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International comparison CCQM-K74: Nitrogen dioxide, 10 µmol/mol

Final Report

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Field: Amount of substance

Organizing Body: CCQM

Index

1. Rationale for comparison

There is a high international priority attached to activities which reduce NO_x in the atmosphere. The current level of permitted emissions is typically between 50 µmol/mol and 100 µmol/mol, but lower values are expected in the future. Currently, ambient air quality monitoring regulations also require the measurement of NO_x mole fractions of 0.2 µmol/mol. The production of accurate standards at these mole fractions requires either dilution of a stable higher concentration gas standard or production by a dynamic technique, for example, one based on permeation tubes.

The CCQM-K74 comparison is designed to evaluate the level of comparability of laboratories' measurement capabilities for nitrogen dioxide (NO_2) at a nominal mole fraction of 10 µmol/mol.

2. Quantities and Units

In this protocol the measurand was the mole fraction of nitrogen dioxide in nitrogen*, with measurement results being expressed in mol/mol and its multiples µmol/mol or nmol/mol.

(*the nitrogen balance gas contains nominally 1000 µmol/mol of oxygen)

3. Schedule

The revised schedule for the project was as follows:

June 2009	Shipment of cylinders to the BIPM
June 2009 – August 2009	Analysis of mixtures at the BIPM
September 2009	Shipment of cylinders from the BIPM to participants
October 2009 – January 2010	Analysis of mixtures by the participants
February 2010	Shipment of cylinders back from participants to the BIPM
March 2010 – May 2010	2nd set of analysis of mixtures at the BIPM
February 2010 – May 2010	Reports of the participants
July 2010	Distribution of Draft A of this report

4. Measurement standards

The gas mixtures circulated as part of the comparison were prepared by VSL. The nitrogen dioxide gas mixtures were contained in passivated aluminium cylinders of 5 L. The cylinders were pressurized at about 12 MPa.

The nitrogen dioxide gas standards were produced by gravimetric preparation in accordance with the International Standard ISO 6142:2001[1].

Each cylinder was value assigned by the BIPM dynamic gas facility as described in ANNEX 1, before and after the participant's measurements. The VSL and BIPM values and measurements are given in Table 1 and Table 2 where:

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[1] ISO 6142:2001: Gas analysis-Preparation of calibration gas mixtures-Gravimetric method.

x_{VSL}	is the value assigned by VSL based on gravimetric preparation;
$u_{\mathrm{prep}}(x_{\mathrm{VSL}})$	the standard uncertainty of the VSL values with contributions due to gravimetry and purity analysis;
$u_{\mathrm{ver}}(x_{\mathrm{VSL}})$	the standard uncertainty including contributions from verification associated with the assigned value x_{VSL};
x_{KCRV}	The Key Comparison Reference Value (KCRV) that is the first BIPM measurement result (prior to sending out cylinders to participants);
$u(x_{\mathrm{KCRV}})$	the standard uncertainty of the KCRV;
x_{BIPM2}	the second BIPM measurement result (on return of cylinders from participants);
$u(x_{\mathrm{BIPM2}})$	the standard uncertainty of the second BIPM measurement result;

From previous studies carried out by the BIPM and VSL it was expected that the mixtures would contain certain amounts of HNO_3. Analysis of the gas mixtures at the BIPM using FT-IR spectroscopy confirmed the presence of and permitted the quantification of nitric acid in the gas mixtures. Table 4 lists the nitric acid mole fractions found in the gas standards. To verify the stability of the gas mixtures the purity analysis was repeated when the gas mixtures were returned to the BIPM provided that the participants returned the cylinders with the minimum gas pressure required as described in the comparison protocol (see Table 3).

Table 4 lists:

Cylinder	the identification code of the cylinder received by the participating laboratory;
$x_{\mathrm{HNO3(1)}}$	the mole fraction of nitric acid measured in the standard by the BIPM (prior to sending standards to participants);
$u(x_{\mathrm{HNO3(1)}})$	the standard uncertainty associated with the nitric acid mole fraction measurement;
$x_{\mathrm{HNO3(2)}}$	the mole fraction of nitric acid measured in the standard by the BIPM (following return of standards to the BIPM);
$u(x_{\mathrm{HNO3(2)}})$	is the standard uncertainty associated with the nitric acid determination by FT-IR spectroscopy after the participant's measurements.

Figure 1 plots the nitrogen dioxide mole fraction reported by VSL for each gas standard. In Figure 1 the error bars represent the standard uncertainty associated with the certified value. The average of nitrogen dioxide mole fractions calculated from VSL values based on gravimetric preparation data was 10.60 µmol/mol with a standard uncertainty of 105 nmol/mol.

The nitrogen dioxide mole fractions measured by the BIPM before and after measurements by participants are shown in Figure 2 and Figure 3. In Figure 2 the error bars represent the standard uncertainty associated with the BIPM measurement results including contributions from the dynamic preparation of nitrogen dioxide gas mixtures, NO_2 losses in the permeation system of the BIPM and an observed drift in the nitrogen dioxide mole fractions measured by the BIPM before and after the participant's measurements. For further information see ANNEX 2- Report of Proposed *u(KCRV)* for the Draft B report of CCQM-K74: Nitrogen dioxide, 10 μmol/mol. The error bars in Figure 3 represent the standard uncertainty associated with the BIPM measurement results including the contributions from the dynamic preparation of nitrogen dioxide gas mixtures.

The average of the BIPM measurement results for all cylinders was 10.334 μmol/mol with a standard deviation of 72 nmol/mol covering all measured values. The amount of nitric acid found in each cylinder was consistent with the difference between the gravimetric preparation value and BIPM's analytical value for the nitrogen dioxide amount fraction, and accounts for the conversion of nitrogen dioxide to nitric acid (reacting with residual water and oxygen in the gas standards) and limited by the amount of water present. Figure 5 and Figure 6 plot the nitric acid mole fractions measured in each gas standard. The amount of nitric acid was measured before and after the measurements of the participating laboratories. Changes in the mole fractions of nitrogen dioxide and nitric acid in each cylinder during the period of the comparison were well within the measurement uncertainties of these values. The uncertainty budget for the key comparison reference value contains a component which covers any change in value due to instability of the gas transfer standard.

The BIPM was unable to perform a second measurement of nitric acid content in gas mixtures 930659, 930649 and 930654, as the participating laboratories that had made measurements on these cylinders had not followed the comparison protocol and returned the cylinders with insufficient gas to make these measurements. Cylinders 930650 and 930722 were not returned to the BIPM on time and no additional measurements could be made on these cylinders.

VSL preparation values

Certificate number	Preparation date	Number of Cylinder	Assigned NO_2 mole fraction x_{VSL} (µmol/mol)	Gravimetric standard uncertainty $u\text{prep}(x_{VSL})$ (µmol/mol)	Certified standard uncertainty $u\text{ver}(x_{VSL})$ (µmol/mol)
3221115-02	24/02/2009	#930659-PRM	10.604	0.003	0.105
3221115-05	18/03/2009	#930650-PRM	10.617	0.002	0.105
3221115-22	09/04/2009	#930655-PRM	10.608	0.003	0.105
3221115-23	09/04/2009	#930662-PRM	10.606	0.003	0.105
3221115-21	08/04/2009	#930649-PRM	10.609	0.003	0.105
3221115-16	03/04/2009	#930671-PRM	10.597	0.003	0.105
3221115-06	19/03/2009	#930660-PRM	10.614	0.002	0.105
3221115-07	19/03/2009	#930667-PRM	10.603	0.002	0.105
3221115-15	02/04/2009	#930661-PRM	10.603	0.003	0.105
3221115-03	25/02/2009	#930673-PRM	10.605	0.003	0.105
3221115-17	03/04/2009	#930675-PRM	10.609	0.003	0.105
3221115-13	01/04/2009	#930654-PRM	10.604	0.002	0.105
3221115-09	20/03/2009	#930674-PRM	10.608	0.002	0.105
3221115-25	10/04/2009	#930676-PRM	10.602	0.003	0.105
3221115-18	03/04/2009	#930713-PRM	10.597	0.003	0.105
3221115-20	08/04/2009	#930722-PRM	10.620	0.003	0.105
3221115-11	01/04/2009	#930697-PRM	10.600	0.003	0.105

Table 1. Characteristics of gravimetric mixtures as provided by VSL.

BIPM measurement results

Number of Cylinder	Measurement date 1st measurement	1st BIPM NO$_2$ mole fraction measurement x_{KCRV} µmol/mol	Standard uncertainty $u(x_{\mathrm{KCRV}})$ µmol/mol	Measurement date 2nd measurement	2nd BIPM assigned NO$_2$ mole fraction x_{BIPM2} µmol/mol	Standard uncertainty $u(x_{\mathrm{BIPM2}})$ µmol/mol	Δx= (x_{BIPM2}- x_{KCRV}) µmol/mol	$u(\Delta x)$ µmol/mol	$2u(\Delta x)$ µmol/mol
#930659-PRM	19/08/2009	10.226	0.042	*					
#930650-PRM	20/08/2009	10.227	0.042	**					
#930655-PRM	18/08/2009	10.347	0.042	01/04/2010	10.351	0.035	0.004	0.055	0.109
#930662-PRM	18/08/2009	10.378	0.042	30/03/2010	10.353	0.035	−0.025	0.054	0.109
#930649-PRM	18/08/2009	10.347	0.042	*					
#930671-PRM	21/08/2009	10.351	0.041	30/03/2010	10.323	0.035	−0.028	0.054	0.109
#930660-PRM	21/08/2009	10.431	0.041	02/04/2010	10.400	0.035	−0.031	0.054	0.109
#930667-PRM	01/09/2009	10.183	0.042	07/04/2010	10.151	0.035	−0.032	0.054	0.109
#930661-PRM	19/08/2009	10.270	0.042	31/03/2010	10.265	0.035	−0.005	0.054	0.109
#930673-PRM	26/08/2009	10.417	0.041	31/03/2010	10.401	0.035	−0.016	0.054	0.109
#930675-PRM	27/08/2009	10.378	0.041	07/04/2010	10.384	0.035	0.006	0.054	0.109
#930654-PRM	25/08/2009	10.299	0.041	*					
#930674-PRM	25/08/2009	10.370	0.041	30/03/2010	10.343	0.035	−0.027	0.054	0.109
#930676-PRM	28/08/2009	10.435	0.042	31/03/2010	10.421	0.035	−0.014	0.055	0.109
#930713-PRM	29/08/2009	10.320	0.042	01/04/2010	10.284	0.035	−0.036	0.055	0.110
#930722-PRM	28/08/2009	10.350	0.042	**					
#930697-PRM	25/08/2009	10.343	0.041	31/03/2010	10.343	0.024	0.000	0.048	0.096

Table 2. Results of BIPM NO$_2$ mole fraction measurements. * Insufficient gas for second measurement ** Standard unavailable for the second measurement.

Departure and return pressure of the gas standards

Lab	Certification date	Number of Cylinder	Date of return	pressure on departure Mpa	pressure on return Mpa
NPL	24/02/2009	#930659-PRM	26/01/2010	9.0	4.0*
NIM	18/03/2009	#930650-PRM	16/04/2010**	10.0	6.0
SMU	09/04/2009	#930655-PRM	02/02/2010	10.0	7.5
NMIA	09/04/2009	#930662-PRM	26/02/2010	9.5	7.0
NMISA	08/04/2009	#930649-PRM	24/02/2010	10.5	2.5*
CERI	03/04/2009	#930671-PRM	01/03/2010	10.0	7.5
METAS	19/03/2009	#930660-PRM	02/02/2010	9.0	7.8
INRIM	19/03/2009	#930667-PRM	02/02/2010	10.0	6.3
KRISS	02/04/2009	#930661-PRM	26/02/2010	9.5	5.5
FMI	25/02/2009	#930673-PRM	16/02/2010	8.7	7.0
LNE	03/04/2009	#930675-PRM	02/02/2010	10.0	8.0
NIST	01/04/2009	#930654-PRM	02/02/2010	10.2	4.0*
VSL	20/03/2009	#930674-PRM	02/02/2010	10.2	7.2
CEM	10/04/2009	#930676-PRM	02/03/2010	10.0	6.2
VNIIM	03/04/2009	#930713-PRM	16/03/2010	10.0	7.2
BAM	08/04/2009	#930722-PRM	***	9.8	**
BIPM	20/03/2009	#930697-PRM	In place	10.0	5.0

Table 3. Departure and return pressure of the gas standards after being measured by the participating laboratories.

* Insufficient gas for 2nd series of BIPM measurements (≤5MPa). ** Standard returned to the BIPM behind schedule. *** Standard not yet returned to the BIPM.

BIPM HNO_3 Measurements

Cylinder	Measurement date	$x_{HNO3(1)}$ (µmol/mol)	$u(x_{HNO3(1)})$ (µmol/mol)	Measurement date	$x_{HNO3(2)}$ (µmol/mol)	$u(x_{HNO3(2)})$ (µmol/mol)	$\Delta x = (x_{HNO3(2)} - x_{HNO3(2)})$ µmol/mol	$u(\Delta x)$ µmol/mol	$2u(\Delta x)$ µmol/mol
#930659-PRM	12/08/2009	0.348	0.027	*					
#930650-PRM	10/08/2009	0.214	0.023	07/05/2010	0.240	0.024	0.026	0.033	0.066
#930655-PRM	30/07/2009	0.114	0.021	20/04/2010	0.133	0.021	0.019	0.030	0.059
#930662-PRM	28/07/2009	0.155	0.022	01/05/2010	0.140	0.021	−0.015	0.030	0.061
#930649-PRM	11/08/2009	0.237	0.024	*					
#930671-PRM	06/08/2009	0.165	0.022	03/05/2010	0.184	0.022	0.019	0.031	0.062
#930660-PRM	11/08/2009	0.137	0.021	20/04/2010	0.152	0.022	0.014	0.030	0.060
#930667-PRM	05/08/2009	0.345	0.027	22/04/2010	0.363	0.028	0.018	0.039	0.077
#930661-PRM	30/07/2009	0.199	0.023	21/04/2010	0.240	0.024	0.041	0.033	0.065
#930673-PRM	04/08/2009	0.119	0.021	29/04/2010	0.114	0.021	−0.005	0.030	0.059
#930675-PRM	07/08/2009	0.148	0.021	21/04/2010	0.144	0.021	−0.004	0.030	0.061
#930654-PRM	11/08/2009	0.234	0.023	*					
#930674-PRM	06/08/2009	0.131	0.021	30/05/2010	0.124	0.021	−0.007	0.030	0.060
#930676-PRM	11/08/2009	0.081	0.020	01/05/2010	0.099	0.021	0.018	0.029	0.058
#930713-PRM	12/08/2009	0.197	0.022	21/04/2010	0.184	0.022	−0.013	0.032	0.063
#930722-PRM	31/07/2009	0.145	0.021	**					
#930697-PRM	28/07/2009	0.141	0.021	30/04/2010	0.172	0.022	0.031	0.031	0.061

Table 4. Nitric acid mole fraction measured in cylinder gas standards by the BIPM using FT-IR spectroscopy. * Insufficient gas for second measurement. ** Standard returned to the BIPM behind schedule. *** Standard not yet returned to the BIPM.

1st BIPM NO_2 mole fraction measurement x_{KCRV} µmol/mol	Standard uncertainty $u(x_{\mathrm{KCRV}})$ µmol/mol	2nd BIPM NO_2 mole fraction measurement x_{BIPM2} µmol/mol	Standard uncertainty $u(x_{\mathrm{BIPM2}})$ µmol/mol	$x_{\mathrm{KCRV}} + x_{\mathrm{HNO3(1)}}$	$u(x_{\mathrm{KCRV}} + x_{\mathrm{HNO3(1)}})$	$2u(x_{\mathrm{KCRV}} + x_{\mathrm{HNO3(1)}})$	$x_{\mathrm{BIPM2}} + x_{\mathrm{HNO3(2)}}$	$u(x_{\mathrm{BIPM2}} + x_{\mathrm{HNO3(2)}})$	$2u(x_{\mathrm{BIPM2}} + x_{\mathrm{HNO3(2)}})$
10.226	0.042	*		10.574	0.050	0.099			
10.227	0.042	**		10.441	0.047	0.095			
10.347	0.042	10.351	0.035	10.461	0.046	0.093	10.484	0.041	0.082
10.378	0.042	10.353	0.035	10.533	0.047	0.094	10.493	0.041	0.082
10.347	0.042	*		10.584	0.048	0.095			
10.351	0.041	10.323	0.035	10.516	0.047	0.094	10.507	0.042	0.083
10.431	0.041	10.400	0.035	10.568	0.047	0.093	10.552	0.041	0.083
10.183	0.042	10.151	0.035	10.528	0.050	0.099	10.514	0.045	0.089
10.270	0.042	10.265	0.035	10.469	0.047	0.095	10.505	0.042	0.085
10.417	0.041	10.401	0.035	10.536	0.046	0.093	10.515	0.041	0.082
10.378	0.041	10.384	0.035	10.526	0.047	0.093	10.528	0.041	0.082
10.299	0.041	*		10.533	0.048	0.095			
10.370	0.041	10.343	0.035	10.501	0.047	0.093	10.467	0.041	0.082
10.435	0.042	10.421	0.035	10.516	0.047	0.093	10.520	0.041	0.081
10.320	0.042	10.284	0.035	10.517	0.048	0.096	10.468	0.042	0.083
10.350	0.042	**		10.495	0.047	0.094			
10.343	0.041	10.343	0.024	10.484	0.047	0.093	10.515	0.032	0.065

Table 5. Summation of Nitrogen Dioxide and Nitric Acid Mole fractions for each standard based on BIPM measurements.

* Insufficient gas for second measurement. ** The standard wasn't available for 2nd measurement

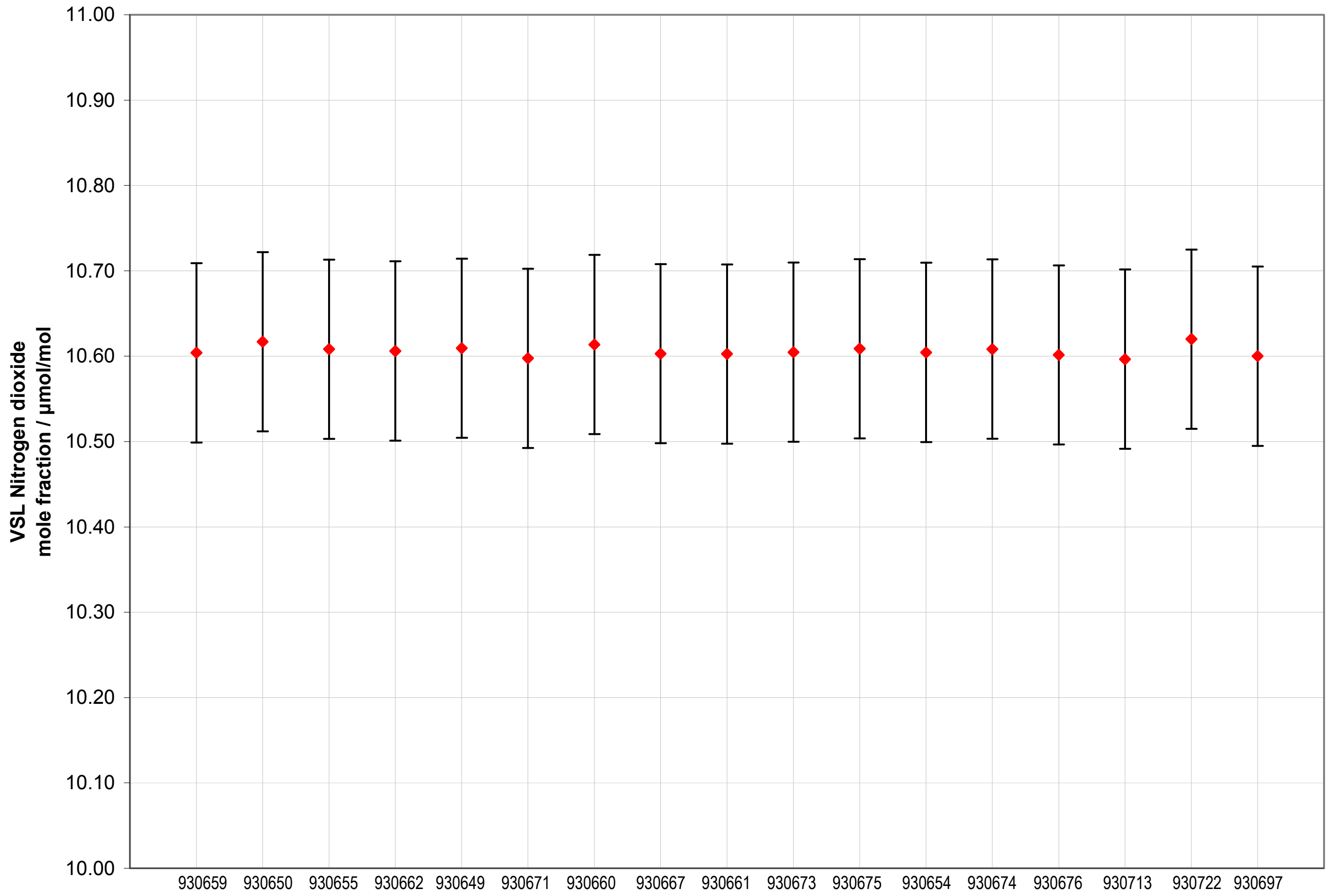

Figure 1. Nitrogen dioxide mole fraction values provided by VSL based on static gravimetric preparation. The error bar represents the standard uncertainty (*k*=1) associated with the certified value.

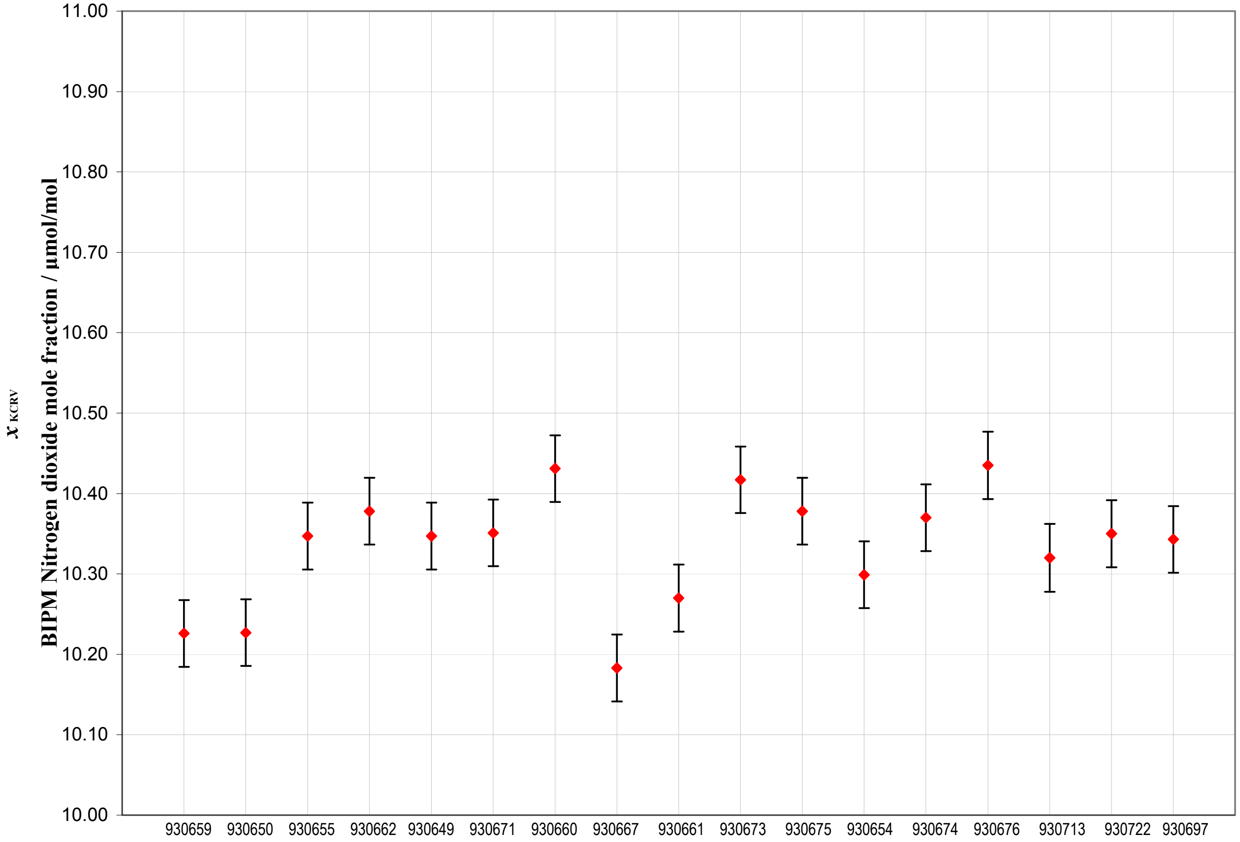

Figure 2. First series of nitrogen dioxide mole fraction measurements by the BIPM (x_{KCRV}), prior to sending standards to participating laboratories. The error bars represent the standard uncertainty (k=1) associated with the BIPM measurement results including contributions from the dynamic preparation of nitrogen dioxide gas mixtures, NO_2 losses in the permeation system of the BIPM and an observed drift in the nitrogen dioxide mole fractions measured by the BIPM before and after the participant's measurements. For further information see ANNEX 2- Report of Proposed u(KCRV) for the Draft B report of CCQM-K74: Nitrogen dioxide, 10 µmol/mol.

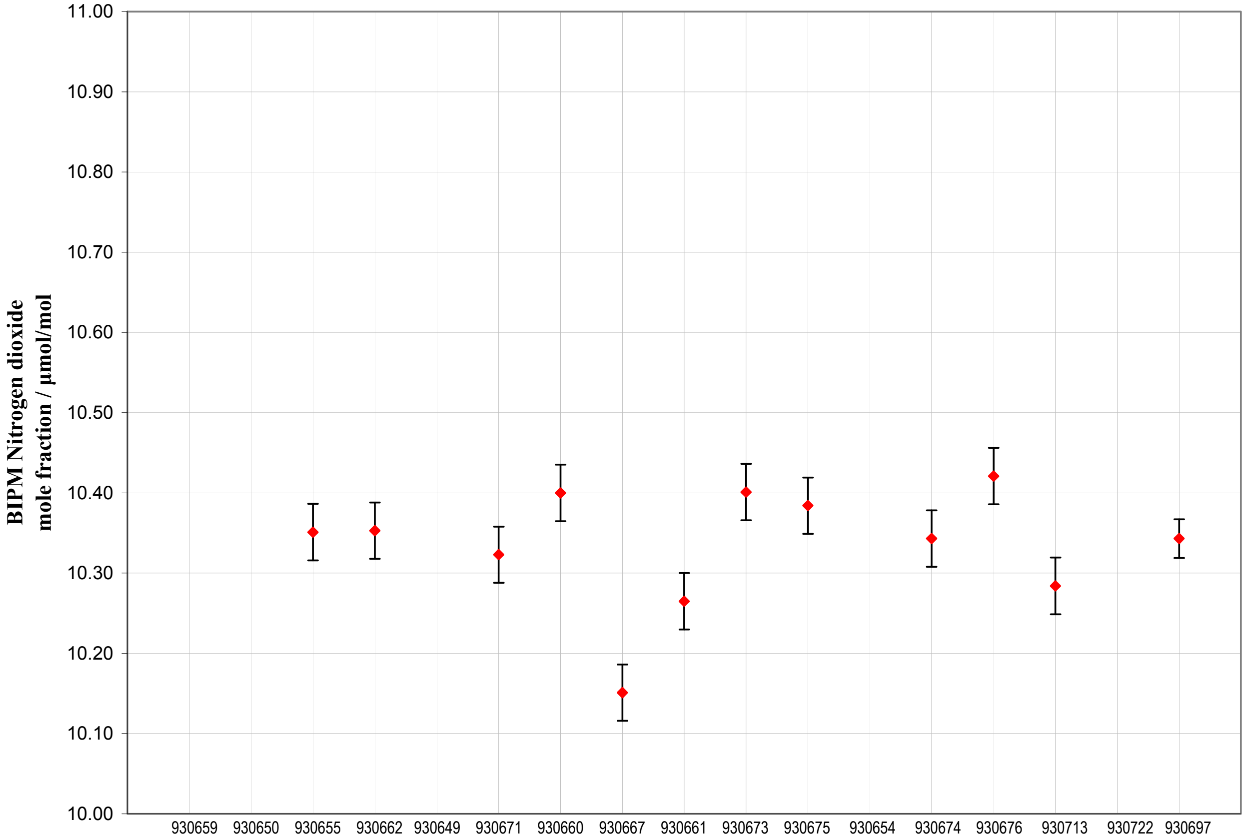

Figure 3. Second series of nitrogen dioxide mole fraction measurements by the BIPM, after return of standards from participating laboratories. The error bars represent the standard uncertainty (*k*=1) associated with the BIPM measurement results including the contributions from the dynamic preparation of nitrogen dioxide gas mixtures.

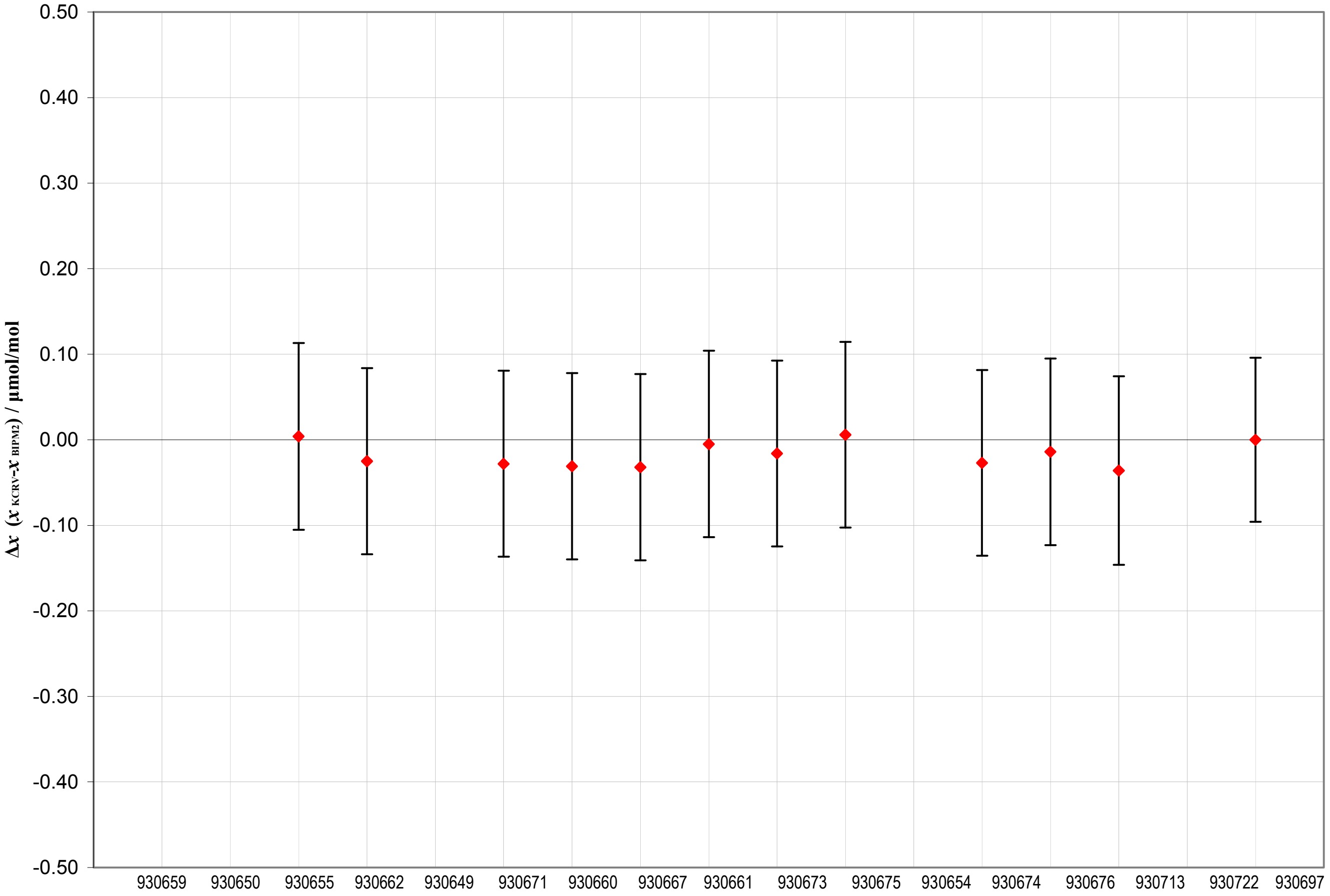

Figure 4. Difference between the BIPM series of measurements for each standard. The error bar represents the expanded uncertainty at a 95 % level of confidence.

