International Key Comparison APMP.QM-K4.1

Final report 24/10/2007

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Field

Amount of substance

Subject

Comparison of primary standards of ethanol in nitrogen

Participants

China (NIM), Korea (KRISS), Japan (CERI),

Background

Reference gases of ethanol in air or nitrogen are used for the calibration of ethanol level in exhalation and are very important in view of legal medicine. The key comparisons CCQM-K4 and APMP.QM-K4, ethanol in air were organized in 1999 and 2000. CERI and NIM (NRCCRM) participated in the CCQM-K4. CERI and KRISS participated in the APMP.QM-K4 from APMP (Asia Pacific Metrology Program) region. Recently preparation technique of reference gases was greatly improved and equivalence level of the participants was expected to enhance. This comparison, APMP.QM-K4.1 was intended to be a rerun of the comparison in APMP region using the same protocol basically. This comparison involved three laboratories. The nominal amount fraction of the standards used for the comparison was 100 to130 μmol/mol. This comparison will link to CCQM-K4 through CERI who participated in CCQM-K4 in the name of NMIJ.

Conduct of the comparison

The Chemicals Evaluation and Research Institute, Japan (CERI) prepared primary standards of ethanol in nitrogen 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. These procedures are the same as those used in APMP.QM-K4.

The pure ethanol used to prepare the standards is a reference material (NIMC CRM 4001-a, NIMC: National Institute of Materials and Chemical Research). The purity is 99.895 % ± 0.05 % ($k = 2.57$). The ethanol was put in an evacuated small vessel (0.25 L) and expanded into a 10 L cylinder. The mass of ethanol is obtained by weighing the small vessel before and after the expansion. Then a balance of nitrogen was added in the cylinder. The mass of nitrogen was measured by weighing the cylinder. The nitrogen was analysed for THC (total hydrocarbons) and found to have less than 10 nmol/mol THC 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 confirmed that ethanol-in-nitrogen standards contained in them were 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 nitrogen. The methods reported are given in **Table 1**. After the completion of the comparison, the standards were returned to CERI where they were re-analysed by comparison with primary standards that had not been distributed. These measurements showed no significant change in the ethanol amount fraction within the estimated uncertainty of the measurements. The combined standard uncertainty estimated by CERI for the gravimetric value of the ethanol amount fraction was 0.08 μmol/mol. CERI reanalyzed the returned cylinders from each participant and evaluated the instability of the cylinders during the comparison. Deviations of ethanol concentration between analytical values measured between before and after the shipment to the participants were -0.02, 0.03 and 0.1 μmol/mol. The instability result of the delivered standards is small enough in this comparison.

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

Laboratory	Cylinder number	Analytical method	Standard	Calibration model	No. of measurements	Total no. of sub-measurements
CERI	CPB-19115	FID THC analyzer	gravimetric	2 point bracketing	5	15
KRISS	CPB-19114	GC-FID	gravimetric	2 independent single point calibration	4	18
NIM	CPB-19113	GC-FID	gravimetric	6 independent single point calibration	4	24

FID: flame-ionization detector
GC-FID: gas chromatograph with FID

Uncertainty of the distributed standards

Each distributed standard materials was prepared using gravimetric method. The uncertainty of the standard gases was 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.
The relative standard uncertainties of distributed standards are given in **Table 2**.

Table 2. The standard uncertainty of distributed standards

components	relative standard uncertainty
purity analyses	0.02 %
weighing	0.02 %
stability (6 months)	0.07 %
Total	0.08 %

Results

The results submitted by the three 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. Expanded uncertainties are calculated using a coverage factor $k = 2$, as an approximation of 95% confidence intervals.

Two of the three participants submitted results that were within 0.1% of the relevant reference value. In these cases, the estimated uncertainty was larger than the deviation from the reference value.

As a conclusion, the agreement of the results in this key comparison is very good.

