CCQM-P176 Final report

Pilot study: CCQM-P176

Carbon monoxide in Synthetic air at ambient level

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Field

Amount of substance

Subject

Carbon monoxide in Synthetic air at ambient level

Participant

Empa

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.

The CCQM-K84 key comparison aimed at supporting measurement capabilities of CO at ambient level (350 nmol/mol). Since Empa was interested to take part, this pilot comparison was carried out in parallel with the CCQM-K84. Therefore the objective of this comparison is to compare EMPA measurement result with the KCRV of the CCQM-K84.

Participant

Empa took part in the study as a CO-WCC under the WMO-GAW program. KRISS coordinated the comparison.

Table 1: List of participants

Acronym	Country	Institute
Empa	CH	Swiss Federal Laboratories for Materials Science and Technology, Switzerland
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea

Schedule

The Schedule for this comparison was proposed 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

Sample preparation

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. This pilot study compares the EMPA result to the key comparison reference values (KCRV) of the CCQM-K84. The pressure in each cylinder was approximately 100 bar; cylinders of 10 dm^3 (Al. Luxfer, UK) were used. 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.

Table 3 identifies CO mole fraction and its uncertainty, including gravimetric preparation and purity analysis, and a composition of each mixture as well.

Table 2. Gravimetric preparation uncertainty of CO gases for a set of cylinders.

Cylinder	CO	$U_{prep.}$, $k = 2$	Ar	O_2	N_2

	[nmol/mol]	[nmol/mol]	[%]	[%]	[%]
D015280	350.60	1.30	0.8907	20.96	78.15
D015286	353.26	1.31	0.9238	20.89	78.19

CO stability in air

In order to verify the mixture's stability, each cylinder was analyzed four times over a 20 months' 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. 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.

Table 4 shows the results of consecutive analyses starting from the preparation of mixtures. The fraction CO appears to have stopped increasing (by ~ 1 %) after an eight-month period from the preparation date. In terms of the two cylinders (D015280, D015286) for the comparison, the increments look stable within 0.1 nmol/mol since the second verification.

Table 3. Stability study data for the comparison

Laboratory	Cylinder	x_{prep} [nmol/mol] Jul. 2012	x_{2nd} [nmol/mol] 2^{nd} ver. May. 2013	x_{3rd} [nmol/mol] 3^{rd} ver. Nov. 2013	x_{4th} [nmol/mol] 4^{th} ver. Mar. 2014
Empa	D015280	350.60	353.99	353.82	354.07
KRISS	D015286	353.26	356.74	356.75	356.80

Since the stability of CO in air was an issue for the CCQM-K84 key comparison which could not be neglected, it was agreed to determine KCRV as the preparation value with stability uncertainty of 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, as listed in the table 5.

Table 5. Reference values 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_tot} [nmol/mol]
Empa	D015280	350.60	1.30	3.39	3.63
KRISS	D015286	353.26	1.31	3.48	3.72

Measurement results

The measurement and calibration methods used by the participating laboratory in this comparison are listed in Table 6. Empa and KRISS used laser spectroscopy and GC, respectively. Empa used WMO standard and KRISS their own standards.

Table 6. Summary of the measurement methods of the participants

Laboratory	Cylinder	Measurement period	Calibration standards	Instrument calibration	Measurement technique
Empa	D015280	Aug. 2012	WMO-2004	multiple point	*ICOS
KRISS	D015286	Jul. 2012 to Sep.	Own standards	single point	GC/FID/Methanator

*ICOS: Off axis integrated cavity output spectroscopy

Preparation values and participants' reported values in this comparison are summarized in Table 7. The differences between reported and prepared were listed in it.

For the sake of consistency between the results of the participating laboratories and the reference value, a difference (Δ_i) in table 7 is expressed as

$$\Delta_i = x_{\mathrm{i}} - x_{\mathrm{i,RV,}} \quad (2).$$

In the above equation, $x_{i,RV}$ is given as x_{prep}, and x_i is the result of laboratory i. Therefore the standard uncertainty of Δ_i based on Table 9 can be expressed as:

$$u^2(\Delta_i) = u^2_{\mathrm{i,lab}}(x_{\mathrm{i}}) + u^2_{\mathrm{i,prep\_tot}}(x_{\mathrm{i,\,RV}}) \quad (3)$$

Assuming that the terms in equation (3) are uncorrelated, the degrees of equivalence $\Delta_i \pm U(\Delta_i)$ are presented in Figure 3, where the solid squares represent the Δ_i and the vertical bars

indicate the associated expanded uncertainty (k = 2). Fig 4 shows all results of K84 and P84 in a time.

