

# Report

## Bilateral Comparison EUROMET 919 Natural gas

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### 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 .....	5
Discussion of results .....	8
Conclusions .....	8
References .....	8
Coordinator .....	9
Project reference .....	9
Completion date .....	9
Annex A: Measurement Reports .....	10
Measurement Report from INTI .....	10
Measurement Report from NMi VSL .....	13

### 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 EUROMET consultation. 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-K23b [1]. The mixture concerned contains nitrogen, carbon dioxide and the alkanes up to butane.

## Participants

As in CCQM-K23b, NMI-VSL was the coordinating laboratory. The natural gas PSM was prepared by NMI-VSL and subsequently checked against other PSMs for consistency. After analysis the mixture was shipped to INTI for measurement.

## Measurement standards

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

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

Component	Amount fractions $x$ ( $10^{-2} \text{ mol mol}^{-1}$ )
Nitrogen	4
Carbon dioxide	1
Ethane	3
Propane	1
<i>n</i> -Butane	0.2
<i>iso</i> -Butane	0.2
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, Nitrogen (6.0) from Air Products, Carbon dioxide (5.2) from AGA, and propane (3.5) from Air Liquide. 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, methane, and ethane) and GC/FID (propane, *iso*-butane, and *n*-butane).

## Measurement protocol

The laboratories were requested to use their normal procedure for the measurement of the composition of the gas mixtures. 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 consultation are based on gravimetry, and the purity verification 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 consultation, 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])

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

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 consultation, 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 consultation<sup>1</sup> can be defined as

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

where

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

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<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].

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 consultation. 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 consultation mixture 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 consultation.

## 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
INTI	2007-01-09 2007-05-09 2007-21-09	2-points	NPL
NMi VSL	2006-08-18	OLS	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

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

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]

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

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

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 the figure 1, 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.

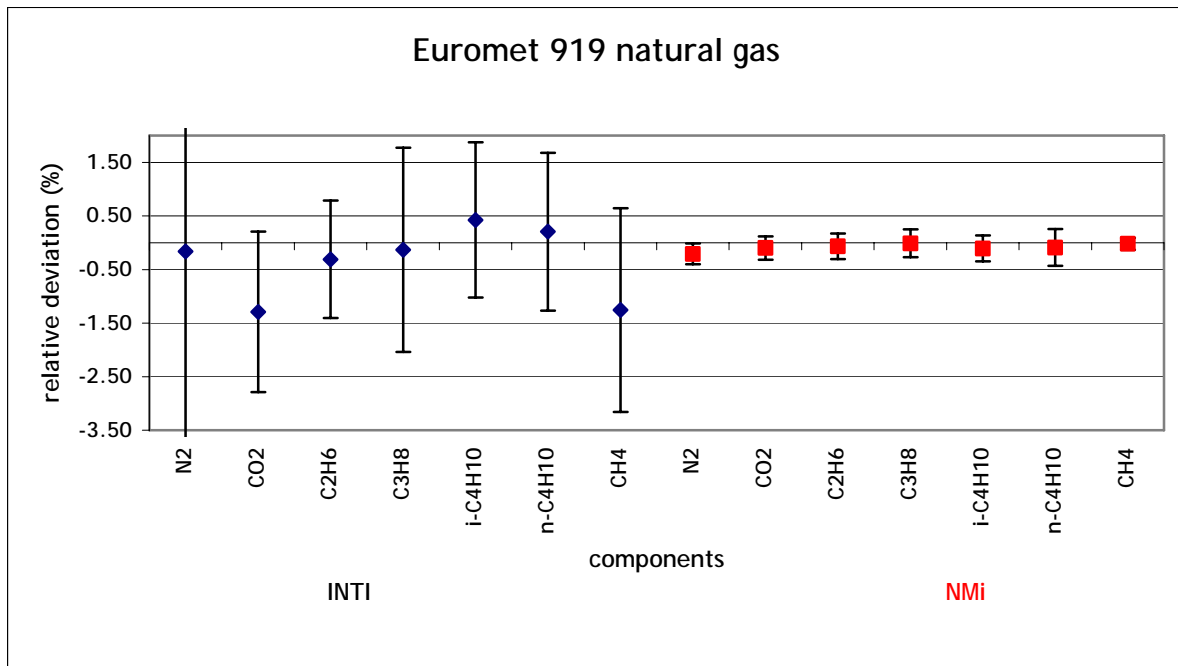


Figure 1: Degrees of equivalence

## Results

In this section, the results of this consultation 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)

