Primary standard gas mixtures for measurement of ambient level of greenhouse gases

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Abstract

Greenhouse gases (GHG) have been known as causing materials of the greenhouse effect. Because it is very important to reduce their emission, they has been paid attention since Kyoto protocol to the United Nations Framework Convention on Climate Change. Accurate observation data of ambient GHG are vital for the study of the relationship between GHGs and global warming, but it is not easy to quantify their mixing ratios owing to their globally and temporally tiny variation. For example, mixing ratio of carbon dioxide in the atmosphere, is reported to be growing by +1.7 ppm (parts per million)/year for recent 10 years according to GAW report.

For the purpose of accurate measurement of GHGs, it is essential to have a accurate standard gas mixtures with global scale under well controlled quality system. We have prepared the standard gas mixtures by using a gravimetric method since 2002 and those of carbon dioxide, methane, nitrous oxide, sulphur hexafluoride, and 3 chloro-fluorocarbons are now available. Their specifications including good inter-comparison results are presented.

➢Keywords: greenhouse gas monitoring, standard gas mixtures, scale harmonization, KGAW station

Greenhouse primary standard gas preparation in KRISS

substance	Preparation method	Impurity analysis	Range of Certified Values in Reference Materials	Uncertainty (k=2) [U=2·u=2· $\sqrt{u_{grav}^2+u_{val}^2+u_{sta}^2}$]	Dissemination	Validity period /cylinder	ref
CO_2	Gravimetry/3 step	CO_2, N_2, O_2, Ar	above 10 μmol/mol	0.06 at 380 μmol/mol	Air /Air modified	2 year/Al*, 29.5L	CCQM-K3, 52
CH_4	Gravimetry/4 step	CH_4, N_2, O_2, Ar	above 100 nmol/mol	0.002 at 1.9 μmol/mol	Air /Air modified	2 year/Al*, 29.5L	CCQM-P41
N_2O	Gravimetry/5 step	N_2O, N_2, O_2	above 50 nmol/mol	0.2 at 320 nmol/mol	Air /Air modified	2 year/Al*, 29.5L	CCQM-K68
SF_6 NF_3	Gravimetry/6 step Gravimetry/6 step	SF_6, N_2, O_2 NF_3, N_2, O_2	above 6 pmol/mol for SF_6 above 1 nmol/mol for NF_3 (0.5 pmol/mol after 2011)	0.06 at 6 pmol/mol for SF_6 0.01 at 1 nmol/mol for NF_3	Air /Air modified	2 year/Al*, 29.5L	CCQM-K15, Paper preparation
PFCs	Gravimetry/6 step	CF_4 (C_2F_6), N_2, O_2	above 10 pmol/mol for CF_4 above 100 μmol/mol for C_2F_6 (50 pmol/mol after 2011)	0.1 at 10 pmol/mol for CF_4	Air /Air modified	2 year/Al*, 29.5L	CCQM-K15, Paper preparation
HFCs	Gravimetry	HFC23, N_2, O_2	above 30 pmol/mol for HFC23 after 2010		Air /Air modified	2 year/Al*, 29.5L	
CFCs HCFCs	Gravimetry/4~5 step	CFC 11,12,113, N_2, O_2	μmol/mol~50 pmol/mol for CFC 11,12,113	0.5 at 50 pmol/mol for CFC	Air /Air modified	2 year/Al*, 29.5L	

➢ traceable to SI, uncertainty level with in WMO recommendation, Additionally δ13C/CO_2, δ13C/CH_4 can be distributed after 2011, Al*: Al Barrel polished (Luxfer or Catrina)

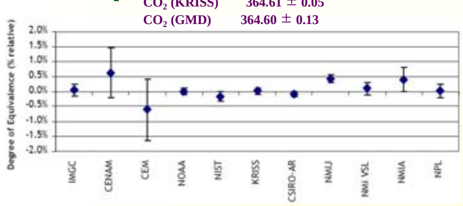
International comparison

International comparison CCQM-P41 Greenhouse gases

- Coordinating Lab: VSL (Netherland)
- Participants: 9 NMIs (2 WMO)
- Subatance: CO_2 and CH_4 ambient level

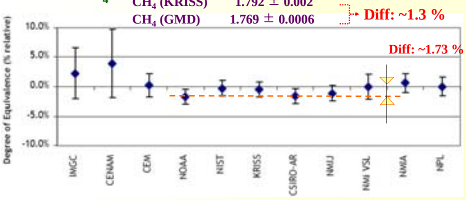
CO_2 [2003]

CO_2 (Reference) 364.60 ± 0.18
CO_2 (KRISS) 364.61 ± 0.05
CO_2 (GMD) 364.60 ± 0.13



CH_4

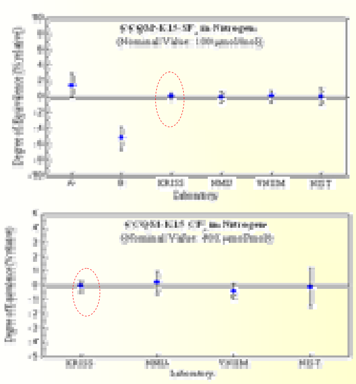
CH_4 (Reference) 1.800 ± 0.011
CH_4 (KRISS) 1.792 ± 0.002
CH_4 (GMD) 1.769 ± 0.0006
Diff: ~1.3 %



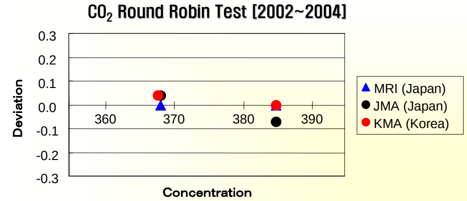
International comparison CCQM-K15 Emission level of CF_4 and SF_6

