

## International Comparison CCQM-K51 Carbon monoxide (CO) in nitrogen (5 µmol.mol<sup>-1</sup>)

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<b>Field</b>	Amount of substance
<b>Subject</b>	Comparison in the field of permanent gases (carbon monoxide in nitrogen)
<b>Organising body</b>	CCQM

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## Introduction

The first key comparison on carbon monoxide (CO) in nitrogen dates back to 1992 (CCQM-K1a) [1]. It was one of the first types of gas mixtures that were used in an international key comparison. Since then, numerous national metrology institutes (NMIs) have been setting up facilities for gas analysis, and have developed claims for their calibration and measurement capabilities (CMCs) for these mixtures. Furthermore, in the April 2005 meeting of the CCQM (Consultative Committee for Amount of Substance) Gas Analysis Working Group, a policy was proposed to repeat key comparisons for stable mixtures every 10 years. This comparison was performed in line with the policy proposal and provided an opportunity for NMIs that could not participate in the previous comparison.

In preparation for this CCQM-K51 key comparison on CO in nitrogen (1 to 10  $\mu\text{mol}\cdot\text{mol}^{-1}$  range) a bilateral comparison (EUROMET 900) was organised between the coordinating laboratory and another laboratory which participated in CCQM-K1. In this bilateral comparison the NMISA (then CSIR NML) prepared two gas mixtures to be analysed by VSL (then NMI-VSL) and VSL also prepared two mixtures to be analysed by NMISA. This allowed for the NMISA to validate its capabilities for this component over this range.

## Participants

Table 1 lists the participants in this key comparison

**Table 1: List of participants**

Acronym	Country	Institute
UBA(D)	DE	Umweltbundesamt (Federal Environment Agency), Langen, Germany
NMIJ	JP	National Metrology Institute of Japan, Tsukuba, Japan
CERI	JP	Chemicals Evaluation and Research Institute, Saitama, Japan
VSL	NL	Van Swinden Laboratorium B V, Delft, the Netherlands
NIST	US	National Institute of Standards and Technology, Gaithersburg, United States of America
CENAM,	MX	Centro Nacional de Metrologia, Queretaro, Mexico
INMETRO	BR	Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, Xerém RJ, Brazil
NPL	UK	National Physical Laboratory, Teddington, Middlesex, United Kingdom
VNIIM,	RU	DI Mendeleev Institute for Metrology, St. Petersburg, Russia
NMISA	ZA	National Metrology Institute of South Africa, Pretoria, South Africa
IPQ,	PT	Instituto Português da Qualidade, Caparica, Portugal
LNE	FR	Laboratoire National d'Essais, Paris, France
JRC-ERLAP	EU	European Commission, Joint Research Centre, Institute for Environment and Sustainability, Ispra, Italy

FMI	FI	Finnish Meteorological Institute, Helsinki, Finland
UBA(A),	AT	Umweltbundesamt GmbH, Department Air Quality Control & Energy, Vienna, Austria
METAS	CH	Swiss Federal Office of Metrology, Bern-Wabern, Switzerland
NMIA	AU	National Metrology Institute of Australia, Lindfield, Australia
CEM	ES	Centro Espanol de Metrologia, Madrid, Spain
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
SMU	SK	Slovak Institute of Metrology, Bratislava, Slovak Republic
GUM	PL	Central Office of Measures (Główny Urząd Miar), Warsaw, Poland
NIM	CN	Institute of Metrology, Beijing, Peoples Republic of China
NIMT	TH	National Institute of Metrology (Thailand), Klong Luang, Pathumthani, Thailand
NPL (India)	IN	National Physical Laboratory, New Delhi, India
BAM	DE	Bundesanstalt für Materialforschung und – prüfung, Berlin, Germany

### Measurement standards

Table 2 gives the nominal composition used throughout this comparison.

**Table 2: Nominal composition for the comparison**

Component	x ( $\mu\text{mol}\cdot\text{mol}^{-1}$ )
Carbon monoxide	5
Nitrogen	balance

### Measurement protocol

A set of mixtures of carbon monoxide in nitrogen at a nominal concentration of  $5 \mu\text{mol}\cdot\text{mol}^{-1}$  was prepared gravimetrically. The mixtures were verified against primary standard mixtures (PSMs). After verification of the composition of the mixtures, the gravimetric value was adopted as key comparison reference value (KCRV). Each cylinder has its own reference value. The pressure in the cylinders was approximately 120 bar and aluminium cylinders of  $5 \text{ dm}^3$  nominal volume were used.

Participating laboratories were requested to specify, in detail, which analytical method(s) were used and how the evaluation of the measurement uncertainty was performed. Each participating laboratory was responsible for the calibration of its own equipment. To ensure a proper evaluation of the data, it was necessary that the calibration method, as well as the way in which the calibration mixtures were prepared, was reported to the co-ordinator. This information was needed for the evaluation of the preparation facilities as an integral part of this comparison.

After each calibration, the measurements on the gas mixture was performed and recorded. Each laboratory was required to express the uncertainty on all results submitted, as expanded uncertainty. The evaluation of measurement uncertainty was required to be in accordance to the “Guide to the expression of uncertainty in measurement” (ISO GUM). The participant should have provided a detailed description of the uncertainty budget, including

- method of evaluation (type A or type B)
- (assumed) probability distribution
- standard uncertainties and sensitivity coefficients

After the measurements, the participants were requested to return the cylinders with a sufficient amount of gas (pressure at least 30 bar) to the coordinating laboratory for re-analysis. Transport of the cylinders to the participating laboratories was arranged by the coordinating laboratory and paid for by each participant. The return of the cylinders was arranged and paid for by the participants.

The measurement report required at least three independent measurements for each cylinder, obtained under repeatability conditions with (at least) three independent calibrations, e.g. calibration → measurement → calibration → measurement → calibration → measurement (etc.). This was a strict requirement to come to proper statistical analysis of the reported data.

### Schedule

The schedule for this part of the comparison is presented in table 3.

**Table 3: Schedule followed for CCQM-K51**

December 2007	Preparation of gravimetric mixtures and first verification measurement
February 2008	Shipment of cylinders to participating laboratories
30 June 2008	Report submission to coordinating laboratory
15 July 2008	Cylinder submission to coordinating laboratory
August 2008	Second verification measurement
October 2008	Draft A report
April 2009	Draft B report

### Measurement methods

The measurement methods used by the participants are described in appendix A of this report. A summary of the calibration methods, dates of measurement and reporting, and the way in which the metrological traceability was established is given in table 4.

**Table 4: Summary of the measurement methods of the participants**

Laboratory code	Measurements	Calibration	Traceability	Measurement technique
NMIJ	22-28/05/2008	ISO-6143	Own standards	GC-FID
NMISA	18,22,24/09/2008	ISO-6143	Own standards	GC-FID
UBA-Germany	18,24,25/04/2008	Bracketing	ISO 6144	Gas filter correlation analyser
VNIIM	22/04/, 23/05 and	ISO-6143	Own standards	GC-FID

	06/06/2008			
SMU	27/03, 04/04 and 07/04/2008	ISO-6143	Own standards	GC-FID
NPL	27 and 28/03/2008	Bracketing	Own standards	GC-FID; NDIR
CERI	25,27,28/03/2008	Bracketing	Own standards	NDIR
BAM	04 to 07/08/2008	ISO-6143	Own standards	NDIR
CEM	24/04, 08,13, 15 and 20/05/2008	ISO-6143	Own standards	GC-HID
CENAM	13, 16 and 17/06/2008	ISO-6143	Own standards	GC-FID
GUM	06, 09 and 12/06/2008	ISO-6143	Own standards	NDIR
INMETRO	18, 22 and 23/07/2008	ISO-6143	VSL	GC-FID
IPQ	21, 22, 23 and 29/04/2008	ISO-6143	Own standards	NDIR
JRC-ERLAP	08, 13, 16 and 22/05/2008	ISO-6143	ISO 6144	NDIR
KRISS	29 and 30/04, 01/05/2008	ISO-6143	Own standards	GC-FID
LNE	27, 28 and 31/03/2008	Ratio	Own standards	Gas filter correlation analyser
METAS	22, 23 and 24/04/2008	ISO-6143	Own standards	GC-FID
NIM	24, 25 and 26/06/2008	ISO-6143	Own standards	GC-FID
NIMT	16, 17 and 18/06/2008	ISO-6143	CERI	NDIR
NIST	14, 15 and 16/04/2008	ISO-6143	Own standards	GC-FID
VSL	25/03 and 23/04/2008	ISO-6143	Own standards	NDIR
NPL-India	03 and 04/08/2008	Ratio	Own standards	GC-FID
UBA-Austria	23 and 24/04, 14 and 20/05, 19 and 25/06/2008	ISO-6143	VSL	NDIR
FMI	02/07/2008	ISO-6143	VSL	NDIR
NMIA	12, 18, 23 and 24/06/2008	ISO-6143	Own standards	FTIR (10m gas cell)

### Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined as [8]

$$\Delta x_i = D_i = x_i - x_{KCRV}, \quad (7)$$

and the uncertainty of the difference  $D_i$  at 95% level of confidence. Here  $x_{KCRV}$  denotes the key comparison reference value, and  $x_i$  the result of laboratory  $i$ <sup>1</sup>. Appreciating the special conditions in gas analysis, it can be expressed as

$$\Delta x_i = D_i = x_i - x_{i,ref}. \quad (8)$$

The standard uncertainty of  $D_i$  can be expressed as

$$u^2(\Delta x_i) = +u_{i,lab}^2 + u_{i,prep}^2 + u_{i,ver}^2, \quad (9)$$

assuming that the aggregated error terms are uncorrelated. As discussed, the combined standard uncertainty of the reference value comprises the uncertainty from preparation and that the uncertainty from verification for the mixture involved.

<sup>1</sup> Each laboratory receives one cylinder, so that the same index can be used for both a laboratory and a cylinder.

## Results

In this section, the results of the key comparison are summarised. In table 5, the following data is presented

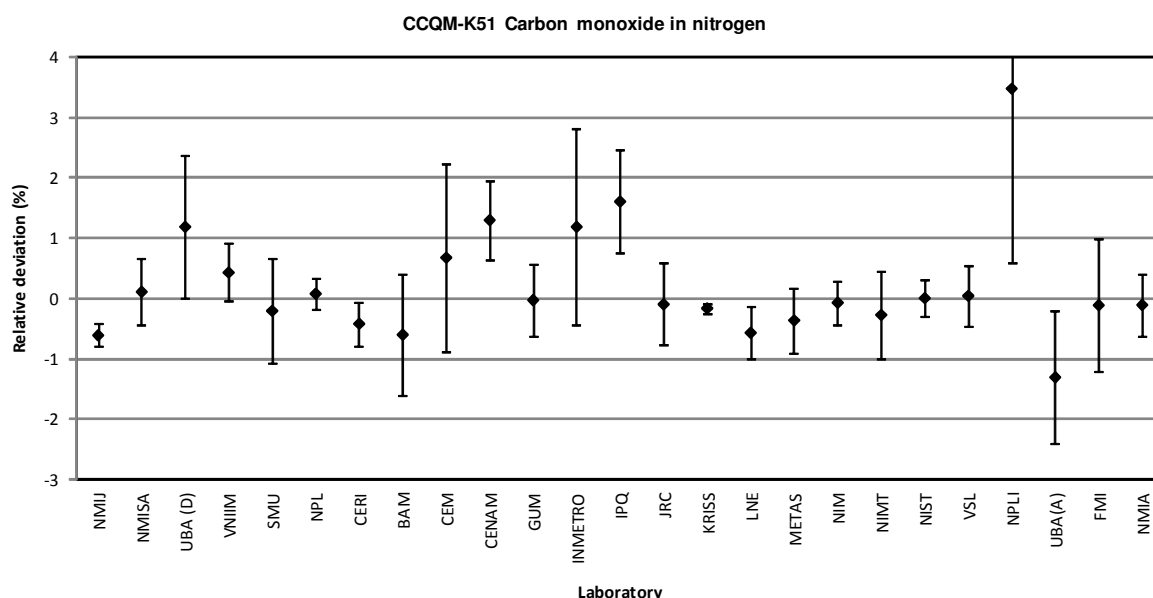
$x_{prep}$	amount of substance fraction, from preparation ( $10^{-6}$ mol.mol <sup>-1</sup> )
$u_{prep}$	uncertainty of $x_{prep}$ ( $10^{-6}$ mol.mol <sup>-1</sup> )
$u_{ver}$	uncertainty from verification ( $10^{-6}$ mol.mol <sup>-1</sup> )
$u_{ref}$	uncertainty of reference value ( $10^{-6}$ mol.mol <sup>-1</sup> )
$x_{lab}$	result of laboratory ( $10^{-6}$ mol.mol <sup>-1</sup> )
$U_{lab}$	stated uncertainty of laboratory, at 95% level of confidence ( $10^{-6}$ mol.mol <sup>-1</sup> )
$k_{lab}$	stated coverage factor
$\Delta x$	difference between laboratory result and reference value ( $10^{-6}$ mol.mol <sup>-1</sup> )
$k$	assigned coverage factor for degrees of equivalence
$U(\Delta x)$	expanded uncertainty of difference, $\Delta x$ , at 95% level of confidence <sup>2</sup> ( $10^{-6}$ mol.mol <sup>-1</sup> )

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<sup>2</sup> As defined in the MRA [7], a degree of equivalence is given by  $\Delta x$  and  $U(\Delta x)$ .

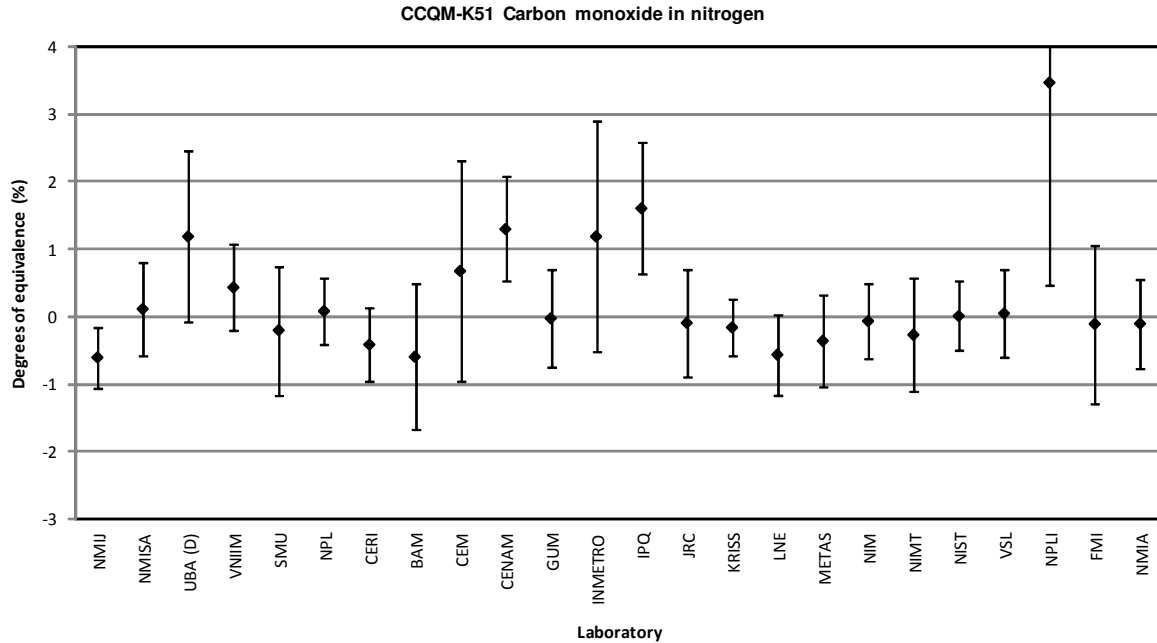
**Table 5: Results**

Laboratory code	Cylinder	$x_{prep}$	$u_{prep}$	$u_{ver}$	$u_{ref}$	$x_{lab}$	$U_{lab}$	$k_{lab}$	$\Delta x$	$k$	$U(\Delta x)$
NMIJ	D95 5680	5.0204	0.0030	0.0100	0.0104	4.9897	0.0091	2	-0.0307	2	0.0228
NMISA	D95 8416	5.0054	0.0030	0.0100	0.0104	5.0108	0.0273	2	0.0054	2	0.0344
UBA(D)	M55 5674	5.0146	0.0030	0.0100	0.0104	5.0740	0.0600	2	0.0594	2	0.0635
VNIIM	M55 5669	5.0195	0.0030	0.0100	0.0104	5.0410	0.0240	2	0.0215	2	0.0318
SMU	M55 5685	5.0134	0.0030	0.0100	0.0104	5.0030	0.0430	2	-0.0104	2	0.0478
NPL	D95 8300	5.0172	0.0030	0.0100	0.0104	5.0210	0.0130	2	0.0038	2	0.0246
CERI	D95 8312	5.0192	0.0030	0.0100	0.0104	4.9980	0.0180	2	-0.0212	2	0.0276
BAM	D95 8369	5.0183	0.0030	0.0100	0.0104	4.9880	0.0499	2	-0.0303	2	0.0541
CEM	M55 5692	5.0163	0.0030	0.0100	0.0104	5.0500	0.0790	2	0.0337	2	0.0817
CENAM	M55 5728	5.0210	0.0030	0.0100	0.0104	5.0860	0.0330	2	0.0650	2	0.0391
GUM	M55 5709	5.0216	0.0030	0.0100	0.0104	5.0200	0.0300	2	-0.0016	2	0.0366
INMETRO	D95 8363	5.0215	0.0030	0.0100	0.0104	5.0810	0.0830	2	0.0595	2	0.0856
IPQ	D95 8407	5.0195	0.0030	0.0100	0.0104	5.1000	0.0440	2	0.0805	2	0.0487
JRC	D95 8393	5.0240	0.0030	0.0100	0.0104	5.0190	0.0340	2	-0.0050	2	0.0399
KRISS	M55 5715	5.0194	0.0030	0.0100	0.0104	5.0110	0.0040	2	-0.0084	2	0.0213
LNE	M55 5708	5.0227	0.0030	0.0100	0.0104	4.9940	0.0220	2	-0.0287	2	0.0303
METAS	M55 5697	5.0214	0.0030	0.0100	0.0104	5.0030	0.0270	2	-0.0184	2	0.0341
NIM	M55 5717	5.0216	0.0030	0.0100	0.0104	5.0180	0.0180	2	-0.0036	2	0.0276
NIMT	M55 5695	5.0178	0.0030	0.0100	0.0104	5.0040	0.0365	2	-0.0138	2	0.0421
NIST	D95 8293	5.0109	0.0030	0.0100	0.0104	5.0110	0.0150	2	0.0001	2	0.0257
VSL	D95 8365	5.0120	0.0030	0.0100	0.0104	5.0140	0.0250	2	0.0020	2	0.0326
NPLI	D95 8294	5.0207	0.0030	0.0100	0.0104	5.1950	0.1500	2	0.1743	2	0.1514
UBA(A)	D95 8320	5.0258	0.0030	0.0100	0.0104	4.9600	0.0550	2	-0.0658	2	0.0590
FMI	M55 5706	5.0258	0.0030	0.0100	0.0104	5.0200	0.0552	2	-0.0058	2	0.0590
NMIA	M55 5726	5.0135	0.0030	0.0100	0.0104	5.0080	0.0260	2	-0.0055	2	0.0333



