

# Final Report

## Bilateral Comparison EUROMET 1028 Natural gas

Rob M. Wessel<sup>1</sup>, Adriaan M.H. van der Veen<sup>1</sup>, Paul R. Ziel<sup>1</sup>, Valnei S. Cunha<sup>2</sup>, C. Ribeiro<sup>2</sup>, C. Augusto<sup>2</sup>

<sup>1</sup> VSL, Thijssseweg 11, 2629 JA Delft, the Netherlands

<sup>2</sup> Instituto Nacional de Metrologia, Normalização e Qualidade Industrial INMETRO, Laboratório de Análise de Gases, Divisão de Metrologia Química – DQUIM, Av. Nossa Senhora das Graças, 50 - Xerém - cep: 25.250-020, Prédio 4 - Duque de Caxias - RJ - Brasil

### Field

Amount of substance

### Subject

Comparison in the field of natural gas analysis

### Table of contents

Field .....	1
Subject .....	1
Table of contents .....	1
Introduction.....	1
Participants.....	2
Measurement standards.....	2
Measurement protocol .....	2
Measurement equation.....	2
Measurement methods .....	4
Degrees of equivalence .....	4
Results.....	7
Discussion of results .....	8
Conclusions.....	8
References.....	8
Coordinator .....	9
Project reference .....	9
Completion date.....	9
Annex A: Measurement Reports.....	10
Measurement Report from Divisão de Metrologia Química/INMETRO .....	10
Measurement Report from NMi VSL .....	14

### Introduction

The measurement of composition of natural gas mixtures is commonly used for the calculation of its calorific value. Natural gas is a fossil fuel and its economic value per unit of volume or mass is mainly determined by its calorific value. Other aspects that might influence the economic value of natural gas, such as its sulphur content, have not been addressed in this key comparison. In most cases, the calorific value and other thermodynamical properties are calculated from composition data.

At the highest metrological level, natural gas standards are commonly prepared gravimetrically as PSMs (Primary Standard Mixtures). This comparison is using the same design as international key

comparison CCQM-K16[1]. The mixture concerned contains nitrogen, carbon dioxide and the alkanes up to n-hexane.

## Participants

As in CCQM-K16, VSL was the coordinating laboratory. The natural gas PSM was prepared by VSL and analysed. After analysis the mixture was shipped to INMETRO for analyses.

## Measurement standard

Table 1 shows the nominal composition of the mixture used (expressed as amount of substance fractions).

**Table 1: Nominal composition of the mixture**

Component	Amount fractions $x$ ( $10^{-2} \text{ mol mol}^{-1}$ )
Nitrogen	1
Carbon dioxide	1,5
Ethane	7
Propane	2,5
<i>n</i> -Butane	0.6
<i>iso</i> -Butane	0.4
<i>n</i> -Pentane	0.03
<i>iso</i> -Pentane	0.03
<i>n</i> -Hexane	0.03
Methane	Balance

The mixture is prepared gravimetrically and subsequently verified.

The preparation of the mixture has been carried out using the normal procedure for the preparation of gas mixtures [6]. The following gases were used: methane (5.5), ethane (5.0), n-butane (3.5) and iso-butane (3.5) from Scott Specialty Gases, propane (3.5), n-pentane and iso-pentane from Air Liquide, n-hexane from Aldrich, Nitrogen (6.0) from Air Products and carbon dioxide (5.2) from AGA. All gases were directly introduced in the final mixture. The final mixture had a pressure of approximately 7 MPa.

After preparation, the mixture was verified by comparing the mixture with PSMs from the standards maintenance programme. The mixtures have been verified using GC/TCD (nitrogen, carbon dioxide and ethane) and GC/FID (other hydrocarbons).

## Measurement protocol

The laboratories were requested to use their normal procedure for the measurement of the composition of the gas mixture. For participation in this bilateral comparison, it had been requested that participants determine all components in the mixture, and not just a subset.

The participants were also requested to describe their methods of measurement, and the models used for evaluating the measurement uncertainty.

## Measurement equation

The reference values used in this key comparison are based on gravimetry, and the purity analysis of the parent gases/liquids.

In the preparation, the following four groups of uncertainty components have been considered:

1. gravimetric preparation (weighing process) ( $x_{i,grav}$ )
2. purity of the parent gases ( $\Delta x_{i,purity}$ )
3. stability of the gas mixture ( $\Delta x_{i,stab}$ )
4. correction due to partial recovery of a component ( $\Delta x_{i,nr}$ )

The amount of substance fraction  $x_{i,prep}$  of a particular component in mixture  $i$ , as it appears during use of the cylinder, can now be expressed as

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} + \Delta x_{i,stab} + \Delta x_{i,nr}, \quad (1)$$

The value obtained from equation (1) is sometimes referred to as “gravimetric value”. Assuming independence of the terms in equation (1), the expression for the combined standard uncertainty becomes

$$u_{i,prep}^2 = u_{i,grav}^2 + u_{i,purity}^2 + u_{i,stab}^2 + u_{i,nr}^2. \quad (2)$$

For the mixtures used in this key comparison, the following statements hold (for all components involved). First of all, the preparation method has been designed in such a way that

$$\Delta x_{i,nr} = 0, \quad (3)$$

and its standard uncertainty as well. Furthermore, long-term stability study data has shown that

$$\Delta x_{i,stab} = 0, \quad (4)$$

and its standard uncertainty as well. In practice, this means that the scattering of the results over time in the long-term stability study can be explained solely from the analytical uncertainty (e.g. calibration, repeatability of measurement). On this basis, using the theory of analysis of variance [8,9] the conclusion can be drawn that the uncertainty due to long-term stability can be set to zero.

