EffecTech
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UKAS PROFICIENCY TESTING
4719

Stack Emissions Proficiency Testing Scheme (SEPTS)

Presentation of Results

Round 2024

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	09 August 2024	Adam Lomax	***Draft 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
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Adam Lomax
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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 2024 (June - July 2024).

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	10 to 200 µmol/mol
propane (C_3H_8) in 10% oxygen / nitrogen	5 to 50 µmol/mol
nitric oxide (NO) in nitrogen	10 to 500 µmol/mol
carbon monoxide (CO) in nitrogen	20 to 500 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	20 to 400 µmol/mol 25 to 500 µmol/mol

Note: all units used in this report are in the SI unit of amount of substance fraction (mol/mol) or in metric prefixes thereof.
500 µmol/mol is equivalent to 500 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-five (35) laboratories signed up to participate in this round. Thirty-five (35) 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 carbon dioxide measurand which was calibrated using a single-point through origin calibration (SPO). Both of these calibration methods are in accordance with ISO 12963 for which EffecTech is accredited to ISO 17025 and ISO 17034 by UKAS.

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

The uncertainty on amount fraction of each measurand in the mixtures resulting from this calibration is termed the characterisation uncertainty, u_{char} (ISO Guide 35 : 2017).

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 : 2017.

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

Reference value assignment

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

The initial combined uncertainty determined for each reference value was calculated from the equation below (ISO Guide 35 : 2017 - section 10.2).

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

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	69.2	1.1	0.72	0.72	0.00
propane	µmol/mol	38.90	0.26	0.34	0.32	0.098
nitric oxide	µmol/mol	133.31	0.66	0.20	0.19	0.060
carbon monoxide	µmol/mol	183.8	1.5	0.42	0.42	0.026
oxygen	%mol/mol	5.352	0.031	0.080	0.079	0.012
carbon dioxide	%mol/mol	7.333	0.032	0.082	0.045	0.069
nitric oxide (NO/NO2 mix)	µmol/mol	69.72	0.41	0.25	0.24	0.081
nitrogen oxides (NO/NO2 mix)	µmol/mol	78.71	0.59	0.37	0.36	0.092

3. Results

3.1 Reported results

There were thirty-five (35) 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	✓	✓	✓	✓			✓	×
P31							✓	✓
P32	✓	✓	✓	✓	✓	✓	✓	✓
P33	✓	✓	✓	✓	✓	✓	✓	✓
P34	✓	✓	✓	✓	✓	✓	✓	✓
P35	✓	✓	✓	✓	✓	✓	✓	✓

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	✓	✓	✓	✓	✓	✓	✓	✓
P31	✓	✓			✓	✓	✓	✓
P32	✓	✓	✓	✓	✓	✓	✓	✓
P33	✓	✓	✓	✓	✓	✓	✓	✓
P34	✓	✓	✓	✓	✓	✓	✓	✓
P35	✓	✓	✓	✓	✓	✓	✓	✓

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

3.2 Measures of performance

z-score

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

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

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

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

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

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

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

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

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

These are given in the tables below.

Table 4: Standard deviation for performance assessment

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

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

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

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

E_n number

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

The E_n number is calculated with the following general formula

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

where x_{meas} is the measured result reported by the laboratory
x_{ref} the assigned reference value and
U_{meas} and U_{ref} their respective uncertainties (using a coverage factor k=2)

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

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

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

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

3.3 Evaluation of results

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

Table 7 - Summary of *z*-scores

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		0.24	0.08		-0.03			
P02					-1.13	1.52		
P03	0.53	0.04	0.06	0.31	0.35	1.14	-0.80	-1.28
P04	0.34	-0.95		-0.88	2.02	1.16	-0.73	1.32
P05	0.50		0.42					
P06	-0.62	-0.22		0.24	0.43		-0.89	-1.26
P07	-0.03	-0.92	-0.04	-0.78	0.50	-0.06	-1.33	-1.59
P08		0.30	0.32	-0.26	0.27	0.97	-0.75	-2.31
P09						3.85		
P10	0.67	-0.15	-0.06	1.29	-0.38	-0.52	-0.15	0.18
P11	0.99	-0.32	0.22	1.07	0.76	-5.20	-0.52	-0.90
P12		0.33						
P13					1.54	5.60		
P14	-0.26	-1.05		-0.85	-0.76	0.94	-0.44	-0.58
P15	2.02	0.38	-0.65	1.07	-1.64	-1.01	-2.06	-1.58
P16			0.56	1.34				
P17		0.24	0.11	-0.17	0.24		-0.52	-0.47
P18				-0.70	-1.22	2.19	-0.32	-0.44
P19		-0.44	1.43	-2.03		1.25	2.46	2.32
P20	0.28	-0.16	-0.78	0.90	0.21			
P21		0.77	-0.12	-1.97	0.36	0.40	-2.64	-2.60
P22	2.42	0.00	0.09	0.11	-0.80	0.78	0.79	0.25
P23	-0.18	0.17	0.63	1.36	-0.16	-0.59	0.07	0.10
P24		-1.09	-0.20	0.48	0.60	-1.72	-1.13	0.64
P25		0.32		0.25		-3.26		
P26	0.90	-1.80		0.58	0.22	-0.01	-1.07	0.90
P27	-4.07	-2.73	-0.87	-1.85	3.27			
P28	2.09		-0.21	-0.07	0.60	-2.20	0.22	0.20
P29	-0.14	-0.42		1.30	1.13	-1.12	2.79	3.27
P30	-13.35	-0.10			1.04	1.09	-1.61	-2.55
P31				-0.54	1.73		0.71	-0.30
P32	-2.00	-0.10	0.09	-0.10	2.28	-0.11	-0.41	-0.42
P33	0.61	0.21	0.63	0.02	-0.31	0.98	-0.52	-0.85
P34	2.42	0.00	0.09	0.11	-0.80	0.78	0.79	0.25
P35	0.42	0.11	-0.04	0.71	0.00	1.60	-0.53	-1.04