**Figure 1:** Relative deviation from the reference value with uncertainties stated by the laboratories ( $k=2$ )

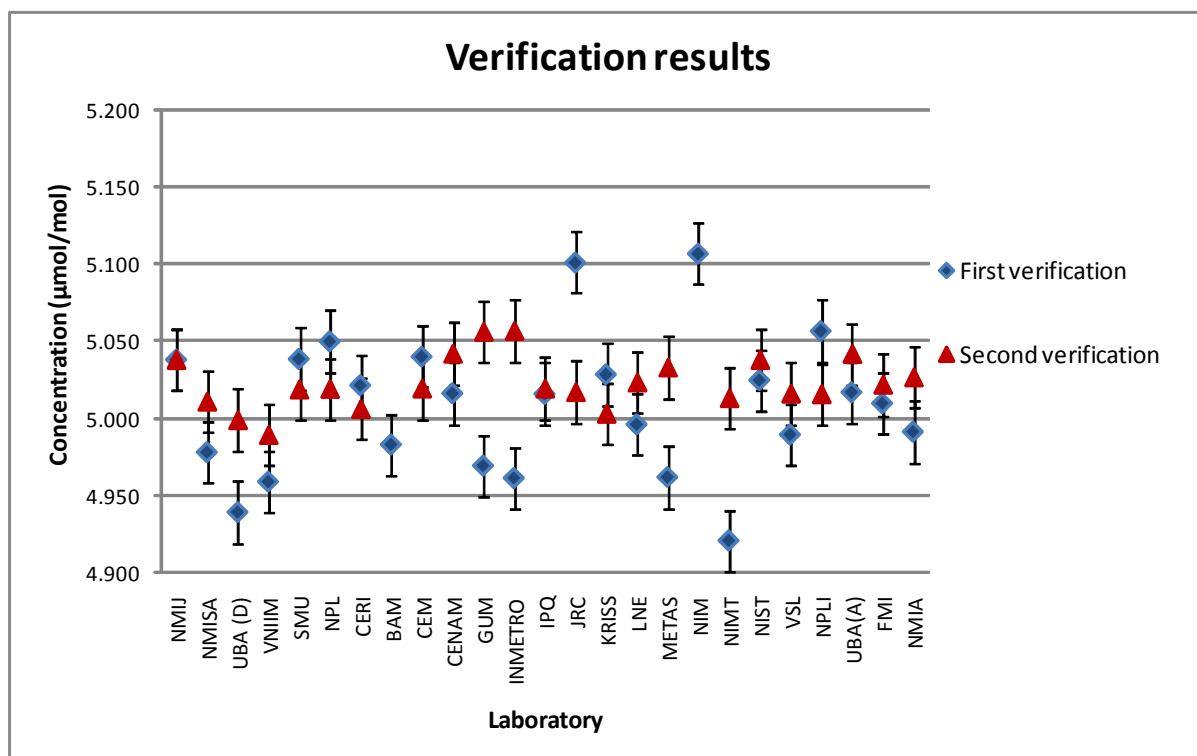




**Figure 2:** Relative degrees of equivalence with uncertainties (k=2)

**Discussion of the results**

The cylinders were verified using GC-FID (methaniser) before and after they were analysed by the participating laboratories (January 2008 and September-October 2008). All the cylinders verified at NMISA showed agreement to the gravimetric reference value with 1% expanded uncertainty. The cylinder from BAM arrived at NMISA empty and could not be verified a second time while the cylinder from NIM (China) was received after the Draft A Report was completed. All of the other cylinders were returned with enough gas pressure to complete the second set of verification measurements. The verification results are summarised in figure 3 below.



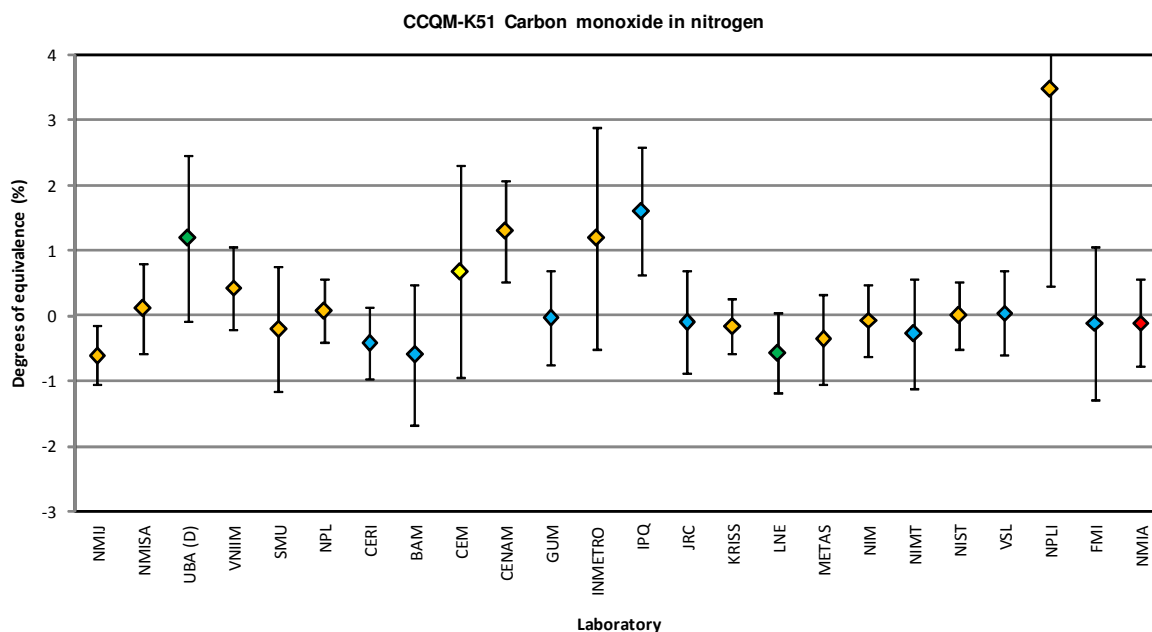
**Figure 3:** A summary of the verification results (Uncertainty bars =  $u_{ver}$ ).

The  $^{13}\text{C}/^{12}\text{C}$  ratio in the NMISA carbon monoxide ( $1 \text{ \%mol.mol}^{-1}$  CO in  $\text{N}_2$  mixture), was tested by KRISS and shown to be normal. This was investigated because it has been previously shown that an abnormal isotope ratio, results in a non-dispersive infrared spectroscopy (NDIR) method versus a gas chromatography (GC) method bias [9]. From figure 4 below, it may be seen that there is no evident bias in the type of measurement method used, since the points are evenly distributed about the reference value.

NPL and VSL both analysed the high purity nitrogen used in making the CO in nitrogen mixtures, and they both returned measurement results that were consistent with the purity analysis performed at NMISA.

VSL tested the CO, carbon dioxide ( $\text{CO}_2$ ), argon and methane ( $\text{CH}_4$ ) content and reported that the NMISA nitrogen contains carbon monoxide at a level of  $5 \pm 3 \text{ nmol.mol}^{-1}$  and carbon dioxide at a level of  $3 \pm 3 \text{ nmol.mol}^{-1}$  using fourier transform infrared spectroscopy (FTIR). Using gas chromatography with pulsed helium discharge ionisation detection (GC-PDHID), argon was estimated at  $110 \pm 20 \text{ } \mu\text{mol.mol}^{-1}$ , and  $\text{O}_2$  could not be quantified due to this large argon content. Methane was estimated at  $10 \pm 6 \text{ nmol.mol}^{-1}$ , using this technique as well.

NPL tested the CO and  $\text{CO}_2$  content, and reported that the NMISA nitrogen contains carbon monoxide at a level below the detection limit of the analytical method used ( $3 \text{ nmol.mol}^{-1}$ ), and carbon dioxide at a level close to the detection limit ( $3 \text{ nmol.mol}^{-1}$ ).



**Figure 4:** Degrees of equivalence plot with different colours showing the different measurement methods used (see table 4).

### How Far Does the Light Shine

This document describes the protocol for a key comparison for carbon monoxide in nitrogen. The nominal amount-of-substance fraction was  $5 \mu\text{mol}\cdot\text{mol}^{-1}$ . This key comparison aims to support CMC claims for carbon monoxide from  $1 \mu\text{mol}\cdot\text{mol}^{-1}$  and higher in a nitrogen matrix. This key comparison can also be used to support CMC claims for carbon monoxide in an air matrix with special consideration for cross interference from the high concentration of oxygen on the CO concentrations especially with measurement techniques, such as NDIR.

### Conclusions

Of the 25 participating laboratories, 19 (76%) showed satisfactory degrees of equivalence to the gravimetric reference value. UBA (Austria) is not a designated institute and participated in the comparison as a pilot study. The results show that the CO concentration is not influenced by the measurement method used, and from this it may be concluded that the pure CO, used to prepare the gas mixtures, was not  $^{13}\text{C}$ -isotope depleted. This was confirmed by the isotope ratio analysis carried out by KRISS on a 1% mixture of CO in nitrogen, obtained from the NMISA.

There is no indication of positive or negative bias in the gravimetric reference value, as the results from the different laboratories are evenly distributed on both sides of the key comparison reference value.

### References

- [1] Alink A., The first key comparison on Primary Standard gas Mixtures, *Metrologia* **37** (2000), pp. 35-49.
- [2] International Organisation for Standardisation, "ISO 6142 -- Gas analysis -- Preparation of calibration gas mixtures -- Gravimetric method", ISO, Geneva (CH), 2001.

- [3] Van der Veen A.M.H., Pauwels J., "Uncertainty calculations in the certification of reference materials. 1. Principles of analysis of variance", *Accreditation and Quality Assurance* **5** (2000), pp. 464-469.
- [4] Alink A., Van der Veen A.M.H., "Uncertainty calculations for the preparation of primary gas mixtures. 1. Gravimetry", *Metrologia* **37** (2000), pp 641-650.
- [5] Van der Veen A.M.H., De Leer E.W.B., Perrochet J.-F., Wang Lin Zhen, Heine H.-J., Knopf D., Richter W., Barbe J., Marschal A., Vargha G., Deák E., Takahashi C., Kim J.S., Kim Y.D., Kim B.M., Kustikov Y.A., Khatskevitch E.A., Pankratov V.V., Popova T.A., Konopelko L., Musil S., Holland P., Milton M.J.T., Miller W.R., Guenther F.R., International Comparison CCQM-K3, Final Report, 2000.
- [6] Van der Veen AMH, *et al.*, "International comparison CCQM-P41 Green house gases." *Metrologia* **44** (2007), 08002.
- [7] CIPM, "Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes", Sèvres (F), October 1999.
- [8] Van der Veen A.M.H., Cox M.G., "Degrees of equivalence across key comparisons in gas analysis", *Metrologia* **40** (2003), pp. 18-23.
- [9] Nieuwenkamp G., van der Veen, A.M.H., "Discrepancy in infrared measurement results of carbon monoxide in nitrogen mixtures due to variations of the  $^{13}\text{C}/^{12}\text{C}$  isotope ratio", *Accreditation and Quality Assurance*, Volume 10, Number 9, January 2006.
- [10] International Organisation for Standardisation, "ISO 6143 -- Gas analysis -- Comparison methods for determining and checking the composition of calibration gas mixtures", ISO, Geneva (CH), 2001.
- [11] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML, "Guide to the expression of uncertainty in measurement", first edition, ISO Geneva, 1995

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**Project reference**

CCQM-K51

**Completion date**

31 May 2009

## APPENDIX: Laboratory Reports

### Report of Isotopic Ratio from KRISS

#### Isotope ratio of CO 1% for K51 (NMISA)

- *Experimental date : Jan. 17, 2008*
- *NMISA Sample gas (NS, M555718) : CO 1 % in N<sub>2</sub>*
- *KRISS reference gas (KR, Z000325): CO<sub>2</sub> 99.99 % ( $\delta^{13}\text{C}_{\text{RM PDB}} = -23.05 \pm 0.06 \text{‰}$ )*
- *Equipment: Precision gas mass spectrometer (Finnigan MAT 271)*

*& Isotope ratio mass spectrometer (Finnigan Delta Plus)*

*(To derive the isotope ratio of NMISA sample, the CO gas of NMISA was converted into CO<sub>2</sub> at O<sub>2</sub> atmosphere generated by the chemical (combustion) reaction of CuO)*

*The following is result of  $\delta^{13}\text{C}_{\text{NS}}$ :*

$$\delta^{13}\text{C}_{(\text{NS-PDB})} = -49.6 \text{‰} \pm 30.4 \text{‰} (k=2).$$

- ⇒ *This carbon isotope ratio is within the range of normal terrestrial carbon.*
- ⇒ *The uncertainty of  $\delta^{13}\text{C}$  value is much larger than that of general  $\delta^{13}\text{C}$  measurement. The reason is that 1 % CO (NS, M555718) can not measure directly by IRMS. We used instead precision gas mass spectrometer to get <sup>45</sup>CO<sub>2</sub>/<sup>44</sup>CO<sub>2</sub> ratio.*

# National Physical Laboratory

Report on Analysis of Sample of BIP nitrogen from BIP cylinder BIP00037

**Customer:** National Metrology Institute of South Africa

**Address:** Meiring Naudé Road  
Brummeria  
Pretoria  
South Africa

**Quotation Reference:** n/a

## Background

A sample of BIP nitrogen was supplied by NMISA for analysis in support of work relating to the key comparison CCQM-K51 [Carbon monoxide (CO) in Nitrogen (N<sub>2</sub>) at 5 µmol/mol]. The gas was supplied in a 5 litre aluminium cylinder. The determination carbon monoxide and carbon dioxide was requested.

### Analytical Methods

1. CO<sub>2</sub> was measured using an Ametek Ta5000F process GC (flame ionisation detector).
2. CO was measured using an Ametek Ta5000R process GC (reduction gas detector). The measurement was made using NPL994 as a reference.

## Results

Results from the analyses outlined above demonstrate that the supplied sample of BIP nitrogen contains carbon monoxide at a level below the detection limit of the analytical method used (3 nmol/mol) and carbon dioxide at a level close to the detection limit (3 nmol/mol). These measurements were made using the same method as that used for the routine purity analysis of pure nitrogen, which is used to prepare gas standards at NPL. From past experience, the level of CO in the NMISA sample was as expected, whereas the level of CO<sub>2</sub> was marginally higher. The total CO + CO<sub>2</sub> observed in the NMISA cylinder was well within the limit specified by the supplier of 0.5 µmol/mol.

### Purity analysis NMISA N<sub>2</sub> used in K51 as performed by VSL

The analysis was focused on CO and CO<sub>2</sub>.  
In addition the nitrogen was run over a GC to check for other potential impurities.

For CO and CO<sub>2</sub> an FT-IR set-up was used with a 96 m multi pass cell.  
Both CO and CO<sub>2</sub> were not detected. Detection limit for CO is 10 nmol/mol and for CO<sub>2</sub> 5 nmol/mol.

The result for this purity analysis is therefore:

CO:  $(5 \pm 3)$  nmol/mol  
CO<sub>2</sub>:  $(3 \pm 2)$  nmol/mol

In addition a check was performed for Ar/O<sub>2</sub> and methane  
The nitrogen was analysed by GC-PDHID over a molsieve column at 25 °C.  
The nitrogen was found to have a high Ar content of over 100 µmol/mol. No oxygen was found but the detection limit for oxygen was limited due to this high amount of Ar.  
Finally the N<sub>2</sub> was analysed by GC-FID-Methaniser for methane.  
No methane was found with a detection limit of 20 nmol/mol.

The result for the GC purity analysis is therefore:

Ar:  $(110 \pm 20)$  µmol/mol  
CH<sub>4</sub>:  $(10 \pm 6)$  nmol/mol

Laboratory name: NMIJ

Cylinder number: D95 5680

## Results

Component	Result ( $\mu\text{mol/mol}$ )	Expanded Uncertainty ( $\mu\text{mol/mol}$ )	Coverage factor <sup>3</sup>
CO	4.9897	0.0091	2

Measurement Date : 22nd-28th, May, 2008

## Reference Method:

Our analysis used a gas chromatograph described in table 1.

Table 1. Analytical conditions.

Body	Shimadzu GC-14B
Software for data collection	GC solution (Shimadzu)
Column	Porapak Q 2m
Oven temp.	45 °C
Detector	FID (with Ni catalyst)
Temp. of Ni catalyst	400 °C
Temp. of detector	200 °C
Carrier gas	N <sub>2</sub>
Volume of sample loop	5 mL
Analytical time for one injection	5 min
Number of injections per one cylinder	10 (However, only last five injections were adopted)

## Calibration Standards:

All measurements used the calibration gas standards in Table 2.

Table 2. Gravimetric concentrations in calibration gas standards. (Units are  $\mu\text{mol/mol}$ ).  
The balance gas of all calibration standards is nitrogen.

(a) calibration standard 1

Component	Gravimetric concentration, $X_1$	Expanded uncertainty [ $k=2$ ], $U(X_1)$
Carbon monoxide	3.6486	0.00220

<sup>3</sup> The coverage factor shall be based on approximately 95% confidence.



(b) calibration standard 2

Component	Gravimetric concentration, $X_2$	Expanded uncertainty [ $k=2$ ], $U(X_2)$
Carbon monoxide	5.5577	0.00362

(c) calibration standard 3

Component	Gravimetric concentration, $X_3$	Expanded uncertainty [ $k=2$ ], $U(X_3)$
Carbon monoxide	6.3047	0.00396

(d) calibration standard 4

Component	Gravimetric concentration, $X_4$	Expanded uncertainty [ $k=2$ ], $U(X_4)$
Carbon monoxide	4.9746	0.00238

Preparation method:

The calibration gas standards were prepared by gravimetric method, according to ISO 6142:2001. An electronic mass-comparator (Mettler Toledo model KA10-3/P, capacity 15 kg, readability 1 mg) with automatic loading system of cylinders [Ref.2] was used for preparation of all calibration gas standards. These calibration gas standards were prepared by 4-step dilution.

Purity analyses :

The impurities in parent gases were determined with various gas analyzers. The mole fractions of the major components were calculated from equation (1) in ISO6142:2001.

Tables 3 and 4 show the results of the impurity analyses.

Table 3. Purity table for high-purity carbon monoxide gas used as parent gas.

Component	Mole fraction $\mu\text{mol/mol}$	Standard uncertainty $\mu\text{mol/mol}$	method
CO	999974.4	2.3	-
N <sub>2</sub>	2.4	1.4	GC-TCD
He	15.54	0.15	GC-TCD
O <sub>2</sub>	1.06	0.61	GC-TCD
H <sub>2</sub> O	0.44	0.25	Capacitance type moisture meter
CO <sub>2</sub>	1.44	0.83	GC-TCD
CH <sub>4</sub>	2.41	1.39	GC-TCD
H <sub>2</sub>	2.35	0.38	GC-TCD

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

Component	Mole fraction $\mu\text{mol/mol}$	Standard uncertainty $\mu\text{mol/mol}$	method
N <sub>2</sub>	999999.55	0.25	-
H <sub>2</sub> O	0.44	0.25	Moisture analyzer
CO	0.0019	0.0011	GC-FID
CH <sub>4</sub>	0.0022	0.0013	GC-FID

## Sample handling:

### Stabilization

The sample cylinder was kept in air conditioned room at approximately 22 °C for more than one day. After that, we started our measurements for this comparison.