Table 7. Measurement Results

Laboratory	Cylinder	x_{prep} [nmol/mol]	u_{prep_tot} k = 2 [nmol/mol]	x_{lab} [nmol/mol]	U_{lab} k = 2 [nmol/mol]	Δx $x_{lab} - x_{prep}$ [nmol/mol]	u(Δx) $U(x_{lab} - x_{prep})$ [nmol/mol]
Empa	D015280	350.60	1.82	342.93	6.71	-7.67	3.81
KRISS	D015286	353.26	1.86	353.25	1.06	-0.01	1.94

Fig 4 shows all results of K84 and P176.

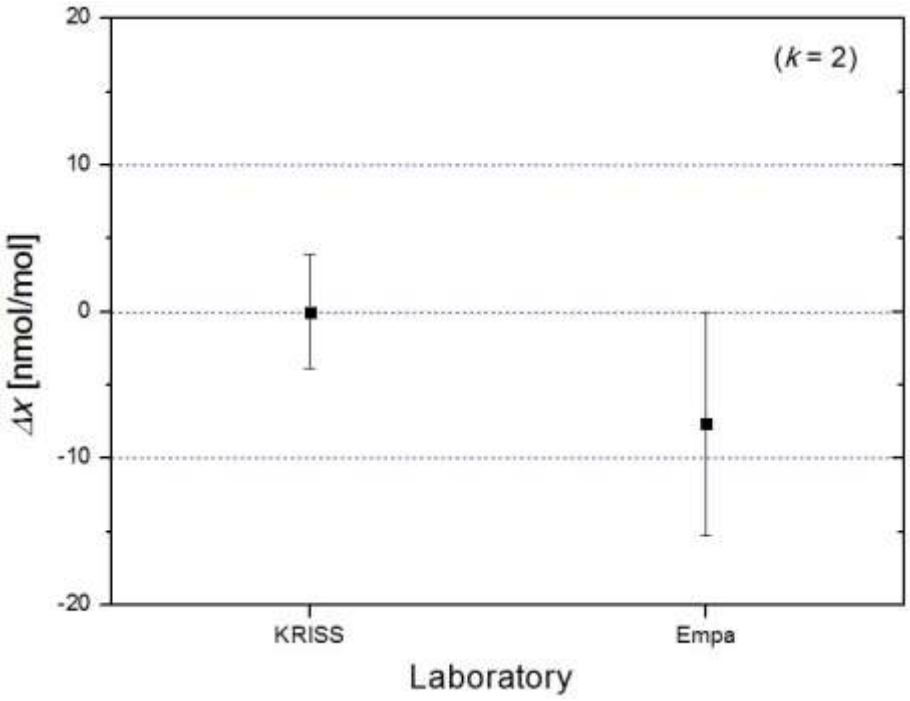

Figure 3. Differences between participants' results and the RV for the comparison, where the vertical bar represents the expanded uncertainty, $U(\Delta_i)$, at the 95 % level of confidence.