†component assessed based on a z' score

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

However, participant **P30** reported an anomalously low measurement for sulphur dioxide. Participants **P11** and **P25** reported low, while **P09** and **P13** reported high measurements respectively, for carbon dioxide.

Eighteen (18) laboratories (**P01**, **P02**, **P03**, **P05**, **P06**, **P07, P10**, **P12**, **P14**, **P16**, **P17**, **P20**, **P23**, **P24**, **P26**, **P31**, **P33** and **P35**) achieved satisfactory results for all measurands for which they reported a result.

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

Table 8 - Summary of E_n-numbers

participant id	sulphur dioxide	propane	nitric oxide	carbon monoxide	oxygen	carbon dioxide	nitric oxide (NO/NO2 mix)	nitrogen oxides (NO/NO2 mix)
P01		1.00	0.27		-0.05			
P02					-0.14	0.25		
P03	0.10	0.02	0.03	0.08	0.07	0.22	-0.21	-0.38
P04	0.47	-1.68		-0.78	0.29	0.19	-1.59	2.59
P05	0.65		0.74					
P06	-0.14	-0.11		0.04	0.66		-0.28	-0.41
P07	-0.02	-1.39	-0.03	-0.63	0.95	-0.14	-0.94	-1.17
P08		1.17	0.49	-0.22	0.26	1.11	-1.18	-2.34
P09						1.27		
P10	0.27	-0.07	-0.04	0.32	-0.17	-0.07	-0.08	0.09
P11	0.46	-0.15	0.23	0.49	0.18	-1.44	-0.26	-0.53
P12		0.13						
P13					0.42	2.42		
P14	-0.34	-1.91		-0.75	-0.09	0.15	-0.86	-1.06
P15	0.77	0.21	-0.38	0.32	-0.74	-0.27	-1.25	-0.94
P16			0.16	0.33				
P17		0.26	0.14	-0.13	0.14		-0.65	-0.27
P18				-0.43	-0.38	0.90	-0.33	-0.44
P19		-1.09	2.99	-2.09		0.71	4.92	4.37
P20	0.14	-0.54	-1.18	0.54	0.12			
P21		0.55	-0.08	-1.04	0.16	0.17	-2.04	-1.99
P22	1.06	0.00	0.03	0.03		0.12	0.26	0.08
P23	-0.07	0.08	0.32	0.34	-0.07	-0.08	0.03	0.04
P24		-2.82	-0.43	0.49	0.63	-1.02	-2.47	1.25
P25		0.42		0.10		-7.47		
P26	1.17	-3.67		0.71	0.06	0.00	-0.91	0.72
P27	-0.74	-1.13	-0.22	-0.28	0.47			
P28	0.31		-0.05	-0.01			0.05	
P29	-0.04	-0.13		0.56	0.40	-0.11	1.84	0.95
P30	-5.16	-0.19			0.94	2.28	-0.57	-1.12
P31				-0.32	0.61		0.45	-0.18
P32	-0.93	-0.15	0.08	-0.05	4.56	-0.25	-0.35	-0.34
P33	0.32	0.42	0.49	0.01	-0.59	2.24	-0.22	-0.38
P34	1.06	0.00	0.03	0.03		0.12	0.26	0.08
P35	0.08	0.06	-0.02	0.18	0.00	0.30	-0.14	-0.30

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

For 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 **P03**, **P06**, **P10**, **P17**, **P23**, **P31** and **P35** 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 **P03**, **P10**, **P23** and **P35** 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	
	69.2	1.1	µmol/mol	1.7	µmol/mol

