



**EffecTech**

Global Leaders in Gas Measurement



## Stack Emissions Proficiency Testing Scheme (SEPTS)

### Presentation of Results

#### Round 2025

EffecTech is accredited by the United Kingdom Accreditation Service (UKAS) to provide this Proficiency Testing Scheme in accordance with the requirements of ISO/IEC 17043 : 2010

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## Revisions History

| Issue | Date         | Author(s)   | Comments                                 |
|-------|--------------|-------------|--|
| 1     | 29 July 2025 | Joey Walker | <b><i>Draft report (for comment)</i></b> |

## Statement of Confidentiality

EffectTech keeps all data regarding the performance of individual participants strictly confidential. Results and performance data are protected, stored and backed up on storage network disks and folders to which access is restricted to the scheme coordinator and the technical authority only.

The relationship between results and the laboratories that submitted them will never be disclosed. The laboratory alone is granted access to its performance through the assigned participant code and through issue of a confidential Certificate of Participation.

Checked by



Steve Price  
**Scheme Coordinator**

Approved by



Joey Walker  
**Technical Authority**

## 1. Introduction

EffecTech provides and organises the Stack Emissions Proficiency Testing Scheme (SEPTS). This report presents data on the reference mixtures in cylinders and the results of the participants for Round 2025 (June - July 2025).

The SEPTS scheme provides an objective way of assessing the performance of each participant by a series of annual inter-laboratory comparisons. The scheme is aimed at laboratories/testing organisations working in the field of continuous emissions monitoring (CEM) of stationary sources often in waste incineration or large combustion plant processes.

In this round participants were given the opportunity of analysing up to eight (8) different measurands in seven (7) gas mixtures. The composition range of each measurand in each mixture is shown in the tables below.

**Table 1: Composition range by gas mixture type**

| measurand  | range                                    |
|--|--|
| sulphur dioxide (SO <sub>2</sub> )<br>in nitrogen                          | 10 to 200 µmol/mol                       |
| propane (C <sub>3</sub> H <sub>8</sub> )<br>in 10% oxygen / nitrogen       | 5 to 50 µmol/mol                         |
| nitric oxide (NO)<br>in nitrogen   | 10 to 500 µmol/mol                       |
| carbon monoxide (CO)<br>in nitrogen  | 20 to 500 µmol/mol                       |
| oxygen (O <sub>2</sub> )<br>in nitrogen                                    | 2 to 14 %mol/mol                         |
| carbon dioxide (CO <sub>2</sub> )<br>in nitrogen                           | 1 to 10 %mol/mol                         |
| nitric oxide (NO) and<br>nitrogen oxides (NO <sub>x</sub> )<br>in nitrogen | 20 to 400 µmol/mol<br>25 to 500 µmol/mol |

Note: all units used in this report are in the SI unit of amount of substance fraction (mol/mol) or in metric prefixes thereof.  
500 µmol/mol is equivalent to  $500 \times 10^{-6}$  mol/mol  
10 %mol/mol is equivalent to 10 dmol/mol is equivalent to  $10 \times 10^{-2}$  mol/mol

Gas mixture preparation, reference value assignment and the assessment of participants' results are all carried out by designated operators and approved signatories within EffecTech and in accordance with our ISO/IEC 17043 accredited processes.

In addition, all logistics management and preparation of shipping documentation is also carried out by designated approved personnel within EffecTech. All shipping, freight forwarding and proficiency testing item distribution is supplied by specialist transport providers.

A total of twenty-seven (27) laboratories signed up to participate in this round. Twenty-seven (27) laboratories to whom items were distributed, submitted results for one or more of the measurands assessed in the scheme.

## 2. Mixture preparation and reference value assignment

### 2.1 Procedure

#### Preparation of mixture batches

For each mixture type, a single large volume parent mixture was prepared by a gravimetric method in accordance with ISO 6142-1. A batch of mixtures of each type was then produced by decanting the parent mixture into a batch of lower volume pre-prepared and evacuated daughter cylinders. The parent mixture and daughter mixtures were then calibrated.

#### Mixture calibration

All parent mixtures were calibrated using a two-point calibration design with bracketing (TPC), with the exception of the carbon dioxide measurand which was calibrated using a single-point through origin calibration (SPO). Both of these calibration methods are in accordance with ISO 12963 for which EffecTech is accredited to ISO/IEC 17025 and ISO 17034 by UKAS.

Every single decant mixture was calibrated by a single point exact matching technique (SPEM) also in accordance with ISO 12963 by the comparison of the decant mixture with its nominally identical parent mixture. A selective batch calibration technique was not used. All mixtures despatched to participants were calibrated individually to provide ultimate assurance in the assigned reference values.

The uncertainty on amount fraction of each measurand in the mixtures resulting from this calibration is termed the characterisation uncertainty,  $u_{\text{char}}$  (ISO 33405).

All calibrations are performed in accordance with EffecTech's ISO/IEC 17025 accredited calibration methods (in-house methods TM014, TM025 or TM026). These can be found in our scope of accreditation published on the United Kingdom Accreditation Service (UKAS) website ([www.ukas.com](http://www.ukas.com)).

#### Reference mixture traceability

An analytical comparison method is used for the calibration of all mixtures in this scheme. In-house primary reference gas mixtures (PRGM) are used for calibration which are traceable by verification to the National Physical Laboratory (NPL, UK) or to the Van Swinden Laboratorium (VSL, NL). Parent mixtures are calibrated either by direct comparison with PRGMs (SPO) or, where diluted, with reference gas mixtures generated dynamically in accordance with ISO 6145-7 (TPC). This process ensured that the values assigned to the mixtures in this scheme are metrologically traceable to international standards, through an unbroken chain of comparisons, and ultimately to the amount of substance (mole) defined in the SI (International System of Units).

#### Homogeneity assessment

Statistical analysis of the spread of reference values obtained for each batch of mixtures (derived through calibration above) is used to assess the homogeneity between the set of decant mixtures to be distributed to each participant. The dispersion of the amount fraction of each component due to batch inhomogeneity is known as the between-bottle standard deviation ( $s_{\text{bb}}$ ). The uncertainty arising from this is the between-bottle uncertainty ( $u_{\text{bb}}$ ). The statistical procedure used for the determination of  $u_{\text{bb}}=s_{\text{bb}}$  can be found in ISO 33405.

The uncertainty associated with within-bottle heterogeneity  $u_{wb}$  is assumed to be zero; EffectTech has conducted numerous measurements and intercomparisons that demonstrate that for well mixed gas mixtures, samples used for analysis are homogenous with the gas mixture within the cylinder. Hence the standard uncertainty associated with heterogeneity  $u_{hom} = u_{bb}$ . This uncertainty should be less than or equal to the characterisation uncertainty,  $u_{char}$ , in order to accept the batch. This condition was met for all components in all mixtures produced for all participants in this round.

### Reference value assignment

For all measurands, each component was assigned a reference value,  $x_{ref}$ , calculated from the average (simple arithmetic mean) of those determined in the calibration stage (see section above).

The initial combined uncertainty determined for each reference value was calculated from the equation below (ISO 33405 – section 10.2).

$$u_c^2 = u_{char}^2 + u_{hom}^2$$

This combined uncertainty,  $u_c$ , is dominated in all cases by the calibration uncertainty,  $u_{char}$

Following this calculation, the expanded uncertainty,  $k \cdot u_c$ , ( $k=2$ ), was compared to the Calibration and Measurement Capability (CMC) for which EffectTech is accredited to ISO/IEC 17025. If  $U_{CMC}$  ( $k=2$ ) was greater than  $k \cdot u_c$  ( $k=2$ ) then the uncertainty on the reference value was assigned to that stated in our published CMC in accordance with accepted practice such that

$$U_{ref} = \max (U_{CMC}, 2u_c)$$

The use of a coverage factor of  $k=2$  in the assignment of  $U_{ref}$  provides a level of confidence of approximately 95%.

The individual calibration data for each suite of decant mixtures is not shown in this report. However, this data is available to all participants on request from EffectTech.

### Stability statement

Over several years EffectTech has built up a history of intercomparisons of mixture types featured in this PT scheme. Data from these intercomparisons show clearly that all mixtures remain stable within their stated uncertainty for a minimum of 12 months.

Hence, the stability of each mixture is guaranteed for a period of 12 months. Within this time period there is no additional uncertainty ascribed to the reference values resulting from the long or short term stability of the mixtures. This is valid providing the mixtures are not used beyond this stability period.

The majority of these mixtures will be stable (within their stated uncertainty) for considerably longer but this period has not been determined.

## 2.2 Assigned reference values

The table below show the reference values assigned to the measurands in the mixtures in cylinders distributed to participants of this scheme.

