EffecTech
Global Leaders in Gas Measurement

UKAS PROFICIENCY TESTING
4719

Stack Emissions Proficiency Testing Scheme (SEPTS)

Presentation of Results

Round 2021

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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Table of Contents

Revisions History

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1	19.08.2021	Dr Gavin Squire	***Final report (for comment)***

Statement of Confidentiality

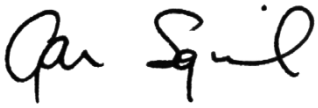
EffecTech keeps all data regarding the performance of individual participants strictly confidential. Results and performance data are protected, stored and backed up on storage network disks and folders to which access is restricted to the scheme coordinator and the technical authority only.

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 2021 (June - July 2021).

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 twenty-five (25) laboratories signed up to participate in this round. Twenty-three (23) 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 6142-1:2015. 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 or 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.

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_{ref}	$U(x_{ref})$	u_c / %	u_{char} / %	u_{bb} / %
sulphur dioxide	µmol/mol	238.5	1.6	0.32	0.32	0.048
propane	µmol/mol	42.69	0.36	0.36	0.36	0.079
nitric oxide	µmol/mol	418.2	1.8	0.13	0.13	0.036
carbon monoxide	µmol/mol	114.20	0.91	0.38	0.38	0.029
oxygen	%mol/mol	4.814	0.029	0.091	0.090	0.010
carbon dioxide	%mol/mol	3.427	0.019	0.13	0.12	0.035
nitric oxide (NO/NO2 mix)	µmol/mol	66.09	0.48	0.36	0.31	0.19
nitrogen oxides (NO/NO2 mix)	µmol/mol	76.9	1.1	0.74	0.74	0.081

3. Results

3.1 Reported results

There were twenty-five (25) 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	✓	✓	✓	✓	✓	✓	✓	✓

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	✓	✓	✓	✓	✓	✓	✓	✓

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 with the exception of participants **P10, P11** and **P12** for which no E_n numbers could be calculated.

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 contributions $S_{PT,rel}$ and $S_{PT,abs}$ by

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

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 (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
$\|\boldsymbol{z}\| \leq 2$	**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

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								
P02	0.62				0.53	-0.80		
P03	0.70	0.00	-0.15	0.70	0.89	-0.07	-1.97	-2.97
P04							0.25	0.43
P05	0.46	-0.15	0.28	-2.10	1.07	-0.70	0.68	0.00
P06	0.08	-0.71	0.61	0.19	0.62	-1.81	-0.72	-1.32
P07	0.41	0.10	0.33	0.61	0.37	-1.83	-0.87	-1.03
P08	-0.63	-0.54	-3.16	-2.20	-0.50	0.16	-0.10	-1.64
P09	0.00	-0.26	0.06	0.53	0.10	-0.18	-1.14	-0.87
P10		-0.21		0.99	3.37	-3.32	0.79	0.05
P11	-2.75	-12.97		1.40	-1.32		-2.05	-2.45
P12	0.13	0.32		2.55		-3.77	0.52	0.52
P13		0.43			-0.24			
P14	5.53	2.65		2.39	0.02	3.68	-3.04	-5.00
P15	0.09	-0.11	0.17	0.31	0.55			
P16				0.31	0.51	0.66	-1.50	-1.65
P17				0.52	1.95		-0.75	0.44
P18	1.00	0.06	0.29	1.30	0.58	-0.37	-0.90	-0.89
P19	3.48	1.29	1.15	0.61	-0.21	4.43	-0.13	0.93
P20								
P21					0.45	0.75		
P22	-0.72	-0.09		0.10	0.45	-0.05	0.05	0.35
P23	-3.15	-1.86	-0.98	-8.12	2.20	-18.68	1.25	0.18
P24	-1.42	-0.92	0.01	1.45	0.46	-0.32	-0.90	-2.28
P25	-1.03	1.08	0.02	0.42	0.83	-1.31	-1.03	-2.24

These results show a mixed performance from the pool of participants. Measurements of all components was generally good.

However, participant **P23** reported anomalously low measurements for sulphur dioxide, carbon monoxide and carbon dioxide.

Participant **P14** struggled with the majority of the measurements with only oxygen reported with a satisfactory amount fraction.

Participant **P11** struggled with the measurement of propane.

