EffecTech
Global Leaders in Gas Measurement

UKAS PROFICIENCY TESTING
4719

Global Gas and LNG
Proficiency Testing (PT) Scheme

Presentation of Results

Round 24Q2

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	23.08.2024	Adam Lomax	***Final report (for comment)***

Statement of Confidentiality

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

The relationship between results and the laboratories that submitted them will never be disclosed. The laboratory alone is granted access to its performance through the assigned participant code and through issue of a confidential Certificate of Participation.

Checked by

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1. Introduction

EffecTech provides and organises the Global Gas and LNG Proficiency Testing Scheme (GGLNG). This report presents data on the reference mixtures and the results of the participants for round 24Q2 (October-December 2023).

The GGLNG scheme provides an objective way of assessing the performance of each participant by a series of quarterly (four rounds per year) inter-laboratory comparisons. The scheme is aimed at laboratories working in the field of liquefied natural gas (LNG) and natural gas processing and transportation.

In this round participants were given the opportunity of measuring up to two (2) different mixture types, a typical LNG composition and a sulphur component mixture. The composition range of each component in each mixture is shown in the tables below.

Table 1.1: Composition range - LNG composition

component	range (% mol/mol)
ethane	0.1 to 14
propane	0.05 to 5
iso-butane	0.01 to 1
n-butane	0.01 to 1
iso-pentane	0.005 to 0.35
n-pentane	0.005 to 0.35
n-hexane	0.001 to 0.35
nitrogen	0.1 to 1
methane	balance

Table 1.2: Composition range - sulphur component mixture

component	range (µmol/mol)
hydrogen sulphide	0.2 to 10
carbonyl sulphide	0.2 to 10
ethyl mercaptan	0.2 to 10
methyl mercaptan	0.2 to 10
dimethyl sulphide	0.2 to 10
methane, ethane & propane	balance

Note: The matrix of the sulphur component mixture is made up of methane, ethane and propane in amount fractions that represent a typical natural gas or LNG matrix. In this way the matrix more accurately represents samples which are measured routinely by your laboratory. Participants are asked to measure and report the sulphur containing components only and are NOT required to report the matrix hydrocarbons in this mixture.

Gas mixture preparation, reference value assignment and the assessment of participants' results are all carried out by designated operators and approved signatories within EffecTech. 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 nine (39) laboratories signed up to participate in this round. Thirty nine (39) participants, to whom items were distributed, submitted results for one or more of the mixture types 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. 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 by a multipoint calibration technique by comparison with a suite of reference mixtures in accordance with the requirements of ISO 6143:2001. Where this was not possible, a bracketing technique was used where one or more reference gases of similar composition and matrix were used.

Every single decant mixture was calibrated by an exact matching technique through comparison 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 TM001 and TM002). These can be found in our scope of accreditation published on the United Kingdom Accreditation Service (UKAS) website (www.ukas.org).

Reference mixture traceability

Gas chromatography was used as the analytical technique for the calibration of all mixtures in this scheme. Each gas chromatograph was calibrated with one or more reference mixtures traceable to either the National Physical Laboratory (NPL, UK) or the Van Swinden Laboratory (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 : 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 both mixture types, 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 6.10).

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

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.

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

2.2 Assigned reference values

In the tables that follow, all reference values and their uncertainties are given as amount of substance fraction in units of %mol/mol (10^{-2} mol/mol) **except** for the sulphur component mixture which is given in µmol/mol (ppm mol/mol).

Table 2.1: Reference values - LNG composition

component	x_{ref}	$U(x_{ref})$	u_c / %	u_{char} / %	u_{bb} / %
nitrogen	0.4054	*0.0060*	0.74	0.74	0.089
carbon dioxide					
methane	94.586	0.015	0.0052	0.0051	0.0010
ethane	2.6402	0.0066	0.11	0.11	0.012
propane	2.0170	0.0061	0.12	0.11	0.030
iso-butane	0.14181	0.00046	0.16	0.16	0.044
n-butane	0.13889	0.00052	0.19	0.18	0.055
iso-pentane	0.03130	0.00026	0.20	0.18	0.093
n-pentane	0.02945	0.00025	0.21	0.17	0.12
n-hexane	0.01020	0.00020	0.27	0.18	0.19

Table 2.2: Reference values - sulphur component mixture

component	x_{ref}	$U(x_{ref})$	u_c / %	u_{char} / %	u_{bb} / %
hydrogen sulphide	1.829	*0.071*	2.0	1.9	0.51
carbonyl sulphide	1.638	*0.067*	2.1	1.9	0.77
methyl mercaptan	1.446	*0.060*	2.1	1.9	0.82
ethyl mercaptan	1.521	*0.070*	2.3	2.3	0.00
dimethyl sulphide	1.284	*0.068*	2.6	2.6	0.00
total sulphur	7.72	*0.15*			

Note: Following examination of the assigned reference values, it was noted that in some cases the assigned uncertainties were not insignificant compared to the expectation of the participants in terms of the standard deviation for performance assessment (SDPA). These are shown in *italics* in the tables above. In these cases, the reference value uncertainties were considered in the calculation of an adjusted z'-score (see section 3.2 below.)

3. Results

3.1 Reported results

There were thirty-nine (39) laboratories who submitted results in this round of the GGLNG PT scheme. Consignments containing one or both mixture types were shipped to the participating laboratories. The table below shows participation and whether results were submitted.

Table 3.1: Participant laboratories and reported results

participant id	LNG mixture		sulphur component mix	
	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			✓	✓
P36	✓	✓	✓	✓
P37	✓	✓	✓	✓
P38	✓	✓	✓	✓
P39	✓	✓	✓	✓

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. For those participants who did not submit any uncertainty estimates E_n-numbers could not be calculated and have not been presented in this report.

All laboratories responded that they had reported normalised results for the LNG mixture. Some laboratories reported normalised results which did not sum to exactly 100% mol/mol due to

rounding errors from truncation of their results. These results were normalised (or re-normalised) before comparison with reference values were made.

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

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 those component failing this condition.

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

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

For the natural gas mixture, the absolute standard deviation used for performance assessment for *non-methane* components is taken as the reproducibility standard deviation, s_R, defined in ISO 6974-3 [A] - Equation (2) where

$$\ln(s_R) = -4.28 + 0.715.\ln(x_{ref}) \quad (3)$$

This gives

$$\sigma = s_R = e^{-4.28 + 0.715.\ln(x_{ref})} \quad (4)$$

For the *methane* component, the reproducibility standard deviation used for performance assessment is 0.09 % relative also specified in ISO 6974 - Part 3 such that

$$\sigma = s_R = \frac{0.09}{100}.x_{ref} \quad (5)$$

These performance measures defined in this international standard are those based on a statistical evaluation of historical data from this PT scheme and so should represent a reasonable expectation of the proven performance capabilities that should be demonstrated by each laboratory in the measurement of the natural gas mixture.

[A] ISO 6974 : 2018 *Natural gas - Determination of composition and associated uncertainty by gas chromatography - Part 3:Precision and bias*

By using equations (4) and (5) and the reference values in table 2.1 we obtain the following

Table 3.2: Standard deviation for performance assessment (LNG mixture)

component	σ (%mol/mol)
nitrogen	0.00726
methane	0.0851
ethane	0.0277
propane	0.0229
iso-butane	0.00343
n-butane	0.00337
iso-pentane	0.001163
n-pentane	0.001113
n-hexane	0.000521

For the sulphur component mixture the absolute standard deviation used for performance assessment, σ, is calculated from the relative standard deviation for performance assessment, S_{PT}, by

$$\sigma = \frac{S_{PT}}{100} . x_{ref} \qquad (6)$$

The relative standard deviation for performance assessment used for calculating the **z**-scores has been fixed for all components in these mixtures and is based upon a reasonable expectation of the performance capabilities that should be demonstrated by each laboratory. These are given in the tables below

Table 3.3: Standard deviation for performance assessment (sulphur component mixture)

component	S_{PT} (% relative)
hydrogen sulphide	5.0 %
carbonyl sulphide	4.0 %
ethyl mercaptan	4.0 %
methyl mercaptan	4.0 %
dimethyl sulphide	4.0 %
total sulphur	5.0 %

The qualification of the **z**-scores is given in table 3.4 below

Table 3.4: 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 reporting estimates of uncertainties associated with their measurement results.

The E_n number is calculated with the following general formula

$$E_n = \frac{x_{meas} - x_{ref}}{\sqrt{U_{meas}^2 + U_{ref}^2}} \quad (7)$$

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 3.5 below

Table 3.5: Relationship between E_n-number and quality of result

z-score	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 them to report an 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.

Overall score

In addition, a score has been calculated which expresses the participants score as percentage of the maximum possible score for each mixture type. The scoring scheme is as follows.

For each parameter in each round points can be earned in accordance with the scheme in table 3.6 below

Table 3.6: Relationship between z-score and quality of result

z-score	score per component
$\|z\| \leq 2$	**1 point**
$2 < \|z\| \leq 2.5$	**0.5 point**
$2.5 < \|z\| \leq 3$	**0.25 point**
$\|z\| > 3$	**no points**

A participant's score for each mixture is then expressed as percentage of the maximum score possible. The maximum score possible is attained when a participant obtains a *z*-score of less than 2 for all components that the laboratory measures in the mixture.

3.3 Evaluation of results

LNG composition (content)

As per the instructions and published protocols, the LNG mixture **did not** contain carbon dioxide in this round to represent a typical vapourised LNG sample. The summary of z-scores is given below.

Table 3.7 - Summary of *z*-scores

participant id	nitrogen	carbon dioxide	methane	ethane	propane	iso-butane	n-butane	iso-pentane	n-pentane	n-hexane
P01	-1.86		0.28	0.01	-0.38	0.08	-0.04	-0.14	-0.42	-0.06
P02	0.35		0.09	-0.37	0.05	-0.04	-0.06	-0.37	-0.67	0.29
P03	-2.63		-3.40	6.49	5.04	1.64	1.93	1.60	1.12	-0.11
P04	0.48		-0.01	0.39	-0.15	-0.41	0.30	-0.08	-0.22	-0.38‡
P05	0.66		0.06	-0.38	0.06	-0.15	-0.02	-0.30	-0.40	-0.38
P06	0.80		0.02	-0.16	-0.16	-0.03	0.21	-0.09	-0.13	-0.67
P07										
P08	-0.71		-0.01	0.96	-0.42	0.08	-0.02	-0.11	-0.39	-19.56
P09	0.16		-0.68	1.79	0.23	0.37	0.33	-0.23	-0.39	-0.38
P10	-0.29		-0.18	0.61	-0.08	0.52	0.48	-0.43	-0.58	-0.58
P11	0.03		0.14	-0.28	-0.28	-0.08	0.74	0.13	0.00	-0.96
P12	-0.52		0.17	-0.18	-0.25	0.03	0.09	-0.09	-0.13	-0.38
P13	0.14		-0.73	1.60	0.55	0.47	0.61	0.15	0.00	-0.16
P14	-1.19		0.43	-0.18	-0.96	-0.02	0.05	-0.09	-0.41	-0.38
P15	11.92		-0.55	-0.85	-1.13	-0.16	-0.19	-0.26	-0.40	8.25
P16	1.31		-0.53	1.22	-0.04	0.49	0.51	-0.60	-0.40	-1.15
P17	1.46		-0.29	1.51	-0.63	-0.72	-3.09	-1.16	-0.31	-0.31
P18	-0.54		0.06	-0.12	0.14	0.15	-0.17	0.22	-1.02	0.15
P19	0.67		-0.49	1.14	0.04	0.70	0.71	-0.60	-0.31	-0.58
P20										
P21	1.02		-0.16	0.18	0.05	-0.09	-0.05	-0.45	0.51	-0.73
P22	-0.54		0.21	-0.28	-0.32	0.00	0.33	-0.13	-0.25	1.20
P23	0.16		-0.66	1.22	0.66	0.74	0.85	0.30	0.15	0.03
P24	1.34		-0.43	0.86	-0.01	0.55	0.57	-0.52	-0.31	-0.58
P25										
P26	1.57		-0.78	1.73	0.16	0.38	0.37	-0.03	-0.27	-0.12
P27										
P28										
P29	0.55		-0.10	0.18	0.06	-0.25	-0.33	-0.77	0.51	-0.49
P30	-51.62		-66.96	71.76	142.90	92.56	92.42	79.85	78.31	78.47
P31	-0.56		-0.65	1.22	0.96	0.64	0.33	-0.26	0.49	-0.38
P32										
P33	2.03		0.12	-0.84	-0.20	0.07	0.12	0.55	0.31	-1.04
P34	0.11		-0.71	1.60	0.51	0.49	0.61	0.11	-0.05	-0.35
P35										
P36	-0.60		0.08	0.03	-0.13	0.05	0.12	-0.14	-0.10	-0.45
P37	-0.83		0.09	0.39	-0.31	-0.22	-0.90	-0.28	-0.42	-0.77
P38	1.12		-1.59	2.84	2.01	0.44	0.33	-0.26	-0.40	-0.38
P39	-0.87		-0.13	0.38	0.11	0.60	0.77	0.09	-0.16	-0.16

Results marked with a ‡ where submitted as less than a given limit of detection and so a one tailed z-test was used instead, for which a result of $|\mathbf{z}|<1.65$ is considered a satisfactory result.

Results for the LNG mixture in this round were excellent with twenty-five (25) out of thirty-two (32) reporting participants achieving a perfect score of 100%. The average score was **93.6%**.

Of those not reporting a perfect score, no particular component was the issue, laboratory **P30** appear to have significantly difficulty with all components suggesting that have possibly submitted the result for a different gas sample.

Table 3.8 - Summary of E_n-numbers

participant id	nitrogen	carbon dioxide	methane	ethane	propane	iso-butane	n-butane	iso-pentane	n-pentane	n-hexane
P01	-0.81		0.05	0.00	-0.07	0.03	-0.01	-0.05	-0.16	-0.01
P02										
P03										
P04	0.50		0.00	0.35	-0.15	-0.66	0.49	-0.15	-0.46	
P05										
P06	0.85		0.01	-0.37	-0.35	-0.15	0.89	-0.25	-0.38	-1.24
P07										
P08	-0.61		-0.02	0.26	-0.14	0.02	-0.01	-0.12	-0.82	-51.00
P09										
P10										
P11										
P12	-0.10		0.15	-0.12	-0.22	0.03	0.07	-0.05	-0.08	
P13										
P14										
P15										
P16										
P17	0.53		-0.03	0.31	-0.14	-0.25	-1.16	-0.45	-0.12	-0.08
P18	-0.71		0.01	-0.50	0.52	1.09	-1.13	0.96	-4.56	0.40
P19										
P20										
P21										
P22										
P23										
P24										
P25										
P26	1.07		-1.79	1.97	0.17	0.64	0.50	-0.04	-0.30	-0.14
P27										
P28										
P29										
P30			-356.78	297.92	513.62	520.11	432.32	283.04	272.34	144.67
P31	-0.26		-1.73	4.66	0.60					
P32										
P33	0.96		0.26	-1.69	-0.03	0.02	0.04	1.17	0.58	-1.44
P34										
P35										
P36	-0.75		0.16	0.06	-0.29	0.11	0.24	-0.30	-0.21	-0.65
P37	-0.74		0.26	0.88	-0.63	-0.15	-0.61	-0.09	-0.14	-0.16
P38										
P39	-0.95		-0.14	0.53	0.06	0.21	0.26	0.05	-0.08	-0.03

Of the fourteen (14) laboratories reporting uncertainties for this mixture, the E_n-numbers are shown above. There were a greater number of unsatisfactory results on the basis of E_n-numbers due to underestimation of uncertainties and potential bias to the nitrogen measurement.

Laboratories **P06, P18** and **P26** scored 100% 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 due to undetected bias in their measurements.

Laboratories **P01, P04, P12, P36, P37** and **P39** reported excellent results with perfect scores on the basis of both performance measures.

LNG composition (physical properties)

Participants were asked to report physical properties (calculated from their measured composition) in order to assess any measurement errors in these properties. This was not a mandatory requirement. However, EffecTech encourages laboratories to submit these calculations if it is a local requirement of their laboratory.

As physical properties can be submitted using a variety of reference methods and conditions, laboratories were allowed to submit their results alongside the methods and references used. For comparison purposes, EffecTech also calculated properties using the same methods submitted by each participant.

The tables in Annex A show the relative difference between reference values (calculated from reference composition) and those submitted by the laboratory (or calculated by EffecTech from reported composition). Data reported by the laboratory is shown with **Blue** markers whereas those calculated by EffecTech are shown in **Red**.

Where results were calculated by EffecTech, these were done using ISO 6976 [ISO6976:1995 *Natural gas - Calculation of calorific values, density, relative density and Wobbe index from composition*] for a real gas at reference temperatures of 15°C (combustion) and 15°C (metering) and a pressure of 101.325 kPa.

As a basis for the performance of these measures has yet to be established, **z**-scores and $\boldsymbol{E_n}$-numbers for these parameters have not been calculated in this round.

Sulphur component mixture

The sulphur mixture contained components at challengingly low amount fractions in accordance with routine measurements made in their laboratories. The matrix gas included methane, ethane and propane in order to more accurately represent the matrix gas in samples routinely measured by the participants. The results for the sulphur component mixture are shown below.

Table 3.9 - Summary of *z'*-scores

participant id	hydrogen sulphide	carbonyl sulphide	methyl mercaptan	ethyl mercaptan	dimethyl sulphide	total sulphur (from speciated)	total sulphur (unspeciated)
P01	-0.89	0.14	-0.29	-0.16	0.42	-0.21	
P02							
P03							
P04	-0.91	-1.74					
P05							
P06							
P07	-0.85	-1.52	-1.26	-1.46	-1.10	-1.14	-0.53
P08							
P09							
P10							
P11							
P12							
P13							
P14							
P15	2.51	2.25	0.96	0.61	2.45	1.69	
P16							
P17							
P18	2.70	-5.50	-2.60	-0.41	1.47	-0.64	
P19							
P20	-2.52	2.43	-3.40	-4.13	-2.78	-1.91	
P21							
P22							
P23							
P24							
P25	-8.12	-3.15	-7.60	-7.74			
P26							
P27	-1.01	-3.10	-0.55	-4.57	-3.80	-2.34	-0.07
P28	-10.80	-17.87	-15.62	-16.51	-15.84	-11.08	-9.45
P29							
P30							
P31							
P32	-3.84				-1.01		
P33							
P34							
P35	2.64		-16.16	-4.60	7.36		
P36		-5.59	-0.81	-0.49	-1.69		
P37							-0.31
P38	0.61	-4.61	-1.01	-0.88	-1.57	-1.28	
P39	-2.62	-0.04	-1.08	-1.25	0.12	-1.05	-0.78

An average set of results were reported for the sulphur component mixture in this round. The overall score was **60.4%**.

Three (3) laboratories **P01**, **P04** and **P07** achieved a perfect 100% on the sulphur components they reported out of fifteen (15) laboratories submitting results. An excellent performance for these laboratories.

