EffecTech
Global Leaders in Gas Measurement

UKAS PROFICIENCY TESTING
4719

Stack Emissions Proficiency Testing Scheme (SEPTS)

Presentation of Results

Round 2017

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

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Statement of Confidentiality

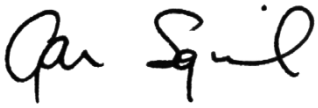
EffecTech keeps all data regarding the performance of individual participants strictly confidential. Results and performance data are protected, stored and backed up on storage network disks and folders to which access is restricted to the scheme coordinator and the technical authority only.

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 2017 (May - July 2017).

The SEPTS scheme provides an objective way of assessing the performance of each participant by a series of annual inter-laboratory comparisons. The scheme is aimed at laboratories/testing organisations working in the field of continuous emissions monitoring (CEM) of stationary sources often in waste incineration or large combustion plant processes.

In this round participants were given the opportunity of analysing up to eight (8) different measurands in seven (7) gas mixtures. The composition range of each measurand in each mixture is shown in the tables below.

Table 1: Composition range by gas mixture type

measurand	range
sulphur dioxide (SO_2) in nitrogen	50 to 1000 µmol/mol
propane (C_3H_8) in 10% oxygen / nitrogen	1 to 50 µmol/mol
nitric oxide (NO) in nitrogen	5 to 500 µmol/mol
carbon monoxide (CO) in nitrogen	50 to 1000 µmol/mol
oxygen (O_2) in nitrogen	2 to 14 %mol/mol
carbon dioxide (CO_2) in nitrogen	1 to 10 %mol/mol
nitric oxide (NO) and nitrogen oxides (NO_X) in nitrogen	40 to 400 µmol/mol 50 to 500 µmol/mol

Note: all units used in this report are in the SI unit of amount of substance fraction (mol/mol) or in metric prefixes thereof.
500 µmol/mol is equivalent to 500 x 10^{-6} mol/mol
10 %mol/mol is equivalent to 10 dmol/mol is equivalent to 10 x 10^{-2} mol/mol

Gas mixture preparation, reference value assignment and the assessment of participants' results are all carried out by designated operators and approved signatories within EffecTech and in accordance with our ISO/IEC 17043 accredited processes.

In addition, all logistics management and preparation of shipping documentation is also carried out by designated approved personnel within EffecTech. All shipping, freight forwarding and proficiency testing item distribution is supplied by specialist transport providers.

A total of twenty-seven (27) laboratories signed up to participate in this round. All participants, to whom items were distributed, submitted results for one or more of the measurands assessed in the scheme.

2. Mixture preparation and reference value assignment

2.1 Procedure

Preparation of mixture batches

For each mixture type, a single large volume parent mixture was prepared by a gravimetric method in accordance with ISO 6142-1:2015. A batch of mixtures of each type was then produced by decanting the parent mixture into a batch of lower volume pre-prepared and evacuated daughter cylinders. The parent mixture and daughter mixtures were then calibrated.

Mixture calibration

All parent mixtures were calibrated using a two-point calibration design with bracketing (TPC), with the exception of propane which was calibrated using a single-point through origin calibration (SPO). Both of these calibration methods are in accordance with ISO 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 and TM025). These can be found in our scope of accreditation published on the United Kingdom Accreditation Service (UKAS) website (www.ukas.org).

Reference mixture traceability

An analytical comparison method is used for the calibration of all mixtures in this scheme. Parent mixtures are calibrated by comparison with reference gas mixtures generated dynamically in accordance with ISO 6145-7. In-house primary reference gas mixtures (PRGM) are used for blending which are traceable by verification to the National Physical Laboratory (NPL, UK) or to the Van Swinden Laboratorium (VSL, NL). This process ensured that the values assigned to the mixtures in this scheme are metrologically traceable to international standards, through an unbroken chain of comparisons, and ultimately to the amount of substance (mole) defined in the SI (International System of Units).

Homogeneity assessment

Statistical analysis of the spread of reference values obtained for each batch of mixtures (derived through calibration above) is used to assess the homogeneity between the set of decant mixtures to be distributed to each participant. The dispersion of the amount fraction of each component due to batch inhomogeneity is known as the between-bottle standard deviation (s_{bb}). The uncertainty arising from this is the between-bottle uncertainty (u_{bb}). The statistical procedure used for the determination of $u_{bb}=s_{bb}$ can be found in ISO Guide 35 : 2006. This uncertainty should be less than or equal to the characterisation uncertainty, u_{char}, in order to accept the batch. This condition was met for all components in all mixtures produced for all participants in this round.

Reference value assignment

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

The initial combined uncertainty determined for each reference value was calculated from the equation below (ISO Guide 35 : 2006 - section 6.2).