Discussion on the link among the results of CCQM-K4, APMP.QM-K4 and APMP.QM-K4.1

The Mutual Recognition Arrangements (MRA) requires that the results of a Key Comparison carried out by a Regional Metrology Organisation should be linked to those of the corresponding key comparison carried out by the CCQM. In this case, it is necessary to demonstrate the link between this comparison and CCQM-K4.
CERI and NIM (NRCCRM) participated in the CCQM-K4 and APMP.QM-K4.1. In CCQM-K4, the results of NIM showed significant deviation from the reference value, NIM's results can not useful in linking the comparisons. CMS-ITRI (Chinese Taipei), KRISS, CERI, CSIR-NML (South Africa) and ERL-HIAST (Syria) and KRISS participated in the APMP.QM-K4. CERI was the link laboratory between CCQM-K4 and APMP.QM-K4. CMS-ITRI and CSIR-NML used primary mixtures of LNE (France) and NMi (The Netherlands). CERI, CMC-ITRI and CSIR-NML showed consistent results in APMP.QM-K4. These results showed the results of CERI were also consistent to CCQM-K4. On the other hand, results of KRISS deviated about 1 % from KCRV. Effect on the concentration of ethanol in KRISS standards caused by

ethanol adsorption on the cylinder wall was concerned. Conclusions are reached that, CERI acts as linking laboratory for these three comparisons.

References

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

Coordinators

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Completion Date

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Table 3. Results of key comparison APMP.QM-K4.1 ethanol in nitrogen

Key comparison APMP.QM-K4.1

MEASURAND: Amount-of-substance fraction of ethanol in nitrogen
NOMINAL VALUE: 100-130 μmol/mol

x_i: result of measurement carried out by laboratory *i*
u_i: combined standard uncertainty of x_i
$x_{i\mathrm{grav}}$: gravimetric value of the ethanol amount-of-substance fraction in the cylinder received by laboratory *i*
$u_{i\mathrm{grav}}$: combined standard uncertainty of $x_{i\mathrm{grav}}$

Lab *i*	**x_i** μmol/mol	**u_i** μmol/mol	**$x_{i\mathrm{grav}}$** μmol/mol	**$u_{i\mathrm{grav}}$** μmol/mol	**Date of measurement**	100*relative difference
CERI	110.20	0.187	110.21	0.08	2005-11	-0.01
KRISS	105.37	0.223	105.32	0.08	2006-4	0.05
NRCCRM	116.4	1.164	113.18	0.08	2006-01,02	2.85

