EffecTech
Global Leaders in Gas Measurement

UKAS PROFICIENCY TESTING
4719

Stack Emissions Proficiency Testing Scheme (SEPTS)

Presentation of Results

Round 2023

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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Author(s): Adam Lomax

Dove House
Dove Fields
Uttoxeter
Staffordshire ST14 8HU
United Kingdom
T +44 (0)1889 569229
F +44 (0)1889 569220
www.effectech.co.uk

Table of Contents

Revisions History

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Statement of Confidentiality

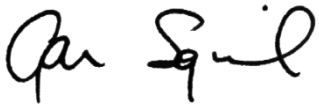
EffecTech keeps all data regarding the performance of individual participants strictly confidential. Results and performance data are protected, stored and backed up on storage network disks and folders to which access is restricted to the scheme coordinator and the technical authority only.

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 2023 (June - July 2023).

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 twenty-nine (29) laboratories signed up to participate in this round. Twenty-nine (29) 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	33.3	1.1	1.6	1.6	0.11
propane	µmol/mol	31.47	0.29	0.37	0.35	0.11
nitric oxide	µmol/mol	163.70	0.78	0.17	0.17	0.045
carbon monoxide	µmol/mol	321.7	2.6	0.22	0.22	0.021
oxygen	%mol/mol	9.378	0.048	0.050	0.050	0.0037
carbon dioxide	%mol/mol	4.210	0.023	0.092	0.092	0.0041
nitric oxide (NO/NO2 mix)	µmol/mol	78.92	0.45	0.23	0.21	0.093
nitrogen oxides (NO/NO2 mix)	µmol/mol	97.89	0.50	0.26	0.22	0.13

3. Results

3.1 Reported results

There were twenty-nine (29) 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	✓	✓	✓	✓			✓	✓

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	✓	✓	✓	✓	✓	✓	✓	✓

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

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	-0.62	0.65	-0.03	0.58	1.52	0.46	-0.08
P02	-1.34	-1.88		-0.17	0.11	-1.32	-0.40	-1.61
P03	-2.21	-0.53	-0.37	-0.05	-0.09	0.52	-0.71	0.50
P04				-0.29	2.57		-0.72	0.33
P05	0.71	-0.97	0.64	0.06	0.77	0.77	0.07	-0.01
P06	-1.39	-0.82		0.57	0.87	-2.40	-1.55	-0.60
P07		-0.43		0.54				
P08	2.67	-0.60	-0.27	0.24	1.08	-1.11	-2.01	-2.82
P09	0.70		5.06	-1.49	0.79	-4.99	1.26	0.94
P10	-0.29	0.24	2.29	0.49	0.29	-0.06	-0.15	0.52
P11	-0.75	0.04	0.81	0.73	-0.48	0.48	0.67	0.21
P12					1.18	0.96		
P13	0.47		0.99		-0.07			
P14							-9.89	-15.71
P15	0.57	0.35	0.33	0.51	0.21	-0.12	-0.77	-0.65
P16	-0.05		0.30	-0.12	-0.20	0.88		
P17				0.11	0.09			
P18			0.62		-0.27			
P19		-0.34	0.34	0.20	0.36	0.67		-3.13
P20	1.43	-0.31		-1.71	0.07	2.51	-1.40	-2.47
P21		0.67						
P22	1.72	0.17	-1.08	0.69	-0.71	0.67	-0.77	-0.22
P23				-0.53	1.25	0.76	-0.34	-0.01
P24	2.73	-0.10	1.30	2.30	-0.01			
P25	-0.19	-1.32	0.60	0.58	0.65	1.92	-0.16	-0.49
P26		-0.76	0.19		-2.46			
P27	-1.45	-0.10	-0.14	0.30	0.00	1.27	-0.58	0.75
P28	-0.83	-1.95		-0.87	1.70	0.24	-1.90	-1.68
P29	1.93	-0.64		0.65	-0.06	-1.07	1.16	-0.02

†component assessed based on a z' score

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

However, participant **P14** reported an anomalously low measurement for mixed nitric oxides, **P09** reported low for carbon dioxide and high for nitric oxide, and **P19** reported low for nitrogen oxides.

Participant **P14** reported very similar amounts of nitric oxide and nitrogen oxides suggesting either an error was made during the measurement or their instrumentation is faulty and not able to measure nitrogen dioxide.

