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UKAS PROFICIENCY TESTING
4719

Stack Emissions Proficiency Testing Scheme (SEPTS)

Presentation of Results

Round 2016

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	15.06.2016	Dr Gavin Squire	***Final report (for comment)***

Statement of Confidentiality

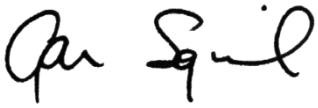
EffecTech keeps all data regarding the performance of individual participants strictly confidential. Results and performance data are protected, stored and backed up on storage network disks and folders to which access is restricted to the scheme coordinator and the technical authority only.

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 2016 (May - June 2016).

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 x 10^{-6} mol/mol
10 %mol/mol is equivalent to 10 dmol/mol is equivalent to 10 x 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 fifteen (15) laboratories signed up to participate in this round. Fourteen (14) 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 propane which was calibrated using a single-point through origin calibration (SPO). Both of these calibration methods are in accordance with ISO/DIS 12963 for which EffecTech is accredited to ISO 17025 by UKAS.

Every single decant mixtures was calibrated by a single point exact matching technique (SPEM) also in accordance with ISO/DIS 12963 by the comparison of the decant mixture with its nominally identical parent mixtures. 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 and TM025). 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. Parent mixtures are calibrated by comparison with reference gas mixtures generated dynamically in accordance with ISO 6145-7. In-house primary reference gas mixtures (PRGM) are used for blending which are traceable by verification to the National Physical Laboratory (NPL, UK). 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	53.72	1.06	1.00	1.00	<0.01
propane	µmol/mol	8.917	0.057	0.32	0.32	<0.01
nitric oxide	µmol/mol	190.22	1.04	0.18	0.18	0.03
carbon monoxide	µmol/mol	177.2	1.6	0.20	0.20	0.01
oxygen	%mol/mol	13.673	0.075	0.087	0.086	0.014
carbon dioxide	%mol/mol	8.202	0.027	0.136	0.136	0.003
nitric oxide (NO/NO_2 mix)	µmol/mol	95.24	0.83	0.44	0.36	0.25
nitrogen oxides (NO/NO_2 mix)	µmol/mol	122.74	0.94	0.38	0.37	0.11

3. Results

3.1 Reported results

There were fifteen (15) 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 table below shows 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	✓	✓	✓	✓			✓	✓

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	✓	✓			✓	✓	✓	✓

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

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

where x_{meas} is the measured result reported by the laboratory
x_{ref} is the assigned reference value and
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

$$\sigma = \frac{S_{PT}}{100} . x_{ref} \quad (2)$$

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. These values have been chosen with reference to relevant CEN standards, the Waste Incineration Directive (WID) and the Large Combustion Plant Directive (LCPD). These are given in the tables below.

Table 4: Standard deviation for performance assessment

measurand	S_{PT} (mol/mol)
sulphur dioxide	5.0 % relative
propane	7.5 % relative
nitric oxide	5.0 % relative
carbon monoxide	3.0 % relative
oxygen	2.0 % relative
carbon dioxide	2.0 % relative
nitric oxide (NO/NO2 mix)	5.0 % relative
nitrogen oxides (NO/NO2 mix)	5.0 % 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
$\|\boldsymbol{z}\| \leq 2$	**satisfactory result**
$2 < \|\boldsymbol{z}\| < 3$	**questionable result**
$\|\boldsymbol{z}\| \geq 3$	**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

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

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

z-score	quality of result
$\lvert E_n \rvert \leq 1$	**satisfactory result**
$\lvert E_n \rvert > 1$	**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								
P02	-0.53	-2.12	-0.58	-0.30	0.14	0.48	-0.72	-1.42
P03				0.27	0.17	0.46	-1.22	-0.80
P04	0.37			-0.02	-0.14	0.09		
P05	-0.43		0.13	0.08		-0.17	0.37	0.31
P06		0.07	0.12	0.18	0.13		0.04	0.18
P07			0.08	0.42	1.00	-0.87	-0.82	-1.42
P08	0.19	-0.10	0.11	-0.04	0.25	0.17	0.06	0.28
P09			-0.66					
P10		0.06	0.04	0.29	-0.83	-0.16	-0.18	0.06
P11	0.93		0.38	0.25	1.64	0.15	0.74	-0.14
P12	0.78	0.17	-0.05	0.05	0.18	-0.49		
P13	-0.02	-0.80	-0.01	0.31	0.10	0.48	-0.14	-1.04
P14	2.34	2.86	0.71	0.09				
P15	-0.60	0.93		0.08	-0.05		0.56	0.09

These results show an excellent performance from the pool of participants, with the majority of results reported with a satisfactory **z**-score.

