ISSN 1831-9424

European Commission

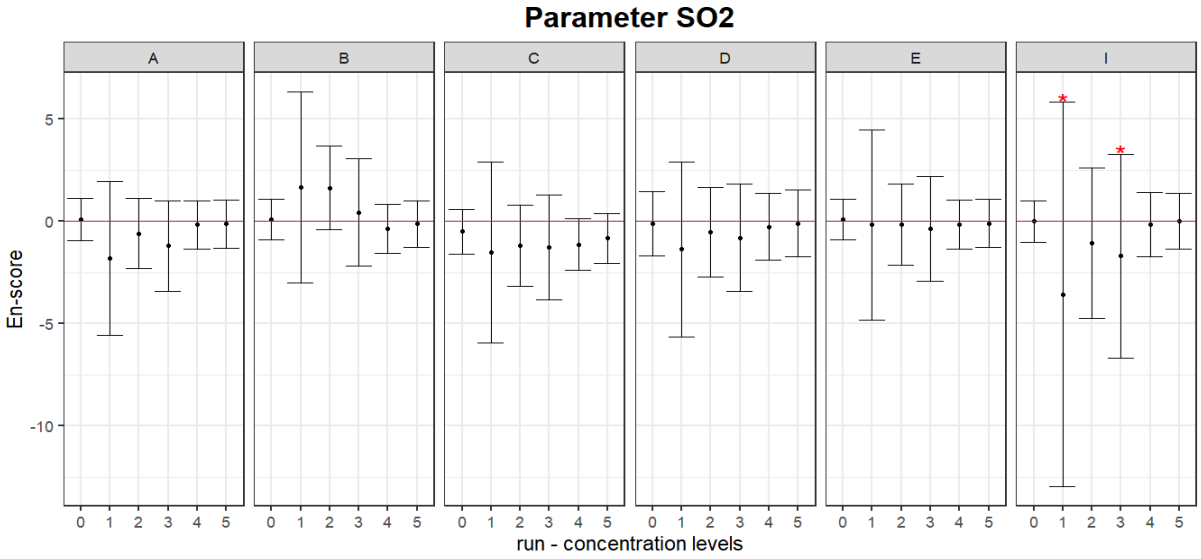
JRC TECHNICAL REPORT

# PROFICIENCY TESTING SCHEME Measurement of inorganic gaseous pollutants ($SO_2$, CO, $O_3$, NO and $NO_2$) in filtered ambient air (27-30 March 2023, Ispra-Italy)

*European Commission harmonisation programme for air quality measurements*

Barbiere M., Tarricone C., Borowiak A.

2023

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JRC134689

EUR 31694 EN

PDF ISBN 978-92-68-08424-3 ISSN 1831-9424 doi:10.2760/434570 KJ-NA-31-694-EN-N

Luxembourg: Publications Office of the European Union, 2023



How to cite this report: Barbiere M., Tarricone C., Borowiak A., *PROFICIENCY TESTING SCHEME, Measurement of inorganic gaseous pollutants ($SO_2$, CO, $O_3$, NO and $NO_2$) in filtered ambient air (27-30 March 2023, Ispra-Italy)*, Publications Office of the European Union, Luxembourg, 2023, doi:10.2760/434570, JRC134689

EUROPEAN REFERENCE LABORATORY FOR AIR POLLUTION - ERLAP

# PROFICIENCY TESTING SCHEME

## Measurement of inorganic gaseous pollutants (SO2, CO, O3, NO and NO2) in filtered ambient air (27-30 March 2023, Ispra-Italy)

European Commission harmonisation programme
for air quality measurements

Barbiere Maurizio, Tarricone Claudia, Borowiak Annette.

PTP N° 0018 P

Joint Research Centre

## Contents

## Abstract

Within the harmonisation programme of Air Quality monitoring in Europe the European Reference Laboratory of Air Pollution (ERLAP) organises Proficiency Tests (PT).
During the period **27-30 of March 2023**, including ERLAP, seven Laboratories of AQUILA (Network of European Air Quality Reference Laboratories) met for a laboratory comparison exercise in Ispra (IT) to evaluate their proficiency in the analysis of inorganic gaseous air pollutants (NO, $NO_2$, $SO_2$, CO and $O_3$) covered by the European Air Quality Directive 2008/50 EC [1] and its last amendments 2015/1480/EC [42].
Two laboratories (D and I) didn't participate for CO measurement.
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.
Based only on the z/z'-score evaluation all results reported were **100%** satisfactory. Considering the En-score, **97%** of all value were found satisfactory. The overall performance for both the indicators has to be considered good.
Considering the repeatability and reproducibility evaluation, the results among AQUILA participants at the highest generated concentration levels are satisfactory for measurements of all pollutants.

## Acknowledgements

Thank you for the participation to: Kiza Christos, Papadopoulos Christos, Wolf Andreas, Köller Alexander, Zang Thorsten, Zang Stefanie, Adams Jan, De Nys Jurgen, Van der Gaag Ed, Van Vliet Wilfred, Parvanova Milena, Panayotov Nikolay.

| | NAME | VERSION | DATE |
|---|---|---|---|
| Edited | M. BARBIERE (Technician/QO)<br>C. TARRICONE (Technician) | DRAFT_0 | 20/05/2023 |
| Reviewed | N. JENSEN (Scientist/QO) | DRAFT_1 | 22/06/2023 |
| Approved | A. BOROWIAK (PT Coordinator) | Final_0 | 10/07/2023 |

The final version of this report will be published on JRC Publication Repository (https://publications.jrc.ec.europa.eu/repository/) and can be found searching the identification number 134689.

# 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 on the basis of 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 the Central Eastern Europe, Caucasus and countries from Central Asia.
Starting in 2004, it has been decided to bring together the efforts of both the JRC-ERLAP and WHO CC and to coordinate activities as far as possible, with a view to optimise resources and improve international harmonisation.
This report deals with the PT that took place in the period **27-30 of March 2023** 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 purposes of the EC legislation and support the implementation of quality schemes by NRLs.
ERLAP is accredited to the standards ISO 17025 and ISO 17043 for the 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 is applied to all PT 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 and z'-score method [13] with the uncertainty requirements for calibration gases stated in the European standards [2], [3], [4] and [5], which are consistent with the DQOs of European Directives.
According to the above-mentioned Directive [1, 42], NRLs with an overall unsatisfactory performance in the z/z'-score evaluation **(one unsatisfactory or two questionable results per parameter)** is 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].
Beside the proficiency of participating laboratories, the repeatability and reproducibility of standardised measurement methods [14], [15] and [16] are evaluated as well. These group evaluations are useful indicators of trends in measurement quality over different proficiency tests.

# 2 Proficiency test organisation

The PT was announced in **November 2022** to the members of the AQUILA network and the WHO CC representative. Registration was opened in **February 2023** and closed the third week of **March 2023**.
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, 27 of March 2023**, 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, Austria, Bulgaria, Cyprus, Belgium, Germany and Netherlands.

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

| Acronym | Laboratory | Country |
|---|---|---|
| EAA | Environment Agency Austria | Austria |
| EEA | Executive Environmental Agency | Bulgaria |
| DLI | Dept. of Labour Inspection | Cyprus |
| VMM | Flemish Environmental Agency | Belgium |
| LANUV | Landesamt fur Natur, Umwelt und Verbraucherschutz | Germany |
| ERLAP | European Reference Laboratory for Air Pollution | European Commission |
| DCMR | Environmental Protection Agency | Netherlands |

Source: JRC 2023

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. This information has been reported by the participants through a web interfaced questionnaire as described in the protocol.
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 cluster during the data evaluation. VMM and DCMR laboratories didn't participate to the testing exercise for CO due to the fact in their country this pollutant is not an issue anymore.

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

| Pollutant | Acronym | Instruments |
|---|---|---|
| $SO_2$ | DCMR | API / T100 |
| | DLI | Serinus S50 |
| | EAA | Thermo Fisher Scientific TEI 43 i-TLE |
| | EEA | Horiba APSA-370 |
| | ERLAP | Thermo 43iTLE, 2009 |
| | LANUV | Horiba APSA 370 |
| | VMM | Horiba APSA-370 |
| $NO/NO_2$ | DCMR | Environment / AC32e |
| | DLI | Serinus S40 |
| | EAA | Horiba APNA 370 |
| | EEA | Horiba APNA 370 |
| | ERLAP | Thermo, TE42i, 2015 |
| | LANUV | Horiba APMA370 |
| | VMM | API/Teledyne T200 |
| CO | DCMR | No participation |
| | DLI | Serinus S30 |
| | EAA | Horiba APMA 370 |
| | EEA | Horiba APMA 370 |
| | ERLAP | Horiba, APMA-370, 2021 |
| | LANUV | Horiba APMA 370, Thermo Modell 48i |
| | VMM | No participation |
| $O_3$ | DCMR | Environnement / 42e |
| | DLI | Thermo Fisher Scientific 49i |
| | EAA | Thermo Fisher Scientific TEI 49 i |
| | EEA | Horiba APOA 370 |
| | ERLAP | Thermo Fisher Scientific, 49i 2014 |
| | LANUV | Horiba APOA 370 |
| | VMM | Envea 0342e |

Source: JRC 2023

# 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 | 100 | X | | | |
| 2 | NO-$NO_2$ | 2nd | 14:00 | 2 | 60 | 50 | | | |
| 1 | $O_3$ | 2nd | 16:00 | 2 | | | 60 | | |
| 3 | NO-$NO_2$ | 2nd | 18:00 | 2 | 30 | X | | | |
| 4 | NO-$NO_2$ | 2nd | 20:00 | 2 | 15 | 10 | | | |
| 2 | $O_3$ | 2nd | 22:00 | 2 | | | 20 | | |
| 5 | NO-$NO_2$ | 3rd | 00:00 | 2 | 60 | X | | | |
| 6 | NO-$NO_2$ | 3rd | 02:00 | 2 | 45 | 25 | | | |
| 3 | $O_3$ | 3rd | 04:00 | 2 | | | 30 | | |
| 7 | NO-$NO_2$ | 3rd | 06:00 | 2 | 480 | X | | | |
| 8 | NO-$NO_2$ | 3rd | 08:00 | 2 | 280 | 100 | | | |
| 4 | $O_3$ | 3rd | 10:00 | 2 | | | 90 | | |
| 9 | NO-$NO_2$ | 3rd | 12:00 | 2 | 300 | X | | | |
| 10 | NO-$NO_2$ | 3rd | 14:00 | 2 | 70 | 120 | | | |
| 5 | $O_3$ | 3rd | 16:00 | 2 | | | 120 | | |
| | / | 3rd | 18:00 | 1 | Calibration | | | | |
| 0 | CO-$SO_2$ | 3rd | 19:00 | 2 | | | | Zero air | |
| 1 | CO-$SO_2$ | 3rd | 21:00 | 2 | | | | 100 | 5 |
| 2 | CO-$SO_2$ | 3rd | 23:00 | 2 | | | | 35 | 9 |
| 3 | CO-$SO_2$ | 4th | 01:00 | 2 | | | | 50 | 7 |
| 4 | CO-$SO_2$ | 4th | 03:00 | 2 | | | | 12 | 1.5 |
| 5 | CO-$SO_2$ | 4th | 05:00 | 2 | | | | 8 | 0.9 |
| | | 4th | 07:00 | 2 | Zero air (not to be reported) | | | | |
| | | 4th | 09:00 | END | | | | | |

Source: JRC 2023

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 NO2 indicated in Table 3 with an X.

The test mixtures were prepared by gas dilution from cylinders containing high concentrations of NO, SO2, or CO using thermal mass flow controllers [8]. O3 was added using an ozone generator and NO2 was produced applying the gas phase titration method [19] in a condition of NO excess or as a possible presence of NO2 in NO cylinders.
The participants were required to report three half-hour-mean measurements for each concentration level (run) in order to evaluate the repeatability of standardised measurement methods. Zero value concentration levels were generated for one hour and was requested to be reported one half-hour-mean measurement so no repeatability was calculated for this run.

# 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 for the whole PT [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, are reported the values of measurement submitted, the mean value, the uncertainties, $\sigma_{pt}$ calculated, z/z`-score and En-score. All this information is presented as a table and in graphical format against the 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). At the moment, document N37 [12], is under revision and any changes discussed till now, have not yet been approved within the AQUILA network.

The performance indicators, z-score and z'-score (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 choice between z/z'-score is consequence to the meeting of the criterion $u_{ref}<0.3\sigma_{pt}$ described in the standard ISO 13528 (par. 9.2) [13], where the uncertainty of the reference value ($u_{ref}$) is compared to $0.3\sigma_{pt}$. 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, that is calculated individually for each participant, from the uncertainty of the participant's measurement result and the uncertainty of the reference value.

## 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:

$$z = \frac{(x_{lab} - X_{ref})}{\sqrt{\sigma_{pt}^2}} = \frac{(x_{lab} - X_{ref})}{\sqrt{(a \cdot X_{ref} + b)^2}} \qquad \text{Equation 1}$$

$$z' = \frac{(x_{lab} - X_{ref})}{\sqrt{\sigma_{pt}^2 + u_{ref}^2}} = \frac{(x_{lab} - X_{ref})}{\sqrt{(a \cdot X_{ref} + b)^2 + u_{ref}^2}} \qquad \text{Equation 2}$$

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

In the $NO/NO_2$, $SO_2$, 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' ($\sigma_{pt}$) 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 $\sigma_{pt}$ 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 ($\sigma_{pt}$).

| Gas | a | b (nmol/mol) |
|---|---|---|
| $SO_2$ | 0.022 | 1 |
| CO | 0.024 | 100 |
| $O_3$ | 0.020 | 1 |
| NO | 0.024 | 1 |
| $NO_2$ | 0.020 | 1 |

Source: JRC 2023

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

$$\sigma_{pt} = (a \cdot X_{ref}) + b \qquad \text{Equation 3}$$

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

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

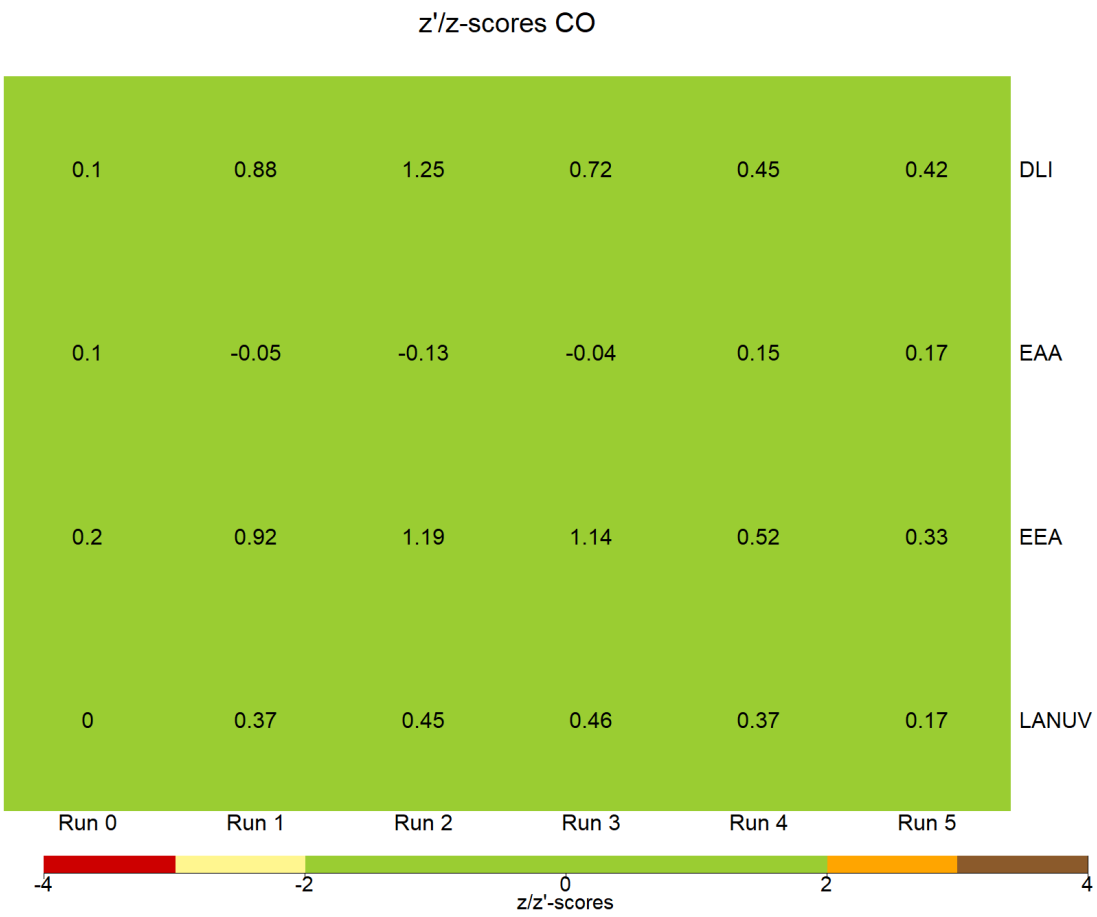
The assessment of results in z/z`-score evaluation is made according to the following criteria:
|z/z'| ≤ 2 are considered satisfactory.
2 < |z/z'| < 3 are considered questionable.
|z/z'| ≥ 3 are considered unsatisfactory. Scores falling in this range are very unusual and are taken as evidence that an 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, no value was found questionable or unsatisfactory.

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 run (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.

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




*Source: JRC 2023*

z/z'-score values are given for each participant and each tested concentration level (run).
For this pollutant, the graphical representation shows a good performance of every participant for all concentration levels generated.

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.

Laboratories DCMR and VMM didn't participate to the PT for this pollutant.

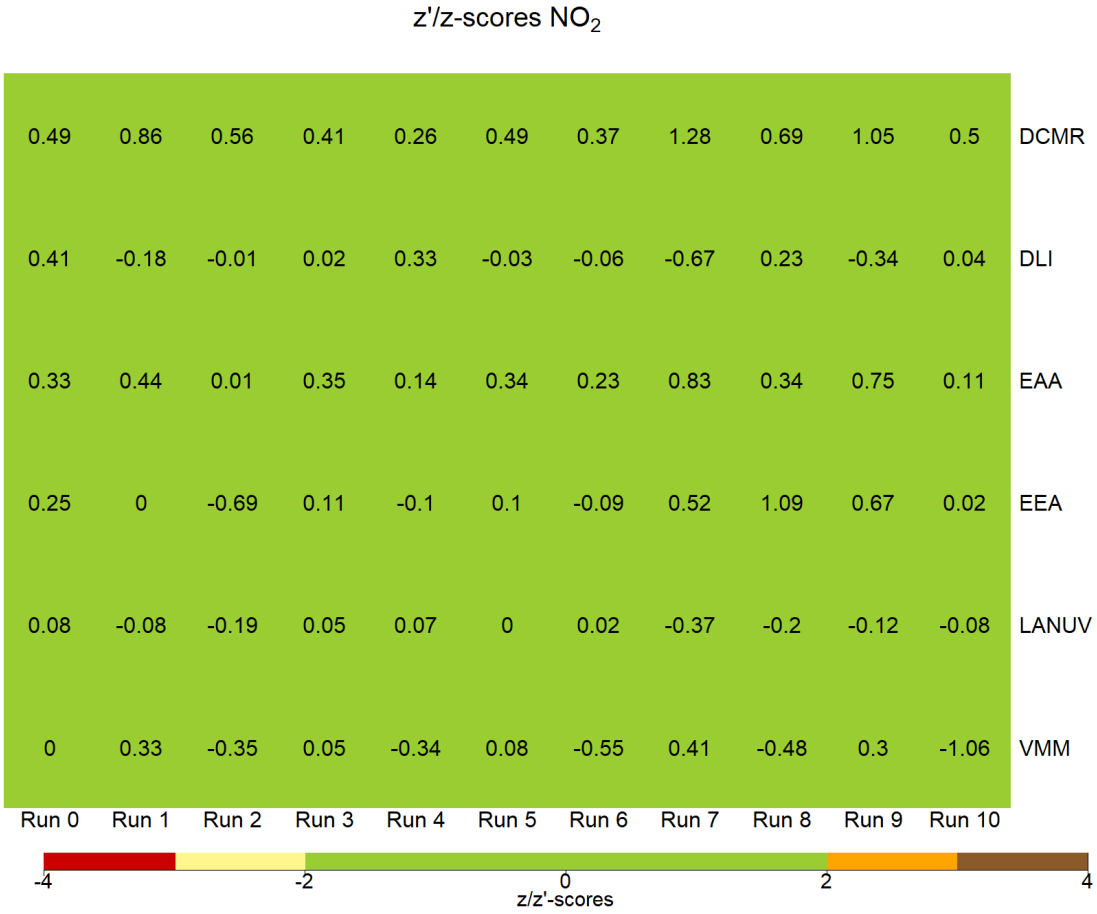
**Figure 2**: graphical matrix of z/z'-score evaluations of NO measurements in nmol/mol


*Source: JRC 2023*

z/z'-score values are given for each participant and each tested concentration level (run).
For this pollutant, the graphical representation shows a good performance of every participant for all concentration levels generated.

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.

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




*Source: JRC 2023*

z/z'-score values are given for each participant and each tested concentration level (run).
For this pollutant, the graphical representation shows a good performance of every participant for all concentration levels generated.

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.