Eighteen (18) laboratories (**P01**, **P02**, **P05**, **P07**, **P11**, **P12**, **P13**, **P15**, **P16**, **P17**, **P18**, **P21**, **P22**, **P23**, **P25**, **P27**, **P28** and **P29**) 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	0.04	-0.70	0.51	-0.02	1.16	3.16	0.33	-0.06
P02	-0.53	-3.48		-0.08	0.04	-0.32	-0.13	-0.55
P03	-1.43	-1.48	-0.27	-0.03	-0.17	0.86	-0.51	0.35
P04				-0.54	5.56		-3.16	1.62
P05	0.37	-1.21	1.00	0.05	1.48	1.60	0.05	-0.01
P06	-0.29	-0.22		0.18	0.27	-0.59	-0.63	-0.27
P07		-1.37		0.65				
P08	0.88	-0.44	-0.25	0.12	0.48	-0.20	-1.87	-2.15
P09	0.12		1.08	-0.18	1.71	-11.30	0.29	0.19
P10	-0.04	0.05	1.37	0.42	0.13	0.00	-0.04	0.15
P11	-0.10	0.01	0.48	0.63	-0.22	0.10	0.19	0.06
P12					0.24	0.10		
P13	0.12		0.74		-0.02			
P14							-26.02	-37.34
P15	0.16	0.16	0.18	0.20	0.05	-0.02	-0.20	-0.17
P16	-0.03		1.10	-0.16	-0.32	1.41		
P17				0.14	0.13			
P18			1.37		-0.27			
P19		-0.26	0.31	0.09	0.15	0.30		-3.08
P20	0.78	-0.52		-2.47	0.03	0.50	-0.67	-1.22
P21		0.25						
P22	0.69	0.10	-0.64	0.21	-0.30	0.19	-0.45	-0.12
P23				-0.33	0.63	0.20	-0.34	-0.01
P24	1.53	-0.29	2.38	2.32	-0.01			
P25	-0.14	-2.80	0.25	0.61	0.11	0.26	-0.07	-0.21
P26		-0.73	0.12		-0.55			
P27	-0.93	-0.28	-0.10	0.18	0.00	2.08	-0.41	0.52
P28	-0.63	-2.90		-1.39	1.54	0.48	-1.40	-1.90
P29	0.68	-1.08		0.39	-0.10	-2.29	0.36	0.00

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 **P06**, **P11**, **P15**, **P22** and **P23** 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 **P11**, **P15** and **P22** 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	
33.3	1.1	µmol/mol	0.8	µmol/mol

Reported data

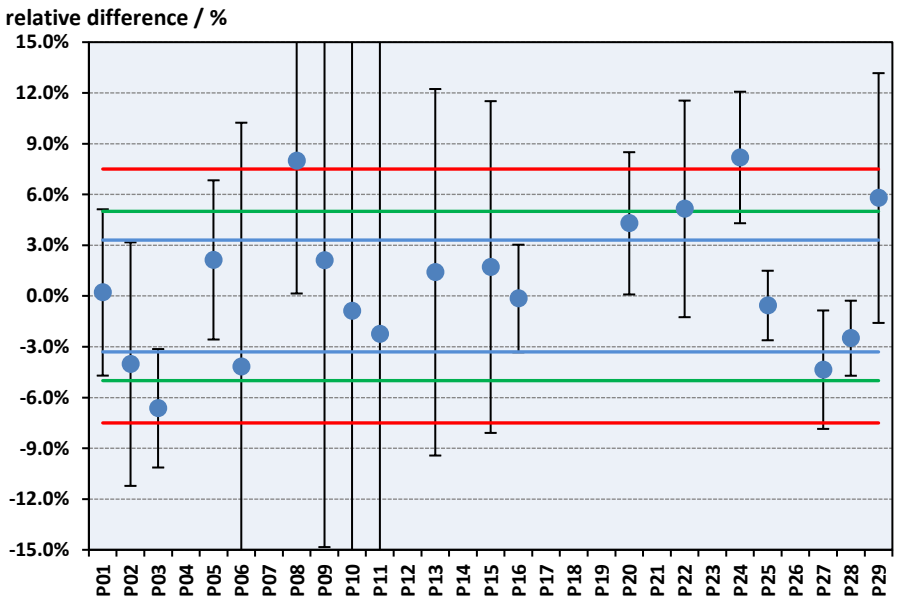
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*Z'*-score	E_n-number
P01	33.4	1.6	0.21%	0.07	0.04
P02	32.0	2.3	-4.03%	-1.34	-0.53
P03	31.1	1.1	-6.64%	-2.21	-1.43
P04					
P05	34.0	1.6	2.13%	0.71	0.37
P06	31.9	4.6	-4.17%	-1.39	-0.29
P07					
P08	36.0	2.8	7.99%	2.67	0.88
P09	34.0	5.8	2.10%	0.70	0.12
P10	33.0	7.3	-0.87%	-0.29	-0.04
P11	32.6	7.4	-2.25%	-0.75	-0.10
P12					
P13	33.8	3.7	1.40%	0.47	0.12
P14					
P15	33.9	3.3	1.71%	0.57	0.16
P16	33.3	1.1	-0.15%	-0.05	-0.03
P17					
P18					
P19					
P20	34.7	1.5	4.29%	1.43	0.78
P21					
P22	35.0	2.2	5.15%	1.72	0.69
P23					
P24	36.0	1.4	8.19%	2.73	1.53
P25	33.1	0.7	-0.56%	-0.19	-0.14
P26					
P27	31.9	1.1	-4.35%	-1.45	-0.93
P28	32.5	0.7	-2.49%	-0.83	-0.63
P29	35.2	2.6	5.79%	1.93	0.68

