International comparison CCQM-K74.2018: Nitrogen dioxide, 10 µmol mol-1

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(Final Report)

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Field: Amount of substance

Organizing Body: CCQM

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1 Executive summary

The CCQM-K74.2018 comparison is a specialised comparison (Track C), organized as a Model 2 Comparison (participants' standards sent to the BIPM for measurement and comparison against each other) initially foreseen with a protocol that anticipated standards that follow a well behaved decay profile, allowing BIPM measurements to be compared to interpolated values for participants' standards.

Several options to calculate the KCRV were proposed during the April 2020 meeting by the BIPM. After an exhaustive analysis and group discussions, it was clear that the nitrogen dioxide (NO_2) amount fractions in some of the standards presented a decay profile that exhibited a power function (an initially faster decay rate than from a linear decay function); therefore, a specific approach to estimate the values of the participants at the time of the KCRV measurement (see details in section 6.2) was to be developed and presented in November 2020.

This approach was presented in November 2020 and chosen by the participants to be used to calculate the degrees of equivalence (see Figure 1, below) in this version. This approach takes into account a decay profile found on similar calibration gas mixtures in cylinders with one of the passivations used in this key comparison. For standards that exhibit a decay, in this approach, NMI values and uncertainties as a function of time are calculated based on the knowledge that these will lie between values predicted by a linear decay function calculated from the first set (before the BIPM analysis) and the second set of the NMI measurements (after the BIPM analysis), and a constant value deduced from the second set of the individual NMI measurement results. This approach does not require the exact decay profile of each standard to be known, but only that it lies within the limits defined above.

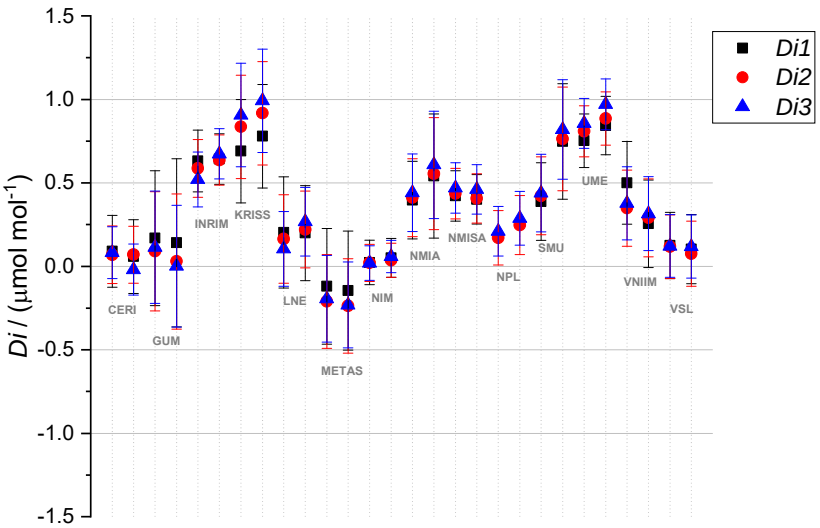

Figure 1. Graph of Equivalence, approach adopted in November 2020 (called option 6 at that time) based on the three series of measurements performed at the BIPM at different times for each of the two standards sent by participants: Black squares – series 1(first series of BIPM measurements) , red circles – series 2 (4 months after first series), blue triangles – series 3 (6 months after first series). The error bar represents the expanded uncertainty at a 95 % level of confidence. The two sets of 3 results for each participants are plotted next to each other's.

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2 Quantities and Units

The measurand was the mole fraction of nitrogen dioxide in nitrogen*, with measurement results being expressed in mol mol^{-1} and its multiples µmol mol^{-1} or nmol mol^{-1}. The terminology "amount fraction" is used throughout this report for the quantity "amount fraction".

(*it was recognized that participants would prepare standards with the nitrogen balance gas containing a small amount of oxygen that normally would not exceed 1000 µmol mol^{-1})

3 Schedule

The revised schedule for the project was as follows:

April 2017	Draft protocol distributed to participants;
May 2017 – April 2018	The participating laboratories prepare the mixtures and carry out their 1st set of analysis (verification and stability test);
May to June 2018	Shipment of cylinders to the BIPM (last cylinder arrived in June);
July 2018 – Mach 2019	Analysis of mixtures at the BIPM;
Mach – April 2019	Shipment of cylinders from the BIPM to participants;
April 2019 – January 2020	2nd set of analysis of mixtures by the participants (stability);
October 2019 – January 2020	Reports of the participants ; and
March 2020	Distribution of Draft A of this report.
March 2020	Distribution of Draft A.2 of this report.
March 2021	Distribution of Draft A.3 of this report.
September 2021	Distribution of Draft B of this report.

4 Standards preparation and measurements of participants

Each laboratory taking part in CCQM-K74.2018 was requested to prepare two nitrogen dioxide gas mixtures contained in cylinders with a minimum volume of 5 L pressurized at about 12 MPa. The choice of the cylinder material and the passivation technology employed remained the choice of the participant. Participants also required to perform measurements on the standards each month during a 3 months period before sending the standards to the BIPM and during an equally long period after their return.

4.1 Summary of participants' reports

Participants were asked to use their usual procedure to prepare and analyse nitrogen dioxide amount fractions in their standards, and to carefully report the date of analysis to the coordinating laboratory in the results forms. All results forms can be found in ANNEX VII - Measurement reports of participants.

Table 1 summarizes information provided by laboratories, as well as additional information which is useful in understanding the results of the comparison. At the Draft

A.3 report stage, some of the information was not available to the coordinating laboratory, in which case the table is empty.

The information summarized in the table below is:

a) information on the calibration standards (including date of preparation) that were used to value assign the sent-in standards for the three measurements before shipping and after returning from the BIPM;
b) the analytical method used for the value assignment of the produced standards and what chemical species produce what significant response in the instrument;
c) the method used to produce the standards that were sent to the BIPM;
d) significant impurities that were detected in each of the participating standards;
e) the characteristics of the cylinders used: e.g., bulk material, surface layer/treatment; and
f) any additional notable comments.

The previous comparison on NO_2 standards, CCQM-K74.2009[1] had highlighted the potential presence of HNO_3 in the gas mixtures and the importance of a correct estimation of its amount fraction to accurately determine NO_2 amount fractions. Therefore, the analytical technique used by participants to perform NO_2 measurements after preparation of the standards is a key information, as well as the quantification of HNO_3.
In Table 1 we can observe that seven laboratories of fourteen used Chemiluminescence (CLD) analysers, which measure NO_x rather than NO_2 only, including HNO_3. Three laboratories used Non-Dispersive Ultraviolet (ND-UV) analysers (NPL, NMISA and VSL), which can measure exclusively NO_2. Three laboratories used Fourier Transformed InfraRed (FT-IR) analysers (LNE, NMIA and VNIIM) which can measure both NO_2 and HNO_3 independently. Among these three laboratories, only LNE and VNIIM reported HNO_3 amount fractions measured in their gas mixtures.

VSL measured HNO_3 by Cavity Ring Down Spectroscopy (CRDS) and NMISA used FT-IR to measure the HNO_3 amount fractions in one of their cylinders according to the reported information included in ANNEX VII - Measurement reports of participants.

No information was reported by GUM.

Table 1. Summary of information submitted by participating laboratories.

Lab	Standards for pre BIPM stability values	Date of prep.	Standards for post BIPM stability values	Date of prep.	Analytical instrument	Responds to	Preparation method	Impurities detected in submitted Standard 1	Impurities detected in submitted Standard 2	Submitted cylinder type	Comments
GUM										Al with coated layers	
INRIM	3 standards same as sent 7-11 ppm	with sent standard	with NPL QC standard		CLD Thermo 42i	NO_x including HNO_3	NO + O_2 reaction			Al	Traceability to NPL NO in N_2 mixtures at 100ppm
KRISS	4 PRMs				CLD Thermo 42i-HL	NO_x including HNO_3					
NPL	Reference gas				UV LIMAS 11	NO_2					
LNE	Dynamic dilution high amount fraction NO_2				FT-IR	NO_2	NO + O_2 reaction	HNO_3	HNO_3		
NMISA	NO_2 10-100ppm multipoint				UV LIMAS	NO_2	NO + O_2 reaction	HNO_3 (below LoD)			
CERI	1 Fresh NO_2 standard	At each stability measurement	1 Fresh NO_2 standard	At each stability measurement	CLD Thermo 42i-HL	NOX including HNO_3	NO+O_2 reaction.	NO 20 ppb at 3rd stability measurement	NO 20 ppb at 3rd stability measurement	Al	

Lab	Standards for pre BIPM stability values	Date of prep.	Standards for post BIPM stability values	Date of prep.	Analytical instrument	Responds to	Preparation method	Impurities detected in submitted Standard 1	Impurities detected in submitted Standard 2	Submitted cylinder type	Comments
NMIA					FT-IR	NO_2					Moisture in regulators
NIM	1 Fresh NO_2 standard	At each stability measurement	1 Fresh NO_2 standard	At each stability measurement	CLD Thermo 42i-HL	NO_X including HNO_3	NO + O_2 reaction			Cylinder heated and exposed to 100 ppm NO_2 for 2 days	0.2 ppm H_2O in N_2
SMU	3 standards 10-15 ppm		3 standards 10-15 ppm		CLD Thermo 42c	NO_X including HNO_3	NO + O_2 reaction			Aculife IV surface	
UME	single point calibration				Single point calibration		CLD Thermo 42i	NO_X including HNO_3	NO + O_2 reaction		
METAS	Dynamic preparation with a new PERM TUBE for each measurement	Dynamic preparation with a new PERM TUBE for each measurement	CLD Thermo 42i-TL	NO_X including HNO_3	VSL standard NO + O_2 reaction				Trace level analyser used at the 50-100 ppb range for NO_2		
VNIIM	6 series were carried out for APEX614632 cylinder and 5 – for cylinder № 5603778				FT-IR	NO_2	NO + O_2 reaction	HNO_3 correction applied to NO_2	HNO_3 correction applied to NO_2		4.8 m FT-IR

Lab	Standards for pre BIPM stability values	Date of prep.	Standards for post BIPM stability values	Date of prep.	Analytical instrument	Responds to	Preparation method	Impurities detected in submitted Standard 1	Impurities detected in submitted Standard 2	Submitted cylinder type	Comments
VSL	5 static primary standard materials (PSM), prepared according to ISO 6142-1:2015, have been analysed to calibrate the analyser in the range of 100 – 10 x 10^{-6} mol mol^{-1} NO_2 in N_2	Less than 12 months before analysis	5 static primary standard materials (PSM), prepared according to ISO 6142-1:2015, have been analysed to calibrate the analyser in the range of 100 – 10 x 10^{-6} mol mol^{-1} NO_2 in N_2	Less than 12 months before analysis	LIMAS	NO_2	NO + O_2 reaction	HNO_3 correction applied to NO_2	HNO_3 correction applied to NO_2	10 litre aluminium cylinder with Alpha Tech NO2 passivation	The gravimetric amount fraction has been corrected for the HNO_3 amount fraction, according to analysis, and the N_2O_4 amount fraction calculated based on literature

4.2 Participants' submitted results

The participants were requested to perform measurements on the standards each month during a 3 month period before sending the standards to the BIPM and during the same period after their return. Table 2 summarises the participants' submitted results where:

NMI	is the acronym of the participating national metrology institute;
Cylinder	identification code of the cylinder sent by the participating laboratory;
Date	date at which the participating laboratory performed the value assignment of the specific standard
x_{NMI}	the NO_2 amount fraction in the standard assigned by the NMI;
$u(x_{NMI})$	the standard uncertainty of the NMI's values.

All participants followed rigorously the monthly measurement sequence except four who reduced the time interval in between some of the measurements (KRISS, NMIA, NPL and VNIIM).

All submitted standard uncertainties are shown in Figure 2. One order of magnitude difference was observed between the smallest ($u(x_{NIM})$= 0.016 µmol mol^{-1}) and the largest ($u(x_{NMIA})$= 0.30 µmol mol^{-1}) submitted uncertainties. The average standard uncertainty value was 0.074 µmol mol^{-1}.

Participants were also asked to report impurities measured in their standards. As the previous comparison CCQM-K74 had shown the importance of a correct estimation of nitric acid (HNO_3) in NO_2 in nitrogen standards, reporting this component is valuable information. In this exercise only four of fourteen participants (LNE, NMISA, VNIIM and VSL) reported HNO_3 as a main impurity, with amount fractions between 0.07 µmol mol^{-1} and 0.17 µmol mol^{-1} (see Table 3).

Table 2. NO_2 amount fraction reported by participants for each of their six measurements. – No measurements available.

NMI	Cylinder	Date of measurement by the NMI	Assigned NO_2 amount fraction x_{NMI} (µmol mol^{-1})	Assigned standard Uncertainty $u(x_{NMI})$ (µmol mol^{-1})	NMI	Cylinder	Date of measurement by the NMI	Assigned NO_2 amount fraction x_{NMI} (µmol mol^{-1})	Assigned standard uncertainty $u(x_{NMI})$ (µmol mol^{-1})
CERI	CPB 25961	15/01/2018	10.098	0.041	GUM	No D298386_1	06/02/2018	10.526	0.117
		16/02/2018	10.052	0.040			07/03/2018	10.619	0.107
		12/03/2018	10.022	0.040			10/04/2018	10.906	0.118
		10/04/2019	9.798	0.039			04/04/2019	10.446	0.119
		23/05/2019	9.742	0.039			16/05/2019	10.355	0.126
		12/07/2019	9.792	0.039			10/07/2019	10.399	0.143
	CPB 18969	15/01/2018	10.088	0.041		No D298387_1	06/02/2018	10.535	0.117
		16/02/2018	10.074	0.041			07/03/2018	10.604	0.108
		12/03/2018	10.044	0.040			10/04/2018	10.827	0.117
		10/04/2019	9.770	0.039			04/04/2019	10.159	0.117
		23/05/2019	9.748	0.039			16/05/2019	10.134	0.124
		12/07/2019	9.772	0.039			10/07/2019	9.989	0.142
INRIM	P27787/D247449	01/12/2017	10.090	0.065	KRISS	D59 6920	17/05/2018	10.030	0.150
		29/01/2018	9.900	0.065			18/05/2018	10.050	0.150
		26/04/2018	9.840	0.065			19/05/2018	10.040	0.150
		18/04/2019	10.100	0.065			20/08/2019	10.050	0.150
		13/05/2019	9.910	0.060			22/08/2019	10.050	0.150
		21/06/2019	10.110	0.075			18/09/2019	10.060	0.150
	D247448	01/12/2017	10.360	0.065		D59 6882	17/05/2018	10.030	0.150
		29/01/2018	10.240	0.065			18/05/2018	10.020	0.150
		26/04/2018	10.210	0.065			19/05/2018	10.030	0.150
		18/04/2019	10.080	0.050			20/08/2019	10.030	0.150
		13/05/2019	10.150	0.050			22/08/2019	10.040	0.150
		21/06/2019	10.250	0.065			18/09/2019	10.050	0.150

NMI	Cylinder	Date of measurement by the NMI	Assigned NO_2 amount fraction x_{NMI} (µmol mol^{-1})	Assigned standard uncertainty $u(x_{NMI})$ (µmol mol^{-1})	NMI	Cylinder	Date of measurement by the NMI	Assigned NO_2 amount fraction x_{NMI} (µmol mol^{-1})	Assigned standard uncertainty $u(x_{NMI})$ (µmol mol^{-1})
LNE	1191	28/02/2018	10.100	0.065	METAS	10918	23/03/2018	9.930	0.155
		28/03/2018	10.020	0.065			17/04/2018	9.670	0.130
		27/04/2018	9.960	0.060			23/05/2018	9.840	0.045
		14/05/2019	9.600	0.060			04/06/2019	9.500	0.030
		20/06/2019	9.570	0.060			03/07/2019	9.250	0.060
		12/07/2019	9.620	0.060			15/08/2019	9.560	0.105
	1183	28/02/2018	10.090	0.065		10919	28/03/2018	9.950	0.155
		28/03/2018	10.010	0.065			18/04/2018	9.690	0.130
		27/04/2018	9.970	0.060			18/05/2018	9.850	0.045
		14/05/2019	9.700	0.060			04/06/2019	9.530	0.030
		20/06/2019	9.690	0.060			02/07/2019	9.300	0.060
		12/07/2019	9.740	0.060			16/08/2019	9.440	0.105
NIM	L62804135	26/01/2018	9.936	0.017	NMIA	MK0806	05/04/2018	9.740	0.160
		02/03/2018	9.904	0.017			05/04/2018	9.970	0.045
		26/03/2018	9.890	0.017			06/04/2018	9.950	0.085
		24/05/2019	9.769	0.017			05/08/2019	9.850	0.300
		28/06/2019	9.806	0.017			06/08/2019	10.010	0.110
		24/07/2019	9.785	0.017			06/08/2019	10.000	0.110
	L62804125	26/01/2018	9.947	0.017		MK0807	05/04/2018	10.270	0.100
		02/03/2018	9.909	0.017			05/04/2018	10.220	0.045
		26/03/2018	9.896	0.017			06/04/2018	10.220	0.075
		29/05/2019	9.737	0.017			05/08/2019	10.020	0.120
		28/06/2019	9.759	0.017			06/08/2019	10.020	0.120
		24/07/2019	9.748	0.017			06/08/2019	10.010	0.120

NMI	Cylinder	Date of measurement by the NMI	Assigned NO_2 amount fraction x_{NMI} (µmol mol^{-1})	Assigned standard uncertainty $u(x_{NMI})$ (µmol mol^{-1})	NMI	Cylinder	Date of measurement by the NMI	Assigned NO_2 amount fraction x_{NMI} (µmol mol^{-1})	Assigned standard uncertainty $u(x_{NMI})$ (µmol mol^{-1})
NMISA	D62 6618	12/03/2018	9.958	0.072	NPL	2448	19/04/2018	10.020	0.035
		15/04/2018	10.029	0.072			03/05/2018	9.990	0.035
		07/05/2018	9.948	0.082			16/05/2018	10.020	0.035
		25/04/2019	10.020	0.045			08/05/2019	9.820	0.050
		27/05/2019	10.010	0.059			-	-	-
		25/07/2019	10.000	0.051			-	-	-
	D62 6554	08/03/2018	9.938	0.068		S357	19/04/2018	10.040	0.035
		15/04/2018	9.943	0.084			03/05/2018	10.010	0.035
		07/05/2018	9.856	0.069			16/05/2018	10.000	0.035
		25/04/2019	10.007	0.046			08/05/2019	9.750	0.050
		27/05/2019	9.985	0.058			03/06/2019	9.880	0.050
		25/07/2019	9.999	0.056			08/07/2019	9.810	0.050
SMU	MY9742	29/01/2018	10.180	0.105	UME	PSM499783	17/01/2018	9.913	0.050
		27/02/2018	10.130	0.105			21/02/2018	9.790	0.049
		28/03/2018	10.110	0.105			21/03/2018	9.819	0.050
		09/04/2019	10.130	0.130			28/05/2019	9.717	0.050
		02/05/2019	10.140	0.115			27/06/2019	9.748	0.049
		05/06/2019	10.130	0.120			25/07/2019	9.745	0.049
	MY9728	29/01/2018	10.050	0.115		PSM499791	17/01/2018	10.028	0.051
		27/02/2018	10.050	0.110			21/02/2018	10.123	0.051
		28/03/2018	10.060	0.110			21/03/2018	10.109	0.051
		09/04/2019	9.870	0.115			28/05/2019	10.003	0.051
		02/05/2019	9.880	0.115			27/06/2019	10.033	0.050
		05/06/2019	9.830	0.150			25/07/2019	10.024	0.050

