REPORT

Final Report of

Key Comparison

CCQM-K4 (ethanol in air)

**M.J.T. Milton, C.Brookes,
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NPL

National Physical Laboratory

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ABSTRACT

CCQM Key Comparison K4 involved primary standards of ethanol in air at a nominal amount fraction 120 μmol/mol. The method used by the pilot laboratory to prepare these standards and the results from the eight participating laboratories are reported.

This report and the results of the comparison were approved by the CCQM in April 2001.

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Background

This key comparison involved primary standards of ethanol in air maintained at eight laboratories. The nominal amount fraction of the standards used for the comparison was 120 µmol/mol which is typical of 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.

The full affiliations of the eight participants are listed in Annex 1.

Conduct of the comparison

The National Physical Laboratory (UK) acted as pilot laboratory for this key comparison. A set of primary standards of ethanol in air were prepared by NPL and one was distributed to each participating laboratory. The standards were prepared using the procedure described in Annex 2.

The participants measured the concentration of ethanol in the standard received with respect to their own primary standards. The methods reported are described below. After the completion of the comparison, each participant returned the standard to NPL where it was re-analysed by comparison with primary standards that had been retained at NPL. These were compared with primary standards maintained in NPL's archive of primary standards. These measurements showed no significant change in the ethanol amount fraction within the estimated uncertainty of the gravimetric values. The uncertainty estimated by NPL for the gravimetric value of the ethanol amount fraction was 0.1 µmol/mol (the derivation of this value is described in Annex 2).

Analysis methods used by participating laboratories

The methods used by each of the participating laboratories to analyse the standards are listed in Table 1. Five laboratories used process gas analysers operating on the flame-ionisation detector (FID) or non-dispersive infrared (NDIR) principles. Three laboratories used gas chromatography with FID detection. Most participants used two point (bracketing or zero-span) calibrations. Only two laboratories used multi-point calibrations. The uncertainties reported for the analysis by each participant include the uncertainty calculated for the

comparison process together with a contribution from the uncertainty of the reference standards used for the comparison.

Table 1. Results of CCQM K4: comparison of ethanol in air standards

Laboratory	Cylinder number	Analytical method	No of standards	Gravimetric amount		Analytical amount		100*Relative Difference
				Amount fraction μ mol/mol	Uncertainty (k=2) μ mol/mol	Result submitted μ mol/mol	Uncertainty (k=2) μ mol/mol	
LNE	A 324	NDIR	2 & zero	120.59	0.10	121.4	2.7	*0.67*
NIST	A 319	GC-FID	7	120.48	0.10	121.5	1.2	*0.85*
NMI	A 322	NDIR	11 & 16	120.84	0.10	120.8	1.2	*-0.03*
NPL	A 317	FID	2	120.49	0.10	120.5	1.0	*0.01*
NRCCRM	A 323	GC	9 independently	120.68	0.10	112	2	*-7.2*
NRLM	A 312	FID	2	120.76	0.10	121.04	0.46	*0.23*
OMH	A 318	GC-FID	1 & zero	120.39	0.10	119.30	0.43	*-0.91*
VNIIM	A 325	GC-FID	1	120.67	0.10	124.7	0.7	*3.3*

FID - flame-ionisation detector
GC-FID - gas chromatography with FID
NDIR - non-dispersive infrared