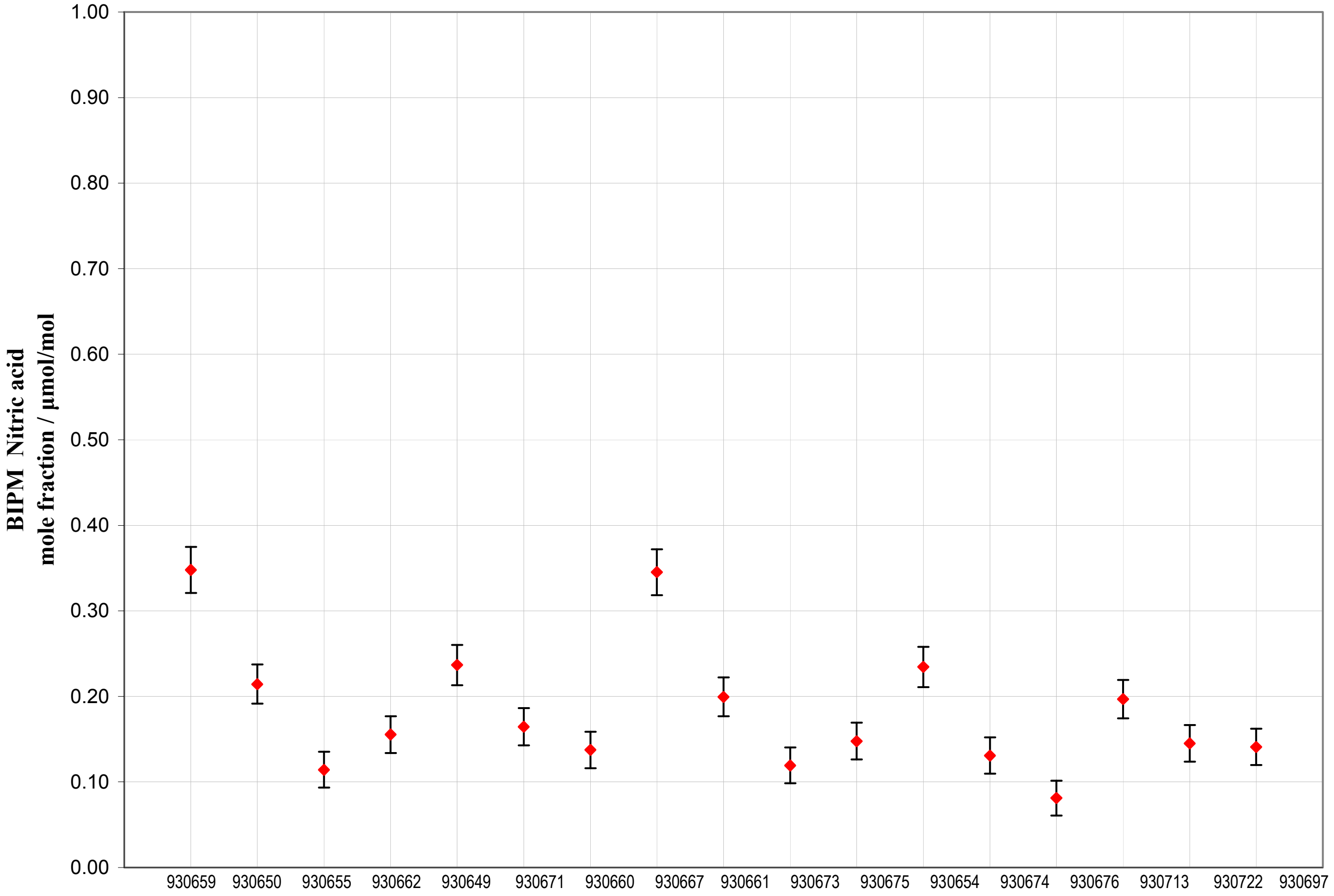

Figure 5. First series of nitric acid mole fraction measurements by the BIPM, prior to sending standards to participating laboratories. The error bar represents the standard uncertainty (*k*=1) associated with the FT-IR measurements.

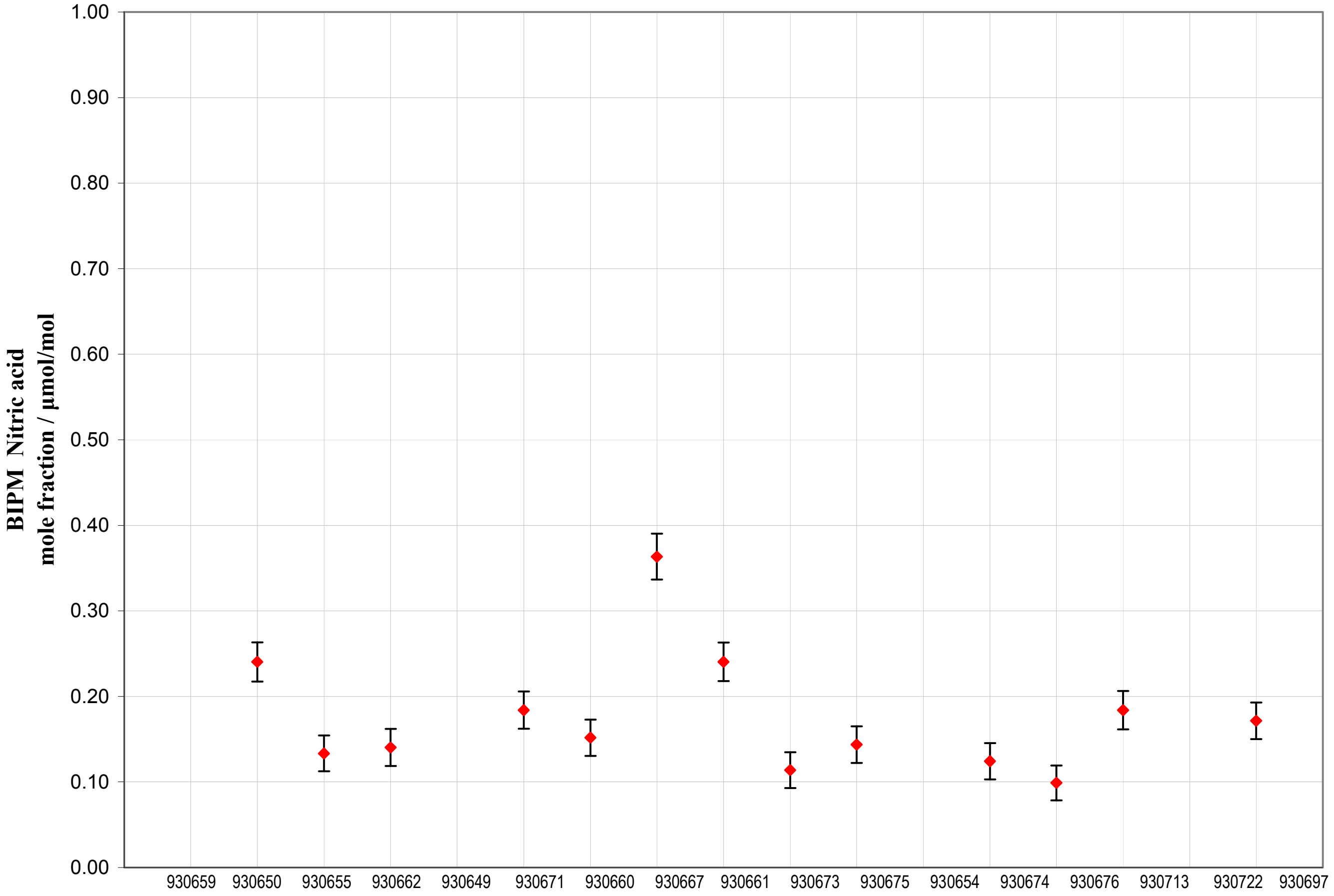

Figure 6. Second series of nitric acid mole fraction measurements by the BIPM, after return of standards from participating laboratories. The error bar represents the standard uncertainty (*k*=1) associated with the FT-IR measurements.

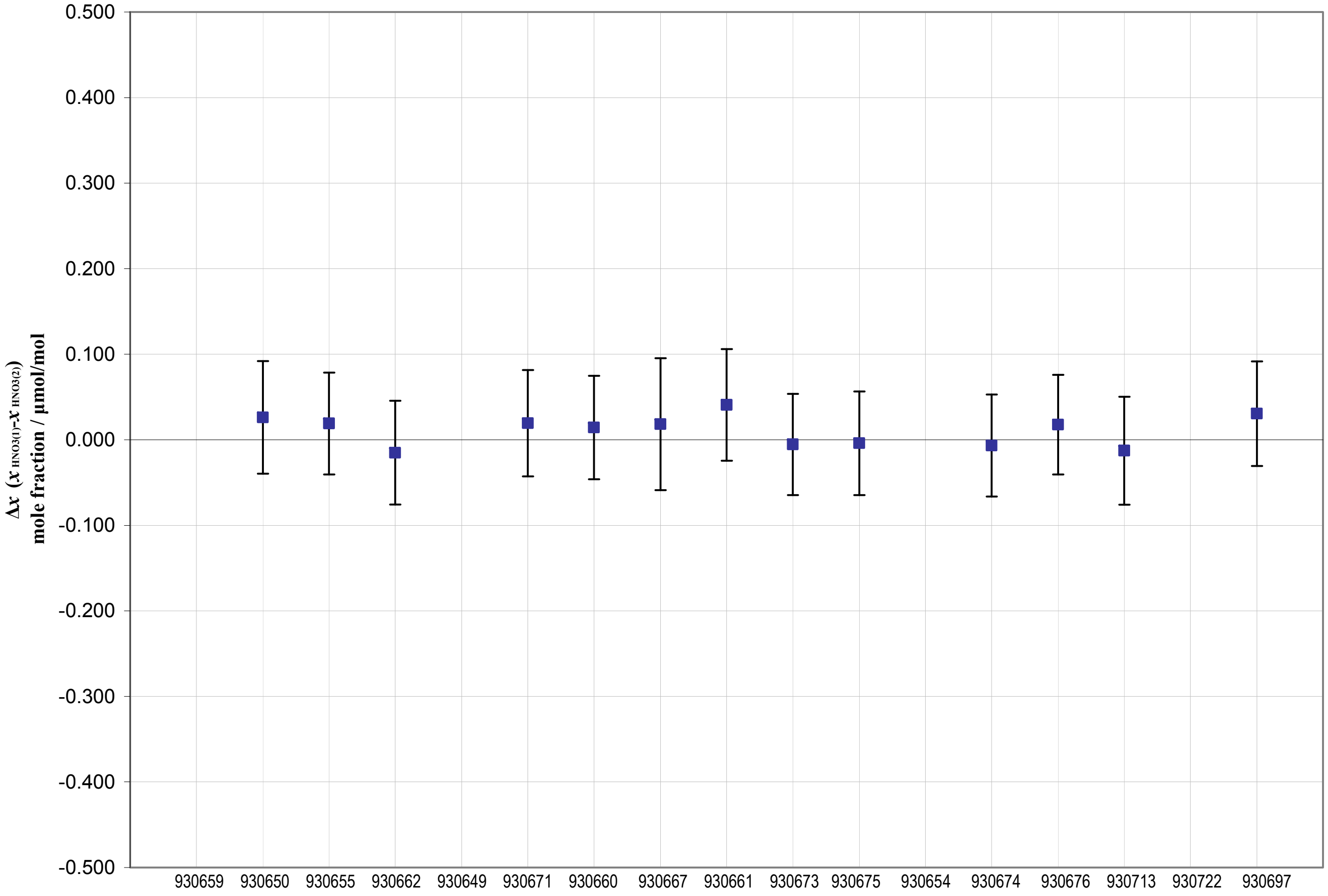

Figure 7. Difference between the first and second series of nitric acid mole fraction measurements by the BIPM. The error bar represents the expanded uncertainty at a 95 % level of confidence.

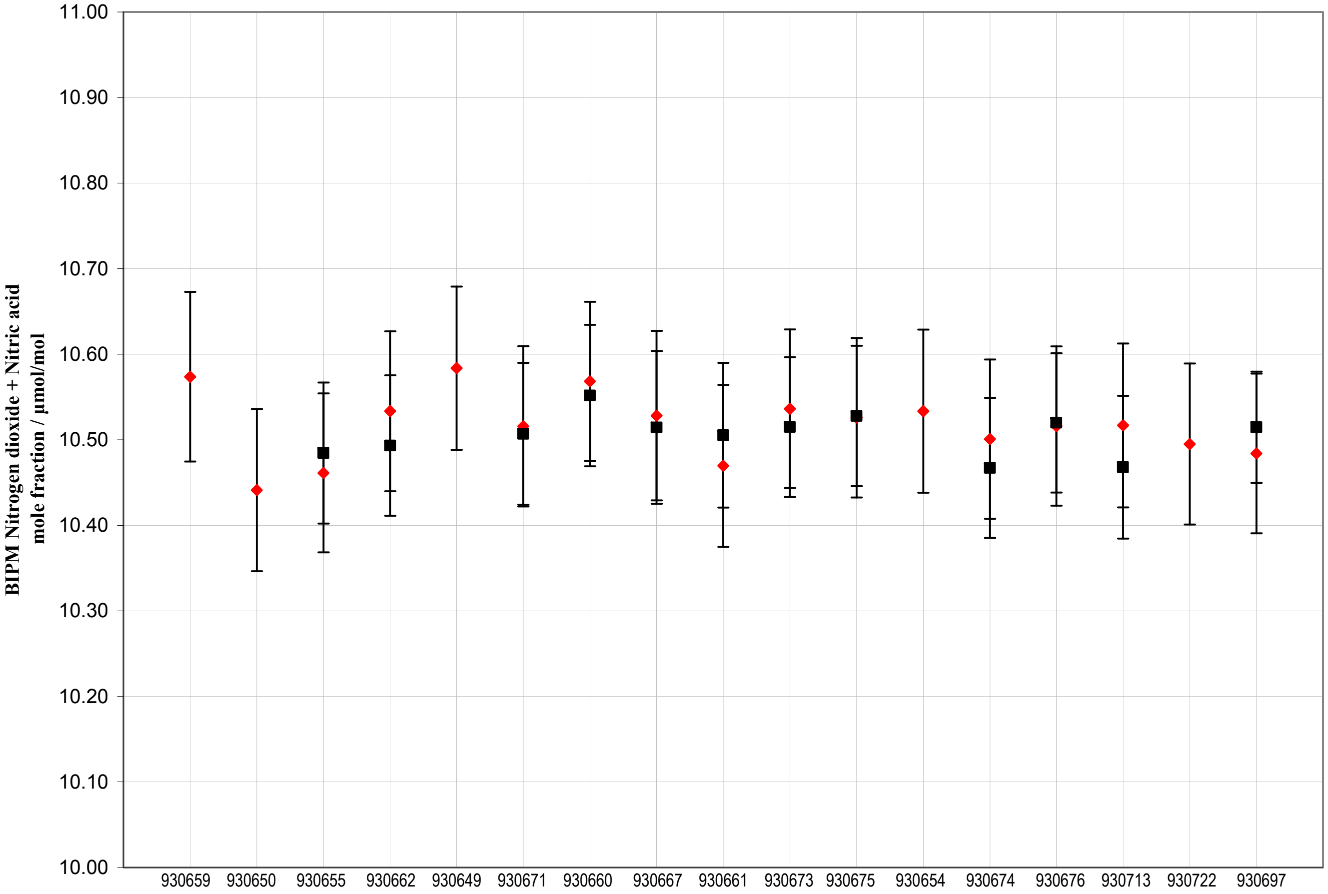

Figure 8. Summation of nitrogen dioxide and nitric acid mole fractions in each standard based on BIPM measurements. Red: First measurements. Black: Second measurements. The error bar represents the expanded uncertainty at a 95 % level of confidence.

5. Reference Values for Cylinders

During the 24th and 25th meetings of the CCQM GAWG it was agreed that the key comparison reference value for CCQM-K74 was to be based on BIPM measurement results prior to distribution of gas standards to participants. The BIPM's measurements clearly indicate the presence of nitric acid in the gas mixtures ranging from 100 nmol/mol to 350 nmol/mol. The gravimetric preparation values provided by VSL were not used as reference values for the comparison of nitrogen dioxide as these do not account for the presence of nitric acid in the standards, arising from the conversion of NO_2 to nitric acid through the reaction with oxygen and residual water in the cylinders. The current hypothesis is that the water must have been present on the cylinder coatings. In the current version of the report, laboratory results are compared to BIPM values, since they correctly account for the presence of nitric acid in the gas mixtures. Furthermore, the agreement between the summation of nitric acid and nitrogen dioxide mole fractions with the initial amount of nitrogen dioxide (prior to any reaction) expected from static gravimetric preparation values further confirms the hypothesis of the loss mechanism of NO_2 in the cylinders.
For each cylinder, the Key Comparison Reference Value is the NO_2 mole fraction assigned by the BIPM (first measurement).

Following the CCQM GAWG guidance, it was decided that the standard uncertainty of the Key Comparison Reference Value (KCRV) was to be calculated from the following equation

$$u_{\mathrm{KCRV}}(x_{\mathrm{NO_2}}) = \sqrt{\left(u(x_{\mathrm{BIPM}})\right)^2 + \left(u(x_{\mathrm{NO_2Losses}})\right)^2 + \left(u(x_{\mathrm{NO_2Drift}})\right)^2} \qquad (1)$$

where $u(x_{\mathrm{BIPM}})$ is the uncertainty associated with the value assigned by the BIPM, $u\left(x_{\mathrm{NO_2Lossess}}\right)$ the uncertainty contribution due to NO_2 losses equivalent to 5.7 nmol/mol and $u(x_{\mathrm{NO_2Drift}})$ the uncertainty contribution due to observed drift of NO_2 estimated to be 21 nmol/mol. This leads to an overall standard uncertainty of the KCRV of 0.041 µmol/mol. A full discussion of the uncertainty of the KCRV is included in Annex 2 of this report.

6. Measurement protocol

The measurement protocol requested participants to provide the value and uncertainty of the nitrogen dioxide mole fraction measured by the laboratory, a complete uncertainty budget and a description of their gas analysis procedure. The procedure employed for the gas analysis was the responsibility of the participating laboratory. (See ANNEX 3 - Measurement reports of participants).

7. Measurement methods

The measurement methods and calibration methods used by the participating organizations in this comparison are listed in Table 6.

Laboratory	Measurement method	Calibration method	Traceability
BIPM	FT-IR, UV	GLS, linear, Bracketing, Permeation-dynamic mixtures	own permeation tube system
NMIA	FT-IR	Bracketing (8-12) µmol/mol	own gravimetric standards
BAM	FT-IR	2 mixtures	own gravimetric standards
NIM	FT-IR , Chemiluminescence	5 mixtures	own gravimetric standards
NPL	UV	1 mixtures	own gravimetric standards
VSL	UV	4 mixtures	own gravimetric standards
CEM	Chemiluminescence	GLS, linear, 3 mixtures	NPL
CERI	Chemiluminescence	Bracketing, 2 mixtures	own gravimetric standards
FMI	Chemiluminescence	GPT , 1 mixture	NPL
INRIM	Chemiluminescence	GLS, linear, 3 mixtures	own gravimetric standards
KRISS	Chemiluminescence	6 mixtures	own gravimetric standards
LNE	Chemiluminescence	Permeation-dynamic mixtures	own permeation tube system
METAS	Chemiluminescence	Permeation-dynamic mixtures	own permeation tube system
NIST	Chemiluminescence	6 mixtures	own gravimetric standards
NMISA	Chemiluminescence	Bracketing (10-100) µmol/mol	own gravimetric standards
SMU	Chemiluminescence	5 mixtures	own gravimetric standards
VNIIM	Chemiluminescence	2 mixtures	own gravimetric standards

Table 6. Measurement and calibration methods used by participating laboratories.

8. Results

The reported nitrogen dioxide mole fractions by participating laboratories are shown in Figure 9. The evaluation of the level of consistency between the participating laboratories was performed by comparison with the BIPM measurements (1st series, the x_{KCRV}) for each cylinder. This decision was taken due to the systematic difference found between the values based on static gravimetric preparation (Table 1) and the BIPM measurements, caused by the presence of nitric acid in the cylinders (Table 2).

The permeation of nitric acid from NO_2 permeation tubes was detected and quantified by the BIPM, and the BIPM's values are corrected to avoid systematic errors caused by this issue. This is fully described in ANNEX 1- BIPM Value assignment procedure.

The consistency between the participating laboratory's results and the Key Comparison Reference Value (the first BIPM value), is presented in terms of a degree of equivalence (*D*) expressed quantitatively in two terms: its deviation from the KCRV value and the uncertainty of this deviation (at 95 % level of confidence).

The degree of equivalence is defined as:

$$D = x_{NMI} - x_{KCRV} \qquad (2)$$

where x_{NMI} denotes the amount of substance fraction as measured by the participating National Metrology Institute (NMI) and x_{KCRV} the reference value given by the BIPM.

The uncertainty in the reference value, x_{KCRV}, is given by the following expression:

$$u_{KCRV}(x_{NO2}) = \sqrt{u(x_{BIPM})^2 + u(x_{NO2Losses})^2 + u(x_{NO2Drift})^2} \qquad (3)$$

where $u(x_{\mathrm{BIPM}})$ is the uncertainty associated with the value assigned by the BIPM following the procedure described in ANNEX 1- BIPM Value assignment procedure and $u(x_{\mathrm{NO_2Lossess}})$ and $u(x_{\mathrm{NO_2Drift}})$ the uncertainty contributions due to NO_2 losses and the observed drift in NO_2 detailed in ANNEX 2- Report of Proposed *u(KCRV)* for the Draft B report of CCQM-K74: Nitrogen dioxide, 10 µmol/mol.

The combined standard uncertainty associated with the deviation from the KCRV can be expressed as:

$$u(D) = \sqrt{u_{NMI}^2 + u_{KCRV}^2} \qquad (4)$$

and the expanded uncertainty, at 95 % confidence level

$$U(D) = k \cdot u(D) \qquad (5)$$

where *k* denotes the coverage factor, taken as $k = 2$ (normal distribution, approximately 95 % level of confidence).

The degrees of equivalence are listed in Table 7 where:

Laboratory	is the acronym of the participating national metrology institute;
Cylinder	the identification code of the cylinder received by the participating laboratory;
x_{KCRV}	the assigned amount of substance fraction of a component by the BIPM (1st series of BIPM measurement results);
$u(x_{\mathrm{KCRV}})$	the uncertainty of the BIPM measurement result
x_{Lab}	the result as reported by the participating laboratory;

$u(x_{\mathrm{Lab}})$ the standard uncertainty associated with the reported value x_{Lab};

D degree of equivalence calculated as the difference in amount of substance fraction as measured by the laboratory and x_{BIPM} the BIPM value; and

$U(D)$ the expanded uncertainty of the degree of equivalence;

The BIPM's reported result is based on the second analysis of a cylinder (#930697-PRM) and compared to the first measurement made on this gas mixture.

The graph of equivalence, based on the difference in nitrogen dioxide reported values by participating laboratories and key comparison reference value, is plotted in Figure 10.

9. Conclusion

The results of the comparison indicate consistency of the majority of measurement results within limits of ± 3 %. This can be compared to a relative standard uncertainty in the key comparison reference value of 0.4 %. The results of only one laboratory lie significantly outside these limits. Its results were based on calibration with nitrogen monoxide and gas phase titration, rather than with statically or dynamically prepared nitrogen dioxide mixtures, as was the case for all other participants.
A full interpretation of the results of the comparison needs to take into account the presence of nitric acid (in the range 100 nmol/mol to 350 nmol/mol) in the cylinders circulated as part of the comparison, as well as the possible presence of nitric acid in the primary standards used by participating laboratories. Furthermore, a number of measurement techniques may not differentiate between nitric acid and nitrogen dioxide. This can occur when using chemiluminescence instrumentation, in which the thermal conversion of nitrogen species to nitrogen monoxide will convert all reactive nitrogen species, nitrogen dioxide as well as nitric acid, into nitrogen monoxide.

The BIPM's FT-IR measurements and dynamic system for the generation of standard gas mixtures has allowed both nitrogen dioxide and nitric acid mole fractions to be quantified, and confirmed by UV absorption measurements, in both the transfer cylinders and permeation tube systems, and were used as the key comparison reference value in the comparison.

10. 'How far the light shines' statement

The following ' How far the light shines' statement is proposed:

The results of this key comparison can be used to support CMC claims for analytical capabilities for NO_2 in nitrogen and synthetic air mixtures in the range 10 µmol/mol to 1000 µmol/mol.

	BIPM			Participants				
Laboratory	Cylinder	x_{KCRV}	$u(x_{\text{KCRV}})$	x_{Lab}	$u(x_{\text{Lab}})$	$D(x_{\text{Lab-}}\ x_{\text{KCRV}})$	$u(D)$	$U(D)$ *(k=2)*
NPL	#930659-PRM	10.226	0.042	10.331	0.040	0.105	0.058	0.115
NIM	#930650-PRM	10.227	0.042	10.150	0.050	−0.077	0.065	0.130
SMU	#930655-PRM	10.347	0.042	10.100	0.060	−0.247	0.073	0.146
NMIA	#930662-PRM	10.378	0.042	10.740	0.315	0.362	0.318	0.635
NMISA	#930649-PRM	10.347	0.042	10.690	0.185	0.343	0.190	0.379
CERI	#930671-PRM	10.351	0.041	10.400	0.190	0.049	0.194	0.389
METAS	#930660-PRM	10.431	0.041	10.630	0.080	0.199	0.090	0.180
INRIM	#930667-PRM	10.183	0.042	9.990	0.100	−0.193	0.108	0.217
KRISS	#930661-PRM	10.270	0.042	10.450	0.155	0.180	0.160	0.321
FMI	#930673-PRM	10.417	0.041	9.880	0.150	−0.537	0.156	0.311
LNE	#930675-PRM	10.378	0.041	10.260	0.065	−0.118	0.077	0.154
NIST	#930654-PRM	10.299	0.041	10.280	0.050	−0.019	0.065	0.130
VSL	#930674-PRM	10.370	0.041	10.510	0.105	0.140	0.113	0.226
CEM	#930676-PRM	10.435	0.042	10.720	0.110	0.285	0.118	0.235
VNIIM	#930713-PRM	10.320	0.042	10.550	0.080	0.230	0.090	0.181
BAM	#930722-PRM	10.350	0.042	10.530	0.375	0.180	0.377	0.755
BIPM	#930697-PRM	10.343	0.041	10.343	0.024	0.000	0.048	0.096

Table 7. Laboratory results for nitrogen dioxide measurements (µmol/mol).

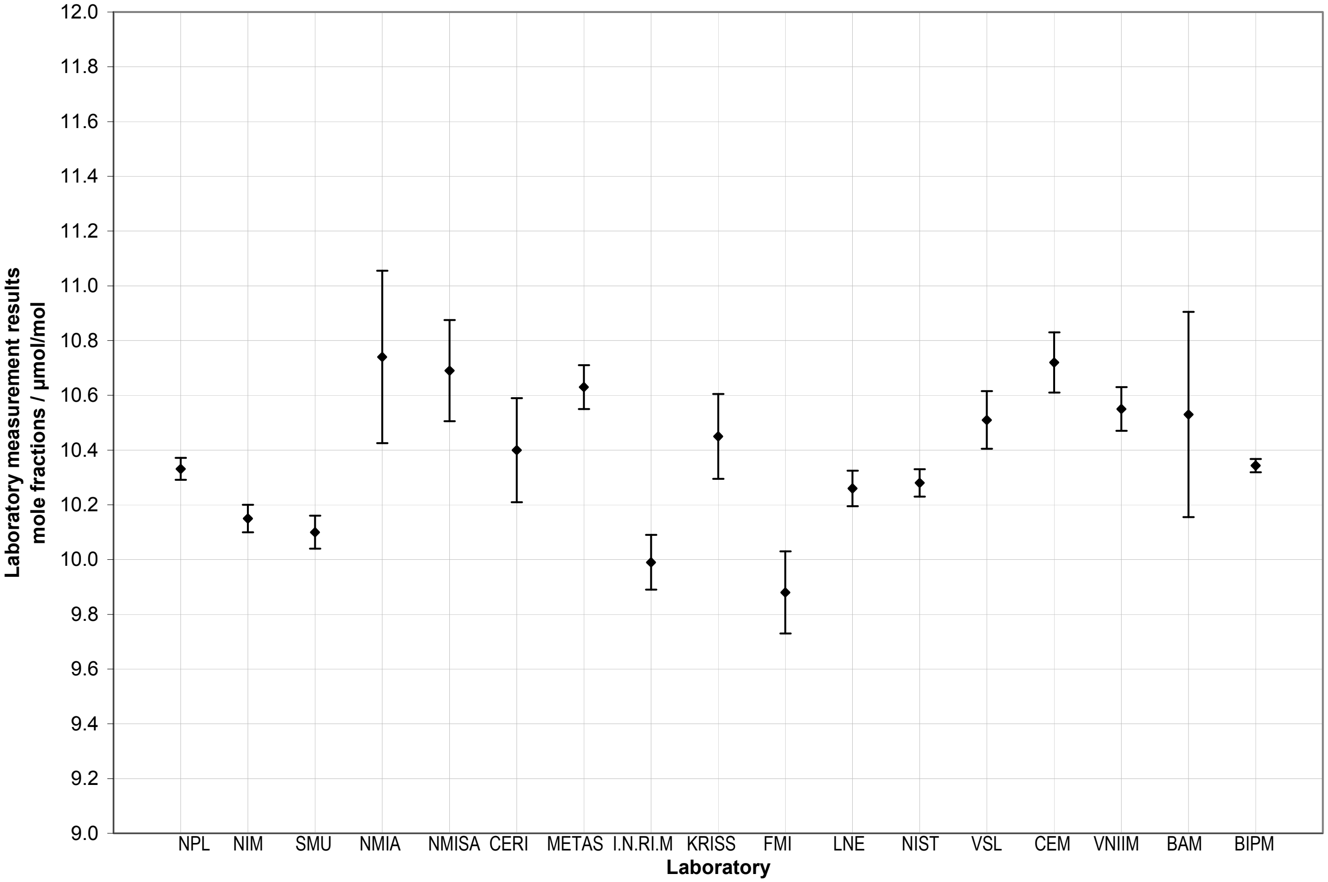

Figure 9. Nitrogen dioxide mole fractions as reported by the participating laboratories. The error bar represents the standard uncertainties reported by participants.