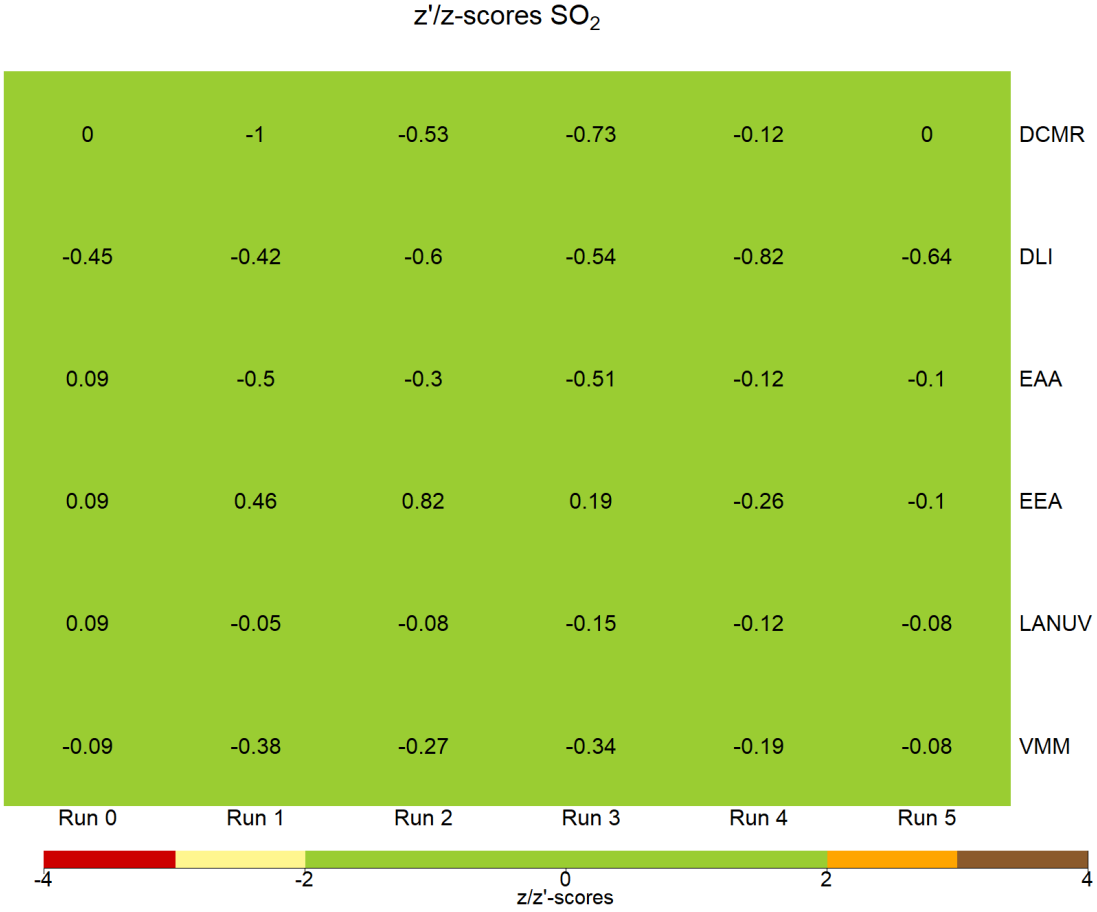
**Figure 4**: graphical matrix of z/z'-score evaluations of $O_3$ measurements in nmol/mol


*Source: JRC 2023*

z/z'-score values are given for each participant and each tested concentration level (run).
For this pollutant, the graphical representation shows a good performance of every participant for all concentration levels generated.

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.

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




*Source: JRC 2023*

z/z'-score values are given for each participant and each tested concentration level (run).
For this pollutant, the graphical representation shows a good performance of every participant for all concentration levels generated.

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.

## 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:

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

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 10 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 evaluation showed in Figures 6, 8, 10, 12, 14 underline few unsatisfactory results for different parameters and concentrations, as reported in table 5.
In Annex B, from table 10 to 15 are reported all En values calculated for each participant, parameter and concentration level.

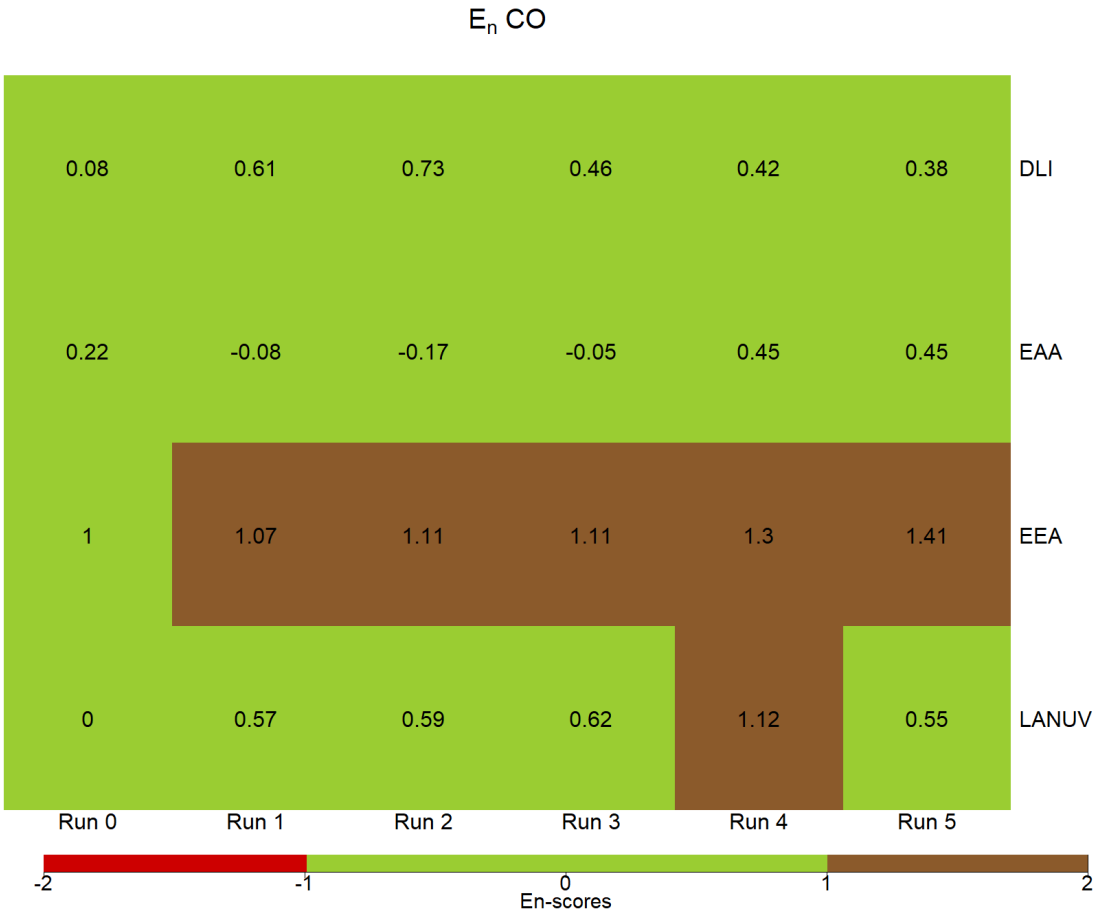
**Table 5**: Unsatisfactory results according to En-score.

| Laboratory | Component | Run | En-score | En evaluation |
|---|---|---|---|---|
| EEA | CO | 1 | 1.07 | unsatisfactory |
| EEA | CO | 2 | 1.11 | unsatisfactory |
| EEA | CO | 3 | 1.11 | unsatisfactory |
| EEA | CO | 4 | 1.30 | unsatisfactory |
| LANUV | CO | 4 | 1.12 | unsatisfactory |
| EEA | CO | 5 | 1.41 | unsatisfactory |
| EEA | O3 | 0 | 1.11 | unsatisfactory |

Source: JRC 2023

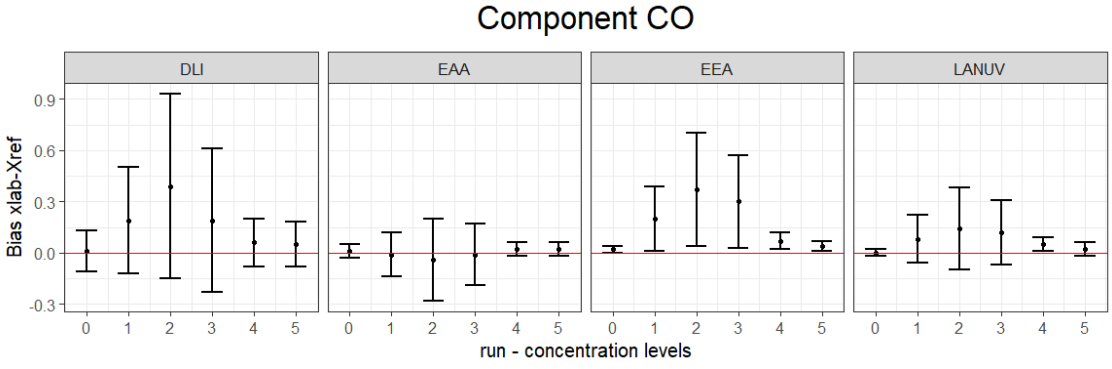
The differences between individual participants' values and reference values (bias $x_{lab}$-$X_{ref}$) are evaluated and presented for each concentration level in the Figures 7, 9, 11, 13, 15.
The expanded uncertainties reported by participants are shown in the graphs for each run as error bar.
These 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 x-axis.
Reported standard uncertainties of the participants, larger than the "standard deviation for proficiency assessments" ($\sigma_{pt}$), are considered not fit-for-purpose (see Annex B).

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




*Source: JRC 2023*

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

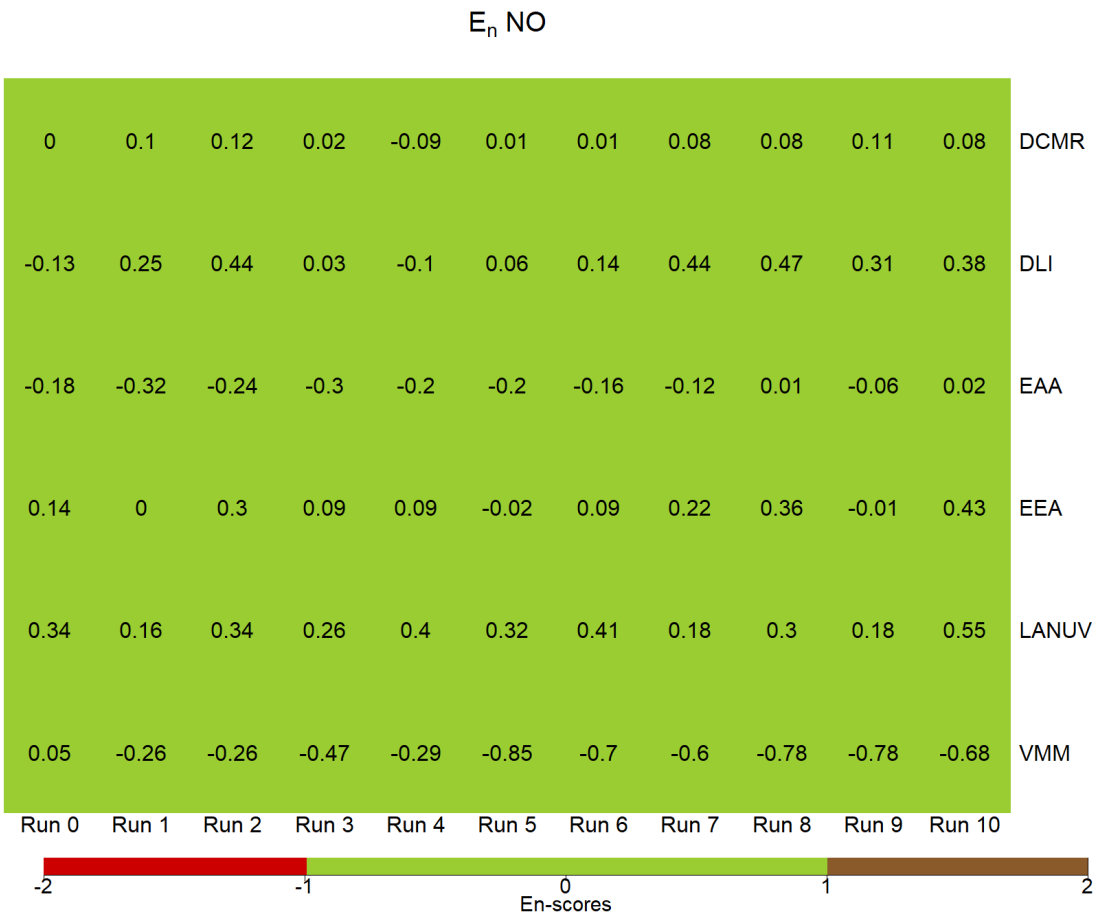



*Source: JRC 2023*

Laboratories DCMR and VMM did not participate to the PT for this pollutant.

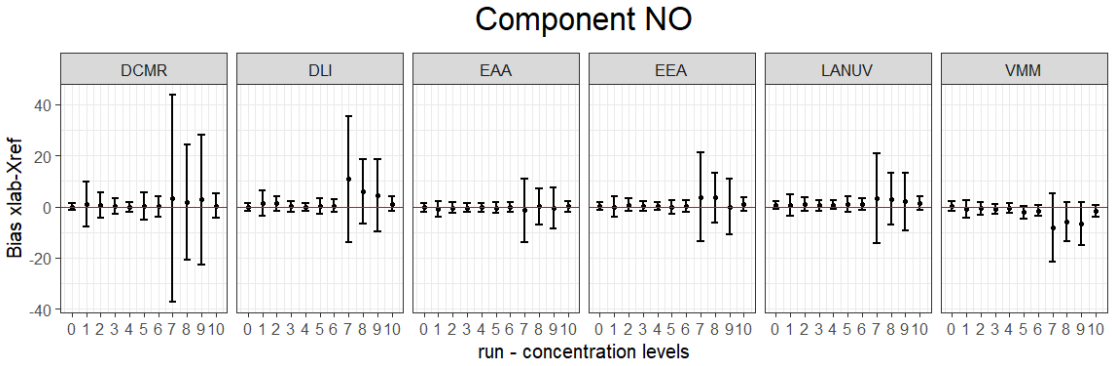
Laboratory EEA overestimates the measurement for this pollutant obtaining unsatisfactory En values. For Run 4 LANUV measurement result is very close to the reference value but due to a small uncertainty, this result gets an En-score above the acceptance criterion.

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




*Source: JRC 2023*

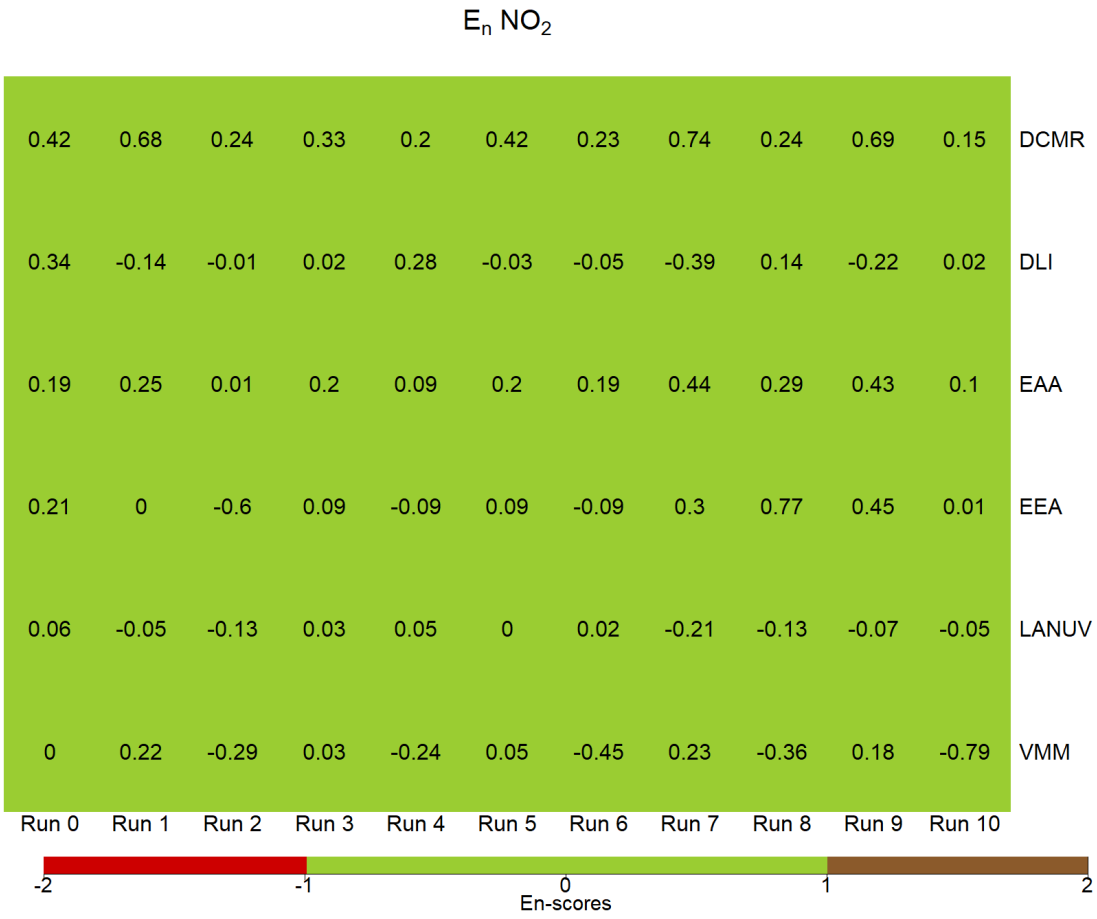
**Figure 9**: Bias of participant's NO measurement results in nmol/mol




*Source: JRC 2023*

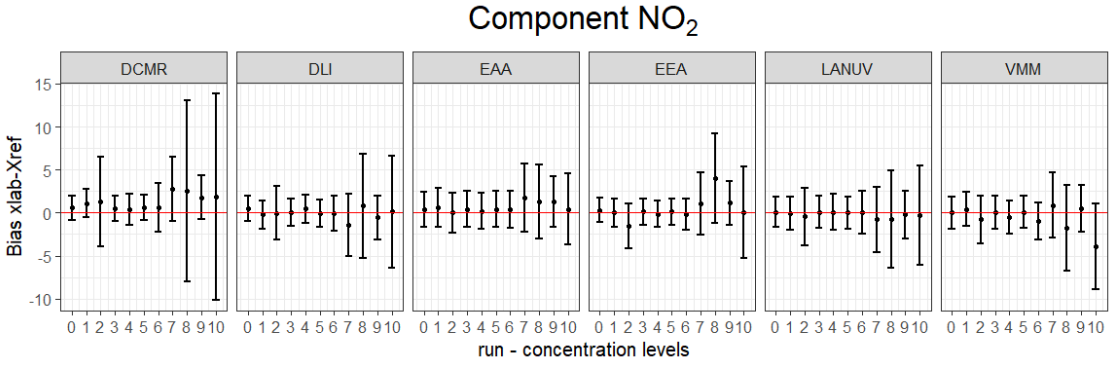
For this pollutant, both graphical representations show a good performance of every participant. For DCMR, in run 7-8-9, can be observed a good precision of the measurement but a slightly high uncertainty.

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




*Source: JRC 2023*

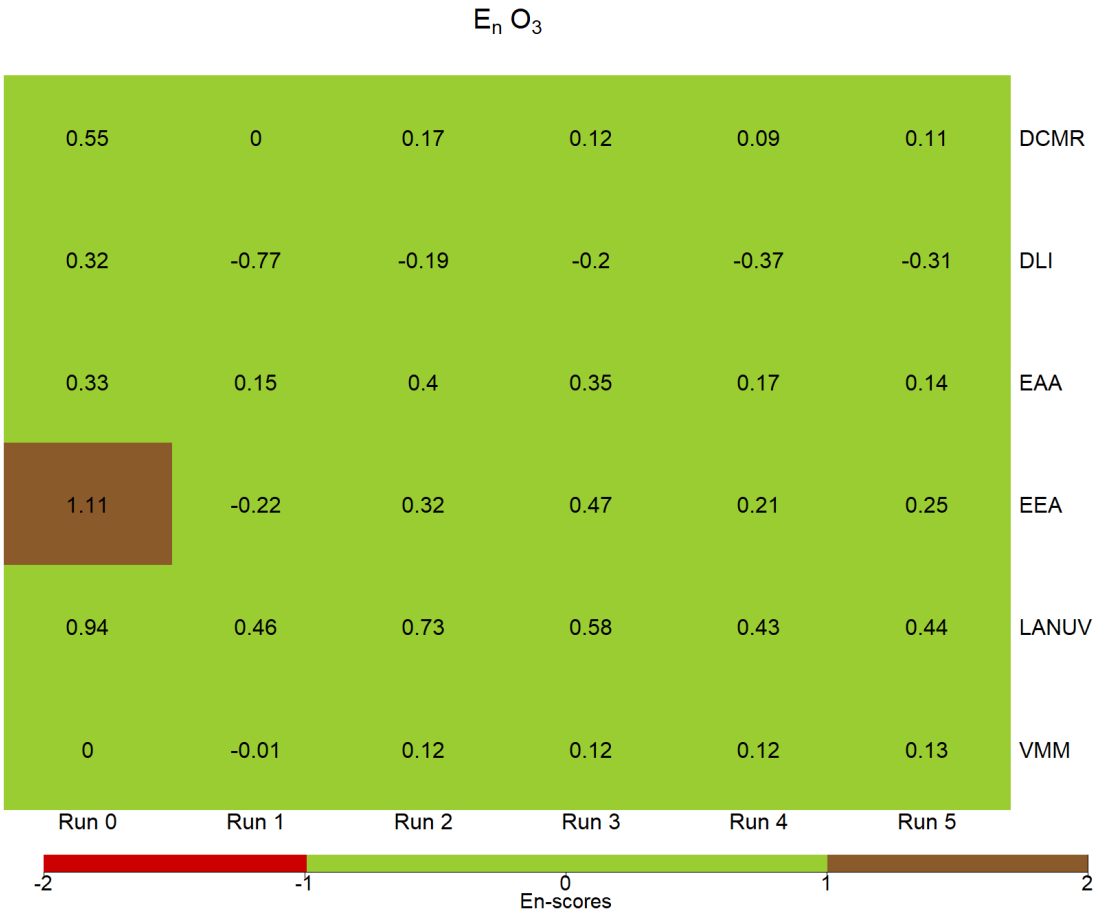
**Figure 11**: Bias of participant's $NO_2$ measurement results in nmol/mol.