Participant **P02** reported a questionable results for the propane measurand as did participant **P14** for both the propane and the sulphur dioxide measurement.

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								
P02	-0.52	-1.68	-0.45	-0.20	0.06	0.15	-0.56	-1.20
P03				0.20	0.07	0.23	-1.27	-0.83
P04	0.79			-0.05	-0.37	0.37		
P05	-0.69		0.23	0.08		-0.14	0.65	0.50
P06		0.30	0.66	0.38	0.18		0.12	0.75
P07			0.06	0.23	0.40	-0.37	-0.59	-1.07
P08	0.18	-0.52	0.27	-0.05	0.35	0.11	0.07	0.24
P09			-3.15					
P10		0.17	0.07	0.32	-0.84	-0.13	-0.32	0.12
P11	0.62		0.38	0.16	0.96	0.06	0.50	-0.11
P12	1.29	0.07	-0.07	0.04	0.12	-0.31		
P13	-0.01	-0.64	0.00	0.11	0.09	0.71	-0.09	-0.65
P14	5.89	2.30	2.78	0.19				
P15	-0.79	1.29		0.08	-0.03		1.03	0.16

Laboratories **P03, P07, P09, P12** and **P15** scored perfectly on the basis of ***z***-scores but failed on one or more components on the basis of E_n-numbers. These laboratories underestimated their uncertainties for failing components.

Laboratories **P04**, **P05**, **P06, P08, P10, P11** and **P13** all reported excellent results with perfect scores on the basis of both performance measures.

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	
53.72	1.06	µmol/mol	2.69	µmol/mol

Reported data

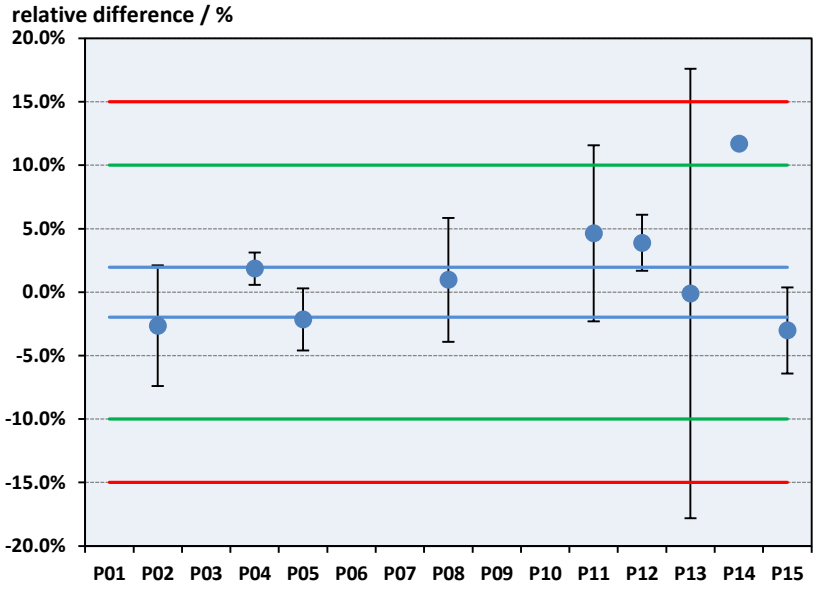
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	z-score	E_n-number
P01					
P02	52.30	2.49	-2.64%	-0.53	-0.52
P03					
P04	54.72	0.69	1.85%	0.37	0.79
P05	52.56	1.29	-2.15%	-0.43	-0.69
P06					
P07					
P08	54.24	2.65	0.97%	0.19	0.18
P09					
P10					
P11	56.21	3.90	4.64%	0.93	0.62
P12	55.81	1.23	3.89%	0.78	1.29
P13	53.66	9.50	-0.11%	-0.02	-0.01
P14	60.00	0.12	11.69%	2.34	5.89
P15	52.10	1.77	-3.02%	-0.60	-0.79

