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EC/WHO Harmonization Programme for Air Quality Measurements:

The evaluation of the Interlaboratory Comparison Exercise for SO_2, O_3, NO and NO_2 Langen 20th-25th September 2009

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WHO COLLABORATING CENTRE FOR AIR QUALITY
MANAGEMENT AND AIR POLLUTION CONTROL

at the

FEDERAL ENVIRONMENTAL AGENCY

Executive Summary

From the 20th to the 25th of September 2009 in Langen (DE), 4 National Reference Laboratories (NRL) of AQUILA network and 3 laboratories of the World Health Organisation (WHO) Euro-Region met for an interlaboratory comparison exercise (IE) to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO_2, NO, NO_2 and O_3).

Most of the laboratories participating in the IE used automated CEN reference methods, which are mandatory in the EU, while some laboratories of the WHO Euro-Region performed analysis using manual methods.
In this report proficiency evaluation was made at different degrees for each laboratory taking into account the differences in the methodologies and the completeness of the information provided by participants. For the laboratories who expressed their uncertainty, performance was evaluated using two criteria, providing information on their proficiency to the European Commission and supporting the national quality control systems.

In terms of criteria imposed by the European Commission (that are not mandatory for WHO laboratories), 71% of the results reported by National Reference Laboratories (AQUILA network) were good both in terms of measured values and reported uncertainties. Another 23% of the results had good measured values, but the reported uncertainties were either too high (19%) or too small (4%). There were neither questionable nor unacceptable values.

AQUILA laboratories presented good comparability among participants for NO_2, O_3, and SO_2. The relative reproducibility limit for NO was above the objective deriving from the standard deviation for proficiency assessment.

For WHO laboratories using automated techniques, the results are satisfactory for SO_2, NO_2 and NO measurement methods, while one laboratory needs further investigation of their O_3 measurements.
The laboratory using manual methods presented results comparable to those of the automated methods for NO and O_3 but there were questionable results for NO_2 and SO_2 and unsatisfactory results for NO_2.

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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 – Interlaboratory comparison [14], [23]
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
UBA	Umweltbundesamt (Germany)
WHO CC-EURO	World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin

Mathematical Symbols:

symbol	*explanation*
E_n	E_n – number statistic (ISO 13528; [14])
r	repeatability limit (ISO 5725; [15])
R	reproducibility limit (ISO 5725; [15])
σ_p	the standard deviation for proficiency assessment (ISO 13528; [14])
x*	robust average (Annex C ISO 13528; [14])
s*	robust standard deviation (Annex C ISO 13528; [14])
s_r	repeatability standard deviation (ISO 5725; [15])
s_R	reproducibility standard deviation (ISO 5725; [15])
U_X	The expended uncertainty of the assigned/reference value (ISO 13528; [14])
U_{xi}	The expended uncertainty of the participant's value
u_X	The standard uncertainty of the assigned/reference value (ISO 13528; [14])
X	Assigned/reference value (ISO 13528; [14])
x_i	the average of three values reported by the participant i (for particular parameter and concentration level) (ISO 5725; [15])
$x_{i,j}$	j-th reported value of participant i (for particular parameter and concentration level) (ISO 5725; [15])
z'	z'-score statistic (ISO 13528; [14])

1. Introduction

Directive 2008/50/EC [1] on ambient air quality and cleaner air for Europe sets a framework for a harmonized air quality assessment in Europe. One important objective of the Directive is that the ambient air quality shall be assessed on the basis of common methods and criteria. It deals with the air pollutants sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and monoxide (NO), particulate matter, lead, benzene, carbon monoxide (CO) and ozone (O_3). Among others it specifies the reference methods for measurements and Data Quality Objectives (DQO) for the accuracy of measurements.

The European Commission (EC) has supported the development and publication of reference measurement methods [2], [3] and [4] as European standards. Appropriate calibration methods [5], [8] and [9] have been standardised by the International Organization for Standardization (ISO).

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

The World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin (WHO CC) is carrying out similar activities since 1994 [10] [11], 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 20th to the 25th of September 2009 in the UBA Pilotstation in Langen (DE) 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), 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 for the organisation of IEs was developed by ERLAP and is described in a position paper on the organization of interlaboratory comparison exercises for gaseous air pollutants [13].

This evaluation scheme was adopted in December 2008 and is applied to all IEs since then. It contains common criteria to alert the EC on possible performance failures which do not rely solely on the uncertainty claimed by participants. The evaluation scheme implements the z'-score method [14] with the uncertainty requirements for calibration gases stated in the European standards [2], [3] and [4], which are consistent with the DQOs of European Directives.
According to AQUILA's view, NRLs with an overall unsatisfactory performance in the z'-score evaluation (one unsatisfactory or two questionable results per parameter) need to repeat their participation in the following IE in order to demonstrate remediation measures [13]. 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's uncertainty [14]. Hence, participants

measurement results (measurement values and uncertainties) are compared to the assigned values applying the E_n – number method [14].

Beside the proficiency of participating laboratories, the repeatability and reproducibility of standardized measurement methods [15], [16] and [17] are evaluated as well. These group evaluations are useful indicators of trends in measurement quality over different IEs.

2. Communication and time schedule

The IE was announced in May 2009 to the members of the AQUILA network and the WHO CC representative. A registration letter was send by WHO to interested parties and the registration was closed with the list of 7 participating laboratories. The participants were required to bring their own measurement instruments, data acquisition equipment and travelling standards (to be used for calibrations or checks during the IE).

The participants were invited to arrive on Sunday 20th September for the installation of their equipment (Table 2). The calibration and generation of NO analysers was carried out on Monday 21st, the calibration and generation of NO_2 analysers was carried out on Tuesday 22nd, the calibration and generation of SO_2 analysers was carried out on Wednesday 23rd and the calibration and generation of O_3 analysers was carried out on Friday 24th. The test gases generation finished on Thursday 24th at 16:45.

3. Participants

All participants were organizations dealing with the routine ambient air monitoring or health related studies. The national representatives came from EU member states Belgium, Bulgaria, Lithuania, Slovenia, and from non EU members Croatia, Ukraine, and Macedonia.

Country	Name of Organization	IE code	Network	method
Germany	Federal Environment Agency	A		automatic
Croatia	Teaching Institute of Public Health	B	WHO	auto/man
Belgium	Institut Scientifique de Service Public (ISSeP) Cellule Interrégionale de l’Environnement (CELINE) Belgium Environmental Agency	C	AQUILA	automatic
Ukraine	State Institution „O.M. Marzeyev Institute for Hygiene and Medical Ecology, Academy of Medical Sciences of Ukraine”, The Laboratory for Ambient Air Hygiene and Risk Assessment	D	WHO	manual
Lithuania	Environmental Protection Agency	E	AQUILA	automatic
Bulgaria	Executive Environment Agency	F	AQUILA	automatic
Slovenia	The Environmental Agency of the Republic of Slovenia	G	AQUILA	automatic
Macedonia	Central environmental laboratory - Calibration Laboratory from Ministry of Environment and Physical Planning	H	WHO	automatic

Table 1: The list of participating organisations.

4. The Analytical methods

NRLs of EU member states are required to implement CEN standard methods while non EU member states of the WHO Euro Region may use either CEN methods or methods officially accepted in their countries.
In the present interlaboratory comparison were used the following CEN automatic methods:

NO	Chemiluminscence [3]
NO_2	Chemiluminscence [3]
SO_2	Ultraviolet fluorescence [2]
O_3	Ultraviolet photometry [4]

In addition, the following manual methods were used:

Teaching Institute of Public Health (Croatia) - IE Code B:

NO_2	Spectrophotometry, modified Griess-Saltzmann [5]

This laboratory provided NO_2 measurements using two different techniques: CEN standard method and the manual method described above. The complete evaluation was made only on the results obtained with the standard method.

Institute for Hygiene and Medical Ecology “Marzeyev” , Academy of Medical Sciences of Ukraine – Laboratory for Ambient Air Hygiene and Risk Assessment (Ukraine) - IE Code D.

NO	Photocolorimetric method, modified Griess-Saltzmann [6]
NO_2	Photocolorimetric method, modified Griess-Saltzmann [6]
SO_2	Photocolorimetric hydrogen peroxide absorption method [6]
O_3	Photocolorimetric Potassium iodide method, [6]

This was the only laboratory providing data measured exclusively with manual methods.

5. The preparation of test mixtures

The UBA Pilotstation facility is described in [10]. During this IE, gas mixtures were prepared for SO_2, O_3, NO and NO_2 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, NO_2 or SO_2 using thermal mass flow controllers [9]. O_3 was added using an ozone generator.

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

day	start time	duration	operation	NO	NO_2	SO_2	O_3
		(h)		(nmol/mol)	(nmol/mol)	(nmol/mol)	(nmol/mol)
20-Sep	15:00	3	installation				
21-Sep	8:00	1	calibration				
21-Sep	9:00	2.30	NO test gas 1	0			
21-Sep	11:45	1.30	NO test gas 2	200			
21-Sep	13:30	1.30	NO test gas 3	20			
22-Sep	8:45	1	NO2 test gas 4		0		
22-Sep	10:00	1.30	NO2 test gas 5		200		
22-Sep	11:45	1.30	NO2 test gas 6		100		
22-Sep	13:30	1.30	NO2 test gas 7		60		
22-Sep	15:15	1.30	NO2 test gas 8		20		
23-Sep	8:45	1	SO2 test gas 9			0	
23-Sep	10:00	1.30	SO2 test gas 10			130	
23-Sep	11:45	1.30	SO2 test gas 11			45	
23-Sep	13:30	1.30	SO2 test gas 12			20	
23-Sep	15:15	1.30	SO2 test gas 13			5	
24-Sep	8:45	1	O3 test gas 14				0
24-Sep	10:00	1.30	O3 test gas 15				300
24-Sep	11:45	1.30	O3 test gas 16				100
24-Sep	13:30	1.30	O3 test gas 17				60
24-Sep	15:15	1.30	O3 test gas 18				20

Table 2:The sequence program of generated test gases.

6. The evaluation of laboratory's measurement proficiency

To evaluate the participants measurement proficiency was applied the methodology described in ISO 13528 [14]. It has been agreed among the AQUILA members to take the measurement results of UBA as the assigned/reference values for the whole IE [13]. The traceability of UBA's measurement results and the method applied to validate them are presented in Annex A.

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

As it is described in the Position Paper [13], 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, taking into account the uncertainty of the participants measurement and the uncertainty of the assigned/reference value.

5.1 z'- score

The z'- score statistic is calculated according to ISO 13528 [14] as:

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

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 [2], [3] and [4] 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) [14] 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. On November 2008 AQUILA members agreed to set σ_p equal to 1 ppb at zero concentration of SO_2, O_3, NO, NO_2.
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:

Gas	σ_p=a·c+b	
	a	b
		nmol/mol
SO_2	0.022	1
O_3	0.020	1
NO	0.024	1
NO_2	0.020	1

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

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'=±2 and z'=±3 lines.

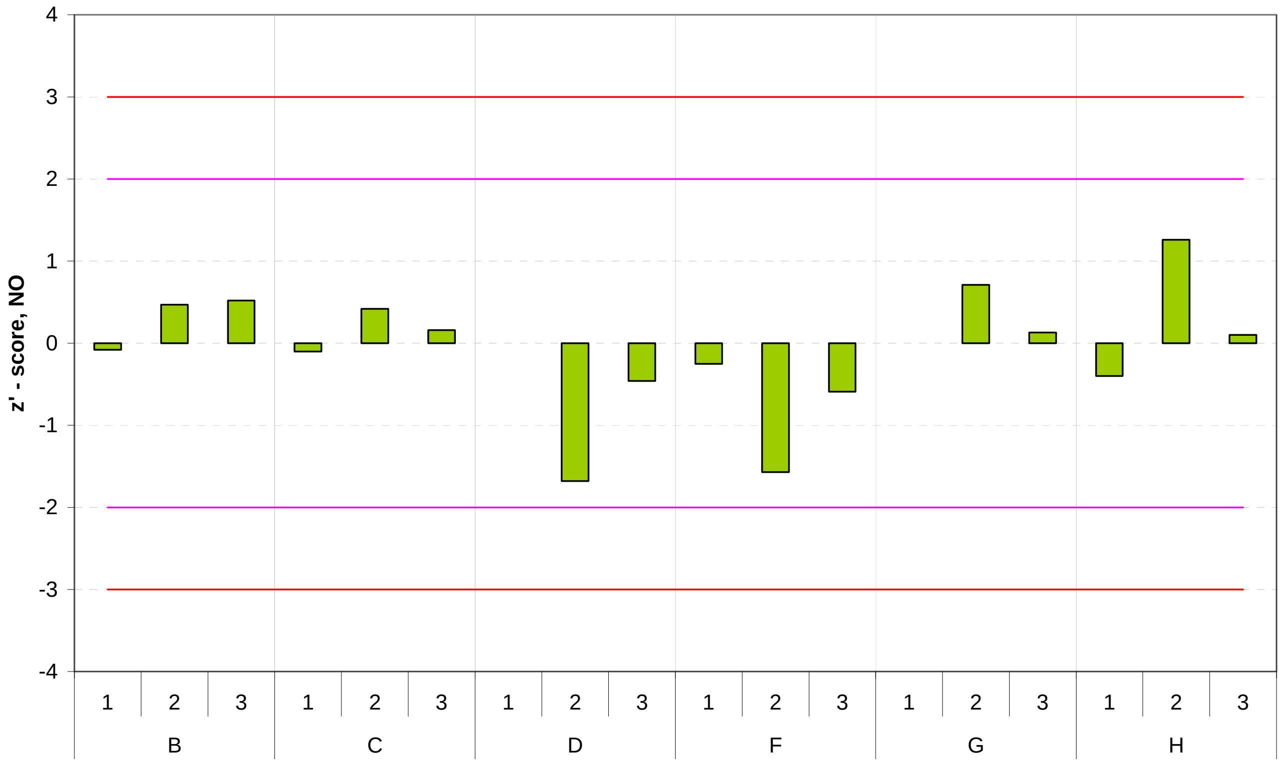

Figure 1:The z'-score evaluations of NO measurements are given for each participant and each tested test gas. The evaluations according to the Test Gas step with nominal concentration are: 1 (0 nmol/mol), 2 (200 nmol/mol), 3 (20 nmol/mol), The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

