International comparison CCQM-K82:
Methane in Air at Ambient level (1800-2200) nmol/mol

(Final report)

Edgar Flores[*1], Joële Viallon[1], Tiphaine Choteau[1], Philippe Moussay[1], Robert I. Wielgosz[1], Namgoo Kang[2], Byung Moon Kim[2], Ewelina Zalewska[3], Adriaan (A.M.H.) van der Veen[3], Leonid Konopelko[4], Hai Wu[5], Qiao Han[5], George Rhoderick[6], Franklin R. Guenther[6], Takuro Watanabe[7], Takuya Shimosaka[7], Kenji Kato[7], Brad Hall[8], Paul Brewer[9].

[1]Bureau International des Poids et Mesures (BIPM), Pavillon de Breteuil, F-92312 Sèvres Cedex, France.
[2]Korea Research Institute of Standards and Science (KRISS),1 Doryong-Dong, Yuseong-Gu, Daejeon 305-340, Republic of Korea.
[3]Dutch Metrology Institute (VSL), Thijsseweg 11 2629 JA Delft The Netherlands.
[4]D.I.Mendeleyev Institute for Metrology (VNIIM), 19 Moskovsky pr., St. Petersburg, 190005 Russia.
[5]National Institute of Metrology (NIM), China, No.18, Bei-San-Huan Dong Str., Beijing 100013, China.
[6]National Institute of Standards and Technology (NIST), 100 Bureau Drive, Gaithersburg, MD 20899-8393, USA.
[7]National Metrology Institute of Japan (NMIJ), 305-8563 1-1-1, Umezono, Tsukuba, Ibaraki 305-8563 Japan.
[8]National Oceanic and Atmospheric Administration (NOAA), 325 Broadway, Mail Stop R.GMD1, Boulder, CO 80305 USA.
[9]National Physical Laboratory (NPL), Hampton Road, Teddington, Middx, TW11 0LW, UK.

Coordinating laboratories:

Bureau International des Poids et Mesures (BIPM)
National Institute of Standards and Technology (NIST)

Study coordinator: Edgar Flores (BIPM)
Correspondence to be addressed to: Edgar Flores edgar.flores@bipm.org
(Tel: + 33 1 45 07 70 92)

Field: Amount of substance

Organizing Body: CCQM

Index

1. Rationale for comparison

The CCQM-K82 comparison was designed to evaluate the level of comparability of NMI preparative capabilities for gravimetric methane in air primary reference mixtures in the range (1800-2200) nmol mol^{-1}. The balance gas for the standards was either scrubbed dry real air or synthetic air.

This study involved a simultaneous comparison of a suite of gas standards with two prepared by each of the eight participating laboratories. The standards were sent to the BIPM where the comparison measurements were performed. The reference value for a given gas standard was calculated from a calibration line derived from a self-consistent subset of the standards. Measurements at the BIPM were performed using two independent analytical methods gas chromatograph (GC-FID) and cavity ring-down spectroscopy (CRDS), and following the advice of the CCQM Gas Analysis Working Group, results from the CRDS method were used to calculate the key comparison reference value.

The performance of the BIPM measurement systems were previously validated using a suite of CH_4 in air standards prepared by the NIST.

2. Quantities and Units

In this comparison the measurand was the amount of substance fraction of methane in either scrubbed dry real air or synthetic air, with measurement results being expressed in mol/mol and its submultiples µmol/mol or nmol/mol.

The table below describes the limits of the gas matrix composition of the scrubbed dry real air and synthetic air, which were to be met by participants:

Component in Air	Minimum amount of substance fraction permitted within submitted cylinder	Maximum amount of substance fraction permitted within submitted cylinder
Nitrogen	0.77849 mol/mol	0.78317 mol/mol
Oxygen	0.20776 mol/mol	0.21111 mol/mol
Argon	8.865 mmol/mol	9.799 mmol/mol
Carbon Dioxide	360 µmol/mol	400 µmol/mol

Table 1. Limits for balance gas composition in standards submitted for the comparison. Based upon the possible biases that could be introduced into the spectroscopic comparison method (CRDS) due to variation in the composition of the air matrix in different standards, participating laboratories were asked to ensure that the composition of their air matrix was within these limits.

3. Schedule

The revised schedule for the project was as follows:

May 2012- April 2013	Mixture preparation, verification and stability tests by participants.
October 2012- May 2013	Shipment of cylinders to the BIPM
May 2013 – June 2013	Analysis of mixtures by the BIPM
July 2013	Shipment of cylinders back from the BIPM to participants
August 2013 – October 2013	2nd set of analysis of mixtures by participants
October 2013	Distribution of Draft A of this report
March 2014	Distribution of Draft B of this report
July 2014	Distribution of final report

4. Measurement standards

The study was organised as a comparison of a suite of 2*n* primary gas standards, two standards prepared by each of the *n* participating laboratories. The reference value for a given gas standard was to be determined from a regression line calculated from all standards, or from a self-consistent subset of the standards. Measurements at the BIPM were performed with two independent analytical methods, notably Cavity Ring Down Spectroscopy (CRDS) and Gas Chromatography with Flame Ionization Detector (GC-FID).

Each participating laboratory was asked to provide one high pressure cylinder standard at the nominal amount of substance fraction of 1800±20 nmol/mol and one high pressure cylinder standard at the amount of substance fraction 2200±20 nmol/mol together with the following information:

In the case of standards produced with synthetic air:

- a purity table with uncertainties for the nominally pure CH_4 parent gas;
- a purity table with uncertainties for the nominally pure N_2, O_2, Ar and CO_2 parent gas;
- a brief outline of the dilution series undertaken to produce the final mixtures;
- a purity table for each of the final mixtures, including gravimetric uncertainties;
- a brief outline of the verification procedure applied to the final mixtures;
- a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

In the case of standards produced with scrubbed 'real' air:

- a purity table with uncertainties for the nominally pure CH_4 parent gas;
- results of the analysis and amount of substance fractions and uncertainties of N_2, O_2, Ar and CO_2 in the scrubbed real air;
- a brief outline of the preparation procedure of the final mixtures;
- a composition table for each of the final mixtures, including gravimetric uncertainties when relevant;
- a brief outline of the verification procedure applied to the final mixtures;
- a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM.

Information submitted by participating laboratories is included in ANNEX 2 - Measurement reports of participants .

The CH_4 amount of substance fractions reported by participants are listed in Table 3, where:

x_{NMI} is the value assigned by the participating NMI based on gravimetric preparation;

$u(x_{NMI})$ is the standard uncertainty including contributions from verification associated with the assigned value x_{NMI};

Figure 1 plots the CH_4 amount of substance fraction reported by the participants for each gas standard. In this figure the error bars represent the standard uncertainty associated with the certified value. In this figure it can be observed that for the amount of substance fraction range (1800±20 nmol/mol) NIST submitted the mixture with the smallest CH_4 amount of substance fraction, 1796.76±1.7 nmol/mol, and NIM with the highest, 1825.6±1.7 nmol/mol, which was outside of the amount of substance fraction range requested. For the amount of substance fraction range (2200±20 nmol/mol) NIM produced the lowest amount of substance fraction, 2193.80±2.00 nmol/mol, and VNIIM the highest, 2214.60±2.5 nmol/mol. The expanded uncertainties reported by the participants are plotted in Figure 2.

All mixtures were within specifications, for gas matrix composition, as required in the comparison protocol[1] (see Table 4). Ten of sixteen standards were produced in synthetic air and the six others in purified (scrubbed) real air (Table 3).

5. Measurement protocol

On receipt by the BIPM, all cylinders were allowed to equilibrate at laboratory temperature for at least 24 hours. All cylinders were rolled for 1 hour to ensure homogeneity of the mixture. Each cylinder was connected from the pressure reducer to one inlet of a 16-inlet automatic gas sampler. The sampler was connected to two analysers, the GC-FID and to the CRDS. The pressure reducer of each cylinder was flushed nine times with the mixture. The cylinder valve was closed leaving the high pressure side of the pressure reducer at the cylinder pressure and the low pressure side of the pressure reducer at ~300 kPa (abs). The cylinders were left stand at least 24 hours, to allow conditioning of the pressure reducers.

Four methodologies were used to measure the cylinders, three based on CRDS, Method 1-A, 1-B and 2, and one on GC-FID.

[1] *This nominal fraction limits were given in order to avoid possible biases that could be introduced into the spectroscopic comparison method (CRDS) due to variation in the composition of the air matrix in different standards.*

In Method 1-A and Method 1-B the BIPM reported values were the CRDS responses defined as the average of the CRDS value over five minutes of measurements. Methods 1-A measurements were made under repeatability conditions over 6 hours. Method 1-B measurements were made under intermediate precision conditions by sequential measurements during thirty days. Method 2 measurements were also made under intermediate precision conditions, over 30 days. In this Method, the BIPM reported value was the drift corrected ratio between the instrument response and a control cylinder.

The cylinders were also analysed by GC-FID, where the BIPM reported value was the drift corrected ratio between the GC-FID response and the control cylinder. These measurements were performed under intermediate precision conditions (thirty days).

6. Comparison results

Measurements were performed at the BIPM from April to June 2013. Table 5 lists the inlet pressure before and after the standards were analyzed by the BIPM.

Each cylinder was value assigned using the methods described in section 5 (details in ANNEX 1- BIPM Value assignment procedure). The results of these series of measurements are listed in Table 6 where:

$\overline{y}_A$ is the reported value based on CRDS measurements by Method 1-A (under repeatability conditions, 6 hour measurement period);

$u\left(\overline{y}_A\right)$ is the standard uncertainty of the reported value based on CRDS measurements by Method 1-A;

$\overline{y}_B$ is the reported value based on CRDS measurements using Method 1-B (response under intermediate precision conditions, measurements over 30 days);

$u\left(\overline{y}_B\right)$ is the standard uncertainty of the reported value based on CRDS measurements by Method 1-B;

$\overline{R}_2$ is the reported value based on CRDS measurements by Method 2 (with control cylinder under intermediate precision conditions, measurements over 30 days);

$u\left(\overline{R}_2\right)$ is the standard uncertainty of the reported value based on CRDS measurements by Method 2;

$\overline{R}_{wGC}$ is the reported value based on GC-FID measurements;

$u\left(\overline{R}_{GC}\right)$ is the standard uncertainty of the reported value based on GC-FID;

To simplify the presentation of the results, Table 6 results were plotted in Figure 3 and Figure 4 overlapping CRDS Method 1-A and CRDS Method 1-B responses and CRDS Method 2 and GC-FID ratios to control standard results respectively. The typical uncertainties for each of the methods used by the BIPM are listed in Table 2. Once returned to the participants, the standards were analyzed by the laboratories in order to verify the stability of the mixtures.

Comparison method name	Measurement quantity	Symbol	unit	Typical relative standard uncertainty (%)
CRDS Method 1-A	Instrument response under repeatability conditions	$\overline{y}_A$	ppb	0.01
CRDS Method 1-B	Instrument response under intermediate precision conditions	$\overline{y}_B$	ppb	0.02
CRDS Method 2	Ratio to control cylinder under intermediate precision condition	$\overline{R}_2$	1	0.025
GC-FID	Ratio to control cylinder under intermediate precision conditions	$\overline{R}_{wGC}$	1	0.025

Table 2. Summary of methods used during the CCQM-K82 international comparison and typical uncertainties obtained by the BIPM.

Participant	Cylinder references	Gas Matrix	NMI's assigned CH_4 amount of substance fraction x_{NMI} (nmol/mol)	NMI's assigned CH_4 expanded uncertainty k=2 $U(x_{NMI})$ (nmol/mol)
KRISS	D929248	Synthetic Air	1797.10	1.00
KRISS	D985705	Synthetic Air	2200.90	1.20
NIM	CAL017763	Synthetic Air	1825.20	1.70
NIM	CAL017790	Synthetic Air	2193.80	2.00
NIST	FB03569	Purified real air	1796.76	1.70
NIST	FB03587	Purified real air	2195.96	1.68
NMIJ	CPB-28035	Synthetic Air	1797.30	1.30
NMIJ	CPB-28219	Synthetic Air	2198.30	1.30
NOAA	FB03578	Purified real air	1812.10	2.60
NOAA	FB03593	Purified real air	2208.90	2.80
NPL	221727	Purified real air	1799.40	3.60
NPL	233097	Purified real air	2199.60	4.40
VNIIM	D249682	Synthetic Air	1812.90	2.60
VNIIM	D249845	Synthetic Air	2214.60	2.50
VSL	D 249292	Synthetic Air	1798.29	4.00
VSL	D 249289	Synthetic Air	2196.33	4.80

Table 3. Characteristics of gravimetric mixtures as provided by participants.

Participant	Number of Cylinder	Gas Matrix	NMI's assigned CH_4 amount of substance fraction x_{NMI} (nmol/mol)	NMI's assigned expanded uncertainty k=2 $U(x_{NMI})$ (nmol/mol)	NMI's assigned CO_2 amount of substance fraction x_{CO2} (μmol/mol)	NMI's assigned expanded uncertainty k =2 $U(x_{CO2})$ (μmol/mol)	NMI's assigned Ar amount of substance fraction x_{Ar} (mmol/mol)	NMI's assigned expanded uncertainty k =2 $U(x_{Ar})$ (mmol/mol)	NMI's assigned O_2 amount of substance fraction x_{O2} (%)	NMI's assigned expanded uncertainty k=2 $U(x_{O2})$ (%)	NMI's assigned N_2 amount of substance fraction x_{N2} (%)	NMI's assigned expanded uncertainty k =2 $U(x_{N2})$ (%)
KRISS	D929248	S. A.	1797.10	1.00	381.76000	0.17000	9.88000	0.01100	20.96007	0.00071	78.05350	0.00110
KRISS	D985705	S. A.	2200.90	1.20	379.70000	0.19000	9.41360	0.00700	20.76648	0.00066	78.25379	0.00091
NIM	CAL017763	S. A.	1825.20	1.70	378.91000	0.08369	9.39110	0.00640	21.01900	0.00108	78.00300	0.00012
NIM	CAL017790	S. A.	2193.80	2.00	377.68000	0.08321	9.36110	0.00631	20.86900	0.00103	78.15700	0.00117
NIST	FB03569	R. A.	1796.76	1.70	390.89300	0.04500	9.37986	0.01274	20.92714	0.00261	78.09558	0.00818
NIST	FB03587	R. A.	2195.96	1.68	390.93900	0.04194	9.37999	0.01223	20.92595	0.00249	78.09671	0.00792
NMIJ	CPB-28035	S. A.	1797.30	1.30	386.66000	0.09000	9.25980	0.00070	21.05380	0.00060	77.98140	0.00060
NMIJ	CPB-28219	S. A.	2198.30	1.30	383.39000	0.09000	9.43990	0.00080	20.92760	0.00070	78.08980	0.00070
NOAA	FB03578	R. A.	1812.10	2.60	376.18000	0.14000	9.33200	0.00600	20.91200	0.01200	78.15500	0.01200
NOAA	FB03593	R. A.	2208.90	2.80	366.98000	0.14000	9.33200	0.00600	20.91200	0.01200	78.15500	0.01200
NPL	221727	R. A.	1799.40	3.60	370.70000	0.70000	9.34500	0.02700	20.92720	0.01300	78.10060	0.04700
NPL	233097	R. A.	2199.60	4.40	372.50000	0.70000	9.34100	0.02700	20.92710	0.01300	78.10080	0.04700
VNIIM	D249682	S. A.	1812.90	2.60	380.75000	0.21000	9.33600	0.00700	20.97670	0.00150	0.00000	0.00000
VNIIM	D249845	S. A.	2214.60	2.50	381.18000	0.23000	9.32400	0.01000	21.02040	0.00180	0.00000	0.00000
VSL	D 249292	S. A.	1798.29	4.00	380.29200	0.02000	9.29510	0.00035	20.89707	0.00027	78.13520	0.00027
VSL	D 249289	S. A.	2196.33	4.80	380.34400	0.22000	9.30828	0.00037	20.90399	0.00027	78.12692	0.00027

Table 4. Purity table of the submitted gas mixtures according to participants' reports in ANNEX 2 - Measurement reports of participants.Synthetic Air is identified as S. A. and Purified real air as R. A.* No data given.

Departure and return pressure of the gas standards

Lab	Number of Cylinder	Date of arrival	Date of return	pressure on arrival Mpa	pressure on departure Mpa
KRISS	D929248	11/02/2013	09/07/2013	8.0	6.5
KRISS	D985705	11/03/2013	09/07/2013	8.5	7.0
NIM	CAL017763	02/05/2013	16/07/2013	8.5	7.0
NIM	CAL017790	02/05/2013	16/07/2013	9.5	8.0
NIST	FB03569	21/12/2012	12/07/2013	7.6	4.5
NIST	FB03587	21/12/2012	12/07/2013	6.9	4.0
NMIJ	CPB-28035	06/11/2012	26/09/2013	10.0	8.5
NMIJ	CPB-28219	06/11/2012	26/09/2013	10.0	8.0
NOAA	FB03578	16/11/2012	12/07/2013	-	8.0
NOAA	FB03593	16/11/2012	12/07/2013	-	8.0
NPL	221727	07/02/2013	05/07/2013	9.0	8.5
NPL	233097	07/02/2013	05/07/2013	9.0	7.5
VNIIM	D249682	30/10/2012	16/07/2013	9.0	7.0
VNIIM	D249845	30/10/2012	16/07/2013	9.0	6.5
VSL	D 249292	09/11/2012	06/09/2013	11.7	9.5
VSL	D 249289	09/11/2012	06/09/2013	11.8	8.0

Table 5. Pressure of the gas standards on arrival and departure from the BIPM.

Participant	Number of Cylinder	x_{NMI} Assigned NMI's CH_4 amount of substance fraction in (nmol/mol)	$u(x_{NMI})$ Assigned NMI's Standard uncertainty (k=1) (nmol/mol)	$\overline{y}_A$ CRDS Method 1-A (Under repeatability conditions) Response of CRDS analyzer in ppb	$u(\overline{y}_A)$ Standard Uncertainty in instrument response ppb	$\overline{y}_B$ CRDS Method 1-B (Under Intermediate precision conditions) Response of CRDS analyzer in ppb	$u(\overline{y}_B)$ Standard Uncertainty in instrument response ppb	$\overline{R}_2$ CRDS Method 2 (Under intermediate precision conditions) Ratios to control cylinder	$u(\overline{R}_2)$ Standard uncertainty in the Ratios to control cylinder	$\overline{R}_{wGC}$ GC-FID (Under intermediate precision conditions) Ratios to control cylinder	$u(\overline{R}_{GC})$ Standard uncertainty in the Ratios to control cylinder
KRISS	D 929248	1797.10	0.50	1799.60926	0.14073	1799.86935	0.38388	0.94490	0.00026	0.94496	0.00024
KRISS	D 985705	2200.90	0.60	2204.16130	0.14480	2204.63154	0.36594	1.15737	0.00026	1.15796	0.00025
NIM	CAL017763	1825.20	0.85	1827.50983	0.15982	1827.63050	0.37394	0.95961	0.00027	0.95978	0.00025
NIM	CAL017790	2193.80	1.00	2195.89326	0.17085	2196.30459	0.38093	1.15314	0.00026	1.15336	0.00025
NIST	FB03569	1796.76	0.85	1798.60535	0.19742	1799.06344	0.35702	0.94449	0.00026	0.94445	0.00024
NIST	FB03587	2195.96	0.84	2196.67296	0.21216	2197.01439	0.36278	1.15345	0.00026	1.15377	0.00025
NMIJ	CPB-28035	1797.30	0.65	1798.14676	0.16347	1798.55020	0.34420	0.94429	0.00026	0.94429	0.00025
NMIJ	CPB-28219	2198.30	0.65	2199.05187	0.26322	2199.62465	0.33020	1.15489	0.00026	1.15506	0.00025
NOAA	FB03578	1812.10	1.30	1816.28065	0.19906	1816.63607	0.41202	0.95368	0.00027	0.95371	0.00024
NOAA	FB03593	2208.90	1.40	2215.77219	0.15564	2216.13485	0.42586	1.16346	0.00026	1.16388	0.00025
NPL	221727	1799.40	1.80	1802.42557	0.16529	1802.70344	0.37915	0.94650	0.00026	0.94659	0.00025
NPL	233097	2199.60	2.20	2203.04409	0.15029	2203.46678	0.37632	1.15683	0.00026	1.15689	0.00024
VNIIM	D 249682	1812.90	1.30	1812.03194	0.18482	1812.06648	0.33792	0.95159	0.00026	0.95151	0.00026
VNIIM	D 249845	2214.60	1.25	2216.42565	0.17334	2217.03717	0.37642	1.16395	0.00026	1.16408	0.00025
VSL	D 249292	1798.29	2.0	1799.61069	0.14994	1799.69072	0.45676	0.94499	0.00027	0.94515	0.00024
VSL	D 249289	2196.33	2.4	2197.31476	0.17831	2197.60865	0.49573	1.15390	0.00026	1.15415	0.00023

Table 6. Results of BIPM CH_4 amount of substance fraction measurements.

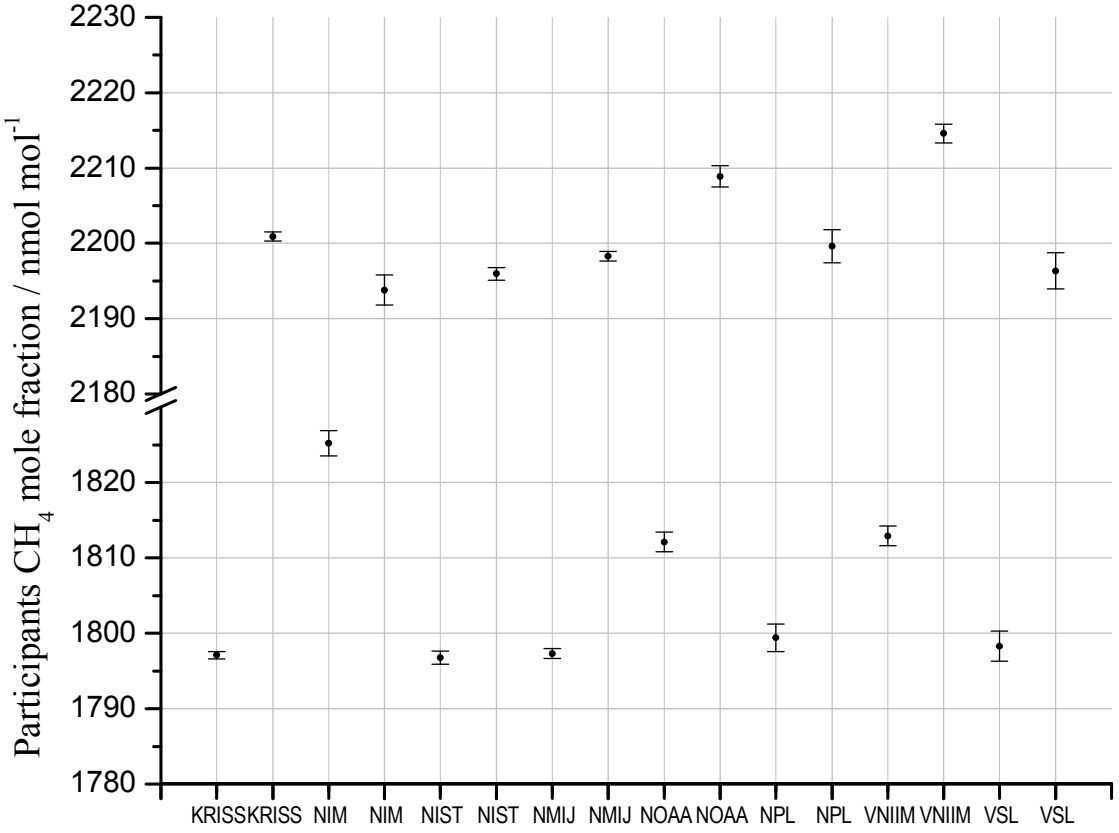

Figure 1. CH_4 amount of substance fractions x_{NMI} provided by participants. The error bars represents the standard uncertainty (k=1) associated with the submitted values.

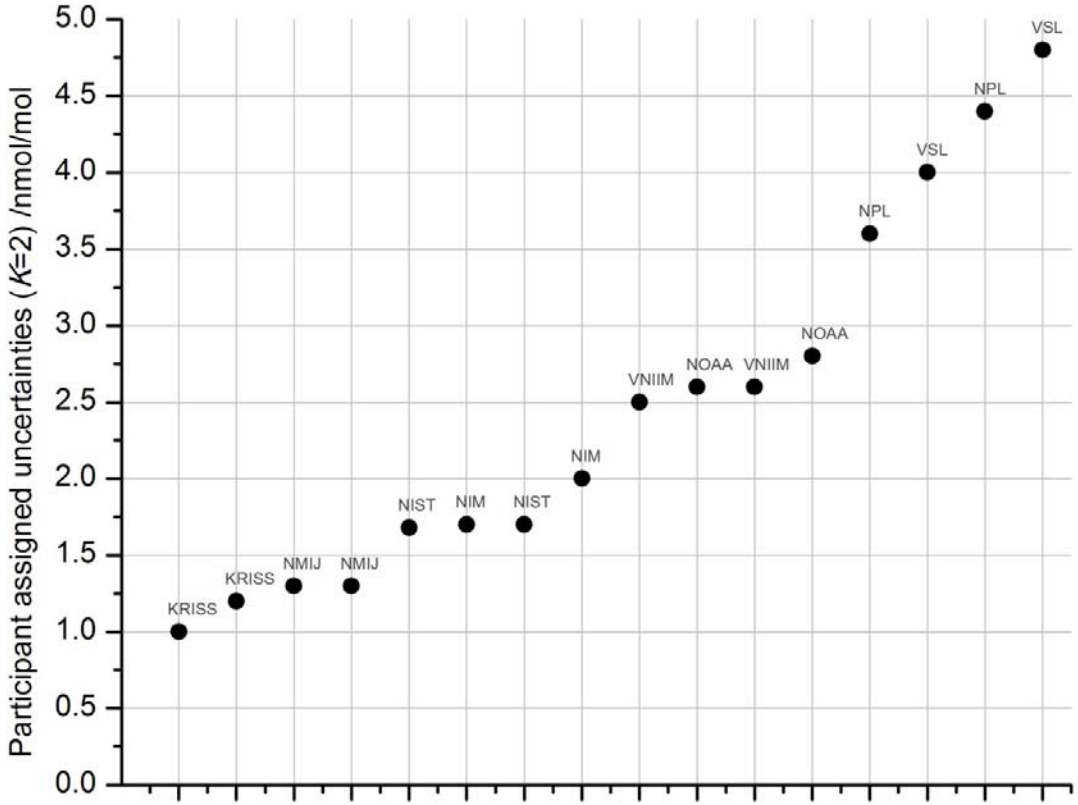

Figure 2. Participants' assigned CH_4 expanded uncertainties $U(x_{NMI})$.

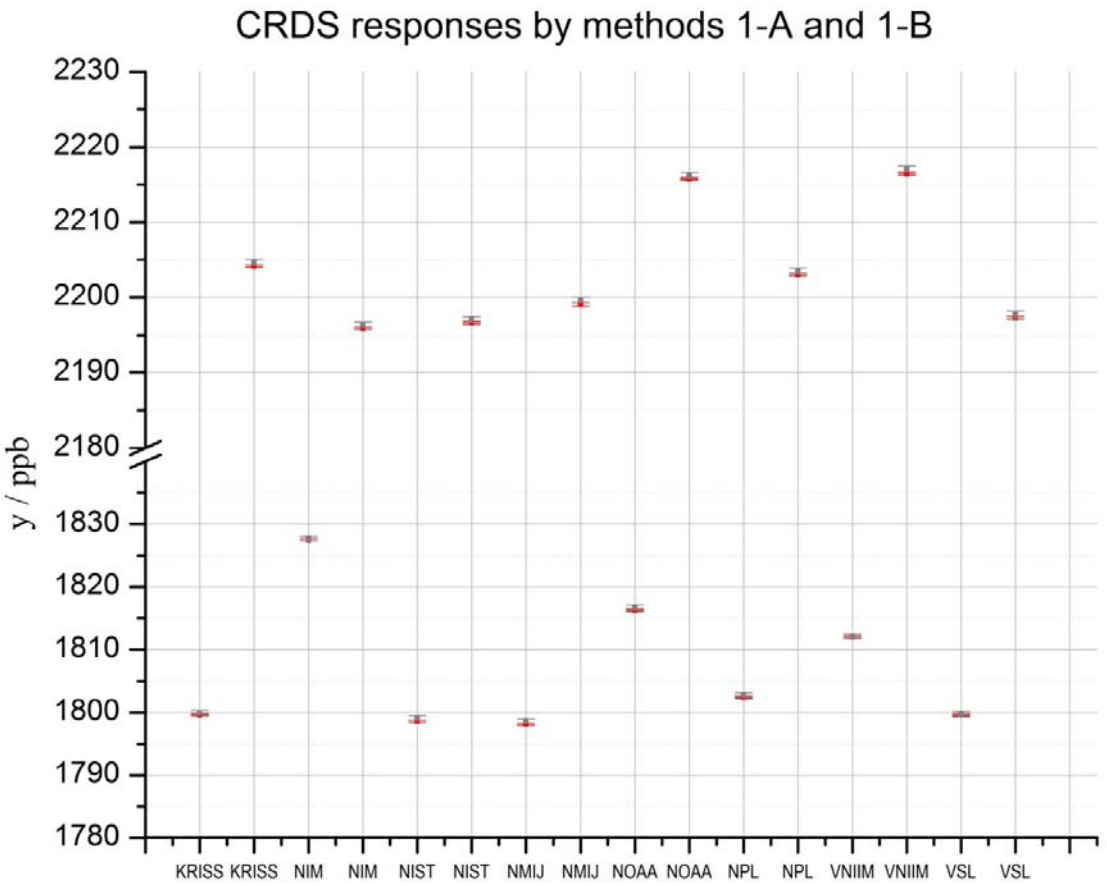

Figure 3. CRDS responses on gas mixtures by Method 1-A (red dots) and Method 1-B (black dots). The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results. For further information see section ANNEX 1- BIPM Value assignment procedure.

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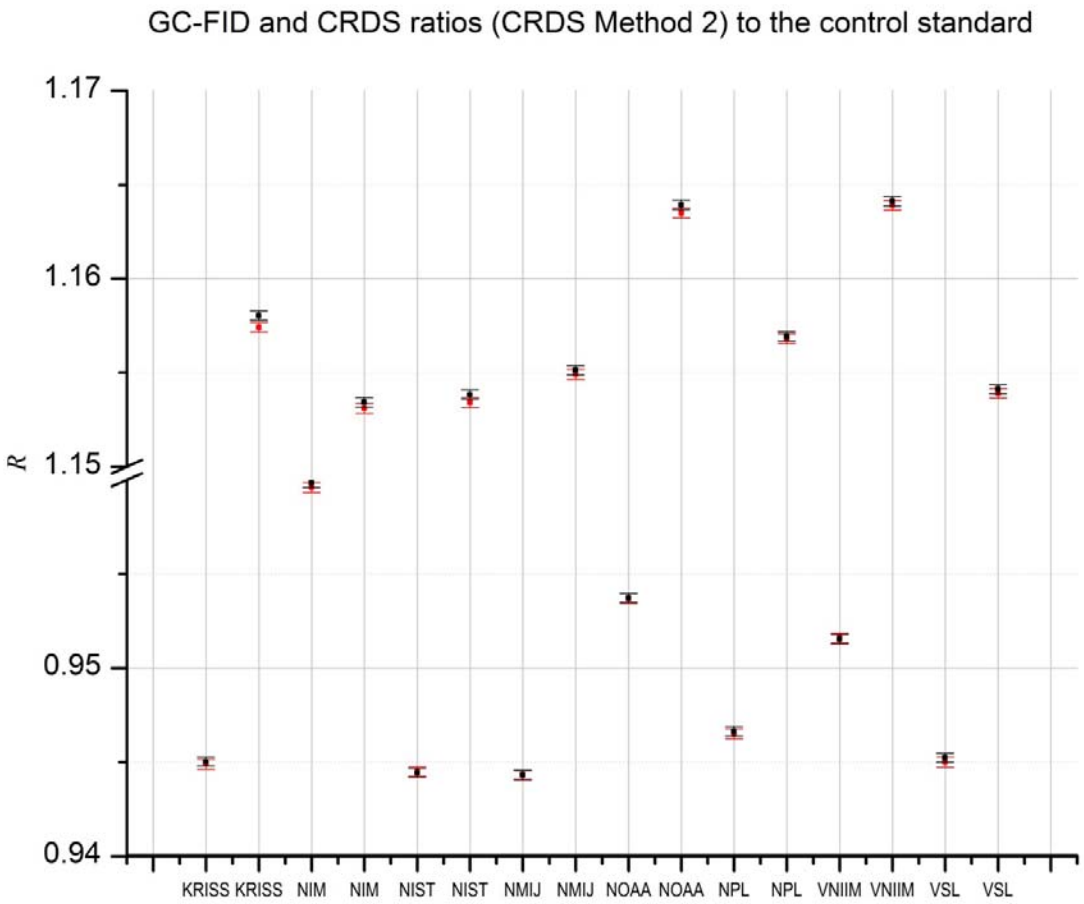


Figure 4. CRDS ratios to the control standard by Method 2, R_2 (black dots) and GC-FID ratios to the control standard, R_{wGC} (red dots). The error bars represent the standard uncertainty (k = 1) associated with the BIPM measurement results. For further information see ANNEX 1- BIPM Value assignment procedure.

Table 7 summarizes the figures showing the measurements results obtained by different methods at the BIPM.

Comparison method	CH_4 amount of substance fraction	Figure
CRDS Method 1-A		
(Instrument responses under repeatability conditions)		
	1750 nmol/mol to 2250 nmol/mol	5
	1795-1830 nmol/mol	6
	2190-2220 nmol/mol	7
CRDS Method 1-B		
(Instrument responses under intermediate precision conditions)		
	1750 nmol/mol to 2250 nmol/mol	8
	1795-1830 nmol/mol	9
	2190-2220 nmol/mol	10
CRDS Method 2		
(Ratio to control cylinder under intermediate precision conditions)		
	1750 nmol/mol to 2250 nmol/mol	11
	1795-1830 nmol/mol	12
	2190-2220 nmol/mol	13
GC-FID		
(Ratio to control cylinder under intermediate precision conditions)		
	1750 nmol/mol to 2250 nmol/mol	14
	1795-1830 nmol/mol	15
	2190-2220 nmol/mol	16

Table 7. List of figures corresponding to results obtained from Methods 1-A, 1-B, 2 and GC-FID.

A key measurement required for the preparation of accurate methane standards is the determination of trace methane in the balance gas[1]. Trace methane levels in balance gas in the standards provided and measured by participants is shown in Figure 17.

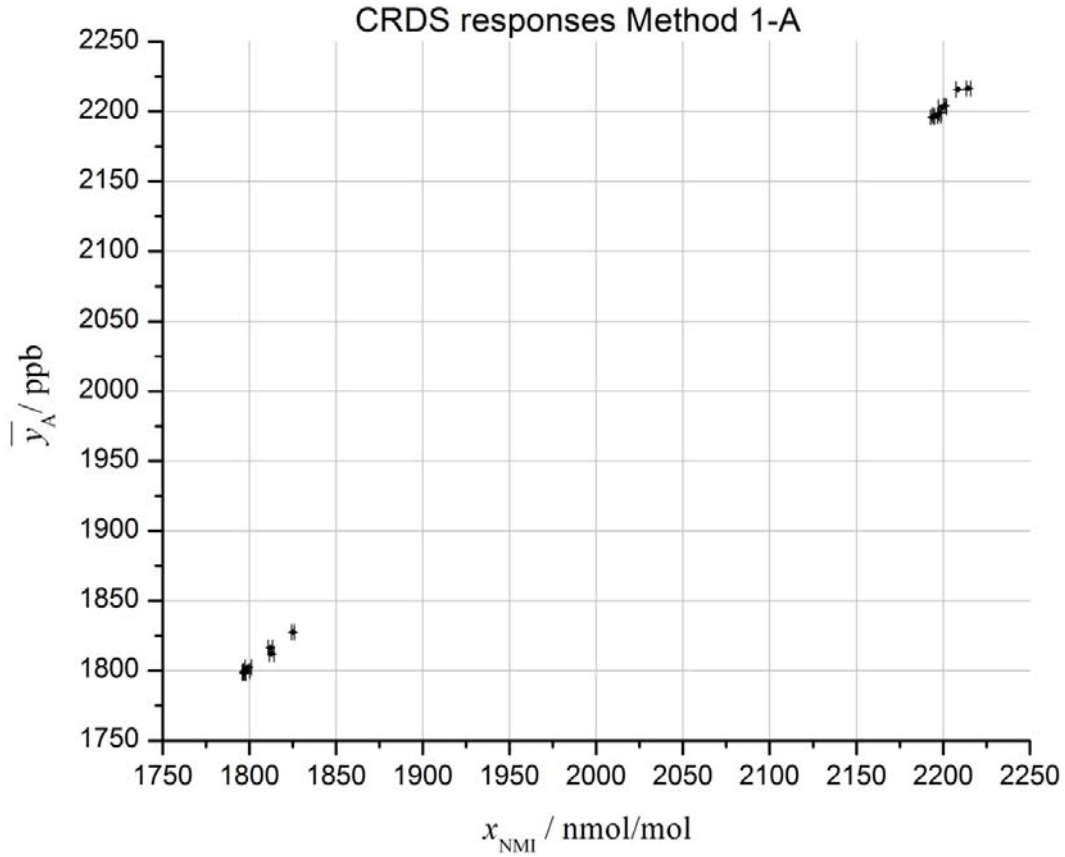


Figure 5. CRDS response to the participants gas mixtures by Method 1-A. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI gravimetric values (x-axis). For further information see section ANNEX 1- BIPM Value assignment procedure.