Consensus values (raw data)

m	54.66	
s_r	0.36	0.66%
s_L	2.82	5.17%
s_R	2.85	5.21%
p	9	

Consensus values (corrected)

m	53.80	
s_r	0.39	0.73%
s_L	1.78	3.31%
s_R	1.82	3.38%
p	8	



Measurand/ Mixture propane

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
8.917	0.057	µmol/mol	0.669	µmol/mol

Reported data

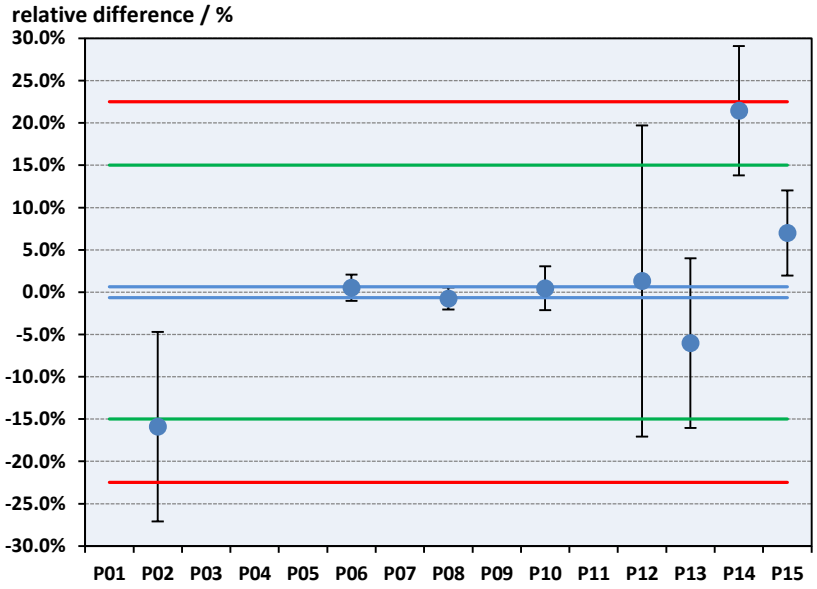
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	z-score	E_n-number
P01					
P02	7.500	0.840	-15.89%	-2.12	-1.68
P03					
P04					
P05					
P06	8.963	0.140	0.52%	0.07	0.30
P07					
P08	8.850	0.115	-0.75%	-0.10	-0.52
P09					
P10	8.958	0.232	0.46%	0.06	0.17
P11					
P12	9.034	1.660	1.31%	0.17	0.07
P13	8.380	0.840	-6.02%	-0.80	-0.64
P14	10.830	0.828	21.45%	2.86	2.30
P15	9.539	0.480	6.98%	0.93	1.29

Consensus values (raw data)

m	9.027	
s_r	0.069	0.77%
s_L	1.013	11.22%
s_R	1.015	11.25%
p	8	

Consensus values (corrected)

m	9.027	
s_r	0.069	0.77%
s_L	1.013	11.22%
s_R	1.015	11.25%
p	8	



Measurand/ Mixture	nitric oxide

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	190.22	1.04	µmol/mol	9.51	µmol/mol

