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UKAS PROFICIENCY TESTING
4719

Stack Emissions Proficiency Testing Scheme (SEPTS)

Presentation of Results

Round 2020

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	20.08.2020	Dr Gavin Squire	***Final report (for comment)***

Statement of Confidentiality

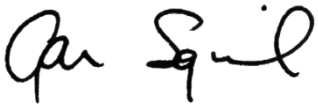
EffecTech keeps all data regarding the performance of individual participants strictly confidential. Results and performance data are protected, stored and backed up on storage network disks and folders to which access is restricted to the scheme coordinator and the technical authority only.

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 2020 (June - July 2020).

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 thirty (30) laboratories signed up to participate in this round. All 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 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.

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	622.3	3.9	0.22	0.22	0.025
propane	µmol/mol	28.32	0.27	0.47	0.46	0.13
nitric oxide	µmol/mol	223.2	1.0	0.14	0.14	0.025
carbon monoxide	µmol/mol	432.3	3.5	0.17	0.17	0.005
oxygen	%mol/mol	6.271	0.035	0.066	0.066	0.006
carbon dioxide	%mol/mol	7.021	0.031	0.11	0.11	0.004
nitric oxide (NO/NO2 mix)	µmol/mol	75.27	0.43	0.22	0.20	0.091
nitrogen oxides (NO/NO2 mix)	µmol/mol	90.80	0.55	0.30	0.29	0.10

3. Results

3.1 Reported results

There were thirty (30) 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	✓	✓						
P29	✓	✓	✓	✓	✓	✓	✓	✓
P30	✓	✓	✓	✓	✓	✓	✓	✓

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					✓	✓	✓	✓
P29			✓	✓				
P30			✓	✓	✓	✓	✓	✓

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 sole exception of participant **P06** 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
$\lvert E_n \rvert \leq 1$	**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			0.07	0.04	-1.05		-0.48	-1.47
P02	-0.05	0.13	-0.05	0.66	0.08	0.49	0.72	0.31
P03				0.17	-0.02	0.83	-0.69	-0.43
P04	-0.35	-0.37	-0.50	-0.48	-2.35	2.28	0.52	0.49
P05					1.28	-0.29		
P06	-1.28	26.23		0.39	-1.11		-1.74	-2.56
P07	0.35						-1.39	-2.71
P08	0.87	-0.38	-0.68	1.87	1.44	3.48	0.76	0.97
P09					10.03	-10.36		
P10	0.56	-0.08	0.18	0.86	0.39			
P11		-0.18	-0.53	0.48	0.61		-1.31	-1.01
P12	2.36			-0.01	-0.18	-1.38	0.09	-0.12
P13		-0.45						
P14	-0.05	0.00	0.16	0.09	-0.26	1.68	-0.58	-1.48
P15	-0.20	-0.72	-1.42	0.34	0.23			
P16	0.06	-2.47		0.04	-2.08		0.43	-1.09
P17	-0.02		-0.13		-0.06			
P18	-0.05	0.16	0.12	0.14	-0.71	0.35	-0.25	-1.10
P19		-0.21		-0.64	0.03			
P20	2.89	-1.38	-0.37	-0.42	1.13	-0.36	-1.00	-1.53
P21		-0.74	3.58	-1.76	0.26	0.90	3.05	2.13
P22	1.50	-1.85	0.59	2.31	0.39	2.64	0.26	-0.33
P23		-2.16		0.89				
P24	-0.20		-0.30	0.48	0.09			
P25			-0.13					
P26			-0.14	-0.01	-0.26		-0.71	-1.56
P27	0.51	-0.29	2.97	-1.73	0.39	-0.97	2.41	1.83
P28	-0.61						-7.05	-6.30
P29	-0.55	-0.30	-0.86	0.37	1.47	4.36		
P30	-0.07	-0.30	-0.54	1.24	0.81	1.11	-0.36	-0.53

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

However, participant **P06** reported an anomalously high propane measurement above the maximum of the range specified in the PT scheme protocol document.

Participant **P09** reported unsatisfactory results for both the oxygen and carbon dioxide measurands they reported.

Participant **P28** struggled with the measurement of the NO/NO_2 mixture.