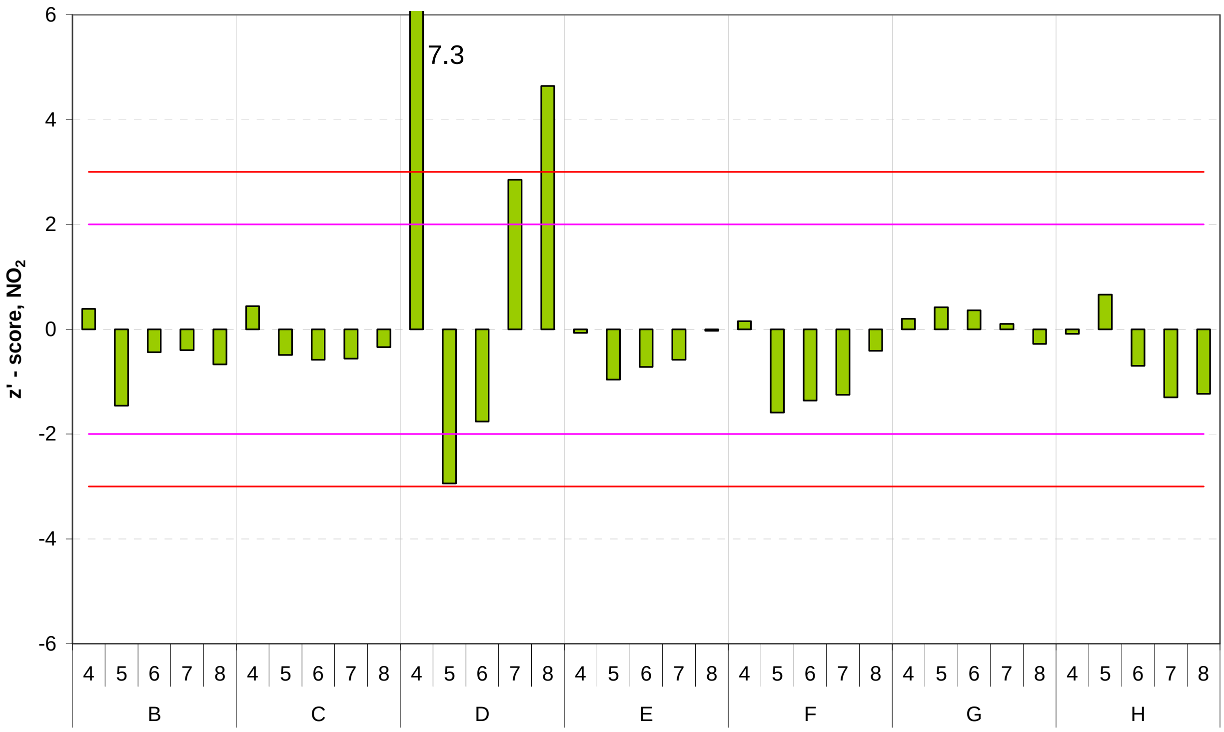

Figure 2:The z'-score evaluations of NO_2 measurements
are given for each participant and each tested gas. The evaluations according to the Test Gas step with nominal concentration are: 4 (0 nmol/mol), 5 (200 nmol/mol), 6 (100 nmol/mol), 7 (60 nmol/mol), 8 (20 nmol/mol). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

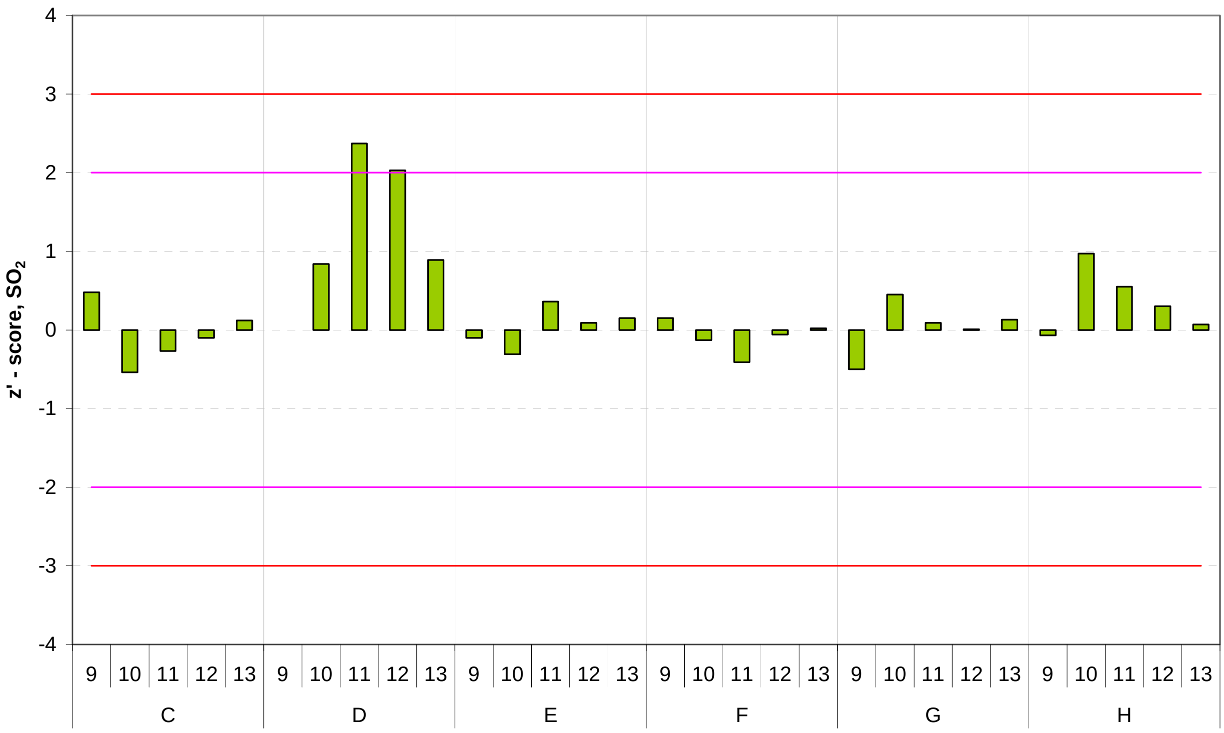

Figure 3:The z'-score evaluations of SO_2 measurements
are given for each participant and each tested concentration level. The evaluations according to the Test Gas step with nominal concentration are is: 9 (0 nmol/mol), 10 (130 nmol/mol), 11 (45 nmol/mol), 12 (20 nmol/mol), 13 (5 nmol/mol). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

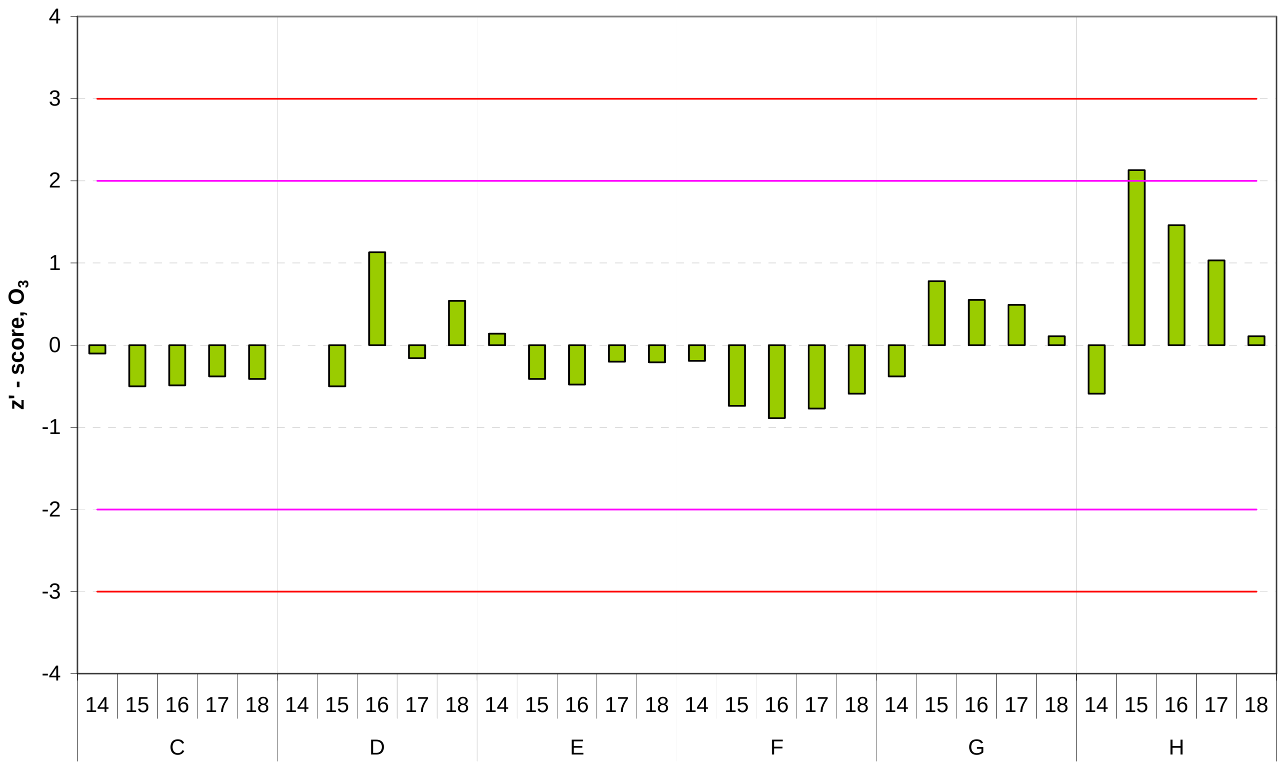

Figure 4:The z'-score evaluations of O_3 measurements
are given for each participant and each tested test gas. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 14 (0 nmol/mol), 15 (300 nmol/mol), 16 (100 nmol/mol), 17 (60 nmol/mol), 18 (20 nmol/mol). The assessment criteria are presented as z'=±2 and z'=±3 lines. They represent the limits for the questionable and unsatisfactory results.

5.2 E_n- number

The normalised deviations [14] (E_n) were calculated according to:

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

where 'X' is the assigned/reference value with an expanded uncertainty 'U_X' and 'x_i' is the participant's average value with an expanded uncertainty 'U_{Xi}'. Satisfactory results are the ones for which $|E_n| \leq 1$.

In Figure 5: to Figure 8: the bias of each participant (x_i-X) are plotted and error bars are used to denote the value of denominator of equation $2\left(\sqrt{U_{x_i}^2 + U_X^2}\right)$. These plots represent also the E_n-number evaluations where, considering the E_n criteria ($|E_n| \leq 1$), all results with error bars touching or crossing x-axis are satisfactory. Reported standard uncertainties (Annex B) that are bigger than "standard deviation for proficiency assessments" (σ_p, Table 3:) are considered not fit-for-purpose and are denoted with "*" in the x-axis of each figure.

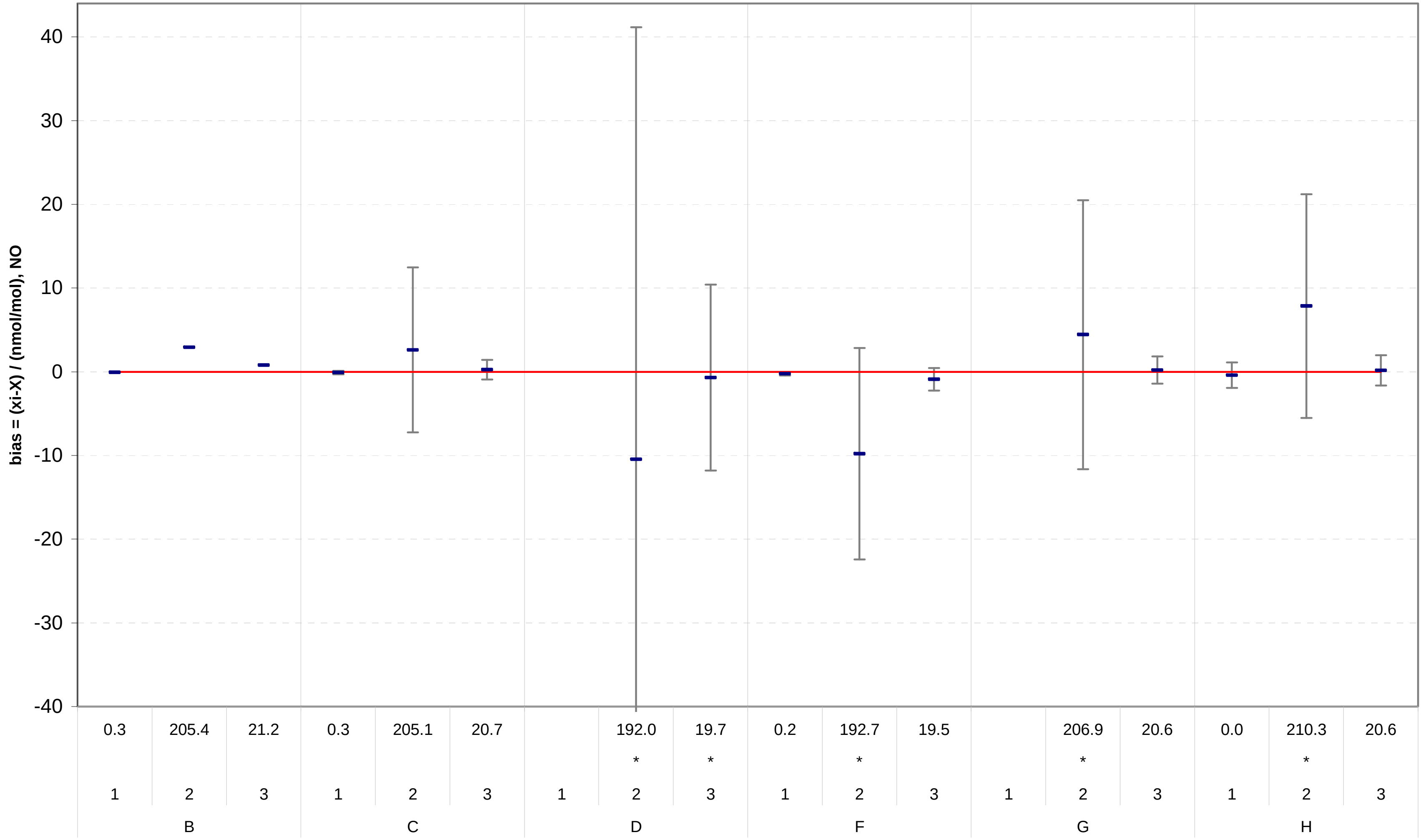

Figure 5:Bias of participant's NO measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested gas (Table 2:). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the test gas step together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