*Source: JRC 2023*

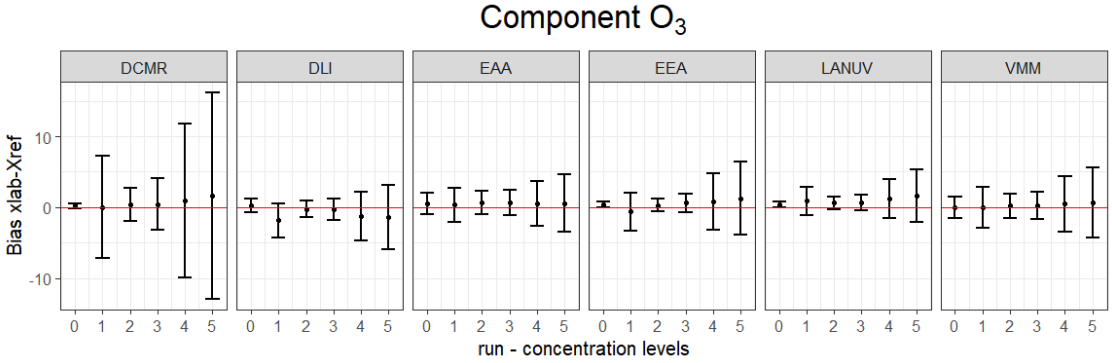
For this pollutant, both graphical representations show a general good performance of every participant. For DCMR, in run 8 and 10, can be observed a good precision of the measurements but slightly high uncertainties.

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




*Source: JRC 2023*

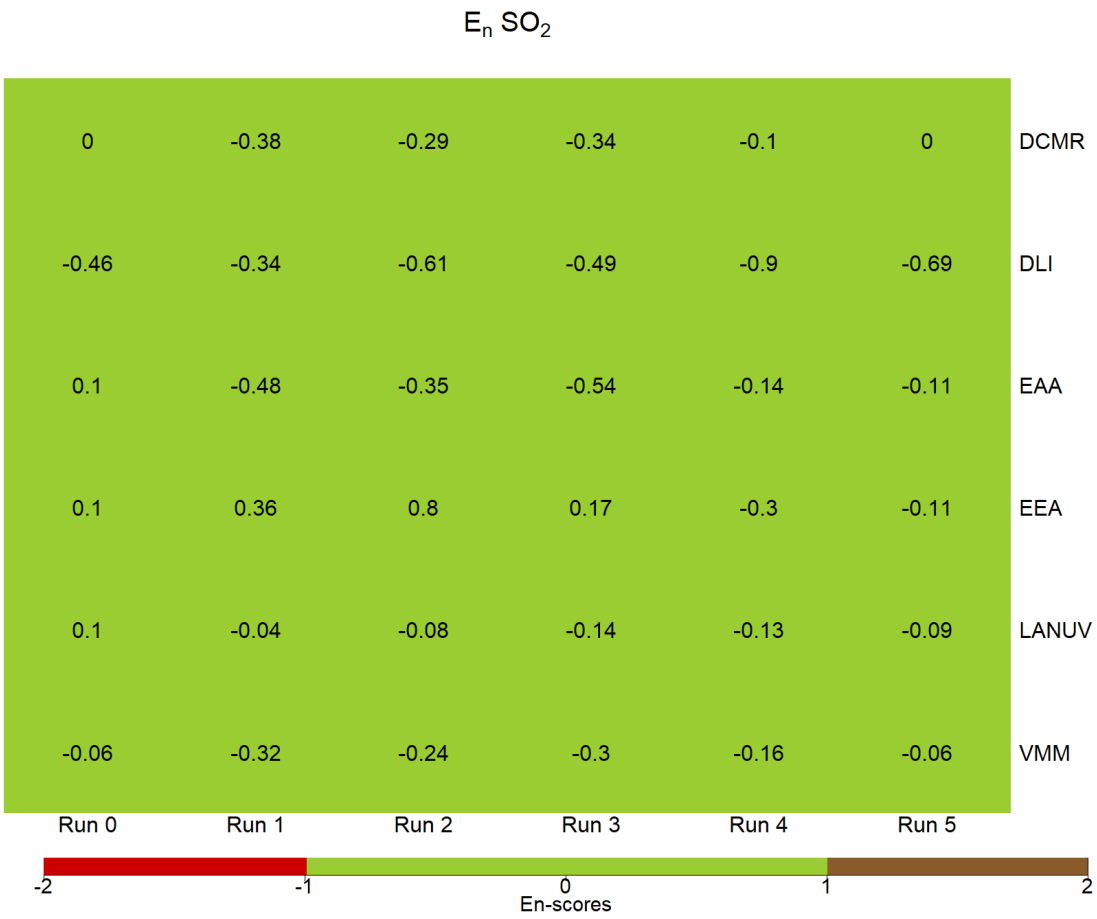
**Figure 13**: Bias of participant's $O_3$ measurement results in nmol/mol




*Source: JRC 2023*

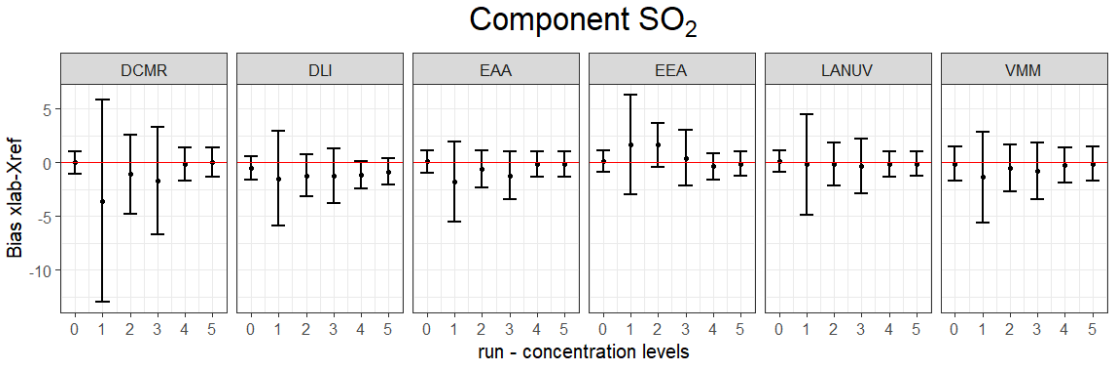
For this pollutant, both graphical representations show a general good performance of every participant. DCMR, in runs 1, 4 and 5, has a good precision of the measurements but slightly high uncertainties. One value of EEA is found out of the acceptability criteria due probably to a very small uncertainty value reported.

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




*Source: JRC 2023*

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




*Source: JRC 2023*

For this pollutant, both graphical representations show a general good performance of every participant. DCMR, in run 1, is not showing a good measurement precision but due to a big uncertainty reported value is not found unsatisfactory.

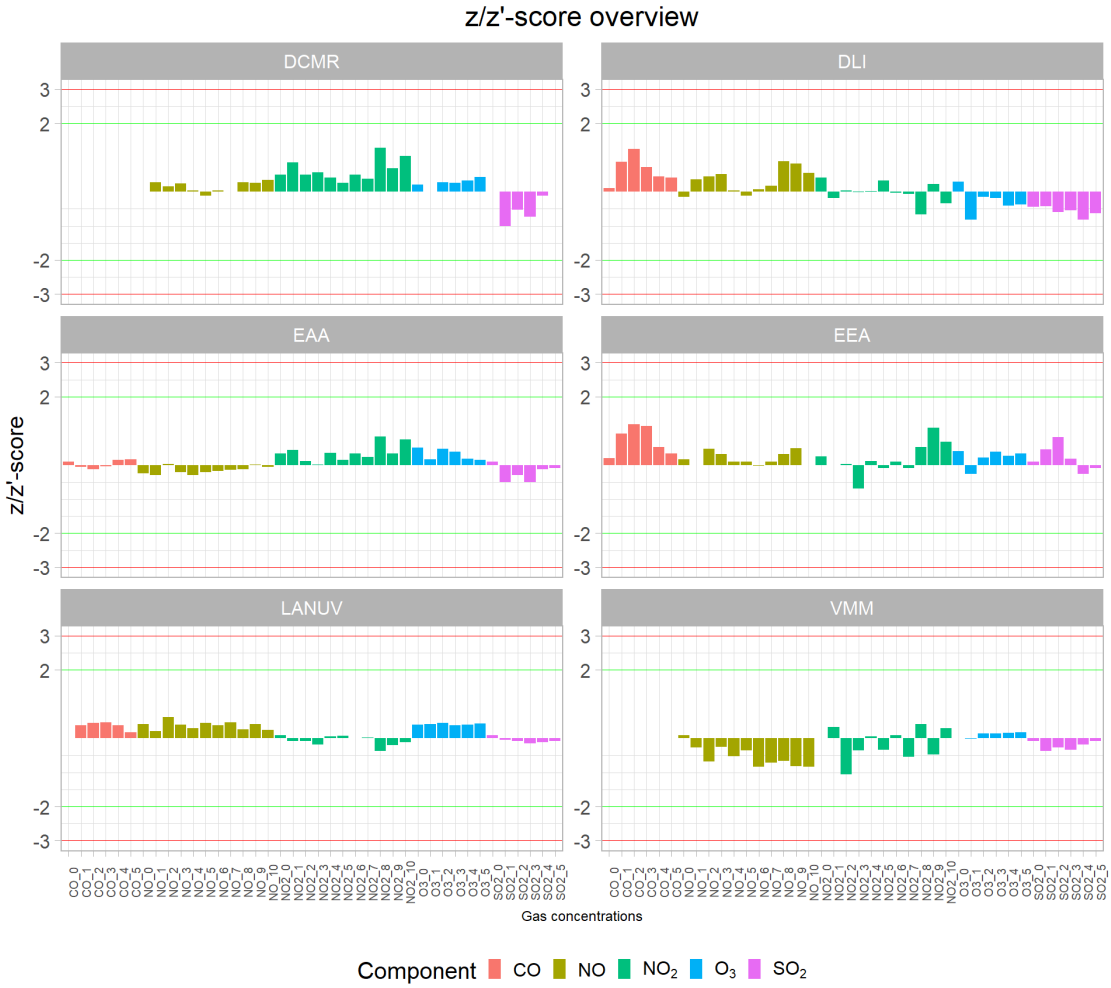
# 6 Conclusions

The proficiency evaluation scheme has provided an assessment of the participants measured values and their evaluated uncertainties through the calculation of two performance indicators (z/z'-score and En-score).
The precision evaluation (Annex C) focuses on data that are as much as possible the reflection of every day work of NRLs and thus represents the comparability of participant's standard operating procedures based on EN standards. As a consequence, a procedure for the detection of exceptional errors (error during typing, slip in performing the measurement or the calculation, wrong averaging interval, malfunction of instrumentation, etc.) is applied. In this procedure is carried out a data consistency evaluation as described in ISO 13528 [13].
Before the release of the draft report, laboratories showing clear form of statistical inconsistencies are requested to investigate the cause of discrepancies and are allowed to correct their results in case of identification of exceptional errors.
Subsequently, data are considered definitive and z/z'-scores calculation is used to estimate the participate performance. The relative reproducibility limits, at the highest studied concentration levels, are 5.5% for $SO_2$, 8.8% for CO, 2.9% for $O_3$, for NO 4.3% and for $NO_2$ 4.5% all within the objective derived from criteria foreseen by the EN standards.

Statistical unsatisfactory results obtained at this stage are not considered as extraordinary errors, but due to significant difference in participant's standard operating procedure.
The precision of standardised measurement methods reported in Annex C are calculated using the data pool without unsatisfactory values.
In this exercise **100%** of the results in the z/z'-score evaluations are satisfactory.
Regarding the En-score parameter **97%** of the results are found satisfactory and **3%** unsatisfactory according to the limits explained in paragraph 5.2.

As in previous PT, the adopted criteria for high concentrations were the standard deviations for proficiency assessment, deriving from the European Standards' uncertainty requirements.
The reproducibility standard deviation obtained and described in Annex C, like previous PTs [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.
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 results of this PT is in line with the performances of previous years as shown by the following Table 6 where the results of z/z'-score in all PT organized in Ispra from 2005 till 2023 are presented.

**Figure 16**: Overview about z/z'-score final evaluation




*Source: JRC 2023*

**Table 6**: z/z'-score summary results of PT organized in Ispra from 2005 to 2023.

| PT | Site | Satisfactory (%) | Questionable (%) | Unsatisfactory (%) |
|---|---|---|---|---|
| Jun_05 | Ispra (IT) | 94.7 | 2.3 | 3.0 |
| Jun_07 | Ispra (IT) | 97.8 | 1.9 | 0.3 |
| 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 | 0.0 |
| Oct_09 | Ispra (IT) | 98.2 | 1.8 | 0.0 |
| Jun_10 | Ispra (IT) | 97.0 | 3.0 | 0.0 |
| Sep_11 | Ispra (IT) | 99.4 | 0.3 | 0.3 |
| Oct_11 | Ispra (IT) | 98.7 | 1.3 | 0.0 |
| Jun_12 | Ispra (IT) | 100.0 | 0.0 | 0.0 |
| Sep_13 | Ispra (IT) | 100.0 | 0.0 | 0.0 |
| Oct_13 | Ispra (IT) | 99.3 | 0.7 | 0.0 |
| May_14 | Ispra (IT) | 98.1 | 0.7 | 1.1 |
| Oct_15_I | Ispra (IT) | 99.4 | 0.6 | 0.0 |
| Oct_15_II | Ispra (IT) | 93.7 | 4.1 | 2.2 |
| Jun_16 | Ispra (IT) | 100 | 0.0 | 0.0 |
| Jun_17_I | Ispra (IT) | 98.9 | 0.7 | 0.4 |
| Jun_17_II | Ispra (IT) | 96.2 | 1.9 | 1.9 |
| Jun_18 | Ispra (IT) | 100 | 0.0 | 0.0 |
| May_19_I | Ispra (IT) | 98.7 | 1.3 | 0.0 |
| May_19_II | Ispra (IT) | 97.5 | 2.5 | 0.0 |
| Mar-22(I) | Ispra (IT) | 97.2 | 1.1 | 1.7 |
| Mar_22_II | Ispra (IT) | 99.3 | 0.7 | 0 |
| Apr_22_III | Ispra (IT) | 91.5 | 3.2 | 5.3 |
| Mar_23 | Ispra (IT) | 100 | 0 | 0 |

Source: JRC 2023

During this PT, in agreement to 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 7 are summarised the reading 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 SO2 measurement in presence of NO and $NO_2$ (for NO with concentration 500 nmol/mol $SO_2$ reading ≤ 5.0 nmol/mol, for $NO_2$ with concentration 200 nmol/mol $SO_2$ 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 7**: $SO_2$ measurement during NO gas generation.

| | JRC | | | Nederland | Cyprus | Germany | Belgium | Bulgaria | Austria |
|---|---|---|---|---|---|---|---|---|---|
| | ERLAP values | | | DCMR | DLI | LANUV | VMM | EEA | EAA |
| | NO | $NO_2$ | $SO_2$ | $SO_2$ | | | | | |
| Run | nmol/mol | | | nmol/mol | | | | | |
| 7 | 464.3 | 7.7 | 3.0 | 7.5 | 4,0 | 2.5 | 4.01 | 2.8 | 2.84 |
| | 464.6 | 7.2 | 2.9 | 7.5 | 3,8 | 2.5 | 3.98 | 2.8 | 2.90 |
| | 464.5 | 7.1 | 3.0 | 7.4 | 3,9 | 2.5 | 4.00 | 2.7 | 2.82 |
| 8 | 257.6 | 115.0 | 1.7 | 4.2 | 1,9 | 1.4 | 2.19 | 1.3 | 1.45 |
| | 257.7 | 115.3 | 1.7 | 4.3 | 1,9 | 1.5 | 2.20 | 1.4 | 1.44 |
| | 257.9 | 115.2 | 1.7 | 4.4 | 1,8 | 1.5 | 2.21 | 1.4 | 1.50 |
| 9 | 289.9 | 4.0 | 1.9 | 4.9 | 2,1 | 1.9 | 2.46 | 1.7 | 1.61 |
| | 290.0 | 3.8 | 1.9 | 4.9 | 2,2 | 1.8 | 2.45 | 1.7 | 1.65 |
| | 289.9 | 3.9 | 1.9 | 4.8 | 2,3 | 1.8 | 2.47 | 1.8 | 1.65 |
| 10 | 50.7 | 135.1 | 0.5 | 1.1 | -0,2 | 0.6 | 0.40 | 0.1 | 0.13 |
| | 50.8 | 135.0 | 0.4 | 1.1 | -0,2 | 0.6 | 0.42 | 0.1 | 0.15 |
| | 50.7 | 135.1 | 0.4 | 1.1 | -0,1 | 0.6 | 0.43 | 0.1 | 0.17 |
| Instrument | | | Thermo 43iTLE | API T100 | Serinus S50 | Horiba APSA-370 | Horiba APSA-370 | Horiba APSA-370 | Thermo 43iTLE |

Source: JRC 2023

## References


1. EC Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, L 152, 11.06.2008
2. CEN, EN 14626:2012, ambient air quality - Standard method for the measurement of the concentration of carbon monoxide by non-dispersive infrared spectroscopy
3. CEN, EN 14212:2012, ambient air quality - Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence
4. CEN, EN 14211:2012, ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence
5. CEN, EN 14625:2012, ambient air quality - Standard method for the measurement of the concentration of ozone by ultraviolet photometry
6. ISO 6143:2001, Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures
7. ISO 6144:2003, Gas analysis - Preparation of calibration gas mixtures - Static volumetric method
8. ISO 6145-7:2001, Gas analysis - Preparation of calibration gas mixtures using dynamic volumetric methods - Part 7: Thermal mass-flow controllers
9. Mücke H.-G., Air quality management in the WHO European Region – Results of a quality assurance and control programme on air quality monitoring (1994-2004), Environment International, EI-01718. 2008
10. Mücke H.-G. et al., European Intercomparison workshop on air quality monitoring vol.4 – Measuring NO, $NO_2$, $O_3$ and $SO_2$ – Air Hygiene Report 13, WHO Collaboration Centre for Air Quality Management and Air Pollution Control, ISSN 0938 – 9822. 2000
11. AQUILA Network of the National Reference Laboratories of the Member States [online]: Info available: https://ec.europa.eu/jrc/en/aquila
12. AQUILA POSITION PAPER N. 37, Protocol for intercomparison exercise. Organisation of intercomparison exercises for gaseous air pollution for EU national air quality reference laboratories and laboratories of the WHO EURO region, 2008 Available: https://ec.europa.eu/jrc/sites/jrcsh/files/aquila-n_37-intercomparison-exercise protocol 2008.pdf
13. ISO 13528:2022, Statistical methods for use in proficiency testing by inter-laboratory comparison
14. ISO 5725-1:1994, Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions
15. ISO 5725-2:2019, Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method
16. ISO 5725-6:1994, Accuracy (trueness and precision) of measurement methods and results - Part 6: Use in practice of accuracy values
17. De Saeger E. et al., Harmonisation of Directive 92/72/EEC on air pollution by ozone, EUR 17662, 1997
18. De Saeger E. et al., European comparison of Nitrogen Dioxide calibration methods, EUR 17661, 1997
19. ISO 15337:2009, Ambient air - Gas phase titration - Calibration of analysers for ozone
20. Kapus M. et al. The evaluation of the Intercomparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ carried out in June 2007 in Ispra. JRC scientific and technical reports. EUR 23804. 2009
21. Kapus M. et al. The evaluation of the Intercomparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ - April 2008. JRC scientific and technical reports. EUR 23805. 2009
22. Kapus M. et al. The evaluation of the Intercomparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ 6-9 October 2008. JRC scientific and technical reports. EUR 23806. 2009
23. Kapus M. et al. The evaluation of the Intercomparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$13-16 October 2008. JRC scientific and technical reports. EUR 23807. 2009
24. Belis C. A. et al. The evaluation of the Interlaboratory comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ Langen 20-25 September 2009. EUR 24376. 2010
25. Belis C. A. et al. The evaluation of the Interlaboratory comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ 19-22 October 2009. EUR 24476. 2010
26. Viallon J. et al. Final report, on-going key comparison BIPM.QM-K1: Ozone at ambient level, comparison with JRC, 2008. Metrologia 46 08017, 2009. doi: 10.1088/0026-1394/46/1A/08017
27. Viallon, J., et al. International comparison CCQM-P28: Ozone at ambient level, Metrologia 43, Tech. Suppl., 08010, 2006. doi:10.1088/0026-1394/43/1A/08010
28. Tanimoto, H., et al. Intercomparison of ultraviolet photometry and gas-phase titration techniques for ozone reference standards at ambient levels, Journal of Geophysical Research, vol. 111, D16313, 2006. doi:10.1029/2005JD006983