**Table 2: Reference values assigned following batch homogeneity assessment**

| measurand                                   | units               | $x_{\text{ref}}$ | $U(x_{\text{ref}})$ | $u_c / \%$ | $u_{\text{char}} / \%$ | $u_{\text{bb}} / \%$ |
|---|---------------------|------------------|---------------------|------------|------------------------|----------------------|
| sulphur dioxide                             | $\mu\text{mol/mol}$ | 115.6            | 1.2                 | 0.51       | 0.50                   | 0.10                 |
| propane                                     | $\mu\text{mol/mol}$ | 27.14            | 0.26                | 0.35       | 0.34                   | 0.082                |
| nitric oxide                                | $\mu\text{mol/mol}$ | 82.45            | 0.46                | 0.23       | 0.22                   | 0.049                |
| carbon monoxide                             | $\mu\text{mol/mol}$ | 235.8            | 1.9                 | 0.35       | 0.35                   | 0.035                |
| oxygen                                      | $\%\text{mol/mol}$  | 6.827            | 0.037               | 0.056      | 0.056                  | 0.0030               |
| carbon dioxide                              | $\%\text{mol/mol}$  | 6.164            | 0.025               | 0.21       | 0.20                   | 0.048                |
| nitric oxide<br>(NO/NO <sub>2</sub> mix)    | $\mu\text{mol/mol}$ | 86.57            | 0.48                | 0.23       | 0.22                   | 0.053                |
| nitrogen oxides<br>(NO/NO <sub>2</sub> mix) | $\mu\text{mol/mol}$ | 97.77            | 0.69                | 0.36       | 0.34                   | 0.11                 |

## 3. Results

### 3.1 Reported results

There were twenty-seven (27) laboratories/organisations signed up for participation in this round of the scheme. Consignments containing up to seven (7) different mixture types were shipped to those participating.

The tables below show participation and whether results were submitted for the mixtures shipped.

**Table 3: Participant laboratories and reported results**

| Participant id | sulphur dioxide |         | propane       |         | nitric oxide  |         | carbon monoxide |         |
|----------------|-----------------|---------|---------------|---------|---------------|---------|-----------------|---------|
|                | participation   | results | participation | results | participation | results | participation   | results |
| P01            | ✓               | ✓       | ✓             | ✓       |               |         | ✓               | ✓       |
| P02            |                 |         |               |         |               |         |                 |         |
| P03            |                 |         |               |         |               |         | ✓               | ✓       |
| P04            |                 |         |               |         |               |         |                 |         |
| P05            |                 |         |               |         | ✓             | ✓       |                 |         |
| P06            | ✓               | ✓       | ✓             | ✓       |               |         | ✓               | ✓       |
| P07            | ✓               | ✓       | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P08            | ✓               | ✓       | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P09            | ✓               | ✓       | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P10            |                 |         |               |         |               |         | ✓               | ✗       |
| P11            | ✓               | ✓       | ✓             | ✓       |               |         | ✓               | ✓       |
| P12            | ✓               | ✓       | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P13            |                 |         | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P14            |                 |         | ✓             | ✓       | ✓             | ✓       |                 |         |
| P15            | ✓               | ✓       | ✓             | ✓       |               |         | ✓               | ✓       |
| P16            |                 |         | ✓             | ✓       |               |         |                 |         |
| P17            | ✓               | ✓       | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P18            | ✓               | ✓       | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P19            |                 |         |               |         |               |         |                 |         |
| P20            |                 |         |               |         |               |         |                 |         |
| P21            | ✓               | ✓       | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P22            | ✓               | ✓       | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P23            | ✓               | ✓       | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P24            | ✓               | ✓       | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P25            | ✓               | ✓       |               |         | ✓             | ✓       | ✓               | ✓       |
| P26            | ✓               | ✓       | ✓             | ✓       | ✓             | ✓       | ✓               | ✓       |
| P27            | ✓               | ✓       | ✓             | ✓       |               |         | ✓               | ✓       |

| Participant id | oxygen        |         | carbon dioxide |         | nitric oxide<br>(NO/NO2 mix) |         | nitrogen oxides<br>(NO/NO2 mix) |         |
|----------------|---------------|---------|----------------|---------|------------------------------|---------|---------------------------------|---------|
|                | participation | results | participation  | results | participation                | results | participation                   | results |
| P01            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P02            |               |         |                |         | ✓                            | ✓       | ✓                               | ✓       |
| P03            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P04            | ✓             | ✓       | ✓              | ✓       |                              |         |                                 |         |
| P05            | ✓             | ✓       | ✓              | ✓       |                              |         |                                 |         |
| P06            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P07            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P08            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P09            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P10            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✗       | ✓                               | ✗       |
| P11            | ✓             | ✓       |                |         | ✓                            | ✓       | ✓                               | ✓       |
| P12            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P13            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P14            | ✓             | ✓       |                |         |                              |         |                                 |         |
| P15            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P16            |               |         |                |         |                              |         |                                 |         |
| P17            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P18            | ✓             | ✓       |                |         |                              |         |                                 |         |
| P19            | ✓             | ✓       | ✓              | ✓       |                              |         |                                 |         |
| P20            | ✓             | ✓       | ✓              | ✗       |                              |         |                                 |         |
| P21            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P22            | ✓             | ✓       | ✓              | ✓       |                              |         |                                 |         |
| P23            | ✓             | ✗       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P24            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P25            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P26            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |
| P27            | ✓             | ✓       | ✓              | ✓       | ✓                            | ✓       | ✓                               | ✓       |

To enable the calculation of  $E_n$  numbers, the laboratory is required to submit an estimate of the uncertainty placed on their measured amount fractions. The majority of participants submitted estimates of measurement uncertainty on the measurands for which they reported a value.

## 3.2 Measures of performance

### z-score

The evaluation of performance was carried out by means of a **z**-score, which gives the relative deviation of the participant's result from the reference value.

The **z**-score is calculated with the following general formula

$$\mathbf{z} = \frac{x_{meas} - x_{ref}}{\sigma} \quad (1)$$

where  $x_{meas}$  is the measured result reported by the laboratory

$x_{ref}$  is the assigned reference value and

$\sigma$  is the absolute standard deviation used for performance assessment (SDPA) which can be calculated from the contributions  $S_{PT,rel}$  and  $S_{PT,abs}$  by

$$\sigma = \frac{S_{PT,rel}}{100} \cdot x_{ref} + S_{PT,abs} \quad (2)$$

If there is concern that the estimation of the **z**-score may be biased due to the magnitude of the uncertainty of the assigned reference value in the case when  $u_{ref} > 0.3\sigma$  then the use of a modified **z'**-score shall be used to evaluation performance for that component failing this condition.

The **z'**-score is calculated with the following general formula.

$$\mathbf{z}' = \frac{x_{meas} - x_{ref}}{\sqrt{\sigma^2 + u_{ref}^2}} \quad (3)$$

The standard deviation for performance assessment used for calculating the **z**-scores has been fixed for all components by EffecTech and based upon a reasonable expectation of the performance capabilities that should be demonstrated by each laboratory for the direct measurement of a gas mixture in a cylinder.

These are given in the tables below.

**Table 4: Standard deviation for performance assessment**

| measurand                       | $S_{PT,rel}$   | $S_{PT,abs}$  |
|---------------------------------|----------------|---------------|
| sulphur dioxide                 | 2.5 % relative |               |
| propane                         | 5.0 % relative |               |
| nitric oxide                    | 2.5 % relative |               |
| carbon monoxide                 | 1.5 % relative |               |
| oxygen                          | 1.0 % relative | 0.01 %mol/mol |
| carbon dioxide                  | 1.0 % relative | 0.01 %mol/mol |
| nitric oxide<br>(NO/NO2 mix)    | 2.5 % relative |               |
| nitrogen oxides<br>(NO/NO2 mix) | 2.5 % relative |               |

The qualification of the z-scores is given in table 5 below

**Table 5: Relationship between z-score and quality of result**

| z-score       | quality of result     |
|---------------|-----------------------|
| $ z  \leq 2$  | satisfactory result   |
| $2 <  z  < 3$ | questionable result   |
| $ z  \geq 3$  | unsatisfactory result |

### **$E_n$ number**

In addition, an  $E_n$  number is calculated which assesses the difference in the reference and measured (reported) values relative to their respective uncertainties. The calculation of  $E_n$  numbers is dependent upon the laboratory estimates of uncertainties associated with their measurement results.

The  $E_n$  number is calculated with the following general formula

$$E_n = \frac{x_{meas} - x_{ref}}{\sqrt{U_{meas}^2 + U_{ref}^2}} \quad (4)$$

where  $x_{meas}$  is the measured result reported by the laboratory

$x_{ref}$  the assigned reference value and

$U_{meas}$  and  $U_{ref}$  their respective uncertainties (using a coverage factor  $k=2$ )

The qualification of the  $E_n$  number is given in table 6 below

**Table 6: Relationship between  $E_n$ -number and quality of result**

| $E_n$ number   | quality of result     |
|----------------|-----------------------|
| $ E_n  \leq 1$ | satisfactory result   |
| $ E_n  > 1$    | unsatisfactory result |

Evaluation of the performance of a laboratory based on  $E_n$  numbers requires a reported estimate of their measurement uncertainty,  $U_{meas}$ . In addition, it is important that the reported uncertainties are in the same order of magnitude as the uncertainties on the reference values. Due to the nature of the formula used to calculate the  $E_n$  number, high reported uncertainties are much more likely to result in very low  $E_n$  numbers.

