International Comparison

APMP.QM-K3, Final Report

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Field

Amount of substance

Subject

Comparison of measurements of carbon monoxide, carbon dioxide, and propane in nitrogen (car exhaust gas measurements)

Participants

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

Organizing Body

APMP

Background

The key comparison CCQM-K3 on “automotive” gas mixtures (CO, CO_2, and C_3H_8 in nitrogen) was organized in 1998 and the final report was approved by CCQM in April 2000. These mixtures are used for calibrating measurement equipments for automotive exhaust gas. This comparison, APMP.QM-K3 is intended to be an equivalent RMO key comparison in APMP (Asia Pacific Metrology Program) region and using basically same protocol as CCQM-K3. This comparison involved five laboratories, three of them have gravimetric primary standards of “automotive” gas mixtures, one used gravimetric reference mixtures prepared by other national laboratories and the other used reference gas mixtures prepared by a specialty gas company.
KRISS operated as pilot laboratory in this comparison. The selected primary gas mixtures for this comparison were individually prepared using gravimetry and thoroughly studied for their chemical composition and stability. A long-term experience in the behaviour of these mixtures is available at the pilot laboratory.

Process of the comparison

The design of the comparison was adopted from CCQM-K3. The individual cylinders for this comparison were prepared by means of primary methods (gravimetry) at the pilot laboratory KRISS.

The pressure in the cylinders was approximately 10 MPa when distributed. Because of individual preparation of gas mixture, there are some differences in the actual property values of these mixtures, which make working with a single reference value undesirable. However, all property values of these mixtures are within the nominal values as proposed in protocol.
The nominal amount of substance ratios of CO, CO_2 and C_3H_8 in nitrogen, as used in this key comparison, are summarised in table 1.

Table 1 : Nominal amount of substance ratios

Component	x (mmol/mol)
CO	28
CO_2	124
C_3H_8	1.95
N_2	Balance

The cylinders were shipped to participants between July and August 2000. A formal deadline for submission of results was not set. Participated laboratories carried out their measurements during October 2000 and June 2001. Reports were received until July 2001.

Measurement methods and calibration procedures

The participants measured the concentration of CO, CO_2 and C_3H_8 in the cylinder received with respect to their own standards. The measurement and calibration methods used in each NMIs are shown in table 2. For the calibration, NMIJ/CERI, CMS/ITRI and KRISS used gravimetric standards prepared by themselves, CSIR-NML used gravimetric standards prepared by NMi, and ERL/HIAST used reference gas mixtures produced by Scott Specialty Gases.

Table 2 : Measurement and calibration methods

Laboratory	Cylinder number	Measurement method	Calibration method
NMIJ/CERI	MD2534	GC-TCD (CO, CO_2); GC-FID (C_3H_8)	Bracketing using two gravimetric standards
CMS/ITRI	MD2524	GC-TCD	Bracketing using two gravimetric standards
CSIR-NML*	MD2514	NDIR (CO, CO_2)	Curve with 6 gravimetric standards
ERL/HIAST	MC9939	GC-TCD (CO, CO_2); GC-FID (C_3H_8)	One point calibration with a reference standard
KRISS	MC9940	GC-TCD (CO, CO_2); GC-FID (C_3H_8)	One point calibration with a gravimetric standard

* CSIR-NML did not report on C_3H_8.
GC-TCD: gas chromatography with thermal conductivity detector
GC-FID: gas chromatography with flame-ionization detector
NDIR: non-dispersive infrared analyzer

Uncertainty of the reference values

Each distributed cylinders were prepared using gravimetric method. The preparation of the gas mixtures has taken place using the substitution method. The uncertainty of the reference value were estimated by combining the uncertainty of weighing, purity analysis of the component gases, the stability of gases in a cylinder and verification to confirm the gravimetric value. The relative expanded uncertainties (k=2) of the reference value for each component are same as 0.10 %, because the verification uncertainty is dominant.

Table 3. The uncertainty on the reference values of distributed cylinders

components	relative expanded uncertainty
purity analysis	0.001 %
weighing	0.02 %
verification of gravimetric value	0.10 %
Total	0.10 %

Results

The results submitted by the five participants are shown in Table 4, 5, and 6.
Symbols for table 4-5 are followings,

x_i result of measurement carried out by laboratory i
u_i combined standard uncertainty of x_i
x_{igrav} assigned amount of substance fraction of a component in the cylinder received by laboratory i
u_{igrav} combined standard uncertainty of x_{igrav}.

In Figure 1, 2, and 3, the results, except ERL/HIAST that is participated as 'study', 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.