Table 3.10 - Summary of E_n-numbers

participant id	hydrogen sulphide	carbonyl sulphide	methyl mercaptan	ethyl mercaptan	dimethyl sulphide	total sulphur (from speciated)	total sulphur (unspeciated)
P01	-0.15	0.01	-0.02	-0.01	0.03	-0.10	
P02							
P03							
P04	-0.81	-1.40					
P05							
P06							
P07							
P08							
P09							
P10							
P11							
P12							
P13							
P14							
P15							
P16							
P17							
P18	1.38	-3.11	-1.30	-0.21	0.70	-0.41	
P19							
P20	-1.43	0.48	-1.63	-2.04	-1.31	-1.06	
P21							
P22							
P23							
P24							
P25							
P26							
P27							
P28							
P29							
P30							
P31							
P32	-0.68				-0.14		
P33							
P34							
P35	0.84				1.35		
P36		-3.67	-0.53	-0.23	-0.99		
P37							-0.19
P38	0.22	-1.65	-0.44	-0.38	-0.71	-0.57	
P39	-0.92	-0.01	-0.24	-0.34	0.03	-0.67	-0.54

Of the ten (10) laboratories reporting uncertainties for one or more of the components in the sulphur mixture, the E_n-numbers are shown above.

Laboratory **P01** achieved a perfect score on the basis of both performance measures for all speciated sulphur components. This is an excellent performance.

Overall scores

The table below shows the ratings calculated for each laboratory expressed as a percentage of the maximum possible score for each mixture.

Table 3.11 - Summary of overall scores for each mixture type

participant id	LNG mixture	sulphur component
P01	**100.0%**	**100.0%**
P02	**100.0%**	
P03	58.3%	
P04	**100.0%**	**100.0%**
P05	**100.0%**	
P06	**100.0%**	
P07		**100.0%**
P08	88.9%	
P09	**100.0%**	
P10	**100.0%**	
P11	**100.0%**	
P12	**100.0%**	
P13	**100.0%**	
P14	**100.0%**	
P15	77.8%	70.8%
P16	**100.0%**	
P17	88.9%	
P18	**100.0%**	58.3%
P19	**100.0%**	
P20		33.3%
P21	**100.0%**	
P22	**100.0%**	
P23	**100.0%**	
P24	**100.0%**	
P25		0.0%
P26	**100.0%**	
P27		41.7%
P28		0.0%
P29	**100.0%**	
P30	0.0%	
P31	**100.0%**	
P32		50.0%
P33	94.4%	
P34	**100.0%**	
P35		6.3%
P36	**100.0%**	75.0%
P37	**100.0%**	**100.0%**
P38	86.1%	83.3%
P39	**100.0%**	87.5%
Average score	**93.6%**	**60.4%**

On the basis of the average scores, the sulphur component mixture once again proved the most challenging measurement in this round of the scheme. Results for this measurement gave an overall score of **60.4%**. Only three (3) laboratories **P01**, **P04** and **P37** achieved a perfect 100% score out of eight (8) submitting results for both PT items.

Twenty-five (25) out of thirty-two (32) participants achieved a perfect score of 100% for the LNG type mixture in this round. The average score was **94.6%**.

Four (4) out of fifteen (15) laboratories achieved a perfect score of 100% for the LNG type mixture in this round. The average score was **60.4%**.

Laboratories **P01**, **P04** and **P37** are worthy of a particular mention in this round producing excellent sets of results achieving a perfect score of 100% for both the LNG mixture and the sulphur component mixture. An excellent performance.

Annex A - Detailed results by component (and property)

Detailed results for all components (and properties) 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 include some additional statistics in this round 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.

LNG composition (content)

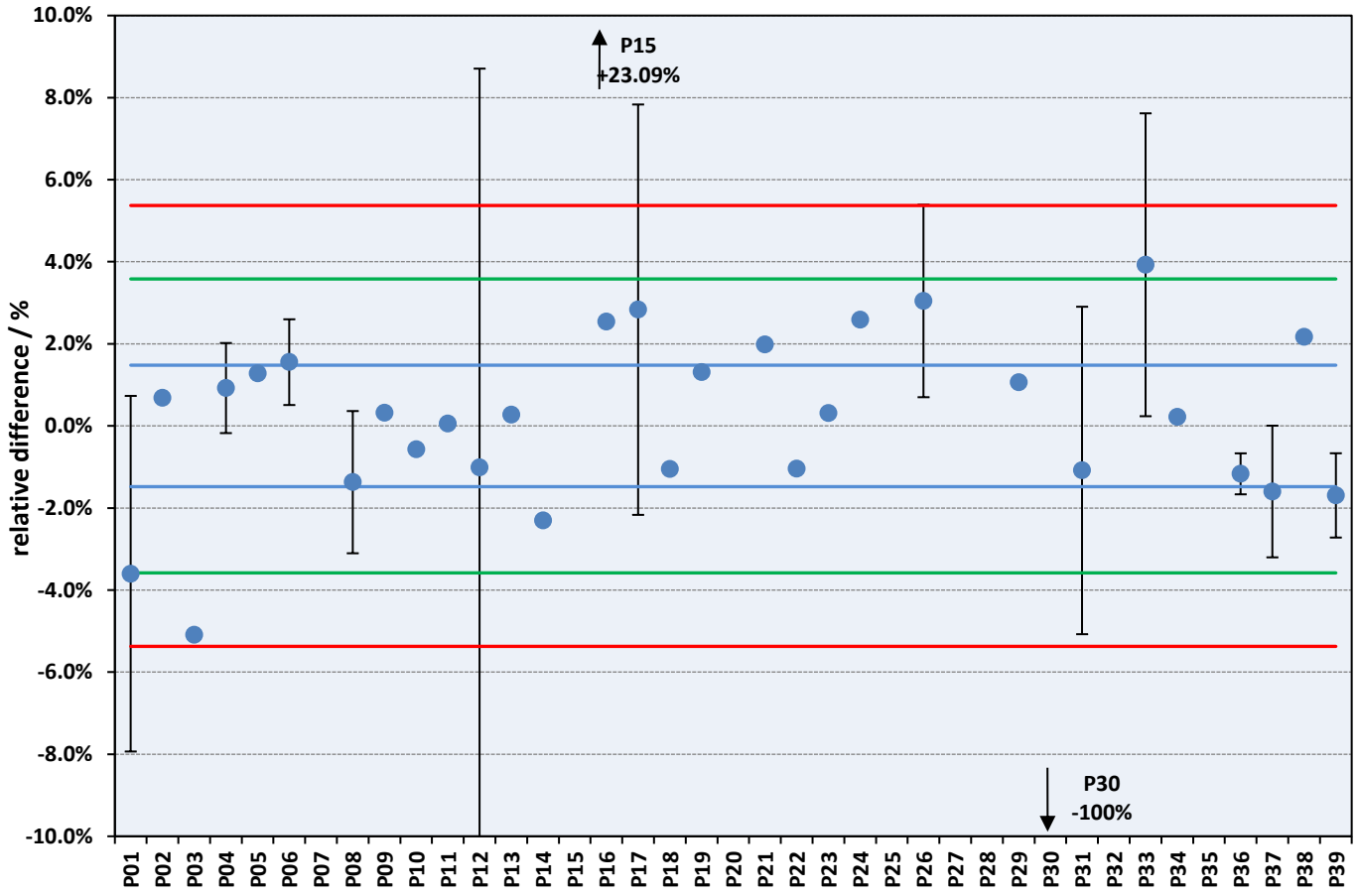
Mixture	LNG
Component	nitrogen

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	0.4054	0.0060	%mol/mol	0.0073	%mol/mol

Reported data

id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z'*-score	E_n-number
P01	0.3908	0.0169	-3.60%	-1.86	-0.81
P02	0.4082		0.68%	0.35	
P03	0.3848		-5.09%	-2.63	
P04	0.4091	0.0045	0.92%	0.48	0.50
P05	0.4106		1.28%	0.66	
P06	0.4117	0.0043	1.55%	0.80	0.85
P07					
P08	0.3998	0.0069	-1.37%	-0.71	-0.61
P09	0.4067		0.32%	0.16	
P10	0.4031		-0.57%	-0.29	
P11	0.4056		0.06%	0.03	
P12	0.4013	0.0390	-1.01%	-0.52	-0.10
P13	0.4065		0.27%	0.14	
P14	0.3961		-2.30%	-1.19	
P15	0.4990		23.09%	11.92	
P16	0.4157		2.54%	1.31	
P17	0.4169	0.0208	2.83%	1.46	0.53
P18	0.4012	0.0000	-1.05%	-0.54	-0.71
P19	0.4107		1.31%	0.67	
P20					
P21	0.4134		1.98%	1.02	
P22	0.4012		-1.04%	-0.54	
P23	0.4067		0.31%	0.16	
P24	0.4159		2.59%	1.34	
P25					
P26	0.4177	0.0098	3.05%	1.57	1.07
P27					
P28					
P29	0.4097		1.07%	0.55	
P30	0.0000		-100.00%	-51.62	
P31	0.4010	0.0160	-1.09%	-0.56	-0.26
P32					
P33	0.4213	0.0155	3.93%	2.03	0.96
P34	0.4063		0.22%	0.11	
P35					
P36	0.4007	0.0020	-1.17%	-0.60	-0.75
P37	0.3989	0.0064	-1.60%	-0.83	-0.74
P38	0.4142		2.17%	1.12	
P39	0.3985	0.0041	-1.69%	-0.87	-0.95

nitrogen in LNG composition



Reference values	
x_{ref}	0.4054
$U(x_{ref})$ k=2	0.0060

Consensus values (raw data)		
m	0.3853	
s_r	0.0028	0.72%
s_L	0.0956	24.80%
s_R	0.0956	24.82%
p	32	

Consensus values (corrected)		
m	0.4073	
s_r	0.0029	0.70%
s_L	0.0169	4.14%
s_R	0.0171	4.20%
p	31	

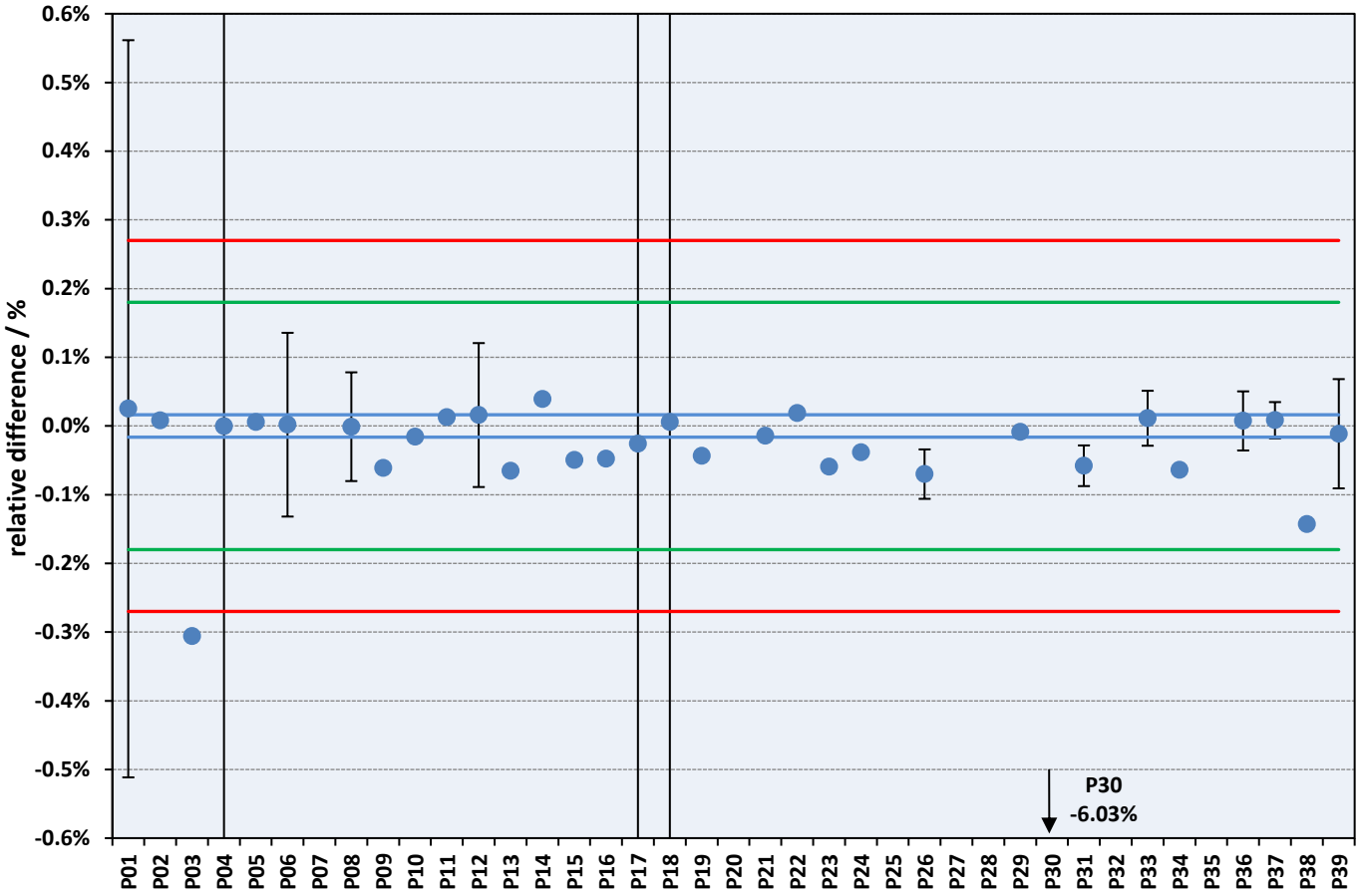
Mixture	LNG
Component	methane

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	94.586	0.015	%mol/mol	0.085	%mol/mol

Reported data

id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01	94.609	0.508	0.03%	0.28	0.05
P02	94.593		0.01%	0.09	
P03	94.296		-0.31%	-3.40	
P04	94.586	0.951	0.00%	-0.01	0.00
P05	94.591		0.01%	0.06	
P06	94.588	0.127	0.00%	0.02	0.01
P07					
P08	94.585	0.075	0.00%	-0.01	-0.02
P09	94.528		-0.06%	-0.68	
P10	94.571		-0.02%	-0.18	
P11	94.598		0.01%	0.14	
P12	94.601	0.099	0.02%	0.17	0.15
P13	94.524		-0.07%	-0.73	
P14	94.623		0.04%	0.43	
P15	94.539		-0.05%	-0.55	
P16	94.541		-0.05%	-0.53	
P17	94.561	0.946	-0.03%	-0.29	-0.03
P18	94.591	0.899	0.01%	0.06	0.01
P19	94.544		-0.04%	-0.49	
P20					
P21	94.572		-0.01%	-0.16	
P22	94.604		0.02%	0.21	
P23	94.530		-0.06%	-0.66	
P24	94.549		-0.04%	-0.43	
P25					
P26	94.519	0.034	-0.07%	-0.78	-1.79
P27					
P28					
P29	94.577		-0.01%	-0.10	
P30	88.886	0.006	-6.03%	-66.96	-356.78
P31	94.531	0.028	-0.06%	-0.65	-1.73
P32					
P33	94.596	0.038	0.01%	0.12	0.26
P34	94.525		-0.06%	-0.71	
P35					
P36	94.593	0.041	0.01%	0.08	0.16
P37	94.594	0.025	0.01%	0.09	0.26
P38	94.451		-0.14%	-1.59	
P39	94.575	0.075	-0.01%	-0.13	-0.14

methane in LNG composition



Reference values	
x_{ref}	94.586
$U(x_{ref})$ k=2	0.015

Consensus values (raw data)		
m	94.241	
s_r	0.009	0.01%
s_L	1.311	1.39%
s_R	1.311	1.39%
p	32	

Consensus values (corrected)		
m	94.547	
s_r	0.008	0.01%
s_L	0.076	0.08%
s_R	0.076	0.08%
p	31	

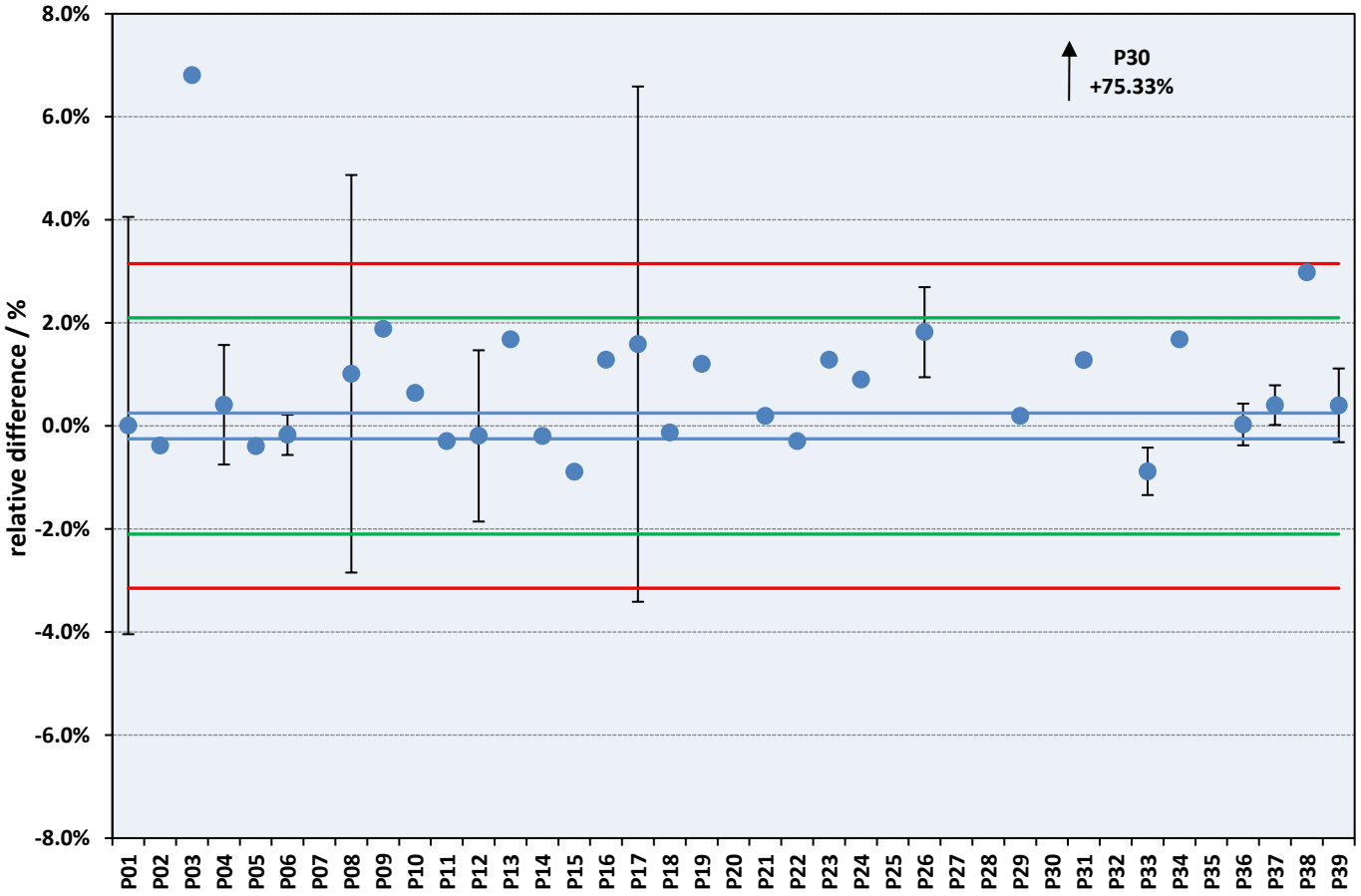
Mixture	LNG
Component	ethane

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	2.640	0.0066	%mol/mol	0.028	%mol/mol

