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CCQM-K93:
Preparative comparison of ethanol in nitrogen

FINAL REPORT

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CCQM-K93:
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EXECUTIVE SUMMARY

This report presents the results of CCQM-K93, a key comparison between 13 National Measurement Institutes (NMIs), which tested the capability of the NMIs to prepare standard gas mixtures of ethanol at a nominal amount fraction of 120 µmol/mol in nitrogen. This composition is typical of the levels used to calibrate evidential breath analysers in many countries. Such standards fulfil the agreed requirements of the International Organization of Legal Metrology (OIML) for the calibration of evidential breath-alcohol analysers.

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1. INTRODUCTION

This key comparison involves standard gas mixtures of ethanol at a nominal amount fraction of 120 µmol/mol in nitrogen. This composition is typical of the levels used to calibrate evidential breath analysers in many countries. Such standards fulfil the agreed requirements of the International Organization of Legal Metrology (OIML) for the calibration of evidential breath-alcohol analysers and provide a more accurate calibration at field level than ethanol/water solution-based simulators, which are highly sensitive to variations in the temperature of the solution.

The comparison uses the preparative model of a key comparison developed by the CCQM GAWG [1,2] and used previously for key comparisons of oxygen (CCQM-K53) [3] and hexane (CCQM-K54) [4]. It requires participants to prepare a standard mixture of ethanol in nitrogen and submit it to the coordinating laboratory for analysis. It provides a direct test of the capability of the participants to prepare accurate reference materials of this type [5,6].

This key comparison of gaseous ethanol in nitrogen follows a series of analytical comparisons each linked to CCQM-K4 (see Table 1). In each of these comparisons travelling standards were prepared by the coordinating laboratory (NPL) and circulated to participating laboratories for them to analyse. These comparisons only tested the capabilities of participants to analyse gas mixtures.

Comparison	Analyte / matrix	Date	Ref
CCQM-K4	Ethanol / air	1999	[7]
EURAMET.QM-K4	Ethanol / air	2000	[8]
APMP.QM-K4	Ethanol / air	2000	[9]
APMP.QM-K4.1	Ethanol / nitrogen	2005-2006	[10]
EURAMET.QM-K4.1	Ethanol / nitrogen	2009	[11]

Table 1. Key comparisons of ethanol in air and nitrogen.

2. OPERATION OF THE COMPARISON

2.1. PARTICIPANTS

The 13 participating laboratories are shown in Table 2 alongside their Calibration and Measurement Capabilities (CMCs) for mixtures of ethanol in nitrogen and air. The matrix gas chosen for this key comparison is nitrogen since it is most widely used matrix by NMIs.

2.2. TIMETABLE

The mixtures were measured by the coordinating laboratory during December 2011 and January 2012.

NMI	Matrix gas	
	Nitrogen	Air
CERI	RM & MC	RM & MC
INMETRO	-	-
IPQ	RM & MC	-
KRISS	RM & MC	RM & MC
LNE	-	-
MKEH	RM & MC	RM & MC
NIM	RM & MC	RM & MC
NIST	RM & MC	-
NMISA	MC	MC
NPL	RM & MC	RM & MC
SMU	RM & MC	-
VNIIM	RM & MC	-
VSL	RM & MC	RM & MC

Table 2. Participants and their CMCs for ethanol in air and nitrogen in this range registered in the Key Comparison Database in April 2011 (RM = reference materials; MC = measurement capability).

2.3. COMPARISON METHOD USED BY THE COORDINATING LABORATORY

The coordinating laboratory developed a highly repeatable gas chromatography method for comparing gas mixtures for CCQM-K93. The method used an Agilent 6890 gas chromatograph with a flame ionisation detector (FID), DB-624 column (75 m long x 0.535 mm diameter with a 3 µm film thickness) and a 0.5 ml sample loop. Ultra-pure helium (Air Products BIP grade) was used as the carrier gas. A schematic diagram of the GC system used is shown in Figure 1. The variation in the response of the FID detector to the amount fraction of ethanol was shown to be linear in nature.

Each comparison consisted of a series of six injections of the 'unknown' NMI standard alternating with six alternate injections of a working reference standard (WRS) with a nominal ethanol amount fraction of 120 µmol/mol. Tests performed during the course of the comparison showed the WRS to be sufficiently stable that no correction for instability needed to be applied to the dataset.

The injections were carried out at intervals of one minute and an example chromatogram is shown in Figure 2. The first and last of these 12 injections was discarded and the ratio of the mean of the remaining five measurements of the NMI standard to the mean of the remaining five measurements of the WRS was evaluated. This sequence was repeated 15 times leading to a value for the ratio r_i:

$$r_i = \frac{1}{15}\sum_{1}^{15}\frac{\sum_{1}^{5} a_i}{\sum_{1}^{5} a_{wrs}} \qquad (1)$$

Where a_i is the peak area recorded from the NMI standard and a_{wrs} is the peak area recorded from the WRS.

An example dataset obtained from the comparison of one NMI standard and the WRS is shown in Table 3. In this example, the relative standard deviation of the 15 values of the ratio of the mean area of the NMI standard to the mean area of the WRS is 0.074 %.

We have considered the whole set of data arising from the comparison against each of the 13 submitted mixtures, and have evaluated the standard deviation of the measured ratios which have been pooled to create a pooled value applicable to all instances of r of $u(r)$ = 0.0651 µmol/mol (corresponding to a relative standard uncertainty of 0.054 %). We have not used the standard error of the mean of these data, since the measurements made in each set of comparisons with the GC are significantly correlated by the drift in the response of the GC detector.

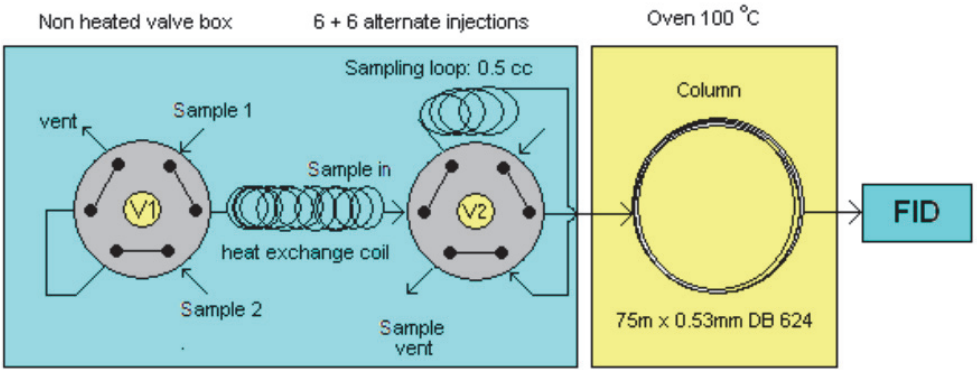

Figure 1. Schematic of the GC system used for comparison of standards by the coordinating laboratory.

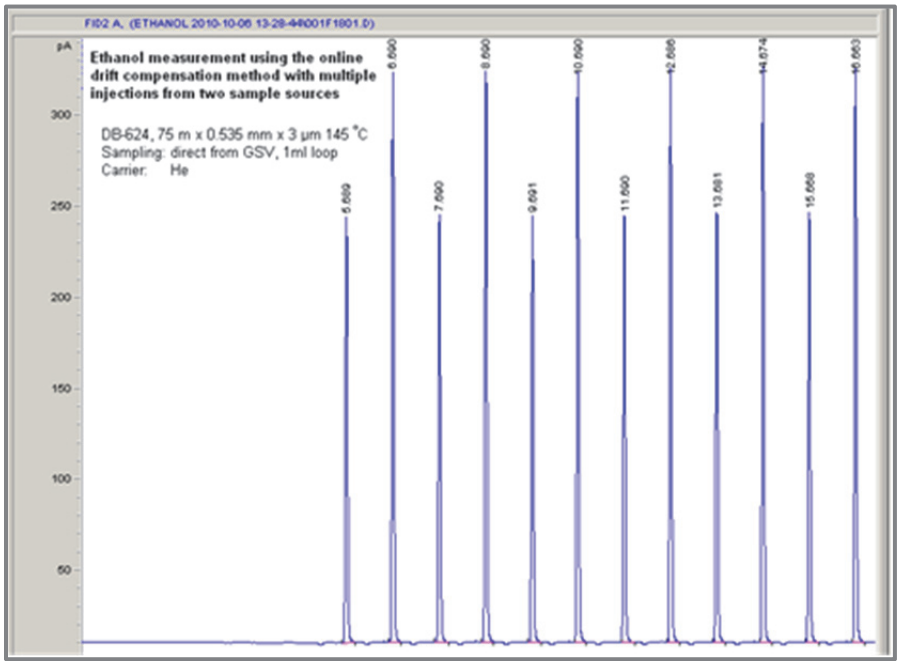

Figure 2. Example of output from the GC in a comparison of two standards. (This example shows two standards with a greater difference in amount fraction than was used in CCQM-K93.)