Consensus values (raw data)

m	33.5	
s_r	0.4	1.18%
s_L	1.5	4.46%
s_R	1.5	4.62%
p	19	

Consensus values (corrected)

m	33.5	
s_r	0.4	1.18%
s_L	1.5	4.46%
s_R	1.5	4.62%
p	19	



Measurand/ Mixture	propane

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	31.47	0.29	µmol/mol	1.57	µmol/mol

Reported data

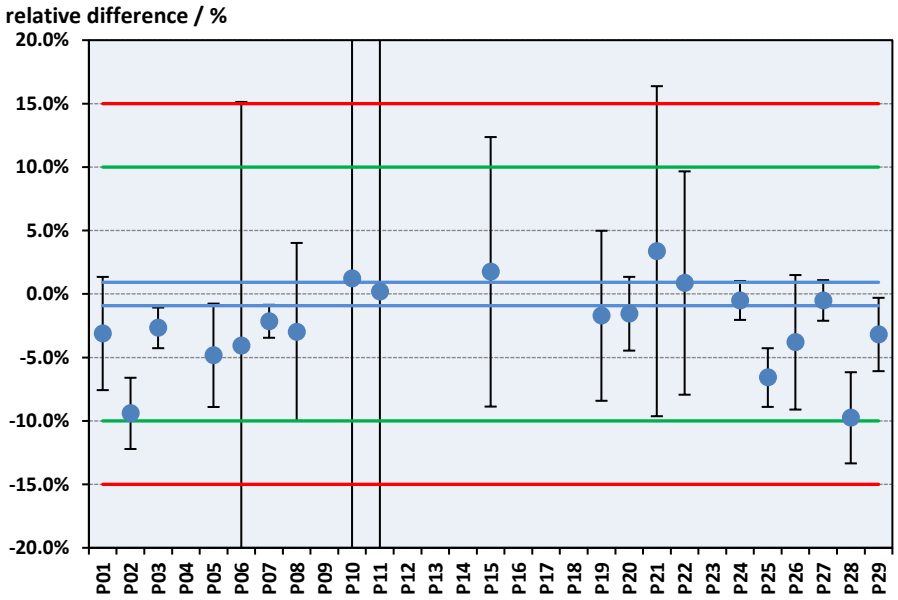
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	30.49	1.36	-3.11%	-0.62	-0.70
P02	28.51	0.80	-9.41%	-1.88	-3.48
P03	30.63	0.49	-2.67%	-0.53	-1.48
P04					
P05	29.95	1.22	-4.83%	-0.97	-1.21
P06	30.19	5.80	-4.08%	-0.82	-0.22
P07	30.79	0.40	-2.15%	-0.43	-1.37
P08	30.53	2.14	-2.99%	-0.60	-0.44
P09					
P10	31.85	7.01	1.22%	0.24	0.05
P11	31.53	6.95	0.18%	0.04	0.01
P12					
P13					
P14					
P15	32.02	3.40	1.75%	0.35	0.16
P16					
P17					
P18					
P19	30.93	2.07	-1.72%	-0.34	-0.26
P20	30.98	0.90	-1.56%	-0.31	-0.52
P21	32.53	4.23	3.37%	0.67	0.25
P22	31.74	2.79	0.86%	0.17	0.10
P23					
P24	31.31	0.48	-0.51%	-0.10	-0.29
P25	29.40	0.68	-6.58%	-1.32	-2.80
P26	30.27	1.60	-3.81%	-0.76	-0.73
P27	31.31	0.50	-0.51%	-0.10	-0.28
P28	28.40	1.02	-9.76%	-1.95	-2.90
P29	30.47	0.88	-3.19%	-0.64	-1.08

Consensus values (raw data)

m	30.65	
s_r	0.15	0.50%
s_L	1.06	3.47%
s_R	1.08	3.51%
p	20	

Consensus values (corrected)

m	30.77	
s_r	0.16	0.51%
s_L	0.94	3.06%
s_R	0.96	3.11%
p	19	



Measurand/ Mixture	nitric oxide

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	163.70	0.78	µmol/mol	4.09	µmol/mol