Reported data

id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	***z***-score	E_n-number
P01	2.640	0.1069	0.01%	**0.01**	**0.00**
P02	2.630		-0.39%	**-0.37**	
P03	2.820		6.81%	**6.49**	
P04	2.651	0.0308	0.41%	**0.39**	**0.35**
P05	2.630		-0.39%	**-0.38**	
P06	2.636	0.0103	-0.17%	**-0.16**	**-0.37**
P07					
P08	2.667	0.1029	1.01%	**0.96**	**0.26**
P09	2.690		1.88%	**1.79**	
P10	2.657		0.64%	**0.61**	
P11	2.632		-0.29%	**-0.28**	
P12	2.635	0.0438	-0.19%	**-0.18**	**-0.12**
P13	2.684		1.68%	**1.60**	
P14	2.635		-0.19%	**-0.18**	
P15	2.617		-0.89%	**-0.85**	
P16	2.674		1.28%	**1.22**	
P17	2.682	0.1341	1.59%	**1.51**	**0.31**
P18	2.637	0.0011	-0.13%	**-0.12**	**-0.50**
P19	2.672		1.20%	**1.14**	
P20					
P21	2.645		0.19%	**0.18**	
P22	2.632		-0.29%	**-0.28**	
P23	2.674		1.28%	**1.22**	
P24	2.664		0.90%	**0.86**	
P25					
P26	2.688	0.0235	1.82%	**1.73**	**1.97**
P27					
P28					
P29	2.645		0.19%	**0.18**	
P30	4.629	0.0010	75.33%	**71.76**	**297.92**
P31	2.674	0.0030	1.28%	**1.22**	**4.66**
P32					
P33	2.617	0.0120	-0.88%	**-0.84**	**-1.69**
P34	2.685		1.68%	**1.60**	
P35					
P36	2.641	0.0107	0.03%	**0.03**	**0.06**
P37	2.651	0.0102	0.40%	**0.39**	**0.88**
P38	2.719		2.98%	**2.84**	
P39	2.651	0.0190	0.40%	**0.38**	**0.53**

ethane in LNG composition



Reference values	
x_{ref}	2.6402
$U(x_{ref})$ k=2	0.0066

Consensus values (raw data)		
m	2.7741	
s_r	0.0069	0.25%
s_L	0.4555	16.42%
s_R	0.4556	16.42%
p	32	

Consensus values (corrected)		
m	2.6681	
s_r	0.0071	0.27%
s_L	0.0464	1.74%
s_R	0.0470	1.76%
p	31	

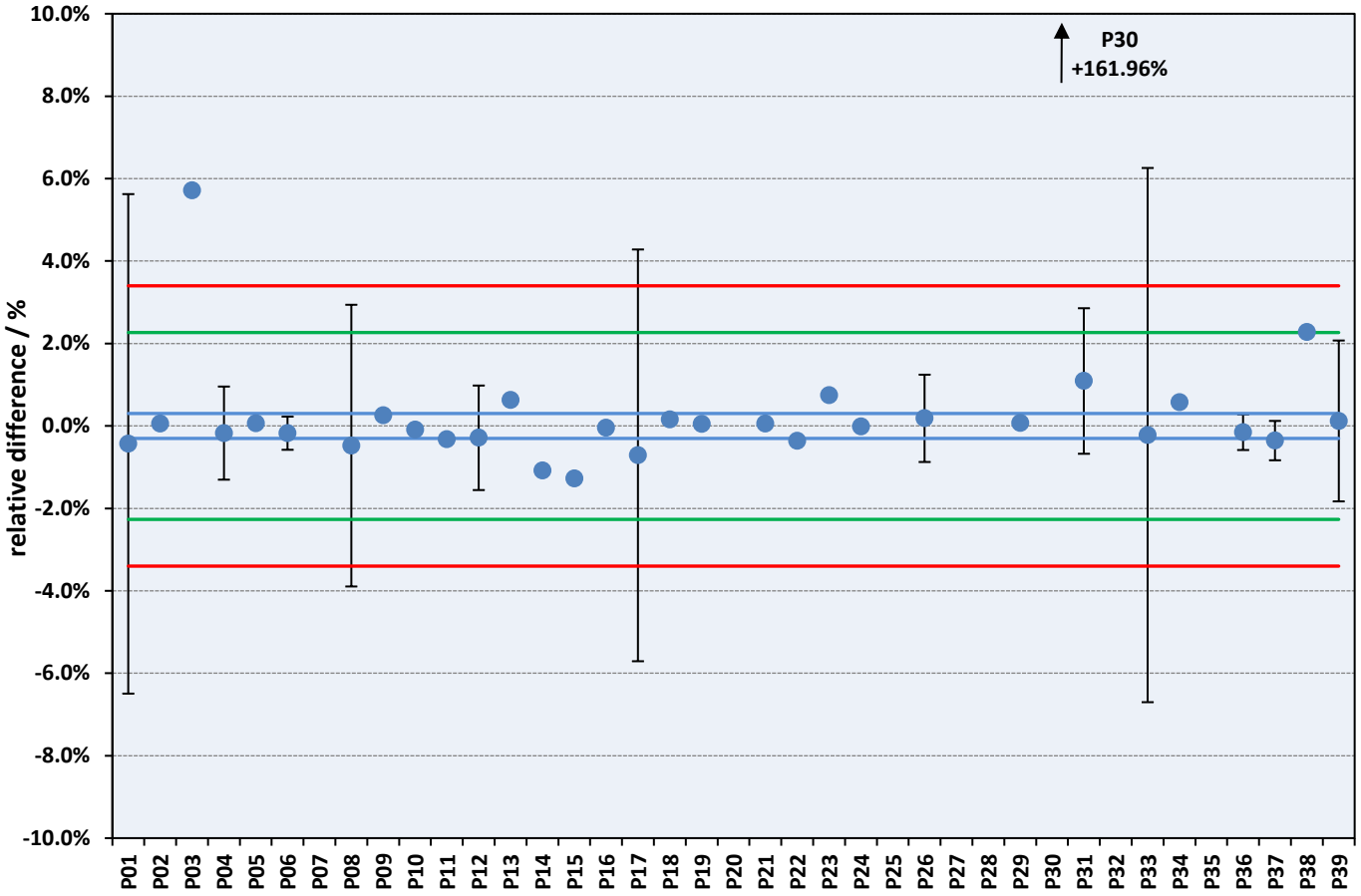
Mixture	LNG
Component	propane

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	2.0170	0.0061	%mol/mol	0.0229	%mol/mol

Reported data

id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	***z***-score	E_n-number
P01	2.0082	0.1217	-0.43%	**-0.38**	**-0.07**
P02	2.0181		0.06%	**0.05**	
P03	2.1322		5.71%	**5.04**	
P04	2.0135	0.0227	-0.17%	**-0.15**	**-0.15**
P05	2.0183		0.06%	**0.06**	
P06	2.0135	0.0081	-0.18%	**-0.16**	**-0.35**
P07					
P08	2.0074	0.0686	-0.48%	**-0.42**	**-0.14**
P09	2.0223		0.26%	**0.23**	
P10	2.0151		-0.09%	**-0.08**	
P11	2.0105		-0.32%	**-0.28**	
P12	2.0112	0.0255	-0.29%	**-0.25**	**-0.22**
P13	2.0297		0.63%	**0.55**	
P14	1.9951		-1.08%	**-0.96**	
P15	1.9913		-1.28%	**-1.13**	
P16	2.0161		-0.04%	**-0.04**	
P17	2.0026	0.1000	-0.71%	**-0.63**	**-0.14**
P18	2.0202	0.0007	0.16%	**0.14**	**0.52**
P19	2.0179		0.04%	**0.04**	
P20					
P21	2.0182		0.06%	**0.05**	
P22	2.0098		-0.36%	**-0.32**	
P23	2.0321		0.75%	**0.66**	
P24	2.0167		-0.01%	**-0.01**	
P25					
P26	2.0207	0.0214	0.18%	**0.16**	**0.17**
P27					
P28					
P29	2.0184		0.07%	**0.06**	
P30	5.2837	0.0018	161.96%	**142.90**	**513.62**
P31	2.0390	0.0360	1.09%	**0.96**	**0.60**
P32					
P33	2.0125	0.1304	-0.22%	**-0.20**	**-0.03**
P34	2.0286		0.57%	**0.51**	
P35					
P36	2.0139	0.0087	-0.15%	**-0.13**	**-0.29**
P37	2.0098	0.0096	-0.36%	**-0.31**	**-0.63**
P38	2.0629		2.28%	**2.01**	
P39	2.0195	0.0394	0.12%	**0.11**	**0.06**

propane in LNG composition



Reference values	
x_{ref}	2.0170
$U(x_{ref})$ k=2	0.0061

Consensus values (raw data)		
m	2.2011	
s_r	0.0021	0.09%
s_L	0.7539	34.25%
s_R	0.7539	34.25%
p	32	

Consensus values (corrected)		
m	2.0250	
s_r	0.0016	0.08%
s_L	0.0308	1.52%
s_R	0.0308	1.52%
p	31	

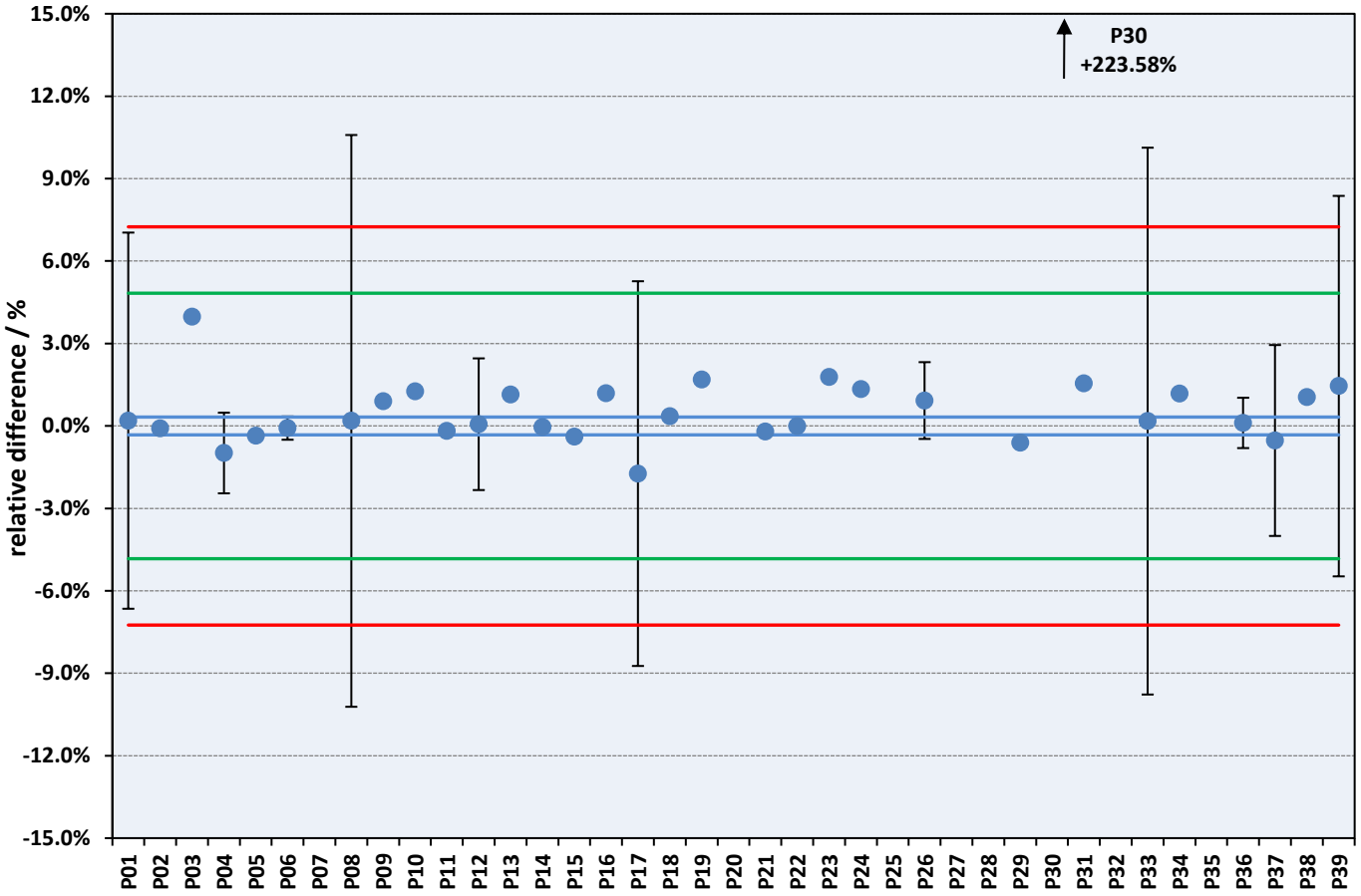
Mixture	LNG
Component	iso-butane

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	0.14181	0.00046	%mol/mol	0.00343	%mol/mol

Reported data

id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01	0.14208	0.00973	0.19%	0.08	0.03
P02	0.14167		-0.10%	-0.04	
P03	0.14744		3.97%	1.64	
P04	0.14041	0.00206	-0.98%	-0.41	-0.66
P05	0.14130		-0.36%	-0.15	
P06	0.14170	0.00060	-0.08%	-0.03	-0.15
P07					
P08	0.14207	0.01478	0.18%	0.08	0.02
P09	0.14309		0.90%	0.37	
P10	0.14360		1.26%	0.52	
P11	0.14155		-0.18%	-0.08	
P12	0.14190	0.00340	0.06%	0.03	0.03
P13	0.14342		1.14%	0.47	
P14	0.14174		-0.05%	-0.02	
P15	0.14125		-0.39%	-0.16	
P16	0.14350		1.19%	0.49	
P17	0.13935	0.00976	-1.73%	-0.72	-0.25
P18	0.14231	0.00001	0.35%	0.15	1.09
P19	0.14420		1.69%	0.70	
P20					
P21	0.14151		-0.21%	-0.09	
P22	0.14180		-0.01%	0.00	
P23	0.14433		1.78%	0.74	
P24	0.14370		1.33%	0.55	
P25					
P26	0.14312	0.00200	0.92%	0.38	0.64
P27					
P28					
P29	0.14095		-0.61%	-0.25	
P30	0.45886	0.00040	223.58%	92.56	520.11
P31	0.14400		1.54%	0.64	
P32					
P33	0.14206	0.01413	0.18%	0.07	0.02
P34	0.14348		1.17%	0.49	
P35					
P36	0.14197	0.00130	0.11%	0.05	0.11
P37	0.14106	0.00490	-0.53%	-0.22	-0.15
P38	0.14330		1.05%	0.44	
P39	0.14387	0.00996	1.45%	0.60	0.21

iso-butane in LNG composition



Reference values	
x_{ref}	0.14181
$U(x_{ref})$ k=2	0.00046

Consensus values (raw data)		
m	0.15971	
s_r	0.00043	0.27%
s_L	0.07312	45.78%
s_R	0.07312	45.78%
p	32	

Consensus values (corrected)		
m	0.14262	
s_r	0.00034	0.24%
s_L	0.00166	1.16%
s_R	0.00169	1.19%
p	31	

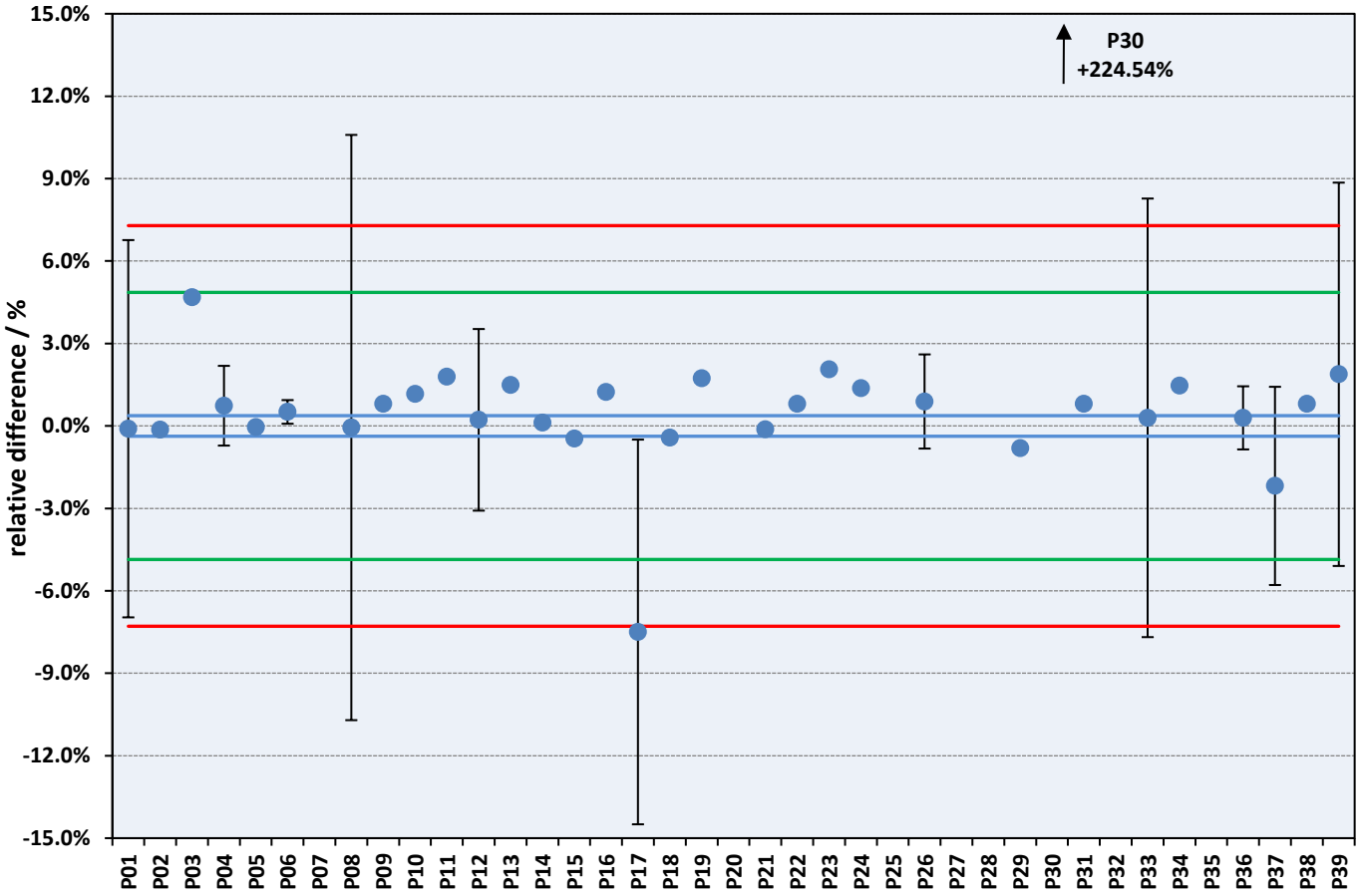
Mixture	LNG
Component	n-butane

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	0.13889	0.00052	%mol/mol	0.00337	%mol/mol