Reported data

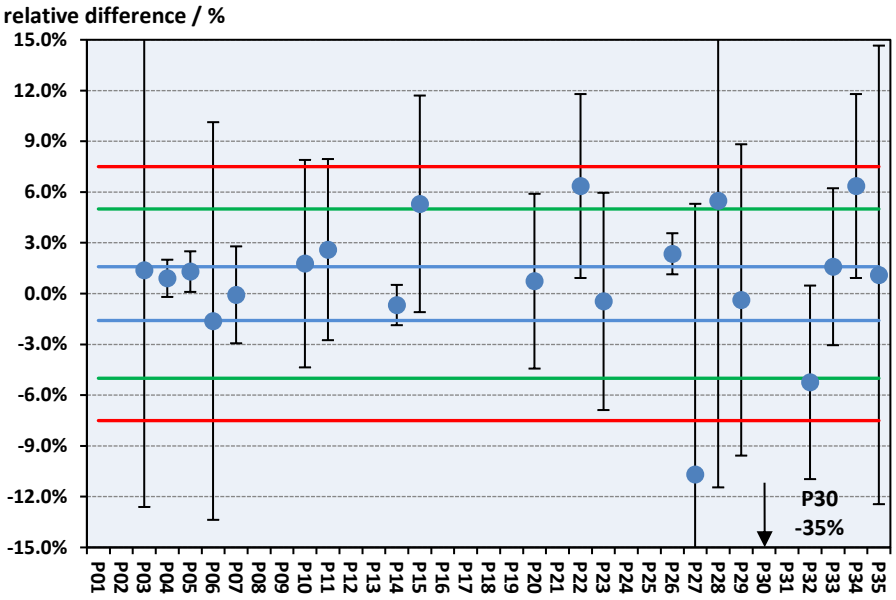
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02					
P03	70.2	9.8	1.39%	0.53	0.10
P04	69.8	0.8	0.90%	0.34	0.47
P05	70.1	0.8	1.30%	0.50	0.65
P06	68.1	8.0	-1.62%	-0.62	-0.14
P07	69.2	2.0	-0.07%	-0.03	-0.02
P08					
P09					
P10	70.4	4.3	1.77%	0.67	0.27
P11	71.0	3.8	2.60%	0.99	0.46
P12					
P13					
P14	68.7	0.8	-0.67%	-0.26	-0.34
P15	72.9	4.7	5.30%	2.02	0.77
P16					
P17					
P18					
P19					
P20	69.7	3.6	0.73%	0.28	0.14
P21					
P22	73.6	4.0	6.36%	2.42	1.06
P23	68.9	4.4	-0.46%	-0.18	-0.07
P24					
P25					
P26	70.8	0.9	2.36%	0.90	1.17
P27	61.8	9.9	-10.69%	-4.07	-0.74
P28	73.0	12.4	5.49%	2.09	0.31
P29	68.9	6.3	-0.37%	-0.14	-0.04
P30	45.0	4.6	-35.04%	-13.35	-5.16
P31					
P32	65.6	3.8	-5.24%	-2.00	-0.93
P33	70.3	3.3	1.59%	0.61	0.32
P34	73.6	4.0	6.36%	2.42	1.06
P35	70.0	9.5	1.11%	0.42	0.08

Consensus values (raw data)

m	69.50	
s_r	0.52	0.74%
s_L	3.4	4.86%
s_R	3.4	4.92%
p	21	

Consensus values (corrected)

m	69.64	
s_r	0.52	0.74%
s_L	2.8	4.02%
s_R	2.8	4.09%
p	20	



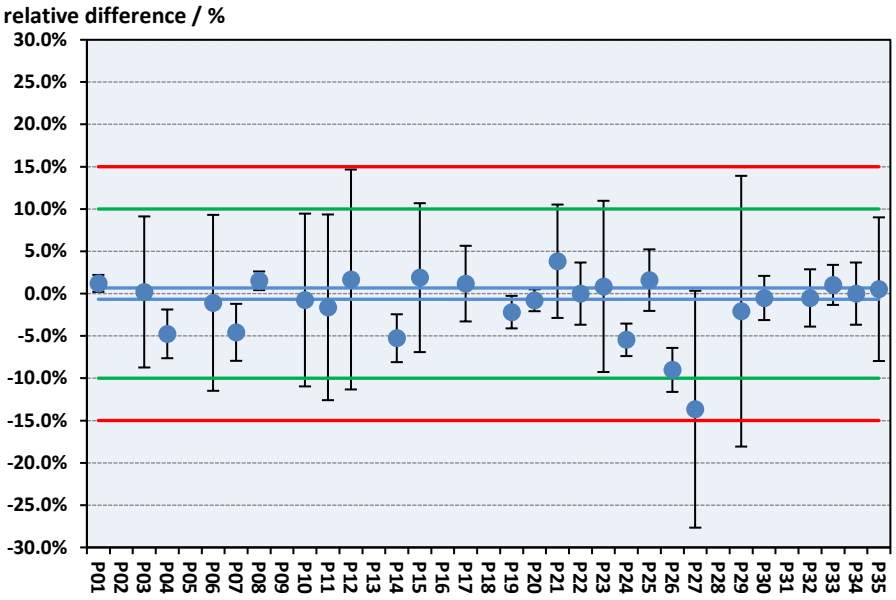
Measurand/ Mixture	propane				
Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	38.90	0.26	µmol/mol	1.94	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	39.37	0.39	1.21%	0.24	1.00
P02					
P03	38.98	3.48	0.20%	0.04	0.02
P04	37.05	1.07	-4.76%	-0.95	-1.68
P05					
P06	38.48	4.00	-1.09%	-0.22	-0.11
P07	37.12	1.25	-4.58%	-0.92	-1.39
P08	39.49	0.43	1.52%	0.30	1.17
P09					
P10	38.61	3.94	-0.76%	-0.15	-0.07
P11	38.27	4.20	-1.62%	-0.32	-0.15
P12	39.55	5.14	1.67%	0.33	0.13
P13					
P14	36.85	1.04	-5.27%	-1.05	-1.91
P15	39.64	3.49	1.89%	0.38	0.21
P16					
P17	39.36	1.76	1.18%	0.24	0.26
P18					
P19	38.05	0.73	-2.19%	-0.44	-1.09
P20	38.60	0.50	-0.78%	-0.16	-0.54
P21	40.39	2.71	3.83%	0.77	0.55
P22	38.90	1.43	0.00%	0.00	0.00
P23	39.23	3.97	0.85%	0.17	0.08
P24	36.78	0.71	-5.46%	-1.09	-2.82
P25	39.52	1.44	1.59%	0.32	0.42
P26	35.39	0.92	-9.02%	-1.80	-3.67
P27	33.59	4.70	-13.66%	-2.73	-1.13
P28					
P29	38.09	6.09	-2.08%	-0.42	-0.13
P30	38.70	1.01	-0.51%	-0.10	-0.19
P31					
P32	38.70	1.31	-0.51%	-0.10	-0.15
P33	39.30	0.93	1.03%	0.21	0.42
P34	38.90	1.43	0.00%	0.00	0.00
P35	39.10	3.32	0.53%	0.11	0.06

