84	3.13	3.17	2.59	2.46	2.98
xi,2	2.94	2.84	3.13	3.16	2.59	2.37	2.98
xi,3	2.97	2.86	3.13	3.17	2.59	2.38	2.99
xi	2.947	2.847	3.130	3.167	2.590	2.403	2.983
si	0.021	0.012	0.000	0.006	0.000	0.049	0.006
u(xi)	0.21	1.00	0.55	0.22	0.26	0.07	0.15
U(xi)	0.42	2.00	1.10	0.44	0.52	0.13	0.30

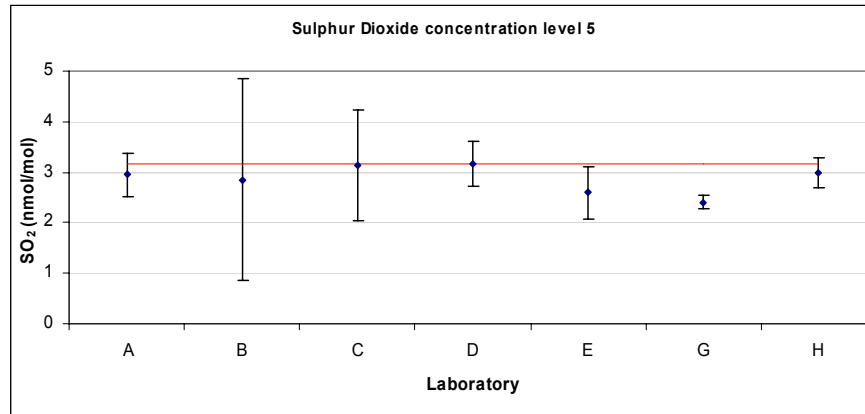


Figure 18: Reported values for SO₂ concentration level 5.

Reported values for CO

Table 13: Reported values for CO concentration level 0.

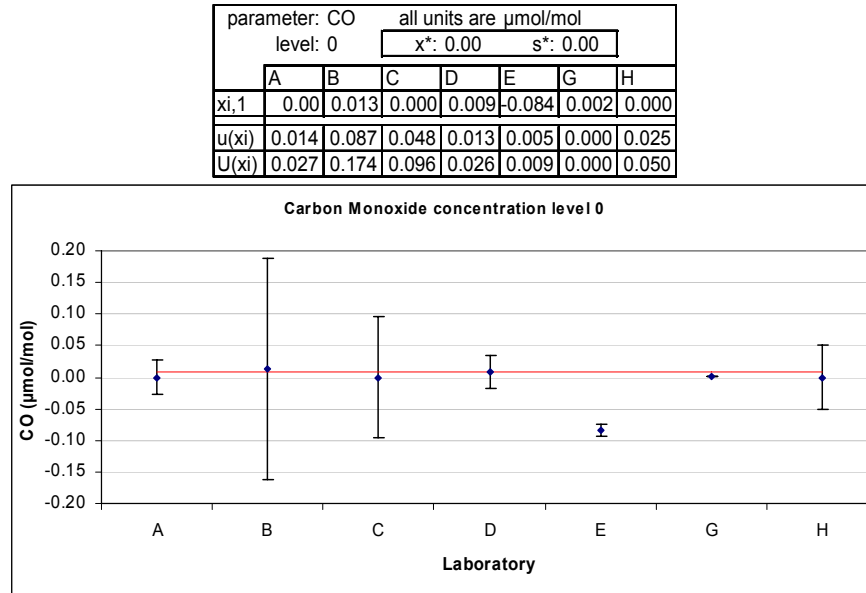


Figure 19: Reported values for CO concentration level 0.

Table 14: Reported values for CO concentration level 1.

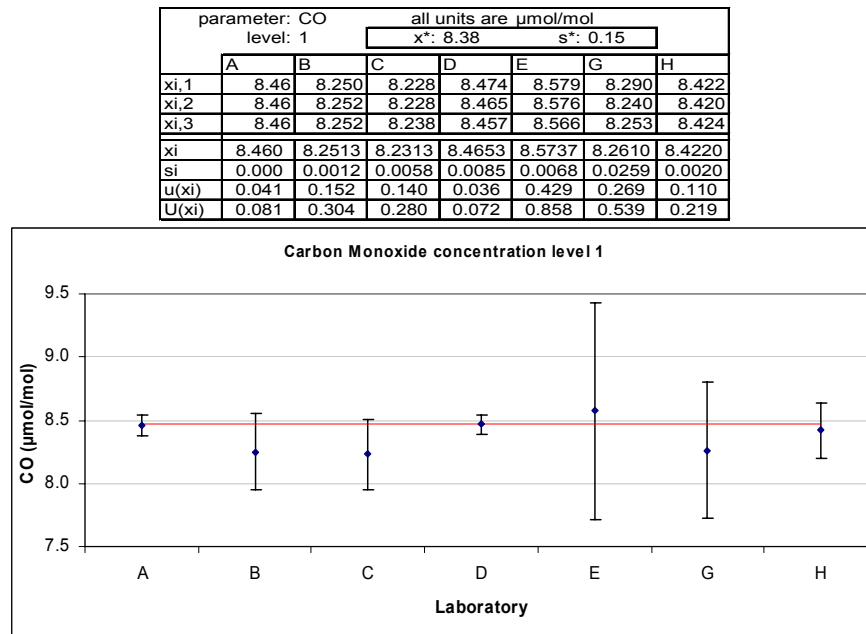


Figure 20: Reported values for CO concentration level 1.

Table 15: Reported values for CO concentration level 2.

parameter: CO		all units are $\mu\text{mol/mol}$					
level: 2		x*: 5.85		s*: 0.10			
	A	B	C	D	E	G	H
xi,1	5.91	5.776	5.751	5.902	5.963	5.754	5.881
xi,2	5.91	5.777	5.751	5.901	5.962	5.750	5.885
xi,3	5.92	5.778	5.762	5.899	5.962	5.754	5.886
xi	5.913	5.7770	5.7547	5.9007	5.9623	5.7527	5.8840
si	0.006	0.0010	0.0064	0.0015	0.0006	0.0023	0.0026
u(xi)	0.032	0.123	0.110	0.026	0.299	0.178	0.077
U(xi)	0.065	0.246	0.210	0.052	0.597	0.357	0.154

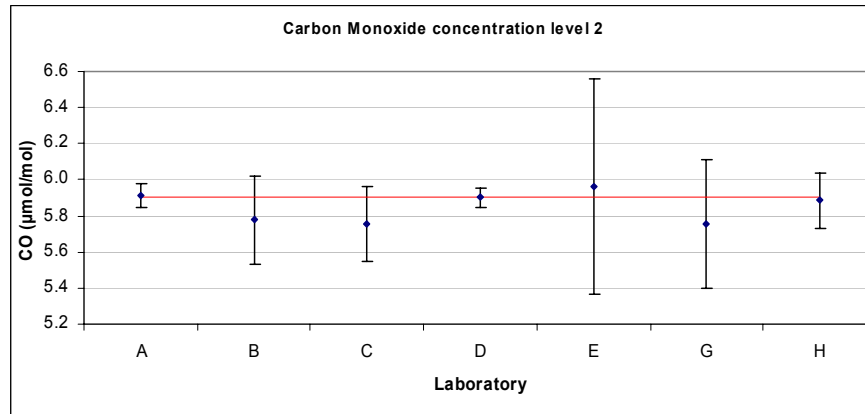


Figure 21: Reported values for CO concentration level 2.

Table 16: Reported values for CO(x) concentration level 3.

parameter: CO		all units are $\mu\text{mol/mol}$					
level: 3		x*: 4.21		s*: 0.05			
	A	B	C	D	E	G	H
xi,1	4.25	4.156	4.135	4.240	4.259	4.067	4.229
xi,2	4.25	4.156	4.135	4.239	4.260	4.064	4.230
xi,3	4.25	4.156	4.135	4.234	4.255	4.061	4.229
xi	4.250	4.1560	4.1350	4.2377	4.2580	4.0640	4.2293
si	0.000	0.0000	0.0000	0.0032	0.0026	0.0030	0.0006
u(xi)	0.027	0.107	0.085	0.021	0.213	0.127	0.055
U(xi)	0.054	0.214	0.170	0.042	0.426	0.250	0.110

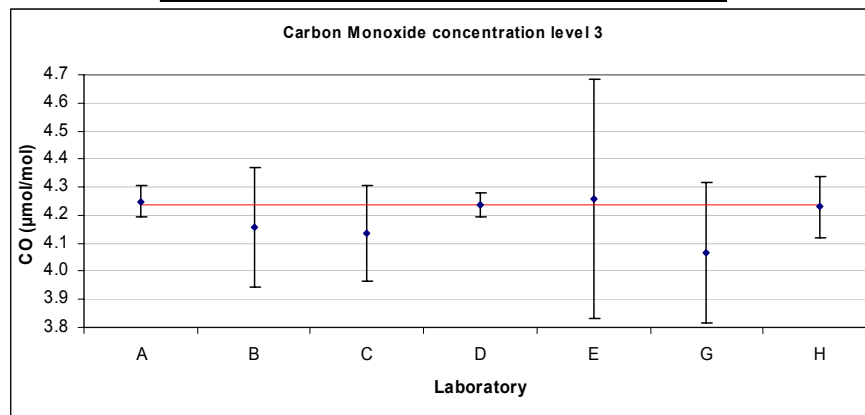


Figure 22: Reported values for CO concentration level 3.

Table 17: Reported values for CO concentration level 4.

parameter: CO		all units are $\mu\text{mol/mol}$						
level: 4		x*: 1.92		s*: 0.03				
	A	B	C	D	E	G	H	
xi,1	1.96	1.926	1.906	1.950	1.909	1.686	1.946	
xi,2	1.95	1.924	1.906	1.948	1.905	1.686	1.944	
xi,3	1.95	1.925	1.906	1.947	1.906	1.686	1.948	
xi	1.953	1.9250	1.9060	1.9483	1.9067	1.6860	1.9460	
si	0.006	0.0010	0.0000	0.0015	0.0021	0.0000	0.0020	
u(xi)	0.020	0.092	0.055	0.015	0.096	0.052	0.026	
U(xi)	0.040	0.184	0.110	0.030	0.191	0.104	0.051	

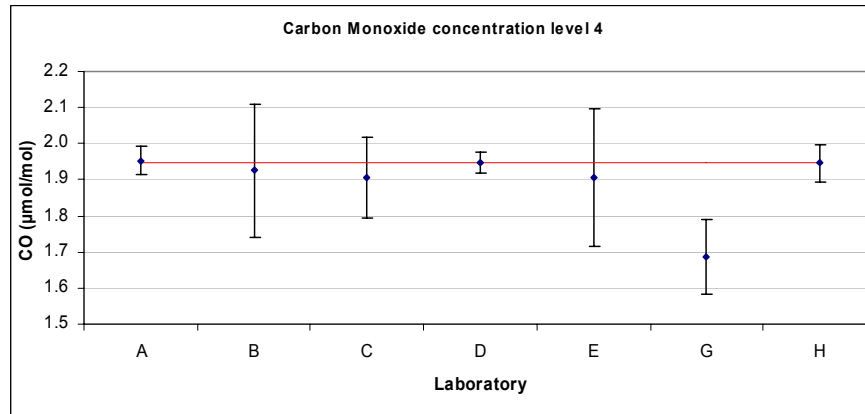


Figure 23: Reported values for CO concentration level 4.