### 3.3 Evaluation of results

The results of the evaluation of z-scores based upon the expectation SDPA are shown in the table below.

**Table 7 - Summary of z-scores**

| <i>z-scores</i> |                 |         |              |                 |        |                |                                       |  |
|-----------------|-----------------|---------|--------------|-----------------|--------|----------------|---------------------------------------|--|
| participant id  | sulphur dioxide | propane | nitric oxide | carbon monoxide | oxygen | carbon dioxide | nitric oxide (NO/NO <sub>2</sub> mix) | nitrogen oxides (NO/NO <sub>2</sub> mix) |
| P01             | 0.26            | -0.03   |              | 0.85            | 0.29   | -0.38          | 0.42                                  | -0.74                                    |
| P02             |                 |         |              |                 |        |                | -4.49                                 | -8.37                                    |
| P03             |                 |         |              | 0.19            | 0.11   | 1.11           | 0.05                                  | -0.05                                    |
| P04             |                 |         |              |                 | -0.15  | 1.41           |                                       |  |
| P05             |                 |         | 0.54         |                 | -0.06  | -1.49          |                                       |  |
| P06             | 1.13            | 0.14    |              | 1.25            | 0.71   | -0.04          | -0.18                                 | -1.17                                    |
| P07             | 0.51            | -0.15   | 0.06         | 0.77            | 0.06   | 0.05           | -0.01                                 | -0.64                                    |
| P08             | 0.27            | -0.54   | -0.74        | 0.10            | -0.13  | -0.31          | -1.18                                 | -1.91                                    |
| P09             | -0.55           | -0.52   | -0.64        | 0.49            | -0.23  | 0.15           | -0.77                                 | -1.55                                    |
| P10             |                 |         |              |                 | -0.09  | 1.06           |                                       |  |
| P11             | -0.31           | -1.13   |              | -2.25           | -7.28  |                | 0.67                                  | 0.46                                     |
| P12             | 0.17            | -0.92   | 0.16         | 2.30            | 0.83   | -2.30          | -0.52                                 | -1.72                                    |
| P13             |                 | -2.45   | 0.37         | 0.03            | 0.74   | -0.32          | -1.80                                 | 1.49                                     |
| P14             |                 | 0.24    | 0.42         |                 | -0.73  |                |                                       |  |
| P15             | -1.89           | -1.74   |              | 0.13            | 2.85   | -0.05          | -1.89                                 | -2.97                                    |
| P16             |                 | 0.10    |              |                 |        |                |                                       |  |
| P17             | -0.01           | -0.23   | 0.32         | -0.45           | 0.93   | 4.69           | 0.85                                  | 1.04                                     |
| P18             | -0.22           | -0.40   | -0.25        | 0.17            | -0.11  |                |                                       |  |
| P19             |                 |         |              |                 | 0.70   | 0.90           |                                       |  |
| P20             |                 |         |              |                 | -0.15  |                |                                       |  |
| P21             | -0.41           | 0.15    | 1.09         | -0.79           | 0.98   | -2.32          | 0.98                                  | 0.21                                     |
| P22             | 0.72            | -0.48   | 0.53         | -0.17           | 0.11   | 0.29           |                                       |  |
| P23             | -0.12           | -0.46   | 0.87         | -0.14           |        | -1.09          | 0.90                                  | 0.68                                     |
| P24             | 0.47            | -1.28   | -0.58        | -0.05           | 0.31   | 1.61           | -2.57                                 | -2.39                                    |
| P25             | 2.21            |         | -6.04        | 0.93            | 0.42   | -2.01          | -6.09                                 | -5.80                                    |
| P26             | -0.50           | 0.00    | 1.14         | -0.94           | 0.65   | -2.21          | 1.04                                  | 0.42                                     |
| P27             | -0.28           | 0.28    |              | 1.33            | -0.01  | 0.10           | -1.28                                 | -1.78                                    |

These results show a generally good performance from the pool of participants.

However, participants **P02**, **P24** and **P25** reported anomalously low measurements for the nitric oxide/nitrogen oxides PT item. Participant **P11** reported low on oxygen, while **P17** reported high for carbon dioxide.

Seventeen (17) laboratories (**P01**, **P03**, **P04**, **P05**, **P06**, **P07**, **P08**, **P09**, **P10**, **P14**, **P16**, **P18**, **P19**, **P20**, **P22**, **P23** and **P27**) achieved satisfactory results for all measurands for which they reported a result.

Performance based upon the  $E_n$ -numbers are given in the table below.

**Table 8 - Summary of  $E_n$ -numbers**

| <i><math>E_n</math>-numbers</i> |                 |         |              |                 |        |                |                                       |  |
|---------------------------------|-----------------|---------|--------------|-----------------|--------|----------------|---------------------------------------|--|
| participant id                  | sulphur dioxide | propane | nitric oxide | carbon monoxide | oxygen | carbon dioxide | nitric oxide (NO/NO <sub>2</sub> mix) | nitrogen oxides (NO/NO <sub>2</sub> mix) |
| P01                             | 0.47            | -0.05   |              | 1.12            | 0.15   | -0.10          | 1.39                                  | -2.17                                    |
| P02                             |                 |         |              |                 |        |                | -6.03                                 | -12.07                                   |
| P03                             |                 |         |              | 0.03            | 0.01   | 0.13           | 0.01                                  | -0.01                                    |
| P04                             |                 |         |              |                 | -0.09  | 0.37           |                                       |  |
| P05                             |                 |         | 0.41         |                 | -0.12  | -3.81          |                                       |  |
| P06                             | 2.21            | 0.21    |              | 1.29            | 1.38   | -0.11          | -0.24                                 | -1.54                                    |
| P07                             | 0.20            | -0.09   | 0.02         | 0.25            | 0.02   | 0.01           | 0.00                                  | -0.20                                    |
| P08                             | 0.11            | -0.44   | -0.24        | 0.02            | -0.03  | -0.04          | -0.40                                 |  |
| P09                             | -0.50           | -0.30   | -0.47        | 0.41            | -0.43  | 0.38           | -0.47                                 | -0.98                                    |
| P10                             |                 |         |              |                 | -0.01  | 0.15           |                                       |  |
| P11                             | -0.13           | -1.18   |              | -0.70           | -7.29  |                | 0.43                                  | 0.27                                     |
| P12                             | 0.06            | -0.87   | 0.14         | 1.11            | 0.36   | -1.04          | -0.45                                 | -1.26                                    |
| P13                             |                 | -8.99   | 0.58         | 0.02            | 0.74   | -0.38          | -2.93                                 | 1.39                                     |
| P14                             |                 | 0.87    | 0.90         |                 | -0.74  |                |                                       |  |
| P15                             | -2.92           | -2.56   |              | 0.19            | 0.87   | -0.01          | -1.63                                 | -2.60                                    |
| P16                             |                 | 0.04    |              |                 |        |                |                                       |  |
| P17                             | 0.00            | -0.11   | 0.16         | -0.13           | 0.21   | 1.20           | 0.42                                  | 0.51                                     |
| P18                             | -0.09           | -0.83   | -0.15        | 0.05            | -0.07  |                |                                       |  |
| P19                             |                 |         |              |                 | 0.53   | 0.88           |                                       |  |
| P20                             |                 |         |              |                 | -0.06  |                |                                       |  |
| P21                             | -0.16           | 0.08    | 0.50         | -0.20           | 0.49   | -0.80          | 0.46                                  | 0.08                                     |
| P22                             | 0.37            | -0.56   | 0.37         | -0.14           | 0.04   | 0.09           |                                       |  |
| P23                             | -0.06           | -0.26   | 0.49         | -0.04           |        | -0.23          | 0.51                                  | 0.38                                     |
| P24                             | 0.18            | -0.68   | -0.28        | -0.01           | 0.15   | 0.53           | -1.30                                 | -0.96                                    |
| P25                             | 0.31            |         | -1.71        | 0.11            |        |                | -1.72                                 |  |
| P26                             | -0.20           | 0.00    | 0.52         | -0.25           | 0.32   | -0.76          | 0.50                                  | 0.16                                     |
| P27                             | -0.42           | 0.42    |              | 0.56            | 0.00   | 0.03           | -0.38                                 | -0.53                                    |

For the laboratories submitting estimates of uncertainty for their measurements, the corresponding  $E_n$ -numbers show fewer satisfactory result to those for z-scores.

For participants reporting unsatisfactory results, this suggests the presence of an undetected measurement bias or an underestimation of their reported uncertainties.

Excellent performances were received from participants **P03, P07, P08, P09, P18, P22, P23** and **P27**, each of whom submitted results for 4 or more measurands achieving 100% perfect score on the basis of both performance measures.

The outstanding laboratories in this round of the PT scheme were participants **P07** and **P09** with a 100% perfect score on the basis of both performance measures for all **eight** measurands.

## Annex A - Detailed results by measurand

Detailed results for all measurands in all mixtures are shown in subsequent charts.

In each chart, the reported results are shown with the dots in terms of a relative difference (in percent) from the assigned reference value. The reported uncertainties (where supplied) are shown as “error bars” on the reported values.

