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1 Introduction

Since 2003, the Dutch Metrology Institute, VSL, organises the PT Hydrocarbons (formerly called the Liquefied Natural Gas Correlation Scheme). These proficiency testing schemes aim to provide laboratories working in the field of liquefied natural gas (LNG) and natural gas. Participation is open to any laboratory providing services in any of the fields.

There are four rounds scheduled a year. The mixtures provided include LNG composition, propane composition, Mixed Refrigerant, and Sulphur in methane.

The mixtures are checked on homogeneity and stability, and reference values are assigned prior to shipment. The mixtures reside after a round at the participant's, so that they remain available as a quality control material (QCM). The preparation and shipment of the mixtures is carried out by Scott Specialty Gases (Scott) in the Netherlands.

2 Points of contact

The schemes are organised by VSL. The contact details of the scheme coordinator and the responsible project manager are given below:

Scheme coordinator:

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The gas and liquid mixtures are prepared by Scott Specialty Gases, that operates as subcontractor and partner in the scheme:

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3 Accreditation status

Like in any laboratory, the quality of the services provided is first priority. For that reason, VSL holds an accreditation for proficiency testing under RvA registration R006, and for calibrations under RvA registration K999. The accreditation is carried out by the Dutch Council for Accreditation RvA in the Netherlands, and is based on the criteria of ILAC-G13 (proficiency testing) and ISO/IEC 17025 (calibration laboratory) respectively.

Scott holds an accreditation as calibration laboratory (RvA registration K064). In addition to this accreditation, VSL audits the services provided by Scott in the schemes biennial on the basis of the relevant criteria of ISO/IEC 17025 and ILAC-G13.

4 Mixtures

The LNGCS comprises four types of mixtures (table 1).

Table 1: Gas mixtures used in the LNGCS

Identification	Description	Cylinder volume (dm^3)	Cylinder Outlet	Nominal pressure (bar)
Mixture I	LNG Composition	5	DIN 1	20
Mixture II	Propane composition	1	DIN 1	5
Mixture III	Mixed refrigerant	1	DIN 1	20
Mixture IV	Sulphur in methane	5	DIN 5	50

4.1 Mixture I – LNG composition

Table 2: Composition mixture I

Component	Range (10^{-2} mol/mol)
Ethane	3 – 9
Propane	2 – 5
i-Butane	0.1 – 1
n-Butane	0.1 – 1
i-Pentane	0.1 – 0.5
n-Pentane	0.1 – 0.5
n-Hexane	0.01 – 0.3
Nitrogen	1 – 8
Carbon dioxide	0.1 – 8
Methane	balance

In rounds with an odd number, the actual mixture is low in nitrogen and carbon dioxide (type Ia) to resemble LNG, whereas in rounds with an even number, the mixture is high in nitrogen and carbon dioxide to resemble feed gas.

4.2 Mixture II – Propane composition

Table 3: Composition mixture II

Component	Range (10^{-2} mol/mol)
Ethane	0.25 – 3
i-Butane	0.03 – 1
n-Butane	0.03 – 1
i-Pentane	0.02 – 0.08
n-Pentane	0.02 – 0.08
Nitrogen	0.1 – 3
Propane	balance

4.3 Mixture III – Mixed refrigerant

Table 4: Composition mixture III

Component	Range (10^{-2} mol/mol)
Ethane	20 – 35
Propane	5 – 15
Nitrogen	4 – 16
Methane	balance

4.4 Mixture IV – Sulphur in methane

Table 5: Composition mixture IV

Component	Range (µmol/mol)
Hydrogen sulphide	10 – 40
Methyl mercaptane	10 – 40
Ethyl mercaptane	10 – 40
Carbonyl sulphide	10 – 40
Dimethyl sulphide	10 – 40
Methane	balance

5 Homogeneity, stability, and reference values

5.1 Homogeneity assessment

The homogeneity of every batch of mixtures is assessed twice: once by Scott on the complete batch of cylinders, and a second time on a randomly selected subset by VSL. The minimum size of the subset is 3 cylinders. Approval of the batch homogeneity is done primarily on VSL's results. The results of the assessment by Scott are included in the approval process.