Table 18: Reported values for CO(x) concentration level 5.

parameter: CO		all units are $\mu\text{mol/mol}$						
level: 5		x*: 0.96		s*: 0.02				
	A	B	C	D	E	G	H	
xi,1	0.98	0.981	0.948	0.967	0.892	0.893	0.974	
xi,2	0.98	0.981	0.948	0.967	0.892	0.893	0.974	
xi,3	0.98	0.981	0.948	0.975	0.896	0.893	0.975	
xi	0.980	0.9810	0.9480	0.9697	0.8933	0.8930	0.9743	
si	0.000	0.0000	0.0000	0.0046	0.0023	0.0000	0.0006	
u(xi)	0.017	0.088	0.050	0.013	0.045	0.027	0.025	
U(xi)	0.033	0.176	0.100	0.026	0.090	0.055	0.050	

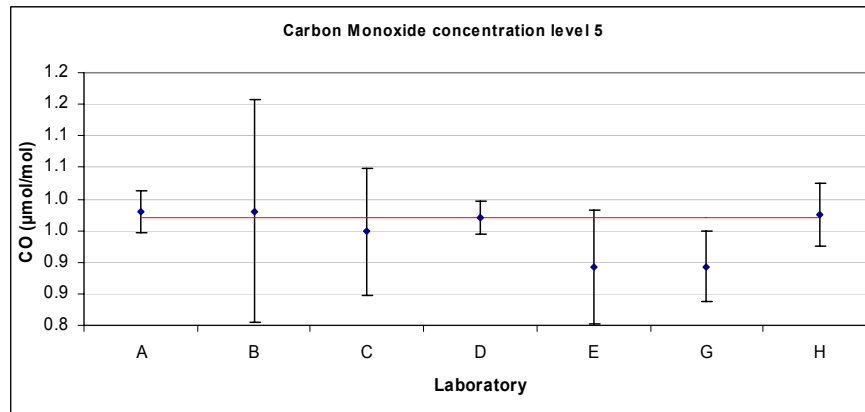


Figure 24: Reported values for CO concentration level 5.

Reported values for O₃

Table 19: Reported values for O₃ concentration level 0.

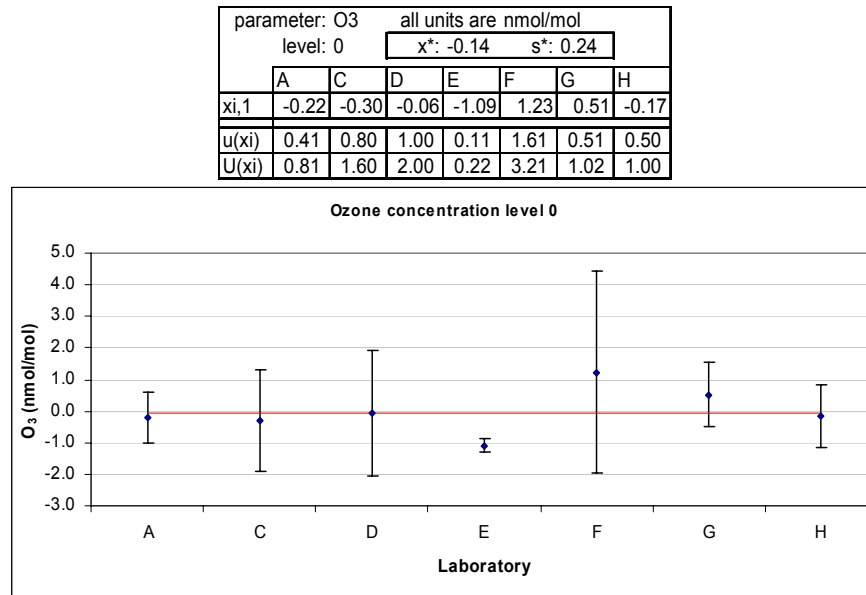


Figure 25: Reported values for O₃ concentration level 0.

Table 20: Reported values for O₃ concentration level 1.

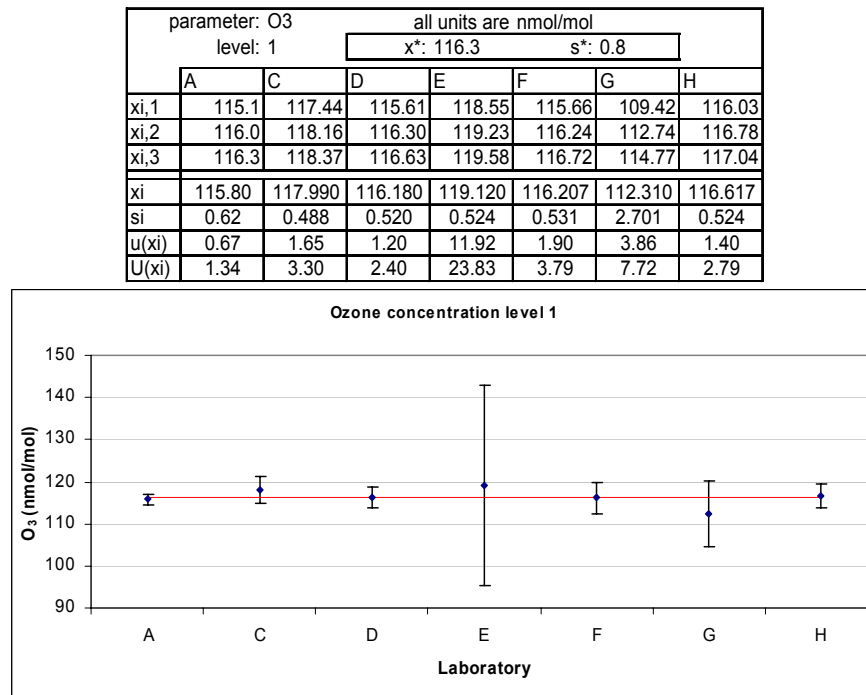


Figure 26: Reported values for O₃ concentration level 1.

Table 21: Reported values for O₃ concentration level 2.

parameter: O ₃		all units are nmol/mol					
level: 2		x*: 100.8		s*: 0.9			
	A	C	D	E	F	G	H
xi,1	99.5	101.21	99.59	101.99	100.13	99.63	100.16
xi,2	100.1	101.83	100.12	102.39	100.73	100.82	100.71
xi,3	100.3	101.93	100.31	102.66	100.86	101.49	100.94
xi	99.97	101.657	100.007	102.347	100.573	100.647	100.603
si	0.42	0.390	0.373	0.337	0.389	0.942	0.401
u(xi)	0.63	1.45	1.00	10.24	1.87	2.66	1.21
U(xi)	1.27	2.90	2.00	20.47	3.73	5.31	2.41

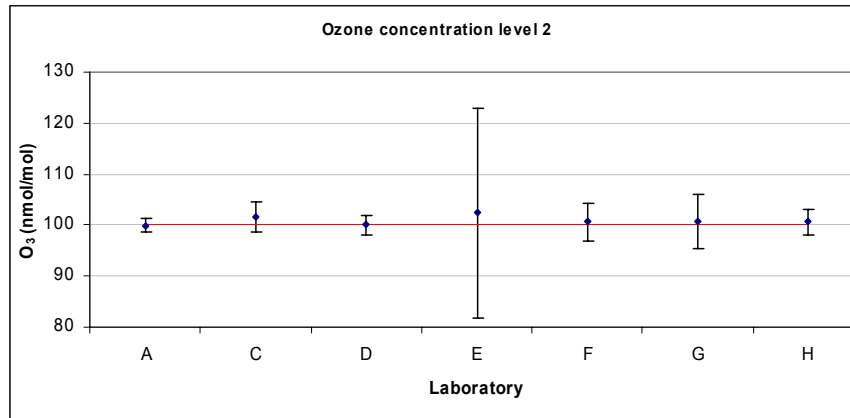


Figure 27: Reported values for O₃ concentration level 2.

Table 22: Reported values for O₃ concentration level 3.

parameter: O ₃		all units are nmol/mol					
level: 3		x*: 58.7		s*: 0.6			
	A	C	D	E	F	G	H
xi,1	57.9	59.18	58.17	58.97	59.10	58.54	58.45
xi,2	58.0	59.18	58.14	59.12	59.22	58.87	58.45
xi,3	58.0	59.18	58.18	59.13	59.23	58.95	58.52
xi	57.97	59.180	58.163	59.073	59.183	58.787	58.473
si	0.06	0.000	0.021	0.090	0.072	0.217	0.040
u(xi)	0.54	1.05	1.00	5.91	1.60	1.57	0.70
U(xi)	1.08	2.10	2.00	11.82	3.20	3.14	1.40

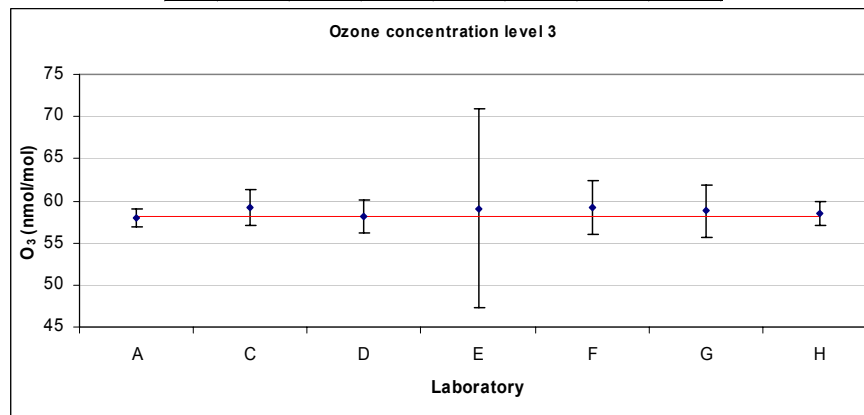


Figure 28: Reported values for O₃ concentration level 3.

Table 23: Reported values for O₃ concentration level 4.

parameter: O ₃		all units are nmol/mol					
level: 4		x*: 20.3		s*: 0.5			
	A	C	D	E	F	G	H
xi,1	19.9	20.65	20.20	19.82	21.75	20.29	20.29
xi,2	19.9	20.65	20.26	19.86	21.74	20.31	20.35
xi,3	19.9	20.65	20.25	19.86	21.74	20.41	20.38
xi	19.90	20.650	20.237	19.847	21.743	20.337	20.340
si	0.00	0.000	0.032	0.023	0.006	0.064	0.046
u(xi)	0.45	0.80	1.00	1.99	1.60	0.87	0.50
U(xi)	0.90	1.60	2.00	3.97	3.19	1.73	1.00

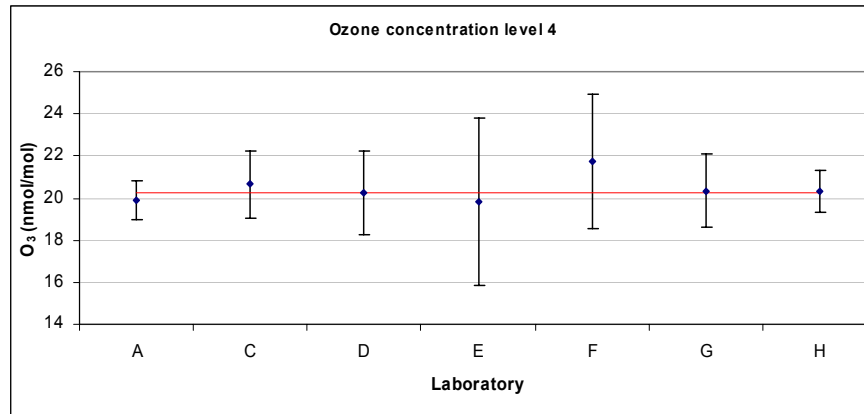


Figure 29: Reported values for O₃ concentration level 4.

Table 24: Reported values for O₃ concentration level 5.

parameter: O ₃		all units are nmol/mol					
level: 5		x*: 13.5		s*: 0.5			
	A	C	D	E	F	G	H
xi,1	13.1	13.77	13.46	12.82	15.22	13.41	13.57
xi,2	13.1	13.77	13.44	12.86	15.12	13.44	13.57
xi,3	13.1	13.97	13.48	12.90	15.23	13.41	13.55
xi	13.10	13.837	13.460	12.860	15.190	13.420	13.563
si	0.00	0.115	0.020	0.040	0.061	0.017	0.012
u(xi)	0.44	0.80	1.00	1.29	1.60	0.73	0.50
U(xi)	0.87	1.60	2.00	2.58	3.20	1.45	1.00

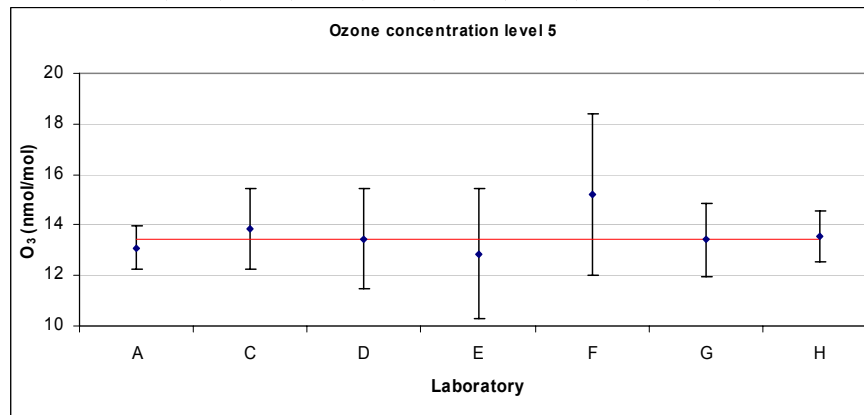


Figure 30: Reported values for O₃ concentration level 5.

