International Comparison

APMP.QM-K4, Final Report 17 July 2002

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Field

Gas standards

Subject

Comparison of measurements of ethanol in air

Participants

JP (NMIJ/CERI), KR (KRISS), TW (CMS-ITRI), ZA (CSIR-NML), SY (ERL-HIAST)*
*ERL participated as a "study". The results will not be included in MRA Appendix B.

Organizing Body

APMP/TCQM

Background

The key comparison CCQM-K4 ethanol in air was organized in 1999 and the final report was approved by CCQM in April 2002. The chairs of the CCQM working groups have approved the publication in the KCDB. This comparison, APMP.QM-K4 is intended to be an equivalent RMO key comparison in the APMP (Asia Pacific Metrology Program) region and uses basically the same protocol. From APMP, two laboratories, NRLM and NRCCRM, participated in the CCQM-K4, but NRCCRM did not participate in this comparison. This comparison involved five laboratories; two of them have their own gravimetric primary standards of ethanol in air, one prepared by a static volumetric method and two purchased cylinder gases of gravimetric mixing from other national laboratories. The nominal amount-of-substance fraction of the standards used for the comparison was 120 μmol/mol, which is a typical level used to calibrate evidential breath analyzers in many countries.

Process of the comparison

The Chemicals Evaluation and Research Institute, Japan (CERI) prepared primary standards of ethanol in air for distribution to each participating laboratory. The standards were prepared using the procedure defined for gravimetric preparation of gas standards [1] with necessary modifications to allow for handling ethanol which condenses into a liquid at room temperature and pressure.

The pure ethanol used to prepare the standards is a reference material (NIMC CRM 4001-a, NIMC: National Institute of Materials and Chemical Research, reorganized into NMIJ in 2001). The purity is 99.895 % ± 0.05 % (k = 2.57). The ethanol was put in a small evacuated vessel (0.25 L) and expanded into a 10 L cylinder. The mass of the ethanol was obtained by weighing the small vessel before and after the expansion. Then a balance of synthetic air was added in the cylinder. The mass of air was measured by weighing the cylinder. The synthetic air was analyzed for total hydrocarbons and found to have less than 10 nmol/mol assumed as methane. The 10 L cylinders were manufactured from aluminium, with a passivated inner surface that minimises the reactivity of the cylinder walls with contents. Tests carried out previously at CERI confirm that ethanol-in-air standards contained in the cylinders are stable over the time-scales required for this comparison. The pressure in the cylinders was approximately 10 MPa when distributed.

The participants measured the concentration of ethanol in the cylinder received with respect to their own standards of ethanol in air. The methods reported are given in Table 1. The expanded uncertainty (k = 2) estimated by CERI for the gravimetric value of the ethanol amount fraction was 0.37 μmol/mol.

Table 1. Conditions of APMP.QM-K4: comparison of ethanol in air standards

Laboratory	Cylinder number	Analytical method	Standard	Calibration model	Number of measure-ments	Total number of sub-measurements	Degree of freedom
CMS-ITRI	CPB-17265	GC-FID	gravimetric (from LNE)	two-point bracketing	3	-	-
KRISS	CPB-17264	GC-FID	gravimetric	4 standards (corrected for adsorption)	4	135	41
NNIJ/CERI	CPB-17262	FID analyzer	gravimetric	two-point bracketing	5	15	14
CSIR-NML	CPB-17267	NDIR	gravimetric (from NMi)	8 standards	3	9	> 90
ERL-HIAST	CPB-17260	GC-FID	static volumetric (injection)	?	4	26	-

FID: flame-ionization detector
GC-FID: gas chromatography with FID
NDIR: non-dispersive infrared analyzer

Uncertainty of the distributed standards

Each distributed standard material was prepared using the gravimetric method. The uncertainties of the standard gases were estimated by combining the uncertainty of weighing including the expansion of a gas cylinder by pressure, purity analysis of the component gases and the stability of gases in a cylinder. Detail of the uncertainty evaluation of the standard gases and gas analysis will be published elsewhere.
The relative standard uncertainty of distributed standards is given in Table 2.

