International Comparison CCQM-K76: Sulfur Dioxide in Nitrogen

Franklin R. Guenther[1], Michael E. Kelley[1], Gerald D. Mitchell[1], Manuel de Jesús Avila Salas[2], Jorge Koelliker Delgado[2], Francisco Rangel Murillo[2], Victor M. Serrano Caballero[2], Alejandro Pérez Castorena[2], Uehara Shinji[3], Dariusz Ciecior[4], Valnei Smarçaro da Cunha[5], Cristiane Rodrigues Augusto[5], Claudia Cipriano Ribeiro[5], Andreia de Lima Fioravante[5], Florbela Dias[6], Oh Sang-Hyub[7], Tatiana Macé [8], Christophe Sutour[8], Tamás Büki[9], Han Qiao[10], Angelique Botha[11], David M. Mogale[11], James Tshilongo[11], Napo Ntsasa[11], Tshepiso Mphamo[11], Ian Uprichard[12], Martin Milton[12], Gergely Vargha[12], Chris Brookes[12], Prabha Johri[13], Ing. Miroslava Valkova[14], Leonid Konopelko[15], Yury Kustikov[15], V.V. Pankratov[15], D.V. Rumyantsev[15], M.V. Pavlov[15], E.V. Gromova[15],Adriaan van der Veen[16], Peter van Otterloo[16], Rob. M. Wessel[16]

[1] National Institute of Standards and Technology (NIST), 100 Bureau Drive, Gaithersburg, MD 20899-8393, USA
[2] Centro Nacional De Metrologíe (CENAM), km 4.5 carretera a Los Cués , Municipio El Marqués, Querétaro CP, 76246 México. Apdo. Postal 1-100 Centro
[3] Chemicals Evaluation and Research Institute (CERI), Japan, 1600 Shimotakano,Sugito-machi, Kitakatsushika-gun,Saitama, 345-0043, Japan.
[4] Central Office of Measures (Glowny Urzad Miar, GUM), Elektorlna 200-139 Warsaw Poland
[5] Instituto Nacional de Metrologia, Normalização e Qualidade Industrial INMETRO
[6] Instituto Português da Qualidade (IPQ), Rua António Gião, 2, 2829-513 Caparica, Portugal
[7] Korea Research Institute of Standards and Science (KRISS),1 Doryong-Dong, Yuseong-Gu, Daejeon 305-340, Korea
[8] Laboratoire National de métrologie et d'Essais (LNE), 1, rue Gaston Boissier, 75 724 Paris Cedex 15
[9] Hungarian Trade Licensing Office (MKEH), H-1124 Budapest, Németvölgyi út 37-39, Hungary
[10] National Institute of Metrology (NIM), China, No.18, Bei-San-Huan Dong Str., Beijing 100013, China.
[11] National Metrology Institute of South Africa (NMISA), CSIR, Building 4 West, Meiring Naude Road Brummeria, 0184, Pretoria, South Africa
[12] National Physical Laboratory (NPL), Module 8 - L10, Hampton Road, Teddington, Middlesex United Kingdom TW11 0LW
[13] National Physical Laboratory India (NPLI), Dr. K.S. Krishnan Road, New Delhi-110012, India
[14] Slovak Institute of Metrology (SMU), Karloveská 63, SK-842 55 Bratislava, Slovak Republic
[15] D.I.Mendeleyev Institute for Metrology (VNIIM), 19 Moskovsky pr., St. Petersburg, 190005 Russia
[16] VSL, Thijsseweg 11 2629 JA Delft The Netherlands

Coordinating Laboratory: National Institute of Standards and Technology (NIST)

Study Coordinators: Michael E. Kelley and Franklin R. Guenther

Field: Amount of Substance

Subject: Sulfur Dioxide in Nitrogen at 100 µmol/mol.

Organizing Body: CCQM

Schedule of comparison:

1) Preparation of cylinders: July 2009
2) Initial verification study: October 2009
3) Cylinders shipped to participants: December 2009
4) Results received from the participants: May through August 2010
5) Cylinders received: May through September 2010
6) Final verification study: October 2010

Introduction

This Key Comparison is designed to test the capabilities of the participants to measure and certify sulfur dioxide in nitrogen, and will provide supporting evidence for the CMCs of institutes for sulfur dioxide. Also, as sulfur dioxide is designated a core compound, and the 100 µmol/mol concentration is within the designated core compound concentration range, this comparison is also designed to demonstrate core capabilities of institutes which qualify under the rules of the Gas Analysis Working Group.

Supported Claims

This Key Comparison provides evidence in support of CMCs for sulfur dioxide in the range of 50 µmol/mol to 1 % mol/mol, in a balance of nitrogen or air. In addition this comparison provides evidence in support of CMC claims extending to all core compounds and concentrations as defined by the Gas Analysis Working Group (GAWG). Institutes which may claim core competences under the rules of the GAWG may use the results of this comparison to support core competency claims.

In order to justify CMCs at amount fractions lower than 50 µmol/mol using this comparison as supporting evidence, it will be necessary for the NMI to provide evidence that they have sufficient capability to analyze the level of impurity of the minor component in the balance gas at less than half their stated uncertainty claim. They must also have analytical methods with sufficient stability and reproducibility to measure changes in concentration of less than their uncertainty over time. In addition, to justify CMCs for CRMs at lower amount fractions it will be necessary to provide evidence of stability trials on cylinders. This comparison shall not be used as evidence for claims below 1 µmol/mol.

Participants

Table 1: List of Participating Laboratories

Acronym	Country	Institute
CENAM	MX	Centro Nacional De Metrologíe
CERI	JP	Chemicals Evaluation and Research Institute
GUM	PL	Central Office of Measures (Glowny Urzad Miar)
INMETRO	BR	National Institute of Metrology, Standardization and Industrial Quality
IPQ	PT	Instituto Português da Qualidade
KRISS	KR	Korea Research Institute of Standards and Science
LNE	FR	Laboratoire National de métrologie et d'Essais
MKEH	HU	Hungarian Trade Licensing Office
NIM	CN	National Institute of Metrology
NIST	US	National Institute of Standards and Technology
NMISA	ZA	National Metrology Institute of South Africa
NPL	GB	National Physical Laboratory
NPLI	IN	National Physical Laboratory India
SMU	SK	Slovak Institute of Metrology
VNIIM	RU	D.I.Mendeleyev Institute for Metrology
VSL	NL	VSL

Preparation of Parent mix cylinder

One aluminum compressed gas cylinder (Cylinder # CC63757) with an internal volume of approximately 30 L was prepared to serve as the parent mixture containing nominal 1500 µmol/mol sulfur dioxide in nitrogen. It was filled in a manner that meets or exceeds the guidelines outlined in ISO 6142.

This candidate parent cylinder was connected to a fill manifold along with premix Cylinder # ALM024297 (2.07124 ± 0.00050% mol/mol SO_2/N_2) and two cylinders of ultra-pure Nitrogen. The contents of the cylinder were vented, purged (138 kPa of ultra-pure Nitrogen) and evacuated a minimum of four times to less than 1.3 Pa. The final evacuation reduced the cylinder pressure to approximately 0.2 Pa. The cylinder was then placed near the double pan balance overnight to allow for the temperature of the cylinder to equilibrate to room temperature. The balance has a capacity of 50.0 kg and a resolution of 0.001 g. The reproducibility is typically ± 0.002 g.

Three replicate measurements of the mass of the evacuated cylinder were made. Each measurement was bracketed by a mass measurement of the control cylinder and a zero mass reading. The evacuated cylinder was then reattached to the manifold and the manifold was purged, vented and evacuated at least four times with ultra-pure Nitrogen and then with the SO_2/N_2 parent mix. The candidate parent cylinder was pressurized to 0.9 kPa with its (2.07124 ± 0.00050) % mol/mol SO_2 premix. It was then allowed to equilibrate for one hour to achieve room temperature. The manifold was then repressurized with the parent mix and the candidate parent cylinder was adjusted to the final fill pressure. The cylinder valve was closed and the cylinder was again placed near the double pan balance overnight to equilibrate the cylinder temperature before weighing. The cylinder was then weighed as before. The cylinder was reattached to the manifold and the manifold was purged, vented and evacuated at least four times with ultra-pure Nitrogen. The candidate cylinder was filled to 12.5 MPa utilizing two cylinders of ultra-pure Nitrogen.

The candidate parent cylinder was allowed to rest for three hours after ultra-pure Nitrogen addition to achieve temperature equilibration with the room. The manifold was then repressurized with ultra-pure Nitrogen and the cylinder was adjusted to the final fill pressure of 12.5 MPa. After filling, the cylinder valve was closed and the cylinder was again placed near the double pan balance overnight to equilibrate the cylinder temperature before weighing. The cylinder was then weighed as before. When weighing was completed, the contents of the cylinder were mixed by rolling for 4 hours on a cylinder roller. The concentration was then calculated from the masses of the added gases and the measured purity of the gases.

Preparation of comparison cylinders

Thirty aluminum compressed gas cylinders with internal volumes of approximately 6 L were purchased from a specialty gas company. and were used to prepare the sample mixtures. They were filled in a manner that meets or exceeds the guidelines outlined in ISO 6142.

The cylinders were connected in groups of five to a five-station fill manifold along with the 1500 µmol/mol parent mix (Cylinder # CC63757) and a cylinder of ultra-pure Nitrogen. The cylinders had been filled by the cylinder provider to 13.8 MPa with a mixture of 100 µmol/mol sulfur dioxide in nitrogen to passivate the cylinder wall. The contents of the five candidate cylinders were vented, purged (138 kPa of ultra-pure Nitrogen) and evacuated a minimum of four times to less than 1.3 Pa. The final evacuation reduced the cylinder pressure to approximately 0.2 Pa. The five cylinders were then placed near the single pan balance overnight to allow for the temperature of the cylinders to equilibrate to room temperature. The single pan balance has a capacity of 10.0 kg and a resolution of 0.01 g. The reproducibility is typically ± 0.02 g.

Four replicate measurements of the mass of each evacuated cylinder were made. Each measurement was bracketed by a mass measurement of the control cylinder and a zero mass reading. The evacuated cylinders were then reattached to the manifold and the manifold was purged, vented and evacuated at least four times with ultra-pure Nitrogen and then with the SO_2/N_2 parent mix. The five candidate cylinders were simultaneously opened and filled with SO_2 parent mix to a predetermined pressure. They were then allowed to equilibrate for one hour to achieve room temperature. The manifold was then repressurized with the parent mix and the cylinders were adjusted to the final fill pressure. The cylinder valves were closed and the cylinders were again placed near the balance overnight to equilibrate the cylinder temperature before weighing. Each cylinder in the group was then weighed as before. The cylinders were then reattached to the manifold and the manifold was purged, vented and evacuated at least four times with ultra-pure Nitrogen. Each candidate cylinder was consecutively opened and filled with ultra-pure Nitrogen to the final predetermined topping pressure. Each group of five candidate samples utilized two cylinders of ultra-pure Nitrogen to fill them to 12.5 MPa.

The candidate cylinders were allowed to rest for three hours after ultra-pure Nitrogen addition to achieve temperature equilibration with the room. The manifold was then repressurized with ultra-pure Nitrogen and each cylinder was adjusted to the final fill pressure of 12.5 MPa. After filling, the cylinder valve was closed and the cylinders were again placed near the balance overnight to equilibrate the cylinder temperature before weighing. The cylinders were then weighed as before. When weighing was completed, the contents of the cylinders were mixed by rolling for 2 hours on a cylinder roller. The concentrations were then calculated from the masses of the added gases.

Verification of Parent Cylinder

The SO_2 content of the parent cylinder was verified using a pulsed fluorescence process analyzer (NIST # 572044). Sample selection was achieved using Computer Operated Gas Analysis System (COGAS # 7). Sample flow of 1 liter/minute was controlled by a mass flow controller.

The parent gas cylinder, CC63757, served as the control cylinder. Fifteen ratios of each of five PSMs to the control cylinder were obtained over a three-day period giving a total of seventy five data points:

PSM cylinder # FF18162	(1725.1 ± 1.3) µmol/mol SO_2/N_2
PSM cylinder # CAL365	(1615.0 ± 1.3) µmol/mol SO_2/N_2
PSM cylinder # FF38016	(1517.8 ± 1.0) µmol/mol SO_2/N_2
PSM cylinder # FF19629	(1402.7 ± 1.0) µmol/mol SO_2/N_2
PSM cylinder # FF16954	(1307.68 ± 0.62) µmol/mol SO_2/N_2

An ISO 6143 data analysis procedure was used to evaluate the data. A linear calibration function was found to give excellent results, the predicted line crossing all calibration points within the assigned uncertainty. The predicted value of cylinder CC63757 using five NIST PSMs was (1546.76 ± 1.54) µmol/mol sulfur dioxide. The gravimetric value assignment was (1546.63 ± 0.54) µmol/mol sulfur dioxide. The parent cylinder passed this verification step.

Verification of Candidate Comparison Cylinders

The SO_2 content of each comparison cylinder was verified prior to shipment to the participants using a pulsed fluorescence process analyzer (NIST # 572044). Sample selection was achieved using Computer Operated Gas Analysis System (COGAS # 7). Sample flow of 1 liter/minute was controlled by a mass flow controller. LS 95-JL-03 served as the control cylinder. Eight ratios of each comparison cylinder to the control cylinder were obtained over a two-day period. The pulsed fluorescence detector response was 1st order and gave excellent results. The ISO 6143 data analysis procedure was used to evaluate the data. The control cylinder contained a gravimetric value assignment of (98.123 ± 0.008) µmol/mol SO_2. The highly collinear response curve demonstrates that the preparation of the gravimetric suite was quite accurate. All comparison cylinder gravimetric values were well within the analytical uncertainty of our measurements. The comparison cylinders passed the verification step and were sent to the participants.