Twelve (12) laboratories (**P02**, **P04**, **P06**, **P07**, **P09**, **P13**, **P15**, **P16**, **P17**, **P18**, **P21**, and **P22**) achieved a 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

participant id	sulphur dioxide	propane	nitric oxide	carbon monoxide	oxygen	carbon dioxide	nitric oxide (NO/NO2 mix)	nitrogen oxides (NO/NO2 mix)
P01								
P02	0.20				0.15	-0.20		
P03	0.40	-0.01	-0.06	0.35	1.55	-0.15	-0.71	-1.12
P04							0.20	0.32
P05	0.28	-0.19	0.17	-0.90	2.10	-1.54	0.40	0.00
P06	0.09	-1.61	1.12	0.15	1.23	-4.15	-1.08	-1.64
P07	0.28	0.09	0.23	0.15	0.07	-0.15	-0.23	-0.27
P08	-0.12	-0.70	-1.53	-0.21	-0.05	0.01	-0.04	-0.74
P09	0.00	-0.53	0.04	0.13	0.16	-0.32	-0.44	-0.33
P10								
P11								
P12								
P13		0.42			-0.06			
P14	4.36	5.44		2.93	0.02	5.94	-0.94	-1.61
P15	0.13	-0.39	0.28	0.21	1.05			
P16				0.22	0.26	0.36	-1.01	-1.24
P17				0.26	0.32		-0.22	0.18
P18	0.67	0.06	0.21	0.36	0.11	-0.03	-0.25	-0.24
P19	1.73	1.28	1.56	0.20	-0.06	0.70	-0.13	1.01
P20								
P21					0.85	1.63		
P22	-0.42	-0.05		0.04	0.16	-0.01	0.03	0.15
P23	-0.61	-2.56	-0.45	-0.87	0.23	-1.45	0.54	0.08
P24	-1.29	-1.43	0.01	0.73	0.24	-0.12	-0.60	-1.48
P25	-0.86	1.51	0.02	0.21	0.42	-0.50	-0.69	-1.45

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 **P07, P09, P17, P18** & **P22** 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, P09** & **P18** 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	
238.5	1.6	µmol/mol	6.0	µmol/mol

Reported data

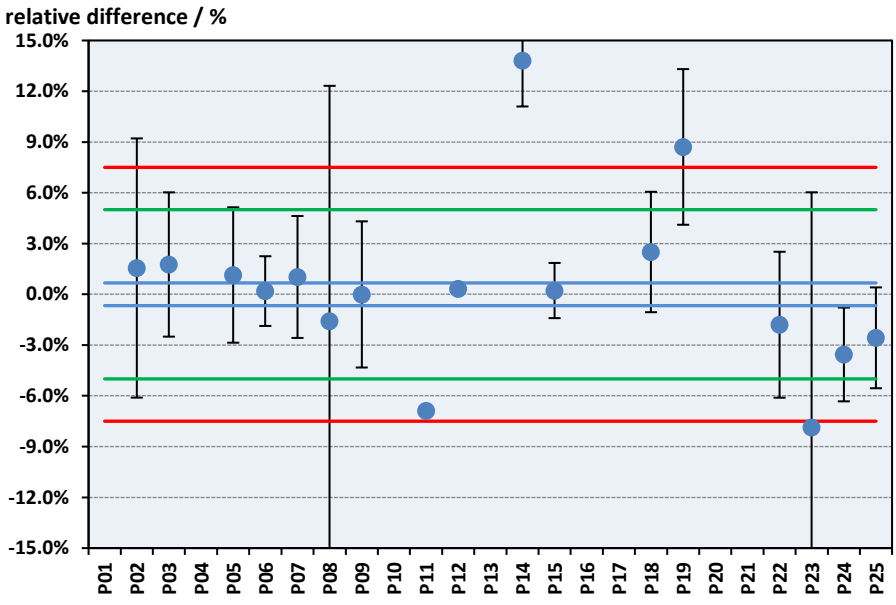
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02	242.2	18.6	1.55%	0.62	0.20
P03	242.7	10.3	1.76%	0.70	0.40
P04					
P05	241.2	9.7	1.14%	0.46	0.28
P06	239.0	4.9	0.19%	0.08	0.09
P07	240.9	8.7	1.02%	0.41	0.28
P08	234.7	32.6	-1.58%	-0.63	-0.12
P09	238.5	10.3	-0.01%	0.00	0.00
P10					
P11	222.1		-6.88%	-2.75	
P12	239.3		0.33%	0.13	
P13					
P14	271.5	7.4	13.82%	5.53	4.36
P15	239.0	3.9	0.22%	0.09	0.13
P16					
P17					
P18	244.5	8.7	2.50%	1.00	0.67
P19	259.3	11.9	8.71%	3.48	1.73
P20					
P21					
P22	234.2	10.1	-1.80%	-0.72	-0.42
P23	219.7	30.5	-7.87%	-3.15	-0.61
P24	230.0	6.4	-3.56%	-1.42	-1.29
P25	232.4	6.9	-2.57%	-1.03	-0.86