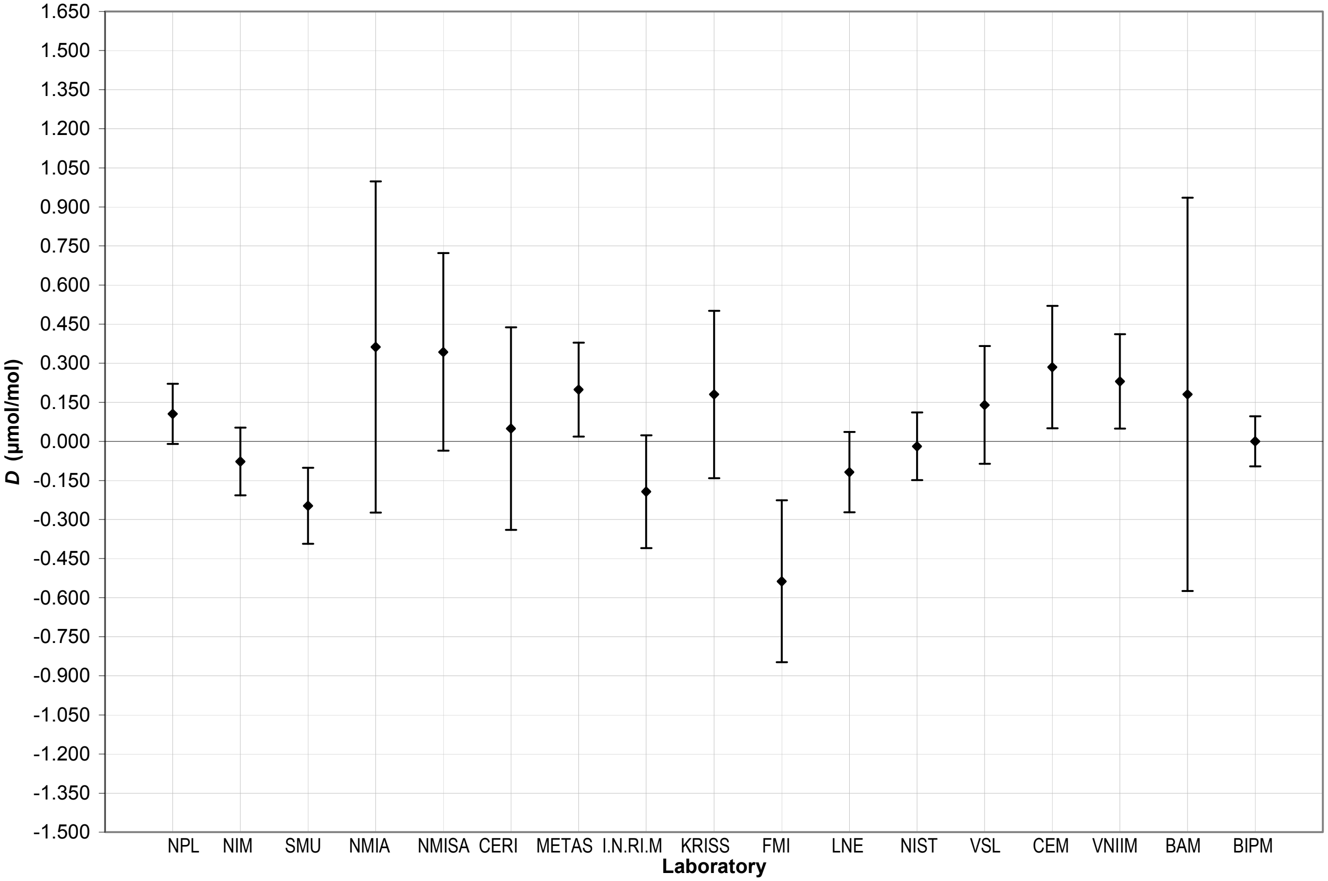

Figure 10**.** Difference between participants' results and the KCRV values for nitrogen dioxide mole fractions. The error bar represents the expanded uncertainty at a 95 % level of confidence.

ANNEX 1- BIPM Value assignment procedure

1. Description of the facility

The BIPM-NO_2 primary gas facility combines gravimetry with dynamic generation of gas mixtures. The facility includes a magnetic suspension balance, a flow control system for the dynamic generation of gas mixtures and a flow control system for nitrogen dioxide gas standards in cylinders. Both the gas cylinder and dynamic sources of NO_2 mixtures are ultimately connected to a continuous gas analyser ABB Limas 11 (AO2020), and to the spectrometer FT-IR Thermo-Nicolet Nexus (See *Figure 11*).

The operation and automation of the ensemble of instruments (NO_2 FT-IR facility-ABB Limas 11-FT-IR) is achieved through a LabView® programme developed by members of the BIPM Chemistry Department. Through a graphical user interface the programme facilitates the setting and monitoring of all relevant instrumental parameters, automated control of complex procedures, the recording of mass measurements and NO_2 analyser readings and related data and the graphical real-time display of many of the instrument readings.

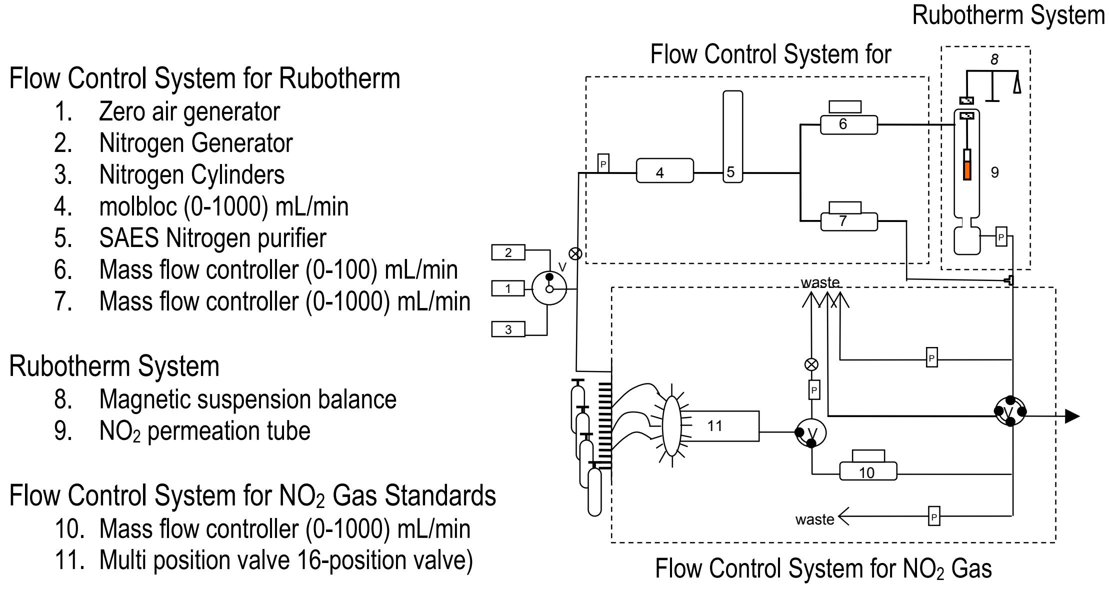

Figure 11: Schematic of the BIPM NO_2 facility

The magnetic suspension balance.

The magnetic suspension balance (MSB; Rubotherm, Germany) is central to the system. An electromagnet is suspended from the base of the weighing pan. Below this electromagnet there is a long vertical glass vessel; the measurement cell of the MSB. At the top of the glass vessel there is a permanent magnet which is held in place by the electromagnet attached to the balance.

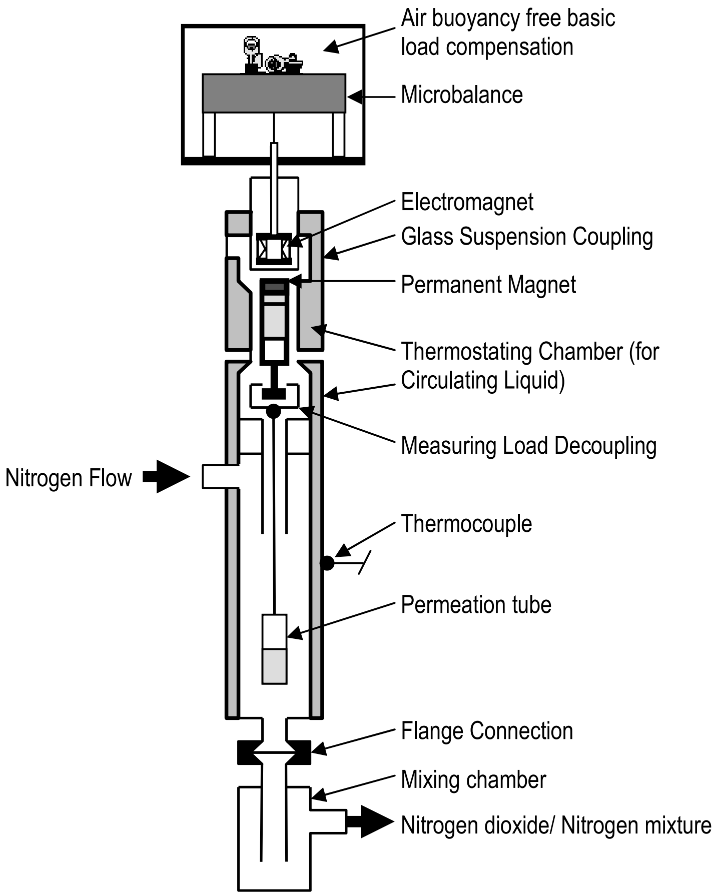

Figure 12: Schematic of the BIPM NO_2 facility permeation tube chamber and magnetic suspension balance.

The position of the permanent magnet is detected electronically and maintained by servo-control of the current of the electromagnet. An NO_2 permeation tube is suspended from the permanent magnet. Thus, the balance measures the mass of the permeation tube without being mechanically in contact with it, since the balance and the weighing load are separated by a layer of glass. The coupling between the permeation tube and the balance is purely magnetic and the sensitive balance is protected from the highly corrosive NO_2 gas and the occasionally elevated temperatures and gas flows surrounding the permeation tube. This facilitates continuous monitoring of the mass loss of the permeation tube, which is located in a temperature controlled environment by means of a double glass-walled jacket containing water circulating at a constant temperature, controlled by a remote thermostat. At constant temperature, the tube emits NO_2 through its permeable fluoropolymer membrane at a constant rate. The balance is a high-resolution comparator (model AT20, Mettler, USA) with a range of 0 g to 22 g and 2 µg resolution. The balance is configured with two mass pieces (see *Figure 12*) which are used to perform an external calibration of the balance. The term external calibration is used to distinguish it from the internal calibration of the balance performed with stainless steel mass standards. The two external calibration mass pieces have nominally the same volume but different mass, as one is made of titanium (Ti) and the other of stainless steel (SS). Briefly, the external calibration mass pieces are used to correct for an effect on the mass measurements arising from changes in the density of the ambient atmosphere surrounding the balance itself. Since it was important to know the mass difference of the Ti and SS pieces with a small uncertainty, the mass and volume of the pieces were calibrated in collaboration with the BIPM Mass Department.

The flow control system for the magnetic suspension balance

To generate primary mixtures using the MSB, a well characterized flow of NO_2-free gas (nitrogen) is required. Once the flow control system receives a pre-selected gas it delivers two well characterized flows to the balance.

The total gas flow is characterized by means of a molbloc®/molbox® facility[2], which was calibrated at the LNE. An electronic digital pressure controller is used to maintain the pressure of the incoming gas entering the molbloc at about 2700 hPa, the optimal pressure to minimize the uncertainty of the molbloc flow measurement (~0.1 %).

The gas flow is then introduced into a gas purifier that removes the remaining water and oxygen that may leak into the gas. The gas flow is then divided into two streams, a carrier and a diluent, both regulated by two mass flow controllers (MFCs).

The flow of the carrier stream is set at a constant value, 100 $mL{\cdot}min^{-1}$, mixing with the NO_2 emerging at constant rate from the permeation tube. The pressure conditions of the permeation chamber are controlled by an electronic digital pressure device to avoid any buoyancy variation.

The gas mixture of the carrier line is then diluted by a larger flow, the diluent stream, varied within the range 0.3 $L{\cdot}min^{-1}$ to 5 $L{\cdot}min^{-1}$ in order to dynamically generate primary NO_2 mixtures in nitrogen (or air) at various concentrations in the range 1 $\mu mol{\cdot}mol^{-1}$ to 15 $\mu mol{\cdot}mol^{-1}$.

Permeation tubes with permeation rates in the range 5000 $ng{\cdot}min^{-1}$ to 10 000 $ng{\cdot}min^{-1}$ are used for this purpose.

The flow control system for NO_2 gas standards

The third module, namely the flow control system for NO_2 gas standards, enables comparison between the dynamically generated gas mixtures and cylinder standards of NO_2 in nitrogen contained in high pressure cylinders (and, alternatively, comparison between various cylinder mixtures). This comparison is achieved via the response of the NO_2 analyser, whether ABB Limas 11 or FT-IR. The continuous gas analyser ABB Limas 11 (part of the AO2020 series) operates according to the NDUV (Non Dispersive Ultraviolet Absorption) measurement principle. The measuring effect is specific radiation absorption of the measured gas component in the UV spectra region to detect NO_2. The FT-IR analyser is a Thermo Nicolet Nexus model enclosed in an isolation box, as described in Section 6.1.

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[2] A molbox® facility is a support unit for making gas flow measurements using molbloc mass flow elements. The molbox® hardware reads calibration data off the molbloc® facility and measures molbloc® upstream and downstream pressure using built-in high precision Reference Pressure Transducers (RPTs). The key molbloc®L measurement is the differential pressure across the element, which is roughly proportional to the mass flow rate through it. The molbloc® elements are calibrated to be used at an absolute pressure which remains nearly constant, while the differential pressure varies with flow rate.

The flow control system enables the sequential sampling of up to 15 standards contained in cylinders by means of a 16 position valve (MPV-16). V2 is a 4-port 2-position valve. It is used to select which sample stream, from either the MSB or from a cylinder, is directed to the analysers, the other stream being directed to waste, without perturbing the flow of either stream.

2. Measurement protocol of the BIPM

On receipt by the BIPM, all cylinders were allowed to equilibrate at laboratory temperature for one week. All cylinders were rolled for 60 minutes to ensure homogeneity of the mixture.

Each cylinder was connected to one inlet of a 16-inlet automatic gas sampler connected to the FT-IR spectrometer and to the BIPM NO_2 dynamic generation facility.

The pressure reducers of each cylinder were flushed nine times with the mixture. The cylinder valves were then closed leaving the high pressure side of the pressure reducer at the cylinder pressure and the low pressure side of the pressure reducer at ~300 kPa. The cylinders were left to stand for at least 24 hours, to allow conditioning of the pressure reducers.

Immediately prior to an analysis, each cylinder valve was opened again and the pressure reducer flushed three times. The suite of cylinders was analysed sequentially.

For the FT-IR spectra acquisition, 120 scans were co-added over a period of 2 minutes to provide one single beam spectrum of a sample. This single beam spectrum was then ratioed with a similar spectrum of ultra-pure nitrogen collected under similar conditions to provide an absorbance spectrum of the gas sample (relative to ultra-pure nitrogen).

For each analyser, a calibration line was evaluated using the Generalized Least Squares approach described by ISO 6143:2001[3].

The assigned BIPM nitrogen dioxide value was then equal to the predicted value from a calibration line calculated from a set of dynamic nitrogen dioxide primary gas mixtures obtained from the BIPM Nitrogen Dioxide (NO_2) Primary Facility.

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[3] ISO 6143:2001: Gas analysis- Comparison methods for determining and checking the composition of calibration gas mixtures.

3. BIPM measurement uncertainties and analyser response

The mole fractions of the dynamically produced gas mixtures obtained with the BIPM facility were calculated by the expression below:

$$x_{\mathrm{NO_2}} = \left(\frac{P \times V_{\mathrm{m}}}{q_v \times M_{\mathrm{NO_2}}} \right) - \left(\frac{M_{\mathrm{HNO_3}} \times x_{\mathrm{HNO_3}}}{M_{\mathrm{NO_2}}} \right) - \sum \left(\frac{M_{\mathrm{imp}} \times x_{\mathrm{imp}}}{M_{\mathrm{NO_2}}} \right) \qquad (6)$$

where:

$x_{\mathrm{NO_2}}$ is the NO_2 mole fraction in µmol·mol^{-1};

P is the NO_2 permeation rate in ng·min^{-1};

V_{m} = 22.4038 L·mol^{-1}, is the molar volume of air/N_2 at standard conditions (273.15 K, 101.3 kPa);

$M_{\mathrm{NO_2}}$ = 46.0055 g·mol^{-1}, is the molar mass of NO_2;

q_v is the total flow of N_2 given by the molbloc®/molbox® facility;

x_{HNO3} is the HNO_3 mole fraction in µmol/mol measured by FT-IR spectroscopy;

$M_{\mathrm{HNO_3}}$ = 60.005 g.mol^{-1} is the molar mass of HNO_3;

x_{imp} are the mole fractions in µmol/mol of other impurities measured by FT-IR Spectroscopy; and

M_{imp} are the molar mass of the impurities;

Applying the uncertainty propagation law and assuming no correlation between the input quantities, the following uncertainty expression was developed:

$$u^2(x_{\mathrm{NO_2}}) = \left(\frac{\partial x_{\mathrm{NO_2}}}{\partial P} \right)^2 \times u^2(P) + \left(\frac{\partial x_{\mathrm{NO_2}}}{\partial V_{\mathrm{m}}} \right)^2 \times u^2(V_{\mathrm{m}}) + \left(\frac{\partial x_{\mathrm{NO_2}}}{\partial M_{\mathrm{NO_2}}} \right)^2 \times u^2(M_{\mathrm{NO_2}}) + \left(\frac{\partial x_{\mathrm{NO_2}}}{\partial q_v} \right)^2 \times u^2(F) +$$
$$\left(\frac{\partial x_{\mathrm{NO_2}}}{\partial x_{HNO3}} \right)^2 \times u^2(x_{HNO_3}) + \left(\frac{\partial x_{\mathrm{NO_2}}}{\partial M_{HNO3}} \right)^2 \times u^2(M_{HNO_3}) + \left(\frac{\partial x_{\mathrm{NO_2}}}{\partial x_{imp}} \right)^2 \times u^2(x_{imp}) + \left(\frac{\partial x_{\mathrm{NO_2}}}{\partial M_{imp}} \right)^2 \times u^2(M_{imp}) \qquad (7)$$

The permeation standard uncertainty, considering a permeation device with a permeation rate equivalent to $P \approx$ 8357 ng·min^{-1}, was estimated to be $u(P) \approx$ 4.18 ng·min^{-1}, assuming a rectangular distribution of the probability that P lies within the interval 8357 ± 6.17 ng·min^{-1}.

The uncertainty in the NO_2 molar mass of 0.00047 g·mol^{-1}, 0.001 % relative, can be derived from the IUPAC Table of Atomic Weights.

The molar volume V_{m} of a real gas at standard conditions (T = 273.15 K, p = 101.325 kPa) is given by the formula

$$V_m = \frac{ZRT}{p} \qquad (8)$$

where Z is the compressibility factor and R is the gas constant, 8.314 472 J·mol^{-1}·K^{-1}, with a relative uncertainty $u(R)$ of 1.8×10^{-6}. Since they are defined by convention there is no uncertainty in T and p.

The compressibility factor of nitrogen obtained from the NIST Refprop database is Z_{N2} = 0.9995434 with a relative uncertainty $u(Z)$ of 15×10^{-6}.

Thus the molar volume of nitrogen and its standard uncertainty are

V_{mN2} = 22.4037 L·mol^{-1}

$u(V_{\mathrm{mN2}})$ = 0.0003 L·mol^{-1}, or 1.5×10^{-5} relative.

The BIPM measured the flow in its system by using molblocs. These were calibrated by the LNE on 27 April 2009. The uncertainty of the BIPM's flow measurements is dominated by on the calibration uncertainty. The uncertainty in the flow measurements $u(q_v)$ was taken from the LNE calibration certificate N° K20869/1. No additional component for the stability of the flow instrument was added, since the time between calibration and the first measurements were short, and no significant deviation between the first and second series of BIPM measurement results was observed for stable cylinder gas standards. The expanded relative uncertainty (k = 2) quoted in the calibration certificate is 0.2 % at the flows used in the comparison. In correspondence between the BIPM and the LNE, the LNE confirmed[4] the relative expanded uncertainties quoted in their CMCs, comparison results and the calibration certificates to be as follows:

- 0.22 % to 0.40 % in LNE's CMCs
- 0.19 % to 0.26 % in the Euramet (1)
- 0.18 % to 0.27 % in the Calibration Certificate K20869/1.

The uncertainty in the calculated nitric acid mole fraction, x_{HNO3}, obtained by FT-IR spectroscopy, is given by:

$$u(x_{HNO3}) \approx \sqrt{(0.02)^2 + (0.015x)^2 + (0.05x)^2} \qquad (9)$$

where x is the mole fraction of nitric acid predicted by FT-IR in the gas mixtures. A future publication will give a detailed description of the measuring methodology and quantification process by FT-IR for the determination of nitric acid.

As for NO_2, the uncertainty in nitric acid molar mass, 0.000561 g·mol^{-1} (0.0009 % relative), was derived from the IUPAC Table of Atomic Weights.

It follows that the uncertainty budget for a NO_2 mixture having a nominal concentration of ~10.0 µmol·mol^{-1} is as tabulated below in Table 8 using nitrogen as diluent gas:

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[4] Private communication with Jean Barbe from LNE.

Quantity x_i	Estimate	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient $c_i=\partial x_{NO2}/\partial x$	Uncertainty contribution $u_i(y)$ mol·mol^{-1}	Index %
P	8.3573 10^{-6}·g·min^{-1}	Normal	4.18 10^{-9}·g·min^{-1}	1.1	4.5 10^{-9}	2.2
V_m	22.4038 L·mol^{-1}	Normal	340.00 10^{-6} L·mol^{-1}	400 10^{-9}	140 10^{-12}	0.0
$q_{v\ molbloc1}$	452 10^{-3}·L·min^{-1}	Normal	455.21 10^{-6} L·min^{-1}	−20 10^{-6}	−9.1 10^{-9}	8.8
M_{NO2}	46.0055 g·mol^{-1}	Normal	1.40 10^{-3} g·mol^{-1}	−190 10^{-9}	−270 10^{-12}	0.0
x_{HNO3}	0.104 10^{-6}mol·mol^{-1}	Normal	0.021 10^{-6}·mol·mol^{-1}	−1.4	−29 10^{-9}	88.5
x_{N2O4}	0 mol·mol^{-1}	Normal	866 10^{-12}·mol·mol^{-1}	−2.0	−1.7 10^{-9}	0.3
x_{N2O3}	0 mol·mol^{-1}	Normal	307 10^{-12}·mol·mol^{-1}	−1.7	−510 10^{-12}	0.0
x_{N2O5}	0 mol·mol^{-1}	Normal	361 10^{-12}·mol·mol^{-1}	−2.3	−850 10^{-12}	0.0
x_{HONO}	0 mol·mol^{-1}	Normal	520 10^{-12}·mol·mol^{-1}	−1.0	−530 10^{-12}	0.0
x_{HO2NO2}	0 mol·mol^{-1}	Normal	572 10^{-12}·mol·mol^{-1}	1.7	−980 10^{-12}	0.1
M_{HNO3}	63.013 g·mol^{-1}	Normal	1.17 10^{-3} g·mol^{-1}	−2.3 10^{-9}	−2.6 10^{-12}	0.0

Quantity	Value	Standard Uncertainty
x_{NO2}	8.86 µmol·mol^{-1}	30 nmol·mol^{-1}

Table 8. Uncertainty budget for a NO_2 /N_2 primary mixture generated with the BIPM facility.
Note: the molar masses M_{N2O4}, M_{N2O3}, M_{N2O5}, M_{HONO}, M_{HO2NO2} were not included in this budget as they represent negligible uncertainty contributions.

The degrees of freedom were numerous, so a coverage factor $k = 2$ was assumed appropriate for the expanded uncertainty. The main uncertainty contributors remain the mole fraction determination of nitric acid and the gas flow measurements. Figure 13 illustrates the new uncertainties in x_{NO_2} for the dynamic generation of NO_2 in nitrogen mixtures over the mole fraction range 8 µmol/mol to 12 µmol/mol, using a permeation tube with permeation rate of 8357 ng·min^{-1} and flows in the range 350 mL·min^{-1} to 450 mL·min^{-1}. The uncertainty is almost a constant and can be fitted by a linear function of the mole fraction. A least squares fit was made using the Excel LINEST function. The standard uncertainties in x_{NO_2} can be modelled by the following linear function (numerical values in µmol/mol):

$$u(x_{\mathrm{NO_2}}) = 0.001036x + 0.020818 \tag{10}$$

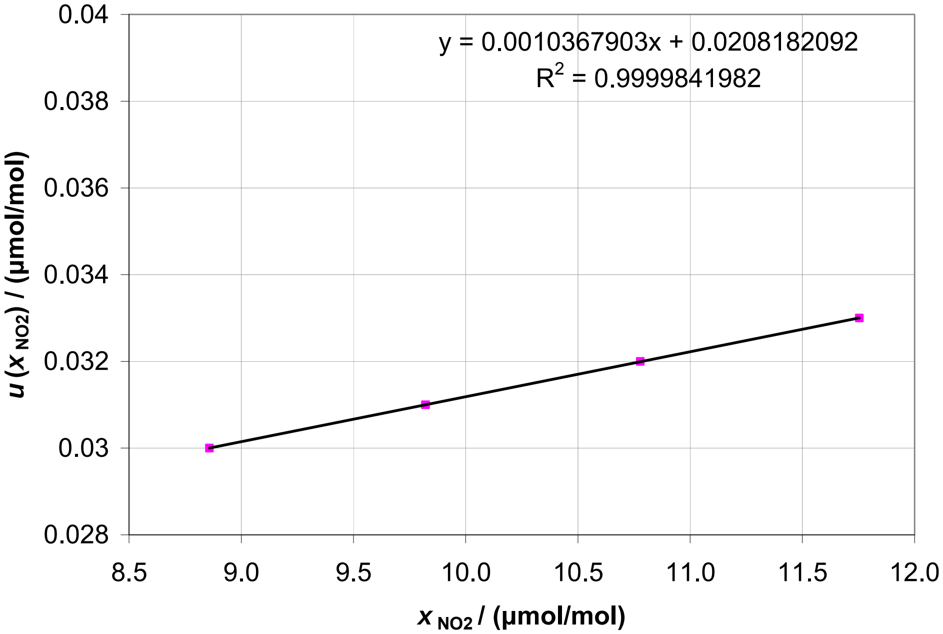

Figure 13. Standard uncertainty of dynamically generated NO_2 mixtures on the BIPM NO_2 facility over a range of x_{NO_2} = (8-12) µmol/mol.

4. Covariance between two dynamically generated gas mixtures

Non-zero covariances, $u(x_{\mathrm{NO_2},i}, x_{\mathrm{NO_2},j})$ were included in the uncertainty calculations because all dynamic mixtures were derived from the same BIPM facility and an error in the analyte content of the one gas is considered to propagate to all gas mixtures in a positive correlated fashion. The covariance between two calibration gas mixtures *i* and *j* is described as follows:

$$u(x_{\mathrm{NO_2},i}, x_{\mathrm{NO_2},j}) = \gamma \left[u(x_{\mathrm{NO_2},i}) \right]^2, \tag{11}$$

Where $u(x_{\mathrm{NO_2},i})$ is the standard uncertainty of the more concentrated mixture as given by equation 10,

$$\gamma = {q_j}/{q_i} \tag{12}$$

is the dilution factor of the total gas flows q_j and q_i (with $q_j < q_i$). Note that as the NO_2 calibration gas mixtures generated with the facility are distributed in a small range of mole fractions (typically 8 nmol/mol to 12 nmol/mol), the dilution factor is often close to 1, and the covariances often close to the variances $u(x_{NO2,i})^2$.

5. The Key Comparison Reference Values and their standard uncertainties

For each cylinder, the Key Comparison Reference Value is the NO_2 mole fraction assigned by the BIPM following the calibration procedure described above.

Following the CCQM GAWG guidance, it was decided that the standard uncertainty of the Key Comparison Reference Value (KCRV) can be quantified by the following equation

$$u_{\mathrm{KCRV}}(x_{\mathrm{NO_2}}) = \sqrt{\left(u(x_{\mathrm{BIPM}})\right)^2 + \left(u(x_{\mathrm{NO_2Losses}})\right)^2 + \left(u(x_{\mathrm{NO_2Drift}})\right)^2} \qquad (13)$$

where $u(x_{\mathrm{BIPM}})$ is the uncertainty associated with the value assigned by the BIPM following the procedure described above, $u\left(x_{\mathrm{NO_2Losses}}\right)$ the uncertainty contribution due to NO_2 losses equivalent to 5.7 nmol/mol and $u(x_{\mathrm{NO_2Drift}})$ the uncertainty contribution due to observed drift in NO_2 estimated in 21 nmol/mol. The additional uncertainties described above increase the KCRV uncertainties from about 0.021 µmol/mol (as reported in the draft A report) to about 0.041 µmol/mol.

6. FT-IR analysis of gas standards

Analysis of all gas standards was undertaken to quantify nitric acid within the gas standards, and to compare these with the impurities and their uncertainties reported by the participating laboratories.

6.1 FT-IR Spectra acquisition procedure

A ThemoNicolet Nexus FT-IR spectrometer was configured with a MCT-high D* liquid N_2-cooled mid-infrared detector and a 6.4 m path-length multipass White cell (Gemini Scientific Instruments, USA) for the purposes of quantitative analysis for gas reference standards. The White cell has wetted surfaces of electropolished stainless steel and gold (mirror coatings) to minimize surface interactions with reactive gas phase species. To keep the internal optical path of the spectrometer free of any interference species this ensemble has been placed in stainless steel enclosure which is constantly purged with ultra high purity nitrogen (dewpoint ~−95°C, i.e. ~200 $\mathrm{nmol{\cdot}mol^{-1}}$ H_2O) flowing at ~15 $\mathrm{L{\cdot}min^{-1}}$.

The gas sample, from either the Rubotherm MSB or from a high pressure cylinder, flows from the NO_2 facility sampling manifold through the White cell, and then to waste. The sample flow rate is controlled immediately downstream of the White cell at ~400 $\mathrm{mL{\cdot}min^{-1}}$. The sample pressure and temperature are measured in real time by means of a calibrated barometer (Series 6000 Digital Pressure Transducer, Mensor, USA) and a calibrated 100 Ω RTD temperature probe attached to the White cell.