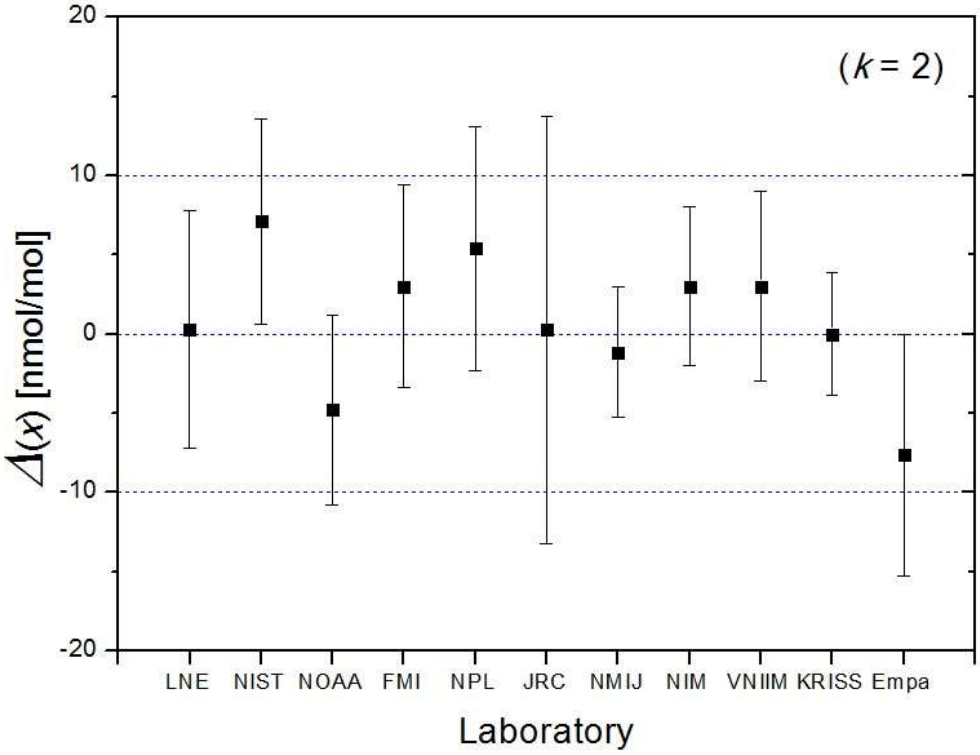

Figure 4. Results for the two comparisons (CCQM-K84 and this pilot study: the last point (Empa) in the graph), where the vertical bar represents the expanded uncertainty, $U(\Delta_i)$, at the 95 % level of confidence.

Conclusions

Around of 1 % of increase in CO mole fraction was observed for the mixtures used for the pilot study. The results of the comparison are consistent with the CCQM-K84 within uncertainties. The results of the comparison demonstrates measurement equivalence between NMIs and WMO.

Acknowledgements

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References

1. Novelli, P. C., J. W. Elkins and L. P. Steele, The Development and Evaluation of a Gravimetric Reference Scale For Measurements of Atmospheric Carbon Monoxide,

Journal of Geophysical Research-Atmospheres, 96 (1991), D7, 13109-13121, JD01108.

2. ESRL Global Monitoring Division, Global view of CO, http://www.esrl.noaa.gov/gmd/ccgg/globalview/co/co_intro.html,.
3. GAW report No. 213, 17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2013), World Meteorological Organization (WMO), Edited by Pieter Tans and Christoph Zellweger
4. International organization for standardization, ISO 6142.2, Gas analysis, "Preparation of calibration gas mixtures, Gravimetric method", ISO, Third edition, 2013(E)

Appendix: Measurement Reports: Empa

Report Form Carbon monoxide in synthetic air

Laboratory name: Empa, Laboratory for Air Pollution/Environmental Technology (C. Zellweger)

Cylinder number: D015280

Measurement # Component CO	Date (dd/mm/yy)	Result (nmol/mol)	Standard dev. (% relative)	Number of replicates
1	15/08/12	342.76	0.01	10
2	24/08/12	342.90	0.01	10
3	24/08/12	342.89	0.01	10
4	24/08/12	342.90	0.01	10
5	24/08/12	342.90	0.01	10
6	24/08/12	342.96	0.01	10
7	24/08/12	342.97	0.01	10
8	27/08/12	342.97	0.01	10
9	27/08/12	342.89	0.01	10
10	27/08/12	342.89	0.01	10
11	27/08/12	342.97	0.01	10
12	27/08/12	342.93	0.01	10
13	27/08/12	342.93	0.01	10
14	27/08/12	342.98	0.01	10
15	27/08/12	342.96	0.01	10
16	27/08/12	342.99	0.01	10
17	28/08/12	343.02	0.01	10
18	28/08/12	342.91	0.01	10
19	28/08/12	342.85	0.01	10
20	28/08/12	343.00	0.01	10
21	28/08/12	342.93	0.01	10
22	28/08/12	342.96	0.01	10
23	28/08/12	342.97	0.01	10
24	28/08/12	342.91	0.01	10
25	28/08/12	342.92	0.01	10

Results

Component	Result (nmol/mol)	Expanded Uncertainty	Coverage factor
CO	342.93	6.71	2

Reference Method:

A cavity enhanced off-axis Integrated Cavity Output Spectroscopy (ICOS) Quantum Cascade Laser (QCL) instrument (Los Gatos Research (LGR) Inc., CA, USA, model LGR-23r) $CO/N_2O/H_2O$ analyzer was used for the calibration of the CCQM-84 cylinder against NOAA CO reference gases. The LGR-23r instrument was featuring the "Enhanced Performance Package" with improved thermal stabilization.

Calibration Standards:

Six reference CO standards from NOAA/ESRL (National Oceanic and Atmospheric Administration / Earth System Research Laboratory) on the WMO-2004 CO calibration scale were used to assign CO mole fractions to four working standards. These four working standards were then used to calibrate the LGR-23r instrument during the measurement of the CCQM-84 cylinder. Table 1 gives an overview of the NOAA reference and working standards.

