Euramet comparison for Ethanol in Nitrogen

EURAMET.QM-K4.1

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Summary

Ethanol measurements in human breath are important for the implementation of legal metrology related to the driving under influence legislation. Measurements are typically performed to calibrate breath testers in accordance with OIML Recommendation R126:1998 (evidential breath analysers) in the range from 50 µmol/mol up to 800 µmol/mol ethanol in nitrogen or air.

Six national metrology institutes participated. The KCRV is based on the gravimetric preparation. Its uncertainty appreciates effects from adsorption of ethanol to the cylinder wall, weighing, and purity analysis. Only VNIIM shows a result which is inconsistent with the KCRV. Both VNIIM and CEM show a result that deviates more than 1% from the reference value.

This Euramet comparison is linked to CCQM-K4; as NPL and VSL participated in both comparisons, this can provide a link between the two comparisons.

Table of contents

1 Introduction

This key comparison involved primary standards of ethanol in nitrogen maintained at six laboratories. The nominal amount fraction of the standards used for the comparison was 120 μmol/mol, which is typical for the levels used to calibrate evidential breath analysers in many countries. Such standards fulfil the agreed OIML requirements for the calibration of evidential breath-alcohol analysers and are able to provide a more accurate calibration at field level than ethanol/water solution-based simulators which have a high sensitivity to variations in the temperature of the solution.

Just as in other key comparisons in the gas analysis area, the values as obtained from gravimetric preparation in accordance with ISO 6142 [1] are taken as reference point.

This Euramet comparison is linked to CCQM-K4 [2]; as NPL and VSL participated in both comparisons, this can provide a link between the two comparisons.

This is the fourth supplementary comparison on ethanol. Within APMP supplementary comparison APMP.QM-K4 [3] and APMP.QM-K4.1 [4] have been reported and within EURAMET this supplementary comparison was preceded by EURAMET.QM-K4 [5].

The matrix gas in this comparison is nitrogen. For 3 of the 4 previous comparisons a mixture of ethanol in synthetic air was circulated. APMP.QM-K4.1 was on ethanol in nitrogen. As most institutes within EURAMET have calibration and measurement capabilities listed for both nitrogen and synthetic air, a EURAMET comparison with nitrogen matrix was favourable.

The full measurement reports of the six participants are stated at the end of the report.

2 Design of the key comparison

2.1 Field of measurement

Amount-of-substance

2.2 Subject

Euramet comparison in the field of environmental and legal measurements (ethanol in nitrogen).

2.3 Participants

The following laboratories participated in the comparison: CEM, INMETRO, NMISA, NPL, VNIIM and VSL (coordinating laboratory).

2.4 Measurement standards

A suite of ethanol in nitrogen mixtures has been gravimetrically prepared for this comparison. The nominal amount of substance fraction is 120 μmol/mol.

The mixtures have been prepared gravimetrically and subsequently verified. The preparation of the mixtures has been carried out using the normal procedure for the preparation of gas mixtures [2]. After preparation, the mixtures have been verified by comparing the key comparison mixtures with PSMs from the standards maintenance programme.

2.5 Conduct of the comparison

VSL acted as pilot laboratory for this Euramet comparison. Each participating laboratory received one mixture and measured the concentration of ethanol with respect to their own primary standards. The methods reported are described below. After the completion of the measurement, each participant was requested to return the standards to VSL to be reanalysed by VSL. Reanalysis showed that the mixtures were stable as was expected from experience with comparable standards at VSL that show stability for more than 4 years.

2.6 Schedule

The schedule for this key comparison reads as follows

June-July 2009	Preparation of gravimetric mixtures + verification measurements
August 2009	Shipment of cylinders to participating laboratories
15 December 2009	Reports due to pilot laboratory
15 December 2009	Cylinders due to pilot laboratory
April 2010	Verification measurements at pilot laboratory
June 2010	Draft A report
September 2010	Draft B report

2.7 Measurement equation

The reference values used in this key comparison are based on gravimetry, and the purity verification of the parent gases/liquids according to ISO 6142. All mixtures underwent verification prior to shipping them to the participants according to ISO 6143. After return of the cylinders, they have been verified once more to reconfirm the stability of the mixtures.