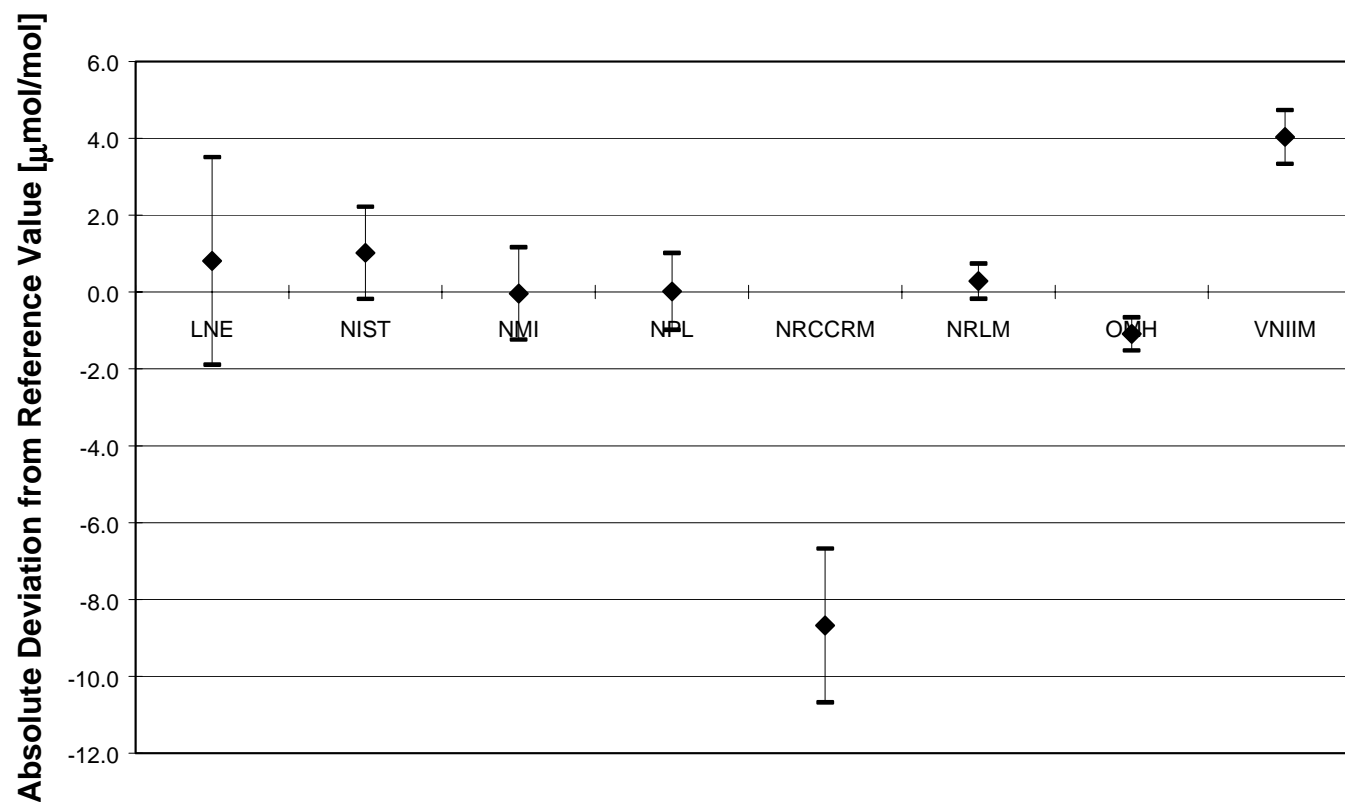**Comparison of 120 ppm ethanol/air standards CCQM-K4**

Figure 1

Results

The results submitted by the eight participants are shown in Table 1. All of the uncertainties represent 95% confidence intervals (expanded using a coverage factor k of 2). In Figure 1 the results are plotted in terms of the difference between the analytical result and the gravimetric value for the relevant standard.

Six of the eight participants submitted results that were within 1% of the relevant reference value. In four of these cases, the estimated uncertainty was larger than the deviation from the reference value.

BAM were unable to submit a result and withdrew from the comparison.

Key Comparison Reference Value, Degrees of Equivalence and Associated Uncertainties

The comparison was performed by submitting different standards to each of the participating laboratories. The pilot laboratory prepared all of these mixtures using the same methods and materials (following the procedure described in Annex 2), so the individual gravimetric values constitute the reference value for each standard. Since these gravimetric values vary by small amounts that are of the same order of magnitude as the observed difference between participants, the use of a single reference value would significantly compromise the accuracy of the comparison.