Table 4. Results of key comparison APMP.QM-K3: CO

Lab i	x_i mmol/mol	u_i mmol/mol	x_{igrav} mmol/mol	u_{igrav} mmol/mol	Date of measurement	100 x relative difference
NMIJ/CERI	28.72	0.06	28.72	0.014	2001-05	0.02
CMS/ITRI	27.79	0.02	27.86	0.014	2000-10	-0.25
CSIR-NML	28.17	0.80	28.11	0.014	2000-10	0.20
ERL/HIAST	26.62	0.06	26.65	0.013	2001-01	-0.12
KRISS	27.55	0.03	27.59	0.014	2001-06	-0.15

Table 5. Results of key comparison APMP.QM-K3: CO_2

Lab i	x_i mmol/mol	u_i mmol/mol	x_{igrav} mmol/mol	u_{igrav} mmol/mol	Date of measurement	100*relative difference
NMIJ/CERI	123.61	0.11	123.55	0.06	2001-05	0.05
CMS/ITRI	124.02	0.05	124.09	0.06	2000-10	-0.05
CSIR-NML	123.22	1.80	122.97	0.06	2000-10	0.20
ERL/HIAST	213.80	11.80	124.84	0.06	2000-09	71.26
KRISS	124.11	0.07	124.16	0.06	2001-06	-0.04

ERL did not report an uncertainty for CO_2. The standard deviation of the measurement data is shown instead of the u_i.

Table 6. Results of key comparison APMP.QM-K3: C_3H_8

Lab i	x_i mmol/mol	u_i mmol/mol	x_{igrav} mmol/mol	u_{igrav} mmol/mol	Date of measurement	100*relative difference
NMIJ/CERI	1.9339	0.0016	1.9365	0.0010	2001-05	-0.13
CMS/ITRI	1.9400	0.0085	1.9515	0.0010	2000-10	-0.59
CSIR-NML						
ERL/HIAST	2.8270	0.1715	1.8887	0.0009	2001-01	49.68
KRISS	1.9547	0.0020	1.9526	0.0010	2001-06	0.11

CSIR-NML did not report a result for the propane.