NMI	Cylinder	Date of measurement by the NMI	Assigned NO_2 amount fraction x_{NMI} (µmol mol^{-1})	Assigned standard uncertainty $u(x_{NMI})$ (µmol mol^{-1})	NMI	Cylinder	Date of measurement by the NMI	Assigned NO_2 amount fraction x_{NMI} (µmol mol^{-1})	Assigned standard uncertainty $u(x_{NMI})$ (µmol mol^{-1})
VNIIM	614632	20/03/2018	9.890	0.070	VSL	VSL105804	05/01/2018	9.875	0.070
		04/04/2018	9.950	0.070			01/03/2018	9.856	0.070
		18/04/2018	9.890	0.070			28/03/2018	9.903	0.070
		16/07/2019	9.810	0.075			21/05/2019	9.785	0.070
		28/08/2019	9.750	0.075			25/06/2019	9.850	0.070
		17/09/2019	9.740	0.075			25/07/2019	9.834	0.070
	5603778	21/03/2018	9.920	0.065		VSL105806	05/01/2018	9.875	0.070
		05/04/2018	9.980	0.065			01/03/2018	9.846	0.070
		19/04/2018	9.930	0.065			28/03/2018	9.844	0.070
		16/07/2019	9.770	0.075			21/05/2019	9.775	0.070
		28/08/2019	9.760	0.075			25/06/2019	9.800	0.070
		17/09/2019	9.750	0.075			25/07/2019	9.754	0.070

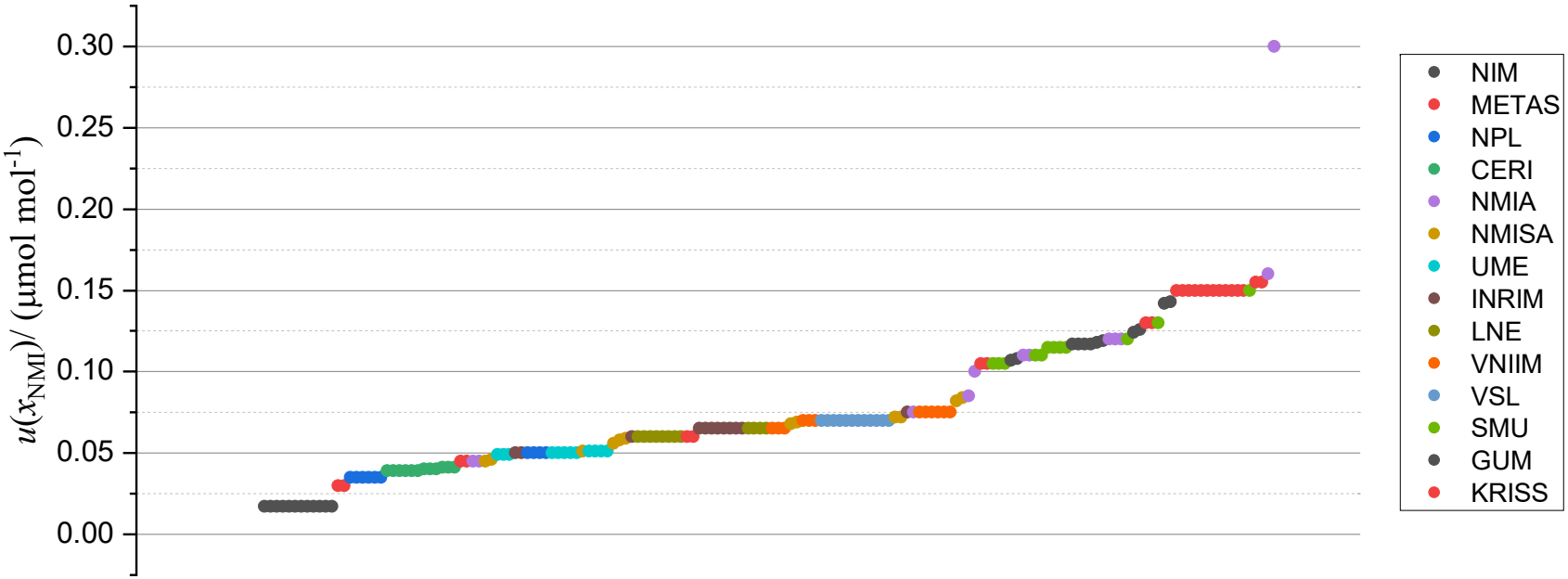

Figure 2. NO_2 amount fraction standard uncertainties (k=1) submitted by participants.

Table 3. Nitric acid amount fractions reported by participants. (The dash indicates -no data submitted).

NMI	Number of Cylinder	Date	$x_{HNO3\,(1)}$ (µmol mol^{-1})	$u(x_{HNO3(1)})$ (µmol mol^{-1})	Date (µmol mol^{-1})	$x_{HNO3(2)}$ (µmol mol^{-1})	$u(x_{HNO3(2)})$ (µmol mol^{-1})	Date (µmol mol^{-1})	$x_{HNO3(3)}$ (µmol mol^{-1})	$u(x_{HNO3(3)})$ (µmol mol^{-1})
LNE	1191	28/02/2018	9.00E-03	4.50E-04	28/03/2018	3.20E-02	2.00E-03	27/04/2018	4.10E-02	2.00E-03
LNE	1183	28/02/2018	4.00E-03	2.00E-04	28/03/2018	3.90E-02	2.00E-03	27/04/2018	5.20E-02	3.00E-03
NMISA	D62 6554	08/05/2018	1.70E-01	6.00E-03	-	-	-	-	-	-
VNIIM	614632	18/04/2018	1.08E-01	1.80E-02	-	-	-	-	-	-
VNIIM	5603778	19/04/2018	5.00E-02	9.00E-03	-	-	-	-	-	-
VSL	VSL105804	17/01/2018	7.00E-02	6.00E-03	28/02/2018	7.80E-02	7.00E-03	29/03/2018	1.13E-01	1.00E-02
VSL	VSL105806	17/01/2018	8.00E-02	7.00E-03	28/02/2018	8.10E-02	7.00E-03	29/03/2018	1.13E-01	1.00E-02

NMI	Number of Cylinder	Date	$x_{HNO3(4)}$ (µmol mol^{-1})	$u(x_{HNO3(4)})$ (µmol mol^{-1})	Date (µmol mol^{-1})	$x_{HNO3(5)}$ (µmol mol^{-1})	$u(x_{HNO3(5)})$ (µmol mol^{-1})	Date (µmol mol^{-1})	$x_{HNO3\,(6)}$ (µmol mol^{-1})	$u(x_{HNO3(6)})$ (µmol mol^{-1})
LNE	1191	14/05/2019	7.00E-02	3.50E-03	20/06/2019	6.60E-02	3.00E-03	12/7/2019	4.30E-02	2.00E-03
LNE	1183	14/05/2019	1.02E-01	5.10E-03	20/06/2019	1.07E-01	5.00E-03	12/7/2019	9.50E-02	5.00E-03
NMISA	D62 6554	-	-	-	-	-	-	-	-	-
VNIIM	614632	-	-	-	-	-	-	-	-	-
VNIIM	5603778	-	-	-	-	-	-	-	-	-
VSL	VSL105804	31/05/2019	1.38E-01	1.20E-02	23/08/2019	1.41E-01	1.30E-02	28/08/2019	1.43E-01	1.30E-02
VSL	VSL105806	31/05/2019	1.41E-01	1.30E-02	23/08/2019	1.51E-01	1.30E-02	28/08/2019	1.44E-01	1.30E-02

5 BIPM measurement results

As described in the comparison protocol each cylinder was value assigned by the BIPM three times during six months, following the procedure described in ANNEX III- BIPM Value assignment procedure. The results of measurements performed during the period July 2018 to March 2019 are listed in Table 4 where:

$x_{BIPM,i}$ is the i^{th} measurement result by the BIPM (i = 1 to 3);

$u(x_{BIPM,i})$ the standard uncertainty of the BIPM measurement;

The reported BIPM measurement results were obtained using an FT-IR system calibrated with NO_2 dynamically generated in nitrogen from a permeation tube, the mass of which was continuously measured with a Magnetic Suspension Balance (MSB). The FTIR measurements were verified by measurements performed with an ND-UV analyzer ABB Limas 11 and are reported in ANNEX IV- ABB LIMAS analyser results. The ND-UV measurements show good agreement between the two instruments. A CAPS detector, which had been described in the comparison protocol, was finally not used because its measurement range is limited to values below 1 µmol mol^{-1}.

The NO_2 amount fraction reported by each participant (black dots) and the BIPM measured values (red dots) are plotted in Figure 3 to Figure 16. The error bars of the participants (black) represent the standard uncertainty associated with the submitted values of the participants. The error bars of the BIPM measured values (red) represent the standard uncertainty associated with the BIPM measurement results. The characteristics of the BIPM measurement system remained effectively unchanged since the CCQM-K74 comparison of 2009, and details can be found in ANNEX III- BIPM Value assignment procedure.

From these plots it can be observed that changes in the NO_2 amount fraction in the cylinder as a function of time needed to be accounted for in the data treatment, as was foreseen in the comparison protocol.

5.1 Analysis of trace components

From previous studies carried out by the BIPM[2-5] 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 again the presence of HNO_3 (see Figure 17 and Table 5) but also other impurities such as H_2O (Figure 19), and even NOCl (Figure 20) and HONO (NPL only in first measurements). The amount of each quantified impurity was calculated using the same spectra as used for the NO_2 value assignment process. For that synthetic calibrations were used anchored to HITRAN 2012 as explained in ANNEX III- BIPM Value assignment procedure. HNO_3 amount fractions measured in VSL standards were also compared with values reported by VSL using Cavity Ring-Down Spectroscopy

anchored to PNNL data (see Figure 18). Consistent values were observed by both institutes when taking into account a linear increase of HNO_3 (which seems to be the most appropriate model in this case), increasing the confidence in measurements performed by FT-IR at the BIPM.

The increase of the HNO_3 amount fraction measured in the VSL standards was also observed in other standards, with some exceptions. The gain in HNO_3 amount fractions is plotted versus the loss in NO_2 over the same period in Figure 21, showing certain correlation for most of the standards. The rate of growth of the impurity varied from cylinder to cylinder.

Table 4. Results of BIPM NO_2 amount fraction measurements.

NMI and BIPM internal cylinder code (1 or 2)	Cylinder	Measurement date 1st measurement	1st BIPM NO_2 amount fraction measurement x_{BIPM1} (µmol mol^{-1})	Standard uncertainty u(x_{BIPM1}) (µmol mol^{-1})	Measurement date 2nd measurement (µmol mol^{-1})	2nd BIPM assigned NO_2 amount fraction x_{BIPM2} (µmol mol^{-1})	Standard uncertainty u(x_{BIPM2}) (µmol mol^{-1})	Measurement Date 3rd measurement (µmol mol^{-1})	3rd BIPM assigned NO_2 amount fraction x_{BIPM3} (µmol mol^{-1})	Standard uncertainty u(x_{BIPM3}) (µmol mol^{-1})
CERI.1	CPB 25961	12/07/2018	9.782	0.038	21/11/2018	9.764	0.038	15/01/2019	9.735	0.038
CERI.2	CPB 18969	20/07/2018	9.806	0.038	11/12/2018	9.748	0.038	06/02/2019	9.819	0.038
GUM.1	No D298386_1	12/07/2018	10.330	0.039	29/11/2018	10.367	0.039	30/01/2019	10.324	0.039
GUM.2	No D298387_1	27/07/2018	10.142	0.039	12/12/2018	10.168	0.038	06/02/2019	10.161	0.038
INRIM.1	D247448	13/07/2018	9.566	0.030	29/11/2018	9.594	0.038	05/02/2019	9.651	0.038
INRIM.2	P27787/D247449	26/07/2018	9.349	0.038	18/12/2018	9.355	0.038	07/02/2019	9.318	0.038
KRISS.1	D59 6882	17/07/2018	9.344	0.038	05/12/2018	9.198	0.038	30/01/2019	9.127	0.038
KRISS.2	D59 6920	25/07/2018	9.267	0.038	06/12/2018	9.130	0.038	07/02/2019	9.055	0.038
LNE.1	1191	13/07/2018	9.558	0.030	22/11/2018	9.532	0.038	06/02/2019	9.554	0.038
LNE.2	1183	19/07/2018	9.628	0.038	06/12/2018	9.557	0.038	07/02/2019	9.488	0.038
METAS.1	10918	17/07/2018	9.707	0.038	03/12/2018	9.739	0.038	21/01/2019	9.703	0.039
METAS.2	10919	26/07/2018	9.728	0.038	17/12/2018	9.754	0.038	04/02/2019	9.725	0.038
NIM.1	L62804125	10/07/2018	9.786	0.038	29/11/2018	9.764	0.038	17/01/2019	9.756	0.038
NIM.2	L62804135	25/07/2018	9.779	0.038	06/12/2018	9.776	0.038	04/02/2019	9.746	0.038
NMIA.1	MK0806	16/07/2018	9.524	0.038	03/12/2018	9.509	0.038	15/01/2019	9.480	0.038
NMIA.2	MK0807	25/07/2018	9.561	0.038	17/12/2018	9.514	0.038	08/02/2019	9.449	0.038
NMISA.1	D62 6618	16/07/2018	9.572	0.038	05/12/2018	9.559	0.038	17/01/2019	9.525	0.038
NMISA.2	D62 6554	20/07/2018	9.553	0.038	12/12/2018	9.548	0.038	11/02/2019	9.494	0.038
NPL.1	2448	13/07/2018	4.961	0.063	03/12/2018	9.689	0.038	30/01/2019	9.635	0.038
NPL.2	S357	20/07/2018	8.228	0.039	11/12/2018	9.611	0.038	08/02/2019	9.556	0.038

NMI and BIPM internal cylinder code (1 or 2)	Cylinder	Measurement date 1st measurement	1st BIPM NO_2 amount fraction measurement x_{BIPM1} (µmol mol^{-1})	Standard uncertainty u(x_{BIPM1}) (µmol mol^{-1})	Measurement date 2nd measurement (µmol mol^{-1})	2nd BIPM assigned NO_2 amount fraction x_{BIPM2} (µmol mol^{-1})	Standard uncertainty u(x_{BIPM2}) (µmol mol^{-1})	Measurement Date 3rd measurement (µmol mol^{-1})	3rd BIPM assigned NO_2 amount fraction x_{BIPM3} (µmol mol^{-1})	Standard uncertainty u(x_{BIPM3}) (µmol mol^{-1})
SMU.1	MY9742	10/07/2018	9.749	0.038	22/11/2018	9.714	0.038	15/01/2019	9.698	0.038
SMU.2	MY9728	27/07/2018	9.175	0.038	18/12/2018	9.128	0.038	08/02/2019	9.060	0.038
UME.1	PSM499791	10/07/2018	9.291	0.038	21/11/2018	9.226	0.038	21/01/2019	9.175	0.039
UME.2	PSM499783	17/07/2018	8.930	0.038	05/12/2018	8.873	0.039	12/02/2019	8.780	0.039
VNIIM.1	614632	16/07/2018	9.324	0.038	22/11/2018	9.457	0.038	21/01/2019	9.419	0.039
VNIIM.2	5603778	19/07/2018	9.577	0.038	11/12/2018	9.515	0.038	11/02/2019	9.479	0.038
VSL.1	VSL105804	12/07/2018	9.717	0.038	21/11/2018	9.718	0.038	17/01/2019	9.710	0.038
VSL.2	VSL105806	19/07/2018	9.701	0.038	12/12/2018	9.716	0.038	11/02/2019	9.668	0.038

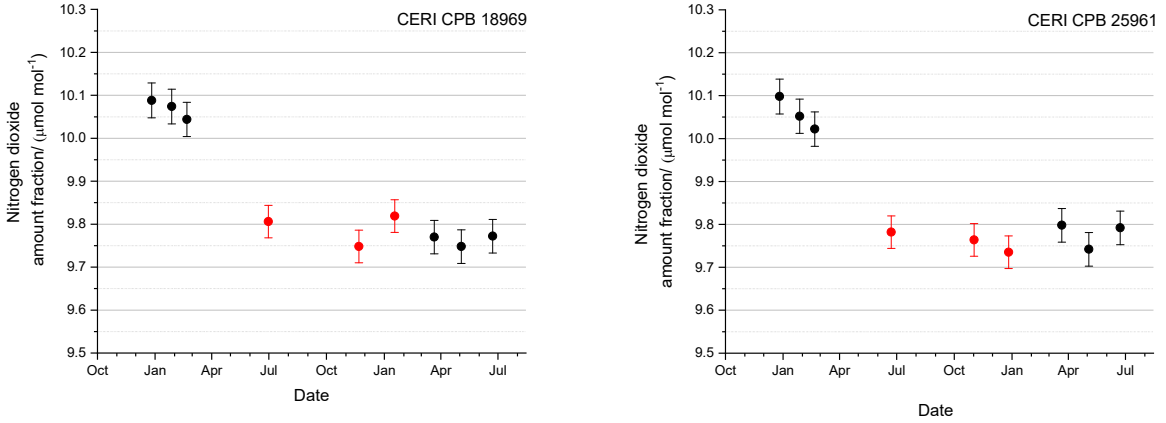

Figure 3. Nitrogen dioxide amount fraction values provided by CERI (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

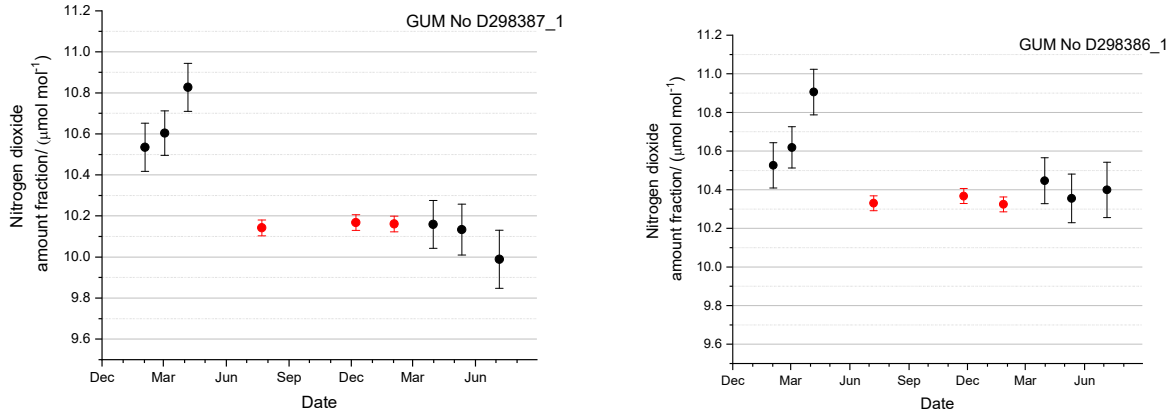

Figure 4. Nitrogen dioxide amount fraction values provided by GUM (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