Consensus values (raw data)		
m	38.30	
s_r	0.28	0.73%
s_L	1.5	3.88%
s_R	1.5	3.95%
p	27	

Consensus values (corrected)		
m	38.49	
s_r	0.28	0.72%
s_L	1.1	2.96%
s_R	1.2	3.05%
p	26	



Measurand/ Mixture	nitric oxide				
Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	133.31	0.66	µmol/mol	3.33	µmol/mol

Reported data

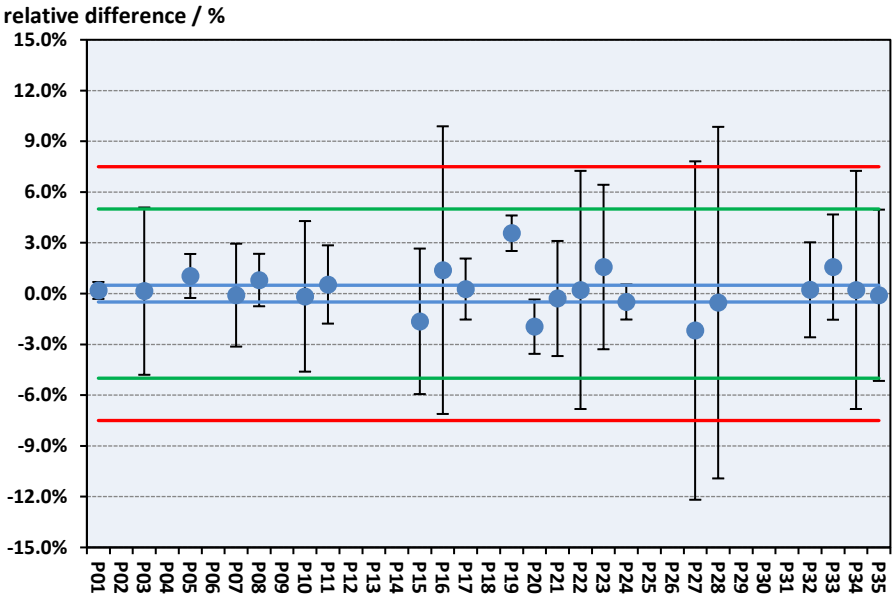
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	133.56	0.67	0.19%	0.08	0.27
P02					
P03	133.51	6.60	0.15%	0.06	0.03
P04					
P05	134.70	1.75	1.04%	0.42	0.74
P06					
P07	133.19	4.05	-0.09%	-0.04	-0.03
P08	134.38	2.08	0.80%	0.32	0.49
P09					
P10	133.09	5.92	-0.16%	-0.06	-0.04
P11	134.03	3.10	0.54%	0.22	0.23
P12					
P13					
P14					
P15	131.13	5.64	-1.64%	-0.65	-0.38
P16	135.16	11.49	1.39%	0.56	0.16
P17	133.67	2.41	0.27%	0.11	0.14
P18					
P19	138.07	1.45	3.57%	1.43	2.99
P20	130.71	2.10	-1.95%	-0.78	-1.18
P21	132.93	4.52	-0.29%	-0.12	-0.08
P22	133.60	9.40	0.22%	0.09	0.03
P23	135.41	6.58	1.57%	0.63	0.32
P24	132.65	1.38	-0.50%	-0.20	-0.43
P25					
P26					
P27	130.40	13.04	-2.18%	-0.87	-0.22
P28	132.60	13.77	-0.53%	-0.21	-0.05
P29					
P30					
P31					
P32	133.61	3.75	0.23%	0.09	0.08
P33	135.40	4.21	1.57%	0.63	0.49
P34	133.60	9.40	0.22%	0.09	0.03
P35	133.18	6.74	-0.10%	-0.04	-0.02

Consensus values (raw data)

m	133.59	
s_r	2.2	1.64%
s_L	1.6	1.22%
s_R	2.7	2.04%
p	22	

Consensus values (corrected)

m	133.34	
s_r	2.3	1.64%
s_L	1.2	1.22%
s_R	2.6	2.04%
p	21	



Measurand/ Mixture	carbon monoxide				
Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	183.8	1.5	µmol/mol	2.8	µmol/mol

