Global Gas and LNG Proficiency Testing (PT) Scheme

Instructions for Participants

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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1. Introduction

EffecTech provides and organises a Global Gas and LNG Proficiency Testing Scheme (formerly called the Gas and Liquefied Natural Gas Correlation Scheme).

Proficiency testing (PT) schemes provide an objective way of assessing the performance of laboratories by a series of regular inter-laboratory comparisons. This PT scheme is aimed at laboratories working in the field of liquefied natural gas (LNG) and natural gas.

The results, reports and certificates issued during this scheme can be used as objective evidence of competence during audits and inspections from interested third parties or accreditation bodies.

In this PT scheme four rounds are scheduled per year. The mixtures provided include LNG composition, propane composition, mixed refrigerant and a sulphur component mixture.

The mixtures are checked for stability and reference values are assigned prior to shipment. After each round, the mixtures will remain at the participant’s laboratories for use in either calibration or quality control.

The gas mixture preparation and assignment of reference values are carried out by EffecTech.

2. References

The following list of references contains information which, through reference in the main body of this document, are necessary to understand fully the provisions of these instruction. At the time of writing, and unless otherwise stated in the main body of this document, these instructions are consistent with the principles contained within all those listed below.

All documents in this list, particularly at the present time, are subject to revision and the provider of this scheme makes every effort to ensure that provisions in more recent revisions than those listed below are adopted.

[1] ISO/IEC 17043 Conformity assessment - General requirements for proficiency testing
[2] ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories
3. Points of contact

The PT scheme is provided by EffecTech.

EffecTech has appointed key personnel and management representatives responsible for providing the scheme. Contact details of the scheme coordinator, the logistics manager and technical authority are given below

**Scheme coordinator**

Mr Steve Price  
EffecTech  
Dove House  
Dove Fields  
Uttoxeter ST14 8HU  
United Kingdom

T: +44 (0)1889 569229  
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F: +44 (0)1889 569220  
E: coordinator@effectech.co.uk

**Logistics (Transport) officer**

Ms Sue Grice  
<address as above>

T: +44 (0)1889 569229  
Direct: +44 (0)1889 598707  
F: +44 (0)1889 569220  
E: logistics@effectech.co.uk

**Technical Authority**

Dr Gavin Squire  
<address as above>

T: +44 (0)1889 569229  
F: +44 (0)1889 569220  
E: gavin.squire@effectech.co.uk
4. Accreditation status

EffecTech provides this proficiency testing scheme in accordance with the requirements of ISO/IEC 17043 [1] (formerly ISO Guide 43) for which it is accredited by the United Kingdom Accreditation Service (UKAS). Please see the UKAS website for our official scope of accreditation (UKAS proficiency testing provider 4719).

EffecTech holds an accreditation awarded by UKAS to ISO/IEC 17025 [2] as a calibration laboratory. Please see the UKAS website for our official scope of accreditation (UKAS calibration laboratory 0590). EffecTech uses these methods for the calibration of gas mixtures issued in this PT scheme.

5. Mixtures

5.1 Introduction

The mixtures issued in this PT scheme comprise four types (see table 1).

Table 1: Gas mixture types

<table>
<thead>
<tr>
<th>description</th>
<th>cylinder volume (dm³)</th>
<th>cylinder outlet</th>
<th>nominal pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNG composition</td>
<td>1</td>
<td>BS341-No.4</td>
<td>20</td>
</tr>
<tr>
<td>propane composition</td>
<td>5</td>
<td>BS341-No.4</td>
<td>5</td>
</tr>
<tr>
<td>mixed refrigerant (MR)</td>
<td>1</td>
<td>BS341-No.4</td>
<td>20</td>
</tr>
<tr>
<td>sulphur component</td>
<td>5</td>
<td>BS341-No.15</td>
<td>50</td>
</tr>
</tbody>
</table>

5.2 LNG composition

Table 2: Composition range

<table>
<thead>
<tr>
<th>component</th>
<th>range (% mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>0.1 to 14</td>
</tr>
<tr>
<td>propane</td>
<td>0.05 to 5</td>
</tr>
<tr>
<td>iso-butane</td>
<td>0.01 to 1</td>
</tr>
<tr>
<td>n-butane</td>
<td>0.01 to 1</td>
</tr>
<tr>
<td>iso-pentane</td>
<td>0.005 to 0.35</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.005 to 0.35</td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.001 to 0.35</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.1 to 8</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>0.1 to 8</td>
</tr>
<tr>
<td>methane</td>
<td>balance</td>
</tr>
</tbody>
</table>
In rounds with an **odd** number, the mixture will contain higher amounts of nitrogen and carbon dioxide to represent feed gas.