Standard	Run														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
WRS	310.08	311.32	310.94	310.27	310.26	310.81	310.55	310.84	311.12	311.11	310.37	310.50	310.34	310.64	310.27
NMI	308.41	308.39	308.59	307.84	307.67	308.61	308.06	307.58	307.85	308.63	307.71	307.38	308.97	308.49	308.05
WRS	311.95	311.89	311.66	310.58	311.73	310.55	310.84	311.59	311.21	311.32	311.44	311.34	311.53	311.86	311.84
NMI	309.34	308.93	308.23	307.50	308.35	307.40	308.26	308.06	307.91	308.74	308.04	307.74	308.87	308.46	307.40
WRS	312.44	312.87	311.74	311.79	312.33	311.21	311.44	311.04	311.08	311.74	312.27	310.92	311.67	312.32	311.58
NMI	308.88	308.61	308.60	307.92	308.94	307.87	307.73	307.77	309.07	308.35	308.94	308.72	309.03	308.21	307.75
WRS	311.97	312.23	312.23	311.52	312.15	311.66	311.77	311.35	312.21	311.69	311.63	311.46	312.34	311.85	311.52
NMI	309.54	308.33	308.48	308.42	308.29	308.26	309.00	308.08	308.23	308.51	308.41	308.26	308.46	308.73	309.18
WRS	313.40	312.01	312.09	310.81	312.08	311.15	311.97	312.31	311.86	311.81	311.69	310.85	311.43	311.91	311.51
NMI	309.01	308.82	308.49	308.52	307.57	307.77	308.76	308.38	309.60	309.06	308.51	307.89	308.15	309.11	308.03
WRS	312.29	311.44	311.32	311.15	310.71	311.22	311.92	311.07	311.74	313.16	311.98	311.25	311.53	311.82	311.11
NMI	309.54	308.10	307.29	308.18	308.43	307.69	307.98	307.64	308.72	309.77	308.82	308.66	309.70	308.99	308.54

Table 3. Peak areas counts from a sequence of alternate injections of WRS and NMI standard over 15 consecutive runs. The first and last value in each run were excluded before calculating the value of r_i.

2.4. MIXTURES SUBMITTED BY PARTICIPANTS

Each of the participating NMIs submitted a mixture together with a value for the amount fraction of ethanol in nitrogen, x_i, and its standard uncertainty, $u(x_i)$. Details of the mixtures and submitted values are given in Tables 4 and 5. It should be noted that due to the short timescale of the comparison, a number of participants submitted values of $u(x_i)$ smaller than those that would be provided routinely to customers (which may include an uncertainty component for the stability of the mixture).

Participant	Cylinder number	Cylinder vol (L)	Cylinder type	Valve type	Valve material	Mixture received
CERI	CPB 19112	9.6	Luxfer (ethanol passivation)	Hamai (G-12)	Brass	08.11.11
INMETRO	MT 4454	5	Scott (Aculife IV)	Cd (98331)	SS	14.12.11
IPQ	S21 4776	5	Scott (Aculife IV)	Cd (D200)	SS	17.11.11
KRISS	D80 7708	10	Luxfer (untreated)	Unknown	SS	25.11.11
LNE	D79 5176	10	Air Products (untreated)	Cd (D200)	SS	10.10.11
MKEH	OMH 138	9.4	Luxfer (untreated)	Unknown	Brass	12.10.11
NIM	CAL017777	5.9	Luxfer (untreated)	Cd (D200)	SS	01.12.11
NIST	CAL017426	5.9	Scott (Aculife IV)	Cd (D200)	Brass	30.11.11
NMISA	D95 8417	5	Luxfer ('fluorination')	Cd (D304)	SS	21.10.11
NPL	A387	10	BOC (Spectraseal)	Cd (D304)	SS	05.12.11
SMU	0023F	5	Scott (Aculife IV)	Cd (98331)	SS	25.10.11
VNIIM	D24 7754	5	Scott (Aculife IV; passivated)	Cd (D200)	SS	25.11.11
VSL	ML 6701	5	Scott (Aculife IV)	Cd (98331)	SS	28.09.11

Table 4. Details of mixtures submitted by participants. Cd indicates Ceodeux; SS indicates stainless steel.

Participant	Purity of ethanol (µmol/mol)	Mass of ethanol added (mg)	Certified value (µmol/mol)
CERI	998950 ± 500	216.97 ± 0.05	118.68 ± 0.065
INMETRO	998504 ± 8	128.0 ± 0.163	119.693 ± 0.12
IPQ	998700 ± 500	115.9 ± 0.024	120.89 ± 0.60
KRISS	999000 ± 250	227.6 ± 0.05	119.87 ± 0.13
LNE	999377 ± 23	259.2 ± 0.053	119.31 ± 0.12
MKEH	999000 ± 600	235.5 ± 0.19	120.03 ± 0.6
NIM	998400 ± 800	137.01 ± 0.016	119.38 ± 0.18
NIST	999682 ± 105	129.4 ± 0.1	121.29 ± 0.31
NMISA	999500 ± 150	150.8 ± 0.05	120.08 ± 0.4
NPL	999780 ± 200	224.52 ± 0.1	120.03 ± 0.054
SMU	996230 ± 670	119.79 ± 0.1	120.72 ± 0.43
VNIIM	878080 ± 50	125.36 ± 0.034	120.30 ± 0.21
VSL	999619 ± 3	139.3 ± 0.1	119.49 ± 0.2

Table 5. Values for the purity of the ethanol, the mass of ethanol added and the certified value for each mixture submitted. All the stated uncertainties are standard (k = 1) uncertainties.

The mixtures submitted by the participants were prepared by adding ethanol to the cylinder using a number of different methods. These are summarised in Table 6, which also indicates whether a buoyancy correction was applied when the mass of ethanol added was calculated.

Participant	Method used for addition of ethanol	Was a buoyancy correction applied?
CERI	Stainless steel vessel	No
INMETRO	Syringe	No
IPQ	Syringe	Yes
KRISS	Syringe	No
LNE	Syringe	Yes
MKEH	Glass container	Yes
NIM	Syringe	Yes
NIST	Syringe	No
NMISA	Stainless steel vessel	No
NPL	Stainless steel vessel	No
SMU	Syringe	No
VNIIM	Capillary purged with nitrogen	No
VSL	Syringe	Yes

Table 6. Details of the preparation method used by each participant

3. RESULTS & DISCUSSION

3.1. RESULTS FROM COMPARISON OF THE MIXTURES

The result of the comparison of each NMI mixture against the working reference standard is a value for r_i as defined by equation (1). As the peak areas represent the amount fraction of ethanol in the mixture, then:

$$r_i = x_i / x_{wrs} \qquad (2)$$

Where x_i is the amount fraction of ethanol in the NMI standard and x_{wrs} is the amount fraction of ethanol in the WRS.

The difference between the value measured with respect to the WRS and the submitted (certified) value is:

$$x_i - x_i^{NMI} = \left(r_i \times x_{wrs}\right) - x_i^{NMI} \qquad (3)$$

Where x_i^{NMI} is the submitted (certified) amount fraction of ethanol in the NMI standard.

In Figure 3, we present the results of the comparisons against the WRS in terms of the relative values of Δ_i given by:

$$\Delta_i = \left(r_i \times x_{wrs} / x_i^{NMI} - 1\right) \times 100 \qquad (4)$$

with error bars equal to ± 0.054 %, which corresponds to the standard uncertainty of the comparison with the WRS. The calculated values of Δ_i are shown in Table 7, and the data are plotted in Figure 3, using a value of x_{wrs} = 120 µmol/mol.

Participant	Date analysed	x_i^{NMI} (µmol/mol)	r_i	Δ_i
IPQ	12.01.12	120.89	1.0010	-0.63%
INMETRO	15.01.12	119.693	0.9920	-0.55%
NMISA	10.01.12	120.08	0.9954	-0.52%
VSL	13.01.12	119.49	0.9913	-0.45%
SMU	11.01.12	120.72	1.0029	-0.31%
LNE	13.12.11	119.31	0.9938	-0.04%
NIST	20.01.12	121.29	1.0109	0.02%
VNIIM	10.01.12	120.30	1.0032	0.07%
NPL	23.01.12	120.03	1.0013	0.10%
NIM	18.01.12	119.38	0.9961	0.13%
CERI	19.01.12	118.68	0.9909	0.19%
KRISS	21.01.12	119.87	1.0023	0.33%
MKEH	23.01.12	120.03	1.0045	0.43%

Table 7. Results of the comparisons against the working reference standard.

3.2 CALCULATION OF THE KEY COMPARISON REFERENCE VALUE

In order to determine the key comparison reference value (KCRV), the value of the WRS must be eliminated from the calculation, and replaced by the consensus value resulting from each of the comparisons. The method used for carrying out this calculation is described in Annex A.

The degrees of equivalence are calculated using:

$$DoE_i = \frac{x_i^{NMI}}{r_i} - x_{KCRV} \qquad (5)$$

Where x_{KCRV} is the KCRV obtained from the inferred amount fractions of ethanol in the NMI standards.