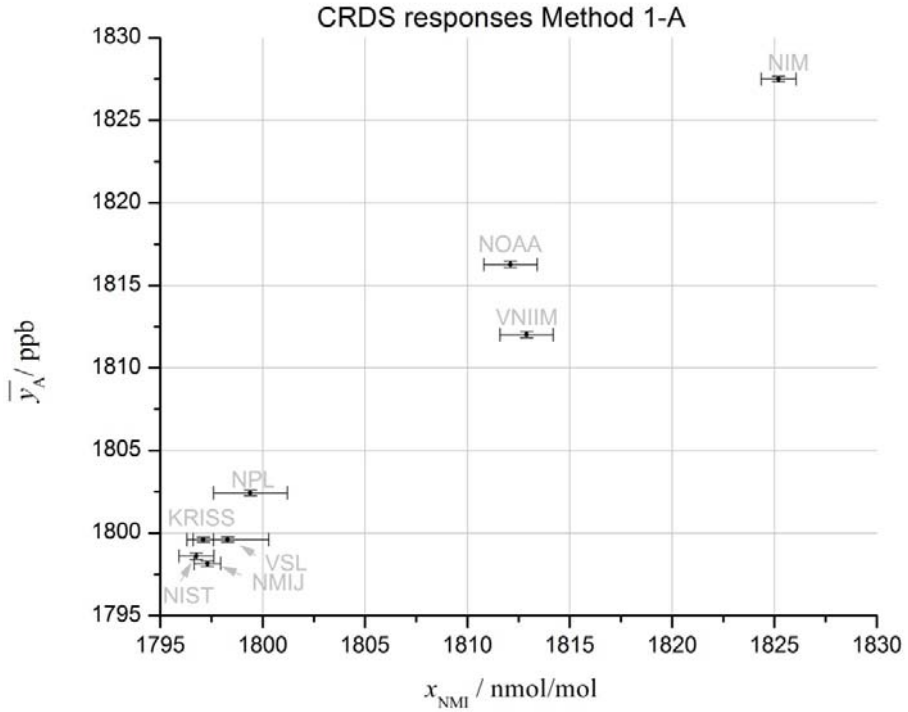


Figure 6. Zoom of the CRDS response to the participants gas mixtures by Method 1-A. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI gravimetric values (x-axis). For further information see section ANNEX 1- BIPM Value assignment procedure.

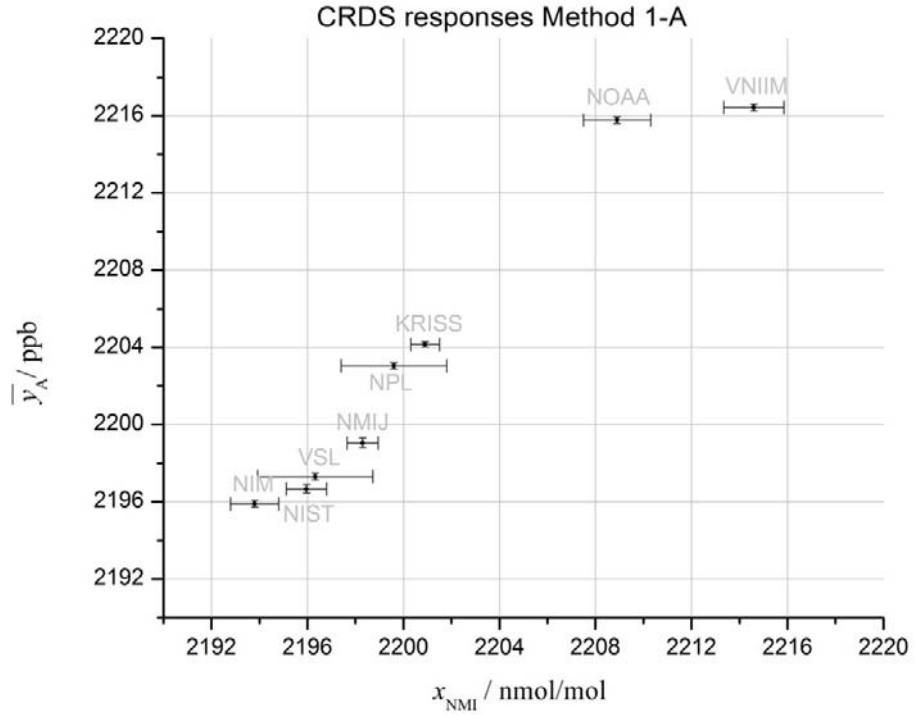


Figure 7. Zoom of the CRDS responses to the participants gas mixtures by Method 1-A. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI gravimetric values (x-axis) . For further information see section ANNEX 1- BIPM Value assignment procedure.

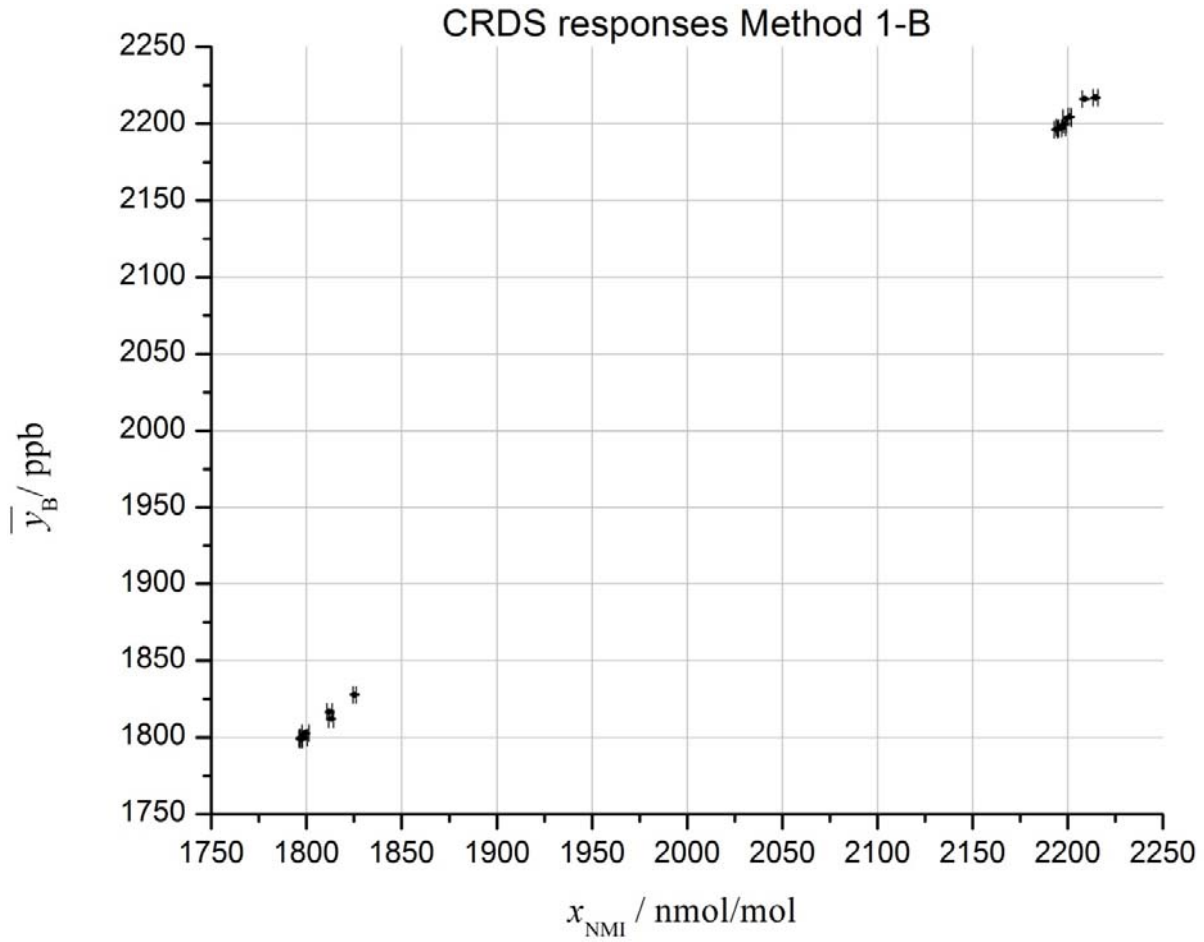


Figure 8. CRDS responses to the participants gas mixtures by Method 1-B. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI gravimetric values (x-axis). For further information see section ANNEX 1- BIPM Value assignment procedure.

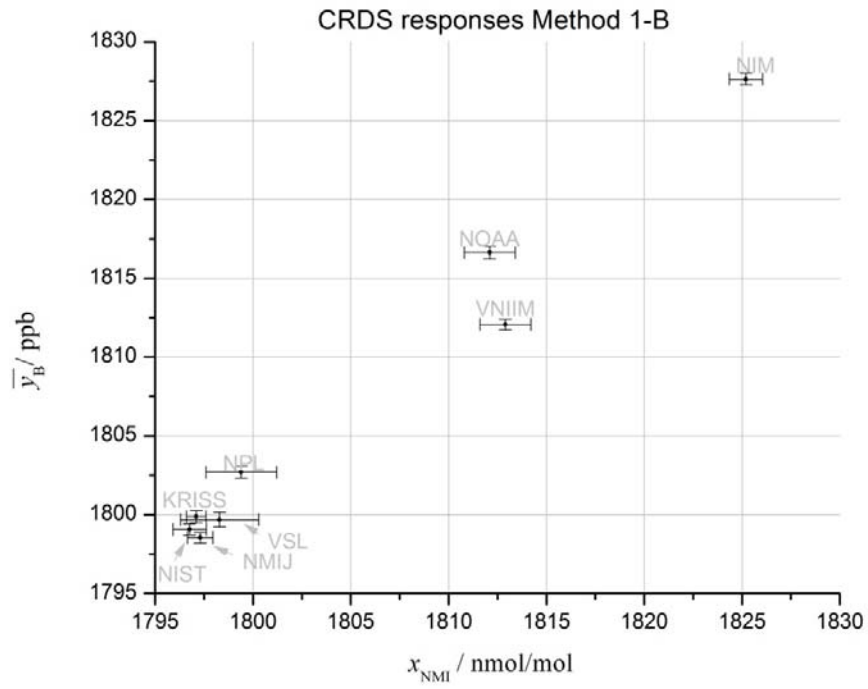


Figure 9. Zoom of the CRDS responses to the participants gas mixtures by Method 1-B. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI gravimetric values (x-axis). For further information see section ANNEX 1- BIPM Value assignment procedure.

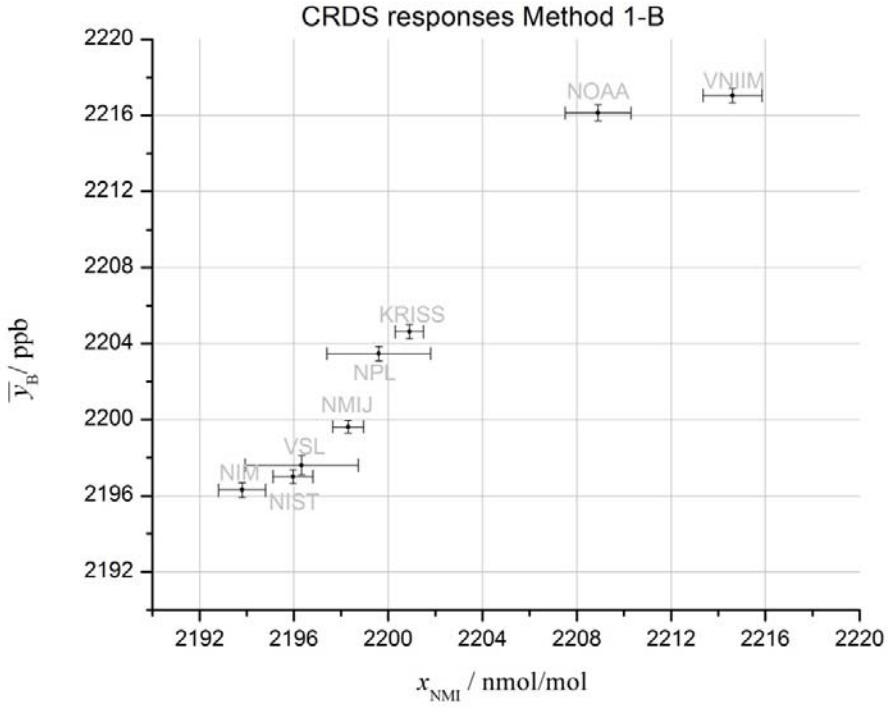


Figure 10. Zoom of the CRDS responses to the participants gas mixtures by Method 1-B. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI gravimetric values (x-axis). For further information see section ANNEX 1- BIPM Value assignment procedure.

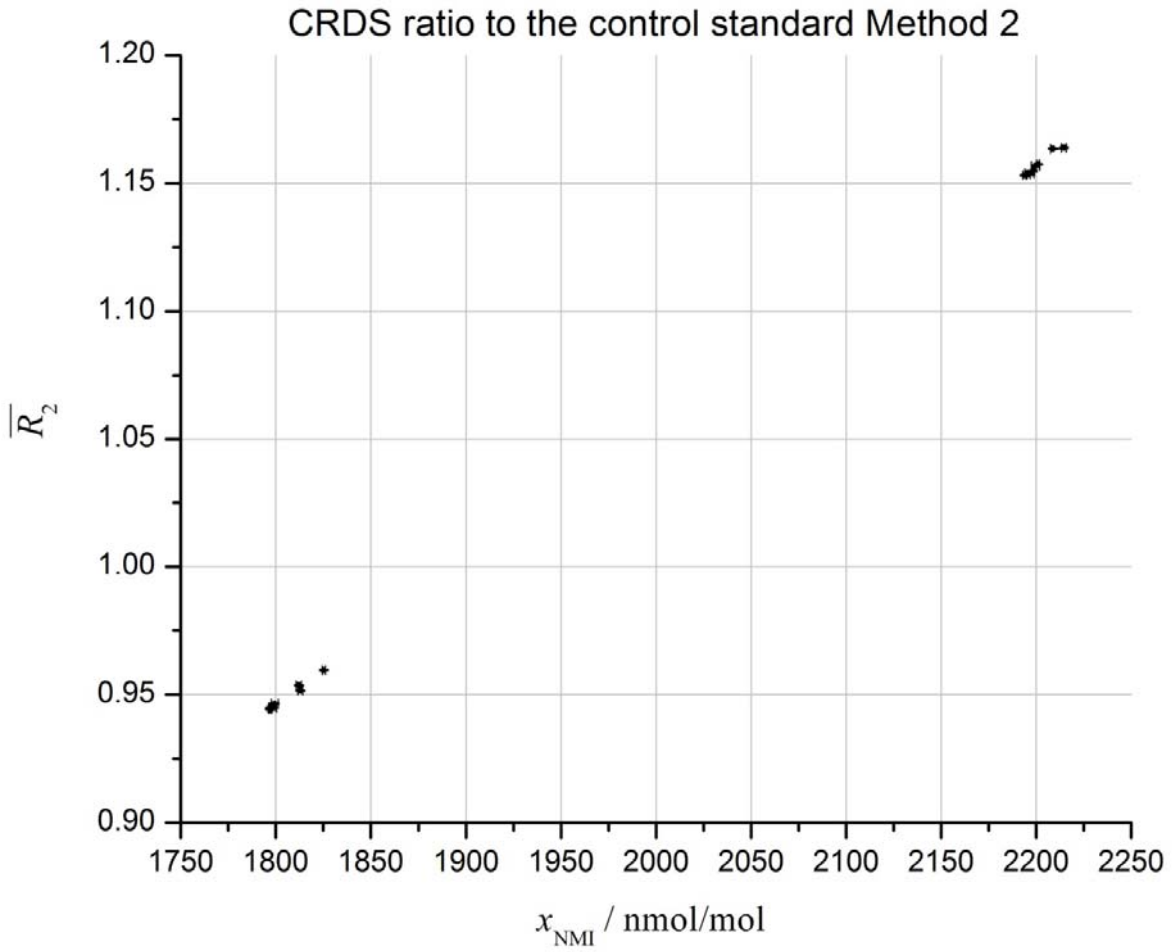


Figure 11. CRDS ratios to control standard (Method 2). The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI gravimetric values (x-axis). For further information see section ANNEX 1- BIPM Value assignment procedure.

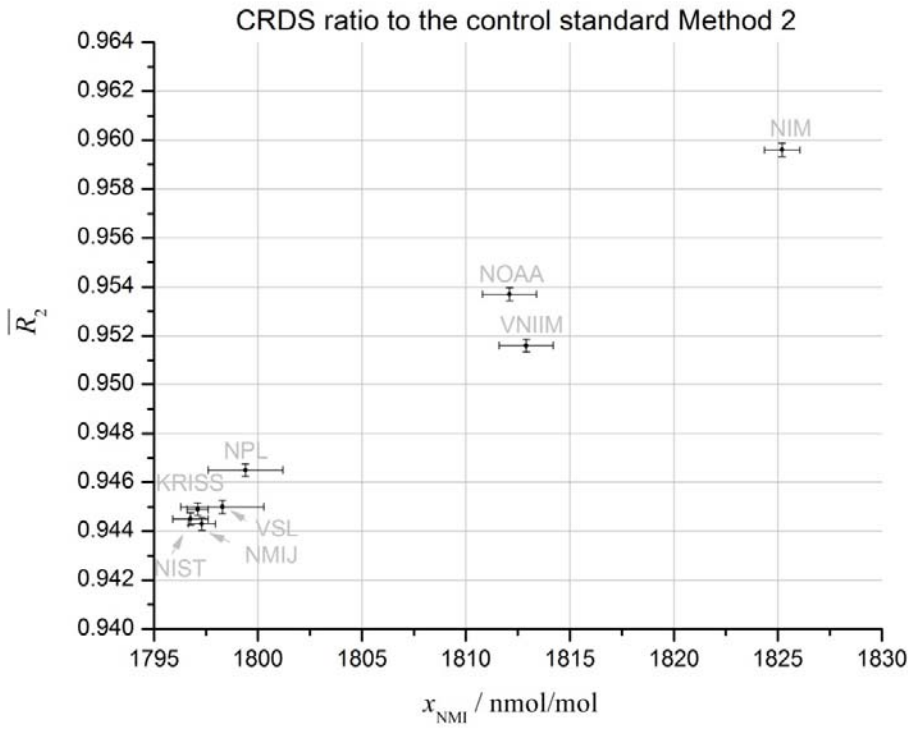


Figure 12. Zoom of the CRDS ratios to control standard (Method 2). The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI gravimetric values (x-axis). For further information see section ANNEX 1- BIPM Value assignment procedure.

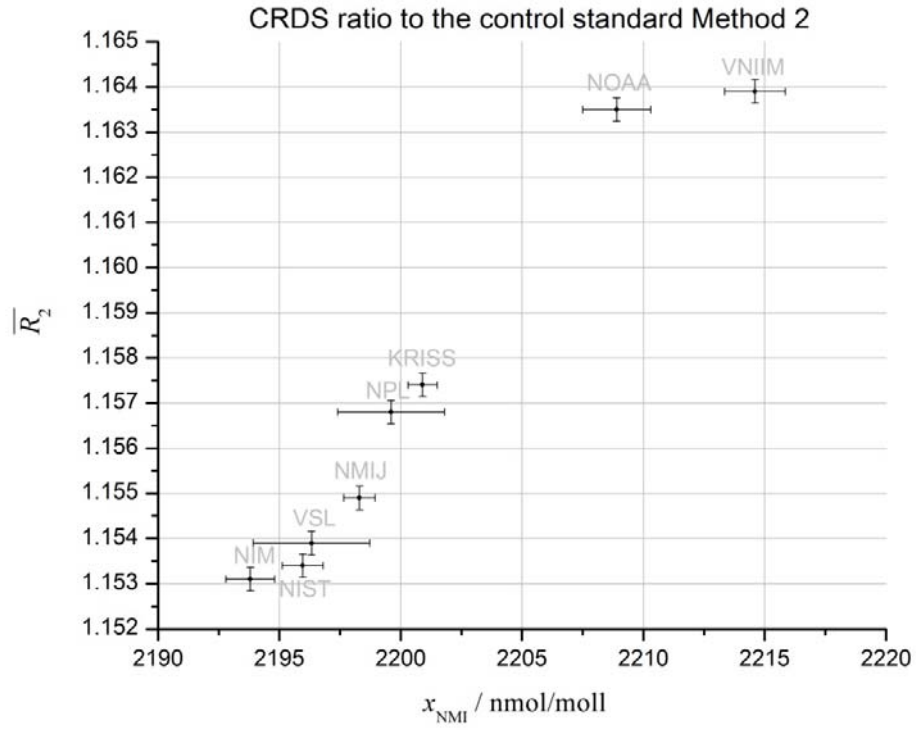


Figure 13. Zoom of the CRDS ratios to control standard (Method 2). The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI gravimetric values (x-axis). For further information see section ANNEX 1- BIPM Value assignment procedure.

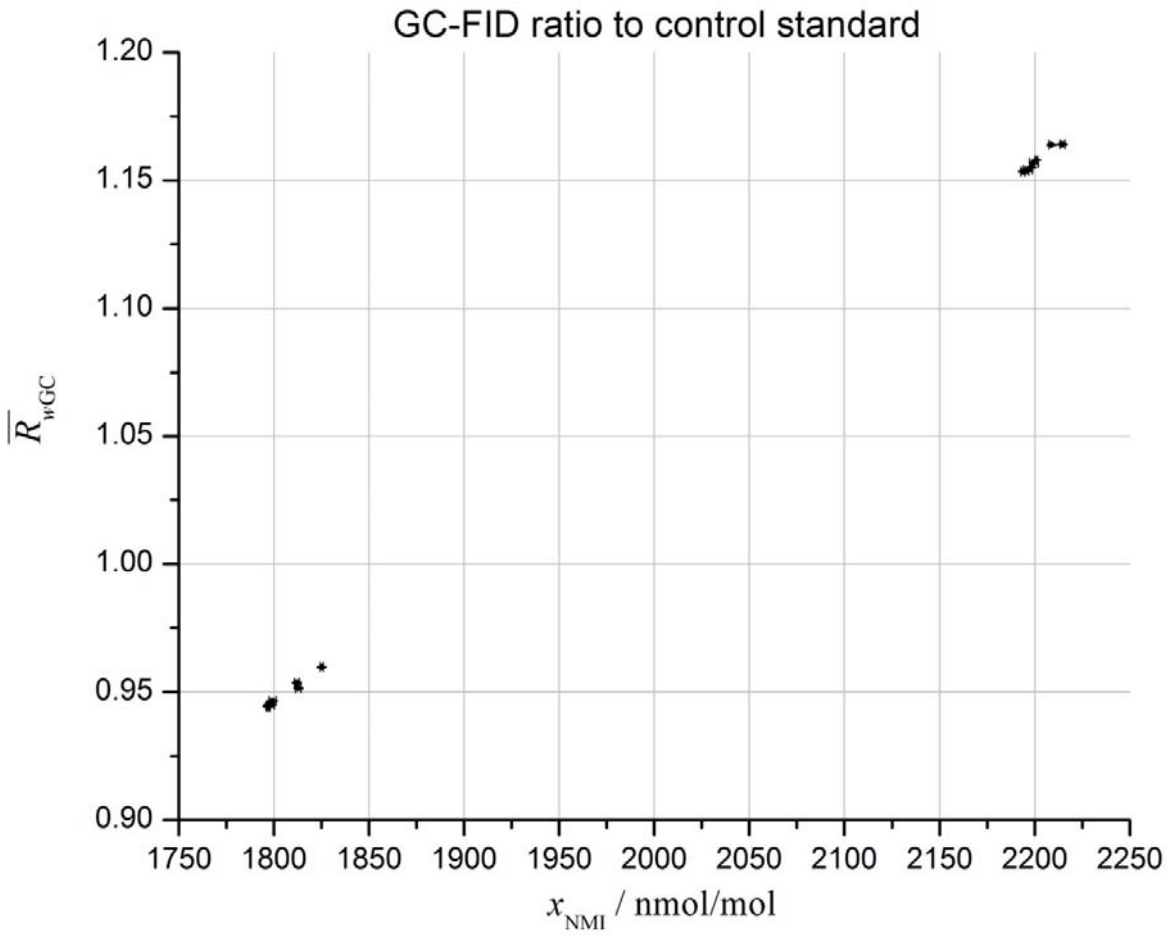


Figure 14. GC-FID ratios to control standard. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI gravimetric values (x-axis). For further information see section ANNEX 1- BIPM Value assignment procedure.

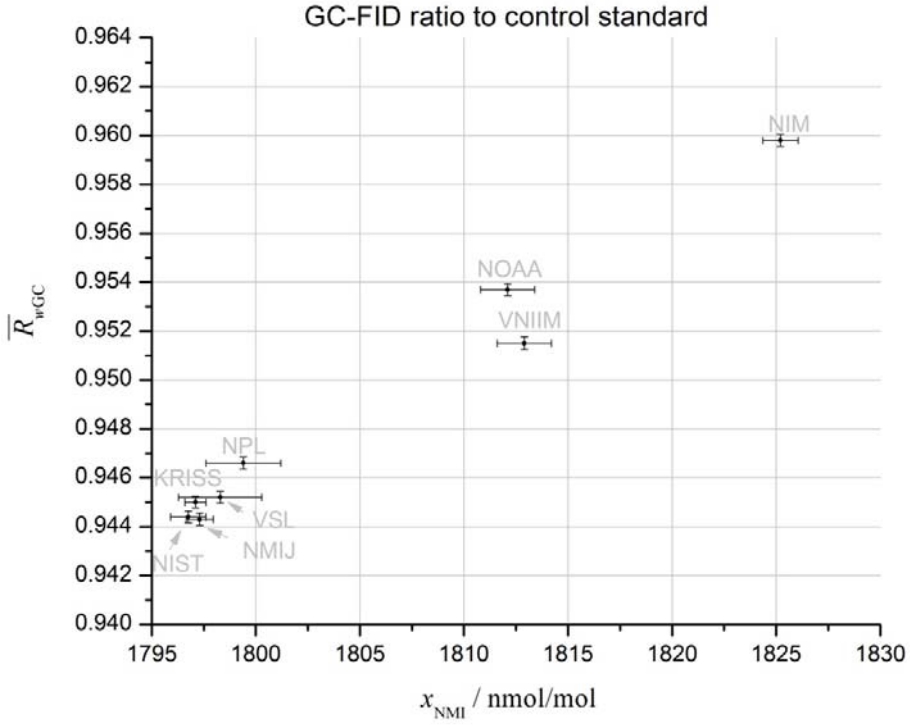


Figure 15. Zoom of the GC-FID ratios to control standard. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results (y- axis) and the NMI gravimetric values (x-axis). For further information see section ANNEX 1- BIPM Value assignment procedure.

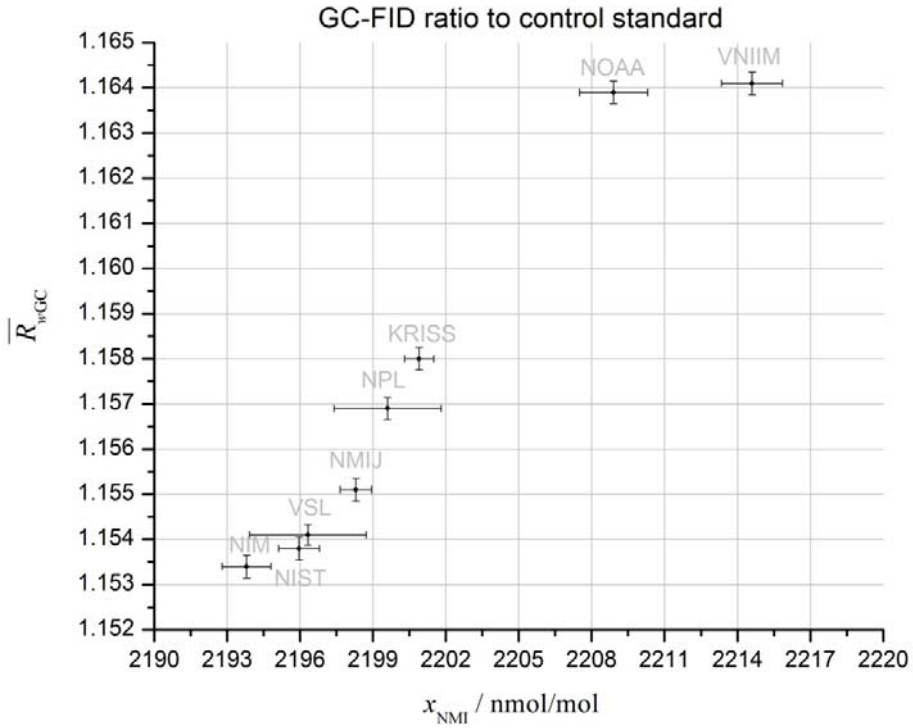


Figure 16. Zoom of the GC-FID ratios to control standard. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results . (y- axis) and the NMI gravimetric values (x-axis)For further information see section ANNEX 1- BIPM Value assignment procedure.

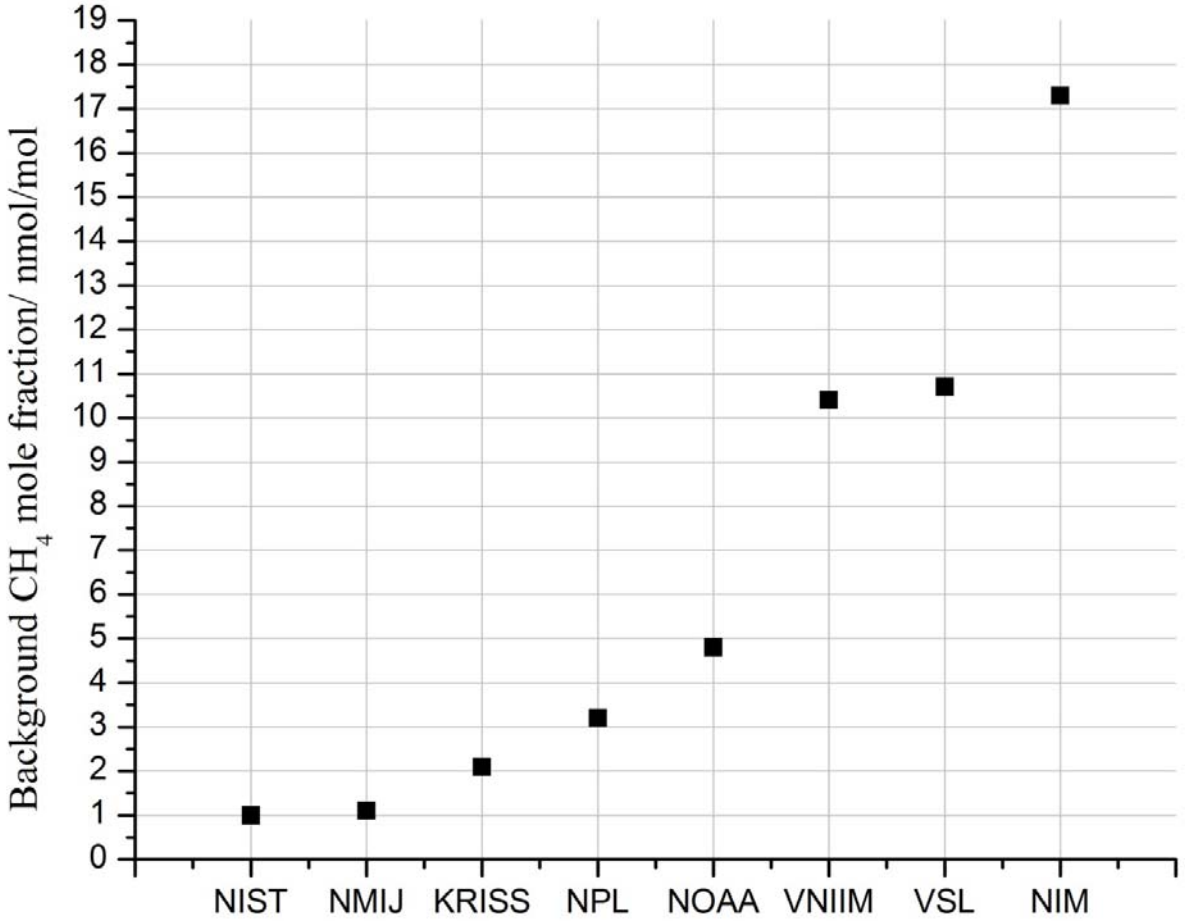


Figure 17. Trace CH_4 mole fractions in balance gas as reported by participating laboratories. See ANNEX 2 - Measurement reports of participants

8. Key Comparison Reference Value

During the 31st meeting of the CCQM GAWG (7-8 April 2014) it was agreed that the key comparison reference value for CCQM-K82 was to be calculated using the measurement results of the CRDS method 2. Furthermore, several statistical approaches, all based on least-square regression, were presented and detailed in the Draft B report (GAWG/14-09). From this analysis, it was agreed to fit the CRDS method 2 results versus the participant's gravimetric values with a line, using the Generalised Least Square approach defined in the standard ISO 6143:2001. It was also agreed to select a subset of cylinders contributing to the regression line so as to obtain a consistent set with regard to the regression, i.e. a set that allows the goodness-of-fit parameter to be less than 2.

Notation

The degree of equivalence is defined as:

$$D = x_{NMI} - x_{KCRV} \quad (1)$$

where

x_{KCRV} is the amount of substance fraction in the cylinder predicted by the linear analysis function for the corresponding analyzer response (ratio to the control cylinder with the CRDS method 2);

$u(x_{KCRV})$ is the uncertainty of the predicted value;

x_{NMI} is the amount of substance fraction submitted by the participating laboratory;

$u(x_{NMI})$ is the standard uncertainty associated with the submitted value x_{NMI};

D is difference in amount of substance fraction as measured by the laboratory and the reference value x; and

$U(D)$ is the expanded uncertainty of this difference.

Degrees of equivalence and graph of equivalence

The analysis of the data from the comparison was done following the procedures outlined in ISO 6143:2001[2] (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures). The regression analysis was performed with XLGenlinev1.1, a computer programme developed by NPL which implements this methodology by taking into consideration uncertainties in both axes.

Standards that were to contribute to the KCRV were selected by applying the regression analysis first to the entire set of cylinders, so as to identify possible outliers, which then were not selected in the next set of data to be analysed. This process lead to a self-consistent set of cylinders comprising all cylinders except one, cylinder FB03593 prepared by NOAA. The goodness-of-fit of the regression performed with this data set is equal to 1.72, demonstrating consistency of the ensemble. Key comparison reference values and degrees of equivalence are listed in Table 8. Degrees of equivalence are plotted in Figure 18. This resulted in only one standard, NOAA cylinder FB03593, not agreeing with the KCRV. .