Reported values for NO

Table 25: Reported values for NO concentration level 0.

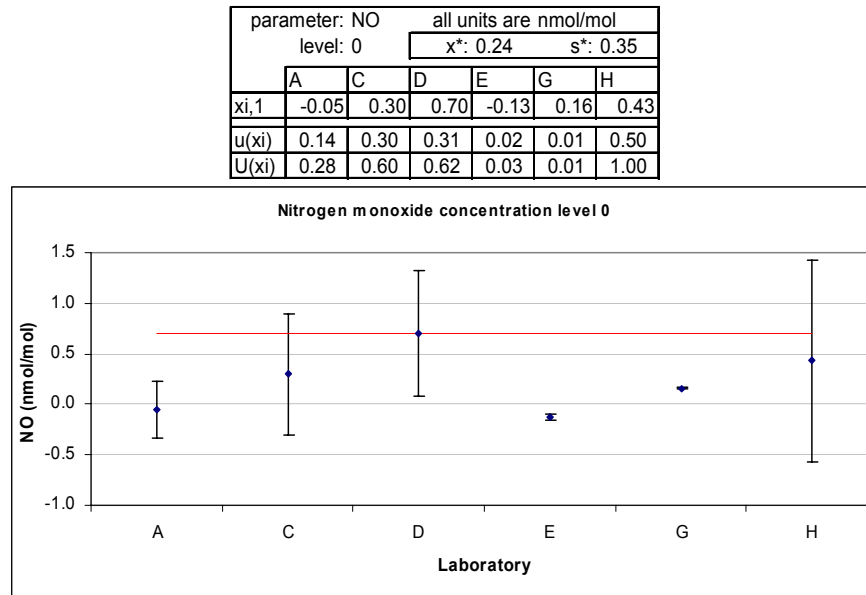


Figure 31: Reported values for NO concentration level 0.

Table 26: Reported values for NO concentration level 1.

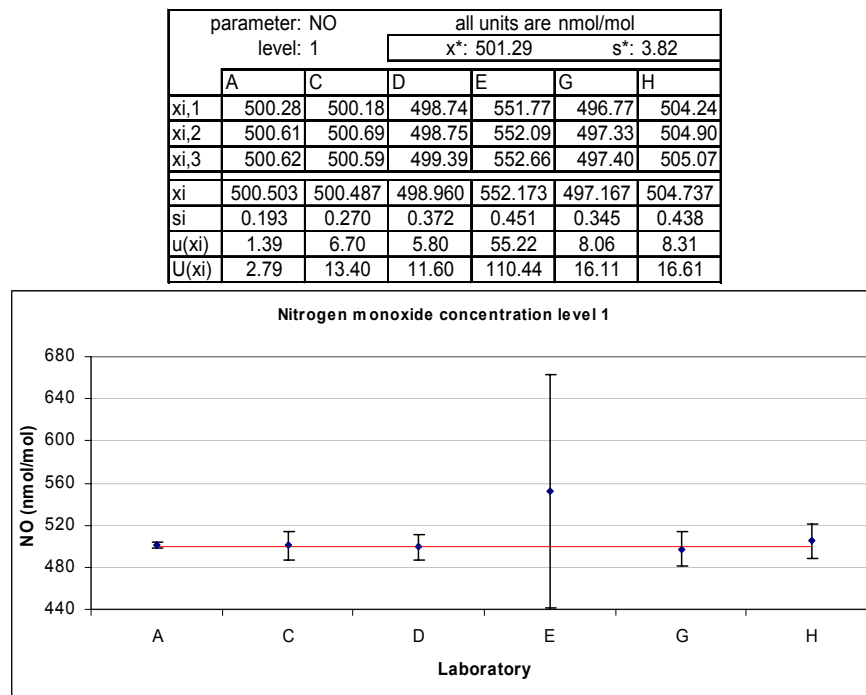


Figure 32: Reported values for NO concentration level 1.

Table 27: Reported values for NO concentration level 2.

parameter: NO		all units are nmol/mol				
level: 2		x*: 382.93		s*: 3.28		
	A	C	D	E	G	H
xi,1	381.84	381.77	380.54	420.73	378.55	385.56
xi,2	382.44	382.29	381.23	421.44	379.68	386.22
xi,3	382.29	382.60	381.36	421.58	379.73	386.51
xi	382.190	382.220	381.043	421.250	379.320	386.097
si	0.312	0.419	0.441	0.456	0.667	0.487
u(xi)	1.10	5.10	4.45	42.13	6.38	6.36
U(xi)	2.20	10.20	8.90	84.25	12.76	12.71

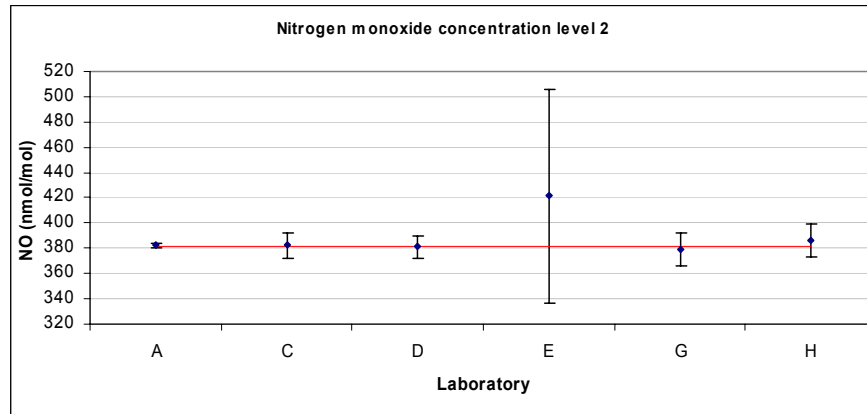


Figure 33: Reported values for NO concentration level 2.

Table 28: Reported values for NO concentration level 3.

parameter: NO		all units are nmol/mol				
level: 3		x*: 252.97		s*: 2.79		
	A	C	D	E	G	H
xi,1	251.92	252.29	252.44	278.54	249.32	255.24
xi,2	251.90	252.40	252.78	278.48	249.42	255.28
xi,3	251.94	252.29	252.70	278.26	249.49	255.33
xi	251.920	252.327	252.640	278.427	249.410	255.283
si	0.020	0.064	0.178	0.147	0.085	0.045
u(xi)	0.77	3.40	2.96	27.85	3.99	4.20
U(xi)	1.54	6.80	5.92	55.69	7.98	8.40

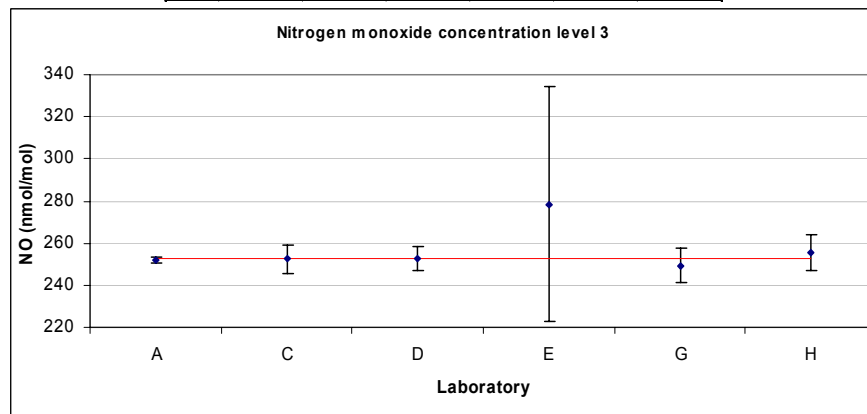


Figure 34: Reported values for NO concentration level 3.

Table 29: Reported values for NO concentration level 4.

parameter: NO		all units are nmol/mol				
level: 4		x*: 150.82		s*: 1.96		
	A	C	D	E	G	H
xi,1	150.03	150.21	150.48	165.27	147.80	152.12
xi,2	150.38	150.51	150.85	165.75	148.02	152.55
xi,3	150.32	150.51	150.78	165.73	147.85	152.60
xi	150.243	150.410	150.703	165.583	147.890	152.423
si	0.187	0.173	0.197	0.272	0.115	0.264
u(xi)	0.52	2.10	1.80	16.56	2.41	2.51
U(xi)	1.03	4.20	3.60	33.12	4.81	5.02

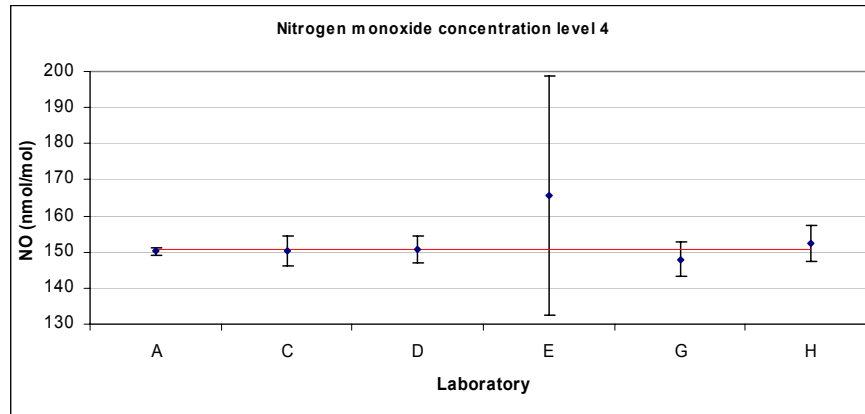


Figure 35: Reported values for NO concentration level 4.

Table 30: Reported values for NO(x) concentration level 5.

parameter: NO		all units are nmol/mol				
level: 5		x*: 150.84		s*: 2.24		
	A	C	D	E	G	H
xi,1	149.86	150.31	151.02	165.98	147.20	152.33
xi,2	149.73	150.41	151.25	166.18	147.13	152.28
xi,3	149.72	150.31	151.14	166.24	146.90	152.28
xi	149.770	150.343	151.137	166.133	147.077	152.297
si	0.078	0.058	0.115	0.136	0.157	0.029
u(xi)	0.52	2.10	1.81	16.62	2.42	2.51
U(xi)	1.03	4.20	3.62	33.23	4.83	5.02

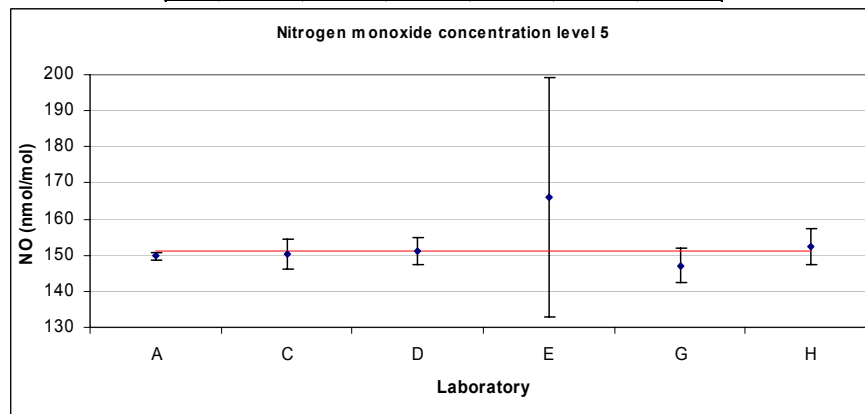


Figure 36: Reported values for NO concentration level 5.