Reported data

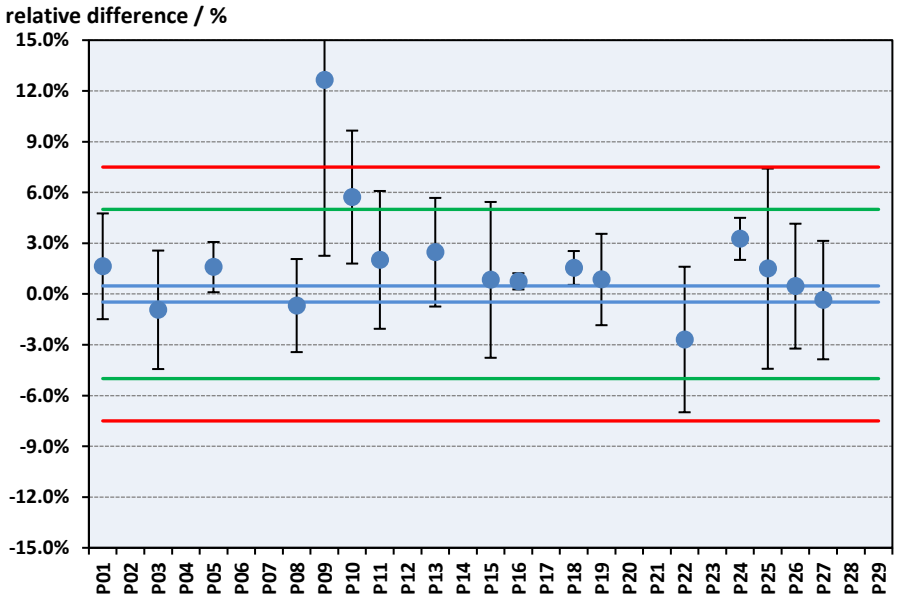
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	166.38	5.20	1.64%	0.65	0.51
P02					
P03	162.17	5.68	-0.93%	-0.37	-0.27
P04					
P05	166.30	2.47	1.59%	0.64	1.00
P06					
P07					
P08	162.58	4.47	-0.68%	-0.27	-0.25
P09	184.40	19.16	12.65%	5.06	1.08
P10	173.08	6.80	5.73%	2.29	1.37
P11	167.00	6.80	2.02%	0.81	0.48
P12					
P13	167.74	5.38	2.47%	0.99	0.74
P14					
P15	165.07	7.60	0.83%	0.33	0.18
P16	164.93	0.79	0.75%	0.30	1.10
P17					
P18	166.22	1.66	1.54%	0.62	1.37
P19	165.10	4.46	0.86%	0.34	0.31
P20					
P21					
P22	159.30	6.85	-2.69%	-1.08	-0.64
P23					
P24	169.03	2.10	3.26%	1.30	2.38
P25	166.15	9.83	1.50%	0.60	0.25
P26	164.46	6.07	0.46%	0.19	0.12
P27	163.11	5.71	-0.36%	-0.14	-0.10
P28					
P29					

Consensus values (raw data)

m	165.69	
s_r	0.43	0.26%
s_L	3.74	2.25%
s_R	3.76	2.27%
p	17	

Consensus values (corrected)

m	165.55	
s_r	0.43	0.26%
s_L	3.36	2.03%
s_R	3.39	2.05%
p	16	



Measurand/ Mixture	carbon monoxide

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
321.7	2.6	µmol/mol	4.8	µmol/mol