The homogeneity test results in a standard deviation that characterises the dispersion of the component amount-of-substance fractions due to batch inhomogeneity, known as "between-bottle standard deviation". This between-bottle standard deviation should be equal or less than a specified upper limit in order to accept the batch.

5.2 Stability of the mixtures

The stability of the mixtures is warranted for a period of at least 6 months. Most of the mixtures will be stable (within the stated uncertainty) for a longer period, but this period has not been determined and therefore is not stated.

In conjunction with reference mixtures with established stability, such as Primary Reference Materials, the mixtures can be used as Quality Control Material after the round in the schemes. Cylinders that are no longer used can be returned directly to Scott, if desired.

5.3 Reference values

In principle, for the four types of mixtures, for each component a reference value and its uncertainty is established by VSL. The results of the analyses for the homogeneity test described in 5.1 are used for the calculation of these values. If reference values are deemed unfeasible, the consensus values will be used instead for rating the laboratories' performance.

The equipment used for homogeneity testing is calibrated with Primary Standard Mixtures, VSL's own primary calibrants, to ensure that the values assigned to the mixtures foreseen to be used in the schemes are metrologically traceable to international standards, and thereby, ultimately to the SI (International System of Units). The approach used is the same as used in the certification of third-party gas mixtures.

The calibration is either carried out by means of a multipoint regression conforming ISO 6143:2001 or through bracketing. In all cases, the matrix of the calibrants closely resembles that of the mixtures to be measured.

5.4 Consensus values

For information purposes, consensus values of the participants' results are calculated and reported. The calculation of the consensus values is carried out in accordance with the classical statistics of ISO 5725-2:1994. Outliers are removed by calculating a Z-score (denoted as Z_{raw}) based on the full dataset. All data that does not comply with the requirement that

$$|Z_{raw}| \leq 3$$

is regarded as outlier. The Z_{raw} is based on a robust estimate of the mean (i.e., the median), and standard deviation (1.4826 * MAD; MAD = median of the absolute deviation).

In those cases where reference values are unavailable, the consensus values will be used for rating the performance of the laboratories.

6 Evaluation of performance

6.1 Rating per component and per mixture type

The evaluation of performance is carried out by means of a Z-score, which gives the relative departure of the participants' results from the reference value. The standard deviation used for calculating the Z-scores has been fixed for all components. The Z-score is calculated with the following formula

$$Z_i = \frac{y_i - y_{ref}}{s_{PT}} \quad (1)$$

where s_{PT} is the standard deviation used for performance rating, y_i the result of laboratory *i* and y_{ref} the reference value for the particular component.

The standard deviations for performance rating are as follows (given relative to the reference value).

Table 6: Performance rating for mixture I (LNG composition)

Component	s_{PT}
Ethane	1.1%
Propane	1.1%
i-Butane	2.2%
n-Butane	2.2%
i-Pentane	2.2%
n-Pentane	2.2%
Hexane[1]	(0.22/x)
Nitrogen	1.1%
Carbon dioxide[2]	2.2%
Methane	0.1%

Table 7: Performance rating for mixture II (Propane composition)

Component	s_{PT}
Ethane	2.0%
i-Butane	2.5%
n-Butane	2.5%
i-Pentane	3.0%
n-Pentane	3.0%
Nitrogen	3.0%
Propane	0.1%

Table 8: Performance rating for mixture III (Mixed Refrigerant)

Component	s_{PT}
Ethane	1.0%
Propane	1.5%
Nitrogen	1.5%
Methane	1.0%

[1] *x denotes the amount-of-substance fraction n-hexane in 10^{-6} mol/mol*

[2] *For amount-of-substance fractions of carbon dioxide exceeding 0.01 mol/mol, s_{PT} = 1.1%*

Table 9: Performance rating for mixture IV (Sulphur in methane)