Table 31: Reported values for NO concentration level 6.

parameter: NO		all units are nmol/mol				
level: 6		x*: 91.31		s*: 1.43		
	A	C	D	E	G	H
xi,1	90.59	90.90	91.60	100.16	88.10	92.16
xi,2	90.58	90.90	91.54	100.09	87.89	92.26
xi,3	90.79	90.90	91.61	100.27	87.93	92.35
xi	90.653	90.900	91.583	100.173	87.973	92.257
si	0.118	0.000	0.038	0.091	0.112	0.095
u(xi)	0.37	1.20	1.13	10.02	1.46	1.52
U(xi)	0.74	2.40	2.26	20.04	2.92	3.04

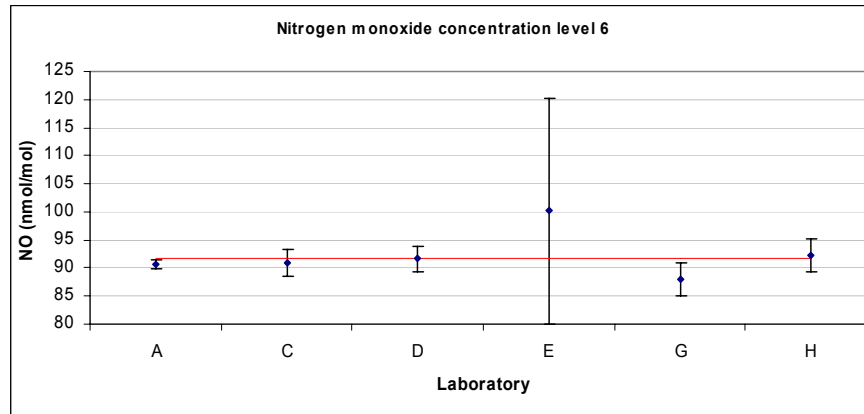


Figure 37: Reported values for NO concentration level 6.

Table 32: Reported values for NO concentration level 7.

parameter: NO		all units are nmol/mol				
level: 7		x*: 50.89		s*: 1.08		
	A	C	D	E	G	H
xi,1	50.03	50.48	51.29	55.53	48.14	51.38
xi,2	50.28	50.58	51.35	55.68	48.18	51.31
xi,3	50.23	50.68	51.31	55.67	48.15	51.42
xi	50.180	50.580	51.317	55.627	48.157	51.370
si	0.132	0.100	0.031	0.084	0.021	0.056
u(xi)	0.27	0.74	0.69	5.57	0.78	0.85
U(xi)	0.53	1.50	1.38	11.13	1.55	1.70

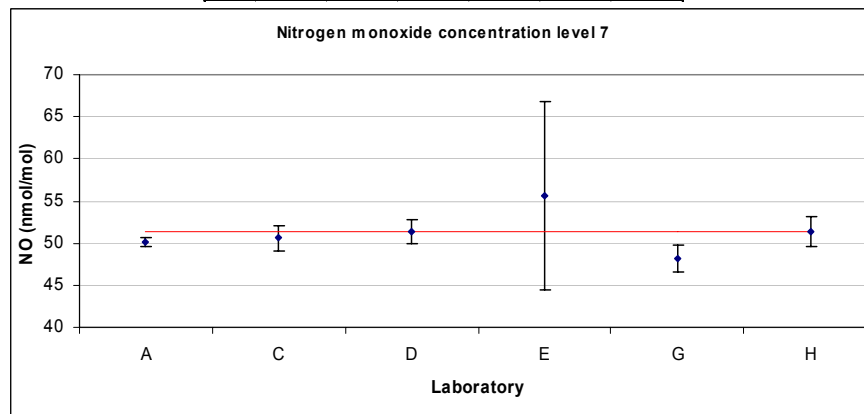


Figure 38: Reported values for NO concentration level 7.

Table 33: Reported values for NO concentration level 8.

	parameter: NO					
	all units are nmol/mol					
level: 8	x*: 30.24			s*: 0.85		
	A	C	D	E	G	H
xi,1	29.73	30.06	30.67	32.88	28.30	30.69
xi,2	29.69	29.96	30.61	32.78	28.15	30.60
xi,3	29.62	29.96	30.57	32.69	28.09	30.43
xi	29.680	29.993	30.617	32.783	28.180	30.573
si	0.056	0.058	0.050	0.095	0.108	0.132
u(xi)	0.22	0.50	0.49	3.28	0.51	0.51
U(xi)	0.43	1.00	0.98	6.56	1.02	1.01

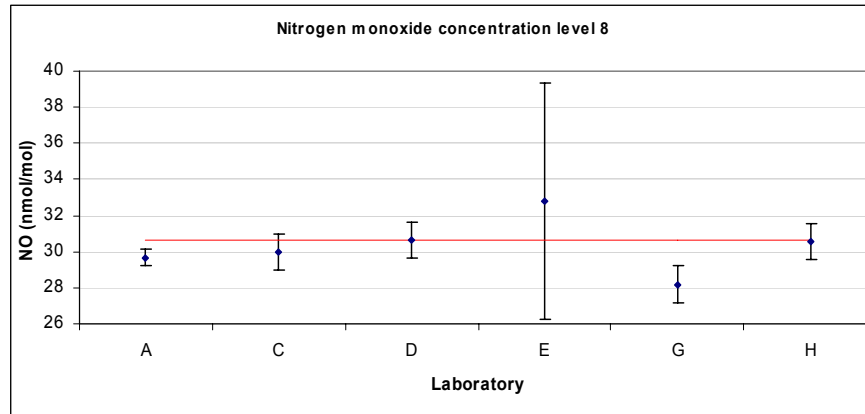


Figure 39: Reported values for NO concentration level 8.

Table 34: Reported values for NO concentration level 9.

	parameter: NO					
	all units are nmol/mol					
level: 9	x*: 15.93			s*: 0.69		
	A	C	D	E	G	H
xi,1	15.48	15.80	16.26	16.91	14.46	16.09
xi,2	15.59	15.70	16.31	16.88	14.49	16.16
xi,3	15.47	15.80	16.28	16.92	14.48	16.13
xi	15.513	15.767	16.283	16.903	14.477	16.127
si	0.067	0.058	0.025	0.021	0.015	0.035
u(xi)	0.18	0.36	0.37	1.70	0.24	0.50
U(xi)	0.36	0.72	0.74	3.39	0.48	1.00

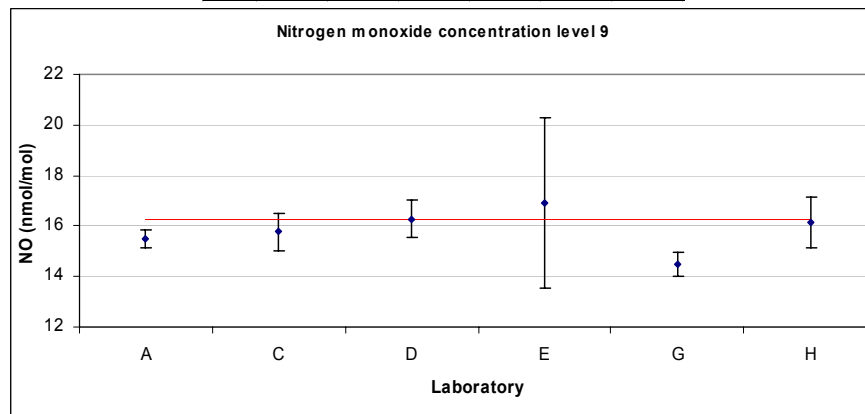


Figure 40: Reported values for NO concentration level 9.

Table 35: Reported values for NO concentration level 10.

parameter: NO		all units are nmol/mol				
level: 10		x*: 2.38		s*: 0.33		
	A	C	D	E	G	H
xi,1	2.28	2.46	2.95	2.30	2.16	2.78
xi,2	2.20	2.46	2.87	2.07	2.10	2.69
xi,3	2.11	2.36	2.78	1.98	2.05	2.55
xi	2.197	2.427	2.867	2.117	2.103	2.673
si	0.085	0.058	0.085	0.165	0.055	0.116
u(xi)	0.15	0.31	0.31	0.22	0.07	0.50
U(xi)	0.29	0.62	0.62	0.43	0.14	1.00

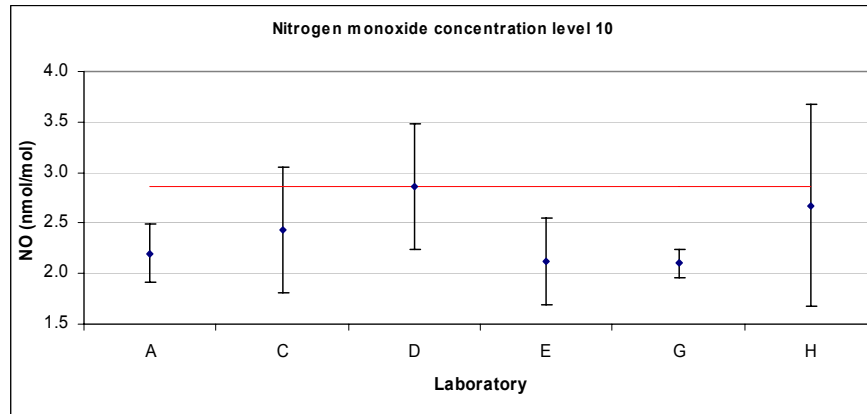


Figure 41: Reported values for NO concentration level 10.

Reported values for NO₂

Table 36: Reported values for NO₂ concentration level 0.

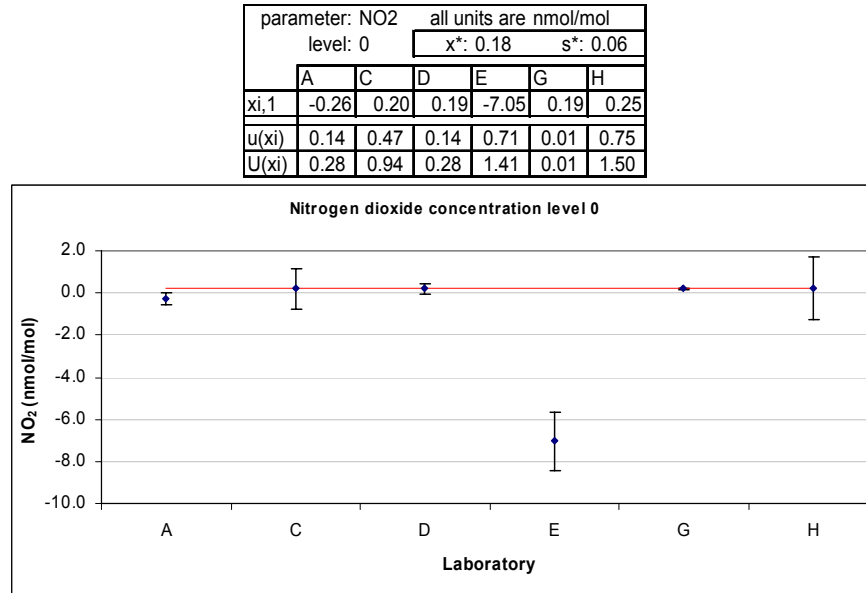


Figure 42: Reported values for NO₂ concentration level 0.

Table 37: Reported values for NO₂ concentration level 1.