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

This combined uncertainty, u_c, is dominated in all cases by the calibration uncertainty, u_{char}

Following this calculation, the expanded uncertainty, $k \cdot u_c$, (k=2), was compared to the Calibration and Measurement Capability (CMC) for which EffecTech is accredited to ISO 17025. If U_{CMC} (k=2) was greater than $k \cdot u_c$ (k=2) then the uncertainty on the reference value was assigned to that stated in our published CMC in accordance with accepted practice such that

$$U_{ref} = \max (U_{CMC} , 2u_c)$$

The use of a coverage factor of k=2 in the assignment of U_{ref} provides a level of confidence of approximately 95%.

The individual calibration data for each suite of decant mixtures is not shown in this report. However, this data is available to all participants on request from EffecTech.

Stability statement

Over several years EffecTech has built up a history of intercomparisons of mixture types featured in this PT scheme. Data from these intercomparisons show clearly that all mixtures remain stable within their stated uncertainty for a minimum of 12 months with the exception of the NO/NO_2 mixture which remains stable for 6 months.

With this exception, the stability of each mixture is guaranteed for a period of 12 months. Within this time period there is no additional uncertainty ascribed to the reference values resulting from the long or short term stability of the mixtures. This is valid providing the mixtures are not used beyond this stability period.

The majority of these mixtures will be stable (within their stated uncertainty) for considerably longer but this period has not been determined.

2.2 Assigned reference values

The table below show the reference values assigned to the measurands in the mixtures in cylinders distributed to participants of this scheme.

Table 2: Reference values assigned following batch homogeneity assessment

measurand	units	x_{ref}	$U(x_{ref})$	u_c / %	u_{char} / %	u_{bb} / %
sulphur dioxide	µmol/mol	109.9	1.3	0.57	0.57	0.087
propane	µmol/mol	24.08	0.15	0.31	0.31	0.032
nitric oxide	µmol/mol	79.78	0.52	0.18	0.17	0.050
carbon monoxide	µmol/mol	200.1	1.5	0.28	0.28	0.012
oxygen	%mol/mol	11.071	0.063	0.13	0.13	0.010
carbon dioxide	%mol/mol	9.685	0.031	0.16	0.16	0.003
nitric oxide (NO/NO_2 mix)	µmol/mol	177.4	1.6	0.44	0.28	0.34
nitrogen oxides (NO/NO_2 mix)	µmol/mol	198.9	1.6	0.41	0.28	0.30

3. Results

3.1 Reported results

There were twenty seven (27) 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	✓	✓	✓	✓	✓	✓	✓	✓

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	✓	✓			✓	✓	✓	✓

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

3.2 Measures of performance

z-score

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

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

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

where x_{meas} is the measured result reported by the laboratory
x_{ref} is the assigned reference value and
σ is the absolute standard deviation used for performance assessment (SDPA) which can be calculated from the relative standard deviation for performance assessment S_{PT} by

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

The relative standard deviation for performance assessment used for calculating the **z**-scores has been fixed for all components by EffecTech and based upon a reasonable expectation of the performance capabilities that should be demonstrated by each laboratory. These values have been chosen with reference to relevant CEN standards, the Waste Incineration Directive (WID) and the Large Combustion Plant Directive (LCPD). These are given in the tables below.

Table 4: Standard deviation for performance assessment

measurand	S_{PT} (mol/mol)
sulphur dioxide	5.0 % relative
propane	7.5 % relative
nitric oxide	5.0 % relative
carbon monoxide	3.0 % relative
oxygen	2.0 % relative
carbon dioxide	2.0 % relative
nitric oxide (NO/NO2 mix)	5.0 % relative
nitrogen oxides (NO/NO2 mix)	5.0 % relative

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

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

z-score	quality of result
$\|z\| \leq 2$	**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

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

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	-0.05	0.20	0.02	0.24	0.71	1.36	0.79	0.50
P02	0.17	-0.29	0.09	0.06	0.05			
P03	-0.09		-0.07	-0.45	0.58	-1.12	1.02	0.83
P04				-0.22				
P05	0.29		0.06	0.04	-0.02	-0.12		
P06	-0.10	-0.10	-0.05	-0.05	0.09	1.47	0.35	0.60
P07			-0.03	0.72	-0.30	-0.08	-0.17	-0.21
P08				-0.35	0.07			
P09	0.30							
P10			0.01	-0.79		-0.50		
P11	-0.55		0.99	-0.63	0.67			0.66
P12	0.01			-0.05				
P13	0.21	0.00	0.16	0.15	-0.06	0.58	0.33	-0.03
P14		1.27	0.04	0.02	0.03		0.58	0.50
P15				0.37	0.14	1.15	0.38	0.29
P16				0.02				
P17		-0.19						
P18			0.40	0.01				
P19	1.30							1.24
P20	-0.25		0.14	0.00		0.42	0.20	0.21
P21	-0.38	1.19	-0.40	0.30	-0.73			
P22	0.75	-0.02	0.48	0.07	7.89	0.26	0.14	0.02
P23	0.49	-0.36	-0.27	0.19	-0.07	0.66	0.03	0.19
P24					-0.46	0.80		
P25	-0.13	0.25		0.27	0.05	0.59	0.22	0.16
P26		0.07	-0.07	-0.18	-0.05	0.09	0.31	0.74
P27	0.29	-0.90	0.36	0.05	0.85		0.36	0.53

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

Participant **P22** reported an unsatisfactory result for the oxygen measurand only.