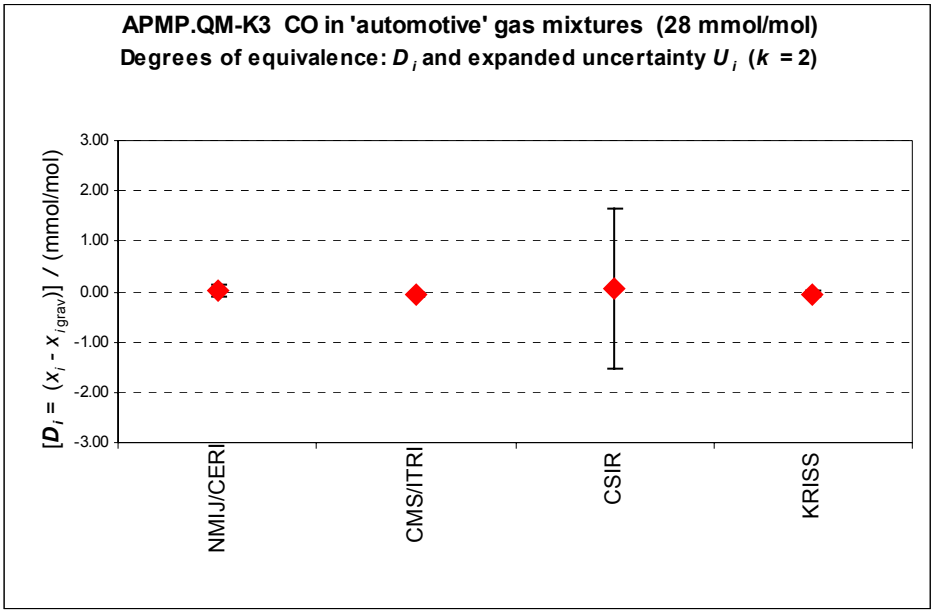

Figure 1. Degree of equivalence for carbon monoxide

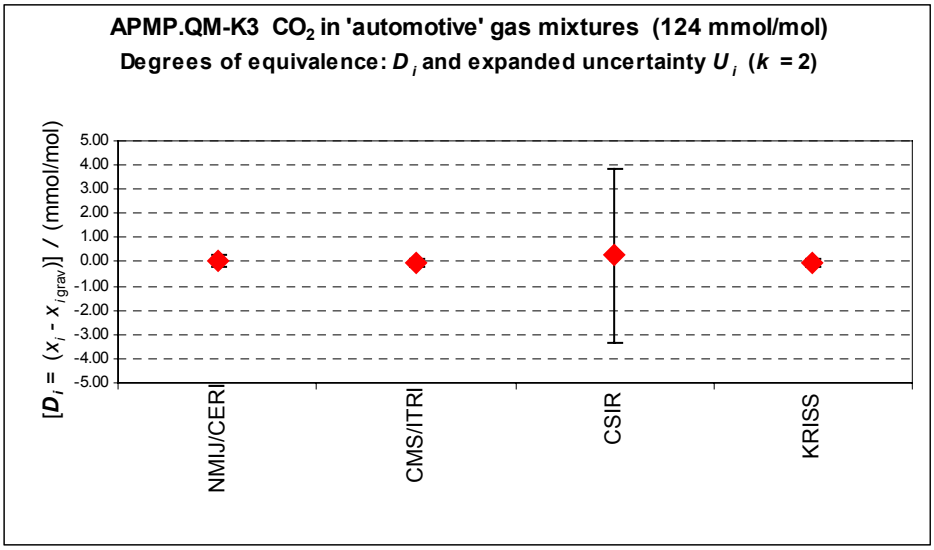

Figure 2. Degree of equivalence for carbon dioxide

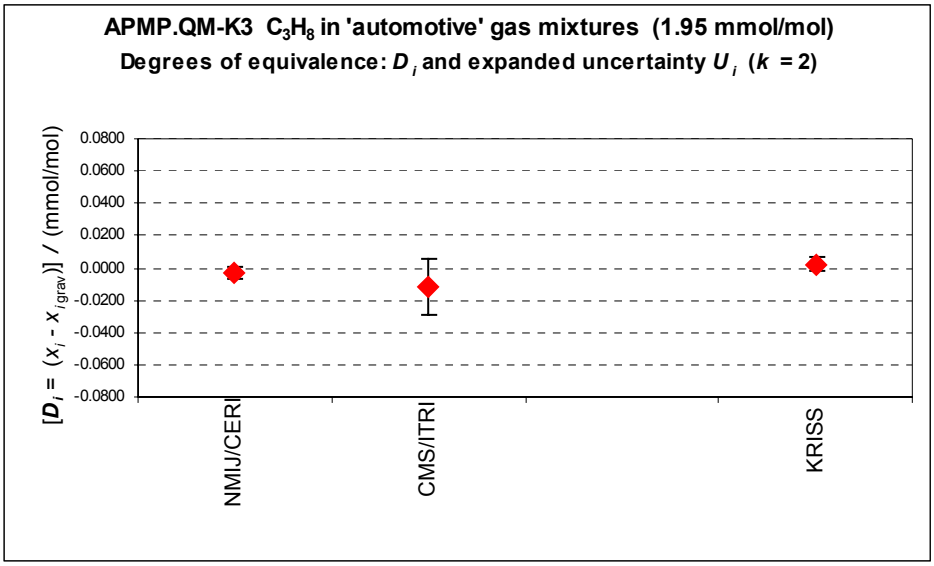

Figure 3. Degree of equivalence for propane

Discussion and Conclusions

All laboratories participated as key comparison submitted results that were within ± 1 % relative to the gravimetric value.

NMIJ/CERI and KRISS are link laboratories for CCQM-K3. The results of this comparison are linked to the key comparison CCQM-K3.

Completion Date

October 31, 2001

Annex 1: Proposal of Degrees of Equivalence

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 mmol/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 mmol/mol

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

Table 7. Degree of equivalence for carbon monoxide

			Lab *j* ⇒ NMIJ/CERI		CMS/ITRI		CSIR-NML		KRISS	
Lab *i* ⇓	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
	mmol/mol		mmol/mol		mmol/mol		mmol/mol		mmol/mol	
NMIJ/CERI	**0.01**	0.12			**0.07**	0.13	**-0.05**	1.60	**0.05**	0.13
CMS/ITRI	**-0.07**	0.05	**-0.07**	0.13			**-0.13**	1.60	**-0.03**	0.08
CSIR-NML	**0.06**	1.60	**0.05**	1.60	**0.13**	1.60			**0.10**	1.60
KRISS	**-0.04**	0.06	**-0.05**	0.13	**0.03**	0.08	**-0.10**	1.60		

Table 8. Degree of equivalence for carbon dioxide

			Lab *j* ⇒ NMIJ/CERI		CMS/ITRI		CSIR-NML		KRISS	
Lab *i* ⇓	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
	mmol/mol		mmol/mol		mmol/mol		mmol/mol		mmol/mol	
NMIJ/CERI	**0.06**	0.25			**0.12**	0.29	**-0.20**	3.61	**0.11**	0.31
CMS/ITRI	**-0.07**	0.16	**-0.12**	0.29			**-0.32**	3.61	**-0.02**	0.24
CSIR-NML	**0.25**	3.60	**0.20**	3.61	**0.32**	3.61			**0.30**	3.61
KRISS	**-0.05**	0.18	**-0.11**	0.31	**0.02**	0.24	**-0.30**	3.61		

Table 9. Degree of equivalence for propane

			Lab *j* ⇒ NMIJ/CERI		CMS/ITRI				KRISS	
Lab *i* ⇓	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
	mmol/mol		mmol/mol		mmol/mol		mmol/mol		mmol/mol	
NMIJ/CERI	**-0.0026**	0.0037			**0.0089**	0.0175			**-0.0047**	0.0058
CMS/ITRI	**-0.0115**	0.0171	**-0.0089**	0.0175					**-0.0136**	0.0177
KRISS	**0.0021**	0.0045	**0.0047**	0.0058	**0.0136**	0.0177				