ISSN 1831-9424

European Commission

PROFICIENCY TESTING SCHEME, Measurements of inorganic gaseous pollutants (SO2, CO, O3, NO and NO2) in filtered ambient air, 18-21 March 2024 Ispra, Italy

European Commission harmonisation programme for air quality measurements

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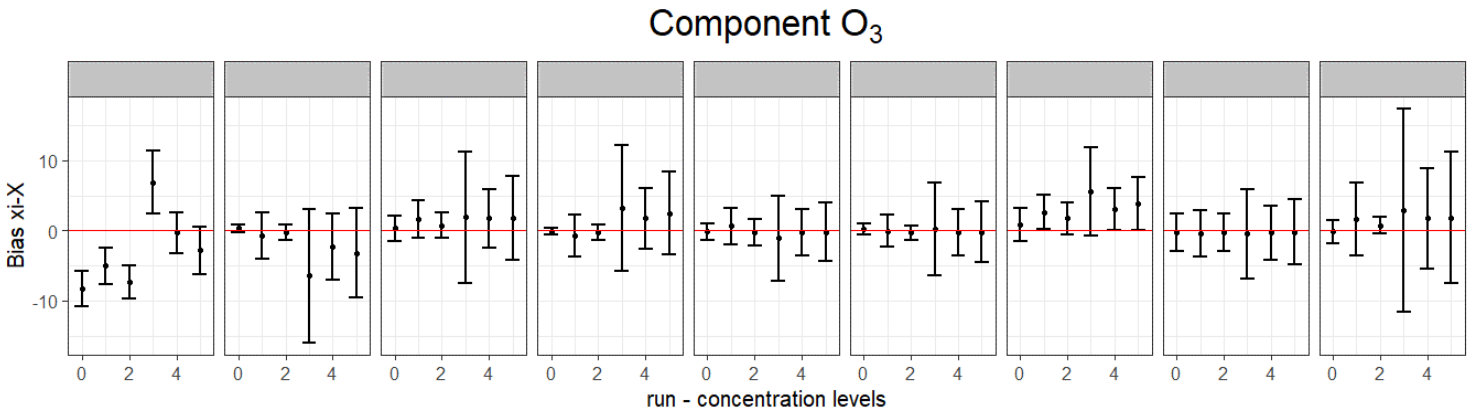
2024



Joint Research Centre

EUR 40125

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EU Science Hub
https://joint-research-centre.ec.europa.eu

JRC139409

EUR 40125

PDF ISBN 978-92-68-22422-9 ISSN 1831-9424 doi:10.2760/1771834 KJ-01-24-163-EN-N

Luxembourg: Publications Office of the European Union, 2024

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How to cite this report: European Commission, Joint Research Centre, Barbiere, M.G., Tarricone, C. and Borowiak, A., *PROFICIENCY TESTING SCHEME, Measurements of inorganic gaseous pollutants (SO2, CO, O3, NO and NO2) in filtered ambient air, 18-21 March 2024 Ispra, Italy*, Publications Office of the European Union, Luxembourg, 2024, https://data.europa.eu/doi/10.2760/1771834, JRC139409.

Contents

PROFICIENCY TESTING SCHEME

Measurement of inorganic gaseous pollutants (SO_2, CO, O_3, NO and NO_2) in filtered ambient air (18-21 March 2024, Ispra-Italy)

European Commission harmonisation programme
for air quality measurements

Barbiere M.G., Tarricone C., Borowiak A.

PTP N° 0018 P

Abstract

Within the harmonisation programme of Air Quality monitoring in Europe the European Reference Laboratory of Air Pollution (ERLAP) organises Proficiency Tests (PT).
From **18-21 March 2024**, eleven Laboratories of AQUILA (Network of European Air Quality Reference Laboratories, including ERLAP) gathered in Ispra, Italy, for a laboratory comparison exercise in Ispra (IT) to assess their proficiency in analysing inorganic gaseous air pollutants (NO, NO_2, SO_2, CO and O_3), covered by the European Air Quality Directive 2008/50 EC [1] and its last amendments 2015/1480/EC [42].

Ecomaks laboratory did not participate to O_3 and ACES laboratory to SO and CO_2 measurements, respectively.

The proficiency evaluation, where each participant's bias was compared to two criteria (z/z'-score and En-score), provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system. In agreement with all participants an evaluation of SO_2 concentration measured as interference during NO_x measurement has been carried out.

Evaluation based on z/z'-scores indicated that **89.2%** of the reported results were satisfactory. In contrast, consideration of the En-score revealed that **78.8%** of all values met satisfactory criteria. Overall, the performance for both indicators was below the average typically achieved in exercises of this type.

Considering the reproducibility evaluation, the results among AQUILA participants at the highest generated concentration levels are 9.9% for CO, 12% for NO, 11% for NO_2, 4.5% for O_3, and 11% for SO_2, all of which fall within the objectives derived from criteria set by EN standards. However, NO, NO_2 and SO_2 show a poor performance, in comparison to the reference value of this PT.

Acknowledgements

Thank you for the participation to:
MARLIERE Fabrice, NATHALIE Bocquet, DÉZSI Viktor, PÓLAY Gábor, DELANEY Lin, RUANE Cathal, BAKRADZE Georgijs, PODSKOCIJS Valters, DAUGE Franck, MARSTEEN Leif, FRACZKOWSKI Tomasz, PINDEL Andrzej, CASIMIRO Susana, MARTINS Ana, BOSKOVIC Stefan, DURICIC Aleksandar, IVANC Natalija, MIKLAVŽINA Iztok, GRAHAM Emelie, PFALLER Stefan.

	NAME	VERSION	DATE
Editing	A. BOROWIAK (PT Coordinator) M. BARBIERE (Technician/QO) C. TARRICONE (Technician)	FINAL REV. 0	30/07/2024
Review	JRC Editorial Review Board (proof reading check with minor remarks)	FINAL REV. 1	03/10/2024
Approval	F. PEKAR (Head of Unit)	FINAL REV. 1	20/09/2024
Authorization	P. SZYMANSKI (Director)	FINAL REV. 1	22/11/2024

1 Introduction

The Directive 2008/50/EC [1] and its last amendments 2015/1480/EC [42] on ambient air quality and cleaner air for Europe sets a framework for a harmonised air quality assessment in Europe.

One important objective of the Directive [1] is that the ambient air quality shall be assessed based on common methods and criteria. It deals with the air pollutants sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and nitrogen monoxide (NO), particulate matter, lead, benzene, carbon monoxide (CO) and ozone (O_3). Among others it specifies the reference methods for measurements and Data Quality Objectives (DQOs) for the accuracy of measurements.

The European Commission (EC) has supported the development and publication of reference measurement methods for CO [2], SO_2 [3], NO-NO_2 [4] and O_3 [5] as European standards. Appropriate calibration methods [6], [7] and [8] have been standardised by the International Organization for Standardization (ISO).

As foreseen in the Air Quality Directive [1, 42], the European Reference Laboratory of Air Pollution (ERLAP) of the Directorate for Energy, Mobility and Climate at the Joint Research Centre (JRC) organises Proficiency Tests (PT) to assess and improve the status of comparability of measurements of National Reference Laboratories (NRL) of the Member States of the European Union.

The World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin (WHO CC) is carrying out similar activities since 1994 [9] [10], [24], [31], [35], [38], [45] and [50], but with a view to obtaining harmonised air quality data for health related studies. Their programme integrates within the WHO EURO region, which includes public health institutes and other national institutes - especially from Central Eastern Europe, Caucasus and countries from Central Asia.

Starting in 2004, it has been decided to bring together the efforts of both the JRC-ERLAP and WHO CC and to coordinate activities as far as possible, with a view to optimise resources and improve international harmonisation.

This report deals with the PT that took place in the period **18-21 of March 2024** in Ispra (IT).

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

ERLAP is accredited to the standard ISO 17043 for the measurement of these air pollutants and EN standard methods used during this proficiency test (EN 14211:2012-NO/NO_2, EN 14212:2012-SO_2, EN 14625:2012-O_3, EN 14626:2012-CO) as proved by the certificates in Annex E.

The methodology for the organisation of PT was developed by ERLAP in collaboration with AQUILA and is described in a paper on the organisation of laboratory comparison exercises for gaseous air pollutants [12].

This evaluation scheme was adopted by AQUILA in December 2008 and has been applied to all PT since then. The evaluation scheme implements the z/z'-score method [13] as performance indicator. According to the above-mentioned document [12], NRLs with an unsatisfactory performance in the z/z'-score evaluation (one unsatisfactory or two questionable results per parameter) are asked to repeat their participation in the following PT in order to demonstrate remediation measures [12].

In addition, considering that the evaluation scheme should be useful to participants for accreditation according to ISO 17025, they are requested to include their measurement uncertainty. Hence, participants' results (measurement values and uncertainties) are also compared to the reference values applying the En–score method [13].

Besides the proficiency of participating laboratories, the reproducibility of standardised measurement methods [14], [15] and [16] are evaluated as well. This group evaluation is a useful indicator of trends in measurement quality over different proficiency tests.

2 Proficiency test organisation

The PT was announced in **September 2023** to the members of the AQUILA network and the WHO CC representative. Registration was opened in **November 2023** and closed the first week of **March 2024**.

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

The participants were invited to arrive on **Monday, 18th March 2024**, for the installation of their equipment. The calibration of NOx and O_3 analysers was carried out the morning of the following day and the generation of NOx and O_3 gas mixtures started at 11:00 on Tuesday.

The calibration of SO_2 and CO analysers was carried out on Wednesday afternoon and the generation of CO and SO_2 gas mixtures started at 20:00 of the same day.

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

3 Participants

All participants (Table 1) were organisations dealing with the routine ambient air monitoring or institutions involved in environmental or public health protection. The national representatives came from Sweden, Portugal, Slovenia, Serbia, Ireland, Poland, Hungary, France, Latvia and Norway.

Table 1: List of participating organizations.

Laboratory Acronym	Complete laboratory name	Country
ACES	Stockholm University	SE
APA	Agencia Portuguesa Do Ambiente	PT
ARSO	Slovenian Environment Agency	SI
Ecomaks	Ecomaks Solutions	RS
EPA	Environmental Protection Agency	IE
ERLAP	European Reference Laboratory for Air Pollution	IT
GIOS	Chief Inspectorate of Environmental Protection	PL
HMS	Hungarian Meteorological Service	HU
INERIS	Institut National de l'Environnement Industriel et des Risques	FR
LVGMC	Latvian Environment, Geology and Meteorology Centre	LV
NILU	Norwegian Institute for Air Research	NO

Source: JRC 2024

The following Table 2 reports the manufacturer and model of the instrumentations used by every participant during the Proficiency Test, including those used in the calculation of the reference values. The list contains technical information and cannot be considered as an implicit or explicit endorsement by the organisers of any specific instrumentation. This list is used to identify presence of clusters during the data evaluation.

ACES laboratory didn't participate to the testing exercise for CO and SO_2 and Ecomaks laboratory for O_3 measurements.

Table 2: List of instruments used by participants.

Laboratory	Analyser SO_2	Analyser CO	Analyser NO	Analyser O_3
ACES	/	/	Environnement SA AS32M	Environnement SA 0342e
APA	Thermo FS 43i	Thermo FS 48i	Thermo FS 42i	Thermo FS 49i
ARSO	Horiba APSA 370	Horiba APMA 370	Horiba APNA 370	Thermo FS 49C
Ecomaks	Teledyne API T100	Teledyne API T300	Teledyne API T200	/
EPA	Teledyne API T100	Teledyne API T300	Teledyne API T200	Teledyne API T400
ERLAP	Thermo FS 43 i-TLE	Horiba APMA 370	Thermo FS 42i	Thermo FS 49i
GIOS	Horiba APSA 370	Horiba APMA 370	Teledyne API T200	Horiba APOA-370
HMS	Thermo FS 43 i-TLE	Thermo FS 48i	Thermo FS 42i	Thermo FS TEI 49 i
INERIS	Teledyne API T100	Horiba APMA 370	Horiba APNA 370	Thermo FS TEI 49 i
LVGMC	Teledyne API T100	Teledyne API T300	Teledyne API T200	Teledyne API T400
NILU	Horiba APSA 370	Horiba APMA 370	Horiba APNA 370	Horiba APOA-370

Source: JRC 2024

4 Preparation of test mixtures

The ERLAP PT facility has been described in several reports [17], [18]. During this PT, gas mixtures were prepared for SO_2, CO, O_3, NO and NO_2 at concentration levels around limit values, critical levels and assessment thresholds set by the European Air Quality Directive [1].

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

Run	Component	Day	Start time	Duration	NO	NO_2	O_3	SO_2	CO
				h	nmol/mol				µmol/mol
	/	1st	09:00		Installation				
	/	2nd	08:00	3	Calibration				
0	$NO-NO_2-O_3$	2nd	11:00	1	Zero air				
1	$NO-NO_2$	2nd	12:00	2	200	0			
2	$NO-NO_2$	2nd	14:00	2	190	10			
1	O_3	2nd	16:00	2			60		
3	$NO-NO_2$	2nd	18:00	2	30	0			
4	$NO-NO_2$	2nd	20:00	2	20	10			
2	O_3	2nd	22:00	2			20		
5	$NO-NO_2$	3rd	00:00	2	60	0			
6	$NO-NO_2$	3rd	02:00	2	45	25			
3	O_3	3rd	04:00	2			180		
7	$NO-NO_2$	3rd	06:00	2	480	7		X	
8	$NO-NO_2$	3rd	08:00	2	280	200		X	
4	O_3	3rd	10:00	2			90		
9	$NO-NO_2$	3rd	12:00	2	300	4		X	
10	$NO-NO_2$	3rd	14:00	2	180	120		X	
5	O_3	3rd	16:00	2			120		
	/	3rd	18:00	2	Calibration				
0	$CO-SO_2$	3rd	20:00	1				Zero air	
1	$CO-SO_2$	3rd	21:00	2				120	0.7
2	$CO-SO_2$	3rd	23:00	2				35	9
3	$CO-SO_2$	4th	01:00	2				5	1
4	$CO-SO_2$	4th	03:00	2				15	2
5	$CO-SO_2$	4th	05:00	2				50	5
		4th	07:00	2	Zero air (not to be reported)				
		4th	09:00	END					

Source: JRC 2024

The sequence program of generated test concentration requested is given in Table 3. In addition, the PT provider, in agreement with the participants, requested also the concentrations of NO_2 and SO_2 indicated in Table 3 with an X.

The test mixtures were prepared by gas dilution from cylinders containing high concentrations of NO, SO_2, or CO using thermal mass flow controllers [8]. O_3 was added using an ozone generator and NO_2 was produced applying the gas phase titration method [19] in a condition of NO excess or as a possible presence of NO_2 in NO cylinders.
The participants were required to report three half-hour-mean measurements for each concentration level (run). Zero value concentration levels were generated for one hour and was requested to be reported one half-hour-mean measurement.

5 The evaluation of laboratory's measurement proficiency

To evaluate the participant's measurement proficiency, the methodology described in ISO 13528 [13] was applied and measurement results of ERLAP were used as the reference values [12].

The traceability of ERLAP's measurement results and the reference values list 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.

In Annex B for each participant and for each run, the values of measurement submitted, the mean value, the uncertainties, σ_{pt} calculated, z-score or z'-score (z/z'-score) and En-score are reported. The data are reported in a table and a graphical format, with all values plotted against the established reference value.

As described in the AQUILA document 37 [12], the proficiency of the participants was assessed by calculating two performance indicators (z/z'-score and En-score).

The performance indicators z/z'-score verify if the difference between the participants measured value and the reference value remains within the limits of a common criterion. The selection of the appropriate indicator, z-score or z'-score, depends on whether the uncertainty of the reference value (u_{ref}) meets the criterion $u_{ref} < 0{,}3\sigma_{pt}$ from ISO 13528 (paragraph 9.2) [13]. When the criterion is met the z-score value is applied, in the other case z'-score is used. The second performance indicator (En-score) verifies if the difference between the participants measured values and reference value remains within the limits of a criterion calculated, from the uncertainty of the participant measurement result and the uncertainty of the reference value.

During the evaluation a process of detection of exceptional errors (error during typing, slip in performing the measurement or the calculation, wrong averaging interval, malfunction of instrumentation, etc.) is applied. In this procedure a data consistency evaluation is carried out as described in ISO 13528 [13].

Before the release of the draft report, laboratories showing clear blunders are requested to investigate the cause of discrepancies and are allowed to correct their results in case of identification of exceptional errors.

After blunders (exceptional error) data are considered definitive, and z/z'-scores calculation is used to estimate the participant performance.

5.1 z-score - z'–score

The z/z'- score performance indicators are calculated according to ISO 13528 (par. 9.4 and 9.5) [13] as:

Equation 1

$$\mathbf{z} = \frac{(\mathbf{x_{lab}} - \mathbf{X_{ref}})}{\sqrt{\boldsymbol{\sigma}_{\mathbf{pt}}^{\mathbf{2}}}} = \frac{(\mathbf{x_{lab}} - \mathbf{X_{ref}})}{\sqrt{(\mathbf{a} \cdot \mathbf{X_{ref}} + \mathbf{b})^{\mathbf{2}}}}$$

Equation 2

$$\mathbf{z'} = \frac{(\mathbf{x_{lab}} - \mathbf{X_{ref}})}{\sqrt{\boldsymbol{\sigma}_{\mathbf{pt}}^{\mathbf{2}} + \mathbf{u}_{\mathbf{ref}}^{\mathbf{2}}}} = \frac{(\mathbf{x_{lab}} - \mathbf{X_{ref}})}{\sqrt{(\mathbf{a} \cdot \mathbf{X_{ref}} + \mathbf{b})^{\mathbf{2}} + \mathbf{u}_{\mathbf{ref}}^{\mathbf{2}}}}$$

z = z-score
z' = z'-score
x_{lab} = participant average values
X_{ref} = reference value
u_{ref} = uncertainty of the reference value
σ_{pt} = Standard deviation for proficiency assessment
a = slope (see table 4)
b = intercept (see table 4)

In the NO_2, SO_2, CO and O_3 EN Standards [2, 3, 4, 5] the uncertainties for calibration gases used in ongoing quality control are prescribed. In fact, it is stated that maximum permitted expanded uncertainty for calibration gases at the calibration point (75% of certification range) is 5% and that 'zero gas' shall not give instrument reading higher than the detection limit. The 'standard deviation for proficiency assessment' (σ_{pt}) is derived in a fitness-for-purpose manner from requirements given in the EN standards, where in place of detection limits criteria, the specifications for purity of zero gas used in type approval as defined in EN Standards are taken.
Over the whole measurement range σ_{pt} is calculated by linear interpolation between the uncertainty of 2.5% at the calibration point (75% of certification range) and the uncertainty at zero level concentration ("b").

Table 4: Standard deviation for proficiency assessment (σ_{pt}).

Gas	a	b (nmol/mol)
SO_2	0.022	1
CO	0.024	100
O_3	0.020	1
NO	0.024	1
NO_2	0.028	1.4

Source: JRC 2024

σ_{pt} is a linear function of concentration (c) with parameters in Table 4 identified "**a**" as slope and "**b**" as intercept.

Equation 3

$$\boldsymbol{\sigma_{pt} = (a \cdot X_{ref}) + b}$$

σ_{pt} = Standard deviation for proficiency assessment
a = slope see table 4
X_{ref} = reference value
b = intercept see table 4

The parameters in table 4 have been discussed and agreed with the AQUILA network through a document named N37 [12].

The assessment of results in z/z`-score evaluation is made according to the following criteria:
$|z/z'| \leq 2$ are considered satisfactory.
$2 < |z/z'| < 3$ are considered questionable.
$|z/z'| \geq 3$ are considered unsatisfactory. Scores falling in this range are very unusual and are taken as evidence that an anomaly has occurred that should be investigated and corrected.

According to z/z'-score calculation, values between 2 and 3 are considered questionable and they deserve a specific check.

In this report, within all the results, many values were found unsatisfactory or questionable as reported in table 5.

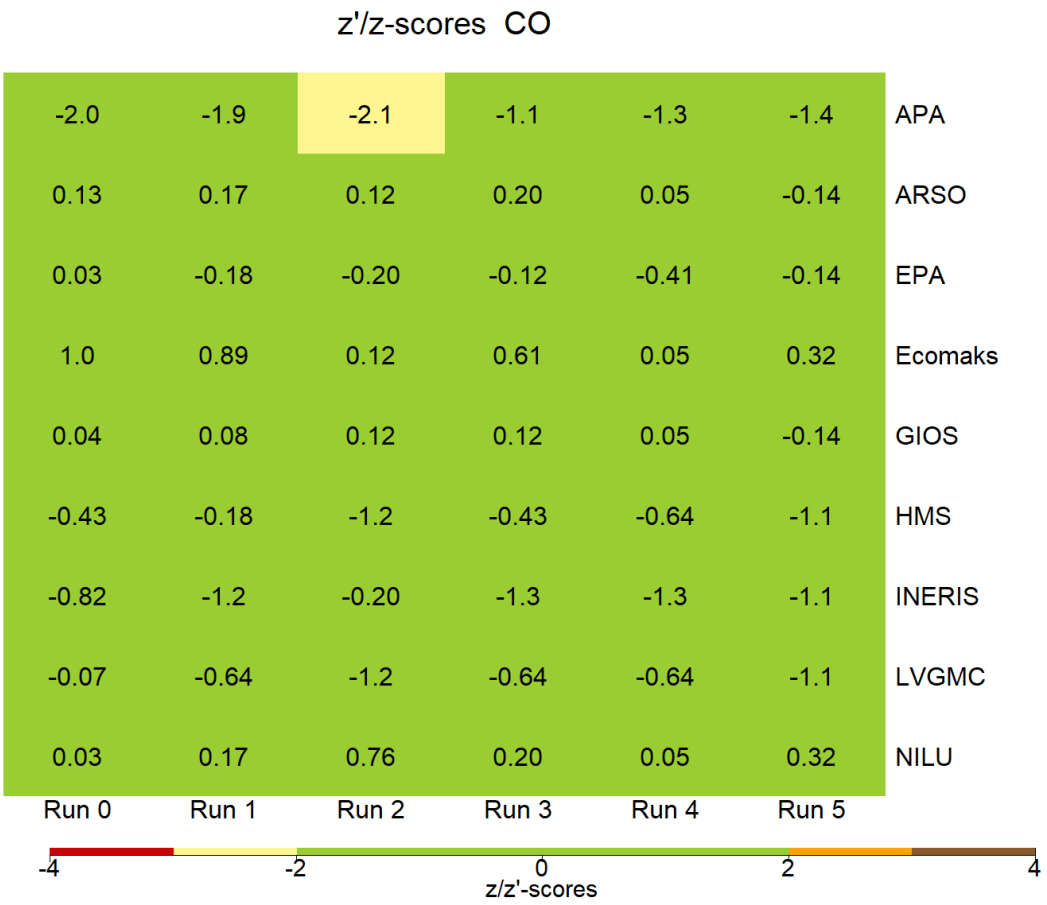
The overall performance of all participants related to the z/z'-score parameters is shown in Figures 1 to 5 as colored graphical matrix where on the x axis are shown the runs (concentration levels) and the y-axis the participants are plotted. The figures, through a bi-dimensional graphical representation, identifies, with different colors according to the criteria explained above, the participant's values of z/z'-score for each concentration level analysed during the PT.
The values of z/z'-score calculated for each participant are reported in the matrix cells.

Table 5: Unsatisfactory/questionable results according to z/z'-score.

Laboratory	Component	Run	z/z'-score value	z/z'-score evaluation
APA	CO	2	-2.1	questionable
ACES	NO	1	-5.6	unsatisfactory
APA	NO	1	-2.1	questionable
ACES	NO	2	-5.4	unsatisfactory
APA	NO	2	-2.0	questionable
ACES	NO	3	-3.3	unsatisfactory
ACES	NO	4	-2.4	questionable
ACES	NO	5	-4.0	unsatisfactory
LVGMC	NO	5	-2.4	questionable
ACES	NO	6	-3.4	unsatisfactory
ACES	NO	7	-3.2	unsatisfactory
LVGMC	NO	7	-2.4	questionable
ACES	NO	8	-3.8	unsatisfactory
LVGMC	NO	8	-2.5	questionable
ACES	NO	9	-4.2	unsatisfactory
LVGMC	NO	9	-3.0	unsatisfactory
ACES	NO	10	-4.3	unsatisfactory
LVGMC	NO	10	-2.7	questionable
INERIS	NO_2	1	-2.3	questionable
INERIS	NO_2	2	-3.0	unsatisfactory
APA	NO_2	7	-2.1	questionable
EPA	NO_2	7	-5.0	unsatisfactory
GIOS	NO_2	7	-3.0	questionable
INERIS	NO_2	7	-4.2	unsatisfactory
EPA	NO_2	8	-2.1	questionable
EPA	NO_2	9	-4.0	unsatisfactory
INERIS	NO_2	9	-2.5	questionable
EPA	NO_2	10	-2.0	questionable
ACES	O_3	0	-8.2	unsatisfactory
ACES	O_3	1	-2.2	questionable
ACES	O_3	2	-5.1	unsatisfactory
APA	SO_2	1	-2.9	questionable
LVGMC	SO_2	1	3.8	unsatisfactory
LVGMC	SO_2	2	2.2	questionable
APA	SO_2	5	-2.0	questionable
LVGMC	SO_2	5	2.9	questionable

Source: JRC 2024

Figure 1: Graphical matrix of z/z'-score evaluations of CO measurements in µmol/mol



Source: JRC 2024

Underestimated unsatisfactory results are marked in red, in yellow underestimated questionable results, in green satisfactory results, in orange overestimated questionable results and in brown overestimated unsatisfactory results.

