International comparison CCQM-P41 Greenhouse gases.
1. Measurement Capability

Final Report

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Field

Amount-of-substance

Subject

Greenhouse gases (methane and carbon dioxide in air)

Participants

NMIA[1] (AU), BAM (DE), CEM (ES), IMGC (IT), NMIJ (JP), KRISS (KR), CENAM (MX), NMi VSL (NL), GUM (PO), NPL (UK), NIST (US)

Laboratories of the WMO[2]: CSIRO-AR (AU), NOAA (US)

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[1] At the time of participation, NMIA was known as CSIRO-National Metrology Laboratory
[2] WMO = World Meteorological Organisation

Organising body

CCQM

Rationale

The World Meteorological Organization (WMO) coordinates worldwide monitoring of greenhouse gases in the background atmosphere. Emissions of the key greenhouse gases such as carbon dioxide and methane are increasing as a result of human activities and are implicated in global climate change. In 1992, the United Nations Framework Convention on Climate Change was established, resulting in the proposal of legally binding limits (the 1997 Kyoto Protocol) aimed at reducing these emissions. The accuracy and traceability of greenhouse gas monitoring over the global space-scale and the decade-to-century time-scale of the enhanced greenhouse effect become critical issues, with an increasing role for National Metrology Institutes (NMIs).

Systematic bias that can occur in the field sampling and laboratory measurement of the real atmosphere, and the high-precision requirements of monitoring background atmospheric values, present significant challenges in linking the atmospheric observations to SI units. This paper describes a comparison to evaluate the measurement capability of representatives of the NMI and WMO community for measuring methane and carbon dioxide at atmospheric levels in synthetic air mixtures.

Measurement standards

The gas mixtures have been prepared gravimetrically at NMi VSL, the coordinating laboratory. The nominal compositions of the mixtures are given in table 1.

Table 1: Specification for mixtures for comparing measurement capabilities

Component	x **(mmol/mol)**
Methane	0.0018
Carbon dioxide	0.365
Argon	9.3
Oxygen	209
Nitrogen	balance

The mixtures have been prepared using two kinds of pre-mixtures:

1. methane and carbon dioxide in nitrogen
2. argon in oxygen

The latter pre-mixture was bought as mixture, made of highest quality argon and oxygen. If the pre-mixture of oxygen and argon had been prepared in-house, the same quality of argon and oxygen would have been used. The argon in oxygen mixture was checked for composition and impurities (in particular carbon dioxide and methane). The other pre-mixture, containing methane and carbon dioxide in nitrogen was made by the coordinating laboratory using nitrogen (grade 6.0) checked specifically for carbon dioxide and methane.

The mixtures have been checked for composition by means of verification with GC-FID[3] (methane) and GC-TCD[4] (carbon dioxide).

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[3] GC-FID = Gas chromatography with flame ionisation detector

[4] GC-TCD = Gas chromatography with thermal conductivity detector

Schedule

The revised schedule of the project has been as follows:

January 15 2003	Shipment of cylinders to participants
March 31 2003	Measurement of cylinders by participants
March 31 2003	Reports due from participants

Measurement protocol

The measurement protocol requested each laboratory to perform at least 3 measurements, with independent calibrations. The replicates, leading to a measurement, were to be carried out under repeatability conditions. The protocol informed the participants about the nominal concentration ranges. The laboratories were also requested to submit a summary of their uncertainty evaluation used for estimating the uncertainty of their result. These descriptions are added as annexes to this report.

Measurement equation

The measurement model has been taken from the CCQM-K1 [1] with the modifications as made for CCQM-K3 [2] and EUROMET.QM-K3 [3]. The mixtures are prepared by means of gravimetry [1,4]; the evaluation of measurement uncertainty of the preparation procedure has been described elsewhere [5].

Four groups of uncertainty components have been considered for the preparation process:

1. gravimetric preparation (weighing process)
2. purity of the parent gases
3. stability of the gas mixture
4. correction due to partial recovery of a component

There has been no evidence that there would be any relevant effect of adsorption, so that only the first three groups of uncertainty components appear in the model for evaluating the uncertainty from gravimetry

$$u^2\left(x_{prep}\right) = u^2\left(x_{weighing}\right) + u^2\left(\Delta x_{purity}\right) + u^2\left(\Delta x_{stab}\right) \qquad (1)$$

where x_{prep} denotes the amount-of-substance fraction as obtained from gravimetry, Δx_{purity} the correction to it from purity verification, and Δx_{stab} the correction due to instability. The latter correction is set to zero.

Measurement methods

The methods of measurement and calibration methods used by the participating organisations in this comparison for carbon dioxide are listed in table 2.

Table 2: Measurement and calibration methods (carbon dioxide)

Laboratory	Measurement method	Calibration method	Traceability
IMGC	NDIR	GLS[5], linear, 3 mixtures	NPL
CENAM	GC-FID, methaniser	GLS, 4 mixtures	own gravimetric standards
CEM	GC-TCD	GLS, linear, 3 mixtures	NMi VSL
NOAA	NDIR	Bracketing	WMO
NIST	NDIR	GLS, linear, 4 mixtures	own gravimetric standards

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[5] GLS = Generalised least squares as defined in ISO 6143 [14]

Laboratory	Measurement method	Calibration method	Traceability
KRISS	NDIR	3 mixtures	own gravimetric standards
CSIRO-AR	GC-FID, Ni-kat	9 mixtures	WMO
NMIJ	GC-FID, Ni-kat	GLS, linear, 3 mixtures	own gravimetric standards
NMi VSL	GC-TCD	OLS[6], linear, 6 mixtures	own gravimetric standards
NMIA	GC-TCD	bracketing	own gravimetric standards
NPL	GC-TCD	Series of ratio measurements	own gravimetric standards

The methods of measurement and calibration methods used by the participating organisations in this comparison for measuring methane are shown in table 3.

Table 3: Measurement and calibration methods (methane)

Laboratory	Measurement method	Calibration method	Traceability
IMGC	GC-FID	GLS, linear, 3 mixtures	NPL
CENAM	GC-FID	GLS, 3 mixtures	own gravimetric standards
CEM	GC-FID	GLS, linear, 3 mixtures	NMi VSL
NOAA	GC-FID	Bracketing	WMO
NIST	GC-FID	GLS, linear, 4 mixtures	own gravimetric standards
KRISS	GC-FID	3 mixtures	own gravimetric standards
CSIRO-AR	GC-FID	2 mixtures	WMO
NMIJ	GC-FID	GLS, linear, 3 mixtures	own gravimetric standards
NMi VSL	GC-FID	OLS, linear, 9 mixtures	own gravimetric standards
NMIA	GC-FID	Bracketing	own gravimetric standards
NPL	GC-FID	Series of ratio measurements	own gravimetric standards

Results

Usually all participants perform analyses on the same artefact and the key comparison reference value is calculated from the mean of the individual results. In the current comparison on gas mixtures, measurements were performed on individually prepared gas mixtures with (slightly) different concentrations. Since the pilot laboratory prepared these mixtures using the same methods and materials, the individual gravimetric values can be adopted as reference values, despite the small differences that exist. The problem is that these small differences are of the same order as the differences found between the national metrological institutes, and thus influence the outcome of the comparison if it would be operated with a single reference value.

In order to evaluate the differences between the participating national metrology institutes, the difference between the gravimetric and analysed values has been taken as starting point. The results are expressed as degree of equivalence, which is expressed quantitatively by two terms: its deviation from the key comparison reference value and the uncertainty of this deviation (at a 95 % level of confidence).

The difference is defined as

$$D = x_{lab} - x_{ref} \tag{2}$$

where x_{lab} denotes the amount-of-substance fraction as measured by the participating laboratory and x_{ref} the reference value. The amount-of-substance fraction value from preparation is taken as reference value.

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[6] OLS = Ordinary least squares, as opposed to GLS as defined in ISO 6143.

The combined standard uncertainty associated with the difference in the degree of equivalence can be expressed as

$$u(D)=\sqrt{u_{lab}^2+u_{ref}^2} \tag{3}$$

and the expanded uncertainty, at a 95% confidence level

$$U(D)=k\cdot u(D) \tag{4}$$

where k denotes the coverage factor. For all degrees of equivalence, $k = 2$ (normal distribution, approximately 95% level of confidence).

In tables 4 and 5 the results of this comparison are presented. The table contains the following information

Cylinder	Identification code of cylinder
x_{ref}	Assigned amount of substance fraction of a component
u_{ref}	Standard uncertainty associated with the assigned value x_{ref}
u_{prep}	Uncertainty from preparation; combination of contributions due to gravimetry and purity analysis
u_{ver}	Uncertainty due to verification of composition of the gas mixture
x_{lab}	Result as reported by the participant
k_{lab}	Coverage factor as reported by participant
U_{lab}	Expanded uncertainty as reported by participant
D_i	Degree of equivalence, difference between laboratory value and the gravimetric value
$U(D_i)$	Expanded uncertainty of the degree of equivalence

The differences between gravimetric and reported value are given as degree of equivalence, that is the difference between the value measured by the laboratory and the gravimetric value and the associated expanded uncertainty.

The uncertainty of the degrees are given with $k = 2$ for all laboratories, taking into consideration both the uncertainty reported from the laboratory as well as the uncertainty from gravimetry (and validation). The combined standard uncertainty of a laboratory has been computed from U_{lab} and k_{lab}. This implies that if a laboratory used a k value deviating from $k = 2$, this information has been taken into account to obtain an estimate for the combined standard uncertainty of the result.

Table 4: Results for methane (µmol/mol)

Lab	Cylinder	x_{ref}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
IMGC	VSL138446	1.814	0.004	0.011	0.012	1.855	0.0742	2	0.041	2.27%	2	0.078	4.28%
CENAM	VSL138504	1.801	0.004	0.011	0.011	1.871	0.1022	2	0.070	3.89%	2	0.105	5.82%
CEM	VSL138511	1.792	0.004	0.011	0.011	1.796	0.026	2	0.004	0.22%	2	0.035	1.93%
NOAA	VSL138529	1.801	0.004	0.011	0.011	1.7693	0.0006	2	-0.031	-1.73%	2	0.023	1.28%
NIST	VSL138541	1.801	0.004	0.011	0.011	1.796	0.01	2	-0.005	-0.30%	2	0.025	1.39%
KRISS	VSL138558	1.800	0.004	0.011	0.011	1.7921	0.0018	2.01	-0.008	-0.44%	2	0.023	1.28%
CSIRO-AR	VSL138554	1.801	0.004	0.011	0.011	1.77082		2	-0.030	-1.68%	2	0.023	1.28%
NMIJ	VSL138572	1.801	0.004	0.011	0.011	1.7802	0.0089	2	-0.021	-1.17%	2	0.025	1.37%
NMi VSL	VSL138586	1.803	0.004	0.011	0.012	1.8024	0.03	2	-0.001	-0.04%	2	0.038	2.10%
NMIA	VSL138542	1.799	0.004	0.011	0.011	1.81	0.02	2.26	0.011	0.61%	2	0.029	1.61%
NPL	VSL138495	1.803	0.004	0.011	0.012	1.802	0.018	2	-0.001	-0.04%	2	0.029	1.62%

Table 5: Results for carbon dioxide (µmol/mol)

Lab	Cylinder	x_{ref}	u_{prep}	u_{ver}	u_{ref}	x_{lab}	U_{lab}	k_{lab}	Δx	$\Delta x/x$	k	$U(\Delta x)$	$U(\Delta x)/x$
IMGC	VSL138446	367.710	0.128	0.121	0.177	367.90	0.63	2	0.190	0.05%	2	0.718	0.20%
CENAM	VSL138504	364.770	0.131	0.120	0.178	367.02	3.05	2	2.250	0.62%	2	3.069	0.84%
CEM	VSL138511	362.980	0.127	0.120	0.174	360.80	3.70	2	-2.180	-0.60%	2	3.716	1.02%
NOAA[7]	VSL138529	364.680	0.129	0.120	0.177	364.68	0.13	2	0.000	0.00%	2	0.376	0.10%
NIST	VSL138541	365.170	0.126	0.121	0.174	364.54	0.41	2	-0.630	-0.17%	2	0.538	0.15%
KRISS	VSL138558	364.600	0.130	0.120	0.177	364.61	0.048	2	0.006	0.00%	2	0.358	0.10%
CSIRO-AR	VSL138554	365.120	0.124	0.120	0.173	364.77		2	-0.350	-0.10%	2	0.346	0.09%
NMIJ	VSL138572	365.160	0.130	0.121	0.177	366.68	0.32	2	1.520	0.42%	2	0.477	0.13%
NMi VSL	VSL138586	365.530	0.126	0.121	0.175	365.87	0.7	2	0.340	0.09%	2	0.782	0.21%
NMIA	VSL138542	364.400	0.130	0.120	0.177	365.81	1.66	2.26	1.410	0.39%	2	1.511	0.41%
NPL	VSL138495	365.140	0.130	0.120	0.177	365.20	0.73	2	0.060	0.02%	2	0.811	0.22%

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[7] Uncertainty is relative to the WMO scale

Measurement traceability of the WMO laboratories

Laboratories within the WMO atmospheric composition monitoring community have two main calibration objectives, to:

1) maintain adequate stability of their laboratories' internal calibration scales and thereby ensure that the atmospheric records they produce are internally consistent in describing spatiotemporal trends

2) maintain close links with other WMO laboratories so that atmospheric data may be reliably merged across multiple laboratories and methods (e.g. GLOBALVIEW-CO_2 2002, GLOBALVIEW-CH_4 2001).

The absolute accuracy of calibration scales used within these programs is usually of secondary importance for interpretation of atmospheric data. A key point to be made here is that for most trace gas species, WMO laboratories can "intercalibrate" more precisely through measurement of air standards than by independently maintaining links to an absolute scale. For example, the WMO CO_2 Calibration Scale is linked to fundamental constants with an uncertainty of about ±0.1 μmol mol^{-1}, yet some laboratories can intercalibrate through exchange of air standards to better than ±0.05 μmol mol^{-1} [6]. This type of disparity is larger for many other trace gas species. Where links to fundamental constants do play a critical role is in providing a benchmark against which to assess and/or define stability of calibration scales, providing these links are sufficiently precise to satisfy the scientific questions being addressed.

Degrees of equivalence

The degrees of equivalence for methane are shown in figure 1. The error bars represent the expanded uncertainty at a 95 % level of confidence. Except for NOAA and CSIRO-AR, all uncertainty bars overlap with the reference value. Possible explanations for NOAA can be that the result is traceable to the WMO scale and/or the uncertainty, given as a standard deviation is only the repeatability of measurement. CSIRO-AR did not state an uncertainty for the methane measurement in its report, which may well explain the observation made above. Between the two WMO laboratories, there is good agreement.