Summarising, the model reduces to

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity}, \quad (5)$$

and for the associated standard uncertainty, the following expression is obtained

$$u_{i,prep}^2 = u_{i,grav}^2 + u_{i,purity}^2. \quad (6)$$

The validity of the mixtures has been demonstrated by verifying the composition as calculated from the preparation data with that obtained from (analytical chemical) measurement. In order to have a positive demonstration of the preparation data (including uncertainty, the following condition should be met [7])

$$|x_{i,prep} - x_{i,ver}| \leq 2\sqrt{u_{i,prep}^2 + u_{i,ver}^2}. \quad (7)$$

The factor 2 is a coverage factor (normal distribution, 95% level of confidence). The assumption must be made that both preparation and verification are unbiased. Such bias has never been observed. The uncertainty associated with the verification highly depends on the experimental design followed. In this particular key comparison, an approach has been chosen which is consistent with CCQM-K3 [10] and takes advantage of the work done in the gravimetry study CCQM-P23 [11].

The reference value of mixture  $i$  in a key comparison<sup>1</sup> can be defined as

$$x_{i,ref} = \langle x_{i,ref} \rangle + \delta x_{i,ref}, \quad (8)$$

where

$$x_{i,ref} = x_{i,prep} + \Delta x_{i,ver}. \quad (9)$$

Since the amount of substance fraction from preparation is used as the basis, the expectation of the correction  $\langle \Delta x_{i,ver} \rangle$  due to verification can be taken as zero, which is consistent with the assumption made earlier that both preparation and verification are unbiased. Thus, (9) can be expressed as

$$x_{i,ref} = \langle x_{i,prep} \rangle + \delta x_{i,prep} + \delta \Delta x_{i,ver}. \quad (10)$$

This expression forms the basis for the evaluation of degrees of equivalence in this key comparison. For all mixtures, it has been required that

$$\Delta x_{i,ver} = 0, \quad (11)$$

that is, there is no correction from the verification. The verification experiments have demonstrated that within the uncertainty of these measurements, the gravimetric values of the key comparison mixtures agreed with older measurement standards.

The expression for the standard uncertainty of a reference value becomes thus

$$u_{i,ref}^2 = u_{i,prep}^2 + u_{i,ver}^2. \quad (12)$$

The values for  $u_{i,ref}$  are given in the tables containing the results of this key comparison.

## Measurement methods

The measurement methods used by the participants are described in annex A of this report. A summary of the calibration methods, dates of measurement and reporting, and the way in which metrological traceability is established is given in table 2.

**Table 2: Summary of calibration methods and metrological traceability**

Laboratory	Measurements	Calibration	Traceability
INMETRO	2008-01-18 2008-01-21 2008-01-23	GLS	NPL (3), VSL (2)
VSL	2007-12-14	GLS	Own standards

## Degrees of equivalence

A unilateral degree of equivalence in comparisons is defined as [4]

$$\Delta x_i = D_i = x_i - x_{RV}, \quad (13)$$

and the uncertainty of the difference  $D_i$  at 95% level of confidence. Here  $x_{RV}$  denotes the reference value, and  $x_i$  the result of laboratory  $i$ .<sup>2</sup> Appreciating the special conditions in gas analysis, it can be expressed as

<sup>1</sup> This definition of a reference value is consistent with the definition of a key comparison reference value, as stated in the mutual recognition arrangement (MRA) [4].

$$\Delta x_i = D_i = x_i - x_{i,ref}. \quad (14)$$

The standard uncertainty of  $D_i$  can be expressed as

$$u^2(\Delta x_i) = +u_{i,lab}^2 + u_{i,prep}^2 + u_{i,ver}^2, \quad (15)$$

assuming that the aggregated error terms are uncorrelated. As discussed, the combined standard uncertainty of the reference value comprises that from preparation and that from verification for the mixture involved. A bilateral degree of equivalence is defined as [4]

$$D_{ij} = D_i - D_j, \quad (16)$$

and the uncertainty of this difference at 95% level of confidence. Under the assumption of independence of  $D_i$  and  $D_j$ , the standard uncertainty of  $D_{ij}$  can be expressed as

$$u^2(D_{ij}) = +u_{i,lab}^2 + u_{i,prep}^2 + u_{i,ver}^2 + u_{j,lab}^2 + u_{j,prep}^2 + u_{j,ver}^2. \quad (17)$$

The assumption of independence is not satisfied by the preparation and verification procedures. It is well known that the use of pre-mixtures leads to correlations in the final mixtures. The standard uncertainty from verification is based on the residuals of a straight line through the data points (response versus composition), and these residuals are correlated too. However, the uncertainty of a degree of equivalence is still dominated by the uncertainty of the laboratory, so that these correlations, which certainly influence  $D_{ij}$  and its uncertainty, will have little practical impact.