In rounds with an **even** number, to accurately represent LNG, the mixture will contain no carbon dioxide and the nitrogen range will be 0.1-1 % (mol/mol).

### 5.3 Propane composition

Table 3: Composition range

<table>
<thead>
<tr>
<th>component</th>
<th>range (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>0.25 to 3</td>
</tr>
<tr>
<td>iso-butane</td>
<td>0.03 to 0.7</td>
</tr>
<tr>
<td>n-butane</td>
<td>0.03 to 0.7</td>
</tr>
<tr>
<td>iso-pentane</td>
<td>0.02 to 0.08</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.02 to 0.08</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.1 to 2</td>
</tr>
<tr>
<td>propane</td>
<td>Balance</td>
</tr>
</tbody>
</table>

### 5.4 Mixed refrigerant (MR)

Table 4: Composition range

<table>
<thead>
<tr>
<th>component</th>
<th>range (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>20 to 35</td>
</tr>
<tr>
<td>propane</td>
<td>5 to 15</td>
</tr>
<tr>
<td>nitrogen</td>
<td>8 to 16</td>
</tr>
<tr>
<td>methane</td>
<td>Balance</td>
</tr>
</tbody>
</table>

### 5.5 Sulphur component mixture

Table 5: Composition range

<table>
<thead>
<tr>
<th>component</th>
<th>range (μmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen sulphide</td>
<td>1 to 10</td>
</tr>
<tr>
<td>methyl mercaptan</td>
<td>1 to 10</td>
</tr>
<tr>
<td>ethyl mercaptan</td>
<td>1 to 10</td>
</tr>
<tr>
<td>carbonyl sulphide</td>
<td>1 to 10</td>
</tr>
<tr>
<td>dimethyl sulphide</td>
<td>1 to 10</td>
</tr>
<tr>
<td>methane, ethane &amp; propane (^1)</td>
<td>Balance</td>
</tr>
</tbody>
</table>

---

\(^{1}\) 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 should measure and report the sulphur containing components only; you are NOT required to report the matrix hydrocarbons in this mixture.
6. Mixture preparation and reference value assignment

6.1 Preparation of mixture batches

One or more parent mixtures are pre-prepared by a gravimetric method in accordance with ISO 6142-1 [3]. A batch of mixtures of each type is then produced by decanting the parent mixture into a batch of lower volume pre-prepared and evacuated daughter cylinders.

The parent mixtures and daughter mixture are then calibrated.

6.2 Mixture calibration

All parent mixtures are calibrated by a multipoint calibration technique by comparison with a suite of reference mixtures in accordance with the requirements of ISO 6143 [4]. Where this is not possible, a bracketing technique is used where one or more reference gases of similar composition and matrix were used.

All decant mixtures were calibrated by an exact matching technique by the comparison of the decant mixture with its nominally identical parent mixtures.

The uncertainty on amount fraction of each measurand in the mixtures resulting from this calibration is termed the characterisation uncertainty, $u_{\text{char}}$ (ISO Guide 35 [5]).

All calibrations are performed in accordance with EffecTech’s ISO 17025 [2] accredited calibration methods.

6.3 Reference mixture traceability

Gas chromatography is used as the analytical technique for the calibration of all mixtures in this scheme. Each gas chromatograph is calibrated with one or several reference mixtures traceable directly to a National Metrology Institute (NMI). This process ensures 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).

6.4 Homogeneity assessment

Statistical analysis of the spread of reference values obtained for each batch of mixtures (derived through calibration in 6.2 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. The uncertainty arising from this is $u_{\text{hom}}$ (ISO Guide 35 [2]). This uncertainty should be less than or equal to the characterisation uncertainty in order to accept the batch.
6.5 Stability of the mixtures

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 stability of the mixtures, $u_{\text{int}}$. This is valid providing the mixtures are not used beyond this stability period.