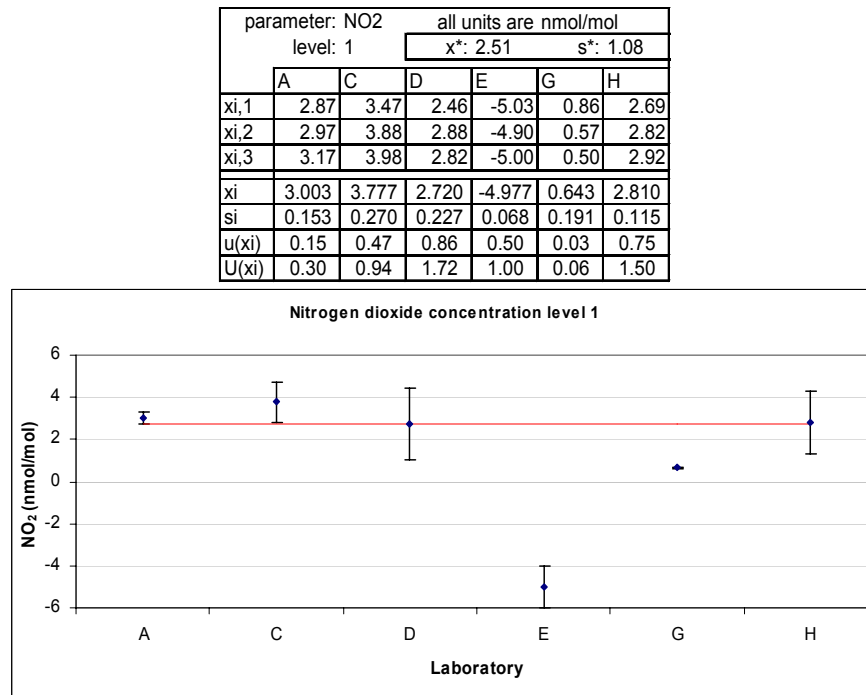


Figure 43: Reported values for NO₂ concentration level 1.

Table 38: Reported values for NO₂ concentration level 2.

parameter: NO2		all units are nmol/mol					
level: 2		x*: 121.73			s*: 1.23		
	A	C	D	E	G	H	
xi,1	121.55	121.70	121.51	125.08	120.63	124.66	
xi,2	121.32	121.30	120.88	124.60	120.23	124.24	
xi,3	121.36	121.40	120.80	124.39	120.28	124.45	
xi	121.410	121.467	121.063	124.690	120.380	124.450	
si	0.123	0.208	0.389	0.354	0.218	0.210	
u(xi)	0.44	2.00	1.73	12.47	2.78	2.54	
U(xi)	0.89	4.00	3.46	24.94	5.56	5.07	

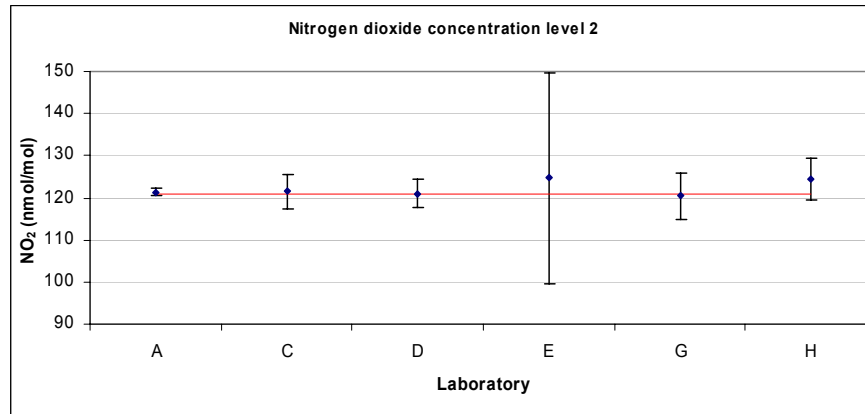


Figure 44: Reported values for NO₂ concentration level 2.

Table 39: Reported values for NO₂ concentration level 3.

parameter: NO2		all units are nmol/mol					
level: 3		x*: 1.08			s*: 0.67		
	A	C	D	E	G	H	
xi,1	1.46	1.63	1.34	-9.83	0.23	1.17	
xi,2	1.53	1.83	1.08	-6.69	0.08	1.28	
xi,3	1.45	1.93	1.33	-6.80	-0.04	1.26	
xi	1.480	1.797	1.250	-7.773	0.090	1.237	
si	0.044	0.153	0.147	1.782	0.135	0.059	
u(xi)	0.15	0.47	0.59	0.78	0.02	0.75	
U(xi)	0.29	0.94	1.18	1.56	0.03	1.50	

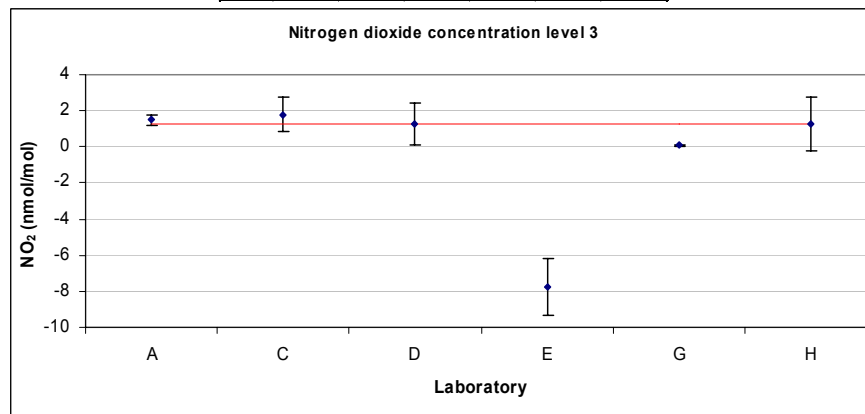


Figure 45: Reported values for NO₂ concentration level 3.

Table 40: Reported values for NO₂ concentration level 4.

parameter: NO2		all units are nmol/mol				
level: 4		x*: 103.31		s*: 0.51		
	A	C	D	E	G	H
xi,1	103.11	103.12	103.60	104.79	103.16	105.99
xi,2	102.91	102.82	103.23	104.56	102.66	105.70
xi,3	102.99	103.02	103.29	104.53	102.61	105.88
xi	103.003	102.987	103.373	104.627	102.810	105.857
si	0.101	0.153	0.199	0.142	0.304	0.146
u(xi)	0.40	1.80	1.42	10.47	2.38	2.16
U(xi)	0.80	3.60	2.84	20.93	4.75	4.32

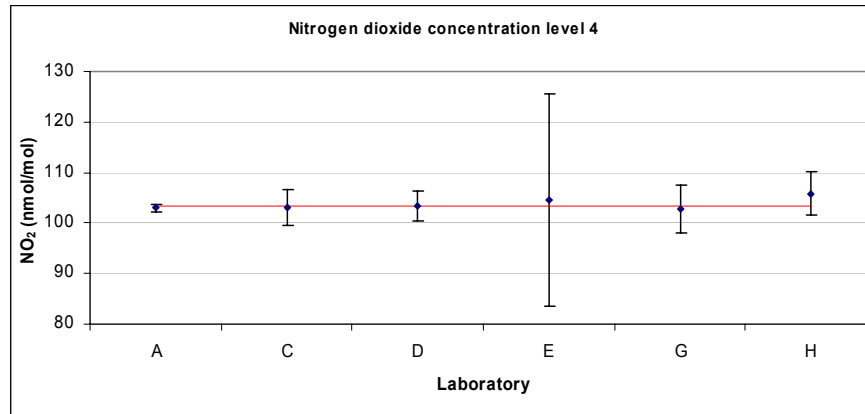


Figure 46: Reported values for NO₂ concentration level 4.

Table 41: Reported values for NO₂ concentration level 5.

parameter: NO2		all units are nmol/mol				
level: 5		x*: 0.26		s*: 0.38		
	A	C	D	E	G	H
xi,1	0.36	0.71	0.45	-8.01	-0.34	0.31
xi,2	0.48	0.71	0.21	-8.01	-0.37	0.37
xi,3	0.47	0.71	0.44	-8.20	-0.39	0.34
xi	0.437	0.710	0.367	-8.073	-0.367	0.340
si	0.067	0.000	0.136	0.110	0.025	0.030
u(xi)	0.14	0.47	0.48	0.81	0.02	0.75
U(xi)	0.28	0.94	0.96	1.62	0.04	1.50

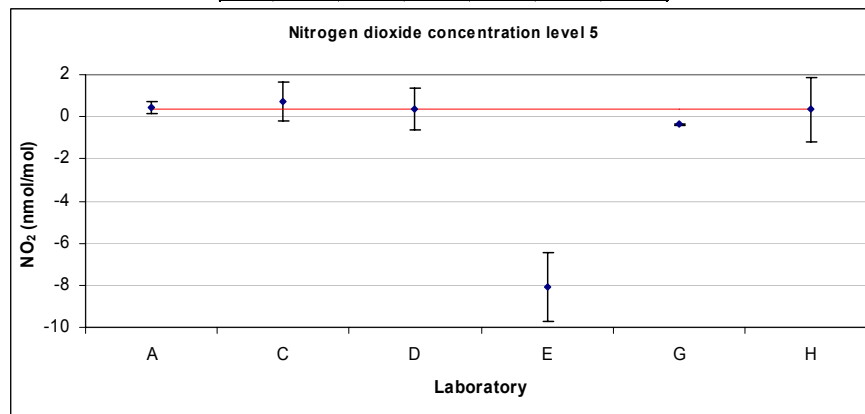


Figure 47: Reported values for NO₂ concentration level 5.

Table 42: Reported values for NO₂ concentration level 6.

parameter: NO2		all units are nmol/mol					
level: 6		x*: 59.33			s*: 1.24		
	A	C	D	E	G	H	
xi,1	59.39	59.44	59.82	56.90	58.52	61.10	
xi,2	59.47	59.54	59.91	56.87	58.44	61.14	
xi,3	59.22	59.54	59.77	56.81	58.35	60.89	
xi	59.360	59.507	59.833	56.860	58.437	61.043	
si	0.128	0.058	0.071	0.046	0.085	0.134	
u(xi)	0.29	1.10	0.85	5.69	1.35	1.25	
U(xi)	0.58	2.20	1.70	11.38	2.70	2.49	

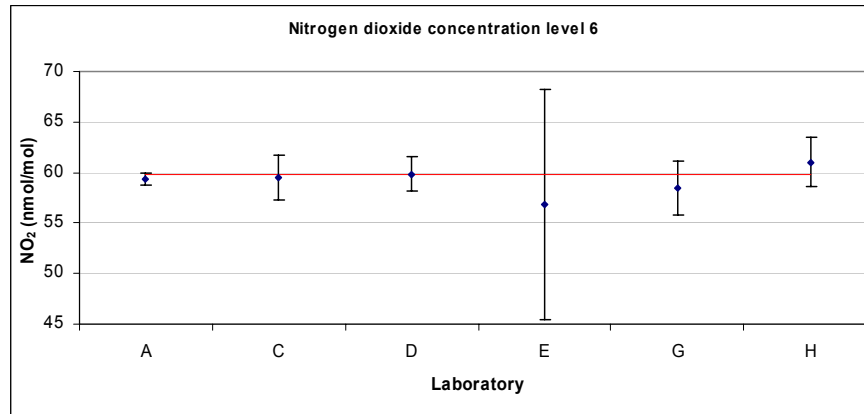


Figure 48: Reported values for NO₂ concentration level 6.

Table 43: Reported values for NO₂ concentration level 7.

parameter: NO2		all units are nmol/mol					
level: 7		x*: -0.04			s*: 0.22		
	A	C	D	E	G	H	
xi,1	-0.13	0.20	0.16	-8.29	-0.11	0.04	
xi,2	-0.11	0.20	0.05	-8.44	-0.10	-0.02	
xi,3	-0.19	0.20	0.11	-8.48	-0.15	0.04	
xi	-0.143	0.200	0.107	-8.403	-0.120	0.020	
si	0.042	0.000	0.055	0.100	0.026	0.035	
u(xi)	0.14	0.47	0.26	0.85	0.01	0.75	
U(xi)	0.28	0.94	0.52	1.69	0.02	1.50	

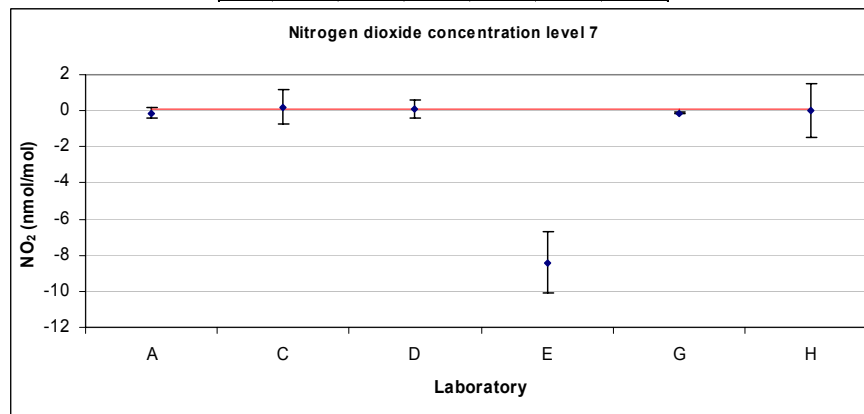


Figure 49: Reported values for NO₂ concentration level 7.