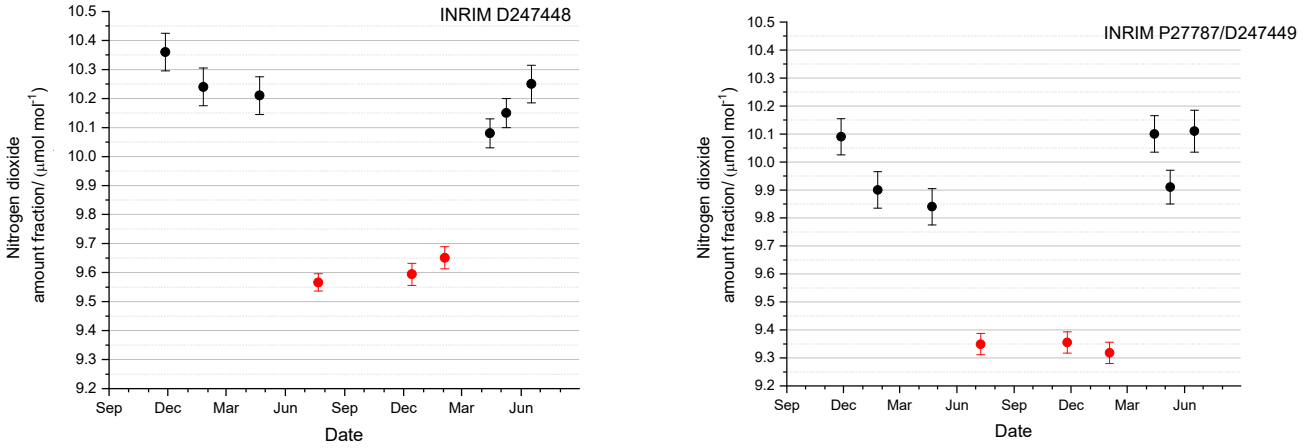

Figure 5. Nitrogen dioxide amount fraction values provided by INRIM (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

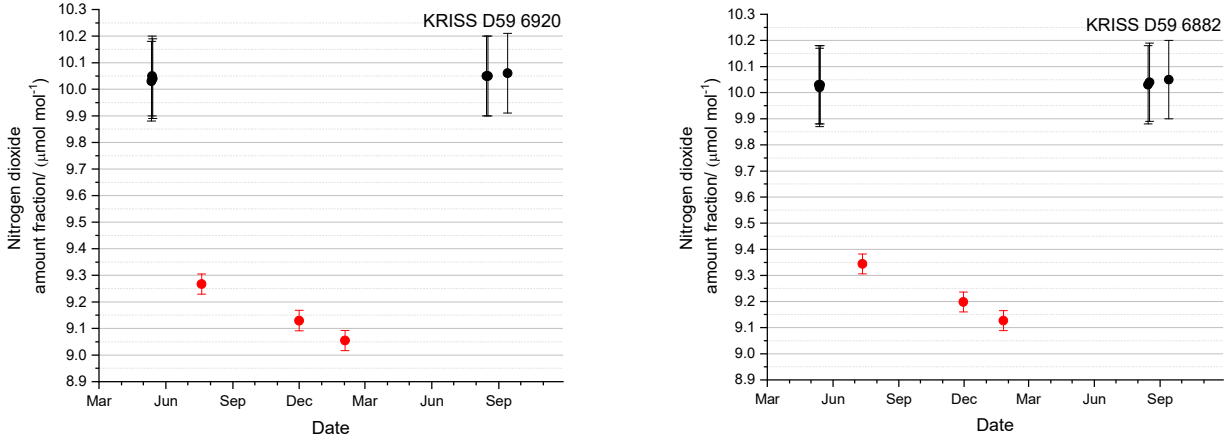

Figure 6. Nitrogen dioxide amount fraction values provided by KRISS (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

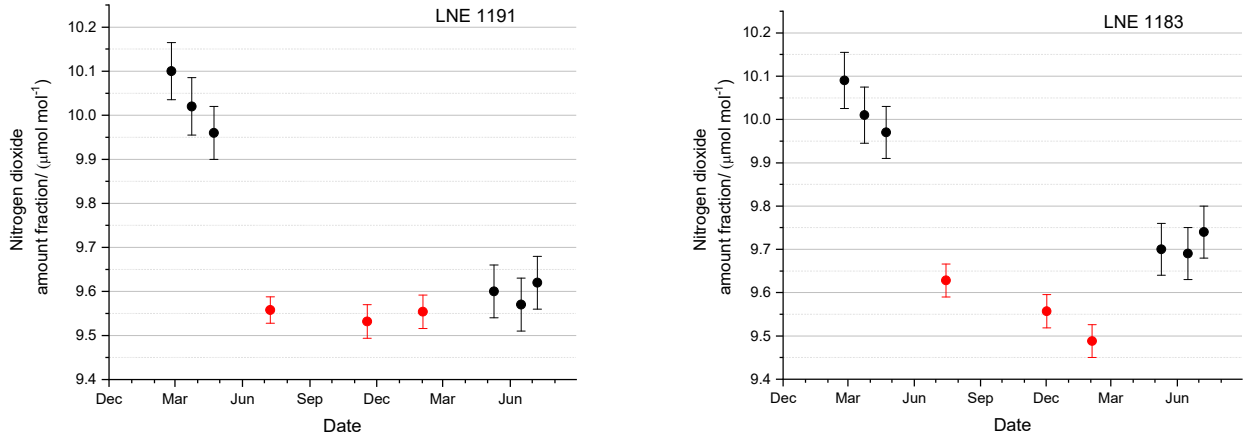

Figure 7. Nitrogen dioxide amount fraction values provided by LNE (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

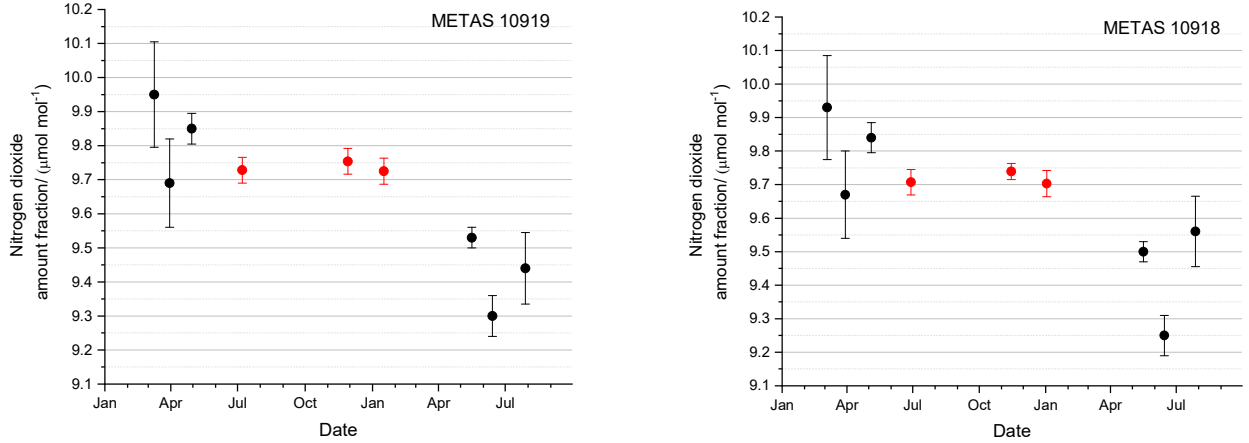

Figure 8. Nitrogen dioxide amount fraction values provided by METAS (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

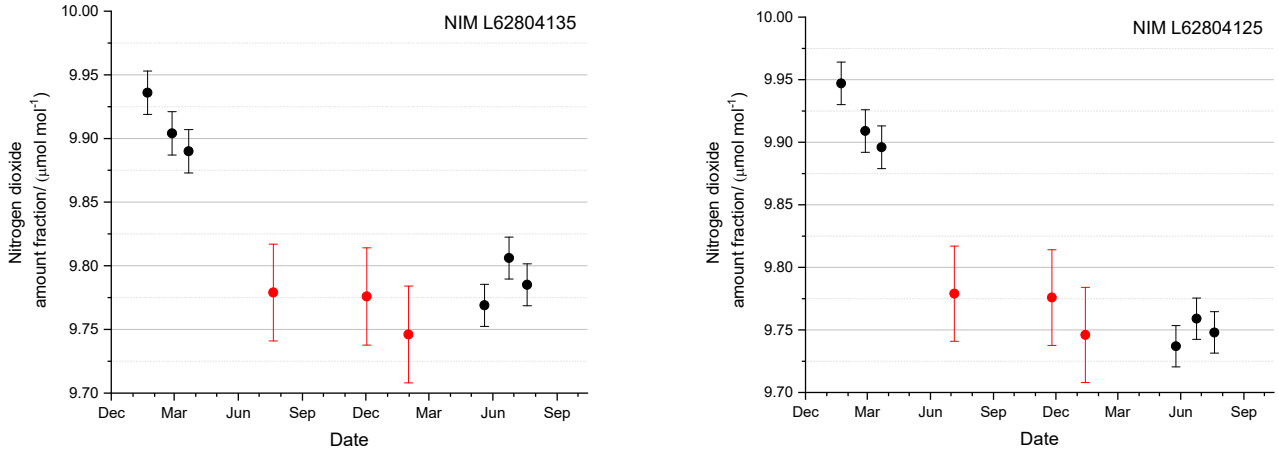

Figure 9. Nitrogen dioxide amount fraction values provided by NIM (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

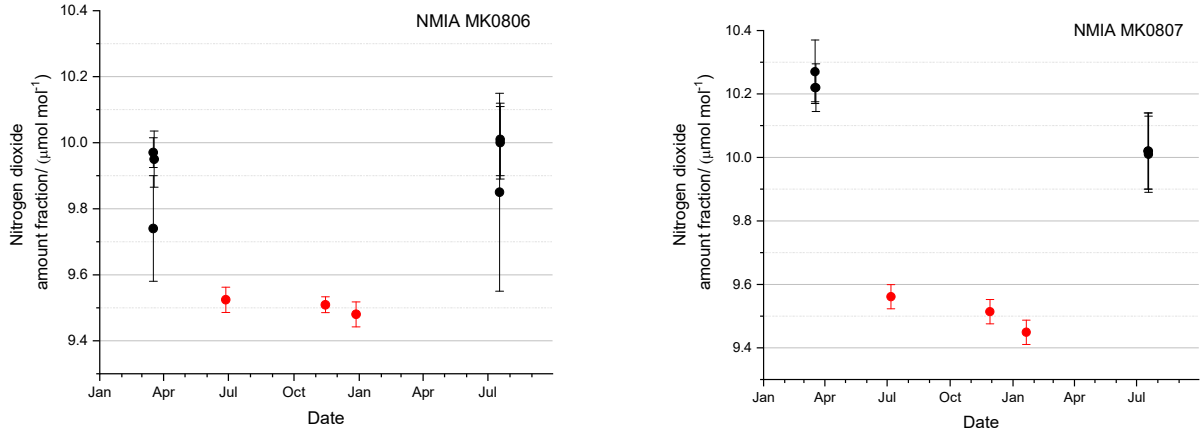

Figure 10. Nitrogen dioxide amount fraction values provided by NMIA (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

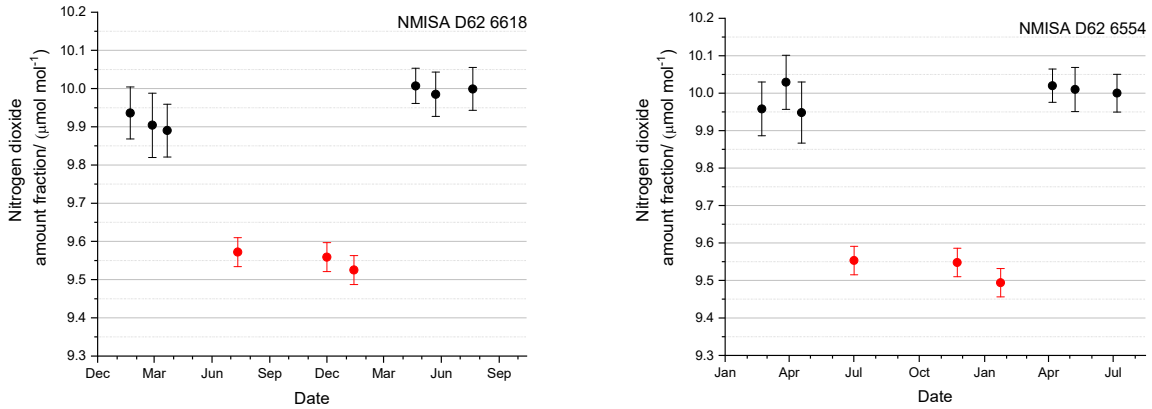

Figure 11. Nitrogen dioxide amount fraction values provided by NMISA (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

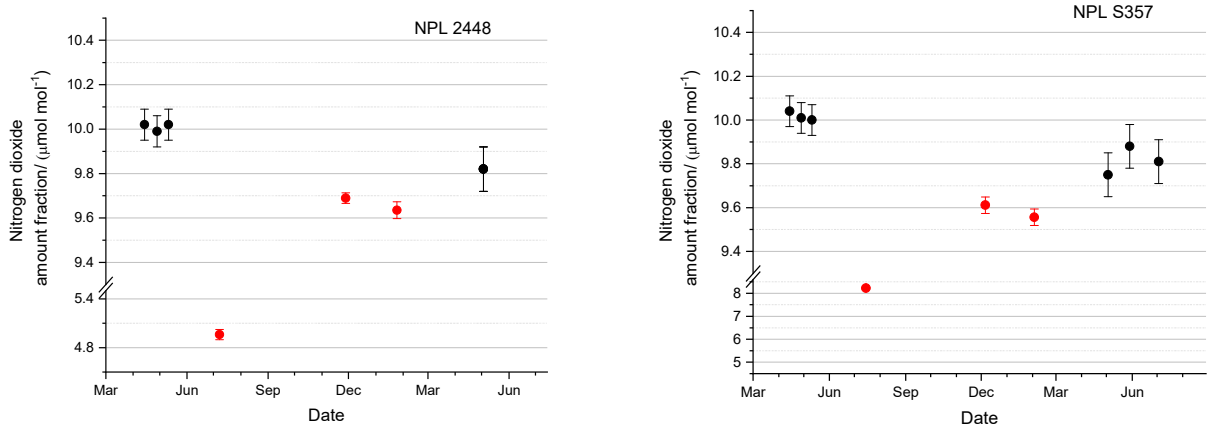

Figure 12. Nitrogen dioxide amount fraction values provided by NPL (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value. Results of the first measurements for NPL were considered as outliers. The first set of BIPM measurements on NPL standards demonstrated very high water levels for both standards (not seen in subsequent measurements).

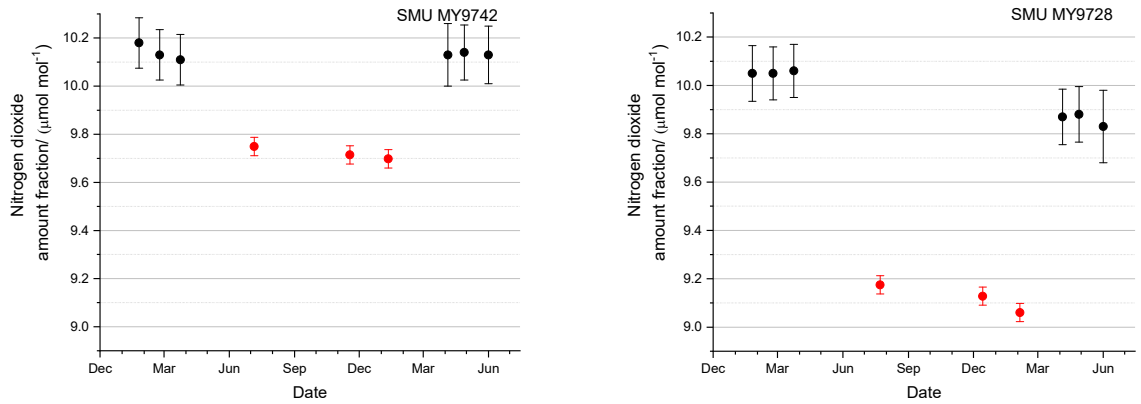

Figure 13. Nitrogen dioxide amount fraction values provided by SMU (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

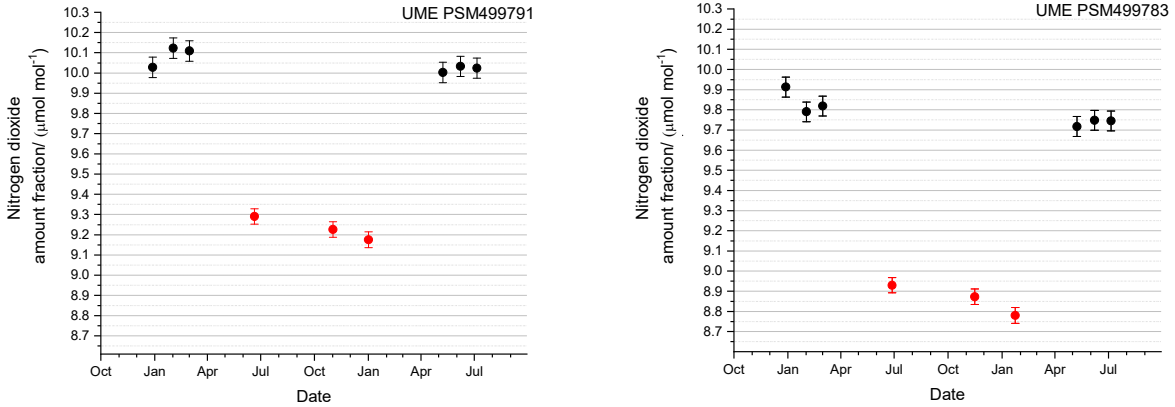

Figure 14. Nitrogen dioxide amount fraction values provided by UME (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

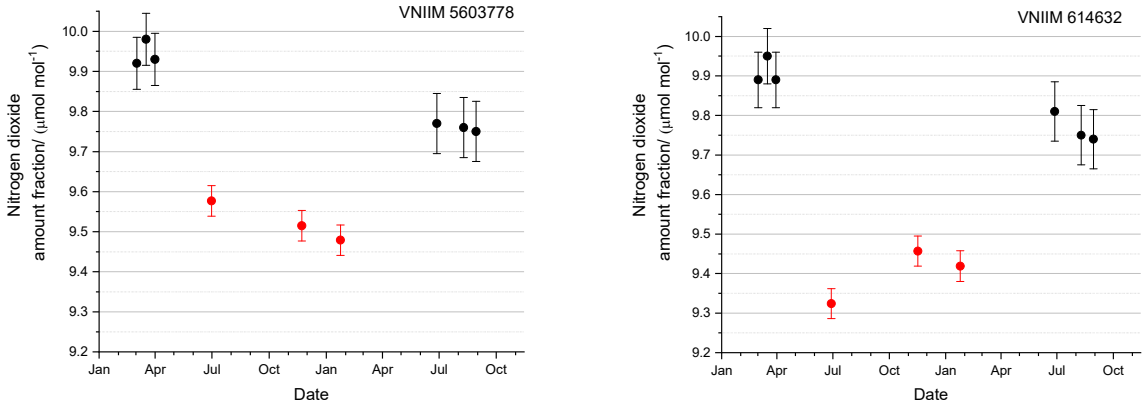

Figure 15. Nitrogen dioxide amount fraction values provided by VNIIM (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (k=1) associated with the measured value.