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			0.03	0.05	-0.34		-0.22	-0.68
P02	-0.03	0.24	-0.02	0.22	0.12	0.84	0.26	0.11
P03				0.27	-0.01	0.40	-0.53	-0.41
P04	-0.33	-0.57	-0.42	-0.25	-0.99	1.37	0.42	0.39
P05					0.51	-0.07		
P06								
P07	1.24						-2.10	-5.35
P08	0.49	-0.49	-0.42	0.75	0.73	0.53	0.25	0.37
P09					3.59	-4.11		
P10	0.78	-0.23	0.26	0.70	0.75			
P11		-0.05	-0.36	0.34	0.15		-0.33	-0.25
P12	1.57			-0.01	-0.34	-1.28	0.05	-0.06
P13		-0.18						
P14	-0.04	0.00	0.11	0.04	-0.08	0.19	-0.20	-0.52
P15	-0.40	-0.47	-0.66	0.32	0.07			
P16	0.01	-1.80		0.01	-0.51		0.12	-0.35
P17	-0.04		-0.25		-0.06			
P18	-0.04	0.14	0.07	0.06	-0.23	0.04	-0.08	-0.36
P19		-0.20		-0.28	0.01			
P20	3.34	-1.70	-0.41	-0.18	0.75	-0.92	-0.50	-0.91
P21		-1.18	3.23	-0.63	0.50	1.91	1.97	1.53
P22	0.81	-1.69	0.82	0.76	0.07	0.50	0.36	-0.44
P23		-0.81		0.26				
P24	-0.40		-0.14	0.45	0.03			
P25			-0.22					
P26			-0.07	-0.01	-0.08		-0.34	-0.79
P27	0.23	-0.19	1.30	-0.54	0.78	-2.37	0.87	0.79
P28	-0.28						-1.95	-1.62
P29	-0.11	-0.11	-0.24	0.07	0.23	0.47		
P30	-0.06	-0.43	-0.47	0.63	0.36	0.34	-0.28	-0.42

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 **P01, P02, P03, P10, P11, P14, P15, P18, P24, P26** & **P30** 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 **P02, P14, P18** & **P30** 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	
622.3	3.9	µmol/mol	15.6	µmol/mol

Reported data

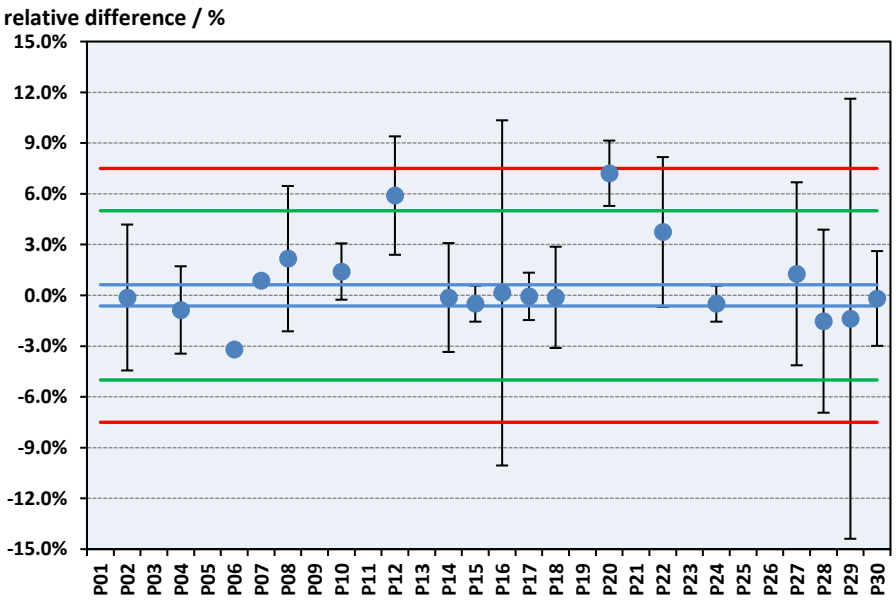
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02	621.5	26.8	-0.13%	-0.05	-0.03
P03					
P04	616.9	15.9	-0.86%	-0.35	-0.33
P05					
P06	602.4		-3.20%	-1.28	
P07	627.7	2.0	0.87%	0.35	1.24
P08	635.8	27.3	2.17%	0.87	0.49
P09					
P10	631.1	10.5	1.41%	0.56	0.78
P11					
P12	659.0	23.1	5.90%	2.36	1.57
P13					
P14	621.5	20.0	-0.13%	-0.05	-0.04
P15	619.3	6.6	-0.49%	-0.20	-0.40
P16	623.2	63.6	0.15%	0.06	0.01
P17	621.9	8.7	-0.06%	-0.02	-0.04
P18	621.6	18.6	-0.12%	-0.05	-0.04
P19					
P20	667.2	12.9	7.22%	2.89	3.34
P21					
P22	645.6	28.6	3.74%	1.50	0.81
P23					
P24	619.3	6.6	-0.49%	-0.20	-0.40
P25					
P26					
P27	630.2	34.1	1.27%	0.51	0.23
P28	612.8	33.2	-1.53%	-0.61	-0.28
P29	613.7	79.8	-1.38%	-0.55	-0.11
P30	621.2	17.4	-0.18%	-0.07	-0.06