The spectrometer user interface is by means of the IMACC software. IMACC allows the automatic setting of all instrument parameters into Thermo's proprietary Omnic software for control, spectra acquisition and on-line analysis.

For the acquisition of high quality spectra suitable for quantitative analysis, 120 scans are co-added over a period of 2 minutes to provide one single beam spectrum of a sample. This single beam spectrum was then ratioed with a similar spectrum of ultra-pure nitrogen collected under similar conditions to provide an absorbance spectrum of the gas sample (relative to ultra-pure nitrogen).

The White cell has a volume of ~750 mL and the sample flows at ~400 $\text{mL}\cdot\text{min}^{-1}$. Assuming perfect mixing in the cell we estimate that an initial sample at time $t = 0$ s has been 99.9 % replaced after 10 min of flow, and 99.9999 % replaced after 20 min. Accordingly, to ensure complete exchange of sample, spectrum acquisition started at $t = 0$ but only the measured spectra obtained after flowing the sample through the White cell for 35 min were used for the mole fraction determination. We also empirically verified that after 30 min of flow, the sample was completely exchanged, within the bounds of measurement uncertainty.

The absorbance spectra of gas reference standards obtained following this procedure had a very high signal: noise ratio, with the level of noise in the baseline being typically $\sim 2 \times 10^{-4}$ abs_{10} peak-peak. By comparison the main NO_2 peak had absorbance in the range (0.04–0.16) abs_{10}.

From times series analysis the uncertainty in the response of the FT-IR spectrometer was estimated in 20 nmol/mol for a 2 minutes average time.

6.2 Quantitative analysis of nitric acid

The determination of nitric acid was assessed configuring the FT-IR facility with a multi pass white cell with an optical path of (48±1.2) m. Spectra were analysed by a non-linear least-square fitting of the measured absorption spectra with synthetic spectra using the program NLM4 (Non Linear MALT). NLM4 included the calculation of synthetic spectra from the HITRAN database of infrared absorption line parameters using the core of the program MALT (an acronym for Multiple Atmospheric Layer Transmission) software developed at the University of Wollongong described in detail by Griffith in 1996(2). The program convolved a stick spectrum calculated from the line parameters with the temperature, pressure, path length, resolution and instrument line shape function specified by the user. Spectra were calculated iteratively from an initial estimate of all input parameters following a modified Levenberg-Marquart algorithm until a least squares best fit to the measured spectrum was obtained. Gas concentrations in the sample were iteratively adjusted during the fit. The quality of the fit could be improved by choosing a proper spectra window of the measured spectrum. Spectra which had been acquired across a total wavelength range of 1660 cm^{-1} to1850 cm^{-1} were fitted on spectral windows according to the impurities of interest, in this case nitric acid.

7. Uncertainty budget

Table 9 below summarizes the uncertainty sources and presents the final combined uncertainty associated with the FT-IR/MATL/CLS measurements of nitric acid at a mole fraction (x) ranging from 100 nmol/mol to 250 nmol/mol with a FT-IR white cell with a 48 m optical path.

Type A	µmol/mol
Stability	0.020
Type B	
MALT	$0.015x$
HITRAN	$0.05x$
Combined uncertainty	$\sqrt{(0.02)^2 + (0.015x)^2 + (0.05x)^2}$

Table 9: uncertainty budget associated with the FT-IR spectrometer used as an absolute method of quantification to determine the concentration of HNO_3 in nitrogen.

8. Regression analysis

The procedure outlined in ISO 6143:2001 (Gas analysis-Comparison methods for determining and checking the composition of calibration gas mixtures) was used for the analysis of the data from the comparison. This required:

- the determination of the analysis function $x=G(y)$ which expressed analyte contents in relation to corresponding measured responses;
- the validation of the analysis function; and
- the prediction of the mole fraction values from the measured responses and comparison to BIPM and NMI's values.

9. Determination and validation of analysis functions

All calculations were performed with B_LEAST, a computer program which implemented the methodology of ISO 6143:2001, and takes into consideration uncertainties in both axes for regression analysis.

Validation studies performed by the BIPM to be published shortly will confirm the linearity of the FT-IR response in the x_{NO2} range 4.5 µmol/mol to15.5 µmol/mol.

ANNEX 2- Report of Proposed *u*(KCRV) for the Draft B report of CCQM-K74: Nitrogen dioxide, 10 µmol/mol

Introduction and summary

During the 24th meeting of the CCQM GAWG in November 2010 the BIPM, in its role as coordinating laboratory of the key comparison CCQM-K74, was asked to investigate additional sources of uncertainty in its measurement results which had been proposed as reference values for the key comparison. The additional sources of uncertainty investigated were:

1. impurity analysis uncertainties;
2. reaction of NO_2 to HNO_3 in the BIPM permeation facility;
3. stability of the gas concentration of the transfer standards (cylinders);
4. contributions from flow measurements;

Version 0.1 of this report, which summarized the results of these investigations, was presented during the 25th CCQM GAWG meeting held in April 2011. During the meeting the value reported for the uncertainty of nitric acid concentrations was questioned. Further review of Version 0.1 of the report by the BIPM has confirmed that incorrect values for the nitric acid concentration were used in both Draft A and Version 0.1 of this report due to an error in the application of equation (8) in the Draft A report. This has been corrected in the current version (0.2) of the report, confirming that the major contributions to the uncertainty of the BIPM measurement results arise from the determination of nitric acid concentrations and the stability of gas mixtures in the transfer standards (cylinders). The inclusion of these components increases the standard uncertainty of the BIPM measurement results and by consequence the standard uncertainties of the proposed key comparison reference values from about 0.02 µmol/mol (as reported in Draft A) to about 0.04 µmol/mol.

1. Impurity analysis

The BIPM undertook additional measurements to verify the purity of the gas permeating from the NO_2 permeation tube. This required: identification of the most likely possible impurities; determination of the limits of detection for the impurities; and measurements of high concentration NO_2 mixtures in order to confirm the absence/presence of such impurities, taking into account their limits of detection.

A survey of literature on NO_2 permeation devices was carried out. A publication from 1977 details the results of purity analysis of a NO_2 permeation device (3). Based on this publication, it was concluded that possible impurities permeating from the tube could include: N_2O_4, N_2O_5, HONO, HO_2NO_2, N_2O_3 and N_2O_4. The possibility of detecting such impurities with the BIPM FT-IR facility was evaluated by comparing their integrated line intensities against HNO_3 in three spectral regions 800 cm^{-1}, 1200 cm^{-1} and 1600 cm^{-1} (see Figure 14 and Table 10). The calculated differences in integrated line intensity, which are listed in Table 11, were subsequently used to calculate limits of detection for each potential impurity by using a ratio to the detection limit of HNO_3. The limit of detection for HNO_3 was determined by calculating the standard deviation of the instrument response measuring ~600 nmol/mol of HNO_3 contained in a 120 µmol/mol NO_2/N_2 gas mixture generated with the NO_2 VICI permeation device. The effective limits of detection at nominally 10 µmol/mol were calculated by dividing the calculated detection limits at high concentration by twelve, as this scale directly with the NO_2 concentration (see *Table 12*). Finally, the standard uncertainty of the impurities at low concentration were calculated assuming a rectangular distribution by the following equation $(A/12)/\sqrt{3}$, except for N_2O_4 and HNO_3 that were experimentally measured.

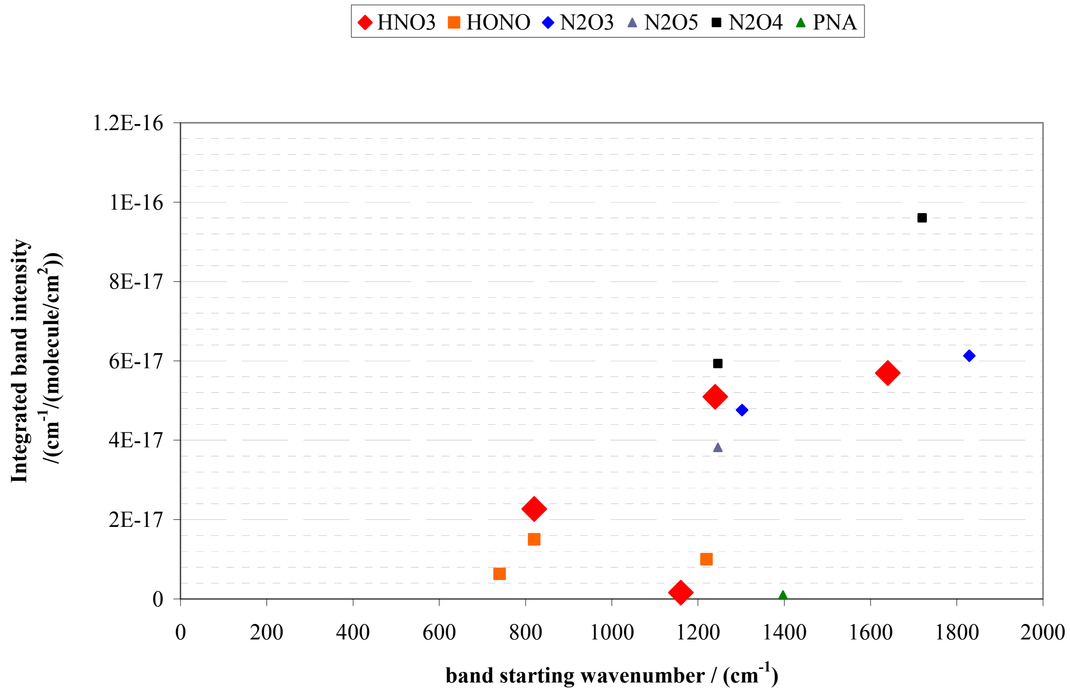

Figure 14. Integrated band intensity $/(\mathrm{cm}^{-1}/(\mathrm{molecule/cm}^2))$ of HNO_3 (4), N_2O_3 (5), N_2O_5 (6), HONO (7), HO_2NO_2 (8) and N_2O_4 (9).

Molecule	Integrated band intensity $/(\mathrm{cm}^{-1}/(\mathrm{molecule/cm}^2))$			
	Spectral region 820 cm^{-1} - 950 cm^{-1}	Spectral region 1160 cm^{-1} -1240 cm^{-1}	Spectral region 1240 cm^{-1} -1400 cm^{-1}	Spectral region 1640 cm^{-1} -1770 cm^{-1}
HNO_3	2.267E-17	1.59E-18	5.095E-17	5.693E-17
HONO	1.50E-17	1.00E-17		
N_2O_3				6.13E-17
N_2O_5			3.82E-17	
N_2O_4			5.93E-17	9.60E-17
PNA			1.00E-18	

Table 10. Integrated band intensities of the molecules HNO_3, N_2O_3, N_2O_4, N_2O_5, HONO, and PNA in different spectral regions.

Molecule	Relative difference (%)
N_2O_3	−6.58
N_2O_5	−25.02
HONO	−80.37
PNA	−98.04

Table 11: Relative difference of the integrated band intensities of the molecules N_2O_3, N_2O_5, HONO, and PNA with respect to HNO_3 in the region 1240 cm^{-1} to 1400 cm^{-1}.

I	II	III	IV	V	VI
IR active impurity	Detection limit (LOD) of impurity in a 120 $\mu mol \cdot mol^{-1}$ NO_2/N_2 gas mixture ($nmol \cdot mol^{-1}$) (A)	Measured mole fraction of impurity in a 120 $\mu mol \cdot mol^{-1}$ NO_2/N_2 gas mixture ($nmol \cdot mol^{-1}$)	Effective limit of detection of impurity in a 10 $\mu mol \cdot mol^{-1}$ NO_2/N_2 gas mixture ($nmol \cdot mol^{-1}$) ($A/12$)	Measured mole fraction of impurity in a 10 $\mu mol \cdot mol^{-1}$ NO_2/N_2 gas mixture ($nmol \cdot mol^{-1}$)	Assigned standard uncertainty in a 10 $\mu mol \cdot mol^{-1}$ NO_2/N_2 gas mixture ($nmol \cdot mol^{-1}$)
HNO_3	6.000	588	0.500	80	20.431
N_2O_3	6.390	0	0.533	0	0.307
N_2O_5	7.500	0	0.625	0	0.361
HONO	10.800	0	0.900	0	0.520
HO_2NO_2	11.880	0	0.990	0	0.572
N_2O_4	1.500	60	0.125	0	0.866

Table 12: I: molecules identified as possible impurities in the nitrogen dioxide gas mixtures generated by the BIPM NO_2 primary facility using a permeation tube. II: limit of detection of the possible impurities at 120 µmol/mol of NO_2/N_2. The limit of detections for HNO_3 and N_2O_4 were experimentally calculated using a long-path FT-IR gas cell. III: measured mole fraction of impurity present in 120 µmol/mol of NO_2/N_2 with the long-path gas cell. IV: calculated effective limit of detection of each impurity at 10 µmol/mol of NO_2/N_2. V: measured mole fraction of each impurity at 10 µmol/mol of NO_2/N_2. VI: Assigned standard uncertainty considering a rectangular distribution ($A/12/\sqrt{3}$).

As previous purity studies did not allow the BIPM to confirm the existence of any other impurity apart from HNO_3, highly concentrated NO_2 gas mixtures were analysed by long-path FT-IR. The mixtures were generated using a NO_2 VICI permeation tube that is a similar permeation device to the one used during the CCQM-K74 comparison.

The preparation of the new gas mixtures was undertaken in a new stainless-steel leak-free permeation chamber. The new permeation chamber had a volume three times smaller than the magnetic suspension chamber and it was specially designed for the purpose. The chamber was placed in the Rubotherm temperature controlled bath and was permanently flushed with a well characterized nitrogen flow as shown in the simplified scheme of Figure 15.

Due to the fact that a carrier gas flow rate of 30 ml/min to 100 ml/min of nitrogen was required for the preparation of the high concentration mixtures, 10 to 13 hours of constant measurements were necessary to obtain a stable response of the FT-IR for each mole fraction. The background stability was achieved by means of the FT-IR enclosure box flushed with 5 l/min of pure nitrogen. Temperature stability was achieved by the Rubotherm system bath and flow stability was accomplished by means of molbloc/molbox measurements and a mass flow controller that was specially designed for small flow rates.

Figure 16 plots the absorbance spectrum of a gas mixture generated with the NO_2 VICI permeation device. NO_2, HNO_3, H_2O, and CO_2 can be easily identified in the spectrum as well as a detected impurity present in the spectral region 1230 cm^{-1} to 1280 cm^{-1}. This impurity was identified as N_2O_4.

The mole fraction of NO_2 was determined using the software MALT and a Classical Least-Square analysis in the region 2820 cm^{-1} to 2940 cm^{-1}, a region where NO_2 absorbs less strongly but is free of HNO_3 and H_2O interferences. The NO_2 mole fraction was verified by the ABB LIMAS analyser which was calibrated for this mole fraction range by means of a gas dilution facility and a highly concentrated gas reference standard. According to the MALT/CLS analysis, the gas mixture contained (106 ±3) µmol/mol of NO_2 [(120 ±1.2) µmol/mol according to the ABB LIMAS] and (588 ± 73) nmol/mol HNO_3.

N_2O_4 was quantified in the spectral region 1230 cm^{-1} to 1280 cm^{-1} using its relative area and by relating this to the HNO_3 absorption band located in 1286 cm^{-1} to 1360 cm^{-1} (see Figure 17). The N_2O_4 calculated mole fraction was (60 ± 6) nmol/mol. A conservative standard uncertainty of 10 % was assigned to the mole fraction determination. Similarly, the N_2O_4 mole fraction was calculated at different NO_2 mole fractions to observe how this changed with changing NO_2 mole fractions (Figure 18).

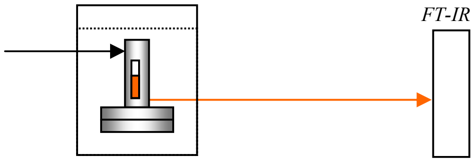

Figure 15. Scheme of the purity analysis experiment for NO_2 permeation tubes.

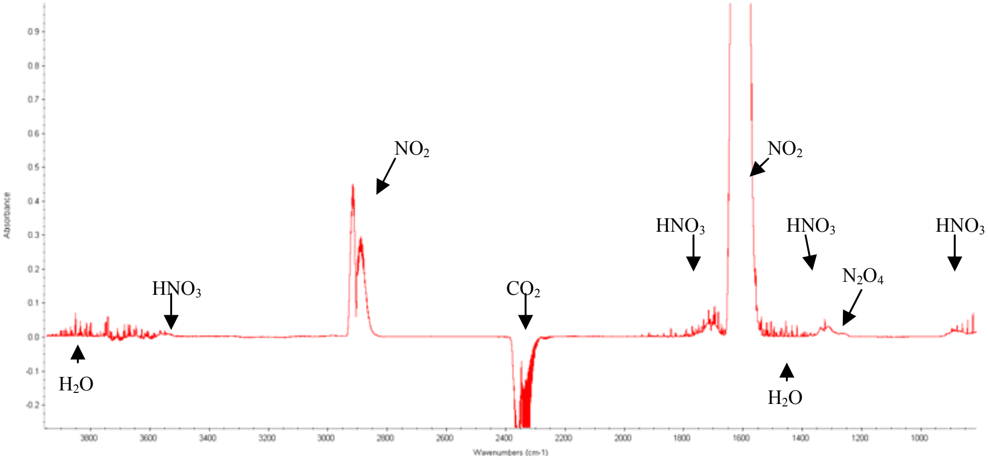

Figure 16. Infrared absorbance spectrum of the purity analysis of a 120 µmol/mol NO_2/N_2 gas mixture generated using a NO_2 permeation tube commercialized by VICI. .

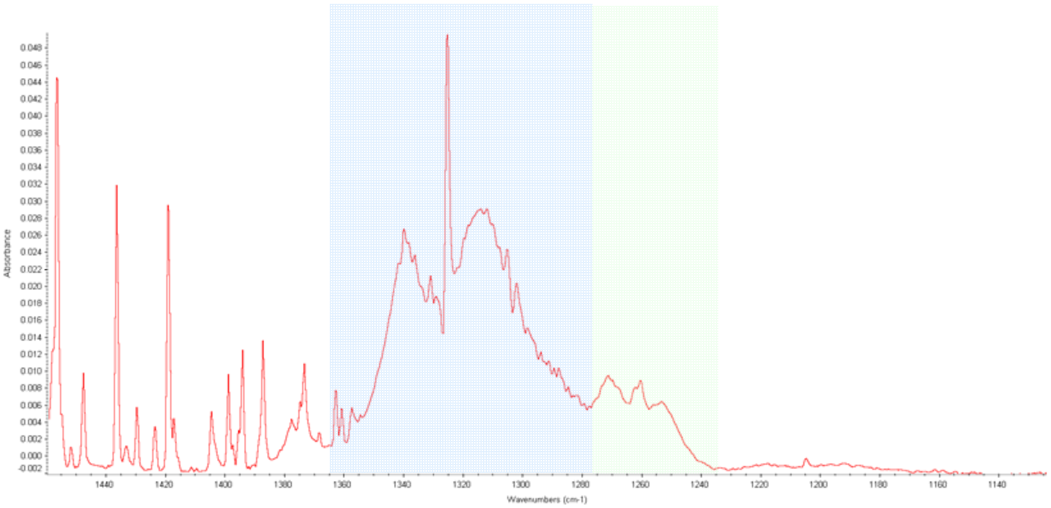

Figure 17. Infrared absorbance spectra of the purity analysis of a 120 µmol/mol NO_2/N_2 gas mixture generated using a NO_2 permeation tube commercialized by VICI in the region 1120 cm^{-1} to 1460 cm^{-1}.

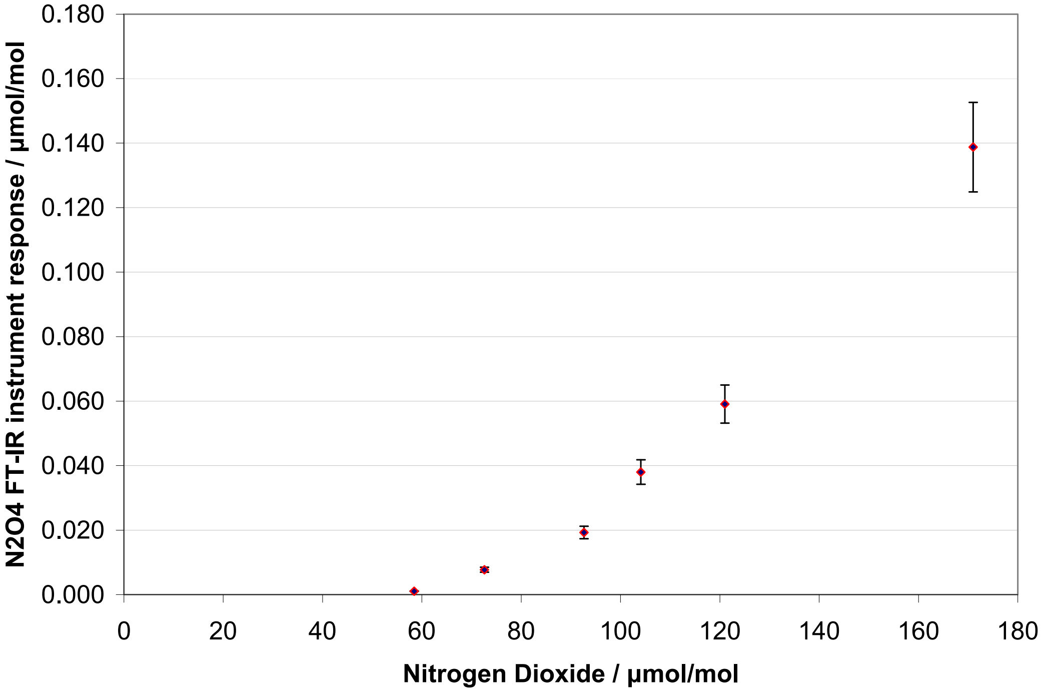

Figure 18. N_2O_4 mole fraction at different NO_2 concentrations of gas mixtures generated by a NO_2 VICI permeation tube.

2. Reaction of NO_2 and HNO_3 in the permeation facility

The possibility of conversion of NO_2 to HNO_3 within the Rubotherm permeation chamber and pneumatic connections was investigated by FT-IR measurements. NO_2 and HNO_3 mole fraction changes were measured when a constant NO_2/N_2 gas mixture was passed through the Rubotherm system. The NO_2/N_2 gas mixtures were, as described in section 1, generated by a NO_2 VICI permeation tube placed into a permeation chamber located in a temperature bath. Figure 19 shows the experimental configuration.

Figure 20 plots the relative difference in nitrogen dioxide when the same gas mixture was passed through the Rubotherm system (A) or went directly to the FT-IR gas cell without passing through the Rubotherm system (B).

The quantitative analysis of the absorbance spectra was performed using a line A spectrum as background until minute 6000 (1200 spectra) where a second background spectrum (in the same position A) was measured. The infrared spectra collection was carried out every 5 minutes. It was noticed that when line A gas mixtures were analysed the relative nitrogen dioxide mole fraction dropped on average 20 nmol/mol. However, when the standard uncertainty due to the instrument response (20 nmol/mol) is plotted in (Figure 20 *i*) the relative difference in the nitrogen dioxide mole fractions measured is equivalent to the measurement uncertainty (Figure 20 *ii*). The nitric acid variations due to changing the flow path (Figure 20 *iii*) again resulted in smaller changes in observed concentration relative to the uncertainty of the instrument response to nitric acid (20 nmol/mol) (Figure 20 *iv*).

Therefore, it is concluded that there is no evidence for the reaction of NO_2 to HNO_3 in the gas phase within the Rubotherm system and that the source of the total HNO_3 measured arises from permeation from the tube. However, an uncertainty component is retained to cover the maximum changes in concentrations observed in these experiments, which was 20 nmol/mol.

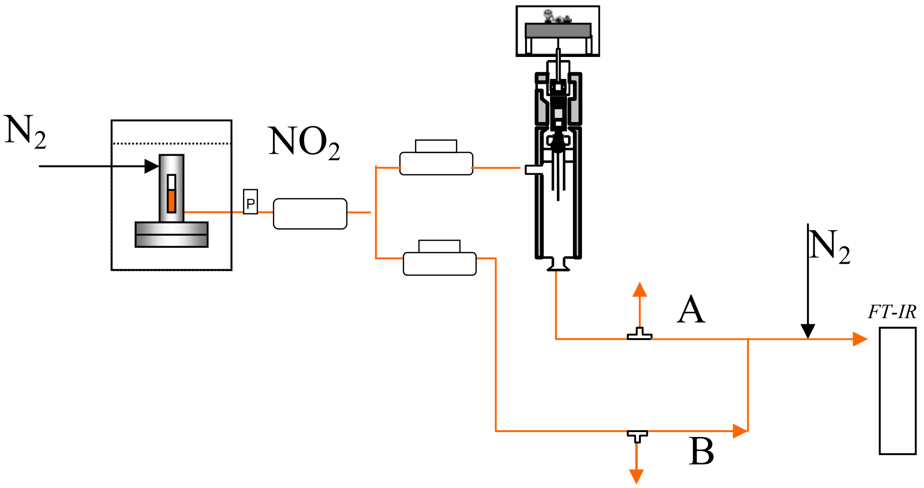

Figure 19. Scheme of the experiment for testing possible absorption/desorption of nitrogen dioxide due to the permeation chamber walls and pneumatic connections.

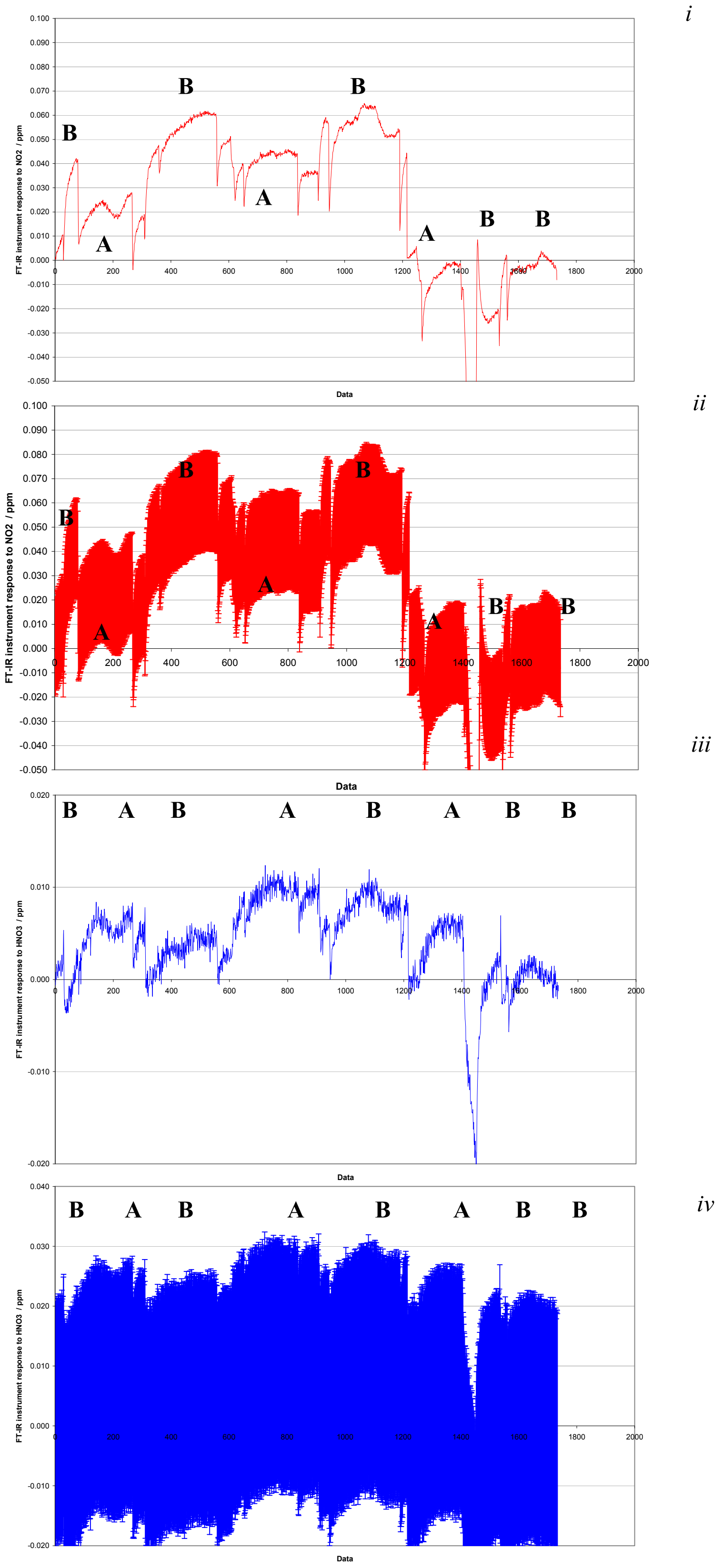

Figure 20. Nitrogen dioxide and nitric acid time series produced by IMACC from gas mixtures A and B (see scheme of Figure 19). The uncertainty bars in the nitrogen dioxide plot on the right are equivalent to the standard uncertainty of the response of the instrument (20 nmol/mol).

3. Cylinder stability/Sampling

The differences between the first and the second nitrogen dioxide value assigned by the BIPM to all cylinders used in the comparison was reanalysed, with the maximum difference observed in the values taken as the basis of an uncertainty component describing the stability of the cylinder over the period of the comparison. The contribution from the gas cylinder stability was evaluated using the equation

$$u^2(x_i) = \frac{(b_+ + b_-)^2}{12} \tag{14}$$

where b_+ and b_- are the upper and the lower boundaries for the nitrogen dioxide difference.

The maximum difference between BIPM assigned values for any particular cylinder was used so that, b_+ and b_- were considered to be 37 nmol/mol each, and by applying equation (14), $u_{\mathrm{Drift}}(x_{\mathrm{NO2}})$ = 21 nmol/mol.

4. Flow

The BIPM measured the flow in its system by using molblocs. These were calibrated by the LNE on 27 April 2009. The uncertainty of the BIPM's flow measurements is dominated by and based on calibration. The uncertainty in the flow measurements was taken from the LNE calibration certificate N° K20869/1. No additional component for the stability of the flow instrument was added, since the time between calibration and the first measurements were short, and no significant deviation between the first and second series of BIPM measurement results was observed for stable cylinder gas standards.

The expanded relative uncertainty (*k*=2) quoted in the calibration certificate is 0.2 % at the flows used in the comparison.

In correspondence between the BIPM and the LNE, the LNE confirmed[5] the relative expanded uncertainties quoted in their CMCs, comparison results and the calibration certificates to be as follows:

0.22 % to 0.40 % in LNE's CMCs
0.19 % to 0.26 % in the Euramet (1)
0.18 % to 0.27 % in the Calibration Certificate K20869/1.