Consensus values (raw data)

m	239.3	
s_r	3.1	1.30%
s_L	12.8	5.35%
s_R	13.2	5.51%
p	17	

Consensus values (corrected)

m	237.0	
s_r	0.6	0.24%
s_L	9.6	4.07%
s_R	9.7	4.08%
p	16	



Measurand/ Mixture	propane

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	42.69	0.36	µmol/mol	2.13	µmol/mol

Reported data

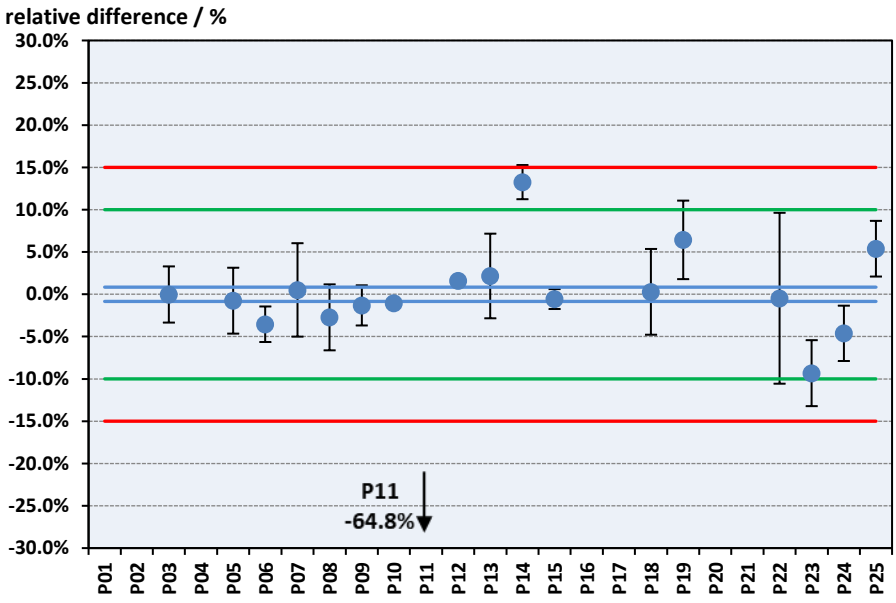
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02					
P03	42.68	1.42	-0.02%	0.00	-0.01
P04					
P05	42.37	1.65	-0.75%	-0.15	-0.19
P06	41.18	0.86	-3.54%	-0.71	-1.61
P07	42.91	2.37	0.52%	0.10	0.09
P08	41.53	1.62	-2.72%	-0.54	-0.70
P09	42.13	1.00	-1.31%	-0.26	-0.53
P10	42.25		-1.03%	-0.21	
P11	15.01		-64.84%	-12.97	
P12	43.37		1.59%	0.32	
P13	43.61	2.18	2.16%	0.43	0.42
P14	48.35	0.98	13.26%	2.65	5.44
P15	42.45	0.50	-0.56%	-0.11	-0.39
P16					
P17					
P18	42.81	2.17	0.29%	0.06	0.06
P19	45.44	2.11	6.43%	1.29	1.28
P20					
P21					
P22	42.49	4.29	-0.47%	-0.09	-0.05
P23	38.71	1.51	-9.32%	-1.86	-2.56
P24	40.72	1.33	-4.61%	-0.92	-1.43
P25	44.99	1.48	5.39%	1.08	1.51

Consensus values (raw data)

m	41.00	
s_r	0.29	0.70%
s_L	7.43	18.13%
s_R	7.44	18.14%
p	18	

Consensus values (corrected)

m	42.82	
s_r	0.26	0.61%
s_L	2.28	5.32%
s_R	2.29	5.36%
p	17	



Measurand/ Mixture

nitric oxide

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
418.2	1.8	µmol/mol	10.5	µmol/mol