In order to evaluate the differences between the participating national metrology institutes, the difference between the gravimetric and analysed values has been taken to represent the Degree of Equivalence with the Key Comparison Reference Value (KCRV):

$$D_i = x_i - x_{igrav}$$

where
$\quad x_i \quad$ = result of measurement carried out by laboratory i
$\quad x_{igrav}$ = gravimetric (reference) value for
$\qquad$ standard analysed by laboratory i

The Degree of Equivalence between laboratories i and j is therefore given by:

$$D_{ij} = D_i - D_j = (x_i - x_{igrav}) - (x_j - x_{jgrav})$$

The uncertainties in each of these quantities is straightforward to calculate using the approach advocated by the ISO "Guide to the Expression of Uncertainty in Measurement" for uncorrelated variables:

$$U_i^2 = 2^2 (u_i^2 + u_{igrav}^2)$$

and

$$U_{ij}^2 = 2^2 (u_i^2 + u_{igrav}^2 + u_j^2 + u_{jgrav}^2)$$

where $\qquad$ u_i = combined uncertainty in measurement carried
out by laboratory i
u_{igrav} = combined uncertainty in gravimetric (reference) value
for standard analysed by laboratory i
U_i = expanded uncertainty in degree of equivalence for laboratory i
U_{ij} = expanded uncertainty in degree of equivalence
between laboratories i and j

The values calculated for the degrees of equivalence and their uncertainty are presented in the format required for the KCDB Appendix B in Annex 3.

Summary

This key comparison demonstrates that the level of comparability between 6 of the 8 participants is adequate to meet the requirement for ethanol/air mixtures at this amount fraction.

The coverage of this key comparison will be extended in linked key comparisons being planned by APMP and EUROMET.

Annex 1 - List of Participants in CCQM K4

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Annex 2 - Preparation of ethanol in air standards at NPL

Cylinders and Valves

The ethanol/air gas mixtures used for this key comparison were contained in size AV (approximate internal volume $10dm^3$) aluminium-alloy cylinders passivated by the British Oxygen Company (BOC) using their proprietary "Spectra-Seal" process. Tests carried out at NPL and elsewhere have shown that moisture standards stored in these cylinders remain stable for periods in excess of two years. The composition of gas standards of CO and CO_2 and more reactive species such as NO or SO_2 also remain stable for periods in excess of three years.

The diaphragm valves used with these cylinders are manufactured by Ceodeux S.A., Luxembourg, and are made from stainless steel. Prior to assembly, these are thoroughly cleaned using hydrocarbon and chlorinated-hydrocarbon free solvents. After filling, the contents of the cylinders are released at controlled pressures using BOC "Spectrol 50S" stainless-steel regulators.

Component Purity

The purity of the ethanol employed for the preparations has a direct effect on the accuracy of the standards produced. The source material was Merck Chemicals "Aristar" grade, which is specified to have a minimum assay of 99.7% with the largest quoted impurity being $\leq 0.2\%$ water. The validity of this assay was confirmed by an independent analysis carried out by an accredited laboratory. The ethanol was further distilled to remove any more volatile compounds that may have been present.

The artificial air used in these standards was analysed by GC and a high-resolution FTIR to measure the levels of impurities present. Some typical results are shown in Table 1.

Procedure

A direct gravimetric preparation procedure has been developed and validated by NPL which enables traceable gaseous ethanol/air (or ethanol/nitrogen) standards to be prepared rapidly and conveniently.

Instrumentation

Two high-precision balances are employed in the procedure:

- A single-pan microbalance (Sartorious Instruments) is used to weigh the ethanol vapour. This has the following specifications:

Maximum capacity:	160 g
Reproducibility:	0.01 mg
Sensitivity:	0.01 mg

- A two-pan, equal-arm balance (Reverifications Ltd, UK) is used to weigh the balance of air added. This is one of three used at NPL for the preparation of all primary gas standards and has the following specifications:

Maximum capacity: 25 kg
Reproducibility: 2 mg
Sensitivity: 1 mg

The ethanol vapour is weighed on the micro-balance in spherical containers designed and manufactured at NPL. These are constructed from thin-walled stainless steel, inert-gas welded into the form of a sphere and electro-polished inside and out. The nominal volume is $1.2 \ dm^3$ and the mass is approximately 130 grams. A lightweight high-vacuum bellows valve is inert-gas welded to the sphere.

The spheres are filled with approximately 160 mg of pure ethanol vapour which is approximately equal to the saturated vapour pressure at ambient temperature. Thus, as the repeatability of the weighing process on the microbalance is specified at ± 0.01 mg, the mass of ethanol vapour can, in principle, be weighed with an accuracy of better than ± 0.01% (relative to its value).