Table 44: Reported values for NO₂ concentration level 8.

parameter: NO ₂		all units are nmol/mol					
level: 8		x*: 20.36			s*: 0.61		
	A	C	D	E	G	H	
xi,1	20.29	20.52	20.72	14.03	19.61	20.80	
xi,2	20.31	20.73	20.80	14.13	19.68	20.96	
xi,3	20.45	20.73	20.83	14.22	19.66	21.06	
xi	20.350	20.660	20.783	14.127	19.650	20.940	
si	0.087	0.121	0.057	0.095	0.036	0.131	
u(xi)	0.19	0.58	0.36	1.42	0.46	0.75	
U(xi)	0.38	1.20	0.72	2.83	0.91	1.50	

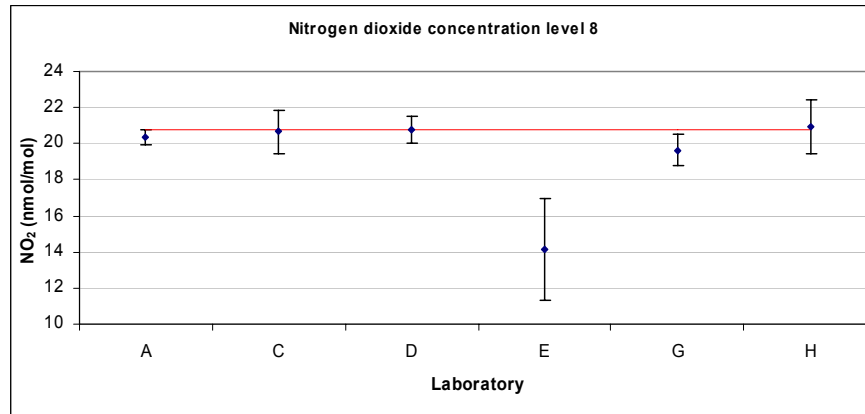


Figure 50: Reported values for NO₂ concentration level 8.

Table 45: Reported values for NO₂ concentration level 9.

parameter: NO ₂		all units are nmol/mol					
level: 9		x*: -0.04			s*: 0.20		
	A	C	D	E	G	H	
xi,1	-0.23	0.20	0.07	-8.49	0.02	0.02	
xi,2	-0.25	0.20	0.00	-8.52	-0.07	0.04	
xi,3	-0.18	0.20	0.05	-8.58	-0.05	0.04	
xi	-0.220	0.200	0.040	-8.530	-0.033	0.033	
si	0.036	0.000	0.036	0.046	0.047	0.012	
u(xi)	0.14	0.47	0.18	0.86	0.01	0.75	
U(xi)	0.28	0.94	0.36	1.71	0.02	1.50	

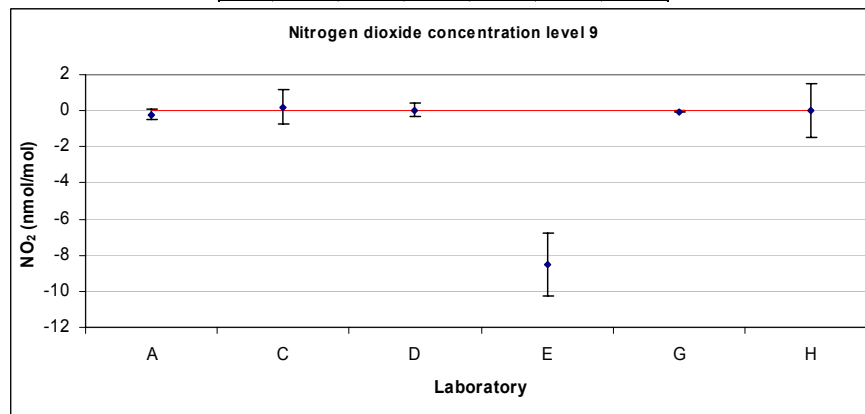


Figure 51: Reported values for NO₂ concentration level 9.

Table 46: Reported values for NO₂ concentration level 10.

parameter: NO ₂		all units are nmol/mol				
level: 10		x*: 13.07		s*: 0.44		
	A	C	D	E	G	H
xi,1	12.96	13.31	13.34	5.66	12.32	13.38
xi,2	12.95	13.31	13.42	6.02	12.39	13.38
xi,3	13.09	13.41	13.52	6.12	12.45	13.49
xi	13.000	13.343	13.427	5.933	12.387	13.417
si	0.078	0.058	0.090	0.242	0.065	0.064
u(xi)	0.17	0.50	0.24	0.60	0.29	0.75
U(xi)	0.35	1.00	0.48	1.19	0.58	1.50

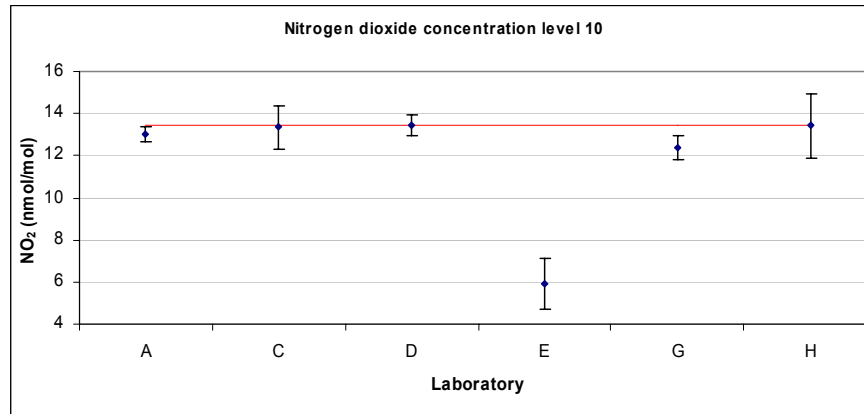


Figure 52: Reported values for NO₂ concentration level 10.

Annex C. The precision of standardized measurement methods

For the main purpose of monitoring trends between different IEs undertaken by ERLAP the precision of standardized SO₂, CO, O₃ and NO_x measurement methods [6], [8], [9] and [10] as implemented by NRLs was evaluated. Applied methodology is described in ISO 5725-1, -2 and -6 [19], [20] and [21]. The precision experiment has involved five laboratories, for NO_x measurement method, and six laboratories, for O₃, CO and SO₂ measurement methods. Six concentration levels were tested, for O₃, CO, SO₂ and NO₂, and eleven for NO. Data consistency and outlier tests have been performed (Annex D).

The repeatability standard deviation (s_r) was calculated in accordance with ISO 5725-2 as the square root of average within laboratory variance. The repeatability limit (r) is calculated using equation 7 [21]. 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.

$$r = t_{95\%,12} \cdot \sqrt{2} \cdot s_r \quad (7)$$

The reproducibility standard deviation (s_R) was calculated in accordance with ISO 5725-2 as the square root of sum of repeatability and between laboratory variance. The reproducibility limit (R) is calculated using equation 8 [21]. 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.

$$R = t_{95\%,5} \cdot \sqrt{2} \cdot s_R \quad (8)$$

The repeatability standard deviation was evaluated with 12 (6·(3-1)) degrees of freedom (ν) and reproducibility standard deviation with 5 (6-1) degrees of freedom. The critical range student factors ($t_{\alpha,\nu}$) are 2,18 and 2,57 respectively.

In Table 47-

The reproducibility and repeatability of NO₂ measurements are dependant on both NO and NO₂ concentrations. In Table 51 both concentrations are given and in Figure 57 R and r are plotted as functions of NO₂ concentration.

Table 51 and Figure 53- Figure 57 the repeatability and reproducibility limits of measurement methods are presented with (r, R) and without (r*, R*) outliers. Also presented is ‘reproducibility from common criteria (R(from σ_p))’ calculated by substituting s_R in equation 8 with a ‘standard deviation for proficiency assessment’ (Table 3). Comparison between R and R(from σ_p) serves to indicate that σ_p is realistic ([18] 6.3.1) or from the other point of view, that the general methodology implemented by NRLs is fit for σ_p.

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

CO data (µmol/mol)						
all data			without outliers			
group average	repeatability limit : r	reproducibility limit : R	group average	repeatability limit : r*	reproducibility limit : R*	reproducibility limit (relative)
0.004		0.021	0.004		0.021	
0.958	0.006	0.124	0.971	0.007	0.053	
1.894	0.008	0.377	1.936	0.009	0.079	
4.179	0.006	0.266	4.179	0.006	0.266	
5.830	0.012	0.279	5.830	0.012	0.279	
8.349	0.036	0.408	8.349	0.036	0.408	4.9%

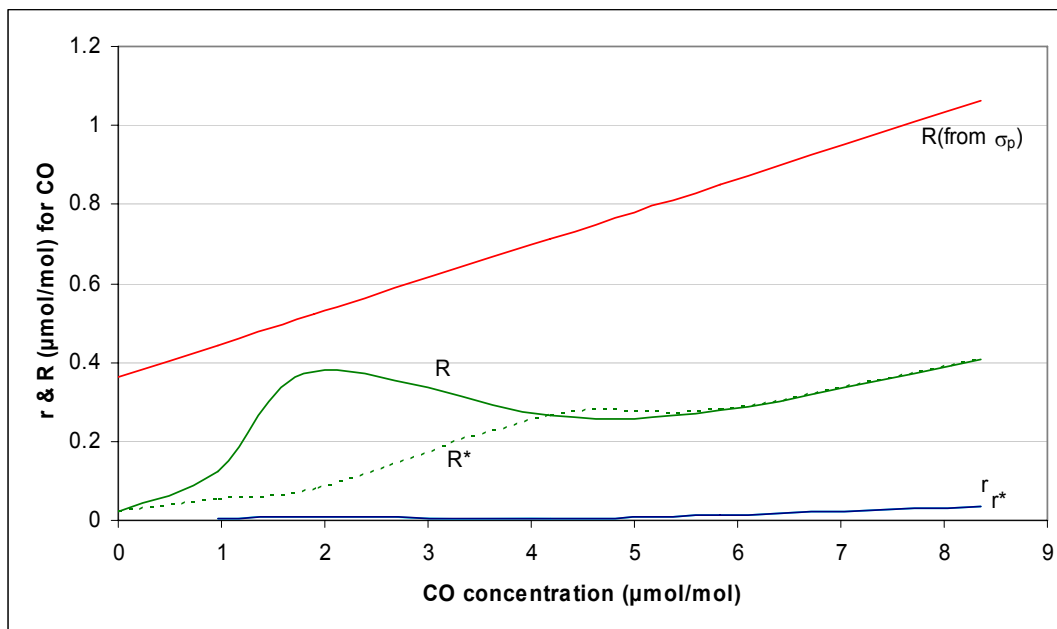


Figure 53: The R and r of CO standard measurement method as a function of concentration.

Table 48: The R and r of O₃ standard measurement method.