5. Modified BIPM uncertainty budget

5.1 Previous uncertainty budget:

The mole fractions of the dynamically produced gas mixtures obtained with the BIPM facility in the Draft A report was calculated by the expression:

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[5] Private communication with Jean Barbe from LNE.

$$x_{\mathrm{NO_2}} = \left(\frac{P \times V_{\mathrm{m}}}{q_v \times M_{\mathrm{NO_2}}} \right) - \left(\frac{M_{\mathrm{HNO_3}} \times x_{\mathrm{HNO_3}}}{M_{\mathrm{NO_2}}} \right) \tag{15}$$

where:

$x_{\mathrm{NO_2}}$ is the NO_2 mole fraction in µmol/mol;

P is the NO_2 permeation rate in $\mathrm{ng \cdot min^{-1}}$;

$V_{\mathrm{m}} = 22.4038\ \mathrm{L \cdot mol^{-1}}$, is the molar volume of air/N_2 at standard conditions (273.15 K, 101.3 kPa);

$M_{\mathrm{NO_2}} = 46.0055\ \mathrm{g \cdot mol^{-1}}$, is the molar mass of NO_2;

q_v is the total flow of N_2 given by the molbloc®/molbox® facility;

x_{HNO3} is the HNO_3 mole fraction in µmol/mol measured by FT-IR spectroscopy.

$M_{\mathrm{HNO_3}} = 63.005\ \mathrm{g.mol^{-1}}$ is the molar mass of HNO_3.

Table 13 shows the Draft A uncertainty budget for the nitrogen dioxide mole fraction determination updated by introducing the correct contribution of the nitric acid mole fraction calculation given by equation 8 of the Draft A report.

Quantity	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient $c_i=\partial x_{\mathrm{NO2}}/\partial x$	Uncertainty contribution $u_i(y)$ $\mathrm{mol \cdot mol^{-1}}$	Index %
P	8.3573 $10^{-6} \cdot \mathrm{g \cdot min^{-1}}$	Normal	4.18 $10^{-9} \cdot \mathrm{g \cdot min^{-1}}$	1.1	4.5 10^{-9}	2.2
V_{m}	22.4038 $\mathrm{L \cdot mol^{-1}}$	Normal	340.00 $10^{-6}\ \mathrm{L \cdot mol^{-1}}$	400 10^{-9}	140 10^{-12}	0.0
$q_{v\ \mathrm{molbloc1}}$	452 $10^{-3} \cdot \mathrm{L \cdot min^{-1}}$	Normal	455.21 $10^{-6}\ \mathrm{L \cdot min^{-1}}$	−20 10^{-6}	−8.2 10^{-9}	7.3
M_{NO2}	46.0055 $\mathrm{g \cdot mol^{-1}}$	Normal	1.40 $10^{-3}\ \mathrm{g \cdot mol^{-1}}$	−190 10^{-9}	−91 10^{-12}	0.0
x_{HNO3}	0.104 10−6mol·mol^{-1}	Normal	0.021 $10^{-6} \cdot \mathrm{mol \cdot mol^{-1}}$	−1.4	−29 10^{-9}	90.4
M_{HNO3}	63.005 $\mathrm{g \cdot mol^{-1}}$	Normal	1.17 $10^{-3}\ \mathrm{g \cdot mol^{-1}}$	−2.3 10^{-9}	−1.3 10^{-12}	0.0

Quantity	Value	Standard Uncertainty
C	8.86 $\mathrm{\mu mol \cdot mol^{-1}}$	30 $\mathrm{nmol \cdot mol^{-1}}$

Table 13. Uncertainty budget for a NO_2 /N_2 primary mixture generated with the BIPM facility, before the introduction of additional components described in this report. The degrees of freedom were numerous, so a coverage factor k = 2 was assumed appropriate for the expanded uncertainty.

In the revised version of the Draft A uncertainty, the contribution of the mole fraction determination of nitric acid became the main uncertainty contributor. Figure 21 illustrates the updated uncertainties in $x_{\mathrm{NO_2}}$ for the dynamic generation of NO_2 in nitrogen mixtures over the mole fraction range 8 µmol/mol to 12 µmol/mol, using a permeation tube with permeation rate 8357 $\mathrm{ng{\cdot}min^{-1}}$ and flows ranging over 350 $\mathrm{mL{\cdot}min^{-1}}$ to 450 $\mathrm{mL{\cdot}min^{-1}}$. A least squares fit of the absolute standard uncertainty $u(x_{\mathrm{NO_2}})$, was made using the Excel LINEST function. The standard uncertainties in $x_{\mathrm{NO_2}}$ can be modelled by the following numerical equation (values given in µmol/mol):

$$u(x_{\mathrm{NO_2}}) = 0.001036x + 0.020818 \qquad (16)$$

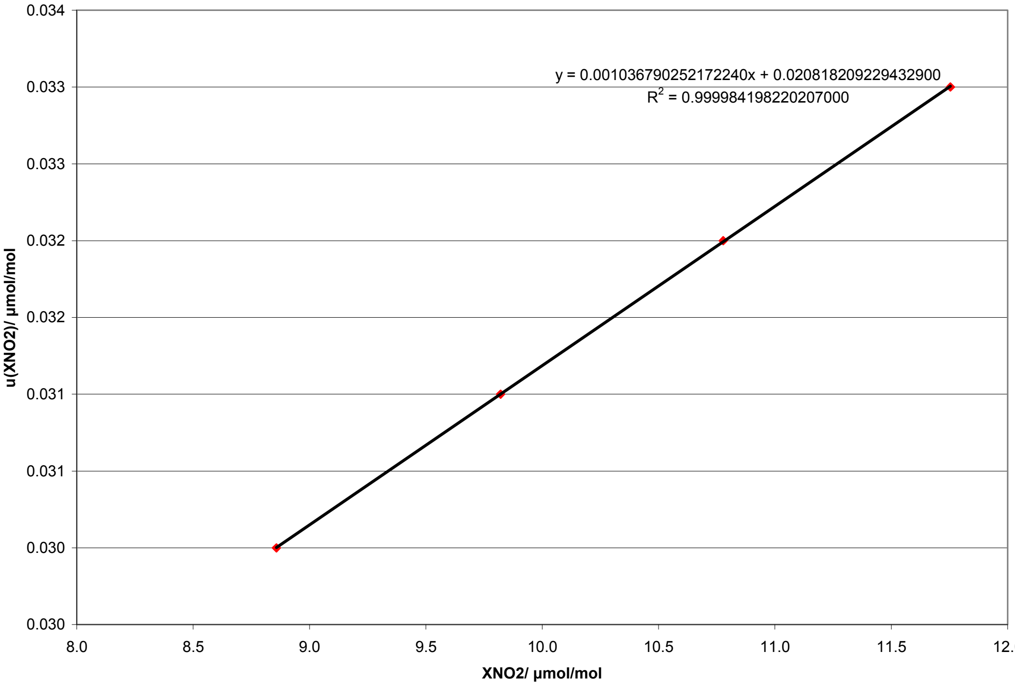

Figure 21. Standard uncertainty of dynamically generated NO_2 mixtures on the BIPM NO_2 Facility over a range of x_{NO_2} = (8-12) µmol/mol, before the introduction of additional components described in this report.

5.2 Additional uncertainty components as a result of this study:

Impurities:

N_2O_4 was the only additional impurity that was detected at a concentration above its limit of detection in the highly concentrated gas mixtures. However, as this is the dimer of NO_2 it is clear that the concentration of N_2O_4 is determined by the equilibrium between the species and the concentration of NO_2. Extrapolation of the measurements of N_2O_4 as a function of NO_2 concentration (see Figure 18) leads to the conclusion that N_2O_4 mole fractions will be smaller than a few nmol/mol when the NO_2 mole fraction is 10 µmol/mol. Therefore, in a 10 µmol/mol nitrogen dioxide gas mixture the most probable concentration of N_2O_4 was taken to be zero, with a conservative uncertainty based on the understanding that the N_2O_4 fraction could not be greater than 1.5 nmol/mol. The associated standard uncertainty was therefore calculated to be $u_{imp}(x_{\mathrm{N2O4}}) = 1.5/\sqrt{3} = 0.866$ nmol/mol.

NO_2 losses:

A maximum variation of 20 nmol/mol was found as a result of the investigation of Section 2 where losses of NO_2 produced by the Rubotherm system were studied. The uncertainty contribution due to this issue in NO_2 is $u_{NO2\ losses}(x_{\mathrm{NO2}}) = 10/\sqrt{3} = 5.7$ nmol/mol.

Cylinder stability:

The contribution of the cylinder stability, is $u_{\mathrm{Drift}}(x_{\mathrm{NO2}}) = 21$ nmol/mol.

5.3 New uncertainty budget:

The measured equation proposed for the mole fraction determination for Draft B is:

$$x_{\mathrm{NO_2}} = \left(\frac{P \times V_{\mathrm{m}}}{q_v \times M_{\mathrm{NO_2}}}\right) - \left(\frac{M_{\mathrm{HNO_3}} \times x_{\mathrm{HNO_3}}}{M_{\mathrm{NO_2}}}\right) - \sum\left(\frac{M_{\mathrm{imp}} \times x_{\mathrm{imp}}}{M_{\mathrm{NO_2}}}\right) \qquad (17)$$

where:

$x_{\mathrm{NO_2}}$ is the NO_2 mole fraction in $\mu\mathrm{mol{\cdot}mol^{-1}}$;

P is the NO_2 permeation rate in $\mathrm{ng{\cdot}min^{-1}}$;

$V_{\mathrm{m}} = 22.4038\ \mathrm{L{\cdot}mol^{-1}}$, is the molar volume of air/N_2 at standard conditions (273.15 K, 101.3 kPa);

$M_{\mathrm{NO_2}} = 46.0055\ \mathrm{g{\cdot}mol^{-1}}$, is the molar mass of NO_2;

q_v is the total flow of N_2 given by the molbloc®/molbox® facility;

x_{HNO3} is the HNO_3 mole fraction in µmol/mol measured by FT-IR spectroscopy;

$M_{\mathrm{HNO_3}} = 60.005\ \mathrm{g.mol^{-1}}$ is the molar mass of HNO_3;

x_{imp} are the mole fractions in µmol/mol of the other impurities measured by FT-IR Spectroscopy; and

M_{imp} are the molar mass of the impurities;

The new uncertainty contributions of the impurities are described in Table 14. The uncertainty in the flow measurements was taken from the LNE calibration certificate N° K20869/1.

It follows that the uncertainty budget for a NO_2 mixture having a nominal concentration of ~8.8 µmol/mol is as shown as follows using nitrogen as the diluent gas:

Quantity	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient $c_i = \partial x_{NO2}/\partial x$	Uncertainty contribution $u_i(y)$ mol·mol^{-1}	Index %
P	8.3573 10^{-6}·g·min^{-1}	Normal	4.18 10^{-9}·g·min−1	1.1	4.5 10^{-9}	2.2
V_m	22.4038 L·mol^{-1}	Normal	340.00 10^{-6} L·mol^{-1}	400 10^{-9}	140 10^{-12}	0.0
$q_{v\ molbloc1}$	452 10^{-3}·L·min^{-1}	Normal	455.21 10^{-6} L·min^{-1}	−20 10^{-6}	−9.1 10^{-9}	8.8
M_{NO2}	46.0055 g·mol^{-1}	Normal	1.40 10^{-3} g·mol^{-1}	−190 10^{-9}	−270 10^{-12}	0.0
x_{HNO3}	0.104 10^{-6}mol·mol^{-1}	Normal	0.021 10^{-6}·mol·mol^{-1}	−1.4	−29 10^{-9}	88.5
x_{N2O4}	0 mol·mol^{-1}	Normal	866 10^{-12}·mol·mol^{-1}	−2.0	−1.7 10^{-9}	0.3
x_{N2O3}	0 mol·mol^{-1}	Normal	307 10^{-12}·mol·mol^{-1}	−1.7	−510 10^{-12}	0.0
x_{N2O5}	0 mol·mol^{-1}	Normal	361 10^{-12}·mol·mol^{-1}	−2.3	−850 10^{-12}	0.0
x_{HONO}	0 mol·mol^{-1}	Normal	520 10^{-12}·mol·mol^{-1}	−1.0	−530 10^{-12}	0.0
x_{HO2NO2}	0 mol·mol^{-1}	Normal	572 10^{-12}·mol·mol^{-1}	1.7	−980 10^{-12}	0.1
M_{HNO3}	63.013 g·mol^{-1}	Normal	1.17 10^{-3} g·mol^{-1}	−2.3 10^{-9}	−2.6 10^{-12}	0.0

Quantity	Value	Standard Uncertainty
x_{NO2}	8.86 µmol·mol^{-1}	30 nmol·mol^{-1}

Table 14. Uncertainty budget for a NO_2 /N2 primary mixture generated with the BIPM facility.
Note: the molar masses M_{N2O4}, M_{N2O3}, M_{N2O5}, M_{HONO}, M_{HO2NO2} were not included in this budget as they represent negligible uncertainty contributions.

The degrees of freedom were numerous, so a coverage factor $k = 2$ was assumed appropriate for the expanded uncertainty. The main uncertainty contributors remain the mole fraction determination of nitric acid and the gas flow measurements. Figure 13 illustrates the new uncertainties in x_{NO_2} for the dynamic generation of NO_2 in nitrogen mixtures over the mole fraction range 8 µmol/mol to 12 µmol/mol, using a permeation tube with permeation rate of 8357 ng·min^{-1} and flows in the range 350 mL·min^{-1} to 450 mL·min^{-1}. The uncertainty is almost a constant and can be fitted by a linear function of the mole fraction. A least squares fit was made using the Excel LINEST function. The standard uncertainties in x_{NO_2} can be modelled by the following linear function (numerical values in µmol/mol):

$$u(x_{\mathrm{NO_2}}) = 0.001036x + 0.020818 \tag{18}$$

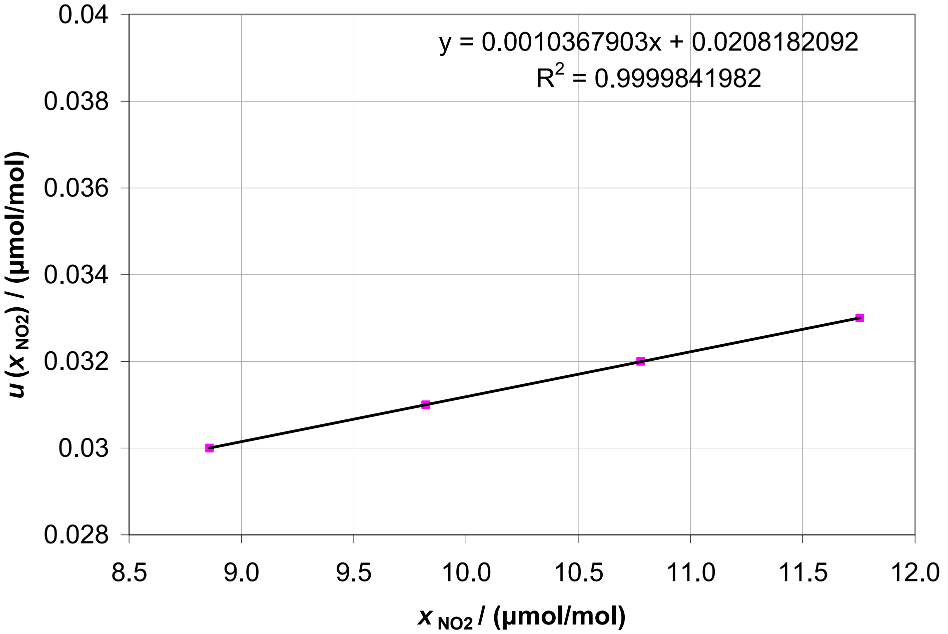

Figure 22. Standard uncertainty of dynamically generated NO_2 mixtures on the BIPM NO_2 facility over a range of x_{NO_2} = (8-12) µmol/mol.

6. Covariance between two dynamically generated gas mixtures

Non-zero covariances, $u(x_{\mathrm{NO_2},i}, x_{\mathrm{NO_2},j})$ were included in the uncertainty calculations because all dynamic mixtures were derived from the same BIPM facility and an error in the analyte content of the one gas is considered to propagate to all gas mixtures in a positive correlated fashion. The covariance between two calibration gas mixtures *i* and *j* is described as follows:

$$u(x_{\mathrm{NO_2},i}, x_{\mathrm{NO_2},j}) = \gamma \left[u(x_{\mathrm{NO_2},i}) \right]^2, \tag{19}$$

Where

$u(x_{\mathrm{NO_2},i})$ is the standard uncertainty of the more concentrated mixture as given by equation 4,

$$\gamma = {}^{q_j}\!/_{q_i} \tag{20}$$

is the dilution factor of the total gas flows q_j and q_i (with $q_j < q_i$). Note that as the NO_2 calibration gas mixtures generated with the facility are distributed in a small range of mole fractions (typically 8 nmol/mol to 12 nmol/mol), the dilution factor is often close to 1, and the covariances often close to the variances $u(x_{NO2,i})^2$.

7. Determination of the calibration function

As in the draft A report, a calibration line was calculated using the Generalized Least Square fitting procedure described in the standard ISO 6143:2001. Uncertainties were calculated according to the budget described in Table 14, and covariances between the calibration mixtures were calculated according to Equation 19.

For each cylinder, the calibration line was calculated using a number n of calibration points, with n ranging from 12 to 36 depending on the measurement conditions. Note that due to the covariance values, this had a negligible effect on the uncertainties of the calibration parameters.

For each cylinder, a predicted NO_2 mole fraction x_{BIPM} was calculated from the FT-IR response using the calibration parameters.

8. The Key Comparison Reference Values and their standard uncertainties

For each cylinder, the Key Comparison Reference Value is the NO_2 mole fraction x_{BIPM} assigned by the BIPM following the calibration procedure described above. The additional uncertainties described in this report do not change the KCRVs calculated in the draft A report but only their associated uncertainties, as can be seen in Table 15 and Table 16.

Following the CCQM GAWG guidance, it was decided that the standard uncertainty of the Key Comparison Reference Value (KCRV) can be quantified by the following equation:

$$u_{\mathrm{KCRV}}(x_{\mathrm{NO_2}}) = \sqrt{\left(u(x_{\mathrm{BIPM}})\right)^2 + \left(u(x_{\mathrm{NO_2 Losses}})\right)^2 + \left(u(x_{\mathrm{NO_2 Drift}})\right)^2} \qquad (21)$$

where $u(x_{\mathrm{BIPM}})$ is the uncertainty associated with the value assigned by the BIPM following the procedure described above, $u\left(x_{\mathrm{NO_2 Lossess}}\right)$ the uncertainty contribution due to NO_2 losses equivalent to 5.7 nmol/mol and $u(x_{\mathrm{NO_2 Drift}})$ the uncertainty contribution due to observed drift in NO_2 estimated in 21 nmol/mol.

The additional uncertainties described in this report increase the KCRV uncertainties from about 0.021 µmol/mol as reported in the draft A report to about 0.041 µmol/mol, as can be seen in Table 15 and Table 16.

Corresponding degrees of equivalence and associated uncertainties are also listed in Table 15 and Table 16 and plotted in Figure 23 and Figure 24.

Draft A measurement results

Laboratory	Cylinder	FT-IR response		BIPM		Participants				
		y_{BIPM}	$u(y_{\mathrm{BIPM}})$	x_{BIPM}	$u(x_{\mathrm{BIPM}})$	x_{Lab}	$u(x_{\mathrm{Lab}})$	$D(x_{\mathrm{Lab}}-x_{\mathrm{BIPM}})$	$u(D)$	$U(D)$ (k=2)
NPL	#930659-PRM	10.715	0.020	10.227	0.021	10.331	0.040	0.104	0.045	0.090
NIM	#930650-PRM	10.716	0.020	10.228	0.021	10.150	0.050	−0.078	0.054	0.108
SMU	#930655-PRM	10.832	0.020	10.347	0.021	10.100	0.060	−0.247	0.064	0.127
NMIA	#930662-PRM	10.864	0.020	10.378	0.021	10.740	0.315	0.362	0.316	0.631
NMISA	#930649-PRM	10.832	0.020	10.347	0.021	10.690	0.185	0.343	0.186	0.372
CERI	#930671-PRM	10.843	0.020	10.352	0.021	10.400	0.190	0.048	0.191	0.382
METAS	#930660-PRM	10.904	0.020	10.432	0.021	10.630	0.080	0.198	0.083	0.165
INRIM	#930667-PRM	10.731	0.020	10.183	0.021	11.470	0.070	1.287	0.073	0.146
KRISS	#930661-PRM	10.766	0.020	10.270	0.021	10.450	0.155	0.180	0.156	0.313
FMI	#930673-PRM	10.984	0.020	10.418	0.021	9.880	0.150	−0.538	0.151	0.303
LNE	#930675-PRM	10.944	0.020	10.378	0.021	10.260	0.065	−0.118	0.068	0.136
NIST	#930654-PRM	10.859	0.020	10.299	0.021	10.280	0.050	−0.019	0.054	0.108
VSL	#930674-PRM	10.933	0.020	10.370	0.021	10.510	0.105	0.140	0.107	0.214
CEM	#930676-PRM	10.991	0.020	10.435	0.023	10.720	0.110	0.285	0.112	0.225
VNIIM	#930713-PRM	10.896	0.020	10.321	0.029	10.550	0.080	0.229	0.085	0.170
BAM	#930722-PRM	10.903	0.020	10.350	0.023	10.530	0.375	0.180	0.376	0.751
BIPM	#930697-PRM	10.905	0.020	10.343	0.021	10.343	0.024	0.000	0.032	0.064

Table 15. Results of the key comparison presented in the draft A report. All values are given in µmol/mol apart from FT-IR response which is in arbitrary units

Draft A - measurement results

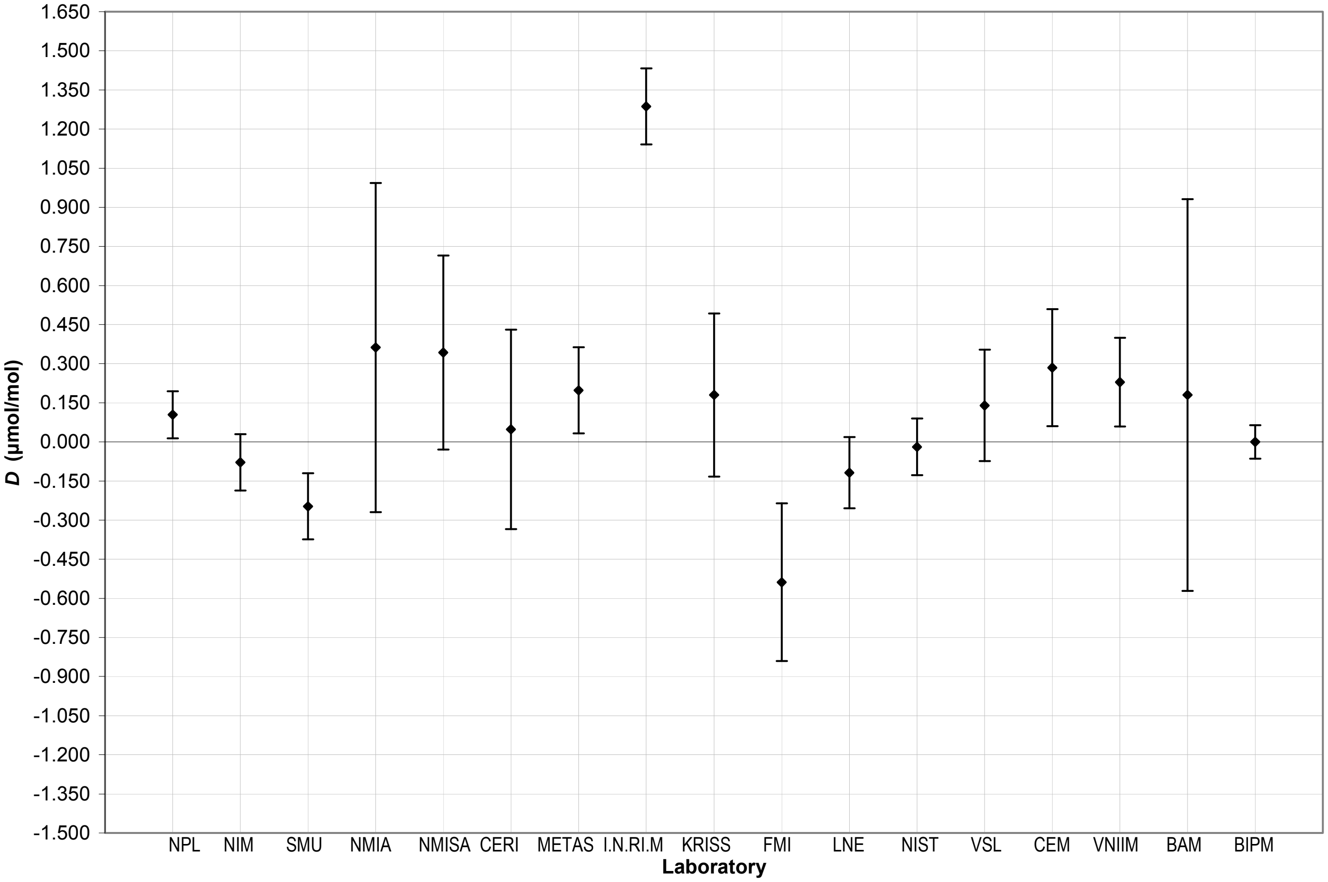

Figure 23. Difference between participants' results and BIPM reported values for nitrogen dioxide mole fractions. The error bar represents the expanded uncertainty at a 95 % level of confidence.

Draft B - measurement results

		FT-IR response		BIPM		Participants		Differences		
Laboratory	Cylinder	y_{BIPM} (µmol/mol)	$u(y_{\mathrm{BIPM}})$	x_{BIPM}	$u(x_{\mathrm{BIPM}})$	x_{Lab}	$u(x_{\mathrm{Lab}})$	$D(x_{\mathrm{Lab}}-x_{\mathrm{BIPM}})$	$u(D)$	$U(D)$ (k=2)
NPL	#930659-PRM	10.715	0.020	10.226	0.042	10.331	0.040	0.105	0.058	0.115
NIM	#930650-PRM	10.716	0.020	10.227	0.042	10.150	0.050	−0.077	0.065	0.130
SMU	#930655-PRM	10.832	0.020	10.347	0.042	10.100	0.060	−0.247	0.073	0.146
NMIA	#930662-PRM	10.864	0.020	10.378	0.042	10.740	0.315	0.362	0.318	0.635
NMISA	#930649-PRM	10.832	0.020	10.347	0.042	10.690	0.185	0.343	0.190	0.379
CERI	#930671-PRM	10.843	0.020	10.351	0.041	10.400	0.190	0.049	0.194	0.389
METAS	#930660-PRM	10.904	0.020	10.431	0.041	10.630	0.080	0.199	0.090	0.180
INRIM	#930667-PRM	10.731	0.020	10.183	0.042	9.990	0.100	−0.193	0.108	0.217
KRISS	#930661-PRM	10.766	0.020	10.270	0.042	10.450	0.155	0.180	0.160	0.321
FMI	#930673-PRM	10.984	0.020	10.417	0.041	9.880	0.150	−0.537	0.156	0.311
LNE	#930675-PRM	10.944	0.020	10.378	0.041	10.260	0.065	−0.118	0.077	0.154
NIST	#930654-PRM	10.859	0.020	10.299	0.041	10.280	0.050	−0.019	0.065	0.130
VSL	#930674-PRM	10.933	0.020	10.370	0.041	10.510	0.105	0.140	0.113	0.226
CEM	#930676-PRM	10.991	0.020	10.435	0.042	10.720	0.110	0.285	0.118	0.235
VNIIM	#930713-PRM	10.896	0.020	10.320	0.042	10.550	0.080	0.230	0.090	0.181
BAM	#930722-PRM	10.903	0.020	10.350	0.042	10.530	0.375	0.180	0.377	0.755
BIPM	#930697-PRM	10.905	0.020	10.343	0.041	10.343	0.024	0.000	0.048	0.096

Table 16. Results of the key comparison taking into account the additional uncertainties presented in this report[6]*. All values are given in µmol/mol apart from FT-IR response which is in arbitrary units (*BIPM reported uncertainty has not been changed from the Draft A value. The corrected standard uncertainty for the BIPM reported value which would result from following the procedure outlined in this document would be 0.035 µmol/mol.)

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[6] *Note: 1 nmol/mol is the maximum observed difference between Draft A and Draft B assigned values by BIPM due to B_Least rounding.*

Draft B - measurement results

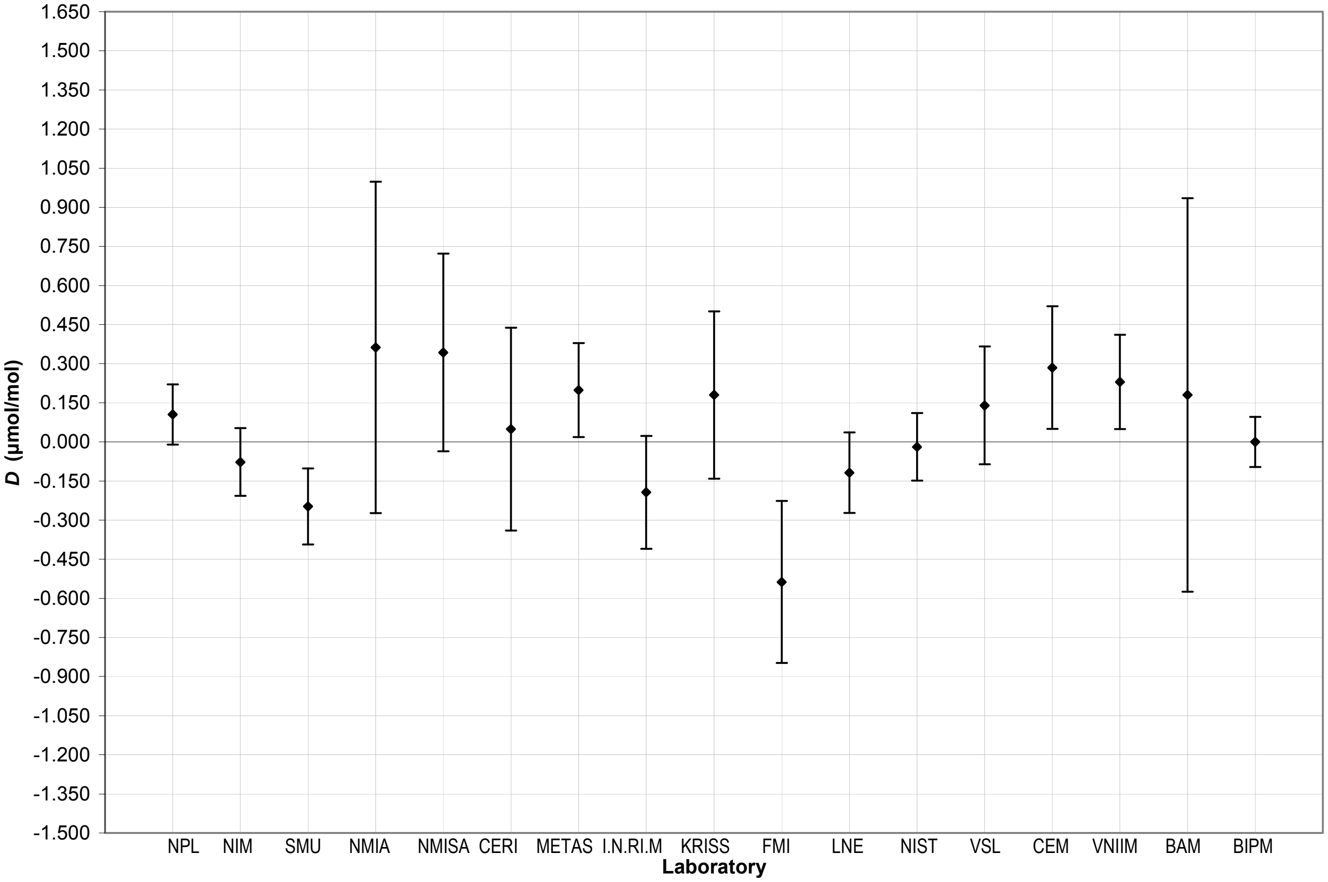

Figure 24. Difference between participants' results and BIPM reported values for nitrogen dioxide mole fractions. The error bar represents the expanded uncertainty at a 95 % level of confidence.