Reported data

id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01	0.13875	0.00953	-0.10%	-0.04	-0.01
P02	0.13870		-0.14%	-0.06	
P03	0.14539		4.68%	1.93	
P04	0.13991	0.00203	0.74%	0.30	0.49
P05	0.13883		-0.05%	-0.02	
P06	0.13960	0.00060	0.51%	0.21	0.89
P07					
P08	0.13881	0.01478	-0.06%	-0.02	-0.01
P09	0.14000		0.80%	0.33	
P10	0.14050		1.16%	0.48	
P11	0.14137		1.79%	0.74	
P12	0.13920	0.00460	0.22%	0.09	0.07
P13	0.14096		1.49%	0.61	
P14	0.13906		0.12%	0.05	
P15	0.13825		-0.46%	-0.19	
P16	0.14060		1.23%	0.51	
P17	0.12848	0.00899	-7.50%	-3.09	-1.16
P18	0.13830	0.00001	-0.42%	-0.17	-1.13
P19	0.14130		1.74%	0.71	
P20					
P21	0.13871		-0.13%	-0.05	
P22	0.14000		0.80%	0.33	
P23	0.14175		2.06%	0.85	
P24	0.14080		1.38%	0.57	
P25					
P26	0.14013	0.00240	0.89%	0.37	0.50
P27					
P28					
P29	0.13776		-0.81%	-0.33	
P30	0.45076	0.00050	224.54%	92.42	432.32
P31	0.14000		0.80%	0.33	
P32					
P33	0.13930	0.01112	0.30%	0.12	0.04
P34	0.14093		1.47%	0.61	
P35					
P36	0.13930	0.00160	0.30%	0.12	0.24
P37	0.13586	0.00490	-2.18%	-0.90	-0.61
P38	0.14000		0.80%	0.33	
P39	0.14150	0.00987	1.88%	0.77	0.26

n-butane in LNG composition



Reference values	
x_{ref}	0.13889
$U(x_{ref})$ k=2	0.00052

Consensus values (raw data)		
m	0.15631	
s_r	0.00048	0.31%
s_L	0.07201	46.07%
s_R	0.07201	46.07%
p	32	

Consensus values (corrected)		
m	0.13949	
s_r	0.00028	0.20%
s_L	0.00284	2.04%
s_R	0.00286	2.05%
p	31	

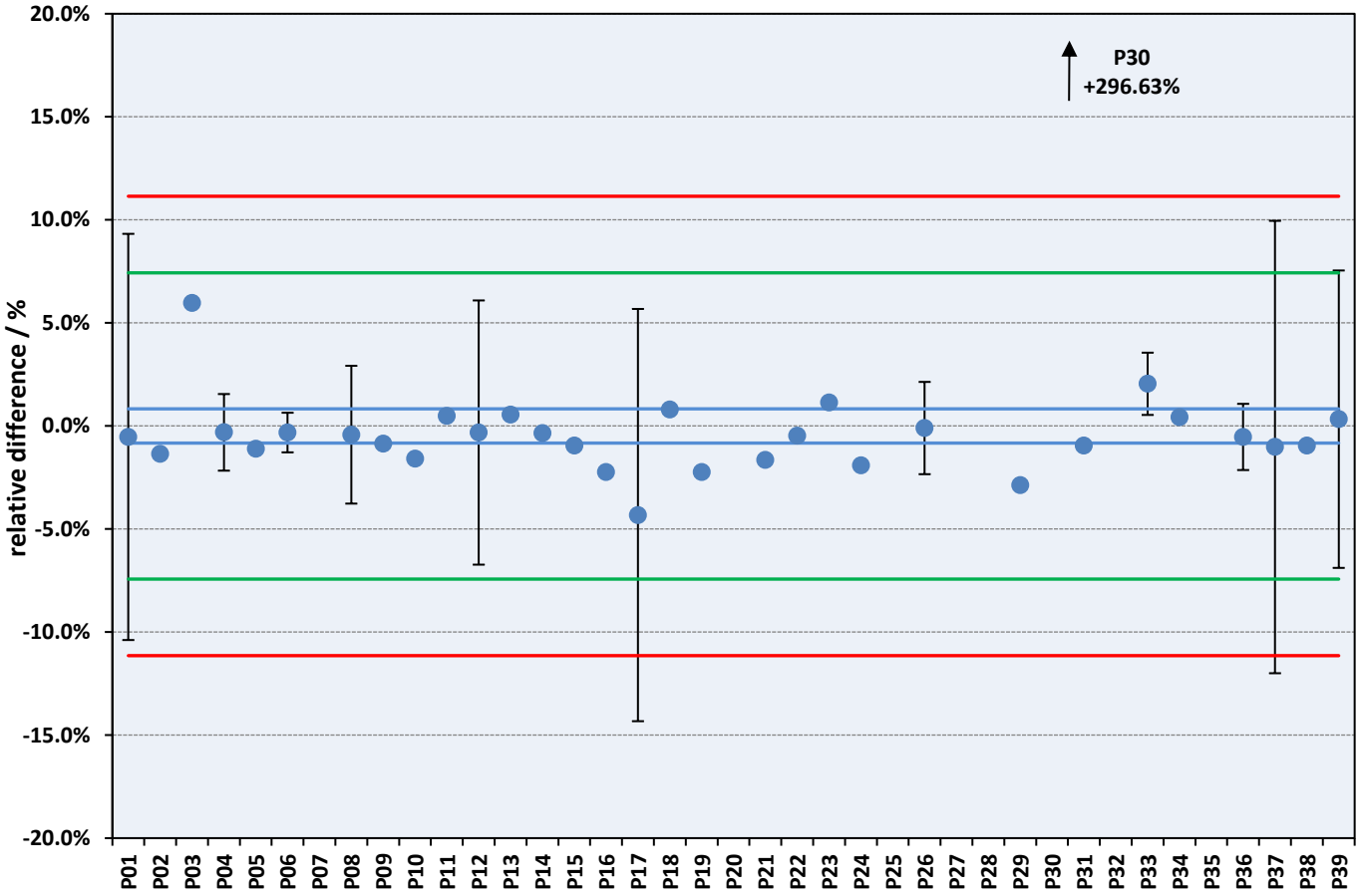
Mixture	LNG
Component	iso-pentane

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	0.03130	0.00026	%mol/mol	0.00116	%mol/mol

Reported data

id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01	0.03113	0.00307	-0.53%	-0.14	-0.05
P02	0.03087		-1.36%	-0.37	
P03	0.03316		5.96%	1.60	
P04	0.03120	0.00058	-0.31%	-0.08	-0.15
P05	0.03095		-1.12%	-0.30	
P06	0.03120	0.00030	-0.32%	-0.09	-0.25
P07					
P08	0.03117	0.00104	-0.42%	-0.11	-0.12
P09	0.03103		-0.86%	-0.23	
P10	0.03080		-1.60%	-0.43	
P11	0.03145		0.48%	0.13	
P12	0.03120	0.00200	-0.32%	-0.09	-0.05
P13	0.03147		0.54%	0.15	
P14	0.03119		-0.35%	-0.09	
P15	0.03100		-0.96%	-0.26	
P16	0.03060		-2.24%	-0.60	
P17	0.02995	0.00300	-4.32%	-1.16	-0.45
P18	0.03155	0.00000	0.80%	0.22	0.96
P19	0.03060		-2.24%	-0.60	
P20					
P21	0.03078		-1.66%	-0.45	
P22	0.03115		-0.48%	-0.13	
P23	0.03165		1.13%	0.30	
P24	0.03070		-1.92%	-0.52	
P25					
P26	0.03127	0.00070	-0.10%	-0.03	-0.04
P27					
P28					
P29	0.03040		-2.88%	-0.77	
P30	0.12414	0.00020	296.63%	79.85	283.04
P31	0.03100		-0.96%	-0.26	
P32					
P33	0.03194	0.00048	2.04%	0.55	1.17
P34	0.03143		0.43%	0.11	
P35					
P36	0.03113	0.00050	-0.53%	-0.14	-0.30
P37	0.03098	0.00340	-1.02%	-0.28	-0.09
P38	0.03100		-0.96%	-0.26	
P39	0.03140	0.00227	0.33%	0.09	0.05

iso-pentane in LNG composition



Reference values	
x_{ref}	0.03130
$U(x_{ref})$ k=2	0.00026

Consensus values (raw data)		
m	0.03626	
s_r	0.00105	2.90%
s_L	0.02148	59.24%
s_R	0.02151	59.31%
p	32	

Consensus values (corrected)		
m	0.03124	
s_r	0.00107	3.42%
s_L	0.00044	1.40%
s_R	0.00115	3.70%
p	31	

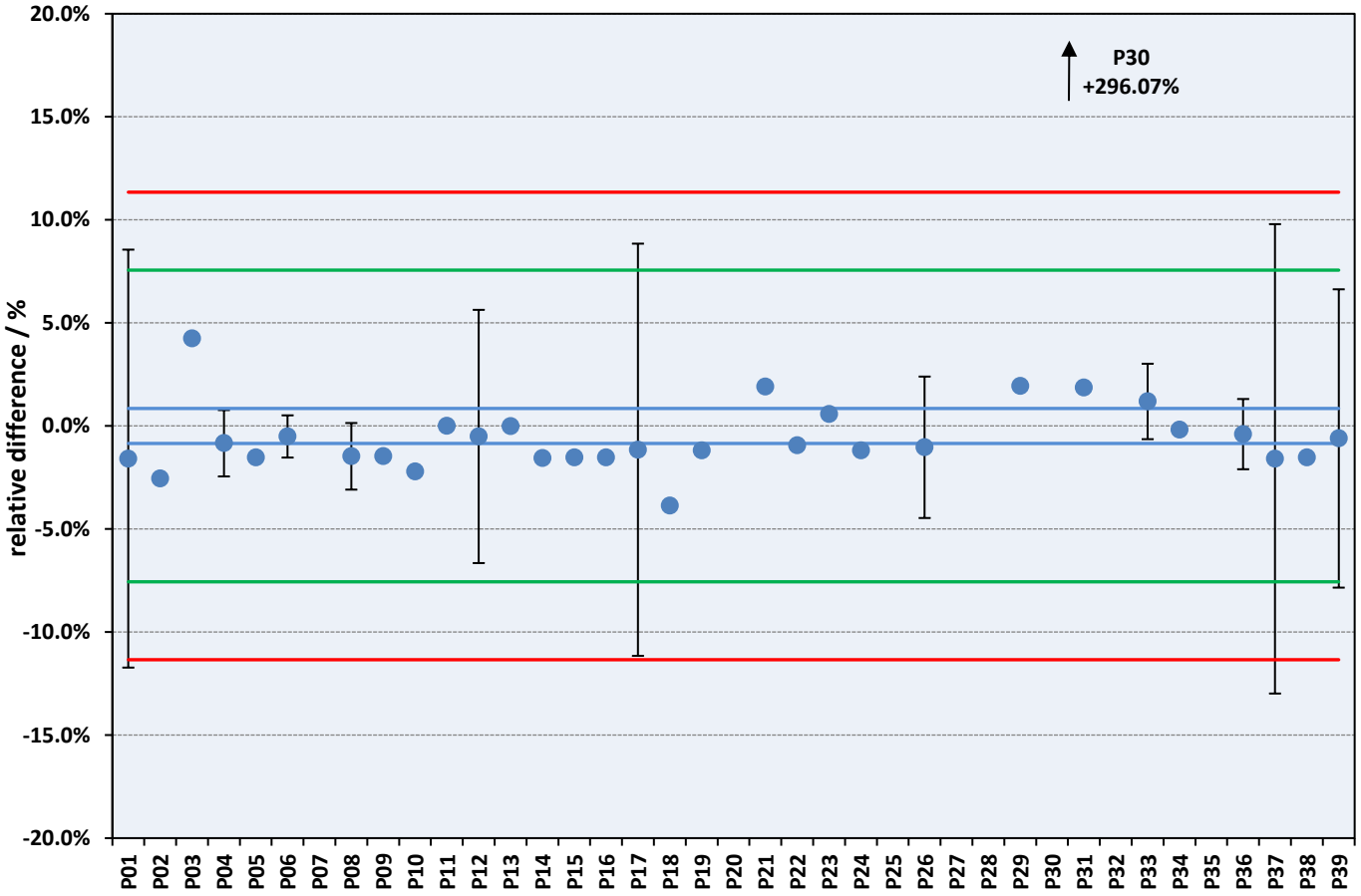
Mixture	LNG
Component	n-pentane

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	0.02945	0.00025	%mol/mol	0.00111	%mol/mol

Reported data

id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	***z***-score	E_n-number
P01	0.02898	0.00294	-1.58%	**-0.42**	**-0.16**
P02	0.02870		-2.55%	**-0.67**	
P03	0.03070		4.24%	**1.12**	
P04	0.02920	0.00047	-0.84%	**-0.22**	**-0.46**
P05	0.02900		-1.53%	**-0.40**	
P06	0.02930	0.00030	-0.51%	**-0.13**	**-0.38**
P07					
P08	0.02902	0.00047	-1.47%	**-0.39**	**-0.82**
P09	0.02902		-1.46%	**-0.39**	
P10	0.02880		-2.21%	**-0.58**	
P11	0.02945		0.00%	**0.00**	
P12	0.02930	0.00180	-0.51%	**-0.13**	**-0.08**
P13	0.02944		-0.02%	**0.00**	
P14	0.02899		-1.56%	**-0.41**	
P15	0.02900		-1.53%	**-0.40**	
P16	0.02900		-1.53%	**-0.40**	
P17	0.02911	0.00291	-1.15%	**-0.31**	**-0.12**
P18	0.02831	0.00000	-3.87%	**-1.02**	**-4.56**
P19	0.02910		-1.19%	**-0.31**	
P20					
P21	0.03001		1.92%	**0.51**	
P22	0.02918		-0.93%	**-0.25**	
P23	0.02962		0.58%	**0.15**	
P24	0.02910		-1.19%	**-0.31**	
P25					
P26	0.02915	0.00100	-1.04%	**-0.27**	**-0.30**
P27					
P28					
P29	0.03002		1.94%	**0.51**	
P30	0.11664	0.00020	296.07%	**78.31**	**272.34**
P31	0.03000		1.87%	**0.49**	
P32					
P33	0.02980	0.00055	1.19%	**0.31**	**0.58**
P34	0.02940		-0.18%	**-0.05**	
P35					
P36	0.02933	0.00050	-0.40%	**-0.10**	**-0.21**
P37	0.02898	0.00330	-1.60%	**-0.42**	**-0.14**
P38	0.02900		-1.53%	**-0.40**	
P39	0.02927	0.00212	-0.61%	**-0.16**	**-0.08**

n-pentane in LNG composition



Reference values	
x_{ref}	0.02945
$U(x_{ref})$ k=2	0.00025

Consensus values (raw data)		
m	0.03403	
s_r	0.00040	1.19%
s_L	0.02019	59.34%
s_R	0.02020	59.35%
p	32	

Consensus values (corrected)		
m	0.02931	
s_r	0.00038	1.29%
s_L	0.00052	1.79%
s_R	0.00065	2.20%
p	31	

Round	24Q2

Mixture	LNG
Component	n-hexane

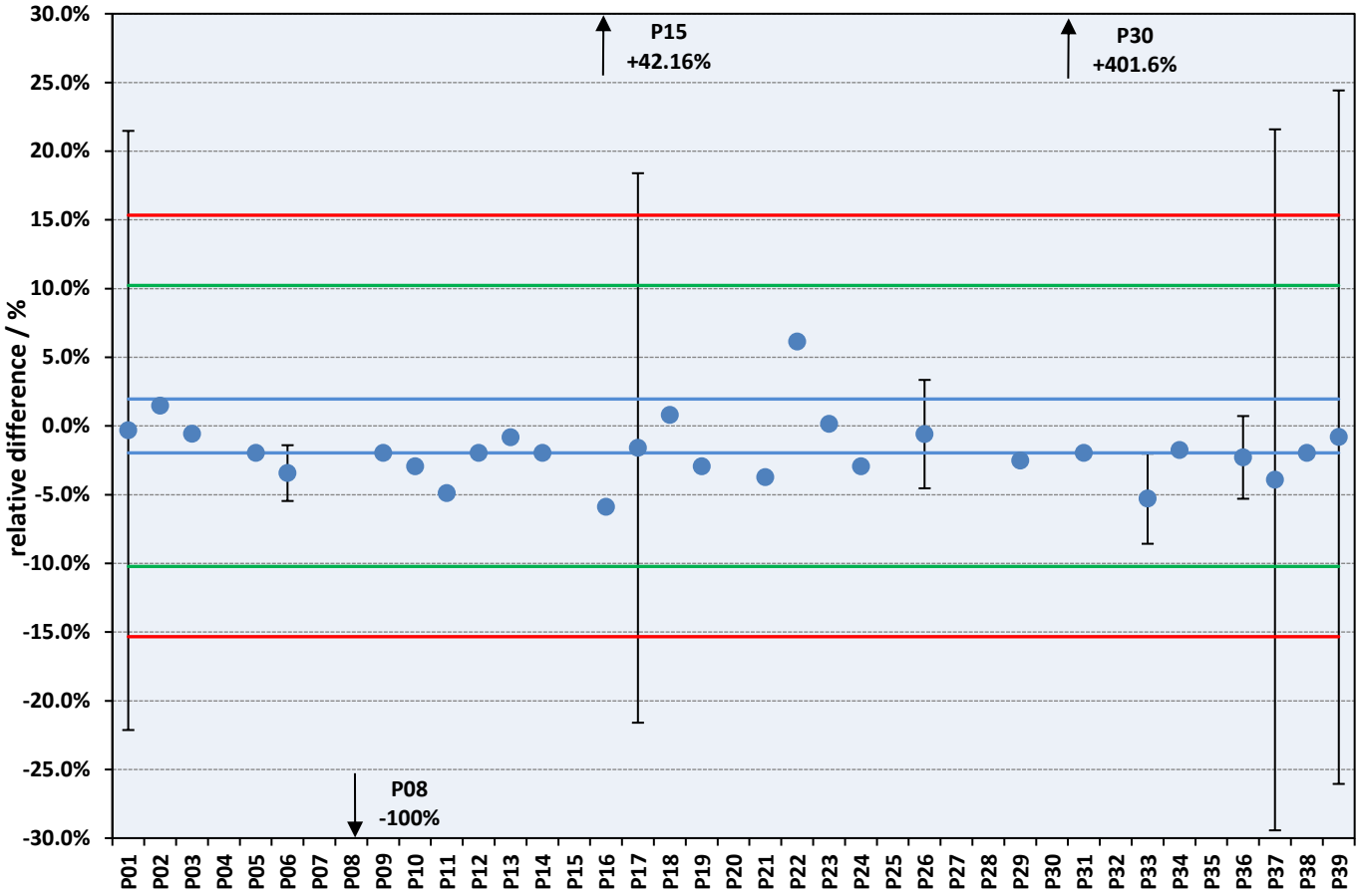
Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	0.01020	0.00020	%mol/mol	0.00052	%mol/mol