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	-0.02	0.06	0.01	0.27	0.12	0.52	0.83	0.60
P02	0.39	-1.19	0.40	0.22	0.17			
P03	-0.08		-0.04	-0.22	0.16	-0.31	0.55	0.50
P04				-0.22				
P05	0.78		0.32	0.12	-0.05	-0.52		
P06	-0.09	-0.49	-0.07	-0.04	0.14	0.61	0.36	0.57
P07			-0.02	0.40	-0.11	-0.02	-0.11	-0.14
P08				-0.34	0.05			
P09	1.18							
P10			0.01	-0.62		-0.20		
P11	-0.14		0.47	-0.32	1.51			0.53
P12	0.05			-0.14				
P13	0.25	0.01	0.29	0.21	-0.05	0.37	0.71	-0.07
P14		8.79	0.13	0.04	0.05		2.40	2.67
P15				0.45	0.11	0.97	0.76	0.58
P16				0.05				
P17		-0.32						
P18			1.25	0.02				
P19	1.13							1.11
P20	-0.47		0.24	0.00		0.34	0.35	0.34
P21	-1.59	1.07	-1.55	0.64	-2.44			
P22	1.58	-0.07	1.13	0.10	6.53	1.37	0.31	0.05
P23	0.52	-0.66	-0.20	0.12	-0.03	0.24	0.03	0.21
P24					-0.35	0.63		
P25	-0.17	0.18		0.22	0.03	0.10	0.24	0.18
P26		0.19	-0.13	-0.20	-0.05	0.08	0.55	1.29
P27	0.07	-0.36	0.18	0.03	1.91		0.17	0.26

Laboratories **P02, P09, P11, P14, P18, P19, P21, P26** and **P27** scored perfectly on the basis of ***z***-scores but failed on one or more components on the basis of E_n-numbers. These laboratories underestimated their uncertainties for failing components.

All other laboratories reported excellent results with perfect scores on the basis of both performance measures.

Annex A - Detailed results by measurand

Detailed results for all measurands in all mixtures are shown in subsequent charts.

In each chart, the reported results are shown with the dots in terms of a relative difference (in percent) from the assigned reference value. The reported uncertainties (where supplied) are shown as "error bars" on the reported values.

In each chart the bound limit lines surrounding the zero relative difference signify

- the percentage relative uncertainty on the reference value, %U(x_{ref}) k=2 (in **blue**)
- the |z|=2 satisfactory limit (in **green**)
- the |z|=3 unsatisfactory limit (in **red**)

This annex also includes additional statistics presenting consensus values from the pool of laboratories on the basis of raw data and correct data (following the removal of outlying reported values).

Additional tables also show repeatability standard deviation (s_r), between laboratory standard deviation (s_L) and reproducibility standard deviation (s_R) on the basis of raw and corrected data. The data has been calculated in accordance with the robust statistical methods in ISO 5725 Parts 1 and 2. The detailed calculations made to derive these results are outside the scope of this report but will be provided to participants on request from the scheme coordinator.

Measurand/ Mixture: sulphur dioxide

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
109.9	1.3	µmol/mol	5.5	µmol/mol

Reported data

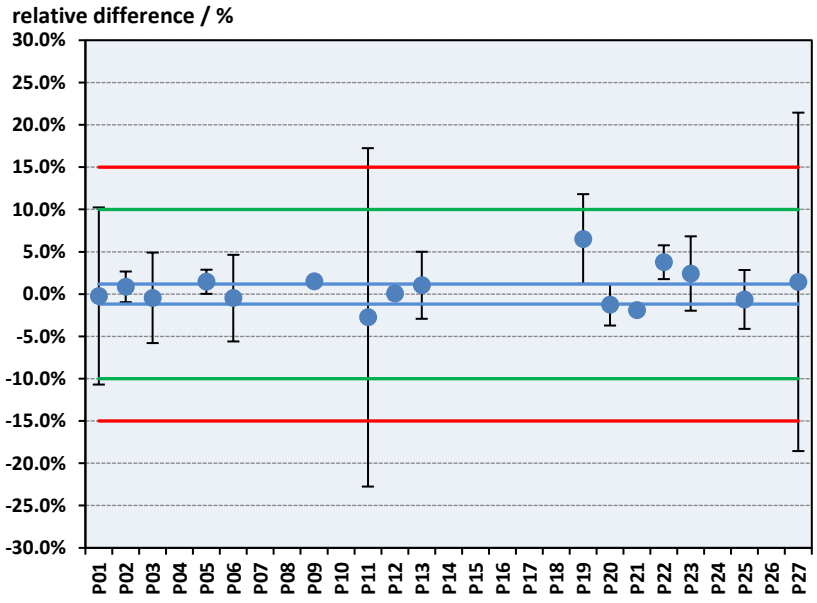
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	109.7	11.5	-0.23%	-0.05	-0.02
P02	110.8	2.0	0.85%	0.17	0.39
P03	109.4	5.9	-0.45%	-0.09	-0.08
P04					
P05	111.5	1.6	1.45%	0.29	0.78
P06	109.4	5.6	-0.48%	-0.10	-0.09
P07					
P08					
P09	111.6	0.6	1.52%	0.30	1.18
P10					
P11	106.9	21.4	-2.75%	-0.55	-0.14
P12	110.0	0.8	0.07%	0.01	0.05
P13	111.0	4.4	1.04%	0.21	0.25
P14					
P15					
P16					
P17					
P18					
P19	117.1	6.2	6.51%	1.30	1.13
P20	108.5	2.7	-1.26%	-0.25	-0.47
P21	107.8	0.2	-1.91%	-0.38	-1.59
P22	114.0	2.3	3.76%	0.75	1.58
P23	112.6	5.0	2.43%	0.49	0.52
P24					
P25	109.2	3.8	-0.64%	-0.13	-0.17
P26					
P27	111.5	22.3	1.44%	0.29	0.07