Reported data

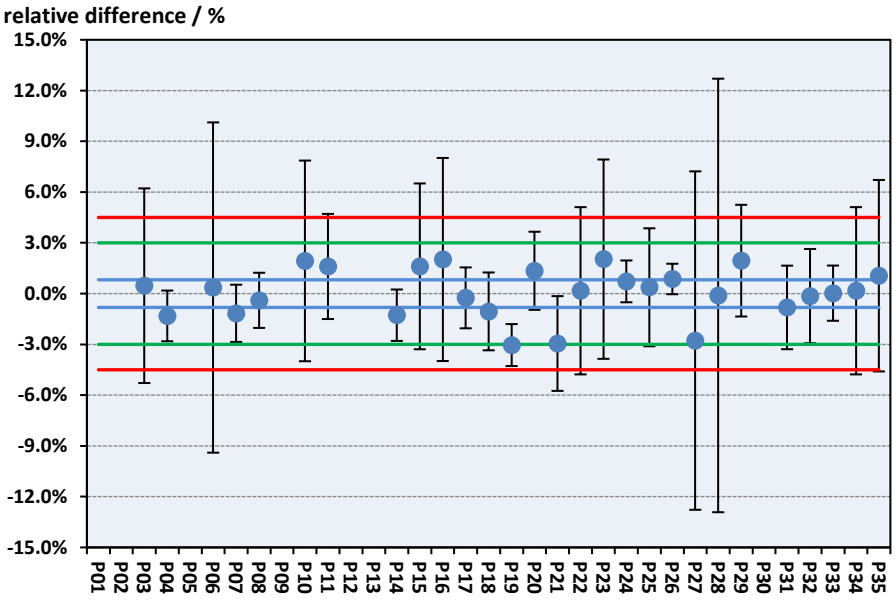
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02					
P03	184.7	10.6	0.47%	0.31	0.08
P04	181.4	2.7	-1.32%	-0.88	-0.78
P05					
P06	184.5	18.0	0.36%	0.24	0.04
P07	181.7	3.1	-1.16%	-0.78	-0.63
P08	183.1	3.0	-0.40%	-0.26	-0.22
P09					
P10	187.4	11.1	1.93%	1.29	0.32
P11	186.8	5.8	1.61%	1.07	0.49
P12					
P13					
P14	181.5	2.8	-1.28%	-0.85	-0.75
P15	186.8	9.2	1.61%	1.07	0.32
P16	187.5	11.3	2.02%	1.34	0.33
P17	183.3	3.3	-0.25%	-0.17	-0.13
P18	181.9	4.2	-1.05%	-0.70	-0.43
P19	178.2	2.2	-3.04%	-2.03	-2.09
P20	186.3	4.3	1.35%	0.90	0.54
P21	178.4	5.0	-2.95%	-1.97	-1.04
P22	184.1	9.1	0.17%	0.11	0.03
P23	187.5	11.0	2.04%	1.36	0.34
P24	185.1	2.3	0.72%	0.48	0.49
P25	184.5	6.4	0.37%	0.25	0.10
P26	185.4	1.7	0.87%	0.58	0.71
P27	178.7	17.9	-2.77%	-1.85	-0.28
P28	183.6	23.5	-0.11%	-0.07	-0.01
P29	187.4	6.2	1.95%	1.30	0.56
P30					
P31	182.3	4.5	-0.82%	-0.54	-0.32
P32	183.5	5.1	-0.15%	-0.10	-0.05
P33	183.9	3.0	0.03%	0.02	0.01
P34	184.1	9.1	0.17%	0.11	0.03
P35	185.7	10.5	1.06%	0.71	0.18

Consensus values (raw data)

m	183.9	
s_r	1.1	0.59%
s_L	2.8	1.50%
s_R	3.0	1.61%
p	28	

Consensus values (corrected)

m	184.3	
s_r	1.0	0.56%
s_L	2.3	1.26%
s_R	2.5	1.37%
p	26	



Measurand/ Mixture	oxygen

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	5.352	0.031	%mol/mol	0.064	%mol/mol

Reported data

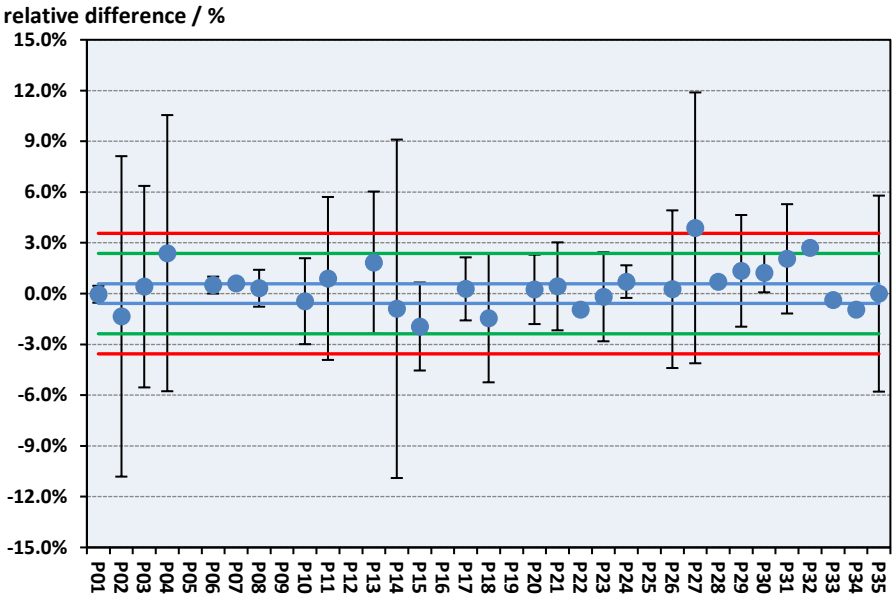
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01	5.350	0.027	-0.04%	-0.03	-0.05
P02	5.280	0.500	-1.35%	-1.13	-0.14
P03	5.374	0.320	0.41%	0.35	0.07
P04	5.480	0.447	2.39%	2.02	0.29
P05					
P06	5.379	0.027	0.50%	0.43	0.66
P07	5.384	0.013	0.60%	0.50	0.95
P08	5.369	0.059	0.32%	0.27	0.26
P09					
P10	5.328	0.135	-0.45%	-0.38	-0.17
P11	5.400	0.260	0.90%	0.76	0.18
P12					
P13	5.450	0.229	1.83%	1.54	0.42
P14	5.304	0.530	-0.90%	-0.76	-0.09
P15	5.248	0.136	-1.94%	-1.64	-0.74
P16					
P17	5.367	0.100	0.28%	0.24	0.14
P18	5.274	0.200	-1.45%	-1.22	-0.38
P19					
P20	5.365	0.110	0.25%	0.21	0.12
P21	5.375	0.140	0.43%	0.36	0.16
P22	5.301	0.000	-0.95%	-0.80	
P23	5.342	0.140	-0.19%	-0.16	-0.07
P24	5.390	0.052	0.71%	0.60	0.63
P25					
P26	5.366	0.250	0.26%	0.22	0.06
P27	5.560	0.445	3.89%	3.27	0.47
P28	5.390	0.000	0.71%	0.60	
P29	5.424	0.179	1.35%	1.13	0.40
P30	5.418	0.063	1.24%	1.04	0.94
P31	5.462	0.176	2.06%	1.73	0.61
P32	5.497	0.007	2.71%	2.28	4.56
P33	5.332	0.013	-0.37%	-0.31	-0.59
P34	5.301	0.000	-0.95%	-0.80	
P35	5.352	0.310	0.00%	0.00	0.00