Reported data

id	value (%mol/mol)	U (k=2) (%mol/mol)	relative difference	*z*-score	E_n-number
P01	0.01017	0.00222	-0.33%	**-0.06**	**-0.01**
P02	0.01035		1.47%	**0.29**	
P03	0.01014		-0.56%	**-0.11**	
P04	<0.0100			**-0.38‡**	
P05	0.01000		-1.96%	**-0.38**	
P06	0.00985	0.00020	-3.43%	**-0.67**	**-1.24**
P07					
P08	0.00000		-100.00%	**-19.56**	
P09	0.01000		-1.96%	**-0.38**	
P10	0.00990		-2.94%	**-0.58**	
P11	0.00970		-4.90%	**-0.96**	
P12	0.01000		-1.96%	**-0.38**	
P13	0.01012		-0.83%	**-0.16**	
P14	0.01000		-1.96%	**-0.38**	
P15	0.01450		42.16%	**8.25**	
P16	0.00960		-5.88%	**-1.15**	
P17	0.01004	0.00201	-1.60%	**-0.31**	**-0.08**
P18	0.01028	0.00000007	0.78%	**0.15**	**0.40**
P19	0.00990		-2.94%	**-0.58**	
P20					
P21	0.00982		-3.74%	**-0.73**	
P22	0.01083		6.13%	**1.20**	
P23	0.01022		0.15%	**0.03**	
P24	0.00990		-2.94%	**-0.58**	
P25					
P26	0.01014	0.00040	-0.59%	**-0.12**	**-0.14**
P27					
P28					
P29	0.00994		-2.52%	**-0.49**	
P30	0.05112	0.00020	401.16%	**78.47**	**144.67**
P31	0.01000		-1.96%	**-0.38**	
P32					
P33	0.00966	0.00032	-5.29%	**-1.04**	**-1.44**
P34	0.01002		-1.77%	**-0.35**	
P35					
P36	0.00997	0.00030	-2.29%	**-0.45**	**-0.65**
P37	0.00980	0.00250	-3.92%	**-0.77**	**-0.16**
P38	0.01000		-1.96%	**-0.38**	
P39	0.01012	0.00255	-0.82%	**-0.16**	**-0.03**

Results marked with a ‡ where submitted as less than a given limit of detection and so a one tailed z-test was used instead, for which a result of |**z**|<1.65 is considered a satisfactory result.

n-hexane in LNG composition



Reference values	
x_{ref}	0.01020
$U(x_{ref})$ k=2	0.00020

Consensus values (raw data)		
m	0.01183	
s_r	0.00023	1.95%
s_L	0.00994	83.97%
s_R	0.00994	83.99%
p	31	

Consensus values (corrected)		
m	0.00958	
s_r	0.00019	2.00%
s_L	0.00252	26.33%
s_R	0.00253	26.40%
p	30	

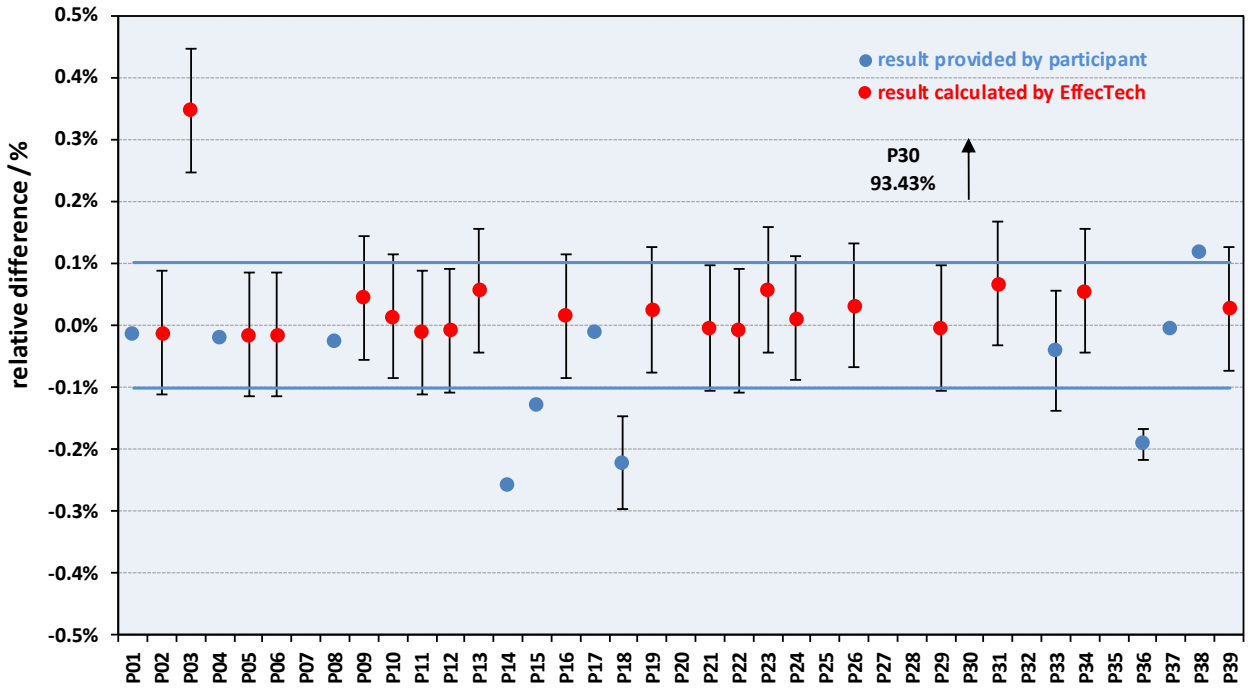
LNG composition (physical properties)

Mixture	LNG
Property	superior calorific value

Reference and reported data

participant id	calculated reference value	assigned uncertainty	participant reported / calculated	reported / calculated uncertainty	relative difference
P01	39.155	0.039	39.148		-0.02%
P02	39.846	0.040	39.842	0.040	-0.01%
P03	39.846	0.040	39.985	0.040	0.35%
P04	39.844	0.040	39.836		-0.02%
P05	39.846	0.040	39.840	0.040	-0.02%
P06	39.846	0.040	39.840	0.040	-0.02%
P07					
P08	1064.9	1.1	1064.6		-0.03%
P09	39.846	0.040	39.864	0.040	0.04%
P10	39.846	0.040	39.852	0.040	0.01%
P11	39.846	0.040	39.842	0.040	-0.01%
P12	39.846	0.040	39.843	0.040	-0.01%
P13	39.846	0.040	39.869	0.040	0.06%
P14	1067.3	1.1	1064.5		-0.26%
P15	39.844	0.040	39.793		-0.13%
P16	39.846	0.040	39.852	0.040	0.01%
P17	39.139	0.039	39.135		-0.01%
P18	1067.3	1.1	1064.9	0.8	-0.22%
P19	39.846	0.040	39.856	0.040	0.02%
P20					
P21	39.846	0.040	39.845	0.040	0.00%
P22	39.846	0.040	39.843	0.040	-0.01%
P23	39.846	0.040	39.869	0.040	0.06%
P24	39.846	0.040	39.851	0.040	0.01%
P25					
P26	39.846	0.040	39.859	0.040	0.03%
P27					
P28					
P29	39.846	0.040	39.845	0.040	0.00%
P30	939.98	0.94	1818.24	13.88	93.43%
P31	39.846	0.040	39.873	0.040	0.07%
P32					
P33	39.846	0.040	39.830	0.039	-0.04%
P34	39.846	0.040	39.868	0.040	0.05%
P35					
P36	39.846	0.040	39.770	0.010	-0.19%
P37	54.703	0.055	54.700		0.00%
P38	11.699	0.012	11.713		0.12%
P39	39.846	0.040	39.857	0.040	0.03%

superior calorific value

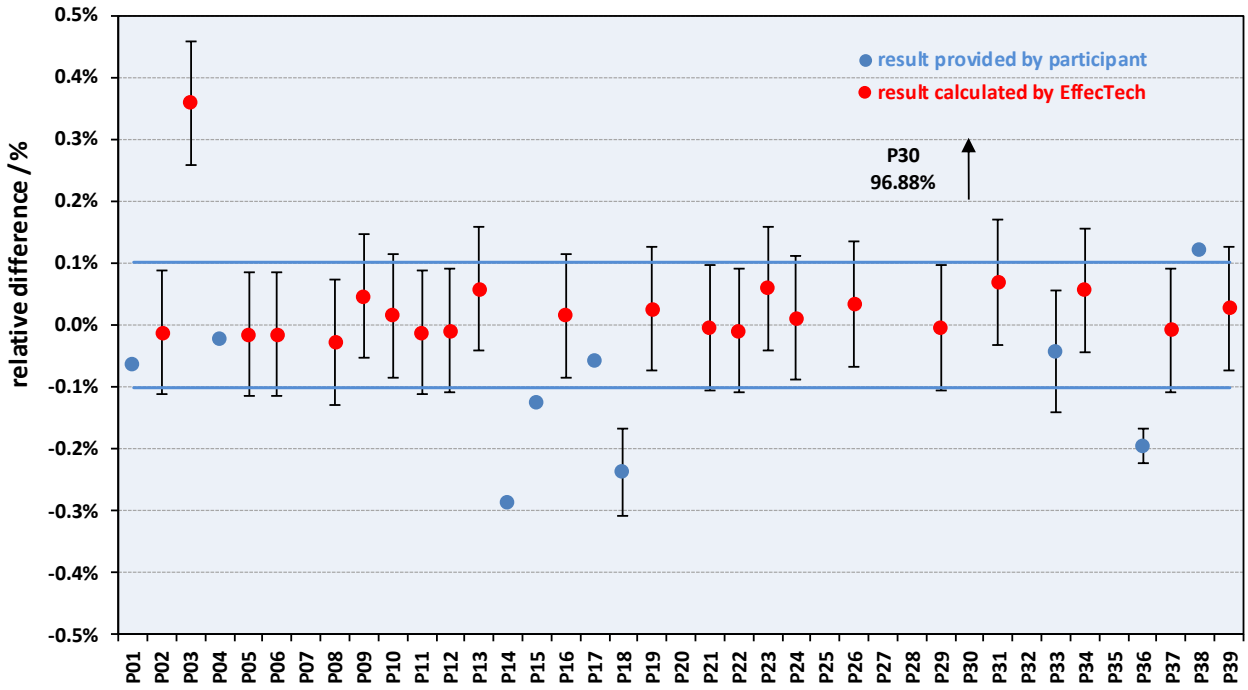


Mixture	LNG
Property	inferior calorific value

Reference and reported data

participant id	calculated reference value	assigned uncertainty	participant reported / calculated	reported / calculated uncertainty	relative difference
P01	35.339	0.035	35.317		-0.06%
P02	35.947	0.036	35.943	0.036	-0.01%
P03	35.947	0.036	36.076	0.036	0.36%
P04	35.945	0.036	35.937		-0.02%
P05	35.947	0.036	35.942	0.036	-0.02%
P06	35.947	0.036	35.942	0.036	-0.02%
P07					
P08	35.947	0.036	35.937	0.036	-0.03%
P09	35.947	0.036	35.964	0.036	0.05%
P10	35.947	0.036	35.953	0.036	0.01%
P11	35.947	0.036	35.943	0.036	-0.01%
P12	35.947	0.036	35.944	0.036	-0.01%
P13	35.947	0.036	35.968	0.036	0.06%
P14	962.95	0.96	960.18		-0.29%
P15	35.945	0.036	35.900		-0.13%
P16	35.947	0.036	35.953	0.036	0.02%
P17	35.325	0.035	35.305		-0.06%
P18	962.95	0.96	960.66	0.67	-0.24%
P19	35.947	0.036	35.957	0.036	0.03%
P20					
P21	35.947	0.036	35.946	0.036	0.00%
P22	35.947	0.036	35.944	0.036	-0.01%
P23	35.947	0.036	35.969	0.036	0.06%
P24	35.947	0.036	35.951	0.036	0.01%
P25					
P26	35.947	0.036	35.959	0.036	0.03%
P27					
P28					
P29	35.947	0.036	35.946	0.036	0.00%
P30	848.00	0.85	1669.58	12.75	96.88%
P31	35.947	0.036	35.972	0.036	0.07%
P32					
P33	35.947	0.036	35.932	0.035	-0.04%
P34	35.947	0.036	35.968	0.036	0.06%
P35					
P36	35.947	0.036	35.877	0.010	-0.20%
P37	35.917	0.036	35.914	0.036	-0.01%
P38	10.540	0.011	10.553		0.12%
P39	35.947	0.036	35.957	0.036	0.03%

inferior calorific value

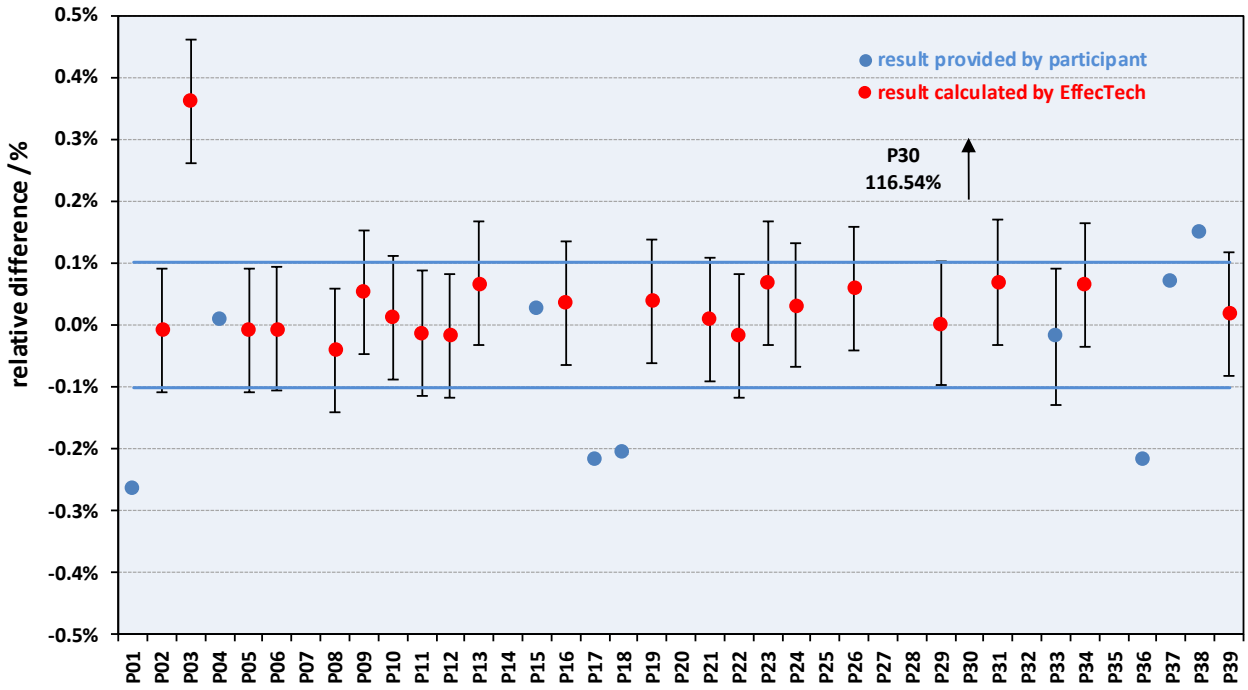


Mixture	LNG
Property	density

Reference and reported data

participant id	calculated reference value	assigned uncertainty	participant reported / calculated	reported / calculated uncertainty	relative difference
P01	0.71630	0.00072	0.71442		-0.26%
P02	0.72857	0.00073	0.72851	0.00073	-0.01%
P03	0.72857	0.00073	0.73121	0.00073	0.36%
P04	0.72854	0.00073	0.72860		0.01%
P05	0.72857	0.00073	0.72852	0.00073	-0.01%
P06	0.72857	0.00073	0.72853	0.00073	-0.01%
P07					
P08	0.72857	0.00073	0.72827	0.00073	-0.04%
P09	0.72857	0.00073	0.72896	0.00073	0.05%
P10	0.72857	0.00073	0.72866	0.00073	0.01%
P11	0.72857	0.00073	0.72848	0.00073	-0.01%
P12	0.72857	0.00073	0.72845	0.00073	-0.02%
P13	0.72857	0.00073	0.72906	0.00073	0.07%
P14	0.72854	0.00073	0.72488		-0.50%
P15	0.72854	0.00073	0.72873		0.03%
P16	0.72857	0.00073	0.72883	0.00073	0.04%
P17	0.71602	0.00072	0.71447		-0.22%
P18	0.04539	0.00005	0.04530	0.00000	-0.21%
P19	0.72857	0.00073	0.72885	0.00073	0.04%
P20					
P21	0.72857	0.00073	0.72864	0.00073	0.01%
P22	0.72857	0.00073	0.72845	0.00073	-0.02%
P23	0.72857	0.00073	0.72907	0.00073	0.07%
P24	0.72857	0.00073	0.72880	0.00073	0.03%
P25					
P26	0.72857	0.00073	0.72900	0.00073	0.06%
P27					
P28					
P29	0.72857	0.00073	0.72859	0.00073	0.00%
P30	0.72857	0.00073	1.57768	0.00320	116.54%
P31	0.72857	0.00073	0.72907	0.00073	0.07%
P32					
P33	0.72857	0.00073	0.72844	0.00080	-0.02%
P34	0.72857	0.00073	0.72904	0.00073	0.06%
P35					
P36	0.72857	0.00073	0.72700		-0.22%
P37	0.72796	0.00073	0.72848		0.07%
P38	0.76891	0.00077	0.77005		0.15%
P39	0.72857	0.00073	0.72871	0.00073	0.02%

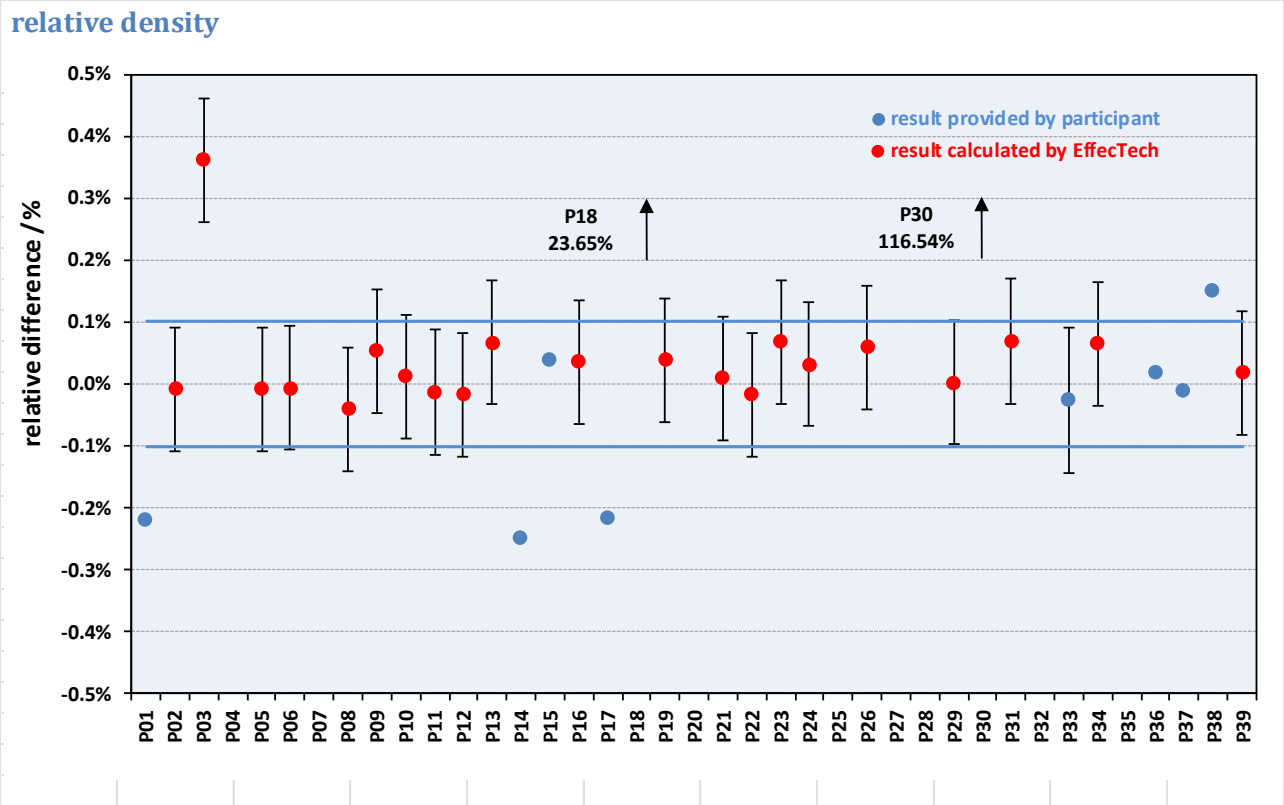
density


result provided by participant
result calculated by EffecTech
P30
116.54%
relative difference /%
0.5%
0.4%
0.3%
0.2%
0.1%
0.0%
-0.1%
-0.2%
-0.3%
-0.4%
-0.5%
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 P36 P37 P38 P39