The uncertainty in the degrees of equivalence is given by:

$$u(DoE_i) = \sqrt{u^2\left(\frac{x_i^{NMI}}{r_i}\right) - u^2\left(x_{KCRV}\right)} \qquad (6)$$

The uncertainty in the KCRV in equation (6) is subtracted because it is correlated with the uncertainties in the NMI values.

At the 29th meeting of the CCQM GAWG in April 2013, discussions were undertaken about the possible influence of absorption effects and buoyancy corrections on the KCRV. All of the participating laboratories were subsequently asked to confirm whether their uncertainty in the submitted (certified) amount fraction of ethanol, $u\left(x_i^{NMI}\right)$, included appropriate contributions for

adsorption effects and buoyancy corrections. The majority of laboratories responded by confirming that they had included appropriate contributions for these effects, but two laboratories (INMETRO and SMU) submitted revised values of $u\left(x_i^{NMI}\right)$.

Following further discussions at the 30th meeting of the CCQM GAWG in November 2013, it was agreed that the results from INMETRO and SMU should therefore *not* contribute to the calculation of the KCRV. The KCRV calculated following the implementation of this decision was:

KCRV = 119.888 ± 0.046 (*k* = 1 uncertainty)

The values of DoE_i and $u(DoE_i)$ calculated using this KCRV are shown in Table 8 and plotted in Figure 4. Note that the results shown for INMETRO and SMU use the values of $u\left(x_i^{NMI}\right)$ originally submitted by these laboratories.

Participant	x_i^{NMI} (µmol/mol)	$u(x_i^{NMI})$ (µmol/mol)	r_i	Inferred value for WRS (µmol/mol)	DoE_i (µmol/mol)	$u(DoE_i)$ (µmol/mol)
IPQ	120.89	0.60	1.0010	120.764	0.876	0.605
INMETRO	119.693	0.12	0.9920	120.658	0.770	0.127
NMISA	120.08	0.40	0.9954	120.633	0.745	0.412
VSL	119.49	0.20	0.9913	120.540	0.651	0.205
SMU	120.72	0.43	1.0029	120.369	0.481	0.435
LNE	119.31	0.12	0.9938	120.050	0.162	0.127
NIST	121.29	0.31	1.0109	119.980	0.092	0.290
VNIIM	120.30	0.21	1.0032	119.915	0.027	0.260
NPL	120.03	0.054	1.0013	119.880	-0.008	0.066
NIM	119.38	0.18	0.9961	119.849	-0.039	0.185
CERI	118.68	0.065	0.9909	119.773	-0.115	0.076
KRISS	119.87	0.13	1.0023	119.601	-0.287	0.137
MKEH	120.03	0.6	1.0045	119.487	-0.401	0.599

Table 8. Calculated degrees of equivalence for participants in CCQM-K93.

4. SUPPORTED CMC CLAIMS

During its 28th meeting in October 2012, the CCQM GAWG agreed that this key comparison can be used to support CMC claims for ethanol over an amount fraction range of 50 – 500 µmol/mol in a matrix of either nitrogen or synthetic air.

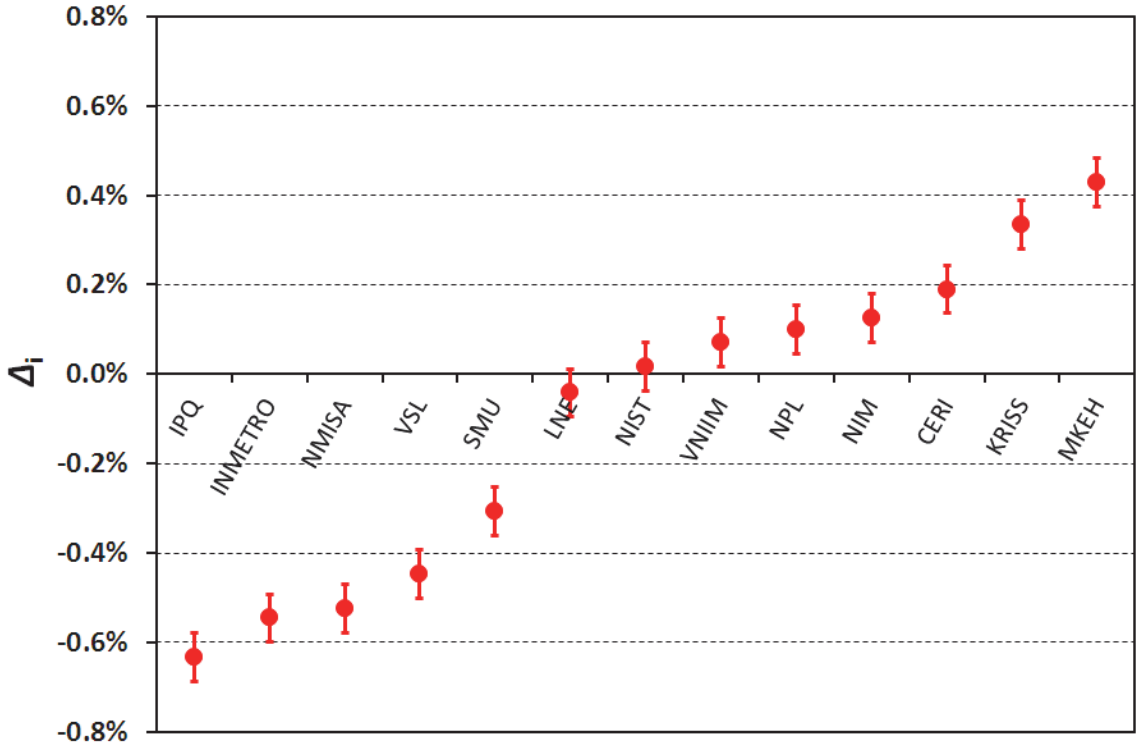

Figure 3. Values of Δ_i relative to the value of the WRS (which has been taken as 120 µmol/mol). The error bars are equal to ± 0.054 %, which corresponds to the standard uncertainty of the comparison with the WRS.

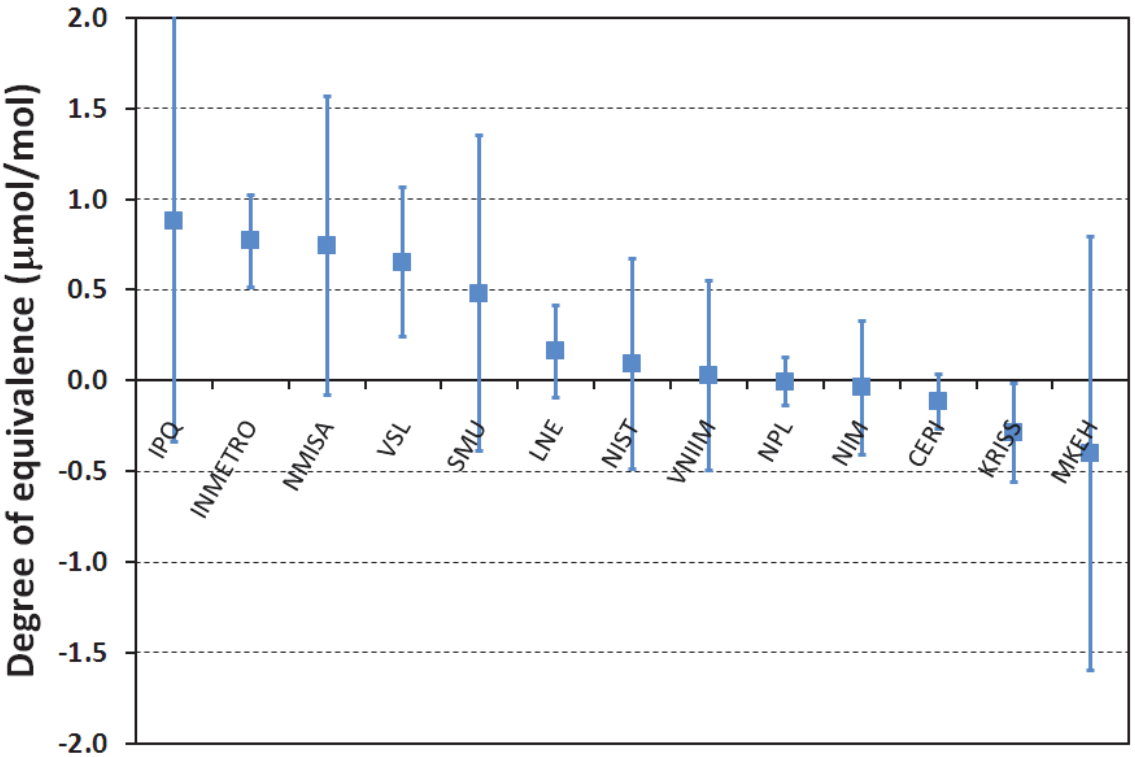

Figure 4. Calculated degrees of equivalence. The error bars represent the expanded uncertainty $U(DoE_i)$ calculated according to equation (6).