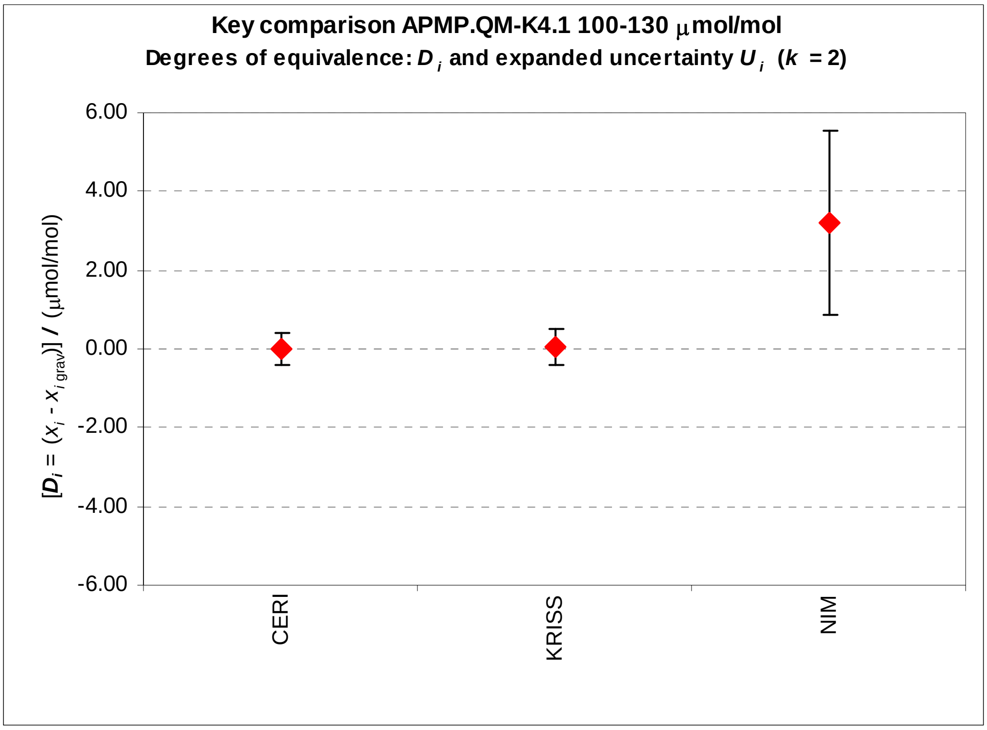

Figure 1. Results of key comparison APMP.QM-K4.1 ethanol in nitrogen

Annex 1 - Degrees of Equivalence

Key comparison APMP.QM-K4.1

MEASURAND: Amount-of-substance fraction of ethanol in nitrogen
NOMINAL VALUE: 100-130 µmol/mol

Key comparison reference value: the value $x_{i\mathrm{grav}}$ 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: $D_i = (x_i - x_{i\mathrm{grav}})$ and $U_i^2 = 2^2(u_i^2 + u_{i\mathrm{grav}}^2)$, its expanded uncertainty (k = 2), both expressed in µmol/mol.

The degree of equivalence between two laboratories is given by a pair of numbers:
$D_{ij} = D_i - D_j = (x_i - x_{i\mathrm{grav}}) - (x_j - x_{j\mathrm{grav}})$ and $U_{ij}^2 = 2^2(u_i^2 + u_j^2 + u_{i\mathrm{grav}}^2 + u_{j\mathrm{grav}}^2)$, its expanded uncertainty (k = 2), both expressed in µmol/mol.

Lab *j* ⇨

Lab i ⇩	D_i	U_i
	µmol/mol	
CERI	**-0.01**	0.41
KRISS	**0.05**	0.47
NIM	**3.22**	2.33

CERI		**KRISS**		**NIM**	
D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
µmol/mol		**µmol/mol**		**µmol/mol**	
		-0.06	0.62	**-3.23**	2.37
0.06	0.62			**-3.17**	2.38
3.23	2.37	**3.17**	2.38		

This comparison is linked to CCQM-K4 through CERI. CERI participated in CCQM-K4 in the name of NMIJ.

Annex 2

Contact persons

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Report from CERI

– Results for C_2H_5OH in nitrogen –

Laboratory : Chemicals Evaluation and Research Institute, Japan
Cylinder number : CPB-19115

NOMINAL COMPOSITION
- ethanol : 100 to 130 .10^{-6} mol/mol
- nitrogen : balance

Measurement No. 1	Date	Result (μmol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	14/11/2005	110.210	0.068	3

Measurement No. 2	Date	Result (μmol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	15/11/2005	110.195	0.085	3

Measurement No. 3	Date	Result (μmol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	16/11/2005	110.182	0.095	3

Measurement No. 4	Date	Result (μmol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	17/11/2005	110.205	0.066	3

Measurement No. 5	Date	Result (μmol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	18/11/2005	110.210	0.088	3

Results:

Analyte	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
C_2H_5OH	110.20	2	0.38

Reference Method:
Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

Instrument for Ethanol gas measurement: FID analyzer
Make: Fisher- Rosemount Co., Ltd.
Type: NGA 2000
Principle: Flame Ionization Detector
Measurement Species: Total Hydrocarbons
Data collection: output of integrateor recording of data

Calibration Standards:
Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

Preparation: gravimetric method

Purity analyses:
Ethanol: Certified by NMIJ.
Thermal analysis by DSC (differential scanning calorimeter)
Temperature calibration : Mercury (NIST SRM 2225), Indium (NIST SRM 1745)
Impurity components: GC-FID and Karl-Fisher (H_2O)

N2 and O2: The impurities in a pure parent gas are determined by analyses and the amount of the major component is conventionally determined by,

$$X_{pure} = 1 - \sum_{i=1}^{N} x_i$$

where:
x_I = mole fraction of impurity i , determined by analysis
N = number of impurities likely in the final mixture
X_{pure} = mole fraction ‘purity’ of the ‘pure’ parent gas

Impurities in the component gases: shown in table 1
Ethanol: NMIJ performed analysis.