Mixture	LNG
Property	relative density

Reference and reported data

participant id	calculated reference value	assigned uncertainty	participant reported / calculated	reported / calculated uncertainty	relative difference
P01	0.59442	0.00059	0.59312		-0.22%
P02	0.59456	0.00059	0.59450	0.00059	-0.01%
P03	0.59456	0.00059	0.59671	0.00060	0.36%
P04	0.59447	0.00059	0.59840		0.66%
P05	0.59456	0.00059	0.59451	0.00059	-0.01%
P06	0.59456	0.00059	0.59452	0.00059	-0.01%
P07					
P08	0.59456	0.00059	0.59431	0.00059	-0.04%
P09	0.59456	0.00059	0.59487	0.00059	0.05%
P10	0.59456	0.00059	0.59463	0.00059	0.01%
P11	0.59456	0.00059	0.59448	0.00059	-0.01%
P12	0.59456	0.00059	0.59445	0.00059	-0.02%
P13	0.59456	0.00059	0.59495	0.00059	0.07%
P14	0.59456	0.00059	0.59308		-0.25%
P15	0.59447	0.00059	0.59470		0.04%
P16	0.59456	0.00059	0.59477	0.00059	0.04%
P17	0.59442	0.00059	0.59313		-0.22%
P18	0.59451	0.00059	0.73509	0.00000	23.65%
P19	0.59456	0.00059	0.59478	0.00059	0.04%
P20					
P21	0.59456	0.00059	0.59461	0.00059	0.01%
P22	0.59456	0.00059	0.59445	0.00059	-0.02%
P23	0.59456	0.00059	0.59496	0.00059	0.07%
P24	0.59456	0.00059	0.59474	0.00059	0.03%
P25					
P26	0.59456	0.00059	0.59491	0.00059	0.06%
P27					
P28					
P29	0.59456	0.00059	0.59457	0.00059	0.00%
P30	0.59456	0.00059	1.28746	0.00260	116.54%
P31	0.59456	0.00059	0.59496	0.00059	0.07%
P32					
P33	0.59456	0.00059	0.59440	0.00070	-0.03%
P34	0.59456	0.00059	0.59494	0.00059	0.06%
P35					
P36	0.59456	0.00059	0.59467		0.02%
P37	0.59456	0.00059	0.59448		-0.01%
P38	0.59465	0.00059	0.59553		0.15%
P39	0.59456	0.00059	0.59467	0.00059	0.02%

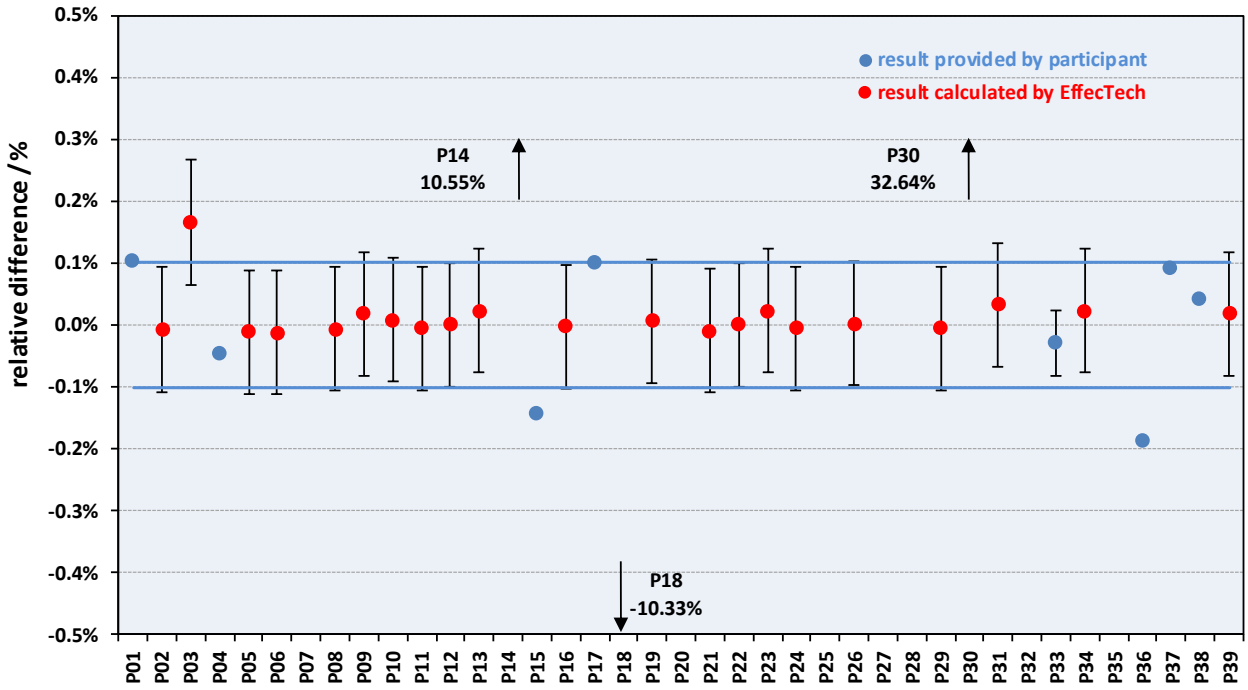

relative density
relative difference /%
0.5%
0.4%
0.3%
0.2%
0.1%
0.0%
-0.1%
-0.2%
-0.3%
-0.4%
-0.5%
result provided by participant
result calculated by EffecTech
P18
23.65%
P30
116.54%
P01 P02 P03 P04 P05 P06 P07 P08 P09 P10 P11 P12 P13 P14 P15 P16 P17 P18 P19 P20 P21 P22 P23 P24 P25 P26 P27 P28 P29 P30 P31 P32 P33 P34 P35 P36 P37 P38 P39

Mixture	LNG
Property	Wobbe index

Reference and reported data

participant id	calculated reference value	assigned uncertainty	participant reported / calculated	reported / calculated uncertainty	relative difference
P01	50.785	0.051	50.837		0.10%
P02	51.677	0.052	51.673	0.052	-0.01%
P03	51.677	0.052	51.762	0.052	0.17%
P04	51.677	0.052	51.652		-0.05%
P05	51.677	0.052	51.671	0.052	-0.01%
P06	51.677	0.052	51.670	0.052	-0.01%
P07					
P08	51.677	0.052	51.673	0.052	-0.01%
P09	51.677	0.052	51.686	0.052	0.02%
P10	51.677	0.052	51.681	0.052	0.01%
P11	51.677	0.052	51.674	0.052	-0.01%
P12	51.677	0.052	51.676	0.052	0.00%
P13	51.677	0.052	51.688	0.052	0.02%
P14	1250.4	1.3	1382.3		10.55%
P15	51.677	0.052	51.603		-0.14%
P16	51.677	0.052	51.675	0.052	0.00%
P17	50.765	0.051	50.815		0.10%
P18	349.051	0.349	312.998	0.040	-10.33%
P19	51.677	0.052	51.680	0.052	0.01%
P20					
P21	51.677	0.052	51.672	0.052	-0.01%
P22	51.677	0.052	51.677	0.052	0.00%
P23	51.677	0.052	51.689	0.052	0.02%
P24	51.677	0.052	51.674	0.052	0.00%
P25					
P26	51.677	0.052	51.678	0.052	0.00%
P27					
P28					
P29	51.677	0.052	51.674	0.052	-0.01%
P30	12351	12	16383	111	32.64%
P31	51.677	0.052	51.693	0.052	0.03%
P32					
P33	51.677	0.052	51.661	0.028	-0.03%
P34	51.677	0.052	51.688	0.052	0.02%
P35					
P36	51.677	0.052	51.580		-0.19%
P37	51.633	0.052	51.680		0.09%
P38	15.171	0.015	15.178		0.04%
P39	51.677	0.052	51.686	0.052	0.02%

Wobbe index


result provided by participant
result calculated by EffecTech
relative difference /%
0.5%
0.4%
0.3%
0.2%
0.1%
0.0%
-0.1%
-0.2%
-0.3%
-0.4%
-0.5%
P14
10.55%
P30
32.64%
P18
-10.33%
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 P36 P37 P38 P39

Sulphur component mixture

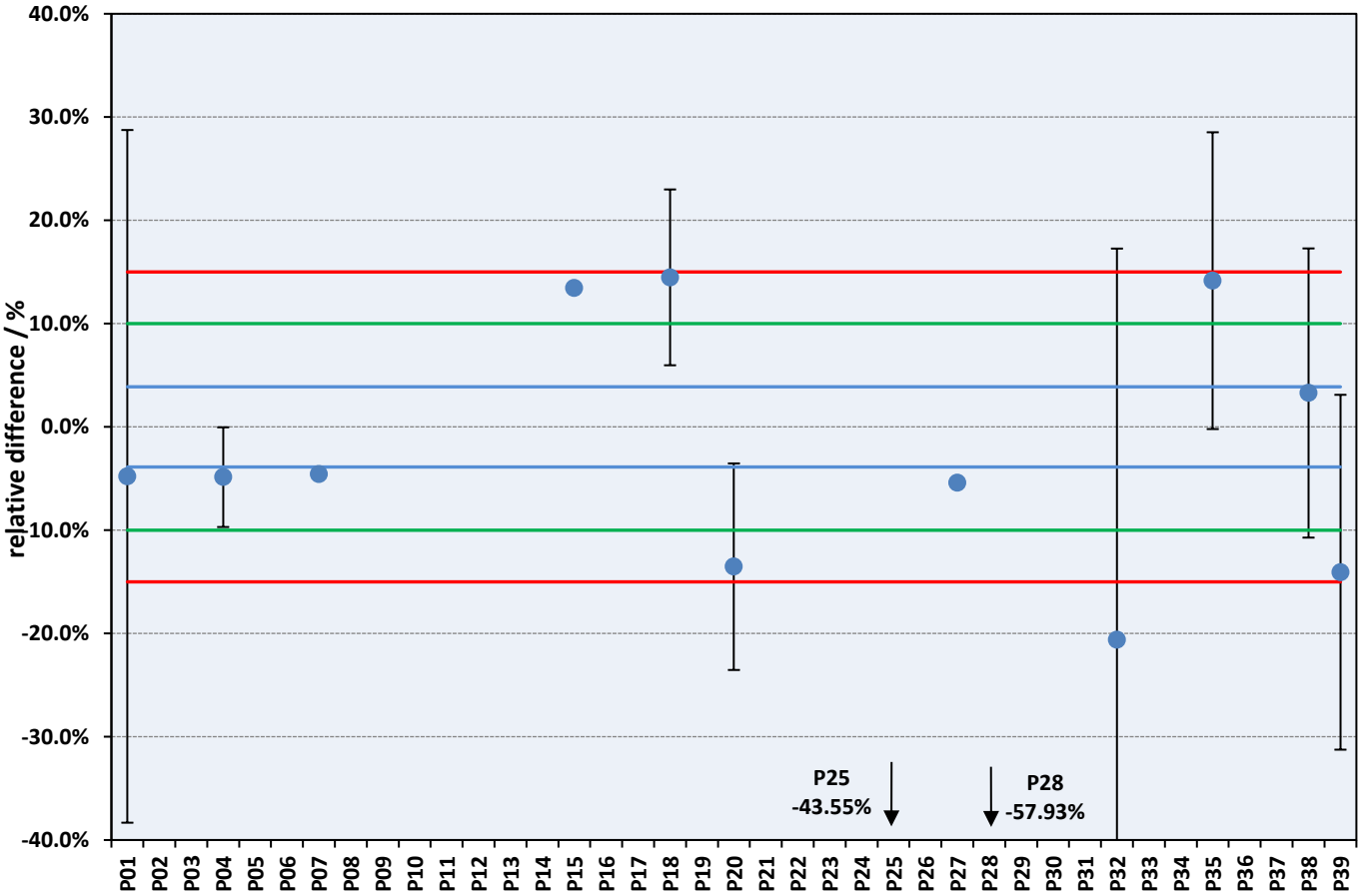
Mixture	sulphur
Component	hydrogen sulphide

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	1.829	0.071	µmol/mol	0.091	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	***z***-score	E_n-number
P01	1.741	0.584	-4.79%	**-0.89**	**-0.15**
P02					
P03					
P04	1.740	0.084	-4.87%	**-0.91**	**-0.81**
P05					
P06					
P07	1.746		-4.56%	**-0.85**	
P08					
P09					
P10					
P11					
P12					
P13					
P14					
P15	2.075		13.44%	**2.51**	
P16					
P17					
P18	2.094	0.178	14.48%	**2.70**	**1.38**
P19					
P20	1.581	0.158	-13.54%	**-2.52**	**-1.43**
P21					
P22					
P23					
P24					
P25	1.033		-43.55%	**-8.12**	
P26					
P27	1.730		-5.41%	**-1.01**	
P28	0.769		-57.93%	**-10.80**	
P29					
P30					
P31					
P32	1.452	0.550	-20.61%	**-3.84**	**-0.68**
P33					
P34					
P35	2.088	0.300	14.16%	**2.64**	**0.84**
P36					
P37					
P38	1.889	0.264	3.28%	**0.61**	**0.22**
P39	1.572	0.270	-14.07%	**-2.62**	**-0.92**

hydrogen sulphide in sulphur composition



Reference values	
x_{ref}	1.829
$U(x_{ref})$ k=2	0.071

Consensus values (raw data)		
m	1.731	
s_r	0.031	1.78%
s_L	0.348	20.11%
s_R	0.349	20.19%
p	13	

Consensus values (corrected)		
m	1.782	
s_r	0.031	1.93%
s_L	0.265	14.85%
s_R	0.267	14.97%
p	12	

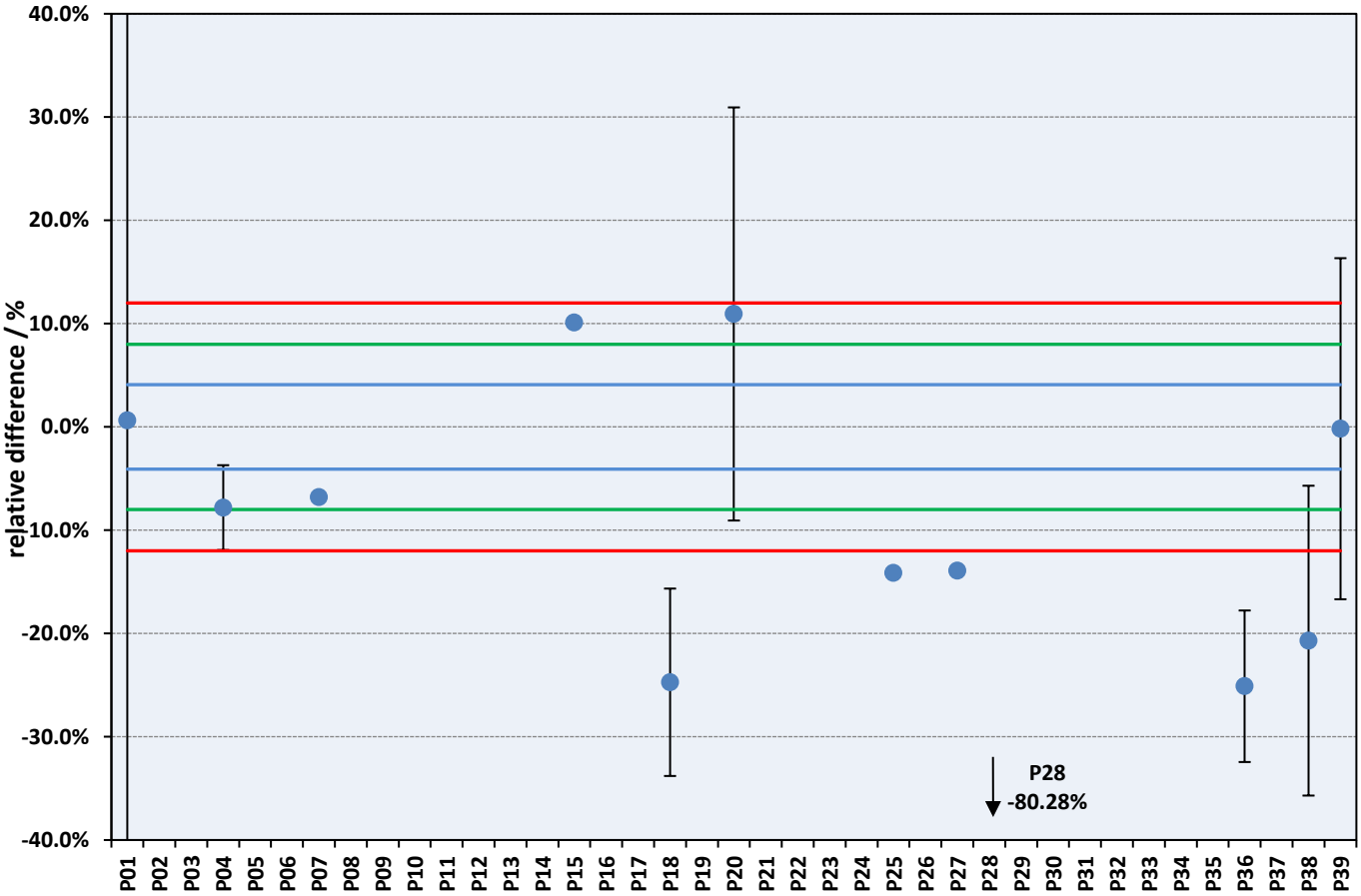
Mixture	sulphur
Component	carbonyl sulphide

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	1.638	0.067	µmol/mol	0.066	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	1.648	0.811	0.62%	0.14	0.01
P02					
P03					
P04	1.510	0.062	-7.81%	-1.74	-1.40
P05					
P06					
P07	1.526		-6.81%	-1.52	
P08					
P09					
P10					
P11					
P12					
P13					
P14					
P15	1.804		10.11%	2.25	
P16					
P17					
P18	1.233	0.112	-24.73%	-5.50	-3.11
P19					
P20	1.817	0.363	10.94%	2.43	0.48
P21					
P22					
P23					
P24					
P25	1.407		-14.13%	-3.15	
P26					
P27	1.410		-13.92%	-3.10	
P28	0.323		-80.28%	-17.87	
P29					
P30					
P31					
P32					
P33					
P34					
P35					
P36	1.227	0.090	-25.11%	-5.59	-3.67
P37					
P38	1.299	0.195	-20.70%	-4.61	-1.65
P39	1.635	0.270	-0.18%	-0.04	-0.01

carbonyl sulphide in sulphur composition



Reference values	
x_{ref}	1.638
$U(x_{ref})$ k=2	0.067

Consensus values (raw data)		
m	1.426	
s_r	0.019	1.35%
s_L	0.381	26.70%
s_R	0.381	26.73%
p	12	