Consensus values (raw data)

m	628.5	
s_r	1.2	0.19%
s_L	17.5	2.79%
s_R	17.6	2.80%
p	19	

Consensus values (corrected)

m	625.7	
s_r	1.2	0.20%
s_L	14.4	2.30%
s_R	14.4	2.31%
p	18	



Measurand/ Mixture: propane

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
28.32	0.27	µmol/mol	1.42	µmol/mol

Reported data

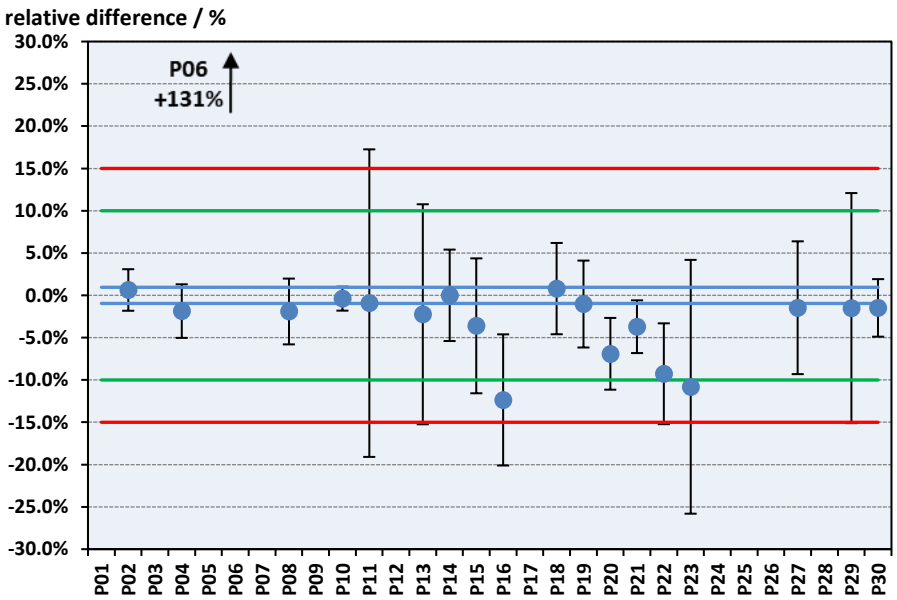
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02	28.50	0.70	0.64%	0.13	0.24
P03					
P04	27.79	0.88	-1.86%	-0.37	-0.57
P05					
P06	65.46		131.13%	26.23	
P07					
P08	27.78	1.08	-1.91%	-0.38	-0.49
P09					
P10	28.21	0.40	-0.39%	-0.08	-0.23
P11	28.06	5.10	-0.92%	-0.18	-0.05
P12					
P13	27.69	3.60	-2.24%	-0.45	-0.18
P14	28.32	1.53	0.00%	0.00	0.00
P15	27.30	2.18	-3.60%	-0.72	-0.47
P16	24.82	1.92	-12.36%	-2.47	-1.80
P17					
P18	28.55	1.54	0.80%	0.16	0.14
P19	28.03	1.44	-1.03%	-0.21	-0.20
P20	26.36	1.12	-6.91%	-1.38	-1.70
P21	27.27	0.85	-3.70%	-0.74	-1.18
P22	25.70	1.53	-9.27%	-1.85	-1.69
P23	25.26	3.79	-10.81%	-2.16	-0.81
P24					
P25					
P26					
P27	27.91	2.19	-1.46%	-0.29	-0.19
P28					
P29	27.89	3.79	-1.51%	-0.30	-0.11
P30	27.90	0.95	-1.48%	-0.30	-0.43

Consensus values (raw data)

m	29.67	
s_r	1.07	3.61%
s_L	9.46	31.88%
s_R	9.52	32.08%
p	19	

Consensus values (corrected)

m	27.35	
s_r	0.14	0.51%
s_L	1.19	4.35%
s_R	1.20	4.38%
p	18	



Measurand/ Mixture	nitric oxide

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	223.2	1.0	µmol/mol	5.6	µmol/mol