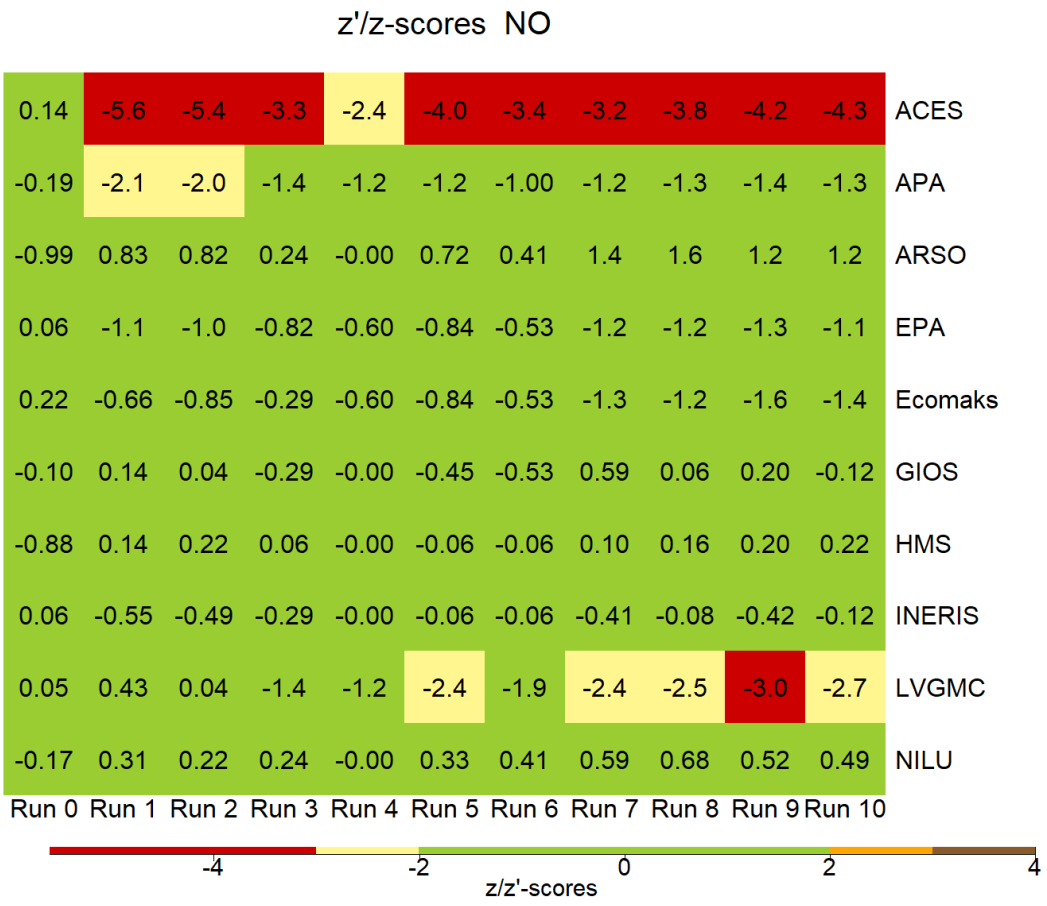
z/z'-score values are given for each participant and each tested concentration level (run).

For this pollutant, the graphical representation shows a general good performance of every participant for all concentration levels generated.

ACES laboratory didn't participate to the measurement of this pollutant.

Only 1 measurement of APA was found questionable.

Figure 2: Graphical matrix of z/z'-score evaluations of NO measurements in nmol/mol



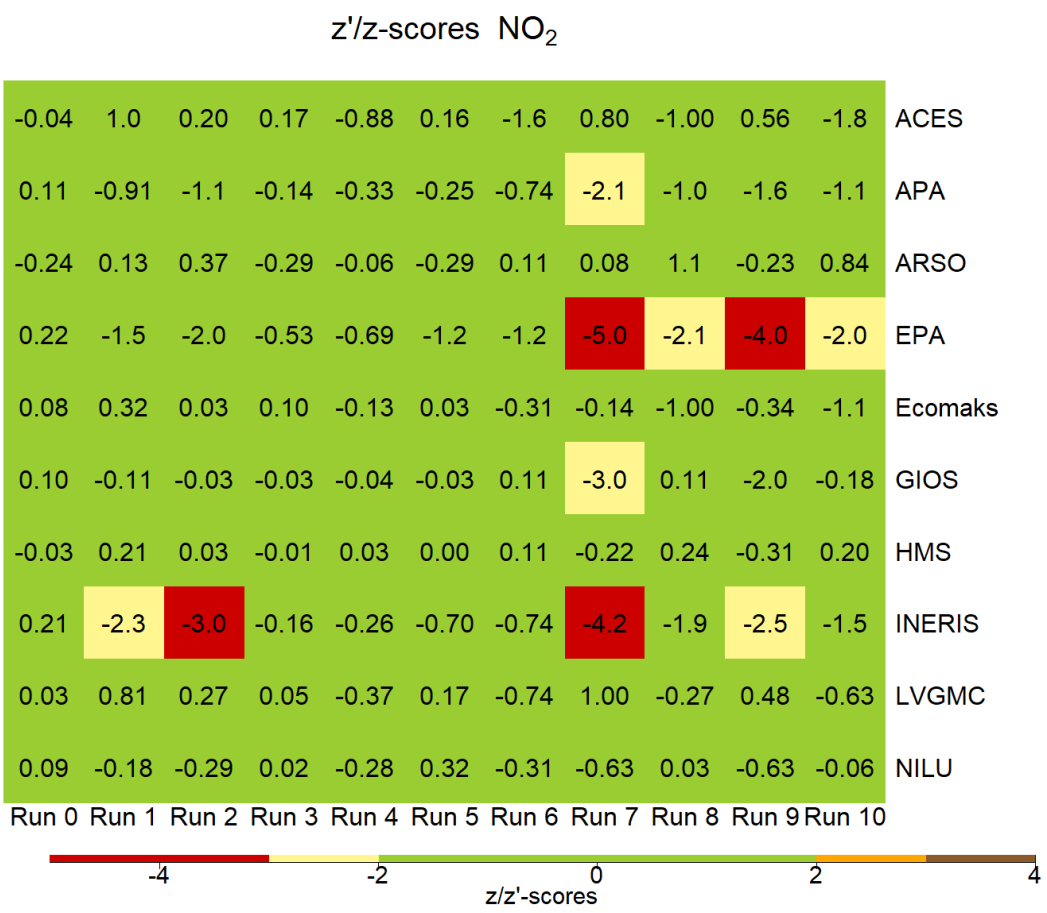
Source: JRC 2024

Underestimated unsatisfactory results are marked in red, in yellow underestimated questionable results, in green satisfactory results, in orange overestimated questionable results and in brown overestimated unsatisfactory results.

z/z'-score values are given for each participant and each tested concentration level (run).

The graphical depiction for this pollutant indicates an overall satisfactory performance, with the exception of three participants.
LVGMC recorded three results that raised concerns and one that was deemed unsatisfactory, ACES exhibited generally inferior performance across most concentration levels. A thorough investigation into the issue should be initiated, beginning with a verification of the standard gas utilized in the calibration process.
Regarding APA, there were two results that were considered questionable.

Figure 3: Graphical matrix of z/z'-score evaluations of NO_2 measurements in nmol/mol



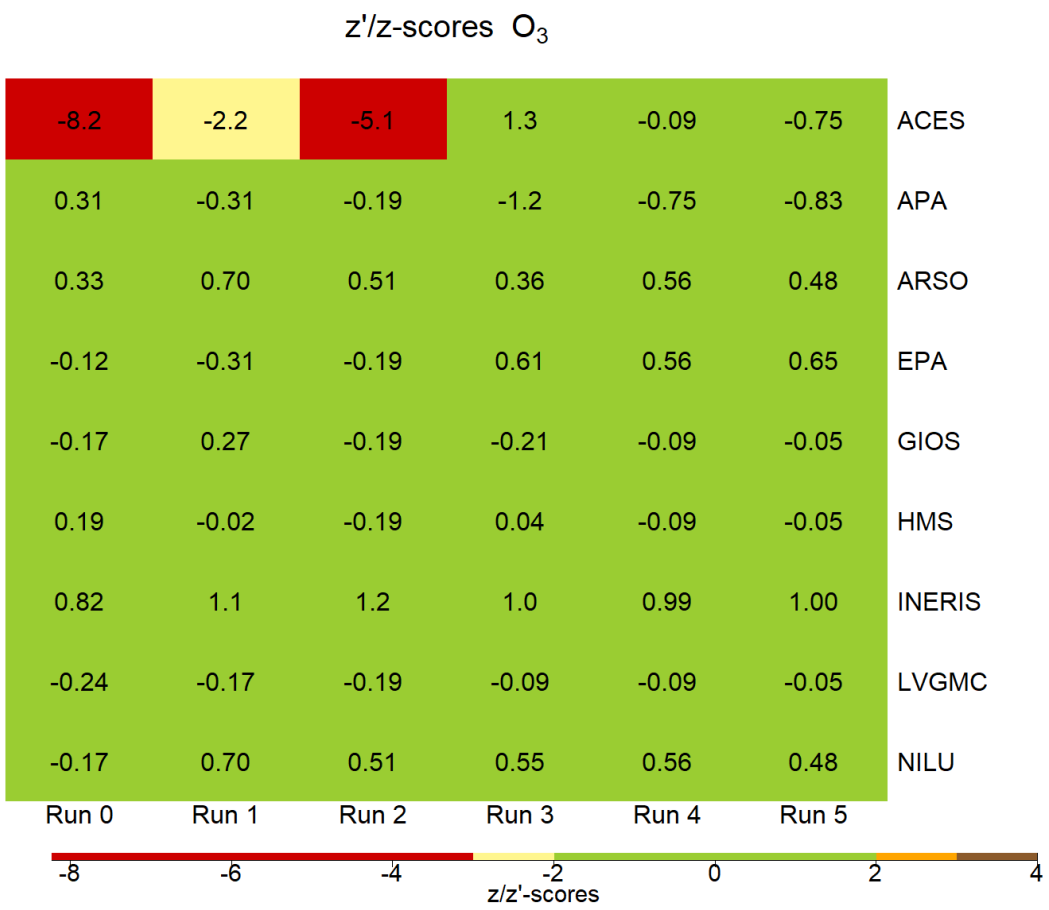
Source: JRC 2024

Underestimated unsatisfactory results are marked in red, in yellow underestimated questionable results, in green satisfactory results, in orange overestimated questionable results and in brown overestimated unsatisfactory results.
z/z'-score values are given for each participant and each tested concentration level (run).

For this pollutant, the graphical representation shows the majority of results as satisfactory for all concentration levels generated.

Only one measurement of APA was found questionable.
For EPA two values questionable and two unsatisfactory were identified for this pollutant measurement.
Only one measurement of GIOS was found questionable.
For INERIS two values questionable and two unsatisfactory were identified for this pollutant measurement.

Figure 4: Graphical matrix of z/z'-score evaluations of O_3 measurements in nmol/mol



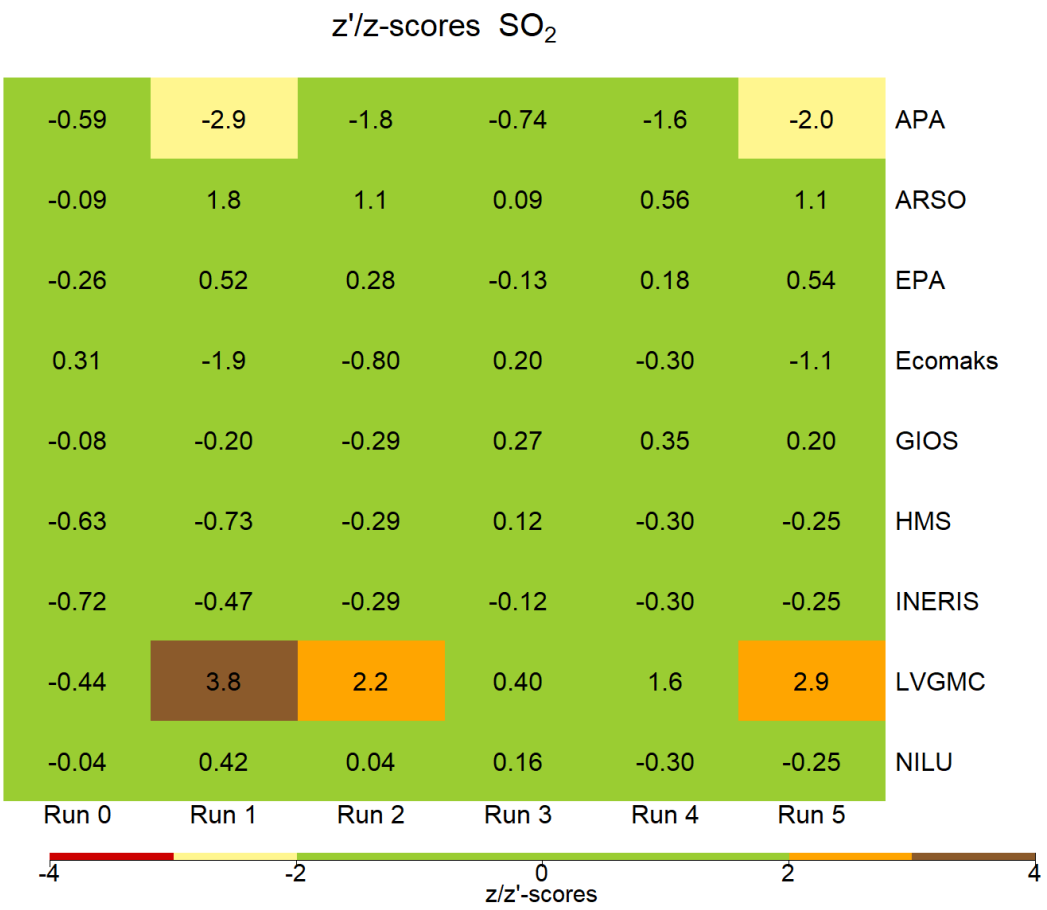
Source: JRC 2024

Underestimated results are highlighted in red for unsatisfactory outcomes and in yellow for questionable ones. Conversely, results meeting expectations are displayed in green, while those that exceeded expectations in a questionable manner are in orange, and clearly excessive unsatisfactory results are in brown.
z/z'-score values are given for each participant and each tested concentration level (run).

The visual depiction of the data indicates that nearly all participants performed well across all generated concentration levels for this pollutant. However, it should be noted that ACES yielded one questionable result and two unsatisfactory results.

Ecomaks laboratory didn't participate in measuring this particular pollutant.

Figure 5: Graphical matrix of z/z'-score evaluations of SO_2 measurements in nmol/mol



Source: JRC 2024

Underestimated unsatisfactory results are marked in red, in yellow underestimated questionable results, in green satisfactory results, in orange overestimated questionable results and in brown overestimated unsatisfactory results.
z/z'-score values are given for each participant and each tested concentration level (run).

ACES laboratory didn't participate to the measurement of this pollutant.

The graphical data for this pollutant illustrates that the majority of participants achieved satisfactory results across all the concentration levels produced. However, APA reported two questionable value and LVGMC, two of their recorded values were deemed questionable and one was considered unsatisfactory.

5.2 En-score

In order to evaluate the participant's ability to have results close to the reference values within their reported uncertainties, the En-score parameters (En) were calculated according to:

$$\textbf{Equation 4}$$
$$En = \frac{x_{lab} - X_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}}$$

En = En-score
x_{lab} = participant average values
X_{ref} = reference value
U_{lab}= expanded uncertainty of the participants
U_{ref}= expanded uncertainty of the reference value

The overall performance of all participants related to the En-score parameters is shown in Figures 6 to 15 as colored graphical matrix where on the x-axis are shown the run (concentration levels) and the y-axis the participants are plotted. The figures, through a bi-dimensional graphical representation, identifies, with different colors, the participant's values of En-score for each concentration level analysed during the PT.
Results with |En-score|<1 are considered satisfactory all the others are unsatisfactory.
The values of En-score calculated for each participant during the PT are reported in the matrix cells. At the bottom of each figure, the legend explains with different colors the identification of the results: in red are marked underestimated unsatisfactory results, in green satisfactory results and in brown overestimated unsatisfactory results. The En evaluations presented in Figures 6, 8, 10, 12, and 14 highlight some unsatisfactory results for different parameters and concentrations, as reported in table 6.
In Annex B, from table 11 to 20 are reported all En values calculated for each participant, parameter and concentration level.

Table 6: Unsatisfactory results according to En-score.

Laboratory	Component	Run	En-score	En evaluation
APA	CO	0	-7.9	unsatisfactory
HMS	CO	0	-1.8	unsatisfactory
APA	CO	1	-7.4	unsatisfactory
APA	CO	2	-3.1	unsatisfactory
HMS	CO	2	-1.5	unsatisfactory
APA	CO	3	-4.0	unsatisfactory
HMS	CO	3	-1.5	unsatisfactory
APA	CO	4	-3.7	unsatisfactory
EPA	CO	4	-1.0	unsatisfactory
HMS	CO	4	-1.7	unsatisfactory
APA	CO	5	-2.5	unsatisfactory
HMS	CO	5	-1.7	unsatisfactory
INERIS	CO	5	-1.1	unsatisfactory
ACES	NO	1	-9.9	unsatisfactory
APA	NO	1	-3.1	unsatisfactory
ACES	NO	2	-9.7	unsatisfactory
APA	NO	2	-3.0	unsatisfactory
ACES	NO	3	-3.5	unsatisfactory
APA	NO	3	-1.4	unsatisfactory
ACES	NO	4	-2.2	unsatisfactory
APA	NO	4	-1.1	unsatisfactory
ACES	NO	5	-5.4	unsatisfactory
APA	NO	5	-1.5	unsatisfactory

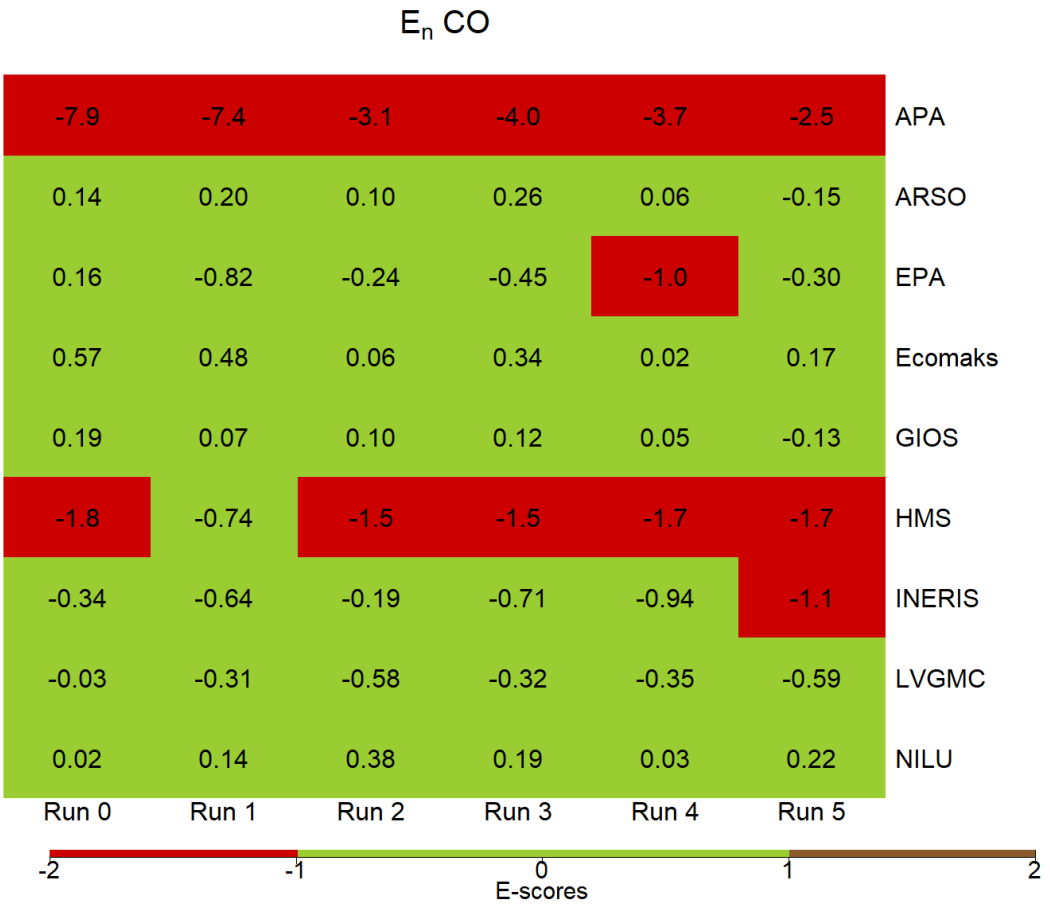
Laboratory	Component	Run	En-score	En evaluation
LVGMC	NO	5	-1.4	unsatisfactory
ACES	NO	6	-3.9	unsatisfactory
APA	NO	6	-1.1	unsatisfactory
LVGMC	NO	6	-1.3	unsatisfactory
ACES	NO	7	-5.4	unsatisfactory
APA	NO	7	-1.7	unsatisfactory
EPA	NO	7	-1.0	unsatisfactory
ACES	NO	8	-6.5	unsatisfactory
APA	NO	8	-1.9	unsatisfactory
ARSO	NO	8	1.1	unsatisfactory
EPA	NO	8	-1.0	unsatisfactory
LVGMC	NO	8	-1.0	unsatisfactory
ACES	NO	9	-7.3	unsatisfactory
APA	NO	9	-2.0	unsatisfactory
EPA	NO	9	-1.1	unsatisfactory
LVGMC	NO	9	-1.3	unsatisfactory
ACES	NO	10	-7.5	unsatisfactory
APA	NO	10	-2.0	unsatisfactory
EPA	NO	10	-1.0	unsatisfactory
LVGMC	NO	10	-1.2	unsatisfactory
EPA	NO_2	1	-1.2	unsatisfactory
INERIS	NO_2	1	-2.0	unsatisfactory
EPA	NO_2	2	-1.9	unsatisfactory
INERIS	NO_2	2	-2.9	unsatisfactory
EPA	NO_2	5	-1.2	unsatisfactory
ACES	NO_2	6	-2.0	unsatisfactory
EPA	NO_2	6	-1.5	unsatisfactory
APA	NO_2	7	-1.3	unsatisfactory
EPA	NO_2	7	-3.3	unsatisfactory
GIOS	NO_2	7	-1.9	unsatisfactory
INERIS	NO_2	7	-2.7	unsatisfactory
ACES	NO_2	8	-1.6	unsatisfactory
APA	NO_2	8	-1.5	unsatisfactory
EPA	NO_2	8	-2.1	unsatisfactory
INERIS	NO_2	8	-1.5	unsatisfactory
APA	NO_2	9	-1.2	unsatisfactory
EPA	NO_2	9	-3.1	unsatisfactory
GIOS	NO_2	9	-1.4	unsatisfactory
INERIS	NO_2	9	-1.9	unsatisfactory
ACES	NO_2	10	-2.9	unsatisfactory
APA	NO_2	10	-1.7	unsatisfactory
EPA	NO_2	10	-2.2	unsatisfactory
INERIS	NO_2	10	-1.3	unsatisfactory
ACES	O_3	0	-3.4	unsatisfactory
ACES	O_3	1	-1.9	unsatisfactory
INERIS	O_3	1	1.1	unsatisfactory
ACES	O_3	2	-3.1	unsatisfactory
ACES	O_3	3	1.5	unsatisfactory
INERIS	O_3	4	1.0	unsatisfactory
INERIS	O_3	5	1.0	unsatisfactory
APA	SO_2	1	-2.4	unsatisfactory
LVGMC	SO_2	1	1.6	unsatisfactory
APA	SO_2	2	-1.9	unsatisfactory
LVGMC	SO_2	2	1.4	unsatisfactory

Laboratory	Component	Run	En-score	En evaluation
APA	SO_2	4	-1.8	unsatisfactory
LVGMC	SO_2	4	1.3	unsatisfactory
APA	SO_2	5	-2.1	unsatisfactory
LVGMC	SO_2	5	1.6	unsatisfactory

Source: JRC 2024

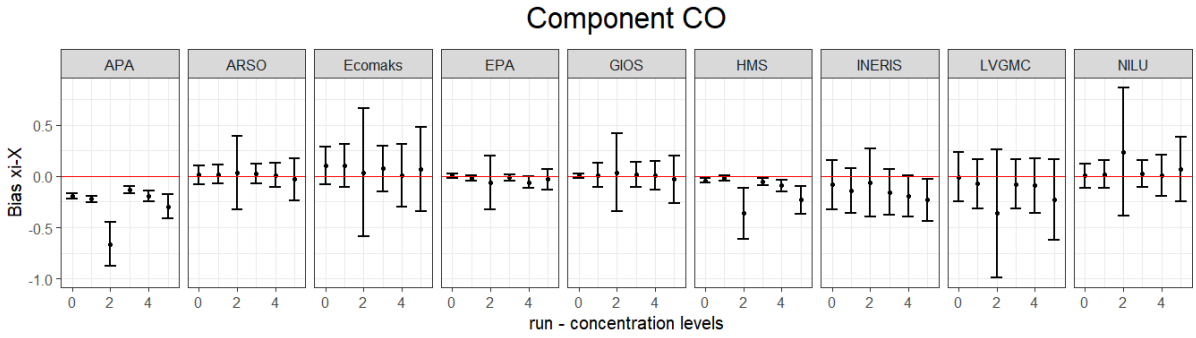
The differences between individual participants' values and reference values (bias x_{lab}-X_{ref}) are evaluated and presented for each concentration level in the Figures 7, 9, 11, 13, 15.
The expanded uncertainties reported by participants are shown in the graphs for each run as error bar.
These plots represent also the En-score evaluations where, considering the En criterion (|En-score|<1), all results are satisfactory if the error bars cross the red line representing the reference value.
Reported standard uncertainties of the participants, larger than the "standard deviation for proficiency assessments" (σ_{pt}), are considered not fit-for-purpose (see Annex B).