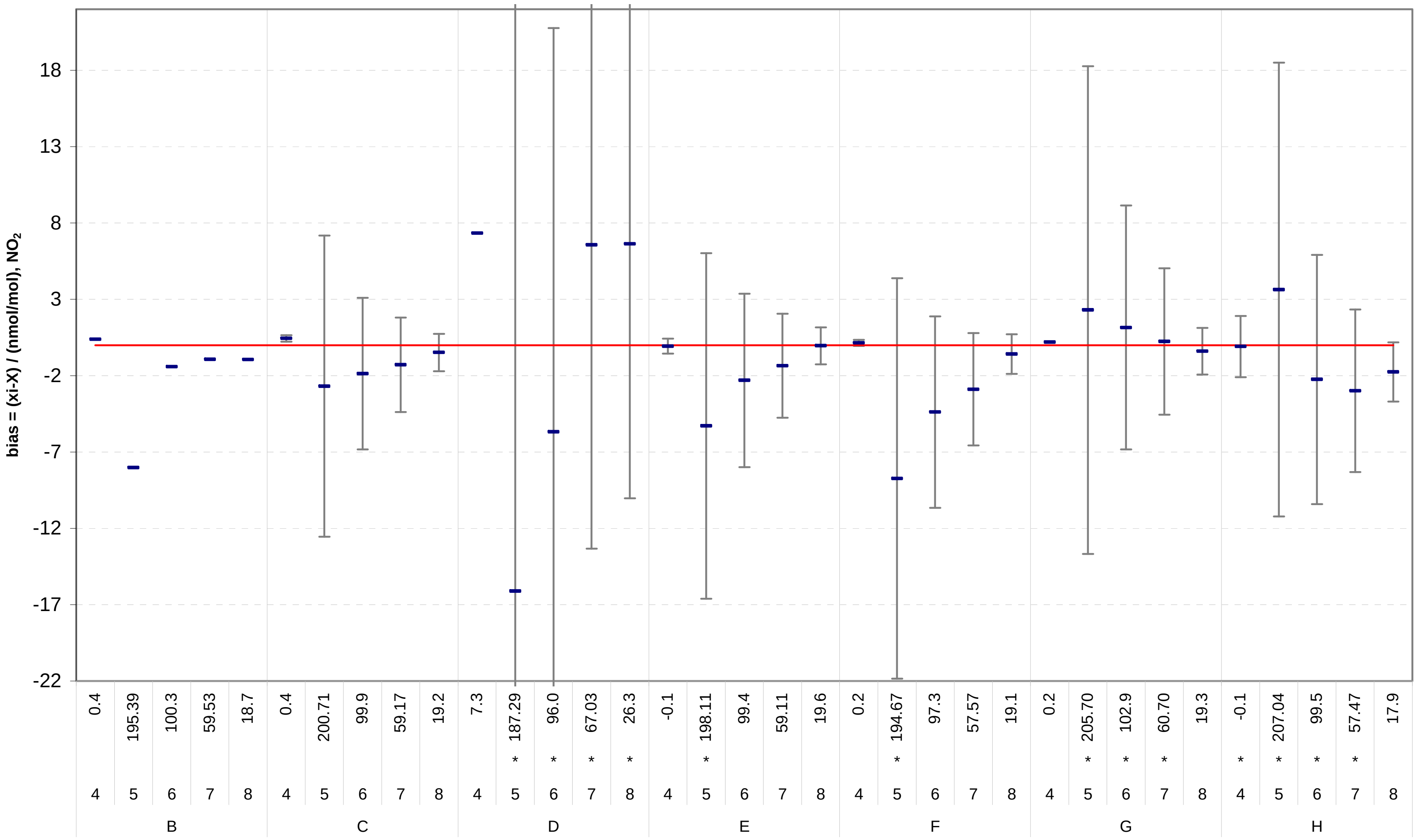

Figure 6:Bias of participant's NO_2 measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested gas (see Table 2:). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the test gas step together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

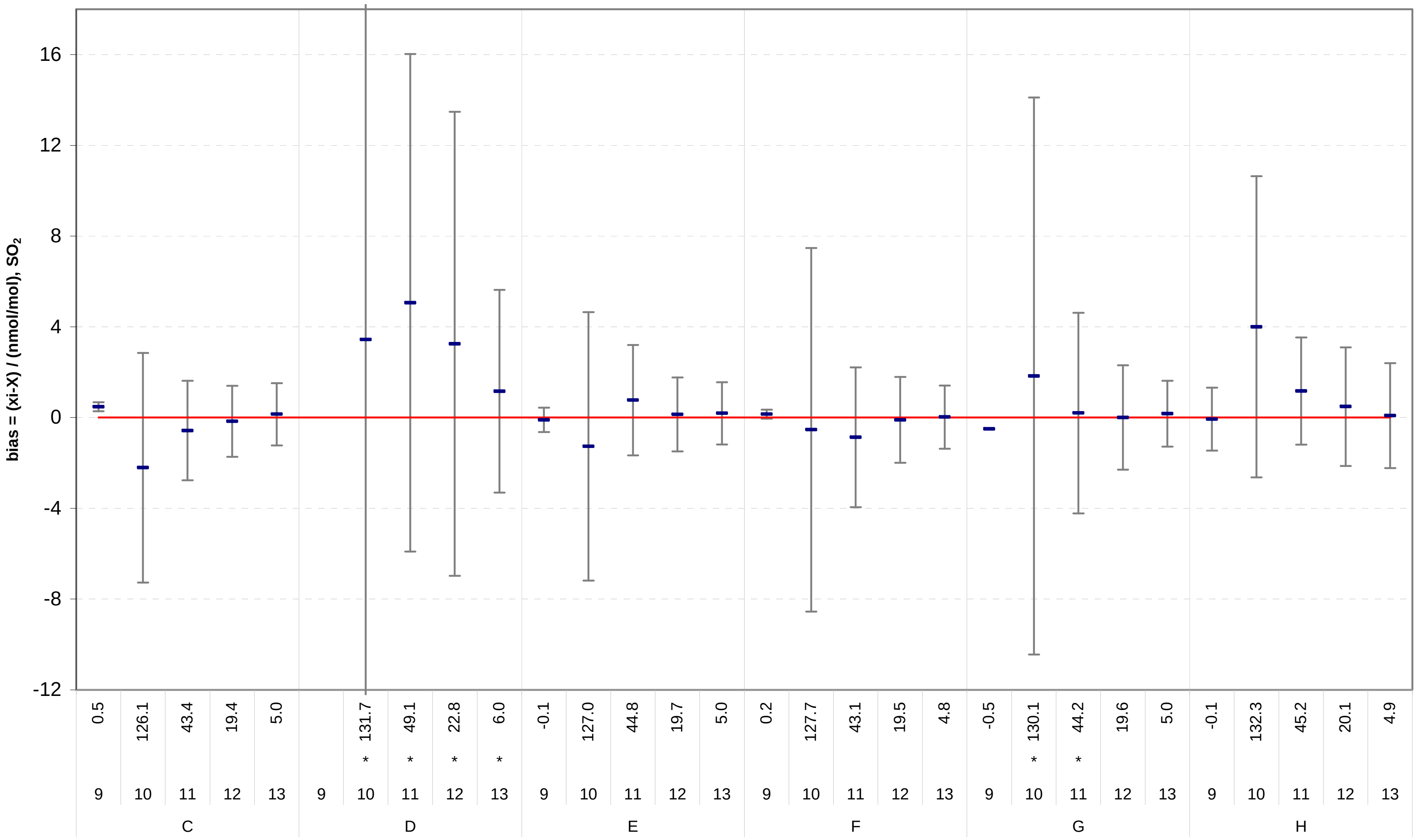

Figure 7:Bias of participant's SO_2 measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested gas (Table 2:). The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the test gas step together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

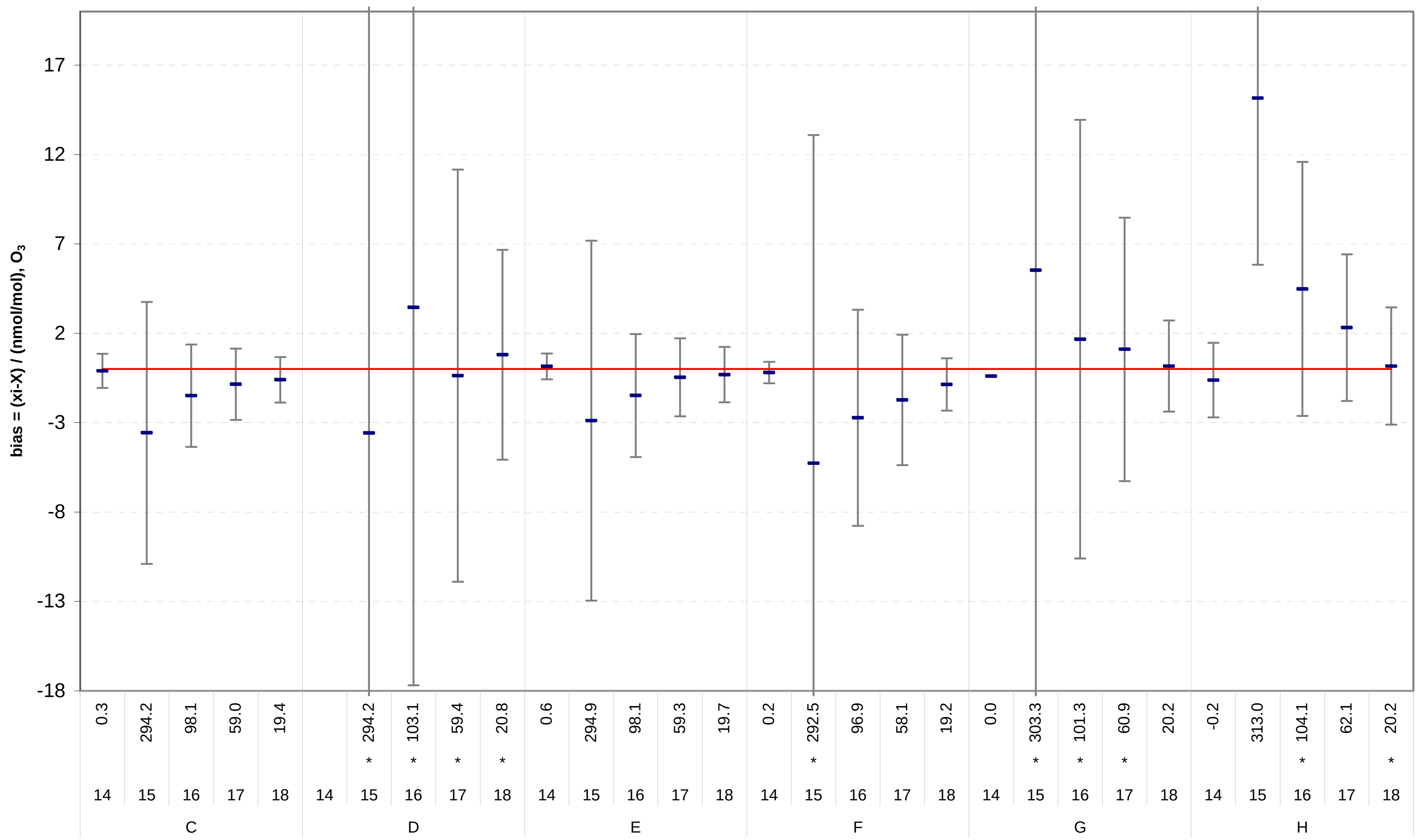

Figure 8:Bias of participant's O_3 measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested gas (see Table 2:). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the test gas step together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p.