Reported data

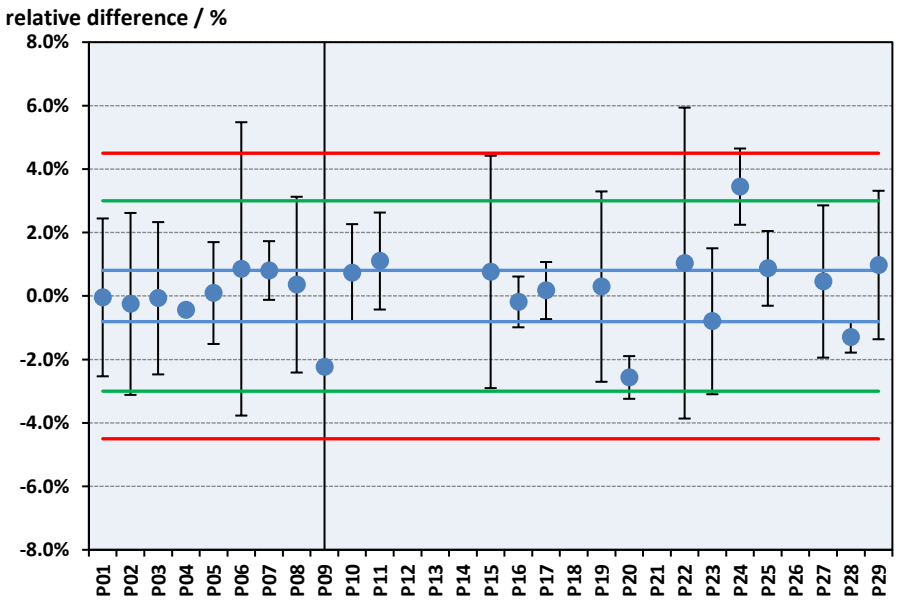
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	321.6	8.0	-0.04%	-0.03	-0.02
P02	320.9	9.2	-0.25%	-0.17	-0.08
P03	321.5	7.7	-0.07%	-0.05	-0.03
P04	320.3	0.0	-0.44%	-0.29	-0.54
P05	322.0	5.2	0.09%	0.06	0.05
P06	324.5	15.0	0.85%	0.57	0.18
P07	324.3	3.0	0.80%	0.54	0.65
P08	322.9	8.9	0.36%	0.24	0.12
P09	314.5	40.3	-2.24%	-1.49	-0.18
P10	324.1	5.0	0.73%	0.49	0.42
P11	325.2	5.0	1.10%	0.73	0.63
P12					
P13					
P14					
P15	324.1	11.9	0.76%	0.51	0.20
P16	321.1	2.6	-0.19%	-0.12	-0.16
P17	322.3	2.9	0.17%	0.11	0.14
P18					
P19	322.7	9.7	0.30%	0.20	0.09
P20	313.4	2.1	-2.57%	-1.71	-2.47
P21					
P22	325.0	15.9	1.04%	0.69	0.21
P23	319.1	7.3	-0.80%	-0.53	-0.33
P24	332.8	4.0	3.45%	2.30	2.32
P25	324.5	3.8	0.87%	0.58	0.61
P26					
P27	323.2	7.8	0.46%	0.30	0.18
P28	317.5	1.5	-1.30%	-0.87	-1.39
P29	324.8	7.6	0.98%	0.65	0.39

Consensus values (raw data)

m	322.6	
s_r	0.5	0.15%
s_L	3.8	1.18%
s_R	3.8	1.19%
p	23	

Consensus values (corrected)

m	322.6	
s_r	0.5	0.16%
s_L	2.2	0.67%
s_R	2.2	0.69%
p	20	



Measurand/ Mixture	oxygen

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	9.378	0.048	%mol/mol	0.104	%mol/mol

Reported data

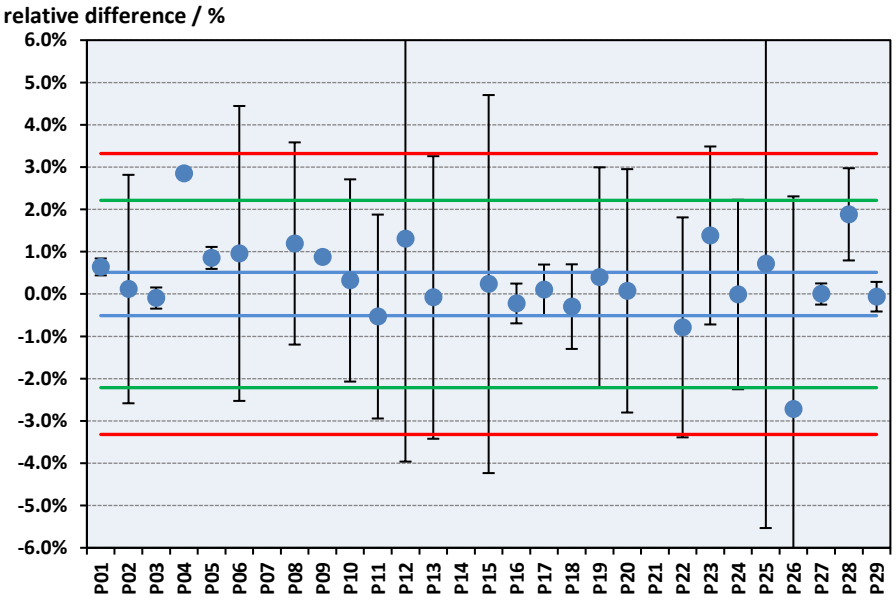
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01	9.438	0.019	0.64%	0.58	1.16
P02	9.389	0.254	0.12%	0.11	0.04
P03	9.369	0.023	-0.10%	-0.09	-0.17
P04	9.645	0.000	2.85%	2.57	5.56
P05	9.458	0.025	0.85%	0.77	1.48
P06	9.468	0.330	0.96%	0.87	0.27
P07					
P08	9.490	0.227	1.19%	1.08	0.48
P09	9.460	0.000	0.87%	0.79	1.71
P10	9.408	0.225	0.32%	0.29	0.13
P11	9.328	0.225	-0.53%	-0.48	-0.22
P12	9.500	0.500	1.30%	1.18	0.24
P13	9.370	0.313	-0.08%	-0.07	-0.02
P14					
P15	9.400	0.420	0.23%	0.21	0.05
P16	9.357	0.044	-0.22%	-0.20	-0.32
P17	9.387	0.056	0.10%	0.09	0.13
P18	9.350	0.094	-0.30%	-0.27	-0.27
P19	9.415	0.245	0.39%	0.36	0.15
P20	9.385	0.270	0.07%	0.07	0.03
P21					
P22	9.304	0.242	-0.79%	-0.71	-0.30
P23	9.508	0.200	1.38%	1.25	0.63
P24	9.377	0.210	-0.01%	-0.01	-0.01
P25	9.445	0.590	0.71%	0.65	0.11
P26	9.123	0.459	-2.72%	-2.46	-0.55
P27	9.378	0.023	0.00%	0.00	0.00
P28	9.555	0.104	1.88%	1.70	1.54
P29	9.372	0.033	-0.06%	-0.06	-0.10

