

PROTOCOL RGCS

Table of contents	Page
1 Introduction	2
2 Points of contact	2
3 Accreditation status	3
4 Mixtures.....	3
4.1 Mixture V – Refinery gas	4
4.2 Mixture VI – Stack gas	4
4.3 Mixture VII – Liquid hydrocarbon mixtures.....	5
5 Homogeneity, stability, and reference values.....	5
5.1 Homogeneity assessment.....	5
5.2 Stability of the mixtures	6
5.3 Reference values.....	6
5.4 Consensus values.....	6
6 Evaluation of performance	7
6.1 Rating per component and per mixture type	7
6.2 Overall rating	8
7 Reports.....	9
7.1 Quarterly reports	9
7.2 Annual report	9
7.3 Executive summary	9
8 Schedule	9
9 Instructions to participants.....	10
9.1 Sample treatment.....	10
9.2 Measurement methods	10
9.3 Submission of results	10
9.4 Specific reporting requirements	10
9.5 Cylinder storage.....	11
9.6 Gas handling	11
9.7 Liquid handling.....	11
9.8 Purging procedure.....	13
9.9 Material integrity and inertness	13

VSL protocol:	VSL-PT-SR/Protocol/010
Application date:	08/05/2009
Version:	00
Page:	2 of 13

PROTOCOL RGCS

1 Introduction

Since 2006, the Dutch Metrology Institute VSL B.V. organises the Refinery Gas Correlation Scheme (formerly part of the Shell Gas Correlation Scheme). This proficiency testing scheme aims to provide laboratories working in the field of refineries with a platform to compare their results. Participation is open to any laboratory providing services in this field.

There are four rounds scheduled a year. In the rounds with odd numbers refinery gas and liquid butane are offered, whereas with even numbers stack gas and liquid propane are offered.

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:

Mrs. Yanaika Quist
VSL B.V.
P.O. Box 654, 2600 AR Delft (mail address)
Thijsseweg 11, 2629 JA Delft (visiting address)
the Netherlands
phone +31 15 269 1500
direct line +31 15 269 1570
facsimile +31 15 261 2971
E-mail YQuist@VSL.nl

Responsible project manager:

Mrs. Annarita Baldan
VSL B.V.
P.O. Box 654, 2600 AR Delft (mail address)
Thijsseweg 11, 2629 JA Delft (visiting address)
the Netherlands
phone +31 15 269 1500
direct line +31 15 269 1728
facsimile +31 15 261 2971
E-mail ABaldan@VSL.nl

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

PROTOCOL RGCS

Mr. J. de Jong
 Scott Specialty Gases Nederland B.V.
 Takkebijsters 48
 4817 BL Breda
 the Netherlands
 phone +31 76 5711828
 facsimile +31 76 5713267
 E-mail JdeJong@Scottgas.com

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

4 Mixtures

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

Table 1: Mixtures used in the RGCS

Identification	Description	Cylinder type (dm ³)	Nominal pressure (bar)
Mixture V	Refinery gas	5	10
Mixture VI	Stack gas	5	150
Mixture VIIa	Propane (liquid)	0.3	35
Mixture VIIb	Butane (liquid)	0.5	14

The net sample mass of propane and butane is 0.15 kg.

PROTOCOL RGCS

4.1 Mixture V – Refinery gas

Table 2: Composition mixture V

Component	Range Mixture Va (10⁻² mol/mol)	Range Mixture Vb (10⁻² mol/mol)
Methane	10 – 12	10 – 12
Ethylene		13 – 15
Ethane	1.5 – 2.5	1.5 – 2.5
Propene		3.5 – 4.5
Propane	0.4 – 0.6	0.4 – 0.6
1,3-Butadiene		0.8 – 1.2
1-Butene		0.4 – 0.6
<i>i</i> -Butene		0.4 – 0.6
Hydrogen	7 – 8	
<i>n</i> -Butane	0.8 – 4.2	0.8 – 4.2
<i>iso</i> -Pentane	0.5 – 1	0.5 – 1
<i>n</i> -Pentane	0.5 – 1	0.5 – 1
<i>n</i> -Hexane	0.01 – 0.1	0.01 – 0.1
Carbon monoxide	1 – 4	1 – 4
Carbon dioxide	0.4 – 0.8	0.4 – 0.8
Hydrogen sulphide	1 – 4	
Nitrogen	balance	balance