Consensus values (corrected)		
m	1.502	
s_r	0.019	1.47%
s_L	0.232	15.41%
s_R	0.232	15.48%
p	11	

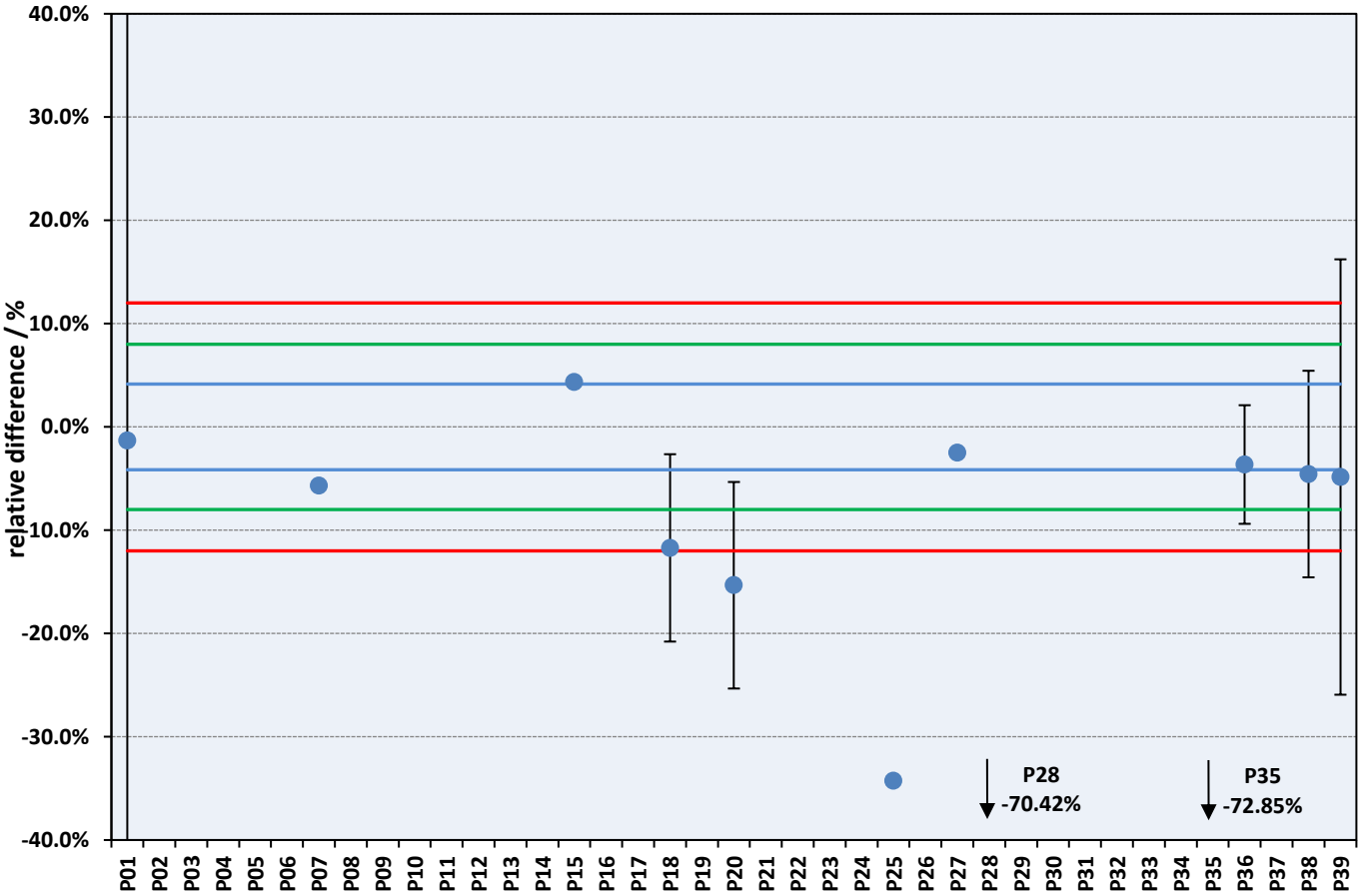
Mixture	sulphur
Component	methyl mercaptan

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	1.446	0.060	µmol/mol	0.058	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	1.427	0.926	-1.31%	-0.29	-0.02
P02					
P03					
P04					
P05					
P06					
P07	1.364		-5.69%	-1.26	
P08					
P09					
P10					
P11					
P12					
P13					
P14					
P15	1.509		4.35%	0.96	
P16					
P17					
P18	1.277	0.116	-11.72%	-2.60	-1.30
P19					
P20	1.224	0.122	-15.33%	-3.40	-1.63
P21					
P22					
P23					
P24					
P25	0.950		-34.27%	-7.60	
P26					
P27	1.410		-2.49%	-0.55	
P28	0.428		-70.42%	-15.62	
P29					
P30					
P31					
P32					
P33					
P34					
P35	0.393		-72.85%	-16.16	
P36	1.393	0.080	-3.64%	-0.81	-0.53
P37					
P38	1.380	0.138	-4.56%	-1.01	-0.44
P39	1.376	0.290	-4.85%	-1.08	-0.24

methyl mercaptan in sulphur composition



Reference values	
x_{ref}	1.446
$U(x_{ref})$ k=2	0.060

Consensus values (raw data)		
m	1.233	
s_r	0.048	3.86%
s_L	0.339	27.51%
s_R	0.342	27.78%
p	12	

Consensus values (corrected)		
m	1.348	
s_r	0.019	1.58%
s_L	0.098	7.21%
s_R	0.100	7.38%
p	10	

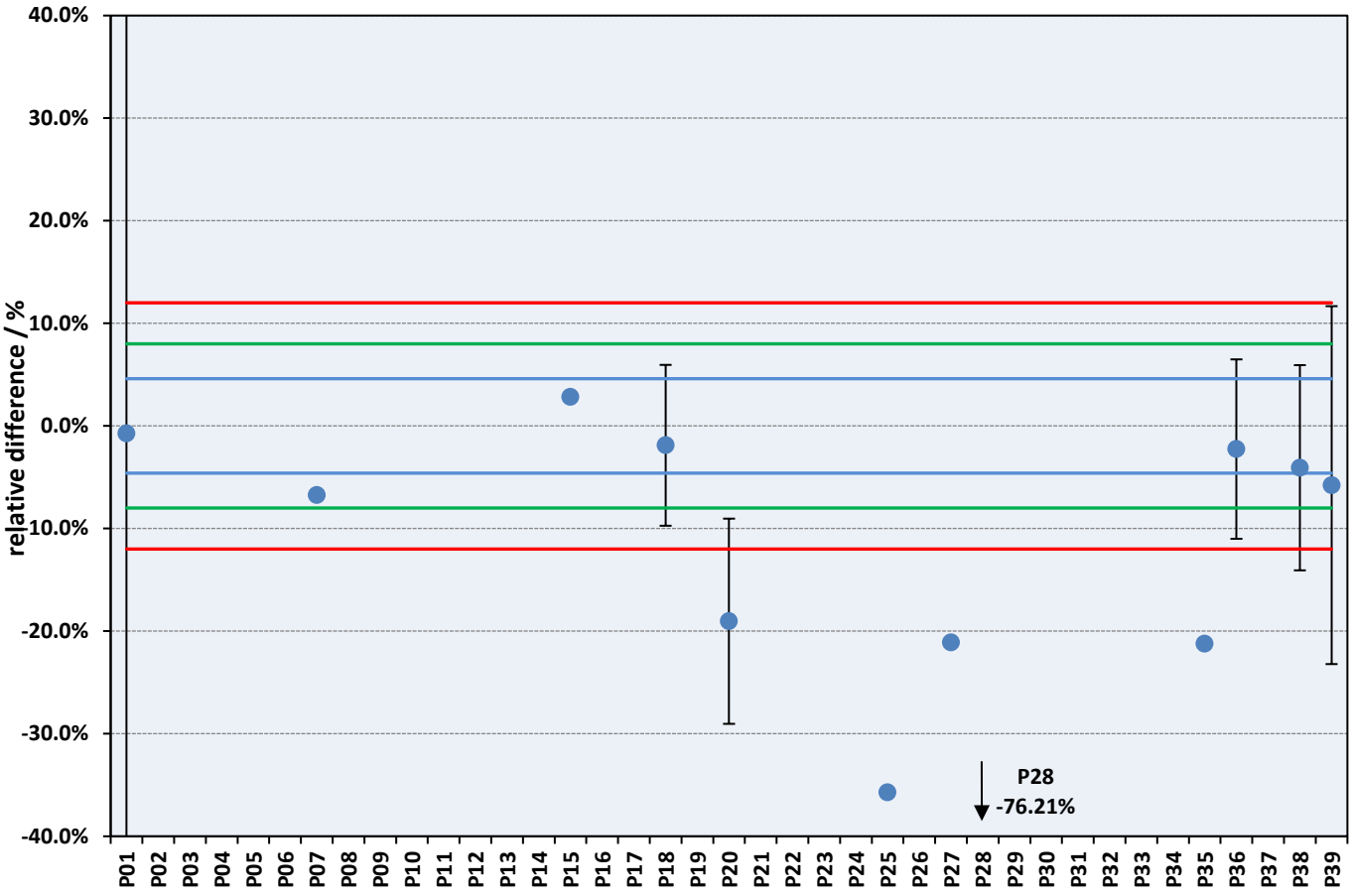
Mixture	sulphur
Component	ethyl mercaptan

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	1.521	0.070	µmol/mol	0.061	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	1.510	0.926	-0.75%	-0.16	-0.01
P02					
P03					
P04					
P05					
P06					
P07	1.418		-6.74%	-1.46	
P08					
P09					
P10					
P11					
P12					
P13					
P14					
P15	1.564		2.84%	0.61	
P16					
P17					
P18	1.492	0.117	-1.89%	-0.41	-0.21
P19					
P20	1.231	0.123	-19.04%	-4.13	-2.04
P21					
P22					
P23					
P24					
P25	0.978		-35.73%	-7.74	
P26					
P27	1.200		-21.10%	-4.57	
P28	0.362		-76.21%	-16.51	
P29					
P30					
P31					
P32					
P33					
P34					
P35	1.198		-21.22%	-4.60	
P36	1.487	0.130	-2.26%	-0.49	-0.23
P37					
P38	1.459	0.146	-4.08%	-0.88	-0.38
P39	1.433	0.250	-5.77%	-1.25	-0.34

ethyl mercaptan in sulphur composition



Reference values

x_{ref}	1.521
$U(x_{ref})$ k=2	0.070

Consensus values (raw data)

m	1.351	
s_r	0.147	10.91%
s_L	0.289	21.43%
s_R	0.325	24.05%
p	12	

Consensus values (corrected)

m	1.415	
s_r	0.152	12.13%
s_L	0.112	5.11%
s_R	0.188	13.16%
p	11	

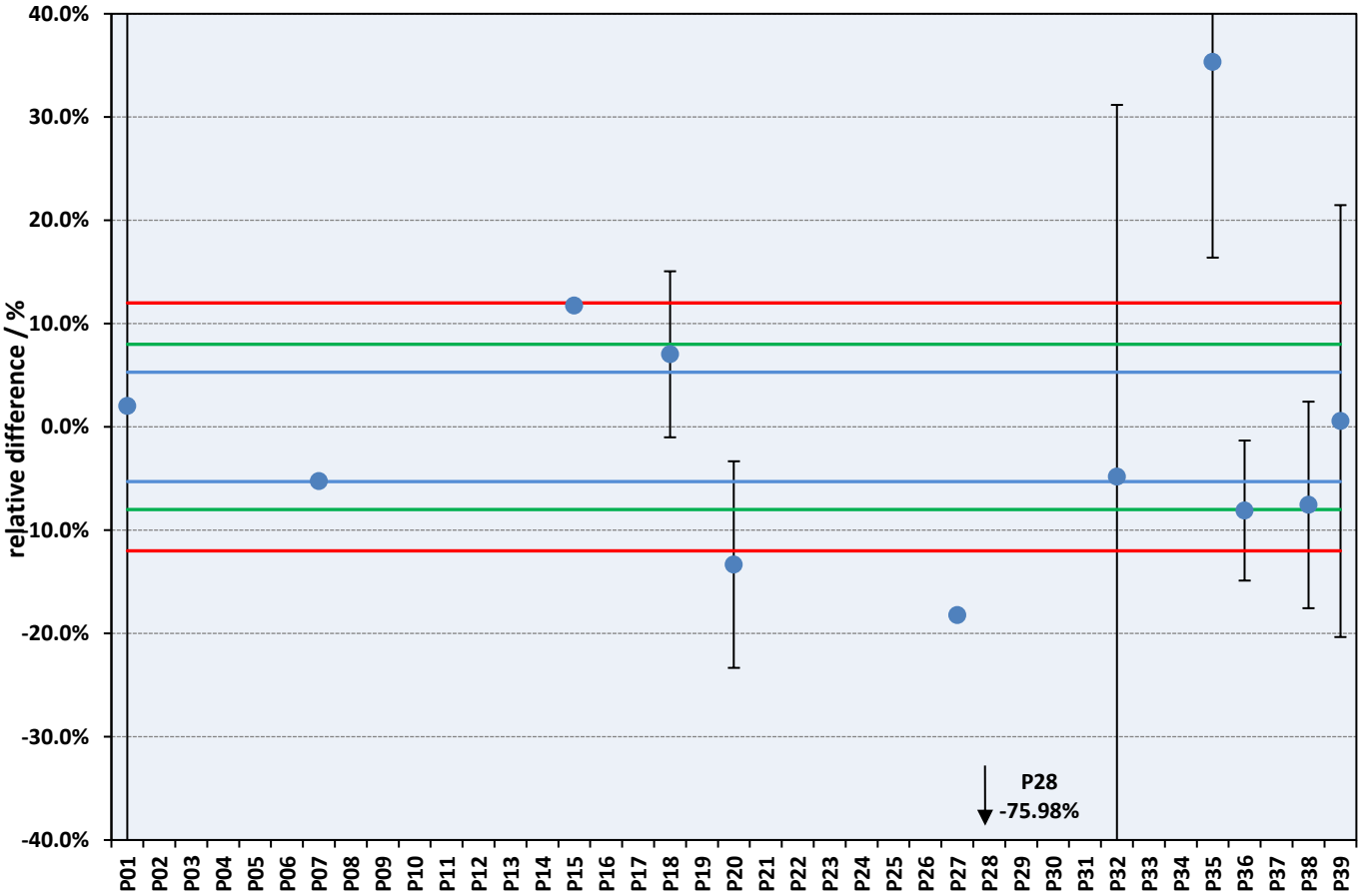
Mixture	sulphur
Component	dimethyl sulphide

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	1.284	0.068	µmol/mol	0.051	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	*z*-score	E_n-number
P01	1.310	0.810	2.03%	**0.42**	**0.03**
P02					
P03					
P04					
P05					
P06					
P07	1.216		-5.26%	**-1.10**	
P08					
P09					
P10					
P11					
P12					
P13					
P14					
P15	1.435		11.73%	**2.45**	
P16					
P17					
P18	1.374	0.110	7.03%	**1.47**	**0.70**
P19					
P20	1.113	0.111	-13.33%	**-2.78**	**-1.31**
P21					
P22					
P23					
P24					
P25					
P26					
P27	1.050		-18.22%	**-3.80**	
P28	0.308		-75.98%	**-15.84**	
P29					
P30					
P31					
P32	1.222	0.440	-4.83%	**-1.01**	**-0.14**
P33					
P34					
P35	1.738	0.329	35.33%	**7.36**	**1.35**
P36	1.180	0.080	-8.10%	**-1.69**	**-0.99**
P37					
P38	1.187	0.119	-7.55%	**-1.57**	**-0.71**
P39	1.291	0.270	0.56%	**0.12**	**0.03**

dimethyl sulphide in sulphur composition



Reference values	
x_{ref}	1.284
$U(x_{ref})$ k=2	0.068

Consensus values (raw data)		
m	1.229	
s_r	0.071	5.80%
s_L	0.274	22.25%
s_R	0.283	23.00%
p	12	

Consensus values (corrected)		
m	1.282	
s_r	0.073	6.31%
s_L	0.149	11.23%
s_R	0.166	12.88%
p	11	