Reported data

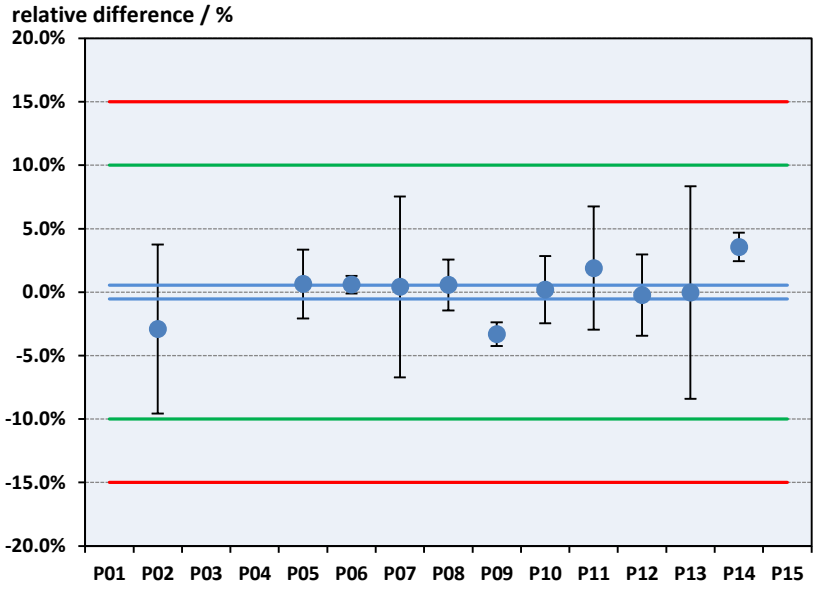
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	z-score	E_n-number
P01					
P02	184.70	12.29	-2.90%	-0.58	-0.45
P03					
P04					
P05	191.45	5.20	0.65%	0.13	0.23
P06	191.34	1.33	0.59%	0.12	0.66
P07	191.01	13.60	0.42%	0.08	0.06
P08	191.30	3.83	0.57%	0.11	0.27
P09	183.91	1.71	-3.32%	-0.66	-3.15
P10	190.58	5.04	0.19%	0.04	0.07
P11	193.83	9.40	1.90%	0.38	0.38
P12	189.77	6.08	-0.23%	-0.05	-0.07
P13	190.17	15.92	-0.03%	-0.01	0.00
P14	197.00	2.21	3.56%	0.71	2.78
P15					

Consensus values (raw data)

m	190.39	
s_r	0.58	0.31%
s_L	3.81	2.00%
s_R	3.86	2.03%
p	11	

Consensus values (corrected)

m	190.39	
s_r	0.58	0.31%
s_L	3.81	2.00%
s_R	3.86	2.03%
p	11	



Measurand/ Mixture	carbon monoxide

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	177.2	1.6	µmol/mol	5.3	µmol/mol

Reported data

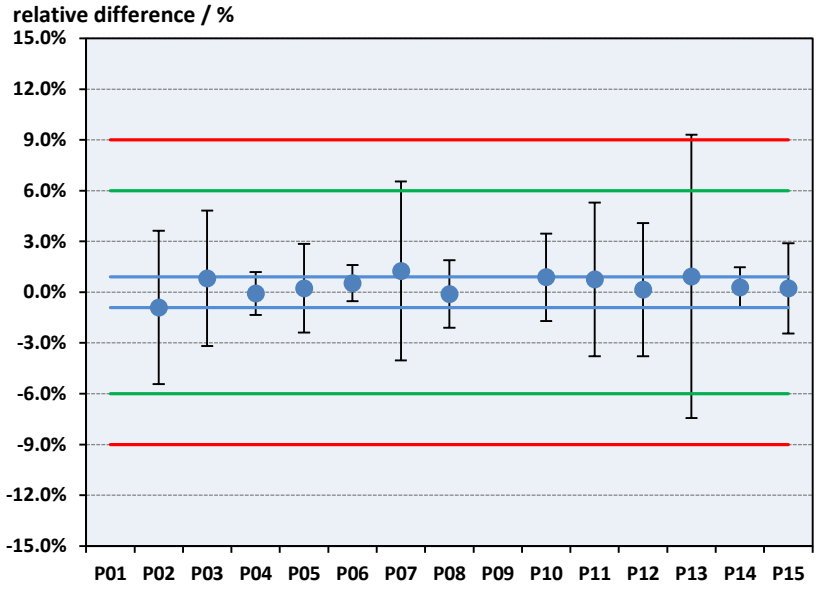
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	z-score	E_n-number
P01					
P02	175.6	8.0	-0.90%	-0.30	-0.20
P03	178.7	7.1	0.82%	0.27	0.20
P04	177.1	2.2	-0.07%	-0.02	-0.05
P05	177.6	4.7	0.23%	0.08	0.08
P06	178.1	1.9	0.53%	0.18	0.38
P07	179.4	9.5	1.25%	0.42	0.23
P08	177.0	3.5	-0.11%	-0.04	-0.05
P09					
P10	178.8	4.6	0.88%	0.29	0.32
P11	178.5	8.1	0.76%	0.25	0.16
P12	177.5	7.0	0.15%	0.05	0.04
P13	178.8	15.0	0.93%	0.31	0.11
P14	177.7	2.1	0.28%	0.09	0.19
P15	177.6	4.7	0.23%	0.08	0.08