In each chart the bound limit lines surrounding the zero relative difference signify

- the percentage relative uncertainty on the reference value,  $\%U(x_{\text{ref}})$   $k=2$  (in blue)
- the  $|z|=2$  satisfactory limit (in green)
- the  $|z|=3$  unsatisfactory limit (in red)

This annex also includes additional statistics presenting consensus values from the pool of laboratories on the basis of raw data and correct data (following the removal of outlying reported values).

Additional tables also show repeatability standard deviation ( $s_r$ ), between laboratory standard deviation ( $s_L$ ) and reproducibility standard deviation ( $s_R$ ) on the basis of raw and corrected data. The data has been calculated in accordance with the robust statistical methods in ISO 5725 Parts 1 and 2. The detailed calculations made to derive these results are outside the scope of this report but will be provided to participants on request from the scheme coordinator.

Measurand/  
Mixture

sulphur dioxide

Reference

| $x_{\text{ref}}$ | $U(x_{\text{ref}}) \ k=2$ | $\sigma$ |
|------------------|---------------------------|----------|
| 115.6            | 1.2                       | 2.9      |

μmol/mol

μmol/mol

Reported data

| id  | value<br>(μmol/mol) | U (k=2)<br>(μmol/mol) | relative<br>difference | z-score | $E_n$ -number |
|-----|---------------------|-----------------------|------------------------|---------|---------------|
| P01 | 116.4               | 1.0                   | 0.65%                  | 0.26    | 0.47          |
| P02 |                     |                       |                        |         |               |
| P03 |                     |                       |                        |         |               |
| P04 |                     |                       |                        |         |               |
| P05 |                     |                       |                        |         |               |
| P06 | 118.9               | 0.9                   | 2.83%                  | 1.13    | 2.21          |
| P07 | 117.1               | 7.3                   | 1.28%                  | 0.51    | 0.20          |
| P08 | 116.4               | 6.8                   | 0.67%                  | 0.27    | 0.11          |
| P09 | 114.0               | 3.0                   | -1.37%                 | -0.55   | -0.50         |
| P10 |                     |                       |                        |         |               |
| P11 | 114.7               | 6.8                   | -0.78%                 | -0.31   | -0.13         |
| P12 | 116.1               | 7.8                   | 0.42%                  | 0.17    | 0.06          |
| P13 |                     |                       |                        |         |               |
| P14 |                     |                       |                        |         |               |
| P15 | 110.1               | 1.4                   | -4.72%                 | -1.89   | -2.92         |
| P16 |                     |                       |                        |         |               |
| P17 | 115.6               | 6.2                   | -0.01%                 | -0.01   | 0.00          |
| P18 | 115.0               | 7.0                   | -0.56%                 | -0.22   | -0.09         |
| P19 |                     |                       |                        |         |               |
| P20 |                     |                       |                        |         |               |
| P21 | 114.4               | 7.3                   | -1.04%                 | -0.41   | -0.16         |
| P22 | 117.7               | 5.4                   | 1.79%                  | 0.72    | 0.37          |
| P23 | 115.3               | 5.8                   | -0.30%                 | -0.12   | -0.06         |
| P24 | 117.0               | 7.5                   | 1.19%                  | 0.47    | 0.18          |
| P25 | 122.0               | 20.7                  | 5.54%                  | 2.21    | 0.31          |
| P26 | 114.2               | 7.3                   | -1.25%                 | -0.50   | -0.20         |
| P27 | 114.8               | 1.5                   | -0.70%                 | -0.28   | -0.42         |

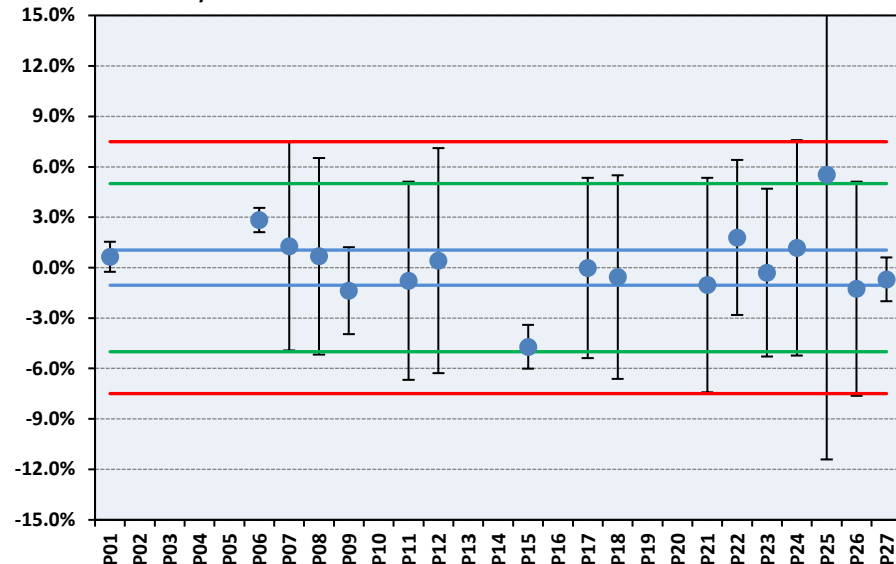
### Consensus values (raw data)

|       |       |       |
|-------|-------|-------|
| $m$   | 115.5 |       |
| $s_r$ | 0.3   | 0.26% |
| $s_L$ | 2.0   | 1.76% |
| $s_R$ | 2.1   | 1.78% |
| $p$   | 17    |       |

### Consensus values (corrected)

|       |       |       |
|-------|-------|-------|
| $m$   | 115.8 |       |
| $s_r$ | 0.3   | 0.27% |
| $s_L$ | 1.4   | 1.22% |
| $s_R$ | 1.4   | 1.25% |
| $p$   | 15    |       |

relative difference / %



Measurand/  
Mixture

propane

Reference

| $x_{\text{ref}}$ | $U(x_{\text{ref}}) \ k=2$ | $\sigma$ |
|------------------|---------------------------|----------|
| 27.14            | 0.26                      | 1.36     |

μmol/mol

μmol/mol

Reported data

| id  | value<br>(μmol/mol) | U (k=2)<br>(μmol/mol) | relative<br>difference | z-score | E <sub>n</sub> -number |
|-----|---------------------|-----------------------|------------------------|---------|------------------------|
| P01 | 27.10               | 0.87                  | -0.15%                 | -0.03   | -0.05                  |
| P02 |                     |                       |                        |         |                        |
| P03 |                     |                       |                        |         |                        |
| P04 |                     |                       |                        |         |                        |
| P05 |                     |                       |                        |         |                        |
| P06 | 27.34               | 0.87                  | 0.72%                  | 0.14    | 0.21                   |
| P07 | 26.94               | 2.15                  | -0.74%                 | -0.15   | -0.09                  |
| P08 | 26.41               | 1.64                  | -2.69%                 | -0.54   | -0.44                  |
| P09 | 26.44               | 2.35                  | -2.58%                 | -0.52   | -0.30                  |
| P10 |                     |                       |                        |         |                        |
| P11 | 25.60               | 1.28                  | -5.67%                 | -1.13   | -1.18                  |
| P12 | 25.89               | 1.42                  | -4.62%                 | -0.92   | -0.87                  |
| P13 | 23.82               | 0.26                  | -12.23%                | -2.45   | -8.99                  |
| P14 | 27.47               | 0.27                  | 1.22%                  | 0.24    | 0.87                   |
| P15 | 24.78               | 0.89                  | -8.70%                 | -1.74   | -2.56                  |
| P16 | 27.28               | 3.55                  | 0.52%                  | 0.10    | 0.04                   |
| P17 | 26.83               | 2.95                  | -1.15%                 | -0.23   | -0.11                  |
| P18 | 26.59               | 0.60                  | -2.01%                 | -0.40   | -0.83                  |
| P19 |                     |                       |                        |         |                        |
| P20 |                     |                       |                        |         |                        |
| P21 | 27.35               | 2.72                  | 0.77%                  | 0.15    | 0.08                   |
| P22 | 26.49               | 1.14                  | -2.41%                 | -0.48   | -0.56                  |
| P23 | 26.52               | 2.33                  | -2.29%                 | -0.46   | -0.26                  |
| P24 | 25.40               | 2.55                  | -6.41%                 | -1.28   | -0.68                  |
| P25 |                     |                       |                        |         |                        |
| P26 | 27.14               | 2.67                  | 0.01%                  | 0.00    | 0.00                   |
| P27 | 27.53               | 0.87                  | 1.42%                  | 0.28    | 0.42                   |