29. ISO, Guide to the expression of uncertainty in measurements, Geneva, 1995, ISBN 92-67-10188-9
30. VDI 2449 Part3: 2001, Measurement methods test criteria- General method for the determination of the uncertainty of calibratable measurement methods.
31. Mücke H-G, et al. European Intercomparison Workshops on Air Quality Monitoring. Vol. 2 – Measuring of CO, NO, $NO_2$ and $O_3$ – Air Hygiene Report 9. Berlin, Germany: WHO Collaborating Centre for Air Quality Management and Air Pollution Control; 1996. ISSN 0938-9822.
32. ISO 17043:2010, Conformity assessment - General requirements for proficiency testing
33. Barbiere M. et al. The evaluation of the Interlaboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ Ispra 14-17 June 2010. EUR 24943. 2011
34. Barbiere M. et al. Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$, 11th-14th June 2012 Ispra. EUR 25536. 2012
35. Barbiere M. et al. Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$, Langen 23rd-28th October 2011. EUR 25387. 2012
36. Barbiere M. et al. Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$, 03rd-06th October 2011 Ispra. EUR 25386. 2012
37. Barbiere M. et al. Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$, 26th-29th September 2011 Ispra. EUR 25385. 2012
38. Barbiere M., Lagler F., Mücke H.G., Wirtz K. and Stummer V. Evaluation of the Laboratory Comparison Exercise for NO, $NO_2$, $SO_2$, CO, and $O_3$ Langen (D) 1st-6th September 2013. EUR 26578. 2014
39. Barbiere M., Lagler F., Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ 30st September-3rd October 2013 Ispra. EUR 26604. 2014
40. Barbiere M., Lagler F., Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ 7st-10th October 2013 Ispra. EUR 26639. 2014
41. Barbiere M., Lagler F., Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ 19th-22nd May 2014 Ispra. EUR 27199. 2014
42. EC COMMISSION DIRECTIVE (EU) 2015/1480 of 28 August 2015 (L226/4) amending several annexes to Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council laying down the rules concerning reference methods, data validation and location of sampling points for the assessment of ambient air quality
43. Lagler F., Barbiere M., Borowiak A. Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$12th-15th October 2015 Ispra. EUR 28097. 2016
44. Barbiere M., Lagler F., Borowiak A. Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ 19th-23rd October 2015 Ispra. EUR 28047. 2016
45. Barbiere M., Lagler F., Mücke H.G., Wirtz K. and Stummer V. Evaluation of the Laboratory Comparison Exercise for NO, $NO_2$, $SO_2$, CO, and $O_3$ Langen (D) 4th-9th October 2015. EUR 27918. 2016
46. Barbiere M., Lagler F., Borowiak A. Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ 13-16 June 2016, Ispra. EUR 28610. 2017
47. Barbiere M., Lagler F., Borowiak A. Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ 19-22 June 2017, Ispra. EUR 29268. 2017
48. Barbiere M., Lagler F., Borowiak A. Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ 26-29 June 2017, Ispra. EUR 29271. 2017
49. Barbiere M., Lagler F., Borowiak A. Evaluation of the Laboratory Comparison Exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ 4-7 June 2018, Ispra. EUR 29671. 2018
50. Barbiere M., Lagler F., Mücke H.G., Wirtz K. and Stummer V. Evaluation of the Laboratory Comparison Exercise for NO, $NO_2$, $SO_2$, CO, and $O_3$ Langen (D) 2-7 September 2018. EUR 29694. 2018
51. Barbiere M., Lagler F., Borowiak A. Evaluation of the Inter-Laboratory Comparison exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ (13-16 May 2019, Ispra). EUR 29898. 2019
52. Barbiere M., Lagler F., Borowiak A. Evaluation of the Inter-Laboratory Comparison exercise for $SO_2$, CO, $O_3$, NO and $NO_2$ (20-23 May 2019, Ispra), Ispra. EUR 29896. 2019
53. Barbiere M., Lagler F., Tarricone C., Borowiak A., PROFICIENCY TESTING SCHEME, Measurements of inorganic gaseous pollutants ($SO_2$, CO, $O_3$, NO and $NO_2$) in filtered ambient air, 21-24 March 2022 Ispra, Italy
54. Barbiere M., Lagler F., Tarricone C., Borowiak A., PROFICIENCY TESTING SCHEME, Measurements of inorganic gaseous pollutants ($SO_2$, CO, $O_3$, NO and $NO_2$) in filtered ambient air, 28-31 March 2022 Ispra, Italy
55. Barbiere M., Lagler F., Tarricone C., Borowiak A., PROFICIENCY TESTING SCHEME, Measurements of inorganic gaseous pollutants ($SO_2$, CO, $O_3$, NO and $NO_2$) in filtered ambient air, 04-07 April 2022 Ispra, Italy

## List of abbreviations

| | |
|---|---|
| AQUILA | Network of National Reference Laboratories for Air Quality |
| CEN | European Committee for Standardization |
| CO | Carbon monoxide |
| CRM | Certified Reference Material |
| DQO | Data Quality Objective |
| ERLAP | European Reference Laboratory for Air Pollution |
| EC | European Commission |
| GPT | Gas Phase Titration |
| 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

| | |
|---|---|
| $\alpha$ | 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) |
| $\sigma_{pt}$ | 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 repeatability variance (ISO 5725) |
| 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) |

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## Annex A. Reference values

The reference values of tested concentration levels (run) were derived from ERLAP's measurements, which are calibrated against the certified reference values of CRMs and are traceable to international standards. In this perspective the reference values are reference values as defined in the ISO 13528 [13].
To foster its reference function ERLAP is participating regularly to key comparisons of the Gas Analysis Working Group within the framework of BIPM's CCQM and it is yearly confirming the compliance to standard ISO 17025 for testing and to ISO 17043, both through an 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 measured 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 reference gas mixture and the calibration experiment evaluation were carried out using two computer applications, the "GUM WORKBENCH" [29] and "B-least" [30] respectively. For extending calibration from the NO to $NO_2$ channel of $NO_X$ analyser the GPT test was performed to establish the efficiency of $NO_2$-converter.
In table 6 the reference values are reported together with their uncertainties.

**Table 8**: Reference values (X)

| Run | Ref value | Ref unc | Ref exp unc | sigmaPT | Unit | z or z' |
|---|---|---|---|---|---|---|
| CO_0 | 0.00 | 0.01 | 0.02 | 0.10 | µmol/mol | z |
| CO_1 | 4.85 | 0.03 | 0.05 | 0.22 | µmol/mol | z |
| CO_2 | 8.79 | 0.04 | 0.09 | 0.31 | µmol/mol | z |
| CO_3 | 6.81 | 0.03 | 0.07 | 0.26 | µmol/mol | z |
| CO_4 | 1.41 | 0.01 | 0.02 | 0.13 | µmol/mol | z |
| CO_5 | 0.83 | 0.01 | 0.02 | 0.12 | µmol/mol | z |
| NO_0 | 0.00 | 0.70 | 1.40 | 1.00 | nmol/mol | z' |
| NO_1 | 99.37 | 0.90 | 1.70 | 3.38 | nmol/mol | z |
| NO_2 | 53.53 | 0.80 | 1.50 | 2.28 | nmol/mol | z' |
| NO_3 | 30.10 | 0.70 | 1.50 | 1.72 | nmol/mol | z' |
| NO_4 | 14.43 | 0.70 | 1.40 | 1.35 | nmol/mol | z' |
| NO_5 | 59.33 | 0.80 | 1.50 | 2.42 | nmol/mol | z' |
| NO_6 | 41.87 | 0.80 | 1.50 | 2.00 | nmol/mol | z' |
| NO_7 | 464.47 | 2.30 | 4.60 | 12.15 | nmol/mol | z |
| NO_8 | 257.73 | 1.40 | 2.80 | 7.19 | nmol/mol | z |
| NO_9 | 289.93 | 1.50 | 3.10 | 7.96 | nmol/mol | z |
| NO_10 | 50.73 | 0.80 | 1.50 | 2.22 | nmol/mol | z' |
| $NO_2$_0 | -0.10 | 0.70 | 1.40 | 1.00 | nmol/mol | z' |
| $NO_2$_1 | 0.20 | 0.80 | 1.60 | 1.00 | nmol/mol | z' |
| $NO_2$_2 | 56.00 | 0.80 | 1.70 | 2.12 | nmol/mol | z' |
| $NO_2$_3 | 0.07 | 0.70 | 1.50 | 1.00 | nmol/mol | z' |
| $NO_2$_4 | 10.77 | 0.70 | 1.50 | 1.22 | nmol/mol | z' |
| $NO_2$_5 | 0.07 | 0.80 | 1.50 | 1.00 | nmol/mol | z' |
| $NO_2$_6 | 27.33 | 0.80 | 1.50 | 1.55 | nmol/mol | z' |
| $NO_2$_7 | 7.33 | 1.80 | 3.60 | 1.15 | nmol/mol | z' |
| $NO_2$_8 | 115.17 | 1.60 | 3.10 | 3.30 | nmol/mol | z' |
| $NO_2$_9 | 3.90 | 1.30 | 2.50 | 1.08 | nmol/mol | z' |
| $NO_2$_10 | 135.07 | 1.10 | 2.20 | 3.70 | nmol/mol | z |
| $O_3$_0 | -0.20 | 0.10 | 0.30 | 1.00 | nmol/mol | z |
| $O_3$_1 | 64.67 | 0.60 | 1.20 | 2.29 | nmol/mol | z |
| $O_3$_2 | 20.60 | 0.20 | 0.50 | 1.41 | nmol/mol | z |
| $O_3$_3 | 32.17 | 0.30 | 0.60 | 1.64 | nmol/mol | z |
| $O_3$_4 | 96.73 | 0.90 | 1.70 | 2.93 | nmol/mol | z' |
| $O_3$_5 | 129.00 | 1.20 | 2.30 | 3.58 | nmol/mol | z' |
| $SO_2$_0 | 0.10 | 0.50 | 1.00 | 1.00 | nmol/mol | z' |
| $SO_2$_1 | 104.47 | 1.40 | 2.70 | 3.30 | nmol/mol | z' |
| $SO_2$_2 | 39.43 | 0.70 | 1.40 | 1.87 | nmol/mol | z' |
| $SO_2$_3 | 54.63 | 0.80 | 1.70 | 2.20 | nmol/mol | z' |
| $SO_2$_4 | 12.93 | 0.50 | 1.10 | 1.28 | nmol/mol | z' |
| $SO_2$_5 | 8.70 | 0.50 | 1.10 | 1.19 | nmol/mol | z' |

Source: JRC 2023

## Homogeneity

This type of PT for inorganic gases foresee a generation of gas mixture that is analysed immediately. The gas isn't stored neither manipulated before the participant's measurement. In this condition, the stability and homogeneity of test item is not fully applicable. In ERLAP, as homogeneity test, all sampling ports, used by participants during the PT, are compared with the last port (port N20) with a running concentration of ozone and the measurement carried out with 2 different analysers of ozone (Thermo Fisher Scientific 49i), calibrated against a SRP photometer primary standard, where used in parallel. The test is considered acceptable when the difference of the two measurements is below 0.5%. This test is part of the equipment checks run before a PT organised by ERLAP in Ispra and its result is reported in Table 9.
The homogeneity of test gas was evaluated comparing the measurement result of the two analysers sampling from port 20a and 20b at the end of the sampling line. The difference between each sampling port and the port 20b was compared to the 20a-20b port initial difference to check the acceptability criteria. The upper and lower limits of bias due to homogeneity were evaluated to be smaller than 0.5%, which constitutes the relative standard uncertainty of 0.3% of each concentration level assuming a rectangular distribution of the bias.

$$u_{fref} = \sqrt{u_{ref}^2 + \left(X_{ref} \cdot u_{homo}\right)^2} \qquad \text{Equation 5}$$

$u_{fref}$ = final reference value combined uncertainty
$u_{ref}$ = reference value uncertainty intermediate
$X_{ref}$ = reference value
$u_{homo}$ = uncertainty contribution from homogeneity test

The standard uncertainties of reference values ($u_{fref}$) were calculated with Equation 5 and used in the proficiency evaluations of chapter 4. The contribution to the uncertainty budget "$u_{ref}$" include repeatability, certified reference material standard uncertainty and drift.

**Table 9**: Homogeneity test.

| Bench position | Sample Analyzer SN15 | Ref. Analyzer SN14 | Diff. nmol/mol | <0.5% passed? |
|---|---|---|---|---|
| 20a/b | 428.2 | 428.5 | 0.0 | Yes |
| 1a | 429.0 | 429.0 | 0.3 | Yes |
| 1b | 428.0 | 428.0 | 0.3 | Yes |
| 2a | 427.0 | 428.0 | -0.7 | Yes |
| 2b | 426.0 | 428.0 | -1.7 | Yes |
| 3a | 426.5 | 428.2 | -1.4 | Yes |
| 3b | 426.5 | 428.5 | -1.7 | Yes |
| 4a | 427.2 | 428.5 | -1.0 | Yes |
| 4b | 427.5 | 428.5 | -0.7 | Yes |
| 5a | 427.8 | 428.2 | -0.1 | Yes |
| 5b | 428.0 | 428.2 | 0.1 | Yes |
| 6a | 428.0 | 428.2 | 0.1 | Yes |
| 6b | 428.0 | 428.0 | 0.3 | Yes |
| 7a | 429.0 | 428.5 | 0.8 | Yes |
| 7b | 427.5 | 428.2 | -0.4 | Yes |
| 8a | 428.5 | 428.5 | 0.3 | Yes |
| 8b | 428.5 | 428.6 | 0.2 | Yes |
| 9a | 427.5 | 428.4 | -0.6 | Yes |
| 9b | 428.0 | 428.0 | 0.3 | Yes |
| 10a | 429.5 | 429.0 | 0.8 | Yes |
| 10b | 429.5 | 429.0 | 0.8 | Yes |
| 11a | 429.0 | 429.0 | 0.3 | Yes |
| 11b | 429.0 | 429.0 | 0.3 | Yes |
| 12a | 428.5 | 429.0 | -0.2 | Yes |
| 12b | 429.0 | 429.0 | 0.3 | Yes |
| 13a | 429.0 | 429.0 | 0.3 | Yes |
| 13b | 429.0 | 429.0 | 0.3 | Yes |
| 14a | 429.0 | 429.0 | 0.3 | Yes |
| 14b | 429.5 | 429.5 | 0.3 | Yes |
| 15a | 429.0 | 429.0 | 0.3 | Yes |
| 15b | 429.0 | 429.5 | -0.2 | Yes |
| 16a | 429.0 | 429.5 | -0.2 | Yes |
| 16b | 429.0 | 429.0 | 0.3 | Yes |
| 17a | 429.5 | 429.0 | 0.8 | Yes |
| 17b | 428.5 | 429.2 | -0.4 | Yes |
| 18a | 428.5 | 429.0 | -0.2 | Yes |
| 18b | 428.0 | 429.0 | -0.7 | Yes |
| 19a | 428.5 | 429.0 | -0.2 | Yes |
| 19b | 428.0 | 429.0 | -0.7 | Yes |
| 21a | 428.0 | 429.0 | -0.7 | Yes |
| 21b | 428.0 | 429.0 | -0.7 | Yes |
| 22a | 428.0 | 429.0 | -0.7 | Yes |
| 22b | 428.0 | 429.0 | -0.7 | Yes |
| 22c | 428.0 | 429.0 | -0.7 | Yes |
| 22d | 428.0 | 429.0 | -0.7 | Yes |
| 23a | 427.5 | 429.0 | -1.2 | Yes |

| Bench position | Sample Analyzer SN15 | Ref. Analyzer SN14 | Diff. nmol/mol | <0.5% passed? |
|---|---|---|---|---|
| 23b | 428.0 | 429.0 | -0.7 | Yes |
| 23c | 427.5 | 429.0 | -1.2 | Yes |
| 23d | 427.5 | 429.0 | -1.2 | Yes |

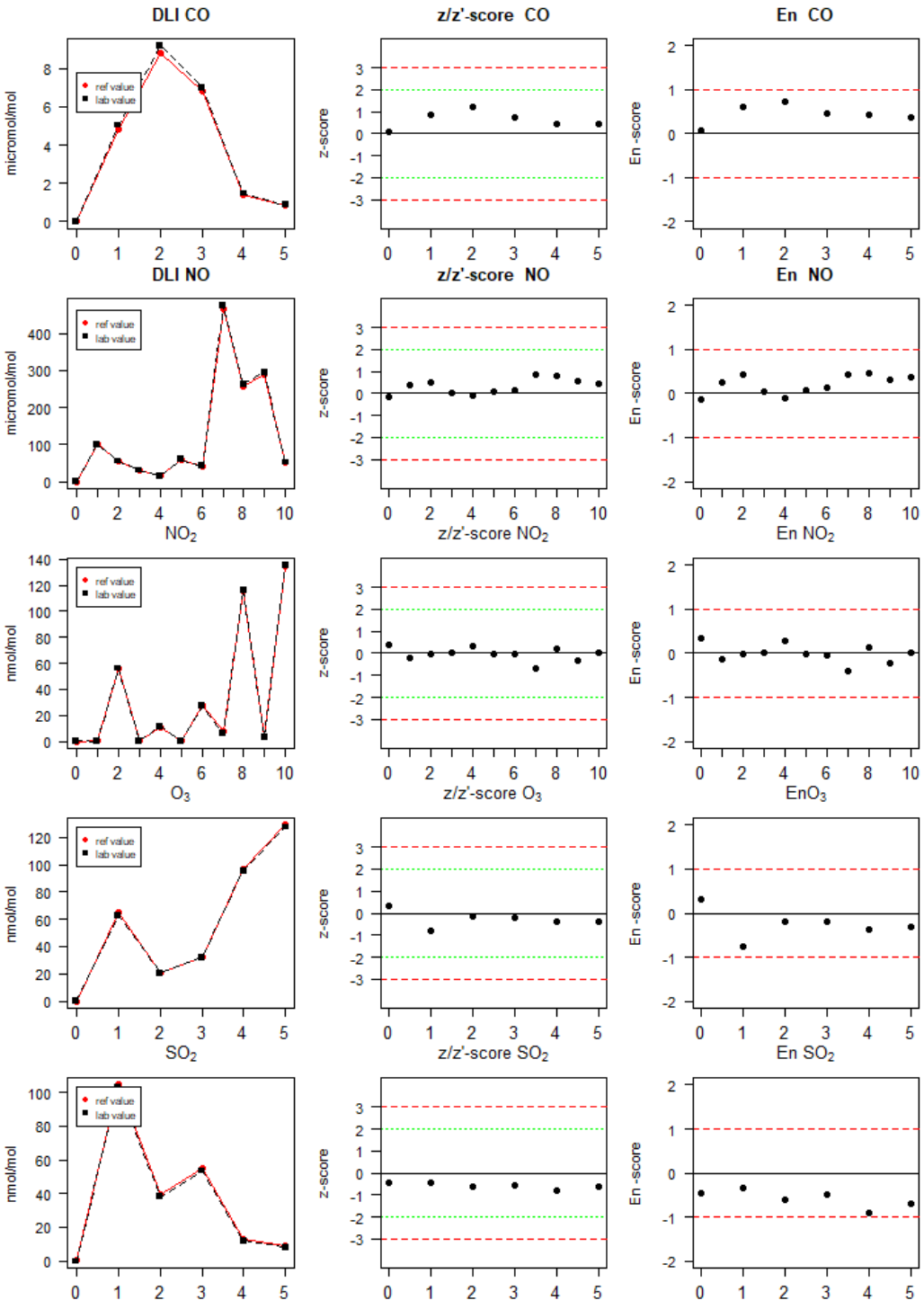
Source: JRC 2023

## Annex B: Results reported by participants

In this annex are reported participant's results, presented both as graphs and tables.
In the graph, from the left and top down, for each pollutant is represented the measurement result submitted 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. "$X_{ref}$" reports the reference values while "$x_{lab}$" is 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 "$u_{lab}$" and "$U_{lab}$" expressed in mol/mol units.