Component	s_{PT}
Hydrogen sulphide	5.0%
Methyl mercaptane	4.0%
Ethyl mercaptane	4.0%
Carbonyl sulphide	4.0%
Dimethyl sulphide	4.0%
Total sulphur	5.0%

The qualification of the Z-scores is as follows:

$\lvert Z\rvert \leq 2$	Satisfactory result
$2 < \lvert Z\rvert < 3$	uestionable result
$\lvert Z\rvert \geq 3$	Unsatisfactory result

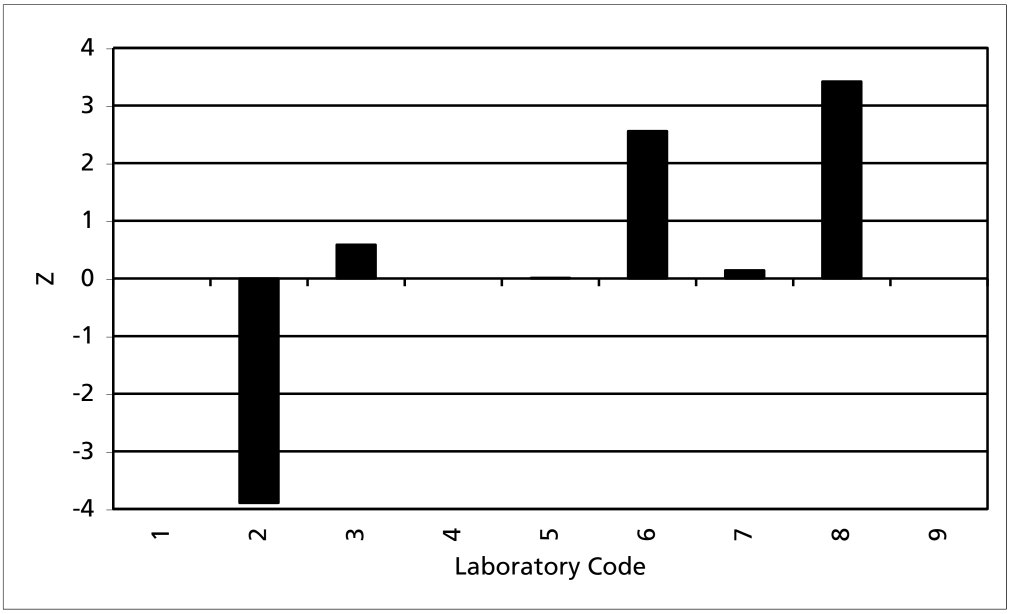

Figure 1: Z-scores for nitrogen in LNG

From the example shown in figure 1, it is clear that laboratories 3, 5, and 7 report a satisfactory result, laboratory 6 a questionable result, and laboratories 2, and 8 an unsatisfactory result.

Additionally, an E_n-score is calculated which assesses the reported result in connection with the stated uncertainty (u_{stat}). It is defined as:

$$E_n = \frac{y_i - y_{ref}}{2\sqrt{u_{ref}^2 + u_{stat}^2}} \qquad (2)$$

The qualification of the E_n-scores is as follows:

$\lvert E_n \rvert \leq 1$	Satisfactory result
$\lvert E_n \rvert > 1$	Unsatisfactory result