Preparation procedure

Before use, a passivated aluminium cylinder and a stainless steel sphere are evacuated. The preparation procedure then involves the following steps:

i.) The aluminium cylinder is weighed (against an identical tare) on the two-pan precision balance. After weighing, it is connected to a vacuum system.

ii.) The evacuated stainless-steel sphere is filled with ethanol by equilibriation with a distilled sample of the pure liquid. The temperature of the liquid ethanol is thermostatically maintained below ambient in order to avoid condensation of the vapour in the remainder of the apparatus.

iii.) The sphere (with ethanol vapour) is weighed on the microbalance. A tare sphere of identical construction is weighed alternately, and the cycle is repeated several times. The standard deviation achieved in practise between these sets of weighings is typically ± 0.05 mg.

iv.) The sphere containing ethanol vapour is then connected to the vacuum system and the interconnecting pipework evacuated.

v.) The ethanol vapour in the sphere is then allowed to equilibrate through the evacuated system into the aluminium cylinder. This results in approximately 80% of the ethanol being transferred into the cylinder. The balance of the gas remains in the sphere with a small quantity (approximately $4.7 \ cm^3$) remaining in the connecting pipework.

vi.) The sphere is then detached from the system and reweighed to determine, by subtraction from the weight measured in (iii), the amount of ethanol removed.

vii.) The aluminium cylinder is then filled with synthetic air to the desired pressure (approximately 50 bar). This filling procedure ensures that most of the small quantity of ethanol vapour remaining in the connecting pipework is forced into the cylinder.

viii.) The aluminium cylinder is disconnected from the filling system and re-weighed on the two-pan balance. The total mass of gas in the cylinder is then calculated by subtraction of the weight obtained in (i).

Analysis of uncertainties

The amount fraction of ethanol in the standard (x) is calculated using the formula:

$$x = \frac{W_e / M_e}{W_e / M_e + W_a / M_a}$$

where:
W_e = mass of ethanol in standard
W_a = mass of air in standard
M_e = relative molecular mass of ethanol
M_a = relative molecular mass of air

The masses of the components are determined from the balance readings as follows:

$$W_e = r_2 - r_1$$

and

$$W_e + W_a = r_4 - r_3$$

where
r_1 = mass of sphere after expansion of ethanol vapour into cylinder
r_2 = mass of sphere with ethanol vapour at SVP following distillation
r_3 = mass of evacuated cylinder
r_4 = mass of cylinder after addition of ethanol and balance gas

Uncertainties in the mass of ethanol vapour

There are a number of sources of uncertainty in the procedure for weighing the ethanol with the microbalance. These are summarised in Table 2 and discussed below.

(i) Uncertainties in an individual weighing

The mass of the sphere when filled with ethanol vapour (r_2) and its mass after the ethanol vapour has been removed (r_1) are obtained from several sequential weighings against a tare. The repeatability of this weighing process has been determined to be ± 0.05 mg (one standard deviation). This value is significantly larger than the resolution of the balance (± 0.01 mg). This is attributed to small variations that might arise from placing and re-replacing the sphere on the balance, and from small changes in the temperature of the sphere when transferring it to and from the ambient laboratory environment.

(ii) Uncertainties due to the calibration of the microbalance

The microbalance is calibrated using an appropriate set of Class E2 mass pieces certified at NPL. The consequent uncertainty from this calibration does not exceed ± 0.01 mg at 100mg or ± 0.005 mg for masses less than 100mg.

(iii)   Uncertainties due to differential buoyancy

Variations in the atmospheric conditions during the weighing procedure can, in principle, give rise to an error in the measured mass of ethanol transferred into the cylinder. The weighing procedure has been designed so that atmospheric variations have an extremely small effect since the tare and sample spheres have nearly identical volumes. We estimate that an upper limit for the difference in volume between two spheres is 13 cm^3 (*ie* approximately 1% of the total volume). We estimate that the maximum variations in ambient temperature, pressure and humidity observed might give rise to a maximum weighing error of ± 0.03 mg. Since this estimate is based on the maximum observed deviation of the influence parameters, it represents a worst-case estimate which should be divided by the square root of 3 to represent the uncertainty (with $k = 1$).

(iv)   Uncertainty arising from linear expansion of the sphere.