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

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

		$x_{prep}$	$\mu_{ref}$	$x_{lab}$	$k_{lab}$	$U_{lab}$	$\Delta x$	$U(\Delta x)$
N <sub>2</sub>	INTI	4.1266	0.0051	4.12	2	0.39	-0.0066	0.390
CO <sub>2</sub>	INTI	1.0129	0.0013	1.000	2	0.015	-0.0129	0.015
C <sub>2</sub> H <sub>6</sub>	INTI	2.9270	0.0036	2.918	2	0.032	-0.0090	0.032
C <sub>3</sub> H <sub>8</sub>	INTI	0.9993	0.0013	0.998	2	0.019	-0.0013	0.019
i-C <sub>4</sub> H <sub>10</sub>	INTI	0.2061	0.0003	0.207	2	0.003	0.0009	0.003
n-C <sub>4</sub> H <sub>10</sub>	INTI	0.2036	0.0002	0.204	2	0.003	0.0004	0.003
CH <sub>4</sub>	INTI	90.5240	0.0720	89.4	2	1.7	-1.1240	1.702
N <sub>2</sub>	NMi	4.1266	0.0051	4.118	2	0.008	-0.0086	0.009
CO <sub>2</sub>	NMi	1.0129	0.0013	1.0119	2	0.0022	-0.0010	0.003
C <sub>2</sub> H <sub>6</sub>	NMi	2.9270	0.0036	2.925	2	0.007	-0.0020	0.008
C <sub>3</sub> H <sub>8</sub>	NMi	0.9993	0.0013	0.9992	2	0.0026	-0.0001	0.003
i-C <sub>4</sub> H <sub>10</sub>	NMi	0.2061	0.0003	0.2059	2	0.0005	-0.0002	0.001
n-C <sub>4</sub> H <sub>10</sub>	NMi	0.2036	0.0002	0.2034	2	0.0007	-0.0002	0.001
CH <sub>4</sub>	NMi	90.5240	0.0720	90.505	2	0.1	-0.0190	0.123

## Discussion of results

In all cases, the departure from the reference value is smaller than the associated expanded uncertainty. For nitrogen, the reported uncertainty for INTI is very large. The laboratory reported that this is caused by the effect that the nitrogen content in Argentine natural gas differs appreciably from the content in this mixture and that the reference gas standards were rather far away from the nominal value.

## Conclusions

The agreement of the results in bilateral comparison is acceptable. For all parameters, the results agree within 1.5% (or better) with the reference value.

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## Annex A: Measurement Reports

### Measurement Report from INTI

Laboratory : INTI (Instituto Nacional de Tecnología Industrial)

Cylinder number : D751971

#### Measurement #1

Component	Date (dd/mm/yy)	Result (%-mol/mol)	Standard deviation (% relative)	number of replicates
Nitrogen	09/01/07	4,1040	1,0	5
Carbon dioxide	09/01/07	1,001	0,3	5
Ethane	09/01/07	2,9076	0,4	5
Propane	09/01/07	0,9972	0,4	5
<i>iso</i> -Butane	09/01/07	0,2070	0,5	5
<i>n</i> -Butane	09/01/07	0,2032	0,5	5
Methane	09/01/07	89,482	0,3	5

#### Measurement #2

Component	Date (dd/mm/yy)	Result (%-mol/mol)	Standard deviation (% relative)	number of replicates
Nitrogen	09/05/07	4,1133	1,4	5
Carbon dioxide	09/05/07	0,999	0,3	5
Ethane	09/05/07	2,9236	0,3	5
Propane	09/05/07	0,9959	0,2	5
<i>iso</i> -Butane	09/05/07	0,2066	0,6	5
<i>n</i> -Butane	09/05/07	0,2031	0,4	5
Methane	09/05/07	89,604	0,3	5

#### Measurement #3

Component	Date (dd/mm/yy)	Result (%-mol/mol)	Standard deviation (% relative)	number of replicates
Nitrogen	21/05/07	4,1456	0,3	7
Carbon dioxide	21/05/07	0,999	0,5	7
Ethane	21/05/07	2,9227	0,3	7
Propane	21/05/07	1,001	0,3	7
<i>iso</i> -Butane	21/05/07	0,2062	0,4	7
<i>n</i> -Butane	21/05/07	0,2043	0,4	7

Methane	21/05/07	89,220	0,3	7
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## Results

Component	Result (%mol/mol)	Expanded Uncertainty (%mol/mol)	Coverage factor <sup>4</sup>
Nitrogen	<b>4,12</b>	0,39	2
Carbon dioxide	<b>1,000</b>	0,015	2
Ethane	<b>2,918</b>	0,032	2
Propane	<b>0,998</b>	0,019	2
<i>iso</i> -Butane	<b>0,207</b>	0,003	2
<i>n</i> -Butane	<b>0,204</b>	0,003	2
Methane	<b>89,4</b>	1,7	2

### Reference Method:

Method: Gas chromatography

Instrument: HP 6890

Columns: HP – PLOT Q 19095P-Q04

HP – PLOT mol Sieve 5A19095P- MSO serial installation

Sample injection: 6 port injection valve, loop 0.5 ml

Detector CO<sub>2</sub>, methane and N<sub>2</sub>: TCD

Detector other components: FID

Carrier: He 5.0

### Calibration Standards:

Primary Reference Gas Mixtures prepared by NPL (Cylinder number A 348, NG 80 and NG 120).