In figure 1, the relative deviations are given and in the figure 2, the degrees of equivalence are given relative to the gravimetric value. The uncertainties are, as required by the MRA [4], given as 95% confidence intervals. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed, and a coverage factor  $k = 2$  was used. For obtaining the standard uncertainty of the laboratory results, the expanded uncertainty (stated at a confidence level of 95%) from the laboratory was divided by the reported coverage factor.

---

<sup>2</sup> Each laboratory receives one cylinder, so that the same index can be used for both a laboratory and a cylinder.

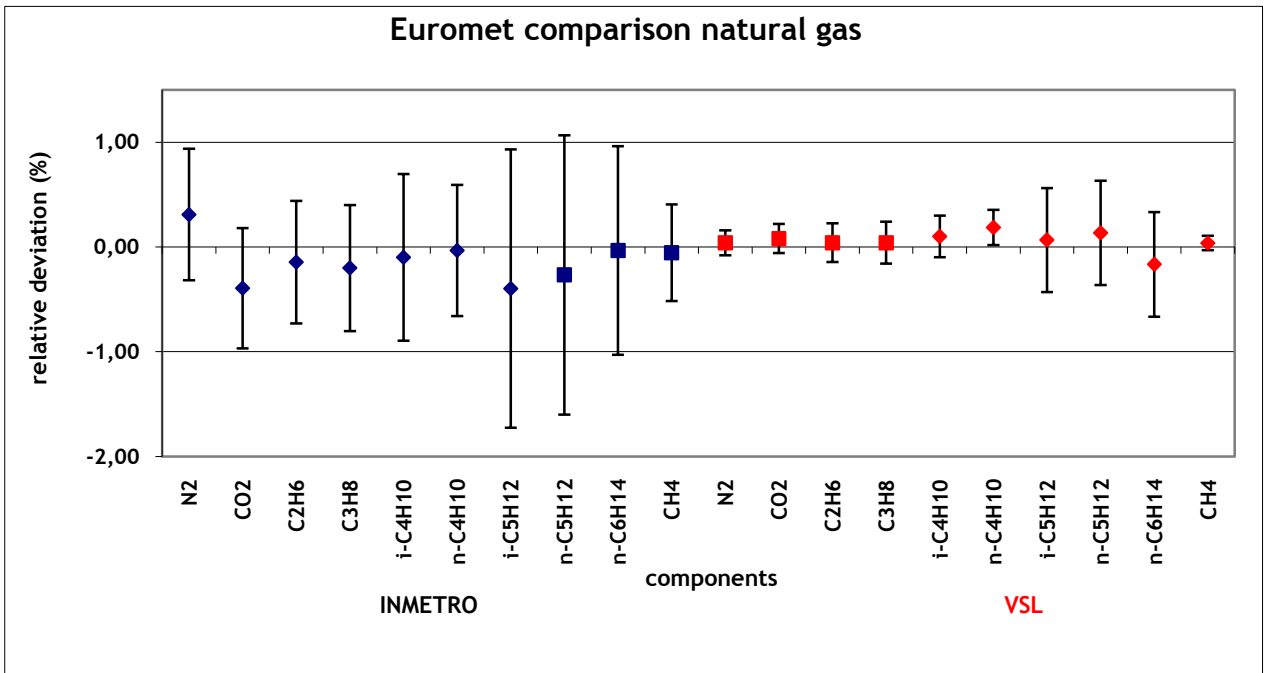


Figure 1: Relative deviation

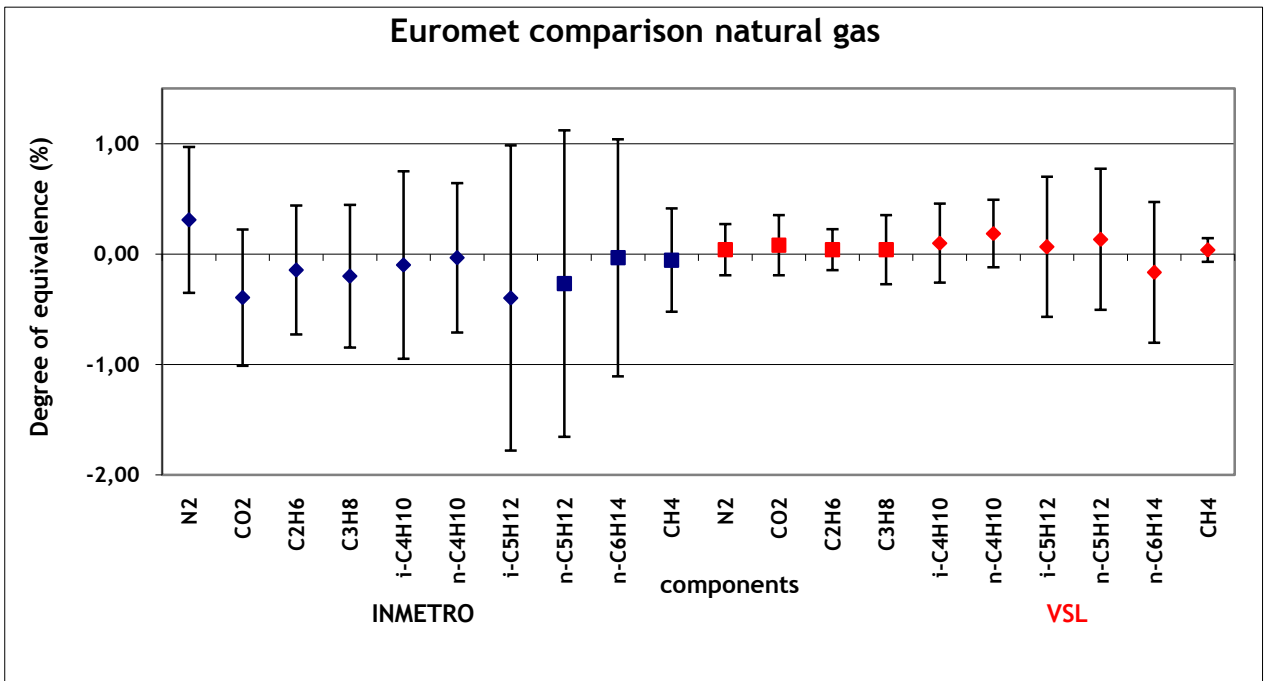


Figure 2: Degree of equivalence

## Results

In this section, the results of the key comparison are summarised. In the tables, the following data is presented

$x_{prep}$	amount of substance fraction, from preparation ( $10^{-2}$ mol/mol)
$u_{prep}$	uncertainty of $x_{prep}$ ( $10^{-2}$ mol/mol)
$u_{ver}$	uncertainty from verification ( $10^{-2}$ mol/mol)
$u_{ref}$	uncertainty of reference value ( $10^{-2}$ mol/mol)
$x_{lab}$	result of laboratory ( $10^{-2}$ mol/mol)
$U_{lab}$	stated uncertainty of laboratory, at 95% level of confidence ( $10^{-2}$ mol/mol)
$k_{lab}$	stated coverage factor
$\Delta x$	difference between laboratory result and reference value ( $10^{-2}$ mol/mol)
$U(\Delta x)$	Expanded uncertainty of difference $\Delta x$ , at 95% level of confidence <sup>3</sup> ( $10^{-2}$ mol/mol)