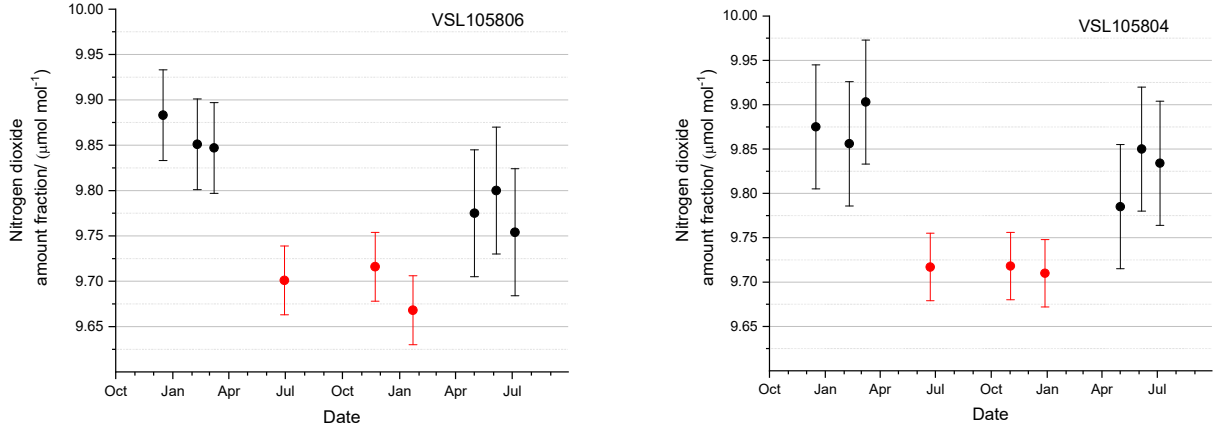

Figure 16. Nitrogen dioxide amount fraction values provided by VSL (black dots) and measured by the BIPM (red dots). The error bar represents the standard uncertainty (*k*=1) associated with the measured value.

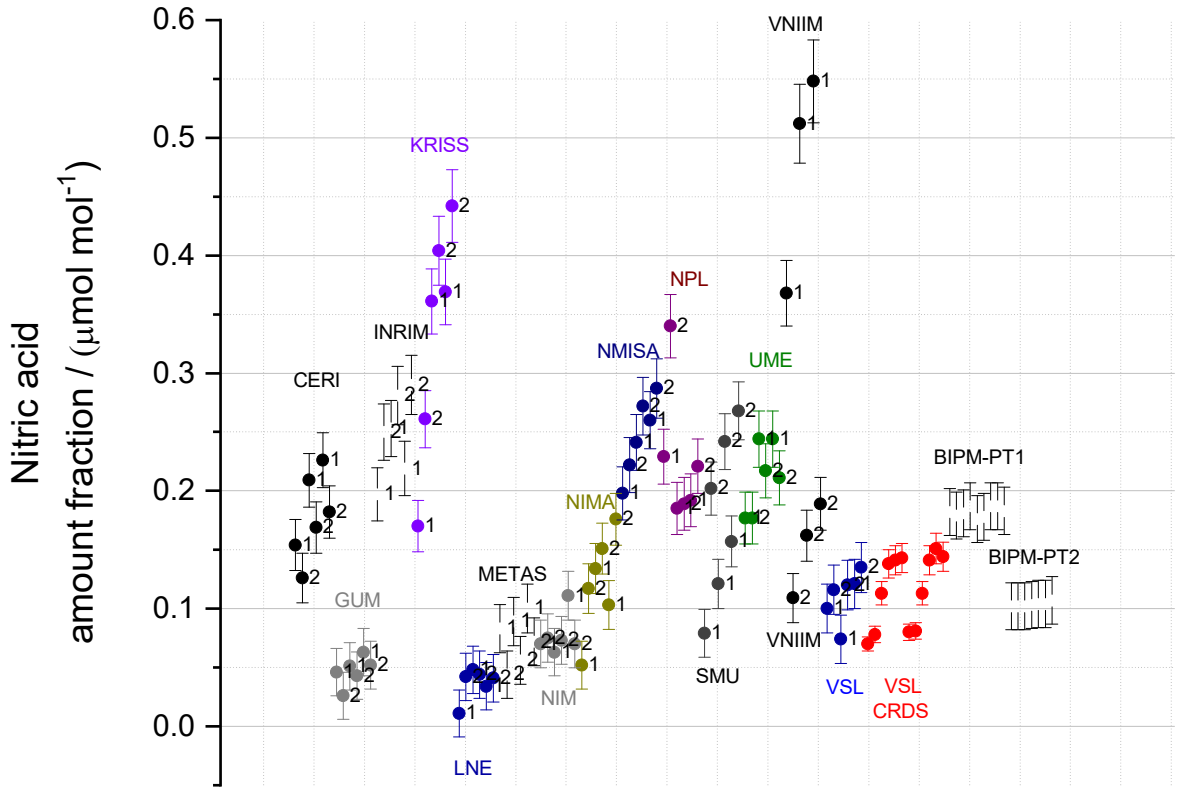

Figure 17. Nitric acid amount fractions measured by the BIPM in participants' standards. The labels 1 and 2 are used to differentiate the two cylinders sent by a laboratory. Three measurements per cylinder were performed. The measurements for each laboratory are organized by date starting from the earliest measurement. HNO_3 amount fractions measured by the VSL by CRDS in its two standards are also indicated as VSL-CRDS (Red dots), as well as the typical amount fraction measured in the BIPM facility using two different types of permeation tubes. The permeation tube type 1, BIPM-PT1, was used from July 10 until August 8, 2018. The permeation tube type 2, BIPM-PT2, was used from August 14, 2018 to February 2019. The error bar represents the standard uncertainty (k=1) associated with the FT-IR measurements.

Table 5. Nitric acid amount fractions measured in cylinder gas standards by the BIPM using FT-IR spectroscopy.

NMI	Cylinder	Measurement date	$x_{HNO3(1)}$ (µmol mol^{-1})	$u(x_{HNO3(1)})$ (µmol mol^{-1})	Measurement (µmol mol^{-1})	$x_{HNO3(2)}$ (µmol mol^{-1})	$u(x_{HNO3(2)})$ (µmol mol^{-1})	Measurement (µmol mol^{-1})	$x_{HNO3(3)}$ (µmol mol^{-1})	$u(x_{HNO3(3)})$ (µmol mol^{-1})
CERI	CPB 25961	12/07/2018	0.154	0.022	21/11/2018	0.209	0.023	15/01/2019	0.226	0.023
CERI	CPB 18969	20/07/2018	0.126	0.021	11/12/2018	0.169	0.022	06/02/2019	0.182	0.022
GUM	No D298386_1	12/07/2018	0.046	0.020	29/11/2018	0.051	0.020	30/01/2019	0.063	0.020
GUM	No D298387_1	27/07/2018	0.026	0.020	12/12/2018	0.043	0.020	06/02/2019	0.052	0.020
INRIM	D247448	13/07/2018	0.197	0.023	29/11/2018	0.253	0.024	05/02/2019	0.219	0.023
INRIM	P27787/D247449	26/07/2018	0.250	0.024	18/12/2018	0.281	0.025	07/02/2019	0.290	0.025
KRISS	D59 6882	17/07/2018	0.170	0.022	05/12/2018	0.361	0.028	30/01/2019	0.369	0.028
KRISS	D59 6920	25/07/2018	0.261	0.024	06/12/2018	0.404	0.029	07/02/2019	0.442	0.031
LNE	1191	13/07/2018	0.011	0.020	22/11/2018	0.048	0.020	06/02/2019	0.034	0.020
LNE	1183	19/07/2018	0.042	0.020	06/12/2018	0.044	0.020	07/02/2019	0.041	0.020
METAS	10918	17/07/2018	0.083	0.020	03/12/2018	0.089	0.021	21/01/2019	0.100	0.021
METAS	10919	26/07/2018	0.044	0.020	17/12/2018	0.056	0.020	04/02/2019	0.072	0.020
NIM	L62804125	10/07/2018	0.070	0.020	29/11/2018	0.063	0.020	17/01/2019	0.111	0.021
NIM	L62804135	25/07/2018	0.075	0.020	06/12/2018	0.073	0.020	04/02/2019	0.070	0.020
NMIA	MK0806	16/07/2018	0.052	0.020	03/12/2018	0.134	0.021	15/01/2019	0.103	0.021
NMIA	MK0807	25/07/2018	0.117	0.021	17/12/2018	0.151	0.022	08/02/2019	0.176	0.022
NMISA	D62 6618	16/07/2018	0.198	0.023	05/12/2018	0.241	0.024	17/01/2019	0.260	0.024
NMISA	D62 6554	20/07/2018	0.222	0.023	12/12/2018	0.272	0.025	11/02/2019	0.287	0.025
NPL	2448	13/07/2018	0.229	0.023	03/12/2018	0.185	0.022	30/01/2019	0.192	0.022
NPL	S357	20/07/2018	0.340	0.027	11/12/2018	0.189	0.022	08/02/2019	0.221	0.023
SMU	MY9742	10/07/2018	0.079	0.020	22/11/2018	0.121	0.021	15/01/2019	0.157	0.022
SMU	MY9728	27/07/2018	0.202	0.023	18/12/2018	0.242	0.024	08/02/2019	0.268	0.025
UME	PSM499791	10/07/2018	0.177	0.022	21/11/2018	0.244	0.024	21/01/2019	0.112	0.021

NMI	Cylinder	Measurement date	$x_{HNO3(1)}$ (µmol mol^{-1})	$u(x_{HNO3(1)})$ (µmol mol^{-1})	Measurement (µmol mol^{-1})	$x_{HNO3(2)}$ (µmol mol^{-1})	$u(x_{HNO3(2)})$ (µmol mol^{-1})	Measurement (µmol mol^{-1})	$x_{HNO3(3)}$ (µmol mol^{-1})	$u(x_{HNO3(3)})$ (µmol mol^{-1})
UME	PSM499783	17/07/2018	0.177	0.022	05/12/2018	0.217	0.023	12/02/2019	0.211	0.023
VNIIM	614632	16/07/2018	0.368	0.028	22/11/2018	0.512	0.034	21/01/2019	0.548	0.035
VNIIM	5603778	19/07/2018	0.109	0.021	11/12/2018	0.162	0.022	11/02/2019	0.189	0.022
VSL	VSL105804	12/07/2018	0.100	0.021	21/11/2018	0.074	0.020	17/01/2019	0.121	0.021
VSL	VSL105806	19/07/2018	0.116	0.021	12/12/2018	0.120	0.021	11/02/2019	0.135	0.021

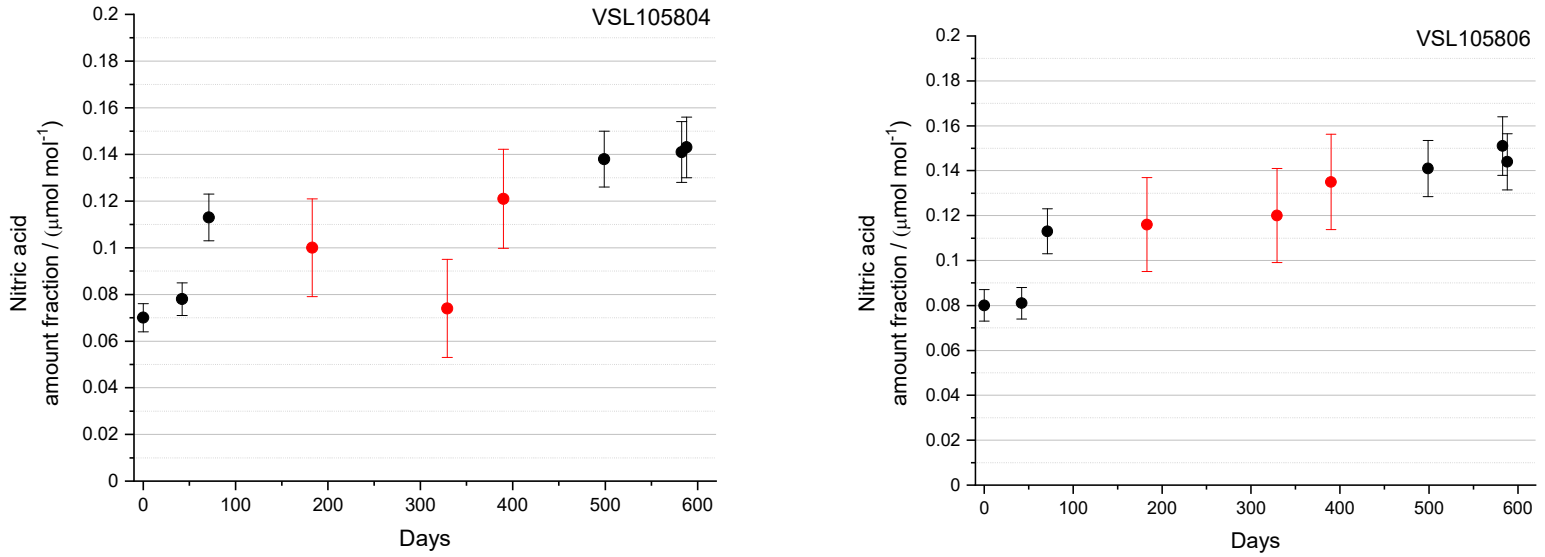

Figure 18. Nitric acid amount fraction measured submitted by VSL (black dots,Table 3) and measured by the BIPM (red dots,Table 5). The error bar represents the standard uncertainty (k=1) associated with the measured value.

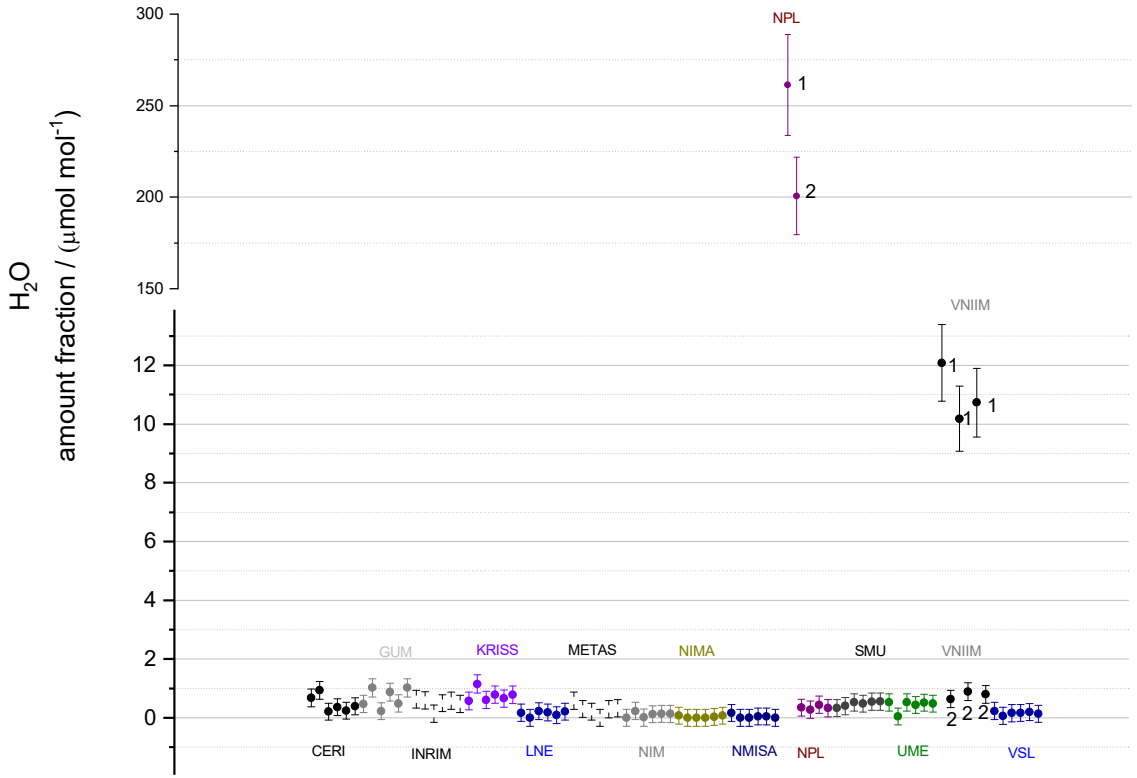

Figure 19. H_2O amount fractions measured by the BIPM in participant's standards. The error bar represents the expanded uncertainty (k=2) associated with the FT-IR measurements. The measurements are organized by laboratory and date starting from cylinder 1 and then cylinder 2 for each laboratory. Three measurements by cylinder were performed.

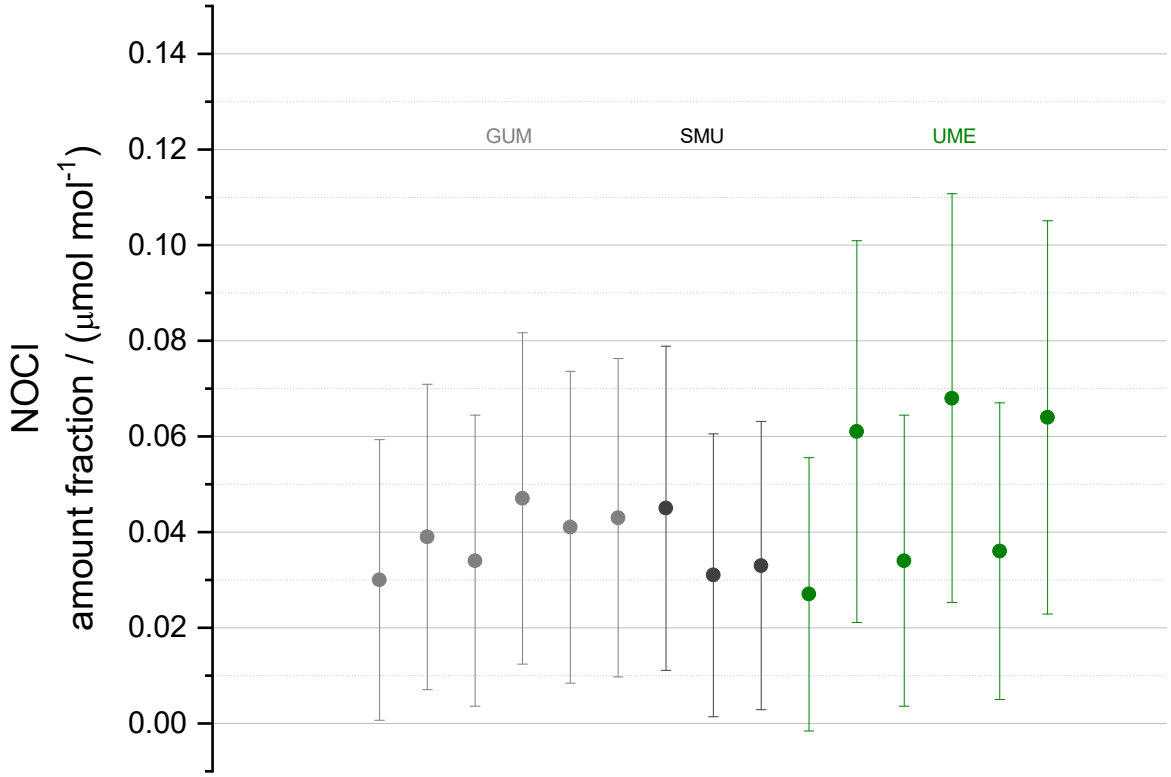

Figure 20. NOCl amount fractions measured by the BIPM in three participants' standards (GUM, SMU and UME). The error bar represents the standard uncertainty (k=1) associated with the FT-IR measurements. The measurements are organized by laboratory and date starting from cylinder 1 and then cylinder 2 for each laboratory. Three measurements by cylinder were performed. For details see ANNEX III- BIPM Value assignment procedure.