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

In conjunction with your existing reference mixtures used for calibration or quality control, these mixtures can be used likewise after the submission of results for each round in this scheme. Cylinders that are no longer required may be returned directly to EffecTech if the costs are not prohibitively expensive.

6.6 Reference value assignment

For all four mixture types, each component is assigned a reference value, $x_{\text{ref}}$, calculated from the average of those determined in the calibration stage (see section 6.2 above).

A combined uncertainty, $u_c$, is first calculated from the equation below. This uncertainty is dominated in all cases by the calibration uncertainty, $u_{\text{char}}$.

$$u_c = u_{\text{char}} + u_{\text{hom}}$$

Following this calculation, the expanded uncertainty, $k\cdot u_c$, ($k=2$), is compared to the Calibration and Measurement Capability (CMC) for which EffecTech is accredited to ISO 17025 (See UKAS calibration laboratory 0590). If $U_{\text{CMC}}$ ($k=2$) is greater than $k\cdot u_c$ ($k=2$) then the uncertainty on the reference value is assigned to that stated in our published CMC in accordance with accepted practice such that

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

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

7.1 Shipping

Four rounds per year will be conducted and mixtures shipped to participants during January, April, July and October.

EffecTech sub-contracts all shipping and freight forwarding to specialist transport providers whose performance has been evaluated by regular and on-going monitoring of their ability to deliver to time and quality.

Participants will be responsible for taking receipt of each consignment and collecting the reference mixtures once they have been notified by EffecTech (or the freight forwarder / courier) that they are due for delivery on site. If the consignment is not received at the destination within one week of the due date of this notification then they should contact EffecTech.

On receipt of the Proficiency Testing item(s) participants will be responsible for completing and returning the “Sample Receipt Form”. This is securely attached to the neck of one of the sample cylinders supplied. The contact details, timescale and methods for return of the completed form are contained on the form itself.

Airfreight delivery to airport
The cargo handling agent at the destination airport will notify the consignee (participant) of the need to clear the goods for customs. Proofs of Delivery (PODs) are requested from the destination cargo handling agent via EffecTech’s freight forwarder. Once beyond the Incoterms™ defined delivery point, EffecTech will periodically request shipment status updates from the participant and their freight forwarder, if known to us, regarding the current status of the shipment at the time of request. Participants should respond to these requests with the latest available information and should, in any event, inform EffecTech of any issues or delays in transportation or customs clearance as soon as they are known.

Airfreight delivery to door
The cargo handling agent at the destination airport will notify the destination freight agent/forwarder (known as the Notify Party) who will in turn notify the consignee (participant). PODs are requested from the Notify Party by EffecTech’s freight forwarder. However, this may be done by EffecTech directly if the Notify Party is known to us.

UK and European road transport
The UK freight forwarder will pass information through the carrier network from carrier to carrier until delivery is made. A Proof of Delivery (POD) will then pass back through the network of carriers to the originating freight forwarder who will then pass back the POD to EffecTech. In the case of UK road transport, EffecTech takes the place of the freight forwarder.

Ex-Works (EXW) & Free Carrier (FCA EffecTech) shipments
For shipments where the participant has elected to arrange their own transportation, EffecTech will notify the participant and their freight forwarder, if supplied, by means of a notification stating the date the samples will be available for collection. This notification will contain an electronic version of all shipping documents generated by EffecTech as well as the collection address, hours of opening and contact details for the collection.
Given the tight timescales involved with this scheme, the availability date given in this notification will start a maximum 5 week (35 day) period for the collection, transit and delivery of the sample(s) to the participant to be completed.

During transportation EffecTech will periodically request information from the participant and their freight forwarder, if known to us, regarding the current status of the shipment at the time of request. Participants should respond to these requests with the latest available information and should, in any event, inform EffecTech of any issues or delays in transportation or customs clearance as soon as they are known.

The participant must notify EffecTech on receipt of the sample(s). This will prompt the reporting form and reporting deadline to be issued. However, should 35 days from the stated sample collection availability date pass without the participant confirming receipt of the sample(s), the reporting form and reporting deadline will be issued automatically to the participant on the 36th day following the sample(s) being made available for collection.