**Table 3: Results (expressed in  $10^{-2}$  mol/mol)**

		$x_{prep}$	$U_{ref}$	$x_{lab}$	$k_{lab}$	$U_{lab}$	$\Delta x$	$U(\Delta x)$
N2	INMETRO	1.0009	0.0020	1.004	2	0.0063	0.0031	0.007
CO2	INMETRO	1.5019	0.0035	1.496	2	0.0086	-0.0059	0.009
C2H6	INMETRO	7.0302	0.0016	7.020	2	0.041	-0.0102	0.041
C3H8	INMETRO	2.496	0.006	2.491	2	0.015	-0.0050	0.016
i-C4H10	INMETRO	0.4026	0.0012	0.4022	2	0.0032	-0.0004	0.003
n-C4H10	INMETRO	0.5902	0.0015	0.5900	2	0.0037	-0.0002	0.004
i-C5H12	INMETRO	0.03022	0.00012	0.0301	2	0.0004	-0.0001	0.000
n-C5H12	INMETRO	0.03008	0.00012	0.0300	2	0.0004	-0.0001	0.000
n-C6H14	INMETRO	0.03011	0.00012	0.0301	2	0.0003	0.0000	0.000
CH4	INMETRO	86.8876	0.0720	86.84	2	0.40	-0.0476	0.406
N2	VSL	1.0009	0.0020	1.0013	2	0.0012	0.0004	0.002
CO2	VSL	1.5019	0.0035	1.5031	2	0.0021	0.0012	0.004
C2H6	VSL	7.0302	0.0016	7.033	2	0.013	0.0028	0.013
C3H8	VSL	2.496	0.006	2.497	2	0.005	0.0010	0.006
i-C4H10	VSL	0.4026	0.0012	0.4030	2	0.0008	0.0004	0.001
n-C4H10	VSL	0.5902	0.0015	0.5913	2	0.0010	0.0011	0.002
i-C5H12	VSL	0.03022	0.00012	0.03024	2	0.00015	0.00002	0.000
n-C5H12	VSL	0.03008	0.00012	0.03012	2	0.00015	0.00004	0.000
n-C6H14	VSL	0.03011	0.00012	0.03006	2	0.00015	-0.00005	0.000
CH4	VSL	86.8876	0.0720	86.92	2	0.06	0.0324	0.094

<sup>3</sup> As defined in the MRA [4], a degree of equivalence is given by  $\Delta x$  and  $U(\Delta x)$ .

## Discussion of results

In all cases, the departure from the reference value is smaller than the associated expanded uncertainty.

## Conclusions

The agreement of the results in bilateral comparison is acceptable. For all parameters, the results agree within 0.5% (or better) with the reference value.

