CCQM-K84 Final Report

International comparison CCQM-K84

Carbon monoxide in Synthetic air at ambient level

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Errata: With Table 10 included

Field

Amount of substance

Subject

Carbon monoxide in Synthetic air at ambient level

Participants

KRISS, NIST, LNE, NIM, NMIJ, VNIIM, FMI, JRC, NOAA, NPL

Organizing body

CCQM GAWG

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Introduction

Carbon monoxide (CO) is reported to be mainly emitted from industries, transportation, and burnings for various usages. Its atmospheric lifetime varies from weeks to months, depending on the mixing ratio of the highly reactive hydroxyl radical. Even though the ambient level of CO varies as a function of regional sources, the mixing ratio of CO ranges from 30 nmol/mol to 300 nmol/mol at the marine boundary layers and from 100 nmol/mol to more than 500 nmol/mol in urban areas(1). In order to study temporal trends and regional variation of the level of CO, the National Oceanic & Atmospheric Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD(2)) has played a key role as the designated Central Calibration Laboratory (CCL) within the frame of the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) program. NOAA/ESRL-GMD provides natural air standards, analyzed for CO, to WMO GAW participants. Since the structure of WMO traceability chain appears hierarchical and explicit all over the world, WMO intends to improve the CO measurement compatibility to up to 2 ppb (in case of extensive compatibility goal: 5 ppb, GAW report No. 213(3)) in order to ensure compatibility through the GAW network. Nevertheless, accurate measurement of CO at ambient level has been proven difficult due to the lack of stability in cylinders. For these reasons, it is necessary that measured results are compared among the values assigned by various NMIs.

This key comparison was initially proposed to aim at a CO/N_2 standard in the 2010 CCQM meeting by KRISS. With participation of FMI, NOAA, and Empa, a modified scheme of CO/air standards was developed for the purpose of atmospheric observations and co-operative support to WMO/GAW activities. Therefore, the purpose of the comparison is to support the measurement capability of CO at ambient level of 350 nmol/mol. Further, this key comparison is expected to contribute to the establishment of traceability to a single scale of CO between NMIs by means of harmonizing the results from different national standards. The Empa result lies in a different report.

Supported claims

This key comparison support the measurement capability, which can be used to support CMC claims, for carbon monoxide in air, synthetic air, and nitrogen from 50 nmol/mol to 1000 nmol/mol.

Participants

A total of ten CCQM members took part in this key. Among them, NOAA, as a WMO designated lab for CO, participated under MRA. The participants are listed in Table 1.

Table 1: List of participants

Acronym	Country	Institute
FMI*	FI	Finnish Meteorological Institute
JRC	IT	Joint Research Center
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
LNE	FR	Laboratoire National d'Essais, Paris, France
NIM	CN	National Institute of Metrology, Beijing, P.R.China
NIST	US	National Institute of Standards and Technology, Gaithersburg, United States of America
NMIJ	JP	National Metrology Institute of Japan, Tsukuba, Japan
NOAA	US, (CCL/WMO)**	National Oceanographic and Atmospheric Administration, Boulder, Colorado, United States of America
NPL	UK	National Physical Laboratory, Teddington, Middlesex, United Kingdom
VNIIM	RU	D.I. Mendeleyev Institute for Metrology, St. Petersburg, Russia

* Standard from the participating laboratory; these laboratories do not make use of their own standards.

**CCL/WMO: Central Calibration Laboratory/ World Meteorological Organization

Schedule

The Schedule for this key comparison was as follows:

Date	
Mar. , 2012	Preparation/verification of mixtures by KRISS
Apr. , 2012	Registration and protocol circulation
Until July , 2012	Shipment of cylinders from KRISS to participants
Until Aug. , 2012	Measurement by participants and sending report to KRISS
Until Mar. , 2013	Return of cylinder to KRISS
Until May, 2013	Second verification for returned cylinders
Until Nov. , 2013	3rd verification
Until Mar. , 2014	4th verification and Draft A report
Until Nov. , 2014	Draft B report

Comparison protocol

A set of mixtures of carbon monoxide in synthetic air of the nominal mole fraction of approximately 350 nmol/mol, were gravimetrically(4) prepared by the coordinating laboratory of KRISS. Each mixture was then verified by means of a GC/FID/Methanator system, against very fresh primary standard gas mixture (PSM) with amount-of-substance fractions of approx. 350 nmol/mol. The amount-of-substance fractions determined by KRISS were adopted as key comparison reference values (KCRV).

Table 2. Nominal composition of mixtures

Component	X (nominal value)
Carbon monoxide [nmol/mol]	350
Argon [%mol/mol]	0.93

Oxygen [%mol/mol]	21
Nitrogen [%mol/mol]	balance

The pressure in each cylinder was approximately 100 bar; cylinders of 10 dm^3 (Al. Luxfer, UK). The amount-of-substance mole fraction obtained from gravimetry, and purity analysis of parent gases, were used as reference values. Accordingly, each cylinder was assigned its own reference value. Impurity analysis was performed using the best analytical method. Participating laboratories were requested to specify in detail which analytical method(s), which standards were used, and how the evaluation of measurement uncertainty was performed.

Each participating laboratory was responsible for the calibration of its own instrument(s) used for the analysis. Applied calibration method should be well established and reported to KRISS. This is an absolute necessity for proper evaluation of the data.

Each laboratory was required to express the uncertainty on all results submitted, as expanded uncertainty. The evaluation of the measurement uncertainty should be in accordance to the “Guide to the expression of uncertainty in measurement” (ISO GUM). The participants should provide a detailed description of the uncertainty budget, including;

- Method of evaluation (type A or type B)
- Assumed Probability distribution
- Standard uncertainties and sensitivity coefficients
- Effective degrees of equivalence (if applicable/used)
- Statistical reasoning behind the coverage factor

After the measurements, the participants were instructed to return the cylinders with a sufficient amount of gas (pressure at least 50 bar) to KRISS for re-analysis.

Additional measurement reports and information can be submitted jointly with the report form to the KRISS, and would be taken into consideration during the evaluation.

Gravimetric preparation

A set of carbon monoxide in synthetic air with the nominal mole fraction of approx. 350 nmol/mol, were gravimetrically(4) prepared through four step dilutions by the coordinating laboratory of KRISS. Each mixture was then verified by means of a GC/FID/Methanator system, against very fresh primary standard gas mixture (PSM) with amount-of-substance fractions of approx. 350 nmol/mol. After purity analysis of the parent gases and verification of the prepared mixtures, the amount-of-substance fractions were adopted as key comparison reference value (KCRV).

For purity analysis of O_2, Ar, and N_2 matrix gases, a GC/FID/Methanator was used and a detection limit for carbon monoxide was set at 0.7 nmol/mol (3σ). A significant amount-of-substance fraction of carbon monoxide impurity was measured by 0.7 nmol/mol in nitrogen and 6.9 nmol/mol in oxygen. Based on this purity results, CO mole fractions are properly applied to every dilution steps. After shipping, the amount of CO mole fraction changed so significantly, which must be taken into account for any further analysis. The stability of the CO in air standards used in this study can be described as follows.

A total of 16 cylinders were prepared for the comparison on July 21st 2012 and analyzed on July 24th 2012. Because a GC/FID/Methanator shows good linearity over the mole fraction range tested in this key comparison, a reference cylinder (A) was measured between sample cylinders as to not only measure sensitivity (Sensitivity = $\text{Response}_{\text{Instrument}}/\text{Mixing ratio}_{\text{Prepared}}$) ratios of sample versus reference but also correct analyzer drift during the comparison analysis in a sequence of A-B-A-C-A-..., and so on. Sensitivity ratios between reference and sample were compared with each other to find that they were within 0.30 % around unity as shown in Fig. 1. Thus, this 0.30% which satisfies a verification criteria was assigned to the analytical uncertainty (k=2) of certified values. In fact, their gravimetric preparation uncertainty including purity analysis was 0.22000%, k = 2. Considering the gravimetric preparation and the analytical uncertainty, the total expanded uncertainty of CO cylinder was calculated to be 0.37%.

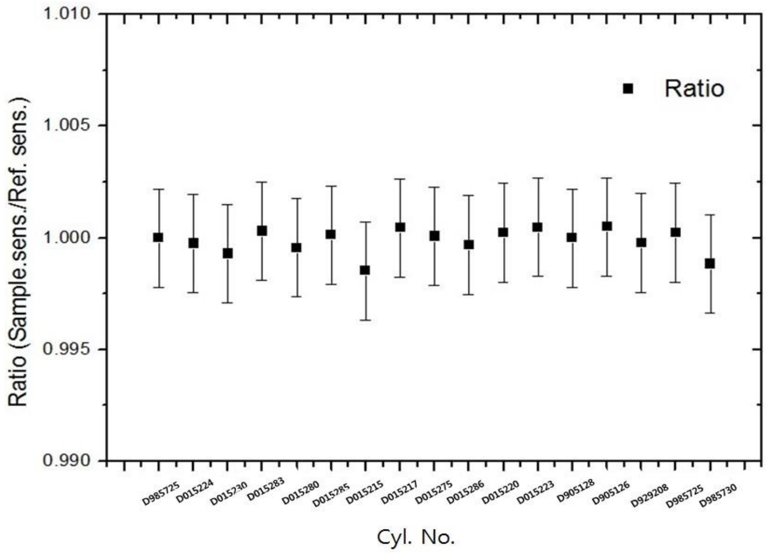

Figure 1. Consistency among the prepared cylinders (July 2012)

Table 3 lists the set of PSMs including their mole fraction composition. From this set ten standards were distributed to participants.

Table 3. Gravimetric preparation uncertainty of CO gases for a set of cylinders.

Cylinder	CO [nmol/mol]	$U_{prep.}$, k = 2 [nmol/mol]	Ar [%mol/mol]	O_2 [%mol/mol]	N_2 [%mol/mol]
D015224	356.33	1.33	0.9161	20.72	78.37
D015230	351.52	1.31	0.8986	20.91	78.19
D015283	350.81	1.31	0.9040	21.10	77.99
D015280	350.60	1.30	0.8907	20.96	78.15
D015285	348.86	1.30	0.9035	20.68	78.42
D015215	349.97	1.30	0.9610	20.96	78.08
D015217	350.83	1.31	0.9529	21.71	77.34
D015275	342.44	1.27	0.9362	20.62	78.45
D015286	353.26	1.31	0.9238	20.89	78.19
D015220	352.35	1.31	0.9184	20.67	78.42
D015223	351.35	1.31	0.8983	21.16	77.95

CO stability in air

In order to verify the mixture's stability, each cylinder was analyzed four times over a 20 month period. Each measurement was carried out against very fresh gravimetric standards aging less than a week, or in case of a reanalysis, a few weeks. First measurement was done, as indicated in the key comparison schedule, before the shipment of the cylinders. Additional three measurements were conducted once the cylinders were returned from the participants. For the second analysis the cylinders were compared to new gravimetric standards produced in March 2013. The second analysis was performed in May 2013. During the second analysis the returned cylinders were compared against the standards prepared in March 2013 (Fig. 2). For the 3th and 4th verifications, the returned cylinders were analyzed in Nov 2013 and Mar 2014 against two newly prepared sets, respectively. The two new sets of standard mixtures had been prepared in Sep. 2013 and Jan 2014, as indicated in figure 2 and table 4.