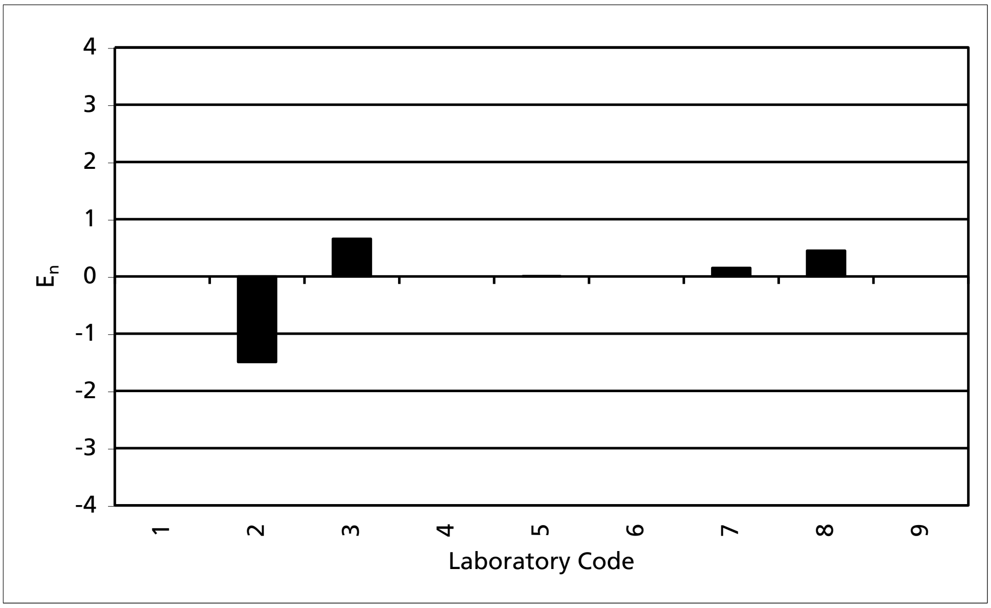

Figure 2: E_n–scores for nitrogen in LNG

From the same dataset as used for figure 1, the E_n–scores are shown in figure 2. For laboratory 6, no E_n score can be calculated because no uncertainty is stated with the result. The E_n value of laboratory 5 is 0.00, and together with laboratories 3, 7, and 8, it forms the group of results with satisfactory performance. Laboratory 2 is in this example the only laboratory with an unsatisfactory result.

6.2 Overall rating

Participants, funded by Shell Global Solutions, who are participating in four rounds and achieving a 100% score will be awarded. There is one award per mixture type.

The overall rating will be expressed as percentage of the maximum possible score. The scoring scheme is as follows. For each parameter in each round, points can be earned according to the following scheme:

$\lvert Z \rvert \leq 2$	1 point
$2 < \lvert Z \rvert \leq 2.5$	0.50 point
$2.5 < \lvert Z \rvert \leq 3$	0.25 point
$\lvert Z \rvert > 3$	no points

Participants, participating in four rounds and achieving a 100% score will be awarded. There is one award per mixture type.

7 Reports

7.1 Quarterly reports

For each round of the PT a report is written containing the following information:

- brief description of the PT results
- results of the homogeneity test
- reference values
- individual results and expanded uncertainties reported by the participants
- consensus values
- rating of the laboratory performance by means of *Z*-scores and E_n-scores.

In the report, the participants are identified by means of a laboratory code, which is assigned by VSL. The assigned code is kept confidential.

7.2 Annual report

Annually a summary report is prepared covering the results of all four rounds.

7.3 Executive summary

An executive summary is prepared from the annual report, highlighting the most important developments in the scheme and the major achievements.

8 Schedule

For schedule details see the VSL ILC schedule scheme.

Participants will be responsible for tracking down and collecting the samples once they have been notified that they have been shipped. If participants are not notified by the courier of the sample arrival at destination within a week, they have to contact us for further information regarding delivery of their samples. In this way, we can take actions and trace back the status of the shipment.

VSL undertakes every reasonable effort to prevent delays in the dispatch of the gas mixtures.

Laboratories are kindly requested to report their results well before the deadline. Results received after the deadline will not be processed and included in the report. In case of foreseeable delays, participants are kindly requested to report such delays to the scheme coordinator with an indication whether results are to be expected and within what time frame. The new date communicated cannot be regarded as a new deadline, unless the scheme coordinator submits a new deadline for reporting results.

9 Instructions to participants

9.1 Sample treatment

Laboratories shall treat the gas mixtures in the same manner as the majority of routinely tested samples.

9.2 Measurement methods

Laboratories shall use to the extent possible their default method for analysing the mixtures. The number of replicates, calibration regime etc., shall be the same as for routinely analysed samples. The laboratories are requested to submit

- the result (with a minimum of two values)
- the (repeatability) standard deviation
- the number of replicates on which the (repeatability) standard deviation is based
- the expanded uncertainty associated with the result, including the coverage factor used.
- The method and type of reference materials used for analysis.