Table 4 certified value of ethanol

	concentration	expanded uncertainty(k=2)	analysis method
Purity of C_2H_5OH	0.99895 mol/mol	0.0004 mol/mol	DSC
Compound in impurity			
CH_3CHO	1.5 E^{-6} g/g	0.1 E^{-6} g/g	GC-FID
$(CH_3)_2CHOH$	5.2 E^{-6} g/g	0.1 E^{-6} g/g	GC-FID
H_2O	18.1 E^{-6} g/g	0.2 E^{-6} g/g	Karl-Fisher

Impurities present in the balance gas: shown in table 2
N2 and O2: CERI performed analysis.

Table 4 impurity of balance gases (10^{-6} mol/mol)

gases	component	Specifications by manufacturer	distribution	analyzed mole fraction	standard uncertainty
O_2	H_2		rectangular	<= 0.1	0.029
	Ar	<= 1	rectangular	<= 0.1	0.029
	N_2	<= 1	rectangular	<= 0.1	0.029
	CO	<= 0.1	rectangular	<= 0.01	0.003
	CO_2	<= 0.1	rectangular	<= 0.01	0.003
	CH_4	<= 0.1	rectangular	<= 0.01	0.003
	C_2H_5OH		rectangular	<= 0.001	0.0003
	H_2O	<= 1	rectangular	<= 1	0.289

	O_2	>= 999995		999998.7	0.29
N_2	H_2	<= 0.05	rectangular	<= 0.05	0.014
	O_2	<= 0.05	rectangular	<= 0.05	0.014
	CO	<= 0.05	rectangular	<= 0.01	0.003
	CO_2	<= 0.05	rectangular	<= 0.01	0.003
	CH_4	<= 0.1	rectangular	<= 0.01	0.003
	C_3H_8	<= 0.05	rectangular	<= 0.01	0.003
	NO_X	<= 0.005	rectangular	<= 0.005	0.001
	SO_2	<= 0.005	rectangular	<= 0.005	0.001
	C_2H_5OH		rectangular	<= 0.001	0.0003
	H_2O	<= 0.5	rectangular	<= 1	0.289
	N_2	>= 999999		999999.4	0.29

Instrument Calibration:

Concentration of Primary standard materials:

Table 2 concentration of PSMs

	Concentration (mol/mol)			
	R_1		R_2	
Component	X_i	$U(X_I)$	X_i	$U(X_I)$
Ethanol	110.210×10^{-6}	0.016×10^{-6}	90.340×10^{-6}	0.015×10^{-6}
Oxygen	20.8972×10^{-2}	0.0005×10^{-2}	20.8986×10^{-2}	0.0005×10^{-2}
Nitrogen	79.0918×10^{-2}	0.0004×10^{-2}	79.0924×10^{-2}	0.0004×10^{-2}

Measurement sequence:

This procedure is for the determination of Ethanol in a sample using a FID analyzer. Flow each gas for 6 minutes. The data are average of FID analyzer output for last 2 minutes using an integrator.

1) Introduce the calibration standard (R_1).
2) Introduce the sample.
3) Introduce the calibration standard (R_2).
4) Calculate the concentration of Ethanol using the formula below.

$$Y = \frac{A(E-D)+B(C-E)}{(C-D)}$$

where *Y*: Concentration of sample
A: Concentration of standard (R_1)
B: Concentration of standard (R_2)
C: Indicated value of standard (R_1)
D: Indicated value of standard (R_2)
E: Indicated value of sample

Following above procedure, 3 measurements are repeated subsequently in a day and iterated for 5 days.

Temperature of the FID case: 45 C
Sample pressure : 130 kPa
Sample flow: 7 ml/min.

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument?(automatic, high pressure, mass-flow controller, dilution etc).:

Stabilization: none

Transfer: manual handling
Sample inlet pressure: 200kPa
Sample flow: 500 ml/min. (with mass-flow controller)
Sample inlet temperature: 60 degrees
Dilution: none

Uncertainty:

μmol/mol

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 of analysis	110.200	normal	0.080	1	0.080
Reference gas R1 preparation	110.210	normal	0.077	0.995	0.077
Reference gas R1 stability	110.210	rectangular	0.150	0.995	0.150
Reference gas R2 preparation	90.340	normal	0.063	0.005	0.0004
Reference gas R2 stability	90.340	rectangular	0.123	0.005	0.0007
total					0.187