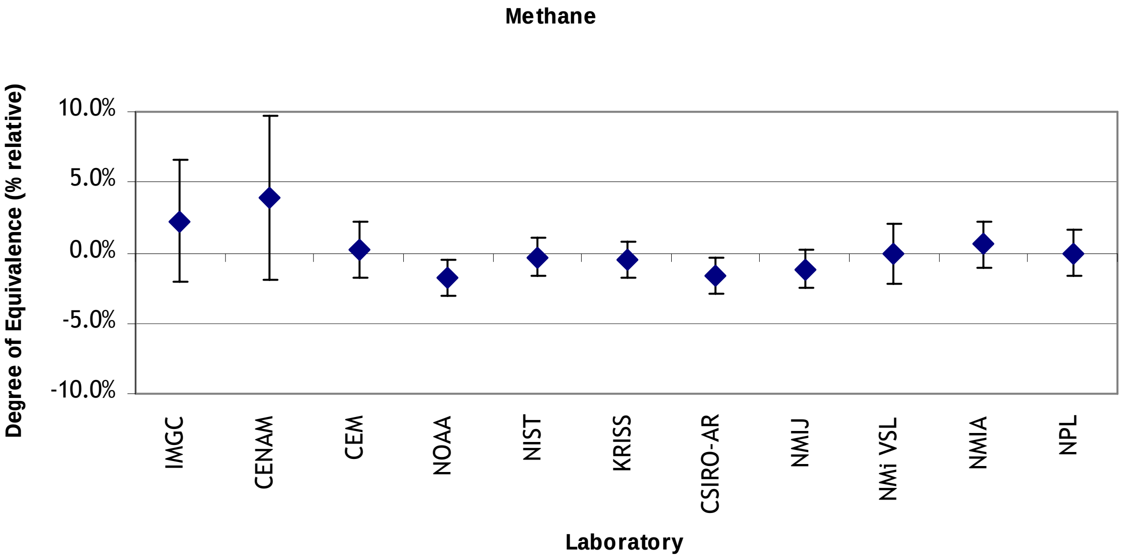

Figure 1: Degrees of equivalence for methane

Comparing the results of the WMO laboratories (NOAA and CSIRO-AR) with the NMIs, it seems that *on average* the results for methane are somewhat higher for the NMI, yet the difference is meaningful.

Both WMO laboratories participating in this exercise (NOAA and CSIRO-AR) report their data in the same nominal CO_2 and CH_4 scales. NOAA is the designated central calibration laboratory (CCL) for maintenance of the WMO CO_2 Calibration Scale and propagation of this scale to other WMO laboratories. The WMO scale is defined and maintained using a manometric technique [7]. CSIRO-AR report their gas chromatography data in this scale, but acknowledge uncertainty in propagating the scale from NOAA to CSIRO-AR and in maintaining stability within CSIRO-AR's internal calibration scheme (see measurement report annexed to this report).

The CH_4 scale maintained by NOAA since 1983 [8,9] was derived from a scale originally established by R. Rasmussen at the Oregon Graduate Center. The NOAA scale was later (in 1990) propagated to CSIRO-AR. Unlike for CO_2, there has been no central CH_4 calibration laboratory within the WMO community until recently (when NOAA was designated as such in September, 2003), and the NOAA scale is not universally used by all WMO laboratories. This scale is known to be inaccurate in absolute terms.

For example, NOAA have participated in intercomparison exercises with Meteorological Research Institute / Geochemical Research Laboratory (MRI) of Tsukuba, Japan [10] and Tohoku University (TU), Japan [11]. The scales of both Japanese laboratories are referenced to CH_4-in-air mixtures gravimetrically prepared by Nippon Sanso Corporation of Japan. Matsueda [10] reported results from MRI/NOAA inter-calibration of a single, high pressure cylinder, yielding a difference of 0.0230 μmol mol^{-1} at 1.7545 μmol mol^{-1} on the MRI scale. This implies a scale relationship of 1.01328 ± 0.00107 (MRI/NOAA) with the uncertainty referring only to precision of measurement.

As suggested by Matsueda [10], the true uncertainty is likely to be higher due to uncertainty in quantification of residual CH_4 (estimated to be 0.0355 μmol mol^{-1}) in the diluent zero air used for the gravimetric preparations. The TU/NOAA inter-calibration reported by Nakazawa et al. [11] compared 3 standards with CH_4 mole fractions of 1.0000, 1.5500 and 2.1800 μmol mol^{-1}. An average difference of 0.0226 ± 0.0008 μmol mol^{-1} was reported, implying a scale ratio of 1.01454 (TU/NOAA) if the difference is applied to the mean mole fraction of all 3 standards. The TU gravimetric standards were prepared at a later date than those of MRI, and using zero air with lower residual CH_4 (Professor Nakazawa, TU, personal communication).

Based on these results, the value reported by NOAA on the NOAA scale as part of the international comparison reported here would be expected to be too low by approximately 0.025 at a CH_4 mole fraction of 1.801 μmol mol^{-1}. This can account for most of the difference (0.031 μmol mol^{-1}) from the gravimetric value in table 5.

CSIRO-AR has obtained and measured a suite of CH_4-in-air mixtures that were also prepared by Nippon Sanso but using a less accurate, volumetric technique. The high precision CH_4 assignments come from extensive analysis at TU against their gravimetrically derived scale. The intercomparison yielded a TU/CSIRO-AR scale ratio of 1.01192 ± 0.00033 (uncertainty due to reproducibility only), equivalent to a difference of 0.021 μmol mol^{-1} (as compared to 0.030 in table 5) at 1.801 μmol mol^{-1}. This estimate of the offset of the CSIRO-AR (and NOAA) scale from absolute values is slightly smaller than those obtained from intercomparisons conducted between NOAA and both MRI and TU, but is nevertheless consistent with most of the differences between NOAA and CSIRO-AR values from the gravimetrically-derived values of the coordinating laboratory (table 5) being due to the origin of the NOAA scale.

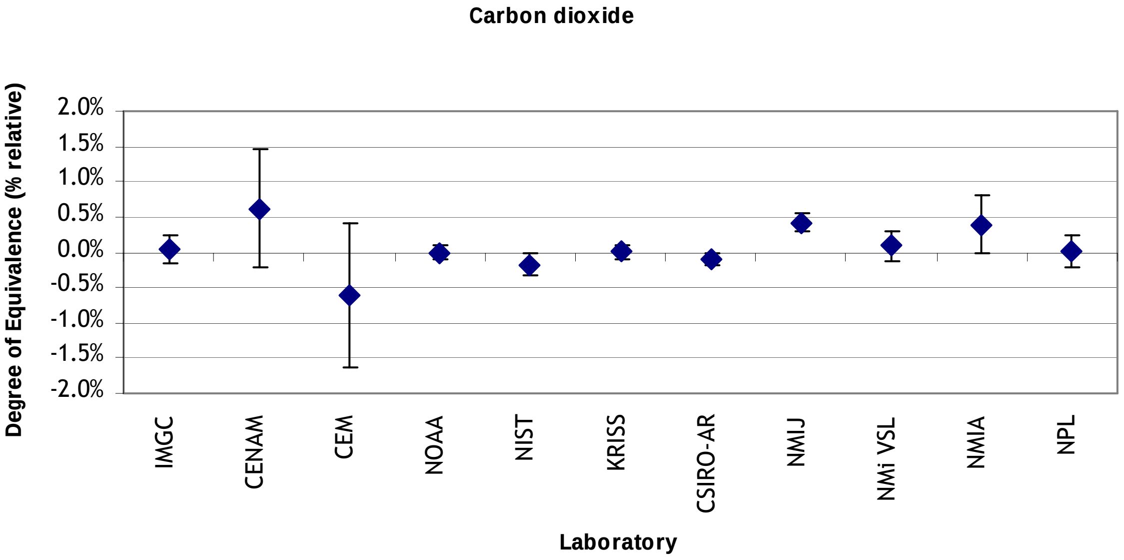

Figure 2: Degrees of equivalence for carbon dioxide

Figure 2 shows the degrees of equivalence for carbon dioxide. Laboratories CSIRO-AR and NMIJ have an uncertainty bar that does not overlap with the reference value. For laboratory CSIRO-AR, this lack over overlap can be due to the fact that no uncertainty of measurement is stated with the result. The overall agreement is good, and there is no indication that there is a systematic difference between the WMO laboratories and the NMIs for carbon dioxide.

Conclusions

There is good agreement between the results of the participants in this comparison for both methane and carbon dioxide. The results for methane agree within 4 % relative, and for most participants even within 2 % relative at an amount of substance fraction level of 1.8 µmol/mol. For carbon dioxide all results agree within 1 % relative, and for most of the agreement is even better: within 0.5 % relative at an amount of substance fraction level of 365 µmol/mol.

Measurement traceability is quite differently established in NMIs and WMO laboratories. This comparison indicates good agreement between the two ‘systems’ for carbon dioxide, whereas the difference observed for methane confirms results from earlier measurement comparisons.

References

[1] Alink A., The first key comparison on Primary Standard gas Mixtures, Metrologia **37** (2000), pp. 35-49

[2] Van der Veen A.M.H, De Leer E.W.B., Perrochet J.-F., Wang Lin Zhen, Heine H.-J., Knopf D., Richter W., Barbe J., Marschal A., Vargha G., Deák E., Takahashi C., Kim J.S., Kim Y.D., Kim B.M., Kustikov Y.A., Khatskevitch E.A., Pankratov V.V., Popova T.A., Konopelko L., Musil S., Holland P., Milton M.J.T., Miller W.R., Guenther F.R., International Comparison CCQM-K3, Final Report

[3] Van der Veen A.M.H., Van Wijk J.I.T., Van Otterloo R.P., Wessel R.M., De Leer E.W.B., Novak J., Sega M., Rakowska A., Castanheira I., Botha A., Musil S., “EU-

ROMET.QM-K3: automotive emission gas measurements", Metrologia **39** (2002), Technical Supplement 08005

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

[5] 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

[6] Toru S., Kazuto S. (eds), "Report of the 11th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Techniques, Tokyo, Japan (25-28 September 2001)" WMO TD No. 1138, Geneva, Switzerland

[7] Zhao, C.L., Tans P.P., Thoning K.W., "A high precision manometric system for absolute calibration of CO_2 in dry air, J. Atmos. Chem. **102** (1997), pp. 5885-5894.

[8] Dlugokencky, E.J., L.P. Steele, P.M. Lang and K.A. Masarie, The growth rate and distribution of atmospheric methane, *J. Geophys. Res.*, 99, 17021-17043, 1994.

[9] Steele, L.P., P.J. Fraser, R.A. Rasmussen, M.A.K. Khalil, T.J. Conway, A.J. Crawford, R.H. Gammon, K.A. Masarie and K.W. Thoning, The global distribution of methane in the atmosphere, *J. Atmos. Chem.*, 5, 125-171, 1987.

[10] Matsueda, H., Intercalibration experiment of methane standard gas scale between NOAA/CMDL and MRI/GRL, *Papers in Meteorology & Geophysics*, 44, 45-56, 1993.

[11] Nakazawa, T., T. Machida, M. Tanaka, Y. Fujii, S. Aoki and O. Watanabe, Differences of the atmospheric CH_4 concentration between the Arctic and Antarctic regions in pre-industrial/pre-agricultural era, *Geophys. Res. Lett.*, 20, 943-946, 1993.

[12] Plassa M., Mosca M., Sega M. "Carbon Dioxide Determination for High Accuracy Weighings" in: *Proceedings of the 16th International Conference IMEKO TC3/APMF '98*, Myung Sai Chung Ed.; Taejon, Korea, **1998**, pp. 183-191

[13] Cox M.G., "The evaluation of key comparison data", *Metrologia*, 2002, **39**, 589-595

[14] International Organization for Standardization, "ISO 6143 Gas analysis - Determination of composition of calibration gas mixtures - Comparison methods", ISO, Geneva, 2001

[15] International Organization for Standardization, "ISO 11095 Linear calibration using reference materials", ISO, Geneva, 1996

[16] Keeling, C.D., Guenther P.R., Moss D.J., "Scripps reference gas calibration system for carbon dioxide-in-air standards: revision of 1985", WMO Environmental Pollution Monitoring and Research Programme No. 42 (1986), Technical Document WMO/TD-No. 125, 42 pp.

[17] Thoning, K.W., Tans P.P., Conway T.J., Waterman L.S., "NOAA/GMCC calibrations of CO2-in-air reference gases: 1979-1985", NOAA Tech. Memo. ERL ARL-150 (1987), 63 pp.

[18] GLOBALVIEW-CH4: Cooperative Atmospheric Data Integration Project - Methane. CD-ROM, NOAA CMDL, Boulder, Colorado [Also available on Internet via anonymous FTP to ftp.cmdl.noaa.gov, Path: ccg/ch4/GLOBALVIEW], 2001.

[19] GLOBALVIEW-CO2: Cooperative Atmospheric Data Integration Project - Carbon Dioxide. CD-ROM, NOAA CMDL, Boulder, Colorado [Also available on Internet via anonymous FTP to ftp.cmdl.noaa.gov, Path: ccg/co2/GLOBALVIEW], 2002.

[20] Masarie, K.A., R.L. Langenfelds, C.E. Allison, T.J. Conway, E.J. Dlugokencky, R.J. Francey, P.C. Novelli, L.P. Steele, P.P. Tans, B. Vaughn and J.W.C. White, NOAA/CSIRO Flask Air Intercomparison Experiment: A strategy for directly assessing consistency among atmospheric measurements made by independent laboratories, *J. Geophys. Res.*, 106, 20445-20464, 2001.

Measurement report of IMGC

Method

The instrument used for CO_2 determination is a NDIR analyser ABB URAS 14, with measurement range from 0 to 1000 μmol mol^{-1} and resolution of 0,1 μmol mol^{-1}. The data are visualized on the instrument display and manually recorded.

The instrument used for methane determination is a gaschromatograph CEINSTRUMENTS GC 8000 Top equipped with a flame ionisation detector. The data are recorded and collected by means of the software ChromCard (CEINSTRUMENTS).