Reported data

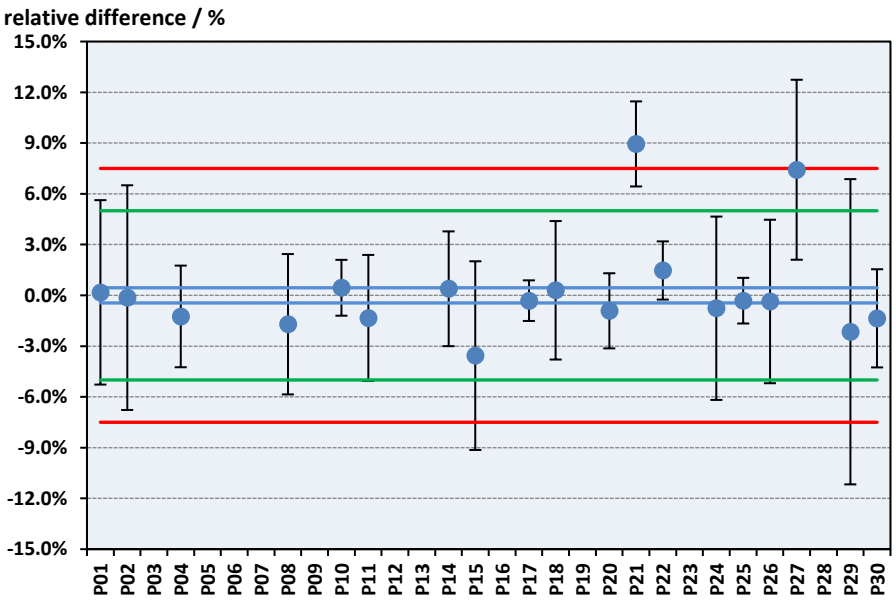
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	223.6	12.2	0.18%	0.07	0.03
P02	222.9	14.8	-0.13%	-0.05	-0.02
P03					
P04	220.4	6.6	-1.25%	-0.50	-0.42
P05					
P06					
P07					
P08	219.4	9.1	-1.71%	-0.68	-0.42
P09					
P10	224.2	3.7	0.45%	0.18	0.26
P11	220.2	8.2	-1.34%	-0.53	-0.36
P12					
P13					
P14	224.1	7.6	0.39%	0.16	0.11
P15	215.3	12.0	-3.56%	-1.42	-0.66
P16					
P17	222.5	2.7	-0.31%	-0.13	-0.25
P18	223.9	9.2	0.30%	0.12	0.07
P19					
P20	221.2	4.9	-0.91%	-0.37	-0.41
P21	243.2	6.1	8.95%	3.58	3.23
P22	226.5	3.9	1.47%	0.59	0.82
P23					
P24	221.5	12.0	-0.76%	-0.30	-0.14
P25	222.5	3.0	-0.31%	-0.13	-0.22
P26	222.4	10.7	-0.36%	-0.14	-0.07
P27	239.8	12.8	7.42%	2.97	1.30
P28					
P29	218.4	19.7	-2.15%	-0.86	-0.24
P30	220.2	6.4	-1.36%	-0.54	-0.47

Consensus values (raw data)

m	224.5	
s_r	1.1	0.50%
s_L	7.2	3.21%
s_R	7.3	3.24%
p	19	

Consensus values (corrected)

m	221.9	
s_r	1.1	0.49%
s_L	2.5	1.12%
s_R	2.7	1.22%
p	17	



Measurand/ Mixture	carbon monoxide

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	432.3	3.5	µmol/mol	6.5	µmol/mol