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

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

For the mixtures used in this key comparison, the following statements hold (for all components involved). Ethanol is a component that tends to adsorb to some extent to the cylinder wall. The average value due to this effect is set to 0,

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

and its associated standard uncertainty is estimated to be 0.25% relative. This uncertainty estimate is based on long-term experience with these mixtures in this particular cylinder type.

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 $u_{\mathrm{i,ver}}$ (e.g. calibration, repeatability of measurement) and other effects.

The analysis performed after the return of the mixtures to VSL confirmed that the mixtures are stable. No significant drift could be observed from the repeat analyses.

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

$$u^2_{i,ref} = u^2_{i,prep} + u^2_{i,ver}. \quad (5)$$

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

2.8 Supported CMC-claims

This Euramet comparison can be used to support analytical capabilities for ethanol in nitrogen and ethanol in air mixtures in the range from 80 to 800 µmol/mol.

2.9 Degrees–of–equivalence

A unilateral degree of equivalence in key comparisons is defined as

$$\Delta x_i = D_i = x_i - x_{\mathrm{KCRV}}, \quad (6)$$

and the uncertainty of the difference D_i at 95% level of confidence. Here x_{KCRV} denotes the key comparison reference value, and x_i the result of laboratory *i*. [1] Appreciating the special conditions in gas analysis, it can be expressed as

$$\Delta x_i = D_i = x_i - x_{i,ref}\,. \tag{7}$$

The standard uncertainty of D_i can be expressed as

$$u^2\left(\Delta x_i\right) = u_{i,lab}^2 + u_{i,prep}^2 + u_{i,ver}^2\,, \tag{8}$$

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.

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[1] Each laboratory receives one cylinder, so that the same index can be used for both a laboratory and a cylinder.

3 Results

3.1 Measurement methods

The methods used by each of the participating laboratories to analyse the standards are listed in table 1. Three laboratories used non-dispersive infrared (NDIR) and 2 laboratories used GC techniques. Furthermore the number of standards the traceability and the calibration model in listed in table 1. The reported calibration methods are two point and multi-point calibration.

Table 1: Analytical methods used

Lab	Analytical method	No. of standards	Traceability to	Calibration model
CEM	GC-TCD	3	IPQ	linear
INMETRO	NDIR	4	VSL	linear
NMISA	NDIR	11	VSL	quadratic
NPL	GC-FID	2	NPL	bracketing
VNIIM	NDIR	2	VNIIM	bracketing
VSL	NDIR	5 and 8	VSL	linear

3.2 Data and evaluation

In this section, the results of the key comparison are summarised. In table 2, the following data is presented

x_{prep}	amount of substance fraction, from preparation
u_{prep}	uncertainty of x_{prep}
u_{ver}	uncertainty from verification
u_{ref}	uncertainty of reference value
x_{lab}	result of laboratory
U_{lab}	stated uncertainty of laboratory, at 95% level of confidence
k_{lab}	stated coverage factor
D_i	difference between laboratory result and reference value
k	assigned coverage factor for degree of equivalence
$U(D_i)$	Expanded uncertainty of difference D_i, at 95% level of confidence[2]

Table 2: Results and degrees–of–equivalence for carbon monoxide

Lab	**Cylinder**	x_{prep} **µmol/mol**	u_{prep} **µmol/mol**	u_{ver} **µmol/mol**	u_{ref} **µmol/mol**	x_{lab} **µmol/mol**	U_{lab} **µmol/mol**	k_{lab}	D_i **µmol/mol**	$\Delta x/x$ **%**	k	$U(D_i)$ **µmol/mol**	$U(D_i)/x$ **%**
CEM	D247878	120.66	0.30	0.11	0.32	122.0	3.8	2	1.34	1.11	2	3.85	3.19
INMETRO	D247873	120.25	0.30	0.11	0.32	121.4	1.6	2	1.15	0.96	2	1.72	1.43
NMISA	D247865	120.45	0.30	0.11	0.32	120.79	0.98	2	0.34	0.28	2	1.17	0.97
NPL	D247880	120.79	0.30	0.11	0.32	120.6	0.4	2	-0.19	-0.16	2	0.75	0.62
VNIIM	D247881	120.36	0.30	0.11	0.32	119.04	0.5	2	-1.32	-1.10	2	0.81	0.67
VSL	D247878	120.66	0.30	0.11	0.32	120.65	0.84	2	0.01	0.01	2	1.06	0.88

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[2] As defined in the MRA [9], a degree of equivalence is given by Δx and $U(\Delta x)$.