Verification of Returned Comparison Cylinders

The participants we asked to return the comparison cylinders to NIST after their analyses were completed. All participants except for NPLI returned their cylinder, and these cylinders were reanalyzed in September and October of 2010. A control cylinder was analyzed along with the returned cylinders according to normal NIST procedures. The control cylinder was then reanalyzed against sulfur dioxide gravimetrically prepared gas standards. The data are presented in Figure 1. No visible trend in the data is apparent, the average of the data indicated a -0.015 µmol/mol bias which was well within the analytical uncertainty of 0.27 µmol/mol. The difference between the NIST gravimetric value and the NIST verification data completed in October of 2010 was added into the overall uncertainty by assuming a rectangular distribution and dividing the difference by the square root of 3.

Cylinder SG080114A, which was sent to NPLI was never returned to NIST, as the cylinder was deemed to hazardous to travel by air freight. It is assumed in this report that this cylinder's stability is in line with the rest of the cylinder population.

After preliminary results were displayed at the CCQM Gas Analysis Working Group meeting in November of 2010, IPQ asked that NIST complete another analysis of their cylinder as the verification demonstrated a possible bias in the positive direction. NIST repeated the verification of this cylinder and obtained a value of 100.31 µmol/mol, which agrees with the previous verification values.

Key Comparison Reference Value

All of the comparison cylinders passed the verification performed in October of 2010 after return from the participants. Therefore, the NIST gravimetrically calculated value and uncertianty is used within this report as the Key Comparison Reference Value (KCRV).

Participant Results

The participants reports are appended to this report. The reported intrumental method and calibration standards used are summarized in Table 1. Four participants reported using primary standards obtained from another NMI (VSL and NMIJ). All other participants reported using primarys standards prepared at their facility from pure sulfur dioxide. A total of eight participants used a pulsed fluorescence instrument, one used a UV absorption, and the remaining seven participants used NDIR. There was no correlation between the degrees of equivalence and the method used, or the source of the primary standards. The analytical results reported by each participant is listed in Table 2, and presented in graphical form in Figure 2.

Table 3 presents the results in tabular form. The gravimetric value and uncertainty was calculated according to ISO 6142 and is the KCRV. The verification results were otained from the analyses conducted on the returned cylinders in October of 2010. The verification uncertainty is a combination of the analytical uncertainty and the primary standard suite uncertainty calculated according to ISO 6143. An additional uncertainty component was included in the verification uncertainty, calculated from the diference between the gravimetric value and the verification value. This uncertainty was considered to have a rectangular distribution. The difference was divided by the square root of 3 and added in quadrature to the verification uncertainty.

Finally, the degrees of equivalence are calculated in the prescribed manner, and presented for each participant in Table 3. The degrees of equivalence are displayed graphically in Figure 3. Finally, results of this comparison are presented inTables 4 and 5, formatted for submission to the Key Comparison Database.

Conclusion

The results of all participants in this key comparison, except for three, are consistent with their KCRV. The three participants which are outside the KCRV interval are NIM, SMU, and NPLI. This compariosn may be used to demonstrate core analytical capabilities in accordance with the rules and procedures of the CCQM Gas Analysis Working group.

Figure 1: Verification of comparison cylinders in September 2009 and October 2010.

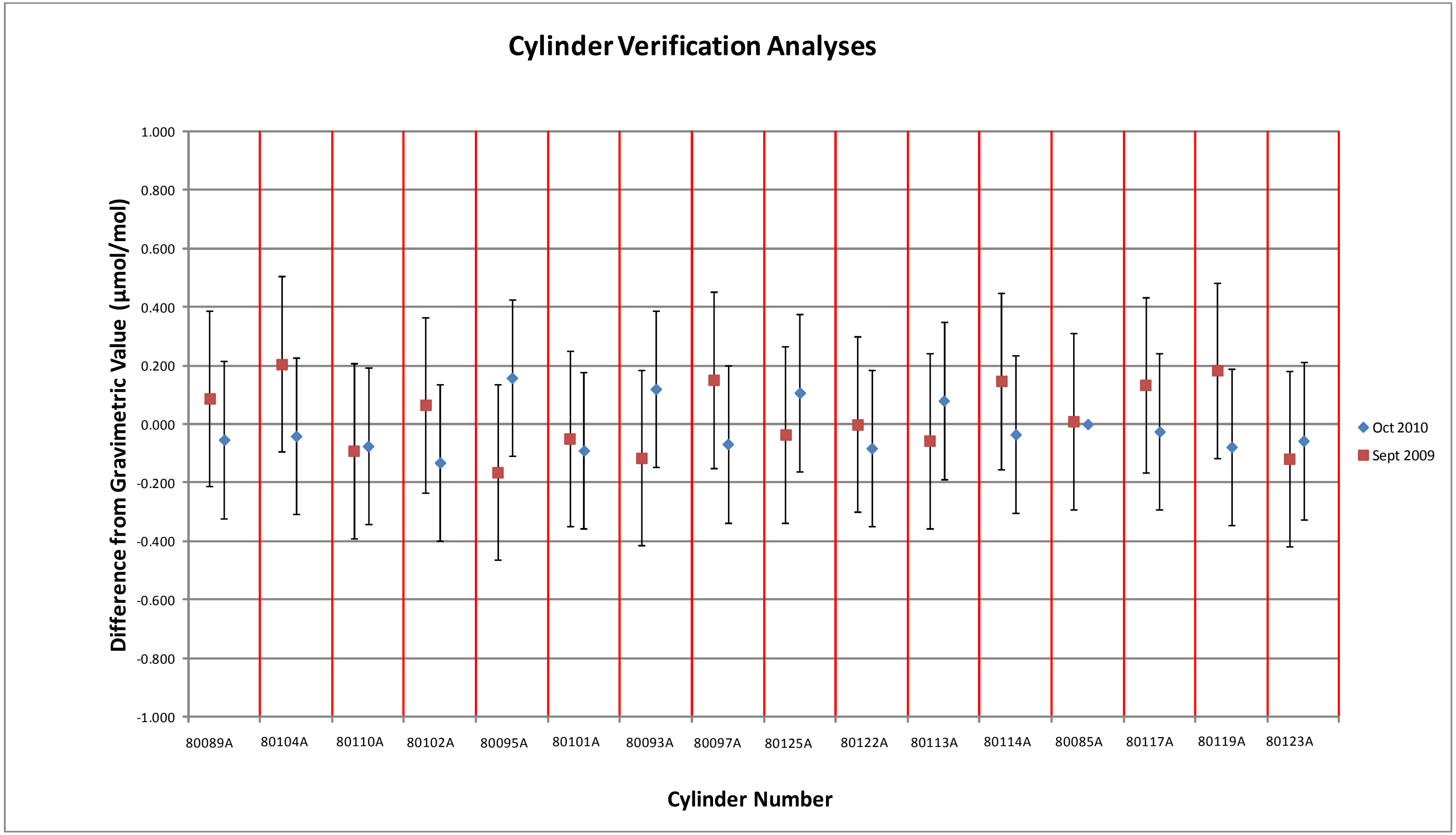


Table 1: Methods used by participating laboratories

Participant	Standards	Instrumentation	Measurements
CENAM	4 Primary Gas Standards prepared ISO 6142, measurement protocol ISO 6143	Pulsed Fluorescence, Thermo Environmental Instruments Model 43C	3 Measurements each with 3 submeasurements
CERI	4 Primary Gas Standards, NMIJ provided pure SO2.	NDIR, Shimadzu URA-107	4 Measurements, each with 3 submeasurements
GUM	7 Gas Standards, 4 certified by VSL, 3 from a producer, measurement protocol ISO 6143	Pulsed Fluorescence, Thermo Environmental Instruments Model 43C	3 Measurements each with 10 submeasurements
INMETRO	5 Gas Standards provided by VSL via ISO 6142, measurement protocol ISO 6143	Infrared Analyzer Horiba VIA-510	6 Measurements each with 8 submeasurements
IPQ	4 Gas Standards provided by VSL via ISO 6142, measurement protocol ISO 6143	NDIR URAS 14	3 Measurements each with 3 submeasurements
KRISS	4 Primary Gas Standards	NDIR Siemens Ultramat 6	3 Measurements each with 4 to 6 submeasurements
LNE	Dynamic dilution using permeation at 350 nmol/mol in air. Comparison Cylinder diluted to 350 nmol/mol with air.	Pulsed Fluorescence, Thermo Environmental Instruments 43-CTL	3 Measurements each with 3 submeasurements
MKEH	4 Primary Gas Standards	NDIR Maihak AG S-715	4 Measurements, each with 3 to 6 submeasurements
NIM	4 Primary Gas Standards prepare ISO 6142, single point calibration (A-B-A-B-A sampling protocol)	Pulsed Fluorescence, Thermo Environmental Instruments Model 43C	6 Measurements each with 4 to 7 submeasurements
NIST	5 Primary Gas Standards, measurement protocol ISO 6143	Pulsed Fluorescence, Thermo Environmental Instruments Model 40B	4 Measurements, each with 4 submeasurements
NMISA	6 Primary Gas Standards prepared ISO 6142, measurement protocol ISO 6143	Fischer-Rosemount NGA 2000 UV Fluorescence	3 Measurements each with 3 submeasurements
NPL	2 Primary Gas Standards, measurement protocol direct comparison	NDIR Horiba VIA-510	8 measurements against each primary standard (2)
NPLI	1 Primary Gas Standard (8.15 µmol/mol), single point calibration	Fluorescent Analyzer, Teledyne 100A	4 Measurements, each with 4 submeasurements
SMU	8 Primary Gas Standards prepared ISO 6142, measurement protocol ISO 6143	Pulsed Fluorescence, Thermo Environmental Instruments Model 43C	3 Measurements each with 20 submeasurements
VNIIM	3 Primary Gas Standards prepared ISO 6142, measurement protocol ISO 6143	UV adsorption, Perkin Elmer Lambda 900	4 Measurements each with4 submeasurements
VSL	11 Primary Gas Standards prepared ISO 6142, measurement protocol ISO 6143	NDIR, ABB URAS-14	3 Measurements each with 3 submeasurements

Table 2: Values reported by participating laboratories

Participant	Comparison cylinder	Reported Value (µmol/mol)	Reported Uncertainty (µmol/mol)
CENAM	SG080089A	**100.26**	0.63
CERI	SG080104A	**100.12**	0.6
GUM	SG080110A	**99.9**	1
INMETRO	SG080102A	**100.3**	0.4
IPQ	SG080095A	**101.02**	0.77
KRISS	SG080101A	**99.97**	0.5
LNE	SG080093A	**99.74**	0.94
MKEH	SG080097A	**100.29**	0.98
NIM	SG080125A	**99.44**	0.51
NIST	SG080122A	**100.40**	0.24
NMISA	SG080113A	**100.48**	0.56
NPL	SG080114A	**100.13**	0.2
NPLI	SG080085A	**102.95**	0.8
SMU	SG080117A	**102.19**	1.02
VNIIM	SG080119A	**100.38**	0.66
VSL	SG080123A	**100.06**	0.12

Figure 2: Results submitted by participants, k=1.