Reported data

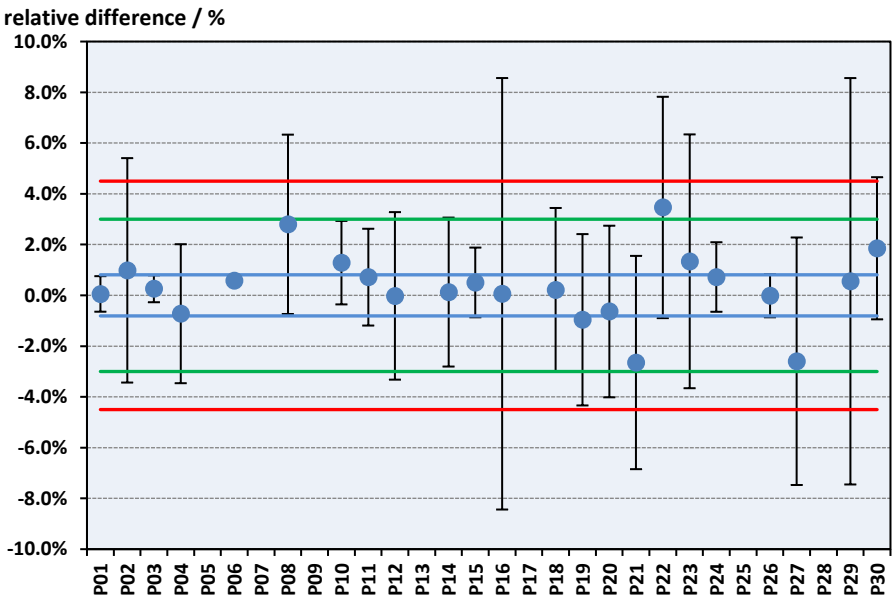
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	432.5	3.0	0.06%	0.04	0.05
P02	436.6	19.3	0.99%	0.66	0.22
P03	433.4	2.3	0.26%	0.17	0.27
P04	429.2	11.8	-0.72%	-0.48	-0.25
P05					
P06	434.8		0.58%	0.39	
P07					
P08	444.4	15.7	2.80%	1.87	0.75
P09					
P10	437.9	7.2	1.29%	0.86	0.70
P11	435.4	8.3	0.72%	0.48	0.34
P12	432.2	14.3	-0.02%	-0.01	-0.01
P13					
P14	432.9	12.7	0.13%	0.09	0.04
P15	434.5	6.0	0.51%	0.34	0.32
P16	432.6	36.8	0.06%	0.04	0.01
P17					
P18	433.2	14.0	0.21%	0.14	0.06
P19	428.1	14.5	-0.96%	-0.64	-0.28
P20	429.6	14.5	-0.64%	-0.42	-0.18
P21	420.9	17.7	-2.65%	-1.76	-0.63
P22	447.3	19.5	3.46%	2.31	0.76
P23	438.1	21.9	1.34%	0.89	0.26
P24	435.4	6.0	0.72%	0.48	0.45
P25					
P26	432.2	3.7	-0.01%	-0.01	-0.01
P27	421.1	20.5	-2.60%	-1.73	-0.54
P28					
P29	434.7	34.8	0.56%	0.37	0.07
P30	440.3	12.3	1.86%	1.24	0.63

Consensus values (raw data)

m	433.4	
s_r	0.7	0.17%
s_L	6.2	1.42%
s_R	6.2	1.44%
p	23	

Consensus values (corrected)

m	434.1	
s_r	0.8	0.18%
s_L	3.8	0.88%
s_R	3.9	0.90%
p	20	



Measurand/ Mixture	oxygen

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	6.271	0.035	%mol/mol	0.073	%mol/mol

Reported data

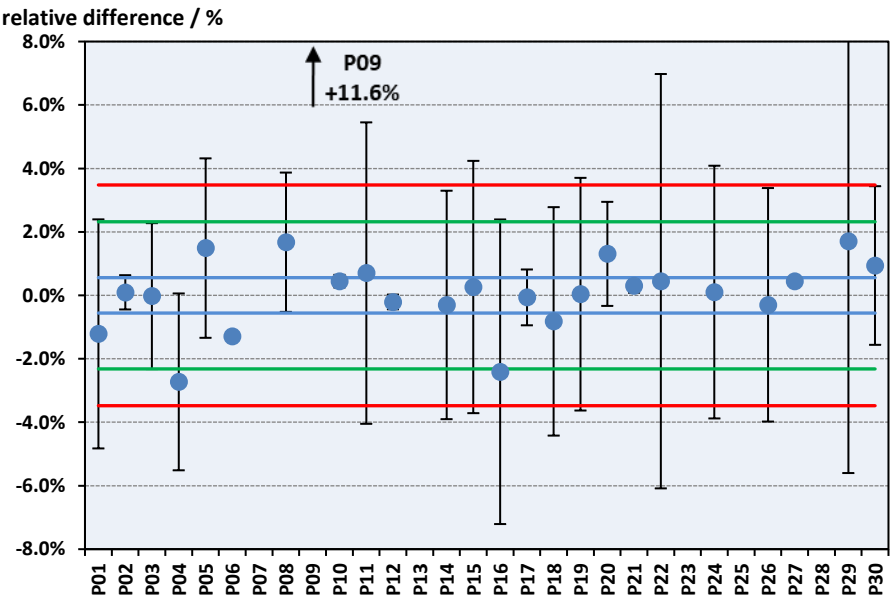
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01	6.195	0.224	-1.21%	-1.05	-0.34
P02	6.277	0.034	0.10%	0.08	0.12
P03	6.269	0.144	-0.02%	-0.02	-0.01
P04	6.100	0.170	-2.73%	-2.35	-0.99
P05	6.364	0.180	1.49%	1.28	0.51
P06	6.190		-1.29%	-1.11	
P07					
P08	6.376	0.140	1.67%	1.44	0.73
P09	7.000	0.200	11.62%	10.03	3.59
P10	6.299	0.013	0.45%	0.39	0.75
P11	6.315	0.300	0.70%	0.61	0.15
P12	6.258	0.014	-0.21%	-0.18	-0.34
P13					
P14	6.252	0.225	-0.30%	-0.26	-0.08
P15	6.288	0.250	0.26%	0.23	0.07
P16	6.120	0.294	-2.41%	-2.08	-0.51
P17	6.267	0.055	-0.06%	-0.06	-0.06
P18	6.220	0.224	-0.82%	-0.71	-0.23
P19	6.273	0.230	0.04%	0.03	0.01
P20	6.353	0.104	1.31%	1.13	0.75
P21	6.290	0.014	0.30%	0.26	0.50
P22	6.299	0.411	0.45%	0.39	0.07
P23					
P24	6.278	0.250	0.10%	0.09	0.03
P25					
P26	6.252	0.230	-0.30%	-0.26	-0.08
P27	6.299	0.009	0.45%	0.39	0.78
P28					
P29	6.378	0.466	1.71%	1.47	0.23
P30	6.330	0.158	0.94%	0.81	0.36