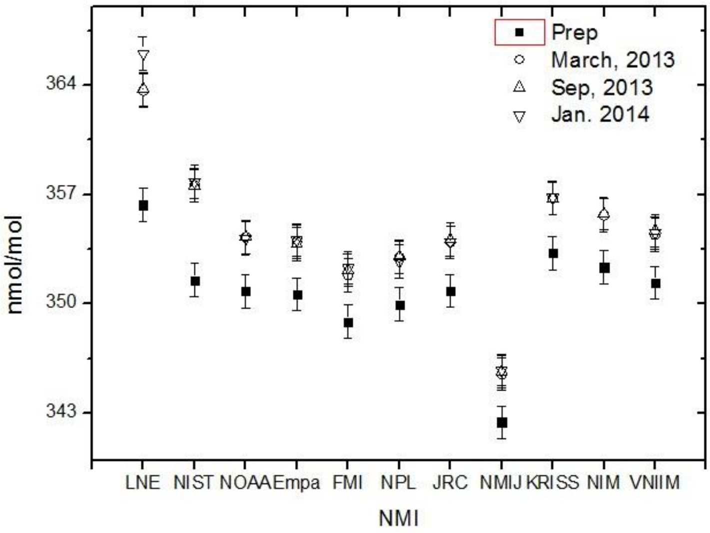

Figure 2. Drift of the cylinders initially prepared for the comparison (from top, filled square: preparation values, circle, upward triangle and downward triangle: measurement values against three sets of standard mixtures prepared in the subsequent times, respectively)

The second and third analysis showed that CO mole fractions increased by an average of 0.93% excluding D985730 and D015224 which increased by more than 1.7% for 14 months. Both Figure 2 and Table 4 show results of consecutive analyses since the preparation of mixtures. CO appears to have stopped increasing after an eight-month period from the preparation date. Due to very low amount of substance in D015220, its fourth analysis was skipped. Stability changes are shown in Figure 3, where the relative differences from the gravimetric values of the cylinders are shown as a function of the analysis time on the x axis. The differences look to have been stable (< 0.1 %) since the second verification, excluding one cylinder that showed continued drift.

Table 4. Temporal variation of the cylinders for the CCQM-K84

Laboratory	Cylinder	x_{prep} [nmol/mol] Jul. 2012	x_{2nd} [nmol/mol] 2nd ver. May. 2013	x_{3rd} [nmol/mol] 3rd ver. Nov. 2013	x_{4th} [nmol/mol] 4th ver. Mar. 2014
LNE	D015224	356.33	363.65	363.77	366.04
NIST	D015230	351.52	357.62	357.57	357.81
NOAA	D015283	350.81	354.28	354.29	354.19
FMI	D015285	348.86	351.82	352.15	352.29
NPL	D015215	349.97	352.99	353.03	352.72
JRC	D015217	350.83	353.96	354.12	353.96
NMIJ	D015275	342.43	345.48	345.67	345.76
KRISS	D015286	353.26	356.74	356.75	356.80
NIM	D015220	352.35	355.67	355.78	-*
VNIIM	D015223	351.35	354.42	354.70	354.55

*NIM cylinder ran out before 4th analysis.

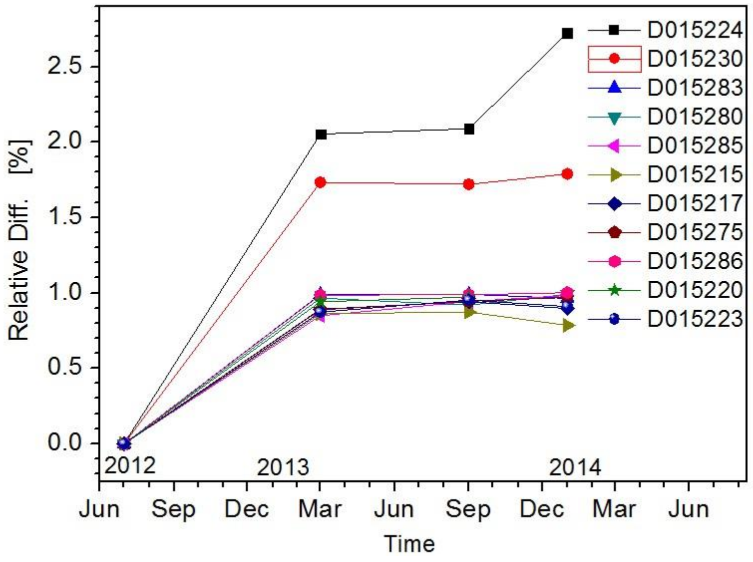

Figure 3. Mole fraction changes since preparation in July 2012.

In order to validate the long-term stability test described in previous section, a set of CO/N_2 cylinders was newly manufactured to be used as a stable reference. It is well known that ambient level of CO in N_2 cylinders have been stable over a few years. Our result shows that

CO in N_2 cylinders are stable within 0.02 % even for four years (Table 5).

Table 5. Details on CO stability tests of CO in N_2 cylinders

	x_{prep} [nmol/mol]	Prep. date	Analysis date	Sensitivity*	Matrix
D015249	344.38	2014.1.11	2014.3.08	0.8485	N_2
D015318	343.35	2014.1.11	2014.3.08	0.8486	N_2
ME2223	400.18	2010.3.15	2014.3.08	0.8486	N_2
ME5576	399.75	2010.3.15	2014.3.08	0.8486	N_2
ME5629	383.25	2010.3.15	2014.3.08	0.8483	N_2

* Sensitivity (S) is defined as a ratio of instrumental response (Res) and the gravimetric concentration (X). S=Res/X.

Contrary to Table 5, Table 6 shows that the sensitivities of CO/air cylinders versus that of CO/N_2 vary by 5 %. Since the stability of CO concentrations in N_2 (Table 5) were ensured by the constant sensitivities among 4-year old cylinders (MEXXXX) and newly prepared gravimetric cylinders (DXXXXXX), it is plausible to set new CO/N_2 cylinders as a reference for the validation test (Table 6), of which measurement sequence is R-A-R-B-R-C-R…. In the series measurement 'R' denotes a reference measurement and the CO/N_2 cylinder (D015249) was used. Ratios between sensitivities of CO/air and CO/N_2, namely S(air)/S(N_2), provides reliable indicator to check the concentration variation within a CO/air cylinder. For instance, the sensitivity ratio value of newly prepared cylinder (D155876/D015249) is lower than that of the older cylinders to exhibit the rate of increase in the CO amounts. As the stability of CO in N_2 cylinders has been proven to be considerably superb (Table 5), a degree of CO-drift among CO/air cylinders can be derived by the comparison of sensitivity ratios of the measurements as follow.

$$\mathrm{RD}_{D155876}^{B,C,D,,,}\,(\%) = \left[\frac{\left|\frac{S(air)}{S(N_2)}\right|_{B,C,D,,,}}{\left|\frac{S(air)}{S(N_2)}\right|_{D155876}} - 1\right] \times 100 \qquad (1)$$

where superscript and subscript stands for measurement index. The value of 'RD" directly denotes the relative deviation of CO concentration determined against sensitivity ratio of cylinder D155876 to D015249 (CO/N_2).

Though the drift rate of CO mole fraction seems to be uneven for every cylinder in Table 6, CO mole fraction tends to sit around 1% incensement. The Cylinders of D015224 (LNE) and D015230 (NIST) were more enormously varied 1.7 % and 2.7 % than the others. In the long run it is the results in table 6 that agree with those in Table 4 and Fig. 3. It can be conclusively said that the stability of cylinders for this key comparison was thoroughly evaluated and confirmed by the means of CO/N_2 referencing method. In future comparisons, the CO stability in air should be monitored for several months prior to distribution.

Table 6. Stability of CO/air against CO/N_2

	x_{prep} [nmol/mol]	Prep. date	Analysis date	Sensitivity	Sensitivity Ratio*	$\mathrm{RD}^{B,C,D,,,}_{D155876}$ [%]	Matrix
D015249	344.38	2014.1.11	2014.3.14	0.8496	1	-	N_2
D155876	344.02	2014.1.11	2014.3.14	0.8646	1.0176	0.0000	Air
D015286	353.26	2012.7.21	2014.3.14	0.8724	1.0268	0.9041	Air
D015224	356.33	2012.7.21	2014.3.14	0.8877	1.0448	2.6730	Air
D015230	351.52	2012.7.21	2014.3.14	0.8807	1.0356	1.7689	Air
D015275	342.43	2012.7.21	2014.3.14	0.8722	1.0270	0.9237	Air

* Ratio of the sensitivities of corresponding raw to D015249 of CO/N_2 in first raw (Ratio $_{\mathrm{air},\ n^{th}}$ = $S_{\mathrm{air},\ n^{th}}/S_{D015249}$)

In 2014 fall meeting, It was agreed that KCRV of each cylinder be a preparation value and associated uncertainty including stability drift, which ($u_{stab.}$) is regarded to be an interval ($u_{stab.}$) between, before (x_{prep} in Table 4), and after (x_{2nd} in Table 4) shipping. Therefore reference value is adopted as the preparation value and its total uncertainty includes changes in CO mole fraction due to mixture drift of positive direction in 10 months. The KCRV and associated expanded uncertainty of each cylinder are listed in Table 7.

Table 7. KCRV and its Uncertainty budget including stability change

Laboratory	Cylinder	x_{prep} [nmol/mol]	U_{prep_i} [nmol/mol]	$U_{stab.}$ (x_{2nd}- x_{prep}) [nmol/mol]	U_{prep_f} [nmol/mol]
LNE	D015224	356.33	1.33	7.32	7.44
NIST	D015230	351.52	1.31	6.10	6.23
NOAA	D015283	350.81	1.31	3.47	3.71
FMI	D015285	348.86	1.30	2.96	3.23
NPL	D015215	349.97	1.30	3.02	3.29
JRC	D015217	350.83	1.31	3.13	3.39
NMIJ	D015275	342.43	1.27	3.04	3.30
KRISS	D015286	353.26	1.31	3.48	3.72
NIM	D015220	352.35	1.31	3.32	3.57
VNIIM	D015223	351.35	1.31	3.07	3.34

Measurement results

The measurement and calibration methods used by the participating laboratory in this comparison are listed in Table 8. Participants used laser spectroscopy, GC with various detectors or NDIR for the gas analysis. It is shown that laser absorption spectroscopy such as cavity ring down spectrometer (CRDS) was preferred by many NMIs. Judging from Figure 4, it was difficult to find which measurement technique would be the best for CO/air analysis. All participants except FMI (NPL standard) used their own standards.

Table 8. Summary of the measurement methods of the participants

Laboratory	Cylinder	Measurement period	Calibration standards	Instrument calibration	Measurement technique
LNE	D015224	Sep. 2012	Own standards	single point	QC-TILDAS
NIST	D015230	Sep. 2012	Own standards	multiple point	*CRDS
NOAA	D015283	Sep to Dec.	WMO-2004	Two point	**ICOS
FMI	D015285	Nov. 2012	NPL	Two point bracket	*CRDS
NPL	D015215	Dec. 2012 to Jan. 2013	Own standards	single point	*CRDS
JRC	D015217	Sep. 2012	Own standards	multiple point	***NDIR

			After 1 step dilution		
NMIJ	D015275	Sep. 2012	Own standards	multiple point	GC-HgO
KRISS	D015286	Jul. 2012 to Sep.	Own standards	single point	GC/FID/Methanator
NIM	D015220	Mar. 2013	Own standards	single point	GC/FID/Methanator
VNIIM	D015223	Sep. 2012	Own standards	single point	GC/FID/Methanator

*CRDS: Cavity ring-down spectrometer, **ICOS: Off axis integrated cavity output spectroscopy, ***NDIR: Non dispersive infrared analysis method

Preparation values and participants' reported values in this comparison are summarized in Table 9 and shown in Figure 4.

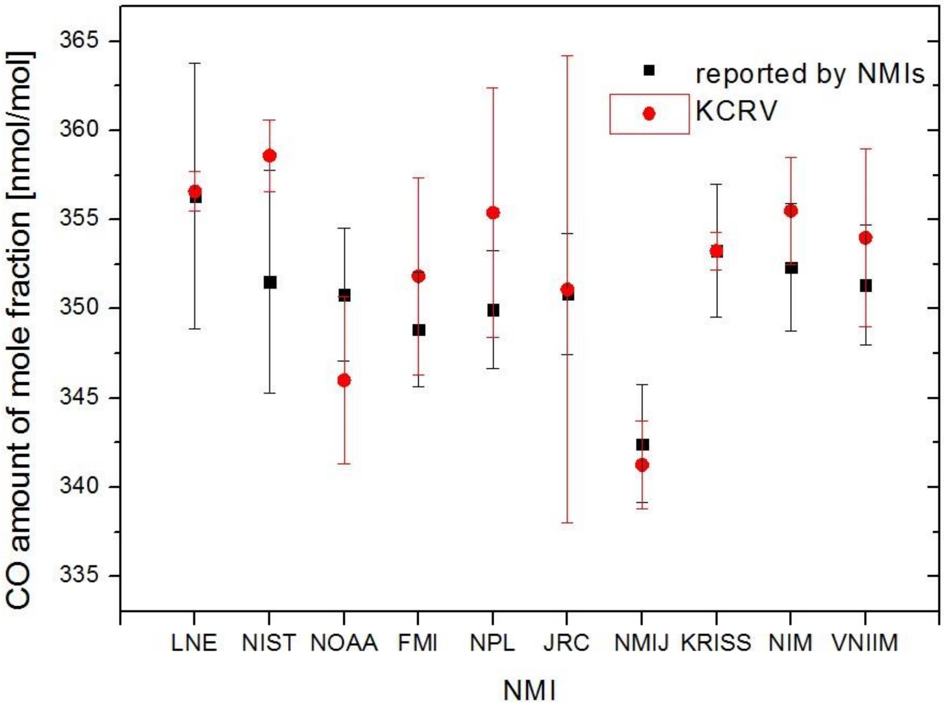

Figure 4. CO mole fractions between reported by participating laboratories (red circle) as well as KCRV (black square), where the vertical bars represent the expanded uncertainty reported by participants (red bar) and KCRV (black bar)

The difference between reported and prepared was listed in Table 9.