Consensus values (raw data)

m	178.0	
s_r	0.4	0.24%
s_L	1.0	0.57%
s_R	1.1	0.62%
p	13	

Consensus values (corrected)

m	178.2	
s_r	0.4	0.24%
s_L	0.7	0.38%
s_R	0.8	0.45%
p	12	



Measurand/ Mixture	oxygen

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	13.673	0.075	%mol/mol	0.273	%mol/mol

Reported data

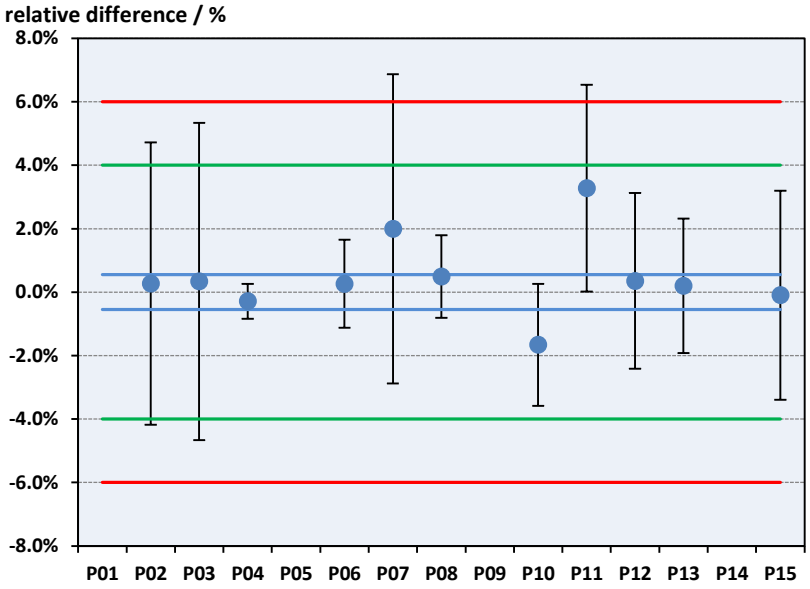
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	z-score	E_n-number
P01					
P02	13.710	0.610	0.27%	**0.14**	**0.06**
P03	13.719	0.686	0.34%	**0.17**	**0.07**
P04	13.634	0.075	-0.29%	**-0.14**	**-0.37**
P05					
P06	13.709	0.190	0.26%	**0.13**	**0.18**
P07	13.946	0.680	2.00%	**1.00**	**0.40**
P08	13.740	0.179	0.49%	**0.25**	**0.35**
P09					
P10	13.446	0.259	-1.66%	**-0.83**	**-0.84**
P11	14.121	0.460	3.28%	**1.64**	**0.96**
P12	13.721	0.380	0.35%	**0.18**	**0.12**
P13	13.700	0.290	0.20%	**0.10**	**0.09**
P14					
P15	13.660	0.450	-0.10%	**-0.05**	**-0.03**

Consensus values (raw data)

m	13.748	
s_r	0.008	0.06%
s_L	0.191	1.39%
s_R	0.191	1.39%
p	11	

Consensus values (corrected)

m	13.700	
s_r	0.007	0.05%
s_L	0.137	1.00%
s_R	0.137	1.00%
p	10	



Measurand/ Mixture	carbon dioxide

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	8.202	0.027	%mol/mol	0.164	%mol/mol