Participant	Cylinder	x_{KCRV} (nmol/mol)	$u(x_{KCRV})$ (nmol/mol)	x_{NMI} (nmol/mol)	$u(x_{NMI})$ (nmol/mol)	$D(x_{NMI} - x_{KCRV})$ (nmol/mol)	$u(D)$ (nmol/mol)	$U(D)$ (k=2) (nmol/mol)
KRISS	D 929248	1797.60	0.69	1797.10	0.50	-0.50	0.85	1.70
KRISS	D 985705	2202.20	0.71	2200.90	0.60	-1.30	0.93	1.85
NIM	CAL017763	1825.60	0.67	1825.20	0.85	-0.40	1.08	2.17
NIM	CAL017790	2194.00	0.70	2193.80	1.00	-0.20	1.22	2.44
NIST	FB03569	1796.80	0.69	1796.76	0.85	-0.04	1.09	2.19
NIST	FB03587	2194.60	0.70	2195.96	0.84	1.36	1.09	2.19
NMIJ	CPB-28035	1796.40	0.69	1797.30	0.65	0.90	0.95	1.89
NMIJ	CPB-28219	2197.50	0.70	2198.30	0.65	0.80	0.96	1.91
NOAA	FB03578	1814.30	0.68	1812.10	1.30	-2.20	1.47	2.93
NOAA	FB03593	2213.80	0.71	2208.90	1.40	-4.90	1.57	3.14
NPL	221727	1800.60	0.69	1799.40	1.80	-1.20	1.93	3.85
NPL	233097	2201.10	0.71	2199.60	2.20	-1.50	2.31	4.62
VNIIM	D 249682	1810.30	0.68	1812.90	1.30	2.60	1.47	2.93
VNIIM	D 249845	2214.60	0.71	2214.60	1.25	0.00	1.44	2.88
VSL	D 249292	1797.80	0.69	1798.29	2.00	0.49	2.11	4.23
VSL	D 249289	2195.60	0.70	2196.33	2.40	0.73	2.50	5.00

Table 8. Degrees of equivalence for the key comparison CCQM-K82

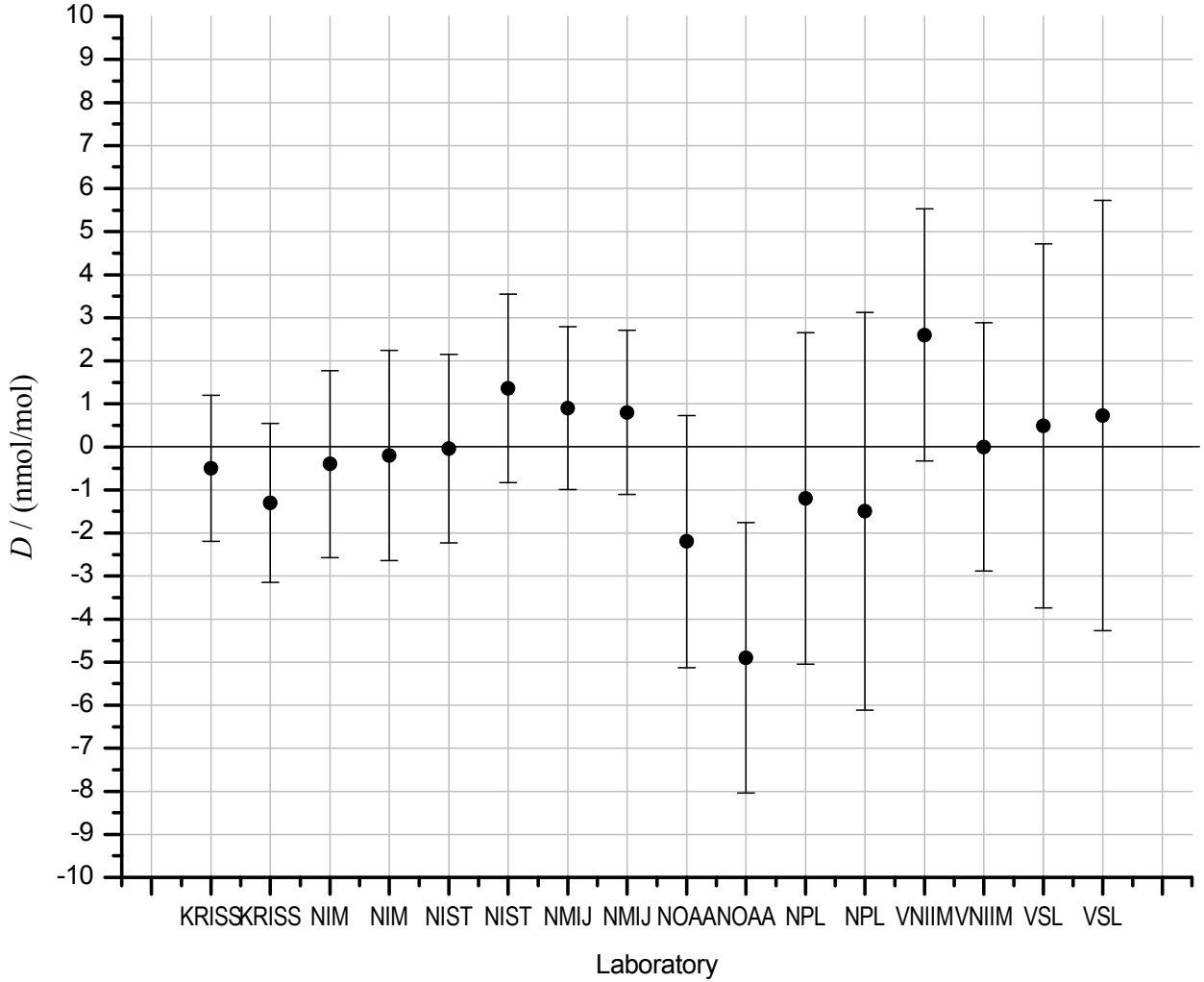


Figure 18. Graph of equivalence for the key comparison CCQM-K82. The error bar represents the expanded uncertainty at a 95 % level of confidence. For the pair of standards the degree of equivalence for the low amount of substance fraction standard is plotted before the high amount of substance fraction standard.

Youden Plot

In order to observe the within-laboratory variability and the between-laboratory variability the graph of equivalence was also represented by a Youden Plot. In a Youden Plot, degrees of equivalence for one standard of each participant are plotted versus degrees of equivalence of the other standard. The Youden plot displayed in Figure 19 shows the degrees of equivalence for the standards prepared with the higher CH_4 amount of substance fraction (around 2200 nmol mol^{-1}) versus the degree of equivalence for the standards prepared with the lower amount of substance fraction (around 1800 nmol mol^{-1}). The $y = x$ line of the plot represents the line on which completely correlated pairs of standards would lie.

Like the graph of equivalence, this plot shows that NOAA cylinder FB03593 is the only standard not in agreement with the reference value. However the two standards from NOAA do appear to have some level of correlation, and are biased in the same direction compared to their KCRVs. On the contrary, the standards from VNIIM would be expected to be correlated due to the same balance gas being used in their preparation. The results of the comparison show that this is not the case, which indicates that another uncorrelated source of uncertainty other than purity measurements needs to be accounted for. The rest of participants seem to be positioned uniformly around the $y = x$ line of the plot, demonstrating that the majority of laboratories have a relatively low within-laboratory variability.

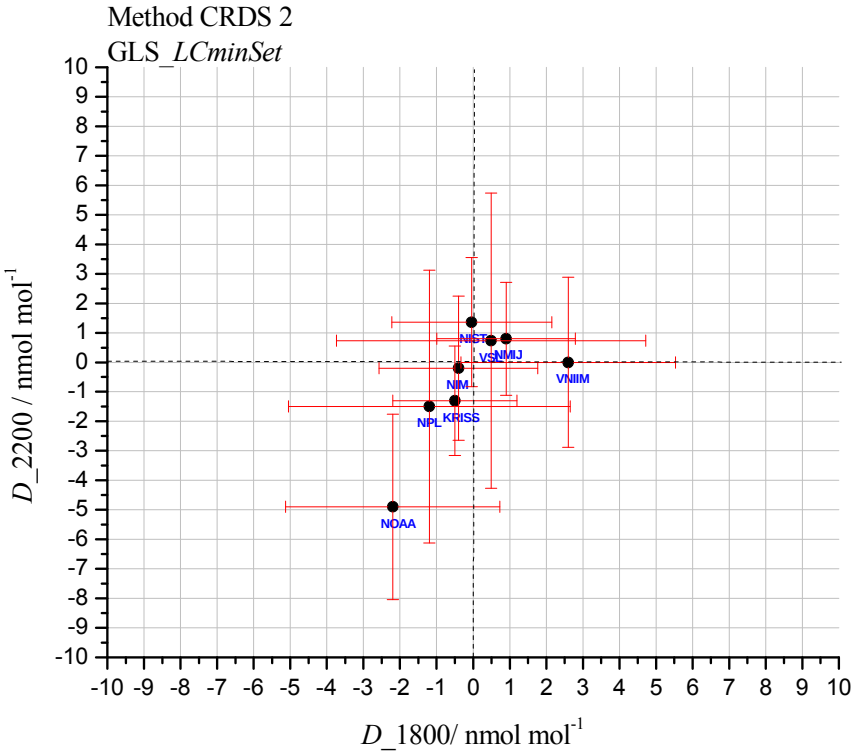


Figure 19. Youden Plot of the CCQM-K82 results. The error bar represents the expanded uncertainty at a 95 % level of confidence.

9. Conclusions

The level of agreement amongst standards improved by a factor of ten compared to a similar comparison exercise performed in 2003 (CCQM-P41).

In most cases a major contributor to reported uncertainty of participants' standards arises from the measurement of trace levels of methane in the balance gas used to prepare their standards.

Youden plot analyses of the comparison results confirm that in most cases the standards within submitted pairs are correlated, and a major reason is that the same balance gas is being used to prepare standards within pairs.

In this comparison reported standard uncertainties ranged from 0.50 nmol/mol to 2.4 nmol/mol and the uncertainties of individual KCRVs ranged from 0.68 nmol/mol to 0.71 nmol/mol.

The standards from VNIIM would be expected to be correlated due to the same balance gas being used in their preparation. The results of the comparison show that this is not the case, which indicates that another uncorrelated source of uncertainty other than purity measurements needs to be accounted for.

The two standards from NOAA do appear to have some level of correlation, and are biased in the same direction compared to their KCRVs.

A very good level of agreement was observed between both techniques, GC-FID and CRDS.

It has been confirmed that the addition of an extra contribution to the uncertainty in CRDS measurements of methane mole fractions arising from possible isotopic variation in the standards has no significant effect on their level of compatibility.

The standard deviation of the ensemble of standards about the KCRV value was 1.70 nmol/mol. This relative standard deviation can be compared to the data compatibility goal set by the World Meteorological Organization – Global Atmospheric Watch for CH_4 in air which are ± 2 nmol/mol (1 SD). In order for a primary standard, or rather a change in primary standard, to have negligible influence on measurement comparability, the standard uncertainty of the primary standard and the standard deviation of a set of compared primary standards should be arguably less than one quarter the value of the compatibility goal, which would be 0.5 nmol/mol. This level of agreement is the goal to set for a future repeat of the CCQM-K82 comparison, and will require further improvements in uncertainties for the measurement of trace level methane in balance gases.

10. Support to Calibration and Measurement Capabilities claims

The results of this key comparison can be used to support:

1) Claimed capabilities CH_4 in synthetic air, scrubbed air, or in nitrogen in the range 1700 nmol/mol to 2500 nmol/mol;

2) Claimed capabilities for CH_4 in nitrogen or in air in the range 2.5 μmol/mol to 25 mmol/mol, where an NMI's smallest claimed relative standard uncertainty is equal or greater to the relative standard uncertainty it reported in CCQM-K82 for results that agree with the KCRV;

3) Claims of purity measurements in nitrogen, oxygen and argon matrix gases for the quantification of methane amount of substance fractions above 1 nmol/mol where the standard uncertainty is equal or greater to u(KCRV).

ANNEX 1- BIPM Value assignment procedure

1. Description of the facility

The BIPM-CH_4 gas facility includes a gas chromatograph (GC-FID), a Cavity ring-down spectrometer (CRDS) and an auto-sampler (Figure 20).

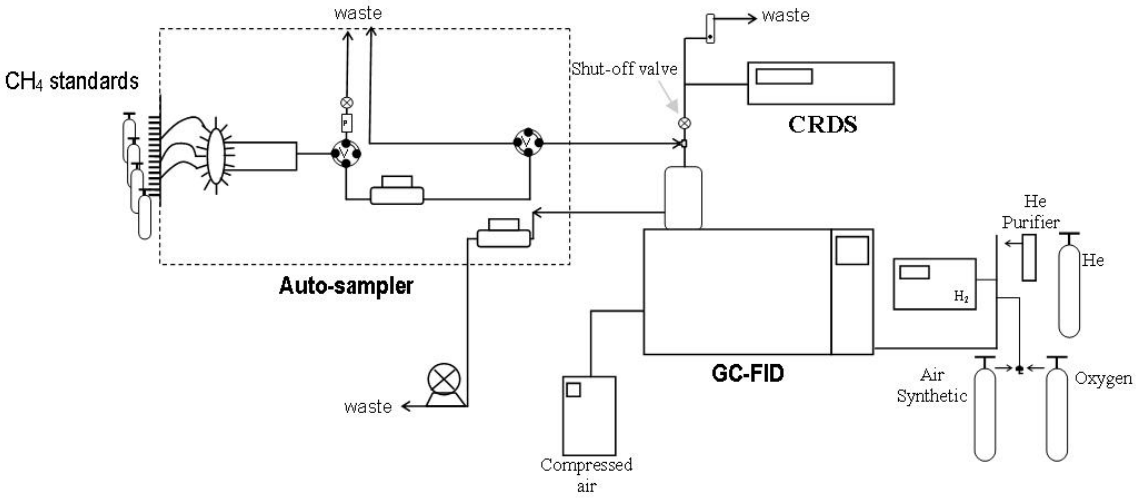


Figure 20 : Schematics of the BIPM Methane facility

1.1 The GC-FID

The GC-FID is a modified Agilent system series 7890A acquired from the SRA Instruments 'France. It is equipped with a flame ionization detector (FID), a stainless steel column packed with Poropak Q (80-100 mesh) and the FID detector is supplied with pure oxygen and hydrogen (see Figure 21).

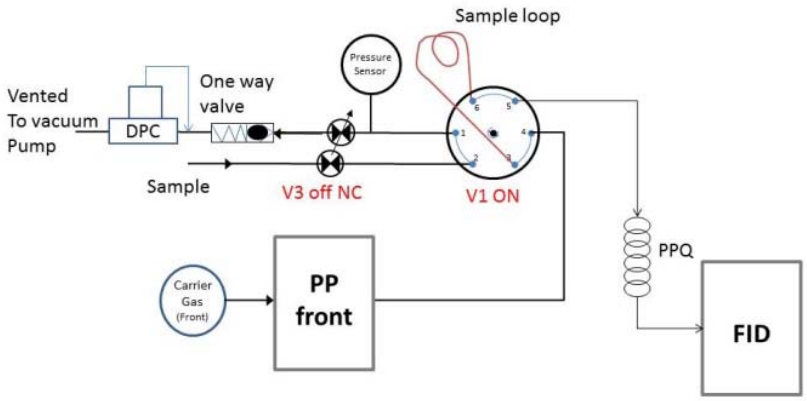


Figure 21 : Internal schematics of the BIPM system for Gas Chromatography with Flame Ionization Detector (GC-FID) comprised by a Poropak Q 80-100 mesh (6 m x 1/8") column, a Sample loop of 5 mL, one Valco two positions six port valves and a FID detector.

The GC-FID is equipped with:

- one 6 port valve V1 (Vici-valco);
- one 5 mL stainless steel injection loop;
- one one-way valve;
- one 6 m stainless steel column packed with Poropak Q (80-100 mesh);
- one flame ionization detector (FID);
- one hydrogen generator;
- one helium purifier;
- one control computer for the GC-FID equipped with:
    - ChemStation version Rev. B.04.02 (118)
    - ProChem Set-up version 2.5.7
    - ProChem software version 2.0.1.
- one barometer (Sensor Technique DC 25/10)

The gas mixtures used for operating the facility were:

- one helium 6.0 gas cylinder, quality 99.9999%
- one oxygen 5.5 in gas cylinder, quality 99.9995 %.
- source of air with pressure of 7 bars .
- one 40 L CH_4/air commercial secondary gas standards (control standard *A*) with an initial internal pressure of 150 bar with the composition specified to be within the following ranges:
    - CH_4: 1950 nmol mol^{-1} to 2050 nmol mol^{-1};
    - CO_2: 360 µmol mol^{-1} to 400 µmol mol^{-1};
    - Ar: 8865 µmol mol^{-1} to 9799 µmol mol^{-1};
    - O_2: 20.77 % to 21.11 %;
    - N_2: Matrix gas.
- Cylinder 589241, used as stability column control standard* with an initial internal pressure of 150 bar with the follow composition:

- CH_4: 3.05 ppm
- CO_2: 388 ppm
- Ar: 9480 ppm
- O_2: 20.5 %
- N_2: Matrix gas

- Two 40 L CH_4/air commercial secondary gas standards with an initial internal pressure of 150 bar and a with the following composition specified to be within the following ranges:
  - CH_4: 1850 nmol mol^{-1} to 3000 nmol mol^{-1}
  - CO_2: 360 µmol mol^{-1} to 400 µmol mol^{-1}
  - Ar: 8865 µmol mol^{-1} to 9799 µmol mol^{-1}
  - O_2: 20.77 % to 21.11 %
  - N_2: Matrix gas

**This control standard was used for quality control of the column retention characteristics.*

1.1.1 GC-FID separation and quantification method

The GC-FID is operated at 250 °C. A 6 m by 6.35 mm stainless steel column packed with Poropak Q (80-100 mesh) was used at a temperature of 35 °C for the analysis. Helium column carrier[2], gas passed through a heated gas purifier, was used at a flow rate of 70 ml min^{-1}. The FID is supplied with 320 ml min^{-1} of pure oxygen[3] and 40 ml min^{-1} of hydrogen[4]. A 5 ml stainless steel sample loop is used to introduce the CH_4/air sample onto the column. The pressure in the sample loop is measured by a calibrated pressure sensor having a resolution of 0.2 hPa and recorded at each injection. Finally the peak areas are measured with an on-line computing integrator.

Pressure correction

Once measured, all peak areas are corrected to the standard pressure using the following expression

$$R_{c,st}C=R_c(p_{st}/p_c) \quad (1)$$

where

$R_{c,st}C$ is the response corrected to standard pressure, arbitrary units (a.u.);

R_c is the measured response, a.u.;

p_c: is the ambient pressure, kPa

p_{st}: is the standard atmospheric pressure (101.325 kPa)

Sampling sequence

[2] The Carrier Gas is He grade 6.0 passing through a SAES getters® PS2-GC50-R-2 for extra purification.
[3] The Flame is produced from Oxygen grade 5.5.
[4] Hydrogen is produced on site by a commercial H_2 generator CG2200 (Claind). It produces grade 6.0 H_2 at a maximum flow rate of 200 ml/min with a purity higher than 99,99999%.

The BIPM measurement procedure for analyzing a set of CH_4/Air gas standards is based on the analysis of two CH_4/Air gas mixtures between a CH_4/Air gas mixture used as control standard (A). The measurement sequence starts by measuring the methane peak area response of three replicate analyses of the control cylinder ($A_{,1}$,$A_{,2}$,$A_{,3}$) and then of two CH_4/air standards (CH_4/air standard one is named Cyl_1 and the second is named Cyl_2) for finalizing again with the control cylinder as illustrated in the sequence below:

Sample Name		
Control Cylinder A_b (before cylinder 1 and 2 measurements)	A_1, A_2, A_3	SUBSET 1
Cylinder 1 measurements	$Cyl_{1,1}$, $Cyl_{1,2}$, $Cyl_{1,3}$	
Cylinder 2 measurements	$Cyl_{2,1}$, $Cyl_{2,2}$, $Cyl_{2,3}$	
Control Cylinder A_a (after cylinder measurements)	A_4, A_5, A_6	

Table 9. Typical sampling sequence.

Since the analysis of each CH_4/Air gas mixture takes 15 minutes this measuring sequence takes about 180 minutes to be completed. Once the sequence is complete a new sequence starts following the same order but using as samples new CH_4/air standards named Cyl_3 and Cyl_4 as shown in the sequence below:

Control Cylinder A_b (before)	A_7, A_8, A_9	SUBSET 2
Cylinder 3	$Cyl_{3,1}$, $Cyl_{3,2}$, $Cyl_{3,3}$	
Cylinder 4	$Cyl_{4,1}$, $Cyl_{4,2}$, $Cyl_{4,3}$	
Control Cylinder A_a (after)	A_{10}, A_{11}, A_{12}	

This sequence is repeated until the last CH_4/air standard is measured.

This sequence is repeated seven times, so that eight days of continuous measurements are necessary to accomplish the measurement of ten cylinders.

Ratios to the control standard

The ratios to the control cylinder are calculated determining first the average responses of three successive measurements performed on the CH_4/air standard gas mixtures as well as on the control cylinder (A). The measurements are performed following the sequence described below for the case of cylinders 1 and 2. Finally the average responses, $\overline{A_b}$, $\overline{C_1}$, $\overline{C_2}$ and $\overline{A_a}$ are calculated for each set of two standard gas mixtures, as described in the equations below:

$$\overline{A_b} = (R_{c,st}A_{,1} + R_{c,st}A_{,2} + R_{c,st}A_{,3})/3 \quad (2)$$

$$\overline{C_1} = (R_{c,st}Cyl_{1,1} + R_{c,st}Cyl_{1,2} + R_{c,st}Cyl_{1,3})/3 \quad (3)$$

$$\overline{C_2} = (R_{c,st}Cyl_{2,1} + R_{c,st}Cyl_{2,2} + R_{c,st}Cyl_{2,3})/3 \quad (4)$$

$$\overline{A_a} = (R_{c,st}A_{,4} + R_{c,st}A_{,5} + R_{c,st}A_{,6})/3 \quad (5)$$

Where $R_{c,st}Cyl_{i,j}$ is the response j (j = 1 to 3) to the gas mixture i corrected to the standard pressure.

The drift of the signal on the entire sequence between the first and last control cylinder measurements is determined as:

$$Drift = \left(\overline{A_b} - \overline{A_a}\right) \quad (6)$$

Considering that all the cylinder analysis is equally spaced in time, the drift a correction to apply between two analyses is:

$$Corr = Drift/3 \quad (7)$$

This correction is then added to the first corrected average response of control cylinder, $\overline{A_b}$, in order to deduce the drift corrected responses factor of the control cylinder for cylinders 1 and 2, $C_{F,1}$ and $C_{F,2}$:

$$C_{F,i} = \overline{A_b} + Corr \quad (8)$$

$$C_{F,i+1} = \overline{A_b} + 2 \cdot Corr \quad (9)$$

The ratios of each standard mixture to the control cylinder A, corrected for the drift of the instrument, are calculated by dividing the average response of the CH_4/air standards mixtures ($\overline{C_1}$ and $\overline{C_2}$) by the drift corrected responses factor $C_{F,1}$ and $C_{F,2}$ respectively:

$$R_{GC\_1,1} = \overline{C}_1 / C_{F,1} \quad (10)$$

$$R_{GC\_2,1} = \overline{C}_2 / C_{F,2} \quad (11)$$

$\overline{R}_{GC}$ is the average of the seven ratios calculated during one set of measurements.

The associated short term stability of the average of the seven ratios calculated during one set of measurements, $u\left(\overline{R}_{GC}\right)$, necessary for the uncertainty determination, was calculated by the standard deviation of the mean as follows:

$$u\left(\overline{R}_{GC}\right)=\sqrt{\frac{\frac{1}{7-1}\sum_{k=1}^{7}\left[\left(\frac{\overline{C_k}}{\overline{A_b}+\left(\frac{\overline{A_b}-\overline{A_a}}{3}\right)}\right)-\overline{R}_{GC}\right]^2}{7}} \tag{12}$$

Weighted means

Since each set, composed of seven sampling sequences, was repeated three or in some cases four times during the entire comparison, the weighted mean was used to combine the means from the sets of measurements.

In this case, the weighted mean, $\overline{R}_{wGC}$, is defined as:

$$\overline{R}_{wGC} = \sum_{l=1}^{s} w_l \overline{R}_{GC\_l} \tag{13}$$

Where *s* is the repeated cycle of seven measurements (3 or 4) and the weights w_l are defined as:

$$w_l = \frac{1/u\left(\overline{R}_{GC\_l}\right)^2}{\sum_{j=1}^{s} 1/u\left(\overline{R}_{GC\_j}\right)^2} \tag{14}$$

Where $u\left(\overline{R}_{GC\_l}\right)$ is the short term stability (standard deviation of the mean) of the l^{th} set of measurements performed on each cylinder calculated with equation (15).

Those weighted means are the final results further used as *y*-axis data, $\overline{R}_{wGC}$. Their associated uncertainties, $u\left(R_{GC}\right)$, are described as follows.

1.1.2 Uncertainty determination

The uncertainty of the weighted mean was determined using the following statistics:

$$u\left(\overline{R}_{wGC}\right)^2 = \frac{1}{\sum_{j=1}^{s} 1/u\left(\overline{R}_{GC\_j}\right)^2} \tag{15}$$

Where *s* is the number of sets.

This uncertainty contribution is then combined with the intermediate precision, $u_{Int\,\mathrm{Pr}\,e}$, determined calculating the standard deviation of the ratio between the cylinder 581087 (installed in position

15) and the control cylinder 597888 during the period of April 5 to May 15 (see Figure 22). The standard deviation resulting of this calculation is $u_{Int\,Pre}$=0.0002.

For completeness reasons the long term stability was determined as well for the standard cylinder 400330 (installed in position 14) during the same period (see Figure 22). The standard deviation resulting of this calculation is 0.00018.

Combined uncertainty

Finally the combined standard uncertainty was determined as follows:

$$u\left(\overline{R}_{GC}\right)=\sqrt{u\left(\overline{R}_{wGC}\right)^2+u_{Int\,Pre}^2} \tag{16}$$

1.1.3 Application of GC-FID method to CCQM –K82 standards

The CCQM-K82 cylinders were measured from April 6 to May 15. Table 10 lists the GC-FID ratios measured during this period.

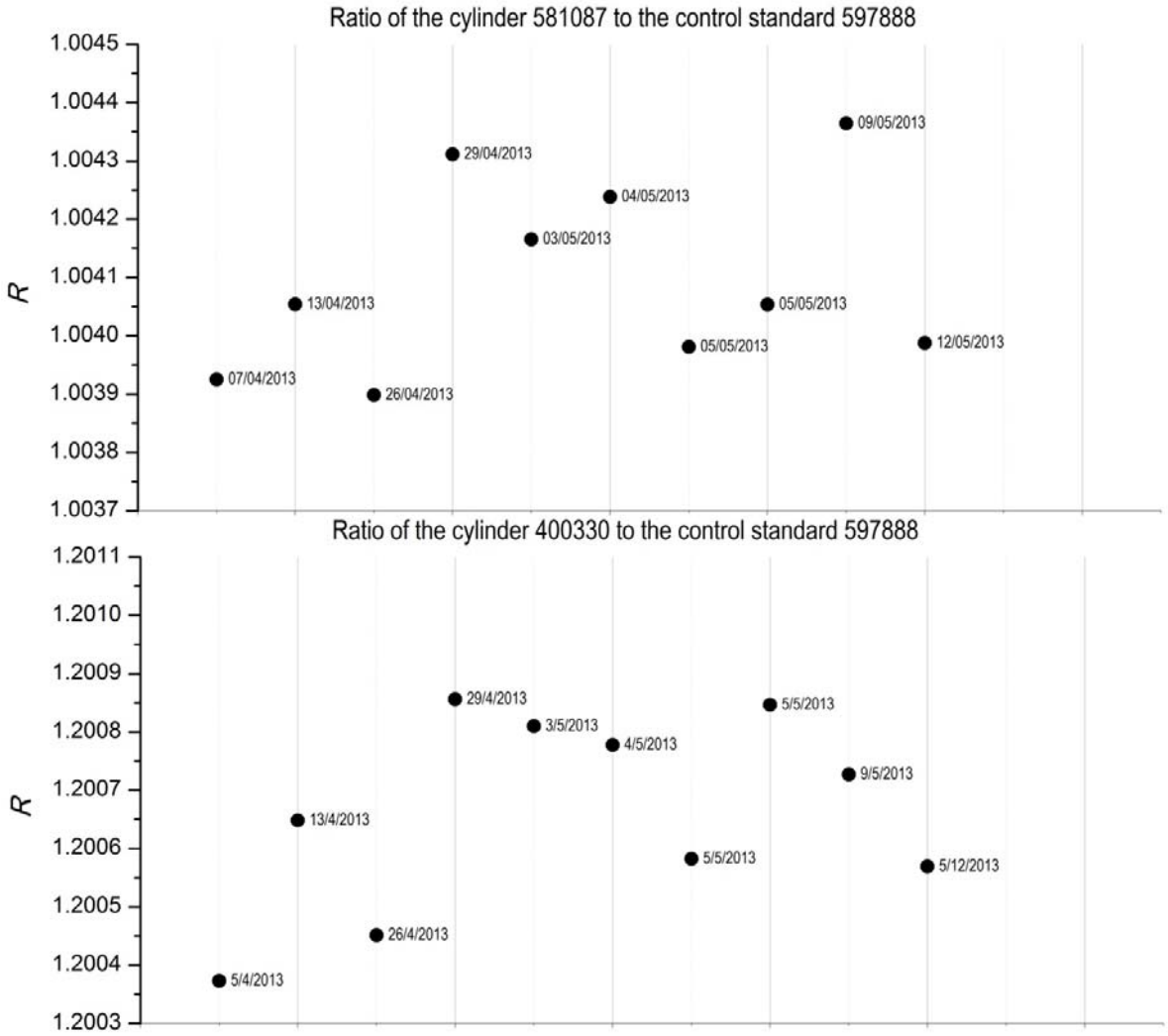


Figure 22 :Ratio of the cylinder 581087 and 400330 to the control cylinder 597888.

Participant-Gas matrix	Number of Cylinder	Assigned NMI's CH_4 amount of substance fraction x_{NMI} (nmol/mol)	Assigned NMI's Standard uncertainty K=1 $u(x_{NMI})$ (nmol/mol)	1st measurement set Date	$\overline{R}_{GC\_1}$	2nd measurement set Date	$\overline{R}_{GC\_2}$	3th measurement set Date	$\overline{R}_{GC\_3}$	4th measurement set Date	$\overline{R}_{GC\_4}$	$\overline{R}_{wGC}$	$u\left(\overline{R}_{GC}\right)$
KRISS-Synthetic Air	D929248	1797.10	0.50	04/06/2013	0.9451	09/05/2013	0.9451	12/05/2013	0.9449	15/05/2013	0.9449	0.9450	0.0002
KRISS-Synthetic Air	D985705	2200.90	0.60	04/06/2013	1.1577	09/05/2013	1.1578	12/05/2013	1.1580	15/05/2013	1.1583	1.1580	0.0003
NIM-Synthetic Air	CAL017763	1825.20	0.85	05/09/2013	0.9597	12/05/2013	0.9597	15/05/2013	0.9600	-	-	0.9598	0.0002
NIM-Synthetic Air	CAL017790	2193.80	1.00	05/09/2013	1.1534	12/05/2013	1.1531	15/05/2013	1.1536	-	-	1.1534	0.0002
NIST-Purified real air	FB03569	1796.76	0.85	06/04/2013	0.9446	13/04/2013	0.9445	26/04/2013	0.9446	29/04/2013	0.9442	0.9444	0.0002
NIST-Purified real air	FB03587	2195.96	0.84	06/04/2013	1.1536	12/04/2013	1.1538	26/04/2013	1.1541	29/04/2013	1.1536	1.1538	0.0003
NMIJ-Synthetic Air	CPB28035	1797.30	0.65	13/04/2013	0.9442	26/04/2013	0.9444	29/04/2013	0.9443	-	-	0.9443	0.0003
NMIJ-Synthetic Air	CPB28219	2198.30	0.65	13/04/2013	1.1552	26/04/2013	1.1551	29/04/2013	1.1549	-	-	1.1551	0.0003
NOAA-Purified real air	FB03578	1812.10	1.30	04/06/2013	0.9535	09/05/2013	0.9537	12/05/2013	0.9539	15/05/2013	0.9539	0.9537	0.0002
NOAA-Purified real air	FB03593	2208.90	1.40	04/06/2013	1.1639	09/05/2013	1.1639	12/05/2013	1.1640	15/05/2013	1.1638	1.1639	0.0002
NPL-Purified real air	221727	1799.40	1.80	04/06/2013	0.9463	12/04/2013	0.9468	25/04/2013	0.9468	29/04/2013	0.9465	0.9466	0.0002
NPL-Purified real air	233097	2199.60	2.20	04/06/2013	1.1569	13/04/2013	1.1570	26/04/2013	1.1567	29/04/2013	1.1570	1.1569	0.0002
VNIIM-Synthetic Air	D249682	1812.90	1.30	12/04/2013	0.9513	25/04/2013	0.9519	29/04/2013	0.9513	-	-	0.9515	0.0003
VNIIM-Synthetic Air	D249845	2214.60	1.25	06/04/2013	1.1644	13/04/2013	1.1637	26/04/2013	1.1642	29/04/2013	1.1643	1.1641	0.0002
VSL-Synthetic Air	D249292	1798.29	2.00	06/04/2013	0.9451	09/05/2013	0.9451	12/05/2013	0.9454	15/05/2013	0.9451	0.9452	0.0002
VSL-Synthetic Air	D249289	2196.33	2.40	06/04/2013	1.1541	09/05/2013	1.1541	12/05/2013	1.1542	15/05/2013	1.1542	1.1541	0.0002

Table 10. GC-FID ratios to the control cylinder A. *i* is the cylinder number.

1.2 The CRDS

The CCQM-K82 comparison cylinders were measured by the Cavity Ring Down Spectrometer (CRDS) Picarro G1202 model using three different methods, two of them based on the instrument response (Method 1-A, Method 1-B) and one in the ratio to a control cylinder (Method 2). In Method 1-A and Method 1-B, the measurand was the CRDS response defined as the average of the CRDS response over five minutes. In Method 1-A, the measurements were done without interruption during 6 hours (under repeatability conditions) and in Method 1-B the measurements were performed sequentially during one month (intermediate precision conditions). .
In the third method, Method-2, the measurand was the ratio of the CRDS response to the control cylinder 597888 (as for the GC-FID Method). The measurements by this method were done over one month as well. The related uncertainties and methodologies of these three methods are fully explained in the coming sections.

1.2.1 Method 1-A : CRDS response during 6 h measurements

As previously described in this method the measurand was the CRDS response defined as the average of the CRDS value over five minutes of measurement, $y_{A,i}$ where each cylinder *i* was measured three times during 6 hours.

The uncertainties related with this methodology were calculated using the following equation:

$$u\left(\bar{y}_A\right)=\sqrt{u_A^2+u_B^2+\overline{\sigma}^2} \qquad (17)$$

where u_A is the Type A uncertianty, u_B the Type B, and $\overline{\sigma}^2$ an additional variance term. These three terms are defined as follows:

Type A uncertainty

This uncertainty component was defined as the combination of the short term repeatability, calculated during the Allan Variance analysis, u_{Allan}, and the instrument drift, u_{Drift}, calculated as the standard deviation of the instrument response to the control cylinder during the measurement period, u_{Drift} (6 hours).

To determine u_{Allan}, Allan variance analysis was applied to time series obtained of CH_4/Air gas mixtures in the amount of substance fraction range of 1.8 μmol mol^{-1} to 2.9 μmol mol^{-1} using Stable 32 software. As can be seen on Figure 23, white noise behavior was observed with a measurement averaging time up to t_{op} = 300 s. The measurement response of the instrument was then associated with an uncertainty equal to the Allan deviation at t_{op}: u_{Alla} = 0.1 ppb. This value was found to be constant over the methane amount of substance fraction range of 1.8 μmol mol^{-1} to 2.9 μmol mol^{-1}.

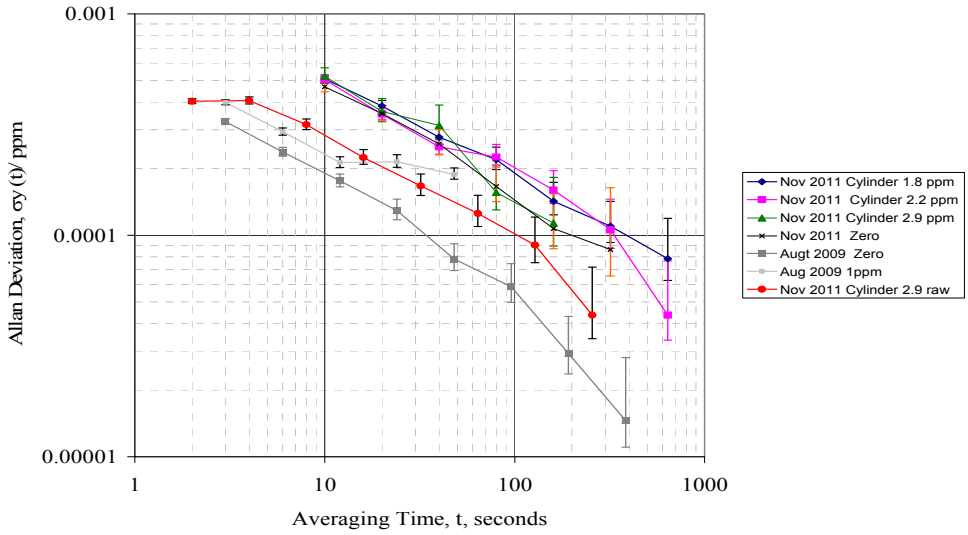


Figure 23 : Allan deviation of the CRDS response to five methane in air gas mixtures and pure nitrogen.

