EffecTech

Global Leaders in Gas Measurement

UKAS
PROFICIENCY TESTING

4719

Stack Emissions Proficiency Testing Scheme (SEPTS)

Presentation of Results

Round 2019

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	19.08.2019	Dr Gavin Squire	***Final report (for comment)***

Statement of Confidentiality

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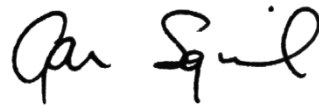
The relationship between results and the laboratories that submitted them will never be disclosed. The laboratory alone is granted access to its performance through the assigned participant code and through issue of a confidential Certificate of Participation.

Checked by

Steve Price
Scheme Coordinator

Approved by

Dr Gavin Squire
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 2019 (June - July 2019).

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_2) in nitrogen	50 to 1000 µmol/mol
propane (C_3H_8) in 10% oxygen / nitrogen	1 to 50 µmol/mol
nitric oxide (NO) in nitrogen	5 to 500 µmol/mol
carbon monoxide (CO) in nitrogen	50 to 1000 µmol/mol
oxygen (O_2) in nitrogen	2 to 14 %mol/mol
carbon dioxide (CO_2) in nitrogen	1 to 10 %mol/mol
nitric oxide (NO) and nitrogen oxides (NO_X) in nitrogen	40 to 400 µmol/mol 50 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 500×10^{-6} mol/mol
10 %mol/mol is equivalent to 10 dmol/mol is equivalent to 10×10^{-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-eight (28) laboratories signed up to participate in this round. Twenty-seven (27) participants, 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 6142-1:2015. 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 oxygen and propane measurands which were 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 17025 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_{char} (ISO Guide 35 : 2006).

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

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_{bb}). The uncertainty arising from this is the between-bottle uncertainty (u_{bb}). The statistical procedure used for the determination of $u_{bb}=s_{bb}$ can be found in ISO Guide 35 : 2006. 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 Guide 35 : 2006 - section 6.2).

$$u^2_c = u^2_{char} + u^2_{bb}$$

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 EffecTech is accredited to ISO 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 EffecTech.

Stability statement

Over several years EffecTech 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 with the exception of the NO/NO_2 mixture which remains stable for 6 months.

With this exception, 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_{ref}	$U(x_{ref})$	u_c / %	u_{char} / %	u_{bb} / %
sulphur dioxide	µmol/mol	388.8	4.0	0.25	0.24	0.042
propane	µmol/mol	38.11	0.33	0.34	0.34	0.063
nitric oxide	µmol/mol	336.2	1.8	0.17	0.16	0.046
carbon monoxide	µmol/mol	597.3	3.9	0.18	0.18	0.007
oxygen	%mol/mol	3.276	0.011	0.17	0.17	0.012
carbon dioxide	%mol/mol	2.682	0.011	0.17	0.17	0.005
nitric oxide (NO/NO2 mix)	µmol/mol	99.16	0.57	0.29	0.15	0.24
nitrogen oxides (NO/NO2 mix)	µmol/mol	107.27	0.65	0.37	0.17	0.33

3. Results

3.1 Reported results

There were twenty eight (28) 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	✓	✗						
P28	✓	✓	✓	✓			✓	✓

Participant id	oxygen		carbon dioxide		nitric oxide (NO/NO2 mix)		nitrogen oxides (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					✓	✗	✓	✗
P28			✓	✓	✓	✓	✓	✓

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. All 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

$$z = \frac{x_{meas} - x_{ref}}{\sigma} \tag{1}$$

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

x_{ref} is the assigned reference value and

σ is the absolute standard deviation used for performance assessment (SDPA) which can be calculated from the relative standard deviation for performance assessment S_{PT} by

$$\sigma = \frac{S_{PT}}{100} \cdot x_{ref} \tag{2}$$

The relative 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} (mol/mol)
sulphur dioxide	2.5 % relative
propane	5.0 % relative
nitric oxide	2.5 % relative
carbon monoxide	1.5 % relative
oxygen	1.0 % relative
carbon dioxide	1.0 % relative
nitric oxide (NO/NO2 mix)	2.5 % relative
nitrogen oxides (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

$$E_n = \frac{x_{meas} - x_{ref}}{\sqrt{U_{meas}^2 + U_{ref}^2}}$$
(3)