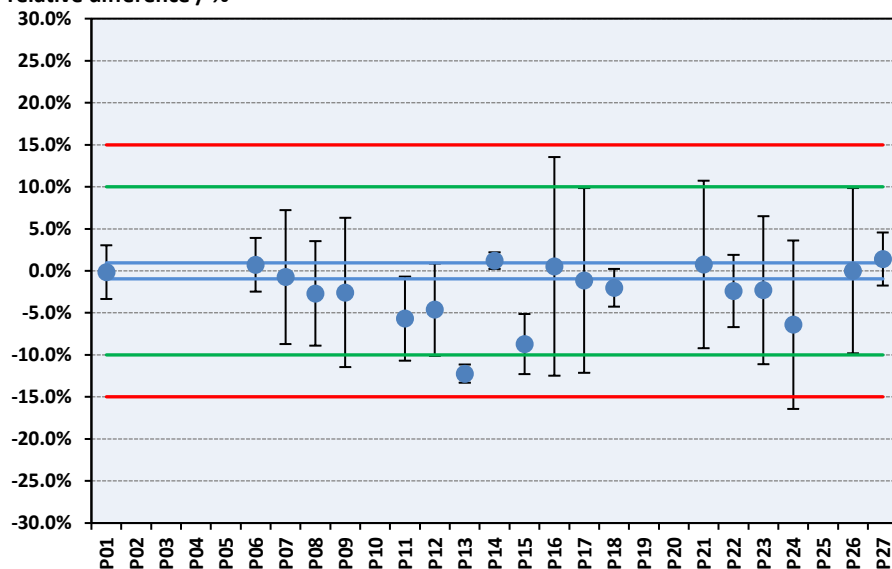
### Consensus values (raw data)

|       |       |       |
|-------|-------|-------|
| $m$   | 26.38 |       |
| $s_r$ | 0.22  | 0.85% |
| $s_L$ | 1.00  | 3.78% |
| $s_R$ | 1.02  | 3.88% |
| $p$   | 19    |       |

### Consensus values (corrected)

|       |       |       |
|-------|-------|-------|
| $m$   | 26.54 |       |
| $s_r$ | 0.23  | 0.87% |
| $s_L$ | 0.78  | 2.92% |
| $s_R$ | 0.81  | 3.05% |
| $p$   | 18    |       |

relative difference / %



Measurand/  
Mixture

nitric oxide

Reference

| $x_{\text{ref}}$ | $U(x_{\text{ref}}) \ k=2$ | $\sigma$ |
|------------------|---------------------------|----------|
| 82.45            | 0.46                      | 2.06     |

$\mu\text{mol/mol}$   $\mu\text{mol/mol}$

Reported data

| id  | value<br>( $\mu\text{mol/mol}$ ) | U (k=2)<br>( $\mu\text{mol/mol}$ ) | relative<br>difference | z-score | $E_n$ -number |
|-----|----------------------------------|------------------------------------|------------------------|---------|---------------|
| P01 |                                  |                                    |                        |         |               |
| P02 |                                  |                                    |                        |         |               |
| P03 |                                  |                                    |                        |         |               |
| P04 |                                  |                                    |                        |         |               |
| P05 | 83.57                            | 2.73                               | 1.36%                  | 0.54    | 0.41          |
| P06 |                                  |                                    |                        |         |               |
| P07 | 82.58                            | 6.61                               | 0.16%                  | 0.06    | 0.02          |
| P08 | 80.92                            | 6.30                               | -1.86%                 | -0.74   | -0.24         |
| P09 | 81.14                            | 2.73                               | -1.59%                 | -0.64   | -0.47         |
| P10 |                                  |                                    |                        |         |               |
| P11 |                                  |                                    |                        |         |               |
| P12 | 82.79                            | 2.40                               | 0.41%                  | 0.16    | 0.14          |
| P13 | 83.22                            | 1.25                               | 0.93%                  | 0.37    | 0.58          |
| P14 | 83.31                            | 0.83                               | 1.04%                  | 0.42    | 0.90          |
| P15 |                                  |                                    |                        |         |               |
| P16 |                                  |                                    |                        |         |               |
| P17 | 83.11                            | 4.07                               | 0.81%                  | 0.32    | 0.16          |
| P18 | 81.94                            | 3.40                               | -0.61%                 | -0.25   | -0.15         |
| P19 |                                  |                                    |                        |         |               |
| P20 |                                  |                                    |                        |         |               |
| P21 | 84.69                            | 4.41                               | 2.72%                  | 1.09    | 0.50          |
| P22 | 83.54                            | 2.93                               | 1.32%                  | 0.53    | 0.37          |
| P23 | 84.25                            | 3.62                               | 2.19%                  | 0.87    | 0.49          |
| P24 | 81.26                            | 4.27                               | -1.44%                 | -0.58   | -0.28         |
| P25 | 70.00                            | 7.27                               | -15.10%                | -6.04   | -1.71         |
| P26 | 84.79                            | 4.44                               | 2.84%                  | 1.14    | 0.52          |
| P27 |                                  |                                    |                        |         |               |

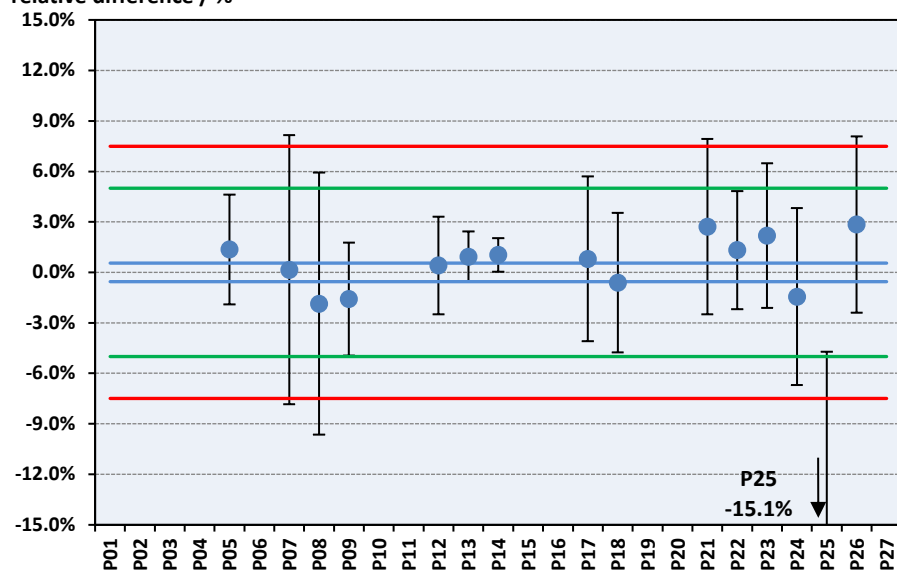
### Consensus values (raw data)

|       |       |       |
|-------|-------|-------|
| $m$   | 82.82 |       |
| $s_r$ | 0.22  | 0.26% |
| $s_L$ | 1.77  | 2.14% |
| $s_R$ | 1.79  | 2.16% |
| $p$   | 15    |       |

### Consensus values (corrected)

|       |       |       |
|-------|-------|-------|
| $m$   | 82.93 |       |
| $s_r$ | 0.22  | 0.26% |
| $s_L$ | 1.32  | 1.59% |
| $s_R$ | 1.34  | 1.61% |
| $p$   | 14    |       |

### relative difference / %



Measurand/  
Mixture

carbon monoxide

Reference

| $x_{\text{ref}}$ | $U(x_{\text{ref}}) \ k=2$ | $\sigma$ |
|------------------|---------------------------|----------|
| 235.8            | 1.9                       | 3.5      |

μmol/mol

μmol/mol

Reported data

| id  | value<br>(μmol/mol) | U (k=2)<br>(μmol/mol) | relative<br>difference | z-score | E <sub>n</sub> -number |
|-----|---------------------|-----------------------|------------------------|---------|------------------------|
| P01 | 238.8               | 1.9                   | 1.28%                  | 0.85    | 1.12                   |
| P02 |                     |                       |                        |         |                        |
| P03 | 236.5               | 23.6                  | 0.29%                  | 0.19    | 0.03                   |
| P04 |                     |                       |                        |         |                        |
| P05 |                     |                       |                        |         |                        |
| P06 | 240.2               | 2.8                   | 1.87%                  | 1.25    | 1.29                   |
| P07 | 238.5               | 10.7                  | 1.15%                  | 0.77    | 0.25                   |
| P08 | 236.1               | 13.7                  | 0.14%                  | 0.10    | 0.02                   |
| P09 | 237.5               | 3.8                   | 0.73%                  | 0.49    | 0.41                   |
| P10 |                     |                       |                        |         |                        |
| P11 | 227.8               | 11.2                  | -3.38%                 | -2.25   | -0.70                  |
| P12 | 244.0               | 7.1                   | 3.46%                  | 2.30    | 1.11                   |
| P13 | 235.9               | 3.8                   | 0.04%                  | 0.03    | 0.02                   |
| P14 |                     |                       |                        |         |                        |
| P15 | 236.3               | 1.5                   | 0.20%                  | 0.13    | 0.19                   |
| P16 |                     |                       |                        |         |                        |
| P17 | 234.2               | 12.4                  | -0.68%                 | -0.45   | -0.13                  |
| P18 | 236.4               | 10.7                  | 0.25%                  | 0.17    | 0.05                   |
| P19 |                     |                       |                        |         |                        |
| P20 |                     |                       |                        |         |                        |
| P21 | 233.0               | 13.5                  | -1.18%                 | -0.79   | -0.20                  |
| P22 | 235.2               | 3.7                   | -0.25%                 | -0.17   | -0.14                  |
| P23 | 235.3               | 11.5                  | -0.22%                 | -0.14   | -0.04                  |
| P24 | 235.6               | 13.5                  | -0.07%                 | -0.05   | -0.01                  |
| P25 | 239.1               | 30.6                  | 1.40%                  | 0.93    | 0.11                   |
| P26 | 232.5               | 13.1                  | -1.41%                 | -0.94   | -0.25                  |
| P27 | 240.5               | 8.2                   | 2.00%                  | 1.33    | 0.56                   |