Consensus values (raw data)

m	110.9	
s_r	0.6	0.51%
s_L	2.7	2.41%
s_R	2.7	2.46%
p	16	

Consensus values (corrected)

m	110.4	
s_r	0.6	0.51%
s_L	1.9	1.73%
s_R	2.0	1.80%
p	15	



Measurand/ Mixture: propane

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
24.08	0.15	µmol/mol	1.81	µmol/mol

Reported data

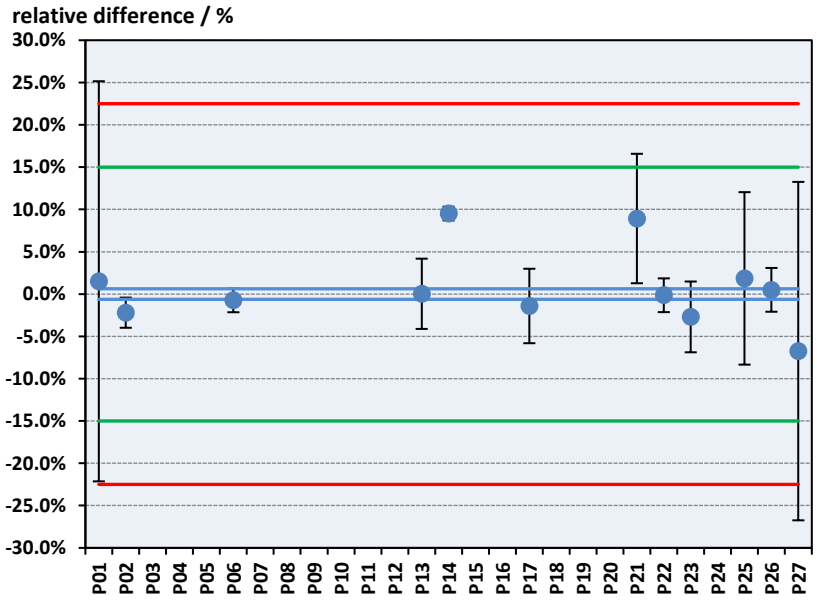
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	24.44	5.78	1.51%	0.20	0.06
P02	23.55	0.42	-2.20%	-0.29	-1.19
P03					
P04					
P05					
P06	23.90	0.33	-0.75%	-0.10	-0.49
P07					
P08					
P09					
P10					
P11					
P12					
P13	24.09	1.00	0.03%	0.00	0.01
P14	26.37	0.21	9.51%	1.27	8.79
P15					
P16					
P17	23.74	1.04	-1.41%	-0.19	-0.32
P18					
P19					
P20					
P21	26.23	2.01	8.93%	1.19	1.07
P22	24.05	0.48	-0.14%	-0.02	-0.07
P23	23.43	0.98	-2.70%	-0.36	-0.66
P24					
P25	24.53	2.50	1.85%	0.25	0.18
P26	24.20	0.63	0.50%	0.07	0.19
P27	22.46	4.49	-6.74%	-0.90	-0.36

Consensus values (raw data)

m	24.44	
s_r	0.15	0.61%
s_L	1.11	4.54%
s_R	1.12	4.58%
p	12	

Consensus values (corrected)

m	24.44	
s_r	0.15	0.61%
s_L	1.11	4.54%
s_R	1.12	4.58%
p	12	



Measurand/ Mixture: nitric oxide

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
79.78	0.52	µmol/mol	3.99	µmol/mol