Consensus values (raw data)

m	6.303	
s_r	0.021	0.33%
s_L	0.175	2.78%
s_R	0.177	2.80%
p	25	

Consensus values (corrected)

m	6.268	
s_r	0.015	0.25%
s_L	0.074	1.18%
s_R	0.076	1.21%
p	24	



Measurand/ Mixture	carbon dioxide

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
7.021	0.031	%mol/mol	0.080	%mol/mol

Reported data

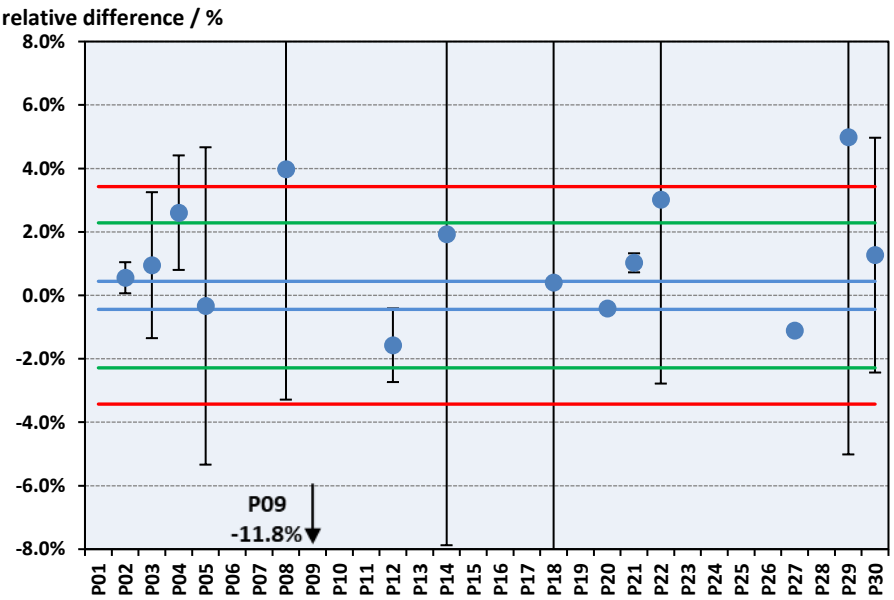
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01					
P02	7.060	0.035	0.56%	0.49	0.84
P03	7.088	0.163	0.95%	0.83	0.40
P04	7.204	0.130	2.61%	2.28	1.37
P05	6.998	0.350	-0.33%	-0.29	-0.07
P06					
P07					
P08	7.300	0.530	3.97%	3.48	0.53
P09	6.190	0.200	-11.84%	-10.36	-4.11
P10					
P11					
P12	6.911	0.080	-1.57%	-1.38	-1.28
P13					
P14	7.156	0.701	1.92%	1.68	0.19
P15					
P16					
P17					
P18	7.049	0.670	0.41%	0.35	0.04
P19					
P20	6.992	0.006	-0.41%	-0.36	-0.92
P21	7.093	0.021	1.03%	0.90	1.91
P22	7.233	0.420	3.02%	2.64	0.50
P23					
P24					
P25					
P26					
P27	6.943	0.011	-1.11%	-0.97	-2.37
P28					
P29	7.371	0.737	4.99%	4.36	0.47
P30	7.110	0.263	1.27%	1.11	0.34