9.3 Submission of results

Laboratories are required to submit their results through the provided spreadsheet. Data reported in deviating formats will not be processed. It is not allowed to make any modifications in the spreadsheet provided, as it prohibits automatic processing.

All reported data, remarks, and other correspondence will be kept confidential. In the scheme reports (see chapter 7.1), results, selected comments, etc. will be reproduced in coded form.

9.4 Specific reporting requirements

The report of the participant should not only contain the measurement results, but also an estimate of the measurement uncertainty. Document EA 4/02 "Expression of the Uncertainty of Measurement in Calibration" describes the preferred method of uncertainty estimation. Following this document a table of the most important sources for uncertainty together with their calculated relative contribution to the total combined uncertainty should be presented.

Document EA-4/02 can be downloaded from the web site of the European accreditation organisation (www.european-accreditation.org).

A more chemistry related document on uncertainty calculation is published by Eurachem and CITAC. This guide CG4 "Quantifying Uncertainty in Analytical Measurements" can be downloaded from www.eurachem.org. These documents can also be obtained through the responsible project manager (see clause 2).

9.5 Cylinder storage

The best way to store the PT gas mixtures for a longer period 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 may require to be re-homogenized if stored for a longer period of time and if exposure to temperatures below the condensation point cannot be excluded. This could be done by bringing up the cylinders to ambient temperature and rolling them in a horizontal position for an appropriate period of time, which may depend on the matrix gas and the components. Apart from transport conditions it is not very obvious that low temperature situations will occur during the PT scheme. Scott will supply a phase diagram for the participant to be able to judge temperature effects.

It is important to temperature stabilize the PT cylinder and the appropriate calibration gases at least 24 hours before analyses.

9.6 Gas handling

Normally the withdrawal of gas from a cylinder is regulated by a pressure reducer and / or flow controller (needle valve, mass flow controller, capillary, etc,). Due to the reversible adiabatic expansion of the gas when withdrawing the gas from the cylinder, cooling of the gas in the cylinder will occur. Furthermore Joule Thomson cooling and / or heating will change the temperature of the transported gas itself. Especially with mixtures containing condensable components, condensation may occur due to these temperature effects. It is important that the pressure drop across flow controllers is minimized. Flow characteristics of flow controllers are normally specified by the manufacturer and give sufficient information to judge whether the requested flow can be controlled by the chosen flow controllers. In calculating the pressure drop, tube sizing (inside diameter and length) should also be considered.

9.7 Purging procedure

The transfer line integrity including the leak tightness and cleanliness of all the components (pressure regulator, valves, transfer line, connections, etc.) must be guaranteed. In order to guarantee this, an appropriate purging procedure shall be used. There are several simple methods, which can be used to purge the transfer system; the most effective method uses a vacuum pump. In any case, it is important to open the cylinder valve not fully and only for a very short time (i.e. 0.5 seconds), both for safety reasons and in order to avoid back contamination.

- If a vacuum pump is available then the purging procedure should be the following: Sequentially evacuate and pressurise the entire transfer line with the gas mixture to be used. This procedure should be repeated several times, typically, three cycles would be sufficient. Make sure that pressure regulators are suited for evacuation and that the purging cycle starts with evacuation.

- If a vacuum pump is not available, the following procedure can be used:
  Sequentially pressurise and vent the transfer system with the gas mixture to be used. This method is not as effective as the vacuum method, hence more cycles would be needed, and typically five to eight cycles are required. The number of cycles depends on the concentration of the measurand; more steps will be necessary for low concentration mixtures.

For both methods, the insertion of a stop valve after the pressure regulator is recommended for safety reasons.

9.8 Material integrity and inertness

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.

For this PT scheme mixtures special attention shall be given to the materials of construction for mixture IV. The low H_2S levels require high purity materials and the reducer is preferably from a stainless steel type. Sample lines are also preferable stainless steel.