4.2 Mixture VI – Stack gas

Table 3: Composition mixture VI

Component	Unit	Range
Carbon monoxide	µmol/mol	10 – 300
Carbon dioxide	10 ⁻² mol/mol	1 – 12
Nitrogen monoxide	µmol/mol	10 – 500
Sulphur dioxide	µmol/mol	50 – 1000
Propane	µmol/mol	3 – 70
Nitrogen		balance

PROTOCOL RGCS

4.3 Mixture VII – Liquid hydrocarbon mixtures

There are two types of liquefied hydrocarbon mixtures: type A (propane) and type B (butane).

Table 4: Composition of mixture VIIa (propane)

Component	Range (10⁻² mol/mol)
Ethane	0.1 – 0.3
Propylene	0.5 – 50
<i>n</i> -Butane	0.1 – 1
<i>i</i> -Butane	0.1 – 3
<i>i</i> -Pentane	0.1 – 1
Propane	Balance

The propane mixture is contained in a piston cylinder.

Table 5: Composition of mixture VIIb

Component	Range (10⁻² mol/mol)
Propane	0.5 – 2.5
Propylene	0.5 – 2.5
<i>n</i> -Butane	0.5 – 10
1,3-Butadiene	0.8 – 1.5
<i>i</i> -Butene	0.5 – 10
1-Butene	0.5 – 10
<i>trans</i> -2-Butene	0.5 – 10
<i>cis</i> -2-Butene	0.5 – 10
<i>i</i> -Pentane	0.4 – 0.8
<i>i</i> -Butane	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.

PROTOCOL RGCS

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 ($1.4826 * MAD$; $MAD = \text{median of the absolute deviation}$).

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

PROTOCOL RGCS

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).

If there are no fixed standard deviations for performance rating, the standard deviations calculated using the approach described in section 5.4 will be used. In those cases, fixed values for s_{PT} will be established on the basis of demonstrated and desired performance.

The qualification of the Z-scores is as follows:

- $|Z| < 2$ Satisfactory result
- $2 < |Z| < 3$ Questionable result
- $|Z| > 3$ Unsatisfactory result

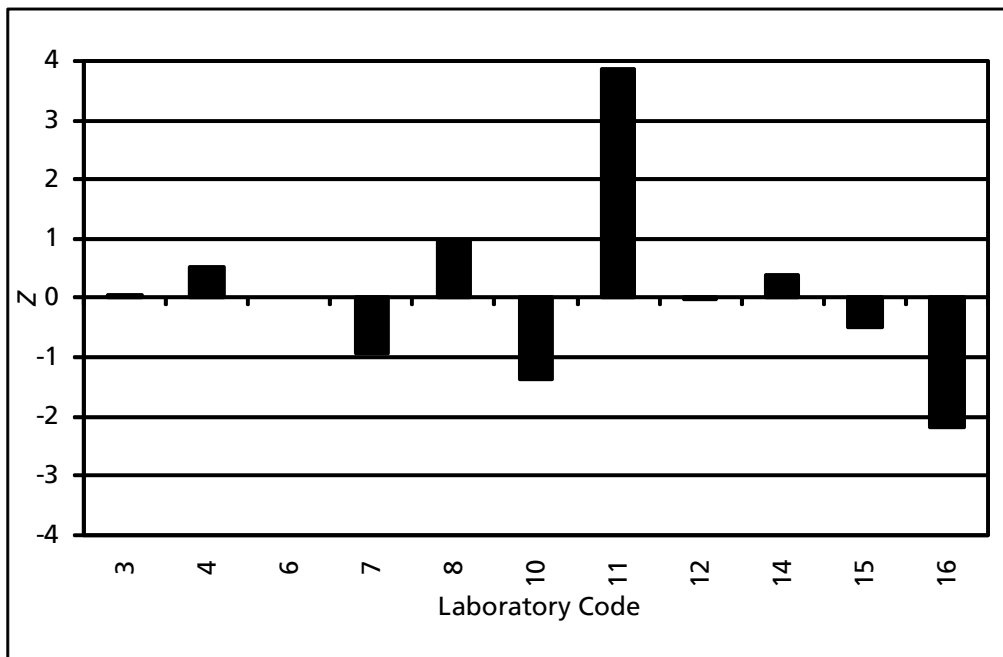


Figure 1: Z-scores for n-butane in refinery gas, mixture Va

PROTOCOL RGCS

$2.5 < |Z| \leq 3$ 0.25 point

$|Z| > 3$ no points

Participants, participating in two 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 both schemes and the major achievements.