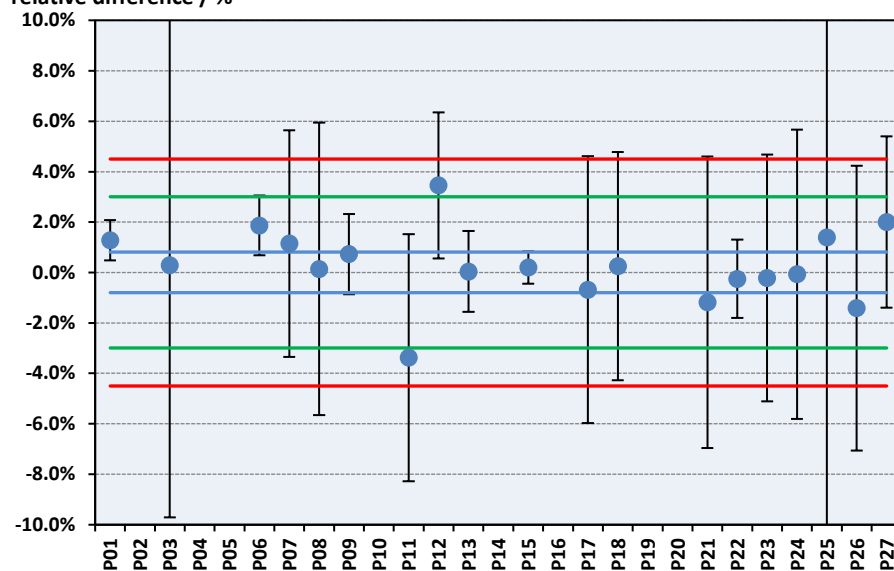
### Consensus values (raw data)

|       |       |       |
|-------|-------|-------|
| $m$   | 236.3 |       |
| $s_r$ | 0.3   | 0.14% |
| $s_L$ | 3.5   | 1.49% |
| $s_R$ | 3.5   | 1.50% |
| $p$   | 19    |       |

### Consensus values (corrected)

|       |       |       |
|-------|-------|-------|
| $m$   | 236.4 |       |
| $s_r$ | 0.4   | 0.15% |
| $s_L$ | 2.3   | 0.97% |
| $s_R$ | 2.3   | 0.98% |
| $p$   | 17    |       |

relative difference / %



Measurand/  
Mixture

oxygen

Reference

| $x_{\text{ref}}$ | $U(x_{\text{ref}}) \ k=2$ |          | $\sigma$ |          |
|------------------|---------------------------|----------|----------|----------|
| 6.827            | 0.037                     | %mol/mol | 0.078    | %mol/mol |

Reported data

| id  | value<br>(%mol/mol) | U (k=2)<br>(%mol/mol) | relative<br>difference | z-score | $E_n$ -number |
|-----|---------------------|-----------------------|------------------------|---------|---------------|
| P01 | 6.850               | 0.144                 | 0.34%                  | 0.29    | 0.15          |
| P02 |                     |                       |                        |         |               |
| P03 | 6.835               | 0.684                 | 0.12%                  | 0.11    | 0.01          |
| P04 | 6.815               | 0.130                 | -0.18%                 | -0.15   | -0.09         |
| P05 | 6.822               | 0.015                 | -0.07%                 | -0.06   | -0.12         |
| P06 | 6.882               | 0.015                 | 0.81%                  | 0.71    | 1.38          |
| P07 | 6.832               | 0.290                 | 0.07%                  | 0.06    | 0.02          |
| P08 | 6.817               | 0.290                 | -0.15%                 | -0.13   | -0.03         |
| P09 | 6.809               | 0.019                 | -0.26%                 | -0.23   | -0.43         |
| P10 | 6.820               | 0.500                 | -0.10%                 | -0.09   | -0.01         |
| P11 | 6.257               | 0.069                 | -8.35%                 | -7.28   | -7.29         |
| P12 | 6.892               | 0.179                 | 0.95%                  | 0.83    | 0.36          |
| P13 | 6.885               | 0.069                 | 0.85%                  | 0.74    | 0.74          |
| P14 | 6.770               | 0.068                 | -0.83%                 | -0.73   | -0.74         |
| P15 | 7.050               | 0.255                 | 3.27%                  | 2.85    | 0.87          |
| P16 |                     |                       |                        |         |               |
| P17 | 6.900               | 0.350                 | 1.07%                  | 0.93    | 0.21          |
| P18 | 6.818               | 0.130                 | -0.13%                 | -0.11   | -0.07         |
| P19 | 6.882               | 0.096                 | 0.80%                  | 0.70    | 0.53          |
| P20 | 6.815               | 0.210                 | -0.18%                 | -0.15   | -0.06         |
| P21 | 6.904               | 0.154                 | 1.13%                  | 0.98    | 0.49          |
| P22 | 6.836               | 0.232                 | 0.13%                  | 0.11    | 0.04          |
| P23 |                     |                       |                        |         |               |
| P24 | 6.851               | 0.153                 | 0.35%                  | 0.31    | 0.15          |
| P25 | 6.860               |                       | 0.48%                  | 0.42    |               |
| P26 | 6.878               | 0.153                 | 0.75%                  | 0.65    | 0.32          |
| P27 | 6.826               | 0.201                 | -0.01%                 | -0.01   | 0.00          |

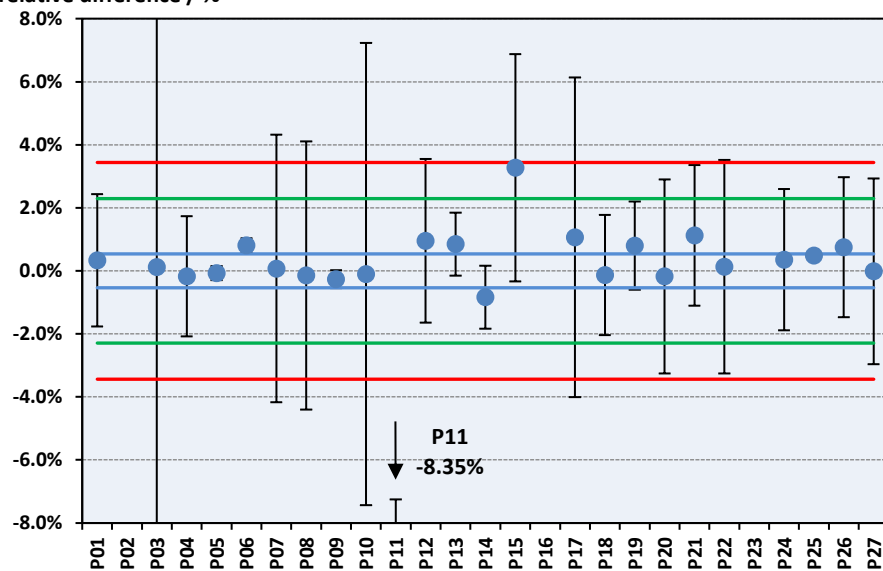
### Consensus values (raw data)

|       |       |       |
|-------|-------|-------|
| $m$   | 6.830 |       |
| $s_r$ | 0.046 | 0.67% |
| $s_L$ | 0.141 | 2.06% |
| $s_R$ | 0.148 | 2.17% |
| $p$   | 24    |       |

### Consensus values (corrected)

|       |       |       |
|-------|-------|-------|
| $m$   | 6.858 |       |
| $s_r$ | 0.015 | 0.21% |
| $s_L$ | 0.055 | 0.81% |
| $s_R$ | 0.057 | 0.83% |
| $p$   | 23    |       |

relative difference / %



Measurand/  
Mixture

carbon dioxide

Reference

| $x_{\text{ref}}$ | $U(x_{\text{ref}}) \ k=2$ |          | $\sigma$ |          |
|------------------|---------------------------|----------|----------|----------|
| 6.164            | 0.025                     | %mol/mol | 0.072    | %mol/mol |