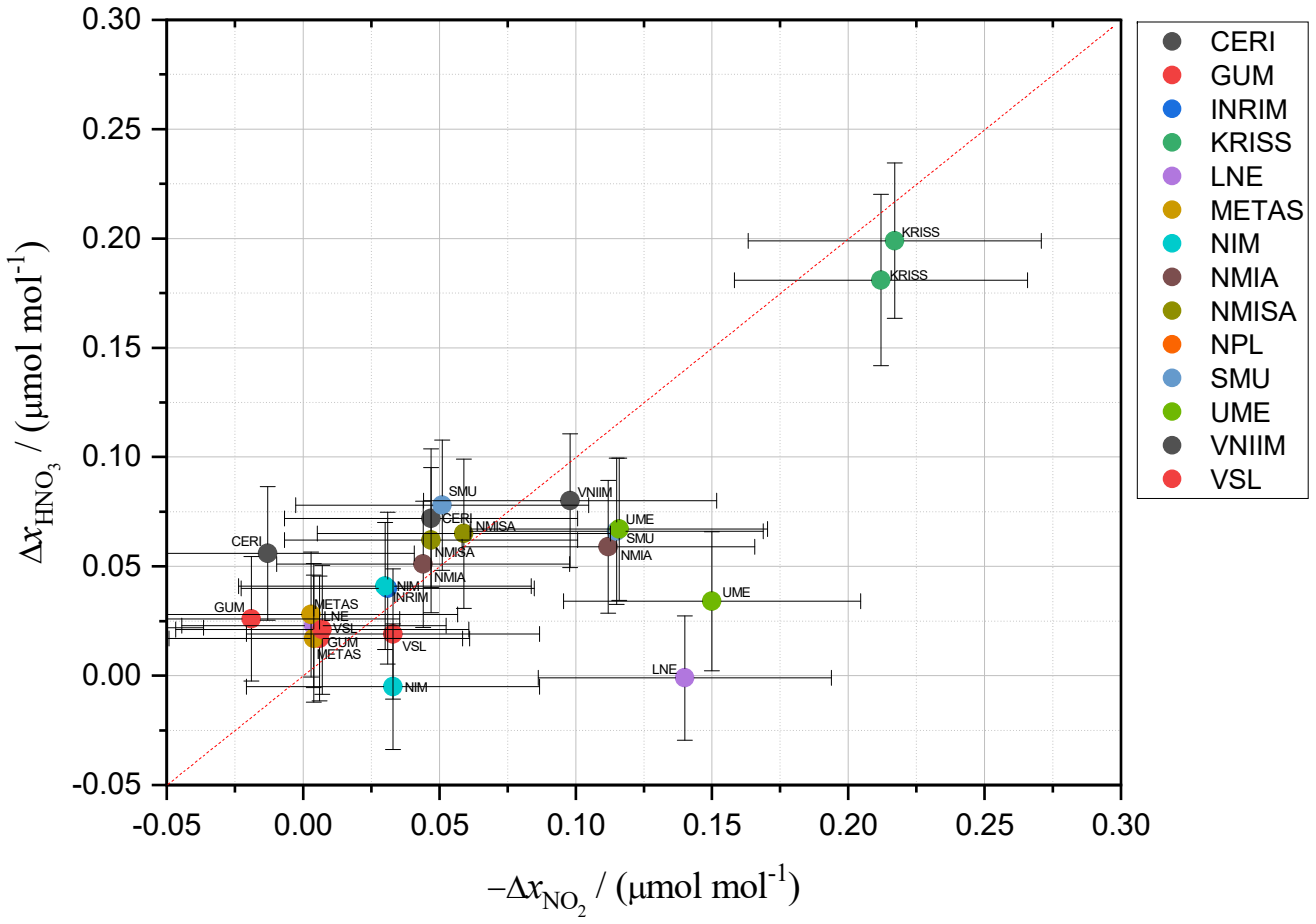

Figure 21. Gain in HNO_3 values against loss in NO_2 amount fraction measurements by the BIPM prior to sending standards back to participating laboratories. The error bar represents the standard uncertainty (k=1). Cylinder 614632 from VNIIM was not included into the plot due to its lack of correlation due its significant level of moisture.

5.2 *Loss of NO_2 versus time*

The NO_2 amount fraction was observed to be decreasing in a number of standards while they were measured at the BIPM. At that time, it was assumed that the decay was linear, and a loss rate was calculated with this assumption. It is provided in this section as additional information on the standards and should not be confused with the linear model applied to participants' results in section 6.2.

The loss rate of NO_2 in each cylinder was calculated after linear regression of the x_{BIPM} (Table 4) versus the time. The NO_2 loss rate in the cylinders, expressed in nmol mol^{-1} d^{-1}, for each is plotted in Figure 22. The treatment, indicated by a marker, of the cylinders is added for information on the same graph. It should be emphasised that little information is known about the details of the treatment, only reported to the coordinating laboratory as a trademark. Furthermore, the loss rate of NO_2 may vary with the age of cylinder in a nonlinear way, as observed during this comparison. Therefore, no further conclusion was drawn regarding the best treatment to ensure stable NO_2 amount fractions in cylinders.

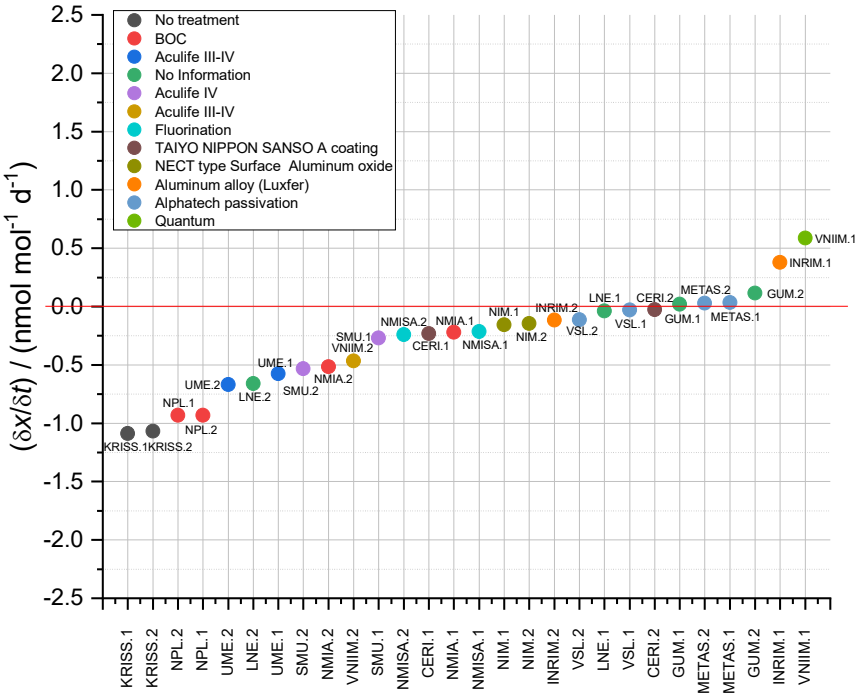

Figure 22: Loss rate of NO_2 in nmol mol^{-1} d^{-1} calculated in the participants' standards from linear regressions of BIPM measurements together with information concerning the cylinder treatment, if any. Note: for NPL Cylinders (2448 and S357) the loss rate was estimated from the two last measurements only, in view of the unexpected values observed during the first measurement.

This graph shows loss rates which can reach 1 nmol mol^{-1} d^{-1} in some cylinders, representing 0.01% of the nominal value lost per day. The data for three cylinders could

be interpreted to infer increase of NO_2 with time, however taking into account the uncertainty of the measurements, other trend lines could be drawn through the data also.

6 Comparison results

Figure 3 to Figure 16 strongly indicate that the decay of the NO_2 amount fraction in the standards was not the same for all standards. For some standards, the decay was faster in the first three months, with a quasi-stable regime observed after. For some others, the decay could be seen as linear, and for some no decay was observed at all (within the measurement uncertainties). For all of them, the frequency of measurements agreed in the protocol did not allow an accurate modelling of the decay function. It was therefore agreed to reflect this lack of knowledge in the estimation of the degrees of equivalence, as explained below.

The graph below shows the principle for the calculation of the comparison results submitted to all participants as approved in November 2020 (called option 6 at that time). The principle of this option is shown with the example of one cylinder provided by CERI. Red dots are the NO_2 amount fractions measured at the BIPM (calibrated with the BIPM dynamic generation system), and the black dots are the values reported by the participant (with its own traceability).

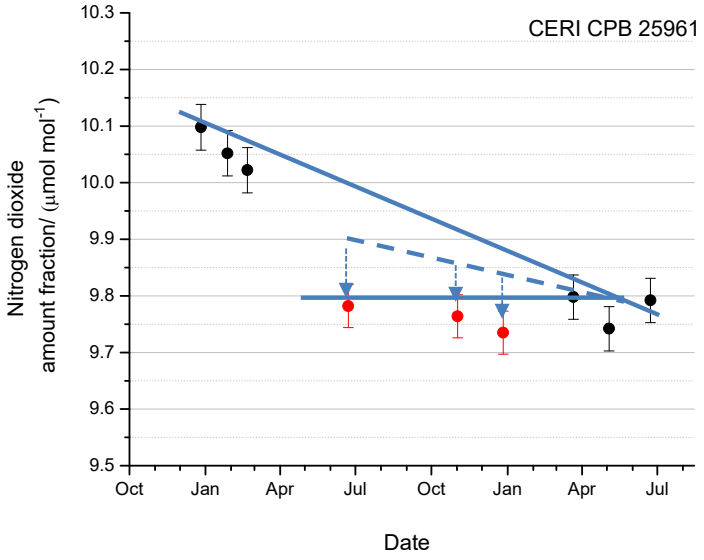

Figure 23. Nitrogen dioxide amount fraction values submitted by CERI for cylinder CPB 25961 (black dots) and BIPM measured values (red dots) during the course of the comparison versus the time. The error bar represents the standard uncertainty (k=1) associated with the measured value.

6.1 The Key Comparison Reference Value

The three values measured at the BIPM constitute the Key Comparison Reference Values, resulting in six values per participant as each of them prepared two standards. They are associated with the date of the measurements.

Each KCRV is associated with a standard uncertainty calculated as explained in ANNEX III- BIPM Value assignment procedure.

To calculate the degrees of equivalence between participants' results and their KCRVs, it was necessary to agree on a model to calculate the participants' NO_2 amount fraction in their standards at the date of the KCRVs (BIPM measurements), as explained below.

6.2 Participants' values at the date of the KCRVs

A difference was made between cylinders with a decay and without, as observed when applying a linear model to participants' results. Table 6 list the parameters (slope and intercept) of a linear regression performed on the NO_2 amount fractions submitted by participants. Calculated decay rates faster than -10^{-4} µmol mol^{-1}/day were taken to indicate a cylinder in which NO_2 was decreasing.

6.2.1 No decay was observed

In this case the participants' value x_{NMI}, is a constant estimated from the average of the six measurements performed by the participant. The standard uncertainty $u(x_{\mathrm{NMI}})$ is the median of the six reported standard uncertainties. Values and uncertainties are detailed in Annex I, Table 8.

6.2.2 A decay was observed

In this case the principle of the approach is that the participants' values must lie between values estimated from a linear decay and the last set of values measured by the participant. Indeed, the frequency of measurements does not allow an accurate observation of the shape of the decay of NO_2 amount fractions during the course of the comparison. However, we can state that this shape is in between a linear decrease, which would result in the largest estimation of NO_2 amount fractions at the KCRV dates, and a decreasing power function ending with constant NO_2 amount fractions. The value x_{NMI} at a specific date was therefore estimated from the average of two values:

- $x_{\mathrm{NMI\_LinPred}}$, the value predicted at that date by the linear regression of the participants' results
- $\bar{x}_{\mathrm{NMI\_3Last}}$, the average of the last three participants' results;

The standard uncertainty of the participant's value, $u(x_{\mathrm{NMI}})$, is estimated from a rectangular distribution delimited by the upper value $x_{\mathrm{NMI\_LinPred}}$ plus its expanded uncertainty and the lower value $\bar{x}_{\mathrm{NMI\_3Last}}$ minus its expanded uncertainty:

$$u(x_{\mathrm{NMI}}) = (x_{\mathrm{NMI_{LinPred}}} + U(x_{\mathrm{NMI_{LinPred}}}) - \bar{x}_{\mathrm{NMI_{3Last}}} + U(\bar{x}_{\mathrm{NMI_{3Last}}}))/(2\sqrt{3}) \quad (1)$$

In which:

$u(x_{\mathrm{NMI_{LinPred}}})$ is the median of the standard uncertainties submitted by the participant for all its six measurements;

$u(x_{\mathrm{NMI}_{3\mathrm{Last}}})$ is the median of the three standard uncertainties submitted by the participant for its last three measurements;

The values $x_{\mathrm{NMI\_LinPred}}$, $\overline{x}_{\mathrm{NMI\_3Last}}$ and their uncertainties are displayed in Annex I, Table 9.

*Table 6. Slopes and intercepts of a linear decay model applied to values submitted by participants. The cylinder is considered decreasing if the slope is lower than -10^{-4} µmol mol^{-1}/day. No uncertainty is provided as the values do not impact the comparison's results. * are those cylinders that do not meet this criterion.*

NMI	Cylinder	Intercept	Slope
		µmol mol^{-1}	*µmol mol^{-1}/day*
CERI	CPB 25961	10.0740	-5.97×10^{-4}
CERI	CPB 18969	10.0857	-6.47×10^{-4}
GUM	No D298386_1	10.6912	-5.99×10^{-4}
GUM	No D298387_1	10.6867	-1.25×10^{-3}
INRIM	P27787/D247449*	9.9462	1.511×10^{-4}
INRIM	D247448	10.2879	-2.43×10^{-4}
KRISS	D59 6920*	10.0398	2.90×10^{-5}
KRISS	D59 6882*	10.0264	2.92×10^{-5}
LNE	1191	10.0547	-9.71×10^{-4}
LNE	1183	10.0436	-7.07×10^{-4}
METAS	10918	9.8332	-8.32×10^{-4}
METAS	10919	9.8524	-9.20×10^{-4}
NIM	L62804125	9.9283	-3.49×10^{-4}
NIM	L62804135	9.9179	-2.55×10^{-4}
NMIA	MK0806*	9.8865	1.37×10^{-4}
NMIA	MK0807	10.2368	-4.51×10^{-4}
NMISA	D62 6618*	9.9772	7.05×10^{-4}
NMISA	D62 6554*	9.9090	1.88×10^{-4}
NPL	2448	10.0168	-5.11×10^{-4}
NPL	S357	10.0217	-5.00×10^{-4}
SMU	MY9742*	10.1422	-2.25×10^{-5}
SMU	MY9728	10.0658	-4.45×10^{-4}
UME	PSM499791	10.0882	-1.25×10^{-4}
UME	PSM499783	9.8487	-2.15×10^{-4}
VNIIM	614632	9.9153	-2.89×10^{-4}
VNIIM	5603778	9.9484	-3.64×10^{-4}
VSL	VSL105804	9.8806	-1.04×10^{-4}
VSL	VSL105806	9.8692	-1.75×10^{-4}

6.3 Degrees of equivalence

One degree of equivalence for one standard of one participant at one date of the measurement performed by the coordinating laboratory is defined as:

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

where x_{NMI} denotes the estimation of the NO_2 amount fraction in the participants' standards at the date of the KCRVs and x_{KCRV} denotes the reference value given by the BIPM on that date.

The combined standard uncertainty associated with the degree of equivalence can be expressed as:

$$u(D) = \sqrt{u(x_{\mathrm{NMI}})^2 + u(x_{\mathrm{KCRV}})^2} \quad (3)$$

and the expanded uncertainty, at 95 % confidence level

$$U(D) = k \cdot u(D) \quad (4)$$

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

As each participant sent two standards which were measured three times at the BIPM, six degrees of equivalence are calculated per participant and listed in Table 7; where:

NMI	is the acronym of the participating national metrology institute;
Cylinder	the identification code of the cylinder sent by the participating laboratory;
x_{NMI}	Is the participants value estimated at the time of the KCRV as explained in section 6.2.
$u(x_{\mathrm{NMI}})$	Is the uncertainty of the participants value estimated at the time of the KCRV as explained in section 6.2.
x_{KCRV}	Is the KCRV measured by the BIPM explained in section 6.1.
$u(x_{\mathrm{KCRV}})$	Is the uncertainty of the KCRV described in ANNEX III- BIPM Value assignment procedure.
D	the degree of equivalence; and
$U(D)$	the expanded uncertainty of the degree of equivalence;

The degrees of equivalence are listed in Table 7 and the corresponding graph of equivalence is plotted in Figure 24.