7. Discussion

For a general assessment of the quality of each result a decision diagram was developed (Figure 9:) 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)

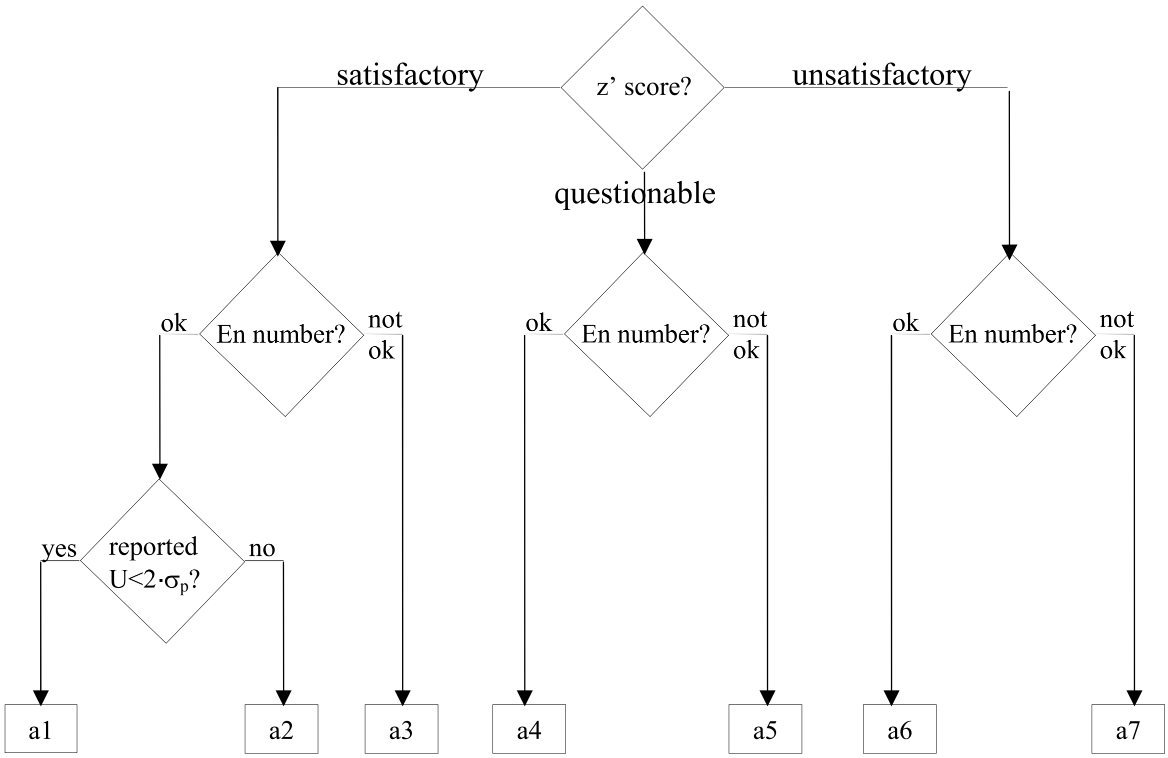

Figure 9:The decision diagram for general assessment of proficiency results.

The results of the IE were assigned to categories according to the diagram given in Figure 9: and are presented in Table 4:.

	run number	conc. level	IE code						
			B	C	D	E	F	G	H
NO (nmol/mol)	1	0.40	NU	a1	NV	NV	a3	NU	a1
	2	202.47	NU	a1	a2	NV	a2	a2	a2
	3	20.43	NU	a1	a2	NV	a1	a1	a1
NO_2 (nmol/mol)	4	0.00	NU	a3	NU	a1	a1	NU	a2
	5	203.40	NU	a1	a4	a2	a2	a2	a2
	6	101.72	NU	a1	a2	a1	a1	a2	a2
	7	60.46	NU	a1	a4	a1	a1	a2	a2
	8	19.67	NU	a1	a6	a1	a1	a1	a1
SO_2 (nmol/mol)	9	0.00	NV	a3	NV	a1	a1	NU	a1
	10	128.27	NV	a1	a2	a1	a1	a2	a1
	11	44.00	NV	a1	a4	a1	a1	a2	a1
	12	19.57	NV	a1	a4	a1	a1	a1	a1
	13	4.80	NV	a1	a2	a1	a1	a1	a1
O_3 (nmol/mol)	14	0.40	NV	a1	NV	a1	a1	NU	a1
	15	297.80	NV	a1	a2	a1	a2	a2	a5
	16	99.60	NV	a1	a2	a1	a1	a2	a2
	17	59.80	NV	a1	a2	a1	a1	a2	a1
	18	20.03	NV	a1	a2	a1	a1	a1	a2

Table 4: The general assessment of proficiency results.
"NV": no values reported; "NU": no uncertainty values reported

8. Conclusions

The proficiency evaluation scheme has provided an assessment of the participants measured values and their evaluated uncertainties. Some of the measured values were provided without an uncertainty estimation (11%), in these cases it was only possible to estimate z' scores. In terms of the criteria imposed by the European Commission (σ_p), 71% of the results reported by NRLs fall into 'a1' category and are good both in terms of measured values and evaluated uncertainties. Most of the remnant measured values are good but the evaluated uncertainties are either too high (19%), category 'a2', or too small, category 'a3' (4%).
The relative number of 'a2' cases, where participant's evaluated uncertainty is higher than the common IE criterion, was lower than in previous IEs but still relevant. The common IE criterion is confirmed to be realistic by comparison to the reproducibility standard deviation obtained at this (Annex C) and other IEs [19]. The mentioned criterion 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 were set by decision of AQUILA members in November 2008. The slight improvement in the compliance of participant's uncertainty at low concentrations with respect to previous IEs is likely ascribable to the application of these new criteria.
No questionable or unsatisfactory results were observed among NRLs.

Concerning WHO laboratories using automated techniques, the results are satisfactory for SO_2, NO_2 and NO measurement methods. The laboratory using manual methods presents results comparable to those of the automated methods for NO and O_3 but their uncertainty is too high.
Considering all WHO laboratories as a whole, there are 12% questionable results, categories 'a4' and 'a5', and one unsatisfactory result ('a6'). Laboratory D, which uses only manual methods, presents two "a4" and one "a6" in its NO_2 measurements while two SO_2 measurements fall in the "a4" category. Laboratory H has one "a5" result in the highest O_3 level. In the first case, the differences are clearly attributable to the use of methods which are not equivalent to CEN reference methods [2], [3]. Laboratory H should investigate the causes of the discrepancy but no action is needed at this stage.

The better comparability among AQUILA-NRL's results is the one observed in SO_2 measurements while NO measurements present the worst performance in terms of reproducibility. The relative reproducibility limits derive from criteria imposed by the European Commission (σ_p). Levels are below the objective at the highest studied concentration: 8.6% for NO_2, 5.8% for O_3, and 4.7% for SO_2. Comparability is considered unsatisfactory for NO where the relative reproducibility limit is 14.2% while the objective is 13.0%. On the other hand, the evaluation of the comparability for this compound has to be interpreted with caution due to the reduced number of levels (only three) and labs (only four). The repeatability and reproducibility of NO_2 depend on the concentration of both NO_2 and NO. Therefore, contemporary acquisition of NO and NO_2 would be necessary to evaluate the combined effect of these two gases.

9. References

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Annex A. Assigned values

The assigned values of tested concentration levels were derived from UBA measurements which are calibrated against the certified reference values of CRMs and are traceable to international standards. In this perspective the assigned values are reference values as defined in the ISO 13528 [14].

UBA SO_2, NO_2 and NO analysers were calibrated using primary calibration gas mixtures prepared according to the methodology described in the ISO 6144 [5]. The procedure and the device for generating primary calibration gases is described elsewhere [18]. Gas mixtures for the calibration experiment were produced from the reference mixtures by dynamic dilution method using mass flow controllers [9].
SO_2, NO_2 and NO gas mixtures manufactured by Air Liquide and certified by UBA (U≤ 2%) were used as internal standards.
For the reference gas mixture composition evaluation and for the calibration experiment evaluation two computer applications were used, the “GUM WORKBENCH” [20] and “ProControl®” [22] .
For O_3 measurements, the primary standard NIST photometer SRP 29 was used [24].

UBA’s measurement results were validated by comparison to the group statistics (x* and s*) for every parameter and concentration level of the IE. These statistics are calculated from participants, applying the robust method described in the Annex C of the ISO 13528 [14]. The validation is taking into account UBA’s measurement result (X) and its standard uncertainty ($u_{X'}$) as given in expression 3 [14]:

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

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

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

run	unit	X	uX’	_x*	_s*	valid.
NO _1	nmol/mol	0.40	0.10	0.25	0.15	OK
NO _2	nmol/mol	202.47	2.10	205.06	3.89	OK
NO _3	nmol/mol	20.43	0.31	20.59	0.22	OK
NO2 _4	nmol/mol	0.00	0.10	0.15	0.24	OK
NO2 _5	nmol/mol	203.40	2.11	200.72	5.55	OK
NO2 _6	nmol/mol	101.72	1.07	99.94	0.86	OK
NO2 _7	nmol/mol	60.46	0.67	59.14	1.43	OK
NO2 _8	nmol/mol	19.67	0.31	19.12	0.56	OK
SO2 _9	nmol/mol	0.00	0.10	-0.02	0.39	OK
SO2 _10	nmol/mol	128.27	1.51	128.41	2.21	OK
SO2 _11	nmol/mol	44.00	0.83	44.12	0.88	OK
SO2 _12	nmol/mol	19.57	0.71	19.59	0.18	OK
SO2 _13	nmol/mol	4.80	0.68	4.90	0.09	OK
O3 _14	nmol/mol	0.40	0.30	0.30	0.20	OK
O3 _15	nmol/mol	297.80	1.54	297.57	5.12	OK
O3 _16	nmol/mol	99.60	0.66	99.31	2.24	OK
O3 _17	nmol/mol	59.80	0.52	59.80	1.52	OK
O3 _18	nmol/mol	20.03	0.43	19.79	0.49	OK

Table 5: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 6.

Due to the reduced length of the bench (only 8 m), compared to those used in other IEs, the lack of homogeneity between the beginning and the end is assumed to be negligible. The evaluation of the uncertainty of the bench confirmed that differences along the distribution line are below the limit of detection.

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 (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 NO

parameter: NO				all units are nmol/mol			
test gas 1				**x*:** 0.3		**s*:** 0.2	
	A	**B**	**C**	**D**	**F**	**G**	**H**
xi,1	0.40	0.32	0.30		0.15	0.00	-0.01
u(xi)	0.10		0.02		0.01		0.76
U(xi)	0.20		0.05		0.02		1.51

Table 6: Reported values for NO test gas 1.

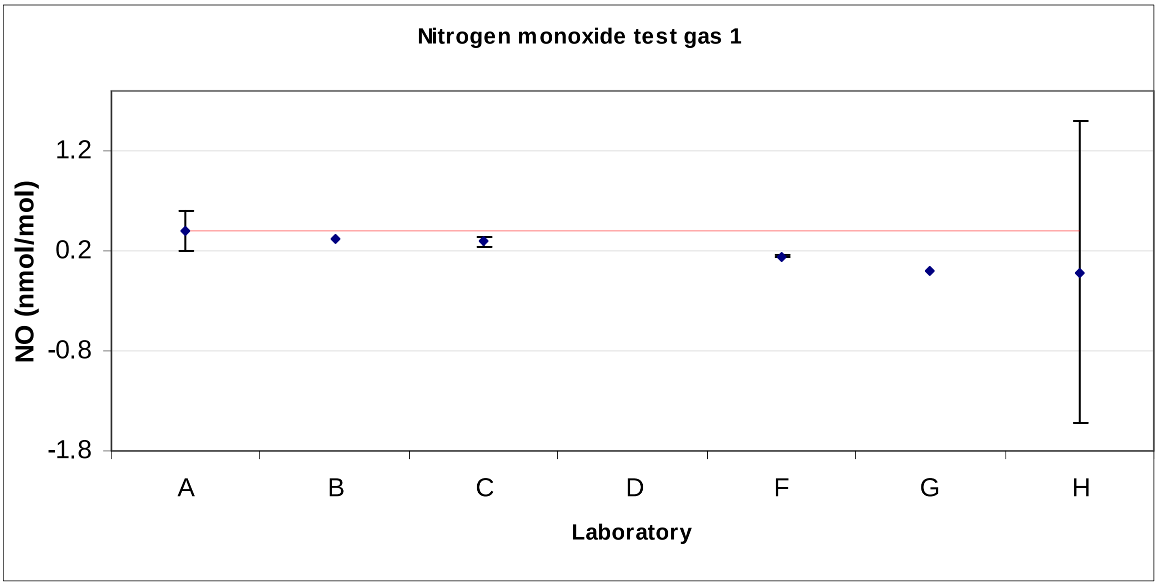

Figure 10: Reported values for NO test gas 1.

parameter: NO				all units are nmol/mol			
test gas 2				205.1		s*: 3.9	
	A	B	C	D	F	G	H
xi,1	202.50	205.54	205.20	192.00	192.00	207.10	210.67
xi,2	202.40	205.07	205.02	208.00	193.00	206.70	210.19
xi,3	202.50	205.58	205.03	176.00	193.00	206.90	210.07
xi	202.47	205.40	205.08	192.00	192.67	206.90	210.31
si	0.06	0.28	0.10	16.00	0.58	0.20	0.32
u(xi)	2.01		4.46	16.17	5.95	7.80	6.35
U(xi)	4.03		8.92	51.44	11.90	15.50	12.69

Table 7: Reported values for NO test gas 2.