O ₃ data (nmol/mol)						
all data			without outliers			
group average	repeatability limit : r	reproducibility limit : R	group average	repeatability limit : r*	reproducibility limit : R*	reproducibility limit (relative)
0.2		2.2	0.0		1.3	
13.8	0.2	2.7	13.5	0.2	1.1	
20.5	0.1	2.3	20.3	0.1	1.1	
58.6	0.3	1.9	58.6	0.3	1.9	
100.6	1.6	2.7	100.6	1.6	2.7	
115.9	3.7	7.8	116.6	1.7	3.8	3.3%

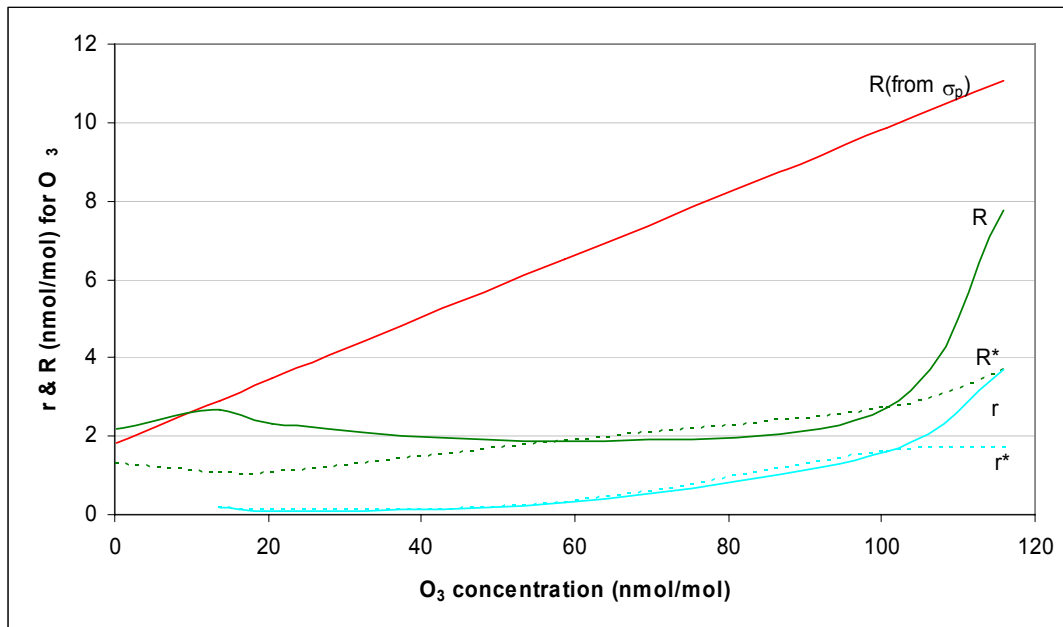


Figure 54: The R and r of O₃ standard measurement method as a function of concentration.

Table 49: The R and r of SO₂ standard measurement method.

SO ₂ data (nmol/mol)						
all data			without outliers			
group average	repeatability limit : r	reproducibility limit : R	group average	repeatability limit : r*	reproducibility limit : R*	reproducibility limit (relative)
-0.1		1.3	0.1		0.4	
2.9	0.1	1.0	3.0	0.0	0.5	
7.4	0.1	0.8	7.4	0.1	0.5	
17.9	0.1	0.9	17.9	0.1	0.9	
46.7	0.2	2.7	46.7	0.2	2.7	
132.4	0.4	8.1	132.4	0.4	8.1	6.1%

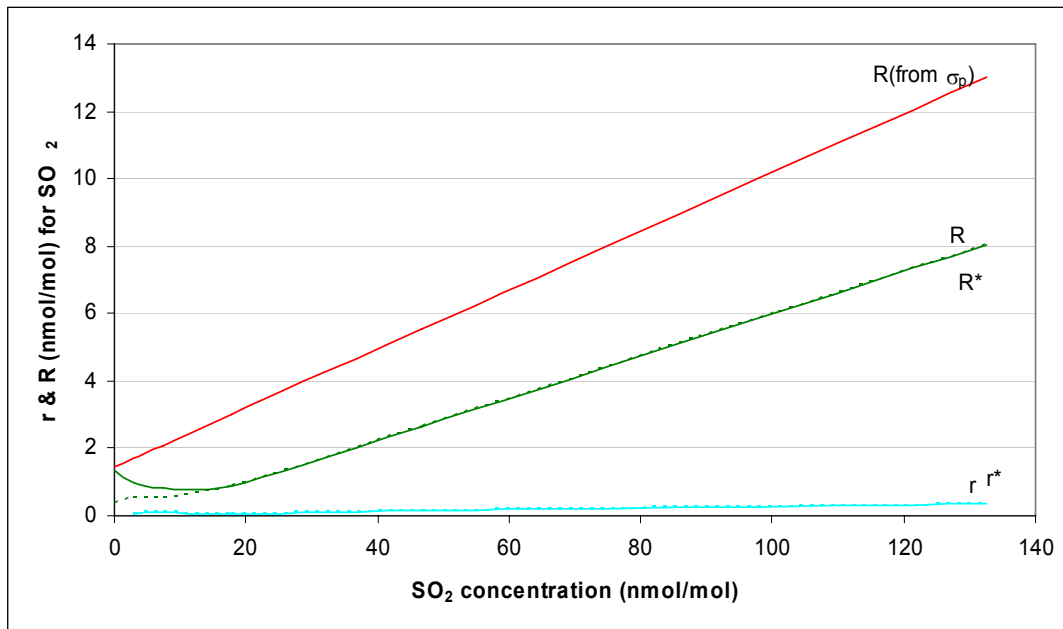


Figure 55: The R and r of SO₂ standard measurement method as a function of concentration.

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

NO data (nmol/mol)			
all data			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.3		1.1	
2.5	0.3	1.3	
15.6	0.1	2.8	
29.8	0.3	3.9	
50.3	0.3	5.1	
90.7	0.3	6.4	
150.1	0.3	7.7	
150.3	0.6	6.4	
252.3	0.3	8.2	
382.2	1.5	9.9	
500.4	1.1	11.0	2.2%

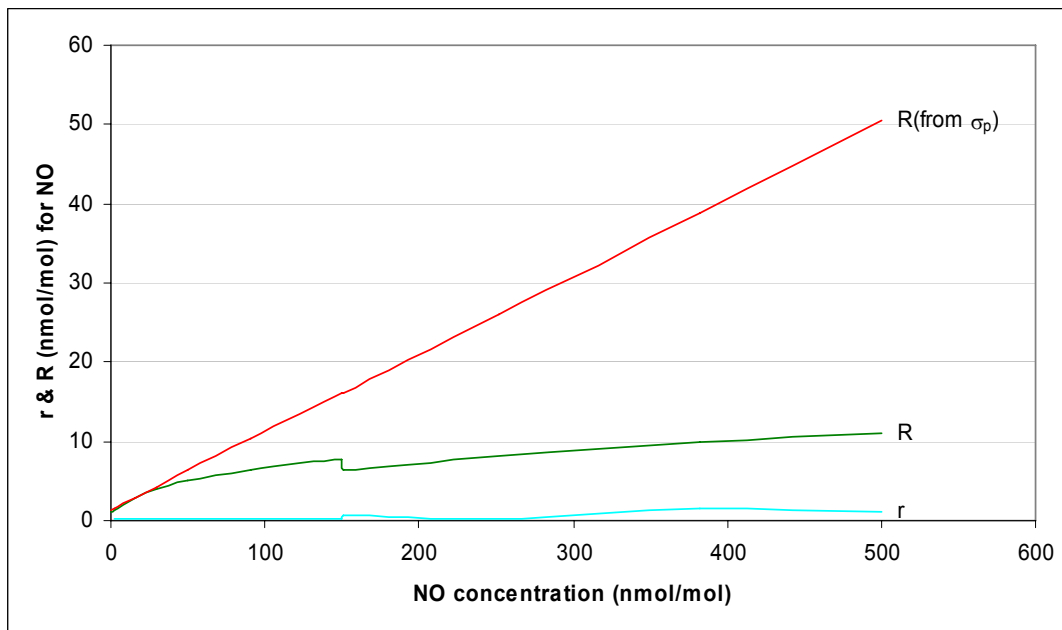


Figure 56: The R and r of NO standard measurement method as a function of concentration.

The reproducibility and repeatability of NO₂ measurements are dependant on both NO and NO₂ concentrations. In Table 51 both concentrations are given and in Figure 57 R and r are plotted as functions of NO₂ concentration.

Table 51: The R and r of NO₂ standard measurement method.

NO ₂ data (nmol/mol)				
all data				
NO	NO ₂	NO ₂		
group average	group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.3	0.1		0.8	
2.5	13.1	0.2	1.8	
15.6	0.0	0.1	0.6	
29.8	20.5	0.3	2.0	
50.3	0.0	0.1	0.6	
90.7	59.6	0.3	3.7	
150.1	0.3	0.2	1.6	
150.3	103.6	0.6	5.0	
252.3	1.2	0.4	2.6	
382.2	121.8	0.8	6.2	5.1%
500.4	2.6	0.6	4.6	

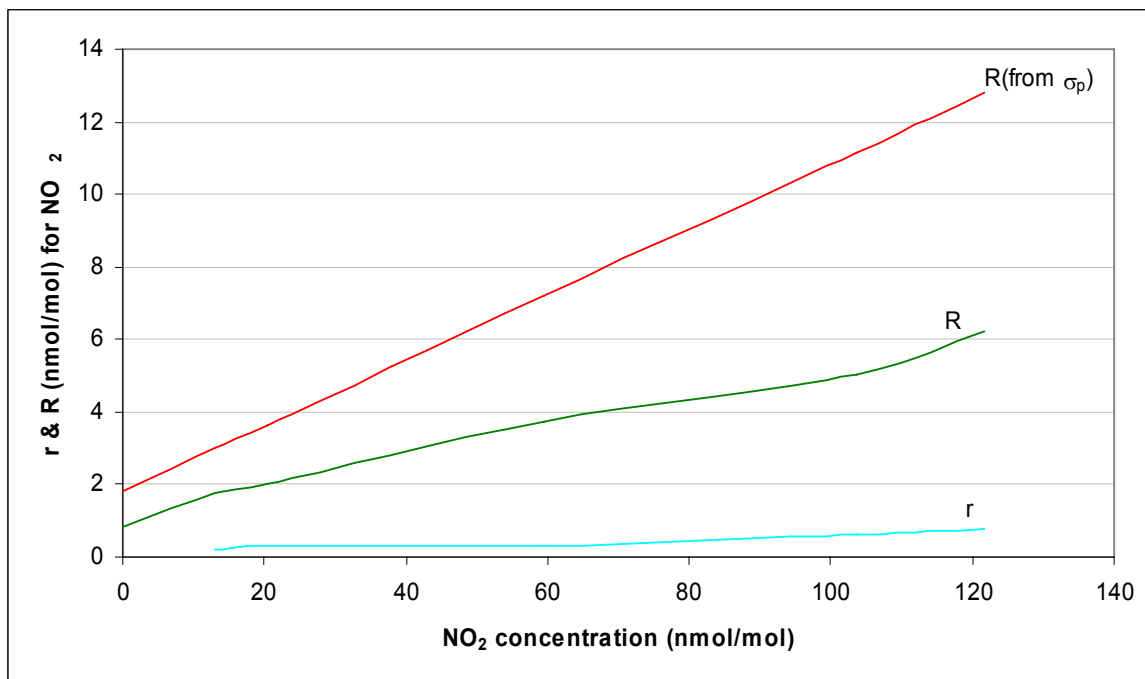


Figure 57: The R and r of NO₂ standard measurement method as a function of concentration.

Annex D. The scrutiny of results for consistency and outliers

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 calculation, the bad averaging interval, malfunction of instrumentation, etc.) was applied. In this procedure the IE data first underwent the scrutiny for its consistency and the detection of statistical outliers as described in ISO 5725-2. Then laboratories showing some form of statistical inconsistency were contacted to try to ascertain the cause of discrepancies. Laboratories were allowed to correct their results and one did so. After that data was considered of appropriate quality and the final tests of statistical outliers were performed.

In this final test “Grubb’s one outlying observation test” was performed Figure 58 to Figure 62. For runs where outliers were detected outliers were removed and “Grubb’s one outlying observation test” was repeated. After this one repetition there were no more outliers in these runs.

Statistical outliers obtained at this stage are not considered as due to extraordinary errors but due to significant difference in participant’s standard operating procedure. These “genuine” statistical outliers are presented in table below:

Table 52: “Genuine” statistical outliers.

Parameter	Run	Participant	Failing test
SO ₂	0	G	“Grubb’s one outlying observation test” (Figure 58)
CO	4,5	G	“Grubb’s one outlying observation test” (Figure 59)
O ₃	0,4,5	F	“Grubb’s one outlying observation test” (Figure 60)

Not to have unrealistic jumps in the evaluation of precision of SO₂ standardized method also data of runs 4 and 5 of participant G were removed from this evaluation. Through exchange of information it was discovered that O₃ analyzer of participant G was failing during run 1 and data of this run is excluded from the evaluation.