Table 9. Measurement Results of CCQM K84

Laboratory	Cylinder	x_{prep} [nmol/mol]	$u_{\text{prep\_tot}}$ [nmol/mol]	x_{lab} [nmol/mol]	U_{lab} [nmol/mol]	Δx $x_{\text{lab}} - x_{\text{prep}}$ [nmol/mol]	$u(\Delta x)$ $u(x_{\text{lab}} - x_{\text{prep}})$ [nmol/mol]
LNE	D015224	356.33	3.72	356.6	1.1	0.3	3.8
NIST	D015230	351.52	3.12	358.6	2.0	7.1	3.3
NOAA	D015283	350.81	1.86	346.0	4.7	-4.8	3.0
FMI	D015285	348.86	1.62	351.84	5.52	2.98	3.20
NPL	D015215	349.97	1.65	355.4	7.0	5.4	3.9
JRC	D015217	350.83	1.7	351.09	13.10	0.26	6.77
NMIJ	D015275	342.43	1.65	341.26	2.46	-1.17	2.06
KRISS	D015286	353.26	1.86	353.25	1.06	-0.01	1.94
NIM	D015220	352.35	1.79	355.5	3	3	3
VNIIM	D015223	351.35	1.67	354	5	3	3

Degrees of equivalence (DoE)

For the sake of consistency between the results of the participating laboratories and the KCRV, a degree of equivalence (d_i) (5) is expressed as

$d_{\text{i}} = x_{\text{i}} - x_{\text{i,KCRV}},$ (2).

In the above equation, $x_{i,KCRV}$ identifies the key comparison reference value which is already mentioned as x_{prep}, and x_i is the result of laboratory *i*. Therefore the standard uncertainty of d_i based on Table 9 can be expressed as:

$u^2(d_{\text{i}}) = u^2_{\text{i,lab}}(x_{\text{i}}) + u^2_{\text{i,prep\_tot}}(x_{\text{i,KCRV}})$ (3).

Assuming that the terms in equation (3) are uncorrelated, the degrees of equivalence d_{i} ± $U(d_{\text{i}})$ are presented in Figure 5, where the solid squares represent the d_i and the vertical bars indicate the associated expanded uncertainty ($k = 2$).

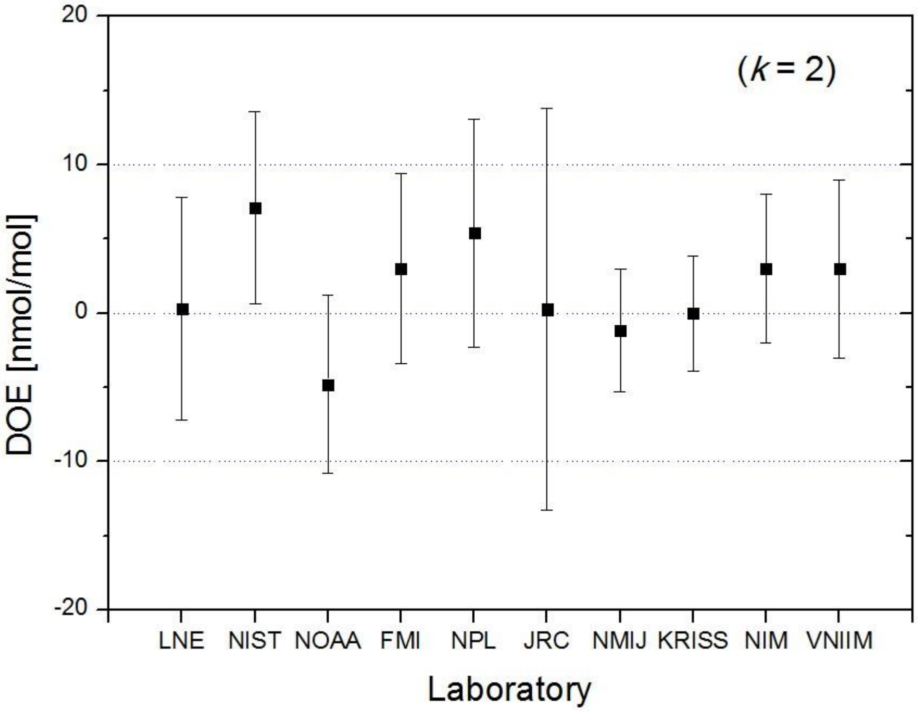

Figure 5. Differences between participants' results and the KCRV for the comparison, where the vertical bar represents the expanded uncertainty, $U(d_i)$, at the 95 % level of confidence.

Table 10. Degrees of equivalence with uncertainties (k=2) of CCQM K84

Laboratory	Cylinder	d_i [nmol/mol]	$U(d_\mathrm{i})$ [nmol/mol]
LNE	D015224	0.3	7.5
NIST	D015230	7.1	6.5
NOAA	D015283	-4.8	6
FMI	D015285	2.98	6.4
NPL	D015215	5.4	7.7
JRC	D015217	0.26	13.53
NMIJ	D015275	-1.17	4.12
KRISS	D015286	-0.01	3.87
NIM	D015220	3	5
VNIIM	D015223	3	6

Conclusions

An increase in CO mole fraction was observed for all cylinders used for this comparison. Since drift rates were not uniform, it was decided to use the prepared values as the KCRV, and to include mole fraction changes in the KCRV uncertainty.

Most of the results in this key comparison are consistent with their KCRV within uncertainties. In order to achieve the WMO recommended comparability goal of ± 2 nmol/mol, the stability of CO in air requires further attention.

This key comparison supports the measurement capability of CO at 350 nmol/mol. The results of the comparison identify measurement equivalence between NMIs and WMO. This key comparison supports the measurement capability of CO in the range of 50 nmol/mol to 1000 nmol/mol.

Acknowledgements

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Appendix: Measurement Reports

Report Form Carbon monoxide in synthetic air

Laboratory name: National Metrology Institute of Japan

Cylinder number: D015275

Measurement #1

Component	**Date (dd/mm/yy)**	**Result (μmol/mol)**	**Standard deviation (% relative)**	**number of replicates**
CO	03/09/12	339.85	0.33	9
CO	03/09/12	340.42	0.40	9
CO	04/09/12	341.93	0.32	9
CO	04/09/12	341.70	0.52	9
CO	05/09/12	343.48	0.53	9
CO	07/09/12	340.91	0.32	9
CO	07/09/12	340.54	0.36	9

Results

Component	**Result (μmol/mol)**	**Expanded Uncertainty (μmol/mol)**	**Coverage factor**[1]
CO	341.26	2.46	2

Method Description Forms

Details of the measurement method used:

Reference Method:

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[1] The coverage factor shall be based on approximately 95% confidence.

Carbon monoxide concentration in synthetic air has been quantified using Peak performer 1 gas chromatography with reducing compound photometer (GC-HgO). Nitrogen purified by getter type purifier was used as carrier gas and the flow rate was 25 ml/min. Column temperature used is 100 ºC. Sample was introduced to GC-HgO using 5mL sample loop and injection volume was corrected by sample temperature and pressure. The sample temperature is temperature of sample loop and the pressure is obtained from the downstream pressure gauge of sample loop.

Calibration standards:

Preparation method

Five calibration standards were used for the determination of carbon monoxide in synthetic air. The standards were prepared from pure carbon monoxide, pure nitrogen, and pure oxygen in accordance with ISO6142:2001 (Gas analysis-Preparation of calibration gases-Gravimetric method. Pure carbon momoxide was from Sumitomo Seika Chemicals Company Limited and pure nitrogen and oxygen from Japan Fine Products. Four-step dilution was used to make the mixtures, with carbon monoxide concentration of 23000-29000 μmol/mol, 610-670 μmol/mol, 13-16 μmol/mol, and 300-370 νmol/mol. Oxygen was added in the last-step dilution. Table 1 shows gravimetric value and expanded uncertainty of the calibration standards.

Table 1. Gravimetric value and expanded uncertainty in calibration standards

Cylinder number	Gravimetric Value (nmol/mol)	Expanded uncertainty [k=2] (nmol/mol)
CPC00873	310.55	0.32
CPB16345	371.07	0.32
CPC00420	300.99	0.32
CPC00414	348.78	0.32
CPC00418	328.87	0.32

Purity analysis

The impurities of carbon monoxide, nitrogen, and oxygen were determined by analytical methods and the amount of the major component is conventionally determined from the following equation,

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

where

x_i: the mole fraction of impurity i, determined by analysis;

N: the number of impurities likely to be present in the final mixture;

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

Table 2-4 shows the results of purity analyses. The purities of carbon monoxide, nitrogen and oxygen were not contributed to the uncertainty of the standard gases prepared by gravimetric method.

Table 2. Purity table of high-purity carbon monoxide used as parent gas

Components	*Applied concentration (μmol/mol)*	*Standard uncertainty (μmol/mol)*	*Distribution*	*Analytical method*
H_2	2.87	0.61	Normal	Micro GC-TCD
He	19.46	0.24	Normal	Micro GC-TCD
N_2	4.27	0.14	Normal	Micro GC-TCD
O_2	1.65	0.19	Normal	Micro GC-TCD
CO_2	0.39	0.22	Rectangular	Micro GC-TCD
N_2O	0.42	0.24	Rectangular	Micro GC-TCD
CH_4	0.75	0.44	Rectangular	Micro GC-TCD
H_2O	0.33	0.02	Rectangular	Capacitance-type moisture meter
CO	999997.36			

Table 3. Purity table of high-purity nitrogen as parent gas

Components	*Applied concentration (μmol/mol)*	*Standard uncertainty (μmol/mol)*	*Distribution*	*Analytical method*
O_2	0.819	0.473	Rectangular	Micro GC-TCD
CO_2	0.010	0.006	Rectangular	FT-IR
CH_4	0.026	0.015	Rectangular	FT-IR
CO	0.00029	0.00016	Rectangular	GC-HgO
H_2O	0.439	0.253	Rectangular	Capacitance-type moisture meter
N_2	999998.48			

Table 4. Purity table of high-purity oxygen as parent gas

Components	*Applied concentration (μmol/mol)*	*Standard uncertainty (μmol/mol)*	*Distribution*	*Analytical method*
N_2	0.090	0.052	Rectangular	GC-TCD
Ar	0.087	0.050	Rectangular	GC-TCD

CO_2	0.056	0.004	Normal	FT-IR
CH_4	0.003	0.002	Rectangular	FT-IR
CO	0.00179 (NSU 12-04) 0.00262 (NSN 75-82)	0.00016 (NSU 12-04) 0.00020 (NSN 75-82)	Normal	GC-HgO
H_2O	0.439	0.253	Rectangular	Capacitance-type moisture meter
O_2	999999.32			

Concentrations of carbon monoxide in nitrogen and oxygen were also measured in detail by FTIR because concentration of carbon monoxide in nitrogen and oxygen, which is close to detection limit, contribute to uncertainty of gravimetric value. In FTIR with path length of 10m and MCT detector, measurement of carbon monoxide in nitrogen and oxygen was performed at high sample pressure of 4000 hPa and integration of 16384 times to achieve high detection sensitivity. The concentration of carbon monoxide obtained using FTIR was agreed with that obtained using GC-HgO within uncertainty.