Consensus values (raw data)

m	5.375	
s_r	0.025	0.47%
s_L	0.073	1.35%
s_R	0.077	1.43%
p	29	

Consensus values (corrected)

m	5.368	
s_r	0.021	0.40%
s_L	0.064	1.19%
s_R	0.067	1.25%
p	28	



Measurand/ Mixture	carbon dioxide				
Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	7.333	0.032	%mol/mol	0.083	%mol/mol

Reported data

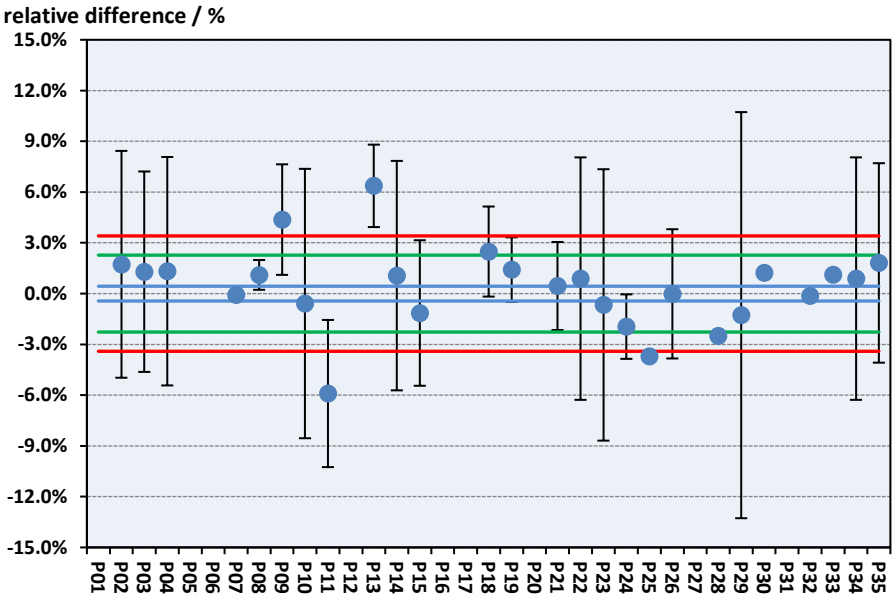
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01					
P02	7.460	0.500	1.73%	1.52	0.25
P03	7.428	0.440	1.30%	1.14	0.22
P04	7.430	0.502	1.32%	1.16	0.19
P05					
P06					
P07	7.328	0.018	-0.07%	-0.06	-0.14
P08	7.414	0.065	1.10%	0.97	1.11
P09	7.654	0.250	4.37%	3.85	1.27
P10	7.290	0.580	-0.59%	-0.52	-0.07
P11	6.900	0.300	-5.90%	-5.20	-1.44
P12					
P13	7.800	0.190	6.37%	5.60	2.42
P14	7.411	0.502	1.06%	0.94	0.15
P15	7.249	0.312	-1.15%	-1.01	-0.27
P16					
P17					
P18	7.515	0.200	2.49%	2.19	0.90
P19	7.437	0.142	1.42%	1.25	0.71
P20					
P21	7.366	0.192	0.45%	0.40	0.17
P22	7.398	0.530	0.89%	0.78	0.12
P23	7.284	0.584	-0.67%	-0.59	-0.08
P24	7.190	0.137	-1.95%	-1.72	-1.02
P25	7.062	0.017	-3.70%	-3.26	-7.47
P26	7.332	0.280	-0.01%	-0.01	0.00
P27					
P28	7.150	0.000	-2.50%	-2.20	
P29	7.240	0.869	-1.27%	-1.12	-0.11
P30	7.424	0.024	1.24%	1.09	2.28
P31					
P32	7.324	0.018	-0.12%	-0.11	-0.25
P33	7.415	0.018	1.12%	0.98	2.24
P34	7.398	0.530	0.89%	0.78	0.12
P35	7.466	0.440	1.81%	1.60	0.30