Reported data

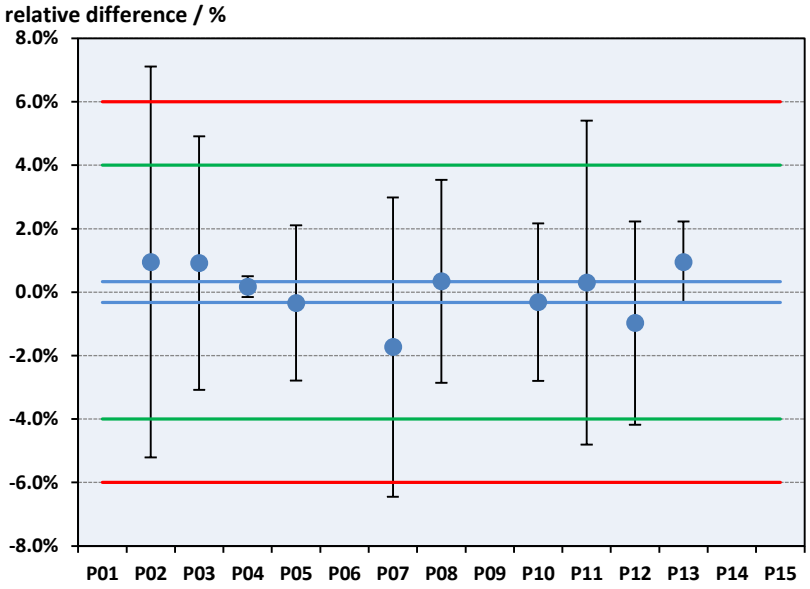
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	z-score	E_n-number
P01					
P02	8.280	0.510	0.95%	0.48	0.15
P03	8.277	0.331	0.92%	0.46	0.23
P04	8.216	0.027	0.17%	0.09	0.37
P05	8.174	0.200	-0.34%	-0.17	-0.14
P06					
P07	8.060	0.380	-1.73%	-0.87	-0.37
P08	8.230	0.263	0.34%	0.17	0.11
P09					
P10	8.176	0.203	-0.32%	-0.16	-0.13
P11	8.227	0.420	0.30%	0.15	0.06
P12	8.122	0.260	-0.98%	-0.49	-0.31
P13	8.280	0.106	0.95%	0.48	0.71
P14					
P15					

Consensus values (raw data)

m	8.196	
s_r	0.017	0.21%
s_L	0.080	0.98%
s_R	0.082	1.00%
p	10	

Consensus values (corrected)

m	8.196	
s_r	0.017	0.21%
s_L	0.080	0.98%
s_R	0.082	1.00%
p	10	



Measurand/ Mixture	nitric oxide (NO/NO2 mix)

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
95.24	0.83	µmol/mol	4.76	µmol/mol

Reported data

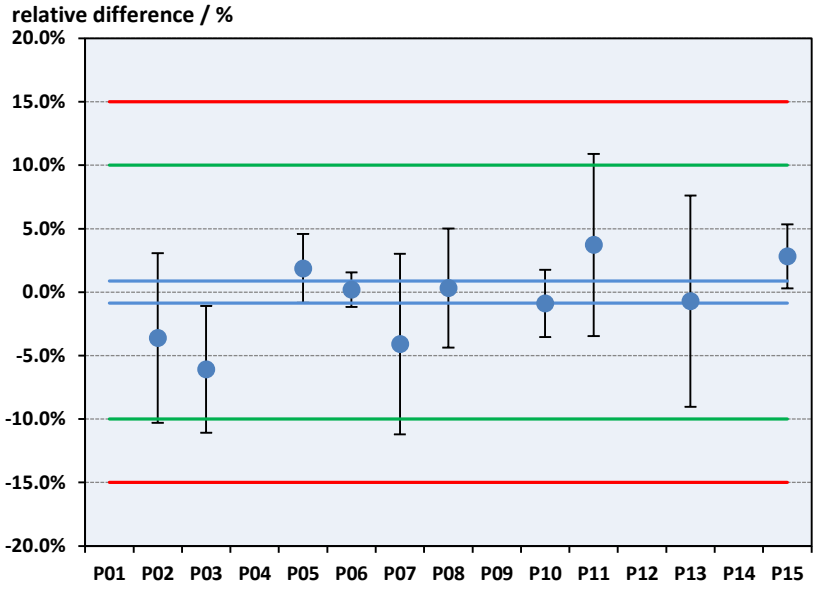
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	z-score	E_n-number
P01					
P02	91.80	6.14	-3.61%	-0.72	-0.56
P03	89.45	4.47	-6.08%	-1.22	-1.27
P04					
P05	97.02	2.63	1.87%	0.37	0.65
P06	95.43	1.30	0.20%	0.04	0.12
P07	91.35	6.50	-4.08%	-0.82	-0.59
P08	95.54	4.48	0.31%	0.06	0.07
P09					
P10	94.40	2.50	-0.88%	-0.18	-0.32
P11	98.78	7.10	3.72%	0.74	0.50
P12					
P13	94.56	7.87	-0.71%	-0.14	-0.09
P14					
P15	97.93	2.47	2.82%	0.56	1.03