Calibration

The Calibration Standards used are Primary Reference Gas Mixtures of CO_2 and methane in a matrix of synthetic air (i.e. argon, oxygen, and nitrogen) purchased from National Physical Laboratory (UK). They were gravimetrically prepared and their expanded uncertainties, based on a standard uncertainty multiplied by a coverage factor k=2 providing a level of confidence of approximately 95%, are from 0,3 to 0,4 μmol mol^{-1} for carbon dioxide and from 0,007 to 0,011 μmol mol^{-1} for methane. As for purity, the certificates declare that all the components had a stated purity of 99,999% or better and no significant levels of carbon dioxide or methane were found in the argon, oxygen and nitrogen.

1) Carbon dioxide

Three standards were used at the following concentrations:

- CO_2 328,7·μmol mol^{-1} U = 0,3 μmol mol^{-1}
- CO_2 363,7 μmol mol^{-1} U = 0,4 μmol mol^{-1}
- CO_2 401,9 μmol mol^{-1} U = 0,4 μmol mol^{-1}

The measurements were carried out at a flow from 58 to 62 L h^{-1}. It was previously proved that this flow variation does not affect the measurement value. The instrument readings were collected after the signal stabilization, i.e. 2 minutes.
No correction for ambient pressure was made because the instrument had been calibrated every day in which measurements were carried out according to the following measurement protocol:
Standard N. 1, Sample, Standard N. 2, Sample, Standard N. 3, Sample, (repeated 3 times).
No correction for ambient temperature was made.
Three different calibration curves were determined, one for each measurement day and they were used to estimate the final result for CO_2.

2) Methane

Three standards were used at the following concentrations:

- CH_4 1,301 μmol mol^{-1} U = 0,007 μmol mol^{-1}
- CH_4 1,799·μmol mol^{-1} U = 0,009 μmol mol^{-1}
- CH_4 2,176 μmol mol^{-1} U = 0,011·μmol mol^{-1}

As for methane, gas-chromatographic injections were made by means of a sampling valve, maintained at a temperature of 30°C. No correction for ambient temperature was made. The ambient pressure was recorded at each injection and the measured response was corrected to standard pressure using the following equation:

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

where:

$R_{c,\,st}$ is the response corrected to standard pressure
R_c is the measured response
p_c is the ambient pressure, [kPa]
p_{st} is standard atmospheric pressure (101,325 kPa)

Measurements were carried out according to the following measurement protocol: Standard N. 1, Sample, Standard N. 2, Sample, Standard N. 3, Sample, (repeated 3 times). Three different calibration curves were determined, one for each measurement day and they were used to estimate the final result for methane.

3) Determination of calibration curves

For both analytes the calibration curves were determined by means of an Excel worksheet, developed at IMGC, based on the Weighted Least Squares method, which calculates a linear correction to be applied to the instrument readings according to the following equation:

$x = y + d(y) = y + \alpha_0 + \alpha_1 y$ (2)

where x is concentration of the analyte in the reference gas mixtures, y is the instrument output and $d(y) = \alpha_0 + \alpha_1 y$ is the correction. The measurands are the polynomial coefficients α_0 and α_1. The estimation algorithm takes care of different sources of uncertainty: the reference gas mixtures uncertainty, the repeatability of the instrument, the lack of fit, the instrument resolution. Being the reference gas mixtures purchased by the same producer, a correlation coefficient of 0,9 was adopted in the calculation. For detailed information see the reference [12].

Evaluation of measurement uncertainty

The contributions to the combined standard uncertainty of the results are due to the calibration curve and to repeatability of readings of sample measurements. From each of the three calibration curves a CO_2 concentration value with its combined standard uncertainty was estimated. The final result is the mean of these three values and its combined standard uncertainty is the largest one among the obtained uncertainties, as they were very close.

The contribution of calibration curve takes into account different sources: the reference gas mixtures uncertainty, the repeatability of the instrument, the lack of fit, the instrument resolution. These sources are merged together in the Excel worksheet for calibration curves calculation, hence it is very difficult to separate each contribution.

After the calibration process α_0 and α_1 being known, if a set of n_r instrument readings, arranged in a vector r, are to be corrected by the calibration algorithm, the matrix R can be defined, whose columns are the first two powers of r:

$R = (r^0 \;\; r)$

The correction vector $d(r)$ can be computed from $d(r) = R\,\alpha$, where α is the vector of the coefficients α_0 and α_1. The corrected readings are:

$q = d(r) + r$ (3)

The covariance matrix of the readings is $\psi_r = s^2\mathbf{I}$, where s is the repeatability standard uncertainty of the instrument and I an identity matrix. The covariance matrix ψ_d of d can be estimated starting from the law of propagation of uncertainty:

$$\psi_d = \nabla_\alpha(\boldsymbol{d})\ \psi_\alpha\ \nabla_\alpha(\boldsymbol{d})^{T} + \nabla_r(\boldsymbol{d})\,\psi_r\,\nabla_r(\boldsymbol{d})^{T}$$

where the symbol $\nabla_z(\boldsymbol{w})$ means the Jacobian matrix, i.e. the matrix derivative, of the vector *w* with respect to the vector *z* and ψ_α is the variance-covariance matrix of the coefficients α_0 and α_1.

From eq. 3 it follows that the combined standard uncertainty of a result derives from a term due to the correction obtained by the calibration curve and from a term due to instrument repeatability:

$u^2_c(q) = u^2(d(r)) + u^2(r)$

Typical evaluation of the measurement uncertainty for **carbon dioxide**:

Quantity X_i	**Estimate** x_i	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$
R	365,6 µmolmol^{-1}	B	Normal	0,16 µmolmol^{-1}	1	0,16 µmolmol^{-1}
$d(r)$	2,5 µmolmol^{-1}	A	Normal	0,26 µmolmol^{-1}	1	0,26 µmolmol^{-1}

<u>Model used for evaluating measurement uncertainty for methane:</u>

Please specify how you assess the combined standard uncertainty of the result, including all components relevant for the measurement uncertainty.

The mathematical model followed to obtain the correct readings for the estimation of the concentration of methane in the unknown sample is the same as used for CO_2. From each of the three calibration curves a methane concentration value with its combined standard uncertainty was estimated. These uncertainties were non-negligibly scattered, because the contribution due to the uncertainty of the reference standard mixtures was negligible with respect to the instrument repeatability. Therefore, it was chosen to express the final result as a weighted mean, calculating the corresponding combined standard uncertainty [13].

Typical evaluation of the measurement uncertainty for **methane**:

Quantity X_i	**Estimate** x_i	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$
R	1,808* µmolmol^{-1}	B	Normal	0,033 µmol mol^{-1}	1	0,033 µmol mol^{-1}
$d(r)$	0,127 µmolmol^{-1}	A	Normal	0,031 µmol mol^{-1}	1	0,031 µmol mol^{-1}

*this value corresponds to the instrument reading expressed as an area multiplied by a numerical conversion factor.

Measurement report of CENAM

Method

Agilent Technologies 6890 Gas Chromatograph Separation System, with FID, split/splitless injector, Ratio Split 5:1, with Ni catalytic methaniser and injection valve, including Chemstation NT to collect and process data. Regulator of low pressure in the outlet of cylinder, with SS tubing of 1/16; with tandem of columns, Col. No 1: Pora-Plot U capillary of 30 m X 0.53 mm X 20 µm; Col. No 2: Pora-Plot Q capillary of 30 m X 0.53 mm X 30 µm.

Oven program: 40 °C, 8 min, isothermal
He flow = 13 ml/min (77 cm/s) , at 113 kPa, constant
Make up N_2: 20 ml/min
FID temperature = 200 °C
Injector temperature = 150 °C
Flame gases flows: air = 400 ml/min, H_2 = 60 ml/min

Calibration

The calibration standards for the measurements were primary standards (primary standard mixtures, PSMs), this mean prepared by weigh, the cylinders were weighted after each compound addition and thermal equilibrium with the room. The method used for the preparation of PSMs was the gravimetric method following the guidelines of the ISO/DIS 6142[1]. The procedure for weighing was a Borda weighing scheme (RTRTRTR). The parent gases were in all cases at least 4.0 of purity and 5.0 for balance. The purity analysis was done by GC-TCD; GC-HDID and GC-FID for the critical impurities. Their uncertainties were calculated by type B evaluation or/and type A evaluation. Dilution scheme for gas mixtures preparation has been done according to the established in Annex A.

The instrument for weighing was a Mettler balance model KB-50-2 (60 kg capacity and 10 mg resolution), serial number 2143212, and sets of weights class E2 (serial number 51496, from 1 to 5000 g – 16 pieces) and E2 (serial number 41003979, from 1 mg to 1 kg – 25 pieces) according to the R 111 of OIML, all of them traceable to CENAM.
According to ISO 6143 [14] using B_Least program software and ISO 11095 [15] for Multi-point Calibration, 4 levels to CO_2 $SmStd_1Std_2SmStd_3Std_4Sm$ five injections each and 3 levels to CH4 $SmStd_1Std_2SmStd_3Sm$ five injections each.

The set of PSM is:

Primary Standard Mixtures.

Cylinder Number	Component	Result (µmol/mol)	U
LL24118	Methane	1.0039	$4.1585 \cdot 10^{-3}$
	Carbon dioxide	350.95	$2.4955 \cdot 10^{-2}$
LL24392	Methane	1.4995	$3.1210 \cdot 10^{-3}$
	Carbon dioxide	400.2	$2.8415 \cdot 10^{-2}$
LL24305	Methane	2.5001	$3.8165 \cdot 10^{-3}$
	Carbon dioxide	301.26	$2.1408 \cdot 10^{-2}$

Cylinder Number	**Component**	**Result (µmol/mol)**	**U**
LL24409	Carbon dioxide	449.69	$3.1944\cdot10^{-2}$

Evaluation of measurement uncertainty

Model used for evaluating measurement uncertainty for methane:

The combined uncertainty has three contributions:

a) Reproducibility. For methane was evaluated by the standard deviation of the mean of nine independent measurements.

b) Repeatability. This contribution was estimated taking in consideration an specific number of replications of one independent measurement of the sample.

c) Method. This component includes the experience and probable bias related to the method for low concentration.

Typical evaluation of the measurement uncertainty for **methane**:

Quantity X_i	**Estimate x_i**	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty $u(x_i)$**	**Sensitivity coefficient c_i**	**Contribution $u_i(y)$**
Reproducibility	-----------	A	Normal	0,0257	1	0,0138
Repeatability	-----------	A	Normal	0,0164	1	0,0090
Method	-----------	B	Rectangular	0,0410	----------------	0,0228

Model used for evaluating measurement uncertainty for carbon dioxide:

Please specify how you assess the combined standard uncertainty of the result, including all components relevant for the measurement uncertainty.

The combined uncertainty has three contributions:

a) Reproducibility. For Carbon dioxide was evaluated by the standard deviation of the mean of eight independent measurements.

b) Repeatability. This contribution was estimated taking in consideration an specific number of replications of one independent measurement of the sample.

c) Method. This component includes the experience and probable bias related to the method for low concentration.

Typical evaluation of the measurement uncertainty for **carbon dioxide**:

Quantity X_i	**Estimate x_i**	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty $u(x_i)$**	**Sensitivity coefficient c_i**	**Contribution $u_i(y)$**
Reproducibility	-----------	A	Normal	0,8982	1	0,0024
Repeatability	-----------	A	Normal	0,4028	1	0,0011
Method	-----------	B	Rectangular	1,1634	----------------	0,0032

Measurement report of CEM

Method

Gas Cromatography, FID detector (CH_4), TCD detector (CO_2), column porapack, CHEMSTATION for data collection. GC configuration with valves and automatic sampler.

Calibration

The calibration standards are prepared by gravimetrical method, and then compare the results by analytical method with NMi VSL standards. The gravimetrical preparation was made in accordance with the ISO 6142 [4], and the analysis in accordance with ISO 6143 [14].

The estimated uncertainty for standards preparation was made with ISO 6142 programme [4] and for analysis with B_LEAST programme [14].

Calibration was carried out using 3 standards using the linear function of B_LEAST programme.
For CH_4, the standards concentrations were: 1,001 μmol/mol; 2,005 μmol/mol; 5,331 μmol/mol
For CO_2, the standards concentrations were: 200,0 μmol/mol; 500,0 μmol /mol; 998,9 μmol/mol

The measurement sequence in both cases was: Standard/sample/standard/standard (in increasing concentration).

There are no corrections for temperature and pressure.

Measurement report of NOAA

Preamble

Measurements of atmospheric trace gases are typically made by comparison to a "known" standard. While the accuracy of the standard is important, a precisely determined standard is even more important for the detection of small but significant spatial and temporal variations. A stable and internally consistent set of precisely determined standards is necessary to insure that observed atmospheric variations are not the result of changing composition of the standard gases. In addition, if different laboratories measuring the same gases use standards tied to the same scale, the data may be compared and combined without the uncertainty introduced by using independent standards. As discussed below, the precision of the NOAA CMDL standards is well-determined while the absolute accuracy is not as well known. It is this precision that NOAA CMDL is attempting to provide to the trace gas measurement community.

Since the mixing ratios of CO_2 and CO may change with time in some cylinders, we recommend that the cylinders be returned to the NOAA CMDL laboratories periodically for recalibration. At pressures below approximately 3500 kPa (~500 psi), drifts in some cylinders become relatively large and nonlinear. The NOAA CMDL measurement programs generally take cylinders off line, perform a final calibration, and refill them when they reach 3500 kPa (500 psi).

Method

HP 6890 GC with FID; HP 35900E A/D; CH_4 separation from air on 10’ long x1/8” o.d. Porapak Q column using N_2 carrier gas and 20% O_2 in N_2 oxidizer gas; ~5 mL sample loop; chromatograms integrated with software developed within our lab.

Calibration

CH_4 standard scale based on two commercial standards purchased in 1982 and subsequently propagated to cylinders of natural air through intensive calibration over two years. Absolute uncertainty on our scale is ±1.5% based on careful comparisons with gravimetric scales. Our scale is propagated to new cylinders with an accuracy of 0.2 nmol mol^{-1}.

Tank # MR8529 was analyzed relative to our standard tank ALM-024316 with assigned CH_4 mole fraction = 1774.4 nmol mol^{-1}. Three determinations of the CH_4 mole fraction in MR8529 were made at least 1 week apart, with 20 aliquots in each determination. Each aliquot of MR8529 was bracketed by aliquots of standard. The CH_4 mole fraction in MR8529 was calculated for each aliquot as follows: $R(MR8529)/R_{avg}(ALM\text{-}024316) \times X(ALM\text{-}024316)$. R is peak area and R_{avg} is the average of the bracketing standard’s peak heights. We assume a linear response of our FID through zero.