      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

participant id	sulphur dioxide	propane	nitric oxide	carbon monoxide	oxygen	carbon dioxide	nitric oxide (NO/NO2 mix)	nitrogen oxides (NO/NO2 mix)
P01		-0.90						
P02					3.48	4.40		
P03	0.33	-0.43		-1.71	0.73	4.03	-2.28	-2.93
P04		-0.34				0.83		
P05	0.94	4.38		-11.37	24.63	7.76	1.12	0.48
P06			0.37	1.47	-4.19	-6.19	0.31	1.55
P07	1.98							
P08	-1.42	-0.43		-0.26	5.31	4.03	0.14	-0.77
P09	0.42	-0.10	0.45	0.01	0.07			
P10		-0.06		1.19	-0.18	5.52	-0.35	-0.77
P11		-0.06				-0.15		
P12	1.25	-0.01	1.25	3.10	-1.07	4.62	0.49	1.06
P13	0.22	1.08		-0.35	-2.38		-0.91	-0.77
P14				-0.58	2.63	5.04	-0.72	0.17
P15	-0.14	-0.22		-1.82	2.87	-8.65	-1.19	-2.82
P16		-0.16		-0.37	-0.18	-1.57	-0.55	0.20
P17		0.01	0.54	0.24	0.37		0.06	0.54
P18	-0.08		-0.27	-0.52				
P19	2.39	-0.33	1.32	1.29	0.89	0.67	0.78	0.05
P20	2.75	-0.95		-1.60	2.56	2.54	-2.12	-2.71
P21	1.45	0.20	0.18	-1.11	-0.49	-0.75	0.38	0.63
P22	0.01			0.55	0.11	0.57		
P23					1.10			
P24	0.74	-1.63		-0.37	-2.63	5.15	-2.12	-1.52
P25	0.77	0.04	0.38	0.16	-4.76	2.16	0.05	0.74
P26	0.84	-3.72	-3.45	-1.21	-0.92	-2.09	0.70	0.86
P27								
P28	1.15	-0.06		-1.04	-5.98	2.16	2.23	2.06

These results show a mixed performance from the pool of participants. Measurements of sulphur dioxide, propane, nitric oxide(s) and carbon monoxide were generally good with the majority of results reported with a satisfactory **z**-score. However, the measurement of oxygen and carbon dioxide at percentage amount fractions proved more challenging with an s_{PT} of 1% relative.

Only six (6) participants reported satisfactory results for **carbon dioxide** from a pool of twenty (20) reported values.

Similarly, only eleven (11) from twenty-two (22) reported satisfactory results for **oxygen**.

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

Table 8 - Summary of E_n-numbers

participant id	sulphur dioxide	propane	nitric oxide	carbon monoxide	oxygen	carbon dioxide	nitric oxide (NO/NO2 mix)	nitrogen oxides (NO/NO2 mix)
P01		-0.36						
P02					1.28	1.67		
P03	0.15	-1.08		-0.55	0.51	0.92	-1.43	-1.86
P04		-0.32				0.18		
P05	0.67	0.76		-6.06	5.97	1.09	0.79	0.25
P06			0.06	0.33	-0.30	-0.83	0.05	0.26
P07	0.93							
P08	-0.67	-1.08		-0.08	3.51	0.92	0.08	-0.46
P09	0.53	-0.17	0.78	0.01	0.16			
P10		-0.14		0.37	-0.13	1.24	-0.21	-0.46
P11		-0.20				-0.20		
P12	0.67	-0.01	1.69	1.01	-0.36	1.47	0.66	1.41
P13	0.52	5.13		-0.79	-7.08		-1.84	-0.96
P14				-1.16	1.10	2.06	-0.73	0.19
P15	-0.07	-0.54		-0.59	1.94	-2.24	-0.73	-1.79
P16		-0.41		-0.12	-0.13	-0.38	-0.33	0.12
P17		0.01	0.21	0.07	0.10		0.02	0.19
P18	-0.09		-0.21	-0.23				
P19	1.69	-0.47	1.90	0.55	2.45	1.56	0.99	0.03
P20	1.17	-2.47		-0.52	1.74	0.59	-1.32	-1.71
P21	0.95	0.14	0.12	-0.29	-0.04	-0.03	0.16	0.25
P22	0.01			0.69	0.12	0.60		
P23						0.17		
P24	0.33	-4.37		-0.12	-1.87	1.16	-1.32	-0.93
P25	0.43	0.08	0.14	0.05	-0.30	0.12	0.02	0.27
P26	0.19	-4.21	-1.55	-0.34	-0.09	-0.06	0.16	0.20
P27								
P28	0.51	-0.14		-0.33	-4.40	0.50	1.25	1.16

For the laboratories submitting estimates of uncertainty for their measurements, the corresponding E_n-numbers show a similar number of satisfactory result to those for **z**-scores.