Figure 6: En-score for CO measurements in matrix view



Source: JRC 2024

Figure 7: Bias of participant's CO measurement results in µmol/mol

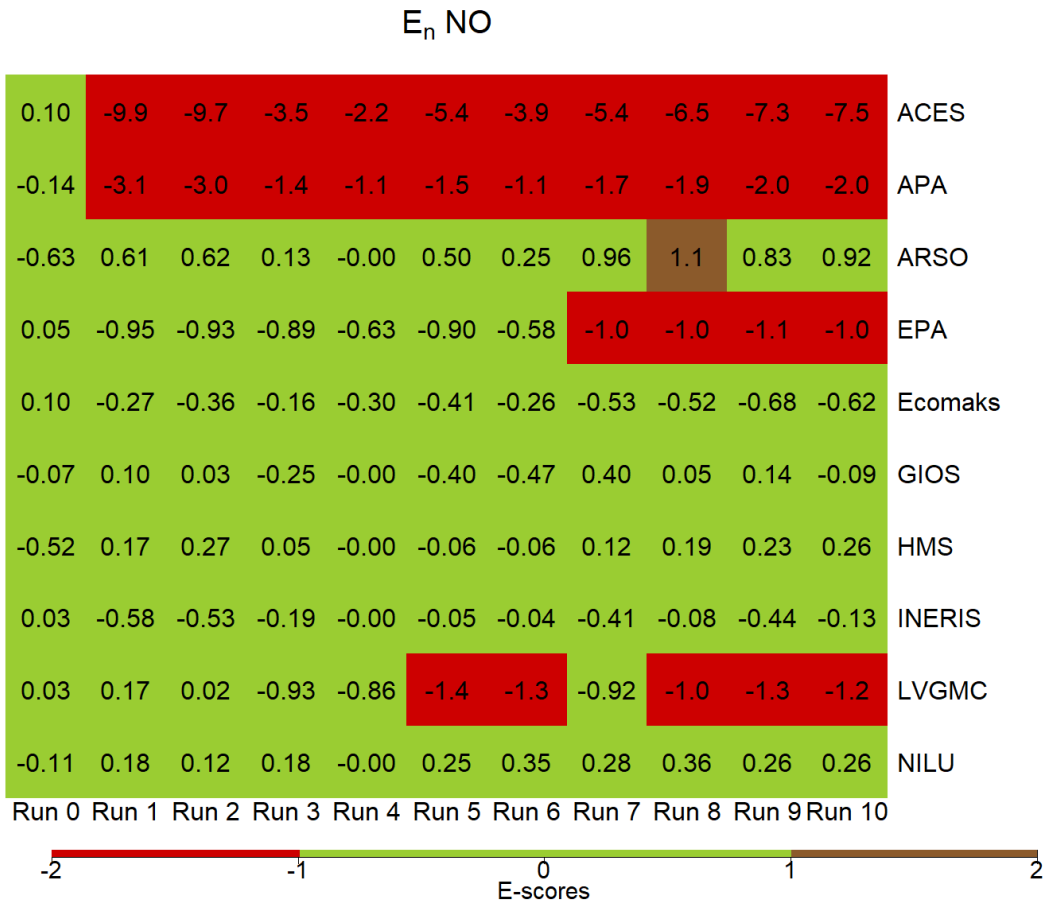


Source: JRC 2024

ACES laboratory didn't participate to the measurement of this pollutant.

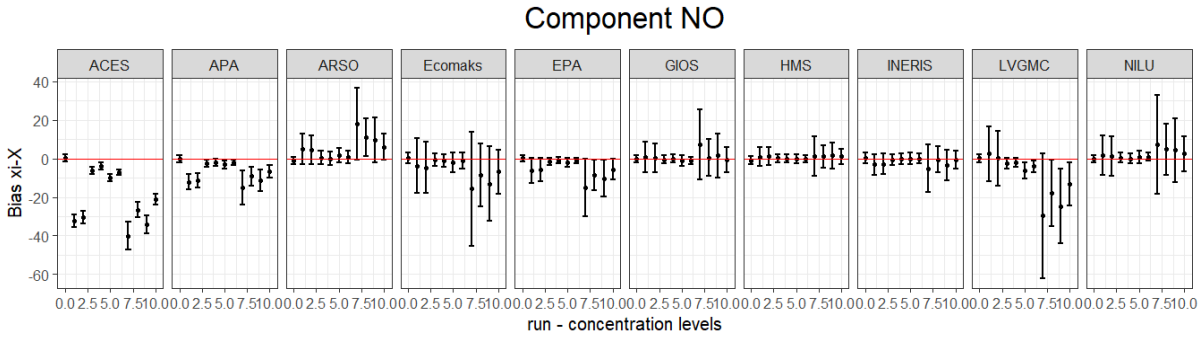
During the En-score evaluation of CO, only 1 measurement of EPA and INERIS was found above the limit while for HMS all values beside one are unsatisfactory and for APA all values are out of the limits. APA reported a small uncertainty and general lower results compared to the assigned value as shown in Fig.7.

Figure 8: En-score for NO measurements in nmol/mol in matrix view



Source: JRC 2024

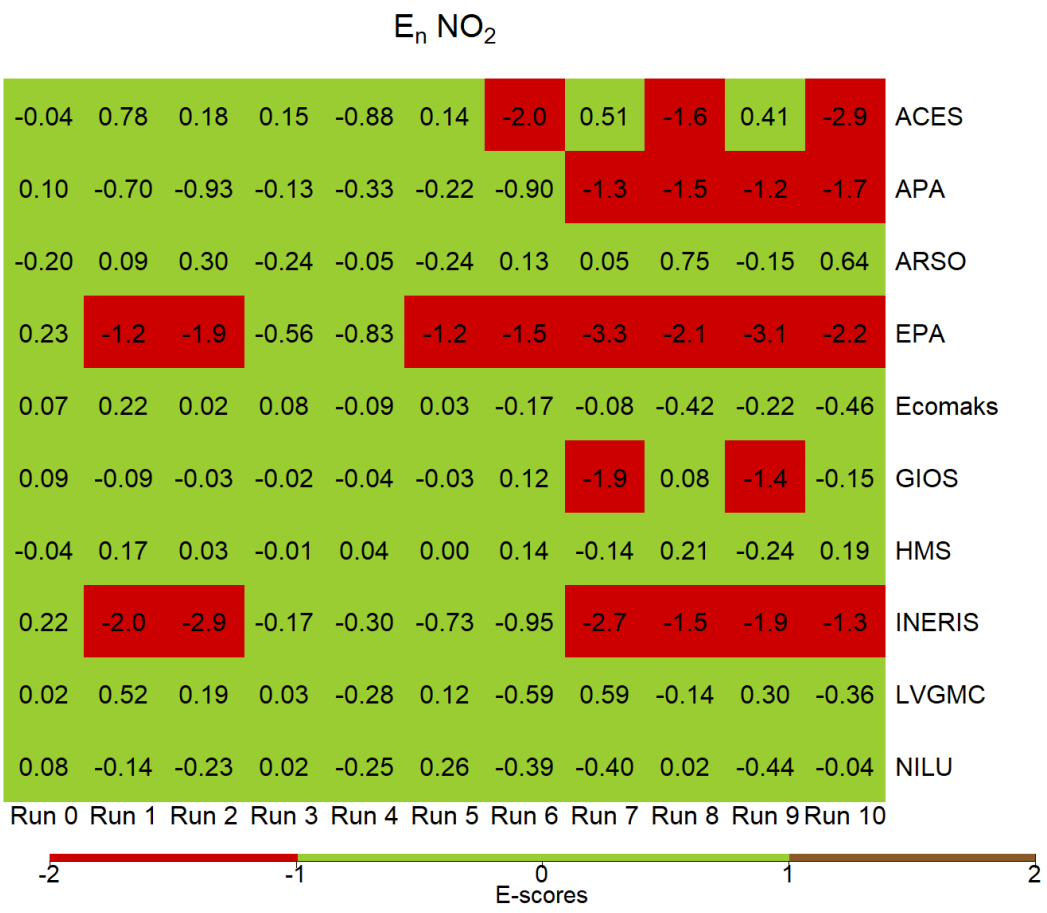
Figure 9: Bias of participant's NO measurement results in nmol/mol



Source: JRC 2024

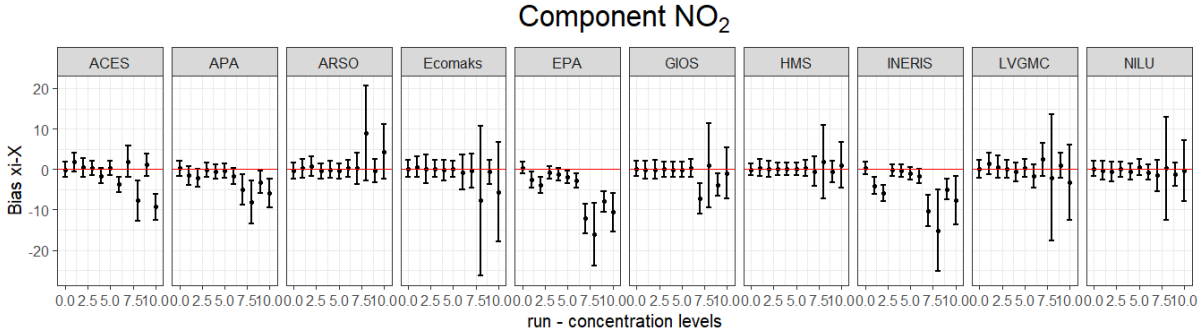
For this pollutant, four laboratories displayed numerous unsatisfactory values during the En-score evaluation. ACES and APA underestimated the measurements in almost all runs except for the zero level. ARSO reported a value that was slightly above the limit. EPA slightly underestimated four values. Five of the values submitted by LVGMC were found to be unsatisfactory.

Figure 10: En-score for NO_2 measurements in nmol/mol in matrix view



Source: JRC 2024

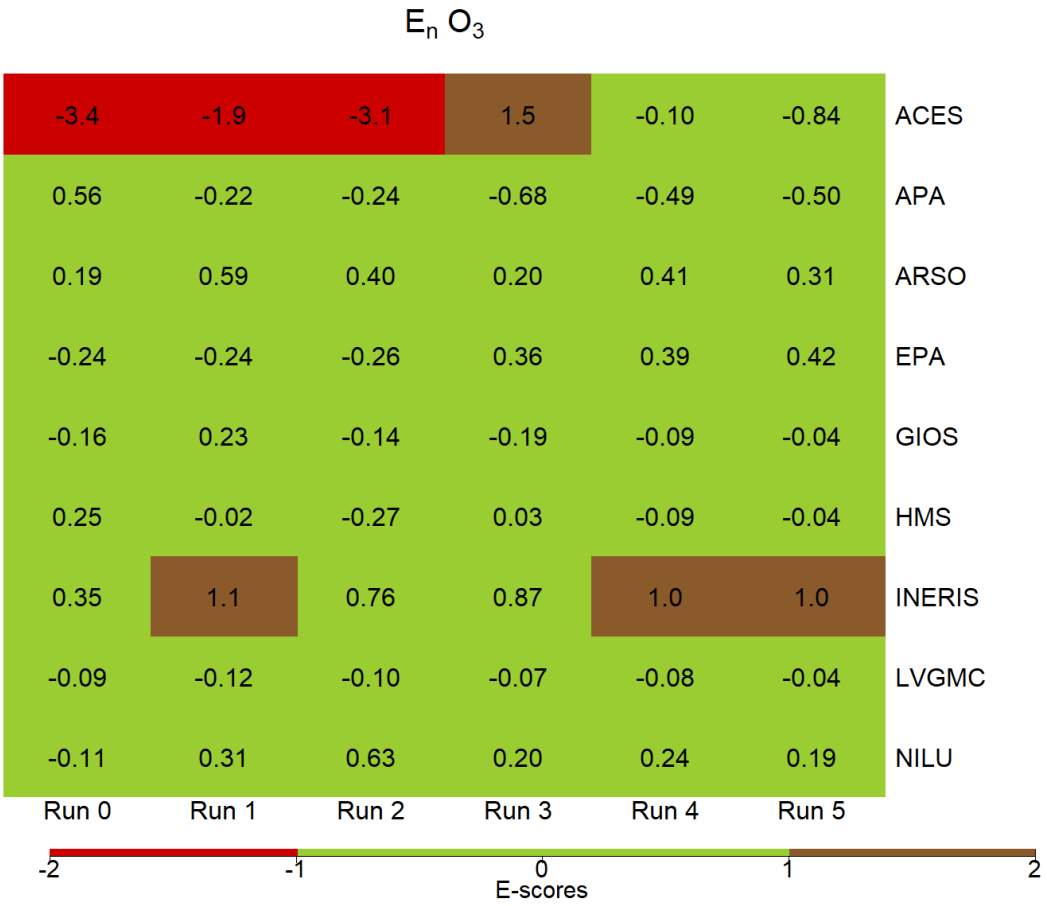
Figure 11: Bias of participant's NO_2 measurement results in nmol/mol.



Source: JRC 2024

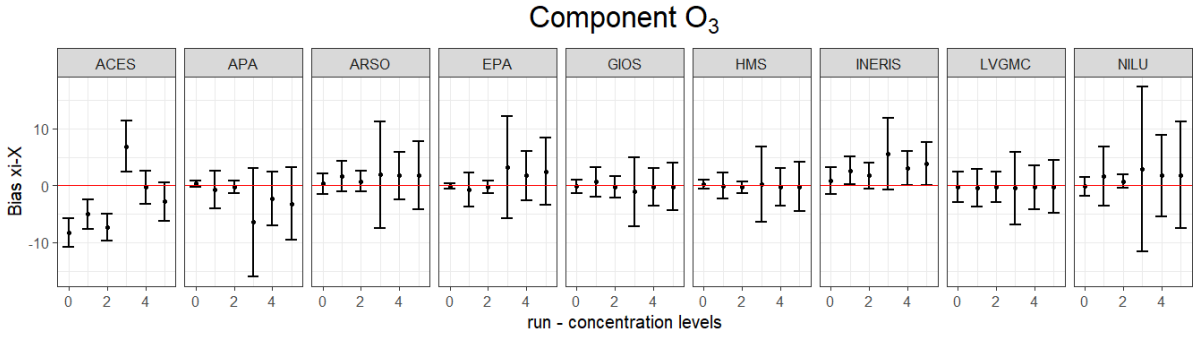
During the En-score evaluation, for this pollutant, both graphical representations show a general poor performance of half of the participants. ACES underestimated 3 values, APA underestimated 4 values, EPA underestimated seven of 11 runs, GIOS underestimated 2 values, INERIS underestimated 6 values.

Figure 12: En-score for O_3 measurements in nmol/mol in matrix view



Source: JRC 2024

Figure 13: Bias of participant's O_3 measurement results in nmol/mol

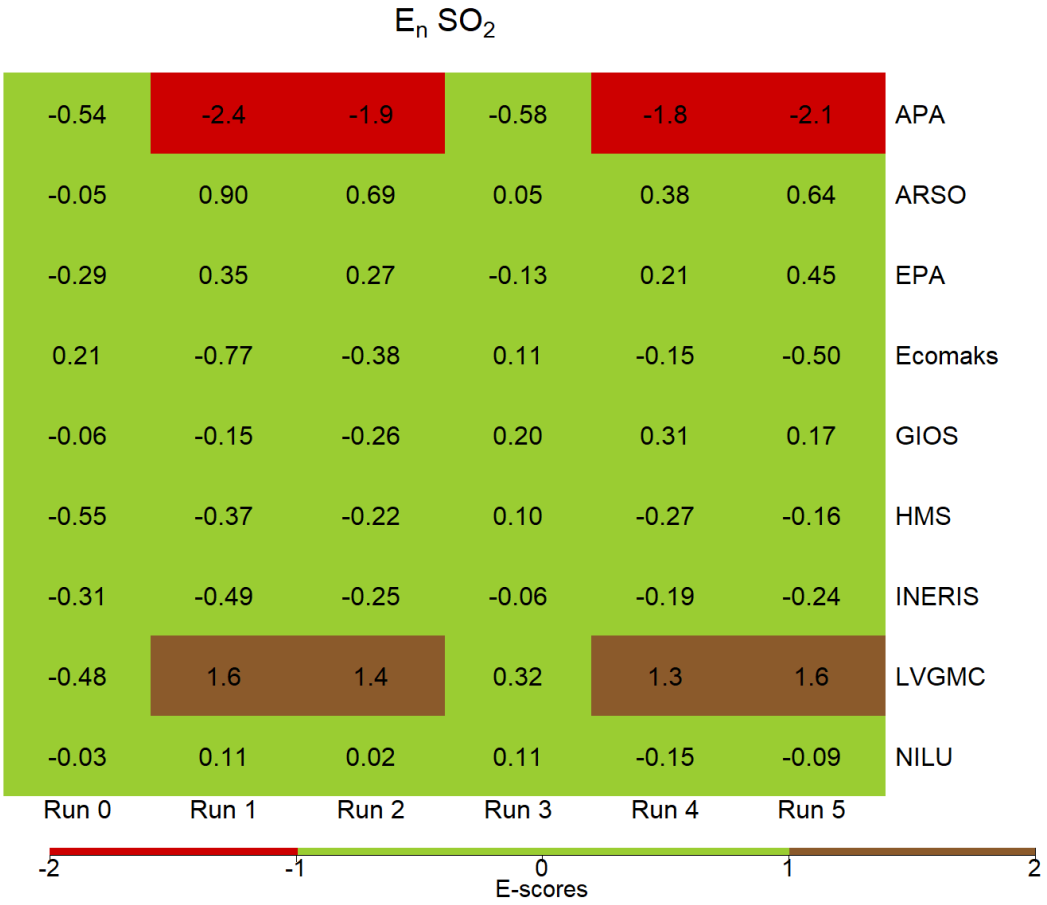


Source: JRC 2024

Ecomaks did not participate to the measurement of this pollutant.

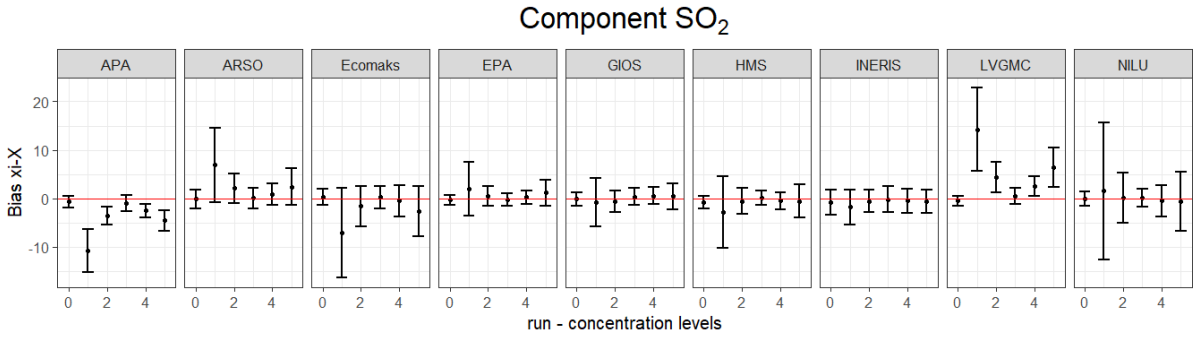
During the En-score evaluation, for this pollutant, both graphical representations show a general good performance of almost every participant, only ACES underestimated three values and overestimated one value. Three results of INERIS were slightly found overestimated.

Figure 14: En-score for SO_2 measurements in nmol/mol in matrix view



Source: JRC 2024

Figure 15: Bias of participant's SO_2 measurement results in nmol/mol



Source: JRC 2024

During the En-score evaluation, the graphical data for this pollutant illustrates that the majority of participants achieved satisfactory results across all the concentration levels produced.
In the case of LVGMC, four of their recorded values were found unsatisfactory while APA submitted four values that were found underestimated.

6 Conclusions

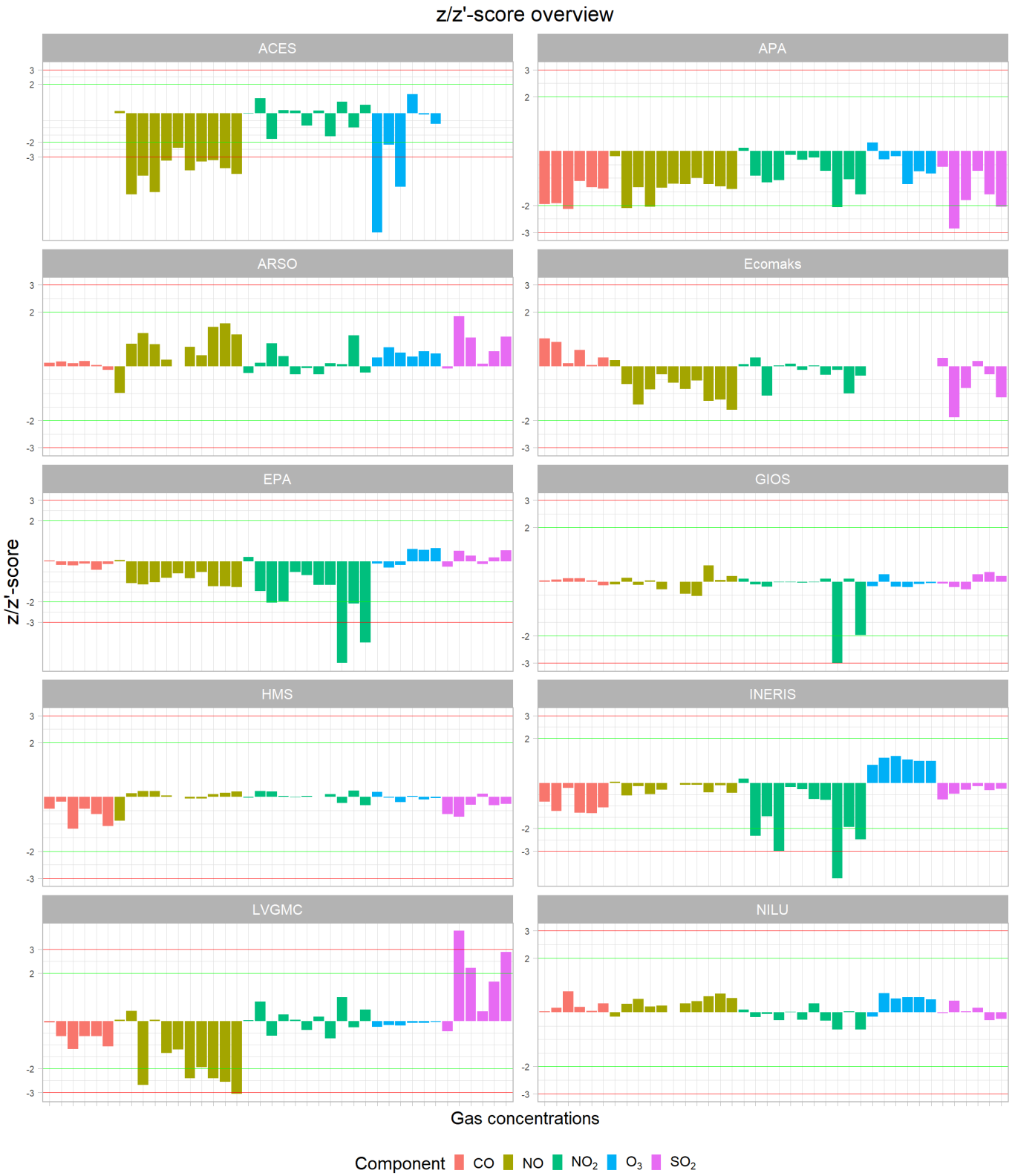
The proficiency evaluation scheme has assessed the participants' measured values and their evaluated uncertainties through calculating two performance indicators (z/z'-score and En-score).

z/z'-scores calculation is used to estimate the participant performance.