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ANNEX A: METHOD USED FOR DETERMINING THE KEY COMPARISON REFERENCE VALUE

Each of the participating NMIs submitted a standard mixture together with a value for the amount fraction of ethanol in nitrogen, x_i, and its standard uncertainty, $u(x_i)$. (The values of $u(x_i)$ are independent).

Each standard submitted by the participants was compared with a working reference standard (WRS) and the following ratio, r_i, was determined for each mixture:

$$r_i = x_i / x_{wrs} \tag{A1}$$

The relative standard uncertainty in the determination of r_i was approximately 0.054 %.

The KCRV was calculated by determining the 'best estimate' of the value of the WRS, $\hat{x}_{wrs}$. This was achieved by solving the following equation:

$$\min \sum_i \frac{\left(x_{wrs} - x_i^{NMI} / r_i\right)^2}{u^2\left(x_i^{NMI} / r_i\right)} \tag{A2}$$

for which the solution [12] is:

$$\hat{x}_{wrs} = KRCV = \frac{\sum_i \left(\frac{1}{u^2(x_i^{NMI} / r_i)} \frac{x_i^{NMI}}{r_i} \right)}{\sum_i \left(\frac{1}{u^2(x_i^{NMI} / r_i)} \right)} \tag{A3}$$

where:

$$\frac{u(x_i^{NMI} / r_i)^2}{(x_i^{NMI} / r_i)^2} = \frac{u(x_i^{NMI})^2}{\left(x_i^{NMI}\right)^2} + \frac{u(r_i)^2}{r_i^2} \tag{A4}$$

$u(r_i)$ is taken as strictly the repeatability of the comparison, in order not to bring any uncertainty due to in the value of x_{wrs} into the calculation.

The uncertainty in the KCRV [12] is given by:

$$u\left(\hat{x}_{wrs}\right) = u\left(KCRV\right) = \sqrt{\frac{1}{\sum_i \left(\frac{1}{u^2(x_i^{NMI} / r_i)} \right)}} \tag{A5}$$

The value component of the degree of equivalence for each participant [12] is then:

$$DoE_i = \frac{x_i^{NMI}}{r_i} - x_{KCRV} \tag{A6}$$

ANNEX B: MEASUREMENT REPORTS

B.1. Measurement report of CERI

Cylinder Number: CPB-19112
Amount fraction of ethanol: 118.68 μmol/mol
Coverage factor: 2
Expanded uncertainty : 0.13 μmol/mol

Purity of ethanol: 0.99895 mol/mol

Component	Amount fraction	Uncertainty (k=2)	Assumed distribution
Ethanol	0.99895 mol/mol	0.0010 mol/mol	Normal

CERI used a NMIJ CRM.

Water concentration for impurity in the ethanol was 18.1 μg/g, acetaldehyde concentration was 1.5 μg/g and 2-propanol concentration was 5.2 μg/g.

Impurities of nitrogen: 0.9999993 mol/mol

Component	Amount fraction μmol/mol	Uncertainty (k=2) μmol/mol	Assumed distribution
Carbon monoxide[1)]	Under 0.003	0.0017	Rectangle
Carbon dioxide[1)]	Under 0.003	0.0017	Rectangle
Methane[1)]	Under 0.004	0.0023	Rectangle
Nitrogen oxide[1)]	Under 0.002	0.0012	Rectangle
Sulfur Dioxide[1)]	Under 0.002	0.0012	Rectangle
Hydrogen[2)]	Under 0.05	0.0029	Rectangle
Oxygen[2)]	Under 0.05	0.0029	Rectangle
Total Hydrocarbon[2)]	Under 0.05	0.0029	Rectangle
Water[2)]	Under 0.5	0.29	Rectangle

1): These components were measured by CERI.
2): These components were measured by a gas manufacture.

Gravimetric Preparation Data

The gas standard for CCQM-K93 was prepared gravimetrically through one step dilution according to ISO6142. CERI used two balances. One was used for weighing of aluminium alloy cylinders, the other was used for weighing of stainless steel vessels. The vessel contained ethanol. And the mass of ethanol filled into the cylinder was calculated from the mass of the vessel before and after the preparation of gas standard.

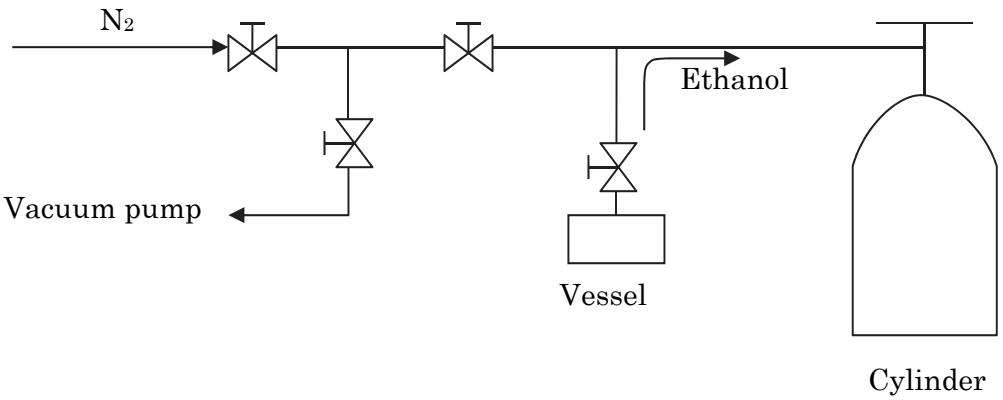

Fig. Preparation system

Specification of Balance for cylinders

Model No.: YMC Co., Ltd. Model: H2-30K
Resolution: 1 mg, Capacity: 30 kg
Uncertainty (k=2): 0.004022 g

Specification of Balance for stainless steel vessels

Model No.: Mettler-Toledo Model AT1005 comparator
Resolution: 0.01 mg, Capacity: 1 kg
Uncertainty (k=2): 6.914×10^{-5} g

Weighing method for cylinders

A-B-A-B substitution method was used for cylinders. A is a K93 cylinder and B is a tare cylinder.

Weighing method for vessels

A'-B'-A'-B'-A'-B'-A'-B' substitution method was used for vessels. A' is a vessel contained ethanol and B' is a tare vessel.

Difference mass between the K93 cylinder and the tare cylinder before preparation: 36.345 g
Difference mass between the K93 cylinder and the tare cylinder after preparation: 1146.938 g
Difference mass between the vessel and the tare vessel before preparation: 2.478445 g
Difference mass between the vessel and the tare vessel after preparation: 2.261478 g

Uncertainty source	Estimate x_i	Assumed distribution	Standard uncertainty $U(x_i)$	Sensitivity factor, $\lvert c_i \rvert$	Contribution to standard uncertainty, $u(y_i)$
Mass of the cylinder, before filling	36.345 g	Normal	0.003597 g	1.069×10^{-7} g^{-1}	3.845×10^{-10}
Mass of the cylinder, after filling	1146.938 g	Normal	0.03071 g	1.069×10^{-7} g^{-1}	3.283×10^{-9}
Mass of the vessel, before filling	2.478445 g	Normal	3.457×10^{-5} g	0.0005470 g^{-1}	1.891×10^{-8}
Mass of the vessel, after filling	2.261478 g	Normal	3.457×10^{-5} g	0.0005470 g^{-1}	1.891×10^{-8}
Purity of ethanol	0.99895 mol/mol	Normal	0.0005 mol/mol	0.0001188	5.940×10^{-8}
Molar mass of ethanol	46.0684 g/mol	Normal	0.0005900 g/mol	2.576×10^{-6} mol/g	1.520×10^{-9}
Molar mass of nitrogen	28.0134 g/mol	Normal	0.0001400 g/mol	4.236×10^{-6} mol/g	5.930×10^{-10}
Impurities in nitrogen	0.6610 μmol/mol	Normal	0.1450×10^{-6} mol/mol	1.187×10^{-4} mol/mol	1.721×10^{-11}
Impurities in ethanol					Negligible for the uncertainty

Combined uncertainty: 0.06525 μmol/mol
Expanded uncertainty: 0.13 μmol/mol

B.2. Measurement report of INMETRO

(Note: this measurement report is that originally submitted by INMETRO at the time of the comparison.)