## References

- [1] Van der Veen A.M.H., Ziel P.R., De Leer E.W.B., Smeulders D., Besley L., Smarçao da Cunha V., Zhou Z., Qiao H., Heine H.-J., Tichy J., Lopez Esteban T., Mace T., Nagyné Szilágyi Z., Kim J.S., Perez Castorena A., Perez Urquiza M., Rangel Murillo F., Serrano Caballero V.M., Carbajal Alarcón C.E., Ramírez Nambo C., Avila Salas M., Rakowska A., Dias F., Konopelko L.A., Popova T.A., Pankratov V.V., Kovrizhnik M.A., Meshkov A.V., Efremova O.V., Kustikov Y.A., Musil S., Milton M.J.T., “Final Report International Comparison CCQM K23ac – Natural gas types I and III”, April 2006
- [2] Alink A., “The first key comparison on Primary Standard gas Mixtures”, *Metrologia* **37** (2000), pp. 35-49
- [3] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML, “Guide to the expression of uncertainty in measurement”, first edition, ISO Geneva, 1995
- [4] CIPM, “Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes”, Sèvres (F), October 1999
- [5] BIPM, Annex B to the MRA, <http://kcdb.bipm.fr/BIPM-KCDB//AppendixB/>
- [6] Alink A., Van der Veen A.M.H., “Uncertainty calculations for the preparation of primary gas mixtures. 1. Gravimetry”, *Metrologia* **37** (2000), pp 641-650
- [7] International Organization for Standardization, ISO 6142:2001 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods, 2<sup>nd</sup> edition
- [8] Van der Veen A.M.H., Pauwels J., “Uncertainty calculations in the certification of reference materials. 1. Principles of analysis of variance”, *Accreditation and Quality Assurance* **5** (2000), pp. 464-469
- [9] Van der Veen A.M.H., Linsinger T.P.J., Lamberty A., Pauwels J., “Uncertainty calculations in the certification of reference materials. 3. Stability study”, *Accreditation and Quality Assurance* **6** (2001), pp. 257-263
- [10] Van der Veen A.M.H., De Leer E.W.B., Perrochet J.-F., Wang Lin Zhen, Heine H.-J., Knopf D., Richter W., Barbe J., Marschal A., Vargha G., Deák E., Takahashi C., Kim J.S., Kim Y.D., Kim B.M., Kustikov Y.A., Khatskevitch E.A., Pankratov V.V., Popova T.A., Konopelko L., Musil S., Holland P., Milton M.J.T., Miller W.R., Guenther F.R., International Comparison CCQM-K3, Final Report, 2000
- [11] Van der Veen A.M.H., Van Wijk J.I.T., “CCQM P23 – Gravimetry”, Protocol, NMi VSL, Delft (NL), October 2000



## **Coordinator**

VSL B.V.  
Rob M. Wessel  
Thijsseweg 11  
2629 JA Delft  
the Netherlands  
Phone +31 15 2691 733  
Fax +31 15 261 29 71  
E-mail [rwessel@vsl.nl](mailto:rwessel@vsl.nl)

## **Project reference**

EUROMET 1028

## **Completion date**

February 2009

## Annex A: Measurement Reports

### Measurement Report from Divisão de Metrologia Química/INMETRO

Laboratory : Laboratório de Análise de Gases/Labag

Cylinder number : D340038

#### Measurement #1

Component	Date (dd/mm/yy)	Result (%-mol/mol)	Standard deviation (% relative)	number of replicates
Nitrogen	18/01/08	1.002	0.15	10
Carbon dioxide	18/01/08	1.495	0.21	10
Ethane	18/01/08	7.020	0.26	10
Propane	18/01/08	2.490	0.33	10
<i>iso</i> -Butane	18/01/08	0.4015	0.26	10
<i>n</i> -Butane	18/01/08	0.5891	0.26	10
<i>iso</i> -Pentane	18/01/08	0.0301	0.46	10
<i>n</i> -Pentane	18/01/08	0.0300	0.61	10
<i>n</i> -Hexane	18/01/08	0.0301	0.40	10
Methane	18/01/08	86.82	0.10	10

#### Measurement #2

Component	Date (dd/mm/yy)	Result (%-mol/mol)	Standard deviation (% relative)	number of replicates
Nitrogen	21/01/08	1.006	0.23	10
Carbon dioxide	21/01/08	1.499	0.15	10
Ethane	21/01/08	7.019	0.26	10
Propane	21/01/08	2.490	0.26	10
<i>iso</i> -Butane	21/01/08	0.4022	0.23	10
<i>n</i> -Butane	21/01/08	0.5901	0.16	10
<i>iso</i> -Pentane	21/01/08	0.0300	0.49	10
<i>n</i> -Pentane	21/01/08	0.0299	0.48	10
<i>n</i> -Hexane	21/01/08	0.0301	0.40	9
Methane	21/01/08	86.82	0.10	10