Statistically unsatisfactory results obtained at this stage are not attributed to extraordinary errors, but rather to significant differences in participants' standard operating procedures.
The precision of standardised measurement methods reported in Annex C are calculated using the whole data pool submitted.
In this exercise **89.2%** of the results in the z/z'-score evaluations are satisfactory.
Regarding the En-score parameter **78.8%** of the results are found satisfactory and **21.2%** unsatisfactory according to the limits explained in paragraph 5.2.

As in previous PT, the adopted evaluation for high concentrations were the standard deviations for proficiency assessment, deriving from the European Standards' uncertainty requirements.
The reproducibility standard deviation obtained and described in Annex C, like previous PT [20], [21], [22], [23], [24], [25], [33], [34], [35], [36], [37], [38], [39], [40], [41], [43], [44], [45], [46], [47], [48], [49], [50], [51], [52], [53], [54] and [55] is comparable to the mentioned criteria. On the other hand, the uncertainty criteria for zero levels were those set in AQUILA's position paper [12].
The following figure 16 is reporting a histogram representation of the overview of the performance indicator z/z'-score results obtained in this PT. All charts indicate the results of each participant for every component analysed at all concentrations generated.
Generally, the overall performance of all laboratories is good and no unsatisfactory results are identified for z/z'-score indicator while a small number of values were found unsatisfactory for the En-score.
The result of this PT is in line with the performances of previous years as shown by the following Table 7 where the results of z/z'-score in all PT organized in JRC Ispra site from 2005 till 2024 are presented.

Figure 16: Overview on z/z'-score final evaluation



Source: JRC 2024

Table 7: z/z'-score summary results of PT organized in Ispra from 2005 to 2024.

PT	Site	Satisfactory (%)	Questionable (%)	Unsatisfactory (%)
Jun_05	Ispra (IT)	94.7	2.3	3.0
Jun_07	Ispra (IT)	97.8	1.9	0.30
Apr_08	Ispra (IT)	93.8	2.1	4.1
Oct_08_I	Ispra (IT)	92.9	4.2	2.9
Oct_08_II	Ispra (IT)	97.0	3.0	0.00
Oct_09	Ispra (IT)	98.2	1.8	0.00
Jun_10	Ispra (IT)	97.0	3.0	0.00
Sep_11	Ispra (IT)	99.4	0.30	0.30
Oct_11	Ispra (IT)	98.7	1.3	0.00
Jun_12	Ispra (IT)	100	0.00	0.00
Sep_13	Ispra (IT)	100	0.00	0.00
Oct_13	Ispra (IT)	99.3	0.70	0.00
May_14	Ispra (IT)	98.1	0.70	1.1
Oct_15_I	Ispra (IT)	99.4	0.60	0.00
Oct_15_II	Ispra (IT)	93.7	4.1	2.2
Jun_16	Ispra (IT)	100	0.00	0.00
Jun_17_I	Ispra (IT)	98.9	0.70	0.40
Jun_17_II	Ispra (IT)	96.2	1.9	1.9
Jun_18	Ispra (IT)	100	0.00	0.00
May_19_I	Ispra (IT)	98.7	1.3	0.00
May_19_II	Ispra (IT)	97.5	2.5	0.00
Mar-22(I)	Ispra (IT)	97.2	1.1	1.7
Mar_22_II	Ispra (IT)	99.3	0.70	0.00
Apr_22_III	Ispra (IT)	91.5	3.2	5.3
Mar_23	Ispra (IT)	100	0.00	0.00
Mar_24_I	Ispra (IT)	98.2	1.8	0.00
Mar_24_II	Ispra (IT)	89.2	5.7	5.1

Source: JRC 2024

During this PT, in agreement with all participants, an extra set of values has been asked to be reported. In order to verify the impact of the interference of NO/NO_2 during SO_2 measurement, all participants quantified sulphur dioxide while, in the sampling tube, was generated high concentration of NO and NO_2.
In table 8 are summarised the readings of all laboratories and the correspondent instrument used. In annex E of the EN 14212 standard is described the type approval required for the instrument used for SO_2 analysis. In table E.1 of this document are listed the relevant performance characteristics and criteria for SO_2 measurement in presence of NO and NO2 (for NO with concentration 500 nmol/mol SO2 reading ≤ 5.0 nmol/mol, for NO2 with concentration 200 nmol/mol SO2 reading ≤ 5.0 nmol/mol). This test is pure indicative and doesn't have the goal of reaching any conclusion about any of the instrumentation used.

Table 8: SO_2 measurement during NO gas generation.

Run	NO ref value	ERLAP1	ERLAP2	INERIS	EPA	GIOS	HMS	NILU	LVGMC	ARSO	APA	ECOMAKS
						SO_2 mol/mol						
7	472	2.9	2.9	1.0	8.3	3.5	2.1	2.8	1.3	2.7	2.2	2.3
7	473	2.9	2.9	1.1	8.3	3.5	2.1	2.8	1.3	2.7	2.1	2.1
7	473	2.9	2.8	1.2	8.3	3.5	2.0	2.8	1.5	2.8	2.2	2.3
8	250	1.7	1.8	0.51	4.4	2.1	0.80	1.3	0.70	1.4	1.00	1.8
8	251	1.7	1.7		4.4	2.0	0.90	1.3	0.76	1.4	0.90	2.0
8	251	1.6	1.7	0.29	4.4	2.0	0.90	1.4	0.81	1.4	0.90	1.9
9	296	1.9	2.0	0.68	5.2	2.2	1.1	1.7	0.94	1.7	1.1	2.0
9	296	1.9	2.0	0.52	5.1	2.3	1.1	1.7	0.89	1.7	1.1	2.2
9	297	1.9	2.0	0.43	5.1	2.3	1.1	1.7	0.80	1.7	1.2	2.0
10	163	1.1	1.4	0.21	2.8	1.3	0.20	0.80	0.43	0.90	0.40	1.3
10	164	1.1	1.4	-0.06	2.8	1.3	0.40	0.80	0.48	0.90	0.50	1.1
10	164	1.1	1.3	0.04	2.8	1.3	0.30	0.80	0.53	0.90	0.40	1.2
		Thermo FS 43iTLE	Horiba APSA-370	Teledyne API T100	Teledyne API T100	Horiba APSA-370	Thermo FS 43i	Horiba APSA-370	Teledyne API T100	Horiba APSA 370	Thermo FS 43i	Teledyne API T100

Source: JRC 2024

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List of abbreviations

AQUILA	Network of National Reference Laboratories for Air Quality
BIPM	Bureau International des Poids et Mesures
CEN	European Committee for Standardization
CO	Carbon monoxide
CRM	Certified Reference Material
DQO	Data Quality Objective
ERLAP	European Reference Laboratory for Air Pollution
EC	European Commission
GPT	Gas Phase Titration
PT	Proficiency Test
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
PT	Proficiency Test
SO_2	Sulphur dioxide
VDI	Verein Deutscher Ingenieure
WHO-CC	World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin

Mathematical Symbols

α	converter efficiency (EN 14211)
Ec	Converter efficiency for NO analyser
En	En–score statistic (ISO 13528)
r	repeatability limit (ISO 5725)
R	reproducibility limit (ISO 5725)
σ_{pt}	standard deviation for proficiency assessment (ISO 13528)
x*	robust average (Annex C ISO 13528)
s*	robust standard deviation (Annex C ISO 13528)
sR	estimate of reproducibility variance (ISO 5725)
U_{ref}	expanded uncertainty of the reference value (ISO 13528)
U_{lab}	expanded uncertainty of the participant's value (ISO 13528)
u_{ref}	standard uncertainty of the reference value (ISO 13528)
X_{ref}	reference value (ISO 13528)
x_{lab}	average of 3 values reported by the participant i (for each parameter and concentration level)
z'	z'-score statistic (ISO 13528)
z	z-score statistic (ISO 13528)

List of figures

List of tables

Annex A. Reference values

The reference values of tested concentration levels (run) were derived, as an average of two set of instruments, from ERLAP's measurements, which are calibrated against the certified reference values of CRMs and are traceable to international standards. In this perspective the reference values are defined as described in the ISO 13528 [13].
To foster its reference function ERLAP is participating regularly to key comparisons of the Gas Analysis Working Group within the framework of BIPM's CCQM and it is yearly confirming the compliance to standard to ISO 17043, through an annual audit run by the competent Italian accreditation body (see annex E).
During this PT ERLAP's SO_2, CO and NO analysers were calibrated according to the methodology described in the standard ISO 6143 [6]. Reference gas mixtures were produced from the primary reference materials (produced and certified by NMi Van Swinden Laboratorium) by dynamic dilution method using mass flow controllers [8].
All flows were verified with a certified molbloc/molbox1 system. For O_3 measurements, the analysers were calibrated using the JRC SRP42 primary standard (constructed by NIST), which has been compared to BIPM primary standard [26]. The photometer absorption cross section uncertainty (1.06%) was included in the uncertainty budget [27], [28].
The calibration functions parameters and uncertainties associated were carried out using VDI 2449 Part3 [30]. The contribution to the uncertainty budget "u_{ref}" include repeatability, certified reference material standard uncertainty, drift and homogeneity. For extending calibration from the NO to NO_2 channel of NO_x analyser, the GPT test was performed to establish the efficiency of NO_2-converter and its contribution is added to the uncertainty.
In table 9 the reference values are reported together with their uncertainties.

Table 9: Reference values (X)

Component	Run	Ref value	Ref unc com	Ref exp unc	sigmaPT	Unit	z or z'
CO	0	-0.00	0.01	0.02	0.10	µmol/mol	z
CO	1	0.62	0.01	0.02	0.11	µmol/mol	z
CO	2	8.8	0.09	0.18	0.31	µmol/mol	z
CO	3	0.92	0.01	0.03	0.12	µmol/mol	z
CO	4	1.9	0.02	0.04	0.15	µmol/mol	z
CO	5	4.8	0.05	0.10	0.22	µmol/mol	z
NO	0	0.23	0.72	1.5	1.0	nmol/mol	z’
NO	1	200	1.3	2.6	5.8	nmol/mol	z
NO	2	191	1.2	2.5	5.6	nmol/mol	z
NO	3	31	0.75	1.5	1.7	nmol/mol	z’
NO	4	21	0.73	1.5	1.5	nmol/mol	z’
NO	5	60	0.80	1.6	2.4	nmol/mol	z’
NO	6	41	0.76	1.5	2.0	nmol/mol	z’
NO	7	473	2.6	5.2	12	nmol/mol	z
NO	8	251	1.5	3.1	7.0	nmol/mol	z
NO	9	296	1.7	3.5	8.1	nmol/mol	z
NO	10	164	1.1	2.3	4.9	nmol/mol	z
NO_2	0	-0.04	0.74	1.5	1.4	nmol/mol	z’
NO_2	1	0.42	1.0	2.0	1.4	nmol/mol	z’
NO_2	2	9.9	1.0	2.0	1.7	nmol/mol	z’
NO_2	3	0.13	0.76	1.5	1.4	nmol/mol	z’
NO_2	4	9.4	0.76	1.5	1.7	nmol/mol	z’
NO_2	5	0.06	0.78	1.5	1.4	nmol/mol	z’
NO_2	6	29	0.80	1.6	2.2	nmol/mol	z’
NO_2	7	7.6	1.8	3.6	1.6	nmol/mol	z’
NO_2	8	228	2.1	4.2	7.8	nmol/mol	z
NO_2	9	4.3	1.3	2.6	1.5	nmol/mol	z’
NO_2	10	136	1.4	2.8	5.2	nmol/mol	z
O_3	0	0.28	0.26	0.52	1.0	nmol/mol	z
O_3	1	65	0.64	1.3	2.3	nmol/mol	z
O_3	2	21	0.29	0.57	1.4	nmol/mol	z
O_3	3	196	1.9	3.8	4.9	nmol/mol	z’
O_3	4	96	0.92	1.8	2.9	nmol/mol	z’
O_3	5	130	1.2	2.5	3.6	nmol/mol	z’
SO_2	0	0.19	0.50	1.0	1.00	nmol/mol	z’
SO_2	1	126	0.97	1.9	3.8	nmol/mol	z
SO_2	2	41	0.58	1.2	1.9	nmol/mol	z’
SO_2	3	4.8	0.64	1.3	1.1	nmol/mol	z’
SO_2	4	20	0.53	1.1	1.4	nmol/mol	z’
SO_2	5	56	0.64	1.3	2.2	nmol/mol	z

Source: JRC 2024

Homogeneity

This type of PT for inorganic gases foresees a generation in real time of gas mixture that is analysed immediately. The gas is not stored nor manipulated before the participant's measurement. In this condition, the stability and homogeneity verification of test item is not fully applicable.

ERLAP verify the homogeneity of the mixture gases, using a ozone mixture because is the most reactive gas. The readings of two identical analysers (Thermo Fisher Scientific 49i), calibrated against an SRP photometer primary standard, are compered, while an ozone concentration is running in the sampling line. The sampling line has 20 positions with 2 connection ports in each position. An analysers measures ozone at the port 20a, the last of the sampling line, and the other one sequentially in the other ports.

The test is considered acceptable when the absolute difference between the initial measurement and all the others is below 0.5%(during this PT equivalent to 2,18 nmol/mol). Assuming a rectangular distribution, it constitutes an uncertainty of 0.3% of each concentration level This test is performed before each inorganic gas PT organised by ERLAP in Ispra.
The homogeneity results are reported in Table10.

Table 10: Homogeneity test.

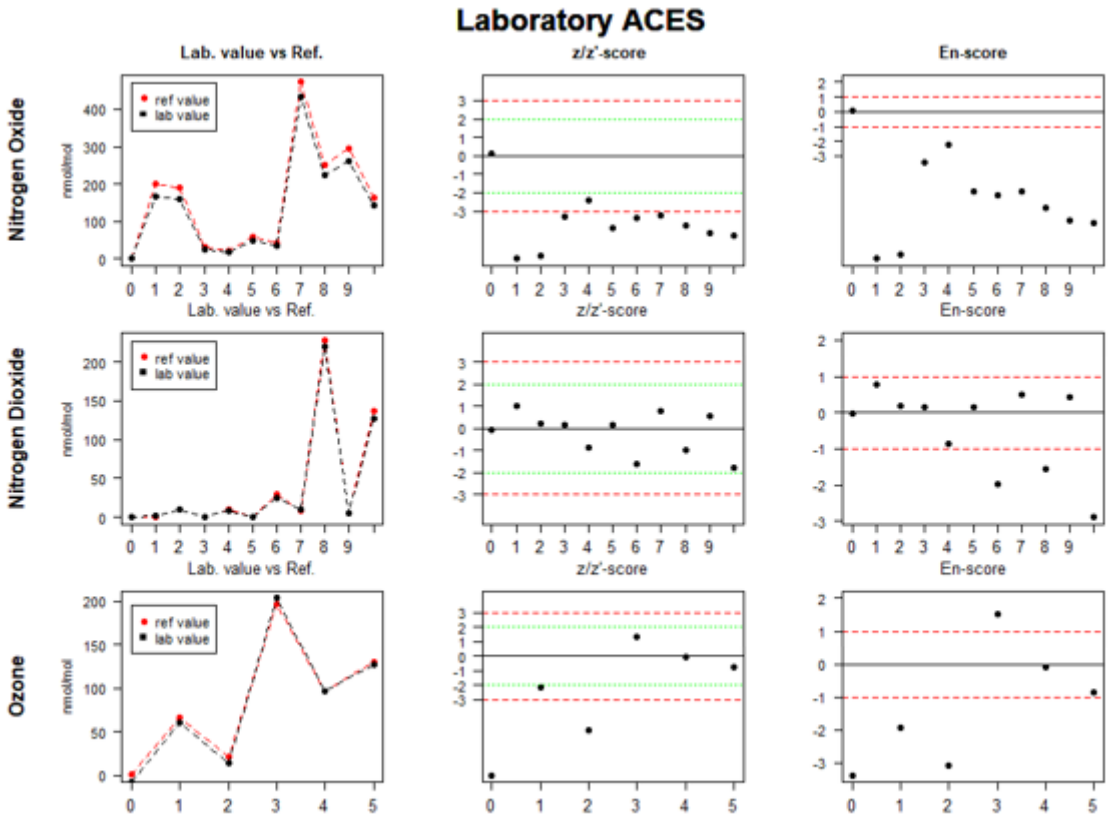
Ref Analyzer (port 20a)	Bench position under test	Diff. between analysers	<0.5%?
nmol/mol		nmol/mol	
436	20b	0.00	Yes
436	1a	-1.00	Yes
435	1b	0.00	Yes
436	2a	0.00	Yes
436	2b	0.50	Yes
437	3a	1.00	Yes
437	3b	1.00	Yes
436	4a	0.80	Yes
438	4b	0.30	Yes
437	5a	0.60	Yes
438	5b	0.40	Yes
438	6a	-1.1	Yes
438	6b	-1.00	Yes
438	7a	-1.00	Yes
438	7b	0.20	Yes
438	8a	-0.40	Yes
438	8b	-0.40	Yes
439	9a	0.40	Yes
439	9b	0.40	Yes
438	10a	-0.40	Yes
438	10b	-0.50	Yes
438	11a	-0.50	Yes
438	11b	0.50	Yes
439	12a	0.40	Yes
439	12b	0.40	Yes
439	13a	0.30	Yes
439	13b	0.30	Yes
439	14a	0.20	Yes
439	14b	0.20	Yes
438	15a	1.00	Yes
439	15b	0.40	Yes
439	16a	0.40	Yes
438	16b	-0.30	Yes
438	17a	1.7	Yes
439	17b	1.3	Yes
439	18a	0.30	Yes
438	18b	0.50	Yes
439	19a	1.3	Yes
439	19b	0.30	Yes
439	20a	0.70	Yes
439	20b	1.4	Yes
440	21a	1.00	Yes
439	21b	0.60	Yes
439	22a	-0.40	Yes
439	22b	0.20	Yes
439	22c	0.40	Yes
439	22d	-0.60	Yes
439	23a	-2.0	Yes
438	23b	1.00	Yes
439	23c	-1.1	Yes
438	23d	-0.50	Yes

Source: JRC 2024

Annex B: Results reported by participants

In this annex are reported all results submitted by the participants and they are presented both as graphs and tables.
In the graph, from the left and top down, for each pollutant is represented the submitted measurement result compared to the reference value, the z/z'-score and En-score calculated and compared to criteria explained in paragraph 5.
In the table are reported all values obtained from the data evaluation of this PT.
From the left "Runs" indicate all gas mixture concentrations generated. In the column "**Lab mean**" is shown the average of the 3 results (Step 1,2,3) representing a measurement of 30 minutes each that every laboratory is asked to report.
The combined and expanded uncertainties of the participant are listed in column "**Lab unc com**" and "**Lab unc exp**", expressed in mol/mol units.
"sigmaPT" column shows the results of the calculation described in paragraph 5.1 using the parameter in Table 4.
"Ref. Val." is showing the calculated reference values.
In column "z/z'-score" and "En-score" are listed the performance indicators values obtained by each participant. "z/z' selection" column indicates for each pollutant's run if it was used z or z' according to the criteria explained in paragraph 5.

Figure 17: Graphical report of results of ACES (Sweden).



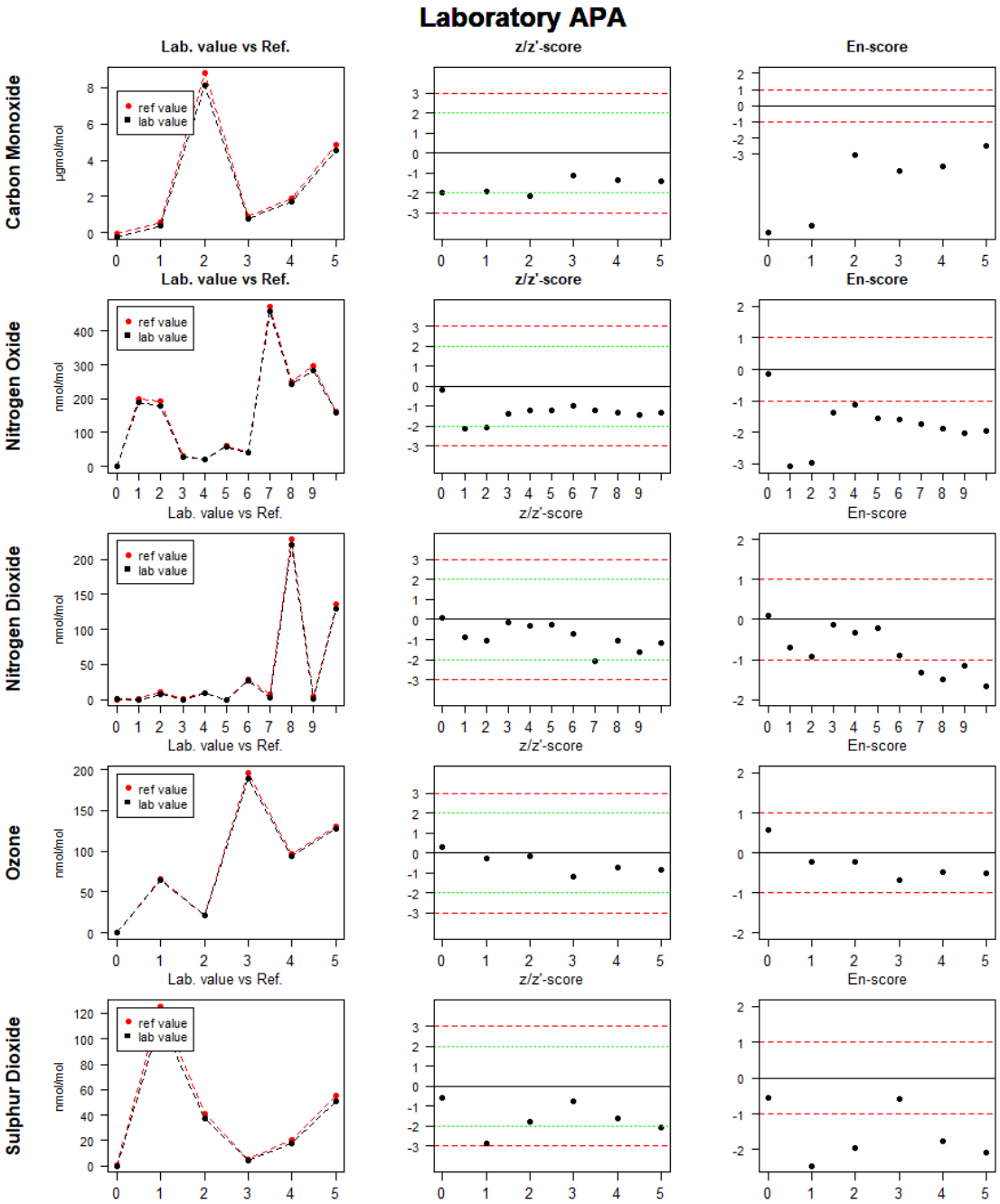
Source: JRC 2024

Table 11: Reported values, uncertainties and performance evaluation results of ACES (Sweden).