- coordinating Lab: KRISS, participants: 6 NMIs
- Participants: SF_6 & CF_4 hundred μmol/mol level
- rational
  - Growth of industry for Semicon, Display: uses many kinds of PFCs during manufacturing process

[2003]



CO2 Round robin test between Japan-Korea



CH_4 reference gas inter-comparison for Asia

Inter-comparison (2001-2002)

Laboratory and Location	Date of Measurement	Conc. (nmol/mol) Cylinder No. CPB13002	Cylinder No. CPB13002
JMA, Headquarters, Tokyo	2001.4.23 – 4.24	**1811.4**	**1963.9**
CMA, CGAWBO at Mt. Waliguan	2001.7.21 – 7.24	**1822.9**	**1980.5**
KMA, Anmyeon-do, Korea	2001.9.3 – 9.5	**1786.4**	**1935.7**
JMA, Headquarters, Tokyo	2001.11.4 – 11.5	**1812.6**	**1964.0**
CMDL, Boulder	2002.2.13 – 3.12	**1787.2**	**1935.9**

- 1.3 % difference between The KRISS Scale and the NOAA Scale

Inter-comparison (2005-2006)

Laboratory and Location	Date of Measurement	Cylinder Number CPB31289 Conc. (ppb)	SD (ppb)	No	CPB31288 Conc. (ppb)	SD (ppb)	No
JMA, Tokyo, Japan	Jul. 6-7, 2005	1696.0	1.6	10	1876.7	1.5	10
CMA, Mt. Waliguan, China	Feb., 2006	1670.1	1.9	103	1845.4	2.3	167
KMA, Anmyeon-do, Korea	Apr.18-27,2006	1695.8	1.5	70	1872.7	1.4	80
KRISS, Daejeon, Korea	Jun.26-30, 2006	1698.3	1.2	9	1877.1	0.9	8
JMA, Tokyo, Japan	Aug.21, 2006	1695.7	1.1	10	1877.3	0.7	9

- The KRISS Scale agree with the NOAA Scale.

Inter-comparison (2008-2009)

Laboratory and Location	Date of Measurement	Cylinder Number CPB13002 Concentration (ppb)	SD (ppb)	No	CPB13003 Concentration (ppb)	SD (ppb)	No	instrument
JMA Tokyo, Japan	May. 1, 2008	1664.4	1.2	10	1848.4	1.8	10	SHIMADZU GC-14BPF
KRISS Daejeon, RP Korea	Sep. -Nov., 2008	1665.1	0.2	5	1851.2	0.2	5	HP-6890
KMA Anmyeon-do, RP Korea	Oct. –Nov., 2008	1665.6	1.2	12	1851.3	1.4	12	HP-6890
CMA Mt. Waliguan, China	Apr. 3-5, 2009	1661.1	0.9	14	1847.0	0.8	14	Agilent-6890N
	Apr. 13-14, 2009	1662.3	0.2	9	1847.2	0.3	9	Picarro G1301
	Apr. 14-16, 2009	1659.3	5.2	10	1846.1	1.9	10	HP-5890
CMA Beijing, China	Apr. 28-29, 2009	1661.9	2.0	10	1847.5	0.6	10	Agilent-6890N
	Apr. 29, 2009	1662.5	0.2	9	1847.3	0.1	9	Picarro G1301
	Apr. 30.2009	1662.2	1.6	12	1847.2	1.8	12	Agilent-6890N
JMA Tokyo, Japan	Jul. 1, 2009	1664.3	1.1	10	1846.8	1.7	10	SHIMADZU GC-14BPF

- The KRISS Scale agree with the NOAA Scale within about 4 ppb.

Japan Meteorological Agency (JMA), Chinese Academy of Meteorological Sciences (CMA)

International comparison CCQM-K52 Carbon dioxide in Synthetic Air

- Coordinating Lab: VSL (Netherland)
- Participants: 17 NMIs (2 WMO)

[2008]

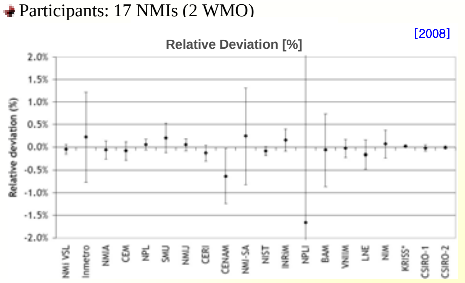
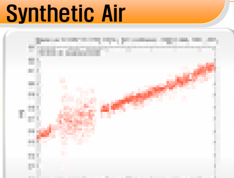


Table 4: Results bilateral NMi-VSL - KRISS

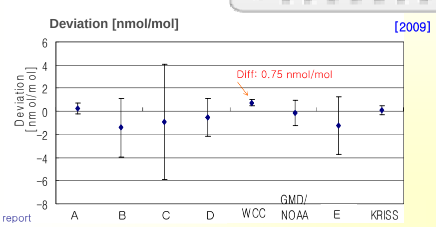
Laboratory	Cylinder	x_{prep}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	k	$U(\Delta x)$
KRISS	D751977	363.12	0.073	0.18	0.20	363.20	0.06	2	0.08	2	0.41

International comparison CCQM-K68 Nitrous oxide in Synthetic Air

- coordinating Lab: KRISS,
- participants: 6 NMIs (2 WMO)
- nominally : N_2O 320 nmol/mol
- scale comparison bet. NMIs and WMO



[2009]



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