Reported data

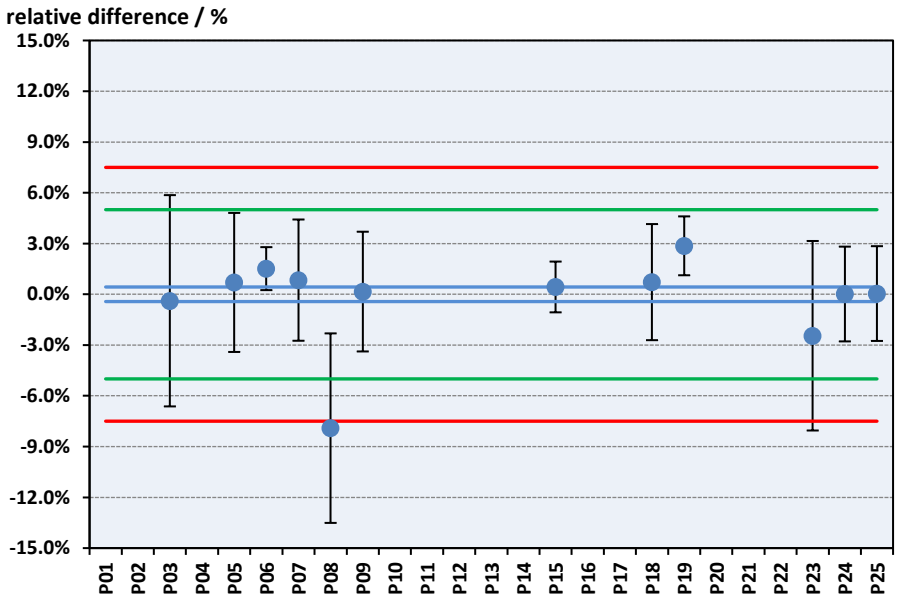
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02					
P03	416.6	26.0	-0.38%	-0.15	-0.06
P04					
P05	421.1	17.3	0.70%	0.28	0.17
P06	424.5	5.4	1.52%	0.61	1.12
P07	421.7	15.1	0.84%	0.33	0.23
P08	385.1	21.6	-7.91%	-3.16	-1.53
P09	418.9	14.8	0.16%	0.06	0.04
P10					
P11					
P12					
P13					
P14					
P15	420.0	6.3	0.43%	0.17	0.28
P16					
P17					
P18	421.2	14.5	0.72%	0.29	0.21
P19	430.2	7.5	2.86%	1.15	1.56
P20					
P21					
P22					
P23	408.0	22.8	-2.45%	-0.98	-0.45
P24	418.3	11.7	0.02%	0.01	0.01
P25	418.4	11.7	0.04%	0.02	0.02

Consensus values (raw data)

m	416.6	
s_r	0.6	0.14%
s_L	11.7	2.81%
s_R	11.7	2.82%
p	12	

Consensus values (corrected)