The CO_2 mixing ratios are reported as mole fractions in dry air (expressed as µmol/mol, or parts per million, ppm). The scale is the WMO (World Meteorological Organization) mole fraction scale, maintained by us in our role as the WMO Central CO_2 Laboratory (CCL). There are fifteen primary WMO CO_2-in-air reference gases that are analyzed manometrically once a year based on the primary quantities volume, temperature, and pressure ([7]. The range of the primaries is from 250 ppm to 520 ppm. The primaries have been analyzed independently at the Scripps Institution of Oceanography (the previous CCL) over two different time periods, and they have been compared to the previous set of WMO primary reference gases still maintained at Scripps [16]. In the range of 250-420 ppm the differences between the CMDL and Scripps analyses of the primaries are less than 0.1 ppm, but at the high end of the range the Scripps analyses are lower than CMDL's by several tenths of a ppm. Based on our error analysis of the analytical method [7], and confirmed by the comparison with the Scripps analyses, our current estimate for the absolute uncertainty of the primary scale is about 0.1 ppm.

The calibration of the primaries is transferred to a set of secondary standards by comparisons on a non-dispersive infrared (NDIR) analyzer, and from the secondaries to all other standard reference air mixtures via the same method. In any such comparison there are always four "known" cylinders, and two to four “unknowns”, to which the calibration of the “known” cylinders is transferred. The comparisons typically take place on different days separated by a week or more. We estimate the precision (1 sigma) of the overall calibration transfer from the primaries to any other standards as 0.06 ppm [17].

The repeatability of the calibrations depends also on the stability of the CO_2 mixing ratio in the cylinder. For cylinders that are stable, the repeatability is on the order of 0.01-0.04 ppm.

Evaluation of measurement uncertainty

Repeatability and selectivity of the analyser: Separation scheme and FID are extremely selective for CH_4. Relative uncertainty in measurement of each aliquot on order of 0.03%.

Appropriateness of the calibration curve (model and its residuals): Linear response of FID has been tested over the nominal range 30 to 2500 nmol mol^{-1}.

Measurement report of NIST

Method

Carbon dioxide was measured using a non-dispersive infrared (NDIR) spectroscopic analyzer. Measurements were made using an instrument range span of 125 part-per-million (ppm). A zero offset or suppressed measuring range was used by using a secondary calibration mixture with a nominal amount of substance value (concentration) of approximately 370 ppm CO_2 as the reference gas supplied to the reference cell. Sample flow of gas in cylinder MR 8541 was controlled by a high-pressure flow controller supplied by NMi VSL. A high-pressure needle valve controlled the sample flow of gas in the NIST calibration mixtures and in the reference gas mixture.

Methane was measured using gas chromatography with a flame Ionization detector (FID/GC). A separation column with a length of 3.66 m and an outside diameter of 3.2 mm containing molecular sieve 13X was operated isothermally at a temperature of 80 ° C. One ultra-high purity gas pressure regulator was used to sample the gas from each of the four NIST calibration mixtures. Sample flow of gas in cylinder MR 8541 was controlled by the high-pressure flow controller. All cylinders were individually sampled manually from the high-pressure regulator to the instrument.

Calibration

Gravimetric preparation of primary standards done using ISO 6142

Purity Table CH_4 **Cylinder No. 4991582**

Component	**MW**	**Mole fraction ppm**	**Uncertainty ppm**
Ethane	30.0690	4.2	0.1
Propane	44.0956	0.4	0.2
Carbon dioxide	44.0095	0.3	0.1
Oxygen	31.9988	1	1
Nitrogen	28.0134	2	1
Total Impurities		**8**	
Methane	16.0425	**999992**	**1.4**

Purity Table of CO_2 **Cylinder No. A-7656**

Component	**MW**	**Mole fraction ppm**	**Uncertainty ppm**
Methane	16.0425	0.6	0.1
Ethane	30.0690	0.2	0.5
Ethylene	28.0532	0.2	0.5
Carbon monoxide	28.0101	0.9	0.5
H_2O	18.0153	4	2
Total Impurities		6	
Carbon dioxide	44.0095	**999994**	2.2

Purity Table Air **SMI Ultrapure Air**

Component	Mole fraction ppm	Uncertainty ppm
Oxygen *	209460	20
Argon *	9340	10
Nitrogen (Diff.)	781200	23
Methane	0.00	0.015 dl
Carbon dioxide	0.03	0.05

Uncertainty of primary standards normally assigned a 0.1 % relative uncertainty. In the case of the methane primary standards, the uncertainty is dominated by the detection limit of methane in the air used to prepare the standards.

Cylinder #	CH_4 Conc.	Uncert (k=1)
CAL-014827	1.905	0.009
X197963	1.886	0.009
CAL-014822	1.805	0.009
CAL-014821	1.698	0.009

Cylinder #	CO_2 Conc.	Uncert (k=1)
X134489	386.10	0.39
X134485	376.79	0.38
X134503	363.11	0.36
X110510	355.98	0.36
C120702	367.82	0.37

Instrument drift was correct using a control cylinder run periodically during the analysis sequence. The calibration was fitted to a linear model using Generalized least squares.

Evaluation of measurement uncertainty

Model used for evaluating measurement uncertainty for methane:

Evaluation of data done using Generalized Least Squares software conforming to ISO 6143 [14]. Uncertainty of the primary standards and instrument reproducibility was propagated using this software. A general summary of the uncertainty follows:

Typical evaluation of the measurement uncertainty for **methane**:

Quantity X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$
Methane Purity	0.999994	A	Gaussian	0.000002	0.000002	Nil
Air CH_4 impurity	0.0000	B	Rectangular	0.0087	1	0.0087 µmol/mol
PSM Prep	1.800	A	Gaussian	0.0018	1	0.0018 µmol/mol
PSM Combined				0.009	1	0.009 µmol/mol
Instr Rep	20000	A	Gaussian	20	1	20

Model used for evaluating measurement uncertainty for carbon dioxide:

Evaluation of data done using Generalized Least Squares software conforming to ISO 6143. Uncertainty of the primary standards and instrument reproducibility was propagated using this software. A general summary of the uncertainty follows:

Typical evaluation of the measurement uncertainty for **carbon dioxide**:

Quantity X_i	**Estimate** x_i	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$
CO_2 Purity	0.999994	A	Gaussian	0.000002	0.000370	Nil
Air CO_2 impurity	0.03	A	Gaussian	0.05	1	0.05 µmol/mol
PSM Prep	370	A	Gaussian	0.37	1	0.37 µmol/mol
PSM Combined	370	A	Gaussian	0.37	1	0.37 µmol/mol
Instr Rep	2.0000	A	Gaussian	0.0040	1	0.0040

Measurement report of laboratory KRISS

Method

CH_4 analyis

We used HP5890 GC/FID for this measurement.

Configuration of analysis system: gas cylinder -> regulator -> MFC -> sample injection valve -> column -> detector -> integrator -> area comparison -> results

Gas Chromatograph with FIDCarrier gas : Helium

Detector Temp. : 200°C Oven Temp. : 35°C

Column: Activated alumina, 80-100 mesh, 6 ft., 1/8" stainless steel tube

Sample loop: 2 cm^3 Sample flow rate: 100 mL/min

- CO_2 analysis

We used NDIR for this measurement (Siemens, Ultramat 6E).

Configuration of analysis system: gas cylinder -> regulator -> MFC -> NDIR-> response comparison-> results

Sample cell flow: 500 mL/min, Reference cell flow: 500 mL/min

Cell pressure: 2.00 Kg/cm^3

Calibration

The calibration standards for CCQM P-41 were prepared by gravimetric method in our institute. All source gases were analyzed impurities for purity analysis. The primary standards with 0.005% ~0.1% overall uncertainty are used.

The ten sets of standard gas with similar concentration were prepared by gravimetric method and checked by GC and NDIR to make sure their accuracy. Finally we used three standard gases for CH_4, Ar, and O_2 measurements, and six standard gases for multi-point calibration in CO_2 measurements.

Evaluation of measurement uncertainty

We estimated the uncertainty in the gravimetric methods and measurements. Their uncertainties are given in Tables.

Uncertainty evaluation of weighing

Uncertainty related to the balance & the weights	Value (mg)	Distribution	Standard uncertainty (mg)
1. Resolution of balance	1	Rectangular	0.289
2. Accuracy of balance including linearity	1	Rectangular	0.577
3. Incorrect zero point	1	Rectangular	0.289
4. Drift(thermal and time effects)	1	Rectangular	0.289
5. Instability due to draught	Negligible		
6. Location of cylinder on the balance pan	Negligible		
7. Uncertainties in the weights used	0.05	Rectangular	0.025

Uncertainty related to the balance & the weights	Value (mg)	Distribution	Standard uncertainty (mg)
8. Buoyancy effects on the weights used	1.68	Rectangular	0.97
Total (mg)			1.235

Uncertainty related to the gas cylinder	Value (mg)	Distribution	Standard uncertainty (mg)
1. Loss of metal, paints or labels from surface of cylinder	0.1	Rectangular	0.058
2. Loss of metal from threads of valve/fitting	0.5	Rectangular	0.289
3. Dirt on cylinder, valves or associated fitting	0.1	Rectangular	0.058
4. Adsorption/desorption effects on the external cylinder surface	0.1	Rectangular	0.058
5. Buoyancy effects on the cylinder itself			
5.1 Cylinder temperature differs from surrounding air due to e.g. filling with gas	0.6	Rectangular	0.346
5.2 Change of cylinder volume during filling	1.1	Rectangular	0.635
5.3 Change of density of surrounding air due to change in temperature, air, pressure, humidity and CO_2 content	Negligible		
6. Uncertainty in determination of external cylinder volume	Negligible		
Total (mg)			0.783

Uncertainties related to the component gases	Value(mg)	Distribution	Standard uncertainty(mg)
1. Residual gases in cylinder	0.057	Rectangular	0.033
2. Uncertainties of leakage of gas			
2.1 Leakage of air into the cylinder after evacuation	1	Rectangular	0.289
2.2 Leakage of gas from the cylinder valve during filling	1	Rectangular	0.289
2.3 Escape of gas from cylinder into transport lines	Negligible		
3. Gas remaining in transfer system when weight loss method is used	Negligible		
4. Absorption/reaction of components on internal cylinder surface	Negligible		
5. Reaction between components	Negligible		
6. Insufficient homogenization	Negligible		
Total (mg)			0.410

Total uncertainties in weighing (1.519 mg: standard uncertainty)

Purity table for N_2

compo-nent	Analysis(10^{-6}mol/mol)	Distribution	Mole fraction (10^{-6} mol/mol)	Uncertainty (10^{-6} mol/mol)
H_2	<0.05	Rectangular	0.025	0.0144
O_2	0.35	Normal	0.35	0.035
CO	<0.1	Rectangular	0.05	0.029
CO_2	<0.01	Rectangular	0.005	0.003
CH_4	0.0013	Normal	0.0013	0.00065
Ar	<0.1	Rectangular	0.05	0.0029
H_2O	1.2	Normal	1.2	0.24
N_2			999998.3	0.246

Purity table for CO_2

compo-nent	Analysis (10^{-6} mol/mol)	Distribution	Mole fraction (10^{-6} mol/mol)	Uncertainty (10^{-6} mol/mol)
H_2	<0.05	Rectangular	0.025	0.0144
O_2+Ar	0.35	Normal	0.35	0.035
CO	<0.1	Rectangular	0.05	0.029
CH_4	0.99	Normal	0.99	0.05
N_2	4.11	Normal	4.11	0.411
H_2O	5	Normal	5	0.5
C_2H_4O	45.1	Normal	45.1	2.26
CO_2			999944.4	0.6509

Purity table for CH_4

compo-nent	Analysis (10^{-6} mol/mol)	Distribution	Mole fraction (10^{-6} mol/mol)	Uncertainty (10^{-6} mol/mol)
H_2	<0.05	Rectangular	0.025	0.0144
O_2+Ar	1.6	Normal	1.6	0.32
CO	<0.1	Rectangular	0.05	0.029
CO_2	2.3	Normal	2.3	0.115
N_2	3.9	Normal	3.9	0.39
H_2O	2.9	Normal	2.9	0.29
THC	<0.1	Rectangular	0.05	0.029
C_2H_6	<1	Rectangular	0.5	0.289
CH_4			999988.7	0.5940

Purity table for Ar

component	Analysis (10^{-6} mol/mol)	Distribution	Mole fraction (10^{-6} mol/mol)	Uncertainty (10^{-6} mol/mol)
H_2	<0.05	Rectangular	0.025	0.0144
O_2	0.41	Normal	0.41	0.041
N_2	1.6	Normal	1.6	0.32
CO_2	<0.01	Rectangular	0.005	0.003
CH_4	<0.003	Rectangular	0.0015	0.001
CO	<0.1	Rectangular	0.05	0.029
H_2O	1.5	Normal	1.5	0.15
THC	<0.1	Rectangular	0.05	0.029
Ar			999996.4	0.3573

Purity table for O_2

component	Analysis (10^{-6} mol/mol)	Distribution	Mole fraction (10^{-6} mol/mol)	Uncertainty (10^{-6} mol/mol)
H_2	<0.05	Rectangular	0.025	0.0144
Ar	<1	Rectangular	0.5	0.289
N_2	2.8	Normal	2.8	0.28
CO_2	<0.01	Rectangular	0.005	0.003
CH_4	<0.003	Rectangular	0.0015	0.001
CO	<0.1	Rectangular	0.05	0.029
H_2O	1.1	Normal	1.1	0.22
THC	<0.1	Rectangular	0.05	0.029
O_2			999995.5	0.3576

Model used for evaluating measurement uncertainty for methane:

Model equation

$C_{sample} = A_{sample} \times C_{std}/A_{std}$

$C_{final} = C_{sample} \times f_{rep}$

Typical evaluation of the measurement uncertainty for **methane**:

Quantity X_i	**Estimate** x_i	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$
A_{sample}	35.4424	A		0.0096127	0.0505642	0.000486
C_{std}	1.80610	B	normal	0.0006000	0.9922578	0.000595
f_{rep}	1.00001	B	normal	0.0001160	1.7920989	0.000208
A_{std}	35.7193	A		0.0071493	-0.0501722	0.000359

A_{sample} : the peak area of sample

C_{std} : the concentration of standard gas (1×10^{-6} mol/mol)

A_{std} : the peak area of standard

f_{rep} : the factor of reproducibility in analysis.