The uncertainty component related to the instrument response drift, u_{Drift}, was determined using the standard deviation of the instrument response to the control cylinder during 6 hours, see Figure 24. For 6 hours measurements u_{Drift} resulted equal to 0.110 ppb.

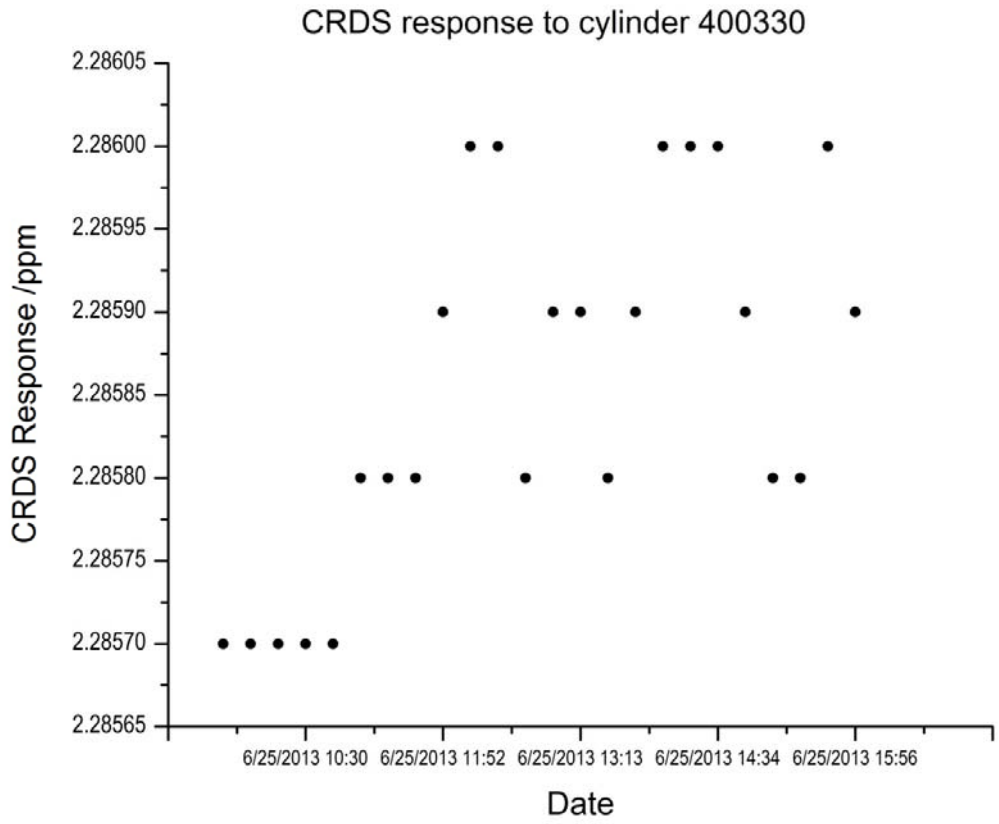


Figure 24 : CRDS response of the control cylinder.

During this analysis all cylinders were analyzed successively and this was repeated three times. The average of the three measurements, $\overline{y}_A$, was calculated and the associated Type A uncertainty determined using equation:

$$u_A = \sqrt{\frac{u_{Allan}^2}{3} + u_{Drift}^2} = 0.124 \text{ ppb} \quad (18)$$

Type B uncertainty

The effects of potential pressure broadening on CH_4 due to the difference in the matrix gas composition was considered as Type B uncertainty, $u_B = u_{Broad}$. The effects were examined using the instrument response function proposed by Nara et al. 2012[3] . Nara et al used a CRDS Picarro model G-1301, an instrument very similar to BIPM's CRDS Picarro G-1202. Nara's equation was interpolated and then its potential on the CH_4 instrument response evaluated using the following equations:

$$\Delta x_{CH4} = -53 \cdot x_{N_2} + 41.378 \quad (19)$$

$$\Delta x_{CH4} = 45 \cdot x_{O_2} - 9.434 \quad (20)$$

$$\Delta x_{CH4} = 104.152 \cdot x_{Ar} - 0.976 \quad (21)$$

where x_{N_2}, x_{O_2} and x_{Ar} are the amount of N_2, O_2 and Ar present in the measured gas mixtures. The uncertainty due to the effects of potential pressure broadening was determined considering the maximum and minimum difference given by equations 19, 20 and 21. These values were used then as limits of a rectangular distribution of the uncertainty due to the independent variation of N_2, O_2 and Ar.

The uncertainty related to the potential broadening effect in the measurements of the CCQM-K82 cylinders was determined using the real purity values of the cylinder mixtures submitted by the participants where ten of the gas mixtures were produced in synthetic and eight in purified real air (see Table 4, section 6).

u_{Broad} was determined by the following equation:

$$u_{Broad} = \sqrt{u_{CRDS}(x_{N2})^2 + u_{CRDS}(x_{O2})^2 + u_{CRDS}(x_{Ar})^2} \quad (22)$$

Where $u_{CRDS}(x_{N2})$, $u_{CRDS}(x_{O2})$ and $u_{CRDS}(x_{Ar})$ were calculated from Table 11.

		N2			O2			Ar		
		Cylinders	Cylinders mole fraction	According Nara et al ΔCH4 (ppb)	Cylinders	Cylinders mole fraction	According Nara et al ΔCH4 (ppb)	Cylinders	Cylinders mole fraction	According Nara et al ΔCH4 (ppb)
		%			%			%		
KRISS-Syn	D929248	78.053500	0.780535	0.009645	20.960070	0.209601	-0.001968	9.480000	0.009480	0.010186
NMIJ-Synt	CPB-28035	77.981400	0.779814	0.047858	21.053800	0.210538	0.040210	9.259800	0.009260	-0.012860
VNIIM-Syn	D249682				20.976700	0.209767	0.005515	9.336000	0.009336	-0.004885
NOAA-Pur	FB03578	78.155000	0.781550	-0.044150	20.912000	0.209120	-0.023600	9.332000	0.009332	-0.005304
NPL-Purifie	221727	78.100600	0.781006	-0.015318	20.927200	0.209272	-0.016760	9.345000	0.009345	-0.003943
NIST-Purifi	FB03569	78.095575	0.780956	-0.012655	20.927138	0.209271	-0.016788	9.379864	0.009380	-0.000294
NIM-Synth	CAL017763	78.003000	0.780030	0.036410	21.019000	0.210190	0.024550	9.391100	0.009391	0.000882
VSL	CAL017790	78.135200	0.781352	-0.033656	20.897070	0.208971	-0.030318	9.295100	0.009295	-0.009166
KRISS-Syn	D985705	78.253790	0.782538	-0.096509	20.766480	0.207665	-0.089084	9.413600	0.009414	0.003237
NMIJ-Synt	CPB-28219	78.089800	0.780898	-0.009594	20.927600	0.209276	-0.016580	9.439900	0.009440	0.005989
VNIIM-Syn	D249845				21.020400	0.210204	0.025180	9.324000	0.009324	-0.006141
NOAA-Pur	FB03593	78.155000	0.781550	-0.044150	20.912000	0.209120	-0.023600	9.332000	0.009332	-0.005304
NPL-Purifie	233097	78.100800	0.781008	-0.015424	20.927100	0.209271	-0.016805	9.341000	0.009341	-0.004362
NIST-Purifi	FB03587	78.096706	0.780967	-0.013254	20.925950	0.209259	-0.017323	9.379985	0.009380	-0.000281
NIM-Synth	CAL017790	78.157000	0.781570	-0.045210	20.869000	0.208690	-0.042950	9.361100	0.009361	-0.002258
VSL	VSL 149289	78.126920	0.781269	-0.029268	20.903990	0.209040	-0.027204	9.308280	0.009308	-0.007786
			Diff Max-Min	Diff Max-Min		Diff Max-Min	Diff Max-Min		Diff Max-Min	Diff Max-Min
			0.002724	-0.144367		0.002873	0.129294		0.000220	0.023046
			$u_{CRDS}(x_{N2})$	-0.041675		$u_{CRDS}(x_{O2})$	0.037324		$u_{CRDS}(x_{Ar})$	0.006653

Table 11. Cylinder amount of substance fractions and difference in CH_4 amount of substance fractions according Nara et al. Red: minimum and maximum mole fraction of N_2 as reported by participants. Orange: maximum and minimum mole fraction of O_2. Yellow: maximum and minimum mole fraction of Ar.

In this manner u_{Broad} was equal to:

$$u_{Broad} = u_B = \sqrt{(-0.04168)^2 + (0.037324)^2 + (0.006653)^2} = 0.056 \text{ ppb} \quad (23)$$

Additional uncertainty variance, $\overline{\sigma}$

As each cylinder was analyzed during a number of *s* sets, it was decided to include the experimental standard deviation of the mean responses of each cylinder as uncertainty contributor to the final uncertainty. For three responses it was calculated by:

$$\overline{\sigma} = \sqrt{\frac{\frac{1}{s-1}\sum_{k=1}^{s}\left(y_{A,k} - \overline{y}_A\right)}{s}} \tag{24}$$

The experimental standard deviations of the mean responses for each mixture are listed in Table 12.

Combined standard uncertainty, $u\left(\overline{y}_A\right)$

Finally the combined uncertainty of all these uncertainty contributors is given by:

$$u\left(\overline{y}_A\right) = \sqrt{u_A^2 + u_B^2 + \overline{\sigma}^2} \tag{25}$$

Where $u\left(\overline{y}_A\right)$ is the standard uncertainty of the CRDS responses for 6 hours of measurements, $\overline{y}_A$. The final combined uncertainties are listed together with CCQM-K82 results in Table 12.

Institute name	Cylinder ID	Gravimetric amount of substance fraction (nmol/mol)	Standard uncertainty (k=1) (nmol/mol)	1st measurement set Date	$y_{A,1}$ (ppb)	2nd measurement set Date	$y_{A,2}$ (ppb)	3th measurement set Date	$y_{A,3}$ (ppb)	$\bar{y}_A$ (ppb)	$\overline{\sigma}$ (ppb)	u_A (ppb)	$u(\bar{y}_A)$ (ppb)
KRISS	D929248	1797.10	0.50	18/6/2013 10:44	1799.55	18/6/2013 12:54	1799.64	18/6/2013 15:05	1799.64	1799.61	0.03	0.14	0.14
KRISS	D985705	2200.90	0.60	18/6/2013 11:00	2204.08	18/6/2013 13:11	2204.16	18/6/2013 15:21	2204.24	2204.16	0.05	0.14	0.14
NIM	CAL017763	1825.20	0.85	18/6/2013 10:28	1827.37	18/6/2013 12:38	1827.50	18/6/2013 14:48	1827.65	1827.51	0.08	0.14	0.16
NIM	CAL017790	2193.80	1.00	18/6/2013 9:39	2195.70	18/6/2013 11:49	2195.95	18/6/2013 14:00	2196.03	2195.89	0.10	0.14	0.17
NIST	FB03569	1796.76	0.85	18/6/2013 9:06	1798.33	18/6/2013 11:17	1798.69	18/6/2013 13:27	1798.80	1798.61	0.14	0.14	0.20
NIST	FB03587	2195.96	0.84	18/6/2013 9:23	2196.37	18/6/2013 11:33	2196.72	18/6/2013 13:43	2196.93	2196.67	0.16	0.14	0.21
NMIJ	CPB28035	1797.30	0.65	18/6/2013 10:52	1797.97	18/6/2013 13:03	1798.20	18/6/2013 15:13	1798.26	1798.15	0.09	0.14	0.16
NMIJ	CPB28219	2198.30	0.65	18/6/2013 8:58	2198.60	18/6/2013 11:09	2199.31	18/6/2013 13:19	2199.24	2199.05	0.22	0.14	0.26
NOAA	FB03578	1812.10	1.30	18/6/2013 9:31	1815.99	18/6/2013 11:41	1816.40	18/6/2013 13:52	1816.44	1816.28	0.14	0.14	0.20
NOAA	FB03593	2208.90	1.40	18/6/2013 10:03	2215.65	18/6/2013 12:14	2215.77	18/6/2013 14:24	2215.90	2215.77	0.07	0.14	0.16
NPL	233097	1799.40	1.80	18/6/2013 10:36	2202.92	18/6/2013 12:46	2203.12	18/6/2013 14:57	2203.08	2203.04	0.06	0.14	0.15
NPL	221727	2199.60	2.20	18/6/2013 9:47	1802.30	18/6/2013 11:57	1802.37	18/6/2013 14:08	1802.60	1802.43	0.09	0.14	0.17
VNIIM	D249682	1812.90	1.30	18/6/2013 9:14	1811.81	18/6/2013 11:25	1812.05	18/6/2013 13:35	1812.24	1812.03	0.12	0.14	0.18
VNIIM	D249845	2214.60	1.25	18/6/2013 9:55	2216.22	18/6/2013 12:06	2216.50	18/6/2013 14:16	2216.56	2216.43	0.11	0.14	0.17
VSL	D249292	1798.29	2.00	18/6/2013 10:20	1799.55	18/6/2013 12:30	1799.55	18/6/2013 14:40	1799.73	1799.61	0.06	0.14	0.15
VSL	D249289	2196.33	2.40	18/6/2013 10:12	2197.09	18/6/2013 12:22	2197.43	18/6/2013 14:32	2197.43	2197.31	0.11	0.14	0.18

Table 12. CRDS responses during a 6hr period.

1.2.2 Method 1-B: CRDS response over 30 days

In this method the measurand was the CRDS response defined as the average of the CRDS value on five minutes of measurement, $y_{B,i}$ where each cylinder *i* was measured three or four times, during approximately 30 days. Method 1-B differs from Method 1-A only by the period during the measurements were completed.

Type A uncertainty, u_A

The Type A uncertainty component was defined as the combination of the short term repeatability, Allan Variance analysis (u_{Allan} = 0.1 ppb), and the intermediate precision u_{Intpre} or drift. u_{Intpre} was determined calculating the standard deviation of the instrument response to the control cylinder during the measurement period, 30 days, that Method 1-B measurements were done. Figure 25 plots the instrument response to the control cylinder during the period 09/04 to 07/05 where u_{Intpre} was equal to 0.319 ppb.

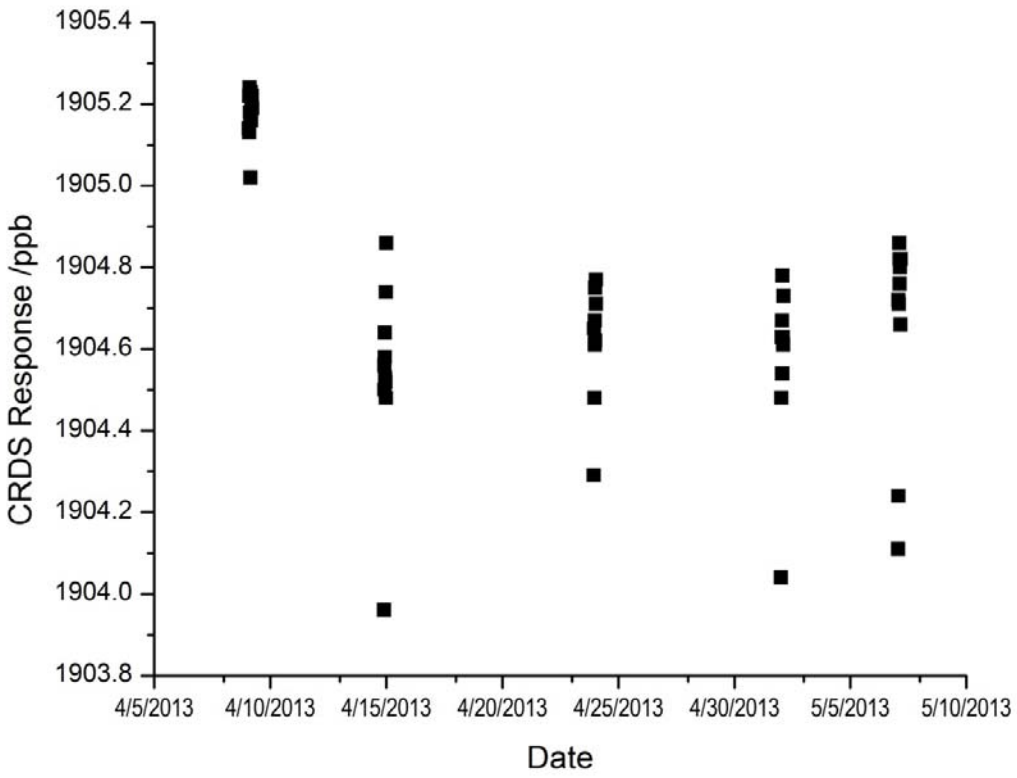


Figure 25 : CRDS response of the control cylinder.

Since the arithmetic mean was used the associated standard uncertainty was calculated by:

$$u_A = \sqrt{\left(\frac{u_{Allan}^2}{s}\right) + u_{Intpre}^2} \quad (26)$$

where *s* is the number of independent observations obtained under the same conditions (3 or 4). For *s* equal to 3 equation 29 was equal to:

$$u_A = \sqrt{\left(\frac{(0.1)^2}{3}\right) + (0.319)^2} = 0.324 \text{ ppb} \quad (27)$$

for *s* equal to 4:

$$u_A = \sqrt{\left(\frac{(0.1)^2}{4}\right) + (0.319)^2} = 0.323 \text{ ppb} \quad (28)$$

Type B uncertainty

Type B uncertainty was the same as Method 1-A, $u_{Broad} = u_B = 0.059$ ppb .

Additional variance, $\overline{\sigma}$

The experimental standard deviation of the mean of the *s* CRDS responses was calculated by the equation:

$$\overline{\sigma} = \sqrt{\frac{\frac{1}{s-1}\sum_{k=1}^{s}\left(y_{B,k} - \overline{y}_B\right)}{s}} \quad (29)$$

where *s* is the number of measurements sets (3 or 4).

Combined standard uncertainty, $u\left(\overline{y}_B\right)$

The combined uncertainty of all this contributors was given by:

$$u\left(\overline{y}_B\right) = \sqrt{u_A^2 + u_B^2 + \overline{\sigma}^2} \; . \quad (30)$$

All measurements results and uncertainties are listed in Table 13.

Institute name	Cylinder ID	Gravimetric amount of substance fraction (nmol/mol)	Standard uncertainty (k=1) (nmol/mol)	1st measurement set Date	$y_{B,1}$ (ppb)	2nd measurement set Date	$y_{B,2}$ (ppb)	3th measurement set Date	$y_{B,3}$ (ppb)	4th measurement set Date	$y_{B,4}$ (ppb)	$\bar{y}_B$ (ppb)	$\overline{\sigma}$ (ppb)	u_A (ppb)	$u(\bar{y}_B)$ (ppb)
KRISS	D929248	1797.10	0.50	9/4/2013	1800.26	7/5/2013	1799.70	17/5/2013	1799.65	-	-	1799.87	0.20	0.32	0.38
KRISS	D985705	2200.90	0.60	9/4/2013	2204.91	7/5/2013	2204.64	17/5/2013	2204.35	-	-	2204.63	0.16	0.32	0.37
NIM	CAL017763	1825.20	0.85	7/5/2013	1827.57	17/5/2013	1827.70	17/5/2013	1827.62	-	-	1827.63	0.04	0.37	0.37
NIM	CAL017790	2193.80	1.00	7/5/2013	2196.43	17/5/2013	2196.16	17/5/2013	2196.32	-	-	2196.30	0.08	0.37	0.38
NIST	FB03569	1796.76	0.85	9/4/2013	1799.48	15/4/2013	1798.86	24/4/2013	1798.94	2/5/2013	1798.98	1799.06	0.14	0.32	0.36
NIST	FB03587	2195.96	0.84	9/4/2013	2197.47	15/4/2013	2196.82	24/4/2013	2196.93	2/5/2013	2196.84	2197.01	0.15	0.32	0.36
NMIJ	CPB28035	1797.30	0.65	15/4/2013	1798.43	24/4/2013	1798.75	2/5/2013	1798.47	-	-	1798.55	0.10	0.32	0.34
NMIJ	CPB28219	2198.30	0.65	15/4/2013	2199.63	24/4/2013	2199.66	2/5/2013	2199.58	-	-	2199.62	0.02	0.32	0.33
NOAA	FB03578	1812.10	1.30	9/4/2013	1817.13	7/5/2013	1816.43	17/5/2013	1816.35	-	-	1816.64	0.25	0.32	0.41
NOAA	FB03593	2208.90	1.40	9/4/2013	2216.67	7/5/2013	2215.92	17/5/2013	2215.81	-	-	2216.13	0.27	0.32	0.43
NPL	221727.00	1799.40	1.80	9/4/2013	1803.25	15/4/2013	1802.36	24/4/2013	1802.62	2/5/2013	1802.58	1802.70	0.19	0.32	0.38
NPL	233097.00	2199.60	2.20	9/4/2013	2204.02	15/4/2013	2203.27	24/4/2013	2203.24	2/5/2013	2203.34	2203.47	0.18	0.32	0.38
VNIIM	D249682	1812.90	1.30	15/4/2013	1811.92	24/4/2013	1812.11	2/5/2013	1812.17	-	-	1812.07	0.07	0.32	0.34
VNIIM	D249845	2214.60	1.25	9/4/2013	2217.58	15/4/2013	2216.88	24/4/2013	2216.91	2/5/2013	2216.78	2217.04	0.18	0.32	0.38
VSL	D249292	1798.29	2.00	9/4/2013	1800.27	7/5/2013	1799.63	17/5/2013	1799.18	-	-	1799.69	0.32	0.32	0.46
VSL	D249289	2196.33	2.40	4/9/2013	2198.35	7/5/2013	2197.23	17/5/2013	2197.25	-	-	2197.61	0.37	0.32	0.50

Table 13. CRDS responses during the period of 09/04 to 07/05, 2013.- No measurement.

1.2.3 Method 2: Uncertainty approach for ratios to the control cylinder 597888

The measurand of this method is the drift corrected ratio between cylinder responses to the control cylinder.

In order to determine the drift corrected ratios for each cylinder the average responses of a CH_4/air standard gas mixture i and control cylinder A are determined following Table 14 scheme:

SampleName		
Control Cylinder before	A_b	SUBSET l
Cylinder i	Cyl_i	
Cylinder i+1	Cyl_{i+1}	
Control Cylinder after	A_a	

Table 14. Typical sampling sequence.

where $Cyl_{i,}$ is the CRDS response to the gas mixture i ($i = A$ for the control or n for the standard gas mixture connected to the autosampler port m). The drift of the signal on the subset l between A_b and A_a, is determined by

$$Corr=(A_b- A_a)/3 \quad (31)$$

considering that all analysis are equally spaced in time.

$Corr$ is then the correction factor to be applied between two mixtures analysis. To calculate the drift corrected responses for Cylinder 1 and 2, $Corr$ is then added to A_b , cylinder 1, and twice to cylinder 2:

$$C_{F,1}= A_b+ Corr \quad (32)$$

$$C_{F,2}= A_b+2\cdot Corr \quad (33)$$

Then, the ratio corrected for the drift of the instrument of each cylinder to the control cylinder A, $R_{CRDS\_1\_1}$ and $R_{CRDS\_2\_1}$, are calculated dividing the response of the CH_4/air standards mixtures (Cyl_1 and Cyl_2) by the drift corrected responses $C_{F,1}$ and $C_{F,2}$ respectively:

$$R_{CRDS\_1\_1} = Cyl_i/C_{F,i} \quad (34)$$

$$R_{CRDS\_2\_1} = Cyl_{i+1}/C_{F,i+1}. \quad (35)$$

Uncertainty

The uncertainties related to the use of CRDS ratios to the control standard *A* were calculated programing equations 37 and 38 in the software GUM Workbench. GUM Workbench is a Windows software to evaluate the uncertainty of measurement based on the "DIN/ISO/BIPM Guide to the expression of uncertainty in measurement". The final equations as programed in GUM were:

For cylinder *i* :

$$R_{2\_i} = \left(\frac{Cyl_i}{A_b + \left(\frac{A_b - A_a}{3} \right)} \right) \tag{36}$$

for cylinder *i*+1:

$$R_{2\_i+1} = \left(\frac{Cyl_{i+1}}{A_b + 2 \cdot \left(\frac{A_b - A_a}{3} \right)} \right) \tag{37}$$

To accomplish this task in GUM, uncertainty values were assigned to each of these parameters. The uncertainty related to the cylinder analysis for cylinders 1 and 2 and control cylinder, $u(Cyl_1)$, $u(Cyl_2)$, $u(A_b)$ and $u(A_a)$ were evaluated as follows:

The uncertainties in the CRDS responses to cylinders 1 and 2 were considered equal to the combination of the short term repeatability, u_{Alla} , and the effect of the difference in air composition between measured gas mixtures, u_{Broad} :

$$u(Cyl_1) = u(Cyl_2) = \sqrt{u_{Allan}^2 + u_{Broad}^2} \tag{38}$$

As described in section 1.2.2, the short term repeatability, given by Allan Variance analysis, u_{Alla} = 0.1 ppb and the effect of the difference in air composition between measured gas mixtures, u_{Broad} = 0.059 ppb.

Finally, the uncertainty in the control cylinder measurements, $u(A_b)$ and $u(A_a)$, was considered equal to the short term repeatability only, u_{Allan} :

$$u(A_B) = u(A_A) = u_{Allan} = 0.1 \text{ ppb} \tag{39}$$

Table 15 and Table 16 list the input parameters used in GUM for cylinders FB03587 and D985705.

Quantity	Instrument response (ppb)	Standard Uncer. (ppb)	Sensitivity coefficient	Uncertainty Contribution	Index %
Cyl_i	2197.473	0.116	5.20E-04	6.10E-05	34.9
A_b	1905.178	0.1	-8.10E-04	-8.10E-05	61.3
A_a	1905.171	0.1	2.00E-04	2.00E-05	3.8

Value	Expanded uncertainty	Coverage factor K
1.15342	2.10E-04	2

Table 15. GUM output values for cylinder 1.

Quantity	Instrument response (ppb)	Standard Uncer. (ppb)	Sensitivity coefficient	Uncertainty Contribution	Index %
Cyl_{i+1}	2204.905	0.116	5.20E-04	6.10E-05	23.8
A_b	1905.178	0.1	-1.00E-03	-1.00E-04	65.7
A_a	1905.171	0.1	4.00E-06	4.00E-05	10.5

Value	Expanded Uncertainty	Coverage Factor K
1.15732	2.50E-04	2

Table 16. GUM output values for cylinder 2.

Intermediate precision, u_{Intpre}

An additional term describing the uncertainty due the intermediate precision of the CRDS ratio measurements was added to $u(R_2)$. This uncertainty term was calculated by the standard deviation of the ratio between the cylinder 400330 (installed in position 14) and the control cylinder 597888 during the period of April 5 to May 15. This term was equivalent to u_{Intpre}=0.000075 (see page 56).

Standard deviation of the mean, $\overline{\sigma}$

The standard deviation of the mean calculated for *s* sets of ratios for each cylinder was also evaluated and it was decided to include this component in the combined uncertainty. The uncertainty for each cylinder measurement is listed in *Table 13*:

$$\overline{\sigma} = \sqrt{\frac{\frac{1}{s-1}\sum_{k=1}^{s}\left(R_{2\_k} - \overline{R}_{2\_k}\right)}{s}} \tag{40}$$

The final expression to determine the global uncertainty for each cylinder *i* is given by equation 44 and the results of the measured cylinders listed in Table 17.

$$u\left(\overline{R}_2\right) = \sqrt{u\left(R_2\right)^2 + u_{Intpre}^2 + \overline{\sigma}^2} \tag{41}$$

Institute name	Cylinder ID	Gravimetric mole fraction (nmol/mol)	Standard uncertainty (k=1) (nmol/mol)	1st measurement set Date	$R_{2,1}$	2nd measurement set Date	$R_{2,2}$	3th measurement set Date	$R_{2,3}$	4th measurement set Date	$R_{2,4}$	$\overline{R}_2$	$\overline{\sigma}$	$u(\overline{R}_2)$
KRISS	D929248	1797.10	0.50	9/4/2013	0.94493	7/5/2013	0.94484	17/5/2013	0.94494	-	-	0.94490	0.00003	0.00026
KRISS	D985705	2200.90	0.60	9/4/2013	1.15733	7/5/2013	1.15738	17/5/2013	1.15740	-	-	1.15737	0.00002	0.00026
NIM	CAL017763	1825.20	0.85	7/5/2013	0.95950	17/5/2013	0.95970	17/5/2013	0.95963	-	-	0.95961	0.00006	0.00027
NIM	CAL017790	2193.80	1.00	7/5/2013	1.15311	17/5/2013	1.15308	17/5/2013	1.15323	-	-	1.15314	0.00004	0.00026
NIST	FB03569	1796.76	0.85	9/4/2013	0.94451	15/4/2013	0.94445	24/4/2013	0.94447	2/5/2013	0.94454	0.94449	0.00002	0.00026
NIST	FB03587	2195.96	0.84	9/4/2013	1.15342	15/4/2013	1.15345	24/4/2013	1.15352	2/5/2013	1.15341	1.15345	0.00002	0.00026
NMIJ	CPB28035	1797.30	0.65	15/4/2013	0.94427	24/4/2013	0.94437	2/5/2013	0.94423	-	-	0.94429	0.00004	0.00026
NMIJ	CPB28219	2198.30	0.65	15/4/2013	1.15492	24/4/2013	1.15491	2/5/2013	1.15485	-	-	1.15489	0.00002	0.00026
NOAA	FB03578	1812.10	1.30	9/4/2013	0.95379	7/5/2013	0.95359	17/5/2013	0.95364	-	-	0.95368	0.00006	0.00027
NOAA	FB03593	2208.90	1.40	9/4/2013	1.16348	7/5/2013	1.16339	17/5/2013	1.16350	-	-	1.16346	0.00003	0.00026
NPL	221727	1799.40	1.80	9/4/2013	0.94649	15/4/2013	0.94646	24/4/2013	0.94649	2/5/2013	0.94657	0.94650	0.00002	0.00026
NPL	233097	2199.60	2.20	9/4/2013	1.15691	15/4/2013	1.15681	24/4/2013	1.15676	2/5/2013	1.15684	1.15683	0.00003	0.00026
VNIIM	D249682	1812.90	1.30	15/4/2013	0.95157	24/4/2013	0.95153	2/5/2013	0.95168	-		0.95159	0.00004	0.00026
VNIIM	D249845	2214.60	1.25	9/4/2013	1.16397	15/4/2013	1.16396	24/4/2013	1.16393	2/5/2013	1.16393	1.16395	0.00001	0.00026
VSL	D249292	1798.29	2.00	9/4/2013	0.94494	7/5/2013	0.94511	17/5/2013	0.94491	-	-	0.94499	0.00006	0.00027
VSL	D249289	2196.33	2.40	9/4/2013	1.15389	7/5/2013	1.15389	17/5/2013	1.15392	-	-	1.15390	0.00001	0.00026

Table 17. CRDS ratios to the control cylinder A. *i* is the cylinder number.

Intermediate precision for ratio CRDS measurements, u_{Intpre}

The intermediate precision was calculated by the standard deviation of the ratio between the cylinder 400330 (installed in position 14) and the control cylinder 597888 during the period of April 5 to May 15 (see *Figure 26*). The standard deviation resulting of this calculation is u_{Intpre}=0.000075.

For completeness reasons the intermediate precision was determined as well for the standard cylinder 581087 (installed in position 15) during the same period (see Figure 26). The standard deviation resulting of this calculation is 0.00006.

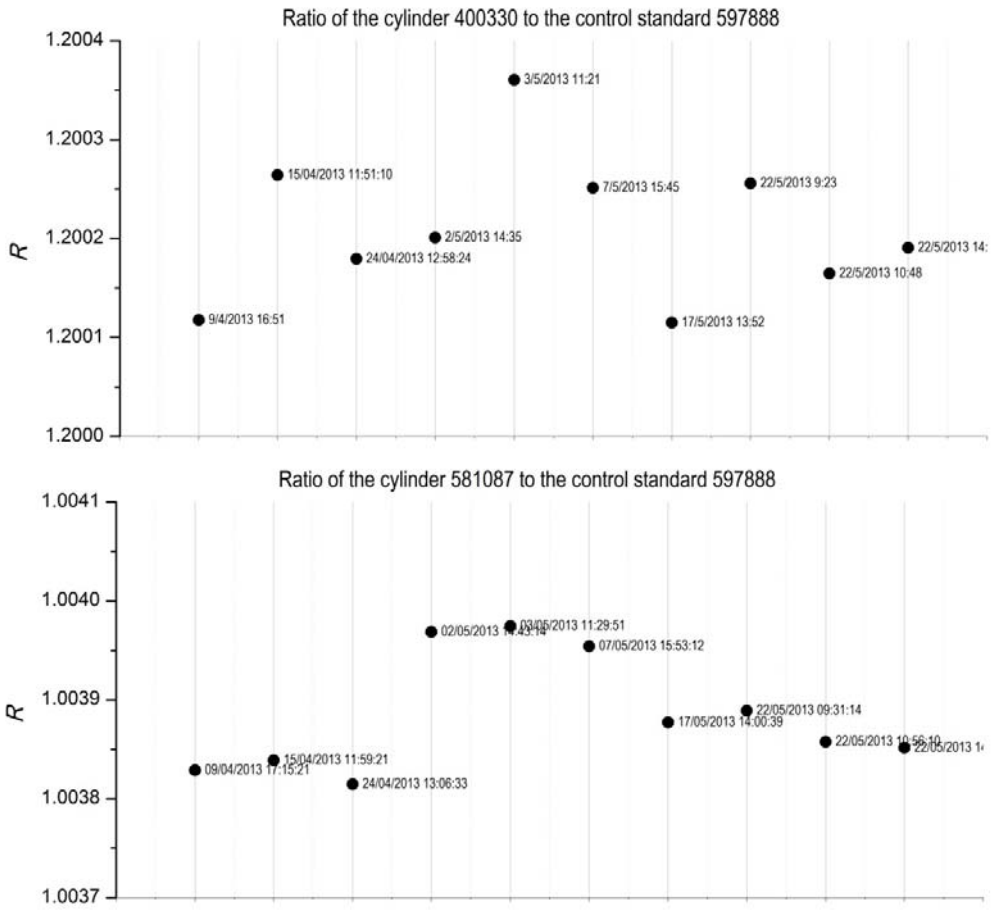


Figure 26 :Ratio of the cylinder 400330 and 581087 to the control cylinder 597888.

ANNEX 2 - Measurement reports of participants

Korea Research Institute of Standards and Science (KRISS)

Key Comparison CCQM-K82
Methane in Air at Ambient level (1800-2200) nmol/mol

Result form CCQM-K82-R

Project name: CCQM-K82 (Methane in Air at Ambient level).

Comparison: Comparability study of laboratories' preparation capabilities for Methane in AirStandards.

Proposed dates: 05/2012 to 03/2013 (to be extended)

Coordinating laboratories:
Bureau International des Poids et Mesures
Chemistry Section
Pavillon de Breteuil
92312 Sevres Cedex, France.

NIST
100 Bureau Drive, Stop 8300, Gaithersburg, MD 20899-8300
US

Study Coordinator: Edgar Flores
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
Email:ejardine@bipm.org

Return of the form:
Please complete and return the form preferably by email to ejardine@bipm.org

The CCQM-K82 comparison is designed to evaluate the level of compatibility of NMI preparative capabilities for gravimetric methane in air primary reference mixtures in the range (1800-2200) nmol/mol. The balance gas for the standards shall be either scrubbed dry real air or synthetic air.