### Transfer of sample gas to the instrument

A pressure regulator with two gauges was attached with the sample cylinder via an adaptor. The pressure of sample gas from the regulator to an electronic mass-flow controller was controlled at 0.1 MPa. The flow rate of sample gas was controlled at approximately 50 mL/min. The sample gas was injected with 6-port valve.

## Instrument Calibration:

A Quality Control (QC) cylinder gas [Ref.1] and other cylinder gases were injected into the GC-FID, alternatively. These cylinders were exchanged automatically after each measurement for one cylinder had finished.

These cylinders were measured by the following order ;

“QC( $i=1$ ) –calibration standard 1– QC( $i=2$ ) –calibration standard 2– QC( $i=3$ )-calibration standard 3– QC( $i=4$ ) –calibration standard 4– QC( $i=5$ ) –sample cylinder–QC( $i=6$ )”

Measurements of peak area (response) were repeated 10 times for each cylinder. The last 5 peak areas were using of the average of peak areas.

Furthermore, this process (“QC( $i=1$ )–……–QC( $i=6$ )”) were repeated  $J$  times. ( $J=9$ )

The following calibration data set can be obtained at  $j$  th round (  $j=1, \dots, 9$  );

- average values of responses to the QC,  $y_{qc, i=1, j}, \dots, y_{qc, i=6, j}$ ,
- average values of responses for calibration standards,  $y_{1, j}, y_{2, j}, y_{3, j}, y_{4, j}$ ,
- average values of responses for sample cylinder,  $y_{s, j}$ ,

The corrected response for calibration standard  $r$  at  $j$  th round,  $Y_{r,j}$ , was calculated from :

$$Y_{r,j} = y_{r,j} / [(y_{qc,i=r,j} + y_{qc,i=r+1,j})/2] \quad (r = 1, 2, 3, 4), \quad (1)$$

The corrected response for sample cylinder at  $j$  th round,  $Y_{s,j}$ , was calculated from :

$$Y_{s,j} = y_{s,j} / [(y_{qc,i=5,j} + y_{qc,i=6,j}) / 2] . \quad (2)$$

Furthermore, the measurements of  $Y_r$  and  $Y_s$  were repeated  $J=9$  times.

$$Y_r = \sum_{j=1}^{J=9} Y_{r,j} / J , \quad (3)$$

$$Y_s = \sum_{j=1}^{J=9} Y_{s,j} / J , \quad (4)$$

These standard uncertainties are ;

$$u^2(Y_r) = \sum_{j=1}^{J=9} (Y_{r,j} - Y_r)^2 / J(J-1) + \sum_{j=1}^{J=9} u^2(Y_{r,j}) / J^2 , \quad (5)$$

$$u^2(Y_s) = \sum_{j=1}^{J=9} (Y_{s,j} - Y_s)^2 / J(J-1) + \sum_{j=1}^{J=9} u^2(Y_{s,j}) / J^2 , \quad (6)$$

where the  $u(Y_{r,j})$  and  $u(Y_{s,j})$  are the standard uncertainty of  $Y_{r,j}$  in eq.(1) and  $Y_{s,j}$  in eq.(2), respectively.

Here, we set that the gravimetric concentration and its uncertainty of calibration standard  $m$  are  $X_r$  and  $u(X_r)$ .

From the data set of  $X_1, X_2, X_3, X_4, Y_1, Y_2, Y_3,$  and  $Y_4$ , the parameters and its uncertainty of the analytical function,  $X_s = b_0 + b_1 \cdot Y_s$ , were calculated by the Deming's least squared method. After that, the analytical content  $X_s$  and its standard uncertainty  $u(X_s)$  of the sample cylinder were calculated from the response,  $Y_s$ , and its uncertainty,  $u(Y_s)$ . The value of goodness-of-fit for this analytical function was 1.08.

## Reference

[1] M.J.T Milton, F. Guenther, W.R. Miller, A.S. Brown, *Metrologia* **43** (2006) pp.L7-L10.

[2] N. Matsumoto, T. Watanabe, M. Maruyama, H. Horimoto, T. Maeda, K. Kato (2004)

*Metrologia* **41** : 178-188.

**Laboratory name: NMISA**

**Cylinder number: D958416**

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	18/09/2008	5,010 x 10 <sup>-6</sup> mol/mol	0,32	10

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	22/09/2008	5,000 x 10 <sup>-6</sup> mol/mol	0,32	10

### Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	24/09/2008	5,022 x 10 <sup>-6</sup> mol/mol	0,32	10

### Result

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor <sup>4</sup>
CO	5,011 x 10 <sup>-6</sup> mol/mol	0,028 x 10 <sup>-6</sup> mol/mol	2

### Reference Method:

The value assigned to the key comparison mixture were obtained by comparing it for carbon monoxide against NMISA's own primary standard gas mixtures (PSMs). The comparison method conforms to ISO 6143 and generalized least squares regression was used for processing the data. A set of six PSMs was used and a quadratic linear calibration model was chosen to fit the data.

### Instrument Calibration:

A set of 6 PSMs of CO in nitrogen ranging from 1 µmol/mol to 10 µmol/mol were used to calibrate the Varian CP3800 GC-FID-methaniser with a 2 ml stainless steel sample loop, Molecular Sieve 13X silicosteel packed column (40/60 mesh size, 1 m length, 2 mm internal diameter).

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<sup>4</sup> The coverage factor shall be based on approximately 95% confidence.

Cylinder No	Gravimetric composition	Standard uncertainty
NML20008384	$1,0219 \times 10^{-6}$ mol/mol	$0,0055 \times 10^{-6}$ mol/mol
NML20005703	$2,0036 \times 10^{-6}$ mol/mol	$0,0055 \times 10^{-6}$ mol/mol
NML20003895	$4,0141 \times 10^{-6}$ mol/mol	$0,0056 \times 10^{-6}$ mol/mol
NML20008404	$6,0235 \times 10^{-6}$ mol/mol	$0,0056 \times 10^{-6}$ mol/mol
NML30003871	$8,0414 \times 10^{-6}$ mol/mol	$0,0055 \times 10^{-6}$ mol/mol
NML40008409	$10,0148 \times 10^{-6}$ mol/mol	$0,0056 \times 10^{-6}$ mol/mol

### Sample handling:

Each cylinder was equipped with a Tescom stainless steel pressure regulator that was adequately purged. The flow rate was set at approx. 100 mL/min.

### Calibration Standards:

The PSM's used for the calibration were prepared from pre-mixtures in accordance with ISO 6142:2001 (Gas analysis - Preparation of calibration gas mixtures - Gravimetric method). After preparation, the composition was verified using the method described in ISO 6143:2001.

BIP Nitrogen (6.0 quality) from Air Products South Africa was used to prepare the PSMs. The nitrogen was analysed to contain less than  $12 \times 10^{-9}$  mol/mol of CO (detection limit of GC-FID-methaniser) in all cases. The uncertainty associated with the CO determination was taken into account during the gravimetric calculations and associated uncertainty evaluation.

After preparation the standards were verified by analytical comparisons against existing gravimetrically prepared standards. Only when no significant difference between the analysed and the calculated gravimetric composition was found, the "new prepared candidate" was accepted as a PSM. The calibration mixtures were prepared between 2007 and 2008.

### Evaluation of measurement uncertainty

The listed gravimetric uncertainty is a combined standard uncertainty and comes from:

- The uncertainty associated with the weighing
- The effect on the buoyancy correction due to cylinder expansion when pressurizing to 120 bar
- The uncertainty associated with the purity analysis
- The uncertainty associated with the molar masses

The listed standard deviations in the three reported measurement cycles are actually the standard uncertainties from the regression analysis, duly propagating the gravimetric uncertainties on the PSMs and the standard deviation in the responses.

All uncertainties were combined in quadrature with the standard deviation for the three values.

Standard uncertainty measurements: = 0,32% rel.  
Standard deviation: 0,22% rel.

$$U_c = \sqrt{[(u_{day1}^2 + u_{day2}^2 + u_{day3}^2)/3]^2 + u_{stddev}^2}$$

Combined: 0,27 % rel.  
Expanded: 0,54 % rel. (k=2)

Laboratory name: UBA (D)

Cylinder number: M555674

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	18/04/08	$5,055 \cdot 10^{-6}$	0,15	5

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	24/04/08	$5,088 \cdot 10^{-6}$	0,19	5

### Measurement #3<sup>5</sup>

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	25/04/08	$5,079 \cdot 10^{-6}$	0,16	5

### Results

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor <sup>6</sup>
CO	$5,074 \cdot 10^{-6}$	$0,060 \cdot 10^{-6}$	2

### Details of the measurement method used:

#### Reference Method:

For analyzing carbon monoxide at the UBA laboratory an IR absorption method based monitor MLU 300 is used.

#### Calibration Standards:

Calibration standard is prepared by volumetric static injection.

<sup>5</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

<sup>6</sup> The coverage factor shall be based on approximately 95% confidence.

Known volumes of the pure gas compound are added to the complementary gas in a vessel of well-defined volume.

The method is described at ISO 6144 and VDI 3490. p. 14

Equipment:

cast iron vessel coated with enamel inside	0.014736 m <sup>3</sup> max. pressure 1000 kPa
Pressure gauge	0-1000 kPa Diptron 3 Wallace&Tiernan
Temperature gauge	SPE-Pt 100 Schwille
Vacuum pump	vacuubrand

Operating material:

Microliter syringe NTL	1000 µl Hamilton series 1001
Nitrogen (balance gas)	6.0 Air Liquide
Carbon monoxide (pure gas)	4.7 Air Liquide; certified by NMI Netherlands

After evacuation the vessel is filled with nitrogen 6.0 at ambient air pressure and temperature. The pure gas is injected by syringe. After that the pressure is increased by introducing additional complementary gas (9-fold ambient air pressure e.g.). The mixture have to re-equilibrate to ambient temperature.

The whole procedure is done in accordance with ISO 6144.

Instrument Calibration:

**Bracketing -Two-point Calibration**

The low and the high standards were prepared by static volumetric injection method .The concentrations were chosen after measuring (estimate) the unknown gas by our reference analyzer.

Measurement result: 5100 nmol/mol  
High standard: 5200 nmol/mol  
Low standard: 4800 nmol/mol

The concentrations were prepared in three steps by pressure reduction and refilling of a base standard.

1. Preparing base concentration 7570 nmol/mol ( p<sub>11</sub>/p<sub>21</sub>)
2. Static dilution to 5200 nmol/mol ( p<sub>12</sub>/p<sub>22</sub>)
3. Static dilution to 4800 nmol/mol ( p<sub>13</sub>/p<sub>23</sub>)

$$C = C_{\text{Vessel}} \cdot \prod_{i=1}^n \frac{p_{1i}}{p_{2i}} \quad (1)$$



$p_1$  = Pressure after reduction

$p_2$  = Pressure after refilling

### Sample Handling:

After arriving the cylinder was kept three weeks in the laboratory (stabilization). In order to take samples at ambient air pressure a pressure regulator was used and via T-piece a little overflow was controlled by a valve. For connecting with the monitor sample inlet ¼" Teflon tubes and stainless steel fittings were used.

The gas flow was about 1.3 l/min.

For this intercomparison we took after a running in period of the pressure regulator (30 min.)

5 samples (6 min.) for each measurement result.

### **Detailed uncertainty budget:**

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

#### Uncertainty:

$$u_c^2 = u_1^2 + u_R^2 + u_M^2 \quad (1)$$

$u_c$  = Combined uncertainty

$u_1$  = Combined uncertainty given by static injection method valid for both bracketing points

$u_R$  = Reproducibility of the static injection method in UBA laboratory

$u_M$  = standard uncertainty of measurements:  $\sqrt{((0,15/\sqrt{5})^2 + (0,19/\sqrt{5})^2 + (0,16/\sqrt{5})^2)}$  = 0,13 % rel.

Calculation of  $u_1$  according to ISO Guide GUM supported by GUM Workbench software. In this calculation is shown the route of traceability to SI.

Standard deviation of the 3 calibrations is included in the reproducibility of the static injection method.

$u_1$  = 0,3 % rel.

$u_R$  = 0,49 % rel.

$u_M$  = 0,13 % rel.

$$u_c = 0,59 \text{ % rel} \quad (1)$$

Coverage factor: 2

**Expanded uncertainty: ± 1, 18 %**

## **Uncertainty calculation of the Static Volumetric Method for the preparation of CO (4,8 µmol/mol) standard gas mixtures**

The procedure is described in ISO 6144

### **Model Equation:**

$$C = ((C_p * V_s / V_d * p_1 / p_2) + C_0) * p_3 / p_4 * p_5 / p_6$$

### **List of Quantities:**

Quantity	Unit	Definition
C		Volume fraction in the resulting mixture of CO
C <sub>p</sub>		Volume fraction of the pure gas CO
V <sub>s</sub>	l	Injected volume by syringe
V <sub>d</sub>	l	Volume of the vessel (complementary gas)
p <sub>1</sub>	kPa	Pressure in the syringe
p <sub>2</sub>	kPa	Final pressure in the vessel
C <sub>0</sub>		CO impurity in the Nitrogen 6.0
p <sub>3</sub>	kPa	Reduced pressure
p <sub>4</sub>	kPa	1. Dilution step
p <sub>5</sub>	kPa	Reduced pressure
p <sub>6</sub>	kPa	2. Dilution step

**C:**

Result

**C<sub>p</sub>:**

Type B rectangular distribution

Value: 0.99999

Halfwidth of Limits: 0.000001

**V<sub>s</sub>:**

Type B rectangular distribution

Value: 1·10<sup>-3</sup> l

Halfwidth of Limits: 50·10<sup>-7</sup> l

**V<sub>d</sub>:**

Type A

Method of observation: Direct

Number of observation: 5

No.	Observation
1	14.736
2	14.733
3	14.738
4	14.734
5	14.737

Arithmetic Mean: 14.735600 l

Standard Deviation: 2.1·10<sup>-3</sup> l

Standard Uncertainty: 927·10<sup>-6</sup> l

Degrees of Freedom: 4

**P<sub>1</sub>:**

Type B rectangular distribution

Value: 101.1 kPa

Halfwidth of Limits: 0.15 kPa

**P<sub>2</sub>:**

Type B rectangular distribution

Value: 909.6 kPa

Halfwidth of Limits: 0.15 kPa

**C<sub>0</sub>:**

Type B rectangular distribution

Value:  $26 \cdot 10^{-9}$

Halfwidth of Limits:  $5 \cdot 10^{-10}$

**P<sub>3</sub>:**

Type B rectangular distribution

Value: 600.0 kPa

Halfwidth of Limits: 0.15 kPa

**P<sub>4</sub>:**

Type B rectangular distribution

Value: 873.3 kPa

Halfwidth of Limits: 0.15 kPa

**P<sub>5</sub>:**

Type B rectangular distribution

Value: 600 kPa

Halfwidth of Limits: 0.15 kPa

**P<sub>6</sub>:**

Type B rectangular distribution

Value: 650 kPa

Halfwidth of Limits: 0.15 kPa

### Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
C <sub>p</sub>	0.99999	$577 \cdot 10^{-9}$	$\infty$	rectangular	$4.8 \cdot 10^{-6}$	$2.8 \cdot 10^{-12}$	0.0 %
V <sub>s</sub>	$1 \cdot 10^{-3}$ l	$2.89 \cdot 10^{-6}$ l	$\infty$	rectangular	$4.8 \cdot 10^{-3}$	$14 \cdot 10^{-9}$	91.1 %
V <sub>d</sub>	14.7356 l	$927 \cdot 10^{-6}$ l	4	normal	$-320 \cdot 10^{-9}$	$-300 \cdot 10^{-12}$	0.0 %
p <sub>1</sub>	101.1 kPa	0.0866 kPa	$\infty$	rectangular	$47 \cdot 10^{-9}$	$4.1 \cdot 10^{-9}$	8.0 %
p <sub>2</sub>	909.6 kPa	0.0866 kPa	$\infty$	rectangular	$-5.3 \cdot 10^{-9}$	$-460 \cdot 10^{-12}$	0.0 %
C <sub>0</sub>	$26 \cdot 10^{-9}$	$289 \cdot 10^{-12}$	$\infty$	rectangular	0.63	$180 \cdot 10^{-12}$	0.0 %
p <sub>3</sub>	600.0 kPa	0.0866 kPa	$\infty$	rectangular	$8.0 \cdot 10^{-9}$	$690 \cdot 10^{-12}$	0.2 %
p <sub>4</sub>	873.3 kPa	0.0866 kPa	$\infty$	rectangular	$-5.5 \cdot 10^{-9}$	$-480 \cdot 10^{-12}$	0.1 %
p <sub>5</sub>	600.0 kPa	0.0866 kPa	$\infty$	rectangular	$8.0 \cdot 10^{-9}$	$690 \cdot 10^{-12}$	0.2 %
p <sub>6</sub>	650.0 kPa	0.0866 kPa	$\infty$	rectangular	$-7.4 \cdot 10^{-9}$	$-640 \cdot 10^{-12}$	0.2 %

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
C	$4.8001 \cdot 10^{-6}$	$14.5 \cdot 10^{-9}$	$\infty$				

**Result:**

Quantity: C

Value:  $4.800 \cdot 10^{-6}$

Relative Expanded Uncertainty:  $\pm 0.60$  %

Coverage Factor: 2.00

Coverage: 95% (normal)

**D.I.MENDELEYEV INSTITUTE FOR METROLOGY (VNIM)  
RESEARCH DEPARTMENT FOR THE STATE MEASUREMENT STANDARDS IN THE  
FIELD OF PHYSICO-CHEMICAL MEASUREMENTS**

**Key Comparison CCQM-K51  
Carbon monoxide in Nitrogen (5  $\mu\text{mol/mol}$ )**

**REPORT**

**Date: 27.06.08**

**Authors:** L.A. Konopelko  
Y.A. Kustikov  
V.V. Pankratov  
I.I. Vasserman  
C.V. Zavyalov  
E.V. Gromova

**Reference method:** GC-FID

**Instrument:** gas chromatograph Agilent 6890N

**Calibration standards**

Characteristics of pure substances used for preparation of the calibration standards are shown in tables 1-2.

Table 1 – Purity table for CO

Component	Mole fraction $10^{-6}$ mol/mol	Expanded uncertainty $10^{-6}$ mol/mol ( $k=2$ )
H <sub>2</sub>	13,20	0,3
O <sub>2</sub> +Ar	14,94	0,42
N <sub>2</sub>	992,9	9,5
CO <sub>2</sub>	26,86	0,28
CH <sub>4</sub>	0,5	0,26
H <sub>2</sub> O	265,0	26,5
CO	998686,60	28,16

Table 2 – Purity table for N<sub>2</sub>

Component	Mole fraction $10^{-6}$ mol/mol	Expanded uncertainty $10^{-6}$ mol/mol ( $k=2$ )
H <sub>2</sub>	0,005	0,003
Ar	11,9	0,5
O <sub>2</sub>	3,6	0,2
CH <sub>4</sub>	0,005	0,003
CO	0,008	0,0046
CO <sub>2</sub>	0,096	0,005
H <sub>2</sub> O	3,2	0,1
N <sub>2</sub>	999981,19	0,55

All standard gas mixtures were prepared in aluminium cylinders with Aculife IV treatment, V= 5 L.

Weighing was performed on the balances 81-V-HCE-20kg (hnu-Voland, USA). Experimental standard deviation for 5 L cylinders: 8 mg.