[1] Hughes E E, Rook H L, Deardorff E R, Margeson J H and Fuerst R G 1977 Performance of a NO_2 permeation device. *Analytical chemistry* **49** (12) 1823–1829

[2] Rothman L S *et al* 2005 The HITRAN 2004 molecular spectroscopic database *Journal of Quantitative Spectroscopy & Radiative Transfer* **96** 139–204

[3] Kagann R H and Maki A G 1984 Infrared absorption intensities for N_2O_3 *Journal of Quantitative Spectroscopy and Radiative Transfer* **31** 173–176

[4] Newnham D, Ballard J and Page M 1993 Infrared absorbance cross-sections for dinitrogen pentoxide vapour *Journal of Quantitative Spectroscopy and Radiative Transfer* **50** 571–577

[5] Barney W S *et al* 2000 Infrared Absorption Cross-Section Measurements for Nitrous Acid (HONO) at Room Temperature *The Journal of Physical Chemistry* **104** (8) 1692–1699

[6] Höjer S, May R D and Miller C E 1999 Intensities of the 1397 cm^{-1} (v_3) band of HO_2NO_2 and feasibility of atmospheric detection *Journal of Quantitative Spectroscopy and Radiative Transfer* **55** 273–278

[7] Hurtmans D, Herman M and Vander Auwera J 1993 Integrated band intensities in N_2O_4 in the infrared range *Journal of Quantitative Spectroscopy and Radiative Transfer* **50** 595–602

[8] Probert C, Johns A I and Metaxiotou Z 2008 An intercomparison of low flow gas facilities at eleven European laboratories using a Molbloc transfer package: EURAMET.MM.FF-S3 (EURAMET Project no 806) *Metrologia* **45,** Tec. Sup. 07012

ANNEX 3 - Measurement reports of participants

Centro Español de metrología (CEM)

A1. General information

Institute	CENTRO ESPAÑOL DE METROLOGÍA (CEM)		
Address	CALLE ALFAR, 2 28760 TRES CANTOS (MADRID) SPAIN		
Contact person	TERESA E. FERNÁNDEZ VICENTE		
Telephone	+ 34 918 074 751	Fax	+ 34 918 074 807
Email*	tefernandez@cem.mityc.es		
Serial number of cylinder received	930676 (D650059)		
Cylinder pressure as received	≈ 95 bar		

A2. Results

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{\mathrm{NO2}})$ / µmol/mol	Coverage factor
10,72	0,22	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The mathematical model used to calculate the uncertainty in the composition of mixture analysed is a linear combination of the sources of uncertainty due to the instrument used and the repeatability of the measurements. This leads to:

$$u = \sqrt{u_{B\_least}^2 + u_r^2}$$

where u_{B_least} is the largest uncertainty among the obtained uncertainties by means of the B_least software (linear fit regression) and u_r is the standard deviation of the mean of the results obtained during the period of measurements (usually from 3 to 5 days).

Table 1 summarizes the uncertainty budget.

Uncertainty source	Assumed distribution	Standard uncertainty / μmol/mol	Sensitivity coefficient	Contribution to standard uncertainty / μmol/mol
u_{B_least}	normal	0,11	1	0,11
u_r	normal	0,0064	1	0,0064
Combined standard uncertainty / μmol/mol				**0,11**
Expanded uncertainty, k[7] = 2 / μmol/mol				**0,22**

Table 1. Detailed uncertainty budget.

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[8].

The mixture was analysed by means of a Thermo 42i chemiluminiscence NO-NO_2-NO_x analyser. Three standards were used with the compositions specified in Table 2:

Species	Amount Fraction NPL1272 / μmol/mol	Amount Fraction NPL1273 / μmol/mol	Amount Fraction NPL1274 / μmol/mol
Nitrogen Dioxide	(5,01 ± 0,10)	(10,00 ± 0,15)	(15,01 ± 0,22)
Oxygen (not certified)	13	22	33
Nitrogen	Balance	Balance	Balance

Table 2. Primary reference gas mixtures used.

All mixtures were prepared gravimetrically and analysed by the Non-Dispersive Ultraviolet (NDUV) technique.

Upon arrival the sample cylinder was rolled and stored in the laboratory under laboratory reference conditions. A pressure reducer was connected to the standards and the sample cylinder. The reducers were carefully flushed as prescribed in International Standard ISO 16664:2004 (Gas analysis – Handling of calibration gases and calibration gas mixtures – Guidelines).

The standards and the sample cylinder were connected to an automatic gas sampler connected to the specific analyser in the increasing order of concentration and the gas outlet pressure was 2 bar. The cylinders were analysed sequentially in three measurement cycles and the data reported came from three independent working days.

B_least software based on International Standard ISO 6143:2001 (Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures) was used to certify the sample cylinder. A calibration curve was fitted to the mean value from three measurement cycles for each standard and the drift among cycles was used as standard uncertainty, because it turned out to be significant. The method used resulted in a calculated mole fraction and standard uncertainty for the sample cylinder. In all cases a linear function was used with a goodness of fit less than 2.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

65 bar approximately.

If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

---

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

[8] The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

Finnish Meteorological Institute (MIKES-FMI)

A1. General information

Institute	Finnish Metrological Institute (MIKES-FMI)		
Address	P.O. BOX 503 FI-00101 HELSINKI FINLAND		
Contact person	Jari Waldén		
Telephone	+358505914615	Fax	+358919295403
Email*	Jari.walden@fmi.fi		
Serial number of cylinder received	APEX 930 673		
Cylinder pressure as received	83 bar		

A2. Results

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
9.88	0.30	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The measurement equation for calculating the concentration of the CCQM-K74 is following:

$$C(NO_2)_{K74} = \frac{\frac{[NO_2]_{K74}}{eff} \cdot C(NO)_{PRM}}{[NO]_{PRM}} \qquad (1)$$

Where [NO2]K74 is the diluted concentration of the gas standard K74 (C(NO2)K74), where [NO2]K74 = [NOx] – [NO] is measured with the analyser APNA-360. The NO2-converter efficiency of the analyser, eff, was defined aso 98.0 %. The concentration of the PRM, C(NO)PRM, was known from the certificate as well as the expanded uncertainty. The PRM was purchased from NPL. The expanded uncertainty can be calculated using the formula of propagation of error.

$$u_c^2 = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial w_i} \right)^2 u_i^2 + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{\partial f}{\partial w_i} \frac{\partial f}{\partial w_j} u_i u_j \rho_{ij} \qquad (2)$$

<u>The combined variance of equation (1) can be expressed as:</u>

$$u(NO2)_{c,K74}^2 = \left(\frac{[NO_2]_{K74}}{eff \cdot [NO]_{PRM}} \right)^2 \cdot u^2(C(NO)_{PRM}) + \left(\frac{C(NO)_{PRM}}{eff \cdot [NO]_{PRM}} \right)^2 \cdot u^2([NO_2]_{K74}) + \left(-\frac{[NO_2]_{K74} \cdot C(NO)_{PRM}}{eff^2 \cdot [NO]_{PRM}} \right)^2 \cdot u^2(eff)$$

$$+ \left(-\frac{[NO_2]_{K74} \cdot C(NO)_{PRM}}{eff \cdot [NO]_{PRM}^2} \right)^2 \cdot u^2([NO]_{PRM}) + 2 \cdot \Bigg\{ \left(\frac{C(NO)_{PRM}}{eff \cdot [NO]_{PRM}} \right) \cdot \Bigg[\left(\frac{[NO_2]_{K74}}{eff \cdot [NO]_{PRM}} \right) \cdot u([NO_2]_{K74}) \cdot u(C(NO)_{PRM}) \cdot r_{[NO_2]_{K74}, C(NO)_{PRM}}$$

$$+ \left(-\frac{[NO_2]_{K74} \cdot C(NO)_{PRM}}{eff^2 \cdot [NO]_{PRM}} \right) \cdot u([NO_2]_{K74}) \cdot u(eff) \cdot r_{[NO_2]_{K74}, eff} + \left(-\frac{[NO_2]_{K74} \cdot C(NO)_{PRM}}{eff \cdot [NO]_{PRM}^2} \right) \cdot u([NO_2]_{K74}) \cdot u([NO]_{PRM}) \cdot r_{[NO_2]_{K74}, [NO]_{PRM}} \Bigg]$$

$$+ \left(\frac{[NO_2]_{K74}}{eff \cdot [NO]_{PRM}} \right) \Bigg[\left(-\frac{[NO_2]_{K74} C(NO)_{PRM}}{eff^2 \cdot [NO]_{PRM}} \right) u(C(NO)_{PRM}) u(eff) r_{C(NO)_{PRM}, eff} + \left(-\frac{[NO_2]_{K74} C(NO)_{PRM}}{eff \cdot [NO]_{PRM}^2} \right) u(C(NO)_{PRM}) u([NO]_{PRM}) r_{C(NO)_{PRM}, [N}$$

$$+ \cdot \left(-\frac{[NO_2]_{K74} \cdot C(NO)_{PRM}}{eff^2 \cdot [NO]_{PRM}} \right) \cdot \left(-\frac{[NO_2]_{K74} \cdot C(NO)_{PRM}}{eff \cdot [NO]_{PRM}^2} \right) \cdot u(eff) \cdot u([NO]_{PRM}) \cdot r_{eff, [NO]_{PRM}} \Bigg\} \qquad (3)$$

<u>The standard uncertainties are listed below:</u>

$u(C(NO)_{PRM}) = 0.25\ \%$ (4)
From the certificate of the PRM

$u([NO_2]_{K74} = 1.1\ \%$ (5)
From the measured value. Uncertainty of the analyser includes: calibration of the analyser, converter efficiency, linearity, repeatability at zero and at measured concentration

$u(eff) = 0.5\ \%,$ (6)
is the uncertainty of the converter efficiency

$u(NO)_{PRM} = 0.9\ \%$ (7)
From the measured value. Uncertainty of the analyser includes: calibration of the analyser, linearity, repeatability at zero and at measured concentration.

<u>The correlation factors are analysed next:</u>

$r_{[NO_2]_{K74}, C(NO)_{PRM}} = 0,$ (8)
No correlation between the concentration of PRM and the concentration of NO_2 was observed at the CCQM-K74 standard

$r_{[NO_2]_{K74}, eff} = -0.004(\% / nmol / mol)$ (9)
Analysed of the converter efficiency as a function of NO_2 concentration during GPT

$r_{[NO_2]_{K74}, [NO]_{PRM}} = 0$ (10)
No correlation between the CCQM-K74 and PRM

$r_{C(NO)_{PRM}, eff} = 0.25(\% nmol / mol)$ (11)
Linked with the uncertainty of the PRM

$$r_{C(NO)_{PRM},[NO]_{PRM}} = 0.01 \tag{12}$$

Dilution ratio of the dilution method

$$r_{eff,[NO]_{PRM}} = 0.004(\%/nmol/mol) \tag{13}$$

Analysed of the converter efficiency as a function of NO concentration during GPT

As a result from the measurements and the values applied in eqs (4) to (13) into eq. (3) the relative combined standard uncertainty was calculated as 1.5 % and 0.151 µmol/mol as an absolute value.

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[9].

The method used for the analysis of the cylinder is the one supported by the laboratory in routine work. The method is based on comparison of the results between the dilutions of the known concentration of the gas standard with the result of the unknown standard at the same dilution stage. The known concentration of the gas standard, PRM, by NPL of 49.86 µmol/mol NO in nitrogen with the relative expanded uncertainty of 0.5 % and the unknown standard was the KC standard (APEX 930 673). Since the gas compound of the KC gas compound was nitrogen dioxide the converter efficiency of the gas analyser, based on chemiluminescence method, was defined prior the measurements. The converter efficiency of the gas analyser used, APNA-360 by Horiba, was defined by the gas phase titration method. In addition the linearity of the APNA-360 analyser was defined in the range covering the concentration range for both of the measurements. The concentration of the KC gas standard was calculated according to equation 1.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

67 bar

If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
NO	2.	0.5 nmol/mol	2	Direct measurement by TEI42C analyser bypassing the NO_2 converter

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[9] The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

Istituto Nazionale di Ricerca Metrologica (INRIM)

A1. General information

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Serial number of cylinder received	930667		
Cylinder pressure as received	90 bar		

A2. Results

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{\mathrm{NO2}})$ / µmol/mol	Coverage factor
11,47	0,14	2

Tab. 1: INRIM results

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The contributions to the combined standard uncertainty of the results are due to the calibration curve and to repeatability of readings of sample measurements. From each of the four calibration curves a NO_2 concentration value with its combined standard uncertainty was estimated. The final result is the mean of these four values and its combined standard uncertainty was calculated by pooling the four variances.

Determination of calibration curves

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

$$x = y + d(y) = y + \alpha_0 + \alpha_1 y \quad (1)$$

where x is concentration of the analyte in the reference gas mixtures, y is the instrument output and $d(y) = \alpha_0 + \alpha_1 y$ is the correction. The measurands are the polynomial coefficients α_0 and α_1. The estimation algorithm takes care of different sources of uncertainty: the reference gas mixtures uncertainty, the repeatability of the instrument, the lack of fit, the instrument resolution. These sources are merged together in the Excel worksheet for calibration curves calculation, hence it is very difficult to separate each contribution. For detailed information see the reference: Plassa M., Mosca M., Sega M. “Carbon Dioxide Determination for High Accuracy Weighings” in: *Proceedings of the 16th International Conference IMEKO TC3/APMF ’98*, Myung Sai Chung Ed.; Taejon, Korea, **1998**, pp. 183-191.

Being the reference gas mixtures prepared at INRIM by diluting the same pre-mixture, a correlation coefficient of 0,9 was adopted in the calculation.

Calibration curve data are summarized in the following tables (Tab. 2-5):

	α	$u_c(\alpha)$	ψ_α	
α_0	1,1E-1	1,8E-01	3,27E-02	-2,97E-03
α_1	-2,4E-02	1,7E-02	-2,97E-03	2,89E-04

Tab. 2: calibration curve parameters of 29/12/09 (first set)

	α	$u_c(\alpha)$	ψ_α	
α_0	6,3E-03	2,0E-01	3,84E-02	-3,69E-03
α_1	-1,6E-02	1,9E-02	-3,69E-03	3,70E-04

Tab. 3: calibration curve parameters of 30/12/09 (second set)

	α	$u_c(\alpha)$	ψ_α	
α_0	-6,7E-02	2,1E-01	4,28E-02	-3,62E-03
α_1	-1,7E-02	1,8E-02	-3,62E-03	3,22E-04

Tab. 4: calibration curve parameters of 04/01/10 (third set)

	α	$u_c(\alpha)$	ψ_α	
α_0	3,3E-02	1,7E-01	2,79E-02	-2,51E-03
α_1	-2,0E-02	1,6E-02	-2,51E-03	2,44E-04

Tab. 5: calibration curve parameters of 05/01/10 (fourth set)

After the calibration process α_0 and α_1 being known, if a set of n_r instrument readings, arranged in a vector $\boldsymbol{r}$, are to be corrected by the calibration algorithm, the matrix R can be defined, whose columns are the first two powers of $\boldsymbol{r}$:
$R = (r^0 \; r)$
The correction vector $\boldsymbol{d}(r)$ can be computed from $\boldsymbol{d}(r) = R\,\boldsymbol{\alpha}$, where $\boldsymbol{\alpha}$ is the vector of the coefficients α_0 and α_1. The corrected readings are:
$q = d(r) + r$ (2)
The covariance matrix of the readings is $\psi_r = s^2\mathbf{I}$, where s is the repeatability standard uncertainty of the instrument and I an identity matrix. The covariance matrix ψ_d of d can be estimated starting from the law of propagation of uncertainty:

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

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

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[10].

The analysis was carried out by means of a chemiluminescence analyser CLD Thermo 42i having resolution of 0,01 µmol mol^{-1}. The data are visualized on the instrument display and manually recorded. For its calibration, a set of three gas mixtures, having the characteristics reported in table 6, were prepared at INRIM by gravimetry. The mixtures were prepared in aluminium alloy cylinders of 5L by diluting with synthetic air N 57 a pre-mixture of NO at the concentration of 99,49 µmol/mol (U=0,80 µmol/mol, k=2) in N_2 purchased from NPL (UK). The gravimetric preparation was carried out following the weighing scheme A-B-B-A.
For the uncertainty evaluation of the gas mixtures prepared at INRIM, the following sources were taken into account: molar masses of parent gases, purity of parent gases, composition of the pre-mixture, weighing of parent gases, covariances between the input quantities.

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[10] The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

The gravimetric preparation was checked twice by comparison with two different sets of three mixtures of NO_2 in synthetic air or purified air: the first set was made by a mixture purchased form NPL and two from an ISO 17025 accredited laboratory; the second set was made by three mixtures purchased from an ISO 17025 accredited laboratory. The analyses confirmed also the complete oxidation of NO into NO_2 during the mixture preparation process.

A mixture of NO_2 at the concentration of 10,07 µmol/mol (U=0,15 µmol/mol, k=2) in synthetic air, purchased form NPL, was used as a quality control standard to validate the calibration curve obtained with INRIM mixtures. The results were satisfactory: the certified value and the analytical values obtained at INRIM are in agreement within the declared uncertainties.
As for purity, the data certified by the producers were used.

Mixture number	Cylinder number	NO_2 molar fraction χ µmol/mol	$U(\chi)$ (k=2) µmol/mol
026	D69 6430	11,88	0,05
028	D56 6403	10,21	0,04
030	D56 6405	8,24	0,03

Tab. 6: calibration mixtures

The measurements were carried out at a flow of approximately 35 L h^{-1}. It was previously proved that small flow variations do not affect the measurement value. The instrument readings were collected after the signal stabilization, i.e. 2 minutes.
No correction for ambient pressure was made because the instrument had been calibrated every day in which measurements were carried out according to the following measurement protocol:
Standard n. 1, Sample, Standard N. 2, Sample, Standard N. 3, Sample, (repeated 3 times). The control standard was analysed at the beginning and at the end of the entire sequence.
No correction for ambient temperature was made.
Four different calibration curves were determined, one for each measurement day and they were used to estimate the final result for NO_2, according to section A3.

The result reported in Table 1 for the estimated concentration of NO_2 if compared with the nominal value of the comparison shows a great discrepancy. Considering that the checking of INRIM calibration standards showed a good comparability between the gravimetric values and the analytical values, and also the NPL mixture of NO_2 used to validate the calibration curves showed a comparability within the declared uncertainty, a possible matrix effect could be the reason of such discrepancy. Indeed, INRIM standard mixtures, the mixtures used for their analytical verification and the NPL mixture used as a control standard have a matrix of synthetic air or purified air, instead the mixture analysed for the comparison has a matrix of nitrogen. This effect was not investigated during the measurements, but some additional measurements are being carried out at INRIM in order to check this aspect.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM: 70 bar

If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique

Result form CCQM-K74-R: Addendum to INRIM report

1. Introduction

In section A 5 it was stated that “The result reported in Table 1 for the estimated concentration of NO_2 if compared with the nominal value of the comparison shows a great discrepancy. Considering that the checking of INRIM calibration standards showed a good comparability between the gravimetric values and the analytical values, and also the NPL mixture of NO_2 used to validate the calibration curves showed a comparability within the declared uncertainty, a possible matrix effect could be the reason of such discrepancy. Indeed, INRIM standard mixtures, the mixtures used for their analytical verification and the NPL mixture used as a control standard have a matrix of synthetic air or purified air, instead the mixture analysed for the comparison has a matrix of nitrogen. This effect was not investigated during the measurements, but some additional measurements are being carried out at INRIM in order to check this aspect.”

Additional measurement were carried out at INRIM to evaluate the possible bias due to the different concentration of O_2 in the CCQM-K74 mixture (0,001 mol/mol) and in the INRIM standards (0,164 mol/mol) used to calibrate the chemiluminescence analyser for the determination of NO_2 mole fraction in the CCQM-K74 cylinder.

2. Evaluation of sensitivity of INRIM chemiluminescence analyser

Gravimetric mixtures containing NO_2 at mole fraction of about 10 µmol/mol and different mole fractions of oxygen prepared at INRIM having composition reported in table 7, were analysed.

Mixture number	Cylinder number	NO_2 mole fraction χ µmol/mol	$U(\chi)$ (k=2) µmol/mol	O_2 mole fraction mol/mol
027	D69 6406	10,20	0,04	0,164
028(*)	D56 6403	10,21	0,04	0,164
032	D56 6404	10,17	0,04	0,045
031	D56 6402	9,94	0,04	0,009
033	D56 6409	9,77	0,04	0,001

Tab. 7: INRIM mixtures used to check the sensitivity of INRIM chemiluminescence analyser having different O_2 mole fractions. (*)One of the 3 mixtures used to calibrate the analyser during the CCQM-K74 measurements (see table 6).

The analyses showed, as expected, a bias affecting the determination of NO_2 mole fraction which is related to the concentration of O_2 present in the mixtures. At the increasing of O_2 concentration, being the nominal mole fraction of NO_2 almost the same, its value, analytically determined by means of the chemiluminescence analyser, increases following a non-linear model.

The sensitivity factor of the analyser itself at the different O_2 mole fractions was calculated by dividing the analyser response by the NO_2 mole fraction. Also the data obtained during the measurements for the CCQM comparison were analysed and the analyser sensitivity for O_2 at 0,164 mol/mol (oxygen mole fraction of INRIM mixtures used for the analyser calibration in the comparison) was determined. The analyser showed comparable values of sensitivity during both the CCQM-K74 analyses and the additional measurements carried out after the comparison, confirming that its performances had remained stable over the time period. Comparing the values, the sensitivity for the analyser for the CCQM-K74 mixture was hence calculated considering an O_2 concentration of 0,001 mol/mol.

3. Determination of the correction

With the same calibration standards used for the CCQM comparison, listed in table 6, INRIM mixture n. 033 containing 0,001 mol/mol of O_2 was analysed following the same protocol used for the comparison and an analytical value for the NO_2 mole fraction, $x_{\text{analytical\_INRIM}}$, was determined. The same quality control standard was also used.

Table 8 reports the calibration curve parameters; table 9 reports the analytical value $x_{\text{analytical\_INRIM}}$, the corresponding gravimetric value $x_{\text{grav\_INRIM}}$ for mixture n. 033 and their standard uncertainties.

	α	$u_c(\alpha)$	ψ_α	
α_0	-5,7E-01	2,5E-01	6,26E-02	-6,20E-03
α_1	-8,0E-02	2,5E-02	-6,20E-03	6,40E-04

Tab. 8: calibration curve parameters of 09/06/10

	NO_2 molar fraction χ µmol/mol	$u(\chi)$ µmol/mol
$x_{\text{analytical\_INRIM}}$	11,25	0,07
$x_{\text{grav\_INRIM}}$	9,77	0,02

Tab. 9: NO_2 molar fractions in INRIM mixture n. 033 with their standard uncertainties

Two different methods were used to calculate the correction for the x_{NO2} value determined during the CCQM-K74 measurements: a multiplicative one, based on the analyser sensitivity, and a additive one based on the difference between the analytical value and the gravimetric one for INRIM mixture n. 033. Due to it being easiest method of estimating the uncertainty of the correction, the additive method was chosen.

The difference $x_{\text{analytical\_INRIM}} - x_{\text{grav\_INRIM}}$ (1,48 µmol/mol), is the correction for the analytical bias due to the effect of O_2.

The corrected mole fraction of NO_2 , $\hat{x}_{\text{NO2}}$, is calculated according to eq. 3:

$$\hat{x}_{\text{NO2}} = x_{\text{NO2}} - (x_{\text{analytical\_INRIM}} - x_{\text{grav\_INRIM}}) \tag{3}$$

where

x_{NO2} :	is the mole fraction of NO_2 analytically determined by INRIM in the analysis of the CCQM-K74 cylinder, reported in table 1;
$x_{\text{grav\_INRIM}}$:	is the mole fraction of NO_2 calculated from the gravimetric preparation of INRIM mixture n. 033 containing 0,001 mol/mol of O_2
$x_{\text{analytical\_INRIM}}$:	is the mole fraction of NO_2 analytically determined in INRIM mixture n. 033 with the parameters reported in table 8.

4. Uncertainty Budget

The combined standard uncertainty of $\hat{x}_{\text{NO2}}$ is calculated according to eq. 4:

$$u(\hat{x}_{\text{NO2}}) = \sqrt{u^2(x_{\text{NO2}}) + u^2(x_{\text{grav\_INRIM}}) + x^2{}_{\text{analytical\_INRIM}} - 2u^2(x_{\text{grav\_INRIM}})} \tag{4}$$

where the last term is due to the covariances between the two series of results x_{NO2} and $x_{\text{analytical\_INRIM}}$ which have been determined using the same set of calibration gas mixtures. The value of $u(x_{\text{grav\_INRIM}})$ was used for the covariance contribution as it represents a typical value of standard uncertainty for the gravimetrically prepared mixtures at INRIM (see also table 6).

The values of the different contributions are shown in table 10.

Quantity	Standard uncertainty µmol/mol
x_{NO2}	0,07
$x_{\mathrm{grav\_INRIM}}$	0,02
$x_{\mathrm{analytical\_INRIM}}$	0,07
	Covariance µmol²/mol²
$x_{\mathrm{grav\_INRIM}}$	-0,0008

Tab. 10: uncertainty contributions for $u_{\mathrm{c}}(x_{\mathrm{NO2}})$

5. Results

Table 11 reports the corrected results for $\hat{x}_{\mathrm{NO2}}$ with its expanded uncertainty.

Nitrogen dioxide mole fraction $\hat{x}_{\mathrm{NO2}}$ / µmol/mol	Expanded uncertainty $U(\hat{x}_{NO2})$ / µmol/mol	Coverage factor
9,99	0,20	2

Tab. 11:corrected results for $\hat{x}_{\mathrm{NO2}}$

The corrected value obtained using the multiplicative factor is $\hat{x}_{\mathrm{NO2}}$ = 10,03 µmol/mol, which is comparable with the value reported in table 11, within the asociated uncertainty.

Korea Research Institute of Standards and Science (KRISS)

A1. General information

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Serial number of cylinder received	D650044		
Cylinder pressure as received	about 85 bar		

A2. Results

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{\mathrm{NO2}})$ / µmol/mol	Coverage factor
10.45	0.31	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Analyte	Relative standard uncertainties / %			Expanded uncertainty / %	Coverage factor
	Gravimetry	Analysis	Stability		
NO_2	0.07	0.25	1.45	2.95	2

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[11].

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[11] The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

The NO_2 was analysed using a chemiluminescent NO/NOx analyser (Thermo Model 42*i*). 6 PRMs, about 10 μmol/mol, were connected to multi-position valve of a computer operated gas sampling system (lab. made). A gas sampling system was used to deliver the sample stream to the NO/NOx analyser and collect responses. Analysis and stability uncertainties were calculated from these data. The K -74 cylinder and 1 PRM (D727632) were analysed likewise. Sample flow (300 ml/min) to the instrument was controlled by MFC (Bronkhorst) during analysis and each sample was purged for three minutes as follows.

PSM(15 minutes) – Nitrogen(3 minutes) – K-74(15 minutes) – Nitrogen(3 minutes) – PSM(15 minutes) …

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

About 55 bar

If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique

Laboratoire National de métrologie et d'Essais (LNE)

A1. General information

Institute	Laboratoire National de métrologie et d'Essais (LNE)		
Address	1, rue Gaston Boissier 75 724 Paris Cedex 15		
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Email*	tatiana.mace@lne.fr		
Serial number of cylinder received	D650058		
Cylinder pressure as received	95 bars		

A2. Results

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{\mathrm{NO2}})$ / µmol/mol	Coverage factor
10,26	0,13	k=2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

First step :

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

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

Uncertainty source	x_I (nmol/mol)	Assumed distribution	Standard uncertainty $u(x_i)$ (nmol/mol)	Sensitivity coefficient c_I	Contribution to standard uncertainty $u_I(y)$
Concentration of the reference gas mixture generated	299.8	-	0.9578	0.993	0.9511

by permeation (C_1)					
Reading for the reference gas mixture generated by permeation (L_1)	304	rectangular	0.577	0.980	0.5655
Reading for the diluted unknown gas mixture (L_2)	302	rectangular	0.577	0.986	0.5690

Concentration of the diluted unknown gas mixture (C_2)	297.84 nmol/mol	1.24 nmol/mol

Then, the standard uncertainty is calculated for each concentration of the unknown gas mixture $C_2^{'}$ as described in the following example.

Uncertainty source	x_I (nmol/mol)	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_2)	297.84	-	1.24	34.40	42.66
Flowrate of the NO_2 unknown gas mixture (NO_2 cylinder) (D_1)	75.126	-	0.19	132.43	25.16
Flowrate of the dilution gas (nitrogen) (D_2)	2509.40	-	6.27	3.96	24.83

Concentration of the unknown gas mixture (C_2')	10246.43 nmol/mol	55.5 nmol/mol

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

Date	Concentrations of the unknown gas mixture (C_2') (nmol/mol)	$u(C_2')$ (nmol/mol)
13/10/2009	10210.967	54.2
13/10/2009	10240.679	54.0
13/10/2009	10241.613	54.0
16/10/2009	10295.842	54.7
16/10/2009	10268.717	55.0
16/10/2009	10307.627	55.1
22/10/2009	10246.432	55.5
22/10/2009	10249.799	55.8
22/10/2009	10281.519	55.8

The mean standard uncertainty is calculated as follows:

$$u_{mean} = \sqrt{\frac{\sum u^2(C_2')}{n}} = 54.91 \ nmol / mol$$

<u>Second step :</u>

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

$$\sigma = 30.61 \, nmol / mol$$

Third step :

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

$$U(x_{NO2}) = 2 \times \sqrt{u_{mean}^2 + \sigma^2} = 0.13\ \mu mol / mol$$

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[12].

Reference Instrument :
A 42C (TEI) analyser based on the principle of chemiluminescence was used to measure the NO_2 concentrations.

Calibration Standard :
A reference dynamic gas mixture of NO_2 in nitrogen (at about 300 nmol/mol) was generated by the LNE reference method which is the permeation method.

Description of the analytical procedure :
A reference gas mixture was generated by permeation at a concentration (C_1 near 300 nmol/mol) slightly higher than the concentration of the unknown gas mixture and injected into the analyser : the response of the analyser was recorded (L_1).

The unknown gas mixture at about 10 µmol/mol was diluted to about 300 nmol/mol : this dynamic unknown gas mixture was then injected into the analyser and the response (L_2) was recorded.