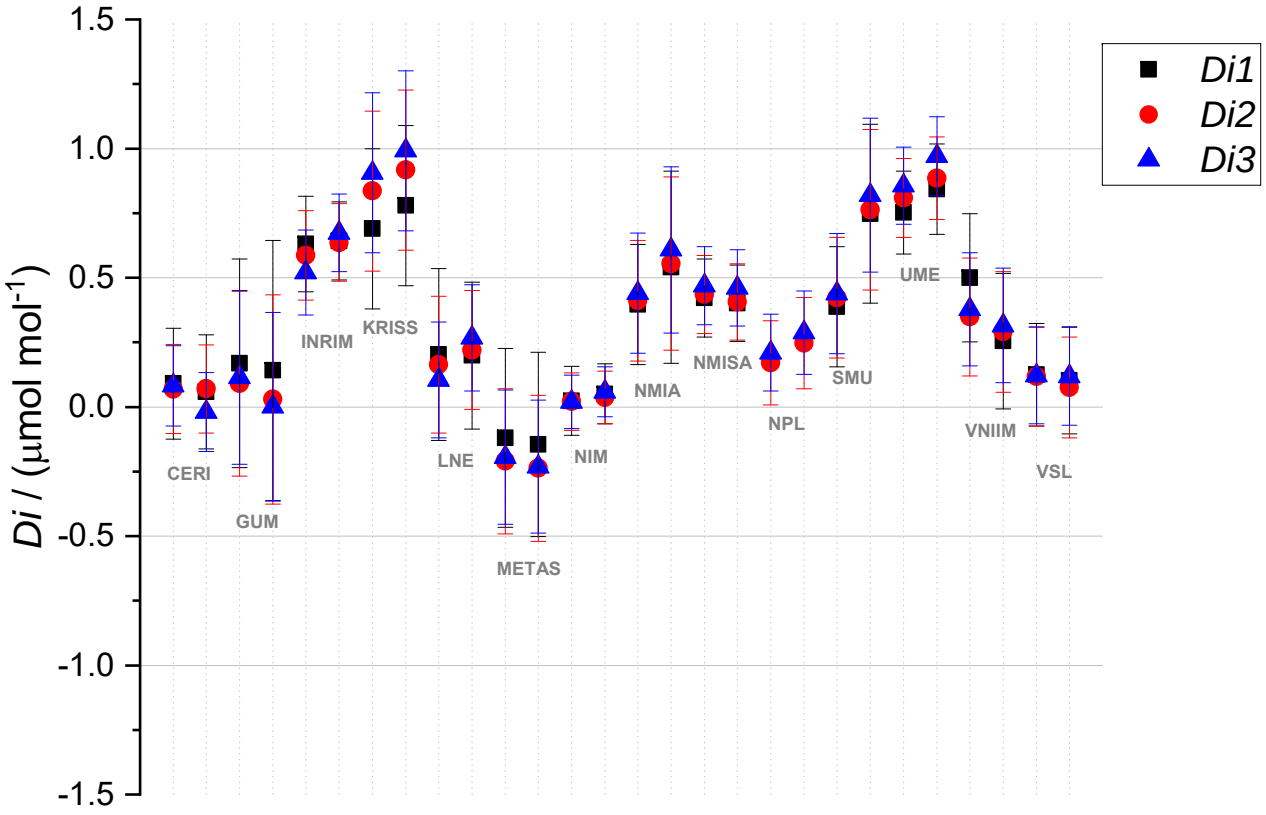

Figure 24. Degrees of equivalence of CCQM-K74.2018 calculated for the two standards sent by participants and based on the three series of measurements performed at the BIPM: Black squares – series 1 , red circles – series 2, blue triangles – series 3. The error bar represents the expanded uncertainty at a 95 % level of confidence. Results of the first measurements for NPL were considered as outliers and are not displayed on the graph.

CCQM-K74.2018: Nitrogen dioxide, 10 µmol mol^{-1}

Table 7. Degrees of equivalence calculated for the two standards sent by participants and based on the three series of measurements performed at the BIPM. All values are expressed in µmol mol-1 .

NMI	Cylinder	D_{i1} (µmol mol^{-1})	$U(D_{i1})$ (µmol mol^{-1})	D_{i2} (µmol mol^{-1})	$U(D_{i2})$ (µmol mol^{-1})	D_{i3} (µmol mol^{-1})	$U(D_{i3})$ (µmol mol^{-1})
CERI	CPB 25961	0.091	0.214	0.069	0.173	0.082	0.156
CERI	CPB 18969	0.058	0.221	0.070	0.171	-0.020	0.153
GUM	No D298386_1	0.169	0.404	0.090	0.357	0.114	0.336
GUM	No D298387_1	0.141	0.503	0.029	0.405	0.001	0.365
INRIM	P27787/D247449	0.631	0.185	0.586	0.173	0.521	0.165
INRIM	D247448	0.643	0.151	0.637	0.151	0.674	0.151
KRISS	D59 6920	0.689	0.309	0.835	0.309	0.906	0.309
KRISS	D59 6882	0.780	0.309	0.917	0.310	0.992	0.309
LNE	1191	0.202	0.333	0.164	0.265	0.105	0.224
LNE	1183	0.199	0.284	0.221	0.230	0.267	0.205
METAS	10918	-0.120	0.346	-0.210	0.281	-0.195	0.259
METAS	10919	-0.145	0.357	-0.238	0.282	-0.231	0.257
NIM	L62804125	0.023	0.133	0.021	0.111	0.020	0.104
NIM	L62804135	0.050	0.116	0.036	0.102	0.059	0.096
NMIA	MK0806	0.396	0.233	0.411	0.233	0.440	0.233
NMIA	MK0807	0.541	0.372	0.555	0.335	0.608	0.321
NMISA	D62 6618	0.422	0.151	0.435	0.151	0.469	0.151
NMISA	D62 6554	0.402	0.147	0.407	0.147	0.461	0.147
NPL	2448	-	-	0.171	0.163	0.210	0.148
NPL	S357	-	-	0.247	0.176	0.288	0.161
SMU	MY9742	0.388	0.233	0.423	0.233	0.439	0.233
SMU	MY9728	0.748	0.347	0.763	0.311	0.819	0.298
UME	PSM499791	0.752	0.161	0.809	0.152	0.856	0.149
UME	PSM499783	0.843	0.175	0.885	0.160	0.971	0.152
VNIIM	614632	0.500	0.248	0.348	0.228	0.378	0.219
VNIIM	5603778	0.255	0.262	0.291	0.233	0.316	0.221
VSL	VSL105804	0.125	0.199	0.117	0.191	0.122	0.188
VSL	VSL105806	0.103	0.208	0.076	0.195	0.119	0.190

7 Results analysis

The results of the comparison indicate agreement of half of the participants with the KCRV but also differences of up to 10 % in some cases.

Similar to the 2009 comparison, the differences may be explained by the presence of nitric acid (in the range 34 nmol mol^{-1} to 548 nmol mol^{-1}) in the cylinders that were circulated by the participants as part of the comparison, as well as the possible presence of nitric acid in the primary standards used by participating laboratories. To test this assumption, the BIPM measured values of NO_2 and HNO_3 were added to obtain $x_{BIPM+HNO3}$ as an alternative reference value to compare against. Results reported in ANNEX I and ANNEX II, show that two participants, NPL and VNIIM, come to an agreement with such reference values in this scenario (see Figure 27). For other participants, the agreement (or disagreement) is maintained, so that a general conclusion of bias correction by just considering all NO_X species in the gas phase cannot de drawn.

NO_2 decays occurring in the time difference between the analysis of the comparison standards and the preparation of the primary standards used for their value assignment (at each of the six dates) could be a possible explanation for remaining differences. According to complementary information submitted by participants in April 2020, nine participants (KRISS, NMIA, SMU, LNE, NMISA, VNIIM, UME, INRIM and VSL) used standards prepared on average more than hundred days before the value assignment of the two standards circulated for the comparison. During this period, the NO_2 amount fraction could have decreased inside the primary standards, following a trend which was not predicted. Consequently, differences between the NO_2 amount fractions in the primary and comparison standards could have varied and impacted the six different measurements. Additionally, three participants (CERI, NIM and NPL) prepared fresh primary standards less than one month before value assigning the comparison standards. Degrees of equivalence are replotted in Figure 25 against the average time difference between the comparison standards' measurements and the primary standards' preparation. Some relationship can be seen, with CERI, NIM and NPL showing good agreement with the KCRV, by minimizing this time difference. However, VSL and LNE show good agreement and have used older primary standards for their value assignments. The agreement can be explained, since VSL standards exhibit very good stability (NO_2 loss rate close to zero as shown in Figure 22) and have corrected for HNO_3 impurity; LNE used a high concentration cylinder prepared two years before (NPL 2164, 200.2 µmol mol^{-1})[1], which had probably reached stability, to value assign their comparison cylinders, and the fractional loss of NO_2 may be considerable smaller in higher concentration standards. METAS results are not plotted on the same graph, as their comparison standards were value assigned a dynamic facility similar to the one used by the BIPM.

[1] Information provided by LNE for the April 2020 meeting.

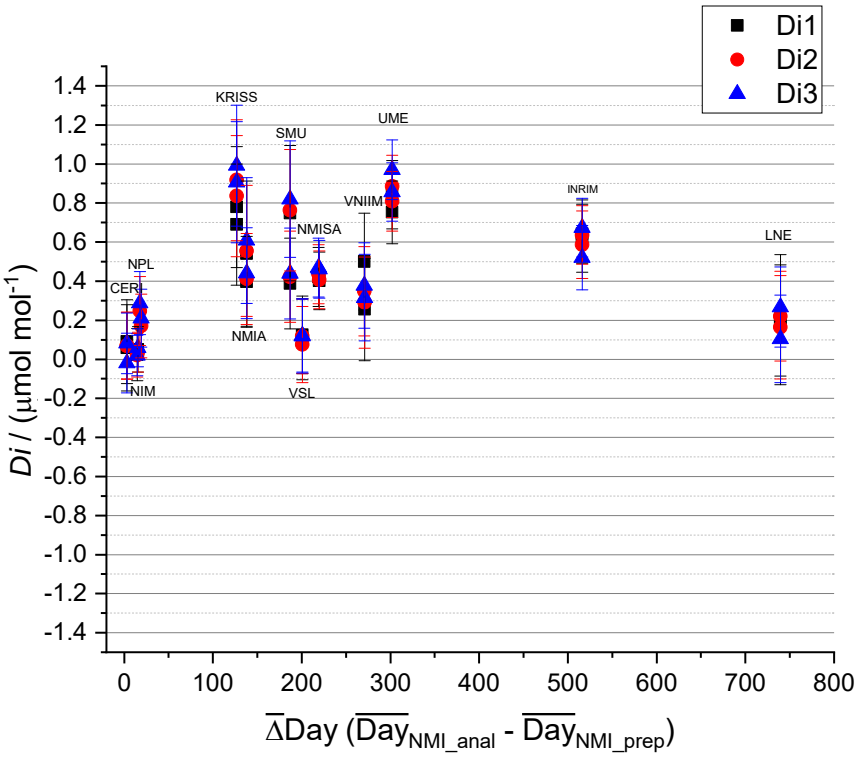

Figure 25. Degrees of equivalence of CCQM-K74.2018 d for the two standards sent by participants and based on the three series of measurements performed at the BIPM: Black squares – series 1 , red circles – series 2, blue triangles – series 3 versus the time difference between the analysis of the standards circulated for the comparison and the preparation of PRM's used for their value assignment. The error bar represents the expanded uncertainty at a 95 % level of confidence. GUM was not included in this plot since no information was provided by the laboratory. METAS was neither included since the reference mixtures were produced on real time by NO_2 permeation.

7.1 Comparison with CCQM-K74 (2009) results

The CCQM-K74 comparison (2009/2010) was organized as a Model 1 comparison, with all cylinders (one per participant) with the same surface treatment, prepared by VSL, and characterized for stability and with reference values provided by the BIPM. A small decay rate was found in the circulated standards, accounted for by the addition of an uncertainty to the reference value, and can be calculated to have been no more than 0.1 nmol mol^{-1} per day loss of NO_2.

In CCQM-K74.2018, standards were prepared by individual NMIs (two per participant), and characterized for stability by participants and the BIPM, the decay rates in different cylinders range over an order of magnitude, and the largest decay rates being an order of magnitude larger than in the original comparison in 2009/2010. Meanwhile the BIPM facility was maintained in the same conditions with the same relative standard uncertainty in the key comparison reference value at 0.4 %. The results from both comparisons are shown in the figure below. From this point of view it can be considered that the CCQM-

K74.2018 comparison was much more challenging, but also provides a clearer picture of the characteristics of different NO_2 standards at this amount fraction range.

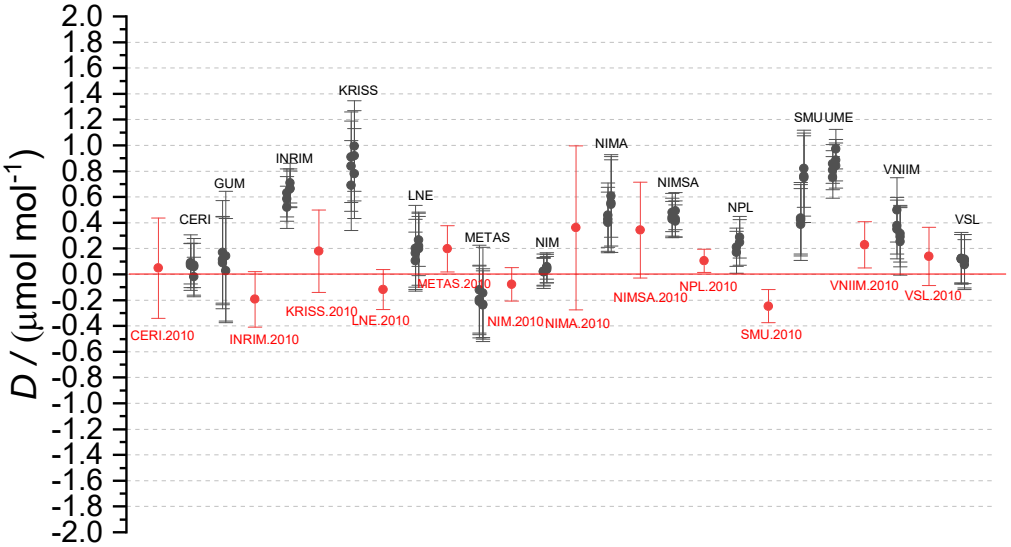

Figure 26. Comparison of degrees of equivalence between the CCQM-K74.2018 comparison (6 black dots per participant as results of 3 repeated measurements by the BIPM on 2 standards) and CCQM-K74 (red dots). The error bar represents the expanded uncertainty at a 95 % level of confidence.

Despite the more challenging nature of the comparison, a general conclusion that can be reached is that the overall spread of results remains similar to that demonstrated in 2009. Areas which were discussed by the GAWG that could lead to improvement in future levels of compatibility were:

a) Systematic application of HNO_3 measurements in NO_2 standard development;
b) Development of best practice procedure for NO_2 standard preparation noting that the instabilities observed would make ISO 6142 processes are not applicable; and
c) Focus on surface treatments and preparation processes to avoid impurities that can lead to decays in NO_2 concentrations.

8 'How far the light shines' statement

The following 'How far the light shines' statement was agreed by participants on November 6, 2020.

The results of this key comparison can be used to support CMC claims for analytical capabilities for NO_2 in nitrogen mixtures in the range from 10 -1000 µmol mol^{-1}, provided the impact of dimerization to N_2O_4 has a negligible effect on the upper limit. The extrapolation scheme described in GAWG/19-41 may be applied across this range. A separate document will be developed to provide further details.

ANNEX I- Participants' values at the date of the KCRVs

More details on the participants' values at the date of the KCRVs are provided below for the two distinct cases:

No decay was observed

In that case the participants' value x_{NMI}, is a constant estimated from the average of the six measurements performed by the participant. The standard uncertainty $u(x_{NMI})$ is the median of the six reported standard uncertainties, as reported below.

Table 8. Participants' values for cylinders without decay.

NMI	Cylinder	Average NO_2 amount fraction $\bar{x}_{NMI}$ (μmol mol^{-1})	Assigned standard uncertainty $u(\bar{x}_{NMI})$ (μmol mol^{-1})
INRIM	P27787/D247449	9.992	0.065
KRISS	D59 6882	10.033	0.150
KRISS	D59 6920	10.047	0.150
NMIA	MK0806	9.920	0.110
NMISA	D62 6618	9.994	0.065
NMISA	D62 6554	9.955	0.063
SMU	MY9742	10.137	0.110

A decay was observed

In that case the value x_{NMI} at a specific date was estimated from the average of two values:

- $x_{NMI\_LinPred}$, the value predicted at that date by the linear regression of the participants' results
- $\bar{x}_{NMI\_3Last}$, the average of the last three participants' results;

The standard uncertainty of the participant's value, $u(x_{NMI})$, is estimated from a rectangular distribution delimited by the upper value $x_{NMI\_LinPred}$ plus its expanded uncertainty and the lower value $\bar{x}_{NMI\_3Last}$ minus its expanded uncertainty, equation 1.

The values $x_{NMI\_LinPred}$, $\bar{x}_{NMI\_3Last}$ and their uncertainties are displayed in the three tables below, corresponding to the three dates of measurements at the BIPM.

Table 9. Average of the last three participants' results and associated uncertainties ($\overline{x}_{\text{NMI-3Last}}$, $u(\overline{x}_{\text{NMI-3Last}})$), value predicted at the first KCRV date by the linear regression of the participants' results $x_{NMI\_LinPred}$, associated uncertainty $u(x_{NMI\_LinPred})$, and resulting participants' values and associated uncertainty.

NMI	Cylinder	$\overline{x}_{\text{NMI-3Last}}$ (µmol mol^{-1})	$u(\overline{x}_{\text{NMI\_3last}})$ (µmol mol^{-1})	$x_{\text{NMI\_LinPred}}$ (µmol mol^{-1})	$u(x_{\text{NMI\_LinPred}})$ (µmol mol^{-1})	$x_{\text{NMI,1}}$ (µmol mol^{-1})	$u(x_{\text{NMI,1}})$ (µmol mol^{-1})
CERI	CPB 25961	9.777	0.039	9.968	0.040	9.873	0.100
CERI	CPB 18969	9.763	0.039	9.965	0.040	9.864	0.104
GUM	No D298386_1	10.400	0.126	10.598	0.119	10.499	0.198
GUM	No D298387_1	10.094	0.124	10.473	0.117	10.283	0.248
INRIM	D247448	10.160	0.050	10.234	0.065	10.197	0.088
LNE	1191	9.597	0.060	9.924	0.060	9.760	0.164
LNE	1183	9.710	0.060	9.944	0.060	9.827	0.137
METAS	10918	9.437	0.060	9.737	0.083	9.587	0.169
METAS	10919	9.423	0.060	9.742	0.083	9.583	0.174
NIM	L62804125	9.748	0.017	9.871	0.017	9.809	0.055
NIM	L62804135	9.787	0.017	9.872	0.017	9.829	0.044
NMIA	MK0807	10.017	0.120	10.187	0.110	10.102	0.182
NPL	2448	9.820	0.050	9.973	0.035	9.897	0.093
NPL	S357	9.813	0.050	9.976	0.043	9.895	0.100
SMU	MY9728	9.860	0.115	9.986	0.115	9.923	0.169
UME	PSM499791	10.020	0.050	10.066	0.049	10.043	0.071
UME	PSM499783	9.737	0.049	9.810	0.051	9.773	0.079
VNIIM	614632	9.767	0.075	9.881	0.073	9.824	0.118
VNIIM	5603778	9.760	0.075	9.905	0.070	9.832	0.126
VSL	VSL105804	9.823	0.070	9.861	0.070	9.842	0.092
VSL	VSL105806	9.776	0.070	9.831	0.070	9.804	0.097

Table 10. value predicted at the second KCRV date by the linear regression of the participants' results $x_{NMI\_LinPred}$, associated uncertainty $u(x_{NMI\_LinPred})$, and resulting participants' values $x_{NMI,2}$ and associated standard uncertainty $u(x_{NMI,2})$.