A further source of uncertainty is due to the expansion of the sphere when it is filled with the ethanol vapour. We estimate that the fractional expansion of a sphere of this construction is 0.0125 (at 10^7 Pa). Hence, the mass of air displaced when 160 mg of ethanol is introduced is calculated to be 0.01mg. Since no correction is made systematically for this effect, we attribute an uncertainty of ± 0.01 mg.

(v)   Uncertainty arising from the transfer of ethanol vapour from sphere to cylinder.

The preparation procedure outlined above for the ethanol/air standards requires that the ethanol vapour weighed in the sphere is transferred into the cylinder. The volume of pipework between the sphere and the cylinder is 4.7 cm^3. Most of the vapour in this pipework is forced into the cylinder when the balance air is introduced. We estimate that the residual amount of ethanol not transferred by this means into the cylinder is no more than 10% of this volume which gives rise to an uncertainty of ± 0.01 mg in the mass of ethanol vapour transferred. This latter figure is considered to represent one standard deviation ($k = 1$).

Uncertainties in the mass of balance gas

A number of uncertainties arise from the procedure for weighing the balance gas into the aluminium cylinder. These are summarised in Table 2 and discussed below.

(i)   Uncertainties in an individual weighing

The mass of the evacuated cylinder (r_3) and the mass of the cylinder with ethanol vapour and balance gas (r_4) are obtained from several sequential weighings against a tare. The repeatability of this weighing process has been determined to be ± 10 mg (one

standard deviation). This value is significantly larger than the resolution of the balance (± 1 mg).

(ii)   Uncertainties due to the standard masses with the two-pan balance

The two-pan balance is calibrated using an appropriate set of Class E2 mass pieces certified at NPL. The consequent uncertainty caused by this calibration does not exceed ± 0.05 mg for a 100g piece, and is not considered further.

(iii)   Uncertainties due to differential buoyancy

Following the above procedure, we estimate that the contribution of differential buoyancy to the mass of the aluminium cylinder due to changes in ambient conditions is less than 1 mg. We do not consider this uncertainty further.

(iv)   Uncertainty arising from linear expansion of the cylinder

A further source of uncertainty is due to the expansion of the cylinder when it is filled with nitrogen. We calculate that the fractional expansion of an aluminium cylinder of this construction is 0.002 at an internal pressure of 10^7 Pa. Hence, the mass of air displaced when 600 g of balance nitrogen is introduced is calculated to be 70 mg. Since no correction is made systematically for this effect, we attribute an uncertainty of ± 70 mg.

Uncertainties arising from Gas Purity

As indicated in Table A1, the largest single impurity in the synthetic air used for these standards is argon. This has a maximum concentration of 50 ppm, which contributes an uncertainty of ±0.005% to the amount fraction of the prepared standard. Table A1 also shows the concentration of a number of hydrocarbons present in this particular example. They result in a total volume fraction of hydrocarbons (excluding ethanol) in the prepared standards of ≤0.02 ppm. This hydrocarbon fraction is small compared with the target ethanol fraction.

The largest impurity in the ethanol used to prepare the standards was found to be water at a volume fraction ≤ 0.2%. Since the ethanol was transferred into the sphere by distillation, we estimate that the amount of water in the final standards is at least 100 times below this level. Other impurities in the ethanol, including carbonyl compounds, constitute about 38 ppm (by volume), and therefore represent an insignificant contribution to the uncertainty in the accuracy of the standards. The ethanol/air standards were also analysed for impurities after preparation. At the time of this analysis, the fraction of acetaldehyde was found to be below the detection limit of the GC-FID at 0.04 µmol/mol.

Total Uncertainty in the Amount Fraction of the Gravimetric Standards

The overall uncertainty in the amount fraction of the prepared standards arises from the individual components discussed above. These are summarised in Table A2 . These lead to a

combined uncertainty of 0.00051 (relative to value). The expanded uncertainty representing a 95% confidence interval is 0.001 (using $k = 2$) or 0.1% (relative to value).