### Measurement #3

Component	Date (dd/mm/yy)	Result (%-mol/mol)	Standard deviation (% relative)	number of replicates
Nitrogen	24/01/08	1,004	0,34	8
Carbon dioxide	24/01/08	1,495	0,23	8
Ethane	24/01/08	7,020	0,32	10
Propane	24/01/08	2,491	0,13	8
<i>iso</i> -Butane	24/01/08	0,4029	0,10	8
<i>n</i> -Butane	24/01/08	0,5908	0,12	8
<i>iso</i> -Pentane	24/01/08	0,0302	0,33	8
<i>n</i> -Pentane	24/01/08	0,0300	0,26	8
<i>n</i> -Hexane	24/01/08	0,0302	0,19	8
Methane	24/01/08	86,89	0,10	10

### Results

Component	Result (%mol/mol)	Expanded Uncertainty (%mol/mol)	Relative Uncertainty (%)	Coverage factor <sup>4</sup>
Nitrogen	<b>1,004</b>	0,0063	0,63	2
Carbon dioxide	<b>1,496</b>	0,0086	0,57	2
Ethane	<b>7,020</b>	0,041	0,59	2
Propane	<b>2,490</b>	0,015	0,60	2
<i>iso</i> -Butane	<b>0,4022</b>	0,0032	0,79	2
<i>n</i> -Butane	<b>0,5900</b>	0,0037	0,63	2
<i>iso</i> -Pentane	<b>0,0301</b>	0,0004	1,32	2
<i>n</i> -Pentane	<b>0,0300</b>	0,0004	1,19	2
<i>n</i> -Hexane	<b>0,0301</b>	0,0003	1,0	2
Methane	<b>86,84</b>	0,40	0,47	2

### Reference Method:

A GC specifically set up for natural gas analysis was used:

---

<sup>4</sup> The coverage factor shall be based on approximately 95% confidence.

-Varian CP-3800 (ISO 6974 configuration) equipped with both TCD and FID detectors. The nitrogen, carbon dioxide and methane were determined using the TCD detector the other components were determined using FID detector.

Carrier gas: Helium.

Columns: 1.5 m x 1/8" ultimetel Molsieve 13X 80/100  
 0.5 m x 1/8" ultimetel Hayesep T 80/100  
 0.5 m x 1/8" ultimetel Hayesep Q 80/100  
 60 m x 0.25 mm CP-Sil 5 CB

Data collection was performed using Star Chromatography Workstation 6.3

### Calibration Standards:

It was used five standards to calibrate the GC. They were prepared according International Standard ISO 6142:2001 by NPL and NMI-VSL.

#### NG 122 (NPL)

Component	Assigned value( $x$ ) $10^{-2}$ mol/mol	Standard uncertainty ( $u(x)$ ) $10^{-2}$ mol/mol
Nitrogen	10,98	0,015
Carbon dioxide	3,021	0,005
Ethane	1,999	0,003
Propane	0,402	0,001
<i>iso</i> -Butane	0,1988	0,0006
<i>n</i> -Butane	1,000	0,003
<i>iso</i> -Pentane	0,01979	0,0001
<i>n</i> -Pentane	0,02019	0,0001
Hexane	0,3257	0,0015
Methane	82,03	0,02

#### NG 132 (NPL)

Component	Assigned value( $x$ ) $10^{-2}$ mol/mol	Standard uncertainty ( $u(x)$ ) $10^{-2}$ mol/mol
Nitrogen	3,166	0,0045
Carbon dioxide	7,126	0,011
Ethane	3,001	0,0045
Propane	1,500	0,0025
<i>iso</i> -Butane	0,2496	0,0006
<i>n</i> -Butane	0,3956	0,001
<i>iso</i> -Pentane	0,01018	0,00007
<i>n</i> -Pentane	0,01027	0,00007
Hexane	0,0983	0,0005
Methane	84,44	0,02

#### NG 126 (NPL)

Component	Assigned value( $x$ ) $10^{-2}$ mol/mol	Standard uncertainty ( $u(x)$ ) $10^{-2}$ mol/mol
Nitrogen	0,5005	0,0025
Carbon dioxide	0,4997	0,00125
Ethane	0,804	0,0016
Propane	4,406	0,0055
<i>iso</i> -Butane	0,07015	0,0004
<i>n</i> -Butane	0,07810	0,0004
<i>iso</i> -Pentane	0,3204	0,00120

<i>n</i> -Pentane	0,3185	0,00120
Hexane	0,01022	0,000075
Methane	92,99	0,025

#### D523411 (NMI)

Component	Assigned value( <i>x</i> ) 10 <sup>-2</sup> mol/mol	Standard uncertainty ( <i>u(x)</i> ) 10 <sup>-2</sup> mol/mol
Nitrogen	10,01	0,02
Carbon dioxide	5,002	0,0125
Ethane	9,985	0,010
Propane	3,990	0,004
<i>iso</i> -Butane	0,994	0,002
<i>n</i> -Butane	1,206	0,005
Methane	68,82	0,05

#### ML 6679 (NMI – recertified at Inmetro)

Component	Assigned value( <i>x</i> ) 10 <sup>-2</sup> mol/mol	Standard uncertainty ( <i>u(x)</i> ) 10 <sup>-2</sup> mol/mol
Nitrogen	4,970	0,011
Carbon dioxide	6,975	0,0215
Ethane	4,992	0,0135
Propane	2,981	0,008
<i>iso</i> -Butane	0,5008	0,0019
<i>n</i> -Butane	0,4912	0,0013
<i>iso</i> -Pentane	0,0200	0,0001
<i>n</i> -Pentane	0,0201	0,00015
Hexane	0,0199	0,00015
Methane	78,98	0,18

#### Instrument Calibration:

The standards used were described in topic above. Temperature and pressure were kept under control at the laboratory. The measurement sequence was injection of the standards and then injection of the sample.