1. CYLINDER DETAILS

Cylinder Number	MT4454
Date of mixture preparation	06/10/2011
Volume (L)	5
Total Pressure (bar)	105
Connection type (e.g. DIN1, BS14 etc.)	DIN1

2. SOURCE OF ETOH

JT Baker – JTBC59

2.1. PURITY TABLE FOR NOMINALLY PURE ETOH

Complete for all components considered:

Component	Method	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
C_2H_5OH	GC-FID	0.998504460	0.000008012
H_2O	Karl Fischer	0.001495540	0.000004786

3. SOURCE OF N_2 (6.0)

White Martins – WMN260

3.1. PURITY TABLE FOR NOMINALLY PURE N_2

Component	Method	Mole Fraction (mol/mol)	Uncertainty (mol/mol)
N_2	ISO 6142 purity estimation from supplier info	0.999999400	0.000000200
CO	ISO 6142 purity estimation from supplier info	0.000000050	0.000000290
H_2O	ISO 6142 purity estimation from supplier info	0.000000250	0.000000140
O_2	ISO 6142 purity estimation from supplier info	0.000000250	0.000000140

C_xH_y*	ISO 6142 purity estimation from supplier info	0.000000050	0.000000029

* total hydrocarbons

4. PREPARATION OF FINAL MIXTURE

Parent gases	$x_{(grav+pur)}$ (mol/mol)	u(x) (mol/mol)
C_2H_5OH	119.693×10^{-6}	0.003×10^{-6}
N_2	0.9998795	0.0000002

5. PURITY TABLE FOR FINAL MIXTURE

Complete for all components considered:

Component	$x_{(grav+pur)}$ (mol/mol)	u(x) (mol/mol)
N_2	0.9998795278953678	0.0000001999784795
CO	0.0000000499940064	0.0000000289965237
H_2O	0.0000004292436668	0.0000001399844082
O_2	0.0000002499700320	0.0000001399832179
C_xH_y	0.0000000499940064	0.0000000289965237
C_2H_5OH	0.0001196929029207	0.0000000031010078

6. VERIFICATION ANALYSIS

The prepared reference gas mixture was measured against Inmetro's PSMs.

The reference values for the amount-of-substance fractions are obtained by interpolation using a calibration curve.

The results that follow are presenting the uncertainty as standard deviation of the measurements, with 08 (eight) repetitions in one single day.

The results from the non-dispersed infrared measurements have been fitted using a linear function, in accordance with ISO 6143, using the software b-least.

The linear function reads for each component as follows: $y = f(x,a) = a_0 + a_1 x$

A. Ethanol

Table A1 – Calibration mixtures for ethanol

Mixture	x μmol mol^{-1}	u(x) μmol mol^{-1}	y	u(y)
PSM107534	99.2107	0.0025	101.98	0.13
PSM146796	119.4433	0.0031	120.39	0.08
PSM116847	199.5495	0.0051	198.53	0.07
PSM133818	282.8684	0.0073	282.54	0.28

Table A2 – Regression coefficients for ethanol

Coefficient		
	value	u
a_0	-4.3393E00	1.7613E-01
a_1	1.0257E00	1.0601E-03

Table A3 – Reference values for ethanol

Mixture	y	u(y)	x_{calib} μmol mol^{-1}	$u(x_{calib})$ μmol mol^{-1}	$u(x_{calib})/x_{calib}$ % rel	X_{prep} μmol mol^{-1}	Δx μmol mol^{-1}	$\Delta x/x_{prep}$ % rel
MT4454	120.79	0.10	119.56	0.12	0.10	119.69	0.13	0.11

7. FINAL RESULTS

The results are presented in following table with data:

x_{prep} amount of substance fraction , from preparation (μmol.mol^{-1})

u_{prep} uncertainty of x_{prep} from gravimetrical preparation and purity (μmol.mol^{-1})

u_{ver} uncertainty from verification (μmol.mol^{-1})

u_{st} uncertainty of stability (μmol.mol^{-1})

u_{cert} final uncertainty of x (μmol.mol^{-1})

U(k=2) stated uncertainty of x, at 95% level of confidence (μmol.mol^{-1})

Standard uncertainty of the mixture was calculated with following formula:

$$u_{cert} = \sqrt{u_{prep}^2 + u_{ver}^2 + u_{st}^2}$$

Component	x_{prep} μmol mol^{-1}	u_{prep} μmol mol^{-1}	u_{ver} μmol mol^{-1}	u_{st} μmol mol^{-1}	u_{cert} μmol mol^{-1}	*X* μmol mol^{-1}	*U(k=2)* μmol mol^{-1}
ETHANOL	119.69	0.0031	0.1210	-	0.12	**119.69**	**0.24**

B.3. Measurement report of IPQ

Gravimetric Results:

Purity of ethanol (µmol/mol)	Mass of ethanol added (mg)	Gravimetric value (µmol/mol)
998700 ± 500	115,9 ± 0,024	120,89

Analytical Results:

Measurement No. 1	Date	Result (10^{-6} mol/mol)	stand. deviation (% relative)	number of sub-measurements
Ethanol	2011-10-18	120,4	0,1	3

Measurement No. 2	Date	Result (10^{-6} mol/mol)	stand. deviation (% relative)	number of sub-measurements
Ethanol	2011-10-19	121,0	0,1	3

Measurement No. 3	Date	Result (10^{-6} mol/mol)	stand. deviation (% relative)	number of sub-measurements
Ethanol	2011-10-20	121,0	0,1	3

Results:

Gas mixture	Result (assigned value) (10^{-6} mol/mol)	Coverage factor	Assigned standard uncertainty (*) (10^{-6} mol/mol)
Ethanol	120,89	2	0,6

Reference Method:
The preparation was done according to ISO 6142:2001- Gravimetric method with syringe introduction.
Non Dispersive Infrared Spectroscopy (NDIR): Analyzer: URAS 4
Data Collection: Auto-sampler - Software Sira version 2.0

Calibration Standards:
It was used three primary standard mixtures from VSL and two primary standard mixtures from NPL.
Composition of calibrants:

Ethanol cylinder	Assigned value(x) (mol/mol)	Standard uncertainty (u(x))
VSL9946	80,1 $x10^{-6}$	0,4 $x10^{-6}$
NPL0296	120,0 $x10^{-6}$	0,5 $x10^{-6}$
VSL3559	220,0 $x10^{-6}$	1,3 $x10^{-6}$
NPL1718	315,0 $x10^{-6}$	1,0 $x10^{-6}$
VSL9944	520,0 $x10^{-6}$	1,3 $x10^{-6}$

Instrument Calibration:
The calibration instrument was done according to ISO 6143. We have used the B_Least program to determine the best model for data handling. All components of mixture have a goodness of fit less than 2 using a linear or quadratic function.
For all components were used a set of five PRM (from VSL and NPL). At least three repeated analyses were performed in three independent days.
Manual calibration (zero and span are calibrated separately by pressing the analyzer system display and control unit softkeys)

Sample Handling:
The cylinder was storage at ambient temperature in a storage room.
The cylinder was connected to a valve to reduce the pressure. The samples were transferred to the analyser through an auto-sampler.

Uncertainty:
The uncertainty measurement was done according ISO GUM: 1995 "Guide to the Expression of Uncertainty in Measurement".
The uncertainty of measurement associated with the final result has been evaluated and includes three main uncertainty sources:

- Uncertainty in calibration;
- Uncertainty of repeatability;
- Uncertainty of reproducibility

These uncertainties were combined and the result was multiplied by a coverage factor with a confidence interval of 95 %.

a) Uncertainty table:

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Repeatability		normal	$2{,}012 \times 10^{-7}$	1	$2{,}012 \times 10^{-7}$
Reproducibility		normal	$7{,}294 \times 10^{-8}$	1	$7{,}294 \times 10^{-8}$
Calibration		normal	$5{,}739 \times 10^{-7}$	1	$5{,}739 \times 10^{-7}$

Coverage factor: 2
Expanded uncertainty: 1,2 $\times 10^{-6}$ mol/mol

B.4. Measurement report of KRISS

Certification of the mixture gas submitted:

The certified concentration of KRISS ethanol gas mixture(cylinder number, D80 7708) for the CCQM–K93 is **119.87×10^{-6} mol/mol ± 0.26×10^{-6} mol/mol (level of confidence, 95 %).**

1 Introduction

For the key comparison and the certification of gas mixture, below steps were strictly followed by the KRISS standard procedure.

1. Purity analysis of ethanol solution and nitrogen gas
2. Preparation of 6 bottles of gas mixture by gravimetric technique
3. Reproducibility test for the gravimetric preparation by GC & FTIR analysis
4. Determination of the adsorption factor to the inside surface of the cylinder wall by GC&FTIR analysis
5. Selection of cylinder and certification for CCQM –K93

2 Preparation

2.1 Purity Analysis

In order to check the purity of ethanol and nitrogen, GC-FID, GC-DID, GC-AED and Karl-Fisher titration method were assisted. Through this step, we determined the purity of ethanol solution was 0.999 mol/mol ± 0.0005 mol/mol(95 % level of confidence) and the purity of nitrogen was 0.999998 mol/mol ± 0.0000005 mol/mol(95 % level of confidence).