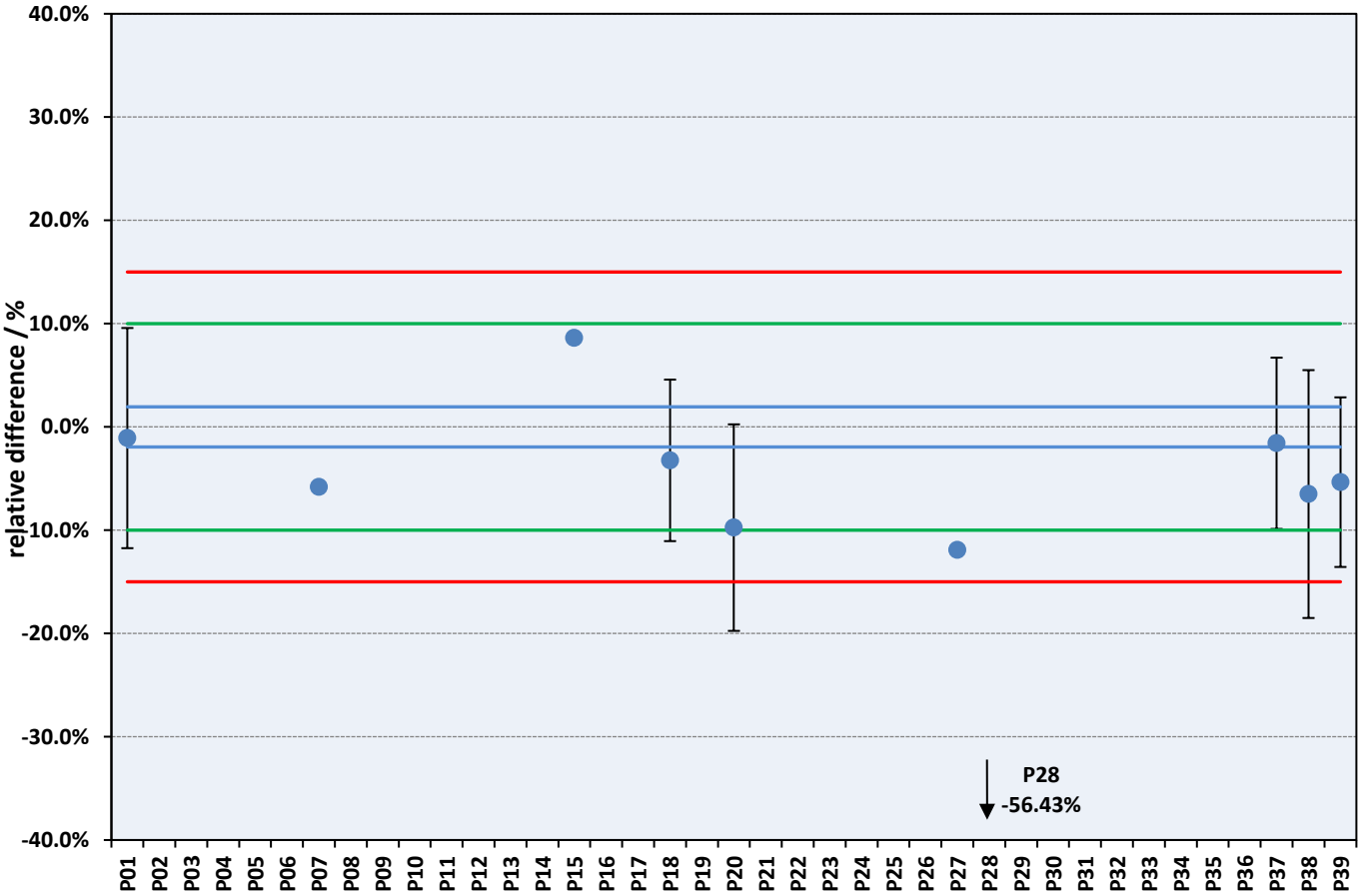
Mixture	sulphur
Component	total sulphur

Reference	x_{ref}	$U(x_{ref})$ k=2		σ	
	7.72	0.15	µmol/mol	0.39	µmol/mol

Reported data

id	value (µmol/mol)	U (k=2) (µmol/mol)	relative difference	***z***-score	E_n-number
P01	7.64	0.81	-1.08%	**-0.21**	**-0.10**
P02					
P03					
P04					
P05					
P06					
P07	7.27		-5.82%	**-1.14**	
P08					
P09					
P10					
P11					
P12					
P13					
P14					
P15	8.39		8.63%	**1.69**	
P16					
P17					
P18	7.47	0.58	-3.24%	**-0.64**	**-0.41**
P19					
P20	6.97	0.70	-9.75%	**-1.91**	**-1.06**
P21					
P22					
P23					
P24					
P25					
P26					
P27	6.80		-11.92%	**-2.34**	
P28	3.36		-56.43%	**-11.08**	
P29					
P30					
P31					
P32					
P33					
P34					
P35					
P36					
P37	7.60	0.63	-1.59%	**-0.31**	**-0.19**
P38	7.22	0.87	-6.50%	**-1.28**	**-0.57**
P39	7.31	0.60	-5.35%	**-1.05**	**-0.67**

total sulphur in sulphur composition



Reference values	
x_{ref}	7.72
$U(x_{ref})$ k=2	0.15

Consensus values (raw data)		
m	7.09	
s_r	0.07	0.95%
s_L	1.15	16.28%
s_R	1.16	16.30%
p	9	

Consensus values (corrected)		
m	7.37	
s_r	0.07	1.05%
s_L	0.35	4.72%
s_R	0.36	4.84%
p	8	

Annex B – Consensus values

Firstly, from the complete set of reported data a grand mean ($\hat{m}$), the repeatability standard deviation (s_r), the between laboratory standard deviation (s_L) and the reproducibility standard deviation (s_R) are calculated.

The consensus value is defined according to

$$\hat{m} = \bar{\bar{y}} = \frac{\sum_{i=1}^{p} n_i \bar{y}_i}{\sum_{i=1}^{p} n_i}$$

where n_i equals the number of results reported by laboratory i, $\bar{y}_i$ the average results of this laboratory and p is the total number of reporting laboratories. The repeatability standard deviation follows from

$$s_r^2 = \frac{\sum_{i=1}^{p}(n_i - 1)s_i^2}{\sum_{i=1}^{p}(n_i - 1)}$$

Where s_i is the repeatability standard deviation of the results of laboratory i.

The between-laboratory standard deviation is calculated according to

$$s_L^2 = \frac{s_d^2 - s_r^2}{\bar{\bar{n}}}$$

where

$$s_d^2 = \frac{1}{p-1}\sum_{i=1}^{p} n_i(\bar{y}_i - \bar{\bar{y}})^2$$

is identical to MS_{among} resulting from unifactorial analysis of variance (ISO Guide 35 - Annex B.1).

$\bar{\bar{n}}$ is defined as

$$\bar{\bar{n}} = \frac{1}{p-1}\left[\sum_{i=1}^{p} n_i - \frac{\sum_{i=1}^{p} n_i^2}{\sum_{i=1}^{p} n_i}\right]$$

The reproducibility standard deviation is calculated according to

$$s_R^2 = s_L^2 + s_r^2$$

The procedure for checking for outliers is different from the methods described in ISO 5725-2 [5]. From the laboratory averages, $\bar{y}_i$, standard deviation s is calculated. This standard deviations is used to calculate a raw z-score according to

$$Z_{RAW,i} = \frac{|\bar{y}_i - \hat{m}|}{s}$$

Where $Z_{RAW,i} > 2$, the result is removed from the dataset. Applying the above equations to the *corrected* data set, revised consensus values and precision measures are then recalculated.

Annex C – A guide to uncertainty

A well-defined uncertainty budget is an integral part of any measurement process; the following section is intended to give an example of a simple uncertainty budget for a typical natural gas type mixture. The simplest method available for calibration is single point through the origin (SPO). It is likely that many laboratories will use more complex measurement and calibration procedures however the basic principles described below should be applicable to any measurement with a differentiable measurement equation.

The methods described below are described in the following standards which will have further guidance on calibration models and uncertainty budget:

- ISO 6974-1:2012— *Determination of composition and associated uncertainty by gas chromatography Part 1: General guidelines and calculation of composition*
- ISO 12963:2017 — *Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration*
- JCGM 100:2008 Evaluation of measurement data — *Guide to the expression of uncertainty in measurement (GUM)*

Measurement equation

A measurement equation or calibration model is used to convert the measurements that are made into an amount fraction. The simplest measurements use a single calibration point and the origin, there are potential biases to this approach; primarily from assuming the origin is a valid point other calibration models can correct for this, however for this example this method will be used. The measurement equation is

$$x_{j,u} = y_{j,u}\frac{q_{j,r}}{y_{j,r}} = \frac{y_{j,u}}{\left(\frac{y_{j,r}}{q_{j,r}}\right)}$$

Where:

q is a normalised amount fraction (in mol/mol)

x is an unnormalised amount fraction (in mol/mol)

y is the instrument response

j is the index of component being calibrated

r indicates it is a property of the reference gas

u indicates it is a property of the unknown gas

The term $\frac{q_{j,r}}{y_{j,r}}$ or $\frac{y_{j,r}}{q_{j,r}}$ are typically called the response factor, both forms can be used and will give the same result.

Measurement uncertainty

The next consideration is the uncertainty on the unnormalised amount fraction this is given by

$$u(x_{j,u}) = x_{j,u}\sqrt{\left(\frac{u(q_{j,r})}{q_{j,r}}\right)^2 + \left(\frac{u(y_{j,r})}{y_{j,r}}\right)^2 + \left(\frac{u(y_{j,u})}{y_{j,u}}\right)^2}$$

where the uncertainties are the standard deviation of the repeat measurements of the reference and unknown gas and from the certificate for the reference gas at k=1. The derivation is given below.

From the GUM, the uncertainty for an uncorrelated system is given by

$$u^2(P) = \sum_{i=1}^{n} \left(\frac{\partial P}{\partial v_i}\right)^2 u^2(v_i).$$

There are 3 variables in the measurement equation which gives

$$u^2(x_{j,u}) = \left(\frac{\partial x_{j,u}}{\partial q_{j,r}}\right)^2 u^2(q_{j,r}) + \left(\frac{\partial x_{j,u}}{\partial y_{j,u}}\right)^2 u^2(y_{j,u}) + \left(\frac{\partial x_{j,u}}{\partial y_{j,r}}\right)^2 u^2(y_{j,r}).$$

Differentiation yields

$$= \left(\frac{y_{j,u}}{y_{j,r}}\right)^2 u^2(q_{j,r}) + \left(-y_{j,u}\frac{q_{j,r}}{y_{j,r}^2}\right)^2 u^2(y_{j,r}) + \left(\frac{q_{j,r}}{y_{j,r}}\right)^2 u^2(y_{j,u}).$$

Dividing through by the unnormalised amount fraction allows the equation to be simplified

$$= (x_{j,u})^2 \left(\frac{\left(\frac{y_{j,u}}{y_{j,r}}\right)^2 u^2(q_{j,r}) + \left(-y_{j,u}\frac{q_{j,r}}{y_{j,r}^2}\right)^2 u^2(y_{j,r}) + \left(\frac{q_{j,r}}{y_{j,r}}\right)^2 u^2(y_{j,u})}{(x_{j,u})^2} \right)$$

$$= (x_{j,u})^2 \left(\frac{\left(\frac{y_{j,u}}{y_{j,r}}\right)^2 u^2(q_{j,r}) + \left(-y_{j,u}\frac{q_{j,r}}{y_{j,r}^2}\right)^2 u^2(y_{j,r}) + \left(\frac{q_{j,r}}{y_{j,r}}\right)^2 u^2(y_{j,u})}{\left(y_{j,u}\frac{q_{j,r}}{y_{j,r}}\right)^2} \right)$$

$$= (x_{j,u})^2 \left(\left(\frac{1}{q_{j,r}}\right)^2 u^2(q_{j,r}) + \left(-\frac{1}{y_{j,r}}\right)^2 u^2(y_{j,r}) + \left(\frac{1}{y_{j,u}}\right)^2 u^2(y_{j,u}) \right)$$

$$= (x_{j,u})^2 \left(\left(\frac{u(q_{j,r})}{q_{j,r}}\right)^2 + \left(-\frac{u(y_{j,r})}{y_{j,r}}\right)^2 + \left(\frac{u(y_{j,u})}{y_{j,u}}\right)^2 \right)$$

giving

$$u(x_{j,u}) = x_{j,u}\sqrt{\left(\frac{u(q_{j,r})}{q_{j,r}}\right)^2 + \left(\frac{u(y_{j,r})}{y_{j,r}}\right)^2 + \left(\frac{u(y_{j,u})}{y_{j,u}}\right)^2}.$$

Normalisation

Maintains the ratio of the components but fixes their sum; this allows for small correction for sample size effects during the calibration.

$$q_j = \frac{x_{j,u}}{\sum_{i=1}^{n} x_i}$$

where n is the number of components and i is the component index.

Uncertainty due to normalisation

The process of normalisation has a significant impact on the uncertainty, propagation of the uncertainty through normalisation is slightly more complex than through the measurement equation, but it can be achieved using the following formula

$$u(q_j) = q_j \sqrt{\left(1 - \frac{2x_j}{\sum_{i=1}^{n} x_i}\right)\frac{u^2(x_j)}{x_j^2} + \frac{\sum_{i=1}^{n} u^2(x_i)}{\left(\sum_{i=1}^{n} x_i\right)^2}}.$$

The derivation of this equation is as follows, first consider the measurement equation

$$q_j = \frac{x_j}{\sum_{i=1}^{n} x_i} = \frac{x_j}{T}$$

where $\mathrm{T} = \sum_{i=1}^{n} x_i$ the unnormalised total. The same equation from the GUM can be used to to determine the uncertainty on normalised composition

$$u^2(P) = \sum_{i=1}^{n} \left(\frac{\partial P}{\partial v_i}\right)^2 u^2(v_i).$$

However, the variables are the unnormalised amount fractions. For a typical natural gas sample this will be a significant amount of variables thus it would be better to consider them in groups. There will be two distinct sensitivity coefficients, one when $i = j$ and the remaining coefficients when $i \neq j$. The differentiation can be achieved by the quotient and chain rules respectively giving

$\frac{\partial z_j}{\partial x_j} = \frac{T - x_j}{T^2}$ and $\frac{\partial z_j}{\partial x_i} = \frac{-x_j}{T^2}$ for all x_i where $i \neq j$.

Thus

$$u^2(q_j) = \left(\frac{T - x_j}{T^2}\right)^2 u(x_j)^2 + \sum_{i=1, i\neq j}^{n} \left(\frac{-x_j}{T^2}\right)^2 u(x_i)^2$$

Now we consider the relative uncertainty

$$\frac{u^2(q_j)}{q_j^2} = \left(\frac{1}{q_j^2}\right)\left(\left(\frac{T - x_j}{T^2}\right)^2 u(x_j)^2 + \sum_{i=1, i\neq j}^{n} \left(\frac{-x_j}{T^2}\right)^2 u(x_i)^2\right).$$

As $q_j = {}^{x_j}/_{T}$ we have

$$\frac{u^2(q_j)}{q_j^2} = \left(\frac{T^2}{x_j^2}\right)\left(\left(\frac{T - x_j}{T^2}\right)^2 u(x_j)^2 + \frac{x_j^2}{T^4} \sum_{i=1, i\neq j}^{n} u(x_i)^2\right)$$

$$= \frac{T^2(T - x_j)^2 u(x_j)^2}{T^4 x_j^2} + \frac{x_j^2 T^2}{x_j^2 T^4} \sum_{i=1, i\neq j}^{n} u(x_i)^2.$$

Simplifying the fractions and expanding the brackets yields

$$\frac{u^2(q_j)}{q_j^2} = \frac{(T^2 - 2tx_j + x_j^2)u(x_j)^2}{T^2 x_j^2} + \frac{1}{T^2} \sum_{i=1, i\neq j}^{n} u(x_i)^2.$$

Splitting the fraction gives

$$\frac{u^2(q_j)}{q_j^2} = \frac{(T^2 - 2tx_j)u(x_j)^2}{T^2x_j^2} + \frac{x_j^2u(x_j)^2}{T^2x_j^2} + \frac{1}{T^2}\sum_{i=1,i\neq j}^{n} u(x_i)^2.$$

Simplifying the fractions yields

$$\frac{u^2(q_j)}{q_j^2} = \left(1 - \frac{2x_j}{T}\right)\frac{u(x_j)^2}{x_j^2} + \frac{u(x_j)^2}{T^2} + \frac{1}{T^2}\sum_{i=1,i\neq j}^{n} u(x_i)^2$$

We can now add the missing term back into the summation thus we have

$$\frac{u^2(q_j)}{q_j^2} = \left(1 - \frac{2x_j}{T}\right)\frac{u(x_j)^2}{x_j^2} + \frac{1}{T^2}\sum_{i=1}^{n} u(x_i)^2$$

$$= \left(1 - \frac{2x_j}{\sum_{i=1}^{n} x_i}\right)\frac{u(x_j)^2}{x_j^2} + \frac{\sum_{i=1}^{n} u(x_i)^2}{\left(\sum_{i=1}^{n} x_i\right)^2}.$$

Rearranging gives

$$u(q_j) = q_j\sqrt{\left(1 - \frac{2x_j}{\sum_{i=1}^{n} x_i}\right)\frac{u^2(x_j)}{x_j^2} + \frac{\sum_{i=1}^{n} u^2(x_i)}{\left(\sum_{i=1}^{n} x_i\right)^2}}.$$

Coverage factor

The coverage factor gives a range that for a certain probability the value will fall it. Uncertainties are typically calculated at k=1, but are expressed at higher converge factors typically k=2. Multiply the uncertainties by k=2 will give a confidence interval of approximately 95%. This is called the expanded uncertainty and the symbol U is used.

Units

The values used in these equations all need to be in mol/mol (which sums to 1). Conversion to %mol/mol simply requires multiplying by the amount fraction and expanded uncertainties by 100.

Below is an example calculation for a natural gas mixture, a version of the spreadsheet is available on request.

component	Reference gas raw data					reference values		Reference gas data summary			response factor
	y(r)1	y(r)2	y(r)3	y(r)4	y(r)5	q(j,r)	u(q(j,r))	y(r)	u(y(r))	%RSD	
	raw areas					mol/mol		mean	standard dev.		q(j,r)/y(r)
nitrogen	7919456	7925766	7921631	7917744	7915844	0.0609700	0.0002350	7920088	3825.11	0.05%	7.6981E-09
carbon dioxide	3196991	3196960	3196271	3195678	3194841	0.0254400	0.0000350	3196148	910.26	0.03%	7.9596E-09
methane	101869624	101889416	101854336	101838416	101814760	0.7846000	0.0003000	101853310	28630.30	0.03%	7.7032E-09
ethane	13739319	13747007	13741495	13738624	13734157	0.1095000	0.0001350	13740120	4683.97	0.03%	7.9694E-09
propane	1112318	1112741	1112117	1112358	1111620	0.0090660	0.0000160	1112231	409.30	0.04%	8.1512E-09
iso-butane	374858	375110	374107	373689	373791	0.0030170	0.0000065	374311	639.63	0.17%	8.0601E-09
n-butane	364282	365188	363104	363796	359486	0.0029990	0.0000070	363171	2195.28	0.60%	8.2578E-09
iso-pentane	267316	266682	267180	267905	269540	0.0022090	0.0000085	267725	1104.40	0.41%	8.2510E-09
n-pentane	261096	263221	262925	263237	260876	0.0021990	0.0000080	262271	1182.16	0.45%	8.3845E-09
n-hexane	0	0	0	0	0	0.0000000	0.0000000	0	0.00	0.00%	0.0000E+00

component	Unknown gas raw data					Candidate gas data summary			Unnormalised			Normalised		Reported	
	y(u)1	y(u)2	y(u)3	y(u)4	y(u)5	y(u)	u(y(u))	%RSD	x(j,u)	u(x(j,u))	u^2(x(j,u))	q(j,u)	u(q(j,u))	q(j,u)	U(q(j,u))
	raw areas					mean	standard dev.		mol/mol		(mol/mol)^2	mol/mol		%mol/mol	
nitrogen	524767	524486	524868	524873	523533	524505	565.90	0.11%	0.004038	0.000016	2.65E-10	0.004061	0.000016	0.4061	0.0033
carbon dioxide	934182	933710	933637	933166	934355	933810	471.72	0.05%	0.007433	0.000011	1.23E-10	0.007476	0.000012	0.7476	0.0023
methane	111724936	111683736	111680400	111730032	111723200	111708461	24252.41	0.02%	0.860517	0.000449	2.02E-07	0.865516	0.000130	86.552	0.026
ethane	9448026	9443364	9447495	9446714	9449990	9447118	2422.33	0.03%	0.075288	0.000098	9.65E-09	0.075725	0.000098	7.572	0.020
propane	4306463	4302337	4301981	4301668	4303210	4303132	1949.47	0.05%	0.035076	0.000065	4.25E-09	0.035279	0.000065	3.528	0.013
iso-butane	558467	557444	558107	557798	558366	558036	420.36	0.08%	0.004498	0.000013	1.64E-10	0.004524	0.000013	0.4524	0.0026
n-butane	548792	547984	548609	548494	549289	548634	473.47	0.09%	0.004531	0.000030	8.77E-10	0.004557	0.000030	0.4557	0.0059
iso-pentane	171815	171355	171950	171633	169822	171315	863.86	0.50%	0.001414	0.000011	1.14E-10	0.001422	0.000011	0.1422	0.0022
n-pentane	168454	169142	168240	167977	179765	170716	5077.18	2.97%	0.001431	0.000043	1.88E-09	0.001440	0.000044	0.1440	0.0087
n-hexane	0	0	0	0	0	0	0.00	0.00%	0.00000	0.00000	0.00E+00	0.000000	0.000000	0	0
								Sum	0.99422338		2.19E-07	1		100	