Table 2. The standard uncertainty of distributed standards

Components	Relative standard uncertainty
purity analysis	0.020 %
weighing	0.015 %
stability (6 months)	0.150 %
combined	0.152 %

Results

The results submitted by the five participants are shown in Table 3 and Figure 1. In Figure 1, the results are plotted in terms of their deviation from the gravimetric value. Symbols for Table 3 are

x_i result of measurement carried out by laboratory i;

u_i combined standard uncertainty of x_i;

x_{igrav} gravimetric value of the ethanol amount-of-substance fraction in the cylinder received by laboratory i;

u_{igrav} combined standard uncertainty of x_{igrav}.

There is no single reference value for this comparison, the value x_{igrav} is taken as the reference value for laboratory i. The table for Degrees of Equivalence and Associated Uncertainties is given in Appendix 1.

Expanded uncertainties are calculated using a coverage factor $k = 2$, as an approximation of 95 % confidence intervals.

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

Table 3. Results of key comparison APMP.QM-K4 ethanol in air

Laboratory i	x_i	u_i	x_{igrav}	u_{igrav}	Date of	100 × relative
	µmol/mol	µmol/mol	µmol/mol	µmol/mol	measurement	difference
CMS-ITRI	121.27	1.76	121.15	0.184	2000-11,12	0.10
KRISS	120.27	0.37	121.57	0.185	2000-07,08,11	-1.07
NMIJ/CERI	119.31	0.16	119.45	0.182	2000-06	-0.12
CSIR-NML	122.31	0.36	121.72	0.185	2000-12	0.48
ERL-HIAST	121.09	6.54*	121.38	0.184	2000-09,10	-0.24

*ERL did not report their uncertainty. This value is the standard deviation of measurement data. The column of 100 × relative difference and the row of ERL-HIAST will not be included in MRA Appendix B.

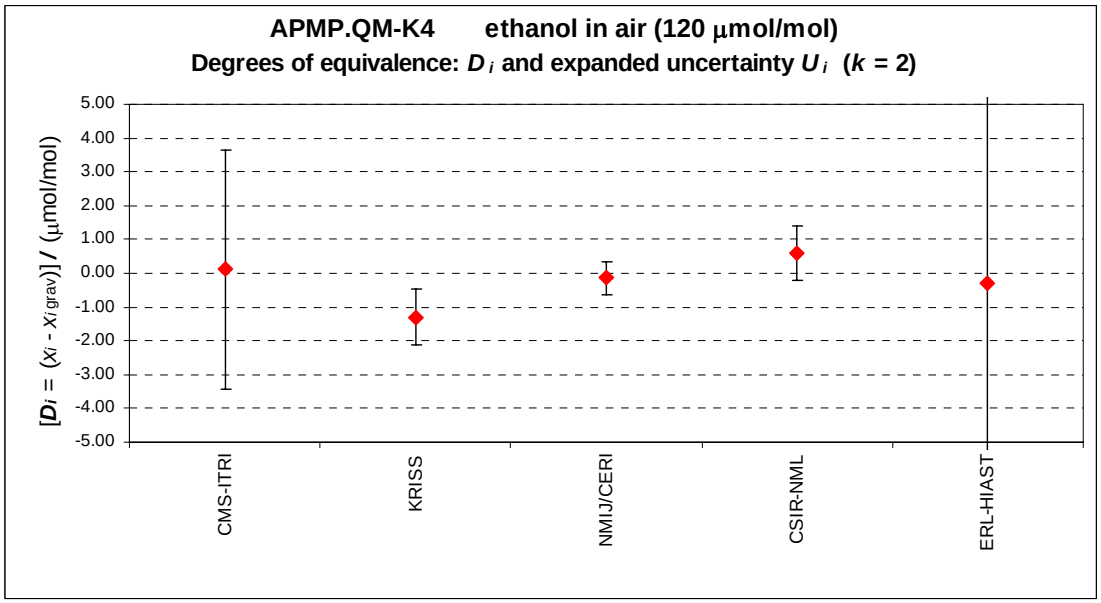

Figure 1. Results of key comparison APMP.QM-K4 ethanol in air. See Appendix 1 for symbols.