Preparation of standard gas mixtures was carried out in 4 stages

1 stage:

Preparation of the first gas pre-mixtures CO/N<sub>2</sub> with CO mole fraction of ≈ 6 %.

Verification of mole fraction was carried out by NDIR analyzer included to the set of National Primary Measurement Standard GET 154. Relative standard deviation for each measurement series was not more than 0,05 %.

2 stage:

Preparation of the second gas pre-mixtures CO/N<sub>2</sub> with CO mole fraction of ≈ 0,1 %.

Verification of mole fraction was carried out by NDIR analyzer included to the set of National Primary Measurement Standard GET 154. Relative standard deviation for each measurement series was not more than 0,06 %.

3 stage:

Preparation of the third gas pre-mixtures CO/N<sub>2</sub> with CO mole fraction of ≈ 0,01 ppm.

Verification of mole fraction was carried out by NDIR analyzer included to the set of National Primary Measurement Standard GET 154. Relative standard deviation for each measurement series was not more than 0,07 %.

4 stage:

Preparation of the calibration gas mixtures CO/N<sub>2</sub> with CO mole fraction of ≈ 5 ppm.

There were prepared 4 standard gas mixtures.

Verification of mole fraction was carried out by gas chromatograph Agilent 6890N included to the set of National Primary Measurement Standard GET 154. Standard deviation for each measurement series was not more than 0,12 %.

The characteristics of calibration standards are shown in table 3.

Table 3 – Characteristics of calibration standards

Standard gas mixture N	Component	Assigned value, 10 <sup>-6</sup> mol/mol	Relative standard uncertainty, %
1	CO	5,054	0,15
	N <sub>2</sub>	balance	-
2	CO	5,061	0,15
	N <sub>2</sub>	balance	-
3	CO	5,079	0,15
	N <sub>2</sub>	balance	-
4	CO	5,079	0,15
	N <sub>2</sub>	balance	-

#### **Instrument calibration**

Linear regression by 4 calibration points was used for instrument calibration.

### Sample handling

Prior to measurements the cylinder was stabilized to room temperature.

### Results of measurements

Results of measurements of CO mole fraction in cylinder № M55 5669 are shown in the table 4

Table 4 - Results of measurements of CO mole fraction in cylinder № M55 5669

#### Measurement #1

Component	Date (dd/mm/yy)	Result ( $10^{-6}$ mol/mol)	Standard deviation (% relative)	number of replicates
CO	22/04/08	5,045	0,14	5

#### Measurement #2

Component	Date (dd/mm/yy)	Result ( $10^{-6}$ mol/mol)	Standard deviation (% relative)	number of replicates
CO	23/05/08	5,040	0,14	5

#### Measurement #3

Component	Date (dd/mm/yy)	Result ( $10^{-6}$ mol/mol)	Standard deviation (% relative)	number of replicates
CO	06/06/08	5,039	0,15	5

### Evaluation of uncertainty of measurements

Total standard uncertainty of CO mole fraction was calculated on the base of the following constituents:

- standard uncertainty of CO mole fraction in calibration gas mixture (including uncertainty of weighing of parent gases and pre-mixtures, uncertainty in the purity of the parent gases, uncertainty from verification);
- standard uncertainty of calibration;
- standard deviation of the measurement result of CO mole fraction in the investigated gas mixture in cylinder № M555669.

Uncertainty budget for CO mole fraction in gas mixture in the cylinder № M55 55669 is shown in the table 5.

Table 5– Uncertainty budget for CO mole fraction in gas mixture in cylinder № M55 55669

№	Source of uncertainty	Type of evaluation	Standard uncertainty, % relative
1	Preparation of the calibration gas mixtures	A, B	0,15
2	Standard uncertainty of calibration	A	0,14
3	Standard deviation of the measurement result	A	0,13
<b>Combined standard uncertainty</b>			<b>0,24</b>
<b>Expanded uncertainty (k=2)</b>			<b>0,48</b>

#### Final result of measurements

Final result of measurements of CO mole fraction in investigated gas mixture in the cylinder № M55 55669 is shown in the table 6

**Table 6**

Component	Result ( $10^{-6}$ mol/mol)	Expanded Uncertainty ( $10^{-6}$ mol/mol)	Relative Expanded Uncertainty (%)	Coverage factor
CO	5,041	0,024	0,48	2



## SMU Report      CCQM-K51 Carbon monoxide in nitrogen

Laboratory name:      Slovak Institute of Metrology, SMU

Cylinder number:      M55 5685

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	27.3.2008	0.000005005	0.45%	6

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	4.4.2008	0.000005000	0.32%	6

### Measurement #3<sup>1</sup>

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	7.4.2008	0.000005004	0.50%	6

### Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor <sup>2</sup>
CO	0.000005003	0.000000043	2

### Details of the measurement method used:

Measured on Thermoquest Trace 2000 gas chromatograph using Porapak&molsieve packed column (2.2m), FID detector, methanizer.

Carrier gas: nitrogen @ 30mL/min

Sample loop: 1 ml

Oven temperature: 40°C

Method time: 10 min. 6 automated runs.

Pressures of all mixtures in sample loop were regulated by pressure controller before entering.

All PSMs as calibration standards were made gravimetrically according ISO 6142 and 6143 in SMU. Impurities in CO Messer 4.7 and Nitrogen Air products BIP Plus were checked on GC and FTIR. Gravimetric values of the CO molar fraction in used PSMs with uncertainties are shown in the table number 1.

Tab. 1

code	x(grav)	u(gr)k=1	u(stab)rel.	u(gr+stab)	U(cert) k=2
0732E_3	0.000001408	0.000000023	0.0025	0.000000023	0.000000046
0102F_1	0.000003514	0.000000018	0.002	0.000000019	0.000000039
0018F_3	0.000005023	0.000000010	0.002	0.000000014	0.000000028
0103F_1	0.000007535	0.000000007	0.002	0.000000017	0.000000033
0097F_4	0.000010700	0.000000015	0.002	0.000000026	0.000000052

All measurements were done in automated way (only in one direction) using electric selector valve. Sequence of 6 measurement cycles with 5 PSMs was used for measurements. All PSMs were used to create calibration curves.

To calculate results following calibration curves were used

- Quadratic (b\_least): FID-area

No corrections were used.

### Detailed uncertainty budget:

Uncertainties of component molar fraction reported in Measurement 1,2 and 3 tables were calculated using b\_least program - according to Deming -weighted least square regression. They are not typically standard deviations, because this program is taking into account both standard uncertainties of mole fractions of the PSMs (which are used for building the calibration curve) and standard uncertainties of responses – signals of PSMs and sample signal. Calibration curves were made from each cycle and the molar fraction of unknown sample with its standard uncertainty was determined by b\_least.

For each  $i^{\text{th}}$  day the average  $\bar{x}_i$  was calculated (1). Standard uncertainty assigned to each  $i^{\text{th}}$  day result (4) is from standard deviation of the average (2) and average from all b\_least uncertainties that day (3).

$$\bar{x}_i = \frac{\sum_{j=1}^n x_j}{n} \quad (1)$$

$$u_1(\bar{x}_i) = \sqrt{\frac{\sum_{j=1}^n (x_j - \bar{x}_i)^2}{n * (n - 1)}} \quad (2)$$

$$u_2(\bar{x}_i) = \sqrt{\frac{\sum_{j=1}^n u(x_j)^2}{n^2}} \quad (3)$$

$$u(\bar{x}_i) = \sqrt{u_1(\bar{x}_i)^2 + u_2(\bar{x}_i)^2} \quad (4)$$

To estimate result uncertainty we have kept "Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method" (Annual Book of ASTM Standards E 691-87) with some approximations.

$$s_R = \sqrt{s_{\bar{x}}^2 + s_r \frac{n-1}{n}} \quad (5)$$

$$s_r = \sqrt{\frac{\sum_{i=1}^p u(\bar{x}_i)^2}{p}} \quad (6)$$

$$s_{\bar{x}} = \frac{\max(\Delta x)}{\sqrt{3}} \quad (7)$$

$$\Delta x = \bar{x}_1 - \bar{x}_2 \quad (8)$$

$p$  – number of days (3)

$n$  – number of measurements in 1 day

index  $i$  represents particular day

index  $j$  represents particular result (evaluated) from one calibration curve

**Final result** is average from 3 day results

$$\bar{x} = \frac{\sum_{i=1}^p \bar{x}_i}{p} \quad (9)$$

As final **standard uncertainty** we assigned to the result (9)  $\max(s_R \text{ or } s_r)$

$$u(\bar{x}) = \max(s_r; s_R) \quad (10)$$

Expanded uncertainty ( $k=2$ ) of final result

$$U(\bar{x}) = 2 \cdot u(\bar{x})$$

To build correct and comprehensive model for partial uncertainties budget is quite difficult. For the clarity and generalisation of the model, simplification was made, that the relative standard uncertainty  $u_{B,rel}(x)$  is built from the relative standard uncertainty of the signal  $u_{rel}(I_{PSM})$ , relative standard uncertainty of the mole fraction of this calibration PSM closest to the sample, 0018F\_3(Tab. 1)  $u_{rel}(x_{PSM})$  and from relative standard uncertainty of the measured sample signal  $u_{rel}(I_{sample})$ .

Estimation of the mole fraction component standard uncertainty measured sample for Measurement 1 is shown in table number 2.

Tab.2

Influence parameter	estimate	Standard uncertainty	Statistical distribution	Sensitivity coefficient	Contribution to rel.uncertainty
$\bar{x}$	0.0000050051 mol/mol	0.0000000063 mol/mol	normal	1.0	0.13%
$I_{PSM}$	2773250 counts	2397 counts	rectangular	1.0	0.09 %
$x_{PSM}$	0.000005023 mol/mol	0.000000014 mol/mol	normal	1.0	0.28%
$I_{sample}$	2765033 counts	6591 counts	rectangular	1.0	0.24%
together					<b>0.40%</b>

Relative standard uncertainty calculated with this simplification does not differ from actual evaluated value by b\_least more than 0.05% (in an absolute value of difference).

Ing. Miroslava Valkova  
Laboratory of gases

09.06.2008

Ing. Stanislav Musil, PhD.  
Deputy for research SMU

## Report from NPL for CCQM-K51 (carbon monoxide in nitrogen)

### Introduction

The cylinder submitted by the coordinating laboratory (D95 8300) has been analysed against two standards (NPL 1230 and NPL 1231) prepared independently at NPL. The analysis was carried out by (NDIR) and also validated by an independent method (GC-me-FID). These are described below.

### NPL Standards used for Analysis

Standard	Amount fraction	Uncertainty ( $k=1$ )
	[ $\mu\text{mol/mol}$ ]	
NPL 1230	4.9761	0.0037
NPL 1231	5.1020	0.0028

**NPL Standard 1230** - was prepared by gravimetric dilution of pure CO in four steps

1. 5%
2. 2000  $\mu\text{mol/mol}$
3. 100  $\mu\text{mol/mol}$
4. 5  $\mu\text{mol/mol}$

**NPL Standard 1231** - was prepared by gravimetric dilution of pure CO in two steps

1. 2040  $\mu\text{mol/mol}$
2. 5  $\mu\text{mol/mol}$

The limiting source of uncertainty was the determination of the purity of the pure nitrogen used for the dilutions. This was BIP+ nitrogen supplied by Air Products. The CO fraction measured at NPL was 3 nmol/mol ( $\pm 2.5$  nmol/mol).

The uncertainty due to weighing the minor component in the last step was

NPL 1230	63.935 g	$\pm 10$ mg
NPL 1231	4.0085 g	$\pm 1$ mg

### Results of Comparison of NPL Standards of CO in Nitrogen

The NDIR analysis was carried out by Ian Uprichard with an ABB NDIR analyser.

In each case the CCQM unknown (D95 8300) was ratioed with standards NPL1230 and NPL1231.

Date	Standard	Amount fraction	SD
		[ $\mu\text{mol/mol}$ ]	
27/03/2008	NPL 1230	5.017	0.004
28/03/2008	NPL 1231	5.025	0.008

	<b>Mean</b>	5.021	0.006
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## Uncertainty

The uncertainty is calculated as the combination in quadrature of the gravimetric uncertainty (0.003  $\mu\text{mol/mol}$ ) with the standard deviation due to the analytical comparisons (0.006  $\mu\text{mol/mol}$ ). The result is 0.0067  $\mu\text{mol/mol}$  ( $k=1$ ).

## Combined Result

**Amount fraction of CO in D95 8300 = 5.021 +/- 0.013 ( $k=2$ )  $\mu\text{mol/mol}$**

*[The uncertainty is equivalent to 0.26% ( $k=2$ )]*

For information, the results presented above were validated with an independent comparison method carried out by Gergely Vargha:

Agilent 6890 with methaniser-FID  
 Column - MS5A PLOT (30m)  
 Temperature 120 deg C  
 Gas sample loop volume 0.5 cm<sup>3</sup>  
 Chemstation software

Each run consisted of 12 injections (the first two were not included in the average). The unknown and the standard were measured in alternate runs. The mean of the ratios of runs was evaluated.

<b>Standard</b>	<b>Amount fraction</b>	<b>SD</b>
	[ $\mu\text{mol/mol}$ ]	
NPL 1230 (ratio)	5.016	0.028
NPL 1231 (ratio)	5.031	0.031

The results of this validation were not included in the calculation of the final result.

Laboratory name: Chemicals Evaluation and Research Institute, Japan

Cylinder number: D958312

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	25/3/2008	4.9993	0.0042	3

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	27/3/2008	5.0020	0.0040	3

### Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	28/3/2008	4.9931	0.0176	3

### Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor <sup>7</sup>
CO	4.998	0.018	2

### Reference Method:

Instruments for CO measurement

Principles: Gas filter correlation CO analyzer (Type: 48i, Make: Thermo electron corporation)

Sample gas flow: 1.5L/min (over flow: 0.5L/min)

### Calibration Standards:

Preparation: Gravimetric method

PRMs based on Japanese Measurement Law (Japan Calibration Service System: JCSS)

Table 1 concentration of PRMs

<sup>7</sup> The coverage factor shall be based on approximately 95% confidence.

Component	Concentration ( $\mu\text{mol/mol}$ )	
	PRM( $R_1$ )	PRM( $R_2$ )
CO	4.993	2.644

Table 2 Uncertainty budget of PRMs (rel %)

Source	PRM( $R_1$ )	PRM( $R_2$ )
Purity of CO, N2	0.03%	0.03%
Impurity(CO) in N2	0.06%	0.11%
Preparation (Balance)	0.05%	0.05%
Stability (6 months)	0.13%	0.13%
Combined	0.16%	0.18%

### Instrument Calibration:

This procedure is for the determination of CO in a sample using CO analyzer.

- 1) Inject the calibration standard ( $R_1$ ) into CO analyzer. Record the output.
- 2) Inject the sample to be tested in same manner as the calibration standard. Record the output.
- 3) Inject the calibration standard ( $R_2$ ). Record the output.
- 4) Calculate the concentration of CO using the formula below.

$$Y = \frac{A(E - D) + B(C - E)}{(C - D)}$$

where Y: Concentration of sample  
A: Concentration of standard ( $R_1$ )  
B: Concentration of standard ( $R_2$ )  
C: Standard ( $R_1$ ) output  
D: Standard ( $R_2$ ) output  
E: Sample output

Following above procedure, 3 measurements are repeated subsequently in a day and iterated for 3 days.

### Uncertainty:

Uncertainty source	Estimate $x_i$ ( $\mu\text{mol/mol}$ )	Assumed distribution	Standard uncertainty $u(x_i)$ ( $\mu\text{mol/mol}$ )	Sensitivity coefficient $c_i$	Contribution to standard uncertainty $u_i(y)$ ( $\mu\text{mol/mol}$ )
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Repeatability of analysis	4.998	normal (A)	0.0034	1	0.0034
PRM <sub>1</sub>	4.993	normal (B)	0.0080	1	0.0080
total					0.0087

Coverage factor: 2

Expanded uncertainty: 0.018  $\mu\text{mol/mol}$



# Report Form CCQM-K51 Carbon monoxide in nitrogen

Laboratory name: AM Bundesanstalt fuer Materialforschung und -pruefung

Cylinder number: D95-8369

## Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	04/08/08	0,000004998	0,2	7

## Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	05/08/08	0,000004987	0,4	7

## Measurement #3<sup>8</sup>

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	06/08/08	0,000005001	0,2	7

## Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	0708/08	0,000004965	0,4	5

## Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor <sup>9</sup>
CO	0,000004988	1 % <sub>rel</sub>	2

## Details of the measurement method used:

<sup>8</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

<sup>9</sup> The coverage factor shall be based on approximately 95% confidence.

The applied method does not correspond to the method which is normally used by BAM for certifying CO (0,1 to 100  $\mu\text{mol} / \text{mol}$ ).

The GC/FID system was defective. Therefore it was not possible to determine the content of CO by use of the GC with methanizer and FID.

The analyser used for the CO determination was a NDIR-System Siemens Ultramat 6, with measurement range: 0,1 to 100  $\mu\text{mol} / \text{mol}$  and resolution 0,01  $\mu\text{mol} / \text{mol}$ !

The data were visualized on the instrument display.

Since the content in this case is very close to the limit of determination for CO, the value of the standard deviation becomes substantially larger.

For the instrument calibration the bracketing technique was used.

### Sample handling:

Each cylinder was equipped with a pressure regulator that was purged three times by sequential evacuation and pressurisation with the gas mixture used.

Continuous flow (300 ml/min) through the analyser.

### Calibration Standards:

All standards are prepared via pre-mixtures according to ISO 6142 "Gas analysis - Preparation of calibration gases - Gravimetric Method".

The content of the impurities in all pure gases were determined before use by GC-PDID and GC-FID .

After preparation the standards were verified by analytical comparisons against existing gravimetrically prepared standards and dyn. vol. prepared standards (by piston pumps).

Only when no significant difference between the analysed and the calculated gravimetric composition is found, the "new prepared candidate " is accepted as a new standard.