For those reporting unsatisfactory results, there seems to be some undetected bias in their measurements or an under-estimation of their uncertainties.

Excellent performances were received from participants **P09**, **P16**, **P17**, and **P22** each of whom submitted results for 4 or more measurands achieving 100% perfect score on the basis of both performance measures.

The outstanding laboratory in this round of the PT scheme was participant **P21** 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_{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_{ref}	$U(x_{ref})$ $k=2$		σ	
388.8	4.0	µmol/mol	9.7	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02					
P03	392.0	21.2	0.82%	0.33	0.15
P04					
P05	398.0	13.1	2.35%	0.94	0.67
P06					
P07	408.0	20.2	4.94%	1.98	0.93
P08	375.0	20.3	-3.55%	-1.42	-0.67
P09	392.9	6.7	1.06%	0.42	0.53
P10					
P11					
P12	400.9	17.8	3.12%	1.25	0.67
P13	390.9	0.0	0.54%	0.22	0.52
P14					
P15	387.4	20.9	-0.36%	-0.14	-0.07
P16					
P17					
P18	388.0	8.0	-0.21%	-0.08	-0.09
P19	412.0	13.2	5.97%	2.39	1.69
P20	415.5	22.4	6.87%	2.75	1.17
P21	402.9	14.2	3.62%	1.45	0.95
P22	388.9	5.0	0.01%	0.01	0.01
P23					
P24	396.0	21.4	1.85%	0.74	0.33
P25	396.3	17.1	1.93%	0.77	0.43
P26	397.0	43.5	2.11%	0.84	0.19
P27					
P28	400.0	21.6	2.88%	1.15	0.51

Consensus values (raw data)

m	397.7	
s_r	3.7	0.94%
s_L	8.0	2.01%
s_R	8.8	2.22%
p	17	

Consensus values (corrected)

m	397.9	
s_r	3.7	0.94%
s_L	7.7	1.93%
s_R	8.6	2.15%
p	16	

relative difference / %
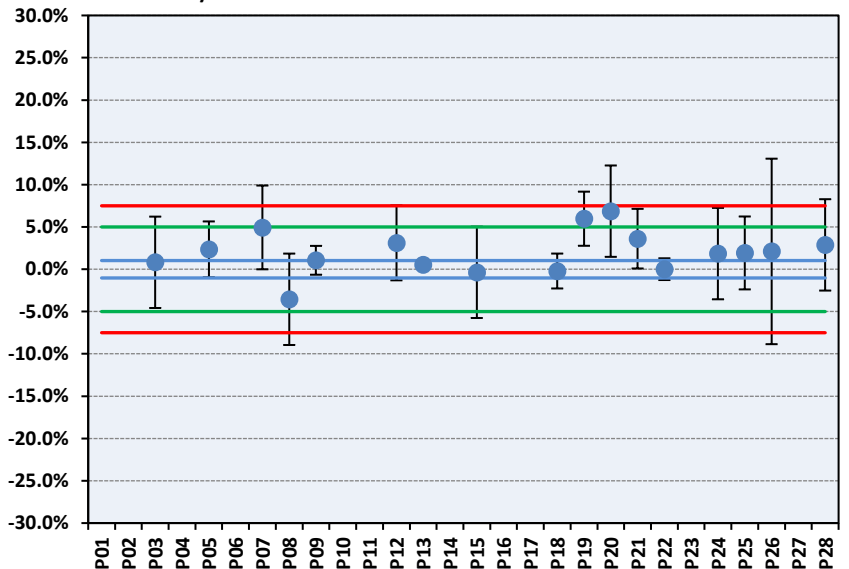
Measurand/ Mixture	propane