Analysis of cylinder gas

CERI analyzed the gases before and after the measurements by participants. The results are shown in Table 4. Two of the cylinders were not returned. The concentration differences between the gravimetric value and the analyzed value and between two analyses were within the expanded uncertainty of analysis (0.32 µmol/mol, k = 2). This shows that no significant change occurred during the comparison. The cylinder that stayed in CERI showed the largest change of concentration.

Table 4. Result of analysis of cylinder gas
x_{igrav} concentration by gravimetric preparation (26 & 27 April 2000);
x_{ia0} concentration by analysis before shipment (11 May 2000);
x_{ia1} concentration by analysis of returned cylinder (25 June 2001).

Cylinder	x_{igrav}	x_{ia0}	x_{ia1}	$x_{ia0} - x_{igrav}$	$x_{ia1} - x_{ia0}$	Laboratory
	µmol/mol	µmol/mol	µmol/mol	µmol/mol	µmol/mol	
CPB-17265	121.150	121.034	-	-0.116		CMS-ITRI
CPB-17264	121.574	121.580	121.497	0.006	-0.083	KRISS
CPB-17262	119.449	119.328	119.372	-0.121	0.044	NMIJ/CERI
CPB-17266	121.721	121.785	121.674	0.064	-0.111	CSIR-NML
CPB-17260	121.379	121.409	-	0.030		ERL-HIAST
CPB-17263	120.974	120.992	120.707	0.018	-0.285	reserve

Discussion

Only NMIJ/CERI is a link laboratory for CCQM-K4 (participated as NRLM). However, CMS-ITRI and CSIR-NML used primary mixtures of LNE and NMi respectively, and both are participants in CCQM-K4. The results in this report reproduce the equivalence in CCQM-K4 results between LNE, NMi and NMIJ/CERI.

The absolute value of the degrees of equivalence of KRISS, $|D_i|$ is larger than its expanded uncertainty, U_i and the relative difference $|D_i|/x_i$ is larger than 1%. KRISS had a correction for the

change of concentration of their standard gas mixture by the ethanol adsorption on the cylinder wall. KRISS, NMi, NMIJ and NPL reported experimental results on the adsorption at the meetings of the CCQM Working Group on Gas Analysis (WGG) held in April 2001 and January 2002. The discussion will be continued at the WGG.

CSIR-NML requested to correct an error for the uncertainty calculation. The expanded uncertainty ($k = 2$) first reported was 4.1 μmol/mol and corrected as 0.72 μmol/mol. The correction was approved by the CCQM.

Summary

This key comparison demonstrates that the level of comparability between 3 of the 4 participants is adequate to meet the requirement for ethanol/air mixtures at this amount fraction.

The results of this comparison are linked to the key comparison CCQM-K4.

References

1. *Gas analysis -- Preparation of calibration gas mixtures -- Gravimetric Method*, ISO 6142, 2001.

2. Milton, M.J.T. et. al., Final Report of Key Comparison CCQM-K4 (ethanol in air), NPL Report COEM 59, March 2001.

Coordinators

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Appendix 1 Proposal of Degrees of Equivalence for the Key Comparison APMP.QM-K4

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

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

and U_i, its expanded uncertainty ($k = 2$), both expressed in μmol/mol

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

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

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

and U_{ij}, its expanded uncertainty ($k = 2$), both expressed in μmol/mol

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

			Lab *j* ⇒							
			CMS-ITRI		**KRISS**		**NMIJ/CERI**		**CSIR-NML**	
***Lab i* ⇓**	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
	μmol/mol		**μmol/mol**		**μmol/mol**		**μmol/mol**		**μmol/mol**	
CMS-ITRI	**0.12**	3.54			**1.42**	3.63	**0.26**	3.57	**-0.47**	3.63
KRISS	**-1.30**	0.82	**-1.42**	3.63			**-1.17**	0.95	**-1.89**	1.15
NMIJ/CERI	**-0.14**	0.48	**-0.26**	3.57	**1.17**	0.95			**-0.73**	0.94
CSIR-NML	**0.59**	0.81	**0.47**	3.63	**1.89**	1.15	**0.73**	0.94		