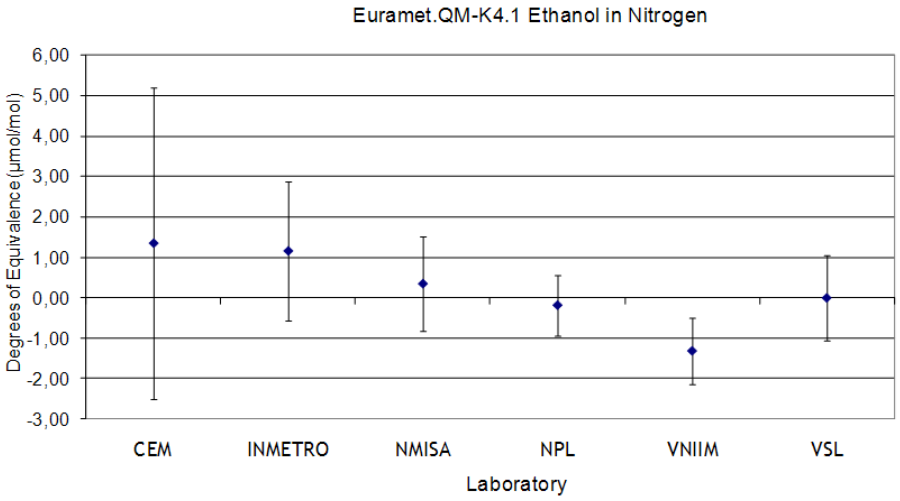

Figure 1: Degrees-of-equivalence (*k* = 2)

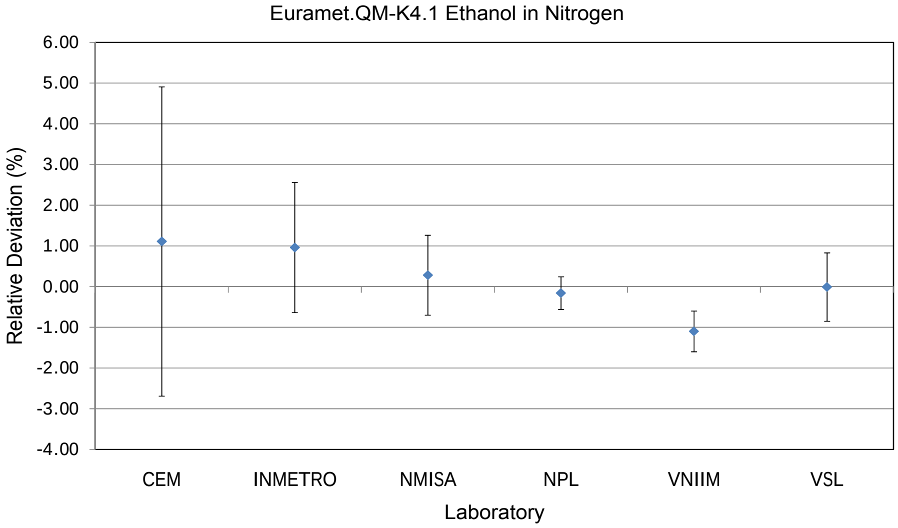

Figure 2: Relative differences (*k* = 2)

4 Discussion and conclusions

The results submitted by the six participants are shown in table 2. The degrees of equivalence are shown in figure 1. Only the result of VNIIM is inconsistent with the KCRV. The relative deviation from the reference values is given in figure 2, both VNIIM and CEM show a deviation of more than 1% relative.

The Mutual Recognition Arrangement (MRA) requires that the result of a Regional Key Comparison should be linked to the corresponding key comparisons carried out by CCQM, in this case the CCQM-K4.

For both comparisons the reference value is the gravimetric values of the ethanol standards at a nominal amount fraction of 120 µmol/mol.

Two laboratories participated in both comparisons: NPL (pilot laboratory for the CCQM-K4) and VSL (pilot laboratory for the EURAMET.QM-K4.1). The results for NPL and VSL in each comparison are shown below.