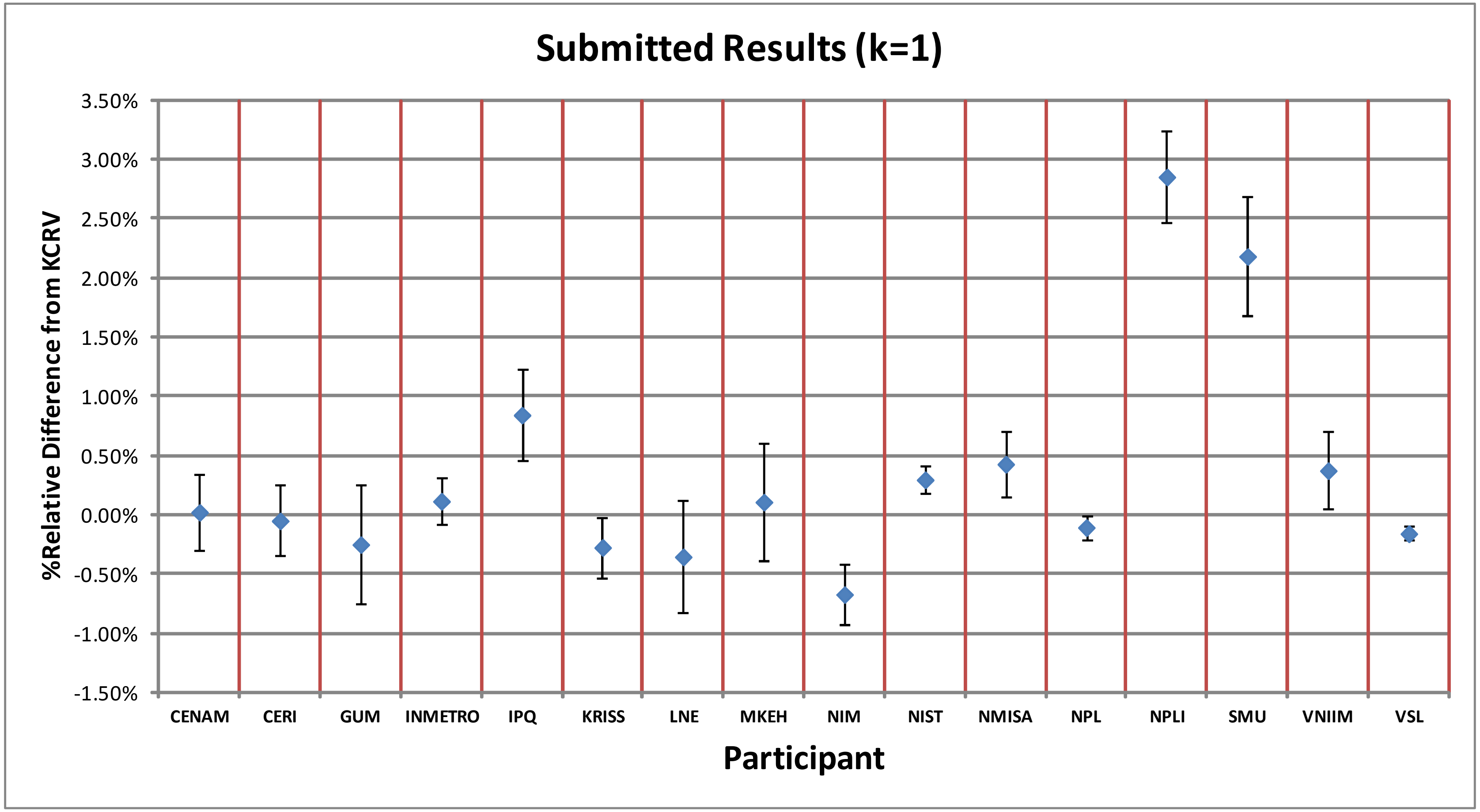


Figure 3: Calculated Degrees of Equivalence

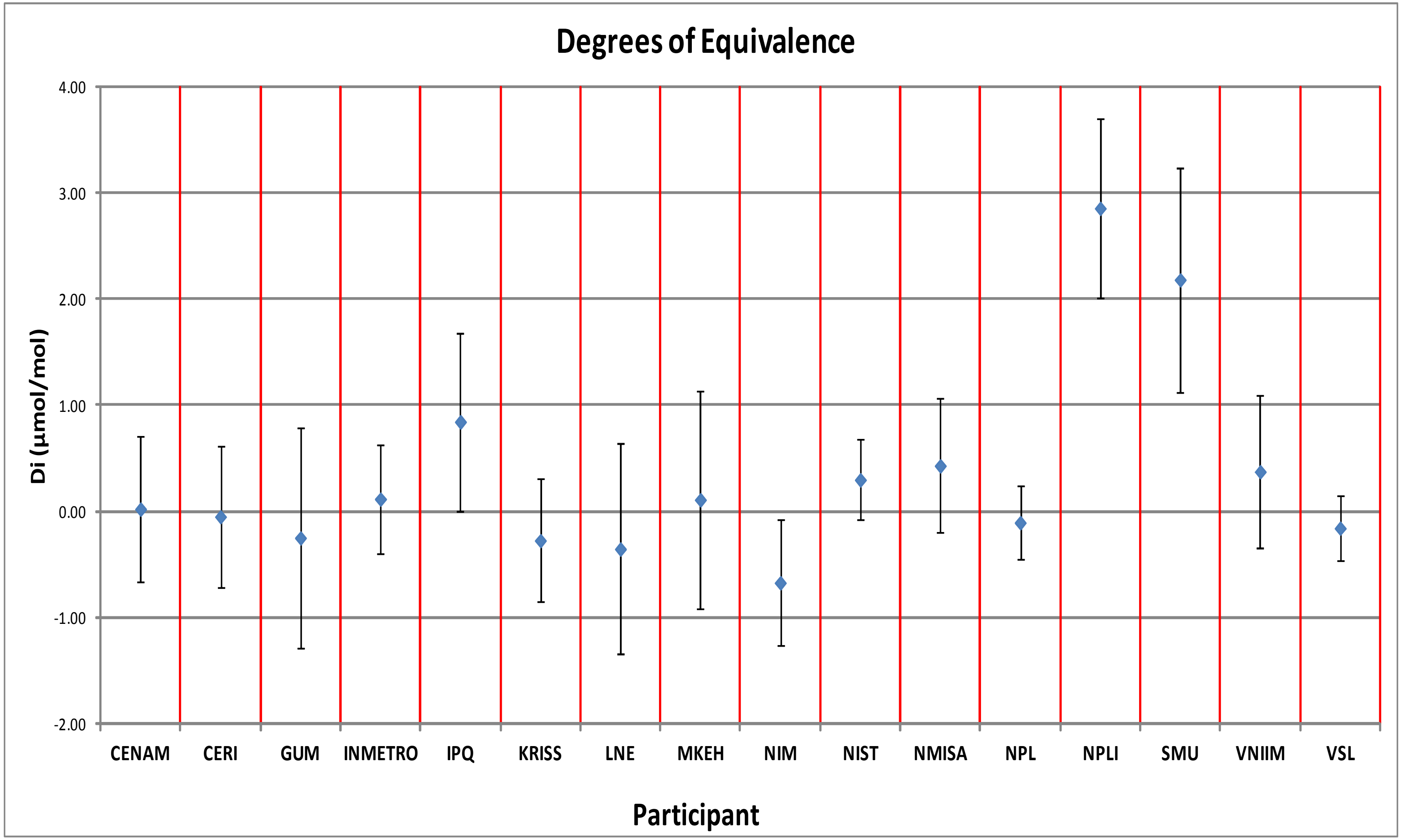


Table 3: Comparison results table with Degrees of Equivalence

Cylinder#	Participant	Grav	uncert	Ver	uVer	$u_{i\,ref}$	Lab Result	uncert	D_i	$u_{i\,ref}$	$U_{i\,ref}$	% rel
$x_{i\,grav}$	$u_{i\,grav}$	$x_{i\,ver}$	$u_{i\,ver}$	$[u_{i\,grav}^2+u_{i\,ver}^2]^{1/2}$	x_i	$u_{i\,res}$	$(x_i - x_{i\,grav})$	$[u_{i\,ref}^2+u_{i\,res}^2]^{1/2}$	$2*u_{i\,ref}$	$(x_i - x_{i\,grav})/x_{i\,grav}$	$x_{i\,grav}$	$u_{i\,grav}$
SG080089A	CENAM	100.238	0.039	100.18	0.14	0.14	100.26	0.32	0.02	0.35	± 0.69	0.02%
SG080104A	CERI	100.170	0.037	100.13	0.13	0.14	100.12	0.30	-0.05	0.33	± 0.66	-0.05%
SG080110A	GUM	100.150	0.037	100.08	0.14	0.14	99.9	0.50	-0.25	0.52	± 1.04	-0.25%
SG080102A	INMETRO	100.184	0.036	100.05	0.15	0.16	100.3	0.20	0.12	0.25	± 0.51	0.12%
SG080095A	IPQ	100.176	0.038	100.33	0.16	0.17	101.02	0.39	0.84	0.42	± 0.84	0.84%
SG080101A	KRISS	100.245	0.037	100.16	0.14	0.15	99.97	0.25	-0.28	0.29	± 0.58	-0.27%
SG080093A	LNE	100.094	0.036	100.21	0.15	0.15	99.74	0.47	-0.35	0.49	± 0.99	-0.35%
SG080097A	MKEH	100.181	0.037	100.11	0.14	0.14	100.29	0.49	0.11	0.51	± 1.02	0.11%
SG080125A	NIM	100.112	0.037	100.22	0.15	0.15	99.44	0.26	-0.67	0.30	± 0.59	-0.67%
SG080122A	NIST	100.103	0.038	100.02	0.14	0.15	100.40	0.12	0.30	0.19	± 0.38	0.30%
SG080113A	NMISA	100.051	0.035	100.13	0.14	0.14	100.48	0.28	0.43	0.32	± 0.63	0.43%
SG080114A	NPL	100.236	0.038	100.20	0.13	0.14	100.13	0.10	-0.11	0.17	± 0.34	-0.11%
SG080085A	NPLI	100.096	0.037		0.13	0.14	102.95	0.40	2.85	0.42	± 0.85	2.85%
SG080117A	SMU	100.009	0.037	99.98	0.13	0.14	102.19	0.51	2.18	0.53	± 1.06	2.18%
SG080119A	VNIIM	100.006	0.037	99.93	0.14	0.14	100.38	0.33	0.37	0.36	± 0.72	0.37%
SG080123A	VSL	100.218	0.041	100.16	0.14	0.14	100.06	0.06	-0.16	0.15	± 0.31	-0.16%

Table 4:

Key comparison CCQM-K76

MEASURAND : Amount-of-substance fraction of Sulfur Dioxide in nitrogen

NOMINAL VALUE : 100 µmol/mol

$x_{\text{Lab}i}$ result of measurement carried out by laboratory *i*
$u_{\text{Lab}i}$ combined standard uncertainty of $x_{\text{Lab}i}$
$x_{i\,\text{ref}}$ reference value for the cylinder sent to laboratory *i* (see page 6 of the Final Report)
$u_{i\,\text{ref}}$ combined standard uncertainty of $x_{i\,\text{ref}}$

Lab *i*	Cylinder number	$x_{\text{Lab}i}$ / (µmol/mol)	$u_{\text{Lab}i}$ / (µmol/mol)	$x_{i\,\text{ref}}$ / (µmol/mol)	$u_{i\,\text{ref}}$ / (µmol/mol)
CENAM	SG080089A	100.26	0.32	100.238	0.14
CERI	SG080104A	100.12	0.30	100.170	0.14
GUM	SG080110A	99.9	0.50	100.150	0.14
INMETRO	SG080102A	100.3	0.20	100.184	0.16
IPQ	SG080095A	101.02	0.39	100.176	0.17
KRISS	SG080101A	99.97	0.25	100.245	0.15
LNE	SG080093A	99.74	0.47	100.094	0.15
MKEH	SG080097A	100.29	0.49	100.181	0.14
NIM	SG080125A	99.44	0.26	100.112	0.15
NIST	SG080122A	100.40	0.12	100.103	0.15
NMISA	SG080113A	100.48	0.28	100.051	0.14
NPL	SG080114A	100.13	0.10	100.236	0.14
NPLI	SG080085A	102.95	0.40	100.096	0.14
SMU	SG080117A	102.19	0.51	100.009	0.14
VNIIM	SG080119A	100.38	0.33	100.006	0.14
VSL	SG080123A	100.06	0.06	100.218	0.14
CENAM	SG080089A	100.26	0.32	100.238	0.14

Table 5:

Key comparison CCQM-K76

MEASURAND : Amount-of-substance fraction of Sulfur Dioxide in nitrogen

NOMINAL VALUE : 100 µmol/mol

Key comparison reference value: there is no single reference value for this comparison, the value $x_{i\,\mathrm{ref}}$ is taken as the reference value for laboratory *i* .

The degree of equivalence of each laboratory *i* with respect to the reference value is given by a pair of terms:

$D_i = (x_{\mathrm{Lab}\,i} - x_{i\,\mathrm{ref}})$, and its associated expanded uncertainty (k = 2) U_i, both expressed in µmol/mol.

No pair-wise degrees of equivalence are computed for this key comparison.

Lab i	D i / (µmol/mol)	U i
CENAM	0.02	0.69
CERI	-0.05	0.66
GUM	-0.25	1.04
INMETRO	0.12	0.51
IPQ	0.84	0.84
KRISS	-0.28	0.58
LNE	-0.35	0.99
MKEH	0.11	1.02
NIM	-0.67	0.59
NIST	0.30	0.38
NMISA	0.43	0.63
NPL	-0.11	0.34
NPLI	2.85	0.85
SMU	2.18	1.06
VNIIM	0.37	0.72
VSL	-0.16	0.31

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory: CENAM

Cylinder number: SG 080089A

Measurement No. 1	Date	Result (% mol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010/05/12	1.0028E-02	1.04E-01	3

Measurement No. 2	Date	Result (% mol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010/05/13	1.0022E-02	6.23E-02	3

Measurement No. 3	Date	Result (% mol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010/05/18	1.0029E-02	1.76E-01	3

Summary Results:

Gas mixture	result (assigned value) (% mol/mol)	Coverage factor	Assigned expanded uncertainty (*) (% mol/mol)
Sulfur Dioxide	1.0026E-02	2	6.3E-05

Reference Method:

The SO_2 content of sample CCQM-K76 was analyzed using a pulsed fluorescence analyzer Thermo Environmental Instruments Inc. model 43 C High level. The sample was compared to four primary standards mixtures prepared gravimetrically using the guide ISO 6142.

It was used a Hewlett Packard model 34401A analog multimeter to collect the responses of the analyzer.

Calibration Standards:

The calibration standards used to calibrate the pulsed fluorescence analyzer model 43C were four primary standards mixtures (PSMs) of SO_2 in N_2. They were prepared according International Standard ISO 6142:2000 by CENAM.