ACES													
Component	**Run**	**Lab mean**	**Step 1**	**Step 2**	**Step 3**	**Lab unc com**	**Lab unc exp**	**unit**	**sigmaPT**	**Ref. Val.**	**z/z'- score**	**z/z' selection**	**En- score**
NO	0	0.40	0.40			0.50	1.00	nmol/mol	1.0	0.23	0.14	z'	0.10
NO	1	168	168	168	167	1.00	2.0	nmol/mol	5.8	200	-5.6	z	-9.9
NO	2	160	160	160	161	0.96	1.9	nmol/mol	5.6	191	-5.4	z	-9.7
NO	3	24	24	24	25	0.50	1.00	nmol/mol	1.7	31	-3.3	z'	-3.5
NO	4	17	17	17	17	0.50	1.00	nmol/mol	1.5	21	-2.4	z'	-2.2
NO	5	50	50	50	50	0.50	1.00	nmol/mol	2.4	60	-4.0	z'	-5.4
NO	6	34	34	34	34	0.50	1.00	nmol/mol	2.0	41	-3.4	z'	-3.9
NO	7	433	432	433	433	2.6	5.2	nmol/mol	12	473	-3.2	z	-5.4
NO	8	224	224	224	224	1.3	2.7	nmol/mol	7.0	251	-3.8	z	-6.5
NO	9	262	262	262	263	1.6	3.1	nmol/mol	8.1	296	-4.2	z	-7.3
NO	10	142	142	142	143	0.85	1.7	nmol/mol	4.9	164	-4.3	z	-7.5
NO_2	0	-0.11	-0.11			0.50	1.00	nmol/mol	1.4	-0.04	-0.04	z'	-0.04
NO_2	1	2.2	2.4	2.2	2.0	0.50	1.00	nmol/mol	1.4	0.42	1.0	z'	0.78
NO_2	2	10	10.0	11	10.0	0.50	1.00	nmol/mol	1.7	9.9	0.20	z'	0.18
NO_2	3	0.41	0.38	0.42	0.42	0.50	1.00	nmol/mol	1.4	0.13	0.17	z'	0.15
NO_2	4	7.8	7.7	7.8	8.0	0.50	1.00	nmol/mol	1.7	9.4	-0.88	z'	-0.88
NO_2	5	0.32	0.38	0.23	0.34	0.50	1.00	nmol/mol	1.4	0.06	0.16	z'	0.14
NO_2	6	25	25	25	25	0.50	1.00	nmol/mol	2.2	29	-1.6	z'	-2.0
NO_2	7	9.5	9.9	9.4	9.2	0.50	1.00	nmol/mol	1.6	7.6	0.80	z'	0.51
NO_2	8	220	221	220	220	1.3	2.6	nmol/mol	7.8	228	-1.00	z	-1.6
NO_2	9	5.4	5.5	5.2	5.5	0.50	1.00	nmol/mol	1.5	4.3	0.56	z'	0.41
NO_2	10	127	127	126	127	0.76	1.5	nmol/mol	5.2	136	-1.8	z	-2.9
O_3	0	-8.0	-8.0			1.2	2.4	nmol/mol	1.0	0.28	-8.2	z	-3.4
O_3	1	60	60	60	61	1.2	2.3	nmol/mol	2.3	65	-2.2	z	-1.9
O_3	2	14	14	14	14	1.2	2.3	nmol/mol	1.4	21	-5.1	z	-3.1
O_3	3	203	202	203	204	1.3	2.5	nmol/mol	4.9	196	1.3	z'	1.5
O_3	4	96	96	96	96	1.2	2.3	nmol/mol	2.9	96	-0.09	z'	-0.10
O_3	5	127	127	127	128	1.2	2.3	nmol/mol	3.6	130	-0.75	z'	-0.84

Source: JRC 2024

Figure 18: Graphical report of results of APA (Portugal).



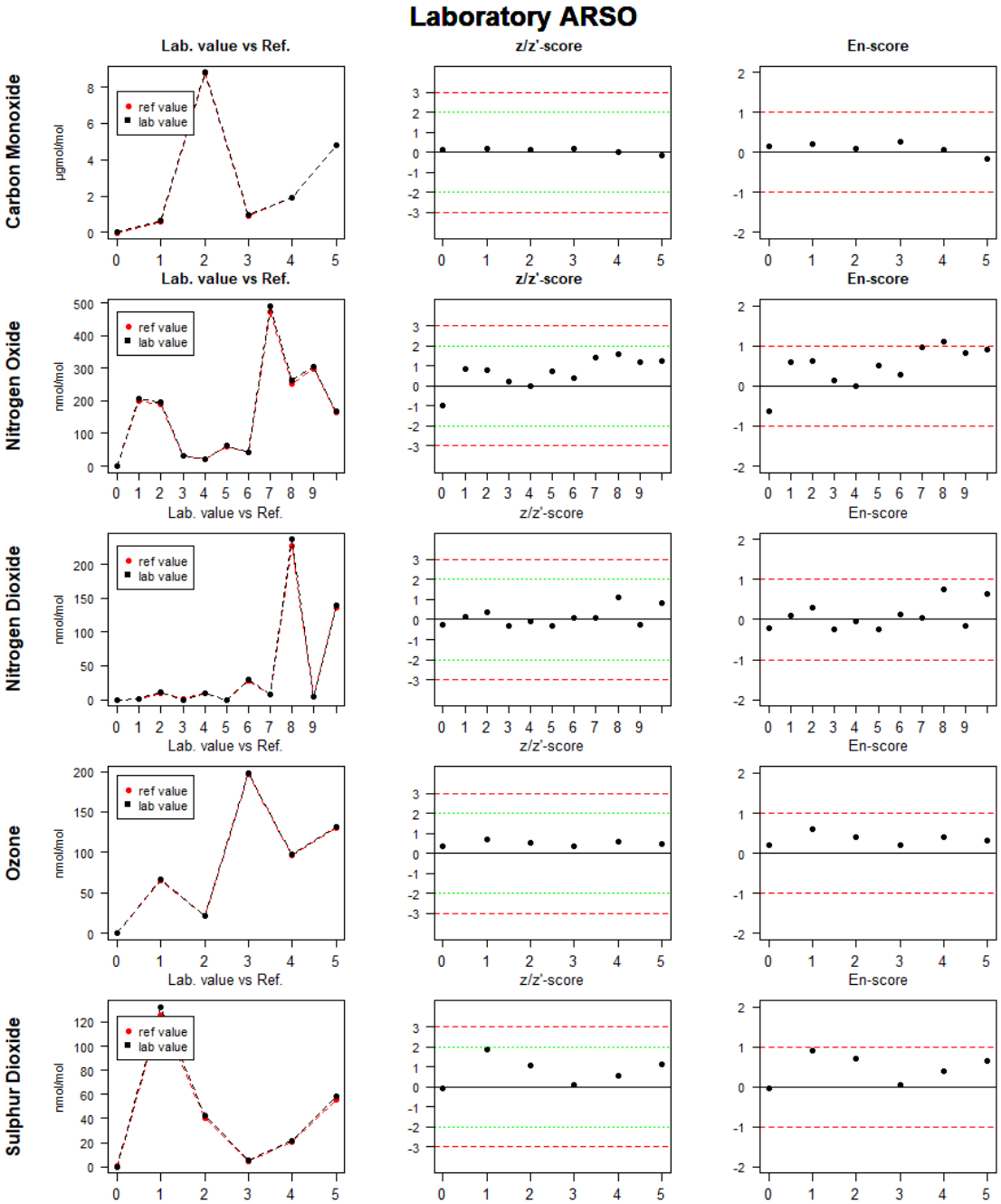
Source: JRC 2024

Table 12: Reported values, uncertainties and performance evaluation results of APA (Portugal).

APA													
Component	**Run**	**Lab mean**	**Step 1**	**Step 2**	**Step 3**	**Lab unc com**	**Lab unc exp**	**unit**	**sigmaPT**	**Ref. Val.**	**z/z'-score**	**z/z' selection**	**En-score**
CO	0	-0.20	-0.20			0.01	0.02	µmol/mol	0.10	-0.00	-2.0	z	-7.9
CO	1	0.40	0.39	0.40	0.41	0.01	0.02	µmol/mol	0.11	0.62	-1.9	z	-7.4
CO	2	8.1	8.1	8.1	8.1	0.06	0.12	µmol/mol	0.31	8.8	-2.1	z	-3.1
CO	3	0.78	0.78	0.78	0.78	0.01	0.02	µmol/mol	0.12	0.92	-1.1	z	-4.0
CO	4	1.7	1.7	1.7	1.7	0.01	0.03	µmol/mol	0.15	1.9	-1.3	z	-3.7
CO	5	4.5	4.5	4.5	4.6	0.03	0.07	µmol/mol	0.22	4.8	-1.4	z	-2.5
NO	0	-0.01	-0.01			0.49	0.97	nmol/mol	1.0	0.23	-0.19	z'	-0.14
NO	1	188	188	188	188	1.5	3.0	nmol/mol	5.8	200	-2.1	z	-3.1
NO	2	179	179	179	180	1.4	2.9	nmol/mol	5.6	191	-2.0	z	-3.0
NO	3	28	28	28	28	0.53	1.1	nmol/mol	1.7	31	-1.4	z'	-1.4
NO	4	19	19	19	19	0.51	1.00	nmol/mol	1.5	21	-1.2	z'	-1.1
NO	5	57	57	57	57	0.65	1.3	nmol/mol	2.4	60	-1.2	z'	-1.5
NO	6	39	39	39	39	0.57	1.1	nmol/mol	2.0	41	-1.00	z'	-1.1
NO	7	458	457	458	458	3.5	6.9	nmol/mol	12	473	-1.2	z	-1.7
NO	8	241	241	241	242	1.9	3.8	nmol/mol	7.0	251	-1.3	z	-1.9
NO	9	285	285	285	285	2.2	4.4	nmol/mol	8.1	296	-1.4	z	-2.0
NO	10	157	157	157	157	1.3	2.5	nmol/mol	4.9	164	-1.3	z	-2.0
NO_2	0	0.13	0.13			0.49	0.97	nmol/mol	1.4	-0.04	0.11	z'	0.10
NO_2	1	-1.2	-1.1	-1.1	-1.3	0.49	0.98	nmol/mol	1.4	0.42	-0.91	z'	-0.70
NO_2	2	7.8	7.7	7.9	7.9	0.49	0.98	nmol/mol	1.7	9.9	-1.1	z'	-0.93
NO_2	3	-0.10	-0.11	-0.09	-0.09	0.49	0.97	nmol/mol	1.4	0.13	-0.14	z'	-0.13
NO_2	4	8.8	8.8	8.8	8.9	0.49	0.98	nmol/mol	1.7	9.4	-0.33	z'	-0.33
NO_2	5	-0.34	-0.31	-0.35	-0.36	0.49	0.97	nmol/mol	1.4	0.06	-0.25	z'	-0.22
NO_2	6	27	27	27	27	0.53	1.1	nmol/mol	2.2	29	-0.74	z'	-0.90
NO_2	7	2.5	2.9	2.5	2.1	0.50	0.99	nmol/mol	1.6	7.6	-2.1	z'	-1.3
NO_2	8	220	220	220	220	1.7	3.4	nmol/mol	7.8	228	-1.0	z	-1.5
NO_2	9	1.1	1.4	0.90	1.00	0.49	0.98	nmol/mol	1.5	4.3	-1.6	z'	-1.2
NO_2	10	130	130	130	130	1.1	2.2	nmol/mol	5.2	136	-1.1	z	-1.7
O_3	0	0.59	0.59			0.12	0.23	nmol/mol	1.0	0.28	0.31	z	0.56
O_3	1	65	64	65	65	1.5	3.0	nmol/mol	2.3	65	-0.31	z	-0.22
O_3	2	21	21	21	21	0.50	1.00	nmol/mol	1.4	21	-0.19	z	-0.24
O_3	3	190	189	190	190	4.4	8.8	nmol/mol	4.9	196	-1.2	z'	-0.68
O_3	4	94	94	94	94	2.2	4.3	nmol/mol	2.9	96	-0.75	z'	-0.49
O_3	5	127	127	127	127	2.9	5.9	nmol/mol	3.6	130	-0.83	z'	-0.50
SO_2	0	-0.47	-0.47			0.33	0.67	nmol/mol	1.00	0.19	-0.59	z'	-0.54
SO_2	1	115	115	115	115	2.0	3.9	nmol/mol	3.8	126	-2.9	z	-2.4
SO_2	2	37	37	37	37	0.71	1.4	nmol/mol	1.9	41	-1.8	z'	-1.9
SO_2	3	3.9	3.1	4.2	4.4	0.51	1.0	nmol/mol	1.1	4.8	-0.74	z'	-0.58
SO_2	4	18	18	18	18	0.46	0.92	nmol/mol	1.4	20	-1.6	z'	-1.8
SO_2	5	51	51	51	51	0.92	1.8	nmol/mol	2.2	56	-2.0	z	-2.1

Source: JRC 2024

Figure 19: Graphical report of results of ARSO (Slovenia).



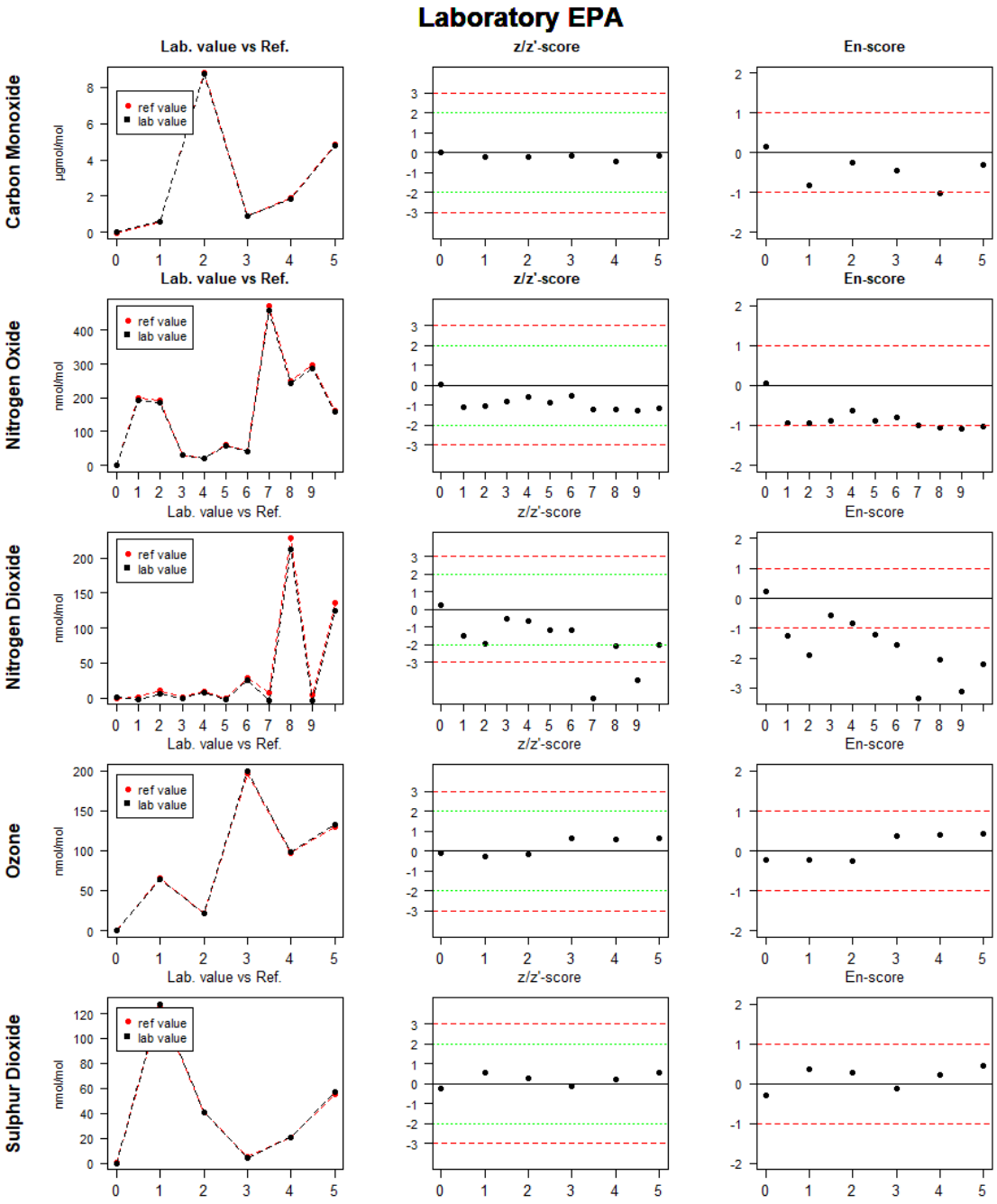
Source: JRC 2024

Table 13: Reported values, uncertainties and performance evaluation results of ARSO (Slovenia).

ARSO													
Component	**Run**	**Lab mean**	**Step 1**	**Step 2**	**Step 3**	**Lab unc com**	**Lab unc exp**	**unit**	**sigmaPT**	**Ref. Val.**	**z/z'- score**	**z/z' selection**	**En- score**
CO	0	0.01	0.01			0.04	0.09	µmol/mol	0.10	-0.00	0.13	z	0.14
CO	1	0.64	0.64	0.64	0.64	0.05	0.09	µmol/mol	0.11	0.62	0.17	z	0.20
CO	2	8.8	8.8	8.8	8.8	0.15	0.31	µmol/mol	0.31	8.8	0.12	z	0.10
CO	3	0.94	0.94	0.94	0.94	0.05	0.09	µmol/mol	0.12	0.92	0.20	z	0.26
CO	4	1.9	1.9	1.9	1.9	0.06	0.11	µmol/mol	0.15	1.9	0.05	z	0.06
CO	5	4.8	4.8	4.8	4.8	0.09	0.18	µmol/mol	0.22	4.8	-0.14	z	-0.15
NO	0	-1.00	-1.00			0.67	1.3	nmol/mol	1.0	0.23	-0.99	z'	-0.63
NO	1	205	205	205	205	3.7	7.4	nmol/mol	5.8	200	0.83	z	0.61
NO	2	195	195	195	196	3.5	7.0	nmol/mol	5.6	191	0.82	z	0.62
NO	3	31	31	31	31	1.5	3.0	nmol/mol	1.7	31	0.24	z'	0.13
NO	4	21	21	21	21	1.5	3.0	nmol/mol	1.5	21	-0.00	z'	-0.00
NO	5	62	62	62	62	1.7	3.3	nmol/mol	2.4	60	0.72	z'	0.50
NO	6	42	42	42	42	1.6	3.1	nmol/mol	2.0	41	0.41	z'	0.25
NO	7	491	490	491	491	8.9	18	nmol/mol	12	473	1.4	z	0.96
NO	8	262	261	262	262	4.7	9.4	nmol/mol	7.0	251	1.6	z	1.1
NO	9	306	306	306	306	5.5	11	nmol/mol	8.1	296	1.2	z	0.83
NO	10	170	169	170	170	3.1	6.2	nmol/mol	4.9	164	1.2	z	0.92
NO_2	0	-0.42	-0.42			0.60	1.2	nmol/mol	1.4	-0.04	-0.24	z'	-0.20
NO_2	1	0.64	0.55	0.57	0.80	0.60	1.2	nmol/mol	1.4	0.42	0.13	z'	0.09
NO_2	2	11	11	10.0	11	0.70	1.4	nmol/mol	1.7	9.9	0.37	z'	0.30
NO_2	3	-0.33	-0.18	-0.31	-0.50	0.60	1.2	nmol/mol	1.4	0.13	-0.29	z'	-0.24
NO_2	4	9.3	9.3	9.3	9.4	0.70	1.4	nmol/mol	1.7	9.4	-0.06	z'	-0.05
NO_2	5	-0.40	-0.28	-0.53	-0.40	0.60	1.2	nmol/mol	1.4	0.06	-0.29	z'	-0.24
NO_2	6	29	29	29	29	0.70	1.4	nmol/mol	2.2	29	0.11	z'	0.13
NO_2	7	7.8	8.0	7.7	7.6	0.70	1.4	nmol/mol	1.6	7.6	0.08	z'	0.05
NO_2	8	237	237	237	237	5.3	11	nmol/mol	7.8	228	1.1	z	0.75
NO_2	9	3.8	3.9	3.9	3.7	0.70	1.4	nmol/mol	1.5	4.3	-0.23	z'	-0.15
NO_2	10	140	141	140	140	3.1	6.2	nmol/mol	5.2	136	0.84	z	0.64
O_3	0	0.61	0.61			0.85	1.7	nmol/mol	1.0	0.28	0.33	z	0.19
O_3	1	67	67	67	67	1.2	2.4	nmol/mol	2.3	65	0.70	z	0.59
O_3	2	22	22	22	22	0.83	1.7	nmol/mol	1.4	21	0.51	z	0.40
O_3	3	198	198	198	198	4.3	8.6	nmol/mol	4.9	196	0.36	z'	0.20
O_3	4	98	98	98	98	1.9	3.7	nmol/mol	2.9	96	0.56	z'	0.41
O_3	5	132	132	132	132	2.7	5.4	nmol/mol	3.6	130	0.48	z'	0.31
SO_2	0	0.09	0.09			0.86	1.7	nmol/mol	1.00	0.19	-0.09	z'	-0.05
SO_2	1	133	133	133	132	3.7	7.4	nmol/mol	3.8	126	1.8	z	0.90
SO_2	2	43	42	43	43	1.4	2.8	nmol/mol	1.9	41	1.1	z'	0.69
SO_2	3	5.0	4.2	5.3	5.4	0.87	1.7	nmol/mol	1.1	4.8	0.09	z'	0.05
SO_2	4	21	22	21	21	1.00	2.0	nmol/mol	1.4	20	0.56	z'	0.38
SO_2	5	58	58	58	58	1.8	3.6	nmol/mol	2.2	56	1.1	z	0.64

Source: JRC 2024

Figure 20: Graphical report of results of EPA (Ireland).



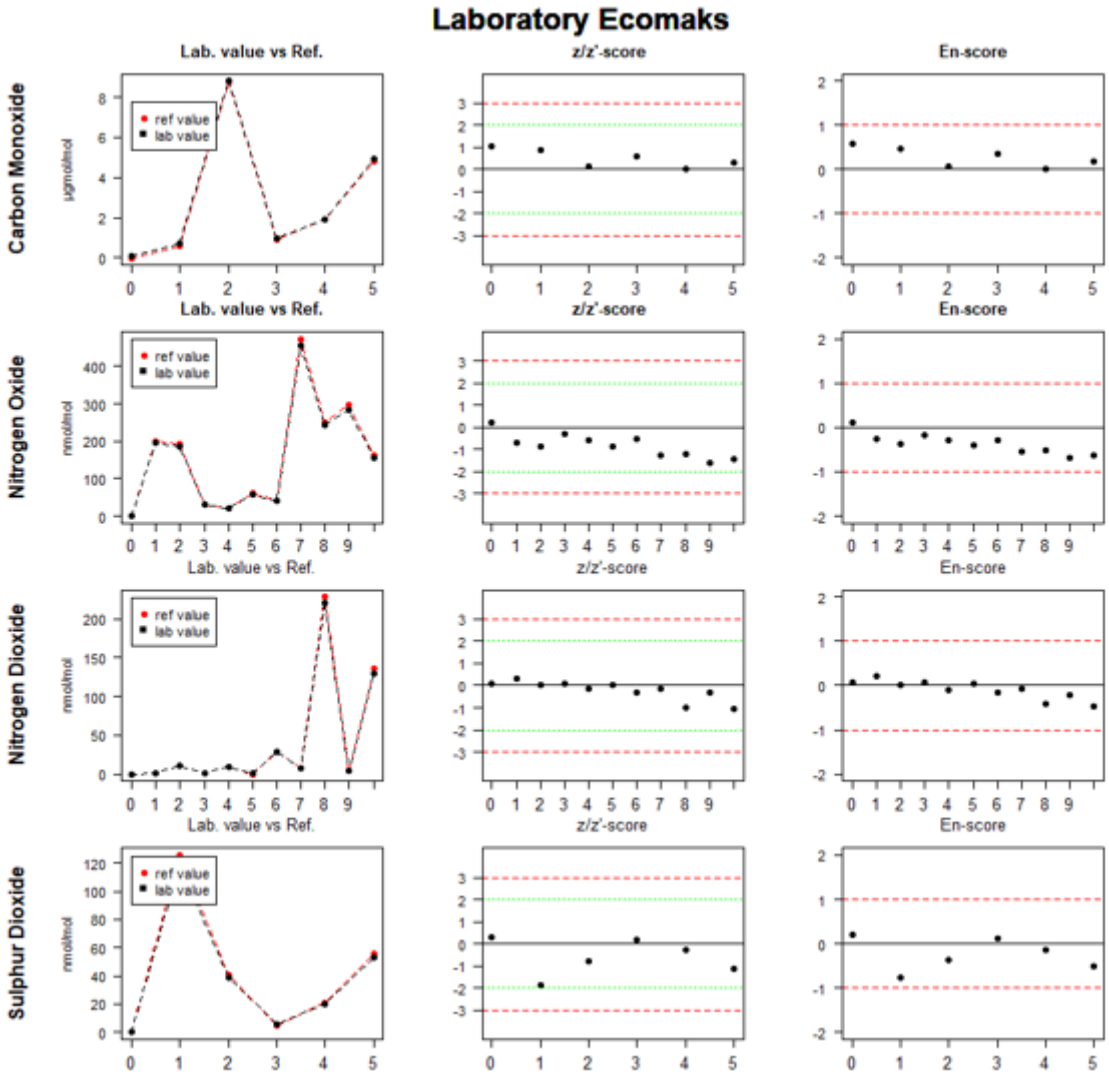
Source: JRC 2024

Table 14: Reported values, uncertainties and performance evaluation results of EPA (Ireland).