8 Schedule

The schedule of the scheme for 2009 is as follows (table 6). Laboratories will receive the mixtures (at minimum) 3 weeks prior to the reporting date for analysis. Reports are due in accordance to the following schedule (table 6).

Table 6: Schedule

Round	Reporting deadline
11	To be determined
12	To be determined
13	To be determined
14	To be determined

VSL protocol:	VSL-PT-SR/Protocol/010
Application date:	08/05/2009
Version:	00
Page:	10 of 13

PROTOCOL RGCS

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
- 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.

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).

VSL protocol:	VSL-PT-SR/Protocol/010
Application date:	08/05/2009
Version:	00
Page:	11 of 13

PROTOCOL RGCS

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 Liquid handling

Constant pressure cylinders are used for liquid propane and butane. Below some brief instruction is given on how to use them.

Mixing Standard

- Mix CPC by holding horizontally at both ends.
- Raise the pre-charge end to a vertical position and hold two to three seconds, then lower to a horizontal position.
- Raise the product end to a vertical position and hold two or three seconds, then lower to a horizontal position.
- Repeat eight to ten times.

PROTOCOL RGCS

Pre-Charge Side

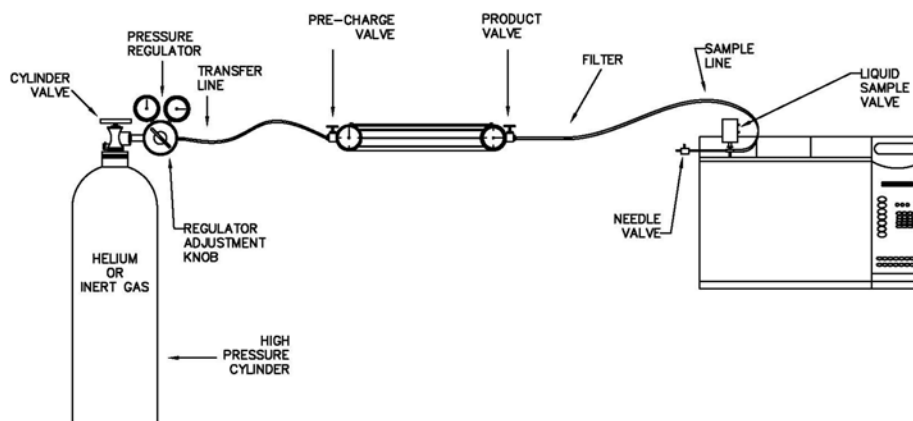
- All CPC's must have constant pressure on the pre-charge valve, ensuring all components remain homogeneous.
- Attach pressure regulator to a high pressure cylinder containing helium or other inert gas.
- Determine the regulator adjustment knob is closed.
- Connect transfer line from regulator to pre-charge valve of CPC.
- Slowly open inert gas cylinder valve.
- Set regulator adjustment knob to sufficient pressure to maintain a single phase; above the vapour pressure of the standard.
- Do not exceed the working pressure of the CPC.
- Purge transfer line.
- Open pre-charge valve on CPC and charge to sufficient pressure.
- Leave pre-charge valve open, maintaining constant pressure during analysis.

Product Side

- Attach filter and sample line to liquid sample valve.
- Verify filter flow direction.
- Connect transfill assembly to product valve of CPC.
- Determine that needle valve on outlet of liquid sample valve is closed.
- Turn on product valve.
- Purge sample line to remove contaminants.
- Inject in manner prescribed by chromatograph manufacturer.

Following sample analysis by GC

- Turn off inert gas cylinder valve, pre-charge valve and product valve on CPC.
- SAFELY RELIEVE PRESURE ON ALL LINES.
- Disconnect sample line from product valve and from pre-charge valve.
- Store, transport or empty contents of CPC according to applicable regulations and company policy.



PROTOCOL RGCS

9.8 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.

9.9 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.