A1. General information

Institute	Korea Research Institute of Standards and Science (KRISS)		
Address	Center for Gas Analysis (Chemistry Building #306 Office #206) Division of Metrology for Quality of Life 267 Gajeong-Ro, Yuseong-Gu Daejeon 305-340, REPUBLIC OF KOREA		
Contact person	Dr. Namgoo Kang		
Telephone	+82-42-868-5221	Fax	+82-42-868-5042
Email*	nkang@kriss.re.kr		
Serial number of cylinder received	**D929248; D985705**		
Cylinder pressure as received	7.0 MPa; 7.0 MPa		

A2. Results

Serial number of cylinder	Methane mole fraction x_{CH4}	Expanded uncertainty $U(x_{CH4})$	Coverage factor (k)
D929248	1797.1nmol/mol	1.0nmol/mol	2
D985705	2200.9nmol/mol	1.2nmol/mol	2

The above results are the gravimetric mole fraction of methane and gravimetric uncertainty at level of confidence of 95%.

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

A3.1. Gravimetric preparation of the cylinders

i) Based on the Protocol of the Key Comparison CCQM-K82 (GAWG/12-36), the above KRISS CH_4 standards were prepared gravimetrically with **synthetic air**.

ii) Specification of the balance was Mettler Toledo Model XP26003L with the resolution of 1 mg and the maximum loading of 26 kg.

iii) A substitution method using the weighing sequence of B-A-B' was used as the weighing method where A denotes a reference (tare) cylinder and B and B' sample cylinders, respectively. The cycle of B-A-B'was repeated 5 times in one measurement and 3 measurement data sets were used to obtain the arithmetic mean and standard deviation of the weighing result. The data for the temperature, atmospheric pressure and relative humidity in the ambient conditions of the balance room were synchronously recorded with the weighing process.

iv) The mole fractions of CH_4 and the other 4 components (CO_2, Ar, O_2, and N_2) in the final mixture were calculated by the equations presented in **A3.2. Model Equation**s based on the equation (3) in ISO 6142:2001.

v) Uncertainties for the mole fractions of the components in the final mixture were estimated using virtually all the uncertainties:i) uncertainties associated with the differencein the readings of the weighing between reference cylinder and sample cylinder; and ii) uncertainties associated with the gravimetric preparation process (U_min **A3.2. Model Equations**) due to the balance, the standard mass pieces (OIML E2 grade), reference cylinders and sample cylinders, potential leakages of cylinders, impurities of source gases, and molar mass of the components.

A3.2. Model Equations:

```
C_Ar = n_comp1 / (n_total) * 100 ;
C_CO2 = n_comp2 / (n_total) * 1000000 ;
C_CH4 = n_comp3 / (n_total) * 1000000000 ;
C_O2 = n_comp4 / (n_total) * 100 ;
C_N2 = (n_bal1 + n_bal2 + n_bal3 + n_bal4 + n_bal)/(n_total)*100;

n_total=n_comp1 + n_comp2  + n_comp3 + n_comp4  + n_bal1 + n_bal2 + n_bal3 + n_bal4 +
n_bal ;

n_comp1 = n_compMother1 / m_Mother1 * m_comp1 ;
n_bal1 = n_balMother1 / m_Mother1 * m_comp1 ;
n_comp2 = n_compMother2 / m_Mother2 * m_comp2 ;
n_bal2 = n_balMother2 / m_Mother2 * m_comp2 ;
n_comp3 = n_compMother3 / m_Mother3 * m_comp3 ;
n_bal3 = n_balMother3 / m_Mother3 * m_comp3 ;
n_comp4 = n_compMother4 / m_Mother4 * m_comp4 ;
n_bal4 = n_balMother4 / m_Mother4 * m_comp4 ;
n_bal = n_balMother / m_balMother * m_bal ;
```

m_Mother1 = n_compMother1 * MW_comp1 + (100 - n_compMother1) * MW_bal ;
m_Mother2 = n_compMother2 * MW_comp2 + (100 - n_compMother2) * MW_bal ;
m_Mother3 = n_compMother3 * MW_comp3 + (100 - n_compMother3) * MW_bal ;
m_Mother4 = n_compMother4 * MW_comp4 + (100 - n_compMother4) * MW_bal ;

m_comp1 = ((SC_comp1 - SC_empty) - (RC_comp1 - RC_empty)) + U_m ;
m_comp2 = ((SC_comp2 - SC_comp1) - (RC_comp2 - RC_comp1)) + U_m ;
m_comp3 = ((SC_comp3 - SC_comp2) - (RC_comp3 - RC_comp2)) + U_m ;
m_comp4 = ((SC_comp4 - SC_comp3) - (RC_comp4 - RC_comp3)) + U_m ;
m_bal = ((SC_bal -SC_comp4) - (RC_bal - RC_comp4)) + U_m;

MW_comp1 = Ar;
MW_comp2 = C+O*2;
MW_comp3 = C+H*4;
MW_comp4 = O*2;
MW_bal = N*2 ;

A3.2. Uncertainty Budgets and List of Quantities:

Uncertainty budget for the mole fraction of CH_4 in the final mixture (D929248)

Quantity	Definition	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
n_total	Total mole of gas	41.275496 mol	1.7E-3 % (rel)				
n_bal	mole of balance gas	29.958859 mol	630E-6 % (rel)				
n_compMother1	mole of component 1 (Ar) in pure Ar	99.9996375 mol	35E-6 % (rel)	normal	-0.12	-2.33E-9 (rel)	0.0%
n_balMother1	mole of balance gas (N2) in pure Ar	160.0E-6 mol	16 % (rel)	normal	-0.17	-2.37E-9 (rel)	0.0%
n_compMother2	mole of component 2 (CO2) in pure CO2	1.999181 mol	0.011 % (rel)	normal	-0.15	-19.0E-9 (rel)	0.0%
n_balMother2	mole of balance gas (N2) in pure CO2	98.00083000 mol	2.6E-6 % (rel)	normal	-0.34	-477E-12 (rel)	0.0%
n_compMother3	mole of component 3 (CH4) in pure CH4	4.99384E-3 mol	0.026 % (rel)	normal	3.60E+05	260E-6 (rel)	84.7%
n_balMother3	mole of balance gas (N2) in pure CH4	99.99950000 mol	2.5E-6 % (rel)	normal	-0.65	-900E-12 (rel)	0.0%
n_compMother4	mole of component 4 (O2) in pure O2	99.9995837 mol	98E-6 % (rel)	rectangular	-3.3	-180E-9 (rel)	0.0%
n_balMother4	mole of balance gas (N2) in pure O2	4.16300E-3 mol	0.035 % (rel)	rectangular	-3.8	-3.03E-9 (rel)	0.0%
n_balMother	mole of balance gas (N2) in pure N2	100.00%	30E-6 % (rel)		-13	-218E-9 (rel)	0.0%
m_balMother	mass of balance gas (N2) in pure N2	2801.34728 g	250E-6 % (rel)		0.47	1.82E-6 (rel)	0.0%
m_comp1	mass of component 1 (Ar) in the final mixture	15.63200 g	0.059 % (rel)				
m_comp2	mass of component 2 (CO2) in the final mixture	22.33200 g	0.021 % (rel)				
m_comp3	mass of component 3 (CH4) in the final mixtue	41.60860 g	0.012 % (rel)				
m_comp4	mass of component 4 (O2) in the final mixture	276.83460 g	2.0E-3 % (rel)				
m_bal	mass of balance gas (N2) in the final mixture	839.25320 g	580E-6 % (rel)				
RC_empty	mass of reference cylinder, empty	13741.58720 g	41E-6 % (rel)	normal	-1.1	-3.40E-6 (rel)	0.0%

SC_empty	mass of sample cylinder, empty	13607.32120 g	44E-6 % (rel)	normal	1.1	3.62E-6 (rel)	0.0%
RC_comp1	mass of reference cylinder, component 1 (Ar)	13741.64040 g	7.5E-6 % (rel)	normal	-0.45	-256E-9 (rel)	0.0%
SC_comp1	mass of sample cylinder, component 1 (Ar)	13623.00640 g	9.5E-6 % (rel)	normal	0.45	320E-9 (rel)	0.0%
RC_comp2	mass of reference cylinder, component 2 (CO2)	13741.673800 g	7.1E-6 % (rel)	normal	43	23.3E-6 (rel)	0.7%
SC_comp2	mass of sample cylinder, component 2 (CO2)	13645.37180 g	8.5E-6 % (rel)	normal	-43	-27.8E-6 (rel)	1.0%
RC_comp3	mass of reference cylinder, component 3 (CH4)	13741.71020 g	12E-6 % (rel)	normal	-43	-41.0E-6 (rel)	2.1%
SC_comp3	mass of sample cylinder, component 3 (CH4)	13687.01680 g	16E-6 % (rel)	normal	43	52.6E-6 (rel)	3.5%
RC_comp4	mass of reference cylinder, component 4 (O2)	13741.75800 g	11E-6 % (rel)	normal	-0.19	-167E-9 (rel)	0.0%
SC_comp4	mass of sample cylinder, component 4 (O2)	13963.89920 g	15E-6 % (rel)	normal	0.19	229E-9 (rel)	0.0%
RC_bal	mass of reference cylinder, balance gas (N2)	13741.773600 g	4.4E-6 % (rel)	normal	1.6	519E-9 (rel)	0.0%
SC_bal	mass of sample cylinder, balance gas (N2)	14803.168000 g	3.0E-6 % (rel)	normal	-1.6	-387E-9 (rel)	0.0%
MW_comp1	molar mass of component 1 (Ar)	39.948000 g/mol	1.3E-3 % (rel)				
MW_comp2	molar mass of component 2 (CO2)	44.009500 g/mol	1.1E-3 % (rel)				
MW_comp3	molar mass of component 3 (CH4)	16.042460 g/mol	2.6E-3 % (rel)				
MW_comp4	molar mass of component 4 (O2)	31.998800 g/mol	940E-6 % (rel)				
MW_bal	molar mass of balance gas (N2)	28.0134800 g/mol	250E-6 % (rel)				
m_Mother1	mass of component 1 (Ar)	3994.7957 g	1.3E-3 % (rel)				
m_Mother2	mass of component 2 (CO2)	2833.32694 g	280E-6 % (rel)				
m_Mother3	mass of component 3 (CH4)	2801.28822 g	250E-6 % (rel)				
m_Mother4	mass of component 4 (O2)	3199.8783 g	940E-6 % (rel)				
U_m	Expanded combined uncertainty for gravimetric preparation process	0.0 g	4.0E-3 g	normal	36	80.3E-6 (rel)	8.1%
H	atomic mass of H	1.0079400 g/mol	3.5E-3 % (rel)	normal	-0.012	-241E-12 (rel)	0.0%
C	atomic mass of C	12.010700 g/mol	3.3E-3 % (rel)	normal	0.021	4.70E-9 (rel)	0.0%
O	atomic mass of O	15.999400 g/mol	940E-6 % (rel)	normal	24	1.9E-6 (rel)	0.0%
N	atomic mass of N	14.0067400 g/mol	250E-6 % (rel)	normal	-120	-2.36E-6 (rel)	0.0%
Ar	atomic mass of Ar	39.948000 g/mol	1.3E-3 % (rel)	normal	0.43	119E-9 (rel)	0.00%
CH4	mole fraction of CH4 in the final mixture	1797.081 nmol/mol	0.028 % (rel)				
C_Ar	mole fraction of Ar in the final mixture	%					
C_CO2	mole fraction of CO2 in the final mixture	umol/mol					
C_CH4	mole fraction of CH4 in the final mixture	nmol/mol					
C_O2	mole fraction of O2 in the final mixture	%					
C_N2	mole fraction of N2 in the final mixture	%					

Uncertainty budget for the mole fraction of CH_4 in the final mixture (D985705)

Quantity	Definition	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
n_total	Total mole of gas	41.444310 mol	1.6E-3 % (rel)				
n_bal	mole of balance gas	29.841873 mol	610E-6 % (rel)				
n_compMother1	mole of component 1 (Ar) in pure Ar	99.9996375 mol	35E-6 % (rel)	normal	-0.15	-2.31E-9 (rel)	0.0%
n_balMother1	mole of balance gas (N2) in pure Ar	160.0E-6 mol	16 % (rel)	normal	-0.21	-2.35E-9 (rel)	0.0%
n_compMother2	mole of component 2 (CO2) in pure CO2	2.000449 mol	0.012 % (rel)	normal	-0.18	-20.1E-9 (rel)	0.0%
n_balMother2	mole of balance gas (N2) in pure CO2	97.99955100 mol	2.6E-6 % (rel)	normal	-0.42	-475E-12 (rel)	0.0%
n_compMother3	mole of component 3 (CH4) in pure CH4	5.01435E-3 mol	0.026 % (rel)	normal	4.40E+05	259E-6 (rel)	87.5%
n_balMother3	mole of balance gas (N2) in pure CH4	99.99498565 mol	2.5E-6 % (rel)	normal	-0.97	-1.10E-9 (rel)	0.0%
n_compMother4	mole of component 4 (O2) in pure O2	99.999584 mol	290E-6 % (rel)	rectangular	-4	-525E-9 (rel)	0.0%
n_balMother4	mole of balance gas (N2) in pure O2	416.30E-6 mol	0.35 % (rel)	rectangular	-4.6	-3.00E-9 (rel)	0.0%
n_balMother	mole of balance gas (N2) in pure N2	100.00%	30E-6 % (rel)		-16	-216E-9 (rel)	0.0%
m_balMother	mass of balance gas (N2) in pure N2	2801.34728 g	250E-6 % (rel)		0.57	1.80E-6 (rel)	0.0%
m_comp1	mass of component 1 (Ar) in the final mixture	15.58540 g	0.038 % (rel)				
m_comp2	mass of component 2 (CO2) in the final mixture	22.28840 g	0.023 % (rel)				
m_comp3	mass of component 3 (CH4) in the final mixtue	50.95800 g	0.011 % (rel)				
m_comp4	mass of component 4 (O2) in the final mixture	275.39940 g	2.0E-3 % (rel)				
m_bal	mass of balance gas (N2) in the final mixture	835.97600 g	550E-6 % (rel)				
RC_empty	mass of reference cylinder, empty	13642.95600 g	17E-6 % (rel)	normal	-1.3	-1.44E-6 (rel)	0.0%
SC_empty	mass of sample cylinder, empty	13687.64040 g	20E-6 % (rel)	normal	1.3	1.63E-6 (rel)	0.0%
RC_comp1	mass of reference cylinder, component 1 (Ar)	13642.98900 g	13E-6 % (rel)	normal	-0.54	-450E-9 (rel)	0.0%
SC_comp1	mass of sample cylinder, component 1 (Ar)	13703.25880 g	13E-6 % (rel)	normal	0.54	452E-9 (rel)	0.0%
RC_comp2	mass of reference cylinder, component 2 (CO2)	13643.02600 g	11E-6 % (rel)	normal	43	29.7E-6 (rel)	1.2%
SC_comp2	mass of sample cylinder, component 2 (CO2)	13725.58420 g	11E-6 % (rel)	normal	-43	-28.7E-6 (rel)	1.1%
RC_comp3	mass of reference cylinder, component 3 (CH4)	13643.06580 g	15E-6 % (rel)	normal	-43	-40.7E-6 (rel)	2.2%
SC_comp3	mass of sample cylinder, component 3 (CH4)	13776.58200 g	18E-6 % (rel)	normal	43	48.2E-6 (rel)	3.0%
RC_comp4	mass of reference cylinder, component 4 (O2)	13643.097000 g	6.6E-6 % (rel)	normal	-0.24	-95.9E-9 (rel)	0.0%
SC_comp4	mass of sample cylinder, component 4 (O2)	14052.01260 g	9.7E-6 % (rel)	normal	0.24	146E-9 (rel)	0.0%
RC_bal	mass of reference cylinder, balance gas (N2)	13643.121200 g	4.9E-6 % (rel)	normal	1.9	571E-9 (rel)	0.0%
SC_bal	mass of sample cylinder, balance gas (N2)	14888.01280 g	10E-6 % (rel)	normal	-1.9	-1.29E-6 (rel)	0.0%
MW_comp1	molar mass of component 1 (Ar)	39.948000 g/mol	1.3E-3 % (rel)				

MW_comp2	molar mass of component 2 (CO2)	44.009500 g/mol	1.1E-3 % (rel)				
MW_comp3	molar mass of component 3 (CH4)	16.042460 g/mol	2.6E-3 % (rel)				
MW_comp4	molar mass of component 4 (O2)	31.998800 g/mol	940E-6 % (rel)				
MW_bal	molar mass of balance gas (N2)	28.0134800 g/mol	250E-6 % (rel)				
m_Mother1	mass of component 1 (Ar)	3994.7957 g	1.3E-3 % (rel)				
m_Mother2	mass of component 2 (CO2)	2833.34722 g	280E-6 % (rel)				
m_Mother3	mass of component 3 (CH4)	2801.28797 g	250E-6 % (rel)				
m_Mother4	mass of component 4 (O2)	3199.8783 g	940E-6 % (rel)				
U_m	expanded combined uncertainty for gravimetric preparation process	0.0 g	4.0E-3 g	normal	35	62.8E-6 (rel)	5.1%
H	atomic mass of H	1.0079400 g/mol	3.5E-3 % (rel)	normal	-0.015	-240E-12 (rel)	0.0%
C	atomic mass of C	12.010700 g/mol	3.3E-3 % (rel)	normal	0.026	4.68E-9 (rel)	0.0%
O	atomic mass of O	15.999400 g/mol	940E-6 % (rel)	normal	29	1.95E-6 (rel)	0.0%
N	atomic mass of N	14.0067400 g/mol	250E-6 % (rel)	normal	-150	-2.34E-6 (rel)	0.0%
Ar	atomic mass of Ar	39.948000 g/mol	1.3E-3 % (rel)	normal	0.52	118E-9 (rel)	0.0%
CH4	mole fraction of CH4 in the final mixture	2200.920 nmol/mol	0.028 % (rel)				
C_Ar	mole fraction of Ar in the final mixture	%					
C_CO2	mole fraction of CO2 in the final mixture	umol/mol					
C_CH4	mole fraction of CH4 in the final mixture	nmol/mol					
C_O2	mole fraction of O2 in the final mixture	%					
C_N2	mole fraction of N2 in the final mixture	%					

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis.

The analysis of CH_4 in the final mixtures of the two gravimetrically prepared cylinders was conducted by using GC-FID. Analytical conditions for gas analysis of CH_4 are presented in the following.

CH_4	**GC-FID**
Column	MS 5A 8 m
Carrier flow	N_2, 70 psi
Oven temperature	65℃, isothermal
Detector temperature	255℃
H_2 flow	65 mL/min
Air flow	550 mL/min
Sample flow	100 mL/min
Sample loop	10 mL

The verification process was based primarily on consistency between mole fraction of CH_4 in the two standard cylinders **(D929248 and D985705)** and other traceable KRISS standard cylinders with comparable CH_4 mole fractions. We examined relative standard deviation of the average ratios of the response factor of CH_4 in the standard to the average response factor in the reference cylinder during the analysis cycle of A-B-A where A and B are the reference cylinder and the sample cylinder, respectively. This process implicitly reflects (i) relative standard deviation of response factors (repeatability); (ii) relative degree of change in the response factors with respect to time (drift); and (iii) relationship between the ratio of responses of sample cylinder and reference cylinder and gravimetric mole factions of CH_4 in sample cylinders for the tested mole fraction range (linearity).

Cylinder ID	Estimated mole fraction of CH_4 predicted from verification analysis $x_{CH4,verif}$	Expanded total uncertainty in the mole fraction of CH_4 $U(x_{CH4,total})$
DS929248	1796.4 nmol/mol	3.9 nmol/mol
DS985705	2201.6 nmol/mol	4.4 nmol/mol

A5. Complementary information

Please include in this section in the case of standards produced with synthetic air:

a) Purity table with uncertainties for the nominally pure CH_4 parent gas

Component	Value [µmol/mol]	Standard uncertainty [µmol/mol] (B type; Rectangular distribution)
H_2	0.2500	0.0808
O_2	1.400	0.162
CO	0.02500	0.00577
CO_2	0.1100	0.0127
N_2	13.10	1.51
C_2H_2	0.01250	0.00577
C_2H_6	0.2550	0.0866
C_2H_4	0.02500	0.00289
C_3H_8	0.1800	0.0208
C_3H_6	0.06500	0.001219
C_4H_{10}	0.6060	0.0700
C_5H_{12}	0.1100	0.0127
C_6	0.100	0.0173
H_2O	11.20	1.29
He	2.500	0.831
Ar	2.500	0.831
CH_4	**999983.5**	**2.4 (level of confidence: 95%, $k = 2$)**

b) Purity table with uncertainties for the nominally pure N_2, O_2, Ar and CO_2 parent gas

Pure N_2

Component	Value [µmol/mol]	Standard uncertainty [µmol/mol] (B type; Rectangular distribution)
H_2	0.0500	0.0144
O_2	0.1800	0.0520

Ar	0.1700	0.0491
CH_4	0.001	0.00289
CO	0.1000	0.0289
CO_2	0.01000	0.00289
C_5	0.1000	0.0289
H_2O	1.200	0.289
N_2	**999998.2**	**0.6 (level of confidence: 95%, $k = 2$)**

Pure O_2

Component	Value [µmol/mol]	Standard uncertainty [µmol/mol] (B type; Rectangular distribution)
H_2	0.0500	0.0144
N_2	2.800	0.808
CH_4	0.003	0.00866
CO	0.1000	0.0289
CO_2	0.01000	0.00289
H_2O	1.100	0.318
C_5	0.1000	0.0289
O_2	**999995.8**	**0.6 (level of confidence: 95%, $k = 2$)**

Pure Ar

Component	Value [µmol/mol]	Standard uncertainty [µmol/mol] (B type; Rectangular distribution)
H_2	0.002500	0.00577
CO	0.0500	0.0173
CH_4	0.030000	0.00577
CO_2	0.010000	0.000577
O_2	0.4100	0.0693
N_2	1.600	0.237
H_2O	1.500	0.248
Ar	**999996.4**	**0.7 (level of confidence: 95%, $k = 2$)**

Pure CO_2

Component	Value [µmol/mol]	Standard uncertainty [µmol/mol] (B type; Rectangular distribution)
H_2	0.02500	0.00577
CO	0.0500	0.0173

CH_4	0.990	0.114
CO_2	0	0.000577
Ar	0.500	0.167
O_2	2.430	0.281
N_2	4.110	0.237
H_2O	5.000	0.577
C_4H_{10}	45.10	1.30
CO_2	**999994.18**	**3 (level of confidence: 95%, $k = 2$)**

c) Brief outline of the dilution series undertaken to produce the final mixtures
All KRISS CH_4standards were prepared with **synthetic air.**

Cylinder ID	Dilution step	Mole fraction of CH_4	Gravimetric uncertainty (level of confidence:95%)
Pure CH_4	0th	99.99835 %	2.4 µmol/mol
D90 5213	1st	5.000 %	0.0018 %
ES0008527	2nd	1981.15 µmol/mol	0.85 µmol/mol
ES0008509	3rd	49.938 µmol/mol	0.026 µmol/mol
DS929248	4th (Final mixture)	1797.1 nmol/mol	1.0 nmol/mol

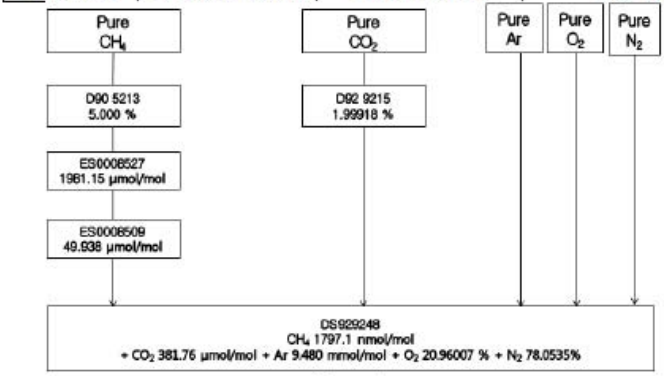


Figure 1

Cylinder ID	Dilution step	Mole fraction of CH_4	Gravimetric uncertainty (level of confidence: 95%)
Pure CH_4	0th	99.99835 %	2.4 µmol/mol
D929221	1st	4.9996 %	0.0019 %
ES0008628	2nd	1983.58µmol/mol	0.87µmol/mol
ES0008689	3rd	50.143µmol/mol	0.026 µmol/mol
DS985705	4th (Final mixture)	2200.9 nmol/mol	1.2 nmol/mol

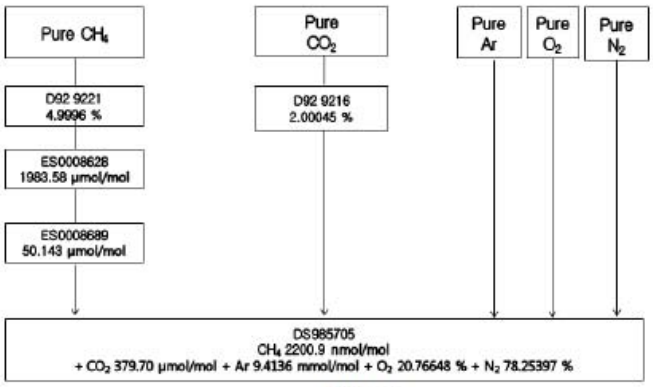


Figure 2

d) Purity table for each of the final mixtures, including gravimetric uncertainties

Cylinder ID : D929248

Component	Gravimetric value	Gravimetricuncertainty (level of confidence: 95%, $k = 2$)
CH_4	1797.1 nmol/mol	1.0 nmol/mol
CO_2	381.76 µmol/mol	0.17 µmol/mol
Ar	9.480 mmol/mol	0.011 mmol/mol
O_2	20.96007 %	0.00071 %
N_2	78.0535 %	0.0011 %

Note: The initial report as of February 1, 2013 contained the gravimetric value for Ar with a trivial numerical typo (9.880). The report also showed an evident record of Ar 9.480 mmol/mol in the lowest box (DS929248) in Figure 1 of Section c). This typo in the purity table above was thus corrected to 9.480.The submitted cylinders were prepared with the mole fractions of Ar within the required range of 8.865 mmol/mol to 9.799 mmol/mol presented in the protocol (GAWG/13-36). The value of 9.880 is far over the maximum value, supporting that this value is a just typo.

Cylinder ID : D985705

Component	Gravimetric value	Gravimetric uncertainty (level of confidence: 95%, $k = 2$)
CH_4	2200.9 nmol/mol	1.2 nmol/mol
CO_2	379.70µmol/mol	0.19µmol/mol
Ar	9.4136 mmol/mol	0.0070 mmol/mol
O_2	20.76648 %	0.00066 %
N_2	78.25379 %	0.00091 %

a) Brief outline of the verification procedure applied to the final mixtures

KRISS analyzed not just CH_4 but also the other components (CO_2, Ar, O_2, and N_2) in the final mixtures for verification purpose. The verification process for the other components was similar to that for CH_4 presented previously in A4. Description of the procedure used during the gas analysis. The analytical conditions of the four components are presented in the following.

CO_2	**GC-FID-Methanizer**
Column	Porapak Q 8/100 12 ft SUS
Carrier flow	N_2, 35 psi
Oven temperature	35 ℃, Isothermal
Detector temperature	250 ℃
Methanizer temperature	385 ℃
H2flow	65 mL/min
Air flow	650 mL/min
Sample flow	100 mL/min
Sample loop	0.5 mL

Ar, O_2, N_2	**GC-TCD**
Column	MoleSieve 5A Capillary 30.0 m x 530 μm x 50.0 μm
Carrier flow	He, 28 mL/min (50 psi)
Oven temperature	-20℃, isothermal
Detector temperature	250℃
Reference flow	40 mL/min
Sample flow	100 mL
Sample loop	1.0 mL

b) a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM

KRISS prepared gravimetrically one ambient-level CH_4in air standard as of 27 September 2008, another standard as of 24 April 2012, and two standards as of 12 September 2012. In the long term stability test, differences in gravimetric and verified mole fraction of CH_4 were less than 0.08%. The verification uncertainty of the two CH_4 standards was about 0.2%. These results suggest that KRISS primary standard gas mixtures of ambient-level CH_4 in air are stable over 4 years.

c) Additional information on cylinder and valve

Cylinder ID	Volume	Valve type (Outlet connection)	Pressure left before shipment to the BIPM
D929248	10 L	JIS B 8246 V2 Type (W22.0, 14 TPI, RH-EXT)	7.0 MPa
D985705	10 L	JIS B 8246 V2 Type (W22.0, 14 TPI, RH-EXT)	7.0 MPa

National Metrology Institute of Japan (NMIJ)

Report for the CCQM-K82

(Methane in air at ambient level, preparation)

National Metrology Institute of Japan (NMIJ), AIST

Takuro WATANABE, Takuya SHIMOSAKA, and Kenji KATO

Report for the CCQM-K82 (methane in air at ambient level, preparation) by NMIJ

A1. General information

Institute	National Metrology Institute of Japan (NMIJ), AIST		
Address	AIST Tsukuba Central 3, 1-1-1, Umezono, Tsukuba, Ibaraki 305-8563, JAPAN		
Contact person	Dr. Takuro WATANABE		
Telephone	+81-29-861-6851	Fax	+81-29-861-6854
E-mail	watanabe-takuro@aist.go.jp		
Serial number of cylinder	CPB-28035 (1797.3 nmol/mol) CPB-28219 (2198.3 nmol/mol)		
Cylinder pressure (at 35 °C)	Approximately 10 MPa (CPB-28035) Approximately 9 MPa (CPB-28219)		

A2. Results

CPB-28035

Methane, mole fraction x_{CH4} / μmol/mol	Expanded uncertainty $U(x_{CH4})$ / μmol/mol	Coverage factor k	Balance
1.7973	0.0013	2	Synthetic air

CPB-28219

Methane, mole fraction x_{CH4} / μmol/mol	Expanded uncertainty $U(x_{CH4})$ / μmol/mol	Coverage factor k	Balance
2.1983	0.0013	2	Synthetic air

A3. Uncertainty budget

Atomic weights and their standard uncertainties were from the atomic weights of the elements 2007.

Two samples of the "methane in air at ambient level" were prepared using 4-steps gravimetric blending as described below in the Section A5. c).

Uncertainty budgets of pure parent gases such as CH_4, N_2, O_2, Ar, and CO_2 were summarized in the Section A5. a) and b) as referred to hereinafter. And, uncertainty budgets of the final mixtures were described below in the Section A5. d).

Average molecular mass ($\overline{M_{gas}}$) of pure parent gases and prepared pre-mixtures were estimated by using the following equation (Equation 1).

$$\overline{M_{gas}} = \sum x_i \cdot M_i \quad \text{(Equation 1)}$$

Where x_i is mole fraction of component i in the pure parent gases or prepared pre-mixtures, and M_i is molecular mass of the component i.

Concentration of the prepared gas mixture was estimated by using the following equation (Equation 2).

$$C_{y,prep} = \frac{\sum_j n'_{y,j}}{\sum_j n_j} = \frac{\sum_j \frac{m_j}{\overline{M_j}} \cdot C_{y,j}}{\sum_j \frac{m_j}{\overline{M_j}}} \quad \text{(Equation 2)}$$

Where $C_{y,prep}$ is mole fraction of compound y in the prepared gas mixture, j is meant filled gas which is pure parent gas or prepared pre-mixture, n_j is filled amount of gas j, $n'_{y,j}$ is filled amount of compound y which is contained in the filled gas j, m_j is mass of filled gas j, $\overline{M_j}$ is average molecular mass of filled gas j, and $C_{y,j}$ is mole fraction of compound y in the filled gas j.

Uncertainty budgets for concentration of methane in pre-mixtures were summarized in six tables (from Table 1 to Table 6). Concentrations and their uncertainties of the other components, nitrogen, oxygen, argon, and carbon dioxide, were estimated using equations 1 and 2. The results were summarized below in Figure 1.

Table 1 Uncertainty table for concentration of methane in the cylinder CPB-29218

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty
Mass of filled methane (mg)	13492	Normal	3.4592
Mass of filled nitrogen (mg)	871291	Normal	3.4630
Average molecular mass of the parent methane (g/mol)	16.0425	Normal	0.0005
Average molecular mass of the parent nitrogen (g/mol)	28.0134	Normal	0.0002
Mole fraction of methane in the parent methane (μmol/mol)	999999.1	Normal	0.2
Mole fraction of methane in the parent nitrogen (μmol/mol)	1.15×10^{-3}	Rectangular	0.67×10^{-3}
Concentration of methane in gas mixture (μmol/mol)	26329		6.6230

Table 2 Uncertainty table for concentration of methane in the cylinder CPB-29219

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty
Mass of filled methane (mg)	19834	Normal	3.4546
Mass of filled nitrogen (mg)	994848	Normal	3.4594
Average molecular mass of the parent methane (g/mol)	16.0425	Normal	0.0005
Average molecular mass of the parent nitrogen (g/mol)	28.0134	Normal	0.0002
Mole fraction of methane in the parent methane (μmol/mol)	999999.1	Normal	0.2
Mole fraction of methane in the parent nitrogen (μmol/mol)	1.15×10^{-3}	Rectangular	0.67×10^{-3}
Concentration of methane in gas mixture (μmol/mol)	33643		5.7562

Table 3 Uncertainty table for concentration of methane in the cylinder CPB-28221

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty
Mass of filled parent CPB-29218 (mg)	21443	Normal	3.6107
Mass of filled carbon dioxide (mg)	193064	Normal	3.6095
Mass of filled nitrogen (mg)	845688	Normal	3.4665
Average molecular mass of the parent CPB-29218 (g/mol)	27.6982	Normal	0.0003
Average molecular mass of the parent carbon dioxide (g/mol)	44.0094	Normal	0.0006
Average molecular mass of the parent nitrogen (g/mol)	28.0134	Normal	0.0002
Mole fraction of methane in the parent CPB-29218 (µmol/mol)	26329	Normal	6.6230
Mole fraction of methane in the parent carbon dioxide (µmol/mol)	8.7×10^{-3}	Normal	1.2×10^{-3}
Mole fraction of methane in the parent nitrogen (µmol/mol)	1.15×10^{-3}	Rectangular	0.67×10^{-3}
Concentration of methane in gas mixture (µmol/mol)	576.62		0.17163

Table 4 Uncertainty table for concentration of methane in the cylinder CPB-28222

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty
Mass of filled parent CPB-29219 (mg)	19644	Normal	3.4628
Mass of filled carbon dioxide (mg)	183767	Normal	3.4553
Mass of filled nitrogen (mg)	858661	Normal	3.4585
Average molecular mass of the parent CPB-29219 (g/mol)	27.6107	Normal	0.0003
Average molecular mass of the parent carbon dioxide (g/mol)	44.0094	Normal	0.0006
Average molecular mass of the parent nitrogen (g/mol)	28.0134	Normal	0.0002
Mole fraction of methane in the parent CPB-29219 (µmol/mol)	33643	Normal	5.7562
Mole fraction of methane in the parent carbon dioxide (µmol/mol)	8.7×10^{-3}	Normal	1.2×10^{-3}
Mole fraction of methane in the parent nitrogen (µmol/mol)	1.15×10^{-3}	Rectangular	0.67×10^{-3}
Concentration of methane in gas mixture (µmol/mol)	673.51		0.16228

Table 5 Uncertainty table for concentration of methane in the cylinder CPB-28223

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty
Mass of filled parent CPB-28221 (mg)	33390	Normal	3.4608
Mass of filled argon (mg)	132190	Normal	3.4553
Mass of filled nitrogen (mg)	798319	Normal	3.4629
Average molecular mass of the parent CPB-28221 (g/mol)	29.9916	Normal	0.0003
Average molecular mass of the parent argon (g/mol)	39.9480	Normal	0.0006
Average molecular mass of the parent nitrogen (g/mol)	28.0134	Normal	0.0002
Mole fraction of methane in the parent CPB-28221 (µmol/mol)	576.62	Normal	0.17163
Mole fraction of methane in the parent argon (µmol/mol)	2.17×10^{-3}	Rectangular	1.25×10^{-3}
Mole fraction of methane in the parent nitrogen (µmol/mol)	1.15×10^{-3}	Rectangular	0.67×10^{-3}
Concentration of methane in gas mixture (µmol/mol)	19.5020		6.152×10^{-3}

Table 6 Uncertainty table for concentration of methane in the cylinder CPB-28224

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty
Mass of filled parent CPB-28222 (mg)	35668	Normal	3.4601
Mass of filled argon (mg)	137948	Normal	3.4552
Mass of filled nitrogen (mg)	799228	Normal	3.4622
Average molecular mass of the parent CPB-28222 (g/mol)	29.8848	Normal	0.0003
Average molecular mass of the parent argon (g/mol)	39.9480	Normal	0.0006
Average molecular mass of the parent nitrogen (g/mol)	28.0134	Normal	0.0002
Mole fraction of methane in the parent CPB-28222 (µmol/mol)	673.51	Normal	0.16228
Mole fraction of methane in the parent argon (µmol/mol)	2.17×10^{-3}	Rectangular	1.25×10^{-3}
Mole fraction of methane in the parent nitrogen (µmol/mol)	1.15×10^{-3}	Rectangular	0.67×10^{-3}
Concentration of methane in gas mixture (µmol/mol)	24.2301		6.290×10^{-3}

A4. Description of the procedure used during the gas analysis

a) Operating conditions for estimation of methane concentrations in the parent nitrogen, oxygen, and argon gases

Operating conditions for estimation of methane concentrations in the parent nitrogen, oxygen and argon were summarized in tables 7, 8, and 9.