EPA													
Component	**Run**	**Lab mean**	**Step 1**	**Step 2**	**Step 3**	**Lab unc com**	**Lab unc exp**	**unit**	**sigma PT**	**Ref. Val.**	**z/z'-score**	**z/z' selection**	**En-score**
CO	0	0.00	0.00	0.00	0.00	0.00	0.00	µmol/mol	0.10	-0.00	0.03	z	0.16
CO	1	0.60	0.60	0.60	0.60	0.01	0.01	µmol/mol	0.11	0.62	-0.18	z	-0.82
CO	2	8.7	8.7	8.7	8.7	0.10	0.19	µmol/mol	0.31	8.8	-0.20	z	-0.24
CO	3	0.90	0.90	0.90	0.90	0.01	0.02	µmol/mol	0.12	0.92	-0.12	z	-0.45
CO	4	1.8	1.9	1.8	1.8	0.02	0.04	µmol/mol	0.15	1.9	-0.41	z	-1.0
CO	5	4.8	4.8	4.8	4.8	0.05	0.01	µmol/mol	0.22	4.8	-0.14	z	-0.30
NO	0	0.30	0.30			0.00	0.01	nmol/mol	1.0	0.23	0.06	z'	0.05
NO	1	194	194	194	194	3.1	6.0	nmol/mol	5.8	200	-1.1	z	-0.95
NO	2	185	185	185	185	3.0	5.7	nmol/mol	5.6	191	-1.0	z	-0.93
NO	3	29	29	29	29	0.47	0.90	nmol/mol	1.7	31	-0.82	z'	-0.89
NO	4	20	20	20	20	0.32	0.62	nmol/mol	1.5	21	-0.60	z'	-0.63
NO	5	58	58	58	58	0.92	1.8	nmol/mol	2.4	60	-0.84	z'	-0.90
NO	6	40	40	40	40	0.63	1.2	nmol/mol	2.0	41	-0.53	z'	-0.58
NO	7	458	457	458	458	7.3	14	nmol/mol	12	473	-1.2	z	-1.0
NO	8	242	241	242	243	3.9	7.5	nmol/mol	7.0	251	-1.2	z	-1.0
NO	9	286	286	286	286	4.6	8.9	nmol/mol	8.1	296	-1.3	z	-1.1
NO	10	158	158	158	158	2.5	4.9	nmol/mol	4.9	164	-1.1	z	-1.0
NO_2	0	0.30	0.30			0.00	0.01	nmol/mol	1.4	-0.04	0.22	z'	0.23
NO_2	1	-2.1	-1.7	-2.2	-2.5	-0.03	-0.07	nmol/mol	1.4	0.42	-1.5	z'	-1.2
NO_2	2	6.1	6.2	6.1	5.9	0.10	0.19	nmol/mol	1.7	9.9	-2.0	z'	-1.9
NO_2	3	-0.72	-0.65	-0.75	-0.75	-0.01	-0.02	nmol/mol	1.4	0.13	-0.53	z'	-0.56
NO_2	4	8.2	8.3	8.0	8.2	0.13	0.25	nmol/mol	1.7	9.4	-0.69	z'	-0.83
NO_2	5	-1.8	-1.9	-1.8	-1.7	-0.03	-0.06	nmol/mol	1.4	0.06	-1.2	z'	-1.2
NO_2	6	26	26	26	26	0.41	0.80	nmol/mol	2.2	29	-1.2	z'	-1.5
NO_2	7	-4.6	-4.4	-4.8	-4.6	-0.07	-0.14	nmol/mol	1.6	7.6	-5.0	z'	-3.3
NO_2	8	212	212	212	212	3.4	6.6	nmol/mol	7.8	228	-2.1	z	-2.1
NO_2	9	-3.7	-3.9	-3.4	-3.7	-0.06	-0.11	nmol/mol	1.5	4.3	-4.0	z'	-3.1
NO_2	10	125	125	125	126	2.0	3.9	nmol/mol	5.2	136	-2.0	z	-2.2
O_3	0	0.15	0.10	0.15	0.20	0.00	0.01	nmol/mol	1.0	0.28	-0.12	z	-0.24
O_3	1	65	64	65	65	1.3	2.7	nmol/mol	2.3	65	-0.31	z	-0.24
O_3	2	21	21	21	21	0.43	0.87	nmol/mol	1.4	21	-0.19	z	-0.26
O_3	3	199	199	199	200	4.0	8.2	nmol/mol	4.9	196	0.61	z'	0.36
O_3	4	98	98	98	98	2.0	4.0	nmol/mol	2.9	96	0.56	z'	0.39
O_3	5	133	132	133	133	2.7	5.4	nmol/mol	3.6	130	0.65	z'	0.42
SO_2	0	-0.10	-0.10	-0.10	-0.10	-0.00	-0.00	nmol/mol	1.00	0.19	-0.26	z'	-0.29
SO_2	1	128	127	128	128	2.6	5.2	nmol/mol	3.8	126	0.52	z	0.35
SO_2	2	41	41	41	41	0.82	1.7	nmol/mol	1.9	41	0.28	z'	0.27
SO_2	3	4.7	3.8	5.1	5.2	0.09	0.19	nmol/mol	1.1	4.8	-0.13	z'	-0.13
SO_2	4	21	21	21	21	0.41	0.85	nmol/mol	1.4	20	0.18	z'	0.21
SO_2	5	57	57	57	57	1.1	2.3	nmol/mol	2.2	56	0.54	z	0.45

Source: JRC 2024

Figure 21: Graphical report of results of Ecomaks (Serbia).



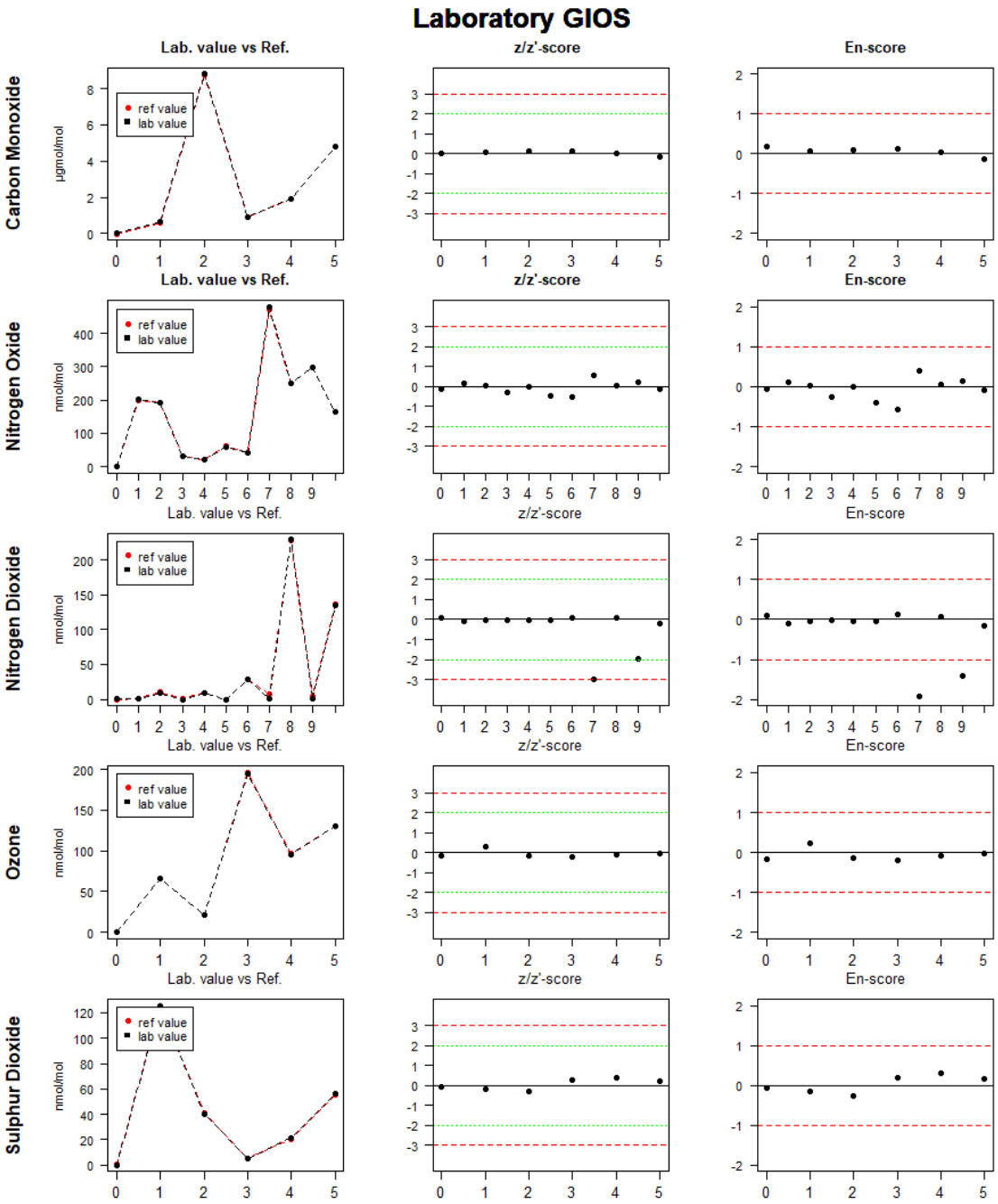
Source: JRC 2024

Table 15: Reported values, uncertainties and performance evaluation results of Ecomaks (Serbia).

Ecomaks													
Component	**Run**	**Lab mean**	**Step 1**	**Step 2**	**Step 3**	**Lab unc com**	**Lab unc exp**	**unit**	**sigmaPT**	**Ref. Val.**	**z/z'- score**	**z/z' selection**	**En- score**
CO	0	0.10	0.10			0.09	0.18	µmol/mol	0.10	-0.00	1.0	z	0.57
CO	1	0.72	0.74	0.72	0.71	0.10	0.21	µmol/mol	0.11	0.62	0.89	z	0.48
CO	2	8.8	8.8	8.8	8.8	0.30	0.60	µmol/mol	0.31	8.8	0.12	z	0.06
CO	3	0.99	0.99	0.99	0.99	0.11	0.22	µmol/mol	0.12	0.92	0.61	z	0.34
CO	4	1.9	1.9	1.9	1.9	0.15	0.30	µmol/mol	0.15	1.9	0.05	z	0.02
CO	5	4.9	4.9	4.9	4.9	0.20	0.40	µmol/mol	0.22	4.8	0.32	z	0.17
NO	0	0.50	0.50			1.2	2.4	nmol/mol	1.0	0.23	0.22	z'	0.10
NO	1	196	197	196	196	7.0	14	nmol/mol	5.8	200	-0.66	z	-0.27
NO	2	186	186	186	186	6.5	13	nmol/mol	5.6	191	-0.85	z	-0.36
NO	3	30	30	30	30	1.5	3.0	nmol/mol	1.7	31	-0.29	z'	-0.16
NO	4	20	20	20	20	1.5	3.0	nmol/mol	1.5	21	-0.60	z'	-0.30
NO	5	58	58	58	58	2.5	5.0	nmol/mol	2.4	60	-0.84	z'	-0.41
NO	6	40	40	40	40	2.0	4.0	nmol/mol	2.0	41	-0.53	z'	-0.26
NO	7	457	457	457	457	14	29	nmol/mol	12	473	-1.3	z	-0.53
NO	8	242	242	242	242	8.0	16	nmol/mol	7.0	251	-1.2	z	-0.52
NO	9	283	283	283	284	9.5	19	nmol/mol	8.1	296	-1.6	z	-0.68
NO	10	157	157	157	156	5.5	11	nmol/mol	4.9	164	-1.4	z	-0.62
NO_2	0	0.09	0.09			0.70	1.4	nmol/mol	1.4	-0.04	0.08	z'	0.07
NO_2	1	0.98	0.95	1.00	1.00	0.75	1.5	nmol/mol	1.4	0.42	0.32	z'	0.22
NO_2	2	10.0	10.0	10.0	10.0	1.5	3.0	nmol/mol	1.7	9.9	0.03	z'	0.02
NO_2	3	0.29	0.34	0.34	0.19	0.71	1.4	nmol/mol	1.4	0.13	0.10	z'	0.08
NO_2	4	9.2	9.1	9.2	9.3	1.0	2.1	nmol/mol	1.7	9.4	-0.13	z'	-0.09
NO_2	5	0.11	0.10	0.14	0.10	0.70	1.4	nmol/mol	1.4	0.06	0.03	z'	0.03
NO_2	6	28	28	28	28	2.0	4.0	nmol/mol	2.2	29	-0.31	z'	-0.17
NO_2	7	7.2	7.7	7.1	6.9	1.00	2.0	nmol/mol	1.6	7.6	-0.14	z'	-0.08
NO_2	8	220	221	220	220	9.0	18	nmol/mol	7.8	228	-1.00	z	-0.42
NO_2	9	3.6	3.6	3.6	3.6	0.85	1.7	nmol/mol	1.5	4.3	-0.34	z'	-0.22
NO_2	10	130	131	130	130	6.0	12	nmol/mol	5.2	136	-1.1	z	-0.46
SO_2	0	0.54	0.54			0.66	1.3	nmol/mol	1.00	0.19	0.31	z'	0.21
SO_2	1	119	118	119	119	4.5	9.0	nmol/mol	3.8	126	-1.9	z	-0.77
SO_2	2	39	39	39	39	2.0	4.0	nmol/mol	1.9	41	-0.80	z'	-0.38
SO_2	3	5.1	4.2	5.5	5.6	0.95	1.9	nmol/mol	1.1	4.8	0.20	z'	0.11
SO_2	4	20	20	20	20	1.5	3.0	nmol/mol	1.4	20	-0.30	z'	-0.15
SO_2	5	53	53	53	53	2.5	5.0	nmol/mol	2.2	56	-1.1	z	-0.50

Source: JRC 2024

Figure 22: Graphical report of results of GIOS (Poland).



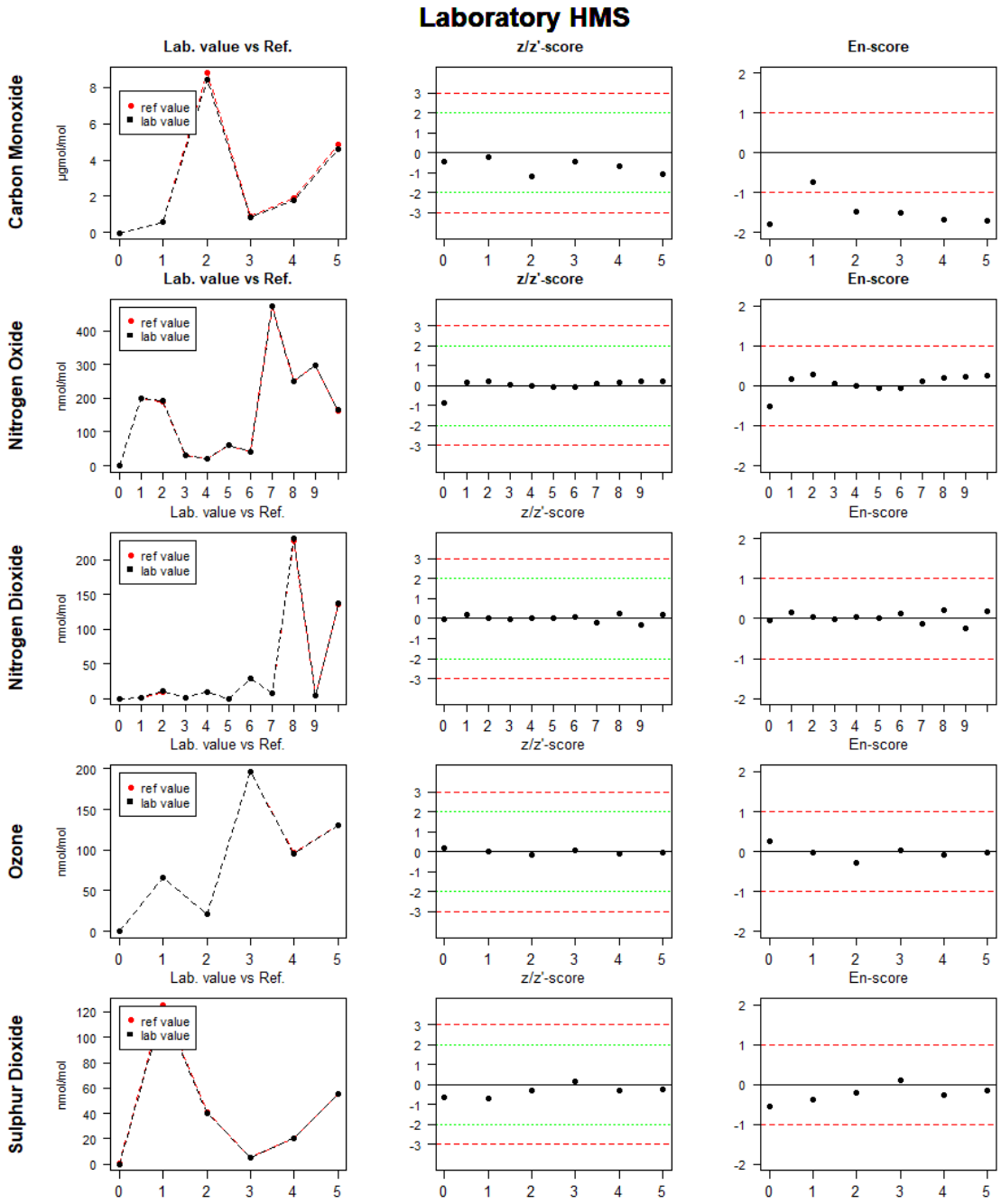
Source: JRC 2024

Table 16: Reported values, uncertainties and performance evaluation results of GIOS (Poland).

GIOS													
Component	**Run**	**Lab mean**	**Step 1**	**Step 2**	**Step 3**	**Lab unc com**	**Lab unc exp**	**unit**	**sigmaPT**	**Ref. Val.**	**z/z'-score**	**z/z' selection**	**En-score**
CO	0	0.00	0.00			0.00	0.01	µmol/mol	0.10	-0.00	0.04	z	0.19
CO	1	0.63	0.63	0.63	0.63	0.06	0.12	µmol/mol	0.11	0.62	0.08	z	0.07
CO	2	8.8	8.8	8.8	8.8	0.17	0.34	µmol/mol	0.31	8.8	0.12	z	0.10
CO	3	0.93	0.93	0.93	0.93	0.06	0.12	µmol/mol	0.12	0.92	0.12	z	0.12
CO	4	1.9	1.9	1.9	1.9	0.07	0.14	µmol/mol	0.15	1.9	0.05	z	0.05
CO	5	4.8	4.8	4.8	4.8	0.10	0.21	µmol/mol	0.22	4.8	-0.14	z	-0.13
NO	0	0.10	0.10			0.50	1.00	nmol/mol	1.0	0.23	-0.10	z'	-0.07
NO	1	201	201	201	201	3.7	7.3	nmol/mol	5.8	200	0.14	z	0.10
NO	2	191	191	191	191	3.5	7.0	nmol/mol	5.6	191	0.04	z	0.03
NO	3	30	30	30	30	0.79	1.6	nmol/mol	1.7	31	-0.29	z'	-0.25
NO	4	21	21	21	21	0.69	1.4	nmol/mol	1.5	21	-0.00	z'	-0.00
NO	5	59	59	59	59	1.2	2.4	nmol/mol	2.4	60	-0.45	z'	-0.40
NO	6	40	40	40	40	0.92	1.8	nmol/mol	2.0	41	-0.53	z'	-0.47
NO	7	480	480	480	480	8.7	17	nmol/mol	12	473	0.59	z	0.40
NO	8	251	251	251	251	4.6	9.1	nmol/mol	7.0	251	0.06	z	0.05
NO	9	298	298	298	298	5.4	11	nmol/mol	8.1	296	0.20	z	0.14
NO	10	163	163	163	163	3.0	6.0	nmol/mol	4.9	164	-0.12	z	-0.09
NO_2	0	0.11	0.11			0.50	1.00	nmol/mol	1.4	-0.04	0.10	z'	0.09
NO_2	1	0.22	0.23	0.24	0.20	0.50	1.00	nmol/mol	1.4	0.42	-0.11	z'	-0.09
NO_2	2	9.9	9.8	9.9	9.9	0.61	1.2	nmol/mol	1.7	9.9	-0.03	z'	-0.03
NO_2	3	0.09	0.16	0.11	0.00	0.50	1.00	nmol/mol	1.4	0.13	-0.03	z'	-0.02
NO_2	4	9.4	9.4	9.3	9.4	0.61	1.2	nmol/mol	1.7	9.4	-0.04	z'	-0.04
NO_2	5	0.01	0.02	0.00	0.01	0.50	1.00	nmol/mol	1.4	0.06	-0.03	z'	-0.03
NO_2	6	29	29	29	29	0.83	1.7	nmol/mol	2.2	29	0.11	z'	0.12
NO_2	7	0.30	0.41	0.28	0.21	0.50	1.00	nmol/mol	1.6	7.6	-3.0	z'	-1.9
NO_2	8	229	229	229	229	4.8	9.5	nmol/mol	7.8	228	0.11	z	0.08
NO_2	9	0.39	0.28	0.44	0.44	0.50	1.00	nmol/mol	1.5	4.3	-2.0	z'	-1.4
NO_2	10	135	135	135	135	2.8	5.7	nmol/mol	5.2	136	-0.18	z	-0.15
O_3	0	0.10	0.10			0.50	1.00	nmol/mol	1.0	0.28	-0.17	z	-0.16
O_3	1	66	66	66	66	1.1	2.3	nmol/mol	2.3	65	0.27	z	0.23
O_3	2	21	21	21	21	0.93	1.8	nmol/mol	1.4	21	-0.19	z	-0.14
O_3	3	195	195	195	195	2.3	4.6	nmol/mol	4.9	196	-0.21	z'	-0.19
O_3	4	96	96	96	96	1.4	2.8	nmol/mol	2.9	96	-0.09	z'	-0.09
O_3	5	130	130	130	130	1.7	3.4	nmol/mol	3.6	130	-0.05	z'	-0.04
SO_2	0	0.10	0.10			0.50	1.00	nmol/mol	1.00	0.19	-0.08	z'	-0.06
SO_2	1	125	125	125	125	2.3	4.7	nmol/mol	3.8	126	-0.20	z	-0.15
SO_2	2	40	40	40	40	0.93	1.9	nmol/mol	1.9	41	-0.29	z'	-0.26
SO_2	3	5.2	5.1	5.2	5.3	0.59	1.2	nmol/mol	1.1	4.8	0.27	z'	0.20
SO_2	4	21	21	21	21	0.69	1.4	nmol/mol	1.4	20	0.35	z'	0.31
SO_2	5	56	56	56	56	1.2	2.3	nmol/mol	2.2	56	0.20	z	0.17

Source: JRC 2024

Figure 23: Graphical report of results of HMS (Hungary).