Model used for evaluating measurement uncertainty for carbon dioxide:

Model equation

$$C_{nmi} = (R_{nmi} - R_1)\times(C_2 - C_1)/(R_2 - R_1) + C_1$$

$$C_{final} = C_{nmi} \times f_{rep} + f_{linearity} + C_{nmi} \times f_{iso}$$

Typical evaluation of the measurement uncertainty for **carbon dioxide**:

Quantity X_i	**Estimate** x_i	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$
R_{nmi}	232.018	A		0.0121967	0.0676593	0.000825
R_1	174.136	A		0.0337712	-0.0401523	-0.001356
R_2	316.509	A		0.0211254	-0.0275070	-0.000581
C_2	370.239	B	normal	0.01850	0.4067148	0.007524
C_1	360.610	B	normal	0.0186667	0.5936862	0.011082
$f_{linearity}$	-0.06520	B	normal	0.0027700	1	0.002770
f_{iso}	0.000416	B	normal	0.0000417	364.52469	0.015201
f_{rep}	0.999985	B	normal	0.0000085	364.52469	0.003098

R_{nmi} : the response of sample in NDIR.
R_1 : the response of standard gas 1 in NDIR.
R_2 : the response of standard gas 2 in NDIR.
C_2 : the concentration of standard gas 1.
C_1 : the concentration of standard gas 2.
$f_{linearity}$: the factor of linearity in NDIR.
f_{iso} : the factor of isotope effect in NDIR.
f_{rep} : the factor of reproducibility in analysis.

Measurement report of laboratory CSIRO-AR

Method

Both CH_4 and CO_2 (in this comparison) are analyzed by gas chromatography (GC) using a Carle “Series 400” instrument with a flame ionization detector (FID). The sample loop volume is 2 ml. Sample air is passed through two columns, the first 8’ x 1/8” O.D. silica gel and the second 3.5’ x 1/8” O.D. molecular sieve 5A. After detection of the CH_4 peak, a valve switch changes the order of the columns, thus ensuring that CO_2 is separated on the silica gel column only without entering the molecular sieve. After separation on the columns, CH_4 is directly detected with the FID, while CO_2 is first catalytically converted to CH_4 with a heated (400°C) nickel catalyst. The carrier gas is ultra high purity He. The catalyst is purged with ultra high purity H_2 and the flame is supported by a mixture of 40% O_2 in N_2. Peaks are integrated by a Hewlett Packard 3396A integrator. All air samples and standards are passed through a chemical drying agent (anhydrous magnesium perchlorate) en route to the sample loops, so that all reported measurements are of mole fraction in dry air.

Calibration

As part of the intercomparison reported here, cylinder standard VSL138554 was analyzed at CSIRO-AR on 3 separate occasions over an 8-day period. Each analysis comprised multiple (13-32) aliquots, with each aliquot from this cylinder bracketed by measured aliquots from a working standard (natural air contained in a high pressure cylinder) with CO_2 and CH_4 assignments propagated from a suite of primary standards.

CO_2

Data are reported in the WMO CO_2 Mole Fraction Scale. The link to this scale was established with 9 primary standards (of a suite of 10 synthetic mixtures of CO_2, CH_4 and CO in zero air purchased from Scott-Marrin, Riverside, CA, USA) in high-pressure cylinders that were calibrated by NOAA in 1992-1994. They span a CO_2 mole fraction range of 291-377 μmol mol^{-1}. Recalibration of a subset of these standards by NOAA in 2001 and recent exchange of other standards between NOAA and CSIRO-AR suggest that CSIRO-AR’s gas chromatograph standards have drifted, resulting in a deviation of CSIRO-AR data from the WMO scale of -0.10 ± 0.05 μmol mol^{-1} at CO_2 mole fractions typical of the background atmosphere and in the vicinity of the cylinder standard measured as part of this intercomparison.

Calibration curves are generated on average every 3 months based on measurement of the 9 primary standards and an additional standard at 422 μmol mol^{-1} (provisional mole fraction assignment based on dilution with zero air to give a CO_2 mole fraction within the range of the primary standards). Instrument response is fitted by a quadratic function passing through zero. Corrections for instrument non-linearity are typically 0.7% of the CO_2 difference between an unknown sample and the working standard at 361 μmol mol^{-1}.

CH_4

CSIRO-AR data are reported in the CSIRO94 CH_4 scale [9], which is derived from, and almost identical to, the CH_4 scale maintained at NOAA. The CSIRO-AR scale was established using two dry, natural air standards in high pressure cylinders calibrated by NOAA between 1987 and 1990. Subsequent exchange between NOAA and CSIRO-AR of 12 other air standards indicated a small difference in the CH_4 scales with CSIRO-AR values being higher than those of NOAA by a factor 1.00021 ± 0.00010, equivalent to a difference of 0.00037 ± 0.00018 μmol mol^{-1} at a CH_4 mole fraction of 1.770 μmol mol^{-1}. There has been no detectable drift in the inter-laboratory difference over more than 10 years of intercomparison activities [20]. The stability of CSIRO-AR's CH_4 scale (and to a lesser extent also the CO_2 scale) is also constrained by the degree of relative stability in CH_4 mole fraction among a suite of more than 30 air standards, stored in different types of containers and with different pressure histories, which have been periodically analysed over periods of up to 20 years.

The instrument response is treated as being linear. Measurements of a suite of CH_4 standards (calibrated against a gravimetrically-defined scale) obtained from Tohoku University (Sendai, Japan) and regular monitoring of standards in the 0.30-1.85 μmol mol^{-1} range indicate the uncertainty due to unaccounted, systematic non-linearity and variability in the response function to be ±0.2% of the CH_4 difference between an unknown sample and the working standard at 1.70 μmol mol^{-1}.

Sample Handling

The cylinder (VSL138554) was fitted (on 11 April 2003) with an ultra-high purity, 2-stage, stainless steel regulator (Tescom Corp., Elk River, Minnesota, USA; series no. 64-3400; serial number JV002029A). The regulator was flushed out (by repeated pressurisation and venting), to remove any trace of ambient air trapped between the cylinder valve and the regulator during the fitting of the regulator. Over the following 3 days the fittings were leak checked to ensure the absence of any leaks. This period also allowed sustained exposure of the internal surfaces to the air in the cylinder, prior to the beginning of the analyses. This conditioning process included periodical purging of air in the regulator to promote equilibration of the internal surfaces with the sample air in relation to surface adsorption processes. For analyses, the delivery pressure of the regulator was set to approximately 10 psig, and left at that setting for the duration of the analysis session. Occasionally during each analysis session, the regulator was purged to ascertain if the time period that air from the cylinder had spent inside the regulator had any discernible effect on the measurement of CH_4 or CO_2. No such effect was observed.

Evaluation of measurement uncertainty

Evaluation of the measurement uncertainty for **methane** in units of μmol mol^{-1} with a coverage factor of k = 2:

Component	Evaluation type (A or B)	Distribution	Contribution $u_i(y)$
Reproducibility	A	Normal	0.0006
Calibration curve	B		0.0003
Sample handling	B	Normal	0.0002
Alignment to scale maintained by NOAA	B		0.0007
CH_4 mole fraction			0.0010

Evaluation of the measurement uncertainty for **carbon dioxide** in units of μmol mol^{-1} with a coverage factor of k = 2:

Component	**Evaluation type (A or B)**	**Distribu-tion**	**Contribution $u_i(y)$**
Reproducibility	A	Normal	0.02
Calibration curve	B		0.02
Sample handling	B	Normal	0.10
Alignment to WMO scale	B		0.15
CO_2 mole fraction			0.18

Measurement report of laboratory NMIJ

Method

Table 1 shows the summary of our instruments used for this comparison.

Table 1. Summary of Instruments

Component	CO_2	CH_4	Ar
Principle	GC-FID with Ni-catalyst	GC-FID, or, GC-FID with pre-concentrator	GC-HID
Equipment	GC-14A (Shimadzu)	GC-14A (Shimadzu) Or, HP6890(HP) with GAS-30(DKK)	HP5820(HP) Detector is the model PDD2(Valco)
Data collection	CDS (DKK)	C-R3A (Shimadzu) or CDS (DKK)	C-R6A (Shimadzu)
Column	Porapack Q (i.d.3 mm, length 2 m, packed, stainless steel)	Unibeads C (i.d.3 mm, length 2 m, packed, stainless steel) or HP-MOLSIV	MS-5A (i.d.1/8inch, length 4m, packed, stainless steel)
Oven temp.	50℃	100℃, or , 40 ℃	-10 ℃
Catalyst temperature	400 to 450℃	-	-
Carrier gas	N_2 (purity 99.999%) in cylinder with purifier	N_2 (99.999%) with purifier or	He (99.9999%) in cylinder
H_2 for FID	H_2 (99.99999%)	H_2 (99.99999%) or Hydrogen generator (STEC model OPGU-1500) with purifier	-
Air for FID	Refined air in cylinder with purifier	Refined air in cylinder with purifier	-

Calibration

Preparation method:

All calibration gas mixtures were prepared by gravimetric method using an electronic mass-comparator (Mettler Toledo model KA10-3/P, capacity 15 kg , readability 1 mg) with automatic loading system of cylinders. The difference on the indication of the mass-comparator between mixture and reference cylinders can be automatically weighed.

Purity analysis :

The impurities in a nominally "pure" parent gas are determined by GC-PID, GC-FID, and, moisture meter. The mole fraction of the major component is conventionally calculated by equation such as ;

$$x_{pure} = 1 - \sum_{i=1}^{N} x_i , \qquad (1)$$

where

x_i = mole fraction of impurity *i*, determined by analysis;

N = number of impurity *i*, determined by analysis;

x_{pure} = mole fraction "purity" of the parent gas.

Table 2, 3, 4, 5, and 6 show the results of impurity analyses.

Table 2 . Purity table for N_2 used as parent gas.

Component	Mole fraction E-06mol/mol	Standard uncertainty E-06mol/mol	Type of Uncertainty	method
CH_4	0.0044	0.0025	B	GC-FID with concentrator
CO_2	0.021	0.012	B	GC-FID with Ni-catalyst
Ar	3.5	2.0	B	GC-HID
O_2	10.3	1.5	A	GC-HID
N_2	999986.1	2.5	-	-
H_2O	0.27	0.16	B	Capacitance-type moisture meter

Table 3 . Purity table for O_2 used as parent gas.

Component	Mole fraction E-06mol/mol	Standard uncertainty E-06mol/mol	Type of Uncertainty	method
CH_4	0.00689	0.00398	B	GC-FID with concentrator
CO_2	0.0044	0.0025	A	GC-FID with Ni-catalyst
Ar	3.5	2.0	B	GC-HID
O_2	999986.1	2.0	-	-
N_2	10.3	1.5	B	GC-HID
H_2O	0.27	0.16	B	Capacitance-type moisture meter

Table 4. Purity table for Ar used as parent gas.

Component	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Type of Uncertainty	Method
CH_4	0.0396	0.0030	A	GC-FID with concentrator
CO_2	0.021	0.012	B	GC-FID with Ni-catalyst
Ar	999989.6	1.5	-	-
N_2	10.3	1.5	B	GC-HID
H_2O	0.27	0.16	B	Capacitance-type moisture meter

Table 5. Purity Table for CO_2 as parent gas.

Component	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Type of Uncertainty	Method
H_2	4.5	2.6	B	GC-TCD
O_2	4.5	2.6	B	GC-TCD
H_2O	4.5	2.6	B	GC-TCD
He	4.5	2.6	B	GC-TCD
N_2	49.7	7.5	A	GC-TCD
CO_2	999919.3	10.2	-	--
C_2H_6	4.5	2.6	B	GC-TCD
C_3H_8	4.5	2.6	B	GC-TCD
CH_4	4.5	2.6	B	GC-TCD

Table 6. Purity Table for CH_4 as parent gas.

Component	Mole fraction µmol/mol	Standard uncertainty µmol/mol	Type of Uncertainty	Method
CO	10	5.8	B	GC-TCD
H_2O	10	5.8	B	GC-TCD
He	10	5.8	B	GC-TCD
N_2	10	5.8	B	GC-TCD
CO_2	10	5.8	A	GC-TCD
C_2H_6	1.0	0.6	-	GC-FID
C_3H_8	1.0	0.6	B	GC-FID
CH_4	999948.0	12.9	B	-

Measurements sequence and mathematical model:

Each measurement #*k* consists of the following procedure.

1) Inject 3 calibration standards (or higher concentration) into the column. Record the retention times and peak areas. The following calibration data set can be obtained;
   - · analyte contents, x_1, x_2, x_3,
   - · standard uncertainties of the analyte contents, $u(x_1)$, $u(x_2)$, $u(x_3)$,
   - · responses to the analyte contents, y_1, y_2, y_3,
   - · standard uncertainties of the responses, $u(y_1)$, $u(y_2)$, $u(y_3)$.

2) Inject the sample with the same manner as the calibration standards. Record the retention times and the peak areas. The response y_k and its standard uncertainty $u(y_k)$ can be obtained.
3) Parameters and its uncertainty of the analytical function $x_k = b_{0,k} + b_{1,k} y_k$ were calculated with ISO6143 [14] implementation software "B_LEAST version 1.11". After that, the analytical content x_k and standard uncertainty $u(x_k)$ of sample cylinder were calculated from peak area y_k and its uncertainty $u(y_k)$.

The analytical functions were validated by Goodness-of-fit. For all analytical functions of our measurements in this comparison values of Goodness-of-fit were less than 2.

Concentration of calibration standards

The following calibration standards were prepared for analyses of CCQM-P41.

Table 7. Concentration and its expanded uncertainty [k=2]
of calibration standards CH_4+CO_2+Ar+O_2 /N_2. The unit of concentration is µmol/mol.

COMPONENT	R_1	R_2	R_3	R_4
CH_4	1.5919 (64)	1.4767 (65)	1.6426 (64)	1.9159 (63)
CO_2	377.61(16)	350.17 (16)	389.70 (17)	454.82 (17)
AR	9257.3 (3.5)	8562.0 (3.5)	9145.3 (3.5)	9688.3 (3.6)

Table 8. Combination of analytes and standared gases.

Analyte	Combination
CH_4	R_2, R_3, R_4
CO_2	R_1, R_2, R_3
Ar	R_2, R_3, R_4

Temperature/pressure correction

None.