Table 7 Operating condition for estimation of methane concentration in the parent N_2

Analytical instrument	GC-FID, Shimadzu GC-2010AF (Shimadzu Corporation, Kyoto, Japan)
Sample injection method	Direct injection using gas sampling valve
Sample volume	2 mL
Column	G-column G-950, 40 m × 1.2 mm i.d., 25 μm thickness (Chemical Evaluation and Research Institute, Saitama, Japan)
Column flow	N_2, 7.3 mL/min
Oven temperature	30 °C, isothermal
FID fuel gas	H_2, 50 mL/min Air, 400 mL/min
FID makeup gas	N_2, 0 mL/min (not used)
FID temperature	250 °C

Table 8 Operating condition for estimation of methane concentration in the parent O_2

Analytical instrument	FT-IR equipped White Cell, NEXUS 670 (Thermo Fischer Scientific Inc., MA, USA)
Detector	Mercury-Cadmium-Telluride, liquid N_2 cooled
Sample injection method	Flowing, 0.1 L/min
Sample pressure	400 kPa abs.
Path length	10.6 m
Resolution	1 cm^{-1}
Apodization function	Blackman Harris
Number of scan	16384

Table 9 Operating condition for estimation of methane concentration in the parent Ar

Analytical instrument	GC/MS, Shimadzu GCMS-QP2010 (Shimadzu Corporation, Kyoto, Japan)
Sample injection method	Direct injection using gas sampling valve
Sample volume	1 mL
Column	ShinCarbon ST 50/80 mesh, micropacked column, 2 m × 1 mm i.d. (Shinwa Chemical Industries Ltd., Kyoto, Japan)
Column flow	He, 8 mL/min
Oven temperature	90 °C, isothermal
Ion source temperature	200 °C
MS ionization method	EI, 70 eV
MS monitoring mode	SIM, m/z = 15 and 16

b) Operating conditions on verification procedures of pre-mixtures

In this verification process, 2nd pre-mixtures and 3rd pre-mixtures were validated. Operating conditions of an analytical instrument were summarized in Tables 10 and 11.

Tables 10 Operating condition on verification process of the 2nd pre-mixtures

Analytical instrument	GC-FID, Shimadzu GC-2010AF (Shimadzu Corporation, Kyoto, Japan)
Injected samples	CPB-28221 (CH_4+CO_2/N_2, CH_4: 576.62 μmol/mol) CPB-28222 (CH_4+CO_2/N_2, CH_4: 673.51 μmol/mol) CPB-29160 (CH_4 /N_2, PRM, CH_4: 766.77 μmol/mol)
Sample injection method	Direct injection using gas sampling valve
Sample volume	0.1 mL
Column	Chrompack Al_2O_3/KCl PLOT, 50 m × 0.53 mm i.d., 10 μm thickness (Agilent Technologies Inc., CA, USA)
Column flow	N_2, 5.6 mL/min
Oven temperature	50 °C, isothermal
FID fuel gas	H_2, 47 mL/min Air, 400 mL/min
FID makeup gas	N_2, 25 mL/min
FID temperature	200 °C

Tables 11 Operating condition on verification process of the 3rd pre-mixtures

Analytical instrument	GC-FID, Shimadzu GC-2010AF (Shimadzu Corporation, Kyoto, Japan)
Injected samples	CPB-28223 (CH_4+CO_2+Ar/N_2, CH_4: 19.502 μmol/mol) CPB-28224 (CH_4+CO_2+Ar/N_2, CH_4: 24.230 μmol/mol) CPB-29166 (CH_4 /N_2, PRM, CH_4: 25.941 μmol/mol)
Sample injection method	Direct injection using gas sampling valve
Sample volume	0.5 mL
Column	Chrompack Al_2O_3/KCl PLOT, 50 m × 0.53 mm i.d., 10 μm thickness (Agilent Technologies Inc., CA, USA)
Column flow	N_2, 5.6 mL/min
Oven temperature	50 °C, isothermal
FID fuel gas	H_2, 47 mL/min Air, 400 mL/min
FID makeup gas	N_2, 25 mL/min
FID temperature	200 °C

Uncertainties of reproducibility of the sample preparations were estimated by the ANOVA. In this estimation, obtained measurement values were normalized with each gravimetric concentration. The between-cylinder variances were negative values in these verification processes. Therefore, the uncertainty of reproducibility of the sample preparations in 2nd pre-mixtures and 3rd pre-mixtures was estimated as zero, respectively.

c) Verification procedure of the final mixtures

Operating condition of an analytical instrument in this verification process was summarized in Tables 12.

Table 12 Operating condition on verification process of the final mixtures

Analytical instrument	GC-FID, Shimadzu GC-2010AF (Shimadzu Corporation, Kyoto, Japan)
Sample injection method	Direct injection using gas sampling valve
Sample volume	2 mL
Column	Carboxen-1006 PLOT, 30 m × 0.53 mm i.d. (Sigma-Aldrich Co. LLC., MO, USA)
Column flow	N_2, 6 mL/min
Oven temperature	40 °C, isothermal
FID fuel gas	H_2, 50 mL/min Air, 400 mL/min
FID makeup gas	N_2, 20 mL/min
FID temperature	250 °C

A5. Complementary information

a) A purity table with uncertainties for the nominally pure CH_4 parent gas

NMIJ CRM 4051-b "Methane" was used as the parent gas. Information of impurities in the parent gas was summarized in Table 13. It was from certificate.

Table 13 Mole fraction of methane and impurities in the parent gas

Component i	Mole fraction x_i / μmol/mol	Standard uncertainty $u(x_i)$ / μmol/mol	Distribution
Methane	999999.14	0.21	-
Nitrogen	0.14	0.08	Rectangular
Oxygen	0.12	0.07	Rectangular
Argon	0.03	0.02	Rectangular
Carbon monoxide	0.13	0.07	Rectangular
Carbon dioxide	0.07	0.04	Rectangular
Hydrogen	0.07	0.04	Rectangular
Ethane	0.02	0.01	Rectangular
Water	0.27	0.16	Rectangular
Other impurities	negligible	-	-

b) A purity table with uncertainties for the nominally pure N_2, O_2, Ar and CO_2 parent gas

1. Nitrogen

Nitrogen was purchased from Japan Fine Products (JFP; Kawasaki, Kanagawa, Japan) and Sumitomo Seika Chemicals Company Limited (SS; Osaka, Japan). In the preparation processes, three cylinders by JFP and two cylinders by SS were used. Information of impurities in the parent gas was summarized in Tables 14 and 15. Checking of methane concentration in all used cylinders was carried out, and obtained highest values were described in the tables.

Table 14 Mole fraction of nitrogen by JFP and impurities in the parent gas

Component i	Mole fraction x_i /μmol/mol	Standard uncertainty $u(x_i)$ /μmol/mol	Distribution
Nitrogen	999999.57	0.16	-
Methane	0.00115	0.00067	Rectangular
Oxygen	0.05	0.03	Rectangular
Carbon monoxide	0.05	0.03	Rectangular
Carbon dioxide	0.05	0.03	Rectangular
Nitrogen monoxide	0.005	0.003	Rectangular
Sulfur dioxide	0.005	0.003	Rectangular
Water	0.27	0.16	Rectangular
Other impurities	negligible	-	-

Table 15 Mole fraction of nitrogen by SS and impurities in the parent gas

Component i	Mole fraction x_i /μmol/mol	Standard uncertainty $u(x_i)$ /μmol/mol	Distribution
Nitrogen	999999.50	0.17	-
Methane	0.00081	0.00047	Rectangular
Oxygen	0.10	0.06	Rectangular
Carbon monoxide	0.10	0.06	Rectangular
Carbon dioxide	0.05	0.03	Rectangular
Water	0.25	0.14	Rectangular
Other impurities	negligible	-	-

2. Oxygen

Oxygen was purchased from Japan Fine Products (Kawasaki, Kanagawa, Japan). In

the preparation processes, only one cylinder was used. Information of impurities in the parent gas was summarized in Table 16.

Table 16 Mole fraction of oxygen and impurities in the parent gas

Component *i*	Mole fraction *xi* /μmol/mol	Standard uncertainty *u*(*xi*) /μmol/mol	Distribution
Oxygen	999999.58	0.17	-
Methane	0.00104	0.00081	Rectangular
Nitrogen	0.10	0.06	Rectangular
Argon	0.03	0.01	Rectangular
Carbon monoxide	0.10	0.06	Rectangular
Carbon dioxide	0.10	0.06	Rectangular
Water	0.27	0.16	Rectangular
Other impurities	negligible	-	-

3. Argon

Argon was purchased from Japan Fine Products (Kawasaki, Kanagawa, Japan). In the preparation processes, only one cylinder was used. Information of impurities in the parent gas was summarized in Table 17.

Table 17 Mole fraction of argon and impurities in the parent gas

Component *i*	Mole fraction *xi* /μmol/mol	Standard uncertainty *u*(*xi*) /μmol/mol	Distribution
Argon	999999.38	0.19	-
Methane	0.00217	0.00125	Rectangular
Nitrogen	0.15	0.09	Rectangular
Oxygen	0.05	0.03	Rectangular
Carbon monoxide	0.05	0.03	Rectangular
Carbon dioxide	0.05	0.03	Rectangular
Hydrogen	0.05	0.03	Rectangular
Water	0.27	0.16	Rectangular
Other impurities	negligible	-	-

4. Carbon dioxide

NMIJ CRM 3407-a "Carbon dioxide" was used as the parent gas. Information of impurities in the parent gas was summarized in Table 18. It was from certificate.

Table 18 Mole fraction of carbon dioxide and impurities in the parent gas

Component i	Mole fraction x_i /μmol/mol	Standard uncertainty $u(x_i)$ /μmol/mol	Distribution
Carbon dioxide	999995.09	1.57	-
Methane	0.0087	0.0012	Normal
Nitrogen	1.55	0.90	Rectangular
Oxygen	0.94	0.55	Rectangular
Hydrogen	1.97	1.14	Rectangular
Water	0.438	0.253	Rectangular
Other impurities	negligible	-	-

c) A brief outline of the dilution series undertaken to produce the final mixtures

The outline of the dilution processes was summarized in Figure 1.

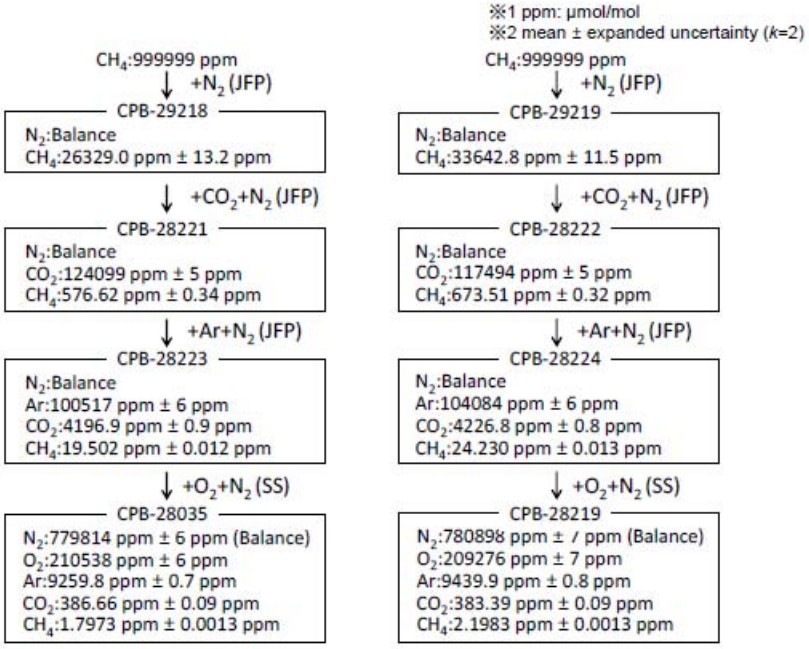


Figure 1 Outline of the dilution series undertaken to produce the final mixtures

d) A purity table for each of the final mixtures, including gravimetric uncertainties

Uncertainty budgets for concentration of methane in final mixtures were summarized in Tables 19 and 20. Concentrations and their uncertainties of the other components, nitrogen, oxygen, argon, and carbon dioxide, were estimated using equations 1 and 2. The results were summarized in Figure 1.

Table 19 Uncertainty table for concentration of methane in the cylinder CPB-28035

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty
Mass of filled parent CPB-28223 (mg)	108318	Normal	3.4616
Mass of filled oxygen (mg)	270545	Normal	3.4611
Mass of filled nitrogen (mg)	784487	Normal	3.4616
Average molecular mass of the parent CPB-28223 (g/mol)	29.2799	Normal	0.0003
Average molecular mass of the parent oxygen (g/mol)	31.9988	Normal	0.0003
Average molecular mass of the parent nitrogen (g/mol)	28.0134	Normal	0.0002
Mole fraction of methane in the parent CPB-28223 (μmol/mol)	19.5020	Normal	6.152×10^{-3}
Mole fraction of methane in the parent oxygen (μmol/mol)	1.04×10^{-3}	Rectangular	0.81×10^{-3}
Mole fraction of methane in the parent nitrogen (μmol/mol)	1.15×10^{-3}	Rectangular	0.67×10^{-3}
Concentration of methane in gas mixture (μmol/mol)	1.7973		6.59×10^{-4}

Table 20 Uncertainty table for concentration of methane in the cylinder CPB-28219

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty
Mass of filled parent CPB-28224 (mg)	99377	Normal	3.4607
Mass of filled oxygen (mg)	250235	Normal	3.4575
Mass of filled nitrogen (mg)	732785	Normal	3.4736
Average molecular mass of the parent CPB-28224 (g/mol)	29.3229	Normal	0.0003
Average molecular mass of the parent oxygen (g/mol)	31.9988	Normal	0.0003
Average molecular mass of the parent nitrogen (g/mol)	28.0134	Normal	0.0002
Mole fraction of methane in the parent CPB-28224 (μmol/mol)	24.2301	Normal	6.290×10^{-3}
Mole fraction of methane in the parent oxygen (μmol/mol)	1.04×10^{-3}	Rectangular	0.81×10^{-3}
Mole fraction of methane in the parent nitrogen (μmol/mol)	1.15×10^{-3}	Rectangular	0.67×10^{-3}
Concentration of methane in gas mixture (μmol/mol)	2.1983		6.64×10^{-4}

e) A brief outline of the verification procedure applied to the final mixtures

Four gas mixtures were prepared in the year of 2012. Two of the four mixtures were made in early June, one was in late of August, and the another one was in early September. Prepared mixtures were included two gas mixtures which were shipped to the BIPM. An uncertainty of reproducibility of the sample preparations was estimated by the ANOVA. In this estimation, verification of the final mixtures was also carried out. Table 21 shows the measurement data of the prepared gas mixtures.

Table 21 Measurement data of the prepared sample gas mixtures (units: μmol/mol)

Cylinder ID	Gravimetric values		Measurement result				
	Mean	Standard uncertainty	#1	#2	#3	#4	#5
CPB-28035	1.7973	6.59×10^{-4}	1.7962	1.8001	1.7973	1.7952	1.7968
CPB-28218	1.8138	6.63×10^{-4}	1.8135	1.8137	1.8160	1.8117	1.8148
CPB-28219	2.1983	6.64×10^{-4}	2.1958	2.1994	2.1975	2.1966	2.2009
CPB-28042	2.2401	6.71×10^{-4}	2.2375	2.2389	2.2405	2.2425	2.2421

The obtained values were normalized with each gravimetric concentration (Table 22).

Table 22 Standardized measurement data of the prepared gas mixtures

Cylinder ID	Measurement result				
	#1	#2	#3	#4	#5
CPB-28035	0.99940	1.00155	1.00002	0.99885	0.99973
CPB-28218	0.99985	0.99995	1.00123	0.99887	1.00056
CPB-28219	0.99887	1.00051	0.99963	0.99924	1.00120
CPB-28042	0.99885	0.99947	1.00020	1.00108	1.00089

The ANOVA shown in Table 23 was computed using our spreadsheet software.

Table 23 ANOVA table for the prepared sample gas mixtures

Source of Variation	S	Degree of freedom	M
Between cylinder	1.89558×10^{-7}	3	6.31860×10^{-8}
Within cylinder	1.47314×10^{-6}	16	8.98215×10^{-7}
Total	1.45610×10^{-6}	19	

The between-cylinder variance u_{bc}^2 is estimated using

$$u_{bc}^{\ 2} = \frac{6.31860\times10^{-8} - 8.98215\times10^{-7}}{5} = -1.67006\times10^{-7} \rightarrow 0$$

Therefore, the between-cylinder standard deviation u_{bc} was zero, and the uncertainty of reproducibility of the sample preparations was estimated as zero.

f) A brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM

Two gas mixtures were prepared at December 2010. Preparation values of

concentrations of methane in these mixtures were 1.9028 μmol/mol ± 0.0028 μmol/mol (k=2) and 2.0373 μmol/mol ± 0.0029 μmol/mol (k=2). The Concentrations in these mixtures were estimated using the calibration curve which was prepared in the verification procedure. This estimation was carried out in September 2012 and it was equivalent to a stability test for 21 months. The period, 21 months, was enough in order to perform this key comparison. Obtained results were summarized in Table 24.

Table 24 Results of a stability test for 21 months

	Prepared values*		Obtained values at the test*		E_n
	Methane	Expanded uncertainty**	Methane	Expanded uncertainty**	
CPB-29198	1.9028	0.0029	1.9040	0.0015	0.29 < 1
CPB-29197	2.0373	0.0029	2.0378	0.0025	0.08 < 1

*: Units of values were μmol/mol.

**: Coverage factor k was 2.

Statistical inspections between the prepared values and the obtained values were carried out using E_n number which was described in the ISO/IEC 17043. The E_n numbers for two cylinders were less than 1 and the inspection results were shown satisfactory performance in 95% confidence level. Therefore, the uncertainty of the stability of the final mixtures was estimated as zero.

g) Cylinder pressure

Cylinder pressure of the final mixtures, CPB-28035 and CPB 28219 is approximately 10 MPa and 9 MPa, respectively. They are the values at 35 degrees Celsius.

Miscellaneous

Two adaptors for JIS-22mm-right to DIN-477 No. 1 and two packing rings for JIS-22mm-right have also been shipped with the cylinders. To attach the adaptor to the valve outlet connection of the cylinder, please lay the cylinder on its side. After that, put a packing ring on the cylinder valve outlet connection as shown in Figure 2 to position the packing ring properly. And then, screw the adaptor onto the connection in order to prevent a leak of sample gas.

Figure 2

National Institute of Metrology (NIM), China

Transmission of International Comparison Results

The title of international comparison: Methane in Air

Serial number for international comparison: CCQM-K82

Comparison experiment period: Jan 2013~Apr 2013

Experiment reporter: HAN Qiao

Phone number of experiment reporter: +86-10-84252300
E-mail: hanqiao@nim.ac.cn
NIM address: No.18, Bei-San-Huan Dong Str., Beijing 100013, China
Phone/Fax number of Department of Metrology Services: +86-10-64213104
Phone/Fax number of Department of R&D and Planning (International Cooperation): +86-10-64218565
E-mail: yw@nim.ac.cn

Transmission date: Apr 24, 2013

Key Comparison CCQM-K82
Methane in Air at Ambient level (1800-2200) nmol/mol

1. General information

Institute	National Institute of Metrology (NIM), China		
Address	No.18, Bei-San-Huan Dong Str., Beijing 100013, China		
Contact person	Dr. Qiao Han, Dr. Hai Wu		
Telephone	+86-10-6452 5330	**Fax**	+86-10-8425 2306
Email	wuhai@nim.ac.cn		
SN of cylinders	CAL017763, CAL017790		
Cylinder pressure	8Mpa		

2. Results

Cylinder No.	**Methane mole fraction x_{CH4} /nmol/mol**	**Expanded uncertainty $U(x_{CH4})$ /nmol/mol**	**Coverage factor**
CAL017763	1825.2	1.7	2
CAL017790	2193.8	2.0	2

3. Purity data of Parent gases

O2, pure, No. 013368#	**fraction**	**Std. u**	**Technique**
Ar(Argon)	5.000E-06	2.887E-06	Product Spec*
CH4(Methane)	7.710E-08	8.190E-10	CRDS
CO(Carbon_monoxide)	5.000E-09	2.887E-09	GC-FID-Cat.**
CO2(Carbon_dioxide)	5.000E-09	2.887E-09	GC-FID-Cat.**
H2(Hydrogen)	1.000E-08	5.774E-09	GC-PDHID
H2O(Water)	5.000E-07	2.887E-07	CRDS
O2(Oxygen)	0.9999894	3.266E-06	/
N2(Nitrogen)	5.000E-06	1.500E-06	GC-PDHID

CO2, pure, No. B5209170#	**fraction**	**Std. u**	**Technique**
Ar(Argon)	2.500E-05	5.000E-06	GC-PDHID
CH4(Methane)	2.415E-06	1.810E-07	GC-FID
CO(Carbon_monoxide)	2.500E-07	5.000E-08	GC-FID-Cat.
CO2(Carbon_dioxide)	0.9999243	8.725E-06	/
H2(Hydrogen)	1.000E-08	1.000E-08	GC-PDHID
H2O(Water)	3.000E-06	1.000E-06	DP meter
O2(Oxygen)	2.500E-05	5.000E-06	GC-PDHID
N2(Nitrogen)	2.000E-05	5.000E-06	GC-PDHID

Ar, pure, BIP	**fraction**	**Std. u**	**Technique**
Ar(Argon)	0.9999896	1.005E-06	GC-PDHID
CH4(Methane)	4.000E-10	2.000E-10	CRDS
CO(Carbon_monoxide)	5.000E-09	2.887E-09	GC-FID-Cat.**
CO2(Carbon_dioxide)	5.000E-09	2.887E-09	GC-FID-Cat.**

H2(Hydrogen)	1.000E-08	2.887E-09	GC-PDHID
H2O(Water)	1.000E-07	5.774E-08	CRDS
O2(Oxygen)	2.600E-07	7.800E-08	O2 anylzer
N2(Nitrogen)	1.000E-05	1.000E-06	/

N2, pure, BIP	**fraction**	**Std. u**	**Technique**
Ar(Argon)	8.600E-05	8.600E-06	/
CH4(Methane)	4.000E-10	2.000E-10	CRDS
CO(Carbon_monoxide)	5.000E-09	2.887E-09	GC-FID-Cat.**
CO2(Carbon_dioxide)	5.000E-09	2.887E-09	GC-FID-Cat.**
H2(Hydrogen)	1.000E-08	2.887E-09	GC-PDHID
H2O(Water)	1.000E-07	5.774E-08	CRDS
O2(Oxygen)	2.600E-07	7.800E-08	Product Spec.*
N2(Nitrogen)	0.9999136	8.601E-06	GC-PDHID

CH4, pure, J01344#	**fraction**	**Std. u**	**Technique**
Ar(Argon)	3.000E-08	2.000E-08	GC-PDHID
CH4(Methane)	0.9999992	1.847E-07	/
CO(Carbon_monoxide)	3.000E-08	1.000E-08	GC-PDHID
CO2(Carbon_dioxide)	9.000E-08	5.000E-08	GC-PDHID
H2(Hydrogen)	6.000E-08	3.000E-08	GC-PDHID
H2O(Water)	2.700E-07	1.600E-07	DP meter
O2(Oxygen)	1.100E-07	6.000E-08	GC-PDHID
N2(Nitrogen)	1.700E-07	1.000E-08	GC-PDHID

* Product Spec., data was from the product specification provided by the manufacturer.
** GC-FID-Cat., GC-FID with methanator catalyst. CO and CO2 were not detected, and thereby half of Detection Limit was taken as their concentration.

4. Gravimetric Preparation of Gas Mixtures

The standard gas mixtures of methane in synthetic air were prepared by using gravimetric method according to ISO6142:2001, and the parent gases were nitrogen, oxygen, argon, carbon dioxide, and methane of high purity. The flow chart below showed dilution from pure gases to the final gas mixtures of CH_4/air.

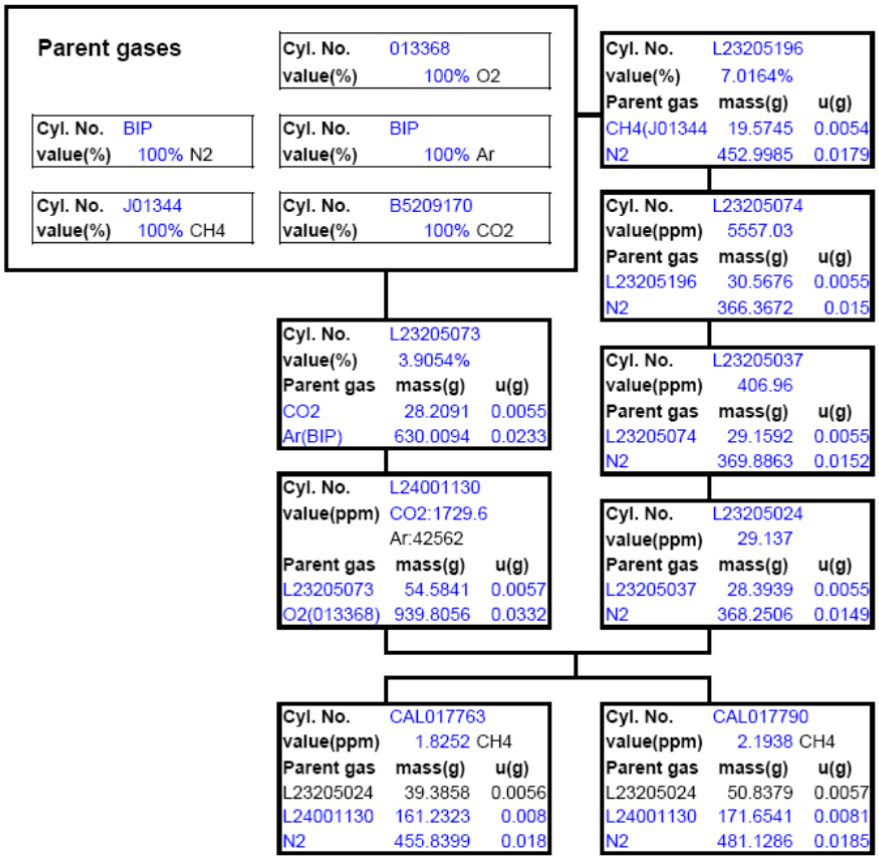


Fig 1. Dilution scheme from pure gases to CH4/syn_air

Mass comparator with capacity of 10kg and resolution of 1mg was provided by Mettler Toledo. Temperature and relative humidity in balance room were controlled at 20°C±1°C and 50%RH±10%RH, respectively. Tare cylinder and substitution method were used during weighing of cylinder in order to cancel buoyancy effect.
Fig.1 showed that standard uncertainty to the mass of added parent gas into the target cylinder was estimated as 0.004g~0.006mg when the added gas was around 30g~40g. By 5-step dilutions, around 2ppm methane in synthetic air could be achieved from the pure gases.

Cyl. No.	**CAL017763**			
Component	**Purity**	**std u_{grav}**	**Exp. U_{grav}**	**Exp.U_{rel}**
Ar(Argon)	9.3911E-03	6.3995E-06	1.2799E-05	0.14%
CH4(Methane)	1.8252E-06	7.9977E-10	1.5995E-09	0.088%
CO(Carbon_monoxide)	6.1439E-09	2.4082E-09	4.8164E-09	78%
CO2(Carbon_dioxide)	3.7891E-04	8.3694E-08	1.6739E-07	0.044%
H2(Hydrogen)	1.0000E-08	2.4081E-09	4.8162E-09	48%
H2O(Water)	1.8518E-07	7.3573E-08	1.4715E-07	79%
O2(Oxygen)	2.1019E-01	1.0780E-05	2.1559E-05	0.010%
N2(Nitrogen)	7.8003E-01	1.2235E-05	2.4470E-05	0.003%

Cyl. No.	CAL017790			
Component	**Purity**	**std u_{grav}**	**Exp. U_{grav}**	**Exp.U_{rel}**
Ar(Argon)	9.3611E-03	6.3108E-06	1.2622E-05	0.14%
CH4(Methane)	2.1938E-06	9.3154E-10	1.8631E-09	0.085%
CO(Carbon_monoxide)	6.1360E-09	2.3788E-09	4.7576E-09	78%
CO2(Carbon_dioxide)	377.68E-09	8.3212E-08	1.6642E-07	0.044%
H2(Hydrogen)	1.0000E-08	2.3787E-09	4.7575E-09	48%
H2O(Water)	1.8457E-07	7.2888E-08	1.4578E-07	79%
O2(Oxygen)	0.20869	1.0260E-05	2.0519E-05	0.010%
N2(Nitrogen)	0.78157	1.1717E-05	2.3433E-05	0.003%

5. Verification

Five newly prepared cylinders together with one old cylinder including methane in synthetic air of 1800ppb~2200ppb were prepared according to above dilution chart, and their internal consistency was also verified by using CRDS (Picarro G2301). The pressure of each sample cylinders was reduced by a regulator, and then the sample gas was introduced into CRDS by using a pump, which was set in downstream of CRDS. Sample gas flow rate was around 400mL/min. Measurement of each cylinder took ~5min, and data during last 30sec were collected and averaged.
Verification was carried out on different days, and the results showed a standard uncertainty (u_{ver}) of 0.3ppb.

6. Stability

Instability of newly prepared cylinders was checked against the old PRM cylinder by using CRDS, and results showed no instability found. Uncertainty due to instability (u_{stab}) was taken as 0.

7. Combined uncertainty

$u_c = \sqrt{u_{grav}^2 + u_{ver}^2}$, in which u_{grav} including the contribution from purity of parent gases.

National Institute of Standards and Technology (NIST)

Report Form CCQM-K82 Methane in real air

Laboratory name: NIST , 100 Bureau Drive, Gaithersburg, MD 20899-8393 USA.

Contacts: Jerry Rhoderick, email: George.rhoderick@nist.gov; phone: 301-975-3937

Franklin, Guenther, email: frank.guenther@nist.gov; 301-975-3939

Cylinder number: FB03569 (1100 psi) and FB03587 (1000 psi)

A2. Results

Methane mole fraction x_{CH4} / µmol/mol	Expanded uncertainty $U(x_{CH4})$ / µmol/mol	Coverage factor (k)
FB03569 = 1.79676	0.00170	2
FB03587 = 2.19596	0.00168	2

A3. Uncertainty Budget

FB03569 **Cylinder # FB03569**

	Value	Standard Uncertainty	Sensitivity Coefficient	Contribution to Uncertainty
Major Component MW	**28.01340**	**0.00028**	**0.0048**	**0.00000**
Minor Component MW	**16.04246**	**0.00081**	**0.0692**	**0.00006**
Mass Parent Gas	**13.09109**	**0.00240**	**0.0012**	**0.00000**
Mass Balance Gas	**539.57759**	**0.00219**	**0.0000**	**0.00000**
Minor Component Wt Fraction	**0.000041987**	**0.000000014**	**257746.07**	**0.00349**
Mass minor component - Parent	**0.00054965**	**0.00000020**	**17159.2786**	**0.00350**
Mass minor component - Bal	**0.00000032**	**0.00000015**	**108.6378**	**0.00002**
Total mass minor component	**0.00054997**	**0.00000025**	**14063.2724**	**0.00356**
Moles of minor component	**0.00003428**	**0.00000002**	**237424.30**	**0.00377**
Balance gas wt fraction (purity)	**0.755278688**	**0.00003290**	**2.7322**	**0.00009**
Mass balance gas - parent	**9.88965160**	**0.00259018**	**0.0068**	**0.00002**
Mass balance gas - balance	**407.53145635**	**0.01783067**	**0.0050**	**0.00009**
Total mass balance gas	**417.42110795**	**0.01801782**	**0.0060**	**0.00011**
Moles of balance gas	**14.90076563**	**0.00066055**	**0.1656**	**0.00011**
Moles impurities from parent	**0.09891309504**	**0.00003285790**	**0.0962**	**0.00000**
Moles impurities from balance	**4.0804534**	**0.0016842**	**0.0244**	**0.00004**

Total Moles of gas	**19.0801664**	**0.0018094**	**0.0855**	**0.00015**
Conc minor component (ppm)	**1.79676**	**0.00085**	**k=1**	
	Relative uncert	**0.047%**	**k=1**	

FB03587	**Cylinder # FB03587**			
		Standard	**Sensitivity**	**Contribution**
	Value	**Uncertainty**	**Coefficient**	**to Uncertainty**
Major Component MW	**28.01340**	**0.00028**	**0.0025**	**0.00000**
Minor Component MW	**16.04246**	**0.00081**	**0.0356**	**0.00003**
Mass Parent Gas	**32.01328**	**0.00174**	**0.0017**	**0.00000**
Mass Balance Gas	**471.68120**	**0.00202**	**0.0000**	**0.00000**
Minor Component Wt Fraction	**0.000019128**	**0.000000006**	**303045.69**	**0.00170**
Mass minor component - Parent	**0.00061235**	**0.00000018**	**9360.7844**	**0.00171**
Mass minor component - Bal	**0.00000026**	**0.00000013**	**282.9510**	**0.00004**
Total mass minor component	**0.00061260**	**0.00000022**	**8207.7027**	**0.00184**
Moles of minor component	**0.00003819**	**0.00000001**	**139587.18**	**0.00197**
Balance gas wt fraction (purity)	**0.755291668**	**0.00003290**	**0.8694**	**0.00003**
Mass balance gas - parent	**24.18102545**	**0.00460394**	**0.0015**	**0.00001**
Mass balance gas - balance	**356.25688192**	**0.01559487**	**0.0018**	**0.00003**
Total mass balance gas	**380.43790737**	**0.01626026**	**0.0022**	**0.00004**
Moles of balance gas	**13.58056885**	**0.00059642**	**0.0613**	**0.00004**
Moles impurities from parent	**0.24201004210**	**0.00007317437**	**0.0175**	**0.00000**
Moles impurities from balance	**3.5668088**	**0.0014723**	**0.0065**	**0.00001**
Total Moles of gas	**17.3894258**	**0.0015902**	**0.0299**	**0.00005**
Conc minor component (ppm)	**2.19596**	**0.00084**	**k=1**	
	Relative uncert	**0.038%**	**k=1**	

A4. Description of procedures for gas analysis

The two K-82 methane primary standard reference materials (PSMs) were compared to 7 existing ambient methane NIST PSMs using a Picarro cavity ring down spectrometer (CRDS). A computer operated gas analysis system was used to select the sample stream to be analyzed. The lot standard (LS) from SRM 1721 Southern Hemisphere Air, was used as a control to bracket two PSMs at a time so as to correct for drift in the instrument. A ratio was determined for each PSM by dividing the CRDS response of the PSM by that of the LS 1721-Al-01. Six independent ratios were determined for each PSM. An average ratio and standard error were calculated from the data for each PSM.