Reference

x_{ref}	$U(x_{ref})$ $k=2$		σ	
38.11	0.33	µmol/mol	1.91	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	**z**-score	**E$_n$**-number
P01	36.40	4.73	-4.50%	-0.90	-0.36
P02					
P03	37.30	0.67	-2.13%	-0.43	-1.08
P04	37.47	1.99	-1.69%	-0.34	-0.32
P05	46.46	10.92	21.91%	4.38	0.76
P06					
P07					
P08	37.30	0.67	-2.13%	-0.43	-1.08
P09	37.92	1.10	-0.50%	-0.10	-0.17
P10	38.00	0.68	-0.29%	-0.06	-0.14
P11	38.00	0.46	-0.29%	-0.06	-0.20
P12	38.08	2.11	-0.07%	-0.01	-0.01
P13	40.17	0.23	5.41%	1.08	5.13
P14					
P15	37.70	0.68	-1.08%	-0.22	-0.54
P16	37.80	0.68	-0.81%	-0.16	-0.41
P17	38.12	1.46	0.03%	0.01	0.01
P18					
P19	37.47	1.33	-1.67%	-0.33	-0.47
P20	36.30	0.65	-4.75%	-0.95	-2.47
P21	38.49	2.77	1.00%	0.20	0.14
P22					
P23					
P24	35.00	0.63	-8.16%	-1.63	-4.37
P25	38.19	0.92	0.21%	0.04	0.08
P26	31.03	1.65	-18.59%	-3.72	-4.21
P27					
P28	38.00	0.68	-0.29%	-0.06	-0.14

Consensus values (raw data)

m	38.19	
s_r	0.24	0.62%
s_L	3.58	9.38%
s_R	3.59	9.40%
p	20	

Consensus values (corrected)

m	38.06	
s_r	0.21	0.56%
s_L	0.97	2.54%
s_R	0.99	2.60%
p	18	

relative difference / %

| Measurand/ Mixture | nitric oxide | | | |

Reference

x_{ref}	$U(x_{ref})$ $k=2$		σ	
336.2	1.8	µmol/mol	8.4	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	z-score	E_n-number
P01					
P02					
P03					
P04					
P05					
P06	339.3	49.5	0.93%	0.37	0.06
P07					
P08					
P09	340.0	4.5	1.13%	0.45	0.78
P10					
P11					
P12	346.7	6.0	3.13%	1.25	1.69
P13					
P14					
P15					
P16					
P17	340.8	22.1	1.35%	0.54	0.21
P18	334.0	10.7	-0.66%	-0.27	-0.21
P19	347.3	5.6	3.31%	1.32	1.90
P20					
P21	337.7	12.1	0.45%	0.18	0.12
P22					
P23					
P24					
P25	339.4	22.5	0.96%	0.38	0.14
P26	307.2	18.6	-8.63%	-3.45	-1.55
P27					
P28					

Consensus values (raw data)

m	336.9	
s_r	1.2	0.34%
s_L	12.3	3.64%
s_R	12.3	3.66%
p	9	

Consensus values (corrected)

m	340.9	
s_r	1.2	0.35%
s_L	4.5	1.32%
s_R	4.7	1.37%
p	8	

relative difference / %

Measurand/Mixture	carbon monoxide

Reference

x_{ref}	$U(x_{ref})$ $k=2$		σ	
597.3	3.9	µmol/mol	9.0	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	z-score	E_n-number
P01					
P02					
P03	582.0	27.4	-2.56%	-1.71	-0.55
P04					
P05	495.5	16.4	-17.05%	-11.37	-6.06
P06	610.5	40.1	2.21%	1.47	0.33
P07					
P08	595.0	28.0	-0.39%	-0.26	-0.08
P09	597.4	8.6	0.02%	0.01	0.01
P10	608.0	28.6	1.79%	1.19	0.37
P11					
P12	625.1	27.3	4.65%	3.10	1.01
P13	594.2	0.6	-0.52%	-0.35	-0.79
P14	592.1	2.3	-0.88%	-0.58	-1.16
P15	581.0	27.3	-2.73%	-1.82	-0.59
P16	594.0	27.9	-0.55%	-0.37	-0.12
P17	599.4	30.1	0.36%	0.24	0.07
P18	592.6	19.9	-0.78%	-0.52	-0.23
P19	608.9	20.6	1.94%	1.29	0.55
P20	583.0	27.4	-2.39%	-1.60	-0.52
P21	587.3	34.7	-1.67%	-1.11	-0.29
P22	602.2	6.0	0.82%	0.55	0.69
P23					
P24	594.0	27.9	-0.55%	-0.37	-0.12
P25	598.7	26.5	0.23%	0.16	0.05
P26	586.5	31.4	-1.81%	-1.21	-0.34
P27					
P28	588.0	27.6	-1.56%	-1.04	-0.33