Presented in the following figures are Grubb's one outlying observation test statistics for the minimum (blue) and maximum (orange with pattern) values of each run. Values between the two lines are considered strugglers and values over violet line are considered outliers.

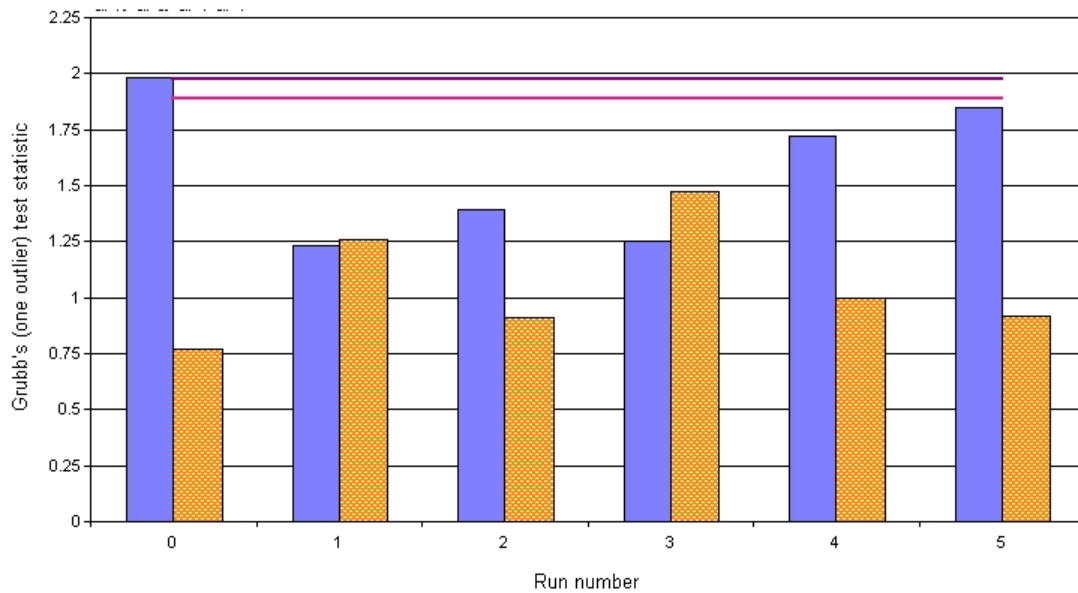


Figure 58: Grubb's one outlying observation test statistics for SO₂ runs.

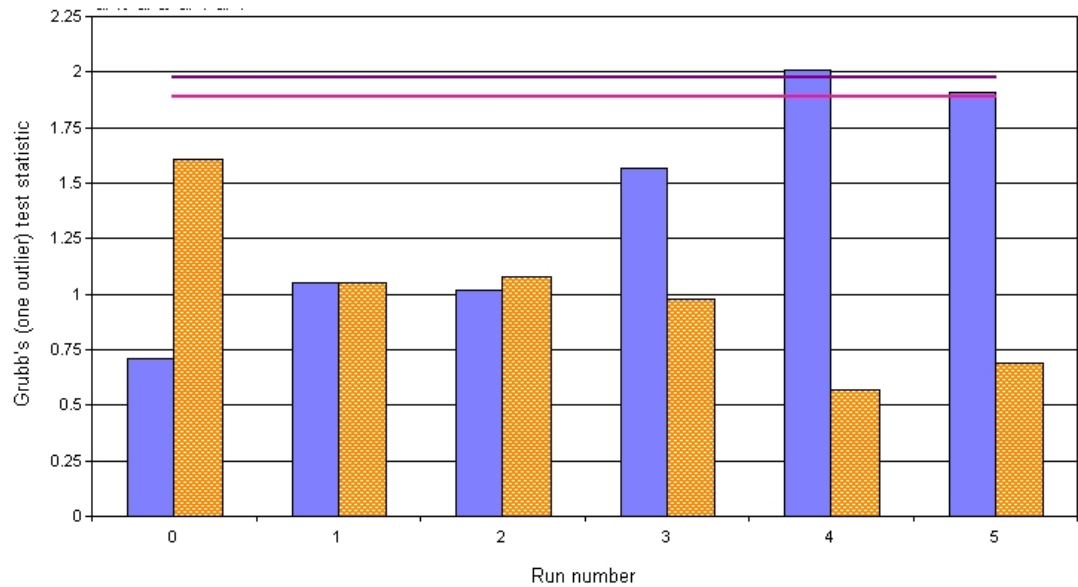


Figure 59: Grubb's one outlying observation test statistics for CO runs.

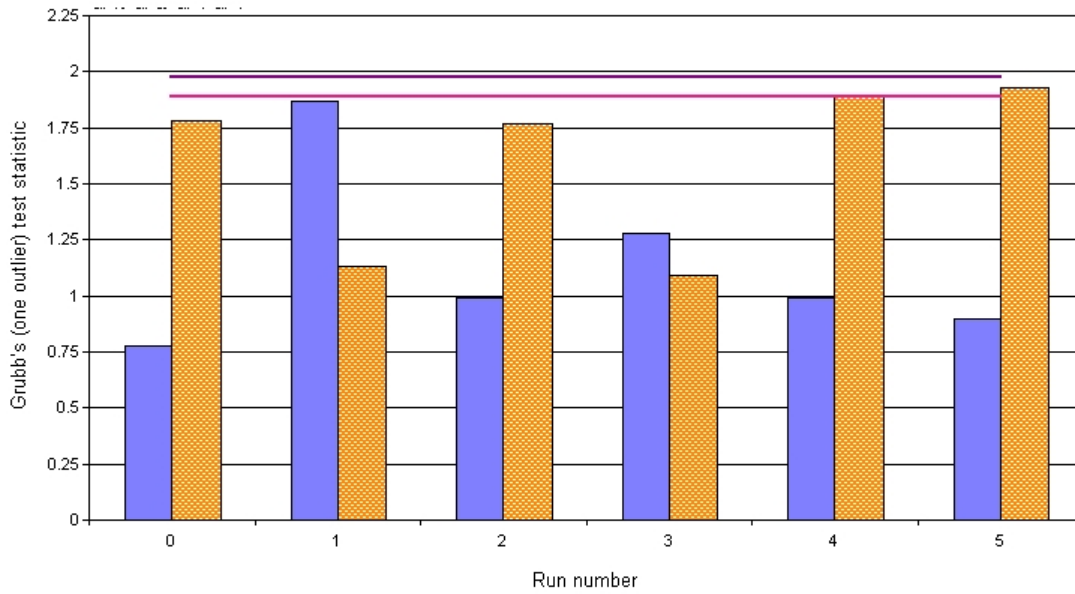


Figure 60: Grubb's one outlying observation test statistics for O₃ runs.

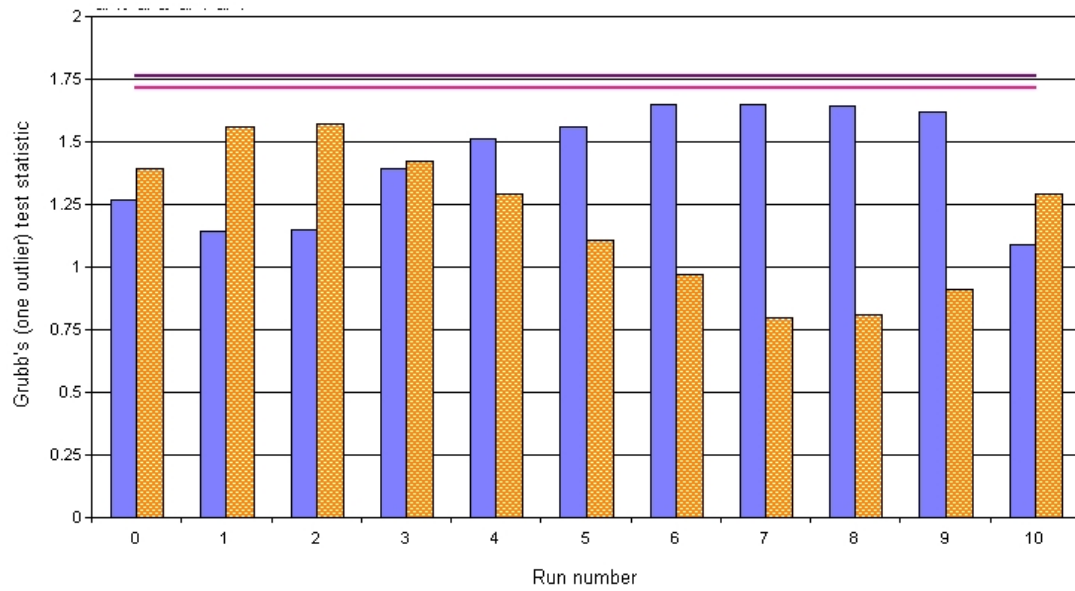


Figure 61: Grubb's one outlying observation test statistics for NO runs.

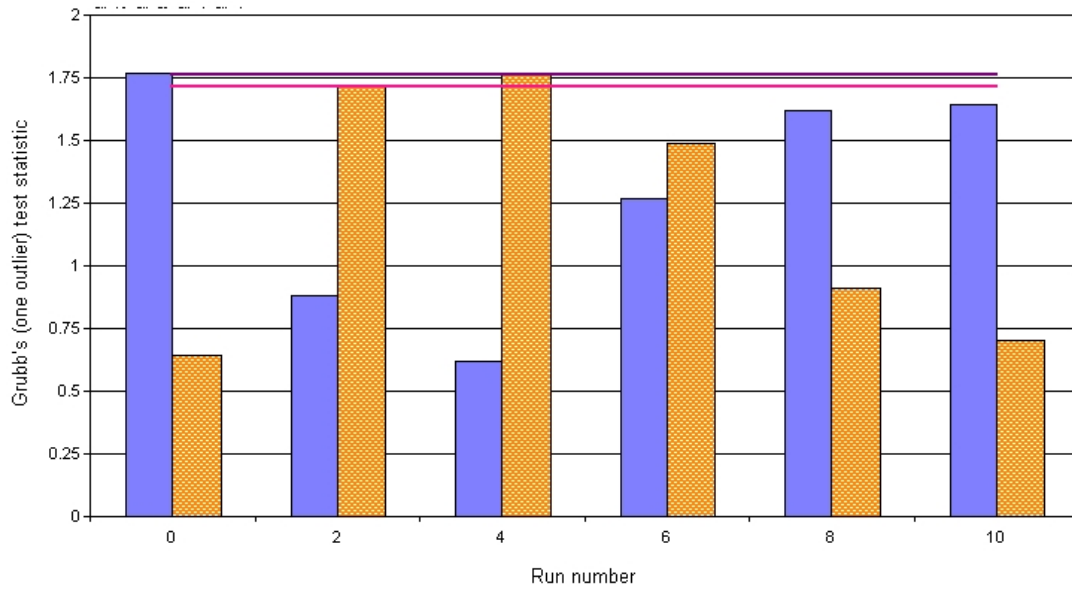


Figure 62: Grubb's one outlying observation test statistics for NO₂ runs.

European Commission

EUR 23805 EN – Joint Research Centre – Institute for Environment and Sustainability

Title: The Evaluation of the Intercomparison Exercise for SO₂, CO, O₃, NO and NO₂ - April 2008

Author(s):

Luxembourg: Office for Official Publications of the European Communities

2009 – 66 pp. – 29.7 x 21.0 cm

EUR – Scientific and Technical Research series – ISSN 1018-5593

ISBN 978-92-79-12169-2

Abstract

In April 2008 in Ispra (IT), 8 AQUILA (Network of European Air Quality Reference Laboratories) laboratories met at an intercomparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO₂, CO, NO, NO₂ and O₃).

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system.

In terms of criteria imposed by the European Commission, 80% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 18% of the results had good measured values, but the reported uncertainties were either too small (7%) or too high (11%).

The comparability of results among AQUILA participants is satisfactory for all studied measurement methods.

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