NMI	Cylinder	$x_{NMI\_LinPred}$ (µmol mol^{-1})	$u(x_{NMI\_LinPred})$ (µmol mol^{-1})	$x_{NMI,2}$ (µmol mol^{-1})	$u(x_{NMI,2})$ (µmol mol^{-1})
CERI	CPB 25961	9.889	0.040	9.833	0.078
CERI	CPB 18969	9.872	0.040	9.818	0.077
GUM	No D298386_1	10.514	0.119	10.457	0.174
GUM	No D298387_1	10.300	0.117	10.197	0.199
INRIM	D247448	10.200	0.065	10.180	0.078
LNE	1191	9.795	0.060	9.696	0.127
LNE	1183	9.845	0.060	9.777	0.108
METAS	10918	9.621	0.083	9.529	0.135
METAS	10919	9.609	0.083	9.516	0.136
NIM	L62804125	9.821	0.017	9.785	0.040
NIM	L62804135	9.838	0.017	9.812	0.034
NMIA	MK0807	10.121	0.110	10.069	0.163
NPL	2448	9.900	0.035	9.860	0.072
NPL	S357	9.904	0.043	9.858	0.079
SMU	MY9728	9.922	0.115	9.891	0.151
UME	PSM499791	10.050	0.049	10.035	0.066
UME	PSM499783	9.779	0.051	9.758	0.070
VNIIM	614632	9.844	0.073	9.805	0.107
VNIIM	5603778	9.852	0.070	9.806	0.110
VSL	VSL105804	9.847	0.070	9.835	0.088
VSL	VSL105806	9.807	0.070	9.792	0.090

Table 11. value predicted at the third KCRV date by the linear regression of the participants' results $x_{NMI\_LinPred}$, associated uncertainty $u(x_{NMI\_LinPred})$, and resulting participants' values $x_{NMI,3}$ and associated standard uncertainty $u(x_{NMI,3})$.

NMI	Cylinder	$x_{NMI\_LinPred}$ (µmol mol^{-1})	$u(x_{NMI\_LinPred})$ (µmol mol^{-1})	$x_{NMI,3}$ (µmol mol^{-1})	$u(x_{NMI,3})$ (µmol mol^{-1})
CERI	CPB 25961	9.856	0.040	9.817	0.068
CERI	CPB 18969	9.835	0.040	9.799	0.066
GUM	No D298386_1	10.477	0.119	10.438	0.163
GUM	No D298387_1	10.230	0.117	10.162	0.178
INRIM	D247448	10.183	0.065	10.172	0.073
LNE	1191	9.722	0.060	9.659	0.105
LNE	1183	9.800	0.060	9.755	0.095
METAS	10918	9.580	0.083	9.508	0.124
METAS	10919	9.564	0.083	9.494	0.123
NIM	L62804125	9.804	0.017	9.776	0.035
NIM	L62804135	9.823	0.017	9.805	0.030
NMIA	MK0807	10.097	0.110	9.939	0.156
NPL	2448	9.871	0.035	9.845	0.064
NPL	S357	9.874	0.043	9.844	0.071
SMU	MY9728	9.899	0.115	9.879	0.144
UME	PSM499791	10.042	0.049	10.031	0.064
UME	PSM499783	9.765	0.051	9.751	0.065
VNIIM	614632	9.827	0.073	9.797	0.102
VNIIM	5603778	9.829	0.070	9.795	0.104
VSL	VSL105804	9.841	0.070	9.832	0.086
VSL	VSL105806	9.797	0.070	9.787	0.087

ANNEX II- HNO_3 and offset vs BIPM reference values

One of the conclusions in the 2010 Key comparison CCQM-K74 report was that a full interpretation of the results of the comparison needed to take into account the presence of nitric acid (in the range 100 nmol mol^{-1} to 350 nmol mol^{-1}) 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.

According to the purity analysis results on this comparison all cylinders contained HNO_3 and other impurities confirming the hypothesis that the primary standards used by participating laboratories in 2010 definitely contained nitric acid.

Under certain scenarios where NMI analytical measurement systems respond to all NO_x species and the BIPM system reports only NO_2, the nitric acid amount fraction in the cylinder can be used to explain the difference between BIPM and NMI reported values. This is tested in Figure 27, where the BIPM measured values of NO_2 and HNO_3 were added to obtain $x_{BIPM+HNO3}$. In a number of cases, there is very good agreement between the values using this treatment. However it is understood that the underlying assumptions may not hold for all cases, and other sources of biases were highlighted in this comparisons, such as the age of the calibration standards used by participants to perform their six different analysis of the comparison standards.

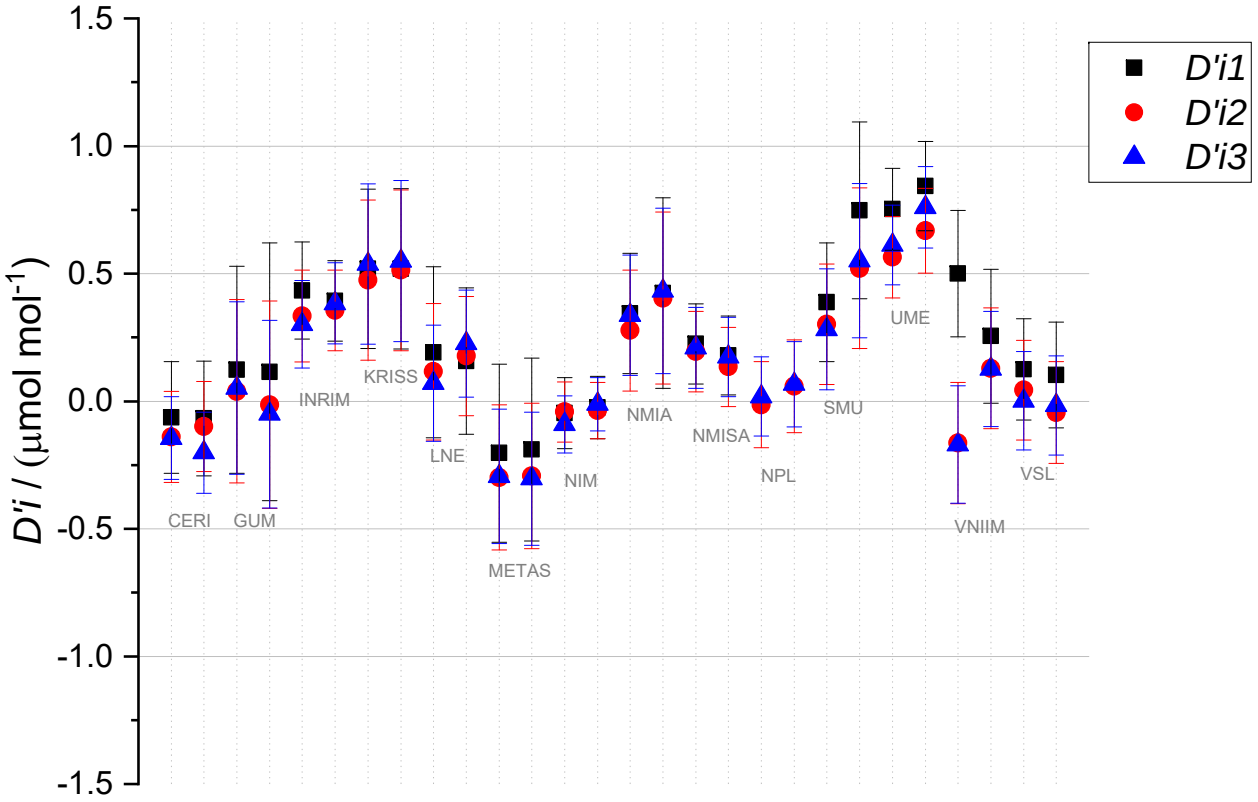

Figure 27. Difference from reference value of CCQM-K74.2018 with the approach adopted in November 2020 (option 6), based on the three series of measurements performed at the BIPM adding the HNO_3 amount of fraction found in each gas mixture: blue diamonds – series 1 , violet diamonds – series 2, cyan diamonds – series 3. The error bar represents the expanded uncertainty at a 95 % level of confidence. Results of the first measurements for NPL were removed.

CCQM-K74.2018: Nitrogen dioxide, 10 µmol mol^{-1}

Table 12. Results interpolated from participants' measurements $x_{NMIPred}$ and reference values x_{BIPM} adding the HNO_3 amount of fraction found in each mixture and difference from reference value D calculated accordingly section 6.2. All values are expressed in µmol mol^{-1}. are the mixtures without decay. For further details see section and and Table 9.*

NMI	Cylinder	D'_{i1} (µmol mol^{-1})	$U(D'_{i1})$ (µmol mol^{-1})	D'_{i2} (µmol mol^{-1})	$U(D'_{i2})$ (µmol mol^{-1})	D'_{i3} (µmol mol^{-1})	$U(D'_{i3})$ (µmol mol^{-1})
CERI	CPB 25961	-0.063	0.219	-0.140	0.179	-0.144	0.163
CERI	CPB 18969	-0.068	0.225	-0.099	0.177	-0.202	0.159
GUM	No D298386_1	0.123	0.406	0.039	0.359	0.051	0.338
GUM	No D298387_1	0.115	0.505	-0.014	0.407	-0.051	0.367
INRIM	P27787/D247449*	0.434	0.191	0.333	0.180	0.302	0.171
INRIM	D247448	0.393	0.158	0.356	0.159	0.384	0.159
KRISS	D59 6920*	0.519	0.313	0.474	0.314	0.537	0.314
KRISS	D59 6882*	0.519	0.313	0.513	0.315	0.550	0.316
LNE	1191	0.191	0.335	0.116	0.268	0.071	0.228
LNE	1183	0.157	0.287	0.177	0.233	0.226	0.209
METAS	10918	-0.203	0.349	-0.299	0.284	-0.295	0.263
METAS	10919	-0.189	0.359	-0.294	0.285	-0.303	0.261
NIM	L62804125	-0.047	0.139	-0.042	0.118	-0.091	0.112
NIM	L62804135	-0.025	0.123	-0.037	0.110	-0.011	0.105
NMIA	MK0806*	0.344	0.236	0.277	0.237	0.337	0.236
NMIA	MK0807	0.424	0.374	0.404	0.337	0.432	0.324
NMISA	D62 6618*	0.224	0.158	0.194	0.158	0.209	0.159
NMISA	D62 6554*	0.180	0.154	0.135	0.155	0.174	0.155
NPL	2448	-	-	-0.014	0.169	0.018	0.155
NPL	S357	-	-	0.058	0.182	0.067	0.168
SMU	MY9742*	0.388	0.233	0.302	0.237	0.282	0.237
SMU	MY9728	0.748	0.347	0.521	0.314	0.551	0.302
UME	PSM499791	0.752	0.161	0.565	0.159	0.612	0.157
UME	PSM499783	0.843	0.175	0.668	0.166	0.760	0.159
VNIIM	614632	0.500	0.248	-0.164	0.238	-0.170	0.230
VNIIM	5603778	0.255	0.262	0.129	0.237	0.127	0.226
VSL	VSL105804	0.125	0.199	0.043	0.196	0.001	0.193
VSL	VSL105806	0.103	0.208	-0.044	0.199	-0.016	0.194

ANNEX III- BIPM Value assignment procedure

The BIPM-NO_2 primary gas facility has been described in detail elsewhere[2-5]. For completeness reasons a summary of the value assignment procedure is presented as follows.

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 Vertex 70V. 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.

The amount fractions of the dynamically produced gas mixtures obtained with the BIPM facility, denoted as x_{BIPM} in this document or x_{NO2} in this section, are calculated by the expression below:

$$x_{\mathrm{NO_2}} = \left(\frac{P \times V_{\mathrm{m}}}{q_v \times M_{\mathrm{NO_2}}} \right) - \left(\frac{M_{\mathrm{HNO_3}} \times x_{\mathrm{HNO_3}}}{M_{\mathrm{NO_2}}} \right) - \sum \left(\frac{M_{\mathrm{imp}} \times x_{\mathrm{imp}}}{M_{\mathrm{NO_2}}} \right) \quad (5)$$

where:

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

P is the NO_2 permeation rate (mass lost rate) in ng min^{-1};

$V_{\mathrm{m}} = 22.4038$ 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 rate of N_2 given by the sum of carrier nitrogen ($q_{v\,\mathrm{molbloc2}}$) and the diluent nitrogen ($q_{v\,\mathrm{molbloc1}}$ and) flow rates in mL min^{-1} at standard conditions (273.15 K. 101.325 kPa);

x_{HNO3} is the HNO_3 amount fraction in μmol mol^{-1} measured by FT-IR spectroscopy (anchored to HITRAN 2012);

$M_{\mathrm{HNO_3}} = 63.013$ g mol^{-1} is the molar mass of HNO_3;

x_{imp} are the amount fractions in μmol mol^{-1} of other impurities measured by FT-IR Spectroscopy (anchored to HITRAN 2012); and

M_{imp} are the molar mass of the impurities in g mol^{-1};

Uncertainties associated with each NO_2 amount fraction x_{NO2} in gas mixtures produced by permeation of nitrogen dioxide, $u(x_{NO2})$, are calculated by means of the software GUM Workbench V.2.3[6]. An example of the uncertainty budget is listed below:

CCQM-K74.2018: Nitrogen dioxide, 10 μmol mol^{-1}

Table 13. 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.

Quantity	Estimate x_i	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient $c_i=\sigma x_{NO2}/\sigma x$	Uncertainty contribution $u_i(y)$ mol·mol^{-1}	Index %
P	11.1239 10^{-6}·g·min^{-1}	Normal	4.18 10^{-9}·g·min^{-1}	0.95	4.0 10^{-9}	1.7
V_m	22.4038 L·mol^{-1}	Normal	340.00 10^{-6} L·mol^{-1}	480 10^{-9}	160 10^{-12}	0.0
$q_{v\ molbloc1}$	511 10^{-3}·L·min^{-1}	Normal	455.21 10^{-6} L·min^{-1}	−21 10^{-6}	−9.5 10^{-9}	9.6
M_{NO2}	46.0055 g·mol^{-1}	Normal	1.40 10^{-3} g·mol^{-1}	−230 10^{-9}	−320 10^{-12}	0.0
x_{HNO3}	0.176 10^{-6}mol·mol^{-1}	Normal	0.021 10^{-6}·mol·mol^{-1}	−1.4	−29 10^{-9}	88.1
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	360 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}	−3.8 10^{-9}	−6.5 10^{-12}	0.0

Quantity	Value	Standard Uncertainty
x_{NO2}	10.45 µmol·mol^{-1}	0.03 µmol·mol^{-1}

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 amount fraction determination of nitric acid and the gas flow rate measurements.

Like in 2009 comparison the HNO_3 uncertainty contribution to the combined uncertainty is significant. This was the subject of specific workshop hold in 2010 by the GAWG and of further publications by the BIPM (see references[2-5]).

An additional uncertainty contribution due to possible NO_2 losses, when analyzing cylinders with the BIPM facility, $u(x_{NO2losses})$, was added as described in the previous comparison CCQM-K74 report. This term corresponds to a bias of zero with an

uncertainty of 5.7 nmol mol^{-1} (see references[2-5]). It was included but its contribution was insignificant (less than 0.4 nmol mol^{-1}).

Correlations

Non-zero covariances, $u(x_{NO_2,i}, x_{NO_2,j})$ 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:

$$u(x_{NO_2,i}, x_{NO_2,j}) = \gamma \left[u(x_{NO_2,i}) \right]^2 . \quad (6)$$

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

$$\gamma = q_j / q_i \quad (7)$$

is the dilution factor of the total gas flow rates 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 amount fractions (typically 8 µmol mol^{-1} to 12 µmol mol^{-1}), the dilution factor is often close to 1, and the covariances often close to the variances $u(x_{NO2.i})^2$.

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. Other impurities were observed, and they are also reported here for information only. These values have no impact on the comparisons results.

FT-IR Spectra acquisition

A vacuum Bruker Vertex 70v FT-IR Spectrometer equipped with a RockSolid interferometer (vacuum better than 0.2 hPa) with 1 cm^{-1} resolution (0.16 cm^{-1} optional), a 40 mm beam diameter, a globar source and CaF_2 beam splitter was used for the study. The spectrometer was configured with a liquid N_2-cooled mid-infrared MCT-high D* detector and a multi-pass White-type gas cell of volume 0.75 L (Gemini Scientific Instruments, USA) with an optical path of 8.88±0.41 m. The wetted surfaces of the gas cell were electro-polished stainless steel treated with Silconert 2000 (Silcotek) and gold (mirror coatings) to minimize surface adsorption and desorption effects for NO_2 and HNO_3. The interferometer was scanned at 64 scans min^{-1} and spectra co-added for five minutes to obtain an acceptable signal-to-noise ratio. The transmission spectra of gas reference standards obtained following this procedure had a very high signal to noise ratio

of typically ~1 x 10^4 peak-peak from (2400-4700) cm^{-1}. By comparison the main NO_2 peak had absorbance in the range (0.04–0.16) abs_{10}.

In order to prevent nonlinear responses produced by excess photon flux reaching the detector special care was put into adjusting the instrument parameters of the software to ensure that the apparent intensity from the detector was zero at 700 cm^{-1}.

The spectrometer user interface was controlled using a BIPM developed software named B-FOS that allowed the automatic setting of all instrument parameters into Bruker's proprietary OPUS software for control, spectral acquisition and on-line analysis through the use of MALT (Multiple Atmospheric Layer Transmission)[7-9] spectrum analysis software version 5.56. MALT retrieves the amount of fractions of each trace gas in the sample from a least-squares fit to the measured spectrum based on a model calculation and Hitran line parameters[10].

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 mL 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. A gradient of temperature was also considered and described in Flores et al.[3]

The White cell has a volume of ~750 mL and the sample flows at ~400 mL 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 amount fraction determination. We also empirically verified that after 30 min of flow, the sample was completely exchanged, within the bounds of measurement uncertainty. For more details see Flores et al.[3]

From times series analysis the uncertainty in the response of the FT-IR spectrometer was estimated in this case of 6 nmol mol^{-1} for a 5 minutes average time. However for conservative reasons 20 nmol mol^{-1} was retained as the uncertainty of the response of the instrument.

Quantitative analysis of nitric acid and other impurities

The determination of nitric acid and other impurities was performed by means of the spectra obtained during the NO_2 value assignment of the participating standards. Since the FT-IR facility was configured with an 8.88±0.41 m multi pass white cell the quantification of certain impurities could be considered as challenging.

Impurities were quantified using the following regions:

- HNO_3: 1709 cm^{-1} (most of the reported integrated band intensities agree in this region within ± 0.2 % [13]);
- CO_2: 2300 to 2400 cm^{-1}

- N_2O: 2100 to 2300 cm^{-1}
- H_2O: 3600 to 4000 cm^{-1}
- HONO: 750 to 900 cm^{-1}
- NOCl: 1760 to 1860 cm^{-1}.

The impurities found are listed in Table 5 for HNO_3, Table 15 for H_2O, Table 16 for CO_2, Table 17 for N_2O, Table 18 for NOCl and Table 19 for HONO where:

NMI	is the identification name of the participating laboratory;
Cylinder	is the identification code of the cylinder given by the participating laboratory;
Date	the date when the BIPM performed the value assignment of the specific standard
$x_{i(j)}$	is the amount fraction of the impurity *i* measured in the standard by the BIPM during the measurement *j* (*j*=1. 2 or 3); and
$u(x_{i\,(j)})$	the standard uncertainty associated with the impurity *i* amount fraction measurement during the measurement *j*;

Uncertainty budget for each impurity

Table **14** below summarizes the uncertainty sources and presents the components of the final combined uncertainty associated with the FT-IR/MALT measurements of: HNO_3 at an amount fraction (x) ranging from 100 nmol mol^{-1} to 250 nmol mol^{-1}; CO_2 at an amount fraction (x) ranging from 10 nmol mol^{-1} to 300 nmol mol^{-1}; N_2O at an amount fraction (x) ranging from 10 nmol mol^{-1} to 50 nmol mol^{-1}; H_2O at an amount fraction (x) ranging from 50 nmol mol^{-1} to 3000 nmol mol^{-1}; HONO at an amount fraction (x) ranging from 10 nmol mol^{-1} to 100 nmol mol^{-1}; and NOCl at an amount fraction (x) ranging from 10 nmol mol^{-1} to 50 nmol mol^{-1}. All impurities were measured with a FT-IR white cell with an 8.88 m optical path. All the components can be combined to give, for example, the following equation for the combined standard uncertainty for HNO_3 measured amount fraction values:

$$u(x_{HNO3}) = \sqrt{(0.02)^2 + (0.017x)^2 + (0.05x)^2} \quad (8)$$

Table 14: uncertainty budget components associated with the FT-IR spectrometer used as an absolute method of quantification to determine the amount fractions of impurities found in the participating standards.