All logistics and delivery queries should be directed to

Ms Sue Grice  
Logistics (Transport) officer  
T:    +44 (0)1889 569229  
Direct:    +44 (0)1889 598707  
F:    +44 (0)1889 569220  
E:    logistics@effectech.co.uk

EffecTech undertakes every reasonable effort to prevent delays in the dispatch of the gas mixtures.
7.2 Reporting

Laboratories are requested to report their results well before the deadline. Participants will be informed of the deadline for reporting which shall usually be 2 weeks after receipt of the cylinders. Results received after the deadline will not be processed or included in the report. In case of foreseeable delays, participants are requested to report such delays to the scheme coordinator with an expected date of submission of their results. The new date requested cannot be regarded as a new deadline unless it is confirmed by the scheme coordinator.

Detailed instructions for reporting your results can be found below in section 8.6 & 8.7.
8. Instructions for measurement

8.1 Sample treatment

Laboratories shall treat the reference gas mixtures in the same manner as they would a routine testing sample.

However, appropriate consideration should be given to the advice below (in sections 8.2, 8.3 & 8.4) concerning storage and use of the gas mixture.

8.2 Cylinder storage

Before and after measurement, the ideal way to store the reference gas mixtures for longer periods is by laying the cylinders in a horizontal position well protected against rolling and falling. For safety reasons it is necessary to separate cylinders containing flammable gases from cylinders containing oxidising components.

Mixtures containing condensable components will always require re-homogenisation following transport or storage below minimum temperatures specified by EffecTech. The minimum recommended storage temperature is calculated specifically for each mixture and can be found on the cylinder extract label affixed to the valve of each cylinder before despatch.

Unless you can confidently confirm that exposure below this temperature has not occurred then the mixture must be allowed to equilibrate to ambient laboratory temperature for a minimum period of 24 hours. During this time, it is good practice to roll the cylinder in a horizontal position, where possible, to encourage mixing during equilibration. These directions provided for re-homogenisation of your mixtures should be strictly followed.

8.3 Gas handling during use

Normally the withdrawal of the reference gas from a cylinder is regulated by a pressure regulator and / or a flow controller (needle valve, mass flow controller or capillary device). Due to reversible adiabatic expansion of the gas on withdrawal from the cylinder, cooling (Joule-Thomson cooling) of the sampled gas mixture will occur. Joule-Thomson cooling occurs particularly with mixtures containing condensable components and can result in retrograde condensation of the sampled gas.

It is important that the pressure drop through pressure regulators and across flow controllers is minimised for mixtures where this is an issue and that withdrawal is done at an appropriate ambient temperature.

The minimum recommended usage temperature based on the fill pressure is calculated specifically for each mixture and can be found on the cylinder extract label affixed to the valve of each cylinder before despatch. The mixture must not be used at ambient temperatures below this recommendation. These directions provided for usage of your mixtures should be strictly followed.

8.4 Sample integrity and handling

It is important to use the most appropriate pressure and flow reduction equipment for a particular requirement. In general terms, this means the equipment needs to be fit for purpose. The equipment needs to regulate to the required pressure and flow and be constructed of the most appropriate material for the gas used.
In many cases the integrity of high quality and expensive calibration gas has been compromised through the use of poor quality or inappropriate pressure and flow reduction equipment.

In this PT scheme special consideration shall be given to the sampling system integrity and materials of construction for the sulphur component mixture. High quality stainless steel regulators and sampling lines are preferable. This will preserve the integrity of the reactive components in this mixture before injection into your instrument.

Adequate leak tightness of the sampling system should be established when sampling your gas mixtures. The mixture should be purged through the pressure reduction and sample conditioning system for an appropriate time such that the sample being injected onto your instrument is truly representative of the contents of the cylinder.

If in doubt, participants should follow the advice given in the International Standard ISO 16664 [6].

### 8.5 Measurement methods

Laboratories shall, wherever possible, use their default method for sampling and analysing the reference mixtures.

The calibration method and number of replicates used for measurement shall be the same as for routinely analysed samples.

### 8.6 Submission of results

Each laboratory is required to submit their results by completing the spreadsheet provided with these instructions. Data reported in an alternative format will not be processed. Please do not make any modifications to the format of the spreadsheet provided as this will prohibit automatic processing. If any participant wishes to comment on this spreadsheet or wishes a revision or update thereof then please send an email request to the [scheme coordinator](mailto:coordinator@effectech.co.uk).