Evaluation of measurement uncertainty

a. Uncertainty related to the balance and the weights.:

b. Uncertainties related to the gas cylinder:

The "apparent" mass difference between reference and mixture cylinders including Al-weighing-pans on the balance, Δm_{cyl}, is expressed as,

$$\Delta m_{cyl} = m_R - m_M - \rho_{air}(V_R - V_M) \quad . \qquad (1)$$

where mR and mM are the mass of cylinders, VR and VM are the volume of cylinders, and ρ_{air} is the air density. Before weighing, the adjustment curves between the difference of indications on the electronic mass comparator □l and □m have been investigated by using standard mass pieces with the uncertainly corresponding to OIML class E2 and by air density measurement. This curve had good linearity. After that, the difference of indication ΔI_{cyl} between reference and mixture cylinders was measured. The Δm_{cyl} was obtained by substituting ΔI_{cyl} to the adjustment curves. The standard uncertainty of ΔI_{cyl}, $u(\Delta I_{cyl})$, was calculated from the pooled estimate standard deviation s_p= 5 mg divided by $\sqrt{n}$ where n=3. The deviation undergoes a simulated filling process.

To obtain the mass of filled gas, m_{gas}, from the “difference” of apparent mass differences Δm_{cyl} between before and after fillings, eq.(1) is recalled. When $\Delta m'_{cyl}$ is the apparent mass difference after filling gas and $\Delta m'_{cyl}$ is before filling,

$$\begin{aligned}\Delta m_{cyl} - \Delta m'_{cyl} &= m'_M - m_M - \rho_{air}(V_R - V_M) + \rho'_{air}(V_R - V'_M) \\ &= m'_M - m_M - (\rho_{air} - \rho'_{air})(V_R - V_M) - \rho'_{air} \cdot \Delta V_{Ml}\end{aligned} \quad , \qquad (2)$$

where,

m_M ; *mass of cylinder before filling ,*
m'_M ; *mass of cylinder after filling ,*
ρ_{air} ; *air density before filling ,*
ρ'_{air} ; *air density after filling ,*
V_R ; volume of cylinder before filling ,
V_M ; volume of mixture cylinder before filling ,
V'_M ; volume of mixture cylinder after filling ,
ΔV_M ; volume of mixture cylinder expanded by filling high-pressure dilution gases (ΔV_M $=V'_M - V_M$) .

The term $(\rho_{air} - \rho'_{air})(V_R - V_M)$ can be ignored, being compared to the term $(m'_M - m_M)$. It has been assumed in this comparison that the term $\rho'_{air} \cdot \Delta V_{Ml}$ could be ignored in eq.(2), although we have never measured the expansion of 10 L Al cylinder by filling high-pressure gas. As the result,

$$m_{gas} = m'_M - m_M = \Delta m_{cyl} - \Delta m'_{cyl} \quad . \qquad \mathbf{(3)}$$

The standard uncertainty of $u(m_{gas})$ includes the following sources of uncertainty.

<Balance>
- Resolution of balance
- Incorrect zero point
- Drift (thermal and time effects)
- Location of cylinder on the balance pan
- Resolution of balance
- Uncertainties in the weights used
- Buoyancy effects on the weights used.
- Accuracy of balance including linearity

< Mechanical handling of cylinder>
- Loss of metal, paints or labels from surface of cylinder:
- Loss of metal from threads of valve /fitting :
- Dirt on cylinder, valves or associated fitting:
- Absorption/ desorption effects on the external cylinder surface:

< Buoyancy effects on the cylinder itself >
- Cylinder temperature differs from surrounding air due to e.g. filling with gas .
- Change of density of surrounding air due to changes in temperature, air pressure, humidity and carbon dioxide content

The results of the mass measurements are tabulated in the following table.

Table 10. Mass and its standard uncertainty of filled into cylinder at the preparation of gas mixtures.

component	Parent gas	mass / g	Standard uncertainty / mg
i		m_{gas}	$u(m_{gas})$
CH_4/N_2 No.1	CH_4	56.8866	4.8
	N_2	905.1960	4.8
CH_4/N_2 No.2	CH_4 / N_2 No.1	24.498	5.3
	N_2	979.187	5.0
CO_2/N_2 No.1	CO_2 / N_2 No.1	105.41	5.0
	N_2	1008.19	4.4
CH_4+CO_2/N_2 No.1	CH_4/N_2 No.2	23.3043	5.0
	CO_2 / N_2 No.1	232.2537	4.4
	N_2	719.6530	4.3
Ar/O_2 No.1	Ar	60.1316	4.5
	O_2	1082.3466	5.7
Ar/O_2 No.2	Ar	52.5637	4.6
	O_2	947.2376	4.4
$CH_4+CO_2+Ar+O_2/N_2$ No.1	CH_4+CO_2/N_2 No.1	23.3164	4.7
	Ar/O_2 No.1	222.1649	4.5
	N_2	670.5061	4.3
$CH_4+CO_2+Ar+O_2/N_2$ No.2	CH_4+CO_2/N_2 No.1	21.2227	4.8
	Ar/O_2 No.1	201.6823	4.5
	N_2	673.9795	4.3
$CH_4+CO_2+Ar+O_2/N_2$ No.3	CH_4+CO_2/N_2 No.1	21.7685	4.5
	Ar/O_2 No.1	198.5500	4.5
	N_2	608.0125	4.3
$CH_4+CO_2+Ar+O_2/N_2$ No.4	CH_4+CO_2/N_2 No.1	24.8254	4.4
	Ar/O_2 No.2	205.7615	4.4
	N_2	580.3987	4.3
$CH_4+CO_2+Ar+O_2/N_2$ No.5	CH_4+CO_2/N_2 No.1	21.5289	4.5
	Ar/O_2 No.2	207.2459	4.4
	N_2	628.2128	4.3

c. Uncertainties related to the component gases

The following uncertainty sources are negligible in this comparison. In our fillings, weight loss method was not used.

— Residual gas in cylinder

(The cylinders were evacuated to about 1 Pa before filling,)

— Leakage of air into the cylinder after evacuation

(The leak check was done with vacuum gauge.)

— Leakage of gas from the cylinder valve during filling

(The leak check was done with high-pressure gauge.)

— Escape of gas from cylinder into transport lines

— Absorption/reaction of components on internal cylinder surface

(There are no reactive gases in this comparison.)

— Reaction between components

(There are no reactive gases in this comparison.)

- Insufficient homogenisation

(After fillings, the homogenisation treatments were performed with a rotating platform. These calibration standards were used for measurements after more than one day.)

The results of impurity analyses are described in the tables of the section "*Calibration standard*". This table shows the following sources.

- Impurities in the component gases: described in above tables.
- Impurities present in the balance gas (or in other components) : described in above tables.
- One or more of the mixture components present in other component gases ;

The molar masses and their uncertainties are calculated from the atomic weights given in the IUPAC publication on the Atomic weights of the Elements (2001). In these calculations, it is assumed that the standard uncertainties of atomic weights of elements are parenthetic values divided by the square root of 3.

Table 11. Molar mass and its standard uncertainty of each component.

Component *i*	Molar mass g/mol	Standard uncertainty g/mol	Type of Uncertainty (A or B)	Distribution
CH_4	16.04246	4.9E-04	B	Rectangular
CO_2	44.0095	8.3E-04	B	Rectangular
Ar	39.948	5.8E-04	B	Rectangular
O_2	31.99880	6.9E-04	B	Rectangular
N_2	28.01340	2.3E-04	B	Rectangular

The mole fractions x_i of the component *i* in the final gas mixture are calculated using eq.(3) of ISO6142. These standard uncertainties $u(x_i)$ were calculated from (A.5) of the same ISO.

$$x_i = \sum_{A=1}^{P}\left(\frac{x_{i,A}\cdot m_A}{\sum_{i=1}^{n} x_{i,A}\cdot M_i}\right) \Bigg/ \sum_{A=1}^{P}\left(\frac{m_A}{\sum_{i=1}^{n} x_{i,A}\cdot M_i}\right) , \qquad \text{(eq. 3 of ISO6142)}$$

$$u^2(x_i) = \sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial M_i}\right)^2 \cdot u^2(M_i) + \sum_{i=1}^{P}\left(\frac{\partial x_i}{\partial m_A}\right)^2 \cdot u^2(m_A) + \sum_{A=1}^{P}\sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial x_{i,A}}\right)^2 \cdot u^2(x_{i,A}) , \quad \text{(eq. A.5 of ISO6142)}$$

where

x_i is the mole fraction of the component *i* in the final mixture, *i* =1,..., *q*-1, *q*, *q*+1,..., *n* ;
P is the total number of the parent gases ;
N is the total number of the components in the final mixture ;
M_A is the mass of the parent gas *A* determined by weighing , *A*=1,..., *r*-1, *r*, *r*+1,..., *P*.

$x_{i,A}$ is the mole fraction of the component *i*, *i* =1 ,…, *n* in the parent gas *A*, *A*=1,…, *r*-1, *r*, *r*+1,…, *P*.

Results of calculating the standard uncertainty and contributions are tabulated in the following table 12. The concentration and its uncertainty were tabulated in Table 7.

Table 12. Contributions to the standard uncertainties of mole fraction by mass measurement, impurity analyses, and, molar mass in pre-mixtures and final-mixtures. The unit of values is E-06mol/mol.

Gas mixture	*i*	x_i	$u(x_i)$	$\sum_{i=1}^{P}\left(\frac{\partial x_i}{\partial m_A}\right)^2 \cdot u^2(m_A)$	$\sum_{A=1}^{P}\sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial x_{i,A}}\right)^2 \cdot u^2(x_{i,A})$	$\sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial M_i}\right)^2 \cdot u^2(M_i)$
CH_4/N_2 No.1	CH_4	98880.0	8.6	7.5	3.2	2.8
CH_4/N_2 No.2	CH_4	2517.27	0.58	5.3E-01	2.3E-01	4.3E-03
CO_2/N_2 No.1	CO_2	62397.0	3.2	2.8	1.2	9.6E-01
CH_4+CO_2/N_2 No.1	CH_4	60.722	1.9E-02	1.3E-02	1.4E-02	2.2E-05
	CO_2	14467.24	8.4E-01	2.3E-01	8.1E-01	1.7E-02
Ar/O_2 No.1	Ar	42608.7	3.8	3.1	1.9	1.1
Ar/O_2 No.2	Ar	42560.9	4.2	3.5	1.9	1.1
$CH_4+CO_2+Ar+O_2/N_2$ No.1 (R1)	CH_4	1.5894	2.1E-03	3.1E-04	2.0E-03	3.7E-05
	CO_2	377.61	7.8E-02	7.4E-02	2.5E-02	8.8E-03
	Ar	9257.3	1.7	1.6E-01	1.7	6.5E-02
$CH_4+CO_2+Ar+O_2/N_2$ No.2 (R2)	CH_4	1.4742	0.0021	3.2E-04	2.1E-03	3.4E-05
	CO_2	350.165	0.081	7.7E-02	2.3E-02	8.2E-03
	Ar	8562.0	1.7	1.6E-01	1.7	6.1E-02
$CH_4+CO_2+Ar+O_2/N_2$ No.3 (R3)	CH_4	1.6401	0.0021	3.3E-04	2.1E-03	3.8E-05
	CO_2	389.699	0.083	7.8E-02	2.6E-02	9.0E-03
	Ar	9145.3	1.7	1.8E-01	1.7	6.4E-02
$CH_4+CO_2+Ar+O_2/N_2$ No.4 (R4)	CH_4	1.9134	0.0021	3.3E-04	2.0E-03	4.4E-05
	CO_2	454.820	0.084	7.8E-02	2.9E-02	1.0E-02
	Ar	9688.3	1.8	1.8E-01	1.8	6.6E-02
$CH_4+CO_2+Ar+O_2/N_2$ No.5	CH_4	1.5685	0.0021	3.2E-04	2.0E-03	3.6E-05
	CO_2	372.628	0.080	7.5E-02	2.5E-02	8.7E-03

Gas mixture	i	x_i	$u(x_i)$	$\sum_{i=1}^{P}\left(\frac{\partial x_i}{\partial m_A}\right)^2\cdot u^2(m_A)$	$\sum_{A=1}^{P}\sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial x_{i,A}}\right)^2\cdot u^2(x_{i,A})$	$\sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial M_i}\right)^2\cdot u^2(M_i)$
(R5)	Ar	9219.0	1.8	1.7E-01	1.8E+00	6.5E-02

d. Uncertainties related to the analysis

GC-HID was used for Ar analysis. This detector is one of universal type detector. In the chromatograph at Argon analysis, the resolution R of peaks between Ar and O_2 is about 1.4 . Here, $R = 2(t_{O2}-t_{Ar})/(W_{O2}+W_{Ar})$, which t_{O2} and t_{Ar} is retention time and W_{O2} and W_{Ar} are the times corresponding to the bottom of each triangle-approximate peak. This R value means that O_2 peak scarcely influences the quantitative analysis of Argon.

GC-FID was used for CO_2 and CH_4 analyses. This detector has selectivity for these analytes, however, the shock due to oxygen in CH_4+CO_2+Ar+O_2/N_2 was observed in chromatogram. Then, the appropriate columns were chosen as the differences of retention times between O_2 shock and CH_4 peak or between O_2 and CO_2 are enough long to do the quantitative analyses.

Final Analytical function x is the average of all measurements.

$$x = \sum_{k=1}^{J} x_k \bigg/ J \quad , \qquad (4)$$

where J is the number of measurement #k and x_k is the analyte content at each measurement #k described in the previous section "*Instrument calibration*".

The standard uncertainty of analyte content at each measurement #k, $u(x_k)$ are evaluated from the following two equations.

$$u^2(x) = \sum_{k=1}^{J} u^2(x_k) \bigg/ J \quad , \qquad (5)$$

$$u^2(x) = \sum_{k=1}^{J} (x_k - x)^2 \bigg/ J\,(J-1)\cdot \qquad (6)$$

If variance of (24) is larger than one of (25), the former value will be adopted, and vice versa.

These uncertainties include the following source of uncertainty;

·Repeatability and selectivity of the analyzer ,

·Appropriateness of the calibration curve (model and its residuals) .