Consensus values (raw data)

m	9.414	
s_r	0.023	0.25%
s_L	0.101	1.07%
s_R	0.104	1.10%
p	26	

Consensus values (corrected)

m	9.417	
s_r	0.024	0.25%
s_L	0.064	0.67%
s_R	0.068	0.72%
p	24	



Measurand/ Mixture	carbon dioxide

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	4.210	0.023	%mol/mol	0.052	%mol/mol

Reported data

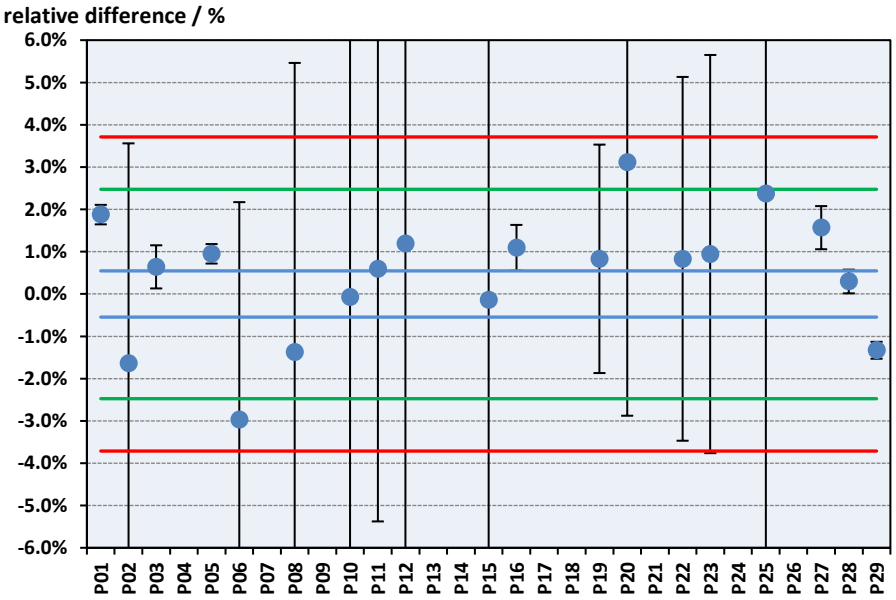
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01	4.289	0.010	1.88%	1.52	3.16
P02	4.141	0.215	-1.64%	-1.32	-0.32
P03	4.237	0.022	0.64%	0.52	0.86
P04					
P05	4.250	0.010	0.95%	0.77	1.60
P06	4.085	0.210	-2.97%	-2.40	-0.59
P07					
P08	4.152	0.284	-1.38%	-1.11	-0.20
P09	3.950	0.000	-6.18%	-4.99	-11.30
P10	4.207	5.780	-0.07%	-0.06	0.00
P11	4.235	0.253	0.59%	0.48	0.10
P12	4.260	0.500	1.19%	0.96	0.10
P13					
P14					
P15	4.204	0.290	-0.14%	-0.12	-0.02
P16	4.256	0.023	1.09%	0.88	1.41
P17					
P18					
P19	4.245	0.115	0.83%	0.67	0.30
P20	4.341	0.260	3.11%	2.51	0.50
P21					
P22	4.245	0.183	0.83%	0.67	0.19
P23	4.250	0.200	0.94%	0.76	0.20
P24					
P25	4.310	0.380	2.38%	1.92	0.26
P26					
P27	4.276	0.022	1.57%	1.27	2.08
P28	4.222	0.012	0.30%	0.24	0.48
P29	4.154	0.008	-1.33%	-1.07	-2.29