Reported data

| id  | value<br>(%mol/mol) | U (k=2)<br>(%mol/mol) | relative<br>difference | z-score | $E_n$ -number |
|-----|---------------------|-----------------------|------------------------|---------|---------------|
| P01 | 6.137               | 0.266                 | -0.44%                 | -0.38   | -0.10         |
| P02 |                     |                       |                        |         |               |
| P03 | 6.244               | 0.624                 | 1.29%                  | 1.11    | 0.13          |
| P04 | 6.265               | 0.270                 | 1.64%                  | 1.41    | 0.37          |
| P05 | 6.057               | 0.013                 | -1.74%                 | -1.49   | -3.81         |
| P06 | 6.161               | 0.016                 | -0.05%                 | -0.04   | -0.11         |
| P07 | 6.167               | 0.270                 | 0.06%                  | 0.05    | 0.01          |
| P08 | 6.142               | 0.520                 | -0.36%                 | -0.31   | -0.04         |
| P09 | 6.175               | 0.014                 | 0.18%                  | 0.15    | 0.38          |
| P10 | 6.240               | 0.500                 | 1.23%                  | 1.06    | 0.15          |
| P11 |                     |                       |                        |         |               |
| P12 | 5.999               | 0.156                 | -2.68%                 | -2.30   | -1.04         |
| P13 | 6.141               | 0.055                 | -0.37%                 | -0.32   | -0.38         |
| P14 |                     |                       |                        |         |               |
| P15 | 6.161               | 0.267                 | -0.06%                 | -0.05   | -0.01         |
| P16 |                     |                       |                        |         |               |
| P17 | 6.500               | 0.280                 | 5.45%                  | 4.69    | 1.20          |
| P18 |                     |                       |                        |         |               |
| P19 | 6.228               | 0.069                 | 1.04%                  | 0.90    | 0.88          |
| P20 |                     |                       |                        |         |               |
| P21 | 5.998               | 0.207                 | -2.69%                 | -2.32   | -0.80         |
| P22 | 6.185               | 0.223                 | 0.34%                  | 0.29    | 0.09          |
| P23 | 6.086               | 0.341                 | -1.27%                 | -1.09   | -0.23         |
| P24 | 6.279               | 0.215                 | 1.87%                  | 1.61    | 0.53          |
| P25 | 6.020               |                       | -2.34%                 | -2.01   |               |
| P26 | 6.006               | 0.206                 | -2.56%                 | -2.21   | -0.76         |
| P27 | 6.171               | 0.268                 | 0.11%                  | 0.10    | 0.03          |

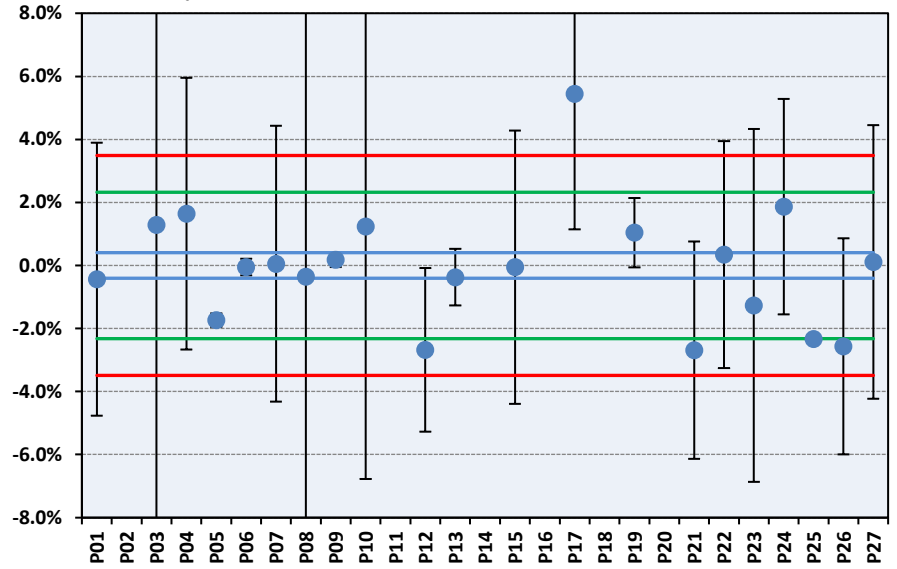
### Consensus values (raw data)

|       |       |       |
|-------|-------|-------|
| $m$   | 6.164 |       |
| $s_r$ | 0.019 | 0.31% |
| $s_L$ | 0.117 | 1.90% |
| $s_R$ | 0.119 | 1.93% |
| $p$   | 21    |       |

### Consensus values (corrected)

|       |       |       |
|-------|-------|-------|
| $m$   | 6.145 |       |
| $s_r$ | 0.020 | 0.32% |
| $s_L$ | 0.087 | 1.42% |
| $s_R$ | 0.090 | 1.46% |
| $p$   | 20    |       |

relative difference / %



Measurand/  
Mixture

nitric oxide  
(NO/NO<sub>2</sub> mix)

Reference

| $x_{\text{ref}}$ | $U(x_{\text{ref}}) \ k=2$ | $\sigma$ |
|------------------|---------------------------|----------|
| 86.57            | 0.48                      | 2.16     |

μmol/mol      μmol/mol

Reported data

| id  | value<br>(μmol/mol) | U (k=2)<br>(μmol/mol) | relative<br>difference | z-score | E <sub>n</sub> -number |
|-----|---------------------|-----------------------|------------------------|---------|------------------------|
| P01 | 87.47               | 0.44                  | 1.04%                  | 0.42    | 1.39                   |
| P02 | 76.86               | 1.54                  | -11.21%                | -4.49   | -6.03                  |
| P03 | 86.68               | 8.67                  | 0.12%                  | 0.05    | 0.01                   |
| P04 |                     |                       |                        |         |                        |
| P05 |                     |                       |                        |         |                        |
| P06 | 86.18               | 1.57                  | -0.45%                 | -0.18   | -0.24                  |
| P07 | 86.54               | 6.92                  | -0.03%                 | -0.01   | 0.00                   |
| P08 | 84.02               | 6.30                  | -2.95%                 | -1.18   | -0.40                  |
| P09 | 84.89               | 3.52                  | -1.94%                 | -0.77   | -0.47                  |
| P10 |                     |                       |                        |         |                        |
| P11 | 88.01               | 3.34                  | 1.66%                  | 0.67    | 0.43                   |
| P12 | 85.44               | 2.48                  | -1.31%                 | -0.52   | -0.45                  |
| P13 | 82.67               | 1.24                  | -4.51%                 | -1.80   | -2.93                  |
| P14 |                     |                       |                        |         |                        |
| P15 | 82.48               | 2.47                  | -4.72%                 | -1.89   | -1.63                  |
| P16 |                     |                       |                        |         |                        |
| P17 | 88.42               | 4.33                  | 2.14%                  | 0.85    | 0.42                   |
| P18 |                     |                       |                        |         |                        |
| P19 |                     |                       |                        |         |                        |
| P20 |                     |                       |                        |         |                        |
| P21 | 88.69               | 4.53                  | 2.44%                  | 0.98    | 0.46                   |
| P22 |                     |                       |                        |         |                        |
| P23 | 88.53               | 3.81                  | 2.26%                  | 0.90    | 0.51                   |
| P24 | 81.01               | 4.26                  | -6.42%                 | -2.57   | -1.30                  |
| P25 | 73.40               | 7.62                  | -15.21%                | -6.09   | -1.72                  |
| P26 | 88.83               | 4.52                  | 2.61%                  | 1.04    | 0.50                   |
| P27 | 83.81               | 7.29                  | -3.19%                 | -1.28   | -0.38                  |

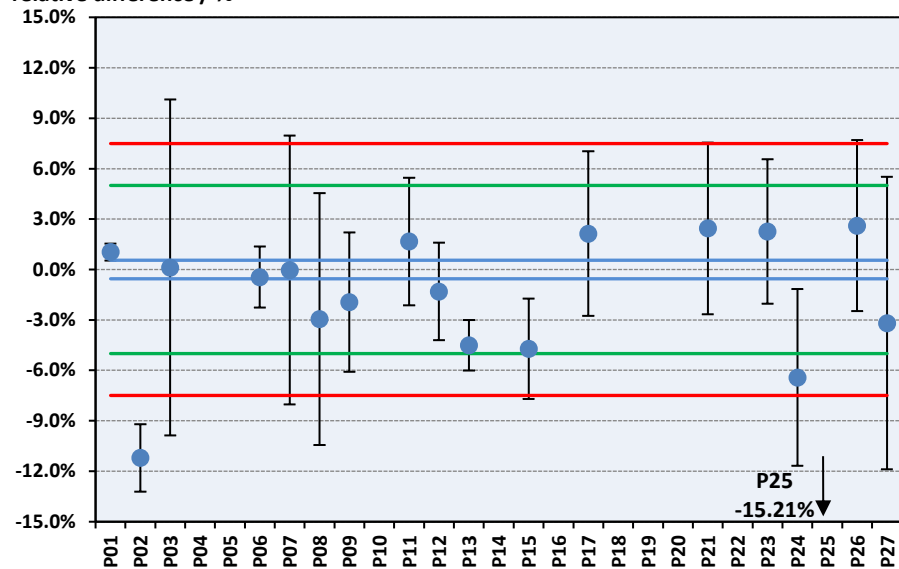
### Consensus values (raw data)

|       |       |       |
|-------|-------|-------|
| $m$   | 85.52 |       |
| $s_r$ | 0.17  | 0.20% |
| $s_L$ | 3.05  | 3.56% |
| $s_R$ | 3.05  | 3.57% |
| $p$   | 18    |       |