2.2 Gravimetric Preparation of gas mixture

For this key comparison, 6 bottles of gas mixture were prepared individually by gravimetric technique. The specification of balances and technique used are summarized as follows;

- Balances used;
  - Mettler Toledo, XP26003L, 1 mg for cylinder weighing
  - OHAUS,USA, EPG214C, 0.1 mg for Syringe weighing
  -
- Technique used;
  - A-B-A, Substitution method

The concentration obtained by gravimetric technique for cylinder(D80 7708) was 120.094×10^{-6} mol/mol and the uncertainty associated with only gravimetric process was evaluated and here are summarized results as follows;

- Uncertainty budget only for the gravimetric process:
  - Model equation; $$C_{grav.} = \frac{P_{EtOH} \cdot \frac{M_{EtOH}}{MW_{EtOH}}}{P_{EtOH} \cdot \frac{M_{EtOH}}{MW_{EtOH}} + \frac{M_{N2}}{MW_{N2}}}$$

− Uncertainty budget

Uncertainty source	Estimate x_i	Type	Assumed distribution	Standard uncertainty $u(x_i)$
Weight of EtOH source	0.2276 g	B	Square	0.5×10^{-4} g
Weight of nitrogen source gas	1151.60 g	B	Square	11.0×10^{-3} g
Molecular weight of EtOH	46.0684 g/mol	B	Normal	0.9×10^{-3} g/mol
Molecular weight of Nitrogen	28.01348 g/mol	B	Normal	0.07×10^{-3} g/mol
EtOH Source purity	0.999 mol/mol	B	Normal	0.00025 mol/mol
Nitrogen Balance purity	0.999998 mol/mol	B	Normal	0.00000025 mol/mol
Concentration by gravimetric preparation	120.094×10^{-6} mol/mol	Combined	Normal	0.032×10^{-6} mol/mol

2.3 Reproducibility test for the gravimetric preparation

For the reproducibility test, 6 bottles of gas mixture prepared were analysed and compared the sensitivities with GC, and verified that the gravimetric values were not deviated from the target values with standard uncertainty of 0.068×10^{-6} mol/mol.

2.4 Determination of the adsorption factor to the inside wall of cylinder

For the determination of the adsorption factor to the inside wall, we transferred the gas mixture to another evacuated and pre-treated cylinder and measured the change of the concentration values by GC. We observed average loss of 0.38 % at the first transferred daughter cylinders. Assuming the surface reaction mechanism(constant adsorption of mole), we assigned the adsorption factor of 0.0019 mol/mol ± 0.00085 mol/mol(standard uncertainty)

3 Conclusion with certification

We selected a cylinder(D80 7708) for the CCQM –K93 and certified the concentration of KRISS ethanol gas mixture. The certified value was obtained with gravimetric value and adsorption factor. As a conclusion, the certified value of the cylinder(D80 7708) for the CCQM–K93 is 119.87×10^{-6} mol/mol ± 0.26 $\times 10^{-6}$ mol/mol(level of confidence, 95 %). Reproducibility of the gravimetric preparation, long-term stability and uncertainty due to adsorption factor were additionally considered to gravimetric uncertainty and the final results of uncertainty budget are summarized as follows;.

− Model equation; $C_{KRISS.} = C_{grav} \cdot f_{repro-prep.} \cdot (1 - f_{adsor.}) \cdot f_{long-stab}$

− Certification; 119.87 x 10^{-6} mol/mol ± 0.26 x 10^{-6} mol/mol(level of confidence, 95 %).
− Uncertainty budget

Uncertainty source	Estimate x_i	Type	Assumed distribution	Standard uncertainty $u(x_i)$
Gravimetric preparation	120.09 x 10^{-6} mol/mol	Combined	Normal	0.032 x 10^{-6} mol/mol
Reproducibility of gravimetry	1	A	Normal	0.00057
Adsorption factor	0.0019	A	Normal	0.00085
Long-term stability	1	A	Normal	0.00029
Concentration of EtOH	119.87 x 10^{-6} mol/mol	Combined	Normal	0.13 x 10^{-6} mol/mol

B.5. Measurement report of LNE

1) Preparation of the gravimetric gas mixture

Pure components :

Pure components used for preparing gravimetric gas mixture are given below :

- ✓ Ethanol from Sigma Aldrich (024183 lot n°BCBD4920V)
- ✓ Nitrogen from Air Product (BIP Nitrogen)

Preparative method :

Gravimetric mixture was prepared in accordance with NF EN ISO 6142: 2001.

The mass of ethanol has been measured by weighing the syringe with a balance Mettler AT261 (resolution of 10 µg) and standard masses (50 mg and 200 mg).

The mass of nitrogen has been measured by comparison between the mass of the cylinder and a standard cylinder (tare) with a comparator METTLER AX3200 (resolution 0,1 mg) and standard masses.

2) Concentration and expanded uncertainty on the gravimetric gas mixture

Specifications :

- ✓ Cylinder n° : APE997362/1052382
- ✓ Preparation date : 13/09/2011
- ✓ Balance gas : Nitrogen
- ✓ Pressure : 114 bars at 20°C
- ✓ Valve : Type C

Gravimetric gas mixture ETHA/N2 0001

- ✓ **Gravimetric concentration : 119.31 µmol/mol**
- ✓ **Expanded uncertainty (k=2) : 0.24 µmol/mol**

The main sources of uncertainty are :

- ✓ The purity of pure ethanol,
- ✓ The purity of pure nitrogen,
- ✓ The mass of ethanol,
- ✓ The mass of nitrogen,
- ✓ The stability of the gravimetric gas mixture on time.

B.6. Measurement report of MKEH

Cylinder number: OMH138

	Date	Result (ppm mol/mol)	Stand. Deviation (ppm mol/mol)
Ethanol	2011.09.12.	120.03	1.20

Standard preparation:
9.4 L aluminum cylinder (Luxfer) with brass valves, pur. ethanol (>99.8%, Merck) and N_2 (99.995%, Messer, Hungary) gas were used for the preparation of the standard gas.
The mass measurement of the ethanol was carried out by an analytical balance and the measurement of the nitrogen gas was carried out by a topload balance.

Uncertainty budget:

Uncertainty source X_i	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Ethanol purity	99.9 %(mol/mol)	Rectangular	0.06 %(mol/mol)	1	0.00060
Ethanol mass	0.2355 g	Normal	0.00019 g	1	0.00081
Nitrogen mass	1193.365 g	Normal	0.058 g	1	0.00005
Ethanol flash	0.2355 g	Normal	0.00115 g	1	0.00488
Variancia					0.00499

Coverage factor: 2
Expanded uncertainty: 1.20 ppm(mol/mol)

B.7. Measurement report of NIM

Cylinder No.: CAL 017777

Concentration of ethanol: 119.38 μmol/mol

Relative Expanded uncertainty: 0.3%

Inner pressure of the comparison cylinder : 8 Mpa

Purity table for N_2

Component	Mole fraction (10^{-6})	Distribution	Uncertainty (10^{-6})
O_2	0.15	Rectangular	0.09
Ar	100	Rectangular	57.74
H_2	0.05	Rectangular	0.03
H_2O	0.2	Rectangular	0.12
CO	0.05	Rectangular	0.03
CO_2	0.1	Rectangular	0.06
CH_4	0.05	Rectangular	0.03
N_2	999899.40	-	57.74

Purity table for C_2H_5OH

Component	Mole fraction (%)	Distribution	Uncertainty (%)
C_2H_5OH	99.84	Normal	0.08
H_2O	0.16	Rectangular	0.10

Gravimetric Preparation Data

Specification of balance (Model No., Readability, etc.)

1) H2-30K, mechanical, capacity 30 kg, Readability 1 mg

2) Sartorius-LE225D, electronical, capacity 220 g, Readability 0.01 mg

Weighing method (A-B-A, Substitution method, etc.,)

Substitution method, reference cylinder (A-B-A)

Concentration's calculation equation is according to ISO 6142:

$$x_i = \frac{\sum_{A=1}^{P}\left(\frac{x_{i,A}\cdot m_A}{\sum_{i=1}^{n}(x_{i,A}\cdot M_i)}\right)}{\sum_{A=1}^{P}\left(\frac{m_A}{\sum_{i=1}^{n}(x_{i,A}\cdot M_i)}\right)}$$

Components uncertainties are calculated with below equation:

$$u^2(x_i) = \sum_{A=1}^{P}\left(\frac{\partial x_i}{\partial m_A}\right)^2 u^2(m_A) + \sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial M_i}\right)^2 u^2(M_i) + \sum_{A=1}^{P}\sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial x_{i,A}}\right)^2 u^2(x_{i,A})$$

Weight of ethanol source gas: 0.13701 g

Weight of nitrogen source gas: 697.396 g

Concentration of ethanol: 119.38 μmol/mol

Coverage factor: 2

Standard uncertainty: 0.18μmol/mol

Uncertainty contribution from weighing

Uncertainty source	Estimate x_i	Distribution	Standard uncertainty $u(x_i)$
Mass of C_2H_5OH	0.13701 g	Normal	0.016 mg
Mass of N_2	697.396 g	Normal	20 mg

Purity table for mixture

Components	Mole fraction (10^{-6})	Uncertainty (10^{-6})
O_2	0.15	0.09
Ar	100	57.74
H_2	0.05	0.03
H_2O	0.39	0.16
CO	0.05	0.03
CO_2	0.10	0.06
CH_4	0.05	0.03
C_2H_5OH	119.38	0.18
N_2	999779.84	57.74

B.8. Measurement report of NIST

Sample: CAL017426

Note: Unless otherwise stated, all Uncertainties are expressed as Expanded (k=2)

Ethanol Gravimetric Content: 121.29 ± 0.61 µmol/mol

Gravimetric Method: Syringe injection of Ethanol followed by direct addition of Nitrogen.