#### Sample Handling:

How were the cylinders treated after arrival (e.g. stabilized) and how were samples transferred to the instrument? (automatic, high pressure, mass-flow controller, dilution etc).:

After arrival the cylinder was stabilized at room temperature (21°C and humidity of 55%) and rolled before measurements. The standards and sample were transferred directly to the GC automatically using a system composed three valves, pressure regulator and flowmeter.

#### Uncertainty:

The uncertainty of the unknown sample was calculated according to ISO 6143, using the software B\_least. The measurements were carried out in three days under repeatability conditions. The final concentrations were a median of the results and the uncertainty is the squared pooling error variance. The combined uncertainty was multiplied by a coverage factor of 2 with a confidence interval of 95%.

# Measurement Report from VSL

## Reference Method:

One GC (specifically set up for natural gas analysis) was used in the analyses.

1. Natural Gas Analyser (NGA):

GC:	HP6890 N (ISO 6974 configuration, Molsieve chanel not used)
Column:	Porapak R , 3 m, 1/8 in od, 80/100 mesh.
Detectors:	1 Thermal Conductivity Detector ( $\mu$ -TCD) and a Flame Ionisation Deterctor (FID) placed at the exhaust of the TCD.
Valves:	1 sampling valve with 0,25 ml sampleloop
Sample introduction:	Multi position gas sampling valves, injection at ambient pressure.
Oven Temperature:	temperature program: 40 °C for 12 minutes, ramp 10 °C/min to 150 °C, hold for 8 minutes.
Carrier:	He
Data Collection:	HP Chemstation software

The temperature program of the Porapak R column results in base-line separation of all the constituents of the samples. The TCD signal is used for the non-combustable components and for the ethane. All other hydrocarbons are analysed using the FID signal.

## Calibration Standards:

All **standards** have been prepared by the **gravimetric method**, according to **ISO 6142**.

Several multi component calibration standards were used, all having methane as balance gas. Depending on the concentrations of the components, standards are prepared directly from pure gases or from so called preliminary mixtures that are prepared from the pure gases. After preparation the standards were verified against existing standards. A detailed composition of the standards is given below.

All pure gases were analysed before use by GC-FID and GC-TCD, except for methane and nitrogen. For nitrogen and methane purity analyses are only performed on selected cylinders using FT-IR and GC-DID in order to check the specifications given by the producer. The results of these purity analyses are expected to be representative for the cylinders that are not tested. The result of these analyses are combined in so called purity tables, that are used to calculate the composition and uncertainties of the gas mixtures that are prepared in the laboratory. The calculated mole fractions of the different components in a mixture therefore are not only based on the purity of the pure substances, but are also based on the presence of this component as an impurity in the other pure gases.

## Instrument Calibration:

The set of standards used for a measurement and the mixtures to be analysed are connected to the gas chromatograph as described in the paragraph "sample handling" . A measurement of a cylinder consist of 5 injections that are averaged and corrected for pressure using the following equation.

$$Y' = Y \cdot \frac{P}{P_0}$$

Where Y' is the corrected response, Y is the average response of the 5 injections, P is the average of the pressures measured when injecting the sample and P<sub>0</sub> is the standard pressure.

The models used for the different curves are in all cases second order and unweighted regression is used.

## Sample Handling:

The cylinders were let to acclimatise to laboratory conditions before analysis was started.

Each cylinder was equipped with a pressure-reducing unit set to approximately 2 bar. These pressure reducers were flushed at least 8 times before the first measurement. These flushings were distributed over a 24 hours time period. After the first measurement the connected reducers remained connected to the cylinder, until all measurements were performed. Before following measurements of the sample the pressure-reducing unit was

flushed only once. Afterwards the cylinders were connected by Teflon tubing to an electronic multiple stream selection valve. Stainless steel tubing to the sample inlet port/ sample loop of the GC connected the outlet valve of this valve. Before starting the automated analysis the Teflon tubings were flushed for 3 minutes and before injection the whole system was (pulsated) flushed for 3 minutes. Just before injection a valve positioned directly behind the stream selection valve is closed and the gas in the sample loop is allowed to reach ambient pressure after which the sample is injected.

## Uncertainty:

### Gravimetric preparation and impurities

The uncertainty of the gravimetric preparation of the standards used was evaluated according to Alink and Van der Veen<sup>5</sup>. The uncertainty in the impurities present in all pure components and mixtures, that are used to prepare the standards are stored in purity tables. When a mixture is prepared, the uncertainty of the components is automatically calculated from the uncertainty of the gravimetric preparation and the uncertainties of the components present in the mother mixtures.