Instrument calibration:

Instrument calibration is performed using NMIJ primary standard gas mixtures. A calibration curve was made between 300 and 370 nmol/mol by measuring the five calibration standards listed in table 1. NMIJ primary standards. The calibration curve was obtained using least square method.

Sample handling:

The sample cylinder had been stood at room temperature for more than a week after arrival. Each cylinder was equipped with a stainless steel pressure regulator that was purged several times by sequential evacuation and pressurisation with the gas mixture used. Samples were transferred to sample loop at flow rate of 80 ml/min using mass-flow controller. Effect of sample pressure and temperature were corrected. The pressure was measured by pressure sensor at downstream of sample loop and the temperature was ambient temperature near sample loop.

Uncertainty:

The uncertainty used for the calibration mixtures contains all sources of gravimetric preparation. Uncertainty for stability is not included because no instability has been detected. The uncertainty in measurement is calculated based on repeatability of the acquired area.

Detailed uncertainty budget:

Please include a list of the uncertainty contributions, the estimate of the standard uncertainty, probability distributions, sensitivity coefficients, etc.

Typical evaluation of the measurement uncertainty for CO:

Quantity X_i	Estimate x_i	Evaluation Type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$
References		A	Gaussian	0.16 µmol/mol		
Repeatability		A	Gaussian	1.22 µmol/mol		
Combined standard uncertainty				1.23 µmol/mol		

Report Form Carbon monoxide in synthetic air

Laboratory name: NIST

Cylinder number: D015230

Analyst: Dr. Gerald Mitchell

The Gas Metrology Group of the Analytical Chemistry Division at NIST participated in the CCQM K84 Key Comparison. One (1) compressed gas cylinder containing carbon monoxide (CO) in a balance of air (cylinder number D015230) was analyzed as part of the comparison sponsored by the Gas Analysis Working Group of the Consultative Committee for Amount of Substance (CCQM). The mixture was prepared gravimetrically according to the CCQM-K84 protocol by the Korea Research Institute of Standard and Science (KRISS).

Analytical Methods

Carbon Monoxide Analysis: The carbon monoxide was analyzed using a Los Gatos Model N_2O/CO-23d analyzer (NIST # 642093). A computer operated gas analysis system (COGAS # 14) was used to deliver the sample stream to the analyzer. Prior to beginning, each analysis the sample line and regulator of each cylinder was purged five (5) times. The analyzer was used to measure the response ratio of each primary standard gas mixture (PSM) cylinder to that of control cylinder (FF10258). During each analytical run, the sample has a purge time of 1.5 minutes before data collection. The analyzer's internal pump used to draw the sample into the analysis cell. The CCQM cylinder and the PSMs listed below were measured against the control cylinder six times during two different analytical periods.

Calibration Standards

Six NIST gravimetrically prepared primary reference materials ranging in concentration from 0.200 µmol/mol to 0.500 µmol/mol were used in this analysis. The PSMs are listed below:

Cylinder Number	Concentration (µmol/mol)	Uncertainty (µmol/mol k=2)
FF10204	0.2015	0.0019
FF10217	0.2526	0.0019
FF10221	0.2996	0.0019
FF10235	0.3483	0.0019
FF10226	0.3940	0.0018

FF10228	0.5032	0.0018

These standards were prepared from three different parent mixtures but all with the same source of balance gas (air). The table 1 gives an assay of the air cylinders used to prepare the standards.

Table 1. Assay of Pure Cylinders

Purity Pure Air (CC101252)	Concentration (µmol/mol)	Uncertainty (µmol/mol)	Purity Pure Air (CC2794)	Concentration (µmol/mol)	Uncertainty (µmol/mol)
N2 (difference)	781000	5	N2 (difference)	780930	9
CO (measured)	0.0077	0.0020	CO (measured)	0.0081	0.0020
CO2 (measured)	397.97	0.075	CO2 (measured)	393.2	0.051
CH4 (measured)	0.0017	0.0009	CH4 (measured)	0.0017	0.0009
Ar (measured)	9352.0	3.0	Ar (measured)	9352.0	8.0
O2 ()measured)	209250	3.4	O2 ()measured)	209325	3.4
Purity Pure Air (CC73041)	Concentration (µmol/mol)	Uncertainty (µmol/mol)	Purity Pure Air (CC81188)	Concentration (µmol/mol)	Uncertainty (µmol/mol)
N2 (difference)	780971	9	N2 (difference)	780885	10
CO (measured)	0.0081	0.0020	CO (measured)	0.0064	0.0020
CO2 (measured)	393.15	0.05	CO2 (measured)	397.10	0.50
CH4 (measured)	0.0017	0.0009	CH4 (measured)	0.0017	0.0009
Ar (measured)	9352.0	8.0	Ar (measured)	9349.0	6.0
O2 ()measured)	209284	3.8	O2 ()measured)	209369.0	8.1

Instrument Calibration: The instrument used in this study is a Los Gatos Model N_2O/CO-23d analyzer. It was calibrated using six gravimetrically prepared PSMs ranging in concentration from 0.200 µmol/mol to 0.500 µmol/mol. The CCQM sample (D015230) was included in the analysis with the PSMs. They were all compared to a control a minimum of six times during each of the two analytical periods. The analytical scheme used was, Control – PSM Standard (1) – Control – PSM Standard (2) Control, etc. The procedure called for each cylinder to have a 1.5 minutes period of equilibration and two-minute data collection period. A calibration curve using all data generated during the two analytical periods was generated using PSM Validator (table 2).

Sample Handling

This analysis is to quantify the CO in a single CCQM-K84 cylinder (D015230). The sample was fitted with a regulator adapted to the fitting supplied by KRISS. The measurements were automated using NIST data system (# 631251) and a computer operated gas analysis system (COGAS # 14). Prior to starting each set of analyses the regulator was flushed five times. The output pressure of each regulator was set so that the slip stream feeding the analyzer has an excess of 200 ml/min.

Amount-of-Substance Fraction

The amount-of-substance fraction (concentration) for carbon monoxide in the K-84 PRM cylinder number D015230 is given in table 3. All measured data and calculations for this CCQM key concentration have been reviewed for sources of systematic and random errors. The uncertainty of the concentration is expressed as an expanded uncertainty, $U = k_c$ with a coverage factor k equal to 2. The true concentration is asserted to lie within the interval defined (0.3586 ± 0.0020) µmol/mol with a level of confidence of approximately 95 % [1]. The uncertainty has been expanded to 0.0020 µmol/mol, as this corresponds to the uncertainty of our primary standards.

Table 2. CCQM-K84 Cylinder D015230 Validation Data

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

	Value	Std Error
b0	0.009141356	0.00265624
b1	0.296060862	0.002296321
cov(b0,b1)		-5.8386E-06
rms residual error		1.217144142

X	Y	X-Solution	Y-Solution	uTest	Cylinder ID
0.6681	0.2051	0.6681	0.2069	PASS	FF10204
0.8176	0.2526	0.8176	0.2512	PASS	FF10217
0.9708	0.2996	0.9709	0.2966	PASS	FF10221
1.1503	0.3483	1.1503	0.3497	PASS	FF10235
1.3069	0.3940	1.3069	0.3961	PASS	FF10226
1.6662	0.5032	1.6662	0.5024	PASS	FF10228

Xin	uXin	Yeval	uYeval	Grav Value (k=2)	Cylinder ID
1.0000	0.0000	0.30520	0.00081	0.3042 ± 0.0039	FF10258
1.1804	0.0003	0.35861	0.00079	Unknown	D015230

Table 3. Amount-of-Substance Fraction (Concentration) for CCQM-K-84 Cylinder # D015230

Cylinder Contents	Measured Value (September 2012)
Carbon monoxide in Air	(0.3586 ± 0.0020) µmol/mol

Appendix A.

Report Form Carbon monoxide in synthetic air

Laboratory name: LNE

Cylinder number: D0152249

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	21/09/2012	356.83	0.03	3

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	27/09/2012	356.82	0.04	3

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	28/09/2012	356.33	0.07	3

Measurement #4

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	01/10/2012	357.07	0.04	3

Measurement #5

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	03/10/2012	356.02	0.05	3

Measurement #6

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	04/10/2012	357.10	0.10	3

Results

Component	Result (nmol/mol)	Expanded Uncertainty (nmol/mol)	Coverage factor[2]
CO	356.6	1.1	2

Method Description Forms

Please complete the following data regarding the description of methods and the uncertainty evaluation.

Details of the measurement method used:

Reference Method:

A Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) developed by Aerodyne Research Inc. is used to quantify CO concentration. This analytical system consists of four pulsed lasers (one for each analyte), an optical system with a 210 m path length absorption cell (Herriott type) and a cooled HgCdTe (MCT) detector.

Calibration standards:

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[2] The coverage factor shall be based on approximately 95 % confidence.

Gravimetric gas mixtures were prepared in accordance with the international standard EN ISO 6142.

Two gas mixtures (CO/Air 0008 and CO/Air 0009) at about 350 nmol/mol of carbon monoxide in synthetic air were prepared using gravimetric method.
Each preparation needed 4 steps (4 gravimetric gas mixtures) to obtain the nominal concentration of 350 nmol/mol.
The mass of each component has been measured by comparison between the mass of the cylinder and a standard cylinder (tare) with a comparator METTLER AX3200 with a resolution of 0.1 mg and standard masses.

Instrument calibration:

The background of the QC-Laser spectrometer was made with zero air. Then, the spectrometer responses were recorded for gravimetric gas mixture and for the unknown gas mixture. The amount fraction of the unknown gas mixture is determined using the amount fraction of the gravimetric gas mixture and the ratio of the spectrometer responses to the gravimetric gas mixture and the unknown gas mixture.
This sequence is repeated three times during a day and on 2 days or 4 days respectively with the CO/Air 0008 gravimetric gas mixture and the CO/Air 0009 gravimetric gas mixture.

Sampling handling:

Cylinders were maintained at a laboratory temperature of (21 ± 2) °C throughout the period of analysis.

Samples were introduced into the analyzer at atmospheric pressure (excess flow was passed to vent) using a low volume gas regulator.

Uncertainty:

<u>1) Gravimetric gas mixtures uncertainties :</u>

- ✓
- ✓ As explained before the preparation of the 2 gravimetric gas mixtures at about 350 nmol/mol needed the preparation of 4 gravimetric gas mixtures.

The last 2 gravimetric gas mixtures at about 350 nmol/mol were obtained by diluting gravimetrically the third gravimetric gas mixture (CO at 10 µmol/mol – CO/N2 0061) with argon, oxygen and nitrogen.