Mass Adds:

Ethanol:	0.129417 ± 0.000200 g
Nitrogen:	648.5902 ± 0.0072 g

Impurities:

In Ethanol:

Water:	116.7 ± 7.7 µmol/mol	(by Karl Fisher)
Methanol:	9 ± 9 µmol/mol	(by Proton NMR)
Diol like:	31 ± 31 µmol/mol	(by Proton NMR)
Acetate like:	3 ± 3 µmol/mol	(by Proton NMR)
Aromtic Hydrocarbons:	< 1 µmol/mol	(by Proton NMR)
Unknown Organics:	158 ± 158 µmol/mol	(by Proton NMR)

In Nitrogen:

Water:	< 0.7 µmol/mol	(by Cavity Ringdown)
Methane:	< 0.005 µmol/mol	(by Cavity Ringdown)
CO:	< 0.1 µmol/mol	(by FTIR)
CO_2:	< 0.5 µmol/mol	(by FTIR)
THC:	< 0.1 µmol/mol	(by FTIR)
O_2:	< 0.7 µmol/mol	(by Fuel Cell)
Ar:	62 ± 12 µmol/mol	(by GC-TCD)

Sources of Uncertainty:

Uncertainty Source X_I	**Assumed Distribution**	**Standard Uncertainty (% Relative), $u(x_i)$. K = 1**
Addition of Ethanol (Minority)	Gaussian	0.077
Addition of Nitrogen (Balance)	Gaussian	0.0005
Known Impurities	Gaussian	0.032
Undetected Impurities	Gaussian	0.10
Ethanol interaction with Syringe	Gaussian	0.15
Ethanol interaction with Sample Line	Gaussian	0.15

Total unexpanded uncertainty, u_C = 0.25 % Relative (k = 1)
Total expanded uncertainty, U_C = 0.50 % Relative (k = 2)

B.9. Measurement report of NMISA

L1. CYLINDER DETAILS

Date of mixture preparation	**28 July 2011**
Volume (L)	**5 ℓ**
Connection type (e.g. e.g. DIN1, BS14 etc.)	**Minimum Dead Volume and CGA 330**
Cylinder number	**D95 8417**
What is the pressure of cylinder before shipping to NPL?	**93 bar**

L2. SOURCE OF ETHANOL

What is the source of your nominally pure ethanol? Or, if you started with a mixture of ethanol already diluted in N_2, what is its source?

Pure ethanol (≥ 99.9%) from Merck

L3. PURITY TABLE FOR NOMINALLY PURE ETHANOL (OR ETHANOL PARENT MIXTURE)

Complete for all components considered:

Component	Method*	Mole Fraction (**x10^{-6}** mol/mol)	Uncertainty (**x10^{-6}** mol/mol)
Ethanol	**Specification**	**0.9995000000**	**0.0003000000**
Water	**Volumetric Karl-Fischer**	**0.0005000000**	**0.0003000000**

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter “specification”.

L4. PURITY TABLE FOR NOMINALLY PURE N_2

Complete for all components considered:

Component	Method*	Mole Fraction (**x10^{-6}** mol/mol)	Uncertainty (**x10^{-6}** mol/mol)
Ar	GC-PDHID	0.000084100	0.000000425
C2H6	GC-FID	0.000000004	0.000000002
CH4	GC-FID	0.000000001	0.000000001
CO	GC-FID	0.000000005	0.000000003
CO2	GC-FID	0.000000006	0.000000003
H2	Specification	0.000000500	0.000000289
H2O	Specification	0.000000010	0.000000006
N2	Specification	0.999915369	0.000000426
O2	Specification	0.000000005	0.000000003

* this may refer to an analytical method (e.g. GC-FID) if you analysed for this impurity. If you are relying on suppliers specifications for this impurity estimate, enter "specification".

H5. PURITY TABLE FOR FINAL ETHANOL/N_2 MIXTURE

Complete for all components considered:

Component	Mole Fraction (**x10^{-6}** mol/mol)	Uncertainty (**x10^{-6}** mol/mol)
N2	999879.8594	8.51841683
ethanol	**$X_{ethanol,\ grav}$: 120.0805157**	**$U\ (X_{ethanol,\ grav})$: k=2 0.08121588**
Ar	84.08989618	8.49897868
H2	0.49993993	0.57693068
H2O	0.07006909	0.03782526
CO2	0.00599928	0.00697916
CO	0.00499940	0.00576931
O2	0.00499940	0.00576931
C2H6	0.00399952	0.00461944
CH4	0.00099988	0.00114986

H7. VERIFICATION

Briefly describe your verification procedure. For example was it by comparison with other traceable Ethanol/N_2 standards; how many such standards; which analytical methods were used? **A set of 7 samples of Ethanol/N_2 mixtures (50 to 550 ppm) was compared with a second set of gravimetrically prepared Ethanol/N_2 standards (50 to 550 ppm). The verification was done using NDIR. The verification runs were performed once every week.**	
What Ethanol mole fraction was predicted from your verification analysis?	$X_{ethanol,anal}$: **120.37 x 10^{-6} mol/mol**
What is your estimate of the uncertainty in $x_{ethanol,anal}$?	($x_{ethanol,anal}$) :k=1 **0,40 x 10^{-6} mol/mol**

H8. STABILITY TESTING

Briefly describe any measures undertaken to confirm the stability of the mixtures in the period between their preparation and their shipping to the NPL.

The stability of the mixture was monitored with a verification run once a week from 30 July 2011 to 28 September 2011 before shipping.

B.10. Measurement report of NPL

1. Cylinder

The mixture was prepared in a 10 Luxfer aluminium cylinder (cylinder number A387) with BOC Spectraseal passivation and a stainless steel Ceodeux valve

2. Preparation method

Following evacuation of the cylinder, (224.52 ± 0.10) mg of ethanol (Fisher) was added from a stainless steel transfer loop. The loop was weighed against a tare, so no buoyancy correction was applied.

(1137.177 ± 0.020) g of nitrogen (Air Products BIP+ grade, with additional purification from a second point-of-fill BIP purifier) was then added directly to the cylinder. The cylinder was weighed against a tare cylinder before and after filling with nitrogen.

3. Purity analysis of 'pure' components

Results of purity analysis of ethanol:

Component	Amount fraction (mol/mol)	Uncertainty (mol/mol)
Ethanol	0.999780	0.000300
Water	0.000220	0.000300

Results of purity analysis of nitrogen:

Component	Amount fraction (mol/mol)	Uncertainty (mol/mol)
Argon	0.0000005000	0.0000000500
Carbon monoxide	0.0000000003	0.0000000002
Oxygen	0.0000000050	0.0000000025
Hydrocarbons	0.0000000050	0.0000000050
Water	0.0000000050	0.0000000020
Nitrogen	0.9999994817	0.0000008735
Nitrogen monoxide	0.0000000005	0.0000000003
Sulphur dioxide	0.0000000005	0.0000000003
Methane	0.0000000010	0.0000000010
Hydrogen	0.0000000010	0.0000000010

4. Calculated amount fraction of submitted mixture

The amount fraction of the mixture submitted for the CCQM-K93 comparison was:
(120.030 ± 0.054) µmol/mol.

B.11. Measurement report of SMU

(Note: this measurement report is that originally submitted by SMU at the time of the comparison.)

Ethanol mixture 0023F_3

1. CYLINDER DETAILS

Date of mixture preparation	5.10.2011
Volume (L)	5
Total Pressure (bar)	100
Connection type (e.g. DIN1, BS14 etc.)	DIN1

2. SOURCE OF ETHANOL AND N_2

The source of nominally pure ethanol was Merck SeccoSolv type ethanol. Source of nitrogen was N_2 BIP Plus 6.0. Purity measurements of pure ethanol and nitrogen were made using following analytical instruments: GC FID- methaniser, GC TCD, Dew-point meter and GC-MS. Mole fraction of undetected, but analysed components were calculated from detection limit of used method. Data for non analysed components were taken from manufacturer specifications.

Parent compounds	$x_{(pur)}$ (mol/mol)	u(x) (mol/mol)
Ethanol	0.99623	0.00067
N_2 BIP	0.99999909	0.00000010

3. PREPARATION OF MIXTURE

Liquid ethanol was inserted to the evacuated gas cylinder by the method of syringe injection. The heated sample loop (70°C) was used for the gasification of ethanol. Weighted syringe with ethanol component (with closed valve) was inserted through septum. Filled cylinder valve and the syringe valve were opened simultaneously. Then the liquid was injected to the sample loop. The liquid was absorbed by vacuum to the cylinder. The syringe valve and cylinder valve were closed after emptying the syringe. Then the sample loop was flushed with nitrogen 4 times. The filled cylinder valve was opened and closed for a moment 4 times simultaneously with flushing.
Following filling with nitrogen were carried out at very low flow. Added amount of liquid component was determined from mass difference of the syringe before and after filling on analytical balance. Added mass of nitrogen was determined from mass difference of filled cylinder before and after filling on automatic balance for 5 L cylinders with comparator.