Reported data

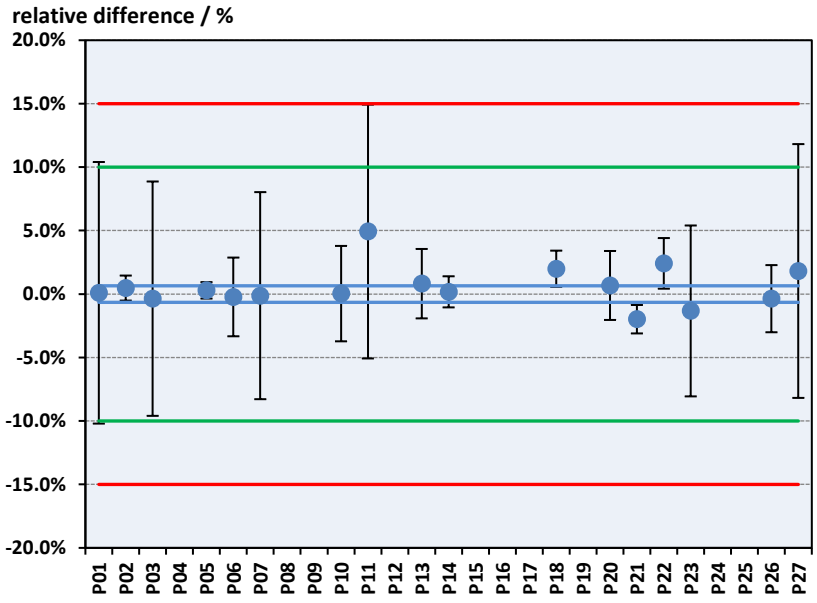
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	79.86	8.23	0.10%	0.02	0.01
P02	80.16	0.79	0.47%	0.09	0.40
P03	79.49	7.34	-0.36%	-0.07	-0.04
P04					
P05	80.01	0.52	0.29%	0.06	0.32
P06	79.60	2.47	-0.23%	-0.05	-0.07
P07	79.68	6.50	-0.13%	-0.03	-0.02
P08					
P09					
P10	79.81	3.00	0.04%	0.01	0.01
P11	83.71	8.37	4.93%	0.99	0.47
P12					
P13	80.43	2.20	0.82%	0.16	0.29
P14	79.92	0.98	0.18%	0.04	0.13
P15					
P16					
P17					
P18	81.37	1.16	2.00%	0.40	1.25
P19					
P20	80.32	2.18	0.68%	0.14	0.24
P21	78.20	0.88	-1.98%	-0.40	-1.55
P22	81.71	1.63	2.42%	0.48	1.13
P23	78.72	5.30	-1.33%	-0.27	-0.20
P24					
P25					
P26	79.49	2.10	-0.36%	-0.07	-0.13
P27	81.23	8.12	1.82%	0.36	0.18

Consensus values (raw data)

m	80.01	
s_r	0.25	0.31%
s_L	1.04	1.29%
s_R	1.06	1.33%
p	17	

Consensus values (corrected)

m	79.95	
s_r	0.23	0.29%
s_L	0.93	1.17%
s_R	0.96	1.20%
p	16	



Measurand/ Mixture: carbon monoxide

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
200.1	1.5	µmol/mol	6.0	µmol/mol

Reported data

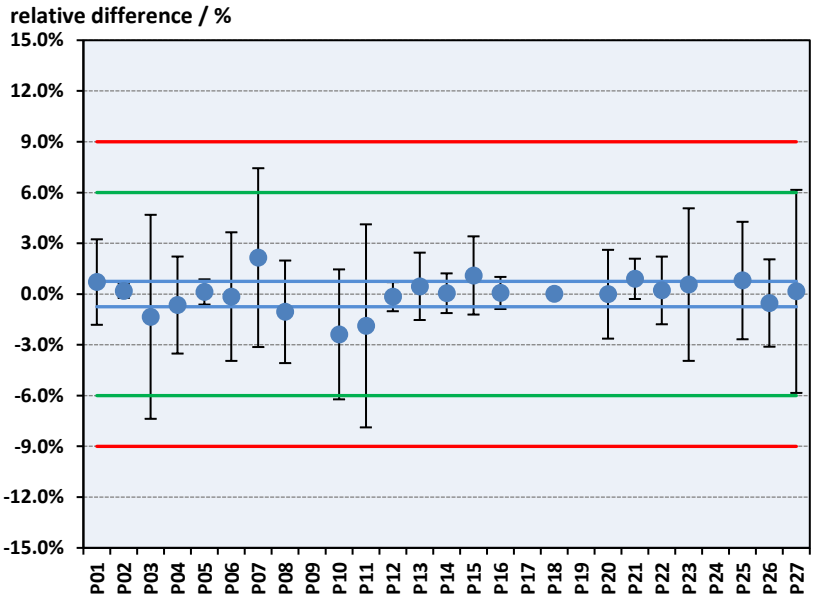
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	201.5	5.1	0.71%	0.24	0.27
P02	200.5	0.8	0.19%	0.06	0.22
P03	197.4	11.9	-1.34%	-0.45	-0.22
P04	198.8	5.7	-0.65%	-0.22	-0.22
P05	200.4	1.5	0.13%	0.04	0.12
P06	199.8	7.6	-0.15%	-0.05	-0.04
P07	204.4	10.8	2.15%	0.72	0.40
P08	198.0	6.0	-1.05%	-0.35	-0.34
P09					
P10	195.3	7.5	-2.38%	-0.79	-0.62
P11	196.3	11.8	-1.88%	-0.63	-0.32
P12	199.8	1.7	-0.15%	-0.05	-0.14
P13	201.0	4.0	0.46%	0.15	0.21
P14	200.2	2.3	0.05%	0.02	0.04
P15	202.3	4.7	1.10%	0.37	0.45
P16	200.2	1.9	0.06%	0.02	0.05
P17					
P18	200.1	0.5	0.02%	0.01	0.02
P19					
P20	200.1	5.2	-0.01%	0.00	0.00
P21	201.9	2.4	0.90%	0.30	0.64
P22	200.5	4.0	0.21%	0.07	0.10
P23	201.2	9.1	0.56%	0.19	0.12
P24					
P25	201.7	7.0	0.80%	0.27	0.22
P26	199.0	5.1	-0.53%	-0.18	-0.20
P27	200.4	12.0	0.16%	0.05	0.03