Consensus values (raw data)

m	7.041	
s_r	0.029	0.41%
s_L	0.291	4.14%
s_R	0.293	4.16%
p	15	

Consensus values (corrected)

m	7.113	
s_r	0.025	0.35%
s_L	0.143	2.01%
s_R	0.145	2.04%
p	14	



Measurand/ Mixture	nitric oxide (NO/NO2 mix)

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
75.27	0.43	µmol/mol	1.88	µmol/mol

Reported data

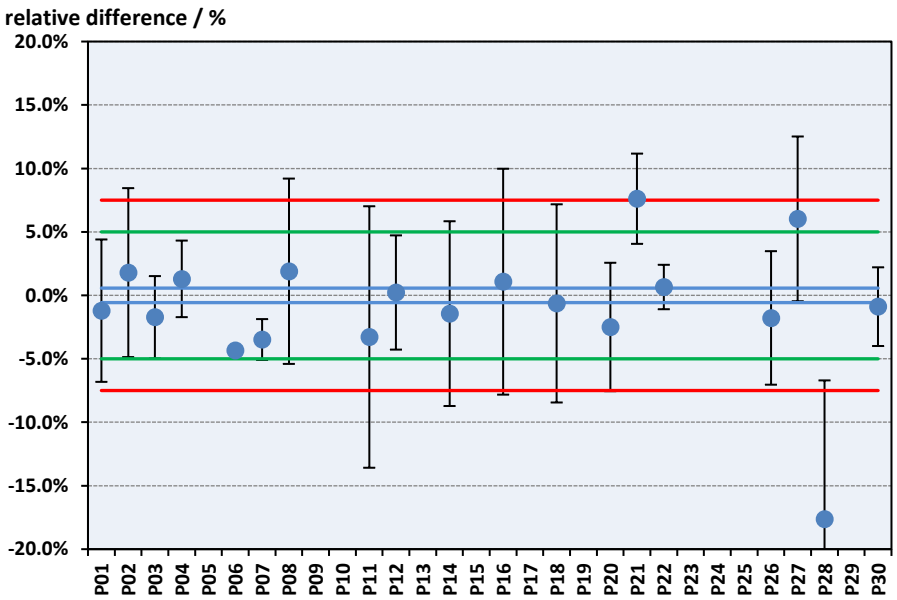
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	74.36	4.17	-1.21%	-0.48	-0.22
P02	76.62	5.10	1.79%	0.72	0.26
P03	73.97	2.40	-1.73%	-0.69	-0.53
P04	76.25	2.30	1.30%	0.52	0.42
P05					
P06	72.00		-4.34%	-1.74	
P07	72.65	1.17	-3.48%	-1.39	-2.10
P08	76.70	5.60	1.90%	0.76	0.25
P09					
P10					
P11	72.80	7.50	-3.28%	-1.31	-0.33
P12	75.44	3.39	0.23%	0.09	0.05
P13					
P14	74.19	5.40	-1.44%	-0.58	-0.20
P15					
P16	76.08	6.77	1.08%	0.43	0.12
P17					
P18	74.79	5.84	-0.63%	-0.25	-0.08
P19					
P20	73.39	3.71	-2.49%	-1.00	-0.50
P21	81.00	2.88	7.61%	3.05	1.97
P22	75.77	1.33	0.66%	0.26	0.36
P23					
P24					
P25					
P26	73.93	3.89	-1.78%	-0.71	-0.34
P27	79.81	5.18	6.03%	2.41	0.87
P28	62.00	6.78	-17.63%	-7.05	-1.95
P29					
P30	74.60	2.31	-0.89%	-0.36	-0.28

Consensus values (raw data)

m	74.66	
s_r	0.44	0.59%
s_L	4.10	5.49%
s_R	4.12	5.52%
p	19	

Consensus values (corrected)

m	75.50	
s_r	0.46	0.60%
s_L	2.43	3.22%
s_R	2.48	3.28%
p	18	



Measurand/ Mixture	nitrogen oxides (NO/NO2 mix)

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
90.80	0.55	µmol/mol	2.27	µmol/mol