DMR-454Ia

Component	Assigned Value mol/mol	Expanded uncertainty
Sulfur dioxide	9.0261E-05	3.0E-07

DMR-454IIa (Control sample)

Component	Assigned Value mol/mol	Expanded uncertainty
Sulfur dioxide	9.4111E-05	3.0E-07

DMR-434b

Component	Assigned Value mol/mol	Expanded uncertainty
Sulfur dioxide	1.01163E-04	3.5E-07

DMR-454IIIa

Component	Assigned Value mol/mol	Expanded uncertainty
Sulfur dioxide	1.06341E-04	2.7E-07

DMR-454IVa

Component	Assigned Value mol/mol	Expanded uncertainty
Sulfur dioxide	1.10922E-04	3.0E-07

Instrument Calibration:

The calibration instrument was done according to ISO 6143. We have used the B_Least program to determine the best model for data handling. To SO_2 have a goodness of fit less than 2 using a linear function. We have used a set of four concentration levels and one control sample in the following sequence:

$$CStd_1CStd_2CMCStd_3CCont.CStd_5C\ldots\ldots$$

At least three repeated analyses were performed in three independent days.

Sample Handling:

After the cylinder arrives to laboratory it was stabilized at room temperature, the cylinder was rolled to homogenize the mixture. Before measurements sample and standards cylinders were equipped with a two stage regulator and flushed by at least five times. To transfer the sample and standard gas to the analyzer was used SS tubing of 1/4”. The flow rate of sample and standard gas was controlled by low pressure regulator.

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 (δ_T) of the reproducibility and repeatability was evaluated by the statistical method of analysis of variance.

b) Mathematical model effect (δ_m).

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

c) Performance instrument (δ_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)"

a) Uncertainty table:

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Repeatibility and Reproducibility	-----------	Normal	0.041	1	0.041
Model	**-----------**	**Normal**	**0.288**	**1**	**0.288**
Performance Instrument	-----------	Rectangular	0.115	--------------	0.115

In addition, we measured the sample by FT-IR. Even agreement between UV-PF and FT-IR was found, a slight difference of the mean value of both methods remains, we do not include in this report the results of the FT-IR measurement because its susceptibility to isotopomeric variation, which was until now not corrected in the results. The FT-IR results could be available if required during the analysis of comparison results.

CENAM Participants List:
Alejandro Pérez Castorena, Manuel de Jesús Avila Salas, Jorge Koelliker Delgado, Francisco Rangel Murillo and Victor M. Serrano Caballero.

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory: Chemicals Evaluation and Research Institute, Japan (CERI)

Cylinder number: SG080104A

Measurement No. 1	Date	Result (μ mol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	15/03/2010	100.06	0.14	3

Measurement No. 2	Date	Result (μmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	16/03/2010	100.12	0.07	3

Measurement No. 3	Date	Result (μmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	17/03/2010	100.22	0.12	3

Measurement No. 4	Date	Result (μmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	25/03/2010	100.08	0.13	3

Summary Results:

Gas mixture	Result (assigned value)	Coverage factor	Assigned expanded uncertainty
Sulfur Dioxide	100.12μmol/mol	2	0.60μmol/mol

Reference Method:

Principle: NDIR

Make: SHIMADZU CORPORATION

Type: URA-107

Calibration Standards:

Preparation method: Gravimetric

Purity analyses

SO_2: NMIJ-CRM

N2: The purity is calculated as below. And impurities in N_2 are determined by analysis.

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

where,

x_i=mole fraction of impurity i

N=number of impurities

x_{pure}=mole fraction purity of pure gas (SO_2)

Instrument Calibration:

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

Calibration Curve,

Quadratic regression was used for calibration curve. Its formula is as follow.

$y = a\,x^2 + b\,x + c$

Where,

y: Sample concentration

n : Standard material quantity

x: Output value of K76 gas mixture

x_i : Output value of gas standard i

y_i : Concentration of gas standard i

$$a = \frac{S(x^2y)S(xx) - S(xy)S(xx^2)}{S(xx)S(x^2x^2) - \{S(xx^2)\}^2}$$

$$b = \frac{S(xy)S(x^2x^2) - S(x^2y)S(xx^2)}{S(xx)S(x^2x^2) - \{S(xx^2)\}^2}$$

$$c = \frac{\sum y_i}{n} - b\frac{\sum x_i}{n} - a\frac{\sum x_i^{\,2}}{n}$$

$$S(xx) = \sum x_i^{\,2} - \frac{\left(\sum x_i\right)^2}{n}, \quad S(xy) = \sum x_i y_i - \frac{\sum x_i \sum y_i}{n}$$

$$S(xx^2) = \sum x_i^{\,3} - \frac{\sum x_i \sum x_i^{\,2}}{n}, \quad S(x^2y) = \sum x_i^{\,2} y_i - \frac{\sum x_i^{\,2} \sum y_i}{n}$$

$$S(x^2x^2) = \sum x_i^{\,4} - \frac{\left(\sum x_i^{\,2}\right)^2}{n}$$

Standards,

4 PRMs were used for this key comparison. Its concentration is as below table.

Table Concentration of PRMs

	Concentration µmol/mol
R_1	122.5
R_2	100.96
R_3	79.72
R_4	59.29

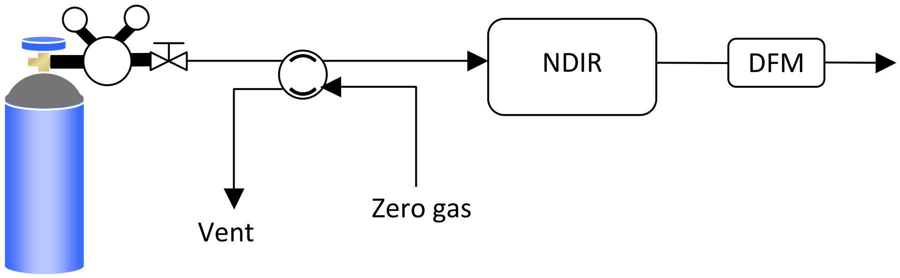
Measurement sequence,

R_1→R_2→K76 gas mixture→R_3→R_4

Sample Handling:

Cylinder – Regulator with needle valve (outlet pressure : 0.05MPa)

– Crossover 4-way valve – NDIR – Digital flow mater (DFM)



Uncertainty:

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

b) Uncertainty table:

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Gravimetric preparation of standard (100.96µmol/mol)	0.02894 µmol/mol	normal	0.01447 µmol/mol	1	0.01447 µmol/mol
Verification	0.2000 µmol/mol	normal	0.1000 µmol/mol	1	0.1000 µmol/mol
Stability	0.3876 µmol/mol	rectangular	0.2238 µmol/mol	1	0.2238 µmol/mol
Repeatability of measurement	0.3358 µmol/mol	normal	0.1679 µmol/mol	1	0.1679 µmol/mol

Combined uncertainty: 0.2975µmol/mol

Coverage factor: 2

Expanded uncertainty: 0.60µmol/mol

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory: Central Office of Measures (GUM)

Cylinder number: SG 080110A

Measurement No. 1	Date	Result (% mol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	11.05.10	0,00992	0,35	10

Measurement No. 2	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	19.05.10	0,01003	0,33	10

Measurement No. 3	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	25.05.10	0,01003	0,34	10

Note: Please copy this table as many times as needed for reporting additional measurements

Summary Results:

Gas mixture	result (assigned value) (% mol/mol)	Coverage factor	Assigned expanded uncertainty (*) (% mol/mol)
Sulfur Dioxide	0,00999	2	0,00010

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

The measurements were repeated 10 times for the standards and sample by pulsed fluorescence SO_2 analyzer, made by Thermo, model 43C.

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

Three standards (No. 1, 3, 6) were prepared by gravimetric method according to ISO 6142 from separate premixtures. The cylinders were evacuated on turbo molecular pump, filled up an weighted on the verification balance. The standards were prepared in aluminum (with coated layers) cylinders. The purity of pure gases used for preparation was taken from the certificates of producer (purity of SO_2 - 3.8; purity of N_2 - 6.0). Four standards (No. 2, 4, 5, 7) were calibrated by VSL.

The standards were (and still are) under metrological control since 2006.

Composition of calibration standards:

No.	Cylinder number	Component	Assigned value (x) [mol/mol]	Expanded uncertainty (u(x)) [mol/mol] (*k*=2)
1	D402375	SO_2	$9{,}9 \cdot 10^{-6}$	$0{,}2 \cdot 10^{-6}$
2	D402405	SO_2	$19{,}92 \cdot 10^{-6}$	$0{,}20 \cdot 10^{-6}$
3	D402379	SO_2	$34{,}2 \cdot 10^{-6}$	$0{,}3 \cdot 10^{-6}$
4	D402434	SO_2	$50{,}1 \cdot 10^{-6}$	$0{,}5 \cdot 10^{-6}$
5	D402398	SO_2	$63{,}1 \cdot 10^{-6}$	$0{,}6 \cdot 10^{-6}$
6	D402370	SO_2	$79{,}1 \cdot 10^{-6}$	$0{,}8 \cdot 10^{-6}$

7	D402419	SO_2	$99{,}8\cdot10^{-6}$	$1{,}0\cdot10^{-6}$

Instrument Calibration:

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

Calibration method according to ISO 6143. The calibration curve was calculated from ratios by the software B_leats.exe (linear case). Measurement sequence: zero gas, standards (for calculation of calibration curve) and sample.

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument? (Automatic, high pressure, mass-flow controller, dilution etc).:

The cylinders (standards and sample) were in the same room for the whole time also during the measurements (temperature stabilization) and the mixtures were mixed up before the measurements. Samples were transferred to the instrument by the manifold.

Uncertainty:

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

The final uncertainty was calculated according to ISO 6143 and consists of the following components:

- the uncertainty of the standards
- the standard deviation of the measurement
- resolution of the analyzer.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

c) Uncertainty table:

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertaint $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
cylinder no. D402375	$9{,}9\cdot10^{-6}$ mol/mol	normal	$0{,}1\cdot10^{-6}$ mol/mol	1	$0{,}1\cdot10^{-6}$ mol/mol
cylinder no. D402405	$19{,}92\cdot10^{-6}$ mol/mol	normal	$0{,}1\cdot10^{-6}$ mol/mol	1	$0{,}1\cdot10^{-6}$ mol/mol
cylinder no. D402379	$34{,}2\cdot10^{-6}$ mol/mol	normal	$0{,}15\cdot10^{-6}$ mol/mol	1	$0{,}15\cdot10^{-6}$ mol/mol
cylinder no. D402434	$50{,}1\cdot10^{-6}$ mol/mol	normal	$0{,}25\cdot10^{-6}$ mol/mol	1	$0{,}25\cdot10^{-6}$ mol/mol
cylinder no. D402398	$63{,}1\cdot10^{-6}$ mol/mol	normal	$0{,}3\cdot10^{-6}$ mol/mol	1	$0{,}3\cdot10^{-6}$ mol/mol
cylinder no. D402370	$79{,}1\cdot10^{-6}$ mol/mol	normal	$0{,}4\cdot10^{-6}$ mol/mol	1	$0{,}4\cdot10^{-6}$ mol/mol
cylinder no. D402419	$99{,}8\cdot10^{-6}$ mol/mol	normal	$0{,}5\cdot10^{-6}$ mol/mol	1	$0{,}5\cdot10^{-6}$ mol/mol
resolution of the analyzer	$0{,}1\cdot10^{-6}$ mol/mol	square	$0{,}1\cdot10^{-6}$ mol/mol	1	$0{,}1\cdot10^{-6}$ mol/mol
standard deviation for cylinder no. D402375	$9{,}6\cdot10^{-6}$ mol/mol	normal	$0{,}1\cdot10^{-6}$ mol/mol	1	$0{,}1\cdot10^{-6}$ mol/mol
standard deviation for cylinder no. D402405	$19{,}4\cdot10^{-6}$ mol/mol	normal	$0{,}2\cdot10^{-6}$ mol/mol	1	$0{,}2\cdot10^{-6}$ mol/mol
standard deviation for cylinder no. D402379	$33{,}3\cdot10^{-6}$ mol/mol	normal	$0{,}4\cdot10^{-6}$ mol/mol	1	$0{,}4\cdot10^{-6}$ mol/mol
standard deviation for cylinder no. D402434	$49{,}2\cdot10^{-6}$ mol/mol	normal	$0{,}4\cdot10^{-6}$ mol/mol	1	$0{,}4\cdot10^{-6}$ mol/mol
standard deviation for cylinder no. D402398	$62{,}3\cdot10^{-6}$ mol/mol	normal	$0{,}6\cdot10^{-6}$ mol/mol	1	$0{,}6\cdot10^{-6}$ mol/mol
standard deviation for cylinder no. D402370	$78{,}4\cdot10^{-6}$ mol/mol	normal	$0{,}6\cdot10^{-6}$ mol/mol	1	$0{,}6\cdot10^{-6}$ mol/mol
standard deviation for cylinder no. D402419	$97{,}7\cdot10^{-6}$ mol/mol	normal	$0{,}9\cdot10^{-6}$ mol/mol	1	$0{,}9\cdot10^{-6}$ mol/mol
Standard deviation for cylinder no. SG 080110A	$98{,}3\cdot10^{-6}$ mol/mol	normal	$0{,}7\cdot10^{-6}$ mol/mol	1	$0{,}7\cdot10^{-6}$ mol/mol

Coverage factor: 2

Expanded uncertainty: 1,0·10^{-6} mol/mol

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory: INMETRO/LABAG

Cylinder number: 05A08

Measurement No. 1	Date	Result (μ mol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	*03/03/2010*	*100.2*	*0.05*	*8*

Measurement No. 2	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	*04/03/2010*	*100.2*	*0.06*	*8*

Measurement No. 3	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	*10/03/2010*	*100.1*	*0.02*	*8*

Measurement No. 4	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	*11/03/2010*	*100.2*	*0.01*	*8*

Measurement No. 5	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	*12/03/2010*	*100.5*	*0.02*	*8*

Measurement No. 6	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	*16/03/2010*	*100.6*	*0.01*	*8*

Note: Please copy this table as many times as needed for reporting additional measurements

Summary Results:

Gas mixture	result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
Sulfur Dioxide	100.3	2	0.4

<u>Reference Method:</u>

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

To analyse the component SO_2, the infrared analyser (HORIBA - model VIA-510) was used.