### Consensus values (corrected)

|       |       |       |
|-------|-------|-------|
| $m$   | 85.83 |       |
| $s_r$ | 0.17  | 0.20% |
| $s_L$ | 2.53  | 2.95% |
| $s_R$ | 2.54  | 2.96% |
| $p$   | 16    |       |

relative difference / %



Measurand/  
Mixture

nitrogen oxides  
(NO/NO<sub>2</sub> mix)

Reference

| $x_{\text{ref}}$ | $U(x_{\text{ref}}) \ k=2$ | $\sigma$ |
|------------------|---------------------------|----------|
| 97.77            | 0.69                      | 2.44     |

μmol/mol      μmol/mol

Reported data

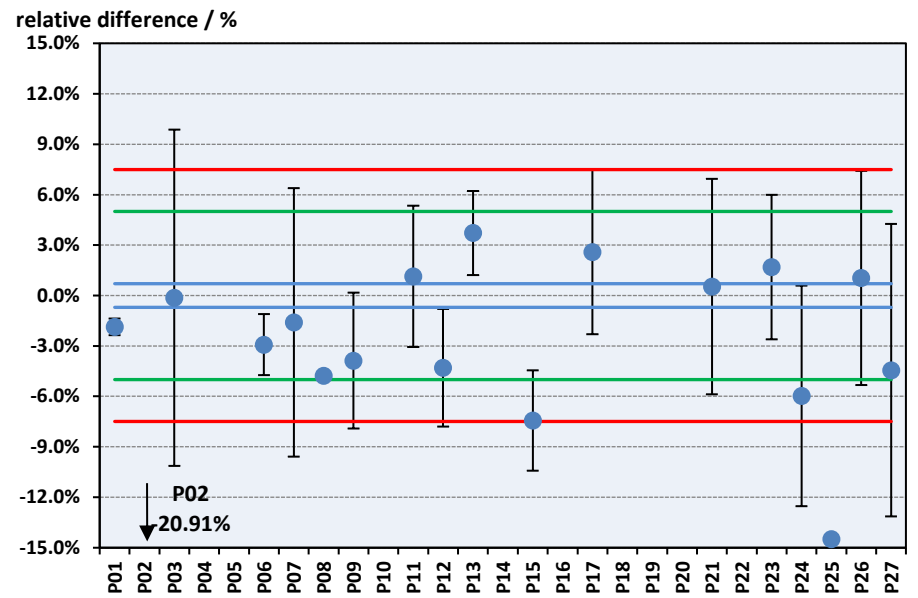
| id  | value<br>(μmol/mol) | U (k=2)<br>(μmol/mol) | relative<br>difference | z-score | E <sub>n</sub> -number |
|-----|---------------------|-----------------------|------------------------|---------|------------------------|
| P01 | 95.95               | 0.48                  | -1.86%                 | -0.74   | -2.17                  |
| P02 | 77.32               | 1.55                  | -20.91%                | -8.37   | -12.07                 |
| P03 | 97.64               | 9.76                  | -0.14%                 | -0.05   | -0.01                  |
| P04 |                     |                       |                        |         |                        |
| P05 |                     |                       |                        |         |                        |
| P06 | 94.91               | 1.72                  | -2.93%                 | -1.17   | -1.54                  |
| P07 | 96.21               | 7.69                  | -1.59%                 | -0.64   | -0.20                  |
| P08 | 93.10               |                       | -4.78%                 | -1.91   |                        |
| P09 | 93.98               | 3.80                  | -3.88%                 | -1.55   | -0.98                  |
| P10 |                     |                       |                        |         |                        |
| P11 | 98.89               | 4.15                  | 1.15%                  | 0.46    | 0.27                   |
| P12 | 93.56               | 3.27                  | -4.31%                 | -1.72   | -1.26                  |
| P13 | 101.41              | 2.54                  | 3.72%                  | 1.49    | 1.39                   |
| P14 |                     |                       |                        |         |                        |
| P15 | 90.50               | 2.71                  | -7.43%                 | -2.97   | -2.60                  |
| P16 |                     |                       |                        |         |                        |
| P17 | 100.30              | 4.91                  | 2.59%                  | 1.04    | 0.51                   |
| P18 |                     |                       |                        |         |                        |
| P19 |                     |                       |                        |         |                        |
| P20 |                     |                       |                        |         |                        |
| P21 | 98.29               | 6.30                  | 0.53%                  | 0.21    | 0.08                   |
| P22 |                     |                       |                        |         |                        |
| P23 | 99.42               | 4.28                  | 1.69%                  | 0.68    | 0.38                   |
| P24 | 91.93               | 6.04                  | -5.97%                 | -2.39   | -0.96                  |
| P25 | 83.60               |                       | -14.49%                | -5.80   |                        |
| P26 | 98.79               | 6.29                  | 1.04%                  | 0.42    | 0.16                   |
| P27 | 93.42               | 8.13                  | -4.45%                 | -1.78   | -0.53                  |

#### Consensus values (raw data)

|       |       |       |
|-------|-------|-------|
| $m$   | 95.59 |       |
| $s_r$ | 0.29  | 0.31% |
| $s_L$ | 4.53  | 4.74% |
| $s_R$ | 4.54  | 4.75% |
| $p$   | 18    |       |

#### Consensus values (corrected)

|       |       |       |
|-------|-------|-------|
| $m$   | 96.06 |       |
| $s_r$ | 0.29  | 0.30% |
| $s_L$ | 3.43  | 3.57% |
| $s_R$ | 3.44  | 3.58% |
| $p$   | 17    |       |



## Annex B - Converter efficiency

If the reported nitric oxide (NO) measurement of the NO/NO<sub>2</sub> mixture, for each participant, is subtracted from that of their reported nitrogen oxides (NO<sub>x</sub>) result, then the nitrogen dioxide (NO<sub>2</sub>) result from their measurements can be directly calculated. This derived NO<sub>2</sub> measurement result can be used to calculate the converter efficiency of their analyser where appropriate.

The table below gives the derived results for nitrogen dioxide and the calculated converter efficiencies for each reporting participant. Their uncertainties have been calculated by adding the uncertainties of their NO and NO<sub>x</sub> reported results in quadrature.

## Reference

| $x_{\text{ref}}$ | $U(x_{\text{ref}}) \ k=2$ |
|------------------|---------------------------|
| 11.20            | 0.84                      |

μmol/mol

## Reported data

| id  | value<br>(μmol/mol) | U (k=2)<br>(μmol/mol) | difference<br>(μmol/mol) | converter<br>efficiency (%) | E <sub>n</sub> -number |
|-----|---------------------|-----------------------|--------------------------|-----------------------------|------------------------|
| P01 | 8.48                | 0.65                  | -2.7                     | 75.7%                       | -2.56                  |
| P02 | 0.46                | 2.18                  | -10.7                    | 4.1%                        | -4.60                  |
| P03 | 10.96               | 13.06                 | -0.2                     | 97.9%                       | -0.02                  |
| P04 |                     |                       |                          |                             |                        |
| P05 |                     |                       |                          |                             |                        |
| P06 | 8.73                | 2.33                  | -2.5                     | 77.9%                       | -1.00                  |
| P07 | 9.67                | 10.35                 | -1.5                     | 86.3%                       | -0.15                  |
| P08 | 9.08                | 6.30                  | -2.1                     | 81.1%                       | -0.33                  |
| P09 | 9.09                | 5.18                  | -2.1                     | 81.1%                       | -0.40                  |
| P10 |                     |                       |                          |                             |                        |
| P11 | 10.88               | 5.33                  | -0.3                     | 97.1%                       | -0.06                  |
| P12 | 8.12                | 4.11                  | -3.1                     | 72.5%                       | -0.73                  |
| P13 | 18.74               | 2.82                  | 7.5                      | 167.3%                      | 2.56                   |
| P14 |                     |                       |                          |                             |                        |
| P15 | 8.02                | 3.66                  | -3.2                     | 71.6%                       | -0.85                  |
| P16 |                     |                       |                          |                             |                        |
| P17 | 11.88               | 6.55                  | 0.7                      | 106.1%                      | 0.10                   |
| P18 |                     |                       |                          |                             |                        |
| P19 |                     |                       |                          |                             |                        |
| P20 |                     |                       |                          |                             |                        |
| P21 | 9.60                | 7.76                  | -1.6                     | 85.7%                       | -0.20                  |
| P22 |                     |                       |                          |                             |                        |
| P23 | 10.90               | 5.72                  | -0.3                     | 97.3%                       | -0.05                  |
| P24 | 10.92               | 7.39                  | -0.3                     | 97.5%                       | -0.04                  |
| P25 | 10.20               | 7.62                  | -1.0                     | 91.1%                       | -0.13                  |
| P26 | 9.96                | 7.75                  | -1.2                     | 88.9%                       | -0.16                  |
| P27 | 9.61                | 10.92                 | -1.6                     | 85.8%                       | -0.15                  |

For appropriate measurement of nitrogen dioxide by the conversion of NO<sub>2</sub> to NO using a converter and subsequent measurement by chemiluminescence, the efficiency of the converter should be above 95% (in accordance with BS EN 14792).