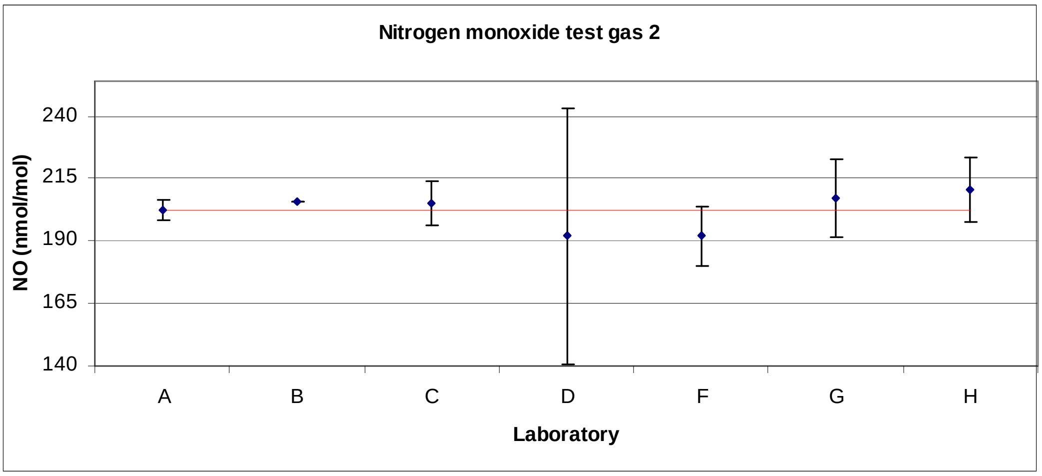

Figure 11: Reported values for NO test gas 2.

parameter: NO				all units are nmol/mol			
test gas 3				x*: 20.6		s*: 0.2	
	A	B	C	D	F	G	H
xi,1	20.50	21.24	20.64	20.80	19.51	20.60	20.56
xi,2	20.40	21.21	20.82	16.00	19.52	20.70	20.52
xi,3	20.40	21.23	20.58	22.40	19.60	20.60	20.69
xi	20.43	21.23	20.68	19.73	19.54	20.63	20.59
si	0.06	0.02	0.13	3.33	0.05	0.06	0.09
u(xi)	0.30		0.50	3.49	0.60	0.80	0.85
U(xi)	0.61		1.00	11.09	1.20	1.50	1.69

Table 8: Reported values for NO test gas 3.

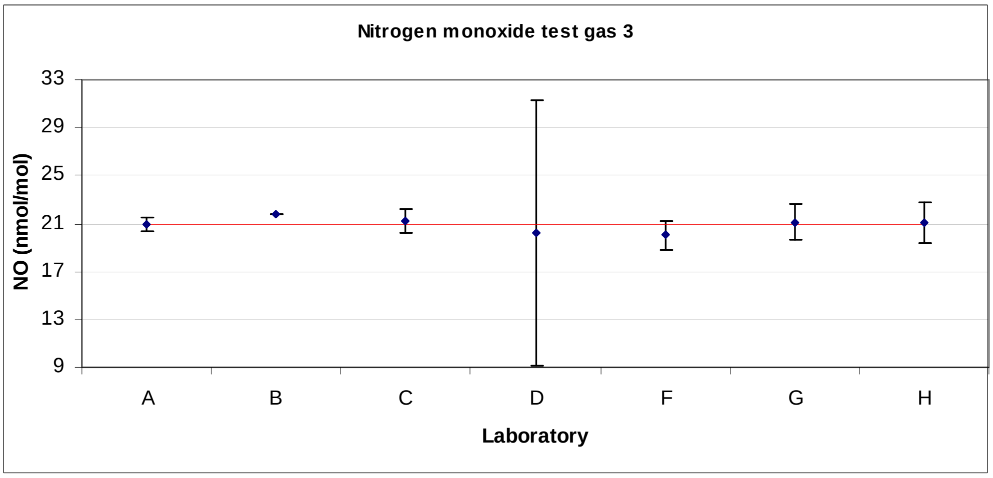

Figure 12: Reported values for NO test gas 3.

Reported values for NO_2

	parameter: NO_2				all units are nmol/mol			
	test gas 4				x*: 0.1		s*: 0.2	
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**
xi,1	0.00	0.39	0.44	7.33	-0.07	0.15	0.20	-0.09
u(xi)	0.10		0.02		0.22	0.01		1.00
U(xi)	0.20		0.05		0.45	0.02		2.00

Table 9: Reported values for NO_2 test gas 4.

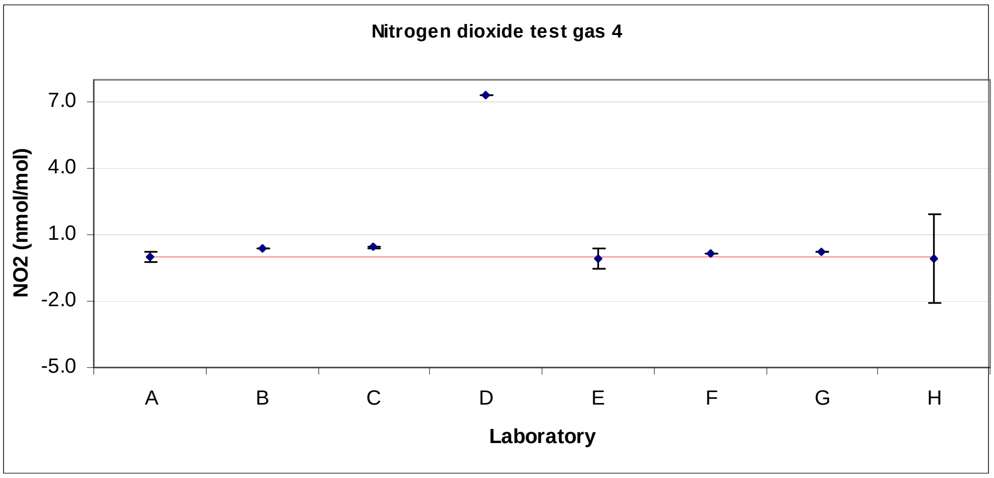

Figure 13: Reported values for NO_2 test gas 4.

	parameter: NO_2				all units are nmol/mol			
	test gas 5				x*: 200.7		s*: 5.6	
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**
xi,1	202.16	194.21	200.58	200.87	198.20	194.00	204.00	206.77
xi,2	203.77	195.31	200.85	191.67	198.49	195.00	206.00	207.11
xi,3	204.28	196.64	200.71	169.32	197.65	195.00	207.10	207.24
xi	203.40	195.39	200.71	187.29	198.11	194.67	205.70	207.04
si	1.11	1.22	0.14	16.23	0.43	0.58	1.57	0.24
u(xi)	2.01		4.46	16.38	5.25	6.21	7.70	7.13
U(xi)	4.03		8.92	52.00	10.50	12.42	15.40	14.25

Table 10: Reported values for NO_2 test gas 5.

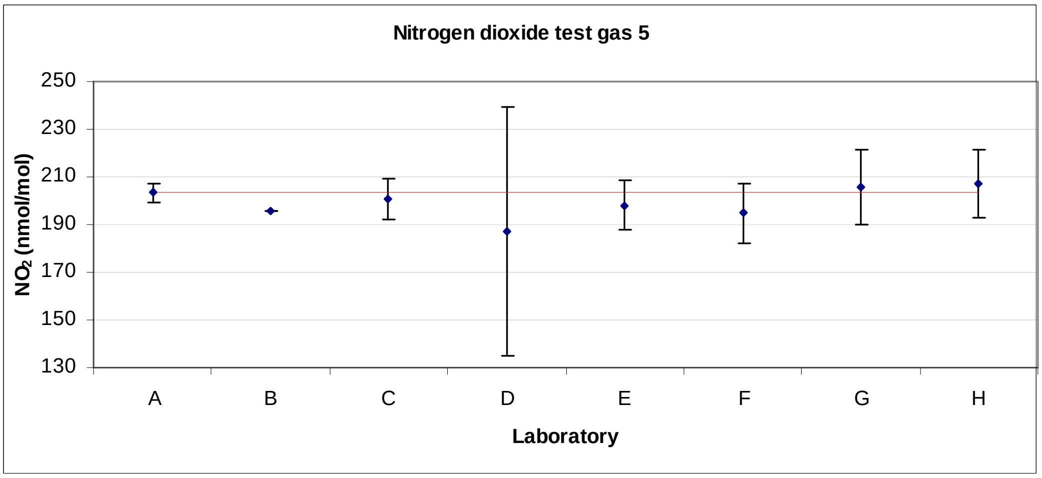

Figure 14: Reported values for NO_2 test gas 5.

parameter: NO_2					all units are nmol/mol			
test gas 6					x*: 99.9		s*: 0.9	
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**
xi,1	101.89	100.03	99.89	95.25	98.85	97.00	103.10	99.95
xi,2	101.68	100.55	99.88	86.96	99.54	97.50	102.90	99.47
xi,3	101.58	100.32	99.78	105.90	99.85	97.50	102.60	99.00
xi	101.72	100.30	99.85	96.04	99.41	97.33	102.87	99.47
si	0.16	0.26	0.06	9.49	0.51	0.29	0.25	0.48
u(xi)	1.03		2.24	8.28	2.63	2.95	3.90	3.94
U(xi)	2.05		4.48	26.35	5.26	5.90	7.70	7.87

Table 11: Reported values for NO_2 test gas 6.

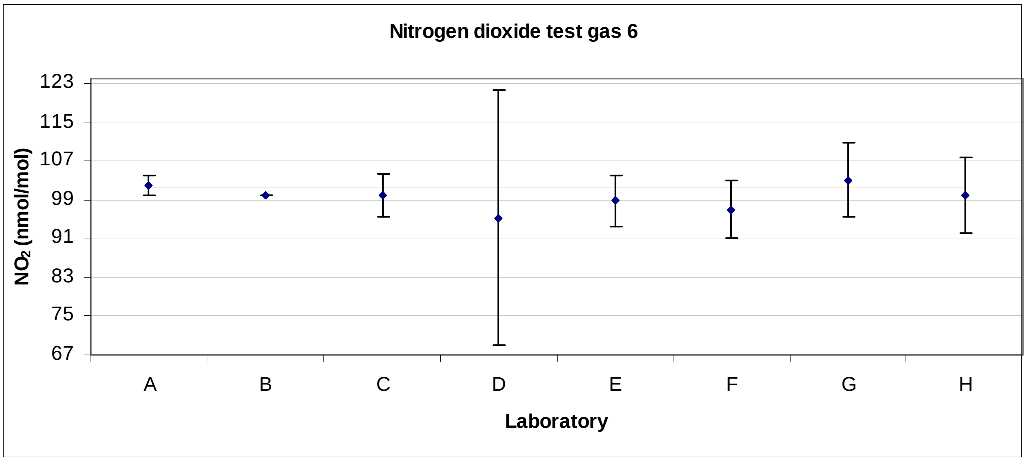

Figure 15: Reported values for NO_2 test gas 6.

parameter: NO_2					all units are nmol/mol			
test gas 7					x*: 59.1		s*: 1.4	
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**
xi,1	60.53	59.72	59.25	74.08	59.30	57.50	60.90	57.67
xi,2	60.22	59.40	59.37	63.50	59.02	57.60	60.60	57.43
xi,3	60.63	59.47	58.89	63.50	59.00	57.60	60.60	57.31
xi	60.46	59.53	59.17	67.03	59.11	57.57	60.70	57.47
si	0.21	0.17	0.25	6.11	0.17	0.06	0.17	0.18
u(xi)	0.64		1.39	6.25	1.56	1.71	2.30	2.58
U(xi)	1.29		2.79	19.85	3.13	3.42	4.60	5.15

Table 12: Reported values for NO_2 test gas 7.

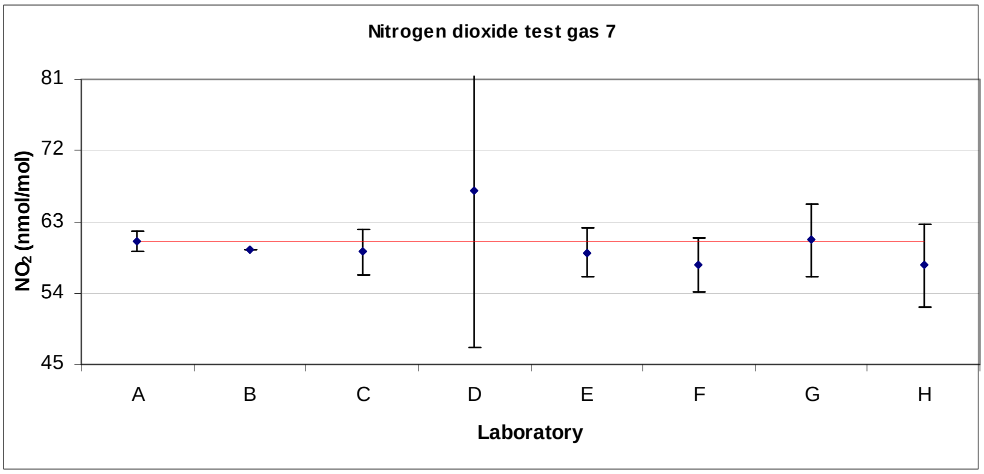

Figure 16: Reported values for NO_2 test gas 7.

parameter: NO_2					all units are nmol/mol			
test gas 8					x*: 19.1		s*: 0.6	
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**
xi,1	19.67	18.86	19.43	21.16	19.47	19.05	19.40	17.94
xi,2	19.47	18.67	19.13	26.45	19.83	19.10	19.30	17.94
xi,3	19.87	18.62	19.02	31.30	19.60	19.10	19.10	17.86
xi	19.67	18.72	19.19	26.30	19.63	19.08	19.27	17.91
si	0.20	0.13	0.21	5.07	0.18	0.03	0.15	0.05
u(xi)	0.30		0.53	5.24	0.52	0.57	0.70	0.92
U(xi)	0.61		1.06	16.66	1.04	1.14	1.40	1.83

Table 13:Reported values for NO_2 test gas 8.