"$\sigma_{PT}$" shows the results of the calculation described in paragraph 5.1 using the parameter in Table 4. In column "z/z'-score" and "En-score" are listed the performance indicators values obtained by each participant. "z/z'" 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 Laboratory DLI (Cyprus)



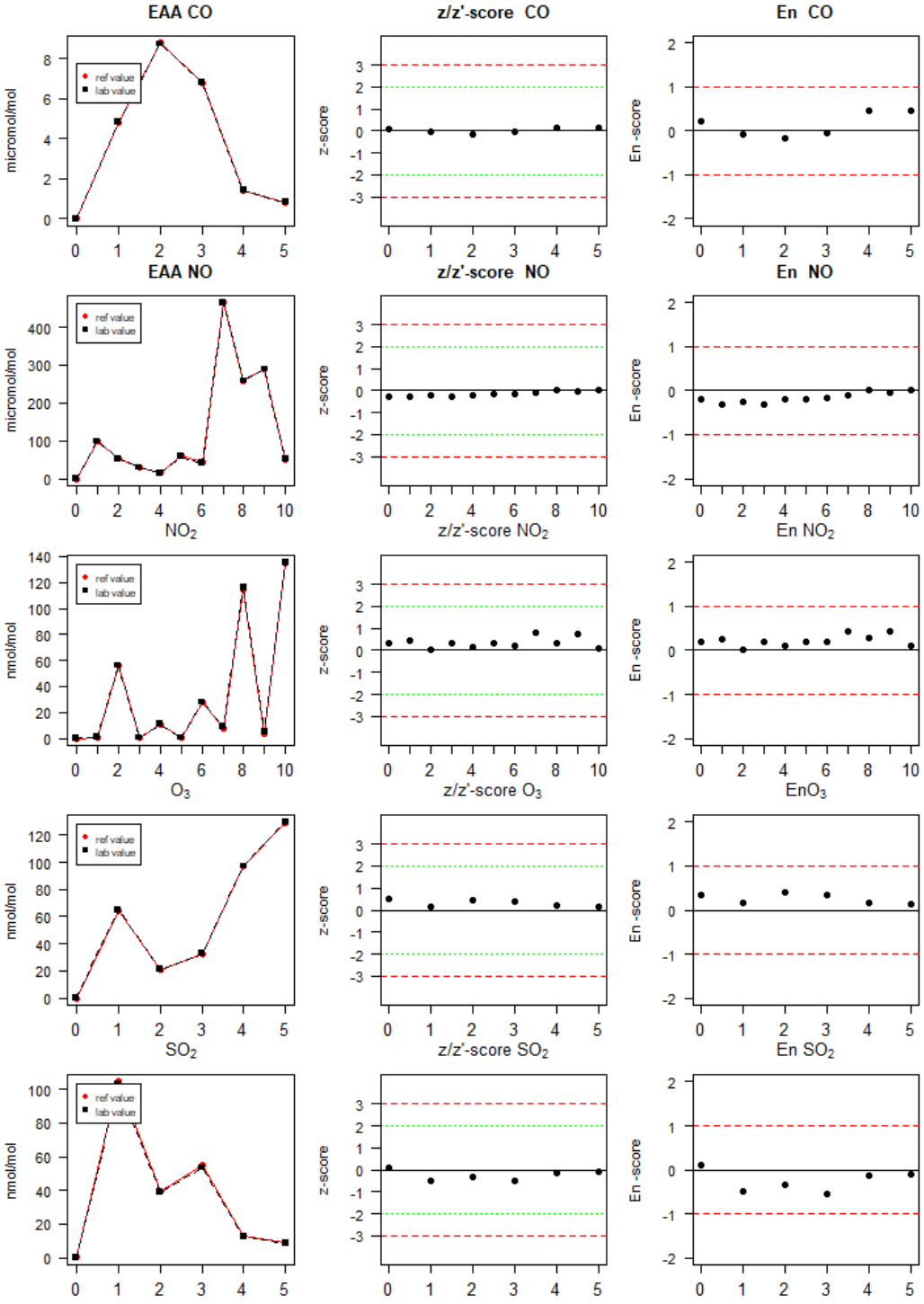

*Source: JRC 2023*

**Table 10**: Reported values, uncertainties and performance evaluation results for Laboratory DLI (Cyprus).

| DLI | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Runs | $X_{ref}$ | $x_{lab}$ | Step 1 | Step 2 | Step 3 | $u_{lab}$ | $U_{lab}$ | $\sigma_{PT}$ | z/z'-score | z/z' | En-score |
| CO_0 | 0.00 | 0.01 | 0.01 | | | 0.06 | 0.12 | 0.10 | 0.10 | z | 0.08 |
| CO_1 | 4.85 | 5.04 | 5.08 | 5.04 | 5.01 | 0.15 | 0.31 | 0.22 | 0.88 | z | 0.61 |
| CO_2 | 8.79 | 9.18 | 9.19 | 9.17 | 9.17 | 0.26 | 0.53 | 0.31 | 1.25 | z | 0.73 |
| CO_3 | 6.81 | 7.00 | 7.02 | 7.01 | 6.98 | 0.21 | 0.41 | 0.26 | 0.72 | z | 0.46 |
| CO_4 | 1.41 | 1.47 | 1.47 | 1.47 | 1.46 | 0.07 | 0.14 | 0.13 | 0.45 | z | 0.42 |
| CO_5 | 0.83 | 0.88 | 0.89 | 0.88 | 0.88 | 0.06 | 0.13 | 0.12 | 0.42 | z | 0.38 |
| NO_0 | 0.00 | -0.20 | -0.20 | | | 0.20 | 0.50 | 1.00 | -0.16 | z' | -0.13 |
| NO_1 | 99.37 | 100.60 | 101.30 | 100.60 | 99.90 | 2.30 | 4.60 | 3.38 | 0.36 | z | 0.25 |
| NO_2 | 53.53 | 54.80 | 55.10 | 54.80 | 54.50 | 1.30 | 2.50 | 2.28 | 0.52 | z' | 0.44 |
| NO_3 | 30.10 | 30.17 | 30.10 | 30.00 | 30.40 | 0.70 | 1.50 | 1.72 | 0.04 | z' | 0.03 |
| NO_4 | 14.43 | 14.27 | 14.20 | 14.50 | 14.10 | 0.40 | 0.80 | 1.35 | -0.11 | z' | -0.10 |
| NO_5 | 59.33 | 59.50 | 59.40 | 59.60 | 59.50 | 1.40 | 2.70 | 2.42 | 0.07 | z' | 0.06 |
| NO_6 | 41.87 | 42.23 | 42.40 | 42.00 | 42.30 | 1.00 | 2.00 | 2.00 | 0.17 | z' | 0.14 |
| NO_7 | 464.47 | 475.27 | 474.70 | 475.30 | 475.80 | 12.10 | 24.20 | 12.15 | 0.89 | z | 0.44 |
| NO_8 | 257.73 | 263.67 | 263.70 | 263.50 | 263.80 | 6.10 | 12.20 | 7.19 | 0.83 | z | 0.47 |
| NO_9 | 289.93 | 294.27 | 293.90 | 294.20 | 294.70 | 6.90 | 13.80 | 7.96 | 0.55 | z | 0.31 |
| NO_10 | 50.73 | 51.80 | 51.70 | 51.80 | 51.90 | 1.20 | 2.40 | 2.22 | 0.45 | z' | 0.38 |
| $NO_2$_0 | -0.10 | 0.40 | 0.40 | | | 0.20 | 0.50 | 1.00 | 0.41 | z' | 0.34 |
| $NO_2$_1 | 0.20 | -0.03 | -0.10 | 0.10 | -0.10 | 0.20 | 0.50 | 1.00 | -0.18 | z' | -0.14 |
| $NO_2$_2 | 56.00 | 55.97 | 55.60 | 55.90 | 56.40 | 1.30 | 2.60 | 2.12 | -0.01 | z' | -0.01 |
| $NO_2$_3 | 0.07 | 0.10 | -0.10 | 0.30 | 0.10 | 0.20 | 0.50 | 1.00 | 0.02 | z' | 0.02 |
| $NO_2$_4 | 10.77 | 11.23 | 11.30 | 11.30 | 11.10 | 0.40 | 0.70 | 1.22 | 0.33 | z' | 0.28 |
| $NO_2$_5 | 0.07 | 0.03 | 0.10 | -0.10 | 0.10 | 0.20 | 0.50 | 1.00 | -0.03 | z' | -0.03 |
| $NO_2$_6 | 27.33 | 27.23 | 26.70 | 27.30 | 27.70 | 0.70 | 1.40 | 1.55 | -0.06 | z' | -0.05 |
| $NO_2$_7 | 7.33 | 5.90 | 6.20 | 5.80 | 5.70 | 0.30 | 0.60 | 1.15 | -0.67 | z' | -0.39 |
| $NO_2$_8 | 115.17 | 116.00 | 116.30 | 116.20 | 115.50 | 2.60 | 5.20 | 3.30 | 0.23 | z' | 0.14 |
| $NO_2$_9 | 3.90 | 3.33 | 3.20 | 3.50 | 3.30 | 0.30 | 0.50 | 1.08 | -0.34 | z' | -0.22 |
| $NO_2$_10 | 135.07 | 135.20 | 135.50 | 135.30 | 134.80 | 3.00 | 6.10 | 3.70 | 0.04 | z | 0.02 |
| $O_3$_0 | -0.20 | 0.10 | 0.10 | | | 0.50 | 0.90 | 1.00 | 0.30 | z | 0.32 |
| $O_3$_1 | 64.67 | 62.80 | 62.40 | 62.90 | 63.10 | 1.10 | 2.10 | 2.29 | -0.82 | z | -0.77 |
| $O_3$_2 | 20.60 | 20.37 | 20.30 | 20.40 | 20.40 | 0.60 | 1.10 | 1.41 | -0.16 | z | -0.19 |
| $O_3$_3 | 32.17 | 31.87 | 31.80 | 31.90 | 31.90 | 0.70 | 1.40 | 1.64 | -0.18 | z | -0.20 |
| $O_3$_4 | 96.73 | 95.47 | 95.50 | 95.40 | 95.50 | 1.50 | 3.00 | 2.93 | -0.41 | z' | -0.37 |
| $O_3$_5 | 129.00 | 127.60 | 127.50 | 127.60 | 127.70 | 1.90 | 3.90 | 3.58 | -0.37 | z' | -0.31 |
| $SO_2$_0 | 0.10 | -0.40 | -0.40 | | | 0.20 | 0.40 | 1.00 | -0.45 | z' | -0.46 |
| $SO_2$_1 | 104.47 | 102.97 | 102.60 | 103.20 | 103.10 | 1.70 | 3.50 | 3.30 | -0.42 | z' | -0.34 |
| $SO_2$_2 | 39.43 | 38.23 | 38.20 | 38.20 | 38.30 | 0.70 | 1.40 | 1.87 | -0.60 | z' | -0.61 |
| $SO_2$_3 | 54.63 | 53.37 | 53.30 | 53.50 | 53.30 | 0.90 | 1.90 | 2.20 | -0.54 | z' | -0.49 |
| $SO_2$_4 | 12.93 | 11.80 | 11.60 | 11.70 | 12.10 | 0.30 | 0.60 | 1.28 | -0.82 | z' | -0.90 |
| $SO_2$_5 | 8.70 | 7.87 | 8.00 | 7.70 | 7.90 | 0.30 | 0.50 | 1.19 | -0.64 | z' | -0.69 |

Source: JRC 2023

**Figure 18**: Graphical report of results of Laboratory EAA (Austria).



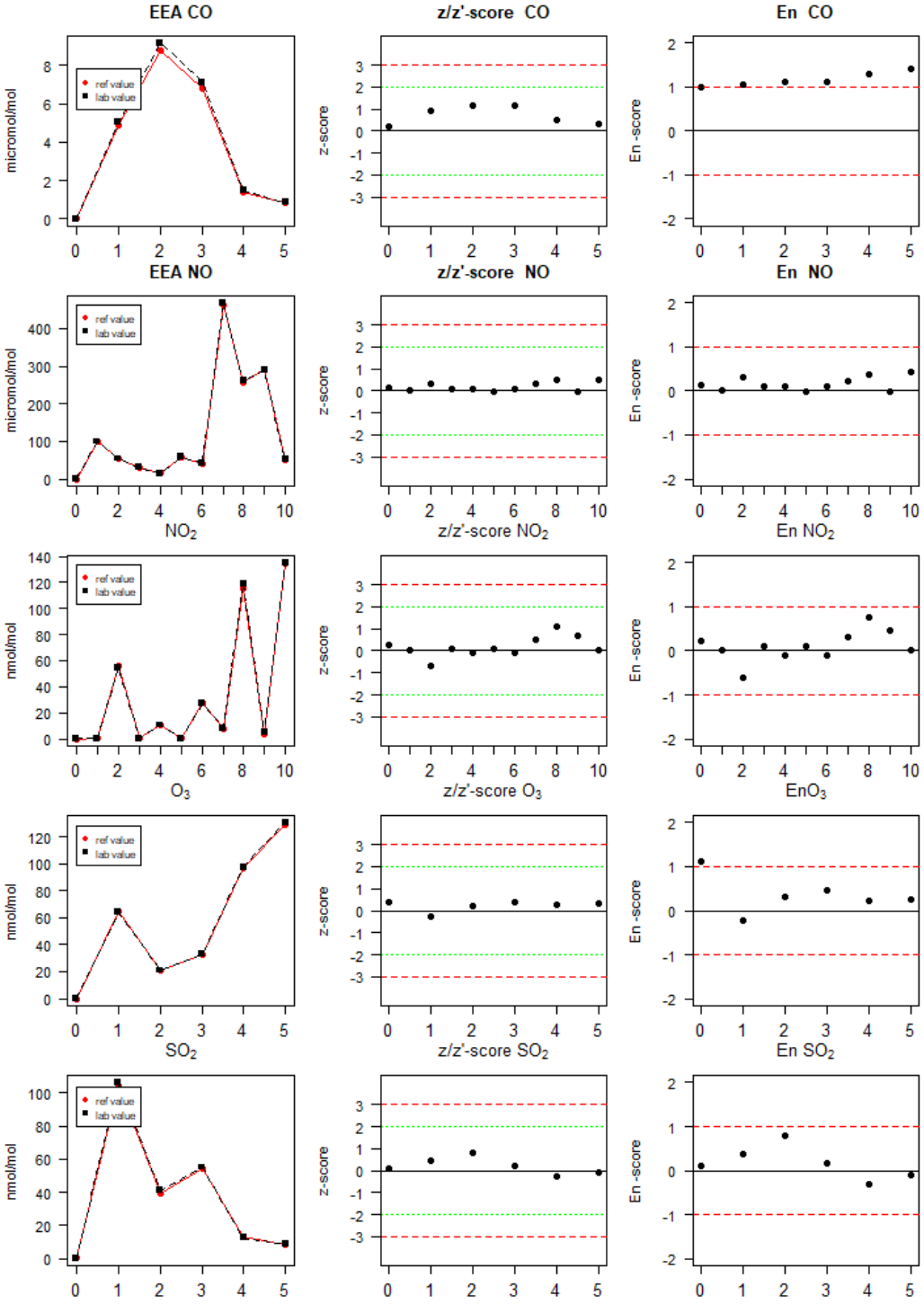

*Source: JRC 2023*

**Table 11**: Reported values, uncertainties and performance evaluation results for Laboratory EAA (Austria).

| EAA | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Runs | $X_{ref}$ | $x_{lab}$ | Step 1 | Step 2 | Step 3 | $u_{lab}$ | $U_{lab}$ | $\sigma_{PT}$ | z/z'-score | z/z' | En-score |
| CO_0 | 0.00 | 0.01 | 0.01 | | | 0.02 | 0.04 | 0.10 | 0.10 | z | 0.22 |
| CO_1 | 4.85 | 4.84 | 4.84 | 4.84 | 4.84 | 0.06 | 0.12 | 0.22 | -0.05 | z | -0.08 |
| CO_2 | 8.79 | 8.75 | 8.75 | 8.75 | 8.76 | 0.11 | 0.22 | 0.31 | -0.13 | z | -0.17 |
| CO_3 | 6.81 | 6.80 | 6.80 | 6.80 | 6.80 | 0.09 | 0.17 | 0.26 | -0.04 | z | -0.05 |
| CO_4 | 1.41 | 1.43 | 1.43 | 1.43 | 1.43 | 0.02 | 0.04 | 0.13 | 0.15 | z | 0.45 |
| CO_5 | 0.83 | 0.85 | 0.85 | 0.85 | 0.85 | 0.02 | 0.04 | 0.12 | 0.17 | z | 0.45 |
| NO_0 | 0.00 | -0.30 | -0.30 | | | 0.50 | 0.90 | 1.00 | -0.25 | z' | -0.18 |
| NO_1 | 99.37 | 98.40 | 98.60 | 98.40 | 98.20 | 1.30 | 2.50 | 3.38 | -0.29 | z | -0.32 |
| NO_2 | 53.53 | 53.03 | 53.10 | 53.00 | 53.00 | 0.70 | 1.40 | 2.28 | -0.21 | z' | -0.24 |
| NO_3 | 30.10 | 29.57 | 29.60 | 29.60 | 29.50 | 0.40 | 0.90 | 1.72 | -0.29 | z' | -0.30 |
| NO_4 | 14.43 | 14.10 | 14.10 | 14.10 | 14.10 | 0.50 | 0.90 | 1.35 | -0.22 | z' | -0.20 |
| NO_5 | 59.33 | 58.90 | 58.90 | 58.90 | 58.90 | 0.80 | 1.50 | 2.42 | -0.17 | z' | -0.20 |
| NO_6 | 41.87 | 41.57 | 41.60 | 41.60 | 41.50 | 0.60 | 1.10 | 2.00 | -0.14 | z' | -0.16 |
| NO_7 | 464.47 | 463.00 | 462.80 | 462.50 | 463.70 | 5.80 | 11.60 | 12.15 | -0.12 | z | -0.12 |
| NO_8 | 257.73 | 257.77 | 257.60 | 257.70 | 258.00 | 3.20 | 6.50 | 7.19 | 0.01 | z | 0.01 |
| NO_9 | 289.93 | 289.47 | 289.30 | 289.50 | 289.60 | 3.60 | 7.30 | 7.96 | -0.06 | z | -0.06 |
| NO_10 | 50.73 | 50.77 | 50.80 | 50.80 | 50.70 | 0.70 | 1.40 | 2.22 | 0.02 | z' | 0.02 |
| $NO_2$_0 | -0.10 | 0.30 | 0.30 | | | 0.80 | 1.50 | 1.00 | 0.33 | z' | 0.19 |
| $NO_2$_1 | 0.20 | 0.77 | 0.80 | 0.70 | 0.80 | 0.80 | 1.60 | 1.00 | 0.44 | z' | 0.25 |
| $NO_2$_2 | 56.00 | 56.03 | 55.90 | 56.10 | 56.10 | 0.80 | 1.60 | 2.12 | 0.01 | z' | 0.01 |
| $NO_2$_3 | 0.07 | 0.50 | 0.50 | 0.50 | 0.50 | 0.70 | 1.50 | 1.00 | 0.35 | z' | 0.20 |
| $NO_2$_4 | 10.77 | 10.97 | 10.90 | 11.10 | 10.90 | 0.80 | 1.50 | 1.22 | 0.14 | z' | 0.09 |
| $NO_2$_5 | 0.07 | 0.50 | 0.50 | 0.50 | 0.50 | 0.80 | 1.50 | 1.00 | 0.34 | z' | 0.20 |
| $NO_2$_6 | 27.33 | 27.73 | 27.70 | 27.70 | 27.80 | 0.80 | 1.50 | 1.55 | 0.23 | z' | 0.19 |
| $NO_2$_7 | 7.33 | 9.10 | 9.30 | 9.10 | 8.90 | 0.80 | 1.70 | 1.15 | 0.83 | z' | 0.44 |
| $NO_2$_8 | 115.17 | 116.43 | 116.40 | 116.40 | 116.50 | 1.50 | 3.00 | 3.30 | 0.34 | z' | 0.29 |
| $NO_2$_9 | 3.90 | 5.17 | 5.30 | 5.20 | 5.00 | 0.80 | 1.60 | 1.08 | 0.75 | z' | 0.43 |
| $NO_2$_10 | 135.07 | 135.47 | 135.40 | 135.50 | 135.50 | 1.70 | 3.50 | 3.70 | 0.11 | z | 0.10 |
| $O_3$_0 | -0.20 | 0.30 | 0.30 | | | 0.80 | 1.50 | 1.00 | 0.50 | z | 0.33 |
| $O_3$_1 | 64.67 | 65.03 | 64.80 | 65.00 | 65.30 | 1.10 | 2.10 | 2.29 | 0.16 | z | 0.15 |
| $O_3$_2 | 20.60 | 21.27 | 21.30 | 21.20 | 21.30 | 0.80 | 1.60 | 1.41 | 0.47 | z | 0.40 |
| $O_3$_3 | 32.17 | 32.80 | 32.80 | 32.80 | 32.80 | 0.90 | 1.70 | 1.64 | 0.38 | z | 0.35 |
| $O_3$_4 | 96.73 | 97.27 | 97.20 | 97.30 | 97.30 | 1.40 | 2.70 | 2.93 | 0.18 | z' | 0.17 |
| $O_3$_5 | 129.00 | 129.57 | 129.50 | 129.60 | 129.60 | 1.70 | 3.40 | 3.58 | 0.15 | z' | 0.14 |
| $SO_2$_0 | 0.10 | 0.20 | 0.20 | | | 0.20 | 0.30 | 1.00 | 0.09 | z' | 0.10 |
| $SO_2$_1 | 104.47 | 102.67 | 102.60 | 102.80 | 102.60 | 1.30 | 2.60 | 3.30 | -0.50 | z' | -0.48 |
| $SO_2$_2 | 39.43 | 38.83 | 38.90 | 38.80 | 38.80 | 0.50 | 1.00 | 1.87 | -0.30 | z' | -0.35 |
| $SO_2$_3 | 54.63 | 53.43 | 53.50 | 53.40 | 53.40 | 0.70 | 1.40 | 2.20 | -0.51 | z' | -0.54 |
| $SO_2$_4 | 12.93 | 12.77 | 12.60 | 12.80 | 12.90 | 0.20 | 0.40 | 1.28 | -0.12 | z' | -0.14 |
| $SO_2$_5 | 8.70 | 8.57 | 8.50 | 8.60 | 8.60 | 0.20 | 0.40 | 1.19 | -0.10 | z' | -0.11 |