Consensus values (raw data)

m	94.77	
s_r	0.39	0.41%
s_L	2.99	3.15%
s_R	3.02	3.18%
p	10	

Consensus values (corrected)

m	94.77	
s_r	0.39	0.41%
s_L	2.99	3.15%
s_R	3.02	3.18%
p	10	



Measurand/ Mixture	nitrogen oxides (NO/NO2 mix)

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
122.74	0.94	µmol/mol	6.14	µmol/mol

Reported data

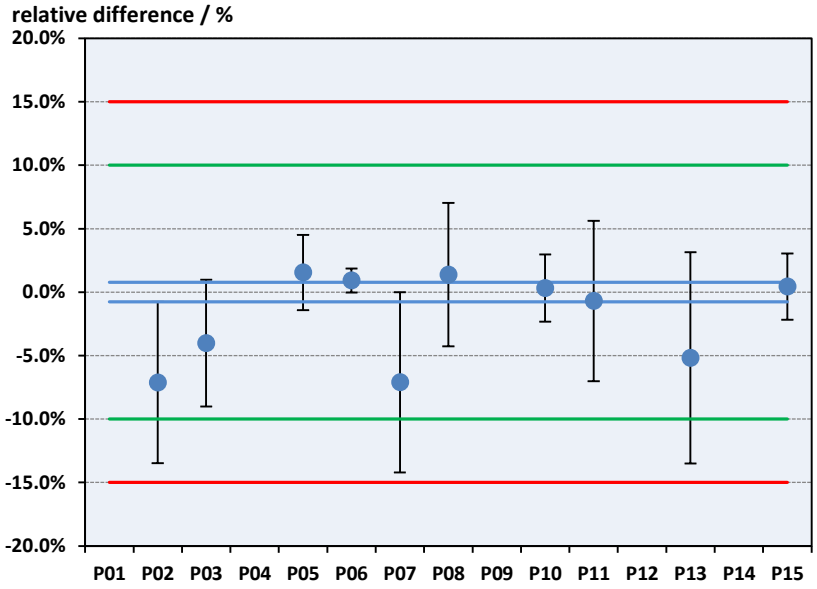
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	z-score	E_n-number
P01					
P02	114.00	7.25	-7.12%	-1.42	-1.20
P03	117.81	5.89	-4.02%	-0.80	-0.83
P04					
P05	124.64	3.69	1.55%	0.31	0.50
P06	123.87	1.17	0.92%	0.18	0.75
P07	114.03	8.10	-7.10%	-1.42	-1.07
P08	124.44	7.03	1.39%	0.28	0.24
P09					
P10	123.13	3.26	0.32%	0.06	0.12
P11	121.89	7.70	-0.69%	-0.14	-0.11
P12					
P13	116.38	9.68	-5.18%	-1.04	-0.65
P14					
P15	123.28	3.23	0.44%	0.09	0.16

Consensus values (raw data)

m	120.04	
s_r	0.44	0.37%
s_L	4.40	3.67%
s_R	4.43	3.69%
p	10	

Consensus values (corrected)

m	120.04	
s_r	0.44	0.37%
s_L	4.40	3.67%
s_R	4.43	3.69%
p	10	



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	
	27.5	1.3	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	difference (µmol/mol)	converter efficiency (%)	E_n-number
P01					
P02	22.2	9.5	-5.3	**80.7%**	**-0.55**
P03	28.4	7.4	0.9	**103.1%**	**0.11**
P04					
P05	27.6	4.5	0.1	**100.4%**	**0.03**
P06	28.4	1.7	0.9	**103.4%**	**0.44**
P07	22.7	10.4	-4.8	**82.5%**	**-0.46**
P08	28.9	8.3	1.4	**105.1%**	**0.17**
P09					
P10	28.7	4.1	1.2	**104.5%**	**0.29**
P11	23.1	10.5	-4.4	**84.0%**	**-0.42**
P12					
P13	21.8	12.5	-5.7	**79.3%**	**-0.45**
P14					
P15	25.4	4.1	-2.1	**92.2%**	**-0.51**

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). Five (5) participants failed to demonstrate converter efficiencies above this 95% expectation.