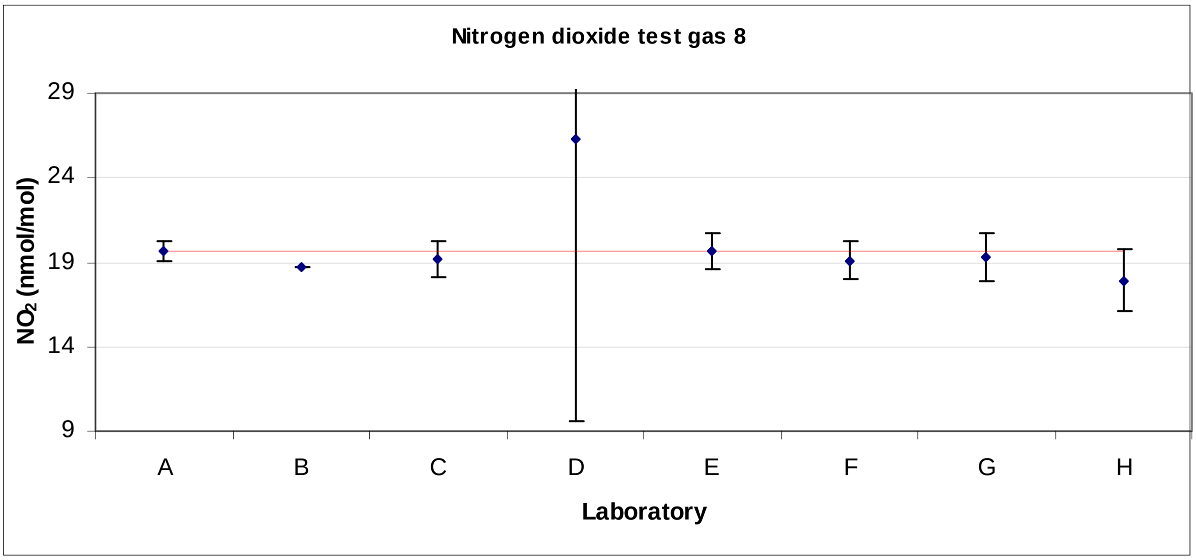

Figure 17: Reported values for NO_2 test gas 8.

Reported values for SO_2

parameter: SO_2				all units are nmol/mol			
test gas 9				x*: 0.0		s*: 0.4	
	A	C	D	E	F	G	H
xi,1	0.00	0.48		-0.10	0.15	-0.50	-0.07
u(xi)	0.10	0.01		0.25	0.01		0.69
U(xi)	0.20	0.02		0.50	0.02		1.37

Table 14: Reported values for SO_2 test gas 9.

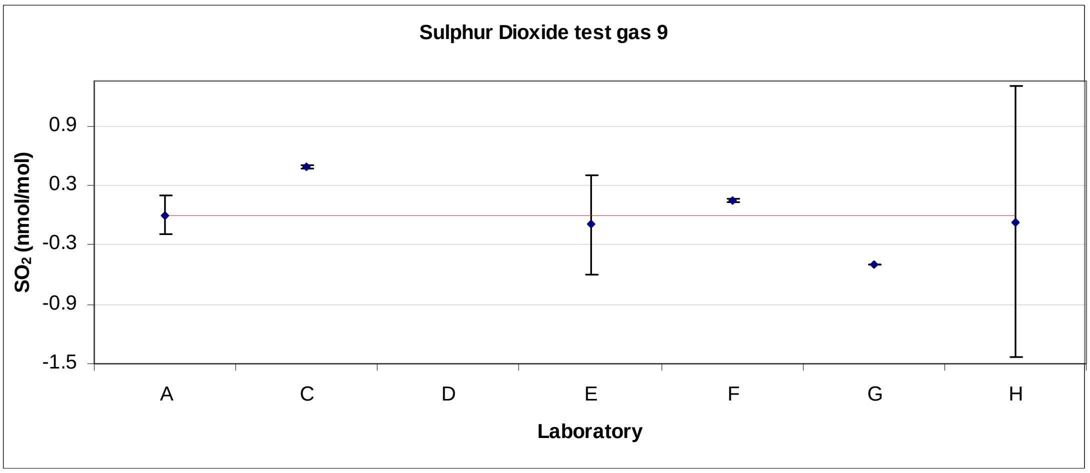

Figure 18: Reported values for SO_2 test gas 9.

parameter: SO_2				all units are nmol/mol			
test gas 10				x*: 128.4		s*: 2.2	
	A	C	D	E	F	G	H
xi,1	128.20	126.06	121.25	126.85	127.20	129.80	132.30
xi,2	128.20	126.14	131.67	126.98	127.80	130.00	132.17
xi,3	128.40	125.99	142.21	127.17	128.20	130.50	132.33
xi	128.27	126.06	131.71	127.00	127.73	130.10	132.27
si	0.12	0.08	10.48	0.16	0.50	0.36	0.09
u(xi)	1.47	2.03	10.65	2.54	3.72	6.00	2.96
U(xi)	2.93	4.05	33.87	5.08	7.42	11.90	5.91

Table 15: Reported values for SO_2 test gas 10.

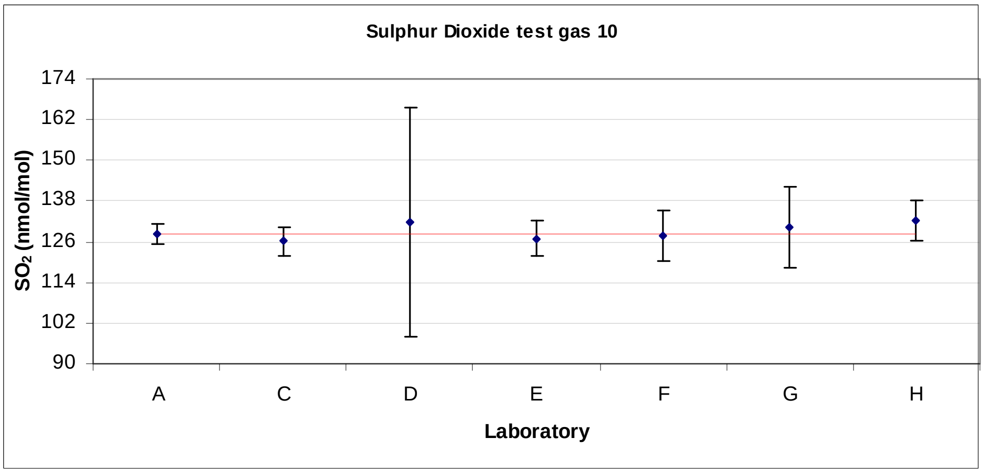

Figure 19: Reported values for SO_2 test gas 10.

parameter: SO_2				all units are nmol/mol			
test gas 11				x*: 44.1		s*: 0.9	
	A	C	D	E	F	G	H
xi,1	44.20	43.59	47.25	44.95	42.90	44.60	45.50
xi,2	43.90	43.42	47.25	44.76	43.20	44.10	45.02
xi,3	43.90	43.28	52.67	44.60	43.30	43.90	44.99
xi	44.00	43.43	49.06	44.77	43.13	44.20	45.17
si	0.17	0.16	3.13	0.18	0.21	0.36	0.29
u(xi)	0.82	0.72	3.40	0.89	1.30	2.00	0.85
U(xi)	1.63	1.44	10.84	1.79	2.60	4.10	1.69

Table 16: Reported values for SO_2 test gas 11.

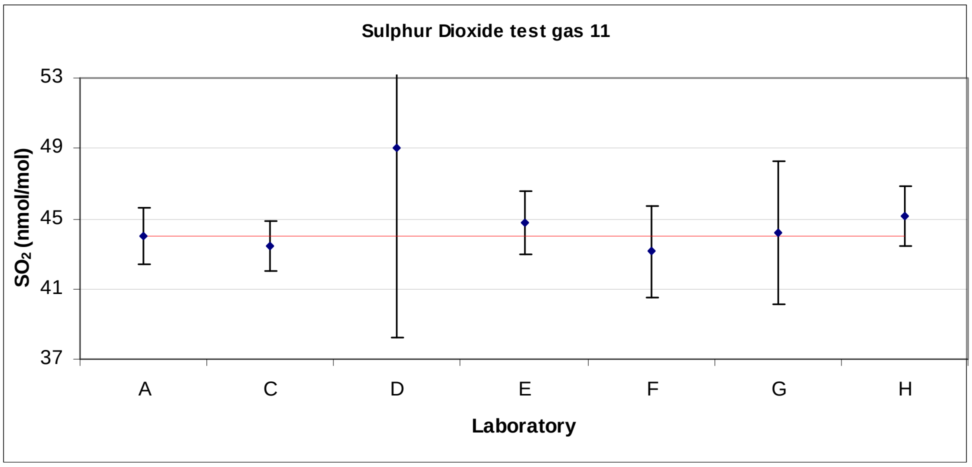

Figure 20: Reported values for SO_2 test gas 11.

parameter: SO_2				all units are nmol/mol			
test gas 12				x*: 19.6		s*: 0.2	
	A	C	D	E	F	G	H
xi,1	19.60	19.40	21.06	19.69	19.50	19.70	20.07
xi,2	19.60	19.38	26.33	19.72	19.40	19.50	20.09
xi,3	19.50	19.42	21.06	19.73	19.50	19.50	20.00
xi	19.57	19.40	22.82	19.71	19.47	19.57	20.05
si	0.06	0.02	3.04	0.02	0.06	0.12	0.05
u(xi)	0.71	0.32	3.18	0.39	0.62	0.90	1.10
U(xi)	1.42	0.64	10.13	0.78	1.24	1.80	2.19

Table 17: Reported values for SO_2 test gas 12.

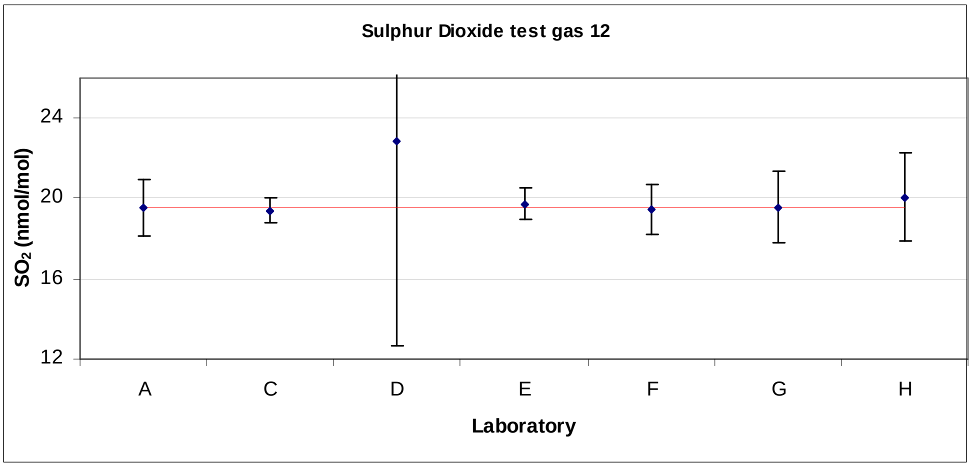

Figure 21: Reported values for SO_2 test gas 12.

parameter: SO_2				all units are nmol/mol			
test gas 13				x*: 4.9		s*: 0.1	
	A	**C**	**D**	**E**	**F**	**G**	**H**
xi,1	4.80	4.99	5.27	5.02	4.80	5.10	4.87
xi,2	4.80	4.94	5.27	4.99	4.83	4.80	4.91
xi,3	4.80	4.91	7.35	4.96	4.83	5.00	4.89
xi	4.80	4.95	5.96	4.99	4.82	4.97	4.89
si	0.00	0.04	1.20	0.03	0.02	0.15	0.02
u(xi)	0.68	0.09	1.34	0.09	0.14	0.20	0.94
U(xi)	1.36	0.18	4.26	0.19	0.28	0.50	1.87

Table 18:Reported values for SO2 test gas 13.

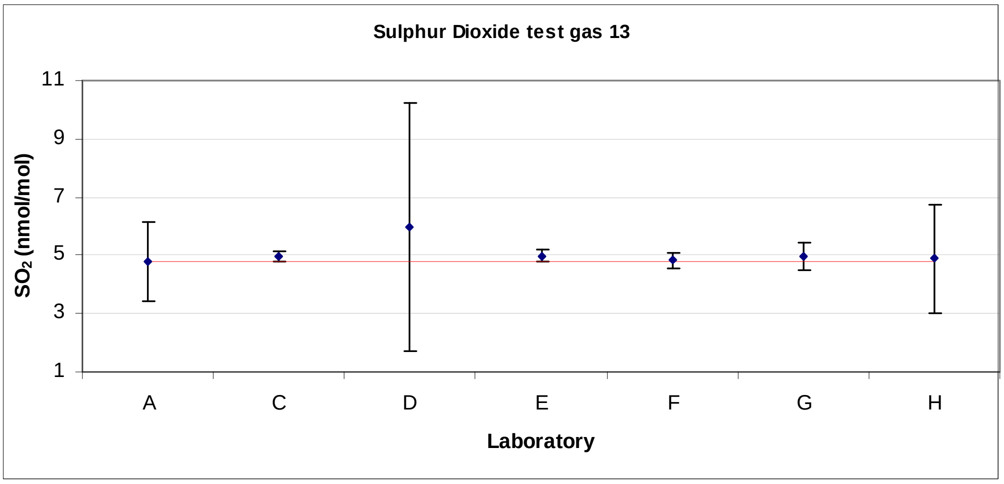

Figure 22: Reported values for SO_2 test gas 13.