Consensus values (raw data)

m	200.2	
s_r	0.5	0.23%
s_L	2.1	1.03%
s_R	2.1	1.05%
p	23	

Consensus values (corrected)

m	200.2	
s_r	0.5	0.24%
s_L	1.4	0.72%
s_R	1.5	0.76%
p	21	



Measurand/ Mixture: oxygen

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
11.071	0.063	%mol/mol	0.221	%mol/mol

Reported data

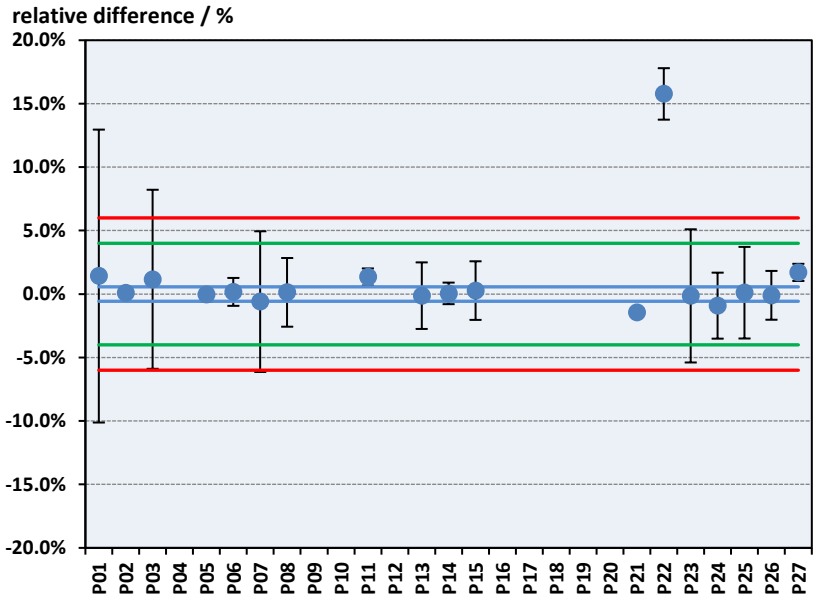
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01	11.228	1.296	1.42%	0.71	0.12
P02	11.082	0.010	0.10%	0.05	0.17
P03	11.200	0.790	1.17%	0.58	0.16
P04					
P05	11.067	0.063	-0.04%	-0.02	-0.05
P06	11.090	0.122	0.17%	0.09	0.14
P07	11.005	0.610	-0.60%	-0.30	-0.11
P08	11.086	0.300	0.14%	0.07	0.05
P09					
P10					
P11	11.220	0.076	1.35%	0.67	1.51
P12					
P13	11.057	0.290	-0.13%	-0.06	-0.05
P14	11.077	0.094	0.05%	0.03	0.05
P15	11.101	0.256	0.27%	0.14	0.11
P16					
P17					
P18					
P19					
P20					
P21	10.910	0.020	-1.45%	-0.73	-2.44
P22	12.817	0.260	15.77%	7.89	6.53
P23	11.055	0.580	-0.14%	-0.07	-0.03
P24	10.970	0.285	-0.91%	-0.46	-0.35
P25	11.083	0.400	0.11%	0.05	0.03
P26	11.060	0.213	-0.10%	-0.05	-0.05
P27	11.260	0.076	1.71%	0.85	1.91

Consensus values (raw data)

m	11.194	
s_r	0.031	0.28%
s_L	0.461	4.12%
s_R	0.462	4.13%
p	18	

Consensus values (corrected)

m	11.075	
s_r	0.030	0.27%
s_L	0.086	0.77%
s_R	0.091	0.82%
p	17	



Measurand/ Mixture carbon dioxide

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
9.685	0.031	%mol/mol	0.194	%mol/mol