✓ *Gravimetric gas mixture n° CO/Air 0008*

✓

- **Purity tables of each component**

✓ Component	Concentration (mol/mol)	Uncertainty (mol/mol)
CO	0.00000998813483	0.00000000669398
N_2	0.99998759588702	0.00000007209187
Ar	0.00000235021068	0.00000006884169
methane	0.00000002549589	0.00000001412405
H_2	0.00000002549090	0.00000001412405
CO_2	0.00000000696628	0.00000000098025
O_2	0.00000000511464	0.00000000284441
H_2O	0.00000000201496	0.00000000117632

Purity table of CO/N2 0061

✓ Component	Concentration (mol/mol)	Uncertainty (mol/mol)
Ar	0.9999998430	0.000000087
N_2	0.000000150	0.000000087
O_2	0.000000005	0.0000000029
methane	0.0000000015	0.000000001
CO_2	0.0000000005	0.000000001
CO	0.000000000	.0000000005
H_2O	0.000000000	0.000000001

Purity table of Argon (BIP+ n°A106273)

Component	Concentration (mol/mol)	Uncertainty (mol/mol)
O_2	0.999997842	0.000001155
CO	0.00000000283	0.0000000008
CO_2	0.000000139	0.000000005
N_2	0.000002000	0.0000011547
methane	0.0000000015	0.000000001
NO_2	0.000000015	0.0000000087
H_2O	0.000000000	0.000000001

Purity table of Oxygen (Alphagaz n°20026895)

Component	Concentration (mol/mol)	Uncertainty (mol/mol)
N_2	0.999999711	0.000000037

O_2	0.000000005	0.0000000029
Ar	0.0000002566	0.000000034
CO_2	0.0000000005	0.000000001
methane	0.0000000015	0.000000001
H_2	0.000000025	0.0000000144
H_2O	0.0000000002	0.0000000012
CO	0.000000000	0.0000000005

Purity table of Nitrogen (BIP+ n°293523)

- **Mass of each component for preparing the gravimetric gas mixture CO/Air 0008**

Component	Mass (g)	Uncertainty (g)
CO/N2 0061	44.888	0.013
Argon BIP + n°A106273	17.952	0.013
Oxygen alphagaz n°20026895	306.523	0.013
Nitrogen BIP+ n°293523	941.596	0.015

✓

- **Composition of the gravimetric gas mixture CO/Air 0008**

Component	Concentration (mol/mol)	Uncertainty (mol/mol)
Carbon monoxide	$354.35\ 10^{-9}$	$0.49\ 10^{-9}$
Argon	$0.99331\ 10^{-2}$	$0.00069\ 10^{-2}$
Oxygen	$21.1726\ 10^{-2}$	$0.00079\ 10^{-2}$
Nitrogen and others impurities	balance	-

- ✓ *Gravimetric gas mixture n° CO/Air 0009*
  - ✓

- **Purity tables of each component**

✓ Component	Concentration (mol/mol)	Uncertainty (mol/mol)
CO	0.00000998813483	0.00000000669398
N_2	0.99998759588702	0.00000007209187
Ar	0.00000235021068	0.00000006884169
methane	0.00000002549589	0.00000001412405
H_2	0.00000002549090	0.00000001412405
CO_2	0.00000000696628	0.00000000098025
O_2	0.00000000511464	0.00000000284441
H_2O	0.00000000201496	0.00000000117632

Purity table of CO/N2 0061

✓ Component	Concentration (mol/mol)	Uncertainty (mol/mol)
Ar	0.9999998430	0.000000087
N_2	0.000000150	0.000000087
O_2	0.000000005	0.0000000029
methane	0.0000000015	0.000000001
CO_2	0.0000000005	0.000000001
CO	0.000000000	.0000000005
H_2O	0.000000000	0.000000001

Purity table of Argon (BIP+ n°A106273)

Component	Concentration (mol/mol)	Uncertainty (mol/mol)
O_2	0.999997842	0.000001155
CO	0.00000000283	0.0000000008
CO_2	0.000000139	0.000000005
N_2	0.000002000	0.0000011547
methane	0.0000000015	0.000000001
NO_2	0.000000015	0.0000000087
H_2O	0.000000000	0.000000001

Purity table of Oxygen (Alphagaz n°20026895)

Component	Concentration (mol/mol)	Uncertainty (mol/mol)
N_2	0.999997648	0.000000073
O_2	0.000000005	0.0000000029
Ar	0.000002288	0.000000070
CO_2	0.000000007	0.000000001
methane	0.000000025	0.0000000144

H_2	0.000000025	0.0000000144
H_2O	0.000000002	0.0000000012
CO	0.000000000	0.0000000005

Purity table of Nitrogen (BIP+ n°082420)

- **Mass of each component for preparing the gravimetric gas mixture CO/Air 0009**

Component	Mass (g)	Uncertainty (g)
CO/N2 0061	44.606	0.013
Argon BIP + n°A106273	17.764	0.013
Oxygen alphagaz n°20026895	300.797	0.013
Nitrogen BIP+ n°082420	939.722	0.015

- **Composition of the gravimetric gas mixture CO/Air 0009**

Component	Concentration (mol/mol)	Uncertainty (mol/mol)
Carbon monoxide	$354.15\ 10^{-9}$	$0.49\ 10^{-9}$
Argon	$0.98874\ 10^{-2}$	$0.00069\ 10^{-2}$
Oxygen	$20.8975\ 10^{-2}$	$0.00080\ 10^{-2}$
Nitrogen and others impurities	balance	-

2) Detailed uncertainty budget:

Uncertainty source	Estimate x_I *(nmol/mol)*	Assumed distribution	Standard uncertainty $u(x_i)$ *(nmol/mol)*
Mean concentration obtained by comparison with the gravimetric gas mixture CO/Air 0008	356.18	Standard deviation of the values	0.25
Mean concentration obtained by comparison with the gravimetric gas mixture CO/Air 0009	356.95	Standard deviation of the values	0.22
Gravimetric gas mixture concentration (CO/Air 0008)	354.35	-	0.49
Gravimetric gas mixture concentration (CO/Air 0009)	354.15	-	0.49

The concentration of the unknown gas mixture D0152249 is the mean concentration of the 2 mean concentrations obtained by comparison with the 2 gravimetric gas mixtures CO/Air 0008 and CO/Air 0009:

$$C_{D0152249} = \frac{356.18 + 356.95}{2} = 356.6\ nmol / mol$$

The uncertainty on the unknown gas mixture concentration is given by:

$$u^2(C_{D0152249}) = \frac{1}{4}(u^2(C_{CO/Air\ 0008}) + s^2_{CO/Air\ 0008} + u^2(C_{CO/Air\ 0009}) + s^2_{CO/Air\ 0009} + 2 \times r \times u^2(C_{CO/Air\ 0008}) \times u^2(C_{CO/Air\ 0009}))$$

$$u^2(C_{D0152249}) = \frac{1}{4}(0.49\text{^}2 + 0.25\text{^}2 + 0.49\text{^}2 + 0.22\text{^}2 + 2 \times 1 \times 0.485 \times 0.485) = 0.26$$

(r is equal to 1 because the 2 gravimetric gas mixtures are correlated)

And $U(C_{D0152249}) = 1.1\ nmol / mol$

Report from Carbon monoxide in synthetic air

Laboratory name: Finnish Meteorological Institute

Cylinder number:

Measurement #1

Component	Date (dd/mm/yy)	Results (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	07/11/2012	351,42	0,04 %	10

Measurement #2

Component	Date (dd/mm/yy)	Results (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	08/11/2012	351,92	0,03 %	10

Measurement #3

Component	Date (dd/mm/yy)	Results (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	08/11/2012	352,17	0,05 %	10

Results

Component	Results (nmol/mol)	Expanded Uncertainty	Coverage factor
CO	351,84	1,57 %	2

Reference Method:

Describe your instrument:

The analyzer used for the measurements was N2O-CO-H2O analyzer by Los Gatos. It is based on cavity enhanced laser absorption technique.

Calibration standards:

The calibration standard was purchased from NPL, UK. The concentration of the gas standard was 20.09 µmol/mol in synthetic air with the standard uncertainty of 0.25 %.

Instrument calibration:

The calibration of the N_2O-CO-H_2O analyzer was made by dilution of the gas standard at the concentration level of CCQM-K84 nominal value. The calibration concentration of 326,4 µmol/mol and 366,1 µmol/mol was used bracketing the CCQM-K84 concentration. The synthetic air was used for dilution of the gas standard. The purity of the synthetic air was examined by comparison of the respond of the instrument for synthetic air and to pure nitrogen gas. The linear regression line was fitted into the measured mean values of the analyzer against the value of the calibration concentration. The gas dilutor, Environics 6100, was calibrated against the flow measurement system of Molbloc laminar flow element by DHI, which was calibrated against the primary flow measurement system by MIKES. Linearity of the analyzer as well as the standard error of the estimate of the regression line was used to examine the performance of the analyzer during calibration. The lack of linearity was included into the uncertainty budget for the measurement results.

During the measurements the temperature and the pressure of the laboratory room was recorded. The changes of both quantities were within the acceptable range and no correction on the results based on these was made.

Sampling handling:

The CCQM-84 cylinder arrived in August when the ambient temperature was well above the condensation temperature in the cylinder i.e. no condensation was expected for gas compound in the cylinder. While in sending the cylinder back to KRISS a week of delay was made in order to wait that the ambient temperature was decreased from – 20 °C to 0 °C. The measurements were made between 7 to 8, November, 2012.

The pressure regulator (two stages) was connected into the cylinder. The pressure regulator was flushed several time with the cylinder gas and finally it was conditioned both the primary and secondary part of the pressure regulator overnight. The sample was injected directly to the analyzer through the tube of stainless steel at room pressure. The excess of about 0.3 to 0.5 l/min was used to maintain the gas at room pressure.

Uncertainty:

Sources of uncertainty of the performance characteristics of the analyzer, gas dilutor, zero air and the gas standard are listed in Table 5

Table 5 Uncertainty budget for the measurement results of CCQM-K84

Quantity Xi	**Estimate Xi(%; nmol/mol)**	**Evaluation Type (A or B)**	**Distribution**	**Standard Uncertainty, u(xi)**	**Sensitivity coefficient, ci**	**Contribution ui(y)**
Detection limit	0,40	B	Gaussian	0,40	1,00	0,40
Repeatability	0,9	A	Rectangular	0,52	1,00	0,52
Linearity	0,25 %	A	Rectangular	0,14 %	1	0,14 %
zero gas, purity	0,5	A	Rectangular	0,29	1,00	0,29
Gas standard	0,25 %	B	Gaussian	0,25 %	1,00	0,25 %
Gas dilution	0,70 %	B	Gaussian	0,70 %	1,00	0,70 %
Combined std uncertainty uc(xi)						0,78 %
Expanded uncertainty U(%)						1,57 %
Coverage factor, k						2

VNIIM Report CCQM-K84: Carbon monoxide in synthetic air

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Laboratory: VNIIM, Research Department for the State Measurement Standards in the field of Physico-Chemical Measurements.

Cylinder number: D015223

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	06/09/2012	353.4	0.43	6

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	06/09/2012	353.3	0.40	6

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol/mol	Standard deviation (% relative)	Number of replicates
CO	12/09/2012	353.2	0.45	6

Measurement #4

Component	Date (dd/mm/yy)	Result (nmol/mol	Standard deviation (% relative)	Number of replicates
CO	12/09/2012	353.3	0.69	6

Measurement #5

Component	Date (dd/mm/yy)	Result (nmol/mol	Standard deviation (% relative)	Number of replicates
CO	20/09/2012	354.9	0.70	6

Measurement #6

Component	Date (dd/mm/yy)	Result (nmol/mol	Standard deviation (% relative)	Number of replicates
CO	20/09/2012	353.9	0.76	6

Result

Component	Result (nmol/mol)	Expanded Uncertainty (nmol/mol)	Coverage factor
CO	**354**	**5**	**2**

Details of the measurement method used:

Reference Method:

Gas chromatography with FID and methanizer;
Instrument: Gas Chromatograph «Agilent 6890»;
Column: CaA 3 m x 3mm;
Carrier gas: helium 30 ml/min;
Oven conditions: 75 ºC for 9 min;
Sample loop: 5 ml;
Data collection: by “ChemStation A.10.02” software.

Calibration Standards:

Calibration was performed using Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 “Gas analysis - Preparation of calibration gas mixtures - Gravimetric method”.
Characteristics of pure substances used for preparation of the calibration gas mixtures are shown in the table 1.

Table 1 – Description of pure substances

Substance	Mole fraction (µmol/mol)	Standard uncertainty (µmol/mol)
Carbon monoxide	999861	22
Nitrogen	999999.0	0.4
Oxygen	999998.4	0.3
Argon	999999.50	0.10

Preparation from pure substances was carried out in 4 stages. On the first stage 3 CO/N_2 gas mixtures were prepared on the concentration level of 2,5 %. On the second and third stages these mixtures were diluted respectively to the concentration levels of 500 and 9 µmol/mol. Then the last mixtures were diluted to target concentration level of 0.3 µmol/mol.

The concentrations and standard uncertainties of carbon monoxide in these mixtures are shown below.

Cylinder number	Component	Concentration (nmol/mol)	Standard uncertainty due to weighing and purity (nmol/mol)
D249246	CO	300.0	1.0
D249373	CO	301.2	1.0
D249403	CO	300.8	1.0

All standard gas mixtures were prepared in aluminum cylinders (Luxfer) with Aculife IV + Aculife III treatment.