All results should be submitted in the approved / supplied spreadsheet before the deadline date and by email to

**GGLNG Scheme Coordinator**

EffecTech
Dove House
Dove Fields
Uttoxeter ST14 8HU
United Kingdom

T: +44 (0)1889 569229
Direct: +44 (0)1889 598716
F: +44 (0)1889 569220
E: coordinator@effectech.co.uk
Each laboratory is requested to submit

- the result (with up to ten repeat measurements)
- the precision / repeatability (expressed as a standard deviation - calculated automatically)
- the expanded uncertainty associated with the result using a coverage factor \( k=2 \) (see section 8.7)
- physical properties (for the LNG composition only) calculated from your measured composition by the method used in your laboratory on a routine basis
- the method and type of calibration gas used for your measurement (included in the Comments section of the form)

Following receipt of each participant’s results by EffecTech they will be acknowledged by the scheme coordinator. The submitted results will then be inspected by a designated authority. Any typographical errors, miscalculations or other gross errors in reporting shall not be referred back to the participant for review. If such errors in reported results are observed then EffecTech will make an explicit note of this in the annual report.

All reported data, comments and other correspondence will be kept strictly confidential by the scheme provider. In the scheme quarterly reports (see section 10.1) results and selected comments will be reproduced using the laboratory’s designated code only.

### 8.7 Reporting of measurement uncertainty

Wherever possible each laboratory should report an estimate of the measurement uncertainty associated with each reported measurement result.


A more chemistry related document on the estimation of uncertainty is published by Eurachem and CITAC. This guide CG4 “Quantifying Uncertainty in Analytical Measurements” can be downloaded from [www.eurachem.org](http://www.eurachem.org).

These documents can also be obtained from the scheme coordinator on request.

### 8.8 Collusion with other participants

In the interests of fairness and accuracy, participants are instructed not to collude or share data with other participants on the results which they have obtained from measurements of any gas mixture.

If you are aware of others that participate in the scheme and wish to share measurement results information with them then, subject to permission from local management, do not do so until the final report has been published by EffecTech.
9. Evaluation of performance

9.1 Rating per component and per mixture type

*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

\[ z = \frac{x_{\text{meas}} - x_{\text{ref}}}{\sigma} \]  \hspace{1cm} (1)

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

\[ \sigma = \frac{S_{PT}}{100} \cdot x_{\text{ref}} \]  \hspace{1cm} (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 are given in the tables below.

**Table 6: Standard deviation for performance assessment (LNG composition)**

<table>
<thead>
<tr>
<th>component</th>
<th>( S_{PT} ) (% relative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrogen</td>
<td>1.1 %</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td></td>
</tr>
<tr>
<td>(0.1 to 1 %mol/mol)</td>
<td>2.2 %</td>
</tr>
<tr>
<td>(1 to 8 % mol/mol)</td>
<td>1.1 %</td>
</tr>
<tr>
<td>methane</td>
<td>0.1 %</td>
</tr>
<tr>
<td>ethane</td>
<td>1.1 %</td>
</tr>
<tr>
<td>propane</td>
<td>1.1 %</td>
</tr>
<tr>
<td>iso-butane</td>
<td>2.2 %</td>
</tr>
<tr>
<td>n-butane</td>
<td>2.2 %</td>
</tr>
<tr>
<td>iso-pentane</td>
<td>2.2 %</td>
</tr>
<tr>
<td>n-pentane</td>
<td>2.2 %</td>
</tr>
<tr>
<td>n-hexane(^\d)</td>
<td>0.0022 %mol/mol</td>
</tr>
</tbody>
</table>

\(^\d\) The standard deviation for performance assessment for n-hexane is given in absolute terms (%mol/mol). Hence \( \sigma = S_{PT} \) for this component.
Table 7: Standard deviation for performance assessment (propane composition)

<table>
<thead>
<tr>
<th>component</th>
<th>$S_{PT}$ (% relative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrogen</td>
<td>3.0 %</td>
</tr>
<tr>
<td>ethane</td>
<td>2.0 %</td>
</tr>
<tr>
<td>propane</td>
<td>0.1 %</td>
</tr>
<tr>
<td>iso-butane</td>
<td>2.5 %</td>
</tr>
<tr>
<td>n-butane</td>
<td>2.5 %</td>
</tr>
<tr>
<td>iso-pentane</td>
<td>3.0 %</td>
</tr>
<tr>
<td>n-pentane</td>
<td>3.0 %</td>
</tr>
</tbody>
</table>