m	419.7	
s_r	0.6	0.13%
s_L	5.7	1.35%
s_R	5.7	1.36%
p	11	



Measurand/ Mixture: carbon monoxide

Reference

x_{ref}	U(x_{ref}) k=2		σ	
114.20	0.91	µmol/mol	1.71	µmol/mol

Reported data

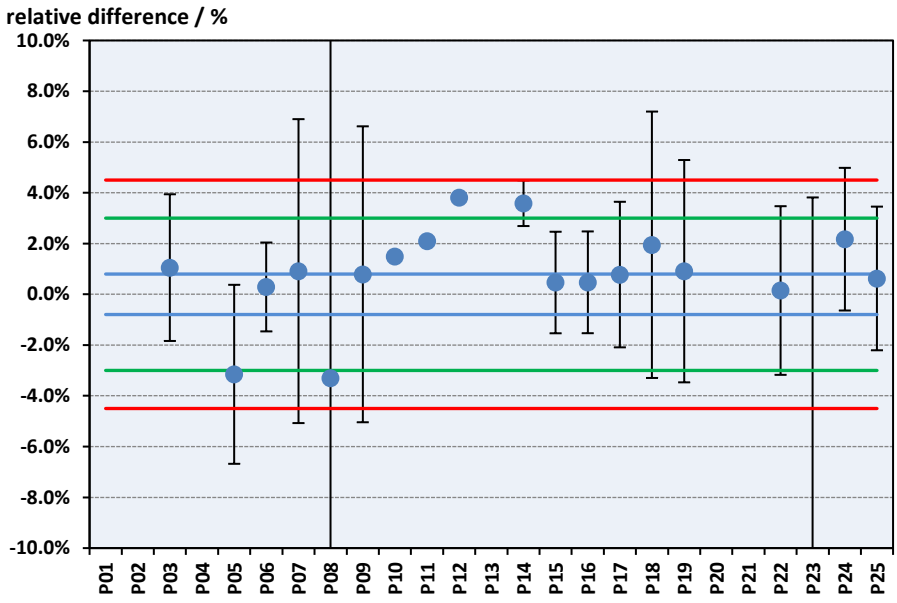
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02					
P03	115.40	3.33	1.05%	0.70	0.35
P04					
P05	110.60	3.90	-3.15%	-2.10	-0.90
P06	114.53	2.00	0.29%	0.19	0.15
P07	115.24	6.90	0.91%	0.61	0.15
P08	110.43	17.67	-3.30%	-2.20	-0.21
P09	115.10	6.71	0.79%	0.53	0.13
P10	115.90		1.49%	0.99	
P11	116.60		2.10%	1.40	
P12	118.56		3.82%	2.55	
P13					
P14	118.30	1.06	3.59%	2.39	2.93
P15	114.73	2.29	0.46%	0.31	0.21
P16	114.74	2.30	0.47%	0.31	0.22
P17	115.09	3.30	0.78%	0.52	0.26
P18	116.43	6.11	1.95%	1.30	0.36
P19	115.24	5.05	0.91%	0.61	0.20
P20					
P21					
P22	114.37	3.80	0.15%	0.10	0.04
P23	100.29	16.05	-12.18%	-8.12	-0.87
P24	116.68	3.28	2.17%	1.45	0.73
P25	114.91	3.25	0.62%	0.42	0.21

Consensus values (raw data)

m	113.97	
s_r	0.32	0.28%
s_L	4.12	3.62%
s_R	4.13	3.63%
p	19	

Consensus values (corrected)

m	114.87	
s_r	0.33	0.28%
s_L	2.04	1.78%
s_R	2.07	1.80%
p	18	



Measurand/ Mixture	oxygen

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
4.814	0.029	%mol/mol	0.058	%mol/mol

Reported data

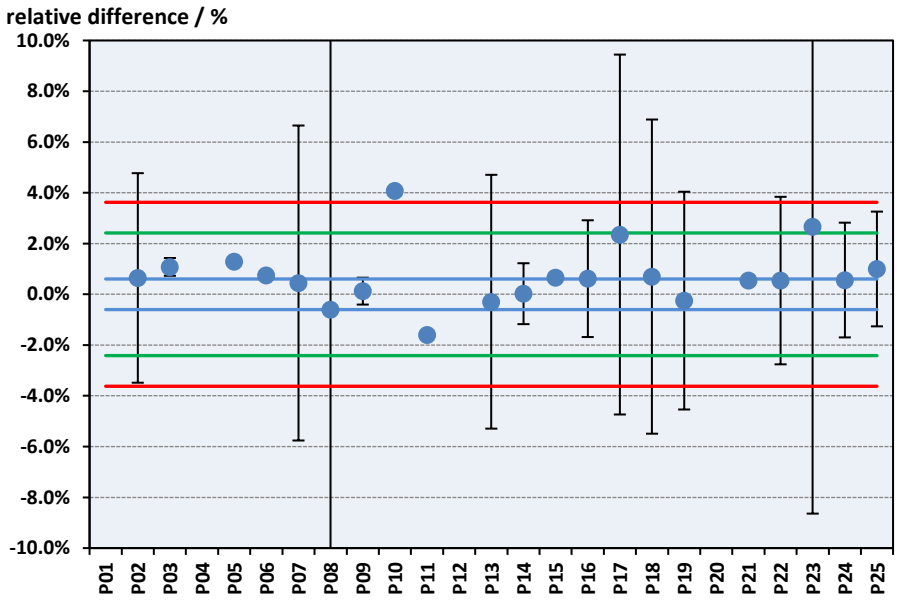
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01					
P02	4.845	0.200	0.64%	0.53	0.15
P03	4.866	0.017	1.08%	0.89	1.55
P04					
P05	4.876	0.005	1.29%	1.07	2.10
P06	4.850	0.004	0.75%	0.62	1.23
P07	4.835	0.300	0.44%	0.37	0.07
P08	4.785	0.541	-0.60%	-0.50	-0.05
P09	4.820	0.026	0.12%	0.10	0.16
P10	5.010		4.07%	3.37	
P11	4.737		-1.60%	-1.32	
P12					
P13	4.800	0.240	-0.29%	-0.24	-0.06
P14	4.815	0.058	0.02%	0.02	0.02
P15	4.846	0.010	0.66%	0.55	1.05
P16	4.844	0.111	0.62%	0.51	0.26
P17	4.927	0.349	2.35%	1.95	0.32
P18	4.848	0.300	0.70%	0.58	0.11
P19	4.802	0.206	-0.25%	-0.21	-0.06
P20					
P21	4.840	0.010	0.54%	0.45	0.85
P22	4.840	0.160	0.54%	0.45	0.16
P23	4.942	0.558	2.66%	2.20	0.23
P24	4.841	0.109	0.56%	0.46	0.24
P25	4.862	0.110	1.00%	0.83	0.42