Reported values for O_3

parameter: O_3				all units are nmol/mol			
test gas 14				x*: 0.3		s*: 0.2	
	A	C	D	E	F	G	H
xi,1	0.40	0.30		0.55	0.20	0.00	-0.22
u(xi)	0.30	0.37		0.20	0.01		1.00
U(xi)	0.60	0.74		0.40	0.02		2.00

Table 19:Reported values for O3 test gas 14

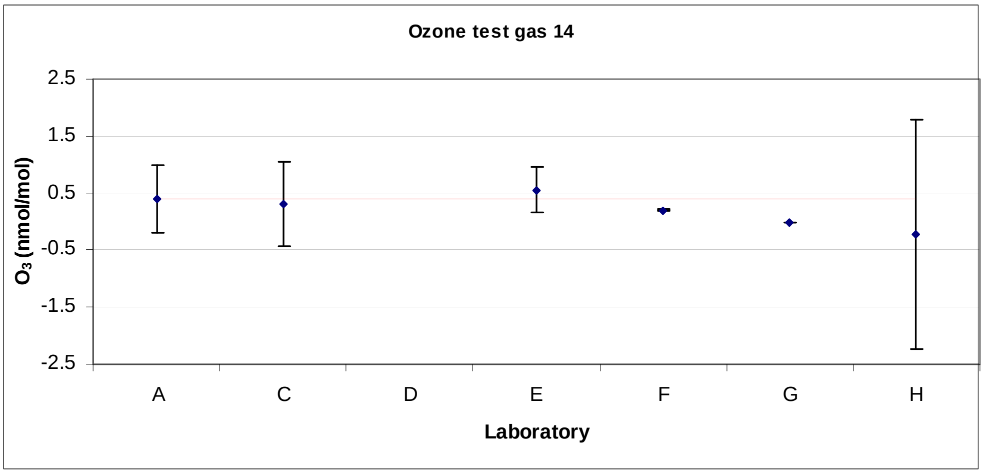

Figure 23: Reported values for O_3 test gas 14.

parameter: O_3				all units are nmol/mol			
test gas 15				x*: 297.6		s*: 5.1	
	A	C	D	E	F	G	H
xi,1	296.60	292.96	282.50	293.43	291.80	301.70	310.76
xi,2	298.10	294.43	308.50	294.85	292.80	303.60	313.22
xi,3	298.70	295.29	291.67	296.44	293.00	304.70	314.87
xi	297.80	294.23	294.22	294.91	292.53	303.33	312.95
si	1.08	1.18	13.19	1.51	0.64	1.52	2.07
u(xi)	1.26	3.33	13.35	4.97	9.05	18.20	4.40
U(xi)	2.51	6.65	42.48	9.58	18.10	36.40	8.79

Table 20:Reported values for O3 test gas 15.

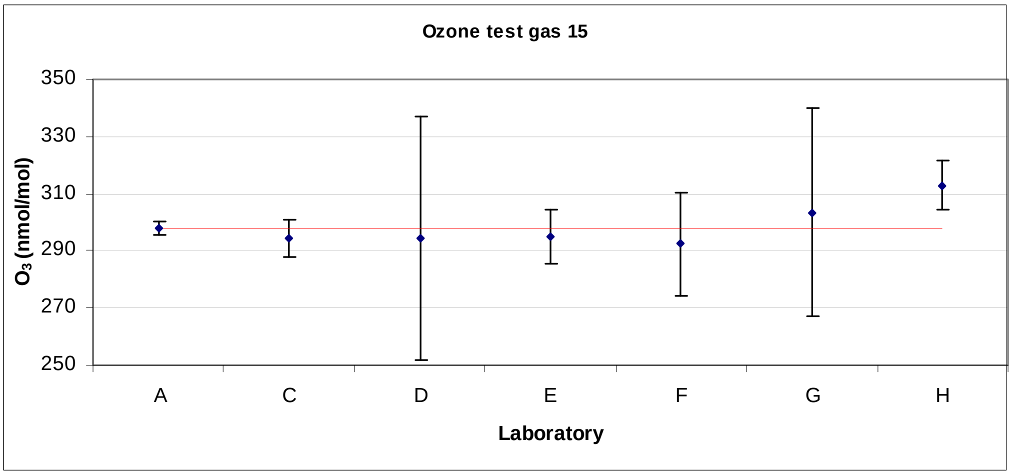

Figure 24: Reported values for O3 test gas 15.

parameter: O_3				all units are nmol/mol			
test gas 16				x*: 99.3		s*: 2.2	
	A	**C**	**D**	**E**	**F**	**G**	**H**
xi,1	100.20	98.59	95.83	98.49	96.60	101.80	104.51
xi,2	99.40	97.97	108.33	98.07	97.00	101.10	103.92
xi,3	99.20	97.78	105.00	97.81	97.00	100.90	103.82
xi	99.60	98.11	103.05	98.12	96.87	101.27	104.08
si	0.53	0.42	6.47	0.34	0.23	0.47	0.37
u(xi)	0.58	1.27	6.63	1.59	2.95	6.10	3.49
U(xi)	1.17	2.54	21.10	3.18	5.90	12.20	6.98

Table 21:Reported values for O_3 test gas 16.

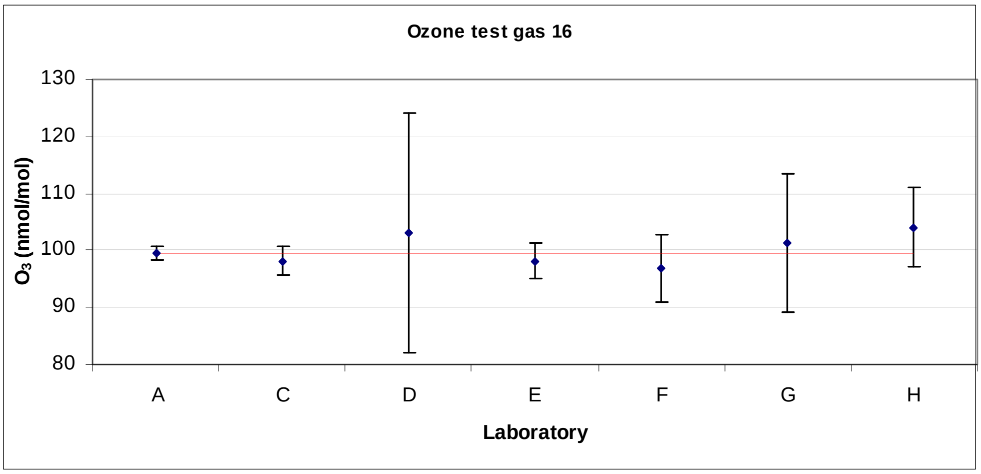

Figure 25: Reported values for O_3 test gas 16.

parameter: O_3				all units are nmol/mol			
test gas 17				x*: 59.8		s*: 1.5	
	A	**C**	**D**	**E**	**F**	**G**	**H**
xi,1	60.00	59.04	58.33	59.48	58.20	61.00	62.31
xi,2	59.70	58.91	63.30	59.32	58.00	60.90	62.05
xi,3	59.70	58.89	56.67	59.22	58.00	60.80	61.99
xi	59.80	58.95	59.43	59.34	58.07	60.90	62.12
si	0.17	0.08	3.45	0.13	0.12	0.10	0.17
u(xi)	0.49	0.85	3.61	0.96	1.75	3.70	1.99
U(xi)	0.98	1.70	11.48	1.92	3.50	7.30	3.97

Table 22:Reported values for O_3 test gas 17.

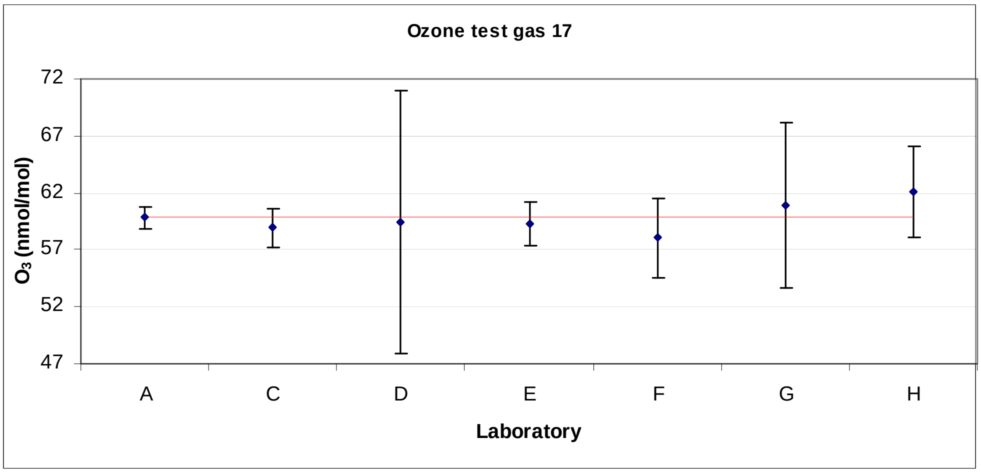

Figure 26: Reported values for O_3 test gas 17.

parameter: O_3				all units are nmol/mol			
test gas 18				x*: 19.8		s*: 0.5	
	A	**C**	**D**	**E**	**F**	**G**	**H**
xi,1	20.00	19.46	19.17	19.69	19.10	20.20	20.23
xi,2	20.00	19.41	22.50	19.74	19.20	20.20	20.18
xi,3	20.10	19.43	20.83	19.73	19.20	20.20	20.19
xi	20.03	19.43	20.83	19.72	19.17	20.20	20.20
si	0.06	0.03	1.67	0.03	0.06	0.00	0.03
u(xi)	0.43	0.46	1.82	0.64	0.59	1.20	1.59
U(xi)	0.86	0.93	5.81	1.28	1.18	2.40	3.17

Table 23: Reported values for O_3 test gas 18.

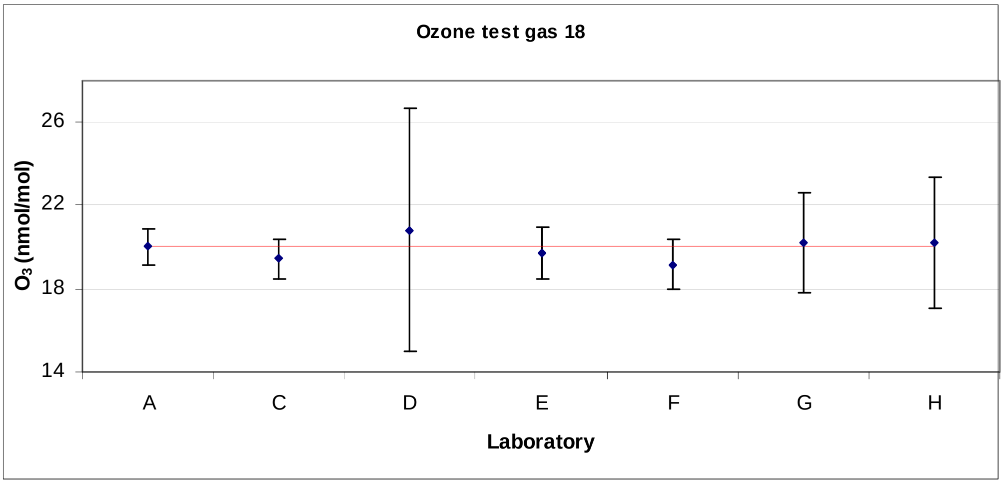

Figure 27: Reported values for O_3 test gas 18.

Annex C. The precision of standardized measurement methods

For the main purpose of monitoring trends between different IEs undertaken in the framework of the EC/WHO Harmonization Programme for Air Quality Measurements, the precision of standardized SO_2, O_3 and NO_X measurement methods [2], [3] and [4] as implemented by NRLs was evaluated. Applied methodology is described in ISO 5725-1, -2 and -6 [15], [16] and [17]. The precision experiment has involved four laboratories, for NO_X, SO_2 and O_3 measurement methods. Five concentration levels were tested, for O_3, SO_2 and NO_2, and three for NO. The data consistency and outlier tests were uncertain due to the small number of participants. No outliers were detected.

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 4 [17]. It represents the biggest difference between two test results found on an identical test gas by one laboratory using the same apparatus within the shortest feasible time interval, that should not been exceeded on average more than once in 20 cases in the normal and correct operation of method.

$$r = t_{95\%,8} \cdot \sqrt{2} \cdot s_r \qquad (4)$$

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 5 [17]. 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.

$$R = t_{95\%,3} \cdot \sqrt{2} \cdot s_R \qquad (5)$$

The repeatability standard deviation was evaluated with 8 (4·(3-1)) degrees of freedom (ν) and reproducibility standard deviation with 3 (4-1) degrees of freedom. The critical range student factors ($t_{\alpha,\nu}$) are 2,31 and 3,18 respectively.

In this annex are presented the repeatability and reproducibility limits of measurement methods (r, R). compared to the reproducibility from common criteria (R(from σ_p))' calculated by substituting s_R in equation 5 with the 'standard deviation for proficiency assessment' (Table 3:). Comparison between R and R(from σ_p) serves to indicate that σ_p is realistic ([14] 6.3.1) and that the general methodology implemented by NRLs fulfil the criteria set in the standard for limiting uncertainty (σ_p).

NO data (nmol/mol)			
AQUILA LABS			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.2		0.6	
20.3	0.3	2.4	
201.8	1.0	28.6	14.2%

Table 24:The R and r of NO standard measurement method.