### Instrument Calibration:

The instrument was calibrated using one point comparison between reference and sample gas.

For each component the reference gas with the most similar concentration to the sample was chosen.

The measurement sequence used was: standard – sample – standard.

The Nitrogen composition in the sample is very different from the typical values found in our country for natural gas. For this reason the composition of our gas standards are not very close to the sample.

Nevertheless, we used the closer standard we have to make the measurement and to check the results we also measured N<sub>2</sub> using a calibration curve made with the three standards already mentioned.

### Sample Handling:

The sample was termostated at room temperature and homogenized by rotation.

Sample injection: Manual, 6 port injection valve

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

**Uncertainty:**

- ❖ The uncertainties of each component in measurements number 1, 2 and 3 were estimated using the following model:

**One point calibration**

$$C_x = C_1 * A_x / A_1$$

Where  $C_x$  = concentration of x component in the sample

$C_1$  = concentration of x component in the calibration gas

$A_x$  = response obtained for x component in the sample

$A_1$  = response obtained for x component in the calibration gas

As both the sample and the calibration gas were analyzed in the same conditions:

$$(U_{C_x} / C_x)^2 = (U_{C_1} / C_1)^2 + (U_{A_x} / A_x)^2 + (U_{A_1} / A_1)^2$$

Where  $U_{C_1}$  = absolute uncertainty of x component in the calibration gas

$U_{C_x}$  = absolute uncertainty of x component in the sample

$U_{A_x}$  = Standard deviation of the response obtained for x component in the sample

$U_{A_1}$  = Standard deviation of the response obtained for x component in the calibration gas.

- ❖ The uncertainties of each component in each measurement were combined to obtain the final uncertainty:

$$(U_{\text{final}})^2 = (U_{\text{measurement 1}})^2 + (U_{\text{measurement 2}})^2 + (U_{\text{measurement 3}})^2$$

# Measurement Report from NMI 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 channel 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 Detector (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 nitrogen, carbon dioxide, methane, and ethane. Propane, iso-butane, and n-butane 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

Standards and their mole fractions per measured component.

### $\text{N}_2$

Cylinder code	Gravimetric Mole fraction
VSL205178	0.006132
VSL307429	0.007994
VSL209604	0.011914
VSL202608	0.024950
VSL203657	0.060075

### $\text{CO}_2$

Cylinder code	Gravimetric Mole fraction
VSL209423	0.003985
VSL205178	0.006135
VSL307429	0.007998
VSL209604	0.011941
VSL203657	0.025174
VSL209546	0.060065
VSL507425	0.12021

### $\text{C}_2\text{H}_6$

Cylinder code	Gravimetric Mole fraction
VSL209423	0.009977
VSL205178	0.014957
VSL202608	0.020020
VSL307429	0.030115
VSL507425	0.045161
VSL209546	0.065695
VSL203657	0.079880
VSL209604	0.110020



**C<sub>3</sub>H<sub>8</sub>**

Cylinder code	Gravimetric Mole fraction
VSL209423	0.0010126
VSL209545	0.001996
VSL202608	0.004005
VSL209604	0.005937
VSL205178	0.007924
VSL507425	0.010020

**i-C<sub>4</sub>H<sub>10</sub>**

Cylinder code	Gravimetric Mole fraction
VSL307429	0.0003027
VSL209423	0.0004963
VSL209545	0.0006967
VSL202608	0.0010037
VSL205178	0.0014751
VSL209546	0.0019668
VSL209604	0.0029989
VSL309424	0.0049685

**n-C<sub>4</sub>H<sub>10</sub>**

Cylinder code	Gravimetric Mole fraction
VSL307429	0.0003018
VSL209423	0.0004959
VSL209545	0.0007027
VSL202608	0.0009978
VSL205178	0.0014822
VSL209604	0.0029997
VSL309424	0.0049843

**CH<sub>4</sub>**

Cylinder code	Gravimetric Mole fraction
VSL209546	0.64776
VSL507425	0.69674
VSL202608	0.74311
VSL203657	0.79689
VSL209604	0.84811
VSL307429	0.89865
VSL223555	0.93855
VSL205178	0.96189
VSL209423	0.98003
VSL209545	0.99210