Consensus values (raw data)

m	4.227	
s_r	0.079	1.88%
s_L	0.062	1.46%
s_R	0.101	2.38%
p	20	

Consensus values (corrected)

m	4.229	
s_r	0.079	1.88%
s_L	0.059	1.38%
s_R	0.099	2.33%
p	19	



Measurand/ Mixture	nitric oxide (NO/NO2 mix)

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
78.92	0.45	µmol/mol	1.97	µmol/mol

Reported data

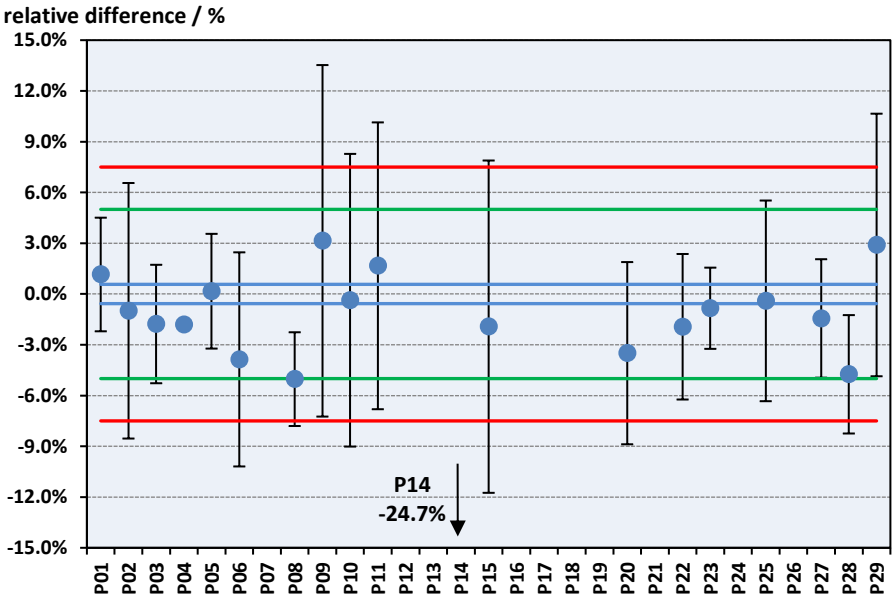
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	79.83	2.68	1.15%	0.46	0.33
P02	78.14	5.90	-0.99%	-0.40	-0.13
P03	77.52	2.71	-1.77%	-0.71	-0.51
P04	77.50	0.00	-1.80%	-0.72	-3.16
P05	79.05	2.68	0.16%	0.07	0.05
P06	75.87	4.80	-3.86%	-1.55	-0.63
P07					
P08	74.95	2.08	-5.03%	-2.01	-1.87
P09	81.40	8.46	3.14%	1.26	0.29
P10	78.63	6.80	-0.37%	-0.15	-0.04
P11	80.24	6.80	1.67%	0.67	0.19
P12					
P13					
P14	59.40	0.60	-24.73%	-9.89	-26.02
P15	77.40	7.60	-1.93%	-0.77	-0.20
P16					
P17					
P18					
P19					
P20	76.16	4.10	-3.50%	-1.40	-0.67
P21					
P22	77.39	3.33	-1.93%	-0.77	-0.45
P23	78.26	1.88	-0.84%	-0.34	-0.34
P24					
P25	78.60	4.66	-0.41%	-0.16	-0.07
P26					
P27	77.78	2.72	-1.44%	-0.58	-0.41
P28	75.17	2.63	-4.75%	-1.90	-1.40
P29	81.21	6.30	2.90%	1.16	0.36

Consensus values (raw data)

m	77.46	
s_r	0.70	0.91%
s_L	3.36	4.33%
s_R	3.43	4.43%
p	19	

Consensus values (corrected)

m	77.90	
s_r	0.71	0.91%
s_L	1.73	2.23%
s_R	1.87	2.40%
p	18	



Measurand/ Mixture	nitrogen oxides (NO/NO2 mix)

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
97.89	0.50	µmol/mol	2.45	µmol/mol