Consensus values (raw data)

m	591.5	
s_r	0.8	0.13%
s_L	30.5	5.16%
s_R	30.5	5.16%
p	21	

Consensus values (corrected)

m	599.4	
s_r	0.8	0.13%
s_L	11.1	1.84%
s_R	11.1	1.85%
p	20	

relative difference / %

Measurand/ Mixture	oxygen	
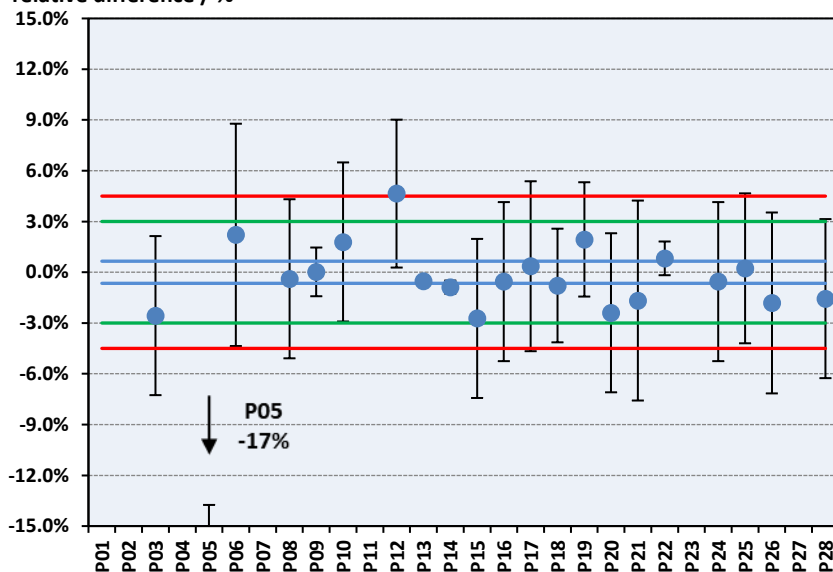
Reference

x_{ref}	$U(x_{ref})$ $k=2$		σ	
3.276	0.011	%mol/mol	0.033	%mol/mol

Reported data

id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	z-score	E_n-number
P01					
P02	3.390	0.088	3.48%	3.48	1.28
P03	3.300	0.046	0.73%	0.73	0.51
P04					
P05	4.083	0.135	24.63%	24.63	5.97
P06	3.139	0.460	-4.19%	-4.19	-0.30
P07					
P08	3.450	0.048	5.31%	5.31	3.51
P09	3.278	0.010	0.07%	0.07	0.16
P10	3.270	0.046	-0.18%	-0.18	-0.13
P11					
P12	3.241	0.097	-1.07%	-1.07	-0.36
P13	3.198	0.001	-2.38%	-2.38	-7.08
P14	3.362	0.077	2.63%	2.63	1.10
P15	3.370	0.047	2.87%	2.87	1.94
P16	3.270	0.046	-0.18%	-0.18	-0.13
P17	3.288	0.120	0.37%	0.37	0.10
P18					
P19	3.305	0.004	0.89%	0.89	2.45
P20	3.360	0.047	2.56%	2.56	1.74
P21	3.260	0.450	-0.49%	-0.49	-0.04
P22	3.280	0.028	0.11%	0.11	0.12
P23	3.312	0.210	1.10%	1.10	0.17
P24	3.190	0.045	-2.63%	-2.63	-1.87
P25	3.120	0.520	-4.76%	-4.76	-0.30
P26	3.246	0.320	-0.92%	-0.92	-0.09
P27					
P28	3.080	0.043	-5.98%	-5.98	-4.40

Consensus values (raw data)

m	3.324	
s_r	0.019	0.57%
s_L	0.236	7.09%
s_R	0.236	7.11%
p	22	

Consensus values (corrected)