	Laboratory	Degree of equivalence D_i (µmol/mol)	Uncertainty in degree of equivalence U_1 (µmol/mol)	D_i / U_1
CCQM-K4	NPL VSL	0.01 -0.04	1.00 0.60	0.01 0.07
EURAMET.QM-K4.1	NPL VSL	0.19 -0.01	0.75 1.06	0.25 0.01

Since the results from both NPL and VSL are comparable with the reference values within their claimed uncertainty in both comparisons, they provide validation that the gravimetric values act as valid reference values. Hence, it is reasonable to conclude that the degrees of equivalence of participants in CCQM-K4 can be linked to those from EURAMET.QM-K4.1 without additional uncertainty.

Therefore we propose that the results of EURAMET.QM-K4.1 are entered into the Appendix C as being comparable with those of CCQM-K4 without correction.

References

[1] International Organization for Standardization, ISO 6142:2001 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods, 2nd edition

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[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] 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

[8] Van der Veen A.M.H., Van Wijk J.I.T., “CCQM P23 – Gravimetry”, Protocol, VSL, Delft (NL), October 2000

[9] CIPM, “Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes”, Sèvres (F), October 1999

Measurement report of CEM

Laboratory : CENTRO ESPAÑOL DE METROLOGÍA (CEM)

Laboratory code :

Cylinder number : D247878

Measurement #1

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**Number of replicates**
Ethanol	27/11/09	$122{,}92\cdot10^{-6}$	1,1	10

Measurement #2

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**number of replicates**
Ethanol	30/11/09	$121{,}08\cdot10^{-6}$	1,0	10

Measurement #3

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**number of replicates**
Ethanol	01/12/09	$122{,}09\cdot10^{-6}$	1,5	10

Result

Component	**Assigned value(x) (mol/mol)**	**Standard uncertainty ($u(x)$)**
Ethanol	$122{,}0\cdot10^{-6}$	$1{,}9\cdot10^{-6}$

Reference Method

The mixture was analysed with microGC-TCD technique. An Agilent 3000A microGC with a 8m x 0,15 mm x 2,0 μm OV-1 capillary column was used for separation. The instrument incorporates a 1,6 μL fixed volume injector. Ethanol was analysed using a thermal conductivity detector.

Data was collected with the Soprane software.

Calibration Standards

Three ethanol in nitrogen mixtures from IPQ were used with the following composition:

- CRM018871: (0,000 080 7 ± 0,000 001 1) mol/mol
- CRM019069: (0,000 138 ± 0,000 001) mol/mol
- CRM018924: (0,000 388 ± 0,000 003) mol/mol

All mixtures were certified by comparison with reference materials according to International Standard ISO 6143:2001.

Instrument Calibration

B_least software based on International Standard ISO 6143:2001 (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures) was used to certify the sample cylinder. A calibration curve was fitted to the mean value from 10 peak area for each CRM and the standard deviation of the 10 measurements was used as standard uncertainty. The method was used resulting in a calculated mole fraction and standard uncertainty for the sample cylinder. In all cases a linear function was used with goodness of fit less than 2.

Sample handling

Upon arrival the sample cylinder was rolled and stored in the laboratory under laboratory reference conditions. The sample was analysed in three consecutive working days.

A pressure reducer was connected to the sample cylinder. The reducer was carefully flushed as prescribed in International Standard ISO 16664:2004 (Gas analysis – Handling of calibration gases and calibration gas mixtures – Guidelines).

Binary CRMs and the sample cylinder were connected one by one to the instrument in the increasing order of concentration and the gas outlet was 1 bar. Before taking the readings, the injector was flushed for several minutes with the mixture to be measured in order to avoid drift.

Evaluation of measurement uncertainty

The mathematical mode used to calculate the uncertainty in the composition of mixture analyzed is a linear combination of the sources of uncertainty due to the instrument used and the repeatability of the measurements. This leads to:

$$u = \sqrt{u_{B\_least}^2 + u_r^2}$$

where u_{B_least} is the largest uncertainty among the obtained uncertainties by means of the B_least software (linear fit regression) and U_r is the standard deviation of the mean of the results obtained along the period of measurements.