4. PURITY TABLE FOR FINAL 0023F 3 MIXTURE

Uncertainties in purity table are in unextended form. Calculation of purity table was made automatically by 2.0 version ISO 6142 software with inputs from gravimetric preparation and purity measurements.

Complete for all components considered:

Mixture data

Cylinder code : 0023F_3
Preparation date : 5.10.2011
Producer : SMU
Maincomponent : Ethanol

Cylinder code:	Producer:	Component:	Transferred gas [g]:	Uncertainty [g]:
1. Etl478.pur	Merck	Ethanol	0.11979	0.0001
2. N399870.pur	Air Products	Nitrogen	601.517	0.013

Purity table

Component:	Formula:	Mass fraction:	Mole fraction:	Uncertainty:
Carbon monoxide	CO	0.00000007497604	0.00000007499091	0.00000000099988
Carbon dioxide	CO2	0.00000005497447	0.00000003499576	0.00000001999758
Hydrogen	H2	0.00000000179867	0.00000002499697	0.00000001399830
Oxygen	O2	0.00000000571018	0.00000000499939	0.00000000299964
Nitrogen	N2	0.99980024340949	0.99987791644273	0.00000016777804
Water	H2O	0.00000064694421	0.00000100606633	0.00000012746568
Methane	CH4	0.00000001145111	0.00000001999758	0.00000001199855
Propane	C3H8	0.00000003147545	0.00000001999758	0.00000001199855
Isopentane	C5H12	0.00000016039823	0.00000006228327	0.00000000314874
n-Pentane	C5H12	0.00000015602940	0.00000006058683	0.00000000302772
n-Hexane	C6H14	0.00000004882720	0.00000001587375	0.00000000520922
Methanol	CH30H	0.00000003464696	0.00000003029342	0.00000001696140
Ethanol	C2H50H	0.00019850380216	0.00012071635811	0.00000010696015
2-Propanone	C3H6O	0.00000001256023	0.00000000605868	0.00000000351382
2-Propanol	C3H7OH	0.00000001299619	0.00000000605868	0.00000000351381

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5. VERIFICATION

The prepared mixture was validated on NDIR analyser. All measurements were done in automatic way using selector gas valve. Before entering sample loops all gas mixtures went through a mass flow controller for regulation. 6 PSM calibration standards used for verification were made gravimetrically according to ISO 6142

and ISO 6143 in SMU. Measurement method with 6 automated runs was used. From each run was made one calibration curve with sample signals. Data were subjected to the b_least program (weighted least square regression). The result of the measurement sequence was the average of molar fractions. Validation criterion in accordance to ISO 6143 was tested.

6. RESULTS

The results are presented in following table with data:

x_{prep} amount of substance fraction , from preparation (mol.mol^{-1})
u_{prep} uncertainty of x_{prep} from gravimetrical preparation and purity (mol.mol^{-1})
u_{ver} uncertainty from verification (mol.mol^{-1})
u_{cert} final uncertainty of x (mol.mol^{-1})
$U(k=2)$ stated uncertainty of x, at 95% level of confidence (mol.mol^{-1})

Standard uncertainty of the mixture was calculated with following formula:

$$u_{cert} = \sqrt{u_{prep}^2 + u_{ver}^2}$$

Component	x_{prep}	u_{prep}	u_{ver}	u_{cert}	x	$U(k=2)$
ethanol	0.00012072	0.00000011	0.00000042	0.00000043	**0.00012072**	**0.00000086**

B.12. Measurement report of VNIIM

Cylinder # D 247754

Gravimetric data

Cylinder number	Component	Mole fraction, µmol/mol	Standard uncertainty (gravimetry), µmol/mol
D 247754	C_2H_5OH (Ethanol)	120,30	0,03
	N_2 (Nitrogen)	balance	-

Pure substances

Purity table for Nitrogen

Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
H_2O (water vapour)	1,00	0,05
O_2 (Oxygen)	0,225	0,005
CO_2 (Carbon Dioxide)	0,030	0,017
CH_4 (Methane)	0,015	0,009
CO (Carbon Monoxide)	0,010	0,006
N_2 (Nitrogen)	999998,72	0,06

Mass fraction of pure Ethanol is **948500 µg/g**, standard uncertainty **55 µg/g** (determined by Digital Density Meter DMA 500, Anton Paar, Austria)

[*Note from NPL*: A revised value for the purity of ethanol of 878080 ± 50 was later submitted]

The results of pure Ethanol analysis (admixtures except water vapour) are shown in the table:

Component	Mass concentration, mg/dm^3	Standard uncertainty, mg/dm^3
C_2H_4O (Acetaldehyde)	0,8	0,1
C_3H_8O (Isopropanol)	1,2	0,2
CH_4O (Methanol)	100	9

Uncertainty evaluation

Source of uncertainty	Standard uncertainty, µmol/mol	Coefficient of sensitivity	Contribution, µmol/mol
Preparation of the gas mixture (gravimetry)	0,03	1	0,03
Verification	0,17	1	0,17
Adsorption of Ethanol by cylinder walls	0,12	1	0,12
Combined standard uncertainty	**0,21**		

B.13. Measurement report of VSL

1 Reference value

The amount–of–substance fraction ethanol in VSL226701 (cylinder number ML 6701) is 119.49 µmol mol^{-1}. The associated standard uncertainty is 0.20 µmol/mol.

2 Preparation method

The gas mixture is prepared using the method described in ISO 6142 [1]. The introduction of the ethanol is done using a syringe. This method complies with the amendment to ISO 6142 [2]. Details of the calculation and uncertainty models used are given elsewhere [3]. The measurement model for the weighing of the transfer vessel (syringe) is the same as for weighing a cylinder except for the term accounting for the expansion, as this expansion does not occur during the process.

3 Results

The weighing results are given in table **1**.

Table 1: Weighing results

	unit	Result	Standard uncertainty
evacuated cylinder	g	398.0083	0.0009
full syringe	g	-1.1932	0.0001
empty syringe	g	-1.3325	0.0001
full cylinder	g	1106.886	0.0053

The compositions of the starting materials are given in table **2** (ethanol) and **3** (nitrogen). The column labelled "*w*" contains the mass fractions, the column labelled *"x*"the amount–of–substance fractions.

Table 2: Purity table ethanol

Component		*w* (g g^{-1})	*x* (mol mol^{-1})	*u*(*x*) (mol mol^{-1})
water	H_2O	0.000149	0.000381	0.000015
ethanol	C_2H_5OH	0.999851	0.999619	0.000003

Table 3: Purity table nitrogen

Component		*w* g g^{-1}	*x* mol mol^{-1}	*u*(*x*) mol mol^{-1}
Argon	Ar	0.000007	0.000005	0.000003
Methane	CH_4	0.000000005	0.000000008	0.000000005
Carbon monoxide	CO	0.000000015	0.000000015	0.000000009
Carbon dioxide	CO_2	0.000000016	0.000000010	0.000000006
Hydrogen	H_2	0.000000002	0.000000025	0.000000015
Water	H_2O	0.000000006	0.000000010	0.000000006
Nitrogen	N_2	0.999993	0.999995	0.000006
Oxygen	O_2	0.000000006	0.000000005	0.000000003

Table 4: Purity table VSL226701 (cylinder ML6701)

Component		*w* g g^{-1}	*x* mol mol^{-1}	*u*(*x*) mol mol^{-1}
Argon	Ar	0.000007	0.000005	0.000003
Methane	CH_4	0.000000005	0.000000008	0.000000005
Carbon monoxide	CO	0.000000015	0.000000015	0.000000009
Carbon dioxide	CO_2	0.000000016	0.000000010	0.000000006
Hydrogen	H_2	0.000000002	0.000000025	0.000000015
Water	H_2O	0.000000036	0.000000056	0.000000006
Nitrogen	N_2	0.999796	0.999875	0.000006
Oxygen	O_2	0.000000006	0.000000005	0.000000003
Ethanol	C_2H_5OH	0.000196494	0.000119494	0.000000016

The masses transferred are summarised in table **5**. The calculation is based on the results given in table **1**. The standard uncertainty is obtained by applying the law of propagation of uncertainty [4] to the relevant expressions.

Table 5: Masses transferred

	unit	Result	Standard uncertainty
m(liquid)	g	0.1393	0.0001
m(gas)	g	708.7384	0.0054
m(EtOH)	g	0.1393	0.0001
m(N2)	g	708.7333	0.0069

In the masses of the components, the purity of the starting materials is appreciated.

4 Uncertainty budget

The largest contributor in the uncertainty budget is the effect of cylinder wall adsorption. For this mixture, the value assigned to this uncertainty component is 0.016% relative to the assigned amount fraction ethanol.

5 References

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

[2] International Organization for Standardization, “ISO 6142:2001/Amd 1:2009 – Liquid introduction”, ISO, Geneva, 2009

[3] 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

[4] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (2008) “Evaluation of measurement data — Guide to the expression of uncertainty in measurement”, first edition, GUM:1995 with minor corrections