Reported data

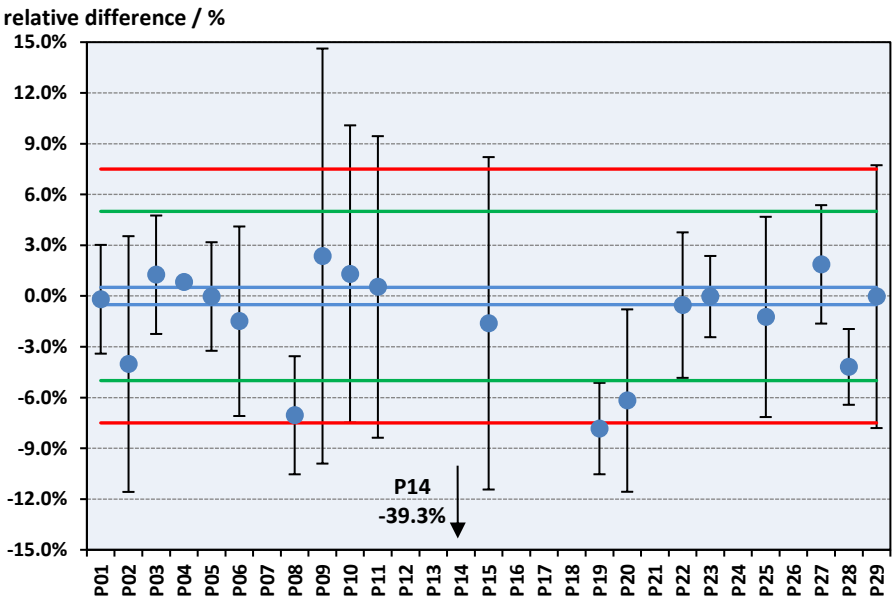
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	97.70	3.14	-0.19%	-0.08	-0.06
P02	93.95	7.10	-4.02%	-1.61	-0.55
P03	99.12	3.47	1.26%	0.50	0.35
P04	98.70	0.00	0.83%	0.33	1.62
P05	97.86	3.14	-0.03%	-0.01	-0.01
P06	96.43	5.40	-1.49%	-0.60	-0.27
P07					
P08	90.99	3.18	-7.05%	-2.82	-2.15
P09	100.20	12.29	2.36%	0.94	0.19
P10	99.16	8.71	1.30%	0.52	0.15
P11	98.41	8.77	0.54%	0.21	0.06
P12					
P13					
P14	59.45	0.90	-39.27%	-15.71	-37.34
P15	96.31	9.46	-1.61%	-0.65	-0.17
P16					
P17					
P18					
P19	90.22	2.44	-7.83%	-3.13	-3.08
P20	91.84	4.95	-6.18%	-2.47	-1.22
P21					
P22	97.36	4.19	-0.54%	-0.22	-0.12
P23	97.86	2.35	-0.03%	-0.01	-0.01
P24					
P25	96.68	5.72	-1.24%	-0.49	-0.21
P26					
P27	99.72	3.49	1.87%	0.75	0.52
P28	93.79	2.10	-4.19%	-1.68	-1.90
P29	97.85	7.60	-0.04%	-0.02	0.00

Consensus values (raw data)

m	95.53	
s_r	0.67	0.70%
s_L	6.31	6.61%
s_R	6.35	6.65%
p	20	

Consensus values (corrected)

m	96.35	
s_r	0.68	0.70%
s_L	2.96	3.08%
s_R	3.04	3.16%
p	19	



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	
18.97	0.76	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	difference (µmol/mol)	converter efficiency (%)	E_n-number
P01	17.87	4.13	-1.1	94.2%	-0.26
P02	15.82	9.23	-3.2	83.4%	-0.34
P03	21.60	4.40	2.6	113.9%	0.59
P04	21.20	0.00	2.2	111.8%	2.93
P05	18.81	4.13	-0.2	99.2%	-0.04
P06	20.56	7.22	1.6	108.4%	0.22
P07					
P08	16.04	3.79	-2.9	84.6%	-0.76
P09	18.80	14.92	-0.2	99.1%	-0.01
P10	20.53	11.05	1.6	108.2%	0.14
P11	18.18	11.10	-0.8	95.8%	-0.07
P12					
P13					
P14	0.04	1.08	-18.9	0.2%	-14.32
P15	18.91	12.13	-0.1	99.7%	0.00
P16					
P17					
P18					
P19					
P20	15.68	6.43	-3.3	82.7%	-0.51
P21					
P22	19.97	5.35	1.0	105.3%	0.19
P23	19.60	3.01	0.6	103.3%	0.20
P24					
P25	18.08	7.38	-0.9	95.3%	-0.12
P26					
P27	21.94	4.43	3.0	115.7%	0.66
P28	18.61	3.37	-0.4	98.1%	-0.10
P29	16.65	9.87	-2.3	87.8%	-0.23

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). Thirteen (13) participants demonstrated converter efficiencies above this 95% expectation.