Source: JRC 2023

**Figure 19**: Graphical report of results of Laboratory EEA (Bulgaria).



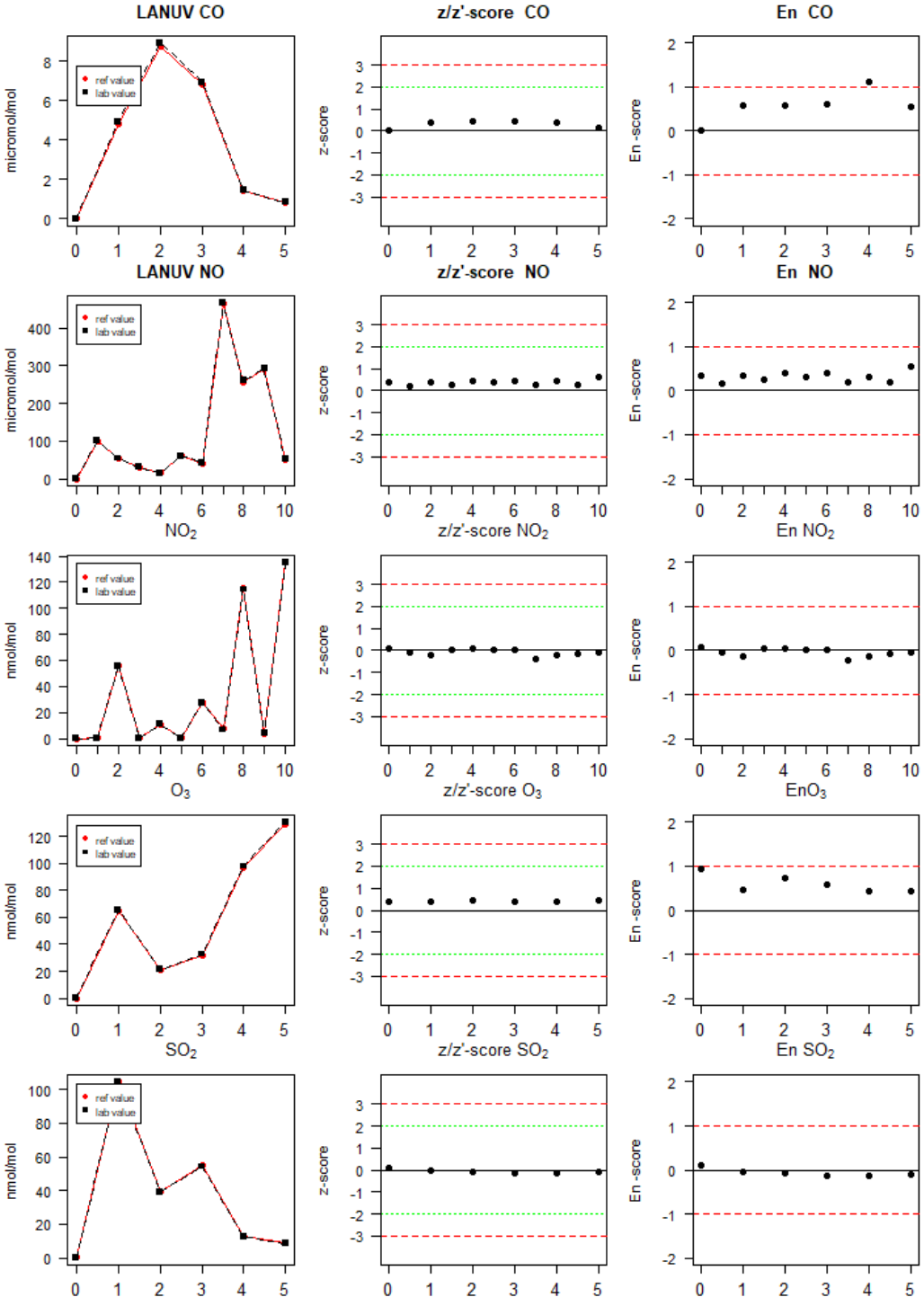

*Source: JRC 2023*

**Table 12**: Reported values, uncertainties and performance evaluation results for Laboratory EEA (Bulgaria).

| EEA | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Runs | $X_{ref}$ | $x_{lab}$ | Step 1 | Step 2 | Step 3 | $u_{lab}$ | $U_{lab}$ | $\sigma_{PT}$ | z/z'-score | z/z' | En-score |
| CO_0 | 0.00 | 0.02 | 0.02 | | | 0.00 | 0.00 | 0.10 | 0.20 | z | 1.00 |
| CO_1 | 4.85 | 5.05 | 5.05 | 5.05 | 5.06 | 0.09 | 0.18 | 0.22 | 0.92 | z | 1.07 |
| CO_2 | 8.79 | 9.16 | 9.16 | 9.16 | 9.16 | 0.16 | 0.32 | 0.31 | 1.19 | z | 1.11 |
| CO_3 | 6.81 | 7.11 | 7.11 | 7.11 | 7.11 | 0.13 | 0.26 | 0.26 | 1.14 | z | 1.11 |
| CO_4 | 1.41 | 1.48 | 1.48 | 1.48 | 1.48 | 0.03 | 0.05 | 0.13 | 0.52 | z | 1.30 |
| CO_5 | 0.83 | 0.87 | 0.87 | 0.87 | 0.87 | 0.01 | 0.02 | 0.12 | 0.33 | z | 1.41 |
| NO_0 | 0.00 | 0.20 | 0.20 | | | 0.00 | 0.10 | 1.00 | 0.16 | z’ | 0.14 |
| NO_1 | 99.37 | 99.37 | 99.30 | 99.40 | 99.40 | 1.80 | 3.60 | 3.38 | 0.00 | z | 0.00 |
| NO_2 | 53.53 | 54.27 | 54.20 | 54.30 | 54.30 | 1.00 | 2.00 | 2.28 | 0.31 | z’ | 0.30 |
| NO_3 | 30.10 | 30.27 | 30.20 | 30.30 | 30.30 | 0.50 | 1.00 | 1.72 | 0.09 | z’ | 0.09 |
| NO_4 | 14.43 | 14.57 | 14.50 | 14.60 | 14.60 | 0.30 | 0.60 | 1.35 | 0.09 | z’ | 0.09 |
| NO_5 | 59.33 | 59.27 | 59.20 | 59.30 | 59.30 | 1.10 | 2.20 | 2.42 | -0.02 | z’ | -0.02 |
| NO_6 | 41.87 | 42.07 | 42.00 | 42.10 | 42.10 | 0.80 | 1.60 | 2.00 | 0.09 | z’ | 0.09 |
| NO_7 | 464.47 | 468.23 | 467.90 | 468.40 | 468.40 | 8.40 | 16.80 | 12.15 | 0.31 | z | 0.22 |
| NO_8 | 257.73 | 261.23 | 260.20 | 260.20 | 263.30 | 4.70 | 9.40 | 7.19 | 0.49 | z | 0.36 |
| NO_9 | 289.93 | 289.87 | 289.80 | 289.80 | 290.00 | 5.20 | 10.40 | 7.96 | -0.01 | z | -0.01 |
| NO_10 | 50.73 | 51.87 | 51.80 | 51.90 | 51.90 | 1.10 | 2.20 | 2.22 | 0.48 | z’ | 0.43 |
| $NO_2$_0 | -0.10 | 0.20 | 0.20 | | | 0.00 | 0.10 | 1.00 | 0.25 | z’ | 0.21 |
| $NO_2$_1 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.00 | 0.10 | 1.00 | 0.00 | z’ | 0.00 |
| $NO_2$_2 | 56.00 | 54.43 | 54.30 | 54.50 | 54.50 | 1.00 | 2.00 | 2.12 | -0.69 | z’ | -0.60 |
| $NO_2$_3 | 0.07 | 0.20 | 0.20 | 0.20 | 0.20 | 0.00 | 0.10 | 1.00 | 0.11 | z’ | 0.09 |
| $NO_2$_4 | 10.77 | 10.63 | 10.30 | 10.80 | 10.80 | 0.20 | 0.40 | 1.22 | -0.10 | z’ | -0.09 |
| $NO_2$_5 | 0.07 | 0.20 | 0.20 | 0.20 | 0.20 | 0.00 | 0.10 | 1.00 | 0.10 | z’ | 0.09 |
| $NO_2$_6 | 27.33 | 27.17 | 27.10 | 27.20 | 27.20 | 0.50 | 1.00 | 1.55 | -0.09 | z’ | -0.09 |
| $NO_2$_7 | 7.33 | 8.43 | 8.30 | 8.50 | 8.50 | 0.20 | 0.40 | 1.15 | 0.52 | z’ | 0.30 |
| $NO_2$_8 | 115.17 | 119.17 | 119.50 | 119.10 | 118.90 | 2.10 | 4.20 | 3.30 | 1.09 | z’ | 0.77 |
| $NO_2$_9 | 3.90 | 5.03 | 4.90 | 5.10 | 5.10 | 0.10 | 0.20 | 1.08 | 0.67 | z’ | 0.45 |
| $NO_2$_10 | 135.07 | 135.13 | 135.20 | 135.20 | 135.00 | 2.40 | 4.80 | 3.70 | 0.02 | z | 0.01 |
| $O_3$_0 | -0.20 | 0.20 | 0.20 | | | 0.00 | 0.20 | 1.00 | 0.40 | z | 1.11 |
| $O_3$_1 | 64.67 | 64.07 | 64.00 | 64.10 | 64.10 | 1.20 | 2.40 | 2.29 | -0.26 | z | -0.22 |
| $O_3$_2 | 20.60 | 20.90 | 20.80 | 20.90 | 21.00 | 0.40 | 0.80 | 1.41 | 0.21 | z | 0.32 |
| $O_3$_3 | 32.17 | 32.80 | 32.70 | 32.80 | 32.90 | 0.60 | 1.20 | 1.64 | 0.38 | z | 0.47 |
| $O_3$_4 | 96.73 | 97.57 | 97.50 | 97.60 | 97.60 | 1.80 | 3.60 | 2.93 | 0.27 | z’ | 0.21 |
| $O_3$_5 | 129.00 | 130.27 | 130.20 | 130.30 | 130.30 | 2.30 | 4.60 | 3.58 | 0.34 | z’ | 0.25 |
| $SO_2$_0 | 0.10 | 0.20 | 0.20 | | | 0.00 | 0.10 | 1.00 | 0.09 | z’ | 0.10 |
| $SO_2$_1 | 104.47 | 106.13 | 106.00 | 106.20 | 106.20 | 1.90 | 3.80 | 3.30 | 0.46 | z’ | 0.36 |
| $SO_2$_2 | 39.43 | 41.07 | 41.00 | 41.10 | 41.10 | 0.70 | 1.50 | 1.87 | 0.82 | z’ | 0.80 |
| $SO_2$_3 | 54.63 | 55.07 | 55.00 | 55.10 | 55.10 | 1.00 | 2.00 | 2.20 | 0.19 | z’ | 0.17 |
| $SO_2$_4 | 12.93 | 12.57 | 12.50 | 12.60 | 12.60 | 0.20 | 0.50 | 1.28 | -0.26 | z’ | -0.30 |
| $SO_2$_5 | 8.70 | 8.57 | 8.50 | 8.60 | 8.60 | 0.20 | 0.30 | 1.19 | -0.10 | z’ | -0.11 |

Source: JRC 2023

**Figure 20**: Graphical report of results of Laboratory LANUV (Germany).



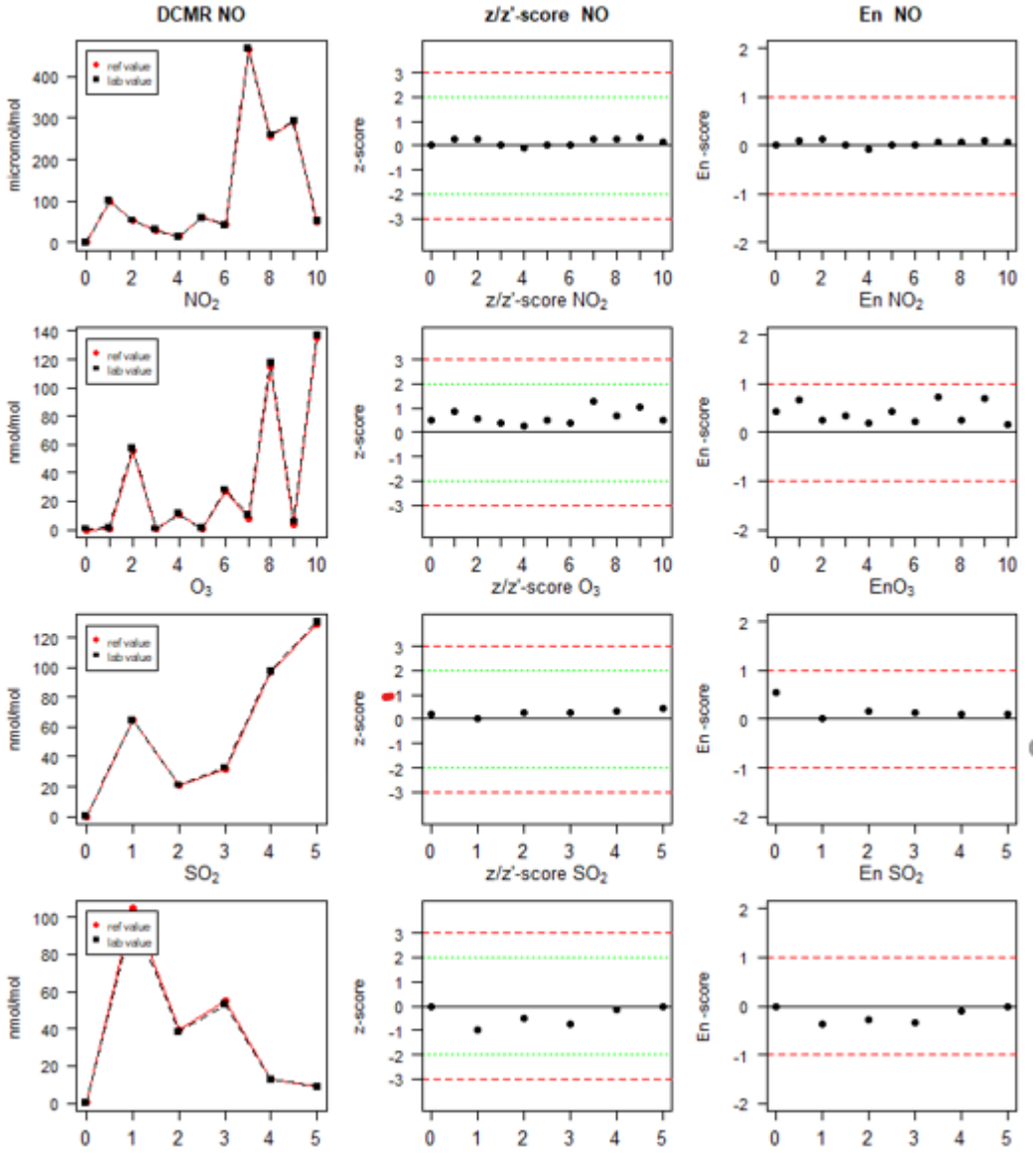

*Source: JRC 2023*

**Table 13**: Reported values, uncertainties and performance evaluation results for Laboratory LANUV (Germany).

| LANUV | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Runs | $X_{ref}$ | $x_{lab}$ | Step 1 | Step 2 | Step 3 | $u_{lab}$ | $U_{lab}$ | $\sigma_{PT}$ | z/z'-score | z/z' | En-score |
| CO_0 | 0.00 | 0.00 | 0.00 | | | 0.00 | 0.01 | 0.10 | 0.00 | z | 0.00 |
| CO_1 | 4.85 | 4.93 | 4.92 | 4.93 | 4.95 | 0.06 | 0.13 | 0.22 | 0.37 | z | 0.57 |
| CO_2 | 8.79 | 8.93 | 8.92 | 8.93 | 8.93 | 0.11 | 0.22 | 0.31 | 0.45 | z | 0.59 |
| CO_3 | 6.81 | 6.93 | 6.94 | 6.93 | 6.93 | 0.09 | 0.18 | 0.26 | 0.46 | z | 0.62 |
| CO_4 | 1.41 | 1.46 | 1.46 | 1.46 | 1.46 | 0.02 | 0.04 | 0.13 | 0.37 | z | 1.12 |
| CO_5 | 0.83 | 0.85 | 0.85 | 0.85 | 0.85 | 0.01 | 0.03 | 0.12 | 0.17 | z | 0.55 |
| NO_0 | 0.00 | 0.50 | 0.50 | | | 0.20 | 0.40 | 1.00 | 0.41 | z' | 0.34 |
| NO_1 | 99.37 | 100.07 | 100.20 | 100.00 | 100.00 | 1.90 | 3.90 | 3.38 | 0.21 | z | 0.16 |
| NO_2 | 53.53 | 54.47 | 54.60 | 54.50 | 54.30 | 1.10 | 2.30 | 2.28 | 0.39 | z' | 0.34 |
| NO_3 | 30.10 | 30.63 | 30.50 | 30.70 | 30.70 | 0.70 | 1.40 | 1.72 | 0.29 | z' | 0.26 |
| NO_4 | 14.43 | 15.10 | 15.20 | 15.00 | 15.10 | 0.40 | 0.90 | 1.35 | 0.44 | z' | 0.40 |
| NO_5 | 59.33 | 60.27 | 60.30 | 60.20 | 60.30 | 1.20 | 2.50 | 2.42 | 0.37 | z' | 0.32 |
| NO_6 | 41.87 | 42.87 | 42.90 | 42.90 | 42.80 | 0.90 | 1.90 | 2.00 | 0.46 | z' | 0.41 |
| NO_7 | 464.47 | 467.63 | 467.10 | 467.90 | 467.90 | 8.50 | 16.90 | 12.15 | 0.26 | z | 0.18 |
| NO_8 | 257.73 | 260.77 | 260.70 | 260.80 | 260.80 | 4.80 | 9.60 | 7.19 | 0.42 | z | 0.30 |
| NO_9 | 289.93 | 291.90 | 291.70 | 292.00 | 292.00 | 5.30 | 10.70 | 7.96 | 0.25 | z | 0.18 |
| NO_10 | 50.73 | 52.20 | 52.30 | 52.20 | 52.10 | 1.10 | 2.20 | 2.22 | 0.62 | z' | 0.55 |
| $NO_2$_0 | -0.10 | 0.00 | 0.00 | | | 0.60 | 1.10 | 1.00 | 0.08 | z' | 0.06 |
| $NO_2$_1 | 0.20 | 0.10 | 0.00 | 0.20 | 0.10 | 0.60 | 1.10 | 1.00 | -0.08 | z' | -0.05 |
| $NO_2$_2 | 56.00 | 55.57 | 55.50 | 55.60 | 55.60 | 1.40 | 2.90 | 2.12 | -0.19 | z' | -0.13 |
| $NO_2$_3 | 0.07 | 0.13 | 0.20 | 0.00 | 0.20 | 0.60 | 1.10 | 1.00 | 0.05 | z' | 0.03 |
| $NO_2$_4 | 10.77 | 10.87 | 10.90 | 10.90 | 10.80 | 0.70 | 1.50 | 1.22 | 0.07 | z' | 0.05 |
| $NO_2$_5 | 0.07 | 0.07 | -0.10 | 0.20 | 0.10 | 0.60 | 1.10 | 1.00 | 0.00 | z' | 0.00 |
| $NO_2$_6 | 27.33 | 27.37 | 27.30 | 27.40 | 27.40 | 1.00 | 2.00 | 1.55 | 0.02 | z' | 0.02 |
| $NO_2$_7 | 7.33 | 6.53 | 7.00 | 6.20 | 6.40 | 0.70 | 1.30 | 1.15 | -0.37 | z' | -0.21 |
| $NO_2$_8 | 115.17 | 114.43 | 114.40 | 114.40 | 114.50 | 2.40 | 4.70 | 3.30 | -0.20 | z' | -0.13 |
| $NO_2$_9 | 3.90 | 3.70 | 3.70 | 3.70 | 3.70 | 0.60 | 1.20 | 1.08 | -0.12 | z' | -0.07 |
| $NO_2$_10 | 135.07 | 134.77 | 134.80 | 134.90 | 134.60 | 2.70 | 5.30 | 3.70 | -0.08 | z | -0.05 |
| $O_3$_0 | -0.20 | 0.20 | 0.20 | | | 0.10 | 0.30 | 1.00 | 0.40 | z | 0.94 |
| $O_3$_1 | 64.67 | 65.60 | 65.40 | 65.60 | 65.80 | 0.80 | 1.60 | 2.29 | 0.41 | z | 0.46 |
| $O_3$_2 | 20.60 | 21.23 | 21.20 | 21.30 | 21.20 | 0.30 | 0.70 | 1.41 | 0.45 | z | 0.73 |
| $O_3$_3 | 32.17 | 32.80 | 32.80 | 32.80 | 32.80 | 0.50 | 0.90 | 1.64 | 0.38 | z | 0.58 |
| $O_3$_4 | 96.73 | 97.93 | 97.80 | 98.00 | 98.00 | 1.10 | 2.20 | 2.93 | 0.39 | z' | 0.43 |
| $O_3$_5 | 129.00 | 130.63 | 130.60 | 130.70 | 130.60 | 1.40 | 2.90 | 3.58 | 0.43 | z' | 0.44 |
| $SO_2$_0 | 0.10 | 0.20 | 0.20 | | | 0.10 | 0.10 | 1.00 | 0.09 | z' | 0.10 |
| $SO_2$_1 | 104.47 | 104.30 | 104.20 | 104.30 | 104.40 | 1.80 | 3.80 | 3.30 | -0.05 | z' | -0.04 |
| $SO_2$_2 | 39.43 | 39.27 | 39.30 | 39.30 | 39.20 | 0.70 | 1.40 | 1.87 | -0.08 | z' | -0.08 |
| $SO_2$_3 | 54.63 | 54.27 | 54.20 | 54.30 | 54.30 | 1.00 | 1.90 | 2.20 | -0.15 | z' | -0.14 |
| $SO_2$_4 | 12.93 | 12.77 | 12.60 | 12.80 | 12.90 | 0.30 | 0.50 | 1.28 | -0.12 | z' | -0.13 |
| $SO_2$_5 | 8.70 | 8.60 | 8.60 | 8.60 | 8.60 | 0.20 | 0.40 | 1.19 | -0.08 | z' | -0.09 |