Measuring range to analyse SO_2: 0-200/1000/1500/2500 ppm. In this case, 0 - 1000 range was utilized.

Analysers out put: 0 – 10 V

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

Four standards were used to calibrate the infrared analyser model VIA-510 to analyse SO_2.

They were prepared according International Standard ISO 6142:2001 by VSL.

PRM 176739SG

Component	*Assigned value(x)* 10^{-6} *mol/mol*	*Standard uncertainty (u(x))* 10^{-6} *mol/mol*
Sulfur dioxide	*60.1*	*0.2*

PRM D751937

Component	*Assigned value(x)* 10^{-6} *mol/mol*	*Standard uncertainty (u(x))* 10^{-6} *mol/mol*
Sulfur dioxide	*120.0*	*0.3*

PRM D751942

Component	*Assigned value(x)* 10^{-6} *mol/mol*	*Standard uncertainty (u(x))* 10^{-6} *mol/mol*
Sulfur dioxide	*180.2*	*0.45*

PRM D751954

Component	*Assigned value(x)* 10^{-6} *mol/mol*	*Standard uncertainty (u(x))* 10^{-6} *mol/mol*
Sulfur dioxide	*250,6*	*0,5*

PRM D751947

Component	*Assigned value(x)* *10^{-6} mol/mol*	*Standard uncertainty (u(x))* *10^{-6} mol/mol*
Sulfur dioxide	*400,1*	*0,8*

Instrument Calibration:

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

The standards used are listed above. The injection was done manually. The order of the injections was: first injection the standards and then injection the sample. They were injected eight times. And the calibration was done according ISO 6143, the best model was determined using the software B_Least, and in this case quadratic model was utilized.

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument? (Automatic, high pressure, mass-flow controller, dilution etc).:

After arrival in the laboratory, the cylinder was stabilised at room temperature (21ºC and humidity of 55%) before measurements. The standards and sample were transferred directly to the infrared analyser using a system composed of pressure regulator, flow meter and control valves.

Uncertainty:

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

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)*

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

d) Uncertainty table:

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$

Coverage factor:

Expanded uncertainty:

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory: KRISS

Cylinder number: NISD100U-A3N

Measurement No. 1	Date	Result (µmol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-04-20	99.82	0.15	4

Measurement No. 2	Date	Result (µmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-04-21	100.04	0.14	6

Measurement No. 3	Date	Result (µmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-04-22	100.05	0.15	6

Summary Results:

Gas mixture	result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
Sulfur Dioxide	99.97 µmol/mol	2	0.50 µmol/mol

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

The SO_2 was analyzed using a NDIR analyzer (Ultramat 6, Siemens). 4 PRMs ranging from 90 to 120 µmol/mol and K76 cylinder were connected to a computer operated gas sampling system. Measurement data was collected and plotted by this system.

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

All PRMs used for the measurement were prepared gravimetrically form the serial dilution of high purity SO_2 gas.

Assigned value (μmol/mol)	Standard uncertainty (μmol/mol)
90.07	0.03
100.07	0.03
109.98	0.03
120.02	0.03

Instrument Calibration:

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

NDIR analyzer was calibrated with 4 PRMs ranging from 90 to 120 μmol/mol and calibration curve was linear. Measurement sequence was as follows :

$PRM_{100} \rightarrow PRM_{90} \rightarrow K76 \rightarrow PRM_{110} \rightarrow PRM_{120} \rightarrow PRM_{100}$

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument? (Automatic, high pressure, mass-flow controller, dilution etc):

K76 cylinder and PRMs were allowed in the laboratory more than 3 days before testing began. 4 PRMs and K76 cylinder were connected to a gas sampling system. Sampling sequences and flow rate (300 ml/min) were controlled by a gas sampling system, and measurement data was collected and plotted in real time.

Uncertainty:

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

e) Uncertainty table:

Analyte	Relative standard uncertainties (%)			Expanded Uncertainty (µmol/mol)	Coverage factor
	Gravimetry	Analysis	Stability		
SO_2	0.03	0.15	0.20	0.50	2

Coverage factor: 2

Expanded uncertainty: 0.50

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory: Laboratoire National de métrologie et d'Essais (LNE)

Cylinder number: SG080093A

Measurement No. 1	Date	Result (µmol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010/02/03	99.749	0.07	3

Measurement No. 2	Date	Result (µmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010/03/18	99.601	0.01	3

Measurement No. 3	Date	Result (µmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010/03/22	99.862	0.04	3

Note: Please copy this table as many times as needed for reporting additional measurements

Summary Results:

Gas mixture	result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)

Sulfur Dioxide	99.74	2	0.94

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

A 43-CTL (TEI) analyser based on the principle of UV fluorescence is used to measure the SO_2 concentrations.

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

Reference dynamic gas mixtures of SO_2 in air (at about 350 nmol/mol) are generated by the LNE reference method which is the permeation method.

Instrument Calibration:

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

A reference gas mixture is generated by permeation at a concentration slightly upper to the concentration of the unknown gas mixture (about 350 nmol/mol) and injected inside the analyser : the analyser is calibrated with this dynamic reference gas mixture.
The unknown gas mixture at about 100 µmol/mol is diluted at about 350 nmol/mol with zero air : this diluted unknown gas mixture is then injected inside the analyser and the response is equal to the concentration of the diluted unknown gas mixture (C').

The SO_2 concentration of the unknown gas mixture C is given by the following formula:

$$C = \frac{C' \times (D_1 + D_2)}{D_1}$$

With : C' the concentration of the diluted unknown gas mixture
D_1 the flowrate of the SO_2 unknown gas mixture (SO_2 cylinder)
D_2 the flowrate of the dilution gas (air)

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

The SO_2 concentration is the mean of the 9 obtained values.

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument? (Automatic, high pressure, mass-flow controller, dilution etc).:

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.

Uncertainty:

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

1) Uncertainty on each concentration of the diluted unknown gas mixture

The first step consists in the estimation of the standard uncertainty on each diluted value.

The SO_2 concentration of the diluted unknown gas mixture *C'* is given by :

$$C' = 10^9 \times \frac{\frac{D_T}{M}}{\frac{D_T}{M} + \frac{D_{Dil}}{V}} \times \frac{L_{sample}}{L_{réf}}$$

With :		
	D_T	the rate of the SO_2 permeation tube
	M	the SO_2 molar mass
	D_{Dil}	the flowrate of the dilution gas (air)
	V	the SO_2 molar volume
	L_{sample}	the reading for the diluted unknown gas mixture
	$L_{réf}$	the reading for the reference gas mixture generated by permeation

An example of an uncertainty budget on one of the 9 obtained diluted values is given in the following table.

Uncertainty source	x_I	Assumed distribution	Standard uncertainty $u(x_i)$ (nmol/mol)	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Rate of the SO_2 permeation tube (D_T)	$803.5\ 10^{-9}$	-	$9.5\ 10^{-10}$	$4.276\ 10^{8}$	$4.062\ 10^{-1}$
SO_2 molar mass (M)	0.79291	-	$1.982\ 10^{-3}$	$4.333\ 10^{2}$	$8.589\ 10^{-1}$
Flowrate of the dilution gas (D_{Dil})	64.0648	-	$3.500\ 10^{-3}$	5.363	$1.877\ 10^{-2}$
SO_2 molar volume (V)	22.414	-	$1.900\ 10^{-4}$	$1.533\ 10^{1}$	$2.913\ 10^{-3}$
Reading for the reference gas mixture generated by permeation ($L_{réf}$)	355	rectangular	$5.774\ 10^{-2}$	$9.678\ 10^{-1}$	$5.588\ 10^{-2}$
Reading for the	344	rectangular	$5.774\ 10^{-2}$	$9.987\ 10^{-1}$	$5.766\ 10^{-2}$

diluted unknown gas mixture (L_{sample})					

Concentration of the diluted unknown gas mixture (*C'*)	343.55 nmol/mol

Expanded uncertainty	1.907 nmol/mol

2) Uncertainty on each concentration of the unknown gas mixture

Then, the standard uncertainty is calculated for each concentration of the unknown gas mixture *C* as described in the following example.

Uncertainty source	x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Concentration of the diluted unknown gas mixture (*C'*)	343.55	-	$9.535\ 10^{-1}$	$2.905\ 10^{-1}$	$2.770\ 10^{-1}$
Flowrate of the SO_2 unknown gas mixture (SO_2 cylinder) (D_1)	34.555	-	$8.639\ 10^{-2}$	2.879	$2.487\ 10^{-1}$
Flowrate of the dilution gas (air) (D_2)	10004.86	-	$2.501\ 10^{1}$	$9.942\ 10^{-3}$	$2.487\ 10^{-1}$

Concentration of the unknown gas mixture (*C*)	99.814 µmol/mol

Expanded uncertainty	0.8954 µmol/mol

3) Uncertainty on the mean concentration of the unknown gas mixture

The standard uncertainties obtained for the 9 values are sum up in the following table.

Date	Concentrations of the unknown gas mixture (C) (µmol/mol)	U(C) (µmol/mol)
2010/02/03	99.814	0.8954
2010/02/03	99.740	0.8946
2010/02/03	99.694	0.8943
2010/03/18	99.609	0.9007
2010/03/18	99.595	0.9005
2010/03/18	99.600	0.9007
2010/03/22	99.860	0.9115
2010/03/22	99.830	0.9114
2010/03/22	99.896	0.9118

The first step consists in calculating the mean standard uncertainty as following:

$$u_{mean} = \sqrt{\frac{\sum u^2(C)}{n}} = 0.452 \ \mu mol/mol$$

The second step consists in the calculation of the standard deviation on the mean of the 9 obtained values.

$$\sigma = 0.119 \, \mu mol/mol$$

The third step consists in the calculation of the expanded uncertainty on the mean concentration of the unknown gas mixture as following:

$$U(C) = 2 \times \sqrt{u_{mean}^2 + \sigma^2} = 2 \times \sqrt{(0.452)^2 + (0.119)^2} = 0.94 \ \mu mol/mol$$

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory: Hungarian Trade Licensing Office (MKEH)

Cylinder number: SG080097A

Measurement No. 1	Date	Result (% mol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010.06.15.	0.010034	0.016	6

Measurement No. 2	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010.06.15.	0.010044	0.014	6

Measurement No. 3	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010.06.16.	0.010015	0.030	5

Measurement No. 4	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010.06.17.	0.010021	0.045	3

Note: Please copy this table as many times as needed for reporting additional measurements

Summary Results:

Gas mixture	result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
Sulfur Dioxide	0.010029 %(mol/mol)	2	0.000098 %(mol/mol)

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

NDIR sulfur dioxide analyzer (S 715, Maihak AG) in combination with a multimeter (model 2000, Keithley) was used to analyze SO_2 gas. The flow rate of the gases was controlled by EPC. The measurement method was direct comparison with a standard which has the same nominal concentration as the sample.

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

4.67 L aluminum cylinders (Luxfer) with brass valves, high purity SO_2 (99.99%, Matheson) and N_2 (99.999%, Messer, Hungary) gases were used for the preparation of the primary standard gases.

The mass measurements of the gases were carried out by a high precision mechanic balance (HCE 25, Voland Corporation, USA) with repeatability of 2.8 mg and capacity of 25 kg.

Instrument Calibration:

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

MKEH primary standards:

OMH272/2010.02.17.	SO_2: 99.92 ppm ± 0.80 ppm(mol/mol)
OMH264/2010.04.06.	SO_2: 100.21 ppm ± 0.80 ppm(mol/mol)
OMH209/2010.06.09.	SO_2: 99.68 ppm ± 0.80 ppm(mol/mol)
NG230/2010.06.11.	SO_2: 99.90 ppm ± 0.80 ppm(mol/mol)

The measurement with a MKEH primary standard with 100 ppm SO_2 nominal concentration.

The standard gas and the sample gas were changed automatically in every 10. minute.

The temperature and pressure correction were not done.

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument? (Automatic, high pressure, mass-flow controller, dilution etc).:

We used sulfinert gas regulator for the cylinders and 70 psi was set up on EPC, so the flow was stable.