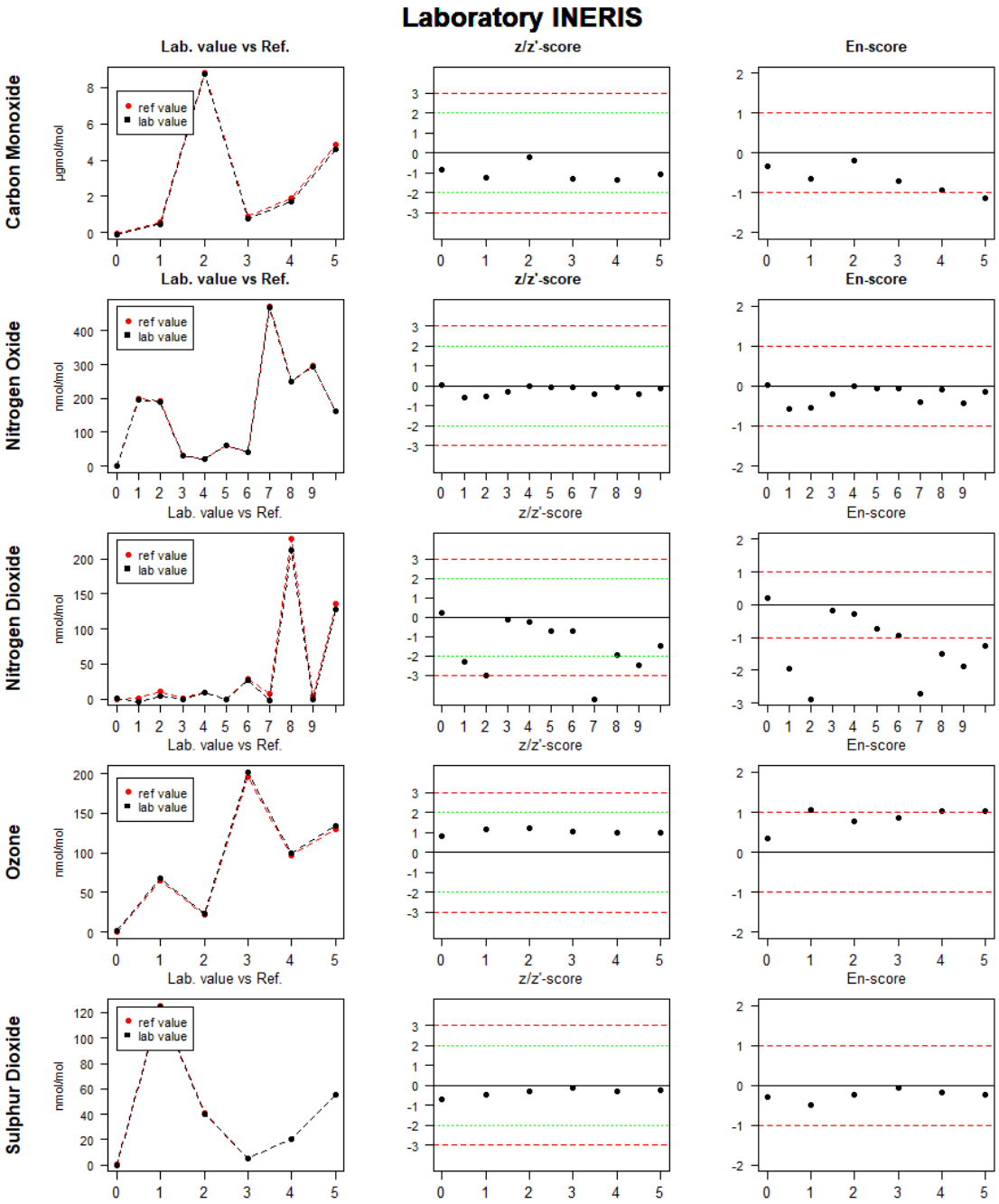
Source: JRC 2024

Table 17: Reported values, uncertainties and performance evaluation results of HMS (Hungary).

HMS													
Component	**Run**	**Lab mean**	**Step 1**	**Step 2**	**Step 3**	**Lab unc com**	**Lab unc exp**	**unit**	**sigmaPT**	**Ref. Val.**	**z/z'-score**	**z/z' selection**	**En-score**
CO	0	-0.05	-0.05			0.01	0.01	µmol/mol	0.10	-0.00	-0.43	z	-1.8
CO	1	0.60	0.60	0.60	0.60	0.01	0.02	µmol/mol	0.11	0.62	-0.18	z	-0.74
CO	2	8.4	8.4	8.4	8.4	0.08	0.17	µmol/mol	0.31	8.8	-1.2	z	-1.5
CO	3	0.86	0.86	0.86	0.87	0.01	0.02	µmol/mol	0.12	0.92	-0.43	z	-1.5
CO	4	1.8	1.8	1.8	1.8	0.02	0.04	µmol/mol	0.15	1.9	-0.64	z	-1.7
CO	5	4.6	4.6	4.6	4.6	0.05	0.09	µmol/mol	0.22	4.8	-1.1	z	-1.7
NO	0	-0.86	-0.86			0.75	1.5	nmol/mol	1.0	0.23	-0.88	z'	-0.52
NO	1	201	201	201	201	2.0	4.1	nmol/mol	5.8	200	0.14	z	0.17
NO	2	192	192	192	192	2.0	3.9	nmol/mol	5.6	191	0.22	z	0.27
NO	3	31	31	30	31	0.80	1.6	nmol/mol	1.7	31	0.06	z'	0.05
NO	4	21	21	21	21	0.78	1.6	nmol/mol	1.5	21	-0.00	z'	-0.00
NO	5	60	60	60	60	0.94	1.9	nmol/mol	2.4	60	-0.06	z'	-0.06
NO	6	41	41	41	41	0.85	1.7	nmol/mol	2.0	41	-0.06	z'	-0.06
NO	7	474	474	474	474	4.5	9.0	nmol/mol	12	473	0.10	z	0.12
NO	8	252	251	252	252	2.5	5.0	nmol/mol	7.0	251	0.16	z	0.19
NO	9	298	298	298	298	2.9	5.8	nmol/mol	8.1	296	0.20	z	0.23
NO	10	165	164	165	165	1.7	3.4	nmol/mol	4.9	164	0.22	z	0.26
NO_2	0	-0.10	-0.10			0.14	0.28	nmol/mol	1.4	-0.04	-0.03	z'	-0.04
NO_2	1	0.78	0.91	0.73	0.70	0.14	0.28	nmol/mol	1.4	0.42	0.21	z'	0.17
NO_2	2	10.0	10.0	10.0	10.0	0.22	0.45	nmol/mol	1.7	9.9	0.03	z'	0.03
NO_2	3	0.12	0.11	0.14	0.11	0.14	0.28	nmol/mol	1.4	0.13	-0.01	z'	-0.01
NO_2	4	9.5	9.5	9.5	9.5	0.22	0.43	nmol/mol	1.7	9.4	0.03	z'	0.04
NO_2	5	0.06	0.13	0.09	-0.04	0.14	0.28	nmol/mol	1.4	0.06	0.00	z'	0.00
NO_2	6	29	29	29	29	0.50	1.1	nmol/mol	2.2	29	0.11	z'	0.14
NO_2	7	7.0	7.3	7.1	6.7	0.19	0.38	nmol/mol	1.6	7.6	-0.22	z'	-0.14
NO_2	8	230	230	230	230	4.0	8.0	nmol/mol	7.8	228	0.24	z	0.21
NO_2	9	3.7	3.8	3.7	3.5	0.15	0.31	nmol/mol	1.5	4.3	-0.31	z'	-0.24
NO_2	10	137	137	137	137	2.4	4.8	nmol/mol	5.2	136	0.20	z	0.19
O_3	0	0.47	0.47			0.30	0.60	nmol/mol	1.0	0.28	0.19	z	0.25
O_3	1	65	65	65	66	0.94	1.9	nmol/mol	2.3	65	-0.02	z	-0.02
O_3	2	21	21	21	21	0.41	0.83	nmol/mol	1.4	21	-0.19	z	-0.27
O_3	3	196	196	196	197	2.7	5.4	nmol/mol	4.9	196	0.04	z'	0.03
O_3	4	96	96	96	96	1.3	2.7	nmol/mol	2.9	96	-0.09	z'	-0.09
O_3	5	130	130	130	130	1.8	3.6	nmol/mol	3.6	130	-0.05	z'	-0.04
SO_2	0	-0.52	-0.52			0.39	0.78	nmol/mol	1.00	0.19	-0.63	z'	-0.55
SO_2	1	123	123	123	123	3.6	7.1	nmol/mol	3.8	126	-0.73	z	-0.37
SO_2	2	40	40	40	40	1.2	2.4	nmol/mol	1.9	41	-0.29	z'	-0.22
SO_2	3	5.0	4.9	5.0	5.1	0.41	0.82	nmol/mol	1.1	4.8	0.12	z'	0.10
SO_2	4	20	20	20	20	0.68	1.4	nmol/mol	1.4	20	-0.30	z'	-0.27
SO_2	5	55	55	55	55	1.6	3.2	nmol/mol	2.2	56	-0.25	z	-0.16

Source: JRC 2024

Figure 24: Graphical report of results of INERIS (France).



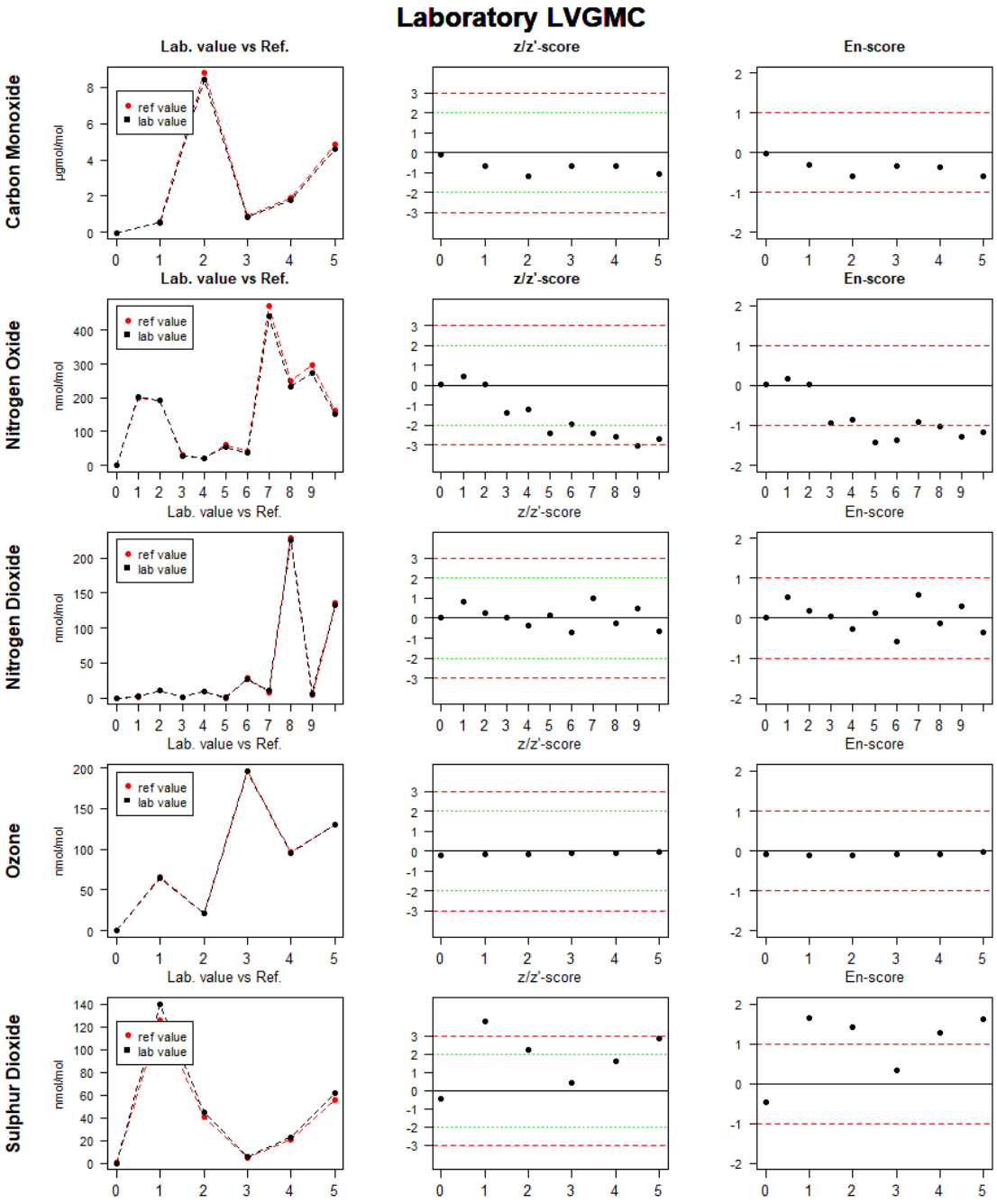
Source: JRC 2024

Table 18: Reported values, uncertainties and performance evaluation results of INERIS (France).

INERIS													
Component	**Run**	**Lab mean**	**Step 1**	**Step 2**	**Step 3**	**Lab unc com**	**Lab unc exp**	**unit**	**sigmaPT**	**Ref. Val.**	**z/z'-score**	**z/z' selection**	**En-score**
CO	0	-0.08	-0.08			0.12	0.24	µmol/mol	0.10	-0.00	-0.82	z	-0.34
CO	1	0.48	0.48	0.48	0.48	0.11	0.22	µmol/mol	0.11	0.62	-1.2	z	-0.64
CO	2	8.7	8.7	8.7	8.7	0.14	0.28	µmol/mol	0.31	8.8	-0.20	z	-0.19
CO	3	0.76	0.76	0.75	0.76	0.11	0.22	µmol/mol	0.12	0.92	-1.3	z	-0.71
CO	4	1.7	1.7	1.7	1.7	0.10	0.20	µmol/mol	0.15	1.9	-1.3	z	-0.94
CO	5	4.6	4.6	4.6	4.6	0.09	0.18	µmol/mol	0.22	4.8	-1.1	z	-1.1
NO	0	0.31	0.31			1.2	2.4	nmol/mol	1.0	0.23	0.06	z'	0.03
NO	1	197	197	197	197	2.4	4.8	nmol/mol	5.8	200	-0.55	z	-0.58
NO	2	188	188	188	188	2.3	4.6	nmol/mol	5.6	191	-0.49	z	-0.53
NO	3	30	30	30	30	1.2	2.4	nmol/mol	1.7	31	-0.29	z'	-0.19
NO	4	21	21	21	21	1.2	2.4	nmol/mol	1.5	21	-0.00	z'	-0.00
NO	5	60	60	60	60	1.3	2.6	nmol/mol	2.4	60	-0.06	z'	-0.05
NO	6	41	41	41	41	1.2	2.5	nmol/mol	2.0	41	-0.06	z'	-0.04
NO	7	468	467	468	468	5.6	11	nmol/mol	12	473	-0.41	z	-0.41
NO	8	250	250	250	250	2.9	5.9	nmol/mol	7.0	251	-0.08	z	-0.08
NO	9	293	293	293	293	3.4	6.9	nmol/mol	8.1	296	-0.42	z	-0.44
NO	10	163	163	163	163	2.0	4.1	nmol/mol	4.9	164	-0.12	z	-0.13
NO_2	0	0.28	0.28			0.00	0.01	nmol/mol	1.4	-0.04	0.21	z'	0.22
NO_2	1	-3.6	-3.9	-3.6	-3.4	0.18	0.35	nmol/mol	1.4	0.42	-2.3	z'	-2.0
NO_2	2	4.0	6.0	0.00	6.1	6.1	0.28	nmol/mol	1.7	9.9	-3.0	z'	-2.9
NO_2	3	-0.12	-0.04	-0.07	-0.26	0.01	0.02	nmol/mol	1.4	0.13	-0.16	z'	-0.17
NO_2	4	9.0	8.9	9.0	9.0	0.14	0.29	nmol/mol	1.7	9.4	-0.26	z'	-0.30
NO_2	5	-1.1	-1.1	-1.1	-1.00	0.04	0.08	nmol/mol	1.4	0.06	-0.70	z'	-0.73
NO_2	6	27	27	27	27	0.45	0.90	nmol/mol	2.2	29	-0.74	z'	-0.95
NO_2	7	-2.7	-2.9	-2.7	-2.4	0.47	0.94	nmol/mol	1.6	7.6	-4.2	z'	-2.7
NO_2	8	213	213	213	213	4.6	9.2	nmol/mol	7.8	228	-1.9	z	-1.5
NO_2	9	-0.65	-0.70	-0.73	-0.53	0.31	0.63	nmol/mol	1.5	4.3	-2.5	z'	-1.9
NO_2	10	128	129	128	128	2.6	5.3	nmol/mol	5.2	136	-1.5	z	-1.3
O_3	0	1.1	1.1			1.2	2.3	nmol/mol	1.0	0.28	0.82	z	0.35
O_3	1	68	68	68	68	1.00	2.1	nmol/mol	2.3	65	1.1	z	1.1
O_3	2	23	23	23	23	1.1	2.2	nmol/mol	1.4	21	1.2	z	0.76
O_3	3	202	201	202	202	2.6	5.1	nmol/mol	4.9	196	1.0	z'	0.87
O_3	4	99	99	99	100	1.1	2.3	nmol/mol	2.9	96	0.99	z'	1.0
O_3	5	134	134	134	134	1.4	2.8	nmol/mol	3.6	130	1.00	z'	1.0
SO_2	0	-0.62	-0.62			1.2	2.4	nmol/mol	1.00	0.19	-0.72	z'	-0.31
SO_2	1	124	124	124	124	1.5	3.0	nmol/mol	3.8	126	-0.47	z	-0.49
SO_2	2	40	40	40	40	1.00	2.0	nmol/mol	1.9	41	-0.29	z'	-0.25
SO_2	3	4.7	3.8	5.0	5.3	1.2	2.3	nmol/mol	1.1	4.8	-0.12	z'	-0.06
SO_2	4	20	20	20	20	1.1	2.2	nmol/mol	1.4	20	-0.30	z'	-0.19
SO_2	5	55	55	55	55	1.00	2.0	nmol/mol	2.2	56	-0.25	z	-0.24

Source: JRC 2024

Figure 25: Graphical report of results of LVGMC (Latvia).



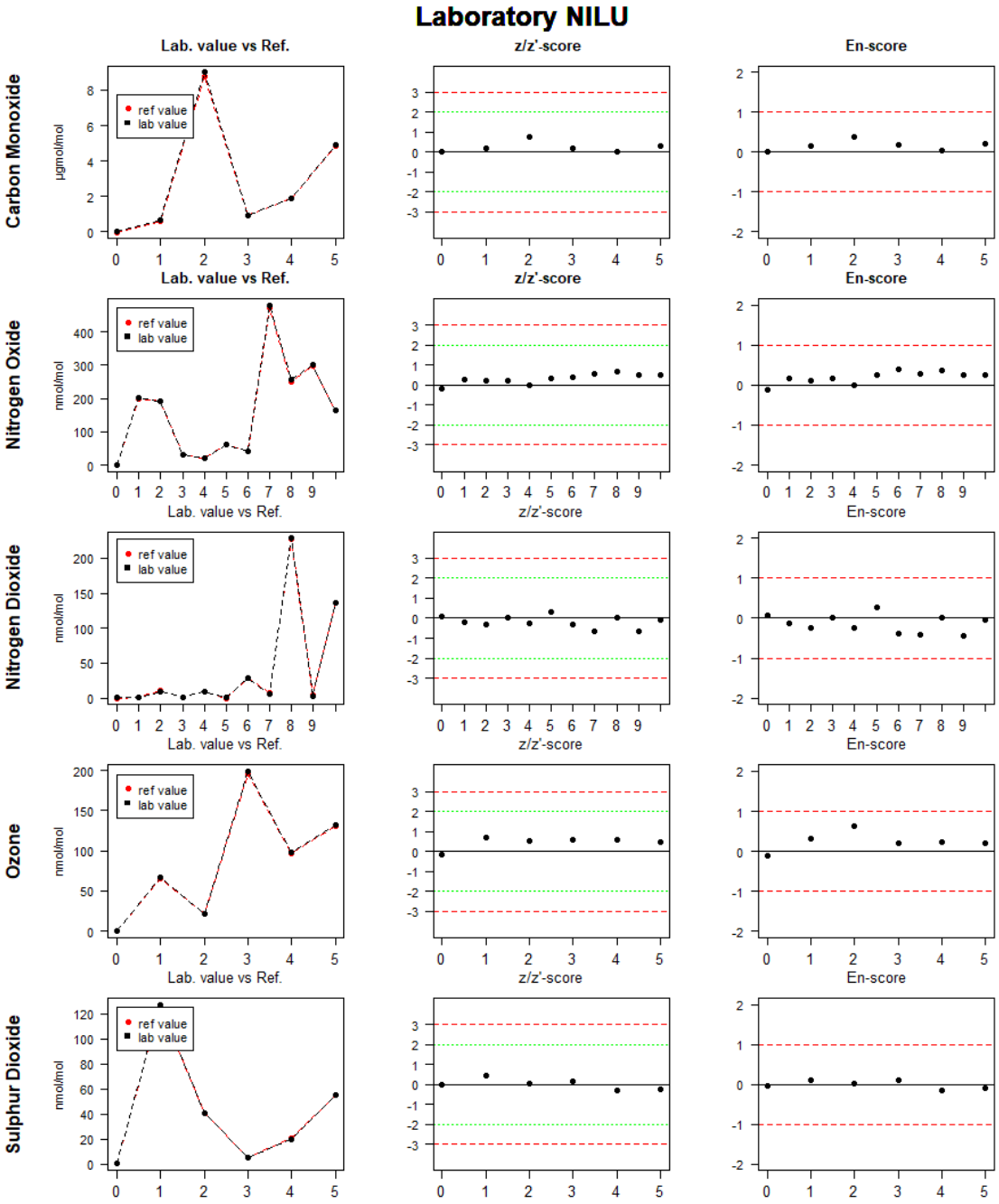
Source: JRC 2024

Table 19: Reported values, uncertainties and performance evaluation results of LVGMC (Latvia).

LVGMC													
Component	**Run**	**Lab mean**	**Step 1**	**Step 2**	**Step 3**	**Lab unc com**	**Lab unc exp**	**unit**	**sigmaPT**	**Ref. Val.**	**z/z'- score**	**z/z' selection**	**En- score**
CO	0	-0.01	-0.01			0.12	0.24	µmol/mol	0.10	-0.00	-0.07	z	-0.03
CO	1	0.55	0.55	0.54	0.55	0.12	0.24	µmol/mol	0.11	0.62	-0.64	z	-0.31
CO	2	8.4	8.4	8.4	8.4	0.30	0.60	µmol/mol	0.31	8.8	-1.2	z	-0.58
CO	3	0.84	0.84	0.83	0.84	0.12	0.24	µmol/mol	0.12	0.92	-0.64	z	-0.32
CO	4	1.8	1.8	1.8	1.8	0.13	0.26	µmol/mol	0.15	1.9	-0.64	z	-0.35
CO	5	4.6	4.6	4.6	4.6	0.19	0.38	µmol/mol	0.22	4.8	-1.1	z	-0.59
NO	0	0.29	0.29			0.63	1.3	nmol/mol	1.0	0.23	0.05	z'	0.03
NO	1	203	204	202	202	7.2	14	nmol/mol	5.8	200	0.43	z	0.17
NO	2	191	194	190	189	6.8	14	nmol/mol	5.6	191	0.04	z	0.02
NO	3	28	28	28	28	1.2	2.3	nmol/mol	1.7	31	-1.4	z'	-0.93
NO	4	19	19	19	19	0.92	1.8	nmol/mol	1.5	21	-1.2	z'	-0.86
NO	5	54	54	54	54	2.0	4.0	nmol/mol	2.4	60	-2.4	z'	-1.4
NO	6	37	37	37	37	1.5	2.9	nmol/mol	2.0	41	-1.9	z'	-1.3
NO	7	443	441	444	444	16	32	nmol/mol	12	473	-2.4	z	-0.92
NO	8	233	232	233	233	8.3	17	nmol/mol	7.0	251	-2.5	z	-1.0
NO	9	272	270	272	273	10.0	19	nmol/mol	8.1	296	-3.0	z	-1.3
NO	10	150	150	150	151	5.4	11	nmol/mol	4.9	164	-2.7	z	-1.2
NO_2	0	0.00	0.00			0.87	1.7	nmol/mol	1.4	-0.04	0.03	z'	0.02
NO_2	1	1.8	1.7	2.0	1.8	0.87	1.8	nmol/mol	1.4	0.42	0.81	z'	0.52
NO_2	2	10	9.4	11	11	0.94	1.9	nmol/mol	1.7	9.9	0.27	z'	0.19
NO_2	3	0.20	0.16	0.25	0.20	0.87	1.7	nmol/mol	1.4	0.13	0.05	z'	0.03
NO_2	4	8.8	8.8	8.7	8.8	0.92	1.8	nmol/mol	1.7	9.4	-0.37	z'	-0.28
NO_2	5	0.33	0.33	0.34	0.32	0.87	1.7	nmol/mol	1.4	0.06	0.17	z'	0.12
NO_2	6	27	27	27	27	1.2	2.5	nmol/mol	2.2	29	-0.74	z'	-0.59
NO_2	7	10.0	10.0	10.0	10.0	0.93	1.9	nmol/mol	1.6	7.6	1.00	z'	0.59
NO_2	8	226	226	226	226	7.4	15	nmol/mol	7.8	228	-0.27	z	-0.14
NO_2	9	5.2	5.3	5.4	5.0	0.89	1.8	nmol/mol	1.5	4.3	0.48	z'	0.30
NO_2	10	133	132	133	133	4.4	8.8	nmol/mol	5.2	136	-0.63	z	-0.36
O_3	0	0.03	0.03			1.3	2.6	nmol/mol	1.0	0.28	-0.24	z	-0.09
O_3	1	65	65	65	65	1.5	3.0	nmol/mol	2.3	65	-0.17	z	-0.12
O_3	2	21	21	21	21	1.3	2.6	nmol/mol	1.4	21	-0.19	z	-0.10
O_3	3	196	195	196	196	2.6	5.1	nmol/mol	4.9	196	-0.09	z'	-0.07
O_3	4	96	96	96	96	1.7	3.4	nmol/mol	2.9	96	-0.09	z'	-0.08
O_3	5	130	130	130	130	2.0	3.9	nmol/mol	3.6	130	-0.05	z'	-0.04
SO_2	0	-0.30	-0.30			0.48	0.00	nmol/mol	1.00	0.19	-0.44	z'	-0.48
SO_2	1	140	140	140	140	4.2	8.4	nmol/mol	3.8	126	3.8	z	1.6
SO_2	2	45	45	45	45	1.4	2.9	nmol/mol	1.9	41	2.2	z'	1.4
SO_2	3	5.4	5.3	5.3	5.5	0.51	1.00	nmol/mol	1.1	4.8	0.40	z'	0.32
SO_2	4	23	23	23	23	0.83	1.7	nmol/mol	1.4	20	1.6	z'	1.3
SO_2	5	62	62	62	62	1.9	3.8	nmol/mol	2.2	56	2.9	z	1.6

Source: JRC 2024

Figure 26: Graphical report of results of NILU (Norway).