Instrument Calibration:

Single point calibration method was used to determine carbon monoxide concentration in the gas mixture to be investigated. Linearity of the carbon monoxide calibration curve (mathematical model of calibration curve y=kx) in the range 0.300 – 0.500 µmol/mol was checked preliminarily using Primary Standard Gas Mixtures.
Measurement sequence was in the order: standard-sample-standard-sample-standard (etc.). Temperature and pressure were not corrected during the calibration procedure due to cited above measurement sequence.

Sample Handling:

Prior to measurements cylinders were stabilized to room temperature. Each cylinder was equipped with a pressure regulator that had been adequately purged before the sample was transferred to the sample loop. The additional valve was installed between the outlet of the column and methanator order to remove oxygen before the methanator.

Uncertainty:

a) Uncertainty related to calibration standards, which takes into consideration uncertainty of the balance, weights and purity analysis of the parent gases, was calculated with the program developed in VNIIM on the base of ISO 6142:2001 “Gas analysis - Preparation of calibration gas mixtures - Gravimetric method”;
b) Uncertainty related to the measurements - S_x was calculated according to the formula

$$S_x = \sqrt{S_R^2 + S_r^2 \frac{n-1}{n}}$$

$$S_R = \sqrt{\frac{\sum_{i=1}^{m}(x_i - x)^2}{m(m-1)}}$$

$$S_r = \sqrt{\frac{\sum_{i=1}^{m} S_{r_i}^2}{m}}$$

$$S_{r_i} = \sqrt{\frac{\sum_{j=1}^{n}(x_{ij} - x_i)^2}{n(n-1)}}$$

where n – number of the results in one measurement series;
m- number of the measurement serieses;
x_{ij} – one of the single results in one of the measurement serieses;
x_i – the average result in one measurement series;
x - overall mean.

Detailed uncertainty budget:

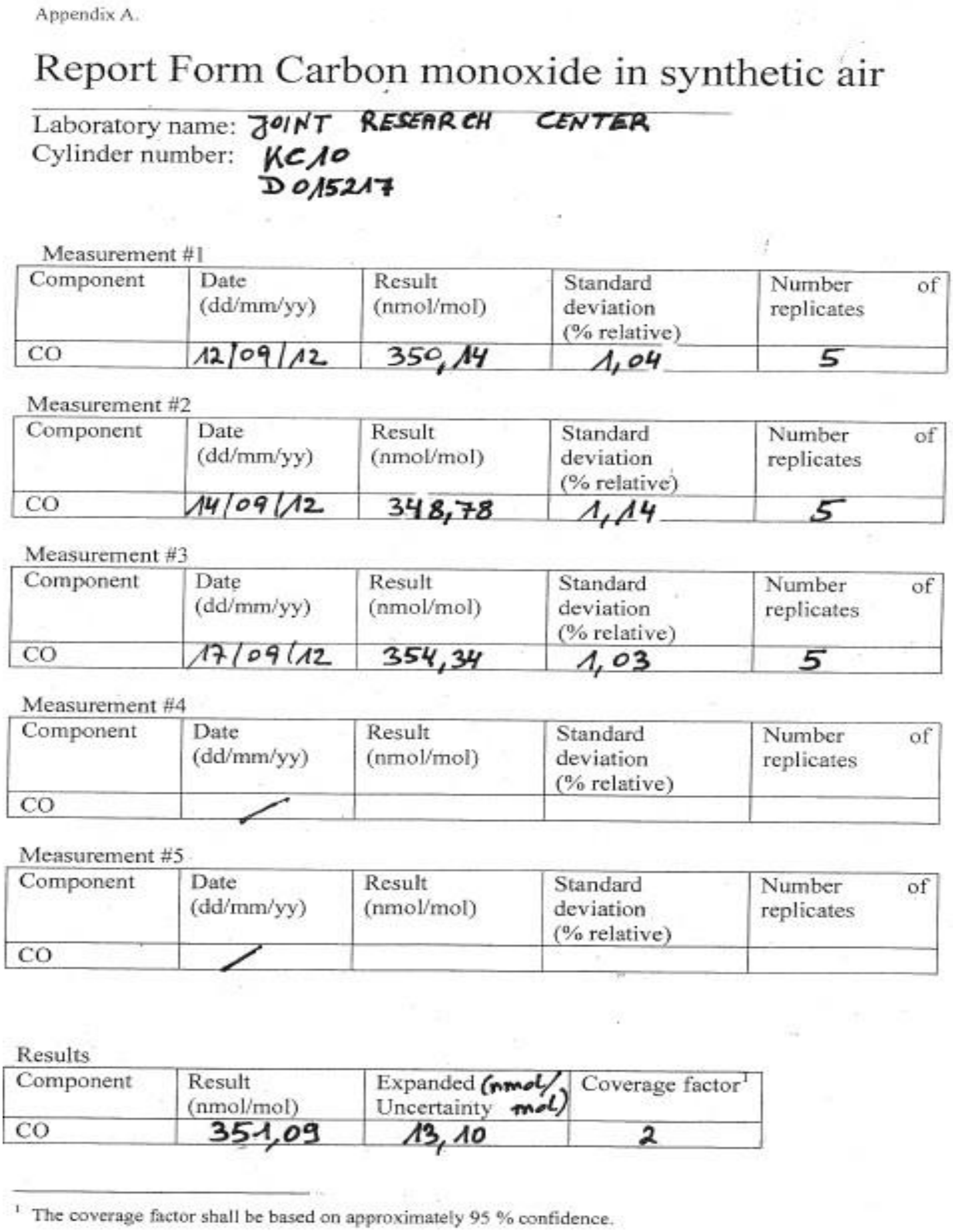
Uncertainty source X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$, %
Calibration standards (weighing + purity)	300.0 (nmol/mol)	A, B	Normal	1.0 (nmol/mol)	1.179	0.333
Between days and within day measurements	353.6 (nmol/mol)	A	Normal	1.92 (nmol/mol)	1	0.544
Combined standard uncertainty						0.638
Expanded uncertainty k=2						1.3

JRC –ERLAP – CCQM-K84

Analysis of Carbon monoxide in Synthetic air at ambient level

Cylinder code: KC10

Cylinder number: D015217



Appendix A.

Report Form Carbon monoxide in synthetic air

Laboratory name: JOINT RESEARCH CENTER
Cylinder number: KC10
D015217

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	12/09/12	350,14	1,04	5

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	14/09/12	348,78	1,14	5

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	17/09/12	354,34	1,03	5

Measurement #4

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	/			

Measurement #5

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	/			

Results

Component	Result (nmol/mol)	Expanded Uncertainty (nmol/mol)	Coverage factor[1]
CO	351,09	13,10	2

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[1] The coverage factor shall be based on approximately 95 % confidence.

Reference Method:

Analyzer: CO analyzer Horiba APMA 370

Method: Non dispersive infrared analysis method

Configuration: Stand alone

Data collection: Data acquisition system with homemade software. Sampling rate is around 2 sec and used to create 1 min averages which are stored in a file. Five consecutive 1 min averages build one measurement.

Calibration Standard:

A dynamic dilution system with thermal mass flow controllers is used to produce gas-mixtures of a desired concentration. A Primary Reference Material (PRM) of $300*10^{-6}$ mol/mol, manufactured by VLS (NL), is diluted with homemade Zero Air. The PRM is produced according to ISO 6142:2001 (Gravimetric preparation) with an expanded uncertainty of 0.3%. The Zero Air is generated from ambient air using a drying system, UV-lamp for oxidation, activated charcoal, molsiev, silicagel and a palladium converter of 380 deg. C for purification. It is compared to a Primary Reference Gas Mixture manufactured by NPL (UK) with an amount fraction of Carbon Monoxide ≤15 nmol/mol and found to be lower by around 10 nmol/mol.

Instrument calibration:

The analyzer is calibrated right before analysis of a client cylinder. Zero air and three gas-mixtures of different concentrations are generated with the dynamic dilution system and measured for 15 min with the analyzer. The last 5 min are used to calculate the measurement result. Immediately after each single gas-mixture the flow-rate of the PRM and the Zero Air are measured independently with a Molbloc/Molbox1 system. The latter one was certified against gravimetric standards at LNE (F) in 2011. Right after the calibration the client cylinder is measured for 15 min, the last five 1 min averages used to calculate the measurement result. As an experiment lasts for less than 2 hours, temperature/pressure corrections are not taken into account.

Sampling handling:

Client cylinder was stabilized to ambient laboratory conditions over more than 2 weeks. A two-stage pressure regulator, manufactured by Veriflow, type 735, with a stainless steel needle valve was attached to the cylinder and evacuated before filled with the cylinder content. Teflon tubing with a t-piece was used to connect it to the analyzer allowing sampling at ambient conditions. In total, three independent calibrations and measurements were performed on Sept. 12th, 14th and 17th, 2012, respectively.

Uncertainty:

Calibration uncertainty:

The uncertainty of the PRM (expanded uncertainty 0.3%), of the Zero Air (7.5 nmol/mol), of the flow-rate (expanded uncertainty 0.3 % or 0.4 % of reading, depending on the flow-rate and used Molbloc) and the repeatability of the analyzer during the sampling of a calibration gas-mixture were taken into account. Uncertainties on compression factors, used to calculate between mol/mol and ppb, were applied but found to be negligible. Analyzer resolution was neglected during calibration as calibration points in the range of 1000 to 3000 nmol/mol were used. Calibration uncertainties were combined using GUM – workbench software to obtain a target value and its associated uncertainty. An example of such a budget is attached. The target values, their uncertainties, the Zero – Air reading and all three calibration readings are entered into ”bleast software” (based on ISO 6143) to calculate the calibration parameters: Linear regression with slope, intercept and associated uncertainties.

Analysis uncertainty:

GUM workbench was used again to calculate the final measurement result out of the calibration parameters, repeatability and analyzer resolution. The latter had to be included at the nominal concentration of the client cylinder, as analyzer resolution is 10 nmol/mol, hence it could have a significant influence on the final result. The three single measurement results and their uncertainty budgets are attached. Finally an average of the three measurements and the three expanded uncertainties was calculated to obtain the final result. The possibility to reduce the variable part of the uncertainty contributions due to the averaging of the final result was discarded.

National Institute of Metrology (NIM), China

Transmission of International Comparison Results

The title of international comparison: Carbon monoxide in synthetic air at ambient level

Serial number for international comparison: CCQM-K84
Comparison experiment period: January, 2013~April, 2013
Experiment reporter: HAN Qiao and HU Shuguo

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

Transmission date: April 9, 2013

International Key Comparison(CCQM-K84) Report
On purity analysis of methane

Lab Information

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Tel.: +86-10-84252300 Fax.: +86-10-84252306
Date of Receiving the Comparison Cylinder: February, 2013
Cylinder No.: 0015220

Measurement and Result

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	25/03/13	355.9	0.06%	2

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	26/03/13	355.4	0.20%	5

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	27/03/13	355.4	0.04%	3

Measurement #4

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	Number of replicates
CO	28/03/13	355.4	0.05%	3

Results

Component	Result (nmol/mol)	Expanded Uncertainty (% relative)	Coverage factor**
CO	355.5	0.8%	2

**The coverage factor *k*=2(95% confidence level)

Method Description

1. Reference Method

CO was analyzed by GC-FID/Methanator (Agilent7890, Agilent, American) with a column of molesieve 5A 80/100(9ft*1/8inch*2.0mm).

GC conditions

Oven temp: 110ºC isotherm 4min

Sample loop: 5mL

Valve #1 load time: 0.1 ~ 0.4min

Carrier gas: N_2

Carrier flow: 75 psi

Sample Flow: 400 mL/min

2. Calibration standard

Cylinder No.: CAL017806

Preparation method

All of the references we used were made by the gravimetric method according to ISO 6142-2006 by ourselves. The parent gases were filled into a 6-liter aluminum cylinder. At least, 10 g parent gas was filled into the cylinder. The cylinder was weighed before and after the filling using a balance with the sensitivity of 1 mg.