Consensus values (raw data)

m	4.842	
s_r	0.035	0.71%
s_L	0.046	0.95%
s_R	0.058	1.19%
p	21	

Consensus values (corrected)

m	4.841	
s_r	0.035	0.71%
s_L	0.045	0.92%
s_R	0.056	1.17%
p	20	



Measurand/ Mixture: carbon dioxide

Reference

x_{ref}	U(x_{ref}) k=2		σ	
3.427	0.019	%mol/mol	0.044	%mol/mol

Reported data

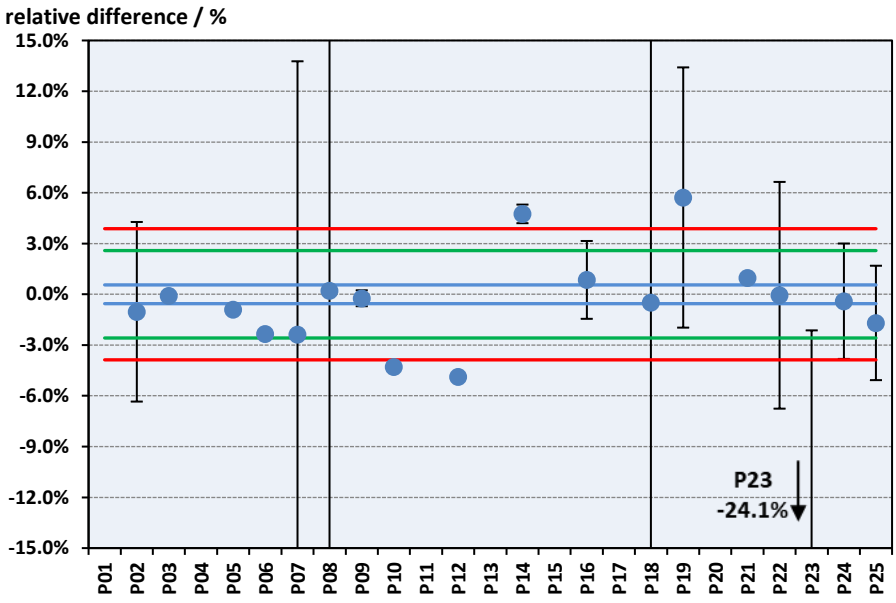
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01					
P02	3.392	0.180	-1.03%	-0.80	-0.20
P03	3.424	0.008	-0.09%	-0.07	-0.15
P04					
P05	3.396	0.007	-0.90%	-0.70	-1.54
P06	3.347	0.003	-2.33%	-1.81	-4.15
P07	3.346	0.540	-2.37%	-1.83	-0.15
P08	3.434	0.755	0.20%	0.16	0.01
P09	3.419	0.016	-0.23%	-0.18	-0.32
P10	3.280		-4.29%	-3.32	
P11					
P12	3.260		-4.87%	-3.77	
P13					
P14	3.590	0.020	4.75%	3.68	5.94
P15					
P16	3.456	0.079	0.85%	0.66	0.36
P17					
P18	3.411	0.550	-0.48%	-0.37	-0.03
P19	3.623	0.279	5.72%	4.43	0.70
P20					
P21	3.460	0.007	0.96%	0.75	1.63
P22	3.425	0.229	-0.06%	-0.05	-0.01
P23	2.600	0.572	-24.13%	-18.68	-1.45
P24	3.413	0.116	-0.41%	-0.32	-0.12
P25	3.369	0.114	-1.69%	-1.31	-0.50