The NO_2 concentration of the diluted unknown gas mixture (C_2) was equal to :

$$C_2 = \frac{C_1 \times L_2}{L_1}$$

The NO_2 concentration of the unknown gas mixture $C_2^{'}$ was :

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[12] The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

$$C_2' = \frac{C_2 \times (D_1 + D_2)}{D_1}$$

With : C_2 the concentration of the diluted unknown gas mixture
D_1 the flowrate of the NO_2 unknown gas mixture (NO_2 cylinder)
D_2 the flowrate of the dilution gas (nitrogen)

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

The NO_2 concentration is the mean of the 9 obtained values.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

The pressure left in the cylinder before shipment to the BIPM was about 80 bar.

If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique

Federal Office of Metrology (METAS)

A1. General information

Institute	METAS		
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Serial number of cylinder received	930660		
Cylinder pressure as received	96 bar		

A2. Results

Measurement #1

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{\mathrm{NO2}})$ / µmol/mol	Coverage factor
10.63	0.17	2

Measurement #2

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
10.62	0.17	2

Measurement #3

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
10.63	0.16	2

Result

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
10.63	0.16	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Model Equation for measurement 2 :

$V_{norm}1=V_{mol}1*f_{5000};$
$V_{norm}2=V_{mol}2*f_{5000};$
$V_{norm}3=V_{mol}3*f_{5000};$

$V_{mfc}mean=(V_{mfc}1+V_{mfc}2+V_{mfc}3)/3;$

$p=(V_{norm}1-V_{norm}mean)*(V_{mfc}1-V_{mfc}mean)+(V_{norm}2-V_{norm}mean)*(V_{mfc}2-V_{mfc}mean)+(V_{norm}3-V_{norm}mean)*(V_{mfc}3-V_{mfc}mean);$
$q=(V_{norm}1-V_{norm}mean)\hat{}2+(V_{norm}2-V_{norm}mean)\hat{}2+(V_{norm}3-V_{norm}mean)\hat{}2;$
$b=p/q;$

$a=V_{mfc}mean-b*V_{norm}mean;$

$V_{norm}bouteille=(V_{mfc}bouteille-a)/b;$

$V_{dilution}norm=V_{dilution}*f_{5000}bis;$

$X_{ppbA1}=((qmC*486.9))/(qv_1*f_{10000});$
$X_{ppbA2}=((qmC*486.9))/(qv_2*f_{10000});$
$X_{ppbA3}=((qmC*486.9))/(qv_3*f_{10000});$

$X_{ppb}meanA=(X_{ppbA1}+X_{ppbA2}+X_{ppbA3})/3-X_{NOx};$
$Anz_{meanA}=(Anz_{ppbA1}+Anz_{ppbA2}+Anz_{ppbA3})/3;$
$p2=(X_{ppbA1}-X_{ppb}meanA)*(Anz_{ppbA1}-X_{NOx}-Anz_{meanA})+(X_{ppbA2}-X_{ppb}meanA)*(Anz_{ppbA2}-X_{NOx}-Anz_{meanA})+(X_{ppbA3}-X_{ppb}meanA)*(Anz_{ppbA3}-X_{NOx}-Anz_{meanA});$
$q2=(X_{ppbA1}-X_{ppb}meanA)^\wedge 2+(X_{ppbA2}-X_{ppb}meanA)^\wedge 2+(X_{ppbA3}-X_{ppb}meanA)^\wedge 2;$
$b2=p2/q2;$
$a2=Anz_{meanA}-b2*X_{ppb}meanA;$

$C_{lu}=(AnzRes-X_{NO2}-a2)/b2$
$C_{bouteille}=C_{lu}*V_{norm}bouteille/(V_{norm}bouteille-V_{dilution}norm);$

List of Quantities:

Quantity	Unit	Definition
V_{norm}mean	ml/min	Average flow normal
V_{norm}1	ml/min	Flow 1 normal
V_{norm}2	ml/min	Flow 2 normal
V_{norm}3	ml/min	Flow 3 normal
V_{mol}1	ml/min	Flow 1 molbloc
f_{5000}		Correction factor for flow calibration 5000 ml/min molbloc
V_{mol}2	ml/min	Flow 2 molbloc
V_{mol}3	ml/min	Flow 3 molbloc
V_{mfc}mean	ml/min	Average flow Mass flow meter
V_{mfc}1	ml/min	Flow 1 mass flow meter overflow
V_{mfc}2	ml/min	Flow 2 mass flow meter overflow
V_{mfc}3	ml/min	Flow 3 mass flow meter overflow
b		Slope of calibration function for flow
p		Numerator for slope of flow calibration function
q		Denominator for slope of flow calibration function
a		Inter of calibration function for flow
V_{norm}bouteille	ml/min	Test mixture flow normal
V_{mfc}bouteille	ml/min	Test mixture flow mass flow meter
$V_{dilution}$norm	ml/min	Dilution flow normal
$V_{dilution}$	ml/min	Dilution flow
f_{5000}bis		Correction factor for flow calibration 5000 ml/min molbloc
$C_{bouteille}$	nmol/mol	Nitrogen dioxide mole fraction in the test mixture
C_{lu}	nmol/mol	Nitrogen dioxide mole fraction diluted
X_{ppbA1}	nmol/mol	Nitrogen dioxide mole fraction balance 1
qmC	ng/min	Mass flow NO_2 permeation unit

Quantity	Unit	Definition
qv_1	ml/min	Flow balance 1
f_{10000}		Correction factor for flow calibration 10000 ml/min molbloc
X_{ppbA2}	nmol/mol	Nitrogen dioxide mole fraction balance 2
qv_2	ml/min	Flow balance 2
X_{ppbA3}	nmol/mol	Nitrogen dioxide mole fraction balance 3
qv_3	ml/min	Flow balance 3
$X_{ppb}meanA$	nmol/mol	Nitrogen dioxide mole fraction balance average
X_{NOx}	nmol/mol	Nitrogen dioxide mole fraction air zero balance
Anz_{meanA}		Display instrument average
Anz_{ppbA1}		Display instrument 1
Anz_{ppbA2}		Display instrument 2
Anz_{ppbA3}		Display instrument 3
b2		Slope of calibration function for instrument indication
p2		Numerator for slope of indication calibration function
q2		Denominator for slope of indication calibration function
a2		Intercept of calibration function for instrument indication
AnzRes		Display test mixture
X_{NO2}	nmol/mol	Nitrogen dioxide mole fraction dilution

V_{mol}1: Type B normal distribution Value: 1140.840929 ml/min Expanded Uncertainty: 0.308797961 ml/min Coverage Factor: 2	**f_{5000}:** Type B normal distribution Value: 1 Expanded Uncertainty: 0.15 % Coverage Factor: 2
V_{mfc}1: Type B normal distribution Value: 99.10032386 ml/min Expanded Uncertainty: 0.136235451 ml/min Coverage Factor: 2	**V_{mfc}bouteille:** Type B normal distribution Value: 99.45063673 ml/min Expanded Uncertainty: 0.137777628 ml/min Coverage Factor: 2
$V_{dilution}$: Type B normal distribution Value: 1101.371378 ml/min Expanded Uncertainty: 0.30 ml/min Coverage Factor: 2	**f_{5000}bis:** Type B normal distribution Value: 1 Expanded Uncertainty: 0.15 % Coverage Factor: 2
qmC: Type B normal distribution Value: 1035.46 ng/min Expanded Uncertainty: 1 % Coverage Factor: 2	**qv_1:** Type B normal distribution Value: 1399.46341 ml/min Expanded Uncertainty: 0.35224 ml/min Coverage Factor: 2
f_{10000}: Type B normal distribution Value: 1 Expanded Uncertainty: 0.15 % Coverage Factor: 2	**X_{NOx}:** Type B normal distribution Value: 0.13 nmol/mol Expanded Uncertainty: 0.02 nmol/mol Coverage Factor: 2
Anz_{ppbA1}: Type B normal distribution Value: 363.31 Expanded Uncertainty: 0.35 Coverage Factor: 2	**AnzRes:** Type B normal distribution Value: 377.21 Expanded Uncertainty: 0.26 Coverage Factor: 2
X_{NO2}: Type B normal distribution Value: 0.1107 nmol/mol Expanded Uncertainty: 0.02 nmol/mol Coverage Factor: 2	

Input Correlation

	f_{5000}	f_{5000} bis	f_{10000}	V_{mol} 1	V_{mol} 2	V_{mol} 3	V_{mfc} 1	V_{mfc} 2	V_{mfc} 3	V_{mfc} bouteille	$V_{dilution}$	qmC	qv_1	qv_2	qv_3	Anz_{ppbA1}	Anz_{ppbA2}	Anz_{ppbA3}	AnzRes
f_{5000}	1	0.95	0.9																
f_{5000}bis	0.95	1	0.9																
f_{10000}	0.9	0.9	1																
V_{mol}1				1	0.9	0.9	0.9	0.9	0.9	0.9	0.9		0.5	0.5	0.5				
V_{mol}2				0.9	1	0.9	0.9	0.9	0.9	0.9	0.9		0.5	0.5	0.5				
V_{mol}3				0.9	0.9	1	0.9	0.9	0.9	0.9	0.9		0.5	0.5	0.5				
V_{mfc}1				0.9	0.9	0.9	1	0.9	0.9	0.9	0.9		0.5	0.5	0.5				
V_{mfc}2				0.9	0.9	0.9	0.9	1	0.9	0.9	0.9		0.5	0.5	0.5				
V_{mfc}3				0.9	0.9	0.9	0.9	0.9	1	0.9	0.9		0.5	0.5	0.5				
V_{mfc}bouteille				0.9	0.9	0.9	0.9	0.9	0.9	1	0.9		0.5	0.5	0.5				
$V_{dilution}$				0.9	0.9	0.9	0.9	0.9	0.9	0.9	1		0.5	0.5	0.5				-1
qmC												1				1	1	1	
qv_1				0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5		1			-0.9			
qv_2				0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5			1			-0.9		
qv_3				0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5				1			-0.9	
Anz_{ppbA1}												1	-0.9			1			
Anz_{ppbA2}												1		-0.9			1		
Anz_{ppbA3}												1			-0.9			1	

Example Uncertainty Budgets (measurement #2):

$C_{bouteille}$: Nitrogen dioxide mole fraction in the test mixture

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$V_{mol}1$	1140.841 ml/min	0.154 ml/min	normal	-180	-28 nmol/mol	1.1 %
f_{5000}	1.000000	0.000750	normal	$-290\cdot10^3$	-220 nmol/mol	54.4 %
$V_{mol}2$	1143.759 ml/min	0.141 ml/min	normal	-87	-12 nmol/mol	0.2 %
$V_{mol}3$	1146.875 ml/min	0.145 ml/min	normal	not valid!	1.8 nmol/mol	0.0 %
$V_{mfc}1$	99.1003 ml/min	0.0681 ml/min	normal	360	25 nmol/mol	0.8 %
$V_{mfc}2$	100.5622 ml/min	0.0672 ml/min	normal	170	12 nmol/mol	0.2 %
$V_{mfc}3$	102.1276 ml/min	0.0721 ml/min	normal	-25	-1.8 nmol/mol	0.0 %
V_{norm}bouteille	1141.540 ml/min	0.871 ml/min				
V_{mfc}bouteille	99.4506 ml/min	0.0689 ml/min	normal	-510	-35 nmol/mol	1.7 %
$V_{dilution}$norm	1101.371 ml/min	0.840 ml/min				
$V_{dilution}$	1101.371 ml/min	0.150 ml/min	normal	260	40 nmol/mol	0.2 %
f_{5000}bis	1.000000	0.000750	normal	$290\cdot10^3$	220 nmol/mol	11.2 %
qmC	1035.46 ng/min	5.18 ng/min	normal	10	53 nmol/mol	34.9 %
qv_1	1399.463 ml/min	0.176 ml/min	normal	-3.6	-0.64 nmol/mol	0.0 %
f_{10000}	1.000000	0.000750	normal	-11000	-8.0 nmol/mol	0.9 %
qv_2	1322.228 ml/min	0.174 ml/min	normal	-2.6	-0.45 nmol/mol	0.0 %
qv_3	1271.393 ml/min	0.199 ml/min	normal	-1.7	-0.33 nmol/mol	0.0 %
X_{NOx}	0.1300 nmol/mol	0.0100 nmol/mol	normal	-29	-0.29 nmol/mol	0.0 %
Anz_{ppbA1}	363.310	0.175	normal	-14	-2.4 nmol/mol	-1.7 %
Anz_{ppbA2}	384.820	0.225	normal	-8.8	-2.0 nmol/mol	-1.4 %
Anz_{ppbA3}	400.370	0.170	normal	-5.2	-0.89 nmol/mol	-0.6 %
AnzRes	377.210	0.130	normal	28	3.6 nmol/mol	-1.8 %
X_{NO2}	0.1107 nmol/mol	0.0100 nmol/mol	normal	-28	-0.28 nmol/mol	0.0 %
$C_{bouteille}$	10617.7 nmol/mol	85.3 nmol/mol				

The uncertainty budget has been calculated using GUM Workbench Pro software (version 2.3.2.36 beta). The main contributions to the combined standard uncertainty are:

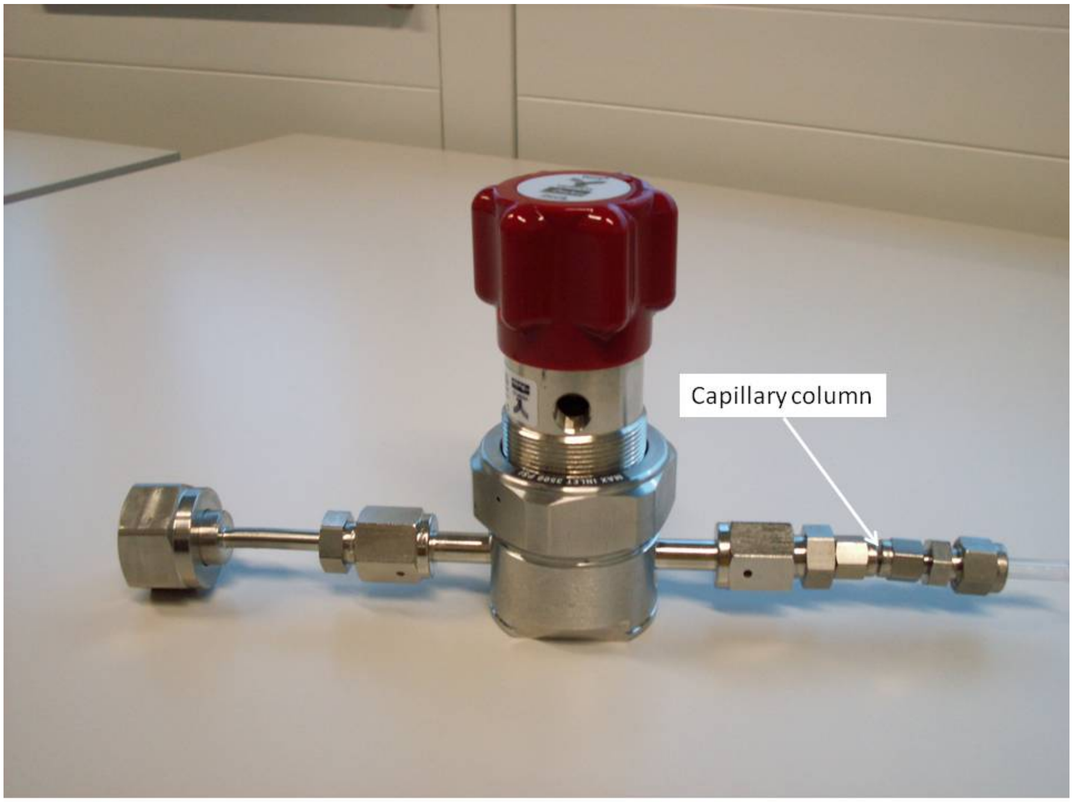
- the standard uncertainty of the NO_2 mass flow from the permeation unit
- the standard uncertainties of the flow measurements

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[13].

A commercial chemiluminescence trace level NO_2-analyser (Thermo 42i -TL) was calibrated with NO_2 calibration standards in the range from 360 nmol·mol^{-1} to 396 nmol·mol^{-1} NO_2 in air. The calibration standards were produced by the METAS primary micro gravimetric standard and a NO_2 permeation unit with purity $\geq$ 99 %. The total zero air dilution gas flow was measured by a molbox-molbloc system. The NO_2 mass flow of the permeation unit was approx. 1035 ng·min^{-1} at 25 °C. This value is an average over 5 days and was used for the 3 calibrations.

The test mixture 930660 was dynamically diluted with zero air by a factor of about 0.036 such that the expected amount of substance fraction of the sample lies within the validated and calibrated range of the analyser and of the METAS micro-gravimetric Standard. The flow of the test mixture was set using a capillary column. The upstream pressure at the capillary column was kept constant by a pressure regulator Parker Veriflo (Hastelloy C-22 alloy).



The flow of the test mixture was calculated by subtracting the dilution gas flow from the total flow going to the instrument. The flow of the dilution gas was regulated with a mass flow controller and measured using a molbox-molbloc system. The total flow was calculated by measuring the “over-flow” of the instrument with a mass flow meter (MFM) as shown in the following scheme.

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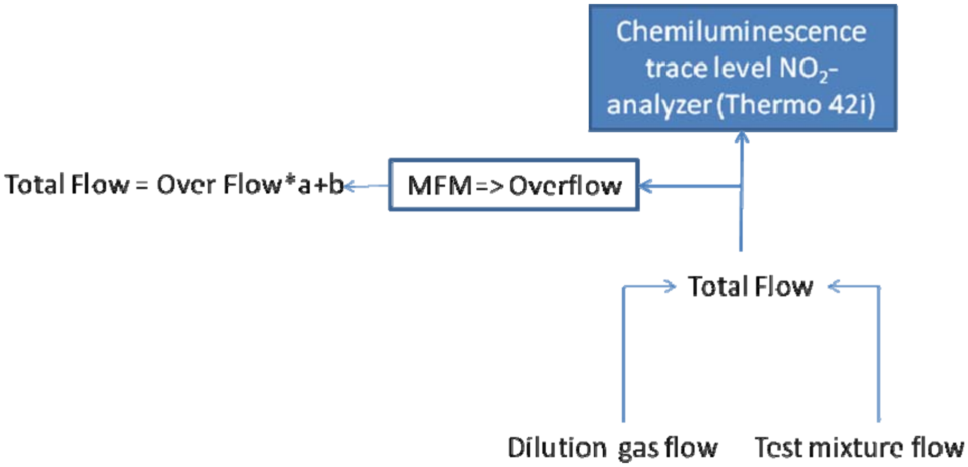
[13] The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.



The linear interpolation was determined experimentally by changing the total flow such that the overflow during the test mixture analysis lies within calibrated range of the mass flow meter.

The resulting gas mixture was measured with the NO_2-analyser and the amount of substance fraction calculated by linear interpolation in agreement with ISO 6143:2001(E).

The molbox-molbloc system was calibrated with the METAS primary standard for low gas flows.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM: 78 bar

If any component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
NO	<1ppb			Chemiluminescence

National Measurement Institute Australia (NMIA)

A1. General information

Institute	NMIA – National Measurement Institute Australia		
Address	Bradfield Road Lindfield NSW 2070 AUSTRALIA		
Contact person	Damian Smeulders		
Telephone	+61 2 84673534	Fax	+61 2 8467 3752
Email*	damian.smeulders@measurement.gov.au		
Serial number of cylinder received	930662		
Cylinder pressure as received	100 bar		

A2. Results

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{\mathrm{NO2}})$ / µmol/mol	Coverage factor
10.74	0.63	2

A3. Uncertainty Budget

Combined standard uncertainty: u = 0.32 µmol/mol

Expanded uncertainty: U = 0.63 µmol/mol

Contributions to uncertainty:
Gravimetric uncertainty: 0.018
Mixture stability and conversion to NO_2: 0.075
Instrument contributions:
    Repeatability: 0.30
    Resolution: 0.020
    Difference due to spectral regions: 0.050

A4. Description of the procedure used during the gas analysis

A Nicolet FT-IR was used to acquire the spectra of the standards and unknown sample. The spectra were run at resolutions of 0.5cm^{-1} and 0.25cm^{-1} with an aperture setting of 2. 100 scans were obtained for each analysis. The background spectra were collected on the evacuated cell. Spectra were collected on a static gas sample with a temperature of 60 ºC at a pressure of 650 Torr.

The strong bands in the region 1530 cm^{-1} to 1670 cm^{-1} and the weaker bands in the region 2840 cm^{-1} to 2940 cm^{-1} were both used for quantitation. The analyses of the standards and sample were repeated three times at each resolution with evacuation and flushing of the cell between tests. The analysis procedure was repeated on several occasions over a two week period.

Four closely bracketed calibration standards containing NO_2 over the concentration range 8 µmol/mol to 12 µmol/mol were used to determine the concentration of NO_2 in the cylinder from the BIPM. Standards were made in uncoated, but passivated 5L Luxfer aluminium cylinders with SS valves. Standards were manufactured from nitrogen oxide that was converted to nitrogen dioxide in the presence of oxygen. Oxygen in the final mixtures was present at approximately 1000 µmol/mol.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM: 78 bar

If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique

National Institute of Metrology (NIM)

Lab Information

Lab Code: 58
Lab Name: National Institute of Metrology (NIM), China
Contact point: Dr. Qiao HAN
Email: hanqiao@nim.ac.cn
Tel.: +86-10-84252300 Fax.: +86-10-84252306
Date of Receiving the Comparison Cylinder: November, 2009
Cylinder No.: 930650

Measurement of NO_2 by 42C NO-NO2-NOx Analyzer

Group #	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
1	26/01/10	10.14	0.13 %	6
2	28/01/10	10.12	0.40 %	4
3	01/02/10	10.18	0.27 %	6
4	02/02/10	10.17	0.17 %	4
5	03/02/10	10.14	0.45 %	3

Measurement of NO_2 by FT-IR

Group #	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
1	27/01/10	10.14	0.55 %	4

Result

Component	Result	Expanded Uncertainty	Coverage factor
NO_2	10.15 µmol/mol	0.10 µmol/mol	2*

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

Method description forms

Reference Method:

NO_2 was analysed by 42C NO-NO2-NOx Analyser (Thermo Environmental Instruments made in the USA), which is based on Chemiluminescence principle, with a measurement range from 0 ppm to100 ppm.

Simultaneously, a FT-IR (Nicolet 5700) with a changeable gas sample cell from Thermo Co was used to compare and check the results from 42C NO-NO2-NOx Analyser.

In the FT-IR system, the detector is MCT/A (mercury cadmium tellurium). Minimum resolution is 0.125cm^{-1}. Beamsplitter is KBr. Optical path length of sample cell is a multi-reflection system changeable from 4m~48m.

The pressure in the cell was controlled at about 50 kPa by the gas inlet system when 10 ppm NO_2 is analysed. The temperature in the gas cell was about 20 ºC. The optical path length is fixed at about 48m, and the resolution is selected at 4cm^{-1} with a 256 times scanning.

Calibration Standards:

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, O_2 and NO. The NO_2 reference gas mixtures came from the gas mixture of NO in nitrogen with some O_2 added into it. The concentration of O_2 was about 1000 ppm in the NO_2 reference gas mixtures.

The parent gases were filled into a 4 litre or 5 litre aluminium cylinder, which received a 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 the gravimetric method and from stability. The uncertainty from stability was evaluated based on short-time and long-time testing. 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 the gravimetric method.

The reference gases used were listed in the following table:

Cylinder Number	Component and assigned value(x) µmol/mol	Relative standard uncertainty ($u(x)$)
499707	9.950	0.36 %
CAL017588	9.857	0.36 %
CAL017592	9.915	0.36 %
CAL017596	9.958	0.36 %
499694	10.395	0.36 %

Instrument Calibration:

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:

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

When testing NO_2 with the 42C NO-NO2-NOx Analyser, the reference and sample gases were directly introduced into the analyser through a “T” type tube by the pump inside the instrument used. The flow rate was about 0.5~1L/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 to make sure that about 100mL/min vented to the atmosphere. The venting flow rate was read from a flow meter.

When FT-IR was used, the gas was introduced into the gas cell by a needle valve, which was between the gas cell and the regulator on the cylinder. The gas cell was vacuumed by a turbo pump before filling it with the gas.

Evaluation of measurement uncertainty

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.

$$u(c_{CCQM})=\sqrt{u^2(c_{PRM})+u^2(H_{CCQM})+u^2(H_{PRM})+u^2(f_{\text{int}ra})+u^2(f_{\text{int}er})}$$

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 42C NO-NO2-NOx Analyser.

$u(H_{PRM})$: Uncertainty of signal reading of the reference gas from 42C NO-NO2-NOx Analyser.

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

$u(c_{PRM})$: Uncertainty of concentration of the reference gas, which was combined by the uncertainty from gravimetric method according to ISO 6142-2001 and the uncertainty from the stability of the reference gas.

$u(f_{\text{int}ra})$: Uncertainty of repeatability in one day or one group. The relative standard uncertainty of $f_{\text{int}ra}$ was calculated from the relative 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.

$u(f_{\text{int}er})$: Uncertainty of reproducibility in different days or groups. The relative standard uncertainty $f_{\text{int}er}$ 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.

Uncertainties estimation for the results is listed in following table.

Uncertainty sources	$u(c_{PRM})$	0.36 %
	$u(H_{CCQM})$	0.10 %
	$u(H_{PRM})$	0.10 %
	$u(f_{\text{int}ra})$	0.26 %
	$u(f_{\text{int}er})$	0.12 %
Uncertainty of measurement result	$u(c_{CCQM})$	0.48 %
	Relative expanded uncertainty (*k*=2, 95 %)	1.0 %

National Institute of Standards and Technology (NIST)

A1. General information

Institute	National Institute of Standards and Technology		
Address	100 Bureau Drive Gaithersburg, MD 20899-8393, USA		
Contact person	Franklin R. Guenther, William J. Thorn III		
Telephone	301-975-3939	Fax	301-977-8392
Email*	fguenther@nist.gov		
Serial number of cylinder received	APEX930654		
Cylinder pressure as received	8.0 MPa		

A2. Results

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
10.28	0.10	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

1) Primary Standard Uncertainty = 0.009 to 0.015 µmol/mol (Gaussian)
2) Instrument precision = 0.01 µmol/mol (Gaussian)
3) Instrument drift = 0.015 to 0.052 µmol/mol (Gaussian)
4) Nitric Acid Determination = 0.06 µmol/mol (Gaussian)

Propagation of these core measurement uncertainties resulted in the following table of results against the 6 primary standards:

	NOx	**std err**	**Uncert**
APEX930654	**10.258**	**0.036**	**0.072**
APEX930654	**10.385**	**0.067**	**0.134**
APEX930654	**10.308**	**0.043**	**0.087**

APEX930654	**10.354**	**0.034**	**0.069**
APEX930654	**10.370**	**0.044**	**0.088**
APEX930654	**10.370**	**0.069**	**0.138**
	NOx		
average	**10.34**	**0.021**	
(Max-Min)/sqrt(12)		**0.037**	
Stderr		**0.042**	
Uncert		**0.08**	

The NOx value for the cylinder then was adjusted by the analysed value for nitric acid of (0.06 ± 0.06) µmol/mol to get (10.28 ± 0.10) µmol/mol.

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[14].

The cylinder was measured for total NOx using chemiluminescence by comparison to six Nitric Oxide primary gas standards. To assure close to 100 % conversion efficiency, NIST used two thermal converters in series. During the analysis, NIST nitrogen dioxide working standards were also compared as controls.

The analysis of the comparison cylinder (APEX930654) was completed over 6 days of analytical comparisons. Each day one of the NIST nitric acid primary standards was compared to a nitrogen dioxide working standard and the comparison cylinders. This resulted in 6 independent analytical values for the comparison cylinder. These 6 independent values were combined by averaging the results into one value, and combining the uncertainties.

The nitric acid value for the cylinder was estimated by directing a gas stream from the cylinder through a trap consisting of a fluorocarbon filter housing containing two 47 mm diameter nylon membrane filters, and on to the chemiluminescence instrument. The value from the instrument without the nylon membranes in the gas stream, and then without the nylon membranes in the gas stream is noted. The difference between these two numbers is the nitric acid value. As this technique has the potential of underreporting nitric acid, or underreporting nitric oxide; the uncertainty is estimated at 0.06 µmol/mol. Attempts to place a value for nitric acid by FT-IR failed due to a detection limit of 0.5 µmol/mol.

The final value for nitrogen dioxide equals the NOx value determined minus the value for the nitric acid.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM: 4 Mpa

If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

---

[14] The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
HNO_3	0.06	0.06	2	chemiluminescence

National Physical Laboratory (NPL)

CCQM-K74 Report from NPL (March 2010)

The unknown cylinder circulated by BIPM to NPL was D65 0042 (930659).

Pressure on receipt (07/09/2009) = 80 bar
Pressure on despatch (25/01/2010) = 40 bar

Introduction

The measurements of cylinder 930659 were made in December 2009 by direct comparison with a nitrogen dioxide in nitrogen standard containing similar nitrogen dioxide (10ppm) and oxygen (1000ppm) amount fractions to the unknown cylinder (NPL 1275R).

The direct comparison measurements were performed, on two separate days, using a ABB Limas UV 11 photometer.

Preparation of NPL 1275R

The standard NPL 1275R was prepared by the following series of dilutions from nominally pure nitric oxide:

Parents	Daughter	
pure NO + N2	50 mmol/mol NO/N_2	*74R2*
50 mmol/mol NO/N_2 + 9 % O_2/N_2 + N_2	4000 µmol/mol NO_2/N_2	*464R*
4000 µmol/mol NO_2/N_2 + N_2	800 µmol/mol NO_2/N_2	*1206R2*
800 µmol/mol + 9 % O_2/N_2 + N_2	100 µmol/mol NO_2/N_2	*1117R4*
100 µmol/mol NO_2/N_2 + N_2	10 µmol/mol NO_2/N_2	*1275R*

The full uncertainty for the final step is given as a Table and shows the standard uncertainty in the prepared amount fraction of NO_2 of 13 nmol/mol.

The best estimate of drift in this value is based on the use of this type of cylinder (BOC Spectraseal) for standards of NO_2 at similar amount fractions. This leads to a standard uncertainty of 10 nmol/mol.

Measurements on 7/12/2009

Sequence	Result µmol/mol
Z	
SU	10.3167
US	10.2871
Z	
SU	10.3643
US	10.3447

Z	
SU	10.3052
US	10.3768
Z	
SU	10.2935
US	10.3626
Mean	**10.3314**
SD	***0.035***

where, Z indicates a measurement of "zero" nitrogen, S indicates a measurement of the standard (NPL1275R) and U a measurement of the unknown (D65 0042).

Measurements on 8/12/2009

Sequence	Result µmol/mol
Z	
SU	10.39822
US	10.35001
Z	
SU	10.26746
US	10.33609
Mean	**10.33795**
SD	***0.054***

Estimation of matrix effect in NDUV analyser

There is a small matrix effect in the NDUV analyser due to the presence of oxygen in the nitrogen. This effect was estimated by carrying out a comparison of the unknown with a standard (NPL 1126R2), which had 26 µmol/mol of oxygen. The comparison was carried out using the sequence described in the previous section. The results were

Date	Result µmol/mol	SD µmol/mol
7-12-2009	10.308	0.035
8-12-2009	10.283	0.020

The mean of these results (10.29 µmol/mol) is 40 nmol/mol lower than the results of the comparison reported in the previous section with a "matching" standard. We therefore attribute an uncertainty of 10 nmol/mol (95 % C/I) to the "uncorrected matrix effect" in the analyser.