#### Composition of calibrants :

##### BAM 6036-080806

Component	Assigned value mol/mol	Standard uncertainty ( $u(x)$ ) ( $k=2$ ) % <sub>rel</sub>
Nitrogen	Balance	0,01
Carbon oxide	0,00000496	0,09

##### BAM 6009-071128

Component	Assigned value mol/mol	Standard uncertainty ( $u(x)$ ) ( $k=2$ ) % <sub>rel</sub>
Nitrogen	Balance	0,01
Carbon oxide	0,00000553	0,10BAM 6020-071029

##### BAM-6020-071029

Component	Assigned value mol/mol	Standard uncertainty ( $u(x)$ ) ( $k=2$ ) % <sub>rel</sub>
Nitrogen	Balance	0,01
Carbon oxide	0,00000652	0,08

##### BAM-6065-080427

Component	Assigned value mol/mol	Standard uncertainty ( $u(x)$ ) ( $k=2$ ) % <sub>rel</sub>
Nitrogen	Balance	0,01

Carbon oxide	0,00001100	0,09
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### Detailed uncertainty budget:

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

The uncertainty of the grav. prepared standards is the combined uncertainty of the following uncertainty sources:

- Uncertainty of the balances (Volland / Sartorius)  $U_{(bal.V)} / U_{(bal.S)}$
- Uncertainty of the impurities of the pure gases  $U_{(imp.)}$
- Uncertainty of the main component of the pure gases  $U_{(pure\ gas)}$
- Residual-uncertainty of non-recovery errors related to the gas cylinder and to the component gas  $U_{(imp./pure\ gas)}$

The uncertainty of the analysis is the combined uncertainty of four uncertainty sources:

- Uncertainty of the grav. prepared calibration gas  $U_{cal\ gas}$
- Standard deviation (Sample measurement)  $U_{NDIR(sample)}$
- Standard deviation (Calibration "measurement")  $U_{NDIR(analysis)}$

Residual-uncertainty of non-recovery errors  $U_{residual}$

Laboratory name: Centro Español de Metrología (CEM)  
 Cylinder number: M55 5692

## Report Form CCQM-K51 Carbon monoxide in nitrogen

Laboratory name: Centro Español de Metrología (CEM)  
 Cylinder number: M55 5692

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation(% relative)	number of replicates
CO	24/04/08	$5,055 \times 10^{-6}$	1,2	10

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation(% relative)	number of replicates
CO	08/05/08	$5,048 \times 10^{-6}$	1,6	10

### Measurement #3<sub>1</sub>

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation(% relative)	number of replicates
CO	13/05/08	$5,042 \times 10^{-6}$	1,3	10

### Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation(% relative)	number of replicates
CO	15/05/08	$5,050 \times 10^{-6}$	1,3	10

### Measurement #5

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation(% relative)	number of replicates
CO	20/05/08	$5,056 \times 10^{-6}$	1,5	10

### Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor <sub>2</sub>
CO	$5,050 \times 10^{-6}$	$0,079 \times 10^{-6}$	2

### Details of the measurement method used:

GC Agilent 6890 Plus,  
 HID detector, 110 °C,  
 Columns: HP-Molesieve  
 Carrier Gas: He

### Detailed uncertainty budget:

The mathematical mode used to calculate the uncertainty of the analysis has been a linear combination of the sources of uncertainty due to the instrument used and the repeatability of the measurements. This leads to:

$$u_{result} = \sqrt{u_{B-Least}^2 + u_{repeat}^2}$$

Where  $u_{B-Least}^2$  is the uncertainty obtained by means of the B\_LEAST software (linear fit regression), and  $u_{repeat}^2$  is the standard deviation of the sample in the case of the single measurements and the standard deviation of the mean in the case of the final result.

Laboratory name: CENAM. Centro Nacional de Metrología. México

Cylinder number: M55 5728

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon Monoxide	13/06/2008	5,094E-06	0,23	3

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon Monoxide	16/06/2008	5,080E-06	0,06	3

### Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Carbon Monoxide	17/06/2008	5,082E-06	0,22	3

### Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor <sup>10</sup>
Carbon Monoxide	5,086E-06	3,3E-08	2

### **Measurement Method:**

Agilent Technologies 6890 Gas Chromatograph, with FID and Ni catalytic methanizer, split/splitless injector, gases injection valve, including Chemstation NT to collect and process data. Regulator of low pressure in the outlet of cylinder, with SS tubing of 1/16. To control the flow of injection was used a mass flow controller. A Molecular Sieve ALLTECH packed column of 60/80 Mesh was used to separate CO peak.

Oven program: 120 °C, 5 min, isothermal

He flow = 180.8 ml/min (65 cm/s) , at 344,7 kPa, constant

Make up N<sub>2</sub>: 25 ml/min

FID temperature = 250 °C

Injector temperature = 150 °C

Flame gases flows: air = 450 ml/min, H<sub>2</sub> = 40 ml/min

### **Calibration Standards:**

The calibration standards for the measurements were primary standards (primary standard mixtures, PSMs), prepared by weigh, the cylinders were weighted after each compound addition and thermal equilibrium with the room. The method used for the preparation of PSMs was the gravimetric method following the guidelines of the ISO/DIS 6142. The procedure for weighing was a Borda weighing scheme (RTRTRTR). The parent gases were in all cases at least 4.0 of purity and 6.0 for balance. Their uncertainties were calculated by type B evaluation or/and type A evaluation.

### **Reference Method:**

The calibration procedure was according to ISO 6143 using B\_Least program software for multipoint Calibration. It was used 5 concentration levels in one control sample in the following sequence: CStd<sub>1</sub>MStd<sub>2</sub>Std<sub>3</sub>Std<sub>4</sub>MCStd<sub>2</sub>....

### **Uncertainty:**

The main sources of uncertainty considered to estimate the combined standard uncertainty are derived from the:

#### **Model used for evaluating measurement uncertainty:**

$$C = \mu + \delta_T + \delta_s + \delta_m$$

The combined uncertainty has three contributions:

a) Reproducibility and Repeatability.

The combined effect ( $\delta_T$ ) of the reproducibility and repeatability was evaluated by the statistical method of analysis of variance.

b) Mathematical model effect ( $\delta_m$ ).

This component corresponds to the estimated uncertainty which come from the B\_Least program software for multipoint Calibration.

c) Performance instrument ( $\delta_s$ )

Variability observed using a Primary Standard Mixture as a sample control.

Coverage factor:  $k=2$

Expanded uncertainty: It was obtained by the product of the combined standard uncertainty and a factor of 2 and it was calculated according to the "Guide to the Expression of Uncertainty in Measurement, BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML (1995)"

### **Uncertainty Measurement to CO**

Quantity $X_i$	Estimate $x_i$	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient $c_i$	Contribution $u_i(y)$
Repeatability and Reproducibility	-----	A	Normal	0,0044	1	0,0044
Model	-----	A	Normal	0,0142	1	0,0142
Performance Instrument	-----	A	Normal	0,0076	1	0,0076

Laboratory name: Central Office of Measures (GUM)

Cylinder number: M555709

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	06.06.2008	0,00000502	0,19	10

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	09.06.2008	0,00000502	0,18	10

### Measurement #3<sup>11</sup>

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	12.06.2008	0,00000502	0,24	10

### Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor <sup>12</sup>
CO	0,00000502	0,00000003	2

### Details of the measurement method used:

Calibration Method according to ISO 6143. The measurements were repeated 10 times for the standards and the sample. The calibration curve was calculated from ratios by the software B\_least.exe (linear case).

Calibration standards were prepared by gravimetric method according to ISO 6142. The standards were prepared from separate premixtures. The cylinders were evacuated on turbo molecular pump, filled up and weighted on the verification balance. The standards were prepared in aluminium (with coated layers) cylinders. The purity of pure gases used for preparation was taken from the certificates of producer.

Composition of calibration standards:

Cylinder number	Component	Assigned value (x)	Standard uncertainty (u(x))
D518840	CO	0,00000451	0,000000005

<sup>11</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

<sup>12</sup> The coverage factor shall be based on approximately 95% confidence.



D518832	CO	0,00000502	0,000000005
D518818	CO	0,00000549	0,000000001

For calibration used analyzer thermo type 48C with NDIR detector.

**Detailed uncertainty budget:**

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

The final uncertainty, calculated according to ISO 6143, consists of the following components;

- the uncertainty of standard preparation calculated according to ISO 6142
- the standard deviation of the measurement
- resolution of the analyzer.

Laboratory name: LABAG/INMETRO

Cylinder number: D958363

### Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	18/07/2008	5,019	0.61	05

### Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	22/07/2008	5.093	0,67	05

### Measurement #3<sup>13</sup>

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CO	23/07/2008	5,132	2,22	05

### Results

Component	Result (µmol/mol)	Expanded Uncertainty	Coverage factor <sup>14</sup>
CO	5.081	0.083	2

### Details of the measurement method used:

The Gas Chromatograph (GC) with catalytic methanizer was used.

Varian CP-3800 GC equipped with of thermal conductivity detector (TCD) and flame ionisation detector (FID). The carbon monoxide was determined with column catalytic methanizer and detects using the flame ionisation detector (FID).

Carrier gas: Helium.

Column: 15 m x 0,25mm x 0,39mm Factorfour capillary column

Data collection was performed using Software Galaxie 1.X.

### Calibration Standards:

It was used three standards to calibrate the GC. They were prepared according International Standard ISO 6142:2001 by NMI-VSL.

<sup>13</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

<sup>14</sup> The coverage factor shall be based on approximately 95% confidence.

PRM MY 9714

Component	Assigned value( x) 10 <sup>-6</sup> mol/mol	Standard uncertainty (u(x)) 10 <sup>-6</sup> mol/mol
Carbon monoxide	2,003	0,005

PRM MY 9716

Component	Assigned value( x) 10 <sup>-6</sup> mol/mol	Standard uncertainty (u(x)) 10 <sup>-6</sup> mol/mol
Carbon monoxide	5,006	0,0125

PRM D244752

Component	Assigned value( x) 10 <sup>-6</sup> mol/mol	Standard uncertainty (u(x)) 10 <sup>-6</sup> mol/mol
Carbon monoxide	7,002	0,0175

### Instrument Calibration:

Describe your Calibration procedure (mathematical model/calibration curve, number and concentrations of standards, measurement sequence, temperature/pressure correction etc.)<sup>15</sup>:

The standards used were described in topic above. Pressure correction was take into account. The measurement was first Injection of the standards and then injection of the sample. Were injected five times. The calibration was done according ISO 6143, the best model was determined using the software B\_Least.

Sample handling:

After arrival in the laboratory the cylinder was stabilised at room temperature (21°C and humidity of 55%) before measurements.

The standards and sample were transferred directly to the GC using a system composed three valves, pressure regulator and flow meter.

### Detailed uncertainty budget:

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

### Evaluation of measurement uncertainty

The uncertainty of the unknown sample was calculated according to ISO 6143, using the software B\_least. The combined uncertainty was multiplied by a coverage factor of 2 with a confidence interval of 95%. Three sources of uncertainty were considered:

- Uncertainty of the standards (certificate - type B)
- Uncertainty of the area (analysis - type A)
- Calibration curve (type A)

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<sup>15</sup> Please state in particular the calibration model, its coefficients, and the uncertainty data (if necessary, as covariance matrix)

Laboratory name: Instituto Português da Qualidade (IPQ)  
Cylinder number: D958407

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	21/04/08	$5,091 \times 10^{-6}$	0,304	3

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	22/04/08	$5,112 \times 10^{-6}$	0,769	3

### Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	23/04/08	$5,103 \times 10^{-6}$	0,469	3

### Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	29/04/08	$5,094 \times 10^{-6}$	0,375	3

### Results

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor <sup>16</sup>
CO	$5,100 \times 10^{-6}$	$0,044 \times 10^{-6}$	2

### Details of the measurement method used:

Reference Method:  
ISO 6143:2001 (E)

Calibration Standards:  
PSM202535 ( $4,746 \times 10^{-6}$ ); PSM202596 ( $4,997 \times 10^{-6}$ ); PSM108342 ( $7,992 \times 10^{-6}$ );  
PSM108337 ( $10,01 \times 10^{-6}$ ); PSM108351 ( $11,99 \times 10^{-6}$ )

#### Instrument Calibration:

Manual calibration (zero and span are calibrated separately by pressing the analyzer system display and control unit softkeys)

Analyzer: Horiba Ambient CO Monitor APMA-360; Non Dispersive Infrared Spectroscopy (NDIR)

<sup>16</sup> The coverage factor shall be based on approximately 95% confidence.

Sample Handling:  
Autosampler / Software Sira version 2.0

**Detailed uncertainty budget:**

Uncertainty table: CO

Uncertainty source  $X_i$	Estimate  $x_i$	Assumed distribution	Standard uncertainty  $u(x_i)$	Sensitivity coefficient  $c_i$	Contribution to standard uncertainty  $u_i(y)$
Repeatability		normal	$1,413 \times 10^{-8}$	1	$1,413 \times 10^{-8}$
Reproducibility		normal	$4,705 \times 10^{-9}$	1	$4,705 \times 10^{-9}$
Calibration		normal	$1,592 \times 10^{-8}$	1	$1,592 \times 10^{-8}$

Laboratory name: European Commission, Joint Research Centre, Institute for Environment and Sustainability, European Reference Laboratory for Air Pollution (ERLAP), Italy

Cylinder number: D958393

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	08/05/08	5021*10 <sup>-9</sup>	0.05	30

\*data acquisition, had 10 seconds sampling time, and 30 measurements are grouped to calculate average and standard deviation

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	13/5/2008	5018*10 <sup>-9</sup>	0.08	30

\*data acquisition, had 10 seconds sampling time, and 30 measurements are grouped to calculate average and standard deviation

### Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	16/5/2008	5014*10 <sup>-9</sup>	0.06	30

\*data acquisition, had 10 seconds sampling time, and 30 measurements are grouped to calculate average and standard deviation

### Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	22/5/2008	5023*10 <sup>-9</sup>	0.09	30

\*data acquisition, had 10 seconds sampling time, and 30 measurements are grouped to calculate average and standard deviation

### Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor <sup>17</sup>
CO	5019*10 <sup>-9</sup>	34*10 <sup>-9</sup> mol/mol	2

### Details of the measurement method used:

CO was measured with a non-dispersive infrared gas filter correlation analyzer (TE 48C).

<sup>17</sup> The coverage factor shall be based on approximately 95% confidence.

The calibration experiment with subsequent determination of the composition of the tested sample was performed on 4 different days. For each calibration experiment three calibration gas mixtures were prepared at fraction levels of 4, 5 and 6  $\mu\text{mol/mol}$ . The calibration gas mixtures were produced by the static volumetric method. Each calibration gas mixture was validated by comparison to a gas mixture produced by a secondary method - the dynamic volumetric method.

#### Calibration gas mixtures

The laboratory procedure implementing methodology of ISO 6144 (static volumetric method) was applied. All influencing quantities are traceable to SI units. A 2.5ml syringe with different volume adapters was used to inject the pure gas into the vessel of known volume (about 110 l), which was then pressurised with zero air. For the evaluation of the amount of CO in the calibration gas mixture and the corresponding uncertainty the 'GUM Workbench' (Danish Technological Institute) computer application was used.

#### Validation gas mixtures

The procedure implementing methodology of ISO 6145-7 (dynamic volumetric method) was applied. A gas cylinder with a CO amount of 45  $\mu\text{mol/mol}$  (produced and certified by NMI Van Swinden Laboratorium) was dynamically diluted using mass flow controllers. For every gas mixture both the total flow and the cylinder flow were measured with Brooks Vol-U-Meters. For the evaluation of the amount of CO in the validation gas mixture and the corresponding uncertainty the 'GUM Workbench' (Danish Technological Institute) computer application was used.

#### Evaluation of the calibration and the measurement result

The methodology of ISO 6143 (comparison method) was applied. For all four calibrations linear calibration functions were evaluated, validated and applied to the measurements of the tested sample. All evaluations of calibrations were performed with the computer application "B-least" (BAM, 1997) described in standard VDI 2449-3.

#### Sampling

The used pressure regulator was vacuumed and purged. The transfer system was tested for suitability as described in ISO 16664.

### **Detailed uncertainty budget:**

The largest contribution to the uncertainty of the calibration gas mixture (relative uncertainty contribution 0.2%) is due to the handling of the syringe (preparation, transport and injection of pure gas) used for the injection in the static volumetric method. It is assessed from systematic comparisons of the Static volumetric method to the Dynamic volumetric method. The second largest contribution to the uncertainty of the calibration gas mixture (relative uncertainty contribution 0.17%) is the temperature of the pure gas in the syringe. The syringe is allowed to reach thermal equilibrium with surroundings and the temperature of the surrounding is measured by a set of thermometers. The third largest contribution to the uncertainty of the calibration gas mixture (relative uncertainty contribution 0.14%) is related to the volume of the syringe. This volume is evaluated by filling the syringe with water and weighing the mass of the squirt. In this procedure the uncertainty of the balance is negligible in comparison to the reproducibility of the procedure. A list of all uncertainty contributions is presented hereafter.

<b>description</b>	<b>relative standard contribution (%)</b>
handling of the pure gas syringe	0.20
temperature of pure gas in the syringe	0.17
mass of water during the calibration of volume of the syringe	0.14
quality of complimentary zero gas	0.11
pressure of pure gas in the syringe	0.08
temperature of final calibration gas mixture in the mixing vessel	0.07
pressure of final calibration gas mixture in the mixing vessel	0.05
density of water that was used for the calibration of volume of the syringe	0.04
volume of the mixing vessel	0.01
Purity of pure gas	0.00



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

Cylinder number: M55 5715

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	29/04/08	$5.010 \times 10^{-6}$	0.05	4
CO	29/04/08	$5.011 \times 10^{-6}$	0.06	4

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	30/04/08	$5.009 \times 10^{-6}$	0.03	4
CO	30/04/08	$5.011 \times 10^{-6}$	0.02	4
CO	30/04/08	$5.011 \times 10^{-6}$	0.05	4
CO	30/04/08	$5.012 \times 10^{-6}$	0.05	4
CO	30/04/08	$5.012 \times 10^{-6}$	0.03	4

### Measurement #3<sup>18</sup>

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	01/05/08	$5.011 \times 10^{-6}$	0.02	4
CO	01/05/08	$5.009 \times 10^{-6}$	0.02	4

### Results

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor <sup>19</sup>
CO	$5.011 \times 10^{-6}$	$0.004 \times 10^{-6}$	2.0

### Details of the measurement method used:

#### Instrument description:

CO analysis ( $\sim 5 \times 10^{-6}$  mol/mol): HP 6980 GAS chromatograph with Flame Ionization detector (GC/FID)

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

#### Analytical condition

<sup>18</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

<sup>19</sup> The coverage factor shall be based on approximately 95% confidence.

Component	Analytical condition
Detector temperature (FID)	280 °
H <sub>2</sub> , Air flow rate	45, 450 mL/min
Methanator Temp.	375 °
Oven Temp.	160 °
Column	Restek MS-5A 80/100 12ft 1/8 inch sus
Carrier flow rate (He)	29mL/min
Sample loop size	2 cc
Sample flow rate	150 ml/min

### Calibration standards:

The calibration standards for CCQM K-51 were prepared by gravimetric method in our institute (KRISS). All impurities in each individual source gas were analyzed for purity analysis. For obtaining the nominal value of CO mixture, 4setp dilutions carried out. The uncertainty of the primary standards prepared during the independent step are within 0.01 % -0.04, k=2.

### Concentration and uncertainty during the preparation of CO mixture

Cylinder no	Preparation concentration (%mol/mol)	Expanded uncertainty (%mol/mol)	Relative expanded Uncertainty (%)	Manufacturing date
EA0003445	4.72734	0.00044	0.0094	
EA0003452	4.73036	0.00045	0.0096	
EA0003454	4.71054	0.00044	0.0094	
EA0003468	4.76455	0.00046	0.0096	

Cylinder no	Preparation concentration (%mol/mol)	Expanded uncertainty (%mol/mol)	Relative expanded uncertainty(%)	Manufacturing date
FF39597	0.22252	0.000039	0.017	
FF39601	0.22581	0.000039	0.017	
FF39628	0.22002	0.000040	0.018	
FF46145	0.22470	0.000039	0.017	

Cylinder no	Preparation concentration (%mol/mol)	Expanded uncertainty (%mol/mol)	Relative expanded uncertainty(%)	Manufacturing date
ME0406	0.0107757	0.0000027	0.025	
ME0407	0.0105829	0.0000027	0.025	
ME0422	0.0103392	0.0000027	0.026	
ME0441	0.0104897	0.0000029	0.025	

Cylinder no	Preparation concentration ( $\mu\text{mol/mol}$ )	Expanded uncertainty ( $\mu\text{mol/mol}$ )	Relative expanded uncertainty(%)	Manufacturing date
ME0431	3.6472	0.0015	0.040	
ME5497	5.2032	0.0018	0.035	
ME5506	4.6764	0.0017	0.036	
ME5525	5.1865	0.0018	0.035	
ME5526	6.0894	0.0020	0.033	
ME0427	6.0951	0.0020	0.033	
ME5535	6.5201	0.0021	0.032	
ME5626	6.6668	0.020	0.033	

### Instrument Calibration:

One set of 8 standard gases with similar concentration was prepared by gravimetric method and verified by GC/FID to make sure their accuracy. Finally we used 2 standard gases (ME5497 and ME5525) for a reference during CO measurements, and the six standard gases left and 1 old standard gas (prepared in 2000) for multi-point calibration in CO measurements.