NIST PSMs used:

FF4267	2.05367 ± 0.00068 µmol/mol; *u* is k=1
FF4287	2.00595 ± 0.00073
FF4295	1.93605 ± 0.00063
FF4249	1.89536 ± 0.00068
FF4288	1.83866 ± 0.00068

FF4283	1.79802 ± 0.00064
FF4260	1.68981 ± 0.00055

A5. Complimentary information

NIST CH_4 standards where prepared gravimetrically with analysed real air as the matrix gas.

a)

b) Pure CH_4 purity table

Component	MW	Mole Fraction µmol/mol[a]	Limit µmol/mol	Analytical Instrumentation
Ethane	30.069	4.2 ± 0.2		GC/FID and HID
Propane	44.0962	0.4 ± 0.4		GC/FID and HID
Carbon dioxide	44.0096	0.3 ± 0.3		GC/HID
Argon	39.948	ND	0.1	GC/TCD/HID
Oxygen	31.9988	0.5 ± 0.2		GC/TCD/HID
Nitrogen	28.0134	1.7 ± 0.2		GC/TCD/HID

Methane Purity = 99.9993 ± 0.00006 %

[a]Relative combined standard uncertainties, k=1.

c) Mole fractions of components in real air matrix gas

Cylinder #	Nitrogen[a] % mol mol^{-1}	Oxygen % mol mol^{-1}	Argon % mol mol^{-1}	Carbon dioxide µmol mol^{-1}	**Methane nmol mol^{-1}**	Carbon monoxide µmol mol^{-1}	Nitrous o µmol m
CC28338	78.0943 ± 0.0020	20.9287 ± 0.0016	0.9378 ± 0.0013	391.44 ± 0.02	0.97 ± 0.50	0.005 ± 0.004	0.321 ± 0

d) Preparation procedure of mixtures

FB03569

Composition Table: Final Mixture		
Compound	mol/mol	Uncert (k=1)
Ar	0.000222062	0.000000516

FB03587

Composition Table: Final Mixture		
Compound	mol/mol	Uncert (k=1)
Ar	0.000596256	7.79304E-07

These methane primary standard mixtures (PSMs) were prepared gravimetrically in accordance with the Gas Metrology Group Quality System (QMIII-646.03) Technical Procedure 646.03.07. The K-82 PSMs, cylinder numbers FB03569 and FB3587, were prepared from parent methane PSMs FF4241 (75.805 ± 0.022) µmol/mol and CAL018213 (34.536 ± 0.009) µmol/mol respectively, and were previously developed and documented in ROAs 639.03-11-039a and 639.03-11-157. Those parent PSMs were prepared from pure methane which was analyzed for purity shown in Table 1. Table 2 lists the analysis for the cylinders of nitrogen used to prepare the original PSM suite, with cylinder number CC28338 being used to prepare these two K-82 PSMs. The preparation procedure used for preparing CH_4 in Air PSMs has been fully documented in "NIST Gravimetrically Prepared Atmospheric Level Methane in Dry Air Standards Suite", Analytical Chemistry, Vol.84 (8) pp. 3802-3810, **2012**.

e) Composition table for final mixtures

O2	0.004952814	0.000001709
CO2	0.000009202	0.000000002
C2H6	0.000000000	0.000000000
C3H8	0.000000000	0.000000000
N2O	0.000000000	0.000000000
Ar	0.009157802	0.000012730
O2	0.204318568	0.000026090
CO2	0.000381690	0.000000044
C2H6	0.000000000	0.000000000
C3H8	0.000000000	0.000000000
N2O	0.000000313	0.000000003
CH4	0.00000179676	0.00000000085
N2	0.780955750	0.000081752
Ar	0.009379864	0.000012740
O2	0.209271383	0.000026146
CO2	0.000390893	0.000000045
C2H6	9.54185E-12	1.95342E-11
C3H8	1.71827E-12	9.79185E-12
N2O	3.1342E-07	2.92911E-09

O2	0.01329597	4.31058E-06
CO2	2.48355E-05	4.89595E-09
C2H6	9.34599E-12	4.61726E-13
C3H8	9.41544E-13	8.80897E-13
N2O	1.89748E-08	1.77375E-10
Ar	0.008783729	1.22077E-05
O2	0.195963526	2.45364E-05
CO2	0.000366104	4.16516E-08
C2H6	1.87288E-12	1.87288E-11
C3H8	9.36442E-13	9.36442E-12
N2O	3.00598E-07	2.80948E-09
CH4	0.00000219596	0.00000000084
N2	0.780967064	7.92252E-05
Ar	0.009379985	1.22326E-05
O2	0.209259496	2.49121E-05
CO2	0.000390939	4.19383E-08
C2H6	1.12189E-11	1.87345E-11
C3H8	1.87799E-12	9.40576E-12
N2O	3.19573E-07	2.81507E-09

f) Outline of verification procedure

The data were then analyzed using an ISO 6143-compliant generalized least squares regression. The average ratio and standard error where plotted on the *x*-axis and the gravimetric concentration and uncertainty were plotted on the *y*-axis for each PSM. In each case, all PSMs passed the *u*-test. This verified the gravimetric concentrations of the K-82 samples to the original ambient methane PSM suite.

Data to be fit to a function using ISO 6143 compliant GenLine

Value of Standards		Analytical Response	
Y-Values, ppb	Y-uncertainty	X-Values	X-uncertainty
1687.15	0.70	0.95258	0.00006
1795.10	0.75	1.01319	0.00004
1796.76	0.85	1.01459	0.00005
1836.16	0.75	1.03694	0.00002
1892.84	0.79	1.06867	0.00004
1933.08	0.78	1.09146	0.00003
2003.44	0.83	1.13133	0.00004
2050.12	0.77	1.15730	0.00007
2195.96	0.84	1.23923	0.00005

Evaluation Data

Responses	
X-Values	X-uncertainty
1.00000	0.00006
1.01510	0.00006

GENLINE - Linear
(y=b0+b1*x)

	Value	Std Error
b0	-2.787	3.433
b1	1773.852	3.192
cov(b0,b1)		-10.927
rms residual error		0.551

PSM	X	Y, ppb	X-Solution	Y-Solution,ppb	uTest	Diff, ppb	% Diff
FF4260	0.95258	1687.15	0.95259	1686.96	PASS	-0.19	-0.01%
FF4283	1.01319	1795.10	1.01320	1794.47	PASS	-0.63	-0.03%
FB03569 (K-82 sample)	**1.01459**	**1796.76**	**1.01459**	**1796.95**	**PASS**	**0.19**	**0.01%**
FF4288	1.03694	1836.16	1.03694	1836.59	PASS	0.43	0.02%
FF4249	1.06867	1892.84	1.06867	1892.88	PASS	0.04	0.00%
FF4295	1.09146	1933.08	1.09146	1933.30	PASS	0.22	0.01%
FF4287	1.13133	2003.44	1.13133	2004.02	PASS	0.58	0.03%
FF4267	1.15730	2050.12	1.15730	2050.10	PASS	-0.02	0.00%
FB03587 (K-82 sample)	**1.23923**	**2195.96**	**1.23924**	**2195.44**	**PASS**	**-0.52**	**-0.02%**

g) Stability testing of K-82 samples.

Stability testing of the NIST K-82 samples was not done. However, the agreement of the K-82 samples with the NIST CH_4/Air suite (labeled NIST-2011) conveys stability to that suite of 7 cylinders which are almost 2 years old. NIST has observed no stability issues with CH4/Air mixtures in the past as documented in "The National Institute of Standards and Technology Ambient Level Methane in Air Standard Reference Material Historical Record", Analytical and Bioanalytical Chemistry, Vol. 403, pp. 537-548, **2012**.

h) Cylinder pressure shipped to BIPM

FB03569 1100 psi (7.6 MPa)
FB03587 1000 psi (6.9 MPa)

D.I.Mendeleyev Institute for Metrology (VNIIM)

Key Comparison CCQM-K82
Methane in Air at Ambient level (1800-2200) nmol/mol
Result form CCQM-K82-R

02/09/2013

A1. General information

Institute	D.I. Mendeleyev Institute for Metrology VNIIM	
Address	19, Moskovsky pr., St. Petersburg, Russia, 190005	
Contact person	Leonid Konopelko, Yury Kustikov	
Telephone	+7 (812) 315-11-45	Fax : +7 (812) 327-97-76
Email*	lkonop@b10.vniim.ru	
Serial number of cylinder sent	D249845; D249682	
Cylinder pressure as received	6.4 MPa for D249845 6.8 MPa for D249682	

A2. Results

Cylinder №	Methane mole fraction *x*CH4 / µmol/mol	Expanded uncertainty* *U* (*x* CH4) / µmol/mol	Coverage factor
D249845	2.2146	0.0025	2
D249682	1.8129	0.0026	2

*****The values of expanded uncertainty do not include the component due to verification

A3. Uncertainty Budget

1 Uncertainty budget (only gravimetry) for the cylinder N D249845

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of N_2		999999.470 µmol/mol	B	Rectangular	0.145 µmol/mol	0.00738	0.00108
Purity of O_2		999998.436 µmol/mol	B	Rectangular	0.142 µmol/mol	0.00163	0.000231
Purity of CO_2		999982.100 µmol/mol	B	Rectangular	0.859 µmol/mol	0.000133	0.000114
Purity of CH_4		999984.660 µmol/mol	B	Rectangular	1.36 µmol/mol	0,0000135	0.0000184
Purity of Ar		999999.496 µmol/mol	B	Rectangular	0.0331 µmol/mol	0.000394	0.00001305
Weighing* 1 stage premixture	CH_4	37.25649 g	A,B	Normal	0.0027g	-0.0572	-0.000155
	N_2	1115.4297 g	A,B	Normal	0.0260 g	0.00191	0.0000497
Weighing* 2 stage premixture	1 pre-mixture	40.3543 g	A,B	Normal	0.0025 g	-0.0527	-0.000132
	N_2	1126.3421 g	A,B	Normal	0.0220 g	0.00189	0.0000416
Weighing* 3 stage premixture	2 pre-mixture	59.1861 g	A,B	Normal	0.0036 g	-0.0353	-0.000127
	N_2	1095.8774 g	A,B	Normal	0.0250 g	0.00191	0.0000477
Weighing* CO_2/N_2 premixture	CO_2	12.9120 g	A,B	Normal	0.0022 g	-0.0000502	-0.000000111
	N_2	576.3338 g	A,B	Normal	0.0130 g	0.00000112	0.0000000146
Weighing* final mixture	3 pre-mixture	12.9261 g	A,B	Normal	0.0026 g	-0.167	-0.000434
	Ar	7.8004 g	A,B	Normal	0.0043 g	0.00253	0.0000109
	CO_2/N_2 premixture	16.0299 g	A,B	Normal	0.0041 g	0.00371	0.0000152
	O_2	140.8709 g	A,B	Normal	0.0060 g	0.00325	0.0000195
	N_2	429.0713 g	A,B	Normal	0.0140 g	0.00377	0.0000528
Combined standard uncertainty							**0.00122**
Expanded uncertainty k=2							**0,0025**

2 Uncertainty budget (only gravimetry) for the cylinder N D249682

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of N_2		999999.470 µmol/mol	B	Rectangular	0.145 µmol/mol	0.00738	0.00108
Purity of O_2		999998.436 µmol/mol	B	Rectangular	0.142 µmol/mol	0.00163	0.000231
Purity of CO_2		999982.100 µmol/mol	B	Rectangular	0.859 µmol/mol	0.000133	0.000114
Purity of CH_4		999984.660 µmol/mol	B	Rectangular	1.36 µmol/mol	0,0000111	0.0000151
Purity of Ar		999999.496 µmol/mol	B	Rectangular	0.0331 µmol/mol	0.000394	0.00001305
Weighing* 1 stage premixture	CH_4	18.3240 g	A,B	Normal	0.0035 g	-0.0952	-0.000333
	N_2	548.447 g	A,B	Normal	0.0160g	0.00318	0.0000509
Weighing* 2 stage premixture	1 pre-mixture	20.2786 g	A,B	Normal	0.0019g	-0.0858	-0.000163
	N_2	568.9606 g	A,B	Normal	0.0130 g	0.00306	0.0000398
Weighing* 3 stage premixture	2 pre-mixture	30.1264 g	A,B	Normal	0.0038 g	-0.0567	-0.000216
	N_2	553.8310 g	A,B	Normal	0.0150 g	0.00309	0.0000463
Weighing* CO_2/N_2 premixture	CO_2	12.9120 g	A,B	Normal	0.0022 g	-0.0000502	-0.000000111
	N_2	576.3338 g	A,B	Normal	0.0130 g	0.00000112	0.0000000146
Weighing* final mixture	3 pre-mixture	10.5493 g	A,B	Normal	0.0031 g	-0.168	-0.000520
	Ar	7.8111 g	A,B	Normal	0.0027 g	0.00205	0.00000554
	CO_2/N_2 premixture	16.0125 g	A,B	Normal	0.0035 g	0.00303	0.0000106
	O_2	140.5831g	A,B	Normal	0.0050 g	0.00265	0.0000133
	N_2	431.7311 g	A,B	Normal	0.0120 g	0.00309	0.0000370
Combined standard uncertainty							**0.00131**

Expanded uncertainty k=2	**0,0026**

*Uncertainty due to weighing includes constituents related to accuracy of balance, buoyancy effect resulting from change of cylinder volume during filling, mass pierces used, drift of balance, residual gas in cylinder.

A4. Description of the procedure used during the gas analysis

Gas chromatography with FID was used for verification
Instrument: Gas Chromatograph «Crystal 5000.2» (Chromatec);
Capillary column: Agilent J&W capillary GC column (HP-PLOT Q; 30 m x 0.530 mm, 40.00 μm);
Carrier gas: helium 100 cm/sec;
Oven conditions: 35 ºC for 40 sec;
Sample loop: 1 ml;
Split:1:2:
Data collection: by “Chromatec Analytic 2.6” software.

3 measurement series with 8 sub-measurements each were carried out.
SD of a single measurement (repeatability within measurement series) was 0,05 % -0,15 %

A5. Complementary information

Please include in this section in the case of standards produced with synthetic air:

a) Purity table with uncertainties for the nominally pure CH_4 parent gas

Cylinder N 62449 Main component CH_4 Mole fraction 99.998466 %		
Component	Mole fraction, μmol/mol	Standard uncertainty, μmol/mol
H_2O	5.0	0.5
N_2	4.5	0.6
CO_2	1.0	0.6
C_2H_4	1.0	0.6
$Ar+O_2$	0.84	0.16
C_2H_6	0.50	0.29
C_4H_6	0.50	0.29
C_3H_6	0.50	0.29
$i\text{-}C_4H_8$	0.50	0.29
$C_4H_8\text{-}1$	0.50	0.29
C_3H_8	0.50	0.29

b) Purity tables with uncertainties for the nominally pure N_2, O_2, Ar and CO_2 parent
gases

Cylinder N 37471 Main component N_2 Mole fraction 99.999947 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
H_2O	0.250	0.145
Ar	0.146	0.004
Ne	0.107	0.006
O_2	0.0160	0.001
CO_2	0.0025	0.0015
H_2	0.0025	0.0015
CH_4	0.0025	0.0015
CO	0.0010	0.0006

Cylinder N 910287 Main component O_2 Mole fraction 99.99984 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
H_2	0.0025	0.0014
Ar	0.1828	0.0042
N_2	0.988	0.024
Kr	0.0010	0.0006
CO	0.0075	0.0043
CH_4	0.0352	0.0010
CO_2	0.0944	0.0048
Xe	0.0025	0.0014
H_20	0.25	0.14

Cylinder N 205863 Main component Ar Mole fraction 99.999950 %		
Component	Mole fraction, µmol/mol	Standard uncertainty, µmol/mol
O_2	0.174	0.004
N_2	0.17	0.03
CH_4	0.0950	0.0014
CO_2	0.030	0.017
H_2	0.025	0.014

CO	0.010	0.006

Cylinder N 226934 Main component CO_2 Mole fraction 99.99821 %		
Component	Mole fraction, μmol/mol	Standard uncertainty, μmol/mol
H_2O	15	0.7
N_2	1.06	0.07
CO	0.5	0.3
CH_4	0.5	0.3
H_2 [	0.5	0.3
O_2	0.3	0.13

c) Brief outline of the dilution series undertaken to produce the final mixtures:

Preparation of final mixtures (methane in synthetic air) was carried out from pure substances in 4 stages.
1-st stage – 3 mixtures CH_4/N_2 –level 5.5 %
2-nd stage – 3 mixtures CH_4/N_2 –level 0.195 %
3-rd stage – 3 mixtures CH_4/N_2 –level 100 μmol/mol
4-th stage – 5 mixtures CH_4/synthetic air – level 2 μmol/mol

The mixtures of 1-3 stages were prepared in Luxfer cylinders (V=10 and 5 dm^3); 5 dm^3 were with Aculife4+Aculife3 coating.

All the mixtures of the 4-th stage were prepared in Luxfer cylinders (V= 5 dm^3) with Aculife4+Aculife3 coating

d) purity table for each of the final mixtures, including gravimetric uncertainties;

Cylinder №: D249845

Component	Mole fraction, μmol/mol	Expanded uncertainty, μmol/mol k=2
O2	210204	18
Ar	9324	10
CO2	381.18	0.23
CH4	2.2146	0.0025
N2	balance	

Cylinder №: D249682

Component	Mole fraction, μmol/mol	Expanded uncertainty, μmol/mol k=2
O2	209767	15

Ar	9336	7
CO2	380.75	0.21
CH4	1.8129	0.0026
N2	balance	

e) brief outline of the verification procedure applied to the final mixtures

Gas chromatography with FID was used for verification
3 measurement series with 8 sub-measurements each were carried out within each verification procedure.
SD of a single measurement (repeatability within one series) was 0,05 % -0,15 %.

f) brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM

The final mixtures were prepared 25.06 -10.07.2012.
First verification measurements were carried out 11.07 -16.07 2012.
Second verification measurements (stability testing) were carried out 25.09 - 28.09.2012.
Verification measurements were performed by checking consistency within the group of the 5 prepared mixtures.
Third verification measurements (stability testing) were carried out 19.09 - 20.09.2013 after return of the cylinders from BIPM.
Verification measurements were performed by checking consistency within the group of the 5 prepared mixtures.

u_{ver} =0,1 %=0,002 µmol/mol

Stability testing did not show instability within the accuracy of the measurement method.

g) cylinder pressure
6.4 MPa for D249845
6.8 MPa for D249682

Dutch Metrology Institute (VSL)

Key Comparison CCQM-K82
Methane in Air at Ambient level (1800-2200) nmol/mol

Result form CCQM-K82-R

Project name: CCQM-K82 (Methane in Air at Ambient level).
Comparison: Comparability study of laboratories' preparation capabilities for Methane in Air Standards.
Proposed dates: 05/2012 to 03/2013.

Coordinating laboratories:

Bureau International des Poids et Mesures
Chemistry Section
Pavillon de Breteuil
92312 Sevres Cedex, France.

NIST
100 Bureau Drive, Stop 8300, Gaithersburg, MD 20899-8300
US

Study Coordinator: Edgar Flores
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:

Please complete and return the form preferably by email to edgar.flores@bipm.org

The CCQM-K82 comparison is designed to evaluate the level of compatibility of NMI preparative capabilities for gravimetric methane in air primary reference mixtures in the range (1800-2200) nmol/mol. The balance gas for the standards shall be either scrubbed dry real air or synthetic air.

A1. General information

Institute	VSL Dutch Metrology Institute		
Address	Thijssseweg 11 2639 JA Delft The Netherlands		
Contact person	Ewelina Zalewska		
Telephone	+31 15 269 15 76	Fax	+31 15 261 29 71

Email*	ezalewska@vsl.nl
Serial number of cylinders received and cylinders pressure as received	D249292 P =117 bar D249289 P = 118 bar

A2. Results

Cylinder number	Methane mole fraction x_{CH4} / µmol/mol	Expanded uncertainty $U(x_{CH4})$ / µmol/mol	Coverage factor
D 249292	1.7983	0.0040	2
D 249289	2.1963	0.0048	2

A3. Uncertainty Budget

The basis for the uncertainty budget is formed by the uncertainty evaluation from the gravimetry and that from purity analysis of the parent gases [1]. The uncertainty evaluation of the weighing is performed using the default procedures [2]. The atomic weights of 2007 [3] have been used, which is in agreement with a resolution taken by ISO/TC158. As the preparation of the gas mixtures is a multistage preparation, the uncertainties in each step are duly propagated. For the propagation of uncertainty, the law of propagation of uncertainty [4] is used.

No allowance is made for stability effects. The maintenance programme for the primary standard gas mixtures (PSMs) indicates that for the amount–of–substance fraction methane, such effects are negligible. A contribution due to sampling from the cylinder is included in the uncertainty budget (0.1% relatieve, k = 1), which is derived from the verification measurements. The verification measurements are performed in accordance with ISO 6143 [5].

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[5].

Methane was analyzed using gas chromatography with flame ionisation detection. A GC was used with the following configuration:
GC - Agilent 6890N
Column – Molsieve 5, 10 ft, 80-100 mesh
FID
Carrier gas - Helium

Cylinders were analyzed against own primary standard gas mixtures. All mixtures were prepared in accordance with ISO 6142 [1]. The verification analysis was performed in accordance with ISO 6143:2001. Eight PSMs with methane in the low ppm range were selected; balance gas was was either synthetic air and nitrogen. Each cylinder was equipped with a pressure regulator. All the cylinders have been flushed three times within 24 hours time period. Cylinders were connected to a sample box equipped with 16-position valve. Every cylinder was injected seven times.

A5. Complementary information

a) a purity table with uncertainties for the nominally pure CH_4 parent gas;

Table 28: Purity table methane (APCH4); all data are given in µmol mol-1

Component	x	u(x)
methane	999998.60	0.60
Carbondioxide	0.05	0.03
Ethane	0.05	0.03
Propane	0.005	0.003
Hydrogen	0.05	0.03
Nitrogen	1.0	0.6
Oxygen	0.25	0.14

All composition data in all purity tables are given in terms of amount–of–substance fractions.

b) a purity table with uncertainties for the nominally pure N_2, O_2, Ar and CO_2 parent gas;
Table 29: Purity table nitrogen (AP6430); all data are given in µmol mol-1

Component	x	u(x)
Argon	3.4	0.34
Methane	0.0005	0.0003
Carbonmonoxide	0.015	0.009
Carbondioxide	0.010	0.006
Hydrogen	0.025	0.015
Water	0.010	0.006
Nitrogen	999996.42	0.35
Oxygen	0.118	0.012

Table 30: Purity table nitrogen (AP6430); all data are given in µmol mol-1

Component	x	u(x)
Argon	1.2	0.12
Methane	0.0005	0.0003
Carbonmonoxide	0.015	0.009
Carbondioxide	0.010	0.006
Hydrogen	0.025	0.015
Water	0.010	0.006
Nitrogen	999998.62	0.12
Oxygen	0.122	0.012

Table 31: Purity table oxygen (AP8381); all data are given in µmol mol-1

Component	x	u(x)
Argon	0.5	0.29
Methane	0.048	0.003
Carbonmonoxide	0.05	0.029
Carbondioxide	0.050	0.029
Water	0.25	0.15
Nitrogen	0.250	0.15
Oxygen	999998.9	1.0

Table 32: Purity table argon (AP8230); all data are given in µmol mol-1

Component	x	u(x)
Argon	999999.8	0.5
Methane	0.025	0.015
Carbonmonoxide	0.013	0.008
Carbondioxide	0.013	0.008
Water	0.01	0.006
Nitrogen	0.150	0.087
Oxygen	0.005	0.003

c) a brief outline of the dilution series undertaken to produce the final mixtures;

The mixtures have been prepared using three different types of pre-mixtures: methane in nitrogen, argon in nitrogen and carbon dioxide in nitrogen. Methane in nitrogen was prepared with five dilution steps, carbon dioxide with two dilution steps. Argon in nitrogen was prepared was prepared using one dilution step.

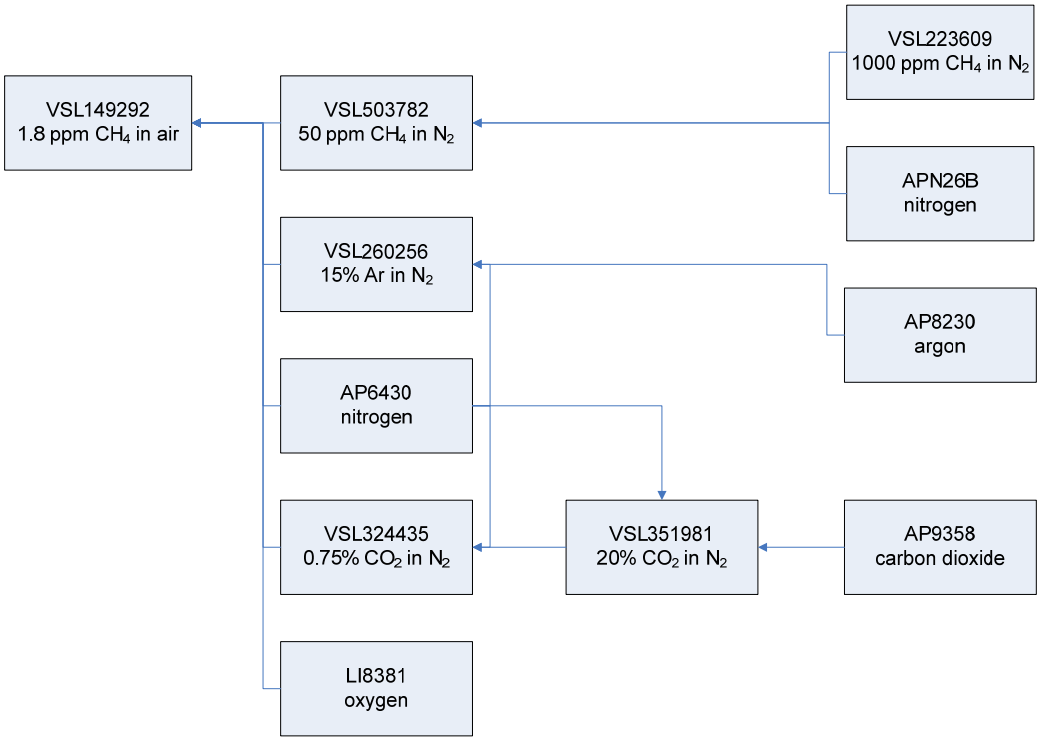


Figure 39: Preparation scheme for VSL149292 (nominal 1.8 µmol mol-1 methane in synthetic air)

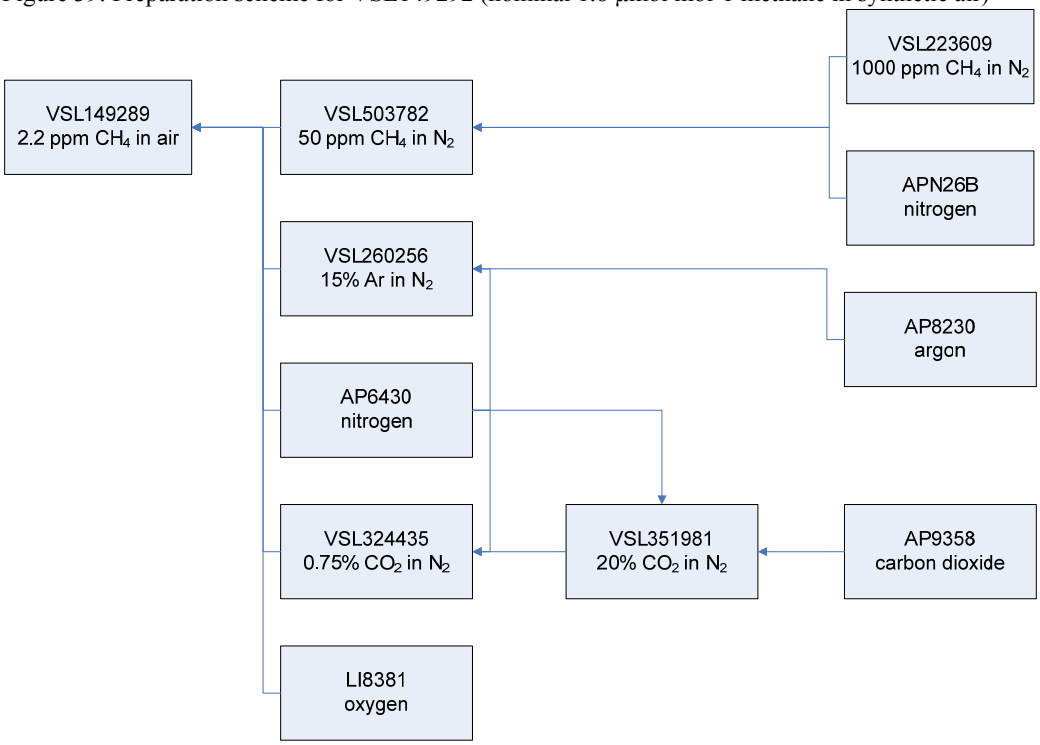


Figure 40: Preparation scheme for VSL149289 (nominal 2.2 µmol mol-1 methane in synthetic air)

d) a purity table for each of the final mixtures, including gravimetric uncertainties;

Table 33: Purity table VSL149289

Component	Unit	y	u(y)
Argon	µmol mol^{-1}	9308.28	0.37
Methane	µmol mol^{-1}	2.19633	0.00088
Carbonmonoxide	µmol mol^{-1}	0.02248	0.00836
Carbondioxide	µmol mol^{-1}	380.344	0.022
Ethene	µmol mol^{-1}	0.0000011	0.0000011
Ethane	µmol mol^{-1}	0.0000011	0.0000011
Propane	µmol mol^{-1}	0.0000011	0.0000011
Hydrogen	µmol mol^{-1}	0.0195	0.0096
Water	µmol mol^{-1}	0.0609	0.0316
Nitrogen	µmol mol^{-1}	781269.2	2.7
Oxygen	µmol mol^{-1}	209039.9	2.7

Table 34: Purity table VSL149292

Component	Unit	y	u(y)
argon	µmol mol^{-1}	9295.10	0.35
methaan	µmol mol^{-1}	1.79829	0.00082
koolstofmonoxide	µmol mol^{-1}	0.02248	0.00841
koolstofdioxide	µmol mol^{-1}	380.292	0.020
etheen	µmol mol^{-1}	0.0000009	0.0000009
ethaan	µmol mol^{-1}	0.0000009	0.0000009
propaan	µmol mol^{-1}	0.0000009	0.0000009
waterstof	µmol mol^{-1}	0.0195	0.0097
water	µmol mol^{-1}	0.0609	0.0316
stikstof	µmol mol^{-1}	781352.0	2.7
zuurstof	µmol mol^{-1}	208970.7	2.7

e) a brief outline of the verification procedure applied to the final mixtures;
f) a brief outline of any stability testing of the mixtures between the time they are prepared and the time they are shipped to the BIPM; and
g) cylinder pressure

A6. References

[1] International Organization for Standardization, “ISO 6142 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods”, ISO Geneva, 2001

[2] Alink A., Van der Veen A.M.H., “Uncertainty calculations for the preparation of primary gas mixtures. 1. Gravimetry”, Metrologia **37** (2000), pp 641-650

[3] Wiesser M.E., Berglund M., “Atomic weights of the elements 2007”, Pure Appl. Chem., **81** (2009), pp. 2131–2156

[4] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (2008) “Evaluation of measurement data — Guide to the expression of uncertainty in measurement”, first edition, GUM:1995 with minor corrections

[5] International Organization for Standardization, "ISO 6143 – Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures ", ISO Geneva, 2001

National Physical Laboratory (NPL)

Key Comparison CCQM-K82
Methane in Air at Ambient Levels (1800-2200) nmol/mol
Result Form CCQM-K82-R

A1 General information

Institute: National Physical Laboratory
Address: Hampton Road, Teddington, TW11 0LW, UK
Contact person: Paul Brewer
Telephone: +44 (0)20 8 943 6007
Email: paul.brewer@npl.co.uk
Serial number of cylinders sent: 221727 (nominal amount fraction: 1800 nmol/mol CH_4) and 233097 (nominal amount fraction: 2200 nmol/mol CH_4)

A2 Results

Component	Amount Fraction (µmol/mol)	Expanded Uncertainty (µmol/mol)
CH_4	1.7994	0.0036
CO_2	370.7	0.7
Ar	9345	27
N_2	781006	470
O_2	209272	130

Table 1: Submitted data for 221727

Component	Amount Fraction (µmol/mol)	Expanded Uncertainty (µmol/mol)
CH_4	2.1996	0.0044
CO_2	372.5	0.7
Ar	9341	27
N_2	781008	470
O_2	209271	130

Table 2: Submitted data for 233097

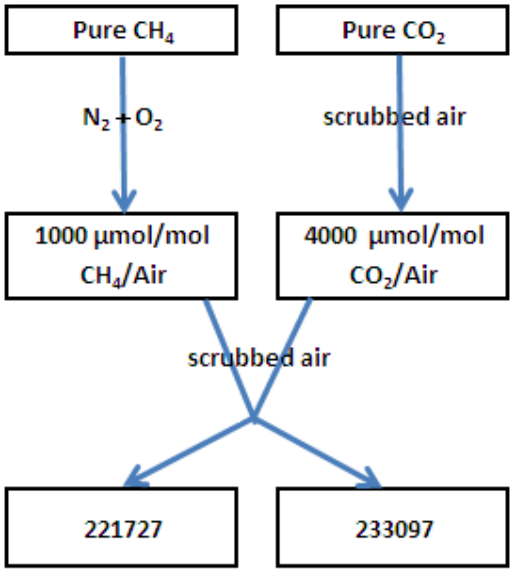
A3 Uncertainty

The estimated uncertainty for the measurement contains the following components:

- Purity analysis of CH_4 and of real scrubbed real air
- Gravimetric preparation (weighing and atomic weight uncertainties)
- Stability
- Transfer losses

A4 Description of the procedure

The two gas mixtures were prepared for this comparison (221727 and 233097) at NPL in real scrubbed air from pure CH_4 (>99.9999%) and pure CO_2 (>99.9999%). The pure industrial source of CO_2 was spiked with pure $^{13}CO_2$ to achieve an isotopic composition close to natural abundance. The mixtures were prepared in BOC 10 litre cylinders with Spectraseal passivation. A second pair of reference standards was prepared and these were used to validate the comparison mixtures. The scheme below shows the gravimetric dilutions with nominal CH_4 and CO_2 amount fractions.



Dilution scheme for gravimetric preparation

A Picarro G2301 Cavity ring-down spectrometer was used to validate the amount fraction of CH_4 in mixtures 221727 and 233097. The analyser response to the matrix gas was recorded. The analyser response to a reference mixture was then recorded for a five minute period followed by the either 221727 or 233097 for the same time. This sequence was repeated four times. At the end of the experiment the analyser response to the matrix gas was recorded a second time. To minimise the effects from zero drift, a mean of the analyser response to the matrix gas before and after the experiment was used. The amount fractions of 221727 and 233097 were then determined by multiplying the ratio of the analyser response to each mixture and the reference mixture (both were corrected for the analyser response to matrix gas) with the amount fraction of the reference mixture. These measurements were used to validate the gravimetric amount fractions submitted.

Cylinders were maintained at a laboratory temperature of (20 ± 3) °C throughout the period of analysis. Samples were introduced into the analyser at atmospheric pressure (excess flow was passed to vent) using a low volume gas regulator.

A5 Complementary information

Purity tables for the CH_4 and real scrubbed air are provided below.

Component	Amount Fraction (µmol/mol)	Expanded Uncertainty (µmol/mol)
CH_4	999999.0	1.0
O_2	0.10	0.10
Ar	0.040	0.040
CO_2	0.035	0.035
CO	0.20	0.20
N_2	0.20	0.20

Table 3: Purity table for CH_4

Component	Amount Fraction (µmol/mol)	Expanded Uncertainty (µmol/mol)
N_2	781280	500
O_2	209350	100
Ar	9365	30
CO_2	0.05	0.05
CO	0.0040	0.0020
CH_4	0.0032	0.0006

Table 4: Purity table for scrubbed real air

The mixtures were prepared on 28th November 2012. Measurements to study the stability of the mixtures were carried out over a 2 month period.

The cylinder pressure of mixtures 221727 and 233097 prior to shipping was > 9 MPa.