Uncertainty:

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

The potential sources of the uncertainty:

Uncertainty of the primary reference material, it was taken into account not only the uncertainty of the preparation but the estimation of the absorption

Uncertainty of the instrument

Standard deviation of the 4 measurement series

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

f) Uncertainty table:

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Standard reference material	0.0100 %(mol/mol)	Normal	0.004	1	0.004
Sulfur dioxide analyzer	0.0100 %(mol/mol)	Normal	0.0025	1	0.0025
Standard deviation of the 4 measurement series	0.010029 %(mol/mol)	Normal	0.0013	1	0.0013
Variancia					0.0049

Coverage factor: 2

Expanded uncertainty: 0.000098 %(mol/mol)

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory:

National Institute of Metrology (NIM), China

Cylinder number:

SG080125A

Measurement No. 1	Date	Result (umol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-5-31	99.49	0.10	4

Measurement No. 2	Date	Result (umol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-6-1	99.36	0.16	6

Measurement No. 3	Date	Result (umol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-6-7	99.50	0.15	6

Measurement No. 4	Date	Result (umol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-6-8	99.49	0.11	8

Measurement No. 5	Date	Result (umol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-6-8	99.37	0.11	8

Measurement No. 6	Date	Result (umol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-6-12	99.43	0.23	7

Note: Please copy this table as many times as needed for reporting additional measurements

Summary Results:

Gas mixture	result (umol/mol) (assigned value)	Coverage factor	Assigned expanded uncertainty (umol/mol)
Sulfur Dioxide	99.44	2	0.51

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

An UV SO2 Analyzer (43C, ThermoElectron, USA) was used to analyze the gas mixtures which the mearsuement range is 0~100μmol/mol. The gas flow was introduced into the analyzer at about 1L/min. In this case, the single point calibration was used to measure the CCQM comparison cylinder.

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

All of the references we used were prepared by the gravimetric method according to ISO 6142-2001 in our lab.

The pure gases were checked before using to make sure that their purities were good enough and the impurities had no effect on the quality of reference gas mixtures. The pure gases included N_2 and SO2.

The parent gases were filled into a 4-liter aluminum cylinder, which has been passed the special treatment. More than 10g parent gas was filled into the cylinder at least. The cylinder was weighed before and after the filling using a balance with a sensitivity of 1 mg.

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

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

The uncertainty of reference gas included the contributions from gravimetric method The uncertainty from gravimetric method was calculated according to the following equation.

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

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

The reference gases used were listed in the following table:

Cylinder Number	Component and assigned value(*x*) □umol/mol	Relative standard uncertainty (*u*(*x*))
500559	100.16	0.22%
521662	100.01	0.22%
500121	101.10	0.22%
522691	100.21	0.22%

Instrument Calibration:

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

Model equation for the measurement of comparison cylinder

$$c_{CCQM} = \frac{H_{CCQM}}{H_{REF}} \cdot c_{REF} \cdot f_{\mathrm{int}\,ro} \cdot f_{\mathrm{int}\,er}$$

c_{CCQM} : Concentration of the SO2 in the comparison cylinder, in unit of μmol/mol;

H_{CCQM} : Signal reading of the comparison gas on SO2 analyzer, in unitofμmol/mol;

H_{REF} : Signal reading of the REF gas on SO2 analyzer, in unit of μmol/mol;

c_{REF} : Concentration of the SO2 in REF cylinder, in unit of μmol/mol;

$f_{\mathrm{int}\,ro}$: repeatability in one day or one group

$f_{\mathrm{int\,er}}$: reproducibility in different days or groups

When testing sample, “A-B-A-B-A” type calibration procedure were used, That means the sample gas and reference gases were measured in the order of Reference – Sample – Reference – Sample – Reference. Single point calibration was used to calculate the concentration of target compound in sample cylinder.

Sample Handling :

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument? (Automatic, high pressure, mass-flow controller, dilution etc).:

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

When testing SO_2 with 43C SO2 Analyzer, the reference and sample gases were directly introduced into the analyzer through a “T” type tube by the pump inside the instrument used. The flow rate was about 1L/min controlled by a flow controller. Another outlet of the “T” tube was vented to the atmosphere. There was a pressure regulator between the cylinder and the inlet of the “T” tube to control the total gas flow rate and make sure that about 100mL/min vent to the atmosphere. The venting flow rate was read from a flow meter.

Uncertainty:

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

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

$$u(c_{CCQM}) = \sqrt{u^2(c_{REF}) + u^2(H_{CCQM}) + u^2(H_{REF}) + u^2(f_{\mathrm{int}\,ra}) + u^2(f_{\mathrm{int}\,er})}$$

Here, u means relative standard uncertainty.

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

$u(H_{CCQM})$: Uncertainty of signal reading of the sample gas from 43C SO2 Analyzer.

$u(H_{REF})$: Uncertainty of signal reading of the reference gas from 43C SO2Analyzer.

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

$u(c_{REF})$: Uncertainty of concentration of the reference gas, which was combined by the uncertainty from gravimetric

$u(f_{\mathrm{int}\,ra})$: Uncertainty of repeatability in one day or one group. The relative standard uncertainty of $f_{\mathrm{int}\,ra}$ was calculated from the rela method according to ISO 6142-2001 and the uncertainty from the stability of the reference gas.tive standard deviation (RSD) of repeating test in one day or one group. The relative standard uncertainty is RSD/sqrt(n), where n is the number of the repeating test.

$u(f_{\mathrm{int}\,er})$: Uncertainty of reproducibility in different days or groups. The relative standard uncertainty $f_{\mathrm{int}\,er}$ was calculated from the relative standard deviation (RSD) of repeating test in different days or groups. The relative standard uncertainty is RSD/sqrt(n), where n is the number of the repeating test.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

g) Uncertainty table:

The uncertainty table was calculated based on one measurement when the cylinder No.is 500559

Uncertainty source X_I	Estimate umol/mol x_I	Assumed distribution	standard uncertainty umol/mol $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty umol/mol $u_I(y)$
H_{CCQM}	97.95	normal	0.049	1.015	0.050
H_{REF}	98.52	normal	0.049	-1.009	0.049
c_{REF}	100.16	normal	0.22	0.9857	0.22
$f_{\text{int}\,ro}$	0.9985	normal	0.001	99.59	0.10
$f_{\text{int er}}$	1.0001	normal	0.0004	99.43	0.04

Result:

Quantity: c_{CCQM}

Value: 99.44μmol/mol

Expanded uncertainty:U=0.5 1 umol/mol

Coverage factor:k=2

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory: National Institute of Standards and Technology

Cylinder number: SG080122A

Measurement No. 1	Date	Result (µmol/mol)	Stand. deviation (µmol/mol)	number of sub-measurements
Sulfur Dioxide	3/19/2010	100.51	0.09	4

Measurement No. 2	Date	Result (µmol/mol)	Stand. deviation (µmol/mol)	number of sub-measurements
Sulfur Dioxide	3/22/2010	100.42	0.15	4

Measurement No. 3	Date	Result (µmol/mol)	Stand. deviation (µmol/mol)	number of sub-measurements
Sulfur Dioxide	3/23/2010	100.20	0.10	4

Measurement No. 4	Date	Result (µmol/mol)	Stand. deviation (µmol/mol)	number of sub-measurements
Sulfur Dioxide	3/24/2010	100.16	0.11	4

Note: Please copy this table as many times as needed for reporting additional measurements
Summary Results:

Gas mixture	result (assigned value) (µmol/mol)	Coverage factor	Assigned expanded Uncertainty (%)
Sulfur Dioxide	100.40 ± 0.12	2	± 0.24

Reference Method:

The sulfur dioxide was analyzed using a ThermoFisher Model 40B Pulsed Fluorescence analyzer (NIST # 572044). A computer-operated gas sampling system (COGAS # 7) was used to deliver the sample stream to the analyzer. Prior to beginning, each analysis the sample line and regulator of each cylinder was purged five (5) times. The analyzer was user to measure the response ratio of each PRM cylinder to that of control cylinder (SG080122A). During each analytical run, the sample has a purge time of 3 minutes before data collection. The analyzer's internal pump would draw the sample into the unit from a 1 L/min slipstream. Each PRM was measured against the control four times during four different analytical periods.

Calibration Standards:

Five NIST gravimetrically prepared primary reference materials ranging in concentration from 120 µmol/mol to 80 µmol/mol were used in this analysis. The PRMs are listed below:

Cylinder Number	Concentration (µmol/mol)	Uncertainty (µmol/mol)
FF19119	120.10	0.16
CAL5769	110.24	0.15
FF38011	100.18	0.13
FF38005	90.11	0.13
CAL7272	80.15	0.12

These standards were prepared from different parent mixtures but all with the same source of balance gas (nitrogen). The table below gives an assay if the nitrogen used to prepare these standards.

Component	Mole fraction µmol/mol	Uncertainty µmol/mol
Sulfur Dioxide	0.05	0.05
Argon	45	3.0
Moisture	0.3	0.3
Carbon Dioxide	0.1	0.1
Nitrogen (Difference)	999954.6	3.0

Instrument Calibration:

The instrument used in this study is a Pulsed Florescence analyzer. The instrument was calibrated using the five gravimetrically prepared PRMs ranging in concentration from 120 µmol/mol to 80 µmol/mol. The CCQM sample (SG080122A) was used as a control and compared to each PRMs a minimum of four times during each analytical periods. The analytical scheme used was, Control – PRM Standard (1) –Control – PRM Standard (2) Control etc. The procedure called for each cylinder to have a three minutes of equilibration and one minute data collection period. A calibration curve with four replicate measurements were run on each of four different days. Each curves were linear.

Sample Handling:

This analysis consist is for a single cylinder identified by CCQM-K76 SG080122A. The sample was fitted with aCGA-660 regulator and measured automatically using NIST data system (#601405) and a computer operated gas analysis system (COGAS #7). Prior to each run the regulator was flushed five times. Each run started and ended with a measurement of the zero gas, house nitrogen. The output pressure of each regulator was set to 206.8 KPa. Cylinder flow was controlled using a mass flow controller. The analyzer has an internal pump that draws in the sample at approximately 800 sccm though a bypass connection. The mass flow is set to provide sample flow in excess of what is needed by the analyzer. The excess sample flow is safely vented.

Uncertainty:

The identified sources of error are measure error; errors associated with the PRMs; within day variability (repeatability); and between day variability (reproducibility). The TYPE A measurement errors are determined from linear calibration data. The Type B errors are associated with the uncertainty of the PRMs. The combined uncertainty is calculated as the square root of the sum of the squares of the standard uncertainties for the within day, between day and PRM uncertainties. The following equations give the algorithm used to calculate the components of the combined uncertainty.

Within Day Standard Uncertainty = 0.25*sqrt (sumsq (A1: Ax)) (1)

Between Day Standard Uncertainty = ABS (MAX (A_1: AX)-MIN (A_1: AX)) / SQRT (12) (2)

Uncertainty of the PRMs = 0.1% (Nominal Reference) (3)

The coverage factor for the expanded uncertainty is 2.

Uncertainty Table:

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard Uncertainty (%) Relative), $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Measurement	0.06%	Gaussian	-.06 to + 0.06	a_1	0.01
Between Day Measurement	0.0008%	Gaussian	-0.08 to + 0.08	a_2	?
Gravimetric Standards	0.1%	Uniform	0.13 to 0.15	a_3 (nominal ref)	1

Coverage factor: 2

Expanded uncertainty: ± 0.24 (%)

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory: National Metrology Institution of South Africa

Cylinder number: 3AL2216

Measurement No. 1	Date	Result (% mol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	24/03/2010	100,37	0,10	3

Measurement No. 2	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	26/03/2010	100,47	0,01	3

Measurement No. 3	Date	Result (% mol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	01/04/2010	100,60	0,23	3

Note: Please copy this table as many times as needed for reporting additional measurements

Summary Results:

Gas mixture	result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
Sulfur Dioxide	100,48	2	0,56

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

The value(s) assigned to the key comparison mixture were obtained by comparing it for sulfur dioxide 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 two of six PSMs was used and a quadratic calibration model was chosen to fit the data.

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

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.

Instrument Calibration:

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

The SO_2 content of sample 3AL2216 was analysed using a UV fluorescence analyser with two sets of 6 gravimetrically prepared binary primary standards mixtures of sulfur dioxide in nitrogen using ISO 6143.

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument? (Automatic, high pressure, mass-flow controller, dilution etc).:

After receipt of sample cylinder 3AL2216 in the laboratory, the cylinder was stabilised at room temperature (22 ºC ± 2 ºC) and humidity of (50 % ± 10%) before checking the pressure and doing measurements. The standards and sample were transferred directly to the UV fluorescence analyser using a system composed of a pressure regulator, mass flow controller and control valves.

Pressure before measurement: 118 bar.

Pressure after measurement: 100 bar.

Uncertainty:

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

The budget of the standard uncertainties for the comparison sample is:

Parameter		**Standard uncertainty**
Gravimetric uncertainty	- Weighing uncertainty - Purity analysis	0,03 % rel.
Verification uncertainty		0,37 % rel.
Stability uncertainty		0,08 % rel.
Regression uncertainty		0,06 % rel.

Coverage factor: 2

Expanded uncertainty: 0,56

Optional

You may provide additional data like the raw measurement data, information on your measurement procedure etc:

CCQM K76 (100 μmol/mol Sulphur Dioxide in nitrogen)

Report of measurements of NIST gas mixture by NPL

Cylinder Identification TC-3ALM153

Overview

The measurements of sulphur dioxide in nitrogen received from the coordinator (NIST) were made during February 2010 by direct comparison with two NPL Primary Standard Mixtures (PSM) of 100 μmol/mol Sulphur Dioxide in nitrogen.

Analytical methods

Horiba VIA-510 NDIR used on 0 to 200 μmol/mol scale.

NPL Primary Standard Mixtures

Two hierarchies of PSMs created at NPL from pure (99.9975%) in 2004 and 2008 were used for the analysis

Nominal amount fraction	**Hierarchy #1**	**Hierarchy #2**
10 mmol/mol	S172	S150
1000 μmol/mol	S186	S151
100 μmol/mol	S187	S152

All standard mixtures were in BOC 10 litre cylinders with Spectraseal passivation.
The detailed composition of S187 is shown in this report.