Measurement Report of INMETRO

Report forms

Laboratory : Laboratório de Análise de Gases - LABAG

Laboratory code : INMETRO
Cylinder number : D247873

Measurement #1

Component	Date (dd/mm/yy)	Result	Unit	Standard deviation (% relative)	number of replicates
C_2H_5OH	11/09/09	120,3	μmol/mol	0,29	8

Measurement #2

Component	Date (dd/mm/yy)	Result	Unit	Standard deviation (% relative)	number of replicates
C_2H_5OH	14/09/09	122,4	μmol/mol	0,38	8

Measurement #3

Component	Date (dd/mm/yy)	Result	Unit	Standard deviation (% relative)	number of replicates
C_2H_5OH	15/09/09	121,6	μmol/mol	0,43	8

Results

Component	Result	Unit	Expanded Uncertainty	Coverage factor
C_2H_5OH	121,4	μmol/mol	1,6	2

Reference Method

To analyse the components ethanol the single beam infrared analysers (Servomex) were used.
Measuring range to analyse: 0-100/0-1000 ppm

Calibration Standards

Four standards were used to calibrate the infrared analyser model 2500 analyse ethanol. They were prepared according International Standard ISO 6142:2001 by NMi-VSL.

PRM D247560

Component	Assigned value(x) 10^{-6} mol/mol	Standard uncertainty (u(x)) 10^{-6} mol/mol
Ethanol	101,7	0,4

PRM D247587

Component	Assigned value(x) 10^{-6} mol/mol	Standard uncertainty (u(x)) 10^{-6} mol/mol
Ethanol	199,0	0,5

PRM D247546

Component	Assigned value(x) 10^{-6} mol/mol	Standard uncertainty (u(x)) 10^{-6} mol/mol
Ethanol	300,6	0,75

PRM MT4454

Component	Assigned value(x) 10^{-6} mol/mol	Standard uncertainty (u(x)) 10^{-6} mol/mol
Ethanol	400,4	1,0

Instrument Calibration

The standards used are listed above. The injection was done manually. The order of the injections was: first injection of the standards and then injection of the sample, and they were injected eight times. And the calibration was done according ISO 6143, the best model was determined using the software B_Least, this case linear models .

Sample handling

After arrival in the laboratory, the cylinder was stabilised at room temperature (21ºC and humidity of 55%) before measurements. The standards and sample were transferred directly to the infrared analyser using a system composed of pressure regulator, flow meter and control valves.

Evaluation of measurement uncertainty

The uncertainty of the unknown sample was calculated according to ISO 6143, using the software B_least. The combined uncertainty was multiplied by a coverage factor of 2 with a confidence interval of 95%. Three sources of uncertainty were considered:

- Uncertainty of the standards (certificate – type B)
- Uncertainty of the area (analysis – type A)
- Calibration curve (type A)

Measurement Report of NMISA

Laboratory : NMISA
Laboratory code :
Cylinder number : D247865

Measurement #1

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**Number of replicates**
C_2H_5OH	03/12/2009	$119,87 \times 10^{-6}$	0,46	3

Measurement #2

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**number of replicates**
C_2H_5OH	04/12/2009	$121,35 \times 10^{-6}$	0,38	3

Measurement #3

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**number of replicates**
C_2H_5OH	08/12/2009	$121,15 \times 10^{-6}$	0,77	3

Result

Component	**Assigned value(*x*) (mol/mol)**	**Standard uncertainty (*u*(*x*)) (mol/mol)**
C_2H_5OH	$120,79 \times 10^{-6}$	$0,49 \times 10^{-6}$

Reference Method

The C_2H_5OH content of sample D247865 was analysed using the siemens ultramat 6 NDIR. The siemens ultramat 6 channel operates according to the NDIR two-beam alternating light principle with double-layer detector and optical coupler. It measures gases highly selectively whose absorption bands lie in the infrared wavelength range from 2 to 9 µm such as, for example, CO, CO_2, NO, SO_2, NH_3, H_2O, CH_4, and other hydrocarbons.

Calibration Standards

The calibration standards were gravimetrically prepared according to International Standard ISO 6142:2001. The calibration standards were imported from NMi-VSL in The Netherlands. The calibration results are traceable to the primary accepted measurement standard.