Model used for evaluating measurement uncertainty for methane:

In the following table, the analytical content x of eq.(4) is also expressed as ;

$$x = \sum_{k=1}^{J} (b_{0,k} + b_{1,k} y_k) \bigg/ J \ , \qquad (7)$$

Its standard uncertainty $u(x)$ was calculated from the following equation based on the eq.(5),

$$
\begin{aligned}
u^2(x) &= \sum_{k=1}^{J} u^2(x_k) \Big/ J \\
&= \sum_{k=1}^{J} \left[b_{1,k}^2 u^2(y_k) + u^2(b_{0,k}) + y_k^2 u^2(b_{1,k}) + 2y_k u(b_{0,k}, b_{1,k}) \right] \Big/ J \quad , \\
&= c_{y_k}^2 u^2(y_k) + c_{b_{0,k}}^2 u^2(y_{b_{0,k}}) + c_{b1,k} u(b_{1,k}) + 2y_k u(b_{0,k}, b_{1,k}) / J
\end{aligned}
\tag{8}
$$

where, sensitivity coefficients are;

$$c_{y_k} = b_{1,k} / \sqrt{J} \ , \tag{9}$$

$$c_{b_{0,k}} = 1/\sqrt{J} \ , \tag{10}$$

$$c_{b_{1,k}} = y_k / \sqrt{J} \ . \tag{11}$$

Also, J=7.

Typical evaluation of the measurement uncertainty for **methane**:

Quantity X_i	**Estimate** x_i	**Standard uncertainty** $u(x_i)$	**Evaluation type (A or B)**	**Distribution**	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$
$y_{k=1}$	2.1012E+04	37.0	A	normal	3.26E-05	1.21E-03
$b_{0,\,k=1}$	-2.2055E-02	1.93E-02	A	normal	3.78E-01	7.31E-03
$b_{1,\,k=1}$	8.6166E-05	1.03E-06	A	normal	7.94E+03	8.17E-03
	$u(b_{0,\,k=1}, b_{1,\,k=1})$	-1.98E-08	$2y_{k=1}u(b_{0,\,k=1}, b_{1,\,k=1})/J$	-3.14E-04	$\lvert\{2y_{k=1}u(b_{0,\,k=1}, b_{1,\,k=1})/J\}^{0.5}\rvert$	1.09E-02
$y_{k=2}$	2.0977E+04	5.5.E+01	A	normal	3.20E-05	1.78E-03
$b_{0,\,k=2}$	3.47E-03	2.61.E-02	A	normal	3.78E-01	9.88E-03
$b_{1,\,k=2}$	8.477E-05	1.32.E-06	A	normal	7.93E+03	1.05E-02
	$u(b_{0,\,k=2}, b_{1,\,k=2})$	-3.43.E-08	$2y_{k=2}u(b_{0,\,k=2}, b_{1,\,k=2})/J$	-5.44E-04	$\lvert\{2y_{k=2}u(b_{0,\,k=2}, b_{1,\,k=2})/J\}^{0.5}\rvert$	1.43E-02
$y_{k=3}$	2.0951E+04	5.01.E+01	A	normal	3.18E-05	1.60E-03
$b_{0,\,k=3}$	1.26E-02	2.97.E-02	A	normal	3.78E-01	1.12E-02
$b_{1,\,k=3}$	8.423E-05	1.46.E-06	A	normal	7.92E+03	1.15E-02
	$u(b_{0,\,k=3}, b_{1,\,k=3})$	-4.30.E-08	$2y_{k=3}u(b_{0,\,k=3}, b_{1,\,k=3})/J$	-6.80E-04	$\lvert\{2y_{k=3}u(b_{0,\,k=3}, b_{1,\,k=3})/J\}^{0.5}\rvert$	1.60E-02
$y_{k=4}$	2.0922E+04	4.87.E+01	A	normal	3.13E-05	1.53E-03
$b_{0,\,k=4}$	4.34E-02	3.38.E-02	A	normal	3.78E-01	1.28E-02
$b_{1,\,k=4}$	8.283E-05	1.69.E-06	A	normal	7.91E+03	1.34E-02
x	$u(b_{0,\,k=4}, b_{1,\,k=4})$	-5.67.E-08	$2y_{k=4}u(b_{0,\,k=4}, b_{1,\,k=4})/J$	-8.97E-04	$\lvert\{2y_{k=4}u(b_{0,\,k=4}, b_{1,\,k=4})/J\}^{0.5}\rvert$	1.84E-02
$y_{k=5}$	2.4094E+05	2.91.E+02	A	normal	2.84E-06	8.27E-04
$b_{0,\,k=5}$	-3.40E-02	1.55.E-02	A	normal	3.78E-01	5.86E-03
$b_{1,\,k=5}$	7.519E-06	6.91.E-08	A	normal	9.11E+04	6.30E-03
	$u(b_{0,\,k=5}, b_{1,\,k=5})$	-1.07.E-09	$2y_{k=5}u(b_{0,\,k=5}, b_{1,\,k=5})/J$	-1.94E-04	$\lvert\{2y_{k=5}u(b_{0,\,k=5}, b_{1,\,k=5})/J\}^{0.5}\rvert$	8.56E-03
$y_{k=6}$	2.3906E+05	6.49.E+01	A	normal	2.99E-06	1.94E-04
$b_{0,\,k=6}$	-1.14E-01	1.87.E-02	A	normal	3.78E-01	7.07E-03
$b_{1,\,k=6}$	7.898E-06	7.98.E-08	A	normal	9.04E+04	7.21E-03
	$u(b_{0,\,k=6}, b_{1,$	-1.48.E-09	$2y_{k=6}u(b_{0,\,k=6}, b_{1,\,k=6})$	-2.68E-04	$\lvert\{2y_{k=6}u(b_{0,\,k=6}, b_{1,\,k=6})/J$	1.01E-02

Quantity X_i	Estimate x_i	Standard uncertainty $u(x_i)$	Evaluation type (A or B)	Distribution	Sensitivity coefficient c_i	Contribution $u_i(y)$
	$_{k=6})$		$/J$		$\}^{0.5}\|$	
$y_{k=7}$	2.3937E+05	1.72.E+02	A	normal	2.82E-06	4.84E-04
$b_{0,\ k=7}$	-4.10E-04	1.74.E-02	A	normal	3.78E-01	6.59E-03
$b_{1,\ k=7}$	7.464E-06	8.07.E-08	A	normal	9.05E+04	7.30E-03
	$u(b_{0,\ k=7}, b_{1,\ k=7})$	-1.40.E-09	$2y_{k=7}u(b_{0,\ k=7}, b_{1,\ k=7}) / J$	-2.53E-04	$\|\{2y_{k=7}u(b_{0,\ k=7}, b_{1,\ k=7}) / J\}^{0.5}\|$	9.79E-03
x	1.7802					4.46E-03

In this table, the units of estimate and its standard uncertainty of y, b_0, b_1 are count, µmol/mol, µmol/mol/count, respectively. Also, the unit of contribution is E-06mol/mol.

Model used for evaluating measurement uncertainty for carbon dioxide:

The standard uncertainty $u(x)$ are calculated from equation (8).

Typical evaluation of the measurement uncertainty for **carbon dioxide**:

Quantity X_i	Estimate x_i	Standard uncertainty $u(x_i)$	Evaluation type (A or B)	Distribution	Sensitivity coefficient c_i	Contribution $u_i(y)$
$y_{k=1}$	63822.9	27.4	A	normal	3.38E-03	9.25E-02
$b_{0,\ k=1}$	-6.80	1.43	A	normal	5.77E-01	8.28E-01
$b_{1,\ k=1}$	5.850E-03	2.22E-05	A	normal	3.68E+04	8.19E-01
	$u(b_{0,\ k=1}, b_{1,\ k=1})$	-0.0000318	$2y_{k=1}u(b_{0,\ k=1}, b_{1,\ k=1})/J$	-4.061053	$\|\{2y_{k=1}u(b_{0,\ k=1}, b_{1,\ k=1})/J\}^{0.5}\|$	1.16
$y_{k=2}$	63924.5	13.1	A	normal	3.21E-03	4.22E-02
$b_{0,\ k=2}$	1.110E+01	1.60	A	normal	5.77E-01	9.25E-01
$b_{1,\ k=2}$	5.5653E-03	2.43E-05	A	normal	3.69E+04	8.97E-01
	$u(b_{0,\ k=2}, b_{1,\ k=2})$	-3.89E-05	$2y_{k=2}u(b_{0,\ k=2}, b_{1,\ k=2})/J$	-4.98E+00	$\|\{2y_{k=2}u(b_{0,\ k=2}, b_{1,\ k=2})/J\}^{0.5}\|$	1.29
$y_{k=3}$	73790.5	33.2	A	normal	2.96E-03	9.82E-02
$b_{0,\ k=3}$	-1.195E+01	2.30	A	normal	5.77E-01	1.33
$b_{1,\ k=3}$	5.1304E-03	3.05E-05	A	normal	4.26E+04	1.30
	$u(b_{0,\ k=3}, b_{1,\ k=3})$	-6.99E-05	$2y_{k=3}u(b_{0,\ k=3}, b_{1,\ k=3})/J$	-1.03E+01	$\|\{2y_{k=3}u(b_{0,\ k=3}, b_{1,\ k=3})/J\}^{0.5}\|$	1.85
x	366.68					0.162

In this table, the units of estimate and its standard uncertainty of y, b_0, b_1 are count, µmol/mol, µmol/mol/count, respectively. Also, the unit of contribution is µmol/mol.

Measurement report of NMi VSL

Method

CO_2 and CH_4 were analysed separately on two different GC's having the following configuration:

General configuration:

- 3 valves:
  1. sampling valve
  2. switching column
  3. switching detector
- Samples are introduced in the sample loop through a Multi Position Valve (MPV) followed by a switching valve (open/close, enabling injection at ambient pressure).
- Both MPV position and measurement sequence are controlled by a BASIC-program running on a HP3396-integrator
- Data processing: Automatic integration by HP-Chemstation through A/D-converter

As no backflush was necessary both valve 2 and 3 could remain in the same position during the entire analysis.

CO_2:

- GC: HP5890 Series II TCD/ELCD
- Column: Porapak R, 10 ft, OD 1/8", 80-100 mesh
- Carrier: Helium, 28 ml/min
- Detector: TCD
- Sampler directly connected to sampling valve

CH_4:

- GC: HP6890 (EPC) FID/PDID
- Column: Molsieve 5A, 6 ft, OD 1/8", 60-80 mesh
- Carrier:N_2 31 ml/min
- Detector: FID
- Sampler connected to sampling valve through electronic pressure controller inside GC.

Calibration

All standards have been prepared by the gravimetric method, according to ISO 6142. After preparation the standards have been verified against existing standards.

Composition:

CO_2

Applied CO_2 standards were blended in synthetic air or nitrogen having mole fractions in the range of 200 – 400 ppm. In this case the standards in synthetic air were prepared from pure CO_2 and synthetic air.

The pure CO_2 was analysed for CO, N_2, O_2, H_2 and C_xH_y using GC-TCD, GC-FID and GC-DID. For N_2 purity analyses are only performed on selected cylinders using FT-IR and GC-DID in order to check the specifications given by the producer. The results of these purity analyses are expected to be representative for the cylinders that are not tested. For synthetic air the O2 content was certified, but no individual purity analyses were performed, which leads to larger uncertainties than for CO_2 in nitrogen.

CH_4

Applied CH_4 standards, having mole fractions in the range of 1 – 10 ppm, were gravimetrically prepared using pure CH_4, oxygen and nitrogen. .

Methane purity analyses are only performed on selected cylinders using FT-IR and GC-DID in order to check the specifications given by the producer. The results of these purity analyses are expected to be representative for the cylinders that are not tested.

The N_2 used for preparation of these standards was specifically analysed for CH_4 and in some cases for CO_2 and CO. For other components purity analyses are only performed on selected cylinders using FT-IR and GC-DID in order to check the specifications given by the producer.

The O_2 was analysed for CH_4, Ar, Ne, CO, CO_2, N_2 and H_2 using GC-DID, GC-TCD and FT-IR.

The set of standards used for a measurement and the comparison mixture are connected to the gas chromatograph as described in the paragraph “sample handling”. A measurement of a cylinder consists of 5 (CH_4) or 7 (CO_2) consecutive injections that are averaged.

The model applied for curve-fitting is a first order polynomial using unweighted regression.

The following cylinders were used for calibration of the instruments:

CO_2 (6 cylinders):

Cylinder	Mole fraction CO_2 *ppm*	Matrix
VSL201009	199.87	Air
VSL228511	200.07	N_2
VSL201004	300.13	Air
VSL201008	350.08	Air
VSL201092	399.27	Air
VSL129389	400.19	N_2

CH_4 (9 cylinders):

Cylinder	Mole fraction CH_4 *ppm*
VSL304151	0.98309
VSL400421	1.003
VSL209579	1.9845
VSL304152	1.9851
VSL209577	3.9816
VSL304144	3.9862
VSL304140	5.9833
VSL404081	7.9866
VSL307330	9.9938

The measurement sequence is by increasing mole fraction. Because the time needed for measurement is limited, no pressure correction has been applied.

Evaluation of measurement uncertainty

Gravimetric preparation and impurities

The uncertainty of the gravimetric preparation of the standards used was evaluated according to Alink and Van der Veen[8]. The uncertainty in the impurities present in all pure components and mixtures, that are used to prepare the standards are stored in purity tables. When a mixture is prepared, the uncertainty of the components is automatically calculated from the uncertainty of the gravimetric preparation and the uncertainties of the components present in the mother mixtures.

Stability, non-recovery and leakages

All new prepared standards are verified for their composition against existing (gravimetrically prepared) standards. This verification is a check of the gravimetric preparation process, which includes determination of errors due to leakage of air into the cylinder, leakage of gas from the cylinder valve during filling, escape of gas from the cylinder, absorption of components on the internal surface of the cylinder. Only when no significant difference between the analysed and the gravimetric composition is found, the cylinder is approved as a new standard. Several selected cylinders covering both components in the respective concentration ranges are used for long term stability testing. During these tests no instability has been detected for any of the components. Because it is difficult or impossible to discern between the different uncertainty contributions, the standard deviation of the results of the stability measurements for a cylinder having a similar mole fraction was chosen to cover these uncertainties.

Appropriateness of the calibration curve (model and its residuals) and repeatability

The uncertainty of the analyses was evaluated using the variance equation for inverse regression of a straight line.

For the equation:

$$\hat{Y} = b_0 + b_1 X$$

The variance can be expressed as:

$$V(\hat{X}) = \frac{k^2 s^2}{b_1^2 (1-g)} \left\{ 1 + \frac{1}{n} + \frac{1}{q} + \frac{(\hat{X} - \overline{X})^2}{S_{XX}} \right\}$$

Where g is:

$$g = \frac{k^2 s^2}{b_1^2 S_{XX}}$$

Where k is the coverage factor (k = 1 results in the standard uncertainty), n is the number of cylinders, q is the number of measurements used to calculate the average response, Sxx is the squared sum of the x’s. The s^2 is the estimate for the variance of a single response and is estimated by:

$$s^2 = \frac{SS_{res}}{n-p}$$

Where n is the number of points used and p is the number of parameters (coefficients in the regression model).