Consensus values (raw data)

m	7.362	
s_r	0.029	0.40%
s_L	0.18	2.38%
s_R	0.18	2.41%
p	26	

Consensus values (corrected)

m	7.363	
s_r	0.031	0.42%
s_L	0.12	1.62%
s_R	0.12	1.67%
p	24	



Measurand/ Mixture	nitric oxide (NO/NO2 mix)				
Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	69.72	0.41	µmol/mol	1.74	µmol/mol

Reported data

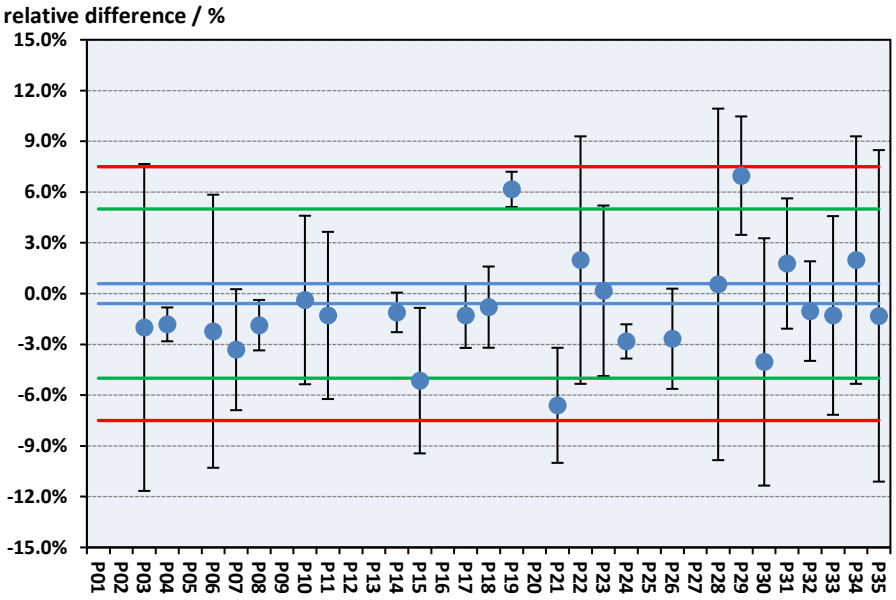
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02					
P03	68.33	6.60	-2.00%	-0.80	-0.21
P04	68.45	0.68	-1.82%	-0.73	-1.59
P05					
P06	68.17	5.50	-2.22%	-0.89	-0.28
P07	67.41	2.41	-3.31%	-1.33	-0.94
P08	68.42	1.02	-1.86%	-0.75	-1.18
P09					
P10	69.46	3.46	-0.38%	-0.15	-0.08
P11	68.82	3.40	-1.29%	-0.52	-0.26
P12					
P13					
P14	68.95	0.81	-1.11%	-0.44	-0.86
P15	66.14	2.84	-5.14%	-2.06	-1.25
P16					
P17	68.82	1.32	-1.29%	-0.52	-0.65
P18	69.16	1.66	-0.80%	-0.32	-0.33
P19	74.02	0.77	6.16%	2.46	4.92
P20					
P21	65.12	2.21	-6.60%	-2.64	-2.04
P22	71.10	5.20	1.98%	0.79	0.26
P23	69.84	3.52	0.17%	0.07	0.03
P24	67.75	0.69	-2.83%	-1.13	-2.47
P25					
P26	67.86	2.01	-2.67%	-1.07	-0.91
P27					
P28	70.10	7.28	0.55%	0.22	0.05
P29	74.58	2.61	6.97%	2.79	1.84
P30	66.91	4.89	-4.04%	-1.61	-0.57
P31	70.96	2.73	1.78%	0.71	0.45
P32	69.00	2.03	-1.03%	-0.41	-0.35
P33	68.82	4.04	-1.29%	-0.52	-0.22
P34	71.10	5.20	1.98%	0.79	0.26
P35	68.80	6.74	-1.31%	-0.53	-0.14

Consensus values (raw data)

m	69.11	
s_r	2.0	2.90%
s_L	2.1	3.00%
s_R	2.9	4.17%
p	25	

Consensus values (corrected)

m	68.62	
s_r	2.1	3.06%
s_L	1.3	1.94%
s_R	2.5	3.62%
p	23	



Measurand/ Mixture	nitrogen oxides (NO/NO2 mix)				
Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	78.71	0.59	µmol/mol	1.97	µmol/mol