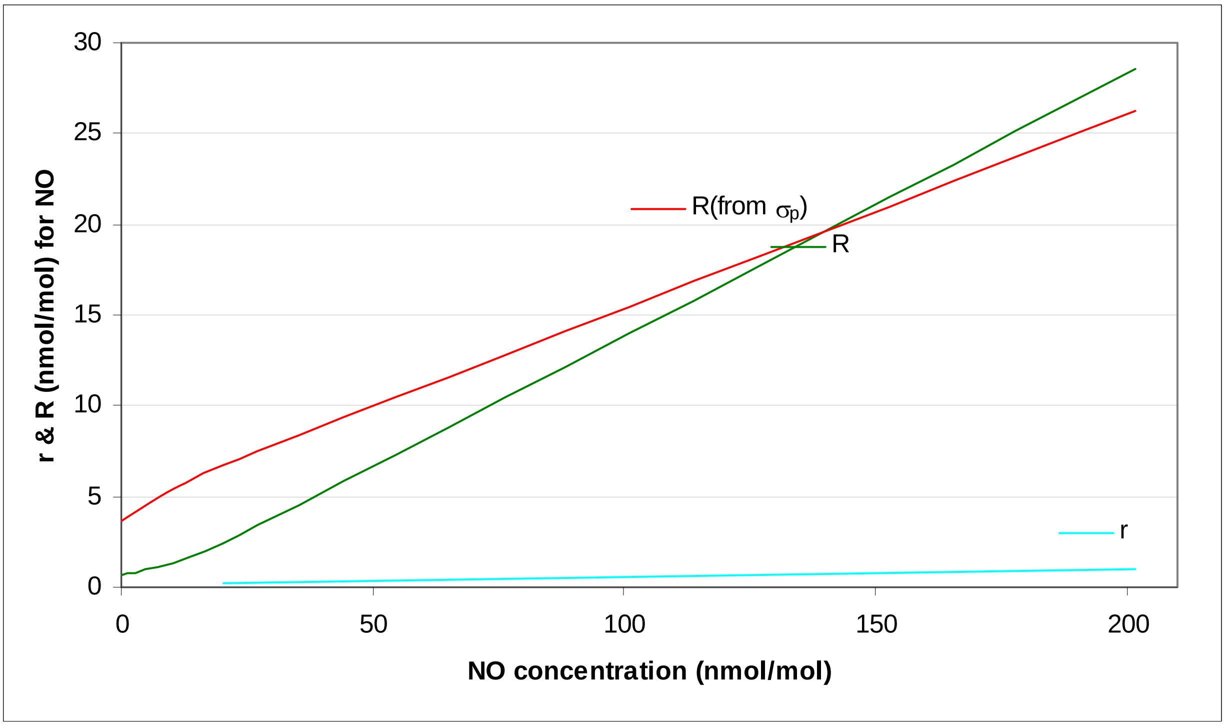

Figure 28: The R and r of NO standard measurement method as a function of concentration.

NO_2 data (nmol/mol)			
AQUILA LABS			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.1		1.0	
19.4	0.5	1.2	
59.4	0.6	5.0	
100.2	0.9	8.5	
200.5	2.9	17.3	8.6%

Table 25:The R and r of NO_2 standard measurement method*.

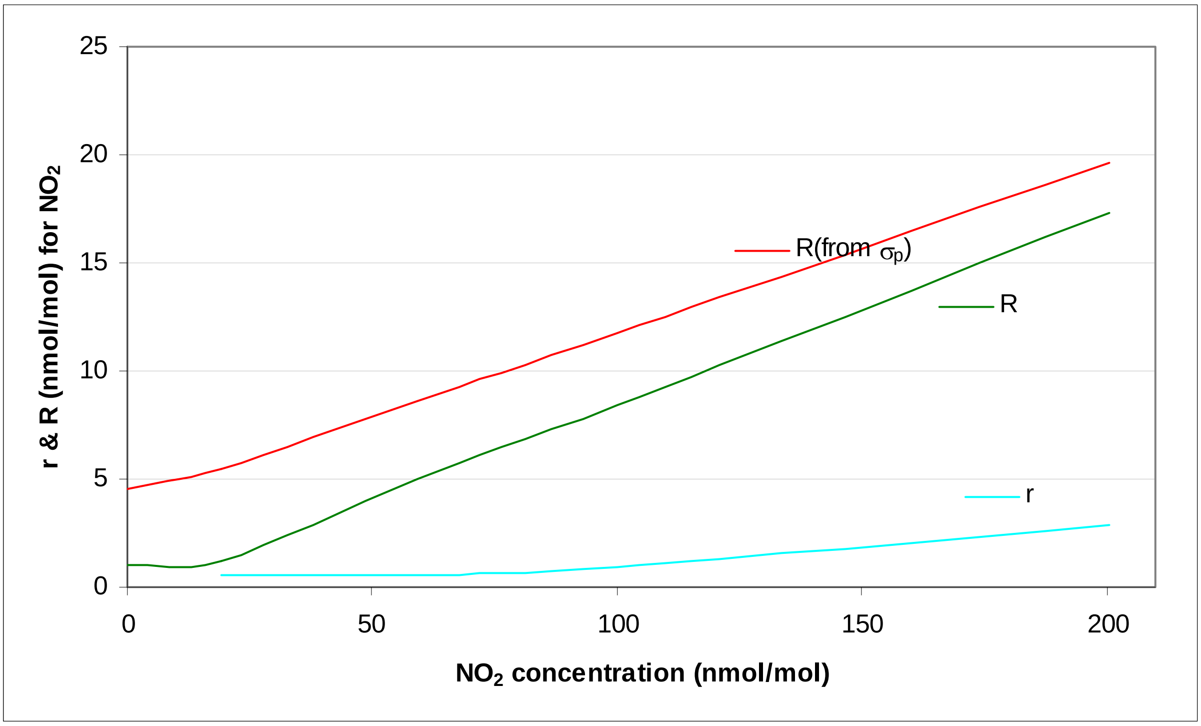

Figure 29: The R and r of NO_2 standard measurement method as a function of concentration*.

*No simultaneous NO, NO_2 data are available for these runs.

SO_2 data (nmol/mol)			
AQUILA LABS			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.1		1.1	
4.9	0.2	0.4	
19.5	0.2	0.5	
43.9	0.7	2.6	
127.8	0.9	6.0	4.7%

Table 26:The R and r of SO_2 standard measurement method.

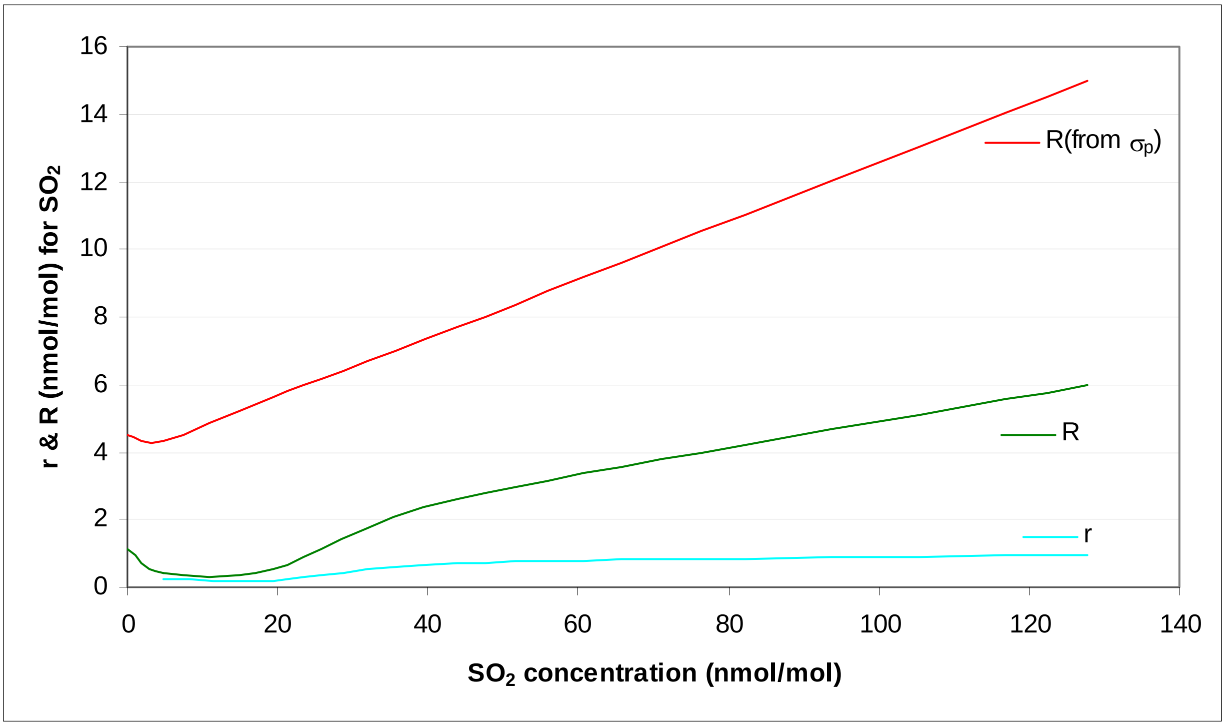

Figure 30: The R and r of SO_2 standard measurement method as a function of concentration.

O_3 data (nmol/mol)			
AQUILA LABS			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.3		0.8	
19.7	0.1	1.7	
59.4	0.4	4.1	
98.8	1.3	6.8	
296.6	3.9	17.1	5.8%

Table 27: The R and r of O_3 standard measurement method.

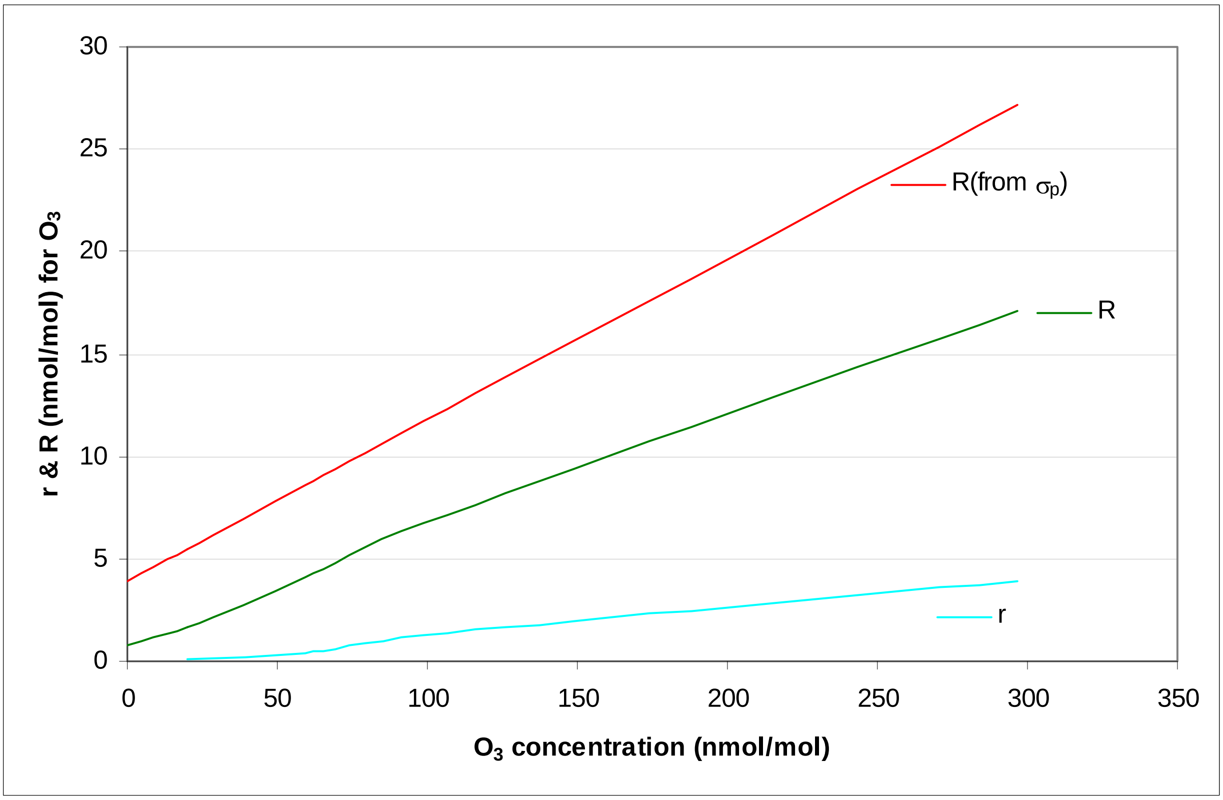

Figure 31: The R and r of O_3 standard measurement method as a function of concentration.

European Commission

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Abstract

From the 20th to the 25th of September 2009 in Langen (DE), 4 national reference laboratories (NRL) of AQUILA network and 3 laboratories of the World Health Organisation (WHO) Euro-Region met for an interlaboratory comparison exercise (IE) to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO_2, NO, NO_2 and O_3).

Most of the laboratories participating in the IE used automated CEN reference methods, which are mandatory in the EU, while some laboratories of the WHO Euro-Region performed analysis using manual methods.
In this report proficiency evaluation was made at different degrees for each laboratory taking into account the differences in the methodologies and the completeness of the information provided by participants. For the laboratories who expressed their uncertainty, performance was evaluated using two criteria, providing information on their proficiency to the European Commission and supporting the national quality control systems.

In terms of criteria imposed by the European Commission (that are not mandatory for WHO laboratories), 71% of the results reported by National Reference Laboratories (AQUILA network) were good both in terms of measured values and reported uncertainties. Another 23% of the results had good measured values, but the reported uncertainties were either too high (19%) or too small (4%). There were neither questionable nor unacceptable values.

AQUILA laboratories presented good comparability among participants for NO_2, O_3, and SO_2. The relative reproducibility limit for NO was above the objective deriving from the standard deviation for proficiency assessment.

For WHO laboratories using automated techniques, the results are satisfactory for SO_2, NO_2 and NO measurement methods, while one laboratory needs further investigation of their O_3 measurements.
The laboratory using manual methods presented results comparable to those of the automated methods for NO and O_3 but there were questionable results for NO_2 and SO_2 and unsatisfactory results for NO_2.

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