This estimation of the uncertainty not only incorporates the appropriateness of the curve, but it also incorporates the repeatability of the measurements.

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[8] A. Alink and A.M.H. van der Veen, Uncertainty Calculations for the preparation of primary gas mixtures, *Metrologia,* **37** (2000) , pp. 641-650.

Model used for evaluating measurement uncertainty for methane:

The uncertainty of the analyses is the combined uncertainty of two uncertainty sources:

- Uncertainty of the component mole fraction in the standards, which is the combined uncertainty for the gravimetrical preparation, impurities, the stability, non recovery and leakages (X_{PSM}).
- Uncertainty of the calibration process, which is uncertainty contribution coming from the appropriateness of the calibration curve (model and its residuals) and the repeatability of the analysis ($\Delta x_{analysis}$)

Typical evaluation of the measurement uncertainty for **methane**:

Quantity X_i	**Estimate** x_i	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$
x_{psm}	1.8e-6	A	Normal	1.4e-8	1	1.4e-8
$\Delta x_{analysis}$	0	A	Normal	4e-9	1	4e-9
$x_{analysis}$	1.8e-6					1.4e-8

Model used for evaluating measurement uncertainty for carbon dioxide:

The uncertainty of the analyses is the combined uncertainty of two uncertainty sources:

- Uncertainty of the component mole fraction in the standards, which is the combined uncertainty for the gravimetrical preparation, impurities, the stability, non recovery and leakages (X_{PSM}).
- Uncertainty of the calibration process, which is uncertainty contribution coming from the appropriateness of the calibration curve (model and its residuals) and the repeatability of the analysis ($\Delta x_{analysis}$)

Typical evaluation of the measurement uncertainty for **carbon dioxide**:

Quantity X_i	**Estimate** x_i	**Evaluation type (A or B)**	**Distribution**	**Standard uncertainty** $u(x_i)$	**Sensitivity coefficient** c_i	**Contribution** $u_i(y)$
x_{psm}	365e-6	A	Normal	2.3e-7	1	2.3e-7
$\Delta x_{analysis}$	0	A	Normal	3e-7	1	3e-7
$x_{analysis}$	365e-6					4e-7

Measurement report of NMIA

Method

Two gas chromatographs were used. Measurement-2 was performed on a Varian GC-3400 and Measurement-1 and Measurement-3 were performed on a Varian GC-3800. In both instruments a thermal conductivity detector was used for CO_2 measurement and a flame ionisation detector was used for CH_4 measurement.

Data collection and the ensuing calculations were performed with Varian Star 5.5 software.

Calibration

Purity analyses of the pure air used were done at a detection limit of about 0.035 µmol/mol for CH_4 in air . The value of 0.014 µmol/mol that was adopted for the concentration of the CH_4 in the pure air was calculated using a graphical method from the response of our GC to methane gravimetric standards at concentrations of 0.01989, 0.04011 and 0.1806 µmol/mol made up with the pure air in question.

We used a two-point calibration model, using the measurement sequence : first standard – CCQM sample- second standard, and assumed that the instrument response between the two standards was linear.

Two calibration standards were used, one at a lower and the second at a higher concentration than the test sample. They were prepared gravimetrically, and the preparation was performed using commercial supplies of pure air, pure methane and pure carbon dioxide.

The concentrations of the two standards used were:

First standard:	CO_2 = **365.71** µmol/mol;	CH_4 = **1.745** µmol/mol
Second standard:	CO_2 = **381.75** µmol/mol;	CH_4 = **1.816** µmol/mol

For each measurement 18 or 27 samples were taken and the last 10 of those were used for the calculations.

Evaluation of measurement uncertainty

Uncertainty:

1. The uncertainty of the calibration of the GC for each series of measurements (standard- sample- standard) was estimated from the difference in the sensitivity factor of the GC for the two standards used.

2. The uncertainty in the value for the concentration of each analyte in the sample was calculated using the following mathematical model for the calculation of the sample concentration:

   $C_x = (C_2 - C_1) . (R_x - R_1) / (R_2 - R_1) + C_1$

   where

   C_x is the sample concentration

C_2 is the concentration of the analyte in the first standard
C_1 is the concentration of the analyte in the second standard
R_x is the response (peak area) of the GC to the sample
R_1 is the response (peak area) of the GC to the first standard
R_2 is the response (peak area) of the GC to the second standard

The total standard uncertainty of each of the three reported results was obtained by combining the values of those two contributory uncertainties.

The reported result for each analyte and its expanded uncertainty were then calculated from the mean of the three results for each.

Carbon Dioxide

Evaluation of the measurement uncertainty for **carbon dioxide measurement 1**

<table>
<tr><th colspan="5"></th><th>Value</th><th>Relative contribution</th></tr>
<tr><td colspan="5">Combined uncertainty (μmol/mol)</td><td>0.484</td><td>100%</td></tr>
<tr><td colspan="5">Uncertainty from calibration of GC (μmol/mol)</td><td>0.354</td><td>53.5%</td></tr>
<tr><td colspan="5">Uncertainty from measurement of sample (μmol/mol)</td><td>0.330</td><td>46.5%</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><th>Quantity X_i</th><th>Estimate x_i</th><th>Evaluation (A or B)</th><th>Distribution</th><th>Std. uncert. $u(x_i)$</th><th>Sens.coeffic. c_i</th><th>Contribution $u_i(y)$%</th></tr>
<tr><td>Standard 1</td><td>365.71</td><td>A</td><td>Normal</td><td>0.13</td><td>0.986</td><td>15.1</td></tr>
<tr><td>Standard 2</td><td>381.75</td><td>A</td><td>Normal</td><td>0.13</td><td>0.014</td><td>0.0</td></tr>
<tr><td>Response 1</td><td>41673</td><td>A</td><td>Normal</td><td>16</td><td>0.0083</td><td>15.9</td></tr>
<tr><td>Response 2</td><td>43584</td><td>A</td><td>Normal</td><td>27</td><td>0.00012</td><td>0.0</td></tr>
<tr><td>Response Sample</td><td>41700</td><td>A</td><td>Normal</td><td>33</td><td>0.0084</td><td>69.0</td></tr>
</table>

Evaluation of the measurement uncertainty for **carbon dioxide measurement 2**

	Value	**Relative contribution**
Combined uncertainty (µmol/mol)	0.677	100%
Uncertainty from calibration of GC (µmol/mol)	0.610	81.1%
Uncertainty from measurement of sample (µmol/mol)	0.294	18.9%

Quantity X_i	**Estimate x_i**	**Evaluation (A or B)**	**Distribution**	**Std. uncert. u(x_i)**	**Sens.coeffic. c_i**	**Contribution $u_i(y)$%**
Standard 1	365.71	A	Normal	0.13	1.0045	19.7
Standard 2	381.75	A	Normal	0.13	0.0045	0.0
Response 1	41414	A	Normal	14	0.0082	15.9
Response 2	43372	A	Normal	24	0.000037	0.0
Response Sample	41405	A	Normal	29	0.0082	64.4

Evaluation of the measurement uncertainty for **carbon dioxide measurement 3**

	Value	**Relative contribution**
Combined uncertainty (µmol/mol)	1.042	100%
Uncertainty from calibration of GC (µmol/mol)	1.04	92.7%
Uncertainty from measurement of sample (µmol/mol)	0.28	7.3%

Quantity X_i	**Estimate x_i**	**Evaluation (A or B)**	**Distribution**	**Std. uncert. u(x_i)**	**Sens.coeffic. c_i**	**Contribution $u_i(y)$%**
Standard 1	365.71	A	Normal	0.13	0.9893	21
Standard 2	381.75	A	Normal	0.13	0.0107	0.0
Response 1	141092	A	Normal	74	0.0023	36.3
Response 2	148076	A	Normal	64	0.000025	0.0
Response Sample	141169	A	Normal	80	0.0023	42.7

Methane

Evaluation of the measurement uncertainty for **methane measurement 1**

	Value	**Relative contribution**
Combined uncertainty (µmol/mol)	0.007	100%
Uncertainty from calibration of GC (µmol/mol)	0.0001	0.03%
Uncertainty from measurement of sample (µmol/mol)	0.007	99.97%

Quantity X_i	**Estimate x_i**	**Evaluation (A or B)**	**Distribution**	**Std. uncert. $u(x_i)$**	**Sens.coeffic. c_i**	**Contribution $u_i(y)$%**
Standard 1	1.745	A	Normal	0.004	0.065	0.4
Standard 2	1.816	A	Normal	0.010	0.94	85.9
Response 1	6445.1	A	Normal	8.8	0.00002	0.0
Response 2	6706.4	A	Normal	5.5	0.0003	3.8
Response Sample	6689.5	A	Normal	8.1	0.0003	9.8

Evaluation of the measurement uncertainty for **methane measurement 2**

	Value	**Relative contribution**
Combined uncertainty (µmol/mol)	0.0078	100%
Uncertainty from calibration of GC (µmol/mol)	0.0044	32.0%
Uncertainty from measurement of sample (µmol/mol)	0.0064	68.0%

Quantity X_i	**Estimate x_i**	**Evaluation (A or B)**	**Distribution**	**Std. uncert. $u(x_i)$**	**Sens.coeffic. c_i**	**Contribution $u_i(y)$%**
Standard 1	1.745	A	Normal	0.004	0.13	2.1
Standard 2	1.816	A	Normal	0.01	0.87	88.9
Response 1	6447.0	A	Normal	6.5	0.00003	0.1
Response 2	6742.7	A	Normal	7.3	0.0002	5.6
Response Sample	6703.3	A	Normal	4.9	0.0002	3.3

Evaluation of the measurement uncertainty for **methane measurement 3**

	Value	**Relative contribution**
Combined uncertainty (µmol/mol)	0.0071	100%
Uncertainty from calibration of GC (µmol/mol)	0.0005	0.5%
Uncertainty from measurement of sample (µmol/mol)	0.0071	99.5%

Quantity X_i	**Estimate x_i**	**Evaluation (A or B)**	**Distribution**	**Std. uncert. $u(x_i)$**	**Sens.coeffic. c_i**	**Contribution $u_i(y)$%**
Standard 1	1.745	A	Normal	0.004	0.05	0.2
Standard 2	1.816	A	Normal	0.0096	0.95	87.3
Response 1	12099.1	A	Normal	9.3	0.000007	0.0
Response 2	12599	A	Normal	15	0.00014	8.0
Response Sample	12574	A	Normal	11	0.00014	4.5

Measurement report of NPL

NPL has prepared a suite of PRMs of carbon dioxide, methane and argon in synthetic air. Binary methane/nitrogen standards were prepared gravimetrically from pure methane at amount fractions of 10% , 1%, 1000 ppm, 100 ppm and 10 ppm. Binary carbon dioxide/nitrogen standards were prepared gravimetrically from pure carbon dioxide at amount fractions of 10% and 5000 ppm. The multi-component “synthetic atmosphere” standards were then prepared by gravimetric mixing of the 5000 ppm carbon dioxide/nitrogen standard with the 10 ppm methane/nitrogen standard and pure argon, oxygen and nitrogen.

Uncertainty in Pure Components

The limiting uncertainties in the final mixture imposed by purity analysis were:

- A detection limit of 100 nmol/mol of carbon dioxide in the pure nitrogen
- A detection limit of 15 nmol/mol of methane in the pure nitrogen

Uncertainty in Gravimetric Preparation Procedure

The uncertainty arising purely from gravimetry was 0.08% (relative, *k*=1) for the carbon dioxide/nitrogen and the methane/nitrogen mixtures. (This corresponds to a weighing uncertainty of 30 mg in the smallest mass of 60 g used in the first step in the process).

Analysis of Carbon Dioxide

GC	Varian Micro GC
Columns	2 x Haysep A (Channel B and D)
Column Temp:	40 Celsius
Carrier Gas	Helium
Runtime:	30 s

“Sandwich” method by alternating the standard and the sample after every 9 runs

Standard [µmol/mol]	***NPL 540***	***NPL 425***	***NG 34***	***NG 35***	***NG 33***	***NPL 552***	**Mean**
Grav value of standard	*369.75*	*365.27*	*348.22*	*372.75*	*360.09*	*356.70*	
Result of ratio comparison	364.9	365.14	365.18	365.62	364.94	365.26	**365.17**
u(x)/x *100	0.15	0.123	0.098	0.12	0.126	0.156	**0.053**

The result of each comparison and the standard deviation of the set of comparisons (expressed relative to value) are shown in the table. These uncertainties have been combined (in quadrature) to generate an estimate of 0.053% for the relative uncertainty due to the repeatability of the analysis. This was then added (in quadrature) to Type B estimates of 0.05% for the gravimetric reference values of the standards and 0.03% for the detection limit of 100 nmol/mol of methane in the balance gas (as a fraction of 360 µmol/mol).

	u(x)/x*100
analysis	**0.05**
grav	**0.05**
purity	**0.03**
Combined *k* =1	**0.08**
Expanded *k* =2	0.16

Analysis of Methane

GC	Varian 3800
Column	Haysep P, 4.4 m, 1/16"OD, 0.75 mm ID micropacked Silicosteel
Column Temp	40 Celsius
Carrier Gas	Helium
	12 injections within one run of 8 minutes "Sandwich" method by alternating the standard and the sample after every run

Standard [µmol/mol]	***NPL 540***	***NPL 425***	***NPL 257***	***NG 34***	***NG 35***	***NPL 552***	
Grav value of standard	*1.829*	*1.802*	*1.896*	*1.739*	*1.86*	*1.771*	
Result of ratio comparison	1.8	1.802	1.803	1.807	1.803	1.799	**1.8023**
u(x)/x [%]	0.17	0.3	0.12	0.15	0.3	0.15	**0.086**
u(x)^2	0.029	0.090	0.014	0.023	0.090	0.023	

The result of each comparison and the standard deviation of the set of comparisons (expressed relative to value) are shown in the table. These uncertainties have been combined (in quadrature) to generate an estimate of 0.086% for the relative uncertainty due to the repeatability of the analysis. This was then added (in quadrature) to Type B estimates of 0.08% for the gravimetric reference values of the standards and 0.53% for the detection limit of 15 nmol/mol of methane in the balance gas (as a fraction of 2 µmol/mol and divided by the square root of 2 because two sources of methane were used in the set of primaries).

	u(x)/x*100
analysis	**0.086**
grav	**0.05**
purity	**0.53**
Combined *k* =1	**0.540**
Expanded *k* =2	1.08