

PROTOCOL PTS NATURAL GAS

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1 Introduction

Since 1996, VSL (Dutch Metrology Institute) organises the Proficiency Testing Scheme Natural Gas. This proficiency testing scheme aims to provide laboratories working in the field of natural gas with a platform to compare their results. Participation is open to any laboratory providing services in this field.

There are two rounds a year.

The gas mixtures are checked on homogeneity and stability, and reference values are assigned prior to shipment.

The preparation and shipment of the mixtures is carried out by Scott Specialty Gases (Scott) in the Netherlands.

2 Points of contact

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

Scheme coordinator:

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Responsible project manager:

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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 the present proficiency testing scheme 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 scheme annually on the basis of the relevant criteria of ISO/IEC 17025 and ILAC-G13.

4 Gas mixture

In each round, a 5 L gas cylinder with is shipped with approximately 20 bars of a synthetic natural gas. The table below gives ranges for the composition, per parameter. On special request, additional components (e.g. He) can be added.

Table 1 Gas composition

Component	Range (% mol/mol)	Component	Range (% mol/mol)
CH ₄	65 - 99	n-C ₄ H ₁₀	0.03 - 0.7
C ₂ H ₆	0.5 - 11	CO ₂	0.2 - 20
C ₃ H ₈	0.1 - 5	N ₂	0.2 - 20
iso-C ₄ H ₁₀	0.03 - 0.7	Other components	optional

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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 6 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 Natural Gas Proficiency Testing Scheme. Cylinders that are no longer used can be returned to VSL, if desired.

5.3 Reference values

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.

The equipment used for homogeneity testing is calibrated with Primary Standard gas Mixtures, VSL's own primary calibrants, to ensure that the values assigned to the mixtures foreseen to be used in the scheme 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.

6 Evaluation of performance

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

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

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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, relative to the reference value, 1.0% for methane and ethane and 1.5% for the other components.

The qualification of the Z-scores is as follows:

$ Z < 2$	Satisfactory result
$2 < Z < 3$	Questionable result
$ Z > 3$	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:

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

where $k=2$, the coverage factor.

The qualification of the E_n -scores is as follows:

$ E_n < 1$	Satisfactory result
$ E_n > 1$	Unsatisfactory result

E_n -scores are given for information purposes only.

7 Submission of results

7.1 General

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 8), results, selected comments, etc. will be reproduced in coded form.

7.2 Specific 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).

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8 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.

9 Schedule

For schedule details see the VSL ILC schedule scheme.

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.

10 Options

At the beginning of each round, a participant may request to have the mixture certified. After completion of the round, a certificate is issued and the mixture can be used as a Certified Reference Material.

Furthermore, the participant may choose not to buy the cylinder. In that case the cylinder should be returned to VSL and only the cylinder rent will be charged for.

11 Instructions to participants

11.1 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.

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

11.2 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.

11.3 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.

11.4 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.