### Sampling handling:

The sample cylinders were stood for more than one week at room temperature to equilibrate temperature.

### Detailed uncertainty budget:

We estimated the uncertainty in the gravimetric methods and measurements. The uncertainties are given in Table.

<Uncertainties during preparation>

Uncertainty related to the balance & the weights	Value (mg)	Distribution	Standard uncertainty (mg)
1. Resolution of balance	1	Rectangular	0.289
2. Accuracy of balance including linearity	1	Rectangular	0.577
3. Incorrect zero point	1	Rectangular	0.289
4. Drift(thermal and time effects)	1	Rectangular	0.289
5. Instability due to draught	Negligible		
6. Location of cylinder on the balance pan	Negligible		
7. Uncertainties in the weights used	0.05	Rectangular	0.025
8. Buoyancy effects on the weights used	1.68	Rectangular	0.97
Total (mg)			1.235

Uncertainty related to the gas cylinder	Value (mg)	Distribution	Standard uncertainty (mg)
1. Loss of metal, paints or labels from surface of cylinder	0.1	Rectangular	0.058

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

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

<Uncertainties in purity analysis>

Purity table for CO

Component	Analytical conc. ( $\mu\text{mol/mol}$ )	Distribution	Applied concentration ( $\mu\text{mol/mol}$ )	Standard uncertainty ( $\mu\text{mol/mol}$ )
H <sub>2</sub>	< 0.5	rectangular	0.25	0.144
H <sub>2</sub> O	15.8	normal	15.8	7.900
CH <sub>4</sub>	< 0.1	rectangular	0.05	0.029
CO <sub>2</sub>	28.9	normal	28.9	5.780
THC	0.3	normal	0.3	0.060
N <sub>2</sub>	6.1	normal	6.1	1.220

O <sub>2</sub>	1.7	normal	1.7	0.340
H <sub>2</sub> S	0.42	normal	0.42	0.084
		Impurity	53.520	9.872
		CO	999946.48	19.744

Purity table for N<sub>2</sub>

Component	Analytical conc. ( $\mu\text{mol/mol}$ )	Distribution	Applied concentration. ( $\mu\text{mol/mol}$ )	Standard uncertainty ( $\mu\text{mol/mol}$ )
H <sub>2</sub>	< 0.5	rectangular	0.025	0.014
H <sub>2</sub> O	1.2	normal	1.2	0.600
CO	< 0.002	rectangular	0.001	0.001
CH <sub>4</sub>	< 0.001	rectangular	0.0005	0.000
CO <sub>2</sub>	< 0.01	rectangular	0.005	0.003
THC	< 0.5	rectangular	0.25	0.144
Ar	< 1.0	rectangular	0.5	0.289
O <sub>2</sub>	0.35	normal	0.35	0.070
Ne	< 0.1	rectangular	0.5	0.289
		Impurity	2.833	0.743
		N <sub>2</sub>	999997.17	1.487

<Total uncertainties>

Uncertainty item	type	Standard uncertainty [%]
Gravimetry uncertainty	B	0.016
Regression uncertainty	A	0.03
Verification uncertainty	A	0.02
Total expanded uncertainty (k=2)		0.08

Laboratory name: LNE

Cylinder number: M555708

### Measurement #1

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	27/03/2008	4.991	0.12	3

### Measurement #2

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	28/03/2008	5.001	0.12	3

### Measurement #3<sup>20</sup>

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	31/03/2008	4.994	0.12	3

### Results

Component	Result ( $\mu\text{mol/mol}$ )	Expanded Uncertainty ( $\mu\text{mol/mol}$ )	Coverage factor <sup>21</sup>
CO	4.994	0.022	2

### Details of the measurement method used:

#### Description of the analyser:

A 48C (TEI) analyser based on the IR principle is used to measure CO concentrations.

#### Description of the calibration standards:

A reference gas mixture of CO in nitrogen at about 5  $\mu\text{mol/mol}$  is used to determine the concentration of the gas mixture M555708.

The reference gas mixture is prepared by a multistage gravimetric method.

<sup>20</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

<sup>21</sup> The coverage factor shall be based on approximately 95% confidence.

**Description of the analytical method:**

The concentration of the gas mixture M555708 is obtained by comparison with the gravimetric reference gas mixture, as following :

$$C_{Gas\ mixture} = C_{Re\ ference\ gas\ mixture} \times \frac{R_{Gas\ mixture}}{R_{Re\ ference\ gas\ mixture}}$$

With :

- $C_{Gas\ mixture}$  the concentration of the gas mixture M555708
- $C_{Re\ ference\ gas\ mixture}$  the concentration of the gravimetric reference gas mixture
- $R_{Gas\ mixture}$  the reading for the gas mixture M555708
- $R_{Re\ ference\ gas\ mixture}$  the reading for the gravimetric reference gas mixture

This procedure is carried out 3 times on 3 different days.

**Sample Handling:**

Cylinders were maintained inside a laboratory at a nominal temperature of (21±2)°C for all the period. Samples were introduced into the analyser via a normal gas regulator and an overflow valve.

**Detailed uncertainty budget:**

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

**Uncertainty:**

First set of results (27/03/2008)

Uncertainty source	Estimate $x_i$	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient $ C_i $	Contribution $u(x_i) \times  C_i $
Gravimetric reference gas mixture	4.991	-	$5.000 \times 10^{-3}$	1.000	$5.000 \times 10^{-3}$
Reading for the gas mixture M555708	4.99	rectangular	$5.7735 \times 10^{-3}$	1.000	$5.774 \times 10^{-3}$
Reading for the gravimetric reference gas mixture	4.99	rectangular	$5.7735 \times 10^{-3}$	1.000	$5.774 \times 10^{-3}$
				$u$ ( $\mu\text{mol/mol}$ )	0.009575

Second set of results (28/03/2008)

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Uncertainty source	Estimate $x_i$	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient $ C_i $	Contribution $u(x_i) \times  C_i $
Gravimetric reference gas mixture	4.991	-	$5.000 \times 10^{-3}$	1.002	$5.010 \times 10^{-3}$
Reading for the gas mixture M555708	5.00	rectangular	$5.7735 \times 10^{-3}$	1.000	$5.774 \times 10^{-3}$
Reading for the gravimetric reference gas mixture	4.99	rectangular	$5.7735 \times 10^{-3}$	1.002	$5.785 \times 10^{-3}$
				$u$ ( $\mu\text{mol/mol}$ )	0.009585

Third set of results (31/03/2008)

Uncertainty source	Estimate $x_i$	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient $ C_i $	Contribution $u(x_i) \times  C_i $
Gravimetric reference gas mixture	4.991	-	$5.000 \times 10^{-3}$	1.001	$5.005 \times 10^{-3}$
Reading for the gas mixture M555708	4.993	rectangular	$5.7735 \times 10^{-3}$	1.000	$5.774 \times 10^{-3}$
Reading for the gravimetric reference gas mixture	4.99	rectangular	$5.7735 \times 10^{-3}$	1.001	$5.779 \times 10^{-3}$
				$u$ ( $\mu\text{mol/mol}$ )	0.00958

Uncertainty on the final result

Uncertainty source	Estimate $x_i$	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient $ C_i $	Contribution $u(x_i) \times  C_i $
Maximum calibration uncertainty	4.994	-	0.009585	1	0.009585
Standard deviation of the mean of the 9 measurements	4.994	-	0.00527	1	0.00527

Coverage factor: 2

Expanded uncertainty:  $U = 0.022 \mu\text{mol/mol}$



Laboratory name: METAS, Analytical Chemistry Section, Gas Analytical Laboratory  
 Cylinder number: M55 5697

#### Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard uncertainty (% relative)	number of replicates
CO	22.04.2008	5.001	-0.23 / +0.26	12

#### Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard uncertainty (% relative)	number of replicates
CO	23.04.2008	5.004	-0.27 / +0.30	12

#### Measurement #3<sup>1</sup>

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard uncertainty (% relative)	number of replicates
CO	24.04.2008	5.003	-0.28 / +0.30	12

#### Result

Component	Result (µmol/mol)	Expanded Uncertainty (µmol/mol)	Coverage factor <sup>2</sup>
CO	5.003	-0.026 / +0.028	2

#### Details of the measurement method used:

The transfer standard has been compared against 6 mixtures by means of a fully automatic pressure controlled GC with methaniser and FID. The mixtures have been prepared by dilution of 2 gravimetric premixtures with nitrogen of quality Alphagaz 2 from Carbagas using a molbloc/molbox system for the flow measurements.

The binary gravimetric premixtures were cylinders out of the set of national reference gas mixtures for CO in nitrogen in the range between 45 µmol/mol to 190 µmol/mol:

Reference 1: Cylinder No. SL 81508 with METAS value (80.11 ± 0.28) µmol/mol

Reference 2: Cylinder No. PG 220123 with METAS value (129.73 ± 0.39) µmol/mol

Three dilutions have been produced for each cylinder to give nominal fractions of 4.95 µmol/mol, 5.00 µmol/mol and 5.05 µmol/mol. The area results (responses) of known calculated mixtures and the unknown mixture have been evaluated using the bracketing technique with a linear regression according to ISO standard 6143 by using the programme B-Least.

<sup>1</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

<sup>2</sup> The coverage factor shall be based on approximately 95% confidence.

The CO molar fraction of the dilution gas has been measured to be < 0.01 µmol/mol (limit of quantification) by means of a CO-analyser Horiba APMA 370 using BIP Plus Nitrogen from air products purified further by a MonoTorr PS3 from pure gas products as zero gas.

### Detailed uncertainty budget:

The uncertainty estimation has been done using GUM Workbench Pro V. 2.3.7.147 and the comparison process using the B-Least method described in ISO standard 6143.

The measurement equation reads as follows:

$$x_{CO(TS)} = x_{CO(grav)} \cdot f_{dil} \cdot K_{comp} + K_{pur}$$

with:

- $x_{CO(TS)}$  being the amount of substance fraction of CO in the transfer standard,
- $x_{CO(grav)}$  being the amount of substance fraction of CO in the gravimetrically prepared CO premixtures used as standards. These are two mixtures in cylinders out of a set forming the national standard gas mixtures.
- $f_{dil}$  being the dilution factor calculated out of the molbloc readings for premixture and dilution gas flow.
- $K_{comp}$  being the correction factor for the comparison method containing the standard deviations of the flow readings and the standard deviations of the GC areas. The standard uncertainty of the flows except for the experimental standard deviations have been accounted for in  $f_{dil}$ . The correction factor is always very near to 1 because of the bracketing technique. Its uncertainty is directly taken from the B-Least result.
- $K_{pur}$  being an additive correction for the CO molar fraction added by the dilution gas. This adder has been set to zero with an uncertainty linked to the limit of quantification. The uncertainty contribution is unilateral because there is only a positive uncertainty contribution and no negative resulting in non symmetric uncertainty statements.

Two example budgets have been prepared to present the best and worst case of the measurements. The differences are mainly in the standard deviation of the GC areas and the slightly different relative uncertainties of the premixtures. Only the expanded uncertainty modulus of the positive part is mentioned. For the negative part the contribution of  $K_{pur}$  has been omitted.

All individual per day standard uncertainties have been combined to the final result taking into account a correlation of 0.95 because most of the uncertainty components are in common.

Example 1 (best case):

#### Uncertainty Budget:

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$x_{CO(grav)}$	129.730 ppm	$1.5 \cdot 10^{-3}$ (rel)	50	normal	0.039	$7.5 \cdot 10^{-3}$ ppm	36.3 %
$f_{dil}$	0.0385281	$1.4 \cdot 10^{-3}$ (rel)	84		130	$7.1 \cdot 10^{-3}$ ppm	32.1 %
$K_{comp}$	1.000600	$800 \cdot 10^{-6}$ (rel)	50	normal	5.0	$4.0 \cdot 10^{-3}$ ppm	10.3 %
$K_{pur}$	0.0 ppm	$5.8 \cdot 10^{-3}$ ppm	$\infty$	rectangular	1.0	$5.8 \cdot 10^{-3}$ ppm	21.4 %
$x_{CO(TS)}$	5.0012 ppm	0.0125 ppm	240				

Result:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$x_{CO(TS)}$	5.001 ppm	0.50 % (relative)	2.00	95% (normal)

Example 2 (worst case):

**Uncertainty Budget:**

Quantity	Value	Standard Uncertainty	Degrees of Freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$x_{CO(grav)}$	80.107 ppm	$1.7 \cdot 10^{-3}$ (rel)	50	normal	0.062	$8.6 \cdot 10^{-3}$ ppm	32.4 %
$f_{dil}$	0.0625494	$1.4 \cdot 10^{-3}$ (rel)	86		80	$6.9 \cdot 10^{-3}$ ppm	21.1 %
$K_{comp}$	0.99846	$1.7 \cdot 10^{-3}$ (rel)	50	normal	5.0	$8.5 \cdot 10^{-3}$ ppm	31.8 %
$K_{pur}$	0.0 ppm	$5.8 \cdot 10^{-3}$ ppm	$\infty$	rectangular	1.0	$5.8 \cdot 10^{-3}$ ppm	14.7 %
$x_{CO(TS)}$	5.0029 ppm	0.0151 ppm	220				

**Result:**

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$x_{CO(TS)}$	5.003 ppm	0.60 % (relative)	2.00	95% (normal)

Date: 25 June 2008

Report prepared by:



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## International Key Comparison Report On CCQM-K51 of CO in Nitrogen

### Lab Information

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 Date of Receiving the Comparison Cylinder: April 2008  
 Cylinder No.: M555717  
 Initial inner pressure of the comparison cylinder when received: 10MPa

### Measurement Report

Table 1. Measurement Report by GC-FID with Methanator

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	24/06/08	5.017	0.14%	5
CO	25/06/08	5.021	0.20%	5
CO	25/06/08	5.022	0.13%	5
CO	26/06/08	5.015	0.21%	5
CO	26/06/08	5.016	0.23%	5
CO	26/06/08	5.018	0.21%	5
Average		5.018		

Table 2. Measurement Report by ThermoElectron 48C CO Analyzer

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	24/06/08	5.019	0.2%	14
CO	24/06/08	5.013	0.2%	14
CO	25/06/08	5.014	0.2%	14
CO	25/06/08	5.023	0.2%	14
Average		5.017		

### Result

Table 3. Reported Result

Component	Result ( $\mu\text{mol/mol}$ )	Expanded Uncertainty ( $\mu\text{mol/mol}$ )	Coverage factor
CO	5.018	0.018*	2**

\* Which is equal to an relative expanded uncertainty of 0.36%;

\*\* The coverage factor was based on approximately 95% confidence.

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### *1 Instrumentation*

A GC-FID with methanator (GC-2010, Shimadzu, Japan) was used to analyze the gas mixtures. A stainless steel column (1m×Ø3mm) packed with TDX-01 was adopted to separate the CO from other gas components.

The gas mixtures in both comparison cylinder and the reference cylinder, via regulators and Teflon tube, were introduced into a 6-port valve. The 6-port valve was driven by compressed air. The size of sample loop used here was 1mL and the gas flow rate through the sample loop was controlled at 125mL/min continuously by an upstream mass flow controller. A restrictor was set at the end of the sample loop in order to increase the injected sample amount and reduce the ambient pressure interferences.

In case of GC-FID used, single point calibration method was used. The comparison cylinder and our reference cylinders were measured in the order of Reference-Sample-Reference-Sample.....

Another instrument was also used to perform this comparison work, and it was the carbon monoxide analyzer (48C, ThermoElectron, USA), of which the measurement range is 0~10µmol/mol. The gas flow was introduced into the analyzer at about 1L/min. In this case, the calibration curve (least square method) was used to measure the CCQM comparison cylinder.

### *2 Comparison Cylinder 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. When a SS regulator was connected to the cylinder, an inner pressure of about 10MPa was read by the gauge.

### 3 Calibration Standards

#### 3.1 Purity Data

The calibration standards of CO in nitrogen were prepared by gravimetric method according to ISO 6142-2001. Of the parent gases, the measured purity data were listed in Table 4-6.

Table 4. Purity data of the High purity N<sub>2</sub> (Cylinder No. C6628043)

Component	Concentration ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Analytical Method
CO	0.310	0.031	GC-PDHID
CO <sub>2</sub>	0.631	0.063	GC-MEN-FID
CH <sub>4</sub>	<0.002	0.001	GC-PDHID
O <sub>2</sub>	0.5	0.05	O <sub>2</sub> Analyzer
N <sub>2</sub>	999985.2	1.4	/
H <sub>2</sub>	0.02	0.01	GC-PDHID
Ar	12.3	1.2	GC-PDHID
H <sub>2</sub> O	<2	0.6	Dew point Meter

Table 5. Purity data of the High purity N<sub>2</sub> (Cylinder No. 1153221)

Component	Concentration ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Analytical Method
CO	0.010	0.002	GC-PDHID
CO <sub>2</sub>	<0.02	0.01	GC-MEN-FID
CH <sub>4</sub>	<0.002	0.001	GC-PDHID
O <sub>2</sub>	0.3	0.03	O <sub>2</sub> Analyzer
N <sub>2</sub>	999970.8	2.8	/
H <sub>2</sub>	0.02	0.004	GC-PDHID
Ar	27.8	2.8	GC-PDHID
H <sub>2</sub> O	<2	0.6	Dew point Meter

Table 6. Purity data of the Pure CO (Cylinder No. 332452)

Component	Concentration ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )	Analytical Method
-----------	--	---	-------------------

CO	999892.1	5.0	/
CO <sub>2</sub>	97	4.9	GC-MEN-FID
CH <sub>4</sub>	1	0.1	GC-FID
O <sub>2</sub>	3.88	0.39	O2 Analyzer
N <sub>2</sub>	5	1	GC-PDHID
H <sub>2</sub> O	<2	0.6	FTIR

### 3.2 Gravimetric Preparation

The calibration gas mixtures of CO in N<sub>2</sub> of about 5µmol/mol were gravimetrically prepared by 4-step dilution. From the pure gases, the CO/N<sub>2</sub> gas mixtures of 2%mol/mol, 0.125%mol/mol, 80µmol/mol, and 5µmol/mol were prepared in sequence. It should be noted that the high purity nitrogen (Cylinder No.: C6628043) was used in first 3 dilution steps, but not used to prepare CO/N<sub>2</sub> of 5µmol/mol. In case of preparation of CO/N<sub>2</sub> of 5µmol/mol, the high purity nitrogen (Cylinder No.: 1153221) was used in order to achieve more precise reference standards. Figure 1 shows a dilution example (Page 5).