Reported data

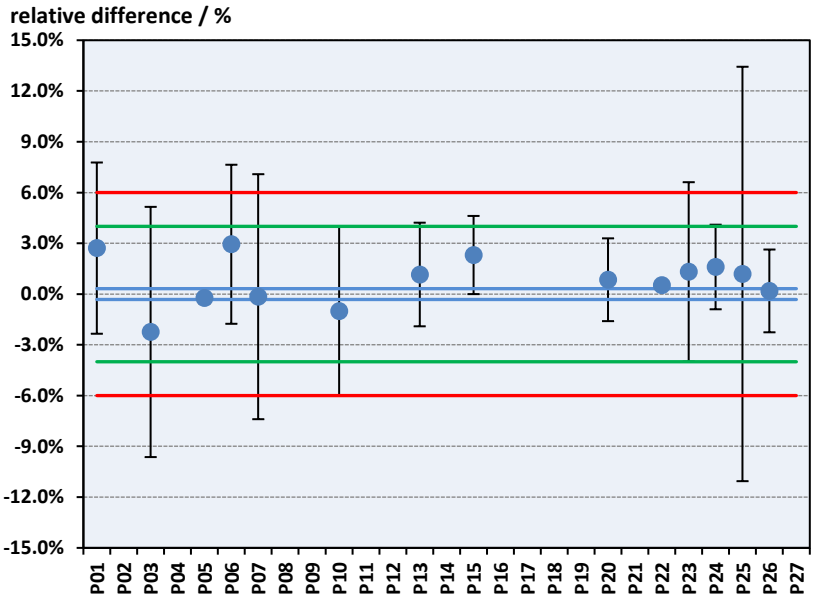
id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01	9.948	0.503	2.72%	1.36	0.52
P02					
P03	9.468	0.700	-2.24%	-1.12	-0.31
P04					
P05	9.662	0.031	-0.24%	-0.12	-0.52
P06	9.970	0.469	2.94%	1.47	0.61
P07	9.670	0.700	-0.15%	-0.08	-0.02
P08					
P09					
P10	9.588	0.480	-1.00%	-0.50	-0.20
P11					
P12					
P13	9.797	0.300	1.16%	0.58	0.37
P14					
P15	9.909	0.229	2.31%	1.15	0.97
P16					
P17					
P18					
P19					
P20	9.767	0.239	0.85%	0.42	0.34
P21					
P22	9.735	0.019	0.52%	0.26	1.37
P23	9.812	0.520	1.31%	0.66	0.24
P24	9.840	0.246	1.60%	0.80	0.63
P25	9.800	1.200	1.19%	0.59	0.10
P26	9.703	0.237	0.19%	0.09	0.08
P27					

Consensus values (raw data)

m	9.753	
s_r	0.020	0.20%
s_L	0.133	1.37%
s_R	0.135	1.38%
p	14	

Consensus values (corrected)

m	9.779	
s_r	0.020	0.20%
s_L	0.105	1.07%
s_R	0.106	1.09%
p	13	



Measurand/ Mixture	nitric oxide (NO/NO2 mix)

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
177.4	1.6	µmol/mol	8.9	µmol/mol

Reported data

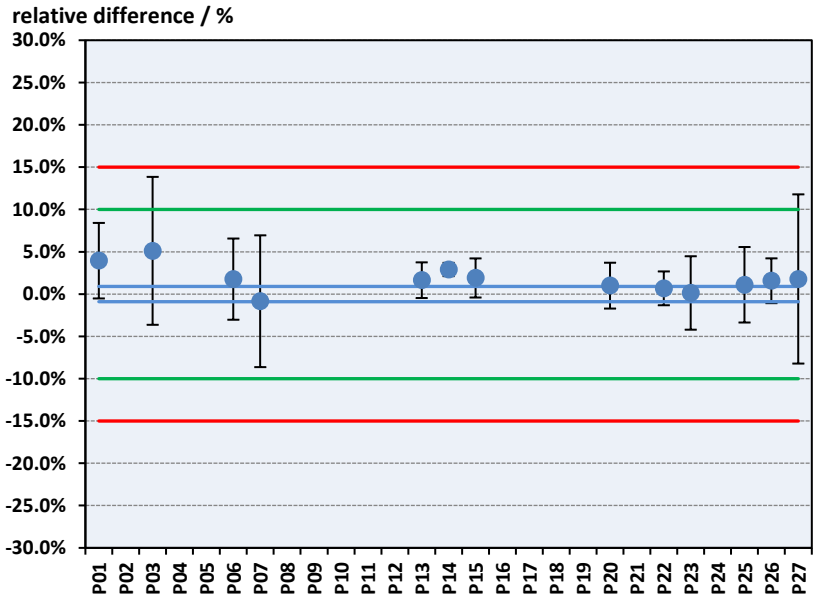
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	184.4	8.2	3.95%	0.79	0.83
P02					
P03	186.5	16.3	5.11%	1.02	0.55
P04					
P05					
P06	180.5	8.7	1.76%	0.35	0.36
P07	175.9	13.7	-0.85%	-0.17	-0.11
P08					
P09					
P10					
P11					
P12					
P13	180.3	3.8	1.64%	0.33	0.71
P14	182.6	1.4	2.90%	0.58	2.40
P15	180.8	4.2	1.90%	0.38	0.76
P16					
P17					
P18					
P19					
P20	179.2	4.9	0.99%	0.20	0.35
P21					
P22	178.6	3.6	0.68%	0.14	0.31
P23	177.6	7.7	0.13%	0.03	0.03
P24					
P25	179.4	8.0	1.10%	0.22	0.24
P26	180.2	4.8	1.57%	0.31	0.55
P27	180.6	18.1	1.78%	0.36	0.17