m	3.263	
s_r	0.020	0.60%
s_L	0.082	2.51%
s_R	0.084	2.58%
p	21	

relative difference / %

Measurand/ Mixture	carbon dioxide
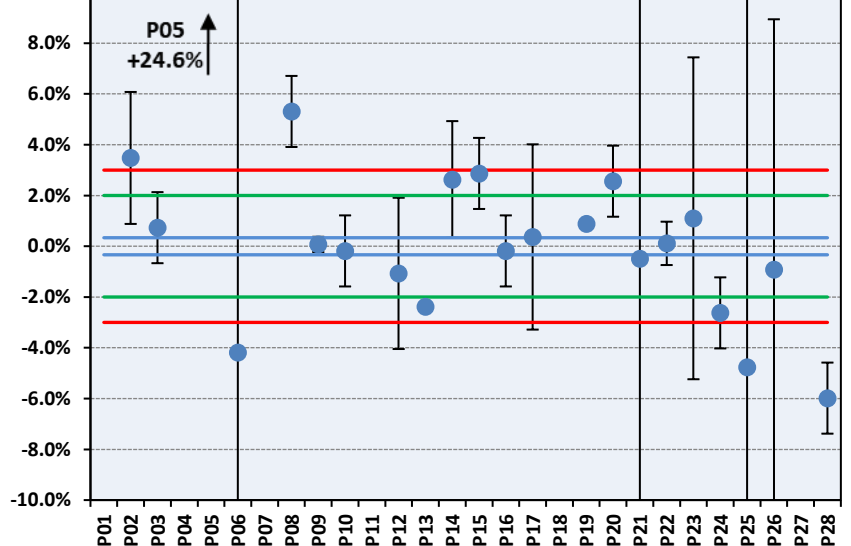
Reference

x_{ref}	$U(x_{ref})$ $k=2$		σ	
2.682	0.011	%mol/mol	0.027	%mol/mol

Reported data

id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01					
P02	2.800	0.070	4.40%	**4.40**	**1.67**
P03	2.790	0.117	4.03%	**4.03**	**0.92**
P04	2.704	0.126	0.83%	**0.83**	**0.18**
P05	2.890	0.191	7.76%	**7.76**	**1.09**
P06	2.516	0.200	-6.19%	**-6.19**	**-0.83**
P07					
P08	2.790	0.117	4.03%	**4.03**	**0.92**
P09					
P10	2.830	0.119	5.52%	**5.52**	**1.24**
P11	2.678	0.017	-0.15%	**-0.15**	**-0.20**
P12	2.806	0.084	4.62%	**4.62**	**1.47**
P13					
P14	2.817	0.065	5.04%	**5.04**	**2.06**
P15	2.450	0.103	-8.65%	**-8.65**	**-2.24**
P16	2.640	0.111	-1.57%	**-1.57**	**-0.38**
P17					
P18					
P19	2.700	0.003	0.67%	**0.67**	**1.56**
P20	2.750	0.116	2.54%	**2.54**	**0.59**
P21	2.662	0.600	-0.75%	**-0.75**	**-0.03**
P22	2.697	0.023	0.57%	**0.57**	**0.60**
P23					
P24	2.820	0.118	5.15%	**5.15**	**1.16**
P25	2.740	0.470	2.16%	**2.16**	**0.12**
P26	2.626	0.900	-2.09%	**-2.09**	**-0.06**
P27					
P28	2.740	0.115	2.16%	**2.16**	**0.50**

Consensus values (raw data)

m	2.726	
s_r	0.019	0.68%
s_L	0.106	3.88%
s_R	0.107	3.94%
p	20	

Consensus values (corrected)

m	2.729	
s_r	0.019	0.68%
s_L	0.103	3.76%
s_R	0.104	3.82%
p	19	

relative difference / %
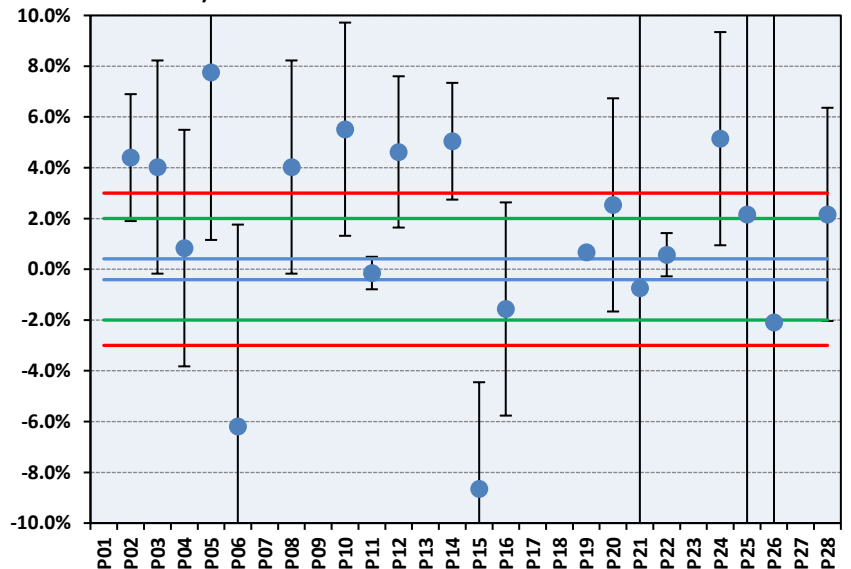
Measurand/ Mixture	nitric oxide (NO/NO2 mix)