Identification of Trace Contamination in the Travelling Standard

Analysis of D65 0042 by FT-IR indicated the presence of approximately 200 nmol/mol of nitric acid. We are unable to measure the cross-sensitivity of the NDUV analyser. From information about the spectroscopy of NO2 and HNO3 we estimate a cross-sensitivity of no more than 0.1. After using a factor of square root(3), we estimate a standard uncertainty due to possible cross-sensitivity of 12 nmol/mol.

Uncertainty

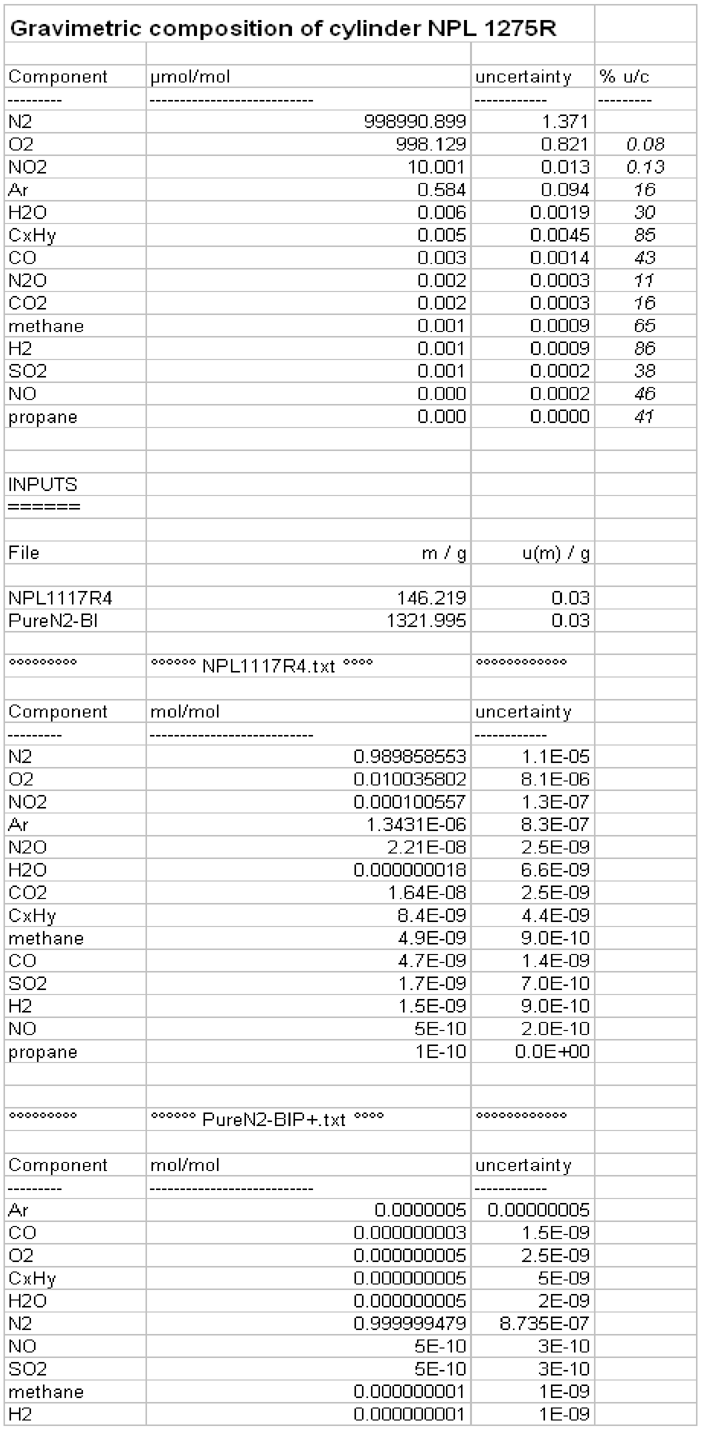
Source of uncertainty	**Estimation Method**	**Standard uncertainty** nmol/mol
Gravimetric preparation of standard	A	13
Drift in gravimetric value of standard	B	10
Repeatability of analysis	A	35

Interference of HNO_3 in analyser	B	12
Matrix effect (oxygen) in analyser	B	5
Combined uncertainty		41

The expanded uncertainty (*k*=2) is 80 nmol/mol.

Final Result

Amount fraction of nitrogen dioxide in D65 0042 = 10.33 +/- 0.08 µmol/mol



Gravimetric composition of cylinder NPL 1275R			
Component	µmol/mol	uncertainty	% u/c
---------	---------------------------	------------	---------
N2	998990.899	1.371	
O2	998.129	0.821	*0.08*
NO2	10.001	0.013	*0.13*
Ar	0.584	0.094	*16*
H2O	0.006	0.0019	*30*
CxHy	0.005	0.0045	*85*
CO	0.003	0.0014	*43*
N2O	0.002	0.0003	*11*
CO2	0.002	0.0003	*16*
methane	0.001	0.0009	*65*
H2	0.001	0.0009	*86*
SO2	0.001	0.0002	*38*
NO	0.000	0.0002	*46*
propane	0.000	0.0000	*41*
INPUTS			
======			
File	m / g	u(m) / g	
NPL1117R4	146.219	0.03	
PureN2-BI	1321.995	0.03	
°°°°°°°°°	°°°°°° NPL1117R4.txt °°°°	°°°°°°°°°°°°	
Component	mol/mol	uncertainty	
---------	---------------------------	------------	
N2	0.989858553	1.1E-05	
O2	0.010035802	8.1E-06	
NO2	0.000100557	1.3E-07	
Ar	1.3431E-06	8.3E-07	
N2O	2.21E-08	2.5E-09	
H2O	0.000000018	6.6E-09	
CO2	1.64E-08	2.5E-09	
CxHy	8.4E-09	4.4E-09	
methane	4.9E-09	9.0E-10	
CO	4.7E-09	1.4E-09	
SO2	1.7E-09	7.0E-10	
H2	1.5E-09	9.0E-10	
NO	5E-10	2.0E-10	
propane	1E-10	0.0E+00	
°°°°°°°°°	°°°°°° PureN2-BIP+.txt °°°°	°°°°°°°°°°°°	
Component	mol/mol	uncertainty	
---------	---------------------------	------------	
Ar	0.0000005	0.00000005	
CO	0.000000003	1.5E-09	
O2	0.000000005	2.5E-09	
CxHy	0.000000005	5E-09	
H2O	0.000000005	2E-09	
N2	0.999999479	8.735E-07	
NO	5E-10	3E-10	
SO2	5E-10	3E-10	
methane	0.000000001	1E-09	
H2	0.000000001	1E-09	

Chemicals Evaluation and Research Institute (CERI)

A1. General information

Institute	Chemicals Evaluation and Research Institute, Japan		
Address	1600 Shimotakano,Sugito-machi, Kitakatsushika-gun,Saitama 345-0043, Japan		
Contact person	Shinji Uehara		
Telephone	+81-480-37-2601	Fax	+81-480-37-2521
Email*	uehara-shinji@ceri.jp		
Serial number of cylinder received	APEX930671		
Cylinder pressure as received	9.7MPa		

A2. Results

Measurement #1

Component	Date (dd/mm/yy)	Result (/µmol/mol)	Standard deviation (% relative)	Number of replicates
NO_2	09/12/09	10.35	0.39	3

Measurement #2

Component	Date (dd/mm/yy)	Result (/µmol/mol)	Standard deviation (% relative)	Number of replicates
NO_2	10/12/09	10.42	0.23	3

Measurement #3

Component	Date (dd/mm/yy)	Result (/µmol/mol)	Standard deviation (% relative)	Number of replicates
NO_2	10/12/09	10.42	0.25	3

Results

Nitrogen dioxide mole fraction x_{NO2}/µmol/mol	Expanded uncertainty $U(x_{NO2})$/ µmol/mol	Coverage factor
10.40	0.38	2

A3. Uncertainty Budget

Source	Estimate	Distribution	Divisor	Standard uncertainty	Sensitivity coefficient	Contribution
Repeatability of measurement	0.1501 µmol/mol	normal	2	0.07505	1	0.07505
Calibration curve	0.03372 µmol/mol	normal	2	0.01686	1	0.01686
Mole fraction of high concentration standard	0.05952 µmol/mol	normal	2	0.02976	1.118	0.03327
Mole fraction of low concentration standard	0.05399 µmol/mol	normal	2	0.02700	0.1183	0.003194
NO in the CCQM-K74 gas mixture	0.0008 µmol/mol	normal	2	0.0004	1	0.0004
Stability	0.34 µmol/mol	normal	2	0.17	1	0.17
		Combined standard uncertainty				0.1896
		Expanded uncertainty (*k*=2)				0.38

A4. Description of the procedure used during the gas analysis

Calibration Standards

Serial number of cylinder	Mole fraction of NO_2 µmol/mol	Expanded uncertainty (*k*=2) µmol/mol	Nominal mole fraction of O_2 µmol/mol
CPB19013	10.184	0.05615	1000
CPB21194	8.398	0.05601	1000

Calibration standards were prepared by gravimetric dilution of pure NO and pure O_2. That procedure is as follows,

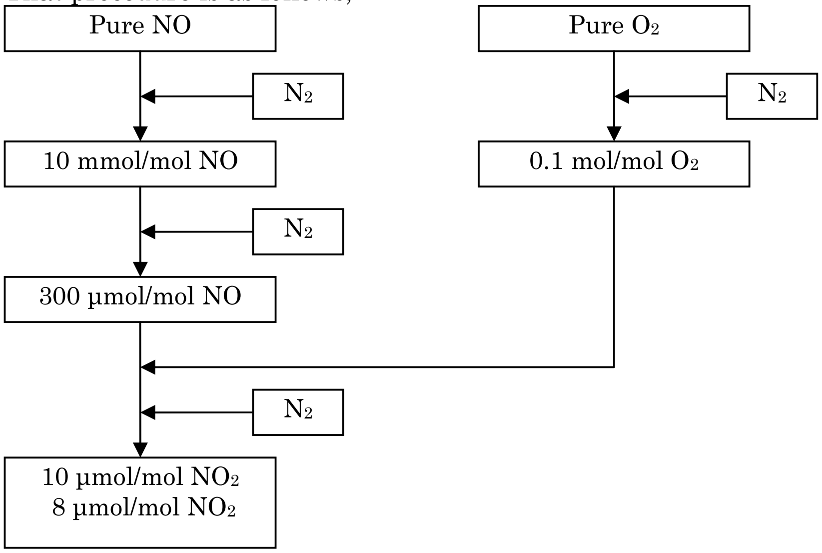


Fig. Procedure of preparation

The analytical method used for gas analysis

Calibration method: Bracketing
Traceability: Own standards
Instrument: Chemiluminescence analyser made by Thermo Fisher Scientific
(Model 42i-HL)
Catalyst of converter: stainless-steel
Measurement Mode: Manual NOx

This instrument has three modes. (Auto mode, Manual NO mode and Manual NOx mode) NO_2 cannot be analysed in “Manual NOx” mode. NOx was regarded as NO_2 in the report. NO_2 can be estimated by subtracting output value of NO from output value of NOx in “Auto mode”. But the observed value of NO is bigger than the accurate one in this mode. Therefore, the uncertainty increases. So “Manual NOx” mode was selected.

Comparisons were made by the following sequence:

$$H_1 \rightarrow K_1 \rightarrow L_1 \rightarrow K_2 \rightarrow H_2 \rightarrow K_3 \rightarrow L_2$$

Where
H_i : measurement of high concentration standard (i=1,2)
L_i: measurement of low concentration standard (i=1,2)
K_i : measurement of the CCQM-K74 gas mixture (i=1,2,3)

Configuration of analysis system:

Gas cylinder → Regulator → Manual 4-way valve → Instrument (Converter → Detector)

The mole fractions of NO_2 in the CCQM-K74 gas mixture were calculated as follows:

$$\frac{1}{3}\left\{(H-L)\left(\frac{K_1^{\ v}-L_1^{\ v}}{H_1^{\ v}-L_1^{\ v}}+\frac{K_2^{\ v}-L_1^{\ v}}{H_2^{\ v}-L_1^{\ v}}+\frac{K_3^{\ v}-L_2^{\ v}}{H_2^{\ v}-L_2^{\ v}}\right)+3B\right\}$$

Where
K_i^v : output value from measurement K_i
H_i^v : output value from measurement H_i
L_i^v : output value from measurement L_i
K_i^v : output value from measurement K_i
H : mole fraction of high concentration standard
L : mole fraction of low concentration standard

A5. Complementary information on the cylinder

The value of the pressure left in the cylinder before shipment to the BIPM: 7.4MPa

If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Component	Mole fraction /nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
NO	0.0036	0.0008	2	Chemiluminescence analyser□NO mode□

National Metrology Institute of South Africa (NMISA)

A1. General information

Institute	National Metrology Institute of South Africa (NMISA)		
Address	CSIR, Building 4 West Meiring Naude Road Brummeria 0184 Pretoria South Africa		
Contact person	Angelique Botha		
Telephone	+27 12 841 3800	Fax	+27 12 841 2131
Email*	abotha@nmisa.org		
Serial number of cylinder received	**D650032**		
Cylinder pressure as received	**96 bar**		

A2. Results

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
10,69	**0,37**	**k = 2**

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

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

Parameter		**Standard uncertainty**
Gravimetric uncertainty	- Weighing uncertainty - Purity analysis	0,14 % rel.
Verification uncertainty (U)		2,05 % rel.
Stability uncertainty (U)		0,77 % rel.

Regression uncertainty (U)	0,06% rel.

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[15].

The NO_2 content of sample D650032 was analysed using a Fischer Rosemount Chemiluminescence analyser calibrated with primary standard mixtures of NO_2-in-nitrogen over the concentration range of 10 ppm to 100 ppm prepared by NMISA.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

The cylinder was left with **23 bar**.

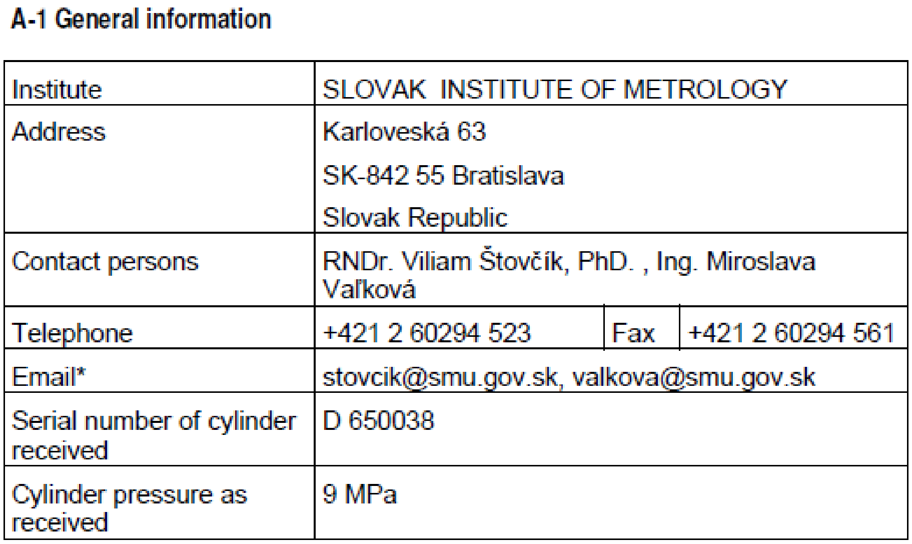
If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique

---

[15] The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

Slovak Institute of Metrology (SMU)



A-1 General information

Institute	SLOVAK INSTITUTE OF METROLOGY		
Address	Karloveská 63 SK-842 55 Bratislava Slovak Republic		
Contact persons	RNDr. Viliam Števčík, 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	D 650038		
Cylinder pressure as received	9 MPa		

A-2 Results

Measuring Month	Nitrogen dioxide mole fraction x_{NO_2} [µmol/mol]	Expanded uncertainty $U(x_{NO_2})$ [µmol/mol]	Coverage Factor
October	10.09	0.13	2
November	10.11	0.13	2
December	10.11	0.11	2
$\overline{X}$	**10.10**	**0.12**	2

A-3 Uncertainty Budget

Combined uncertainty of the NO₂ mole fraction (analysed by chemiluminescence method) was calculated according to the formula:

$$U_C(x) = 2 * \sqrt{u_A(x_{NO_2})^2 + u_B(x_{NO_2})^2}$$

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= 0.01 µmol/mol; discernment of analyzer

$u_{cal} = 0.05 \mu mol / mol$

u_{cal} is the standard uncertainty of *10 µmol/mol* NO₂ PSM used for the analyzer calibration

To estimate result uncertainty from 3 measurement results we have kept "Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method" (Annual Book of ASTM Standards E 691-87) with some approximations.

$$s_R = \sqrt{{s_{\overline{x}}}^2 + s_r \frac{n-1}{n}}$$

$$s_r = \sqrt{\sum_{i=1}^{p} u(\overline{x}_i)^2 \Big/ p}$$

$$s_{\overline{x}} = \frac{\max(\Delta x)}{\sqrt{3}}$$

$$\Delta x = \overline{x}_1 - \overline{x}_2$$

p – Number of measurements
n – Number of replicates

Final result is average from 3 measurement results

$$\overline{X} = \frac{\sum_{i=1}^{p} \overline{x}_i}{p}$$

As final standard uncertainty we assigned to this result max (s_R or s_r)

$$u(\overline{X}) = \max(s_r; s_R)$$

Expanded uncertainty (k=2) of final result

$$U(\overline{X}) = 2 \cdot u(\overline{X})$$

A-4 Description of the procedure used during the gas analysis

The concentration of NO_2 was determined by chemiluminescence method in gas laboratory. Thermo Vision 42C analyzer was used for measurements. SMU own PSM prepared gravimetrically in according to ISO 6142 was used for the calibration of the analyzer before each measurement. NO_2 content was measured after receiving the cylinder from pilot laboratory and then two times after 4 weeks. 5 out of different PSMs in the mole fraction range *(1-10) µmol/mol* NO_2 were used to make a calibration curve and afterwards from calibration curve were constated an unknown quantity of assay. The same fabrics was used for monitoring NO component (NO was found as an impurity). Each measurement was performed under stable conditions:

Pressure: 172.5 mmHg
Flow: 0.720 l per min.
Integration time: 30 sec

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

The laboratory conditions:
Temperature: 20-23℃
Pressure: 98. 9-101.325 KPa
Rel. humidity: 20%-35%.

A-5 Complementary information on the cylinder

Measurement of the NO component was executed by the same method as well as for than NO_2 and its mole fraction are in the table below:

Component	Mole fraction µmol/mol
NO	0.065

The value of the pressure left in the cylinder before shipment to the BIPM:
p= 70, 0 MPa

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

Ing. S. Musil, PhD.
Deputy of research SMU

Mendeleyev Institute for Metrology (VNIIM)

A1. General information

Institute	**D.I.Mendeleyev Institute for Metrology (VNIIM)**		
Address	19 Moskovsky pr., St. Petersburg, 190005 Russia		
Contact person	Leonid Konopelko, Elena Gromova		
Telephone	+7 812 327 57 11	Fax	+ 7 812 327 97 76
Email*	lkonop@b10.vniim.ru		
Serial number of cylinder received	930713		
Cylinder pressure as received	10 MPa		

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[1] CCQM-K74 is fully described in the document: Protocol for CCQM-K74 and CCQM-P110 – Nitrogen dioxide in nitrogen (10 µmol/mol) page 5.

A2. Results

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
10.55	**0.16**	**2**

A3. Uncertainty Budget

Combined standard uncertainty of NO_2 mole fraction was calculated on the base of the following constituents:

- uncertainty of NO_2 mole fraction in the calibration gas mixtures (including uncertainty of weighing of parent gases and pre-mixtures, uncertainty of the purity of the parent gases);

- uncertainty due to sorption of the component by cylinder inner walls and long-term instability of standard gas mixtures;

- standard deviation of the measurement results of NO_2 mole fraction.

Uncertainty budget for NO_2 mole fraction in gas mixture in the cylinder 930713 is given below.

№	Source of uncertainty	Type of evaluation	Standard uncertainty, % relative
1	Preparation of the calibration gas mixtures	A, B	0,1
2	Sorption of the component by cylinder inner walls and long-term instability of standard gas mixture	B	0,5
3	Standard deviation of the measurement results of NO_2 mole fraction	A	0,54
Combined standard uncertainty			**0,74**
Expanded uncertainty (*k*=2)			**1,5**

A4. Description of the procedure used during the gas analysis

Reference Method:

The mole fraction of NO_2 was determined by chemiluminescence method. The measurements were carry out by chemiluminescence analyzer AC 30M (Environnement S.A., France) which is a part of equipment of the State Primary Standard of mole fraction and mass concentration of components in gas media GET 154-01.

Calibration standards:

There were two Primary Standard Gas Mixtures (calibration gas mixtures) of NO_2 10 µmol/mol in Nitrogen prepared gravimetrically in accordance with the ISO 6142:2001. Preparation of the calibration mixtures was carried out using high purity NO_2 and high purity Nitrogen in 3 stages:

1st stage - preparation of the first gas pre-mixtures NO_2/N_2 with NO_2 mole fraction of about 0,01 mol/mol.

2nd stage – preparation of the second gas pre-mixtures NO_2/N_2 with NO_2 mole fraction of about 300 µmol/mol (the Nitrogen balance gas contains nominally 0,03 mol/mol of Oxygen),

3rd stage – preparation of calibration gas mixtures NO_2/N_2 with NO_2 mole fraction of about 10 µmol/mol (the Nitrogen balance gas contains nominally 1000 µmol/mol of Oxygen).

All gas mixtures were prepared in aluminum cylinders with Experis treatment for NO_2. The gas mixtures were verified according to the ISO 6143:2001.

Instrument calibration:

The single calibration point method was used for instrument calibration.

There were five independent measurements made under repeatability conditions with five independent calibrations. Measurement sequence was in order of standard-sample- standard-sample- etc.

Sample handling:

Prior to measurements the cylinders were rolling 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 cleaned at least 10 times by sequential purging over a two day period. 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 analyzer. Both sample and calibration mixtures responses were collected.

A5. Complementary information on the cylinder

The value of the pressure left in the cylinder before shipment to the BIPM:

7.2 MPa

Authors:
L.A. Konopelko
Y.A. Kustikov
V.V. Pankratov
A.V. Malginov
E.V. Gromova

The single calibration point method was used for instrument calibration. There were four independent measurements made under repeatability conditions with four independent calibrations. Measurement sequence was in order of standard-sample- standard-sample- etc.

Sample handling:

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

A stainless steel metering valve was connected with the sample cylinder. The valve was cleaned at least 10 times by sequential purging over a two day period. Directly before the measurements the valve was purged another 3 times.

A pressure regulator for high concentration gas pre-mixture of NO_2 in Nitrogen was purged for 5 times. Then it was left under pressure for 24 hours and directly before measurements it was purged another 3 times.

After each measurement, pure Nitrogen was flushed through the analyzer. Both sample and dynamic mixtures responses were collected.

Appendix A

The results obtained in additional investigations with alternative reference standards (Dynamic volumetric method)

Results

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
10,59	0,14	2

Uncertainty Budget

№	Source of uncertainty	Type of evaluation	Relative standard uncertainty, %
1	Preparation of standard gas mixture 317,9 µmol/mol	A, B	0,07
2	Sorption of the component by cylinder inner walls and long-term instability of standard gas mixture	B	0,10
3	Dynamic dilution	B	0,42
4	Standard deviation of measurement results	A	0,50
Total relative standard uncertainty			**0,66**
Relative expanded uncertainty (*k*=2)			**1,3**

Description of the procedure used during the gas analysis

Reference Method:

AC 30 M (Environnement S.A.) chemiluminescence analyzer was used to measure the NO_2.

Calibration Standards:

There was a gas mixture with NO_2 mole fraction of 320 µmol/mol used for the dynamic dilution and prepared independent from the static gravimetric mixtures pointed in the main part of the report.

Investigations of the stability of the gas mixture during one month were made.

Then, a gas mixture of NO_2 in Nitrogen at about 10 µmol/mol was generated by diluting the gravimetric gas mixture with NO_2 mole fraction of 320 µmol/mol with Nitrogen by using thermal mass-flow controller system. Flow controllers were calibrated by Gas Flow Calibrator Cal=Trak SL-800 (Sierra Instruments, Inc.).

Federal Institute for Materials Research and Testing (BAM)

Institute	BAM Federal Institute for Materials Research and Testing		
Address	Unter den Eichen 87 12205 Berlin Germany		
Contact person	Dirk Tuma		
Telephone	+49 30 8104 4113	Fax	+49 30 8104 3207
Email*	dirk.tuma@bam.de		
Serial number of cylinder received	930722 TC1		
Cylinder pressure as received	98 bar		

A2. Results

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{\text{NO2}})$ / µmol/mol	Coverage factor *k*
10.5_3	0.7_5	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Three terms go with the calculation of *U*: u_{meas} = standard deviation from the measurement (three scans) of the sample; u_{cal} = standard deviation from the measurement of the two calibration gases (three scans for each calibration gas, the value for u_{cal} is the arithmetic mean); $u_{\text{intrinsic}}$ = an intrinsic uncertainty of the calibration gas of 2 % (considers stability)

$$U\left(x_{\text{NO}_2}\right) = \sqrt{\left(u_{\text{meas}}\right)^2 + \left(u_{\text{cal}}\right)^2 + \left(u_{\text{intrinsic}}\right)^2}$$

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[16].

---

[16] The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

The analytical method was FT-IR spectroscopy (cf. protocol P-110 for details).

Prior to the analysis, the cell was evacuated and flushed with dry nitrogen to remove any impurities that absorb infrared energy. A 10-m gas cell was employed.

Background was collected in the evacuated cell. Subsequently, the gas pressure was adjusted to a constant pressure of 100 kPa, and several test runs provided identical spectra.

Sample spectra of each gas were recorded three times maintaining equal conditions. For each measurement, a new gas portion was loaded from the cylinder. A background scan was done before each sample scan. The analysis resorted to the area below the first overtone, i.e., approximately between 2800 and 2950 cm^{-1}.

Two calibration gases were employed; *x*(cal. sample # 1) = 12.28 µmol/mol, *x*(cal. sample # 2) = 9.43 µmol/mol. The calibration samples were prepared gravimetrically. The NO_2 mole fraction of the test sample was calculated via linear interpolation (bracketing method).

Date of analysis: 02-06-2010

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

Cylinder pressure: 87 bar

If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique

Dutch Metrology Institute (VSL)

A1. General information

Institute	VSL		
Address	Thijsseweg 11 2629 JA Delft The Netherlands		
Contact person	G. Nieuwenkamp MSc		
Telephone	+31 15 26 91 682	Fax	+31 15 26 12 971
Email*	gnieuwenkamp@vsl.nl		
Serial number of cylinder received	APEX 930674		
Cylinder pressure as received	10.7 MPa		

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[1] Protocol A is fully described in the document: Pilot Study CCQM-P110 – Nitrogen dioxide in Nitrogen (10 µmol/mol) page 5.

Date of measurement	Measurement technique	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
2009-12-17	UV	10.505	0.22	2
2009-12-18	UV	10.484	0.21	2
2009-12-24	UV	10.528	0.21	2
2009-12-31	CLD	10.524	0.20	2
average		**10.51**	**0.21**	**2**

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Uncertainty source	Relative standard deviation $u(x_i)$	Coverage factor k
Gravimetric standards	0.03 %	
Stability related uncertainty	0.5 %	
Monitor response	0.21 %	
	Relative Expanded uncertainty $U(x_i)$	
Calculated with ISO6143 software	**2.0 %**	**2**

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[2].

The NO_2 content is analyzed by using an ABB LIMAS UV monitor. Calibration is performed with μmol/mol. A linear curve model has been applied. The cylinder is equipped with a stainless steel pressure regulator and flushed prior to use. One single pressure regulator is used for all cylinders, after the analysis the regulator is connected to the next cyilinder. A flow of 500 ml/min, controlled by a Bronkhorst mass flow controller (low Δp type, with Kalrez seals), is led to the monitor. After 30 minutes of flushing, the average response over the next 15 minutes is recorded. Linear curve fitting is performed using ISO6143 software.

An additional measurement is performed with a Thermo 17C NO-NO2-NH3 CLD analyser. The same reference materials and the same method have been used, only with a flow of 600 ml/min. The sample is led over a stainless steel convertor, operated at 750 °C. All nitrogen containing species are converted to NO and analysed as N_t (= total nitrogen).

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

Cylinder pressure (2010-01-04) : 7.2 MPa

If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique

Bureau International des Poids et Mesures (BIPM)

A1. General information

Institute	Bureau International des Poids et Mesures (BIPM)
Address	92312 Sèvres Cedex, France.
Contact person	Edgar Flores
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Email*	edgar.flores@bipm.org
Serial number of cylinder received	930697
Cylinder pressure as received	11MPa

A2. Results

The BIPM result is given in the following table:

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{\mathrm{NO2}})$ / µmol/mol	Coverage factor
10.343	0.048	2

Note: In the version Draft A of this report erroneously the preliminary result 10.329 µmol/mol was reported as the nitrogen dioxide mole fraction of the standard 930697 being the correct value, 10.343 µmol/mol, used in all calculations of this report.

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The uncertainty budget of the BIPM-NO_2 facility is presented in section 3 of ANNEX 1.

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[17].

The method used for the analysis of the cylinder was based on primary reference mixtures generated by the BIPM-NO_2 facility. The BIPM-NO_2 facility comprises a magnetic suspension balance, a flow control system for the dynamic generation of the gas mixtures and a flow control system for static nitrogen dioxide gas standards. Both, static and dynamic sources of NO_2 mixtures are ultimately connected to a continuous gas analyser ABB Limas 11 (AO2020), and to a FT-IR spectrometer. The operation and automation of the ensemble of instruments (NO_2 FT-IR facility-ABB Limas 11-FT-IR) is achieved through a LabView® programme. Through a graphical user interface the program facilitates the setting and monitoring of all relevant instrumental parameters, automated control of complex procedures, the recording of mass measurements and NO_2 analyser readings and related data to file and the graphical real-time display of many of the instrument readings.

Nitric acid was the main impurity in the nitrogen dioxide gas mixtures generated by the BIPM NO_2 facility and this was corrected by quantifying the mole fraction of nitric acid directly using FT-IR spectroscopy with traceability to line parameters within the HITRAN database. The determination of nitric acid was assessed using a (48 ±1.2) m multipath gas cell in the FT-IR system.

A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM:

If any other component other than NO_2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Component	Mole fraction / nmol/mol	Expanded uncertainty nmol/mol	Coverage factor	Measurement technique
HNO_3	141	85	2	FT-IR Spectroscopy

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[17] The choice of the procedure used for gas analysis is the responsibility of the participating laboratory. Nevertheless, for a proper evaluation of the data, it is necessary that the calibration method, as well as the way in which the calibration mixtures have been prepared is reported to the co-ordinators.

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