Reported data

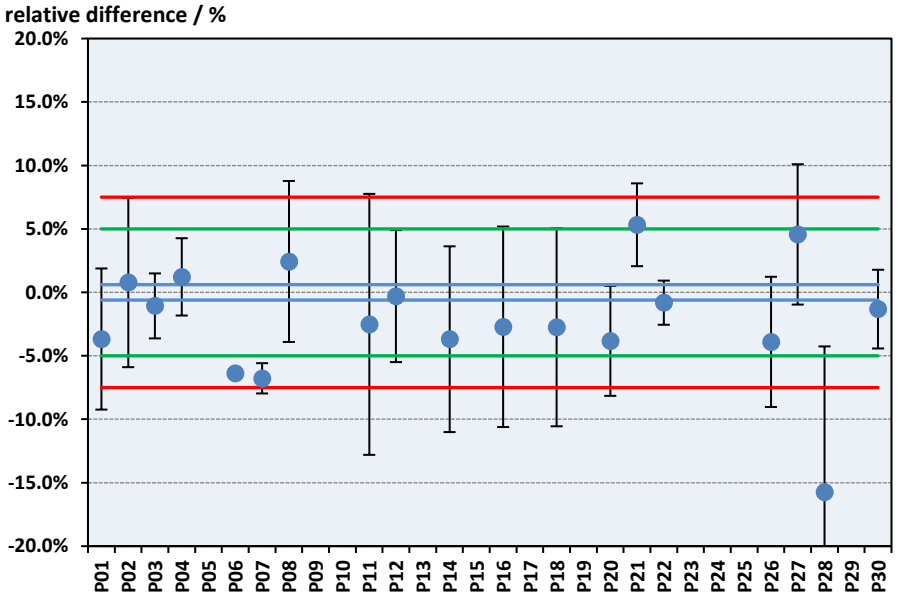
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	87.46	4.86	-3.68%	-1.47	-0.68
P02	91.50	6.10	0.77%	0.31	0.11
P03	89.83	2.30	-1.07%	-0.43	-0.41
P04	91.91	2.80	1.22%	0.49	0.39
P05					
P06	85.00		-6.39%	-2.56	
P07	84.65	1.01	-6.77%	-2.71	-5.35
P08	93.01	5.90	2.43%	0.97	0.37
P09					
P10					
P11	88.51	9.10	-2.52%	-1.01	-0.25
P12	90.53	4.71	-0.29%	-0.12	-0.06
P13					
P14	87.45	6.40	-3.69%	-1.48	-0.52
P15					
P16	88.34	6.98	-2.71%	-1.09	-0.35
P17					
P18	88.30	6.89	-2.75%	-1.10	-0.36
P19					
P20	87.33	3.78	-3.82%	-1.53	-0.91
P21	95.64	3.12	5.32%	2.13	1.53
P22	90.06	1.57	-0.81%	-0.33	-0.44
P23					
P24					
P25					
P26	87.25	4.48	-3.90%	-1.56	-0.79
P27	94.95	5.25	4.56%	1.83	0.79
P28	76.50	8.79	-15.75%	-6.30	-1.62
P29					
P30	89.60	2.78	-1.32%	-0.53	-0.42

Consensus values (raw data)

m	89.12	
s_r	0.55	0.62%
s_L	4.48	5.03%
s_R	4.51	5.06%
p	19	

Consensus values (corrected)

m	89.97	
s_r	0.55	0.61%
s_L	3.04	3.38%
s_R	3.09	3.43%
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	
	15.53	0.70	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	difference (µmol/mol)	converter efficiency (%)	E_n-number
P01	13.10	6.41	-2.4	84.3%	-0.38
P02	14.88	7.95	-0.7	95.8%	-0.08
P03	15.86	3.32	0.3	102.1%	0.10
P04	15.66	3.62	0.1	100.8%	0.04
P05					
P06	13.00		-2.5	83.7%	
P07	12.00	1.55	-3.5	77.3%	-2.08
P08	16.31	8.13	0.8	105.0%	0.10
P09					
P10					
P11	15.71	11.79	0.2	101.2%	0.02
P12	15.09	5.80	-0.4	97.2%	-0.07
P13					
P14	13.26	8.37	-2.3	85.4%	-0.27
P15					
P16	12.26	9.72	-3.3	78.9%	-0.34
P17					
P18	13.51	9.03	-2.0	87.0%	-0.22
P19					
P20	13.93	5.30	-1.6	89.7%	-0.30
P21	14.64	4.25	-0.9	94.2%	-0.21
P22	14.30	2.05	-1.2	92.1%	-0.57
P23					
P24					
P25					
P26	13.32	5.93	-2.2	85.8%	-0.37
P27	15.14	7.38	-0.4	97.5%	-0.05
P28	14.50	11.10	-1.0	93.4%	-0.09
P29					
P30	15.00	3.61	-0.5	96.6%	-0.14

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). Eleven (11) participants failed to demonstrate converter efficiencies above this 95% expectation.