Coverage factor : 2
Expanded uncertainty: 0.38 μmol/mol
Relative expanded uncertainty: 0.35 %

Report from KRISS

– Results for C_2H_5OH in nitrogen –

Laboratory : KRISS
Cylinder number : CPB19114

NOMINAL COMPOSITION
- ethanol : 100 to 130 .10^{-6} mol/mol
- Nitrogen : balance

Measurement No. 1	Date	Result (umol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	2006/04/29	105.44	0.10	4

Measurement No. 2	Date	Result (umol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	2006/04/29	105.38	0.02	4

Measurement No. 3	Date	Result (umol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	2006/04/30	105.35	0.10	5

Measurement No.	Date	Result (umol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	2006/04/30	105.32	0.08	5

Results:

Analyte	Result (assigned value) (umol/mol)	Coverage factor	Assigned expanded uncertainty (umol/mol)
C_2H_5OH	**105.37**	**2.31**	**0.52**

Reference Method:

1. Gravimetrical preparation of standard gas
2. Comparison with GC

Calibration Standards:

1. Gravimetrical preparation at KRISS

2. Standard cylinder No. Gravimetrical values (C'_{std}) Expanded uncertainty (CL, 95%)*

Standard cylinder No.	Gravimetrical values (C'_{std})	Expanded uncertainty (CL, 95%)*
a. ME5508	105.556 umol/mol	0.18 %(Relative)
b. ME5510	105.601 umol/mol	0.18 %(Relative)

* Uncertainty due to only gravimetrical preparation.
* LUXFUR cylinders from Australia were used after soaking.

Instrument Calibration:

1. Independent single point calibration with each of above standards.

Sample Handling:

1. Storage at Lab. temperature before analysis

Uncertainty:

- Model Equation; $C = C^0 \cdot f_{\mathrm{adsor}} \cdot f_{\mathrm{purity}} \cdot f_{\mathrm{grav}}$

Uncertainty source	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Reproducibilty (measurement)	105.62 umol/mol	t- distribution (DF, 3)	0.173 umol/mol	0.9976	0.170 umol/mol
Relative difference due to adsorption	0.9976	t- distribution (DF, 7)	0.00086	105.62 umol/mol	0.091 umol/mol
Relative error due to purity	1	Square - Distribution (DF, ∞)	0.00058	105.37 umol/mol	0.061 umol/mol
Relative error due to gravimetry	1	Normal- Distribution (DF, ∞)	0.00090	105.37 umol/mol	0.094 umol/mol
Combined standard uncertainty	105.37 umol/mol	t- distribution (DF, 8)	0.223 umol/mol	1	0.223 umol/mol

Coverage factor: 2.31

Expanded uncertainty: **0.52 umol/mol (Level of confidence, 95 %)**

Report from NIM

CCQM Bilateral Comparisons Ethanol in nitrogen

Measurement report

Laboratory : NRCCRM
Cylinder number : CPB19113

NOMINAL COMPOSITION
- ethanol : 100 to 130 ×10^{-6} mol/mol
- nitrogen : balance

Measurement No. 1	Date	Result (×10^{-6}mol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	Jan. 18, 2006	116.3	0.5	6

Measurement No. 2	Date	Result (×10^{-6}mol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	Jan. 25, 2006	116.5	0.5	6

Measurement No. 3	Date	Result (×10^{-6}mol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	Feb. 10, 2006	116.1	0.5	6

Measurement No. 4	Date	Result (×10^{-6}mol/mol)	stand. deviation (% relative)	number of sub-measurements
C_2H_5OH	Feb. 13, 2006	116.7	0.4	6

Results:

Analyte	Result (assigned value) (×10^{-6}mol/mol)	Coverage factor	Assigned expanded uncertainty
C_2H_5OH	116.4	2	2%

Reference Method:

Two different systems were used to analyse the ethanol in nitrogen.