The concentration of reference gas was calculated according to the following equation.

$$x_i = \frac{\sum_{A=1}^{P}\left(\frac{x_{i,A}\cdot m_A}{\sum_{i=1}^{n} x_{i,A}\cdot M_i}\right)}{\sum_{A=1}^{P}\left(\frac{m_A}{\sum_{i=1}^{n} x_{i,A}\cdot M_i}\right)}$$

The uncertainty of reference gas included the contributions from gravimetric method and from stability. The uncertainty from stability was evaluated based on short-time and long-time testing before this comparison. The uncertainty from gravimetric method was calculated according to the following equation.

$$u^2(x_i) = \sum_{r=1}^{q}\left(\frac{\partial f_i}{\partial f_r}\right)^2 \cdot u^2(y_r) + 2\sum_{r=1}^{q-1}\sum_{s=r+1}^{q}\left(\frac{\partial f_i}{\partial f_r}\right)\left(\frac{\partial f_i}{\partial f_s}\right)\cdot u(y_r, y_s)$$

Mass of parent gas filled, molecular weight and mole fraction of compound were the main sources of the uncertainty of gravimetric method.

Purity analysis

N_2, **O_2** and **Ar** were analyzed by GC-PDHID(Photo discharged helium ionization detector, Agilent 7890, American) with two columns of molesieve 5A (30m*0.53mm*15μm and 50m*0.53mm*15μm).

CO were analyzed by GC-PDHID and GC-FID with a column of Al_2O_3/KCl(50m*0.53mm*15μm).

Uncertainty of calibration standard

Component	Mole fraction 10^{-6} mol/mol	Expand Uncertainty(*k*=2)

		(10^{-6} mol/mol)
CO	0.3631	0.0024
H_2	0.0500	0.0474
H_2O	0.1298	0.1581
CO_2	0.0100	0.0095
CH_4	0.0200	0.0102
Ar	9981.0691	17.1687
O_2	209081.9828	26.7492
N_2	780936.3802	30.4943

3. Instrument calibration

When CO was analyzed, ‘A-B-A-B-A’ type calibration was used. That means the sample gas and our reference gas were measured in the order of Reference – Sample – Reference – Sample – Reference. The gas pressure at the sample loop of GC was controlled at almost same value during one analysis sequence. Single point calibration was used to calculate the concentration of target compound in sample cylinder.

4. Sampling handling

When package box including comparison cylinder arrived at the lab, it was in good state. Then the box was unpacked and the comparison cylinder was stored at room temperature. A SS regulator was connected to the cylinder.

During the analysis, the gas mixtures in both comparison cylinder and the reference cylinder, via regulators without pressure gauge, 1/8 inch stainless steel tube, were introduced into a 6-port valve. The pressure gauge and the mass flow meter were connected to the inlet of the 6-port valve to show the pressure and flow rate. The 6-port valve was driven by Nitrogen. The gas pressure before the sample loop was controlled at 0.1 MPa by regulator.

Evaluation of measurement uncertainty

The contributions of measurement uncertainty were from reference gas, signal readings of the sample gas and reference gas, reproducibility in different days or groups.

$$u(c_{CCQM}) = \sqrt{u^2(c_{PRM}) + u^2(A_{CCQM}) + u^2(A_{PRM}) + u^2(f_{\text{inter}})}$$

Here, *u* means relative standard uncertainty.

$u(c_{CCQM})$: Measurement uncertainty of concentration of the target component in the comparison sample gas cylinder.

1. $u(A_{CCQM})$: Uncertainty of signal reading of the sample gas from peak area on GC.
2. $u(A_{PRM})$: Uncertainty of signal reading of the reference gas from peak area on GC.

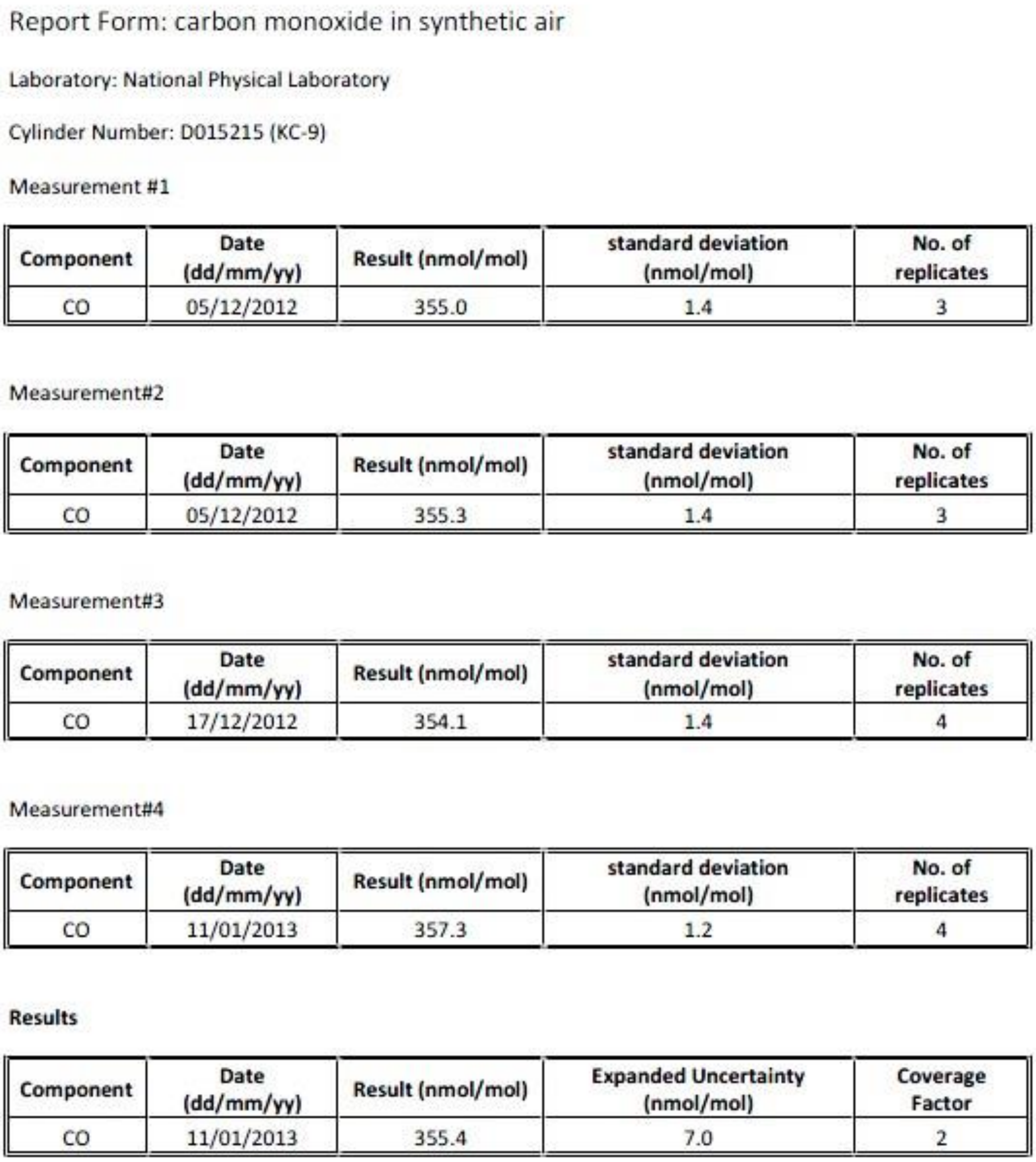
For the A_{CCQM} and A_{PRM} , the relative standard uncertainty could be calculated from the relative standard deviation (RSD) of the signal reading. The relative standard uncertainty is RSD/sqrt(n), where n is the number of signal reading.

3. $u(c_{PRM})$: Uncertainty of concentration of the reference gas, which was combined by the uncertainty from gravimetric method according to ISO 6142-2006 and the uncertainty from the stability of the reference gas.
4. $u(f_{\text{inter}})$: Uncertainty of reproducibility in different days or groups. The relative standard uncertainty f_{inter} was calculated from the relative standard deviation (RSD) of repeating test

in different days or groups. The relative standard uncertainty is RSD/sqrt(n), where n is the number of the repeating test.

Source of uncertainty	$u(c_{PRM})$	$u(A_{CCQM})$	$u(A_{PRM})$	$u(f_{\mathrm{int}er})$
Relative standard uncertainty	0.33%	0.13%	0.13%	0.13%
Relative expanded uncertainty**	0.8%			

**The coverage factor *k*=2(95% confidence level)



Report Form: carbon monoxide in synthetic air

Laboratory: National Physical Laboratory

Cylinder Number: D015215 (KC-9)

Measurement #1

Component	**Date (dd/mm/yy)**	**Result (nmol/mol)**	**standard deviation (nmol/mol)**	**No. of replicates**
CO	05/12/2012	355.0	1.4	3

Measurement#2

Component	**Date (dd/mm/yy)**	**Result (nmol/mol)**	**standard deviation (nmol/mol)**	**No. of replicates**
CO	05/12/2012	355.3	1.4	3

Measurement#3

Component	**Date (dd/mm/yy)**	**Result (nmol/mol)**	**standard deviation (nmol/mol)**	**No. of replicates**
CO	17/12/2012	354.1	1.4	4

Measurement#4

Component	**Date (dd/mm/yy)**	**Result (nmol/mol)**	**standard deviation (nmol/mol)**	**No. of replicates**
CO	11/01/2013	357.3	1.2	4

Results

Component	**Date (dd/mm/yy)**	**Result (nmol/mol)**	**Expanded Uncertainty (nmol/mol)**	**Coverage Factor**
CO	11/01/2013	355.4	7.0	2

Details of the measurement method used

Reference method

A Picarro G2401 Cavity ring-down spectrometer was used to measure the amount fraction of CO in the comparison cylinder.

Calibration standards

Three reference standards were prepared at NPL in real scrubbed air from pure CO (99.9975%) and used in the analysis. All mixtures were prepared in BOC 10 litre cylinders with Spectraseal passivation. The scheme below shows the gravimetric dilutions with nominal CO amount fractions.

Pure
↓
100 mmol/mol
↓
10 mmol/mol
↓
1000 µmol/mol
↓
100 µmol/mol
↓
10 µmol/mol
↓
350 nmol/mol

Instrument calibration

The reference gas mixtures were prepared with CO amount fractions which lie within 2% of the comparison mixture. The analyser response to the matrix gas was recorded. A comparison of the reference mixture to the comparison mixture was achieved by measuring the analyser response to the reference mixture for a five minute period followed by the comparison mixture for the same time. This sequence was repeated a number of times (see results table). At the end of the experiment the analyser response to the matrix gas was recorded a second time. To minimise the effects from zero drift, a mean of the analyser response to the matrix gas before and after the experiment was used. The amount fraction of CO in the comparison mixture was determined using the amount fraction of the reference mixture and the ratio of the analyser response to the reference and unknown mixtures (both were corrected for the analyser response to matrix (zero) gas).

Sample handling

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

Uncertainty

The estimated uncertainty for the measurement contains the following components:

- Purity analysis of CO and scrubbed real air
- Gravimetric preparation
- Analytical uncertainty from the spectrometer (drift and instrument noise)

Uncertainty budget

The amount fraction of the comparison mixture, x_c, was determined using the following expression:

$$x_c = \frac{x_r(y_c - y_z)}{(y_r - y_z)}$$

where x_r is the amount fraction of the reference standard, y_c, y_r and y_z are the analytical measurements of the comparison mixture, the reference standard and zero respectively. Both y_c and y_r are dominated by instrument repeatability. For the purposes of the uncertainty calculation, the equation above represents a situation where repeatability of the measurement takes into account any drift over the measurement period.

The uncertainty in the amount fraction of the comparison cylinder was determined by adding the four components in quadrature. The table which follows details the uncertainty analysis.

quantity	units	example value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
x_r	nmol/mol	353.5	2.0	1.008	2.012	A	normal
y_z	nmol/mol	3.1	1.5	0.008	0.011	A	normal
y_r	nmol/mol	353.2	2.0	-1.017	-2.035	A	normal
y_c	nmol/mol	355.8	2.0	1.010	2.020	A	normal
x_c	nmol/mol	356.1					
$u(x_c)$	nmol/mol	3.5					
$U(x_c)$	nmol/mol	7.0					

Report Form Carbon monoxide in synthetic air
Key Comparison CCQM-K84

Laboratory Information.
Institute: NOAA/OAR/ESRL/GMD
Address: 325 Broadway street
Mail Stop R.GMD1
Boulder, Colorado USA 80305
Contact: Brad Hall, Paul Noveilli
Tel: +1 303.497.7011
Email: Bradley.Hall@noaa.gov

Serial no. DO15283

Reference Method.