National Oceanic and Atmospheric Administration (NOAA)

Key Comparison CCQM-K82
Methane in Air at Ambient level (1800-2200) nmol/mol
Result form CCQM-K82-R
Project name: CCQM-K82 (Methane in Air at Ambient level).
Date: Nov. 9, 2012 (updated Feb. 5, 2013)

1.0 General Information

Institute: NOAA
Address: 325 Broadway
Mail Stop R.GMD1
Boulder, CO 80305 USA
Contact: Brad Hall
Tel: + 1 303 497 7011
Email: Bradley.Hall@noaa.gov

Serial Numbers: FB03578, FB03593

2.0 Results:

Cylinder	CH_4 (nmol/mol)*	Uncertainty (nmol/mol)	Coverage factor	CO_2 (mmol/mol)
FB03578	1812.1	2.6	k=2	376.2
FB03593	2208.9	2.8	k=2	367.0

*WMO X2004 CH_4 Reference Scale

3.0 Uncertainty Budget

Purity Table: CH_4

Component	Mole fraction	Uncertainty
O2	< 100 ppm	
N2	< 100 ppm	
H2O	< 10 ppm	
CH4	0.9998+	0.0002

Purity Table: CO_2

Component	Mole fraction	Uncertainty
N2O	2 ppb	
CH4	< 1 ppm	
CO2	0.99999	0.00001

Purity Table: Dilution Gas (scrubbed real air)

Component	Mole fraction	Uncertainty (k=1)
O2	0.20912	0.00006
N2	0.78155	0.00006
Ar	0.009332	0.000003
CO2	< 1e-6	0.5e-6
CH4	4.8e-9	0.7e-9

3.1 Uncertainty Components

Component	Fractional Uncertainty	Fractional Uncertainty
Cylinder	FB03578	FB03593
MW CH4	2.49e-5	2.49e-5
MW dilution gas	6.91e-5	6.91e-5
Mass of dilution gas	9.30e-6	9.34e-6
Mass of CH4 aliquot	6.124e-4	5.466e-4
CH4 in dilution gas	3.867-4	3.168e-4
Total	7.280e-4	6.361e-4

3.2 Summary of Results and Uncertainties

Cylinder: FB03578 (CH_4 in purified real air)

Component	Mole fraction	Uncertainty (k=2)
O_2	0.20912	0.00012
N_2	0.78155	0.00012
Ar	0.009332	0.000006*
CO_2†	$376.18 \cdot 10^{-6}$	$0.14 \cdot 10^{-6}$
CH_4	$1812.1 \cdot 10^{-9}$	$2.6 \cdot 10^{-9}$

* estimated
† analyzed, WMO X2007 Reference Scale

Cylinder: FB03593 (CH_4 in purified real air)

Component	Mole fraction	Uncertainty (k=2)
O_2	0.20912	0.00012
N_2	0.78155	0.00012
Ar	0.009332	0.000006*
CO_2†	$366.98 \cdot 10^{-6}$	$0.14 \cdot 10^{-6}$
CH_4	$2208.9 \cdot 10^{-9}$	$2.8 \cdot 10^{-9}$

* estimated
† analyzed, WMO X2007 scale

Samples FB03578 and FB03593 were prepared by gravimetric dilution of a 1.06% CH_4-in-air primary standard. Gravimetrically-prepared values of CH_4 in these samples are consistent with the WMO X2004 scale. Analyzed values are reported in section 2.0 and 3.2. Uncertainties are derived from components listed in section 3.1 and are consistent with uncertainties associated with standards that define the WMO X2004 scale.

Impurities in CO_2 were not included in the uncertainty budget for this comparison. Pure CO_2 was analyzed by GCMS and by GC-ECD. CH_4 was not detected. However, the WMO X2004 CH_4 scale is based on primary standards that do not contain CO_2. Therefore any contribution to uncertainty from CO_2 would be inconsistent with the WMO X2004 CH_4 scale.

4.0 Analysis System

The current analytical system for calibrations is based on a Hewlett-Packard 6890 gas chromatograph with flame ionization detector, multi-position stream selection valves for sample selection, a two-position, six-port valve for injection of gas onto the GC column, and custom software for valve control and chromatogram peak integration. A single, 3.2 mm OD, 3 m long

column packed with 80/100 mesh HayeSep Q at 40°C is used for CH_4 separation. Sample loop volume is 5 mL. Carrier gas is 99.9995% N_2 purified by passing it through a heated metal-oxide catalyst (Trace Analytical CAT-1) and a 50 cm long, 2.1 cm ID trap filled with a 50/50 mixture of 13X (8–12 mesh) and 5A (0.16 cm) molecular sieve pellets. Carrier gas column head pressure is set with one of the GC's electronic pressure controllers to give a flow rate of 36 mL min^{-1}. The flame is fueled by 40 mL min^{-1} H_2 (99.999%) and supported by 250 mL min^{-1} 40% O_2 (99.98%) in N_2.

The WMO X2004 CH_4 reference scale is based on 16 gravimetrically-prepared standards, with a nominal range of 300-2600 nmol/mol (see Dlugokencky et al., 2005). Cylinders FB03578 and FB03593 were analyzed over a period of 11 days. The standard deviations of analysis results from three separate analysis periods were 0.13 nmol mol^{-1} and 0.06 nmol mol^{-1} for cylinders FB03578 and FB03593, respectively.

5.0 References

Dlugokencky, E. J., R. C. Myers, P. M. Lang, K. A. Masarie, A. M. Crotwell, K. W. Thoning, B. D. Hall, J. W. Elkins, and L. P. Steele (2005), Conversion of NOAA atmospheric dry air CH4 mole fractions to a gravimetrically prepared standard scale, *J. Geophys. Res.*, *110*, D18306, doi:10.1029/2005JD006035.

ANNEX 3- Validation data

Validation of BIPM's measurement systems with a suite of standards produced by the NIST

In preparation for CCQM-K82 the BIPM conducted a number of studies to validate the performance and uncertainty of its analytical systems.

Compressed gas mixtures containing CH_4 in a balanced air were prepared gravimetrically by the NIST and sent to the BIPM. Six standards were used in the validation study presented here. The preparation procedure used for preparing CH_4 in Air PSM's has been fully documented by Rhoderick et al.[1]

Table 18 lists the characteristics of the methane gas standards along with the gravimetric concentration and its relative uncertainty expressed at a level of confidence of approximately 68% (k = 1) as reported by NIST used in this validation study. The mole fraction and relative uncertainty of NIST standards are plotted in Figure 27.

Number of Cylinder	Assigned CH_4 mole fraction x_{NIST} (nmol mol^{-1})	Certified standard uncertainty $u_{ver}(x_{NIST})$ (nmol mol^{-1})	Matrix
CAL018193	1637.42	0.56	Real Air
FF4234	1815.72	0.66	Synthetic Air
CAL018226	1906.34	0.66	Real Air
FF4190	1929.63	0.64	Synthetic Air
CAL018216	1969.34	0.75	Synthetic Air
CAL018191	1970.9	0.74	Real Air

Table 18. Characteristics of gravimetric mixtures as provided by NIST

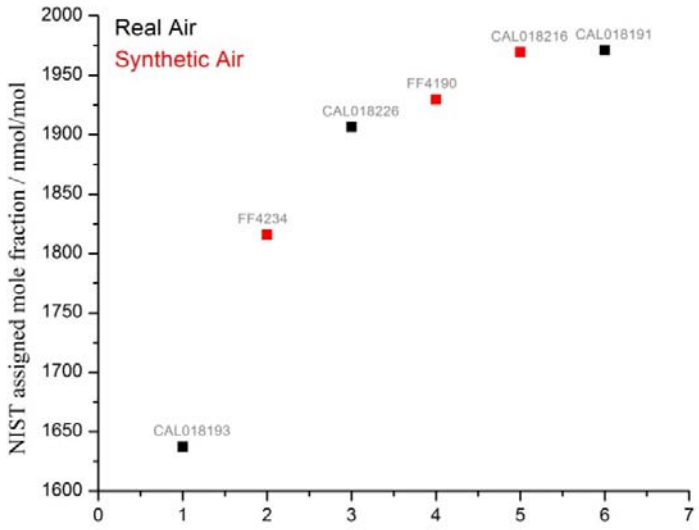


Figure 27 : Methane mole fractions of NIST standards

NIST standards were analyzed by the CRDS Method 2 and then by GC-FID on July 2013. Table 19 lists the results obtained by both methods (bold type writing) together with the results of the CCQM-K82 comparison extracted from Table 6.

To observe the consistency between the CRDS Method 2 and GC-FID , the CRDS Method 2 responses were plotted against GC-FID ratio responses in Figure 28. As can be observed, there were no apparent outliers or deviations from a linear relationship.

In order to verify more carefully the linearity of both methods, the regression analysis was performed including NIST validation standards with the ensemble of standards contributing to the regression in the key comparison. The cylidner FB03593 from NOAA was not consider as part of the set of cylinders used to produce the KCRV (for more information see section 8).

The resulting goodness of fit, listed in Table 20, confirmed the agreement between the analysis function and calibration data in both cases. The difference (Δx_{CH4}) between predicted and gravimetric values for the methane mole fraction for CRDS Method 2 are listed in Table 21 and for GC-FID in Table 22.

The differences (Δx_{CH4}) between CH_4 gravimetric mole fractions and predicted values using CRDS analysis Method 2 are plotted in Figure 29 for CCQM-K82 participants and NIST validation cylinders. The differences (Δx_{CH4}) between CH_4 gravimetric mole fractions and predicted values using GC-FID analysis are plotted in Figure 30, also for CCQM-K82 participants and NIST validation cylinders.

Based on these results the response functions of both methods can be considered as linear within the mole fraction range of 1600 nmol/mol to 2250 nmol/mol and the stated uncertainties of Table 6.

Participant	Number of Cylinder	NMI's assigned CH_4 mole fraction x_{NMI} (nmol/mol)	NMI's assigned Standard uncertainty k=1 $u(x_{NMI})$ (nmol/mol)	$\overline{R}_2$ CRDS Method 2 (Under intermediate precision conditions) Ratios to control cylinder	$u(\overline{R}_2)$ Standard uncertainty in the Ratios to control cylinder	$\overline{R}_{wGC}$ GC-FID (Under intermediate precision conditions) Ratios to control cylinder	$u(\overline{R}_{GC})$ Standard uncertainty in the Ratios to control cylinder
KRISS	D 929248	1797.10	0.50	0.94490	0.00026	0.9450	0.00024
KRISS	D 985705	2200.90	0.60	1.15737	0.00026	1.1580	0.00025
NIM	CAL017763	1825.20	0.85	0.95961	0.00027	0.9598	0.00025
NIM	CAL017790	2193.80	1.00	1.15314	0.00026	1.1534	0.00025
NIST	FB03569	1796.76	0.85	0.94449	0.00026	0.9444	0.00024
NIST	FB03587	2195.96	0.84	1.15345	0.00026	1.1538	0.00025
NIST	**CAL018193**	**1637.42**	**0.56**	**0.86128**	**0.00026**	**0.86115**	**0.00022**
NIST	**FF4234**	**1815.72**	**0.66**	**0.95409**	**0.00026**	**0.95421**	**0.00023**
NIST	**CAL018226**	**1906.34**	**0.66**	**1.00178**	**0.00027**	**1.00186**	**0.00021**
NIST	**FF4190**	**1929.63**	**0.64**	**1.01422**	**0.00027**	**1.01428**	**0.00023**
NIST	**CAL018216**	**1969.34**	**0.75**	**1.03493**	**0.00027**	**1.03520**	**0.00022**
NIST	**CAL018191**	**1970.9**	**0.74**	**1.03579**	**0.00027**	**1.03625**	**0.00022**
NMIJ	CPB-28035	1797.30	0.65	0.94429	0.00026	0.9443	0.00025
NMIJ	CPB-28219	2198.30	0.65	1.15489	0.00026	1.1551	0.00025
NOAA	FB03578	1812.10	1.30	0.95368	0.00027	0.9537	0.00024
NOAA	FB03593	2208.90	1.40	1.16346	0.00026	1.1639	0.00025
NPL	221727	1799.40	1.80	0.94650	0.00026	0.9466	0.00025
NPL	233097	2199.60	2.20	1.15683	0.00026	1.1569	0.00024
VNIIM	D 249682	1812.90	1.30	0.95159	0.00026	0.9515	0.00026
VNIIM	D 249845	2214.60	1.25	1.16395	0.00026	1.1641	0.00025
VSL	D 249292	1798.29	2.00	0.94499	0.00027	0.9452	0.00024
VSL	D 249289	2196.33	2.40	1.15390	0.00026	1.1541	0.00023

Table 19. Results of BIPM CH_4 mole fraction validation measurements. NIST validation standards are shown in bold type.

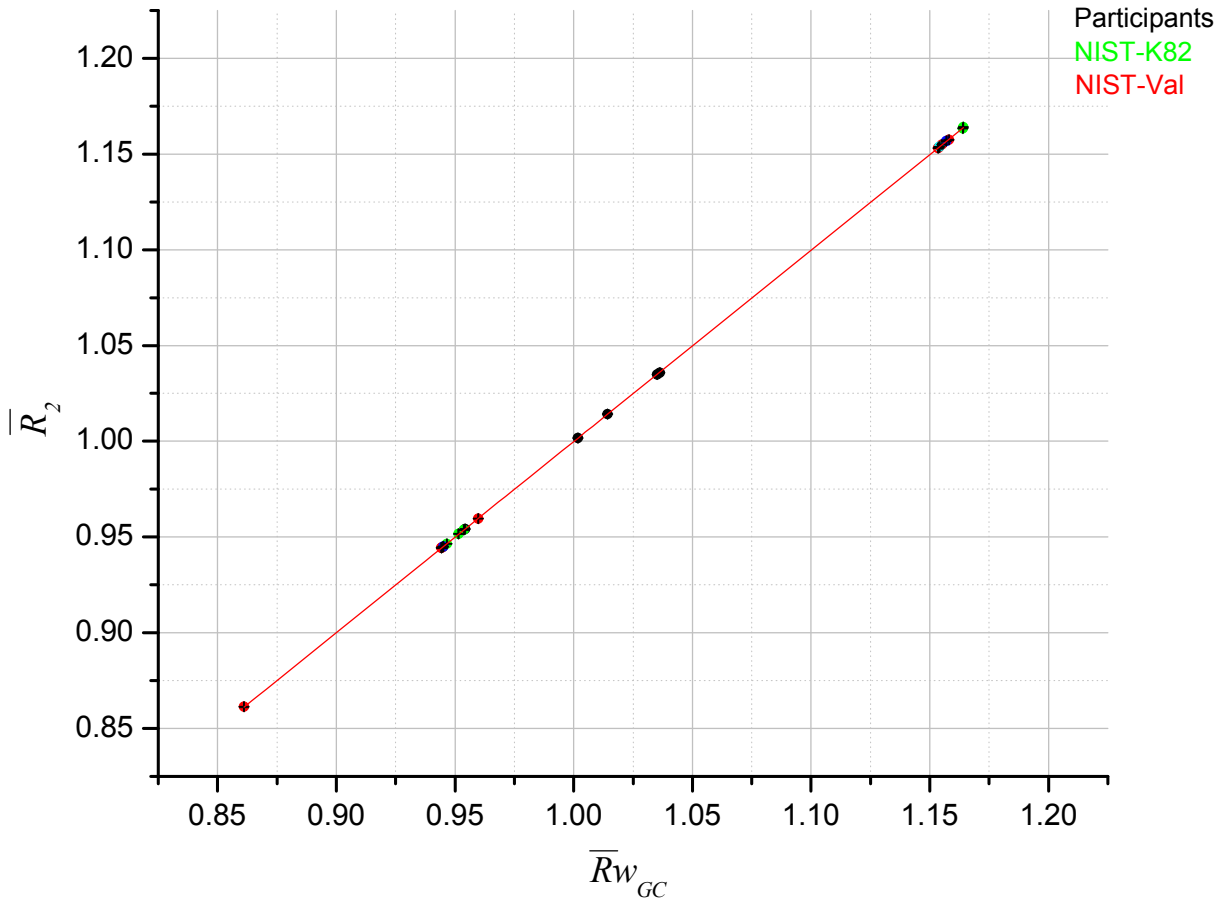


Figure 28. CRDS ratios to control standard Messer 597888 (Method 2) vs GC-FID ratios to control standard. Error bars representing the standard uncertainty (k=1) associated with the BIPM measurement results are plotted but cannot be seen on the graph. For further information see section ANNEX 1- BIPM Value assignment procedure.

Parameter	CRDS Method 2	GC-FID
bo	-2.705	-0.30361
b1	$1.905 \cdot 10^3$	$1.9026 \cdot 10^3$
$u(b_0)$	2.2963	2.2245
$u(b_1)$	2.2497	2.1835
Covariance	-5.1433	-4.836
Remaining SSD	16.547	21.20
Goodness -of-fit measurements	1.74	1.94

Table 20. Regression analysis parameters for CRDS Method 2 and GC-FID using the ensemble of contributing cylinders in CCQM-K82 together with NIST validation cylinders in the linear regression.

Participant	Number of Cylinder	NMI's assigned CH_4 mole fraction x_{NMI} (nmol/mol)	NMI's assigned Standard uncertainty k=1 $u(x_{NMI})$ (nmol/mol)	$\overline{R}_{2\_pred}$ (nmol/mol)	$u\left(\overline{R}_{2\_pred}\right)$ (nmol/mol)	$\Delta x_{CH_4} = \left(x_{NMI} - \overline{R}_{2\_pred}\right)$ (nmol/mol)	$u\left(\Delta x_{CH_4}\right)$ (nmol/mol)	$U\left(\Delta x_{CH_4}\right)$ (k=2) (nmol/mol)
KRISS	D 929248	1797.10	0.50	1797.54	0.57	-0.44	0.76	1.51
KRISS	D 985705	2200.90	0.60	2202.34	0.63	-1.44	0.87	1.74
NIM	CAL017763	1825.20	0.85	1825.56	0.57	-0.36	1.02	2.04
NIM	CAL017790	2193.80	1.00	2194.28	0.63	-0.48	1.18	2.36
NIST	FB03569	1796.76	0.85	1796.76	0.57	0.00	1.02	2.04
NIST	FB03587	2195.96	0.84	2194.87	0.63	1.09	1.05	2.09
NIST	**CAL018193**	**1637.42**	**0.56**	**1638.22**	**0.65**	**-0.80**	**0.86**	**1.71**
NIST	**FF4234**	**1815.72**	**0.66**	**1815.05**	**0.57**	**0.67**	**0.87**	**1.74**
NIST	**CAL018226**	**1906.34**	**0.66**	**1905.90**	**0.56**	**0.44**	**0.87**	**1.73**
NIST	**FF4190**	**1929.63**	**0.64**	**1929.61**	**0.56**	**0.02**	**0.85**	**1.70**
NIST	**CAL018216**	**1969.34**	**0.75**	**1969.07**	**0.55**	**0.27**	**0.93**	**1.86**
NIST	**CAL018191**	**1970.9**	**0.74**	**1970.71**	**0.56**	**0.19**	**0.93**	**1.85**
NMIJ	CPB-28035	1797.30	0.65	1796.37	0.57	0.93	0.87	1.73
NMIJ	CPB-28219	2198.30	0.65	2197.62	0.63	0.68	0.90	1.81
NOAA	FB03578	1812.10	1.30	1814.25	0.57	-2.15	1.42	2.84
NOAA	FB03593	2208.90	1.40	2213.93	0.64	-5.03	1.54	3.08
NPL	221727	1799.40	1.80	1800.59	0.57	-1.19	1.89	3.77
NPL	233097	2199.60	2.20	2201.31	0.63	-1.71	2.29	4.58
VNIIM	D 249682	1812.90	1.30	1810.29	0.57	2.61	1.42	2.84
VNIIM	D 249845	2214.60	1.25	2214.87	0.64	-0.27	1.40	2.81
VSL	D 249292	1798.29	2.00	1797.70	0.58	0.59	2.08	4.16
VSL	D 249289	2196.33	2.40	2195.72	0.62	0.61	2.48	4.96

Table 21. Difference Δx_{CH4} of CH_4 mole fractions assigned by participants from predicted values using Method CRDS 2 for the twenty two gas standards in the validation study set. NIST validation standards are shown in bold type.

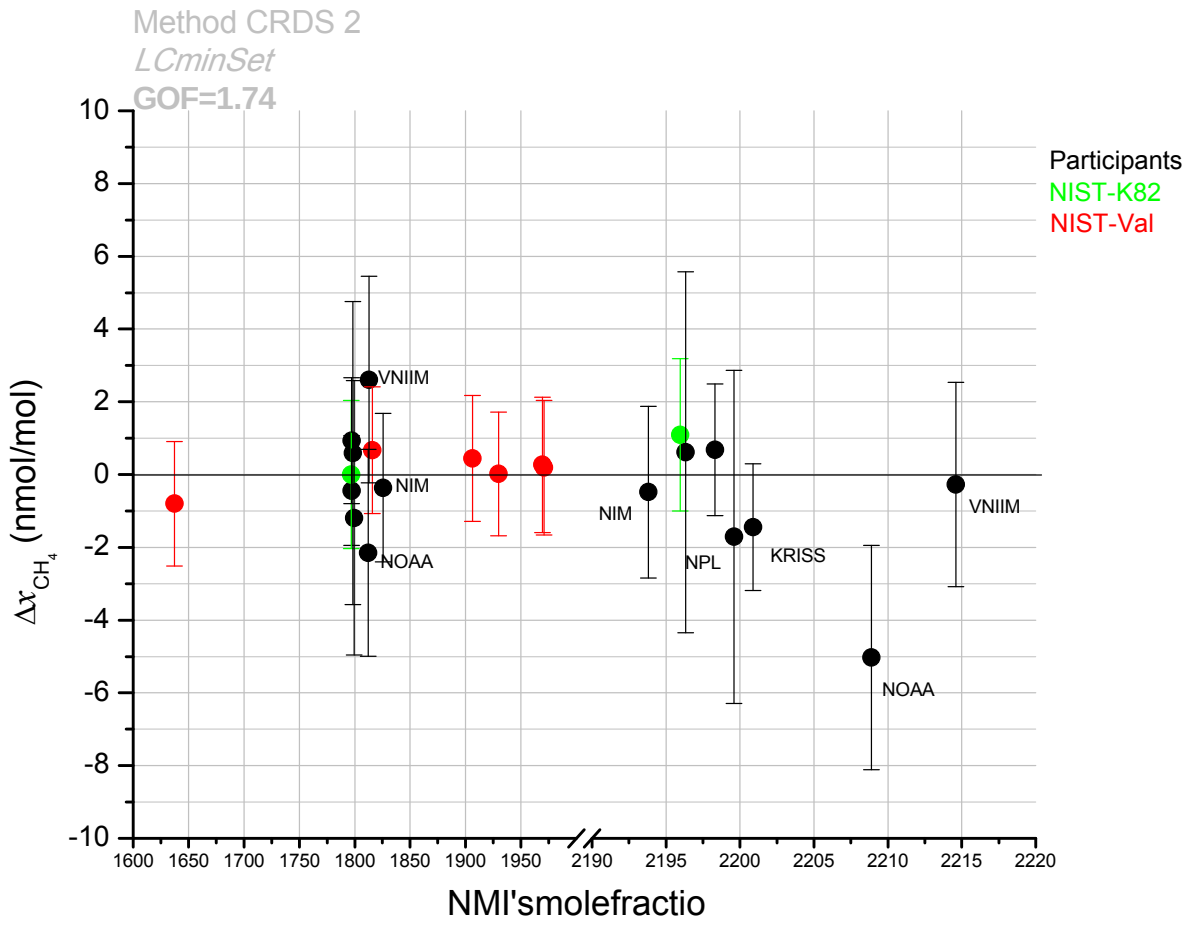


Figure 29. Difference between CH_4 gravimetric mole fractions and predicted values using CRDS Method 2, including CCQM-K82 participants (black dots) and NIST validation cylinders (red dots). The error bar represents the expanded uncertainty at a 95 % level of confidence.

Participant	Number of Cylinder	Assigned NMI's CH_4 mole fraction x_{NMI} (nmol/mol)	Assigned NMI's Standard uncertainty K=1 $u(x_{NMI})$ (nmol/mol)	$\overline{R}_{wGC\_Pred}$ (nmol/mol)	$u(\overline{R}_{wGC\_Pred})$ (nmol/mol)	$\Delta x_{CH_4} = (x_{NMI} - \overline{R}_{wGC\_Pred})$ (nmol/mol)	$u(\Delta x_{CH_4})$ (nmol/mol)	$U(\Delta x_{CH_4})$ (k=2) (nmol/mol)
KRISS	D 929248	1797.10	0.50	1797.56	0.53	-0.46	0.73	1.46
KRISS	D 985705	2200.90	0.60	2202.80	0.61	-1.90	0.85	1.71
NIM	CAL017763	1825.20	0.85	1825.76	0.53	-0.56	1.00	2.00
NIM	CAL017790	2193.80	1.00	2194.04	0.60	-0.24	1.16	2.33
NIST	FB03569	1796.76	0.85	1796.58	0.53	0.18	1.00	2.00
NIST	FB03587	2195.96	0.84	2194.83	0.60	1.13	1.03	2.07
NIST	**CAL018193**	**1637.42**	**0.56**	**1638.09**	**0.58**	**-0.67**	**0.81**	**1.61**
NIST	**FF4234**	**1815.72**	**0.66**	**1815.16**	**0.50**	**0.56**	**0.83**	**1.65**
NIST	**CAL018226**	**1906.34**	**0.66**	**1905.81**	**0.46**	**0.53**	**0.80**	**1.61**
NIST	**FF4190**	**1929.63**	**0.64**	**1929.45**	**0.49**	**0.18**	**0.81**	**1.61**
NIST	**CAL018216**	**1969.34**	**0.75**	**1969.23**	**0.46**	**0.11**	**0.88**	**1.76**
NIST	**CAL018191**	**1970.9**	**0.74**	**1971.24**	**0.48**	**-0.34**	**0.88**	**1.76**
NMIJ	CPB-28035	1797.30	0.65	1796.28	0.54	1.02	0.85	1.69
NMIJ	CPB-28219	2198.30	0.65	2197.29	0.60	1.01	0.89	1.78
NOAA	FB03578	1812.10	1.30	1814.20	0.52	-2.10	1.40	2.80
NOAA	FB03593	2208.90	1.40	2214.07	0.61	-5.17	1.53	3.05
NPL	221727	1799.40	1.80	1800.66	0.54	-1.26	1.88	3.76
NPL	233097	2199.60	2.20	2200.76	0.60	-1.16	2.28	4.56
VNIIM	D 249682	1812.90	1.30	1810.01	0.56	2.89	1.41	2.83
VNIIM	D 249845	2214.60	1.25	2214.44	0.61	0.16	1.39	2.78
VSL	D 249292	1798.29	2.00	1797.92	0.52	0.37	2.07	4.14
VSL	D 249289	2196.33	2.40	2195.55	0.58	0.78	2.47	4.94

Table 22. Difference Δx_{CH4} of CH_4 mole fractions predicted from the analysis function GC-FID versus gravimetric values assigned by participants for the twenty two gas standards in the validation study set. NIST validation standards are shown in bold type.

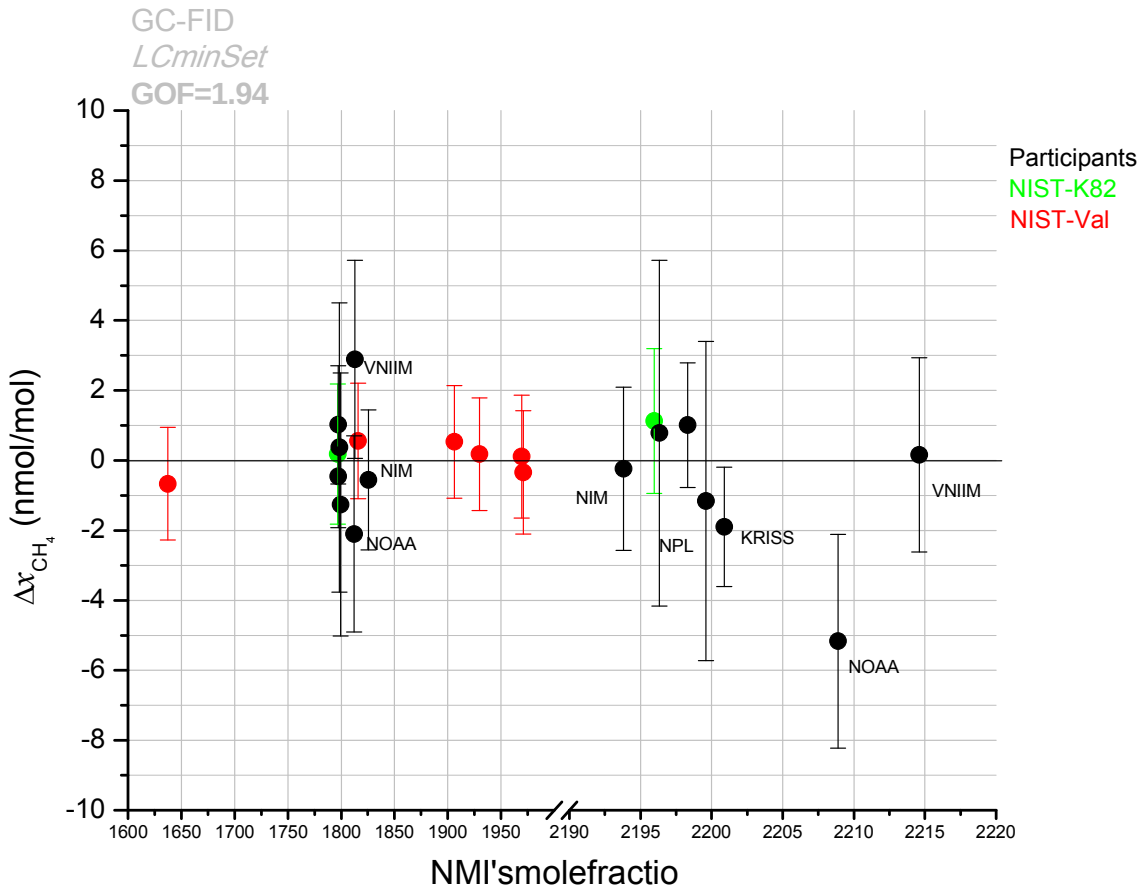


Figure 30. Difference between CH_4 gravimetric mole fractions and predicted values using GC-FID analysis, including CCQM-K82 participants (black dots) and NIST validation cylinders (red dots). The error bar represents the expanded uncertainty at a 95 % level of confidence.

Analysis of effect of input port and regulator on method reported uncertainties

The variability in BIPM measurement results introduced by using either different regulators or different input ports of the auto sampler was studied.

Input ports consistency test:

A consistency test was performed using a manifold to simultaneously connect all the auto-sampler inputs to a single cylinder with a single pressure reducer then analysing the measurements given by each port to a control cylinder.

Three repeats of this analysis led to the conclusion that all the input ports where equivalent within the measurement uncertainties (the standard deviation of the 36 ratios measured during the test was equivalent to: 0.14 nmol/mol). The measurements were performed from November 29 to December 3 2012.

Pressure reducer consistency test:

This test was performed using a manifold to simultaneously connect one cylinder to all pressure reducers, each connected to an input port of the auto-sampler. Measurements were also repeated three times and again no difference was found within the measurement uncertainties (the standard deviation of the 36 ratios measured was equivalent to: 0.13 nmol/mol). The measurements were performed from December 6 to 7 2013.

In the current uncertainty budgets described in this report, no component of uncertainty has been included for port and regulator effect, as they were assumed negligible in comparison to the uncertainty arising from instrument repeatability.

ANNEX 4- Potential biases due to isotope ratio effects

Previous publications[3] have concluded that the isotopic bias for CH_4 measurements with CRDS are not significant as the potential bias is of the same magnitude as their reported analytical precision of their CRDS instrument of ±0.3 nmol mol^{-1}.

This conclusion is re-examined taking into account the uncertainties reported in this comparison. Assuming that pure methane used in the preparation of standards originates from natural gas, the reported[4] mean isotopic composition and (±1 SD) range around the mean that could be expected is –(43±7) ‰ for δ^{13}C (VPDB) and –(185±20) ‰ for δD (VSMOW). Gas samples at the extremes of this range would lead[3] to biases in the CRDS measured methane mole fraction values of +0.34 nmol mol^{-1} and -0.38 nmol mol^{-1}. Considering a rectangular probability distribution between these limits, allows a type B standard uncertainty to be calculated to cover potential variations in CRDS measurements occurring due to potentially different isotopic mixtures in the gas measured, u_δ =0.21 ppb. This is an additional uncertainty component that should be added to CRDS methods used to compare standards produced with different methane source.

The final expression to determine the global uncertainty for each cylinder using CRDS method 2 is given in section 1.2.3 by the equation 38. This corresponds to a relative standard uncertainty of 0.025 %, using the largest values obtained in a conservative approach. Adding an uncertainty component to cover variance arising in CRDS response due to possible isotopic variation in the methane in different standards (u_δ, was computed to be 0.21 ppb) would result in a value of $u(\bar{R}_2)$ of 0.031% when expressed as a relative standard uncertainty. Figure 31 plots the Youden Plot without (a) and with (b) such additional uncertainty component to cover variance arising in CRDS response due to possible isotopic variation. As can be observed (Figure 31) the addition of the extra contribution to the uncertainty in CRDS measurements of methane mole fractions arising from possible isotopic variation in the standards has no significant effect on their level of compatibility.

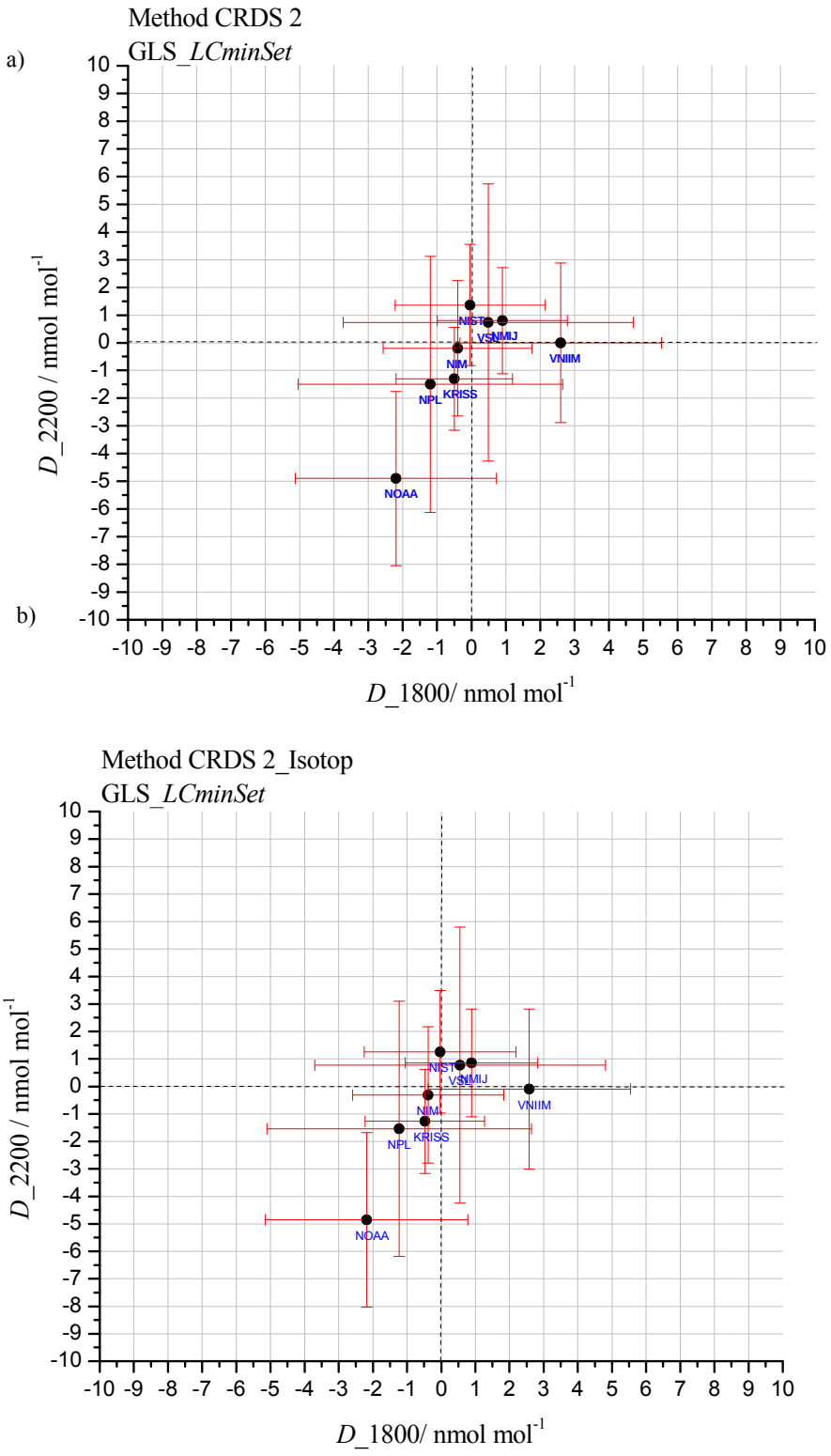


Figure 31. Youden Plot of the CCQM-K82 results. The error bar represents the expanded uncertainty at a 95 % level of confidence.

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(2) ISO."Gas analysis- Comparison methods for determining and checking the composition of calibration gas mixtures".2001.

(3) Nara, H.; H. Tanimoto; Y. Tohjima; H. Mukai; Y. Nojiri; K. Katsumata; C. W. Rella. *Atmos. Meas. Tech.* 2012, 5(11): 2689-2701.

(4) Quay, P.; J. Stutsman; D. Wilbur; A. Snover; E. Dlugokencky; T. Brown. *Global Biogeochemical Cycles* 1999, 13(2): 445-461.