Table 1: NOAA and working standards at Empa

Cylinder #	NOAA assigned CO (nmol/mol)	NOAA uncertainty (nmol/mol) (k=1)	Empa assigned CO (nmol/mol)	Empa uncertainty (nmol/mol) (k=1)
NOAA Reference Standards				
CB09700	141.50	1.0	142.0	1.0
CB09677	143.26	1.0	143.4	1.0
CB09648	230.77	1.6	230.1	1.6
CB09159	234.83	1.6	233.8	1.7
CB09339	506.01	5.1	506.5	3.6
CB09161	519.10	5.2	519.2	3.7
Working Standards				
CC339524			391.0	2.8
CC339523			348.4	2.7
CC311846			167.3	1.2
CA05373			130.2	0.9

Instrument calibration

The LGR-23r instrument was calibrated using four working standards during each analysis. Each standard and the sample were measured for 12-20 minutes, and the last 10 minutes were used for further data processing. The standard measurements were bracketing the sample analysis. A linear regression analysis was applied to calculate the mole fraction of the unknown sample.

Sample handling

The cylinder with the unknown sample was stored in the air conditioned laboratory (23±1°C) during the whole period. Immediately after arrival of the cylinder, a regulator (Scott Specialty Gases Model 514) was connected using the adapter provided by KRISS. The regulator was carefully flushed before each analysis. Storage time before the first analysis was nine days.

The cylinder was connected to a VICI selection valve using 1/16 inch stainless steel tubing, and the flow was controlled by a Red-y Mass Flow Controller. After the MFC, the gas was supplied to the instrument using ¼ inch Synflex-1300 tubing. An excess flow of approx. 30 ml/min was maintained throughout the measurements.

Detailed uncertainty budget

The largest contribution to the uncertainty is the uncertainty of the NOAA standards; additional uncertainty arises from the propagation of the NOAA standards to the sample and the repeatability. In addition, a further contribution to the uncertainty budget was considered (matrix effect). The sample was additionally measured on other instruments employing different analytical techniques (Aerolaser AL5001, UV fluorescence; Aerodyne mini-cw, mid-IR absorption; Picarro G2401, Cavity Ring Down Spectroscopy), which resulted in very reproducible but different results. A possible explanation would be a bias of the different analytical techniques due to matrix effects.

Quantity Xi	Estimate xi	Type	Distribution	Standard Uncertainty u(xi)	Sensitivity coeff. ci	Contribution ui (y)
NOAA scale	343	B		0.007*xi	1	2.40
Scale propagation	343	A	rectangular	0.00077*xi	1	0.26
Repeatability	343	A	normal	0.03	1	0.03
Reproducibility	343	A	normal	0.06	1	0.06
Matrix effect	343	A	rectangular	2.33	1	2.33
					Combined standard uncertainty u (k=1)	3.36 nmol/mol

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[1]
CO	353.25	1.06	2

Method Description Forms

Details of the measurement method used:

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

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).

<Analytical condition>

Detector : FID/Methanator

Detector temp. : 275 ^{o}C

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

Oven temp. : 80 ^{o}C

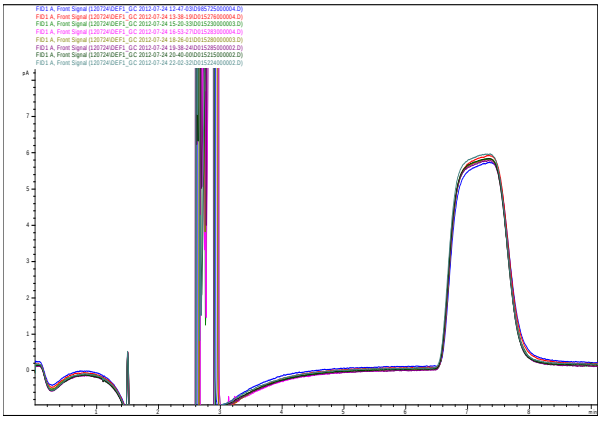
Column : Restek Molesieve 5A, 80/100 16ft*1/8" SS

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

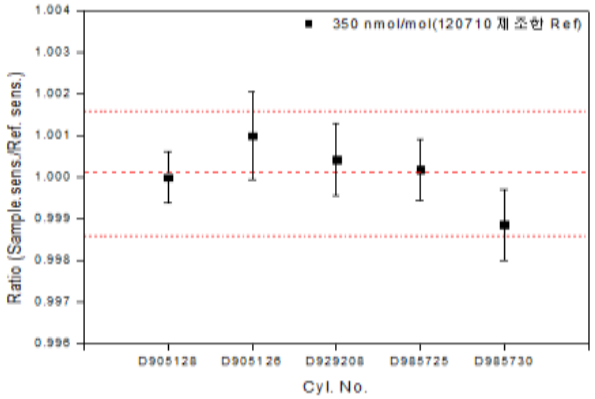


Figure 1. Consistency among primary standard mixtures

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	f*f

					(umol/mol)	
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	