Components	C_2H_5OH	C_2H_5OH
Chromatography	6890 (Agilent)	6890 N (Agilent)
Detector	FID	FID
Column	Alltech capillary column with 30 m × 0.25 mm ×0.25 μm column	PORA capillary column with 50 m × 0.30 mm ×0.5 μm
Oven temperature	80 ºC, constant	100 ºC, constant
Inlet temperature	100 ºC	120 ºC
Carrier gas	He	He
Injection	Manual switch valve	Automatic switch valve
Other parameter	Flow rate of carrier gas: 1.5 ml/min	Flow rate of carrier gas: 1.5 ml/min

Calibration Standards:

Six ethanol in nitrogen gas mixtures were used as calibration standards to analyse the sample. The calibration standards were prepared by injection gravimetric method according to ISO 6142 and the detail information was listed in table 1. The impurities of complementary gas and impurities of components interested were determined with a standard normalized method by gas chromatography instrument. Experiments showed that the impurities of the material gases have no effects to the results within the measurement uncertainties. So the purity of pure gases used for preparation was taken from the certificates of producer. Their uncertainties were calculated by type B evaluation.

Table 1 Calibration Standards

Components	Assigned value (x) ($\times 10^{-6}$ mol/mol)						Relative standard uncertainty ($u(x)$),%
Cylinder number	356774	356717	L3K09019	L3K09191	ME1580	ME1567	
Ethanol in nitrogen	114.82	114.77	114.50	115.07	114.80	114.74	0. 8

Instrument Calibration:

One point calibration method was used to analyse the sample mixture. Concentrations of six standards mixture listed in table 1. The sample was measured in four different days based upon the six calibration standards. One measurement sequence was in the order of standard A - sample - standard A’ - standard B - sample - standard B’ -……- standard G - sample - standard G’. After averaging two response values of the same calibration standard, the concentration of sample mixture was calculated by direct comparison based on the following equation (1).

$$C_{sample,i} = \frac{A_{sample,i}}{A_{st,i}} \cdot C_{st,i} \qquad (1)$$

$C_{sample,i}$ is the concentration of component i in sample mixture to be calculated,

$A_{sample,i}$ is the response value of component i in sample mixture,

$A_{st,i}$ is the response value of component i in the calibration standard mixture,

$C_{st,i}$ is the concentration of component *i* in the calibration standard mixture.

Temperature and pressure were not corrected during the calibration procedure.

Sample Handling:

Sample cylinder after arrival was stored in the room temperature. Sample and standard gas were all directly led to gas chromatography by a regulator, a mass flow control meter and a Teflon pipe. Before each sample injection, the pipe system was purged for five minutes.

Uncertainty:

For ethanol component, we established three types of uncertainties:

- Standard mixture uncertainty, which mainly depend upon the gravimetric method uncertainty
- stability uncertainty
- Analytical uncertainty

The Gravimetric method uncertainty contributions included:

- Balance uncertainty
- Buoyancy of cylinders
- Impurity of gases
- Absorption

The stability uncertainty is evaluated according to the past experimental results.

The analytical uncertainty was evaluated by repeatability of the measurements.

The relative standard uncertainty of ethanol component in sample mixture was evaluated by equation (3)

$$u^2(C_{sample,i},\%) = u_{gravi}{}^2 + u_{stab}{}^2 + u^2{}_{repea} \qquad (2)$$

The relative standard uncertainty of standard mixture included the gravimetric method uncertainty, stability uncertainty and analytical uncertainty. The relative standard uncertainty of repeatability was the RSD% of the four concentration values of the component, which were determined in four different days.

The amount of each contribution to the measurement uncertainty was listed in table 2.

The absolute standard uncertainty was calculated by:

$$u(C_{sample,i}) = u(C_{sample,i},\%) \cdot C_{sample,i} \qquad (3)$$

Expanded uncertainty can be calculated with a confidence interval 95% and a coverage factor k= 2. The expanded uncertainty was:

$$U_i = k \cdot u(C_{sample,i},\%)$$

Table 2 Uncertainty Evaluation

Uncertainty source	Estimate (relative,%) X_i	Assumed distribution	Standard uncertainty (relative,%) $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_i(y)$ (relative,%)
Gravimetric method	1.3	Rectangle	0.8	1	0.8
Stability	0.5	Normal	0.2	1	0.2
Analytical	0.3	Normal	0.2	1	0.2

Coverage factor: 2
Expanded uncertainty: 2%