Source: JRC 2023

**Figure 21**: Graphical report of results of Laboratory DCMR (Netherlands).



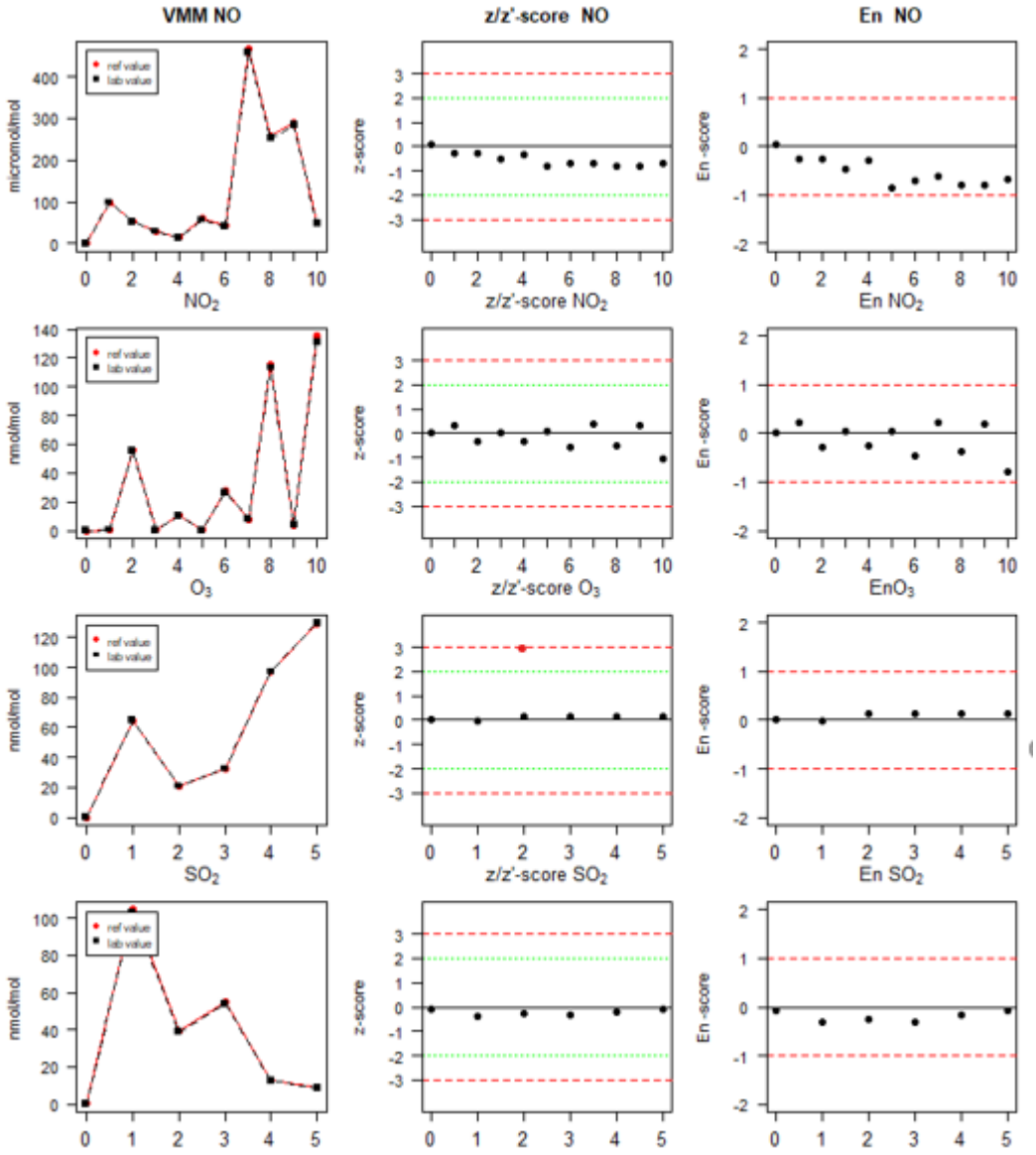

*Source: JRC 2023*

**Table 14**: Reported values, uncertainties and performance evaluation results for Laboratory DCMR (Netherlands).

| DCMR | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Runs | $X_{ref}$ | $x_{lab}$ | Step 1 | Step 2 | Step 3 | $u_{lab}$ | $U_{lab}$ | $\sigma_{PT}$ | z/z'-score | z/z' | En-score |
| NO_0 | 0.00 | 0.00 | 0.0 | | | 0.1 | 0.2 | 1.00 | 0.00 | z' | 0.00 |
| NO_1 | 99.37 | 100.27 | 100.3 | 100.3 | 100.2 | 4.3 | 8.6 | 3.38 | 0.27 | z | 0.10 |
| NO_2 | 53.53 | 54.10 | 54.2 | 54.1 | 54.0 | 2.3 | 4.7 | 2.28 | 0.24 | z' | 0.12 |
| NO_3 | 30.10 | 30.17 | 30.1 | 30.2 | 30.2 | 1.3 | 2.6 | 1.72 | 0.04 | z' | 0.02 |
| NO_4 | 14.43 | 14.27 | 14.4 | 14.2 | 14.2 | 0.6 | 1.2 | 1.35 | -0.11 | z' | -0.09 |
| NO_5 | 59.33 | 59.40 | 59.4 | 59.4 | 59.4 | 2.6 | 5.1 | 2.42 | 0.03 | z' | 0.01 |
| NO_6 | 41.87 | 41.90 | 41.9 | 41.8 | 42.0 | 1.8 | 3.6 | 2.00 | 0.01 | z' | 0.01 |
| NO_7 | 464.47 | 467.73 | 467.0 | 468.0 | 468.2 | 20.1 | 40.2 | 12.15 | 0.27 | z | 0.08 |
| NO_8 | 257.73 | 259.57 | 259.4 | 259.6 | 259.7 | 11.2 | 22.3 | 7.19 | 0.26 | z | 0.08 |
| NO_9 | 289.93 | 292.73 | 292.2 | 292.9 | 293.1 | 12.6 | 25.2 | 7.96 | 0.35 | z | 0.11 |
| NO_10 | 50.73 | 51.10 | 51.1 | 51.1 | 51.1 | 2.2 | 4.4 | 2.22 | 0.16 | z' | 0.08 |
| $NO_2$_0 | -0.10 | 0.50 | 0.5 | | | 0.1 | 0.2 | 1.00 | 0.49 | z' | 0.42 |
| $NO_2$_1 | 0.20 | 1.30 | 1.3 | 1.3 | 1.3 | 0.1 | 0.2 | 1.00 | 0.86 | z' | 0.68 |
| $NO_2$_2 | 56.00 | 57.27 | 57.1 | 57.3 | 57.4 | 2.5 | 4.9 | 2.12 | 0.56 | z' | 0.24 |
| $NO_2$_3 | 0.07 | 0.57 | 0.6 | 0.6 | 0.5 | 0.1 | 0.2 | 1.00 | 0.41 | z' | 0.33 |
| $NO_2$_4 | 10.77 | 11.13 | 11.1 | 11.2 | 11.1 | 0.5 | 1.0 | 1.22 | 0.26 | z' | 0.20 |
| $NO_2$_5 | 0.07 | 0.70 | 0.7 | 0.7 | 0.7 | 0.1 | 0.2 | 1.00 | 0.49 | z' | 0.42 |
| $NO_2$_6 | 27.33 | 27.97 | 28.0 | 28.0 | 27.9 | 1.2 | 2.4 | 1.55 | 0.37 | z' | 0.23 |
| $NO_2$_7 | 7.33 | 10.07 | 10.4 | 10.1 | 9.7 | 0.4 | 0.9 | 1.15 | 1.28 | z' | 0.74 |
| $NO_2$_8 | 115.17 | 117.70 | 117.7 | 117.7 | 117.7 | 5.1 | 10.1 | 3.30 | 0.69 | z' | 0.24 |
| $NO_2$_9 | 3.90 | 5.67 | 5.8 | 5.7 | 5.5 | 0.2 | 0.5 | 1.08 | 1.05 | z' | 0.69 |
| $NO_2$_10 | 135.07 | 136.93 | 137.0 | 136.9 | 136.9 | 5.9 | 11.8 | 3.70 | 0.50 | z | 0.15 |
| $O_3$_0 | -0.20 | 0.00 | 0.0 | | | 0.1 | 0.2 | 1.00 | 0.20 | z | 0.55 |
| $O_3$_1 | 64.67 | 64.67 | 64.0 | 65.0 | 65.0 | 3.6 | 7.1 | 2.29 | 0.00 | z | 0.00 |
| $O_3$_2 | 20.60 | 21.00 | 21.0 | 21.0 | 21.0 | 1.2 | 2.3 | 1.41 | 0.28 | z | 0.17 |
| $O_3$_3 | 32.17 | 32.60 | 32.5 | 32.8 | 32.5 | 1.8 | 3.6 | 1.64 | 0.26 | z | 0.12 |
| $O_3$_4 | 96.73 | 97.70 | 97.1 | 98.0 | 98.0 | 5.4 | 10.7 | 2.93 | 0.32 | z' | 0.09 |
| $O_3$_5 | 129.00 | 130.63 | 130.4 | 130.7 | 130.8 | 7.2 | 14.4 | 3.58 | 0.43 | z' | 0.11 |
| $SO_2$_0 | 0.10 | 0.10 | 0.1 | | | 0.1 | 0.2 | 1.00 | 0.00 | z' | 0.00 |
| $SO_2$_1 | 104.47 | 100.90 | 100.6 | 101.0 | 101.1 | 4.5 | 9.0 | 3.30 | -1.00 | z' | -0.38 |
| $SO_2$_2 | 39.43 | 38.37 | 38.3 | 38.4 | 38.4 | 1.7 | 3.4 | 1.87 | -0.53 | z' | -0.29 |
| $SO_2$_3 | 54.63 | 52.93 | 53.0 | 52.8 | 53.0 | 2.4 | 4.7 | 2.20 | -0.73 | z' | -0.34 |
| $SO_2$_4 | 12.93 | 12.77 | 12.6 | 12.8 | 12.9 | 0.6 | 1.1 | 1.28 | -0.12 | z' | -0.10 |
| $SO_2$_5 | 8.70 | 8.70 | 8.7 | 8.7 | 8.7 | 0.4 | 0.8 | 1.19 | 0.00 | z' | 0.00 |

*Source: JRC 2023*

**Figure 22**: Graphical report of results of Laboratory VMM (Belgium).




*Source: JRC 2023*

**Table 15**: Reported values, uncertainties and performance evaluation results for VMM (Belgium).

| VMM | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Runs | $X_{ref}$ | $x_{lab}$ | Step 1 | Step 2 | Step 3 | $u_{lab}$ | $U_{lab}$ | $\sigma_{PT}$ | z/z'-score | z/z' | En-score |
| NO_0 | 0.00 | 0.10 | 0.1 | | | 0.6 | 1.2 | 1.00 | 0.08 | z' | 0.05 |
| NO_1 | 99.37 | 98.47 | 98.7 | 98.4 | 98.3 | 1.5 | 3.0 | 3.38 | -0.27 | z | -0.26 |
| NO_2 | 53.53 | 52.90 | 53.1 | 52.9 | 52.7 | 0.9 | 1.9 | 2.28 | -0.26 | z' | -0.26 |
| NO_3 | 30.10 | 29.13 | 29.2 | 29.1 | 29.1 | 0.7 | 1.4 | 1.72 | -0.52 | z' | -0.47 |
| NO_4 | 14.43 | 13.90 | 13.9 | 13.9 | 13.9 | 0.6 | 1.2 | 1.35 | -0.35 | z' | -0.29 |
| NO_5 | 59.33 | 57.20 | 57.3 | 57.2 | 57.1 | 1.0 | 2.0 | 2.42 | -0.83 | z' | -0.85 |
| NO_6 | 41.87 | 40.33 | 40.4 | 40.4 | 40.2 | 0.8 | 1.6 | 2.00 | -0.71 | z' | -0.70 |
| NO_7 | 464.47 | 456.37 | 456.1 | 456.8 | 456.2 | 6.3 | 12.6 | 12.15 | -0.67 | z | -0.60 |
| NO_8 | 257.73 | 251.83 | 251.7 | 251.8 | 252.0 | 3.5 | 7.0 | 7.19 | -0.82 | z | -0.78 |
| NO_9 | 289.93 | 283.30 | 283.1 | 283.4 | 283.4 | 4.0 | 7.9 | 7.96 | -0.83 | z | -0.78 |
| NO_10 | 50.73 | 49.13 | 49.0 | 49.2 | 49.2 | 0.9 | 1.8 | 2.22 | -0.68 | z' | -0.68 |
| $NO_2$_0 | -0.10 | -0.10 | -0.1 | | | 0.6 | 1.2 | 1.00 | 0.00 | z' | 0.00 |
| $NO_2$_1 | 0.20 | 0.63 | 0.6 | 0.7 | 0.6 | 0.6 | 1.2 | 1.00 | 0.33 | z' | 0.22 |
| $NO_2$_2 | 56.00 | 55.20 | 55.2 | 55.2 | 55.2 | 1.1 | 2.2 | 2.12 | -0.35 | z' | -0.29 |
| $NO_2$_3 | 0.07 | 0.13 | 0.1 | 0.2 | 0.1 | 0.6 | 1.2 | 1.00 | 0.05 | z' | 0.03 |
| $NO_2$_4 | 10.77 | 10.30 | 10.4 | 10.3 | 10.2 | 0.6 | 1.2 | 1.22 | -0.34 | z' | -0.24 |
| $NO_2$_5 | 0.07 | 0.17 | 0.2 | 0.1 | 0.2 | 0.6 | 1.2 | 1.00 | 0.08 | z' | 0.05 |
| $NO_2$_6 | 27.33 | 26.37 | 26.4 | 26.3 | 26.4 | 0.7 | 1.5 | 1.55 | -0.55 | z' | -0.45 |
| $NO_2$_7 | 7.33 | 8.20 | 8.4 | 7.7 | 8.5 | 0.6 | 1.2 | 1.15 | 0.41 | z' | 0.23 |
| $NO_2$_8 | 115.17 | 113.40 | 113.6 | 113.4 | 113.2 | 2.0 | 3.9 | 3.30 | -0.48 | z' | -0.36 |
| $NO_2$_9 | 3.90 | 4.40 | 4.8 | 4.1 | 4.3 | 0.6 | 1.2 | 1.08 | 0.30 | z' | 0.18 |
| $NO_2$_10 | 135.07 | 131.13 | 131.2 | 131.1 | 131.1 | 2.3 | 4.5 | 3.70 | -1.06 | z | -0.79 |
| $O_3$_0 | -0.20 | -0.20 | -0.2 | | | 0.7 | 1.5 | 1.00 | 0.00 | z | 0.00 |
| $O_3$_1 | 64.67 | 64.63 | 64.3 | 64.7 | 64.9 | 1.3 | 2.6 | 2.29 | -0.02 | z | -0.01 |
| $O_3$_2 | 20.60 | 20.80 | 20.7 | 20.8 | 20.9 | 0.8 | 1.6 | 1.41 | 0.14 | z | 0.12 |
| $O_3$_3 | 32.17 | 32.40 | 32.3 | 32.4 | 32.5 | 0.9 | 1.8 | 1.64 | 0.14 | z | 0.12 |
| $O_3$_4 | 96.73 | 97.20 | 97.0 | 97.3 | 97.3 | 1.7 | 3.5 | 2.93 | 0.15 | z' | 0.12 |
| $O_3$_5 | 129.00 | 129.63 | 129.4 | 129.7 | 129.8 | 2.2 | 4.4 | 3.58 | 0.17 | z' | 0.13 |
| $SO_2$_0 | 0.10 | 0.00 | 0.0 | | | 0.6 | 1.2 | 1.00 | -0.09 | z' | -0.06 |
| $SO_2$_1 | 104.47 | 103.10 | 102.9 | 103.1 | 103.3 | 1.7 | 3.3 | 3.30 | -0.38 | z' | -0.32 |
| $SO_2$_2 | 39.43 | 38.90 | 38.9 | 38.9 | 38.9 | 0.8 | 1.7 | 1.87 | -0.27 | z' | -0.24 |
| $SO_2$_3 | 54.63 | 53.83 | 53.9 | 53.8 | 53.8 | 1.0 | 2.0 | 2.20 | -0.34 | z' | -0.30 |
| $SO_2$_4 | 12.93 | 12.67 | 12.5 | 12.7 | 12.8 | 0.6 | 1.2 | 1.28 | -0.19 | z' | -0.16 |
| $SO_2$_5 | 8.70 | 8.60 | 8.6 | 8.6 | 8.6 | 0.6 | 1.2 | 1.19 | -0.08 | z' | -0.06 |

Source: JRC 2023

## Annex C: Repeatability and reproducibility

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, in particular for CO, 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 seven laboratories, the actual number of laboratories (***p***) is listed in Table 16 according to the data reported.
Six concentration levels (for run 0 only one value is requested so repeatability cannot be evaluated) were tested for $O_3$, CO, $SO_2$ and $NO_2$, and eleven for NO. Performance tests for each participant are performed and results are reported in Annex B.
In ISO 5725 repeatability (r) and reproducibility (R) limits are defined. These limits are the values less than or equal to which the absolute difference between two test results, obtained under either repeatability or reproducibility conditions, may be expected to be with (1 - α) probability level.
The repeatability standard deviation (***$s_r$***) was calculated as the square root of average within-laboratory variance at the 95% confidence level. The repeatability limit (***r***) is calculated using Equation 7 [16].

$$r = t_{\nu/\alpha} \cdot \sqrt{2} \cdot Sr \qquad \text{Equation 7}$$

r = repeatability limit
$t_{\nu/\alpha}$ = *t* Student distribution value
$S_r$ = estimate of repeatability variance

The reproducibility standard deviation (*SR*) was calculated as the square root of sum of repeatability and between-laboratory variance at the 95% confidence level (α). The reproducibility limit (R) is calculated using Equation 8 [16].

$$R = t_{\nu/\alpha} \cdot \sqrt{2} \cdot SR \qquad \text{Equation 8}$$

R = reproducibility limit
$t_{\nu/\alpha}$ = *t* Student distribution value
SR = estimate of reproducibility variance

The repeatability standard deviation was evaluated with (p *(3-1)) degrees of freedom (ν) and reproducibility standard deviation with (p-1) degrees of freedom (ν).
The critical range Student factors, for r and R, corresponding to defined confidence level (α) and degree of freedom (ν) are reported in Table 16.