Analytical results

Date	**04/02/2010**	**04/02/2010**
Analysis against PSM	**S187**	**S152**
Amount fraction of unknown [μmol/mol]	100.079	100.185
Standard deviation of 8 measurements [μmol/mol]	0.047	0.036

Std dev [Relative to value]	*0.05%*	*0.04%*

Uncertainty Calculation

Sulphur dioxide	Uncertainty [µmol/mol]	*Uncertainty [%]*
Repeatability of analysis	0.04	
Gravimetric uncertainty of standard	0.07	
Combined uncertainty	**0.081**	
Expanded uncertainty (*k*=2)	**0.16**	***0.16***

Result

The final result was determined as the mean of the results form analysis against the two hierarchies.

Sulphur dioxide amount fraction in cylinder TC-3ALM153

= 100.13 µmol/mol +/- 0.20 µmol/mol (*k*=2)

Gravimetric Uncertainty for one of the NPL PSM used in the Analysis

```
Component       µmol/mol            uncertainty     % u/c

---------------------------------------------------------

N2             999899.4393          0.78574022      0.000

SO2                100.0147554      0.06625719      0.066

Ar                   0.49994998     0.04522811      9.047

O2                   0.01000126     0.00455038     45.498

NO                   0.00999900     0.00904562     90.465

CO2                  0.00700247     0.00100031     14.285

H2O                  0.00499950     0.00180912     36.186

CxHy                 0.00499950     0.00452931     90.595

methane              0.00299970     0.00452281    150.775

H2                   0.00299970     0.00452281    150.775

CO                   0.00297297     0.00226141     76.065
```

```
INPUTS
======


File               Mass (g)    u/c (g)
--------------------------------------
s186.txt           130.2473    0.02000
BIPLUSN2.txt       1170.996    0.02000


INPUT DATA FILES
================


°°°°°°°°°°°°°°°°°°° s186.txt °°°°°°°°°°°°°°°°°°°


Component       mol/mol             uncertainty
------------------------------------------------
N2              0.9989990758        0.0000010252
SO2             0.0010002710        0.0000006430
Ar              0.0000004995        0.0000000453
CO2             0.0000000700        0.0000000100
O2              0.0000000550        0.0000000067
NO              0.0000000100        0.0000000091
H2O             0.0000000050        0.0000000018
CxHy            0.0000000050        0.0000000051
methane         0.0000000030        0.0000000045
H2              0.0000000030        0.0000000045
CO              0.0000000027        0.0000000023
```

```
°°°°°°°°°°°°°°°°° BIPLUSN2.txt °°°°°°°°°°°°°°°°°


Component       mol/mol             uncertainty

------------------------------------------------

Ar              0.0000005000        0.0000000500

CO              0.0000000030        0.0000000025

O2              0.0000000050        0.0000000050

CxHy            0.0000000050        0.0000000050

H2O             0.0000000050        0.0000000020

N2              0.9999994560        0.0000008655

NO              0.0000000100        0.0000000100

SO2             0.0000000100        0.0000000100

methane         0.0000000030        0.0000000050

H2              0.0000000030        0.0000000050
```

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory: National Physical Laboratory New Delhi India

Cylinder number: SG 080085A

Measurement No. 1	Date	Result (µmol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	21/06/10	102.81	0.04	4

Measurement No. 2	Date	Result (µmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	21/06/10	102.93	0.03	5

Measurement No. 3	Date	Result (µmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	23/06/10	102.99	0.04	4

Measurement No. 4	Date	Result (µmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	23/06/10	103.06	0.02	4

Note: Please copy this table as many times as needed for reporting additional measurements

Summary Results:

Gas mixture	result (assigned value) (μmol/mol)	Coverage factor	Assigned expanded uncertainty (*) (μmol/mol)
Sulfur Dioxide	102.95	2	0.80

Reference Method:

Describe your instrument(s) (principles, make, type, configuration, data collection etc.):

SO_2 Fluorescent Analyzer Model 100A, nominal working range (0.05 to 20 μmol/mol)

Make: Teledyne Instruments, Advanced Pollution Instrumentation Division (T-API),6565 Nancy Ridge Drive San Diego, CA 92121-2251

Data was collected in computer through RS232 port.

Calibration Standards:

Describe your Calibration Standards for the measurements (preparation method, purity analyses, estimated uncertainty etc.):

The calibration standards were prepared gravimetrically using pure SO_2 gas and high purity nitrogen gas according to the ISO 6142. The purity of SO_2 was 99.98%. The first SO_2 gas mixture of concentration 15427.66 (μmol/mol) was prepared in an aluminum cylinder of 10 litre capacity. This gas mixture was subsequently diluted to the concentration of 8.15 ± 0.0316 μmol/ mol SO_2 in nitrogen. This standard was used for the calibration of SO2 Fluorescent Analyzer.

Instrument Calibration:

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

Calibration of the instrument was carried out by single point calibration method using gravimetrically prepared SO_2 gas standard at NPL India, having concentration 8.15 ± 0.0316 μmol/mol in nitrogen.

Sample Handling:

How were the cylinders treated after arrival (stabilized) and how were samples transferred to the instrument? (Automatic, high pressure, mass-flow controller, dilution etc).:

Cylinders were maintained inside a laboratory at a nominal temperature for $30\pm3^{o}C$ for all the period.

The CCQM K-76 inter-comparison cylinder, gas sample was gravimetrically diluted with nitrogen gas in an evacuated 10 liter aluminum cylinder. The dilution factor by weight is 12.462. The pressure of the diluted prepared gas cylinder is 140 Bar.

The diluted sample was analyzed using SO2 fluorescent analyzer.

Uncertainty:

There are potential sources that influence the uncertainty of the final measurement result. Depending on the equipment, the applied analytical method and the target uncertainty of the final result, they have to be taken into account or can be neglected.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

a) Uncertainty table:

Uncertainty source X_I	Estimate x_I	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Reproducibility	102.95 µmol/mol	Normal	0.033 µmol/mol		0.033
Standard SO_2 Gas mixture	8.15 µmol/mol	Normal	0.0316 µmol/mol		0.00388
Dilution Factor due to Balance	12.462	Normal	$2x10^{-9}$		$2x10^{-9}$

Result Value = 102.95 µmol/mol

Combined Uncertainty = ± 0.40 µmol/mol

Coverage factor: 2

Expanded uncertainty = ± 0.80 µmol/mol

Percentage Contribution = 0.39 %

CCQM-K76 Comparison
Measurement report: Sulphur dioxide in nitrogen

Laboratory: VSL

Cylinder number: SG080123A

Measurement No. 1	Date	Result (µmol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulphur Dioxide	2010-02-03	99.954	0.07	3

Measurement No. 2	Date	Result (µmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulphur Dioxide	2010-03-01	100.126	0.05	3

Measurement No. 3	Date	Result (µmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulphur Dioxide	2010-04-28	100.089	0.02	3

Note: Please copy this table as many times as needed for reporting additional measurements

Summary Results:

Gas mixture	result (assigned value)	Coverage factor	Assigned expanded uncertainty (*)
Sulphur Dioxide	100.06	2	0.12

Reference Method:

The analysis were performed conform the standard procedures within the VSL's quality system. For the analysis of 100 µmol mol^{-1} SO_2, an analyser with a NDIR detector was used.

Calibration Standards:

Calibration is performed using the Dutch Primary Standard gas Mixtures (PSMs). A total of 11 PSMs, all prepared by the gravimetric method according to ISO 6142:2001, have been used in this exercise. These PSMs were prepared during normal maintenance work over the past years.

Instrument Calibration:

Analyser : ABB URAS 14 with NDIR detector.

A cubic calibration curve was made between 10 and 100 µmol/mol by measuring PSMs with a molar fraction of 10(3), 20(3), 30, 40, 60, 80 and 100 µmol/mol SO_2 in nitrogen.

Sample Handling:

All cylinders were stored between 15 °C and 25 °C at VSL for at least 24 hours before analysis. 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.

Uncertainty:

The uncertainty used for the calibration mixtures contains all sources of gravimetric preparation. The major source of the uncertainty in the measurement is the determination of the respons of the analyser and this uncertainty on the response was used to determine the molar fraction of the unknown by comparison with the calibration mixtures according to ISO 6143. The reported uncertainty is the combined uncertainty of the 3 analyses (as calculated via ISO 6143) and multiplied by the coverage factor k=2.

Describe in detail how estimates of the uncertainty components were obtained and how they were combined to calculate the overall uncertainty:

The standard uncertainty associated with the amount–of–substance fractions of the PSMs is estimated to be 0.045 µmol mol^{-1}; this value exceeds the uncertainty estimate obtained from the weighing process and the purity analysis and accounts for small but not negligible stability effects. The uncertainty associated with the response is 0.02 a.u., which accounts for gas handling effects (reducers, tubing etc.).

The model reads as

$$y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 \qquad (1)$$

The coefficients and their uncertainties of all measurements are given below.

Table 1: Regression coefficients and associated uncertainties of the 1st measurement

Coefficient	value	standard uncertainty
a_0	-0.00327	0.06595
a_1	0.97864	0.00573
a_2	$-7.36\cdot10^{-5}$	$1.28\cdot10^{-4}$
a_3	$-4.81\cdot10^{-7}$	$8.02\cdot10^{-7}$

Table 2: Covariance matrix associated with regression coefficients of the 1st measurement

Coefficient	a_0	a_1	a_2	a_3
a_0	$4.34951\cdot10^{-3}$	$-3.56559\cdot10^{-4}$	$7.39453\cdot10^{-6}$	$-4.30715\cdot10^{-8}$
a_1	$-3.56559\cdot10^{-4}$	$3.28107\cdot10^{-5}$	$-7.18437\cdot10^{-7}$	$4.31214\cdot10^{-9}$
a_2	$7.39453\cdot10^{-6}$	$-7.18437\cdot10^{-7}$	$1.64668\cdot10^{-8}$	$-1.01809\cdot10^{-10}$
a_3	$-4.30715\cdot10^{-8}$	$4.31214\cdot10^{-9}$	$-1.01809\cdot10^{-10}$	$6.43121\cdot10^{-13}$

Table 3: Regression coefficients and associated uncertainties of the 2nd measurement

Coefficient	value	standard uncertainty
a_0	-0.039717	0.068067
a_1	0.986063	0.005971
a_2	$-3.31\cdot10^{-4}$	$1.32\cdot10^{-4}$

a_3	$1.30 \cdot 10^{-6}$	$8.23 \cdot 10^{-7}$

Table 4: Covariance matrix associated with regression coefficients of the 2nd measurement

Coefficient	a_0	a_1	a_2	a_3
a_0	$4.63311\cdot10^{-3}$	$-3.84433\cdot10^{-4}$	$7.86749\cdot10^{-6}$	$-4.52810\cdot10^{-8}$
a_1	$-3.84433\cdot10^{-4}$	$3.56555\cdot10^{-5}$	$-7.69892\cdot10^{-7}$	$4.56960\cdot10^{-9}$
a_2	$7.86749\cdot10^{-6}$	$-7.69892\cdot10^{-7}$	$1.75074\cdot10^{-8}$	$-1.07581\cdot10^{-10}$
a_3	$-4.52810\cdot10^{-8}$	$4.56960\cdot10^{-9}$	$-1.07581\cdot10^{-10}$	$6.77767\cdot10^{-13}$

Table 5: Regression coefficients and associated uncertainties of the 3rd measurement

Coefficient	value	standard uncertainty
a_0	0.031307	0.068273
a_1	0.986948	0.005994
a_2	$-1.66\cdot10^{-4}$	$1.33\cdot10^{-4}$
a_3	$1.24\cdot10^{-7}$	$8.27\cdot10^{-7}$

Table 6: Covariance matrix associated with regression coefficients of the 3rd measurement

Coefficient	a_0	a_1	a_2	a_3
a_0	$4.66123\cdot10^{-3}$	$-3.86975\cdot10^{-4}$	$7.92145\cdot10^{-6}$	$-4.55988\cdot10^{-8}$
a_1	$-3.86975\cdot10^{-4}$	$3.59223\cdot10^{-5}$	$-7.75949\cdot10^{-7}$	$4.60657\cdot10^{-9}$
a_2	$7.92145\cdot10^{-6}$	$-7.75949\cdot10^{-7}$	$1.76546\cdot10^{-8}$	$-1.08517\cdot10^{-10}$
a_3	$-4.55988\cdot10^{-8}$	$4.60657\cdot10^{-9}$	$-1.08517\cdot10^{-10}$	$6.83850\cdot10^{-13}$

The value for the amount–of–substance fraction SO_2 in the key comparison mixture is obtained by reverse use of the calibration curve. The associated uncertainty is obtained using the law of propagation of uncertainty.
Using the above data, the following results were obtained:

Table 7: Assigned value first measurement

Mixture	y a.u.	$u(y)$ a.u.	x µmol mol^{-1}	$u(x)$ µmol mol^{-1}
NI0123	96.600267	0.039068	99.954	0.063

Table 8: Assigned value second measurement

Mixture	y a.u.	$u(y)$ a.u.	x µmol mol^{-1}	$u(x)$ µmol mol^{-1}
NI0123	96.678	0.032	100.126	0.059

The assigned value for the key comparison mixture NI0123 from the first measurement is given in table 9.