Consensus values (raw data)

m	3.380	
s_r	0.018	0.52%
s_L	0.228	6.73%
s_R	0.228	6.75%
p	18	

Consensus values (corrected)

m	3.435	
s_r	0.018	0.53%
s_L	0.081	2.35%
s_R	0.083	2.41%
p	17	



Measurand/ Mixture	nitric oxide (NO/NO2 mix)

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
66.09	0.48	µmol/mol	1.65	µmol/mol

Reported data

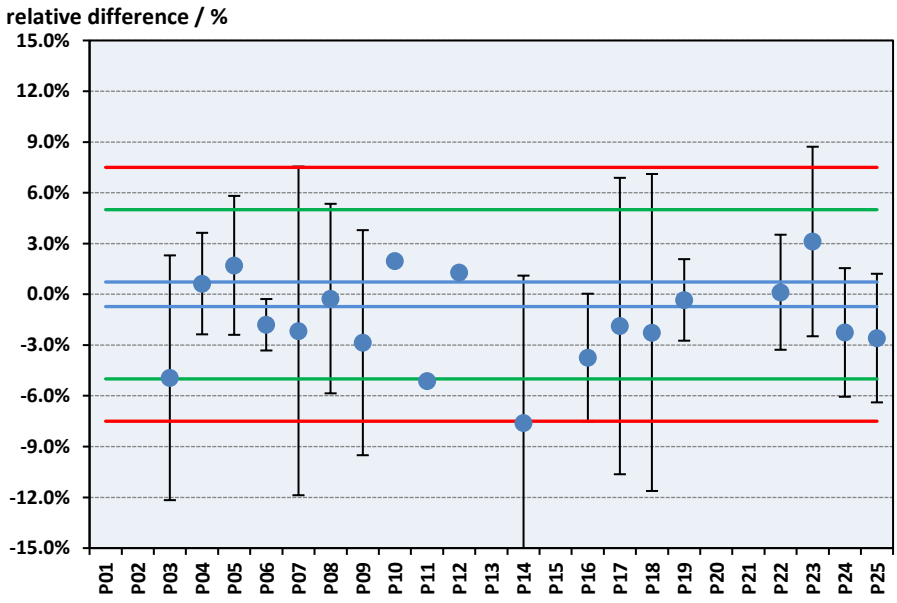
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02					
P03	62.83	4.54	-4.93%	-1.97	-0.71
P04	66.51	2.00	0.63%	0.25	0.20
P05	67.22	2.76	1.71%	0.68	0.40
P06	64.90	0.99	-1.80%	-0.72	-1.08
P07	64.66	6.28	-2.16%	-0.87	-0.23
P08	65.92	3.69	-0.25%	-0.10	-0.04
P09	64.20	4.27	-2.86%	-1.14	-0.44
P10	67.40		1.98%	0.79	
P11	62.70		-5.13%	-2.05	
P12	66.95		1.30%	0.52	
P13					
P14	61.07	5.31	-7.60%	-3.04	-0.94
P15					
P16	63.62	2.40	-3.74%	-1.50	-1.01
P17	64.85	5.68	-1.88%	-0.75	-0.22
P18	64.60	6.05	-2.26%	-0.90	-0.25
P19	65.87	1.59	-0.33%	-0.13	-0.13
P20					
P21					
P22	66.17	2.25	0.12%	0.05	0.03
P23	68.15	3.82	3.12%	1.25	0.54
P24	64.60	2.45	-2.25%	-0.90	-0.60
P25	64.38	2.45	-2.59%	-1.03	-0.69

Consensus values (raw data)

m	64.79	
s_r	0.58	0.90%
s_L	1.85	2.85%
s_R	1.94	2.99%
p	19	

Consensus values (corrected)

m	65.07	
s_r	0.31	0.47%
s_L	1.60	2.45%
s_R	1.63	2.50%
p	18	



Measurand/ Mixture	nitrogen oxides (NO/NO2 mix)

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
76.9	1.1	µmol/mol	1.9	µmol/mol