Analytical methods: The CO mole fraction in cylinder DO15283 (Table 1) was determined using enhanced off-axis integrated-cavity output spectroscopy (ICOS). A CO/N_20 analyzer from Los Gatos Research Inc. (Mountain View California, USA, model 907-0015, serial no. 09-007) was used. The instrument was upgraded with software for Los Gatos to improve resolution of the instrument signal.

Reference Gases: Measurements are referenced to the WMO CO X2004 scale (WMO, 2010) and reported in nmol CO per mol dry air. The primary standards which define the scale were prepared by a gravimetric method. Secondary standards were assigned mole fractions by calibration against two sets of primary standards. Uncertainty in the scale is obtained from measured differences in mole fraction results for standards calibrated using independent sets of primary standards.

Calibration procedure: Instrument response was modeled as a nonlinear function. Response curves were obtained from measurement signals of nine secondary standards covering 25 to 500 nmol mol-1. The one-second instrument measurement signals approach a Gaussian distribution and were averaged over 90s. The mean instrument response of each standard, obtained from eight individual determinations of 90 1 Hz measurements, were fit with an orthogonal polynomial (n=2) to define instrument response.

Sample mole fractions are obtained from sample measurement response and the response curve. Four calibration events were conducted over an 8-week period. Each event consisted of 15 determinations of sample response (mean of 90 1 Hz signals) translated to mole fraction. The value reported here represents the mean of four calibrations events.

Uncertainty of Results: The uncertainty of measurement results is estimated by a statistical approach to yield a combined standard uncertainty expanded to the 95% confidence level (coverage factor = 2). The combined uncertainty includes scale and measurement uncertainties obtained by propagation in quadrature of the uncertainties in the WMO CO X2004 reference scale, the response curve and the repeatability of multiple calibration events of the sample.

Table1. Nominal composition of mixture

Component	X (nominal value)
Carbon Monoxide [nmol/mol]	300
Argon [% mol/mol]	0.93
Oxygen (% mol/mol]	21
Nitrogen (5 nmol/mol]	balance

Table 2. Uncertainty components

Component	Mean Uncertainty 1 σ [nmol/mol]	Fractional uncertainty (%)
Gravimetric Standards		
Weighing uncertainty	1.21	0.35
CO in dilution gas	2	0.58
Analytical		
Response curve	0.24	0.07
Reproducibility	0.17	0.05
Total Combined	2.35	0.68

Results

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol /mol)	Standard Deviation (% relative to Result)	Number of replicates
CO	24/09/12	346.06	3.22e-4	14

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol /mol)	Standard Deviation (% relative to Result)	Number of replicates
CO	23/10/12	346.13	3.47e-4	14

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol /mol)	Standard Deviation (% relative to Result)	Number of replicates
CO	21/11/12	346.36	1.76e-4	14

Measurement #4

Component	Date (dd/mm/yy)	Result (nmol /mol)	Standard Deviation (% relative to Result)	Number of replicates
CO	03/12/12	347.01	4.62e-4	14

Result

Component	**Result (nmol /mol)**	**Expanded Uncertainty (nmol / mol)**	**Coverage Factor**
CO	**346.0**	**4.7**	**2**

Note: CO contained in cylinders of the size and material comparable to those used in this experiment has been known to change with time.

Appendix A.

Report Form Carbon monoxide in synthetic air

Laboratory name: Korea Research Institute of Standards and Science (KRISS)

Cylinder number: D015286

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol /mol)	Standard deviation (nmol /mol)	number of replicates
CO	26/07/12	353.16	0.50	4
	4/09/12	353.34	0.60	4
	4/09/12	353.22	0.64	3
	5/09/12	353.18	0.50	4
	14/09/12	353.36	0.74	4

Results

Component	Result (nmol/mol)	Expanded Uncertainty (nmol /mol)	Coverage factor[3]
CO	353.25	1.06	2

Method Description Forms

Details of the measurement method used:

Analysis method:

Carbon monoxide concentration in synthetic air has been quantified using gas chromatograph thermal conductivity detector with Methanator (GC-TCD/Methanator). Figure 1 shows an analytical condition of the analyzer and its chromatogram.

To achieve analytical interval of ± 0.1 % (standard deviation) the instrument drift and standard deviation of the response were controlled carefully. The cylinder D015286 were analyzed against the primary reference mixture of D985725 (prepared in July, 2012).

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[3] The coverage factor shall be based on approximately 95% confidence.

<Analytical condition>

Detector : FID/Methanator

Detector temp. : 275 ^{o}C

H_2 : 95 mL/min, Air : 350 mL/min

Oven temp. : 80 ^{o}C

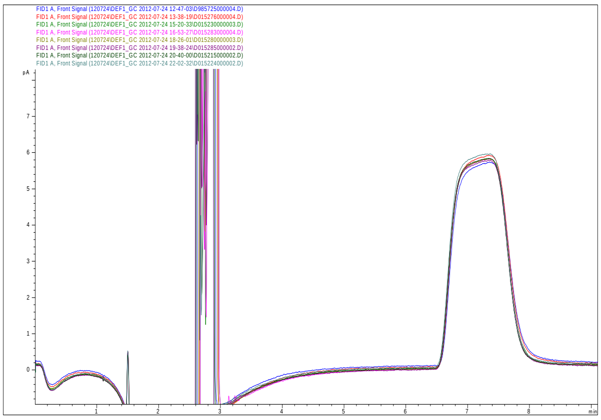
Column : Restek Molesieve 5A, 80/100 16ft*1/8" SS

Carrier gas : N2, 95 psi

Sample loop vol. : 10 mL with restrictor

Sample flow : 80 mL/min

matrix effect (no consideration), valve(0.1/1.1)



Instrument calibration:

Instrument calibration is performed using KRISS primary standard mixtures. One point calibration was done with a cylinder of nominal value ~ 350 nmol/mol which was very close to the target cylinder.

Sample handling:

The sample cylinder had put in the laboratory with room temperature for several days after preparation. Each cylinder was equipped with a stainless steel pressure regulator that was purged more than 7 times after connection to the analysis line. Samples were transferred to sample loop at flow rate of 80 ml/min using mass-flow controller.

Calibration standards:

Preparation method

5 primary standard mixtures were used for the determination of carbon monoxide in synthetic air. The standards were prepared from pure carbon monoxide, pure nitrogen, and pure oxygen in accordance with ISO6142:2001 (Gas analysis-Preparation of calibration gases-Gravimetric method. Pure carbon monoxide was diluted by 4 step and purity analysis for every pure gases were done. Table 1 shows gravimetric value and expanded uncertainty of the calibration standards. They agreed within 0.1 % as shown in Figure 1.

Table 1. Gravimetric value and expanded uncertainty in calibration standards

Cylinder number	Gravimetric Value (nmol/mol)	Expanded uncertainty [k=2] (nmol/mol)
D905128	351.08	0.72
D905126	347.61	0.69
D929208	348.75	0.70
D985725	341.52	0.68
D985730	342.95	0.68

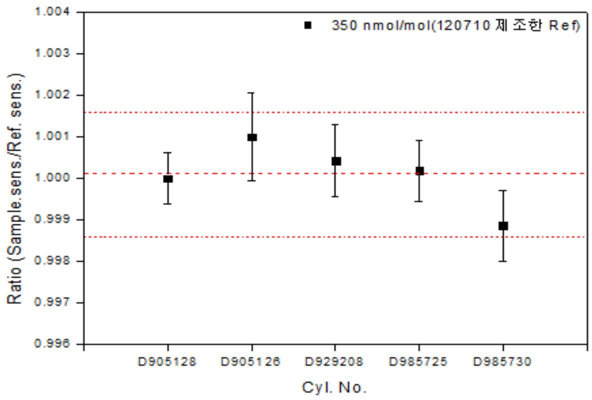


Figure 5. Consistency among primary standard mixtures

Purity analysis

The impurities of carbon monoxide, nitrogen, and oxygen were determined by analytical methods and the amount of the major component is conventionally determined from the following equation,

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

where

x_i: the mole fraction of impurity i, determined by analysis;

N: the number of impurities likely to be present in the final mixture;

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

Table 2-4 shows summarized results of purity analyses for CO, N_2, and O_2. The purity results of them were considered in gravimetric preparation, CO in Oxygen was added to the gravimetric value as well as the uncertainty. Tatal uncertainty of CO was calculated with GUM program. For purity analysis GC-AED, TCD, and PDD were applied. High value of CO in Oxygen acts as a major contributor of uncertainty during preparation.

Table 2. Results of Purity analysis of carbon monoxide (QA8272, 50L Al)

component	analytical conc. (umol/mol)	distribution		applied conc. (umol/mol)	standard uncertainty (umol/mol)	f*f
H2	< 0.26	rectangular	1.732	0.13	0.075	0.005633
H2O	<1.0	rectangular	1.732	0.5	0.289	0.083333
CH4	<0.08	rectangular	1.732	0.04	0.023	0.000533
CO2	<1.02	rectangular	1.732	0.51	0.294	0.086700
THC	<1.0	rectangular	1.732	0.5	0.289	0.083333
N2	4.13	normal	0.2	4.13	0.413	0.170569
O2+Ar	0.93	normal	0.2	0.93	0.093	0.008649
		impurities		6.740	0.662	0.438751
		CO		999993.260	1.325	k=2

Table 3. Results of Purity analysis of Nitrogen

component	analytical conc. (umol/mol)	distribution		applied conc. (umol/mol)	standard uncertainty (umol/mol)	f*f
H2	< 0.5	rectangular	1.732	0.25	0.144	0.020833
H2O	1.2	normal	0.2	1.2	0.120	0.014400
CO	<0.002	rectangular	1.732	0.001	0.001	0.000000
CH4	< 0.001	rectangular	1.732	0.0005	0.000	0.000000
CO2	< 0.01	rectangular	1.732	0.005	0.003	0.000008
THC	< 0.5	rectangular	1.732	0.25	0.144	0.020833
Ar	< 1.0	rectangular	1.732	0.5	0.289	0.083333
O2	0.35	normal	0.2	0.35	0.035	0.001225
Ne	< 1.0	rectangular	1.732	0.5	0.289	0.083333
		impurities		3.057	0.473	0.223967
		N2		999996.944	0.947	k=2

Table 4. Results of Purity analysis of Oxygen

component	analytical conc. (umol/mol)	distribution		applied conc. (umol/mol)	standard uncertainty (umol/mol)	f*f
H2	< 0.1	rectangular	1.732	0.05	0.029	0.000833
H2O	1.54	normal	0.2	1.54	0.154	0.023716
CO	0.00685	normal	0.5	0.00685	0.00171	0.00000293
CH4	< 0.1	rectangular	1.732	0.05	0.029	0.000833
CO2	0.22	normal	0.2	0.22	0.022	0.000484
THC	< 0.3	rectangular	1.732	0.15	0.087	0.007500
Ar	< 1.0	rectangular	1.732	0.5	0.289	0.083333
N2	5.84	normal	0.2	5.84	0.584	0.341056
		impurities		8.357	0.677	0.457759
		O2		999991.643	1.353	k=2

Uncertainty:

The uncertainty used for the calibration mixtures contains all sources of gravimetric preparation. Uncertainty for stability is not included because no instability has been detected. An analysis uncertainty is calculated based on repeatability and drift of analyzer of the acquired area.

Detailed uncertainty budget:

Please include a list of the uncertainty contributions, the estimate of the standard uncertainty, probability distributions, sensitivity coefficients, etc.

Typical evaluation of the measurement uncertainty for CO:

Quantity X_i	Estimate x_i	Evaluation Type (A or B)	Distribution	Standard uncertainty $u(x_i)$ [nmol/mol]	Sensitivity coefficient Rel. $u(x_i)$ [%]	Contribution $u_i(y)$
References		A	Gaussian	0.35	0.1	
Sample		A	Gaussian	0.35	0.1	
References prepared grav.		A	Gaussian	0.42	0.12	
Combined standard uncertainty				0.65	0.18	