Table 8: Standard deviation for performance assessment (mixed refrigerant)

<table>
<thead>
<tr>
<th>component</th>
<th>$S_{PT}$ (% relative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrogen</td>
<td>1.5 %</td>
</tr>
<tr>
<td>methane</td>
<td>1.0 %</td>
</tr>
<tr>
<td>ethane</td>
<td>1.0 %</td>
</tr>
<tr>
<td>propane</td>
<td>1.5 %</td>
</tr>
</tbody>
</table>

Table 9: Standard deviation for performance assessment (sulphur component mixture)

<table>
<thead>
<tr>
<th>component</th>
<th>$S_{PT}$ (% relative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen sulphide</td>
<td>5.0 %</td>
</tr>
<tr>
<td>carbonyl sulphide</td>
<td>4.0 %</td>
</tr>
<tr>
<td>ethyl mercaptan</td>
<td>4.0 %</td>
</tr>
<tr>
<td>methyl mercaptan</td>
<td>4.0 %</td>
</tr>
<tr>
<td>dimethyl sulphide</td>
<td>4.0 %</td>
</tr>
<tr>
<td>total sulphur</td>
<td>5.0 %</td>
</tr>
</tbody>
</table>

The qualification of the z-scores is given in table 10 below

Table 10: Relationship between z-score and quality of result

<table>
<thead>
<tr>
<th>z-score</th>
<th>quality of result</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>z</td>
</tr>
<tr>
<td>$2 &lt;</td>
<td>z</td>
</tr>
<tr>
<td>$</td>
<td>z</td>
</tr>
</tbody>
</table>
Figure 1: z-scores

From the example shown in figure 1, it is clear that laboratories P01, P02, P03, P05, P06, P07, P08, P09, P11 and P12 report a satisfactory result, laboratory P10 a questionable result and laboratories P13 and 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. Laboratories are encouraged to report such estimates in accordance with accepted practices (see section 8.7).

The $E_n$ number is calculated with the following general formula

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

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 11 below.

<table>
<thead>
<tr>
<th>$z$-score</th>
<th>quality of result</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>E_n</td>
</tr>
<tr>
<td>$</td>
<td>E_n</td>
</tr>
</tbody>
</table>

Table 11: Relationship between $E_n$-number and quality of result
Reference  \[ x_{ref} \]  \[ U(x_{ref}) \]  \( k=2 \)  \( S_{PT} \)  \( \%\text{mol/mol} \)  \( \%\text{mol/mol} \)

<table>
<thead>
<tr>
<th>participant id</th>
<th>value ( %\text{mol/mol} )</th>
<th>U ( (k=2) ) ( %\text{mol/mol} )</th>
<th>relative difference</th>
<th>( z )-score</th>
<th>( E_n )-number</th>
</tr>
</thead>
<tbody>
<tr>
<td>P01</td>
<td>0.998</td>
<td>-0.16%</td>
<td>-0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P02</td>
<td>0.996</td>
<td>0.012</td>
<td>-0.36%</td>
<td>-0.36</td>
<td>-0.31</td>
</tr>
<tr>
<td>P03</td>
<td>1.001</td>
<td>0.016</td>
<td>0.14%</td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>P04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P05</td>
<td>0.999</td>
<td>0.006</td>
<td>-0.06%</td>
<td>-0.09</td>
<td>-0.13</td>
</tr>
<tr>
<td>P06</td>
<td>1.006</td>
<td></td>
<td>0.64%</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>P07</td>
<td>0.989</td>
<td>0.063</td>
<td>-1.06%</td>
<td>-1.00</td>
<td>-0.17</td>
</tr>
<tr>
<td>P08</td>
<td>0.989</td>
<td>0.009</td>
<td>-1.06%</td>
<td>-1.00</td>
<td>-1.07</td>
</tr>
<tr>
<td>P09</td>
<td>0.986</td>
<td></td>
<td>-1.36%</td>
<td>-1.27</td>
<td></td>
</tr>
<tr>
<td>P10</td>
<td>1.026</td>
<td></td>
<td>2.64%</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>P11</td>
<td>1.010</td>
<td>0.080</td>
<td>1.04%</td>
<td>0.91</td>
<td>0.12</td>
</tr>
<tr>
<td>P12</td>
<td>1.001</td>
<td>0.017</td>
<td>0.14%</td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>P13</td>
<td>1.050</td>
<td>0.034</td>
<td>5.04%</td>
<td>4.55</td>
<td>1.45</td>
</tr>
</tbody>
</table>