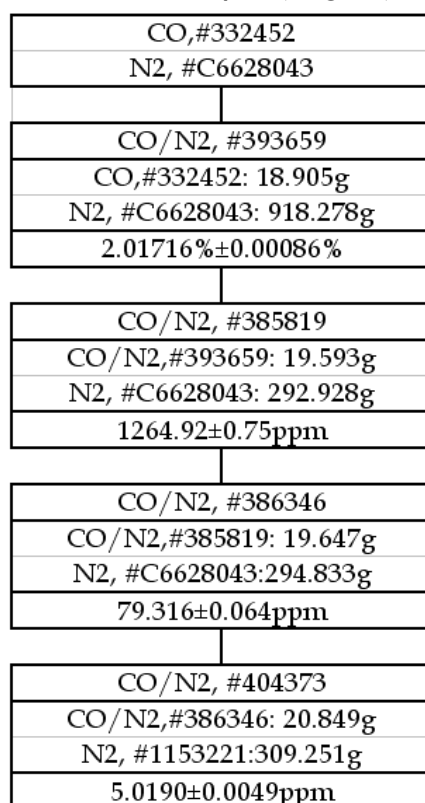


Figure 1. Stepwise dilution for preparation of CO/N<sub>2</sub>

### 3.3 Evaluation of the uncertainty sources in gravimetric preparation

Regarding the uncertainty of our own prepared reference gas mixtures, it was evaluated according to ISO6142-2001.

Balance description: Mettler Toledo product, Capacity: 10Kg, Resolution: 1mg.

Weighing Method: Substitution method.

Table 7. Uncertainty in the balance system and weights used

Uncertainty in the balance system and weights( $u_1$ )	Value(mg)	Distr.	St. u (mg)
1. Uncertainty in balance reading			0.645
1.1 Resolution of the balance	1	Rect.	0.289
1.2 Accuracy of balance including non-linearity	1	Rect.	0.577
1.3 Repeatability	Ng	-	0
2. Uncertainty due to balance drift and condition change			0.289
2.1 Drift of balance	1	Rect.	0.289
2.2 Instability due to draught	Ng	-	0
2.3 Location of cylinder on the balance pan	Ng	-	0
3. Uncertainty in the weights used			
	Case A: 20g	-	0.008
	Case B: 900g	-	0.240
Uncertainty in the 10Kg weight	16	E2 class	2.667
Component gas A: 30g	-	-	0.008
Balance gas B: 900g	-	-	0.240
<b>Total</b>	<b>(Maximum)</b>		<b>1.37</b>

Note:

- 1) The Mettler Toledo balance was calibrated by using 10Kg (E2 Class) weight everyday. In case of balance gas weighing, the standard uncertainty could be derived from the equation:  $16\text{mg}/6 \cdot (900\text{g}/1000/10\text{Kg}) = 0.240\text{mg}$ ;
- 2) In order to obtain the amount of gas filled into the cylinder, we have to read balance 4 times (In turn of Tare-Sample-Tare-Sample). So, the uncertainty in balance reading should be counted for 4 times, while the uncertainty due to balance drift and condition change counted for 2 times, and the uncertainty in weights used only counted once. That is, the combined uncertainty contributed by the sources in this table was  $u = \sqrt{4 \cdot 0.645^2 + 2 \cdot 0.289^2 + 0.240^2} = 1.374\text{mg}$ .

Table 8. Uncertainty related to the cylinders

Uncertainty related to the cylinders( $u_2$ )	Value(mg)	Distr.	St. u (mg)



			)
1. Buoyancy effects			13.603
1.1 Due to volume difference between sample and tare cylinders	2.720	Rect.	1.577
1.2 Volume change due to filling gas	23.286	Rect.	13.444
1.3 Volume change due to cylinder temperature rise	2.328	Rect.	1.344
2. Uncertainty due to handle of sample cylinder			3.267
2.1 Loss of metal, paints or labels from surface of cylinder	5	Rect.	2.887
2.2 Loss of metal from threads of valve/fitting	5	Rect.	2.887
3. Uncertainty due to adsorption			0.082
3.1 Dirt on cylinder, valves or associated fittings	4	Rect.	2.309
3.2 Moisture adsorption onto surface cylinders	0.1	Rect.	0.058
<b>Total</b>	Major component		<b>13.99</b>
	Minor Component		<b>3.87</b>

Note:

- 1) Ambient air parameters records: Atm. Press=997~1002 hPa; T=25~27 °C RH=50%~65%. The air density could be derived as: 1.1575~1.1711 Kg/m<sup>3</sup>. Average air density was 1.1643Kg/m<sup>3</sup>; the maximum difference in air density was 0.0136Kg/m<sup>3</sup>.
- 2) Buoyancy effects due to external volume difference between sample and tare cylinder: the volume difference was supposed not more than 0.2L, and the maximum value of this effect was 2.720mg. The distribution could be regarded as rectangular.
- 3) Volume change due to filling balance gas of N<sub>2</sub>: in our cases, the PRM cylinder (4L) was filled not more than 7.5MPa, therefore this volume change was supposed no more than 20cm<sup>3</sup>. The uncertainty maximum value from this source 1.1643\*20=23.286mg. Supposed rectangular distribution, and the standard uncertainty was 23.286/sqrt (3) =13.444.
- 4) Before each weighing, the cylinder was kept in the balance room for at least 8h so that the cylinder temperature could get equilibrium with the room temperature. So given the cylinder external volume change due to temperature rise was less than 2 cm<sup>3</sup>, the uncertainty from this source could be 2\*1.1643=2.328mg. Take rectangular distribution, the standard uncertainty should be 1.344mg.
- 5) The Loss of metal, paints or labels from cylinder surface was estimated based on experience as no more than 5mg. The loss of metal from the threads of fittings was also no more than 5mg.
- 6) The uncertainty due to adsorption of dirt onto the fittings was estimated within 4mg, while the uncertainty due to adsorption of water onto the cylinder surface was negligible.

**Table 9. Uncertainties related to the component gases**

Uncertainties related to the component gases ( $u_3$ )	Value(mg)	Distr.	St. u(mg)
1. Residual gases in cylinder	0.108	Rect.	0.062
2. Uncertainties of leakage of gas			0.409
2.1 Leakage of air into the cylinder after evacuation	1	Rect.	0.289
2.2 Leakage of gas from the cylinder valve during filling	1	Rect.	0.289
2.3 Escape of gas from cylinder into transport lines	Ng		0
3. Gas remaining in transfer system for weight-loss method	Ng		0
4. Absorption/reaction of components on Cyl. internal surface	Ng		0
5. Reaction between components	Ng		0
6. Insufficient homogenization	Ng		0
<b>Total (mg)</b>			<b>0.41</b>

Note:

- 1) Residual gases in cylinder. All of the cylinders were heating evacuated to  $1 \times 10^{-4}$  Pa before filling gas components. According to the idea gas law, the residual gas (supposed to be  $N_2$ ) amount was 0.108mg. Basing on rectangular distribution, the standard uncertainty was calculated as 0.062mg.
- 2) The leakage of air into the cylinder after evacuation and the leakage of gas from the cylinder valve during filling were estimated no more than 1mg.

For each filled gas component, the standard uncertainty could calculate from  $u_1$ ,  $u_2$ , and  $u_3$  in Table 4-6.

$$u_{majorcomp} = \sqrt{u_1^2 + u_2^2 + u_3^2}$$

$$u_{minorcomp} = \sqrt{u_1^2 + u_2^2 + u_3^2}$$

### 3.4 Primary Standards List

Table 10. Primary Standards list

Cyl. No.	Conc. ( $\mu\text{mol/mol}$ )	Stand. Uncert. ( $\mu\text{mol/mol}$ )	Relat. Uncert
#403811	4.8766	0.0048	0.10%
#404406	4.9403	0.0046	0.09%
#404466	5.0164	0.0049	0.10%
#404373	5.0190	0.0049	0.10%
#404694	5.0795	0.0047	0.09%
#404378	5.1496	0.0050	0.10%
#403922	5.2766	0.0051	0.10%

#### 4 Model equation for the measurement of comparison cylinder

$$c_{CCQM} = \frac{H_{CCQM}}{H_{PRM}} \cdot c_{PRM} \cdot f_r$$

$c_{CCQM}$  : Concentration of the CO in the comparison cylinder, in unit of  $\mu\text{mol/mol}$ ;

$H_{CCQM}$  : Peak height of the comparison cylinder on GC-FID, in unit of pA;

$H_{PRM}$  : Peak height of the PRM cylinder on GC-FID, in unit of pA;

$c_{PRM}$  : Concentration of the CO in PRM cylinder, in unit of  $\mu\text{mol/mol}$ ;

$f_r$  : Reproducibility between day and day.

For the  $H_{CCQM}$  and  $H_{PRM}$ , the relative standard uncertainty could be calculated from the relative standard deviation(RSD). Take the maximum RSD of 0.23% basing on 5 replicates, the relative standard uncertainty is  $0.23\%/\sqrt{5}=0.10\%$ .

For  $c_{PRM}$ , the relative standard uncertainty was 0.10%.

The relative standard uncertainty of  $f_r$  could be calculated from the 6 measurements on different day, and was  $\text{RSD}/\sqrt{6}=0.06\%/\sqrt{6}=0.02\%$ .

Table 11. Uncertainty estimation for the results.

Quantity	Value	Standard uncertainty	Type	Sensitivity Coefficient	Uncertainty Contribution
$c_{PRM}$	5.0189	0.0049	A	0.999880	0.00490
$H_{CCQM}$	6649.1	6.6491	A	0.000755	0.00502
$H_{PRM}$	6645.8	6.6458	A	-0.000756	-0.00502
$f_r$	0.999384	0.0002	A	5.021392	0.00100
$c_{CCQM}$	5.0183	0.0087			

Result:

Quantity:  $c_{CCQM}$

Value:  $5.018\mu\text{mol/mol}$

Expanded Uncertainty:  $0.018\mu\text{mol/mol}$  (Relative Expanded  $U=0.36\%$ )

$k=2$ (95% confidence level)

Laboratory name: National Institute of Metrology (Thailand)  
Cylinder number: M555695

### Measurement #1

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	16/06/08	5.008	0.56	3

### Measurement #2

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	17/06/08	4.992	0.44	3

### Measurement #3<sup>22</sup>

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	18/06/08	5.013	0.38	3

### Results

Component	Result ( $\mu\text{mol/mol}$ )	Expanded Uncertainty (% relative)	Coverage factor <sup>23</sup>
CO	5.004	0.73	2

### Details of the measurement method used:

The analysis is performed by using the ND-IR analyzer. The gas flowrate was set at 1.7 L/min.

### Reference Gas Mixture

All measurements used the reference gas mixtures in Table 1. These standards were prepared by designated calibration laboratory, Chemicals Evaluation and Research Institute (CERI), Japan.

<sup>22</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

<sup>23</sup> The coverage factor shall be based on approximately 95% confidence.

Table 1. Concentration of carbon monoxide gas mixture.

Nominal concentration	Cylinder number	Certified concentration	Expanded uncertainty (Relative value, $k = 2$ )
50 $\mu\text{mol/mol}$	CPC-00752	50.38 $\mu\text{mol/mol}$	0.40%
25 $\mu\text{mol/mol}$	CPC-00751	25.12 $\mu\text{mol/mol}$	0.60%
5 $\mu\text{mol/mol}$	CPC-00750	4.958 $\mu\text{mol/mol}$	0.60%

### Instrument Calibration

A zero gas was injected into the ND-IR analyzer before and after the measurement of reference gases and sample gas. The measurement procedure is shown as follow;

“Calibration 1 - Sample CCQM-K51 - Calibration 2 - Sample CCQM-K51 - Calibration 3 - Sample CCQM-K51

Record 3 responses per cylinder.

### **Detailed uncertainty budget:**

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

- This procedure describes the procedure for the estimation of measurement uncertainty of calibration procedure following a 3-point calibration.
- After completely doing the calibration procedure, the following data set can be obtained to calculate the carbon monoxide content and its uncertainty;

(“Reference gas mixture 1 - Reference gas mixture 2 - Reference gas mixture 3 - Sample CCQM-K51 ”)

- Reference gas contents,  $X_1, X_2, X_3$
- Standard uncertainties of the reference gases,  $u(X_1), u(X_2), u(X_3)$
- Average response of reference gases at  $j$  the cycle,  $y_{1,j}, y_{2,j}, y_{3,j}$
- Standard uncertainties of the response of reference gases at  $j$  cycle,  $u(y_{k,j})$
- Average response of sample gas at  $j$  the cycle,  $y_{s,j}$
- Standard uncertainties of the response of sample gas at  $j$  the cycle,  $u(y_{s,j})$
- The measurement response of reference gases,  $Y_k$  (repeated 3 times)

$$Y_k = \sum_{j=1}^3 y_{k,j} / J, \quad J = \text{number of cycles}$$

- The measurement response of sample,  $Y_s$

$$Y_s = \sum_{j=1}^3 y_{s,j} / J, \quad J = \text{number of cycles}$$

- Standard uncertainties of measurement response of reference gases,  $u(Y_k)$
- Standard uncertainties of measurement response of sample,  $u(Y_s)$

**Note:** number of cycles = number of measurement

- The uncertainty of calibration by 3-point calibration is calculated as follow;
  1. The standard uncertainties of the reference gases content,  $u(X_1)$ ,  $u(X_2)$ ,  $u(X_3)$  are associated with reference standards. In the case, the expanded uncertainty ( $U$ ) is given in the certificate,  $U$  must be divided by the coverage factor state in the certificate (usually  $k = 2$ ) as follows;

$$u(X_i) = \frac{U}{2} \tag{1}$$

Where

$U$  = the expanded uncertainty of reference standards

2. The standard uncertainties of the response of reference gases at  $j$  cycle,  $u(y_{k,j})$  are from the repeatability of ND-IR analyzer responds and estimated by equation 2.

$$u(y_{k,j}) = \frac{SD}{\sqrt{n}} \tag{2}$$

where

$SD$  = the standard deviation of measurement results of response of reference standard

$$= \sqrt{\frac{\sum_{i=1}^3 (y_i - \bar{y})^2}{n-1}}$$

3. The standard uncertainties of the response of sample gas at  $j$  the cycle,  $u(y_{s,j})$  are from the repeatability of ND-IR analyzer responds and estimated by equation 3.

$$u(y_{s,j}) = \frac{SD}{\sqrt{n}} \quad (3)$$

where

$SD$  = the standard deviation of measurement results of response of sample gas

$$= \sqrt{\frac{\sum_{i=1}^3 (y_i - \bar{y})^2}{n-1}}$$

4. The standard uncertainty of measurement response of reference gas,  $u(Y_k)$  is evaluated from the following equations;

$$u^2(Y_k) = u^2(Y_k)_{between-cycle} + u^2(Y_k)_{within-cycle} \quad (4)$$

$$u^2(Y_k) = \sum_{j=1}^3 (y_{k,j} - Y_k)^2 / J(J-1) + \sum_{j=1}^3 u(y_{k,j})^2 / J^2 \quad (5)$$

where

$$Y_k = \sum_{j=1}^3 y_{k,j} / J \quad \dots\dots J = \text{number of cycles}$$

5. The standard uncertainty of measurement response of sample gas,  $u(Y_s)$  is evaluated from the following equations;

$$u^2(Y_s) = u^2(Y_s)_{between-cycle} + u^2(Y_s)_{within-cycle} \quad (6)$$

$$u^2(Y_s) = \sum_{j=1}^3 (y_{s,j} - Y_s)^2 / J(J-1) + \sum_{j=1}^3 u(y_{s,j})^2 / J^2 \quad (7)$$

where

$$Y_s = \sum_{j=1}^3 y_{s,j} / J \quad \dots\dots J = \text{number of cycles}$$

6. From the data set of  $X_1, X_2, X_3, Y_1, Y_2, Y_3$  and the parameters with its uncertainty of the analytical function,  $x_s = b_0 + b_1 \cdot Y_s$ , were calculated with ISO6143 implementation software "B\_LEAST version 1.11". After that, the standard uncertainty  $u(x_s)$  of the sample cylinder were calculated as follows.

$$u^2(x_s)_{6143} = \left(\frac{\partial G}{\partial Y_s}\right)^2 u^2(Y_s) + \sum_{j=0}^N \left(\frac{\partial G}{\partial b_{j,k}}\right)^2 u^2(b_{j,k}) + 2 \sum_{j=0}^{N-1} \sum_{l=j+1}^N \left(\frac{\partial G}{\partial b_{j,k}}\right) \left(\frac{\partial G}{\partial b_{l,k}}\right) u(b_{j,k}, b_{l,k}) \quad (8)$$

where

$u(x_s)_{6143}$  = the standard uncertainty of the carbon monoxide content  
 $x_s$ , calculated using  $x_s=G(Y)$

$u(Y_s)$  = the standard uncertainty of the response  $Y_s$

$u^2(b_{j,k})$  = the variance of the parameter  $b_{j,k}$  of the analysis function

$u(b_{j,k}, b_{l,k})$  = the covariance of the parameters  $b_{j,k}, b_{l,k}$  of the analysis function

function

The variances,  $u^2(b_j)$ , and  $u(b_j, b_l)$ , of the parameters of the analysis function are calculated from the calibration data as follows;

$$u^2(b_j) = \sum_{i=1}^n \left[\frac{\partial b_j}{\partial x_i}\right]^2 u^2(x_i) + \sum_{i=1}^n \left[\frac{\partial b_j}{\partial y_i}\right]^2 u^2(y_i) + 2 \sum_{i=1}^{n-1} \sum_{h=i+1}^n \left[\frac{\partial b_j}{\partial x_i}\right] \left[\frac{\partial b_j}{\partial x_h}\right] u(x_i, x_h) \quad (9)$$

$$u(b_j, b_l) = \sum_{i=1}^n \left[\frac{\partial b_j}{\partial x_i}\right] \left[\frac{\partial b_l}{\partial x_i}\right] u^2(x_i) + \sum_{i=1}^n \left[\frac{\partial b_j}{\partial y_i}\right] \left[\frac{\partial b_l}{\partial y_i}\right] u^2(y_i) + \sum_{i=1}^{n-1} \sum_{h=i+1}^n \left[ \left(\frac{\partial b_j}{\partial x_i}\right) \left(\frac{\partial b_l}{\partial x_h}\right) + \left(\frac{\partial b_l}{\partial x_i}\right) \left(\frac{\partial b_j}{\partial x_h}\right) \right] u(x_i, x_h)$$

(10)

where

$u^2(x_i)$  = the variance of the analyte content  $x_i$

$u^2(y_i)$  = the variance of the corresponding response  $y_i$

$u(x_i, x_h)$  = the covariance of the analyte contents  $x_i$  and  $x_h$  of the gas mixture

mixture



Note: In most cases, in both equations (9, 10) the third term can be considered equal to zero.

7. The expanded uncertainty,  $U$ , is given by equation 11, where a coverage factor,  $k$ , is two.

$$(11) \quad U(x_s)_{6143} = k \cdot u(x_s)_{6143} = 2 \cdot u(x_s)_{6143}$$

8. Uncertainty budget.

Uncertainty of calibration following a 3-point calibration when  $x_s = b_0 + b_1 \cdot y$

uncertainty source	Estimate	Standard uncertainty	Sensitivity coefficient	Contribution to standard uncertainty ( $\mu\text{mol/mol}$ )
- response of sample gas	5.1843	0.0059	0.9707	0.0057
- the parameter $b_0$ of the analysis function	-0.0285	0.0223	1.000	0.0223
- the parameter $b_1$ of the analysis function	0.9707	0.0020	5.1843	0.0105
- covariance of the parameters $b_0, b_1$ of the analysis function	-	0.0000	3.220	0.0000
- analytical concentration of sample	5.004			0.0183
Expanded uncertainty ( $k = 2$ )				0.0366

9. Reference:

- [1] ISO 6143, Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures.