Table A1 - Typical analysis of 'Metrology Grade' Air used to prepare the Ethanol Standards

Constituent	Amount Fraction
Oxygen	0.209
Nitrogen	Balance
Argon	< 50 ppm
Xylene	0.005 ppm
Decane	0.004 ppm
Benzene	0.0015 ppm
Methyl benzene	0.001 ppm
Other hydrocarbons	< 0.002 ppm

Quantity	Uncertainty [mg]	Sensitivity Coefficient	Contribution to combined uncertainty
Mass of Ethanol Vapour			
Mass of sphere	0.05	0.0067	0.00033
Mass of sphere + ethanol	0.05	0.0067	0.00033
Calibration of mass pieces	0.01	0.0067	0.00007
Differential buoyancy	0.015	0.0067	0.00010
Linear expansion of sphere	0.01	0.0067	0.00007
Transfer efficiency correction	0.01	0.0067	0.00007
Mass of Ethanol Vapour			
Mass of cylinder + ethanol	10	0.000002	0.00002
Mass of cylinder+ethanol+balance gas	10	0.000002	0.00002
Linear expansion of cylinder	70	0.000002	0.00012
Combined Uncertainty (k=1)			0.00051

Table A2 - Uncertainties in the Gravimetric Value for the Amount Fraction

Annex 3 – Entry in Appendix B (including degrees of equivalence)

x_i: **result of measurement carried out by laboratory i**

u_i: **combined standard uncertainty of x_i**

$x_{i\,grav}$:   **gravimetric value of the ethanol amount-of-substance fraction in the cylinder received by laboratory i**

$u_{i\,grav}$:   **combined standard uncertainty of $x_{i\,grav}$**

Lab i	x_i μmol/mol	u_i μmol/mol	$x_{i\,grav}$ μmol/mol	$u_{i\,grav}$ μmol/mol	Date of measurement
LNE	121.40	1.35	120.59	0.05	99-08
NIST	121.50	0.60	120.48	0.05	99-03
NMI	120.80	0.60	120.84	0.05	99-05
NPL	120.50	0.50	120.49	0.05	99-10
NRCCRM	112.0	1.0	120.68	0.05	99-07
NRLM	121.04	0.23	120.76	0.05	99-04
OMH	119.30	0.22	120.39	0.05	99-05
VNIIM	124.70	0.35	120.67	0.05	99-06

CCQM-K4

Degrees of equivalence for ethanol in air at nominal value 120 μmol/mol
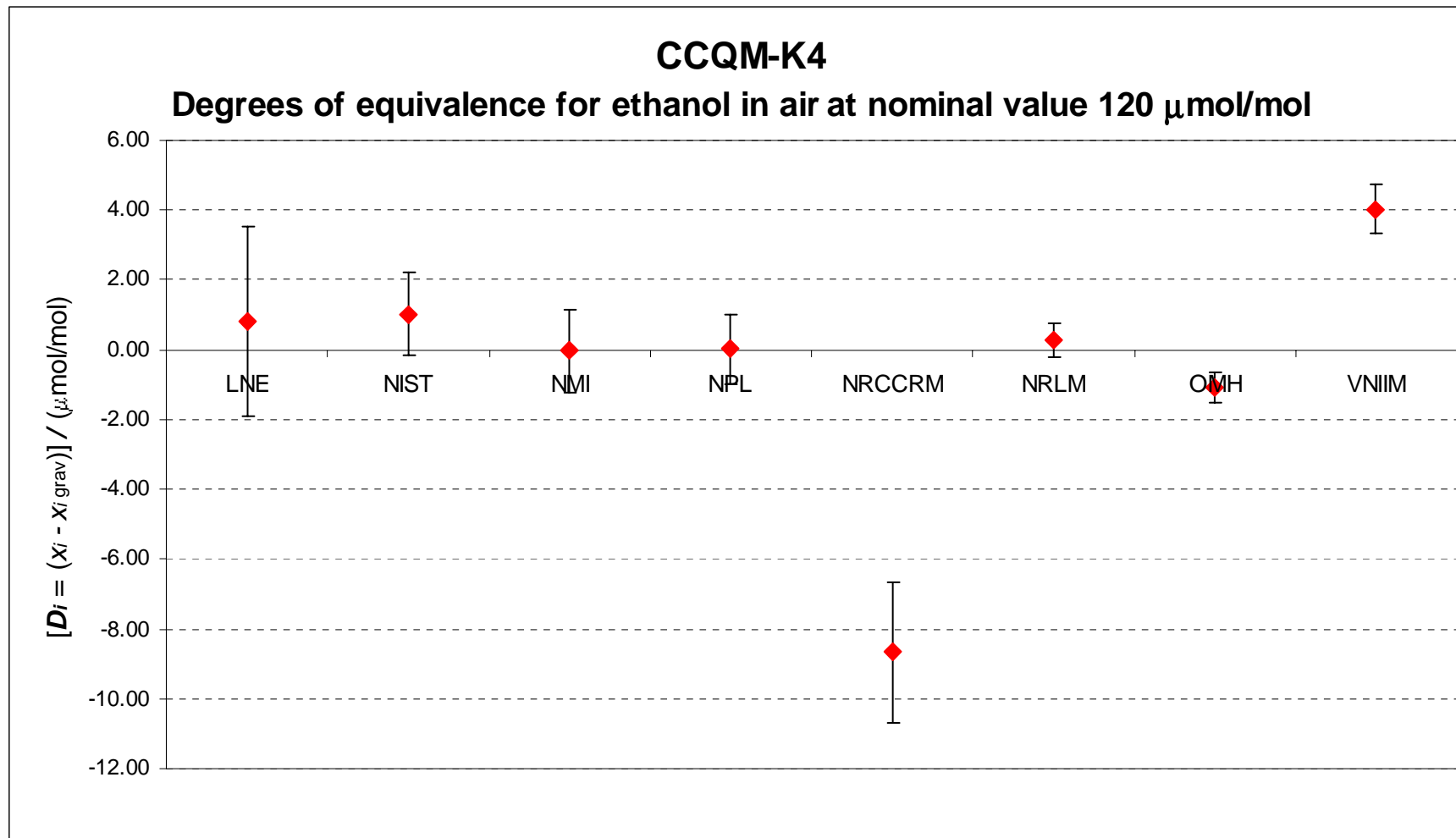
~~Key comparison reference value~~: there is no single reference value for this comparison,