Instrument Calibration

The instrument was calibrated with 11 ethanol standards shown on the table below:

Cylinder Numbers	**Concentration ($\times 10^{-6}$ mol/mol)**	**Standard uncertainty ($\times 10^{-6}$ mol/mol)**
MY9696	327.022557	0.820900803

D518877	82.15088778	0.212826134
MR8423	207.8399219	0.516863469
MR8371	548.2401216	1.368168005
D523449	328.7251661	0.820900803
MY9678	82.39411765	0.212826134
D247809	78.6	0.35
D247870	157	0.4
D247859	471.5	1.15
D247841	262.4	0.65
D247894	365.7	0.9

The calibration method was in accordance with ISO 6143, on three different days. The temperature of the laboratory was regulated at 22 ± 2 ºC and the relative humidity of 40 ± 10%.

Sample handling:

The sample was kept at laboratory temperature with calibration standards. The samples were introduced to the instrument on the rotatube 2 L\min measured with the Brooks electronic flow controller.

Evaluation of measurement uncertainty

The budget of the standard uncertainties for the comparison sample is:

Parameter	**Standard uncertainty**
PRM uncertainty	0,5% rel.
Verification uncertainty	0,4% rel.
Stability uncertainty	0,2% rel.

Measurement Report of NPL

Cylinder number D247880

Analytical Method

Agilent gas chromatograph with Chemstation data processing software.

Column: 4.4 m x 0.75 mm ID Silicosteel, packed with 100/120 mesh Porapak PS

Oven: isothermal, 190 °C

Carrier gas: He, 12 bar head pressure

Sampling: 12 Repeated alternate injections from the unknown and the standard using a gas sampling valve with a 100 µl loop and a separate sample selection valve.

Calibration Standards

Two standards were prepared: A 357 A (120.026 µmol/mol) and A 358 A (120.803 µmol/mol)

Preparation Method: Loop injection into evacuated cylinder, with evacuated MDV (minimized dead volume) connector and without using any purging gas

Example: Gravimetric composition of cylinder A358A

```
Mass of ethanol added            =  0.23210 +/-  0.00010 g
Masss of nitrogen added          =  1167.944 +/- 0.02000 g

    Component     µmol/mol         uncertainty    % u/c
    ---------------------------------------------------------
    N2           999878.6155        0.86774975     0.000
    ethanol           120.8031      0.05425253     0.045
```

Instrument Calibration

Multiple alternate injection with in situ bracketing (linear) calibration. No calibration curve, using standards with very close concentration. Non-linearity within the measurement range was not experienced.

Sample handling

Before doing any measurement cylinder was left in the laboratory for two weeks. Samples were taken at constant flow by using the NPL developed MDV connectors and adjustable restrictor valves.

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
Ethanol	14/09/09	120.61	0.14	3

Measurement #2

Component	**Date (dd/mm/yy)**	**Result (µmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
Ethanol	14/09/09	120.53	0.05	4

Measurement #3

Component	**Date (dd/mm/yy)**	**Result (mol/mol)**	**Standard deviation (% relative)**	**number of replicates**
Ethanol	15/09/09	120.72	0.04	5

Result

Component	**Assigned value(*x*) (µmol/mol)**	**Standard uncertainty (*u*(*x*))**
Ethanol	120.6	0.4 µmol/mol

Evaluation of measurement uncertainty

Contributing uncertainties (k=1)

Ethanol purity: 0.05 % rel.

Standard preparation: 0.04 % rel.

Average measurement uncertainty: 0.1 % rel.

Preferential adsorption of Ethanol on the cylinder wall: 0.1% rel.

Combined uncertainty (k=1): 0.16 % rel. (0.2 µmol/mol Ethanol)

Expanded uncertainty (k=2): 0.31 % rel. (0.4 µmol/mol Ethanol)

Measurement Report of VNIIM

Cylinder number: D 247881

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
C_2H_5OH	20.11.2009	119,11	0,17	4

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
C_2H_5OH	26.11.2009	119,01	0,05	3

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
C_2H_5OH	03.12.2009	119,00	0,17	5

Result

Component	Assigned value (x), µmol/mol	Standard uncertainty (u(x)) (% relative)
C_2H_5OH	119,04	0,25

DESCRIPTION OF THE METHOD

Object of analysis

The object of analysis was ethanol in nitrogen gas mixture in the cylinder under pressure with the nominal ethanol mole fraction 120 μmol/mol.
The gas mixture was in the aluminium cylinder with special treatment,
number: D 247881, V=5 L.