Reported data

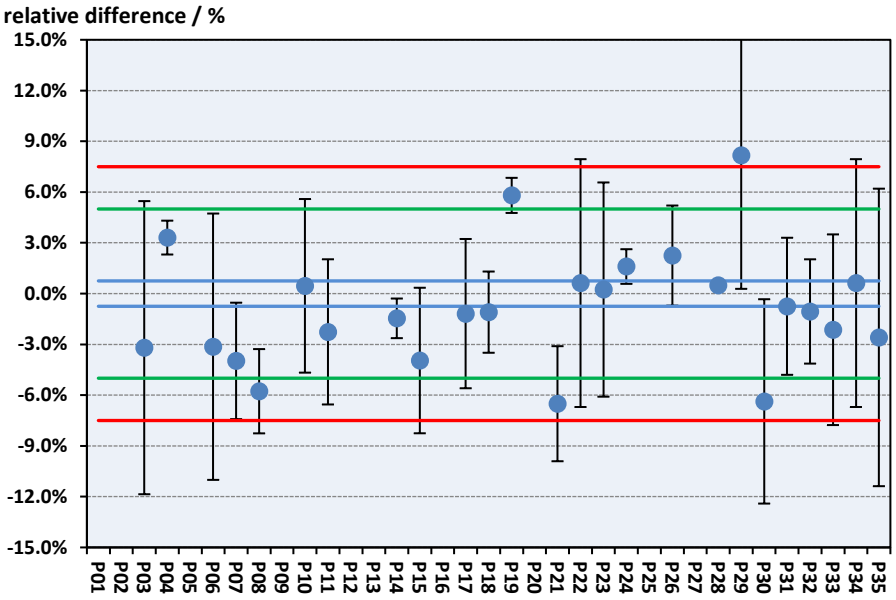
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01					
P02					
P03	76.20	6.60	-3.19%	-1.28	-0.38
P04	81.32	0.81	3.31%	1.32	2.59
P05					
P06	76.24	6.00	-3.14%	-1.26	-0.41
P07	75.58	2.60	-3.98%	-1.59	-1.17
P08	74.17	1.85	-5.77%	-2.31	-2.34
P09					
P10	79.07	4.06	0.46%	0.18	0.09
P11	76.93	3.30	-2.26%	-0.90	-0.53
P12					
P13					
P14	77.56	0.91	-1.46%	-0.58	-1.06
P15	75.60	3.25	-3.95%	-1.58	-0.94
P16					
P17	77.78	3.43	-1.18%	-0.47	-0.27
P18	77.85	1.87	-1.09%	-0.44	-0.44
P19	83.28	0.86	5.80%	2.32	4.37
P20					
P21	73.59	2.50	-6.51%	-2.60	-1.99
P22	79.20	5.80	0.62%	0.25	0.08
P23	78.90	4.99	0.24%	0.10	0.04
P24	79.97	0.82	1.60%	0.64	1.25
P25					
P26	80.48	2.38	2.25%	0.90	0.72
P27					
P28	79.10	0.00	0.50%	0.20	
P29	85.15	6.73	8.18%	3.27	0.95
P30	73.70	4.45	-6.37%	-2.55	-1.12
P31	78.12	3.16	-0.75%	-0.30	-0.18
P32	77.88	2.40	-1.05%	-0.42	-0.34
P33	77.03	4.34	-2.13%	-0.85	-0.38
P34	79.20	5.80	0.62%	0.25	0.08
P35	76.67	6.74	-2.59%	-1.04	-0.30

Consensus values (raw data)

m	78.05	
s_r	0.31	0.40%
s_L	2.8	3.62%
s_R	2.8	3.65%
p	25	

Consensus values (corrected)

m	77.73	
s_r	0.32	0.41%
s_L	2.4	3.12%
s_R	2.4	3.15%
p	24	



Annex B - Converter efficiency

If the reported nitric oxide (NO) measurement of the NO/NO_2 mixture, for each participant, is subtracted from that of their reported nitrogen oxides (NO_X) result, then the nitrogen dioxide (NO_2) result from their measurements can be directly calculated. This derived NO_2 measurement result can be used to calculate the converter efficiency of their analyser where appropriate.

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

Component/ Mixture	nitrogen dioxide (NO2)

Reference	x_{ref}	$U(x_{ref})$ k=2	
	8.99	0.72	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	difference (µmol/mol)	converter efficiency (%)	E_n-number
P01					
P02					
P03	7.87	9.33	-1.1	87.5%	-0.12
P04	12.86	1.06	3.9	143.1%	3.02
P05					
P06	8.07	8.14	-0.9	89.8%	-0.11
P07	8.17	3.55	-0.8	90.9%	-0.23
P08	5.75	2.11	-3.2	64.0%	-1.45
P09					
P10	9.62	5.33	0.6	107.0%	0.12
P11	8.11	4.74	-0.9	90.2%	-0.18
P12					
P13					
P14	8.61	1.21	-0.4	95.8%	-0.27
P15	9.46	4.32	0.5	105.3%	0.11
P16					
P17	8.96	3.68	0.0	99.7%	-0.01
P18	8.69	2.50	-0.3	96.6%	-0.12
P19	9.26	1.16	0.3	103.0%	0.20
P20					
P21	8.47	3.34	-0.5	94.2%	-0.15
P22	8.10	7.79	-0.9	90.1%	-0.11
P23	9.06	6.11	0.1	100.8%	0.01
P24	12.22	1.07	3.2	135.9%	2.51
P25					
P26	12.62	3.12	3.6	140.4%	1.14
P27					
P28	9.00	7.28	0.0	100.1%	0.00
P29	10.57	7.22	1.6	117.6%	0.22
P30	6.79	6.61	-2.2	75.5%	-0.33
P31	7.16	4.18	-1.8	79.6%	-0.43
P32	8.88	3.14	-0.1	98.8%	-0.03
P33	8.21	5.93	-0.8	91.3%	-0.13
P34	8.10	7.79	-0.9	90.1%	-0.11
P35	7.87	9.53	-1.1	87.5%	-0.12

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).