Laboratory name: NIST

Cylinder number: D95 8293

### Measurement #1

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	14/04/08	5.012	0.04	3

### Measurement #2

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	15/04/08	5.009	0.04	3

### Measurement #3<sup>24</sup>

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	16/04/08	5.013	0.04	3

### Results

Component	Result ( $\mu\text{mol/mol}$ )	Expanded Uncertainty	Coverage factor <sup>25</sup>
CO	5.011	0.015	2

### Details of the measurement method used:

The CO content of sample D95 8293 was analyzed using a gas chromatograph (NIST # 550285) equipped with a Flame Ionization Detector and a Methanator (GC/Meth/FID). The components were separated using a 1.83 m x 3.2 mm column packed with Molecular Sieve 5A and which was operated isothermally at 140 °C with a carrier gas flow of 30 mL/min. helium. A sample volume of 10 mL was injected onto the head of the column. The FID and methanator were operated at 385 °C. A computer operated gas sampling system (COGAS # 3) was used to deliver the sample stream to the GC/Meth/FID at ~ 30 mL/min. The sample flow was diverted 6 seconds prior to each injection to ensure that the pressure

<sup>24</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

<sup>25</sup> The coverage factor shall be based on approximately 95% confidence.

in the sample loop was at ambient pressure and, therefore, that the sample volume injected was the same from inject to inject.

The GC/FID/Meth was calibrated with six gravimetrically prepared primary gas mixtures [PSM] containing [nominal] from 3 to 7  $\mu\text{mol/mol}$  of CO in a balance of nitrogen. Sample D95 8293 was used as the analytical control to monitor the detector performance. It was rigorously compared to the PSMs a total of nine times [three times each during three analytical periods]. D95 8293 was sampled before and after each sampling of the PSMs. The alternate sampling of D95 8293 during these intercomparisons allowed correction of the CO response for instrument drift throughout the day. A response ratio for each measurement was determined by dividing the CO response measured for each PSM by the drift corrected CO response for D95 8293.

### Detailed uncertainty budget:

All measured certification data and calculations for the CO concentration of D95 8293 have been reviewed for sources of systematic and random errors. The review identified three sources of uncertainty whose importance required quantification as estimated % Relative uncertainties. These uncertainties are:

Uncertainty source $X_i$	Assumed distribution	Standard uncertainty (% Relative) $u(x_i)$	Sensitivity coefficient $C_i$	Gravimetric Standard or Analytical Component
Gravimetric Standards	gaussian	0.04 - 0.19 %	0.42	gravimetric
Bias	rectangular	0.15 %	0.85	gravimetric
Ratio Reproducibility	gaussian	0.11 - 0.19 %	0.30	analytical

The data was reduced using the protocols listed in ISO6143 which pools the data collected from each analytical day yielding both a predicted concentration and uncertainty. The final concentration was calculated by averaging the data from the three analytical days. The final uncertainty result assembles the uncertainties from the three analytical days using the errors in variables regression model of ISO 6143, and an observed bias between the new and old PSMs which was treated as a rectangular uncertainty and added in quadrature.

Laboratory name: VSL  
 Cylinder number: D958365

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	25/03/2008	$5,0162 \cdot 10^{-6}$ mol/mol	0,12	3

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	23/04/2008	$5,0115 \cdot 10^{-6}$ mol/mol	0,07	5

### Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor <sup>26</sup>
CO	$5,014 \cdot 10^{-6}$ mol/mol	$0,025 \cdot 10^{-6}$ mol/mol	2

### Reference Method:

The value(s) assigned to the key comparison mixture were obtained by comparing it for carbon monoxide against NMI VSL's own primary standard gas mixtures (PSMs). The comparison method is conforming ISO 6143 and generalized distance regression (GDR) was used for processing the data. 7 PSMs were used and a cubic calibration model was chosen to fit the data.

### Instrument Calibration:

The following PSMs were used to calibrate the NDIR analyser (ABB URAS 14). All 7 PSMs contained CO in a matrix of nitrogen similar to the sample mixture.

<sup>26</sup> The coverage factor shall be based on approximately 95% confidence.

Cylinder No	Gravimetric composition	standard uncertainty
VSL205201	$0,9998 \cdot 10^{-6}$ mol/mol	$0,0018 \cdot 10^{-6}$ mol/mol
VSL305260	$2,0012 \cdot 10^{-6}$ mol/mol	$0,0018 \cdot 10^{-6}$ mol/mol
VSL205149	$3,9915 \cdot 10^{-6}$ mol/mol	$0,0019 \cdot 10^{-6}$ mol/mol
VSL308613	$5,0013 \cdot 10^{-6}$ mol/mol	$0,0028 \cdot 10^{-6}$ mol/mol
VSL300990	$6,0014 \cdot 10^{-6}$ mol/mol	$0,0022 \cdot 10^{-6}$ mol/mol
VSL308615	$7,9997 \cdot 10^{-6}$ mol/mol	$0,0030 \cdot 10^{-6}$ mol/mol
VSL238362*	$9,9971 \cdot 10^{-6}$ mol/mol	$0,0026 \cdot 10^{-6}$ mol/mol
VSL160344**	$10,018 \cdot 10^{-6}$ mol/mol	$0,0032 \cdot 10^{-6}$ mol/mol

\*cylinder used in measurement #1

\*\*cylinder used in measurement #2

### Sample handling:

Each cylinder was equipped with a stainless steel pressure regulator that was adequately purged.

The flow rate was set at approx. 350 mL/min. Before taking the readings, the measurement cell was flushed for 3 minutes with the mixture to be measured.

### Calibration Standards:

The PSM's used in calibration are prepared from pre-mixtures in accordance with ISO 6142:2001

(Gas analysis - Preparation of calibration gas mixtures - Gravimetric method). After preparation, the composition was verified using the method described in ISO 6143:2001. For nitrogen 6.0 Quality from 3 different suppliers (Linde, Scott, Air Products) was used. The nitrogen was analysed to contain less than  $6 \cdot 10^{-9}$  mol/mol of CO (detection limit of FT-IR) in all cases. The uncertainty associated with the CO determination is taken into account during the gravimetric calculations and associated uncertainty evaluation.

After preparation the standards were verified by analytical comparisons against existing gravimetrically prepared standards. Only when no significant difference between the analysed and the calculated gravimetric composition is found, the "new prepared candidate" is accepted as a PSM. The calibration mixtures were prepared between 2002 and 2006.

### Evaluation of measurement uncertainty

The listed gravimetric uncertainty is a combined standard uncertainty and comes from:

- The uncertainty associated with the weighing (pooled estimate of 3 mg on minimum 20 g)
- The effect on the buoyancy correction due to cylinder expansion when pressurizing to 120 bar (approx. 20 mg on 600 g)
- The uncertainty associated with the purity analysis
- The uncertainty associated with the molar masses

The listed standard deviations in the two reported measurement cycles are actually the standard uncertainties from the GDR, duly propagating the gravimetric uncertainties on the PSMs and the standard deviation in the responses.

Both uncertainties can be combined in quadrature

Standard uncertainty measurements:  $\sqrt{(0,12^2 + 0,07^2)} = 0,14\%$  rel.

Standard uncertainty in gravimetry: 0,18% rel.

Combined: 0.23 % rel.

Expanded: 0.5 % rel. (k=2)

Laboratory name: National Physical Laboratory, India, (NPL-I)

Cylinder number: D95 8294

### Measurement #1

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	3/8/08	5.187	0.289	3

### Measurement #2

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	3/8/08	5.187	0.403	3

### Measurement #3<sup>27</sup>

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
CO	4/8/08	5.203	0.294	3

### Results

Component	Result ( $\mu\text{mol/mol}$ )	Expanded Uncertainty	Coverage factor <sup>28</sup>
CO	5.195	0.150	2

### Details of the measurement method used:

#### Reference Method:

Agilent GC model 6890N with FID and methanizer were used for analysis of the mixture. GSV valve C was used with 2 ml sample loop. The sample was passed through loop during analysis. The GC column was Molecular Sieve 13x, 10" with helium as carrier gas at the flow 30ml/min. GC conditions kept for the analysis were; Oven temperature 80°C, Injector temperature 150°C, -Methanizer at 350°C and FID Detector temperature 250 °C.

#### Calibration Standard:

The calibration of the GC was done with the Primary Standard Gas Mixture of CO in Nitrogen prepared gravimetrically at NPLI having concentration 5.25  $\mu\text{mole/mole}$ .

### Detailed uncertainty budget:

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

#### Expanded Uncertainty Estimation:

<sup>27</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

<sup>28</sup> The coverage factor shall be based on approximately 95% confidence.

(A). Uncertainty in Primary Standard Gas Mixture of CO prepared at NPLI (Type B)

CO concentration =  $5.252 \mu\text{mol/mol} \pm 0.964$

Relative Standard Uncertainty (RSU) of PSM = 0.009

(B). Uncertainty of GC (Type A)

The Primary Standard Gas Mixture of CO prepared gravimetrically at NPLI had been used to evaluate GC instrument uncertainty i.e. Relative Standard Uncertainty (RSU) of GC due to repeatability = 0.011

(C). Uncertainty related to CCQM K-51 Inter comparison sample (Type A)

i.e. RSU = 0.0006

(D) Sum of % Relative Standard Uncertainty =  $(A^2+B^2+C^2)^{0.5}$

(E) Standard Uncertainty =  $C_{\text{mix}} * (A^2+B^2+C^2)^{0.5} = 0.075$

Expanded Uncertainty = (E) x 2 = 0.150 [with coverage factor 2]



Laboratory name: Umweltbundesamt GmbH, Spittelauer Laende 5, 1090 Vienna, Austria

Cylinder number: D958320

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	23/04/08	4,959E-6 mol/mol	0,2%	5

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	24/04/08	4,959E-6 mol/mol	0,2%	5

### Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	14/05/08	4,958E-6 mol/mol	0,2%	5

### Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	14/05/08	4,973E-6 mol/mol	0,2%	5

### Measurement #5

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	20/05/08	4,950E-6 mol/mol	0,2 %	5

### Measurement #6

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	19/06/08	4,959E-6 mol/mol	0,2 %	5

## Measurement #7

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	25/06/08	4,963E-6 mol/mol	0,2 %	5

## Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor <sup>29</sup>
CO	4,96E-6 mol/mol	0,055E-6 mol/mol	2,0

## Details of the measurement method used:

### Detailed uncertainty budget:

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

Instrument: Horiba APMA 360CE, SN: 8907040114

Calibrated at -5 ppm by dilution system: PLPGG Horiba HA 0214, dilution ratio measured by molblocks

Primary Reference Material used: NMI v.S.L. 250,0 ppm CO ± 0,5 ppm, S.Nr.: D523440, valid trough 13.9.2009

Molblock (A) 3322 (up to 100ml), Certificate: ± 0,2%  
Molblock (B) 3283 (up to 5000ml), Certificate: ± 0,2%

Dilution Ratio: 76 ml/3720 ml, nominal concentration for Calibration of instrument: 5,01E-6 mol/mol.

Uncertainty budget:  
all distribution are regarded as normal distributions

Uncertainty source	value	standard uncertainty	sensitivity coefficient	contribution to uncertainty <i>u</i>
Primary reference material	250 ppm	0,250 ppm	2,00E-2	5,01E-3
Reproducibility instrument, calibration		0,015 ppm	-	1,500E-2
Molblock (A)	76 ml	0,01 ml	6,586E-2	6,6E-4

<sup>29</sup> The coverage factor shall be based on approximately 95% confidence.

Certificate of Molblock (A)	0,20% rel.	0,20 ml	6,586E-2	1,317E-2
Molblock (B)	3720 ml	2,0 ml	1,32E-3	2,64E-3
Certificate of Molblock (B)	0,20% rel.	7,5 ml	1,32E-3	9,89E-3
Reproducibility instrument, measurement		0,015 ppm	-	1,500E-2
Combined standard uncertainty				0,028 ppm

Laboratory name: Finnish Meteorological Institute, Finland

Cylinder number: M555706

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	02/07/2008	$5.02 \cdot 10^{-6}$	0.14 %	10

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	02/07/2008	$5.02 \cdot 10^{-6}$	0.14 %	10

### Measurement #3<sup>30</sup>

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	02/07/2008	$5.02 \cdot 10^{-6}$	0.16 %	10

### Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor <sup>31</sup>
CO	$5.02 \cdot 10^{-6}$	$\pm 1.1 \%$	k = 2

<sup>30</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

<sup>31</sup> The coverage factor shall be based on approximately 95% confidence.

## Details of the measurement method used:

The equipments used for the analysis of the CCQM-K51 gas cylinder:

- Horiba APMA-370 s/n A60V
- Dynamic dilution device for testing the linearity of the analyser: Sonimix 6000A1, LN-Industries, Switzerland. Gas standard for dilution: NPL 1204,  $1998 \pm 10$   $\mu\text{mol/mol}$  in nitrogen. Dilution and zero gas: Nitrogen (Linde 6.0).
- Calibration of the analyser by a gas standard from NMI ( $5.00 \pm 0.05$   $\mu\text{mol/mol}$  in nitrogen).
- Zero by nitrogen ( $\text{N}_2$ ) 6.0
- Measurements were conducted according to the sequence:
  - Linearity check of the analyser (range 0 - 6  $\mu\text{mol/mol}$ )
  - Measurement #1: Calibration - zero - measurement of CCQM-K51 sample - zero.
  - Measurement #2: Calibration - zero - measurement of CCQM-K51 sample - zero
  - Measurement #3: Calibration - zero - measurement of CCQM-K51 sample - zero
  - Linearity check of the analyser (range 0 - 6  $\mu\text{mol/mol}$ )

A 20 min time was allowed for the analyser for each of the measurements to reach the stable reading. The last 10 data points were used to calculate the mean and the standard deviation of the results. The recording of the results was ( $\text{min}^{-1}$ ).

## Detailed uncertainty budget:

The uncertainty budget for the measurements is built by including the following uncertainty components (ISO):

Type A:

- linearity of the analyzer:  $u_{\text{lin}} = \text{largest residual from the regression equation}/\sqrt{3}$   
 $= 0.0125/\sqrt{3}$   $\mu\text{mol/mol} = 0.007$   $\mu\text{mol/mol}$ , rectangular distribution :
- repeatability of the analyzer;
  - $u_{\text{rep, z}} = s_{r,z}/m^{1/2} = 0,005/(16.2)^{1/2} = 0.001$   $\mu\text{mol/mol}$  (EN 14626)
  - $u_{\text{rep, s}} = s_{r,s}/m^{1/2} = 0,01/(16.2)^{1/2} = 0.002$   $\mu\text{mol/mol}$  (EN 14626)

where

$$m = \left( \frac{t}{(t_r + t_f)/2} \right) = \left( \frac{600}{(36_r + 38_f)/2} \right) = 16.2$$

$s_{r,z}$  = standard deviation at zero

$s_{r,s}$  = standard deviation at 5  $\mu\text{mol/mol}$

$t_r$  and  $t_f$  are the rise and fall time of the analyser

$t$  = the time for average calculation (=10 min = 600 s)

**Type B:**

- uncertainty of the gas standard:  $u_{\text{cal}} = 0,5 \% = 0.025 \mu\text{mol/mol}$  (NMI 3220818)
- uncertainty of the data acquisition system:  $u_{\text{dat}} = 0,005 \mu\text{mol/mol}$
- uncertainty of the impurity of nitrogen gas:  $u_{\text{imp}} = 0,005 \mu\text{mol/mol}$

**Combined standard uncertainty:**

$$- u_{\text{comb}} = [u_{\text{lin}}^2 + u_{\text{rep,z}}^2 + u_{\text{rep,s}}^2 + u_{\text{cal}}^2 + u_{\text{dat}}^2 + u_{\text{imp}}^2]^{1/2} = 0.027 \mu\text{mol/mol}$$

**Expanded uncertainty:**

$$U = 2 \times u_{\text{comb}} = 0.054 \mu\text{mol/mol}$$

**Relative expanded uncertainty:**

$$U(\%) = \frac{0.054 \mu\text{mol/mol}}{5.02 \mu\text{mol/mol}} = 1.1 \%$$

**Reference:**

EN 14626 Ambient air quality. Standard method for the measurement of the concentration of carbon monoxide by nondispersive infrared spectroscopy

ISO. Guide to the expression of uncertainty in measurements (GUM). International Organization for Standardization, ISO, 1995.pp 101

Laboratory name: NMIA

Cylinder number: M555726

### Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	12/06/2008	$5.0092 \times 10^{-6}$	0.14	8

### Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	18/06/2008	$4.9971 \times 10^{-6}$	0.14	8

### Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	23/06/2008	$5.0160 \times 10^{-6}$	0.14	8

### Measurement #4

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
CO	24/06/2008	$5.0084 \times 10^{-6}$	0.14	8

### Results

Component	Result (mol/mol)	Expanded Uncertainty (mol/mol)	Coverage factor <sup>32</sup>
CO	$5.008 \times 10^{-6}$	$0.026 \times 10^{-6}$	2

<sup>32</sup> The coverage factor shall be based on approximately 95% confidence.

## Details of the measurement method used:

Analysis was performed by FTIR.

Instrument: Thermo Nicolet 6700 FTIR spectrometer with 10m gas cell, with 0.25cm<sup>-1</sup> resolution over the 2000-2400cm<sup>-1</sup> region. Absorbance peaks in the region 2150-2190 cm<sup>-1</sup> were used for quantification.

## Detailed uncertainty budget:

Five calibration standards were used in this study for the determination of the carbon monoxide concentration. The concentrations of the carbon monoxide in the calibration standards closely matched the expected concentration of carbon monoxide in the sample cylinder.

The calibration standards were prepared gravimetrically in the NMIA laboratory from pure carbon monoxide and nitrogen, in accordance with ISO6142:2001.

### Calibration standard 1: MK0821

Component	Assigned value (x)	Expanded uncertainty
Carbon monoxide	5.004 µmol/mol	0.011 µmol/mol

### Calibration standard 2: MK0815

Component	Assigned value (x)	Expanded uncertainty
Carbon monoxide	4.996 µmol/mol	0.011 µmol/mol

### Calibration standard 3: MK0816

Component	Assigned value (x)	Expanded uncertainty
Carbon monoxide	4.983 µmol/mol	0.011 µmol/mol

### Calibration standard 4: MK0813

Component	Assigned value (x)	Expanded uncertainty
Carbon monoxide	5.282 µmol/mol	0.011 µmol/mol

### Calibration standard 5: MK0814

Component	Assigned value (x)	Expanded uncertainty
Carbon monoxide	4.6919 µmol/mol	0.011 µmol/mol

The uncertainty budget for the analysis of the CO sample from NMISA includes contributions from the instrumental analysis and the uncertainty of the composition of the gas standards.



Uncertainty contribution	Standard uncertainty	Sensitivity coefficient	Units	Contribution
Concentration of standards	0.0055	1	µmol/mol	25 %
Instrument uncertainty	0.0098	1	µmol/mol	44 %
Reproducibility of measurement	0.0070	1	µmol/mol	31 %
<b>Combined standard uncertainty: 0.013 µmol/mol</b>				