Measurement method

Ethanol mole fraction in the gas mixtures was determined by NDIR method.
Analysis was carried out by the gas analyzer "Aeronica - 04" (development of VNIIM) which is a part of equipment of the State Primary Standard of mole fraction and mass concentration of components in gas media GET 154-01.

Calibration standards

Characteristics of pure substances used for preparation of the calibration standards are shown in table 1.

Table 1 – Characteristics of pure substances

Component	Fraction of pure substance	Standard uncertainty	Standard uncertainty, (% relative)
Ethanol	948200 μg/g	55 μg/g	0,006
Nitrogen	999995,3 μmol/mol	0,5 μmol/mol	0,00005

The calibration standards were prepared gravimetrically by one step dilution.
There were prepared two calibration gas mixtures with ethanol mole fraction 118,45 μmol/mol and 119,17 μmol/mol.
The calibration standards were prepared in aluminium cylinders with Aculife IV treatment (Scott Gases), V = 5 L.
Verification of mole fraction was carried out by "Aeronica - 04".
Characteristics of calibration standards are shown in the table 2.

Table 2 – Characteristics of the calibration standards

Cylinder number	Component	Ethanol's mole fraction, (μmol/mol)	Standard uncertainty (gravimetry), (% relative)
D 247764	Ethanol	118,45	0,03
	Nitrogen	balance	
5700267	Ethanol	119,17	0,03
	Nitrogen	balance	

Instrument calibration

Single calibration point was used for instrument calibration.
There were made 3-5 independent measurements under repeatability conditions with 3 independent calibrations (in 3 days during 14 days period).

Sample handling

Prior to measurements the cylinders was stabilized to temperature (20±2)°C during 24 hours.

Evaluation of uncertainty of measurements

Combined standard uncertainty of ethanol mole fraction was calculated on the base of the following constituents:
- standard uncertainty of ethanol mole fraction in calibration gas mixture;
- standard uncertainty of calibration;
- standard deviation of the measurement result of ethanol mole fraction in the gas mixture (cylinder № D247881).

Uncertainty budget for ethanol mole fraction in the gas mixture (cylinder № D247881) is shown in the table 3.

Table 3 – Uncertainty budget for ethanol mole fraction in the gas mixture (cylinder № D247881).

Source of uncertainty	Type of evaluation	Standard uncertainty, $u(x_i)$, % (relative)	Coefficient of sensitivity	Contribution, $U_i(y)$, % (relative)
Preparation of the calibration gas mixture (gravimetry)	B	0,03	1	0,03
Calibration	A	0,16	1	0,16
Standard deviation of measurement result of ethanol mole fraction	A	0,18	1	0,18
Combined standard uncertainty				**0,25**
Expanded uncertainty (*k*=2)				**0,5**

Measurement Report of VSL

Laboratory : VSL
Laboratory code :
Cylinder number : D247878

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
Ethanol	2009-08-20	120,62 10^{-6}	0,36	2

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Ethanol	2009-08-26	120,64 10^{-6}	0,42	2

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Ethanol	2009-10-22	120,71 10^{-6}	0,25	2

Result

Component	Assigned value(x) (mol/mol)	Standard uncertainty ($u(x)$)
Ethanol	120,65 10^{-6}	0,42 10^{-6}

Method description

Reference Method

A Servomex Xendos 2500 NDIR is used for the analysis. The unknown mixture is measured by comparison with a suit of standards covering the range from 100 to 400 ppm (2009-08-20 and 2009-10-22) or 50 – 125 ppm (2009-08-26). Three series of measurements are made and from the second and third series the average is taken as one measurement result.

Calibration Standards

The standards are prepared by gravimetry. The ethanol is introduced into the cylinder as a liquid and vaporized. Quality of the ethanol is better than 99,9% and the water content is determined by Karl fisher. 6.0 nitrogen is used. The uncertainty in the standards is 0,25% rel.

Instrument Calibration

Between 5 and 8 standards are measured. The responses are corrected for pressure and zero measurement and used to make a first order calibration curve.

Sample handling:

The mixture was stored at ambient temperature in the same manner as the standards. All mixtures were connected to the analyser by using a pressure reducing valve and a mass flow controller.

Evaluation of measurement uncertainty

The uncertainty of the measurement directly comes from using ISO6143 with the mixture as the unknown and the standards to form the calibration curve. The uncertainty of the determined ethanol molar fraction is the pooled average of the 3 individual results.