**Figure 2:** \( E_n \) numbers

From the same dataset as used for figure 1, the \( E_n \) numbers are shown in the far right hand column of figure 2. The \( E_n \) numbers of laboratories P08 and P13 are unsatisfactory. However, the performance of all other laboratories is satisfactory by this measure (for those reporting uncertainties).

### 9.2 Overall rating

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 12 below

**Table 12: Relationship between \( z \)-score and quality of result**

<table>
<thead>
<tr>
<th>( z )-score</th>
<th>score per component</th>
</tr>
</thead>
<tbody>
<tr>
<td>(</td>
<td>z</td>
</tr>
<tr>
<td>( 2 &lt;</td>
<td>z</td>
</tr>
<tr>
<td>( 2.5 &lt;</td>
<td>z</td>
</tr>
<tr>
<td>(</td>
<td>z</td>
</tr>
</tbody>
</table>

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.
10. Reports

10.1 Confidentiality

In all reports bound for general distribution, the participants are identified by means of a laboratory code (P01, P02,...,Pxx) which is assigned by EffecTech. Hence, the details of all participating laboratories, their results and their performance assessment are anonymous.

The laboratory code assigned to each participant will be kept strictly confidential and is known only to the scheme coordinator and technical authority within EffecTech.

In addition, on the day of publication of the quarterly report (see section 10.2 below), the registered contact at each laboratory shall also be informed of their laboratory code.

Only the Certificate of Participation (see section 10.3 below) includes details of the laboratory name, address, results and performance in the current round of the scheme. This is ONLY submitted to the registered contact at the participant laboratory.

10.2 Quarterly Report

Following each round of the scheme a report will be issued containing at least the following information:

- calibration and reference value assignment by EffecTech
- individual results and expanded uncertainties reported by each participant
- ratings of each laboratory’s performance by means of z-scores, $E_r$ numbers and overall score
- graphical displays showing participants’ results against reference values and the range of a satisfactory result
- general observations shall be made based upon the participants’ results including advice on the interpretation and comments or recommendations based on the outcome of the round.

10.3 Certificate of Participation

Following each round an individual Certificates of Participation shall be issued to the registered contact at the participant laboratory. This can be used, for example, as a proof of competence during inspections and audits by interested third parties or accreditation bodies.

The Certificate of Participation shall include the name of the scheme and round number, the participant’s name and address and a table of each gas mixture type each containing

- reference values and their uncertainties assigned by EffecTech
- results reported by the individual laboratory for which the certificate is created
- $z$-scores, $E_r$-numbers and overall scores for the laboratory
- statement of authenticity issued, dated and signed by the scheme coordinator and technical authority
10.4 Certificate of Achievement

Participants achieving an overall score of 100% (full conformity) for any mixture type in any of the rounds shall be awarded a Certificate of Achievement.

Individual Certificates of Achievement shall be issued to the registered contact at the participant laboratory.

The Certificate of Achievement shall include
- the name of the scheme and round number
- the participant’s name and address
- the mixture type indicating an overall score of 100% for their measurement
- statement of authenticity issued, dated and signed by the scheme coordinator and technical authority

11. Appeals

Following issue of a report or certificate, participants may appeal their results or scores should they consider the assessment presented is unfair, incorrect or misleading.

All appeals should be reported directly to the scheme coordinator in the first instance who will acknowledge and then consider the appeal. He may, if necessary, refer the appeal to the technical authority for a final decision to be agreed.

Following a successful appeal the laboratory shall be informed of the outcome in the first instance. A new revision of the quarterly report shall be issued to all participants. In addition, dependent upon the consequences of the appeal, it may be necessary to issue one or more Certificates of Participation.