Source: JRC 2024

Table 20: Reported values, uncertainties and performance evaluation results of NILU (Norway).

NILU													
Component	**Run**	**Lab mean**	**Step 1**	**Step 2**	**Step 3**	**Lab unc com**	**Lab unc exp**	**unit**	**sigmaPT**	**Ref. Val.**	**z/z'- score**	**z/z' selection**	**En- score**
CO	0	0.00		0.00	0.00	0.06	0.12	µmol/mol	0.10	-0.00	0.03	z	0.02
CO	1	0.64	0.64	0.64	0.64	0.06	0.13	µmol/mol	0.11	0.62	0.17	z	0.14
CO	2	9.0	9.0	9.0	9.0	0.30	0.60	µmol/mol	0.31	8.8	0.76	z	0.38
CO	3	0.94	0.94	0.94	0.94	0.07	0.13	µmol/mol	0.12	0.92	0.20	z	0.19
CO	4	1.9	1.9	1.9	1.9	0.10	0.20	µmol/mol	0.15	1.9	0.05	z	0.03
CO	5	4.9	4.9	4.9	4.9	0.20	0.30	µmol/mol	0.22	4.8	0.32	z	0.22
NO	0	0.02		0.05	0.00	0.58	1.2	nmol/mol	1.0	0.23	-0.17	z'	-0.11
NO	1	202	202	202	202	5.0	10.0	nmol/mol	5.8	200	0.31	z	0.18
NO	2	192	192	192	192	5.0	10.0	nmol/mol	5.6	191	0.22	z	0.12
NO	3	31	31	31	31	1.00	2.0	nmol/mol	1.7	31	0.24	z'	0.18
NO	4	21	21	21	21	1.00	2.0	nmol/mol	1.5	21	-0.00	z'	-0.00
NO	5	61	61	61	61	2.0	3.0	nmol/mol	2.4	60	0.33	z'	0.25
NO	6	42	42	42	42	1.00	2.0	nmol/mol	2.0	41	0.41	z'	0.35
NO	7	480	480	480	480	12	25	nmol/mol	12	473	0.59	z	0.28
NO	8	255	255	255	256	7.0	13	nmol/mol	7.0	251	0.68	z	0.36
NO	9	301	300	301	301	8.0	16	nmol/mol	8.1	296	0.52	z	0.26
NO	10	166	166	166	166	4.0	9.0	nmol/mol	4.9	164	0.49	z	0.26
NO_2	0	0.10		0.10	0.10	0.58	1.2	nmol/mol	1.4	-0.04	0.09	z'	0.08
NO_2	1	0.10	0.10	0.10	0.10	0.58	1.2	nmol/mol	1.4	0.42	-0.18	z'	-0.14
NO_2	2	9.4	9.3	9.3	9.5	0.60	1.3	nmol/mol	1.7	9.9	-0.29	z'	-0.23
NO_2	3	0.17	0.10	0.10	0.30	0.58	1.2	nmol/mol	1.4	0.13	0.02	z'	0.02
NO_2	4	8.9	8.9	8.9	9.0	0.60	1.3	nmol/mol	1.7	9.4	-0.28	z'	-0.25
NO_2	5	0.57	0.50	0.60	0.60	0.58	1.2	nmol/mol	1.4	0.06	0.32	z'	0.26
NO_2	6	28	28	28	28	1.00	1.00	nmol/mol	2.2	29	-0.31	z'	-0.39
NO_2	7	6.0	6.3	6.0	5.8	0.60	1.2	nmol/mol	1.6	7.6	-0.63	z'	-0.40
NO_2	8	228	229	228	228	6.0	12	nmol/mol	7.8	228	0.03	z	0.02
NO_2	9	3.0	3.2	3.0	2.9	0.60	1.2	nmol/mol	1.5	4.3	-0.63	z'	-0.44
NO_2	10	136	136	135	136	4.0	7.0	nmol/mol	5.2	136	-0.06	z	-0.04
O_3	0	0.10		0.10	0.10	0.78	1.6	nmol/mol	1.0	0.28	-0.17	z	-0.11
O_3	1	67	67	67	67	2.0	5.0	nmol/mol	2.3	65	0.70	z	0.31
O_3	2	22	22	22	22	1.00	1.00	nmol/mol	1.4	21	0.51	z	0.63
O_3	3	199	199	199	199	7.0	14	nmol/mol	4.9	196	0.55	z'	0.20
O_3	4	98	98	98	98	3.0	7.0	nmol/mol	2.9	96	0.56	z'	0.24
O_3	5	132	132	132	132	5.0	9.0	nmol/mol	3.6	130	0.48	z'	0.19
SO_2	0	0.15		0.15	0.15	0.59	1.2	nmol/mol	1.00	0.19	-0.04	z'	-0.03
SO_2	1	127	127	128	127	7.0	14	nmol/mol	3.8	126	0.42	z	0.11
SO_2	2	41	41	41	40	2.0	5.0	nmol/mol	1.9	41	0.04	z'	0.02
SO_2	3	5.0		5.0	5.1	0.70	1.3	nmol/mol	1.1	4.8	0.16	z'	0.11
SO_2	4	20	20	20	20	1.00	3.0	nmol/mol	1.4	20	-0.30	z'	-0.15
SO_2	5	55	55	55	55	3.0	6.0	nmol/mol	2.2	56	-0.25	z	-0.09

Source: JRC 2024

Annex C: Reproducibility

1 Introduction

In this PT the standard ISO 5725 was used to confirm the test method's validity and reliability through the calculation of reproducibility.

The instruments used in these exercises have consistently demonstrated very high repeatability. Confirming observations made over the last 15 years, no significant variability has been noted among any of the participants. Consequently, due to the limited utility of this assessment, ERLAP has decided to omit repeatability from the report.

Reproducibility is defined as the closeness of the agreement between the results of measurements of the same measurand carried out under various conditions: different operators, different equipment, different equipment calibration etc.

During the PT the participants were invited to use, as much as possible, their own everyday work procedure.

The reproducibility limit (R) is a quantitative measure indicating the maximum difference in results that can be expected under reproducibility conditions for a given level of probability, usually 95%.

For the main purpose of monitoring trends between different PT undertaken by ERLAP, the precision of standardized SO_2, CO, O_3 and NO_X measurement methods [2], [3], [4] and [5] as implemented by NRLs, is evaluated. Due to the small number of participants the reproducibility results doesn't give an accurate response about the quality of the methods application during the PT. Applied methodology is described in ISO 5725-1, 5725-2 and 5725-6 [14], [15] and [16]. The precision experiment has involved a maximum of eleven laboratories, the actual number of laboratories (p) is listed in Table 21 according to the data reported.

Six concentration levels were tested for O_3, CO, SO_2 and NO_2, and eleven for NO. Performance tests for each participant are performed and results are reported in Annex B.

In ISO 5725 reproducibility (R) limits is defined. This limit is the value less than or equal to which the absolute difference between two test results, obtained under reproducibility conditions, may be expected to be with (1 - α) probability level.

The reproducibility standard deviation (*SR*) was calculated as the square root of sum of reproducibility of between-laboratory variance at the 95% confidence level (α). The reproducibility limit (R) is calculated using Equation 5 [16].

Equation 5

$$R = t_{\nu/\alpha} \cdot \sqrt{2} \cdot SR$$

R = reproducibility limit

$t_{\nu/\alpha}$ = *t* Student distribution value

SR = standard deviation of between-lab reproducibility.

The reproducibility standard deviation with (p-1) degrees of freedom (ν) and the critical range Student factors, for R, corresponding to defined confidence level (α) and degree of freedom (ν), are reported in Table 21.

Table 21: Critical values of t used in the reproducibility (R) evaluation.

parameter	run	p	t critical value 95% for R
CO	1	9	2.306
CO	2,3,4,5	10	2.262
NO	6	9	2.306
NO	7	11	2.228
NO	1,2,3,4,5,8,9,10	10	2.262
NO_2	2	9	2.306
NO_2	4	10	2.262
NO_2	6,8,10	11	2.228
O_3	1,2	9	2.306

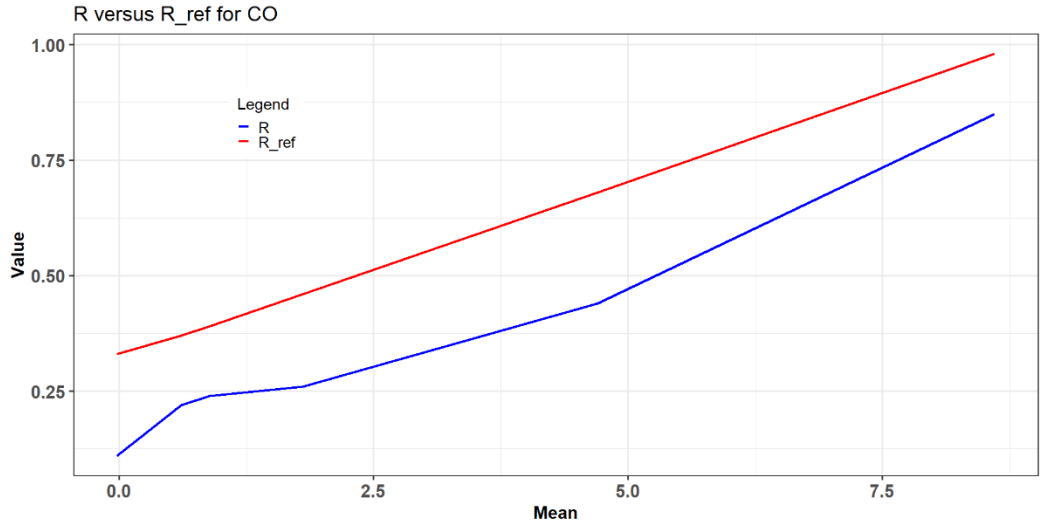
O_3	3,4,5	10	2.262
SO_2	2	7	2.447
SO_2	1,3,4,5	8	2.365

Source: JRC 2024

2 Results

The Reproducibility (R) limits of measurement methods are presented from Figure 27 to Figure 31. It is reported also the 'reproducibility from common criteria (R_Ref.)' calculated by substituting *SR* in Equation 5 with a 'standard deviation for proficiency assessment'(σ_{pt}) (see Table 4). Comparison between R and R_Ref. serves to indicate that σ_{pt} is realistic [13] or from the other point of view, that the general methodology implemented by NRLs is appropriate for σ_{pt}.

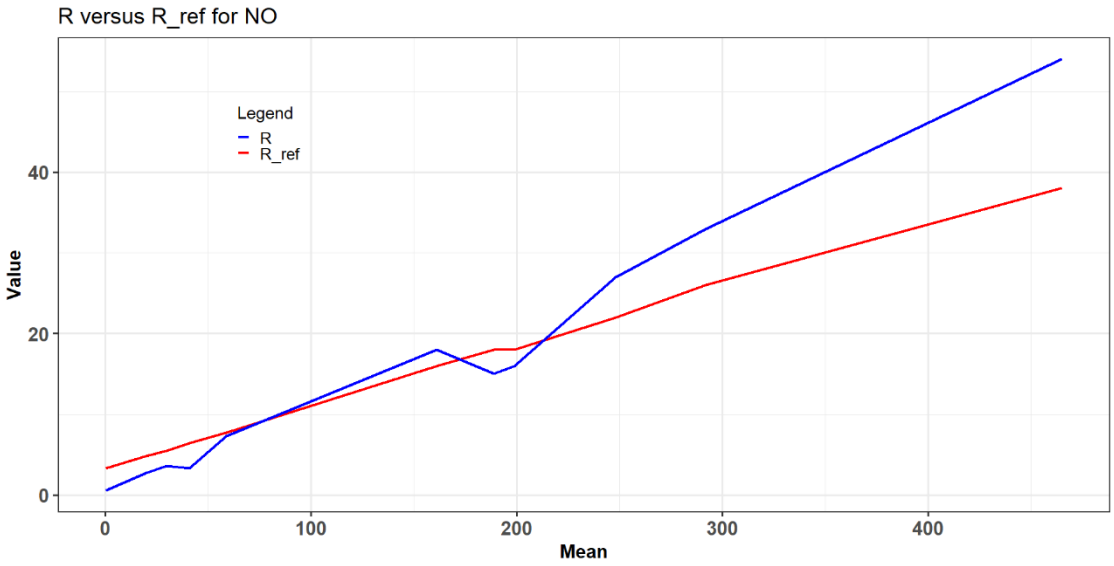
Figure 27: R of CO standard measurement method as a function of concentration.



Component	Run	Mean	R	R_ref	R%	unit
CO	0	-0.02	0.11	0.33		µmol/mol
CO	1	0.61	0.22	0.37	36	µmol/mol
CO	3	0.89	0.24	0.39	27	µmol/mol
CO	4	1.8	0.26	0.46	14	µmol/mol
CO	5	4.7	0.44	0.68	9.4	µmol/mol
CO	2	8.6	0.85	0.98	9.9	µmol/mol

Source: JRC 2024

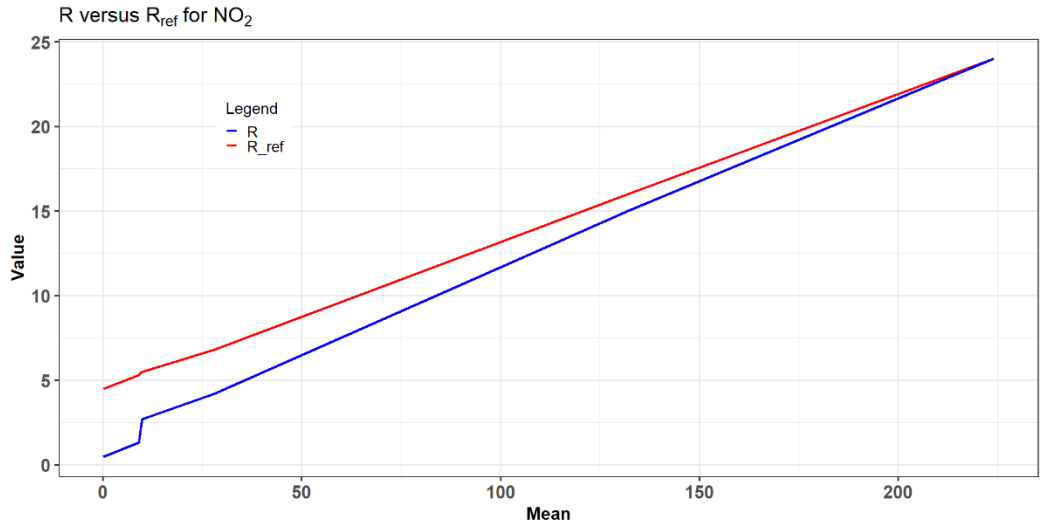
Figure 28: R of NO standard measurement method as a function of concentration.



Component	Run	Mean	R	R_ref	R%	unit
NO	0	0.24	0.56	3.3		nmol/mol
NO	4	20	2.7	4.8	14	nmol/mol
NO	3	30	3.6	5.5	12	nmol/mol
NO	6	41	3.3	6.4	8.0	nmol/mol
NO	5	59	7.3	7.7	12	nmol/mol
NO	10	161	18	16	11	nmol/mol
NO	2	189	15	18	7.9	nmol/mol
NO	1	199	16	18	8.0	nmol/mol
NO	8	248	27	22	11	nmol/mol
NO	9	292	33	26	11	nmol/mol
NO	7	465	54	38	12	nmol/mol

Source: JRC 2024

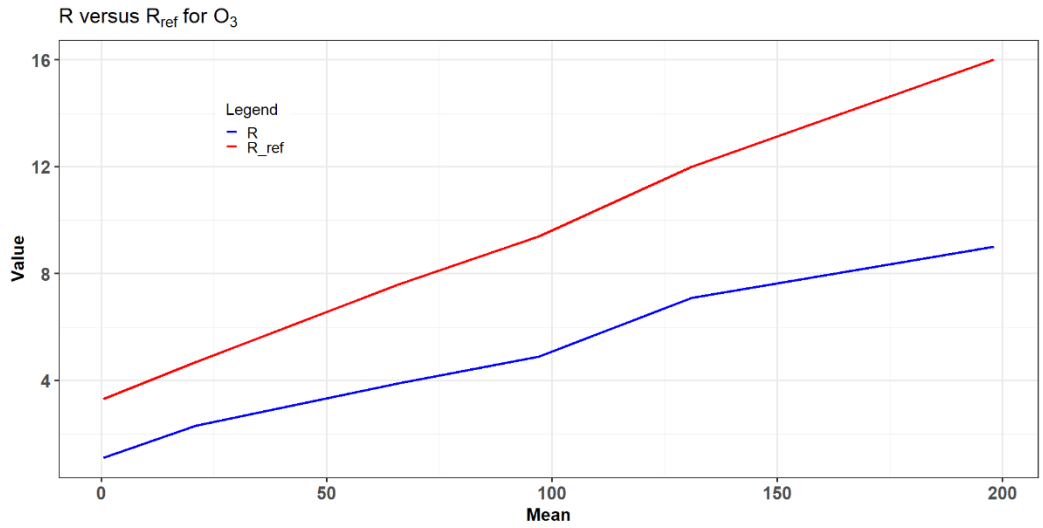
Figure 29: R of NO_2 standard measurement method as a function of concentration.



Component	Run	Mean	R	R_ref	R%	unit
NO_2	0	0.08	0.46	4.5		nmol/mol
NO_2	4	9.1	1.3	5.3	14	nmol/mol
NO_2	2	9.8	2.7	5.5	28	nmol/mol
NO_2	6	28	4.2	6.8	15	nmol/mol
NO_2	10	132	15	16	11	nmol/mol
NO_2	8	224	24	24	11	nmol/mol

Source: JRC 2024

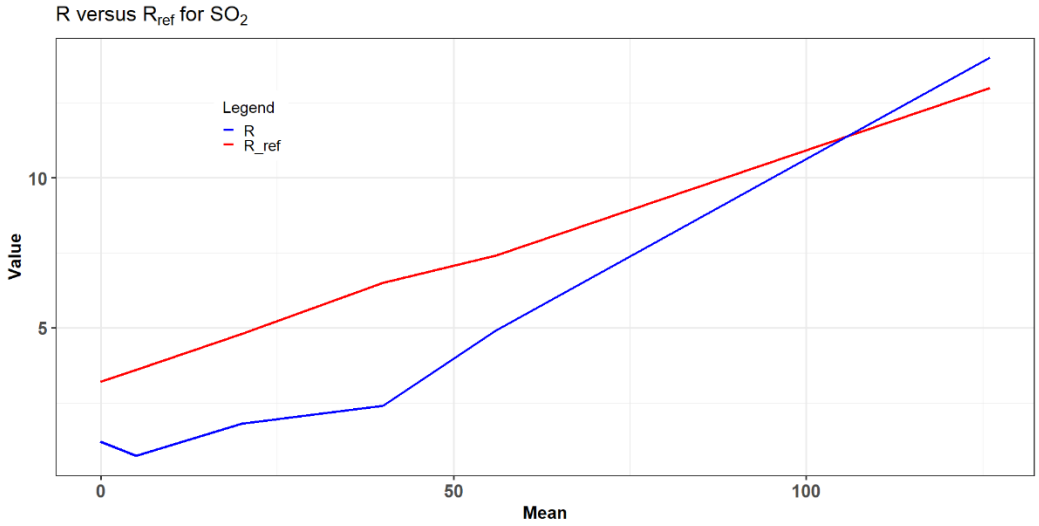
Figure 30: R of O_3 standard measurement method as a function of concentration.



Component	Run	Mean	R	R_ref	R%	unit
O_3	0	0.38	1.1	3.3		nmol/mol
O_3	2	21	2.3	4.7	11	nmol/mol
O_3	1	66	3.9	7.6	5.9	nmol/mol
O_3	4	97	4.9	9.4	5.1	nmol/mol
O_3	5	131	7.1	12	5.4	nmol/mol
O_3	3	198	9.0	16	4.5	nmol/mol

Source: JRC 2024

Figure 31: R of SO_2 standard measurement method as a function of concentration.



Component	Run	Mean	R	R_ref	R%	unit
SO_2	0	-0.09	1.2	3.2		nmol/mol
SO_2	3	5.0	0.73	3.6	15	nmol/mol
SO_2	4	20	1.8	4.8	9.0	nmol/mol
SO_2	2	40	2.4	6.5	6.0	nmol/mol
SO_2	5	56	4.9	7.4	8.8	nmol/mol
SO_2	1	126	14	13	11	nmol/mol

Source: JRC 2024

3 Conclusions

Before assessing reproducibility in this proficiency test (PT), outliers were identified and excluded using boxplot analysis.
A boxplot, or box and whisker diagram, is the tool used to depict the distribution of a dataset and to identify outliers among the participants' results. The plot highlights the lower quartile, median, and upper quartile, while the "whiskers" extend to the last data points not considered abnormal. Any data point that falls outside the 1.5 times the interquartile range (IQR) is considered an outlier, indicating a result significantly different from the norm.
The outliers were removed before proceeding with the reproducibility evaluation. At the highest concentration levels, the relative reproducibility limits are 9.9% for CO, 12% for NO, 11% for NO_2, 4.5% for O_3, and 11% for SO_2.
Graphical representations of reproducibility for CO and O_3 showed no intersection of the blue line (R) with the reference red line, signaling overall satisfactory performance for all pollutants measured. For NO, NO_2 and SO_2 the graphs show a poor performance of the measurement during this PT. As reported in Table 7 this proficiency test, when compared to nearly two decades of historical data, has regrettably been deemed the poorest in terms of the total number of z-score valid values.

Annex D: Confidentiality

Results of the PT are published according to the agreements included in the document AQUILA-N37 [12] approved by all NRL of the AQUILA network.
In order to ensure confidentiality of the laboratories information, ERLAP guarantees the submitted data as follows:

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

The form LAB-REC-2000 (Confidentiality involvement form) is asked to be signed by the participants during their first participation to a PT organized by ERLAP.

Annex E: Accreditation certificates

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European Reference Laboratory for Air Pollution (ERLAP)
Clean Air and Climate Unit
Directorate C. Energy, Mobility and Climate
Joint Research Centre -European Commission
Sede/Headquarters:
- Via E. Fermi 2749 - 21027 Ispra VA

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MD-CA-01 rev. 06

Data di 1ª emissione *1st issue date*	Data di revisione *Review date*	Data di scadenza *Expiring date*
17-01-2019	**03-02-2023**	**15-01-2027**

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	Revisione: **0** Data: **17/01/2019**
	pag. **1** di **1** UNI CEI EN ISO/IEC 17043:2010

ELENCO SCHEMI ACCREDITATI - CATEGORIA: 0

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

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