Consensus values (raw data)

m	180.5	
s_r	0.6	0.33%
s_L	3.0	1.64%
s_R	3.0	1.68%
p	13	

Consensus values (corrected)

m	179.9	
s_r	0.4	0.22%
s_L	2.4	1.31%
s_R	2.4	1.33%
p	12	



Measurand/ Mixture	nitrogen oxides (NO/NO2 mix)

Reference

x_{ref}	$U(x_{ref})$ k=2		σ	
198.9	1.6	µmol/mol	9.9	µmol/mol

Reported data

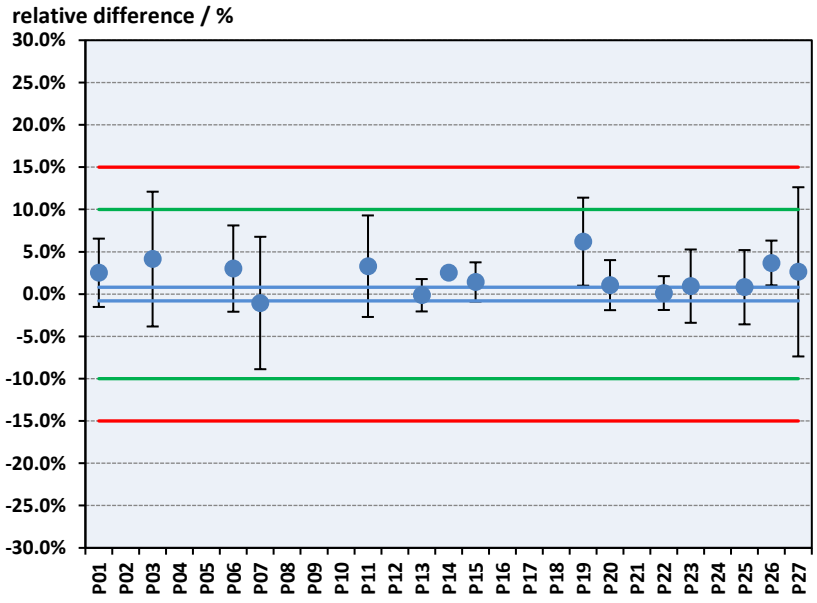
id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	203.9	8.2	2.51%	0.50	0.60
P02					
P03	207.1	16.5	4.13%	0.83	0.50
P04					
P05					
P06	204.9	10.4	3.01%	0.60	0.57
P07	196.8	15.4	-1.06%	-0.21	-0.14
P08					
P09					
P10					
P11	205.5	12.3	3.29%	0.66	0.53
P12					
P13	198.6	3.8	-0.14%	-0.03	-0.07
P14	203.9	1.0	2.52%	0.50	2.67
P15	201.8	4.7	1.44%	0.29	0.58
P16					
P17					
P18					
P19	211.2	11.0	6.19%	1.24	1.11
P20	201.0	5.9	1.05%	0.21	0.34
P21					
P22	199.1	4.0	0.12%	0.02	0.05
P23	200.8	8.7	0.94%	0.19	0.21
P24					
P25	200.5	8.8	0.81%	0.16	0.18
P26	206.2	5.5	3.68%	0.74	1.29
P27	204.1	20.4	2.63%	0.53	0.26

Consensus values (raw data)

m	202.7	
s_r	0.7	0.35%
s_L	4.0	1.98%
s_R	4.1	2.01%
p	15	

Consensus values (corrected)

m	201.9	
s_r	0.7	0.36%
s_L	3.2	1.57%
s_R	3.3	1.61%
p	14	



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	
21.4	2.2	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	difference (µmol/mol)	converter efficiency (%)	E_n-number
P01	19.5	11.6	-1.9	91.1%	-0.16
P02					
P03	20.7	23.2	-0.7	96.5%	-0.03
P04					
P05					
P06	24.4	13.6	3.0	113.8%	0.22
P07	20.9	20.6	-0.5	97.7%	-0.02
P08					
P09					
P10					
P11					
P12					
P13	18.3	5.4	-3.1	85.6%	-0.53
P14	21.4	1.7	0.0	99.8%	-0.01
P15	21.0	6.3	-0.4	98.0%	-0.06
P16					
P17					
P18					
P19					
P20	21.8	7.7	0.4	102.0%	0.05
P21					
P22	20.5	5.3	-0.9	96.0%	-0.15
P23	23.1	11.6	1.7	108.1%	0.15
P24					
P25	21.2	11.9	-0.2	98.9%	-0.02
P26	26.0	7.2	4.6	121.6%	0.61
P27	23.6	27.3	2.2	110.1%	0.08

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). Only two (2) participants failed to demonstrate converter efficiencies above this 95% expectation.