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
99.16	0.57	µmol/mol	2.48	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02					
P03	93.50	3.93	-5.71%	-2.28	-1.43
P04					
P05	101.93	3.47	2.80%	1.12	0.79
P06	99.93	14.60	0.78%	0.31	0.05
P07					
P08	99.50	4.18	0.34%	0.14	0.08
P09					
P10	98.30	4.13	-0.87%	-0.35	-0.21
P11					
P12	100.37	1.75	1.22%	0.49	0.66
P13	96.90	1.09	-2.28%	-0.91	-1.84
P14	97.37	2.40	-1.81%	-0.72	-0.73
P15	96.20	4.04	-2.99%	-1.19	-0.73
P16	97.80	4.11	-1.37%	-0.55	-0.33
P17	99.30	6.95	0.14%	0.06	0.02
P18					
P19	101.10	1.87	1.96%	0.78	0.99
P20	93.90	3.94	-5.30%	-2.12	-1.32
P21	100.10	6.00	0.95%	0.38	0.16
P22					
P23					
P24	93.90	3.94	-5.30%	-2.12	-1.32
P25	99.29	6.60	0.13%	0.05	0.02
P26	100.89	10.96	1.74%	0.70	0.16
P27					
P28	104.70	4.40	5.59%	2.23	1.25

Consensus values (raw data)

m	99.51	
s_r	0.45	0.46%
s_L	1.98	1.99%
s_R	2.03	2.04%
p	18	

Consensus values (corrected)

m	99.57	
s_r	0.45	0.46%
s_L	1.89	1.89%
s_R	1.94	1.95%
p	17	

relative difference / %
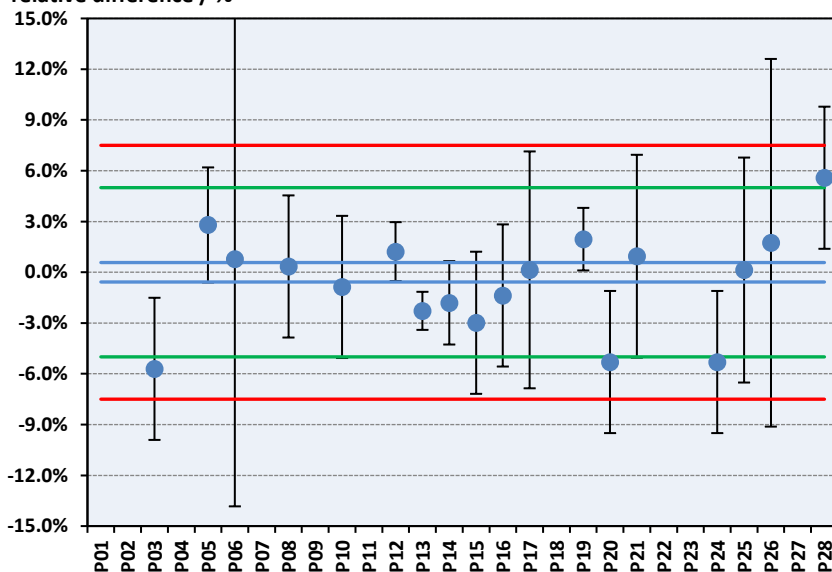
Measurand/ Mixture	nitrogen oxides (NO/NO2 mix)

Reference

x_ref	U(x_ref) k=2		σ	
107.27	0.65	µmol/mol	2.68	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	z-score	E_n-number
P01					
P02					
P03	99.40	4.17	-7.34%	-2.93	-1.86
P04					
P05	108.56	5.10	1.21%	0.48	0.25
P06	111.43	16.30	3.88%	1.55	0.26
P07					
P08	105.20	4.42	-1.93%	-0.77	-0.46
P09					
P10	105.20	4.42	-1.93%	-0.77	-0.46
P11					
P12	110.12	1.92	2.66%	1.06	1.41
P13	105.20	2.05	-1.93%	-0.77	-0.96
P14	107.72	2.30	0.42%	0.17	0.19
P15	99.70	4.19	-7.06%	-2.82	-1.79
P16	107.80	4.53	0.49%	0.20	0.12
P17	108.73	7.61	1.36%	0.54	0.19
P18					
P19	107.40	4.45	0.12%	0.05	0.03
P20	100.00	4.20	-6.78%	-2.71	-1.71
P21	108.96	6.60	1.58%	0.63	0.25
P22					
P23					
P24	103.20	4.33	-3.79%	-1.52	-0.93
P25	109.25	7.26	1.85%	0.74	0.27
P26	109.57	11.77	2.14%	0.86	0.20
P27					
P28	112.80	4.74	5.16%	2.06	1.16