the value $x_{i\text{grav}}$ is taken as the reference value for laboratory *i*.

The degree of equivalence of each laboratory with respect to the reference value is given by a pair of numbers:

$D_i = (x_i - x_{i\text{grav}})$ and U_i, its expanded uncertainty ($k = 2$), both expressed in μmol/mol

$U_i^2 = 2^2(u_i^2 + u_{i\text{grav}}^2)$

The degree of equivalence between two laboratories is given by a pair of numbers:

$D_{ij} = D_i - D_j = (x_i - x_{i\text{grav}}) - (x_j - x_{j\text{grav}})$ and U_{ij}, its expanded uncertainty ($k = 2$), both expressed in μmol/mol

$U_{ij}^2 = 2^2(u_i^2 + u_j^2 + u_{i\text{grav}}^2 + u_{j\text{grav}}^2)$

Lab *j* ⟹

Lab *i* ⇓	D_i	U_i	LNE D_{ij}	U_{ij}	NIST D_{ij}	U_{ij}	NMi D_{ij}	U_{ij}	NPL D_{ij}	U_{ij}	NRCCRM D_{ij}	U_{ij}	NRLM D_{ij}	U_{ij}	OMH D_{ij}	U_{ij}	VNIIM D_{ij}	U_{ij}
	μmol/mol		μmol/mol		μmol/mol		μmol/mol		μmol/mol		μmol/mol		μmol/mol		μmol/mol		μmol/mol	
LNE	0.81	2.70																
NIST	1.02	1.20	0.21	2.96														
NMI	-0.04	1.20	-0.85	2.96	-1.06	1.70												
NPL	0.01	1.00	-0.80	2.88	-1.01	1.57	0.05	1.57										
NRCCRM	-8.68	2.00	-9.48	3.36	-9.69	2.34	-8.64	2.34	-8.69	2.24								
NRLM	0.28	0.47	-0.53	2.74	-0.74	1.29	0.32	1.29	0.27	1.11	8.96	2.06						
OMH	-1.09	0.44	-1.90	2.74	-2.11	1.28	-1.05	1.28	-1.10	1.10	7.58	2.05	-1.37	0.65				
VNIIM	4.03	0.71	3.23	2.79	3.01	1.40	4.07	1.40	4.02	1.23	12.71	2.12	3.75	0.85	5.12	0.83		