Table 9: Assigned value third measurement

Mixture	y a.u.	$u(y)$ a.u.	x µmol mol^{-1}	$u(x)$ µmol mol^{-1}
NI0123	97.274	0.017	100.089	0.052

The final result is obtained by averaging the assigned values from the three measurements and by pooling the associated uncertainties. The overall uncertainty budget appreciates that

1. the same suite of PSMs has been used for all measurements
2. the uncertainty associated with the composition of the PSMs is dominating the uncertainty budget of the measurements
3. by implication, the results are not independent

Table 10: Final result

Measurement	x µmol mol^{-1}	u(x) µmol mol^{-1}
#1	99.954	0.063
#2	100.126	0.059
#3	100.089	0.052
Overall	100.056	0.058

The expanded uncertainty is 0.12 µmol mol^{-1}, using k = 2. The relative expanded uncertainty is 0.12%.

Coverage factor: 2

Expanded uncertainty: 0.12 µmol mol^{-1}.

CCQM-K76 Comparison
Measurement report: Sulfur dioxide in nitrogen

Laboratory: Instituto Português da Qualidade
Cylinder number: NIST2216

Measurement No. 1	Date	Result (µmol/mol)	Stand. Deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-02-02	101,26	0,24	3

Measurement No. 2	Date	Result (µmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-03-08	100,91	0,10	3

Measurement No. 3	Date	Result (µmol/mol)	Stand. deviation (% relative)	number of sub-measurements
Sulfur Dioxide	2010-03-09	100,90	0,19	3

Summary Results:

Gas mixture	result (assigned value) (µmol/mol)	Coverage factor	Assigned expanded uncertainty (*)
Sulfur Dioxide	101,02	1,98	0,77

Reference Method:
Non Dispersive Infrared Spectroscopy (NDIR): Analyzer: URAS 14
Data Collection: Auto-sampler - Software Sira version 2.0

Calibration Standards:
The preparation was done according to ISO 6142:2001- Gravimetric method
The estimated uncertainty was done according ISO GUM: 1995 "Guide to the Expression of Uncertainty in Measurement".
It was used four primary standard mixtures from VSL.

Composition of calibrants:

Component	Assigned value(x) (mol/mol)	Standard uncertainty (u(x))
SO_2	PRM 6729: $25{,}02 \times 10^{-6}$	$0{,}21 \times 10^{-6}$
	PRM 6829: $100{,}10 \times 10^{-6}$	$0{,}28 \times 10^{-6}$
	PRM 7897: $299{,}70 \times 10^{-6}$	$0{,}75 \times 10^{-6}$
	PRM 3836: $500{,}3 \times 10^{-6}$	$1{,}5 \times 10^{-6}$

Instrument Calibration:
The calibration instrument was done according to ISO 6143. We have used the B_Least program to determine the best model for data handling. All components of mixture have a goodness of fit less than 2 using a linear or quadratic function.
For all components were used a set of four PRM (from VSL). At least three repeated analyses were performed in three independent days.
Manual calibration (zero and span are calibrated separately by pressing the analyzer system display and control unit softkeys)

Sample Handling:
After arrival the cylinder was storage at ambient temperature in a storage room.
The cylinder was connected to a valve to reduce the pressure. The samples were transferred to the analyser through an auto-sampler.

Uncertainty:

The uncertainty measurement was done according ISO GUM: 1995 "Guide to the Expression of Uncertainty in Measurement".

The uncertainty of measurement associated with the final result has been evaluated and includes three main uncertainty sources:

- Uncertainty in calibration;
- Uncertainty of repeatability;
- Uncertainty of reproducibility

These uncertainties were combined and the result was multiplied by a coverage factor with a confidence interval of 95 %.

a) Uncertainty table:

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	$1{,}031 \times 10^{-7}$	1	$1{,}031 \times 10^{-7}$
Reproducibility		normal	$1{,}212 \times 10^{-7}$	1	$1{,}212 \times 10^{-7}$
Calibration		normal	$3{,}521 \times 10^{-7}$	1	$3{,}521 \times 10^{-7}$

Coverage factor: 1,98

Expanded uncertainty: 0,77 µmol/mol

Caparica, 1 de Junho de 2010

SMU REPORT CCQM-K76

General information

Institute	SLOVAK INSTITUTE OF METROLOGY		
Address	Karloveská 63 SK-842 55 Bratislava Slovak Republic		
Contact persons	RNDr. Viliam Štovčík, PhD. , Ing. Miroslava Vaľková		
Telephone	+421 2 60294 523	Fax	+421 2 60294 561
Email*	stovcik@smu.gov.sk, valkova@smu.gov.sk		
Serial number of cylinder received	S6080117A		
Cylinder pressure as received	12 MPa		

Results

Measuring Month	Sulfur dioxide mole fraction x_{SO_2} [µmol/mol]	Expanded uncertainty $U(x_{SO_2})$ [µmol/mol]	Coverage Factor
30. March	102.18	1.03	2
20. April	102.15	0.99	2
26. May	102.23	1.04	2
$\overline{X}$	**102.19**	**1.02**	2

Uncertainty Budget

Combined uncertainty of the SO_2 mole fraction (analysed by fluorescence method) was calculated according to the formula:

$$U_C(x) = 2 * \sqrt{u_A(x_{SO_2})^2 + u_B(x_{SO_2})^2}$$

Where:

$u_A(x): square\, deviation\, of\, measure\, (SD)$

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{X})^2}{(n-1)}}$$

n= 20; number of replicates

$$u_B(x) = \sqrt{(x_{\max} - x_{\min})^2 + d^2 + u_{cal}^2}$$

d= 0.1 µmol/mol; discernment of analyzer

$u_{cal} = 0.20 \mu mol/mol$

u_{cal} is the standard uncertainty of *50 µmol/mol* SO_2 PSM used for the analyzer calibration

Code	Assigned value(x) (µmol/mol)	Expanded uncertainty (U(x) k=2) (µmol/mol)
MY 9736	0.9973	0.0090
MY 9737	2.430	0.020
MY 9732	5.016	0.042
MY 9738	9.848	0.080
MY 9735	24.38	0.20
MY 9734	48.99	0.40
MY 9733	75.01	0.66
MY 9731	113.62	0.96

The concentration of SO_2 was determined by fluorescence method in gas laboratory. Thermo Vision 43C analyzer was used for measurements. The SMU`s PSM prepared gravimetrically was used for the calibration of the analyzer before each measurement. SO_2 content was measured after receiving the cylinder from pilot laboratory and then two times after 4 weeks. 8 out of different PSMs in the mole fraction range *(1-115) µmol/mol* SO_2 were used to make a calibration curve and afterwards from calibration curve were constated an unknown quantity of assay. Each measurement was performed under stable conditions:

Pressure: 723.5 mmHg
Flow: 0.487 l per min.
Integration time: 30 sec

The FT-IR method with MCT detector was also used for detection and control of SO_2 content in cylinders. The values of SO_2 content in PSMs mixtures and unknown mixture ordered by FT-IR method was not accounting in this study. However, the values of SO_2 content were significant to those obtained from fluorescence.

Before measuring process the cylinders were homogenized and stabilized for laboratory temperature about 60 minutes.

The laboratory conditions:
Temperature: 20-23℃
Pressure: 98.90 -101.325 KPa,
Rel. humidity: 20%-35%.

Complementary information on the cylinder

The value of the pressure left in the cylinder before shipment:
p= 9.9 MPa

RNDr. V. Števčík, PhD., Ing. M.Valková
Laboratory of gases SMU

CCQM-K76 Comparison

Measurement report: Sulfur dioxide in nitrogen

Laboratory: D.I.Mendeleyev Institute for Metrology (**VNIIM**)
Scientific Research Department for the State Measurement
Standards in the Field of Physical-Chemical Measurements

Cylinder number: SG 080119A

Measurement No. 1	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard Deviation (% relative)	Number of sub-measurements
Sulfur Dioxide	20/05/2010	100,39	0,18	4

Measurement No. 2	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard Deviation (% relative)	Number of sub-measurements
Sulfur Dioxide	31/05/2010	100,33	0,15	4

Measurement No. 3	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard Deviation (% relative)	Number of sub-measurements
Sulfur Dioxide	03/06/2010	100,37	0,25	4

Measurement No. 4	Date (dd/mm/yy)	Result (10^{-6} mol/mol)	Standard Deviation (% relative)	Number of sub-measurements
Sulfur Dioxide	17/06/2010	100,43	0,1	4

Summary Results:

Gas mixture	**Result (assigned value), 10^{-6} mol/mol**	**Coverage factor**	**Assigned Expanded Uncertainty, 10^{-6} mol/mol**	**Relative Expanded Uncertainty, %**
Sulfur Dioxide	**100,38**	**2**	**0,66**	**0,66**

Reference Method: UV absorption

Instrument: Spectrophotometer Lambda 900 ("Perkin Elmer", USA) included into the set of National Primary Measurement Standard GET 154-01

Length of the cell – 14 cm.

Calibration standards:

The calibration standards 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. The verification process is used to confirm the gravimetric composition as checking internal consistency between prepared cylinders, in accordance with requirements of ISO 6143:2001 (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures).

Characteristics of pure substances used for preparation of the calibration standards are shown in Table 1.

Table 1 – Description of pure components

Component	Mole fraction 10^{-6} mol/mol	Standard uncertainty 10^{-6} mol/mol
SO_2	999799	70
N_2	999996,27	0,15

The calibration standards were prepared in aluminium cylinders with Aculife IV treatment, V = 5 L. Preparation of the calibration standards was carried out in 3 stages.

1 stage:

Preparation of the first gas pre-mixtures SO_2/N_2 with SO_2 mole fraction of $1{,}5 \cdot 10^{-2}$ mol/mol. Relative standard deviation for each measurement series was not more than 0,08 %.

2 stage:

Preparation of the second gas pre-mixtures SO_2/N_2 with SO_2 mole fraction of $0{,}1 \cdot 10^{-2}$ mol/mol. Relative standard deviation for each measurement series was not more than 0,07 %.

3 stage:

Preparation of the calibration gas mixtures SO_2/N_2 with SO_2 mole fraction of $100 \cdot 10^{-6}$ mol/mol. Relative standard deviation for each measurement series was not more than 0,25 %.

There were prepared 3 standard gas mixtures.

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

Verification of SO_2 mole fraction was carried out by "Lambda 900" ("Perkin Elmer", USA) spectrophotometer.

Instrument calibration:

The characteristics of the calibration standards are shown in table 2.

Table 2 – Characteristics of calibration standards

Standard gas mixture N	Component	Assigned value, 10^{-6} mol/mol	Standard uncertainty (gravimetry), 10^{-6} mol/mol
1	SO_2	100,50	0,05
	N_2	balance	-
2	SO_2	99,96	0,05
	N_2	balance	-
3	SO_2	99,74	0,05
	N_2	balance	-

Single point calibration method was used to determine SO_2 mole fraction.

There were made 4 independent measurements under repeatability conditions with 4 independent calibrations. One single measurement consisted of 4 sub-measurements.

Sample handling:

Prior to measurements the cylinders were being rolled to ensure homogeneity of the mixtures for two hours and then stored at room temperature at least 24 hours.

Stainless steel metering valves were connected with the cylinders. The valves were purged with SO_2 gas mixture at least 5 times. Then they were left under pressure for 24 hours. Directly before the measurements the valves were purged another 3 times.

After each measurement pure Nitrogen was flushed through the spectrophotometer.

All the measurement results were normalized to temperature 293 K and pressure 101.325 kPa.

Evaluation of uncertainty of measurements:

Total standard uncertainty of SO_2 mole fraction was calculated on the base of the following constituents:

- standard uncertainty of SO_2 mole fraction in standard gas mixture (including uncertainty of weighing of parent gases and pre-mixtures, uncertainty of the purity of the parent gases);
- standard deviation of calibration;
- standard deviation of the measurement result of SO_2 mole fraction in cylinder № SG 080119A;
- standard uncertainty due to pressure measurements;
- standard uncertainty due to temperature measurements.

Uncertainty budget for SO_2 mole fraction in the gas mixture in the cylinder № SG 080119A is shown in the table 3.

Table 3– Uncertainty budget for SO_2 mole fraction in gas mixture in cylinder № SG 080119A

Uncertainty source X_i	**Estimate** x_i	**Evaluation type (A or B)**	**Assumed distribution**	**Standard uncertainty** $u(x_i)$	**Sensitivity coefficient** c_i	**Contribution to standard uncertainty** $u_i(y)$
Calibration standard (gravimetry + purity)	100,50 10^{-6} mol/mol	A,B	Normal	0,05 10^{-6} mol/mol	0,99881	0,05 10^{-6} mol/mol
Standard deviation of calibration	0,111649	A	Normal	0,000278	899,281	0,25 10^{-6} mol/mol
Standard deviation of measurement result	0,112075	A	Normal	0,000223	896,861	0,20 10^{-6} mol/mol
Standard uncertainty due to pressure	101,325 kPa	B	Rectangular	0,010 kPa	1	0,01 10^{-6} mol/mol
Standard uncertainty due to temperature	293 K	B	Rectangular	0,15 K	0,3333	0,05 10^{-6} mol/mol

Coverage factor: 2
Expanded uncertainty: 0,66·10^{-6} mol/mol

Date: 30.06.10

Authors:

L.A. Konopelko, Y.A. Kustikov, V.V. Pankratov, D.V. Rumyantsev, M.V. Pavlov, E.V. Gromova