Consensus values (raw data)

m	108.38	
s_r	0.59	0.54%
s_L	2.47	2.28%
s_R	2.54	2.35%
p	18	

Consensus values (corrected)

m	108.65	
s_r	0.59	0.54%
s_L	1.91	1.76%
s_R	2.00	1.84%
p	15	

relative difference / %
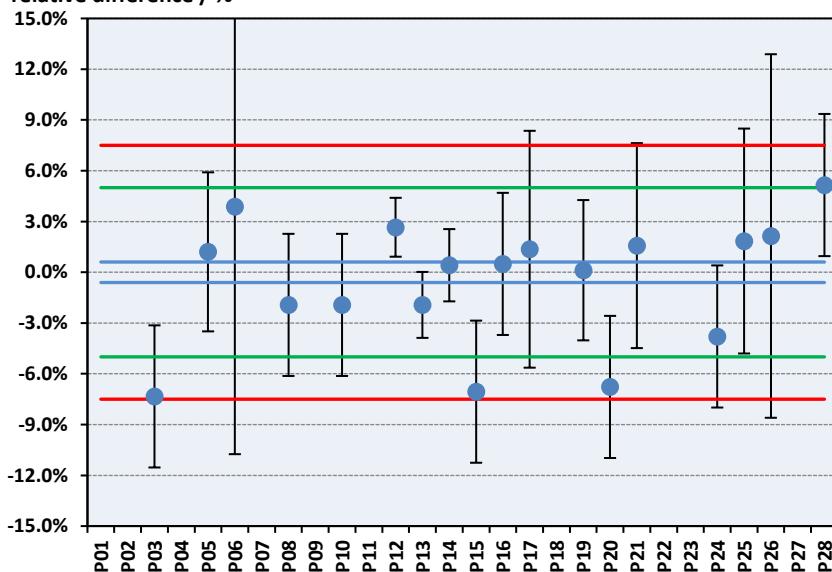
Annex B - Converter efficiency

If the reported nitric oxide (NO) measurement of the NO/NO$_2$ mixture, for each participant, is subtracted from that of their reported nitrogen oxides (NO$_X$) result, then the nitrogen dioxide (NO$_2$) result from their measurements can be directly calculated. This derived NO$_2$ 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$_X$ reported results in quadrature.

Component/ Mixture	nitrogen dioxide (NO2)

Reference

x_{ref}	$U(x_{ref})$ k=2	
8.11	0.86	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	difference (µmol/mol)	converter efficiency (%)	E_n-number
P01					
P02					
P03	5.90	5.73	-2.2	72.7%	-0.38
P04					
P05	6.63	6.17	-1.5	81.8%	-0.24
P06	11.50	21.88	3.4	141.8%	0.15
P07					
P08	5.70	6.08	-2.4	70.3%	-0.39
P09					
P10	6.90	6.05	-1.2	85.1%	-0.20
P11					
P12	9.75	2.59	1.6	120.2%	0.60
P13	8.30	2.32	0.2	102.3%	0.08
P14	10.35	3.32	2.2	127.6%	0.65
P15	3.50	5.82	-4.6	43.2%	-0.78
P16	10.00	6.11	1.9	123.3%	0.31
P17	9.43	10.31	1.3	116.3%	0.13
P18					
P19	6.30	4.83	-1.8	77.7%	-0.37
P20	6.10	5.76	-2.0	75.2%	-0.35
P21	8.86	8.92	0.8	109.2%	0.08
P22					
P23					
P24	9.30	5.86	1.2	114.7%	0.20
P25	9.96	9.81	1.8	122.8%	0.19
P26	8.68	16.08	0.6	107.0%	0.04
P27					
P28	8.10	6.46	0.0	99.9%	0.00

For appropriate measurement of nitrogen dioxide by the conversion of NO$_2$ 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). Seven (7) participants failed to demonstrate converter efficiencies above this 95% expectation.