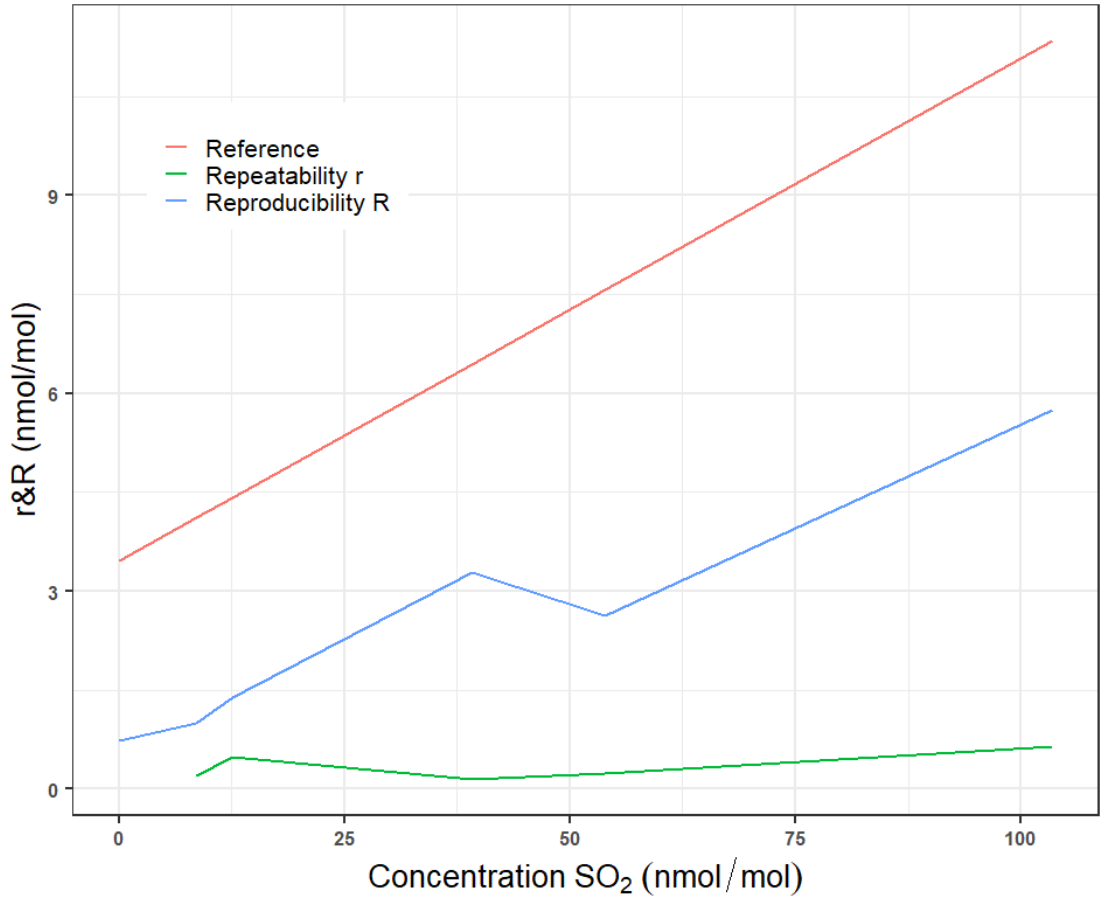
**Table 16**: Critical values of t used in the repeatability (r) and reproducibility (R) evaluation.

| parameter | run | p | t critical value 95% for r | t critical value 95% for R |
|---|---|---|---|---|
| CO | 1,2,3,4,5 | 5 | 2.228 | 2,776 |
| NO | 1,2,3,4,5,6,7,8,9,10 | 7 | 2.145 | 2,447 |
| $NO_2$ | 2,4,6,8,10 | 7 | 2.145 | 2,447 |
| $O_3$ | 1,2,3,4,5 | 7 | 2.145 | 2,447 |
| $SO_2$ | 1,2,3,4,5 | 7 | 2.145 | 2,447 |

Source: JRC 2023

The repeatability (r) and reproducibility (R) limits of measurement methods are presented from Figure 23 to Figure 27. It is reported also the 'reproducibility from common criteria (Reference)' calculated by substituting *SR* in Equation 8 with a 'standard deviation for proficiency assessment' (see Table 4). Comparison between R and Reference serves to indicate that $\sigma_{pt}$ is realistic [13] or from the other point of view, that the general methodology implemented by NRLs is appropriate for $\sigma_{pt}$.

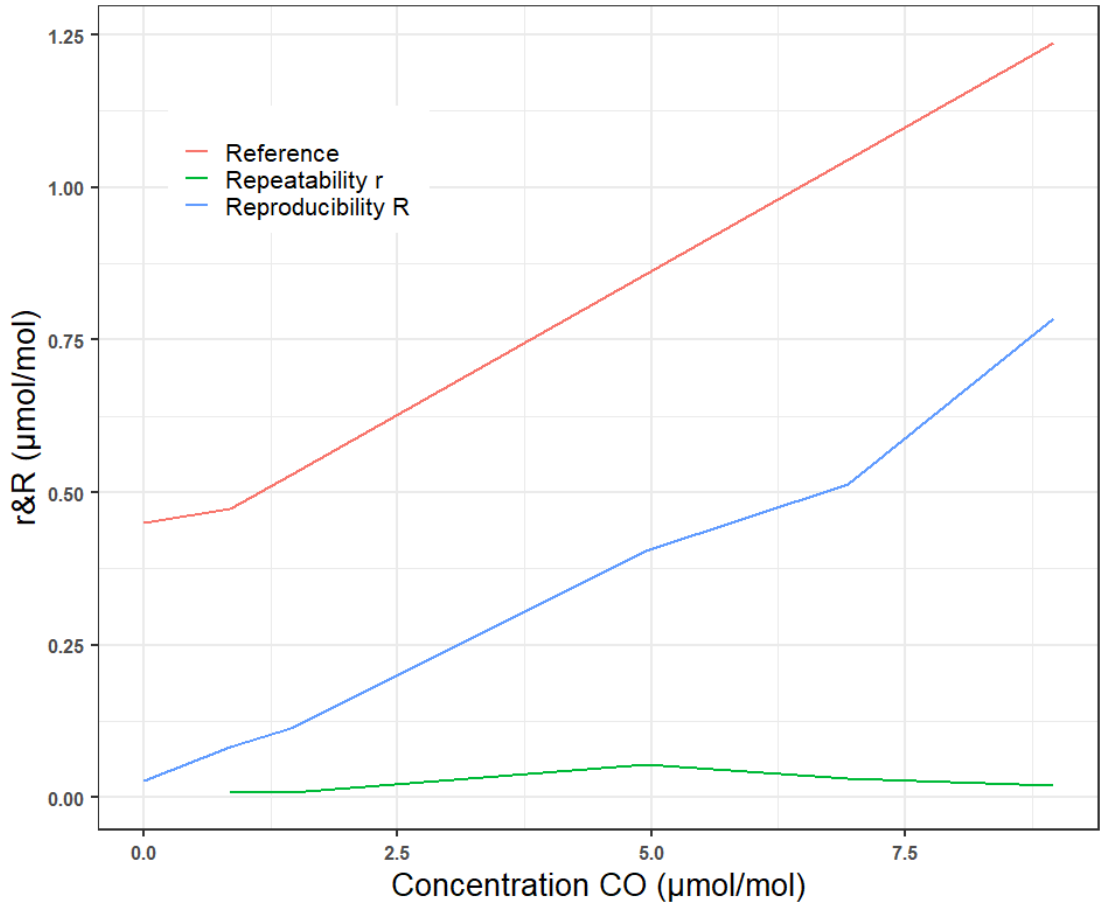
**Figure 23:** The R and r of $SO_2$ standard measurement method as a function of concentration.




| Parameter | Conc.(nmol/mol) | r(nmol/mol) | R(nmol/mol) | R (%) | Reference |
|---|---|---|---|---|---|
| $SO_2$ | 0.06 | | 0.73 | | 3.47 |
| $SO_2$ | 8.52 | 0.21 | 1.00 | | 4.11 |
| $SO_2$ | 12.61 | 0.49 | 1.38 | | 4.42 |
| $SO_2$ | 39.16 | 0.15 | 3.29 | | 6.44 |
| $SO_2$ | 53.93 | 0.24 | 2.63 | | 7.57 |
| $SO_2$ | 103.51 | 0.64 | 5.74 | 5.5 | 11.34 |

*Source: JRC 2023*

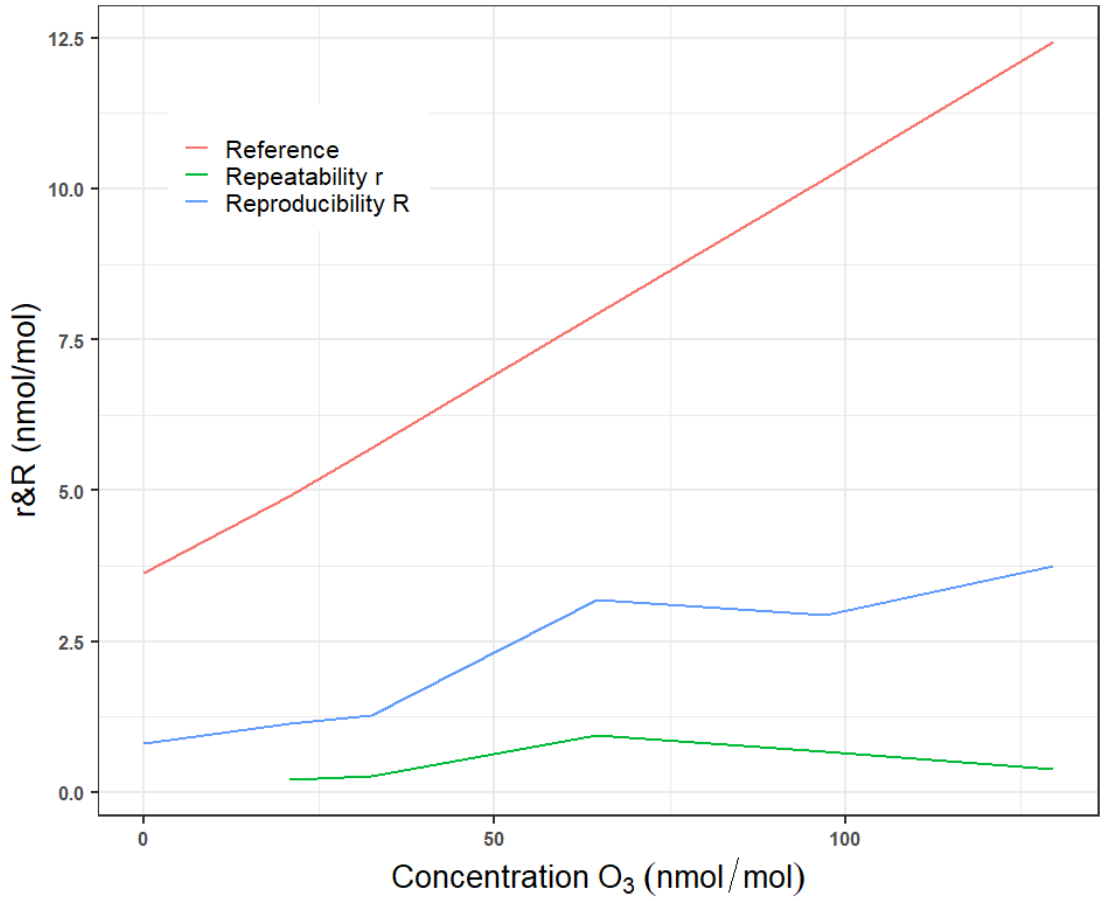
**Figure 24:** The R and r of CO standard measurement method as a function of concentration.




| Parameter | Conc.(µmol/mol) | r(µmol/mol) | R(µmol/mol) | R (%) | Reference |
|---|---|---|---|---|---|
| CO | 0.005 | | 0.027 | | 0.451 |
| CO | 0.857 | 0.009 | 0.082 | | 0.473 |
| CO | 1.449 | 0.009 | 0.114 | | 0.529 |
| CO | 4.944 | 0.054 | 0.404 | | 0.858 |
| CO | 6.932 | 0.032 | 0.514 | | 1.046 |
| CO | 8.961 | 0.019 | 0.785 | 8.8 | 1.237 |

*Source: JRC 2023*

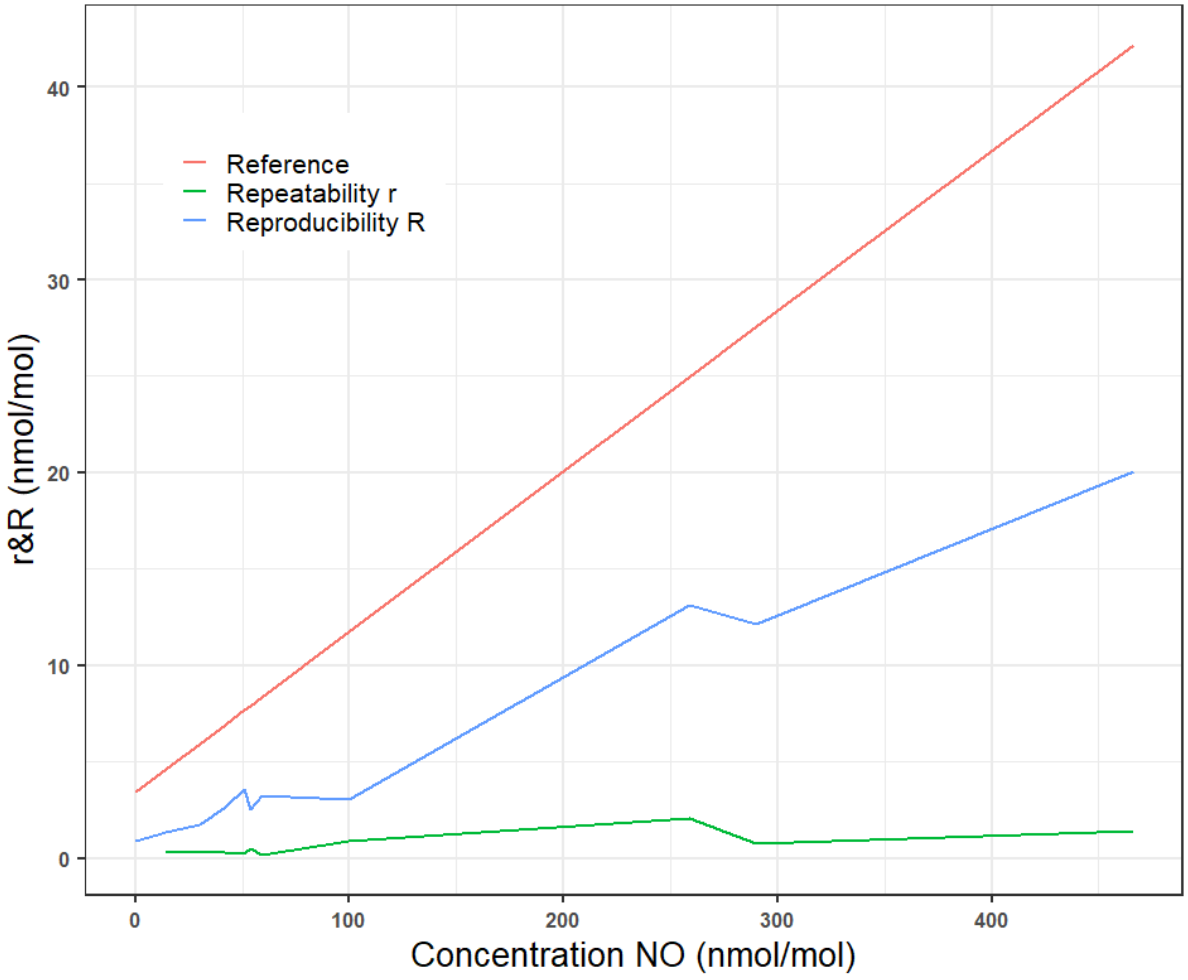
**Figure 25:** The R and r of $O_3$ standard measurement method as a function of concentration.




| Parameter | Conc.(nmol/mol) | r(nmol/mol) | R(nmol/mol) | R (%) | Reference |
|---|---|---|---|---|---|
| $O_3$ | 0.07 | | 0.80 | | 3.64 |
| $O_3$ | 20.88 | 0.21 | 1.14 | | 4.91 |
| $O_3$ | 32.49 | 0.27 | 1.28 | | 5.71 |
| $O_3$ | 64.50 | 0.94 | 3.18 | | 7.92 |
| $O_3$ | 97.12 | 0.67 | 2.94 | | 10.18 |
| $O_3$ | 129.62 | 0.39 | 3.74 | 2.9 | 12.43 |

*Source: JRC 2023*

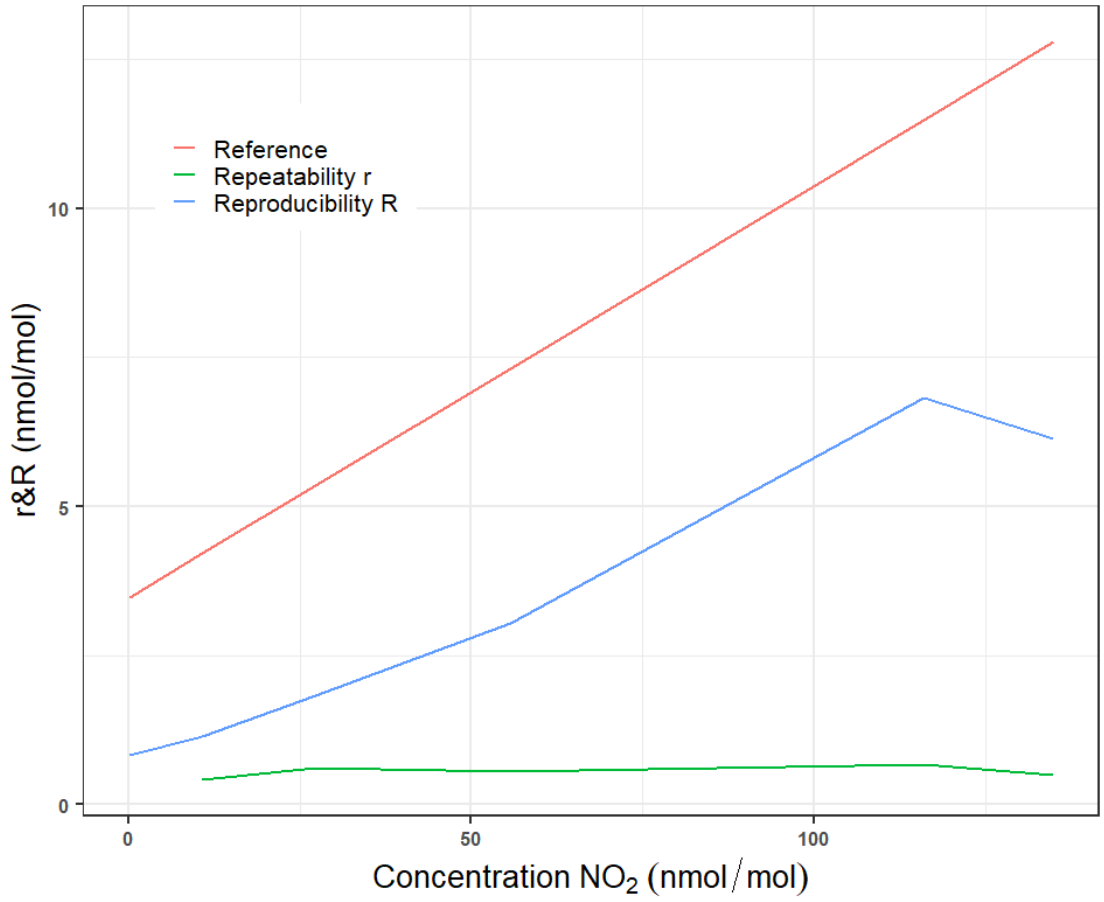
**Figure 26:** The R and r of NO standard measurement method as a function of concentration.




| Parameter | Conc.(nmol/mol) | r(nmol/mol) | R(nmol/mol) | R (%) | Reference |
|---|---|---|---|---|---|
| NO | 0.04 | | 0.90 | | 3.46 |
| NO | 14.38 | 0.3 | 1.35 | | 4.65 |
| NO | 30.01 | 0.3 | 1.73 | | 5.95 |
| NO | 41.83 | 0.33 | 2.70 | | 6.93 |
| NO | 51.09 | 0.24 | 3.60 | | 7.70 |
| NO | 53.87 | 0.49 | 2.56 | | 7.93 |
| NO | 59.12 | 0.21 | 3.29 | | 8.37 |
| NO | 99.51 | 0.91 | 3.08 | | 11.73 |
| NO | 258.94 | 2.09 | 13.15 | | 24.97 |
| NO | 290.21 | 0.79 | 12.18 | | 27.56 |
| NO | 466.10 | 1.43 | 20.04 | 4.3 | 42.17 |

*Source: JRC 2023*

**Figure 27:** The R and r of $NO_2$ standard measurement method as a function of concentration.




| Parameter | Conc.(nmol/mol) | r(nmol/mol) | R(nmol/mol) | R (%) | Reference |
|---|---|---|---|---|---|
| $NO_2$ | 0.17 | | 0.83 | | 3.47 |
| $NO_2$ | 10.84 | 0.42 | 1.14 | | 4.21 |
| $NO_2$ | 27.31 | 0.61 | 1.83 | | 5.35 |
| $NO_2$ | 55.78 | 0.55 | 3.05 | | 7.32 |
| $NO_2$ | 116.04 | 0.67 | 6.82 | | 11.49 |
| $NO_2$ | 134.81 | 0.49 | 6.13 | 4.5 | 12.79 |

*Source: JRC 2023*

## 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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L'ENTE ITALIANO DI ACCREDITAMENTO
Membro degli Accordi di Mutuo Riconoscimento EA, IAF e ILAC
Signatory of EA, IAF and ILAC Mutual Recognition Agreements

ilac-MRA

DL0018P/003

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EMESSO DA / *ISSUED BY* **DIPARTIMENTO LABORATORI DI PROVA**

SI DICHIARA CHE / *WE DECLARE THAT*

**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

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

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

QUALE / *AS*: **Organizzatori di prove valutative interlaboratorio**

***Proficiency Testing Provider***

MD-CA-01 rev. 06

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

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DL1362L/003

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**European Reference Laboratory for Air Pollution (ERLAP) Air and Climate Unit Directorate C.Energy, Transport and Climate Joint Research Centre -European Commission**

Sede/Headquarters:
- Via E. Fermi 2749 - 21027 Ispra VA

È CONFORME AI REQUISITI DELLA NORMA: UNI CEI EN ISO/IEC 17025:2018

*MEETS THE REQUIREMENTS OF THE STANDARD:* *ISO/IEC 17025:2017*

QUALE / *AS*: **Laboratorio di Prova** / ***Testing Laboratory***

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