### Stability, non-recovery and leakages

All new prepared standards are verified for their composition against existing (gravimetrically prepared) standards. This verification is a check of the gravimetric preparation process, which includes determination of errors due to leakage of air into the cylinder, leakage of gas from the cylinder valve during filling, escape of gas from the cylinder, absorption of components on the internal surface of the cylinder. Only when no significant difference between the analysed and the gravimetric composition is found, the cylinder is approved as a new standard. Several selected cylinders covering the concentration ranges of all constituents in the natural gas standards are used for long term stability testing. During these tests no instability has been detected for any of the components. Because it is difficult or impossible to discern between these different uncertainty contributions, the standard deviation of the results of the stability measurements for a cylinder having a similar mole fraction was chosen to cover these uncertainties.

### Calibration curve and repeatability

The calibration curves were constructed using software based on ISO 6143.

As indicated, second order curves were used. Together with the uncertainty of the gravimetric concentrations of the calibration mixtures and the repeatability of the analyses of the calibration mixtures and the sample mixture, the concentration and its accompanied uncertainty were calculated for each constituent.

### Model used for evaluating measurement uncertainty:

The uncertainty of the analyses is the combined uncertainty of two uncertainty sources:

- Uncertainty of the component mole fraction in the standards, which is the combined uncertainty for the gravimetric preparation, impurities, the stability, non recovery and leakages ( $X_{PSM}$ ).
- Uncertainty of the calibration process, which is uncertainty contribution coming from the appropriateness of the calibration curve (model and its residuals) and the repeatability of the analysis ( $\Delta x_{analysis}$ )

Typical evaluation of the measurement uncertainty for **nitrogen**:

Quantity $X_i$	Estimate $x_i$ <i>mol/mol</i>	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ <i>% relative</i>	Sensitivity coefficient $c_i$	Contribution $u_i(y)$ <i>% relative</i>
$x_{psm}$	0.07034	B	Normal	0.05	1	0.05
$\Delta x_{analysis}$	0	A	Normal	0.04	1	0.08
Total:						
$x_{analysis}$	0.07034					0.10

<sup>5</sup> A. Alink and A.M.H. van der Veen, Uncertainty Calculations for the preparation of primary gas mixtures, *Metrologia*, **37** (2000), pp. 641-650.

Typical evaluation of the measurement uncertainty for **carbon dioxide**:

Quantity $X_i$	Estimate $x_i$ <i>mol/mol</i>	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ <i>% relative</i>	Sensitivity coefficient $c_i$	Contribution $u_i(y)$ <i>% relative</i>
$x_{\text{psm}}$	0.02994	B	Normal	0.06	1	0.06
$\Delta x_{\text{analysis}}$	0	A	Normal	0.05	1	0.09
Total:						
$x_{\text{analysis}}$	0.02994					0.11

Typical evaluation of the measurement uncertainty for **ethane**:

Quantity $X_i$	Estimate $x_i$ <i>mol/mol</i>	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ <i>% relative</i>	Sensitivity coefficient $c_i$	Contribution $u_i(y)$ <i>% relative</i>
$x_{\text{psm}}$	0.09415	B	Normal	0.09	1	0.09
$\Delta x_{\text{analysis}}$	0	A	Normal	0.07	1	0.07
Total:						
$x_{\text{analysis}}$	0.09415					0.12

Typical evaluation of the measurement uncertainty for **propane**:

Quantity $X_i$	Estimate $x_i$ <i>mol/mol</i>	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ <i>% relative</i>	Sensitivity coefficient $c_i$	Contribution $u_i(y)$ <i>% relative</i>
$x_{\text{psm}}$	0.03394	B	Normal	0.12	1	0.12
$\Delta x_{\text{analysis}}$	0	A	Normal	0.02	1	0.04
Total:						
$x_{\text{analysis}}$	0.03394					0.13

Typical evaluation of the measurement uncertainty for **iso-butane**:

Quantity $X_i$	Estimate $x_i$ <i>mol/mol</i>	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ <i>% relative</i>	Sensitivity coefficient $c_i$	Contribution $u_i(y)$ <i>% relative</i>
$x_{\text{psm}}$	0.007967	B	Normal	0.07	1	0.10
$\Delta x_{\text{analysis}}$	0	A	Normal	0.03	1	0.06
Total:						
$x_{\text{analysis}}$	0.007967					0.12

Typical evaluation of the measurement uncertainty for **n-butane**:

Quantity $X_i$	Estimate $x_i$ <i>mol/mol</i>	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ <i>% relative</i>	Sensitivity coefficient $c_i$	Contribution $u_i(y)$ <i>% relative</i>
$x_{\text{psm}}$	0.009960	B	Normal	0.14	1	0.14
$\Delta x_{\text{analysis}}$	0	A	Normal	0.04	1	0.08
Total:						
$x_{\text{analysis}}$	0.009960					0.17

Typical evaluation of the measurement uncertainty for **methane**:



Quantity $X_i$	Estimate $x_i$ <i>mol/mol</i>	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$ <i>% relative</i>	Sensitivity coefficient $c_i$	Contribution $u_i(y)$ <i>% relative</i>
$x_{\text{psm}}$	0.7537	B	Normal	0.04	1	0.04
$\Delta x_{\text{analysis}}$	0	A	Normal	0.03	1	0.03
Total:						
$x_{\text{analysis}}$	0.7537					0.05