Reported data

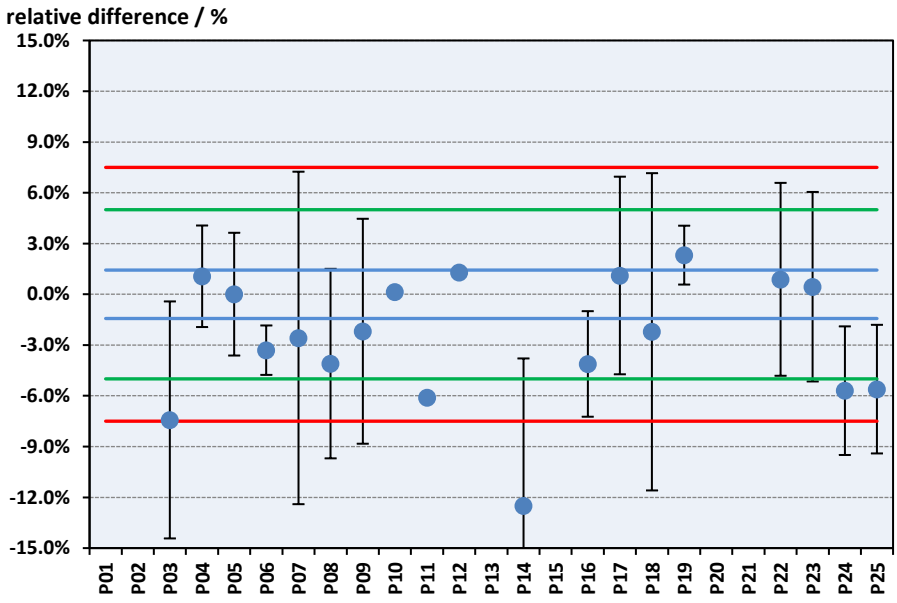
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02					
P03	71.2	5.0	-7.43%	-2.97	-1.12
P04	77.7	2.3	1.06%	0.43	0.32
P05	76.9	2.8	0.01%	0.00	0.00
P06	74.4	1.1	-3.30%	-1.32	-1.64
P07	74.9	7.4	-2.58%	-1.03	-0.27
P08	73.8	4.1	-4.09%	-1.64	-0.74
P09	75.2	5.0	-2.18%	-0.87	-0.33
P10	77.0		0.13%	0.05	
P11	72.2		-6.11%	-2.45	
P12	77.9		1.30%	0.52	
P13					
P14	67.3	5.9	-12.49%	-5.00	-1.61
P15					
P16	73.7	2.3	-4.12%	-1.65	-1.24
P17	77.8	4.5	1.11%	0.44	0.18
P18	75.2	7.1	-2.22%	-0.89	-0.24
P19	78.7	1.4	2.31%	0.93	1.01
P20					
P21					
P22	77.6	4.4	0.88%	0.35	0.15
P23	77.2	4.3	0.45%	0.18	0.08
P24	72.5	2.8	-5.70%	-2.28	-1.48
P25	72.6	2.8	-5.60%	-2.24	-1.45

Consensus values (raw data)

m	74.5	
s_r	0.6	0.83%
s_L	3.0	4.05%
s_R	3.1	4.14%
p	19	

Consensus values (corrected)

m	75.0	
s_r	0.3	0.45%
s_L	2.4	3.19%
s_R	2.4	3.22%
p	18	



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	
10.8	1.2	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	difference (µmol/mol)	converter efficiency (%)	E_n-number
P01					
P02					
P03	8.4	6.7	-2.4	77.4%	-0.36
P04	11.2	3.1	0.4	103.8%	0.12
P05	9.7	0.4	-1.1	89.7%	-0.88
P06	9.5	1.5	-1.3	87.6%	-0.71
P07	10.3	9.7	-0.5	95.0%	-0.06
P08	7.8	5.5	-3.0	72.5%	-0.52
P09	11.0	6.6	0.2	102.0%	0.03
P10	9.6		-1.2	88.9%	
P11	9.5		-1.3	88.0%	
P12	11.0		0.2	101.4%	
P13					
P14	6.2	7.9	-4.6	57.6%	-0.57
P15					
P16	10.1	3.3	-0.7	93.7%	-0.19
P17	12.9	7.3	2.1	119.5%	0.29
P18	10.6	9.3	-0.2	98.1%	-0.02
P19	12.8	2.1	2.0	118.6%	0.83
P20					
P21					
P22	11.4	5.0	0.6	105.6%	0.12
P23	9.1	5.8	-1.7	84.2%	-0.29
P24	7.9	3.7	-2.9	73.3%	-0.74
P25	8.2	3.7	-2.6	76.0%	-0.67

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). Twelve (12) participants failed to demonstrate converter efficiencies above this 95% expectation.