Uncertainty	HNO_3 /µmol mol^{-1}	CO_2 µmol mol^{-1}	N_2O µmol mol^{-1}	H_2O µmol mol^{-1}	HONO µmol mol^{-1}	NOCl µmol mol^{-1}
Type A						
Instrument stability	0.020	0.010	0.010	0.003	0.020	0.025
Type B						
MALT	0.017x	0.015x	0.015x	0.017x	-	
HITRAN	0.05x	0.03x	0.03x	0.05x	-	
Reference spectra	-	-	-	-	0.1x	0.1x
Area measurement	-	-	-	-	0.5x	0.5x

Table 15. H_2O amount fraction measured in cylinder gas standards by the BIPM using FT-IR spectroscopy.

NMI	Cylinder	Measurement date	$x_{H2O(1)}$ (μmol mol^{-1})	$u(x_{H2O(1)})$ (μmol mol^{-1})	Measurement date	$x_{H2O(2)}$ (μmol mol^{-1})	$u(x_{H2O(2)})$ (μmol mol^{-1})	Measurement date	$x_{H2O(3)}$ (μmol mol^{-1})	$u(x_{H2O(3)})$ (μmol mol^{-1})
CERI	CPB 25961	12/07/2018	0.678	0.107	21/11/2018	0.210	0.102	15/01/2019	0.242	0.102
CERI	CPB 18969	20/07/2018	0.937	0.113	11/12/2018	0.364	0.103	06/02/2019	0.392	0.103
GUM	No D298386_1	12/07/2018	0.469	0.104	29/11/2018	0.230	0.102	30/01/2019	0.484	0.104
GUM	No D298387_1	27/07/2018	1.017	0.114	12/12/2018	0.867	0.111	06/02/2019	1.023	0.115
INRIM	D247448	13/07/2018	0.631	0.106	29/11/2018	0.142	0.101	05/02/2019	0.575	0.106
INRIM	P27787/D247449	26/07/2018	0.596	0.106	18/12/2018	0.496	0.104	07/02/2019	0.471	0.104
KRISS	D59 6882	17/07/2018	0.572	0.105	05/12/2018	0.606	0.106	30/01/2019	0.659	0.107
KRISS	D59 6920	25/07/2018	1.150	0.118	06/12/2018	0.790	0.109	07/02/2019	0.785	0.109
LNE	1191	13/07/2018	0.172	0.101	22/11/2018	0.227	0.102	06/02/2019	0.092	0.101
LNE	1183	19/07/2018	0.000	0.101	06/12/2018	0.178	0.101	07/02/2019	0.212	0.102
METAS	10918	17/07/2018	0.581	0.106	03/12/2018	0.210	0.102	21/01/2019	0.296	0.102
METAS	10919	26/07/2018	0.302	0.102	17/12/2018	0.000	0.101	04/02/2019	0.326	0.103
NIM	L62804125	10/07/2018	2.129	0.151	29/11/2018	0.008	0.101	17/01/2019	0.138	0.101
NIM	L62804135	25/07/2018	0.233	0.102	06/12/2018	0.123	0.101	04/02/2019	0.128	0.101
NMIA	MK0806	16/07/2018	0.076	0.101	03/12/2018	0.001	0.101	15/01/2019	0.027	0.101
NMIA	MK0807	25/07/2018	0.001	0.101	17/12/2018	0.000	0.101	08/02/2019	0.074	0.101
NMISA	D62 6618	16/07/2018	0.160	0.101	05/12/2018	0.000	0.101	17/01/2019	0.040	0.101
NMISA	D62 6554	20/07/2018	0.002	0.101	12/12/2018	0.039	0.101	11/02/2019	0.000	0.101
NPL	2448	13/07/2018	261.204	13.795	03/12/2018	0.345	0.103	30/01/2019	0.440	0.104
NPL	S357	20/07/2018	200.657	10.597	11/12/2018	0.278	0.102	08/02/2019	0.327	0.103
SMU	MY9742	10/07/2018	0.334	0.103	22/11/2018	0.525	0.105	15/01/2019	0.544	0.105
SMU	MY9728	27/07/2018	0.401	0.103	18/12/2018	0.483	0.104	08/02/2019	0.550	0.105
UME	PSM499791	10/07/2018	0.526	0.105	21/11/2018	0.524	0.105	21/01/2019	0.512	0.105
UME	PSM499783	17/07/2018	0.040	0.101	05/12/2018	0.435	0.104	12/02/2019	0.483	0.104

NMI	Cylinder	Measurement date	$x_{H2O(1)}$ (µmol mol^{-1})	$u(x_{H2O(1)})$ (µmol mol^{-1})	Measurement date	$x_{H2O(2)}$ (µmol mol^{-1})	$u(x_{H2O(2)})$ (µmol mol^{-1})	Measurement date	$x_{H2O(3)}$ (µmol mol^{-1})	$u(x_{H2O(3)})$ (µmol mol^{-1})
VNIIM	614632	16/07/2018	12.080	0.646	22/11/2018	10.182	0.547	21/01/2019	10.727	0.575
VNIIM	5603778	19/07/2018	0.640	0.107	11/12/2018	0.892	0.111	11/02/2019	0.799	0.110
VSL	VSL105804	12/07/2018	0.231	0.102	21/11/2018	0.159	0.101	17/01/2019	0.194	0.102
VSL	VSL105806	19/07/2018	0.067	0.101	12/12/2018	0.160	0.101	11/02/2019	0.134	0.101

Table 16. CO_2 amount fraction measured in cylinder gas standards by the BIPM using FT-IR spectroscopy.

NMI	Cylinder	Measurement date	$x_{CO2(1)}$ (µmol mol^{-1})	$u(x_{CO2(1)})$ (µmol mol^{-1})	Measurement date	$x_{CO2(2)}$ (µmol mol^{-1})	$u(x_{CO2(2)})$ (µmol mol^{-1})	Measurement Date	$x_{CO2(3)}$ (µmol mol^{-1})	$u(x_{CO2(3)})$ (µmol mol^{-1})
CERI	CPB 25961	12/07/2018	0.018	0.017	21/11/2018	0.033	0.017	15/01/2019	0.036	0.017
CERI	CPB 18969	20/07/2018	0.020	0.017	11/12/2018	0.047	0.017	06/02/2019	0.051	0.017
GUM	No D298386_1	12/07/2018	0.000	0.017	29/11/2018	0.019	0.017	30/01/2019	0.022	0.017
GUM	No D298387_1	27/07/2018	0.010	0.017	12/12/2018	0.024	0.017	06/02/2019	0.025	0.017
INRIM	D247448	13/07/2018	0.010	0.017	29/11/2018	0.018	0.017	05/02/2019	0.017	0.017
INRIM	P27787/D247449	26/07/2018	0.003	0.017	18/12/2018	0.019	0.017	07/02/2019	0.019	0.017
KRISS	D59 6882	17/07/2018	0.000	0.017	05/12/2018	0.027	0.017	30/01/2019	0.028	0.017
KRISS	D59 6920	25/07/2018	0.022	0.017	06/12/2018	0.002	0.017	07/02/2019	0.024	0.017
LNE	1191	13/07/2018	0.000	0.017	22/11/2018	0.004	0.017	06/02/2019	0.005	0.017
LNE	1183	19/07/2018	0.000	0.017	06/12/2018	0.004	0.017	07/02/2019	0.001	0.017
METAS	10918	17/07/2018	0.015	0.017	03/12/2018	0.010	0.017	21/01/2019	0.012	0.017
METAS	10919	26/07/2018	0.024	0.017	17/12/2018	0.013	0.017	04/02/2019	0.014	0.017
NIM	L62804125	10/07/2018	0.000	0.017	29/11/2018	0.015	0.017	17/01/2019	0.016	0.017
NIM	L62804135	25/07/2018	0.013	0.017	06/12/2018	0.015	0.017	04/02/2019	0.018	0.017
NMIA	MK0806	16/07/2018	0.007	0.017	03/12/2018	0.015	0.017	15/01/2019	0.018	0.017
NMIA	MK0807	25/07/2018	0.012	0.017	17/12/2018	0.021	0.017	08/02/2019	0.021	0.017
NMISA	D62 6618	16/07/2018	0.000	0.017	05/12/2018	0.003	0.017	17/01/2019	0.002	0.017
NMISA	D62 6554	20/07/2018	0.000	0.017	12/12/2018	0.003	0.017	11/02/2019	0.004	0.017
NPL	2448	13/07/2018	0.002	0.017	03/12/2018	0.003	0.017	30/01/2019	0.007	0.017
NPL	S357	20/07/2018	0.010	0.017	11/12/2018	0.013	0.017	08/02/2019	0.014	0.017
SMU	MY9742	10/07/2018	0.000	0.017	22/11/2018	0.013	0.017	15/01/2019	0.013	0.017
SMU	MY9728	27/07/2018	0.002	0.017	18/12/2018	0.022	0.017	08/02/2019	0.024	0.017
UME	PSM499791	10/07/2018	0.007	0.017	21/11/2018	0.031	0.017	21/01/2019	0.009	0.017
UME	PSM499783	17/07/2018	0.035	0.017	05/12/2018	0.058	0.017	12/02/2019	0.059	0.017

NMI	Cylinder	Measurement date	$x_{CO2(1)}$ (µmol mol^{-1})	$u(x_{CO2(1)})$ (µmol mol^{-1})	Measurement date	$x_{CO2(2)}$ (µmol mol^{-1})	$u(x_{CO2(2)})$ (µmol mol^{-1})	Measurement Date	$x_{CO2(3)}$ (µmol mol^{-1})	$u(x_{CO2(3)})$ (µmol mol^{-1})
VNIIM	614632	16/07/2018	0.007	0.017	22/11/2018	0.020	0.017	21/01/2019	0.021	0.017
VNIIM	5603778	19/07/2018	0.002	0.017	11/12/2018	0.015	0.017	11/02/2019	0.018	0.017
VSL	VSL105804	12/07/2018	0.000	0.017	21/11/2018	0.011	0.017	17/01/2019	0.011	0.017
VSL	VSL105806	19/07/2018	0.003	0.017	12/12/2018	0.011	0.017	11/02/2019	0.011	0.017

Table 17. N_2O amount fraction measured in cylinder gas standards by the BIPM using FT-IR spectroscopy.

NMI	Cylinder	Measurement date	$x_{N2O(1)}$ (µmol mol^{-1})	$u(x_{N2O(1)})$ (µmol mol^{-1})	Measurement date	$x_{N2O(2)}$ (µmol mol^{-1})	$u(x_{N2O(2)})$ (µmol mol^{-1})	Measurement date	$x_{N2O(3)}$ (µmol mol^{-1})	$u(x_{N2O(3)})$ (µmol mol^{-1})
CERI	CPB 25961	12/07/2018	0.012	0.015	21/11/2018	0.017	0.015	15/01/2019	0.018	0.015
CERI	CPB 18969	20/07/2018	0.013	0.015	11/12/2018	0.019	0.015	06/02/2019	0.016	0.015
GUM	No D298386_1	12/07/2018	0.000	0.015	29/11/2018	0.009	0.015	30/01/2019	0.011	0.015
GUM	No D298387_1	27/07/2018	0.010	0.015	12/12/2018	0.009	0.015	06/02/2019	0.007	0.015
INRIM	D247448	13/07/2018	0.017	0.015	29/11/2018	0.019	0.015	05/02/2019	0.018	0.015
INRIM	P27787/D247449	26/07/2018	0.015	0.015	18/12/2018	0.018	0.015	07/02/2019	0.019	0.015
KRISS	D59 6882	17/07/2018	0.005	0.015	05/12/2018	0.009	0.015	30/01/2019	0.011	0.015
KRISS	D59 6920	25/07/2018	0.015	0.015	06/12/2018	0.007	0.015	07/02/2019	0.011	0.015

NMI	Cylinder	Measurem date	$x_{N2O(1)}$ (μmol mol^{-1})	$u(x_{N2O(1)})$ (μmol mol^{-1})	Measurem date	$x_{N2O(2)}$ (μmol mol^{-1})	$u(x_{N2O(2)})$ (μmol mol^{-1})	Measure date	$x_{N2O(3)}$ (μmol mol^{-1})	$u(x_{N2O(3)})$ (μmol mol^{-1})
LNE	1191	13/07/2018	0.000	0.015	22/11/201	0.008	0.015	06/02/201	0.004	0.015
LNE	1183	19/07/2018	0.000	0.015	06/12/201	0.007	0.015	07/02/201	0.007	0.015
META	10918	17/07/2018	0.008	0.015	03/12/201	0.010	0.015	21/01/201	0.011	0.015
META	10919	26/07/2018	0.007	0.015	17/12/201	0.011	0.015	04/02/201	0.013	0.015
NIM	L62804125	10/07/2018	0.000	0.015	29/11/201	0.014	0.015	17/01/201	0.015	0.015
NIM	L62804135	25/07/2018	0.012	0.015	06/12/201	0.014	0.015	04/02/201	0.016	0.015
NMIA	MK0806	16/07/2018	0.020	0.015	03/12/201	0.023	0.015	15/01/201	0.022	0.015
NMIA	MK0807	25/07/2018	0.037	0.015	17/12/201	0.040	0.015	08/02/201	0.039	0.015
NMIS	D62 6618	16/07/2018	0.000	0.015	05/12/201	0.008	0.015	17/01/201	0.009	0.015
NMIS	D62 6554	20/07/2018	0.009	0.015	12/12/201	0.009	0.015	11/02/201	0.010	0.015
NPL	2448	13/07/2018	0.012	0.015	03/12/201	0.016	0.015	30/01/201	0.017	0.015
NPL	S357	20/07/2018	0.018	0.015	11/12/201	0.020	0.015	08/02/201	0.021	0.015
SMU	MY9742	10/07/2018	0.005	0.015	22/11/201	0.043	0.015	15/01/201	0.041	0.015
SMU	MY9728	27/07/2018	0.045	0.015	18/12/201	0.046	0.015	08/02/201	0.047	0.015
UME	PSM499791	10/07/2018	0.020	0.015	21/11/201	0.010	0.015	21/01/201	0.011	0.015
UME	PSM499783	17/07/2018	0.008	0.015	05/12/201	0.011	0.015	12/02/201	0.011	0.015

NMI	Cylinder	Measurem date	$x_{N2O(1)}$ (μmol mol^{-1})	$u(x_{N2O(1)})$ (μmol mol^{-1})	Measurem date	$x_{N2O(2)}$ (μmol mol^{-1})	$u(x_{N2O(2)})$ (μmol mol^{-1})	Measure date	$x_{N2O(3)}$ (μmol mol^{-1})	$u(x_{N2O(3)})$ (μmol mol^{-1})
VNIIM	614632	16/07/2018	0.007	0.015	22/11/201	0.009	0.015	21/01/201	0.011	0.015
VNIIM	5603778	19/07/2018	0.000	0.015	11/12/201	0.009	0.015	11/02/201	0.009	0.015
VSL	VSL105804	12/07/2018	0.000	0.015	21/11/201	0.010	0.015	17/01/201	0.002	0.015
VSL	VSL105806	19/07/2018	0.008	0.015	12/12/201	0.010	0.015	11/02/201	0.011	0.015

Table 18. NOCl amount fraction measured in cylinder gas standards by the BIPM using FT-IR spectroscopy.

NMI	Cylinder	Measurement date	$x_{NOCL(1)}$ (μmol mol^{-1})	$u(x_{NOCL(1)})$ (μmol mol^{-1})	Measurement date	$x_{NOCL(2)}$ (μmol mol^{-1})	$u(x_{NOCL(2)})$ (μmol mol^{-1})	Measurement date	$x_{NOCL(3)}$ (μmol mol^{-1})	$u(x_{NOCL(3)})$ (μmol mol^{-1})
GUM	No D298386_1	12/07/2018	0.030	0.029	29/11/2018	0.034	0.030	30/01/2019	0.041	0.033
GUM	No D298387_1	27/07/2018	0.039	0.032	12/12/2018	0.047	0.035	06/02/2019	0.043	0.033
SMU	MY9728	27/07/2018	0.045	0.034	18/12/2018	0.031	0.030	08/02/2019	0.033	0.030
UME	PSM499791	10/07/2018	0.027	0.029	21/11/2018	0.034	0.030	21/01/2019	0.036	0.031
UME	PSM499783	17/07/2018	0.061	0.040	05/12/2018	0.068	0.043	12/02/2019	0.064	0.041

Table 19. HONO amount fraction measured in cylinder gas standards by the BIPM using FT-IR spectroscopy.

NMI	Cylinder	Measurement date	$x_{HONO(1)}$ (μmol mol^{-1})	$u(x_{HONO(1)})$ (μmol mol^{-1})
NPL	2448	13/07/2018	0.101	0.055
NPL	S357	20/07/2018	0.028	0.025

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 amount fraction values from the measured responses and comparison to NMI's values.

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.

ANNEX IV- ABB LIMAS analyser results

The NO_2 amount fraction measurements done by FT-IR were verified by the continuous gas analyzer ABB Limas 11 (part of the AO2020 series) analyzer. The Limas 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 difference is defined as:

$$D'' = x_{\mathrm{NMI}} - x_{\mathrm{UV}} \quad (9)$$

where x_{NMI} denotes the estimation of the NO_2 amount fraction in the participants' standards at the date of the KCRVs according sections 6.2.1 and 6.2.2 criteria and $x_{\_\mathrm{UV}}$ denotes the reference value given by the BIPM on that date based on the measurements ABB Limas 11 analyzer.

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

$$u(D'') = \sqrt{u(x_{\mathrm{NMI}})^2 + u(x_{\mathrm{UV}})^2} \quad (10)$$

and the expanded uncertainty, at 95 % confidence level

$$U(D'') = k \cdot u(D'') \quad (11)$$

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

The proposed difference from reference value are listed in Table 20 where:

NMI	is the acronym of the participating national metrology institute;
Cylinder	the identification code of the cylinder received by the participating laboratory;
D''	is the difference; and
$U(D'')$	the expanded uncertainty of that difference;

The graph of equivalence, based on the difference in nitrogen dioxide between participating laboratories based on ABB Limas 11 analyzer measurements and the BIPM are plotted in Figure 28 and listed in Table 20.
When comparing D (Figure 24) against D'' (Figure 28), meaning forty two FTIR calculated results against NDUV, no disagreement was identified between both techniques considering the stated uncertainties.

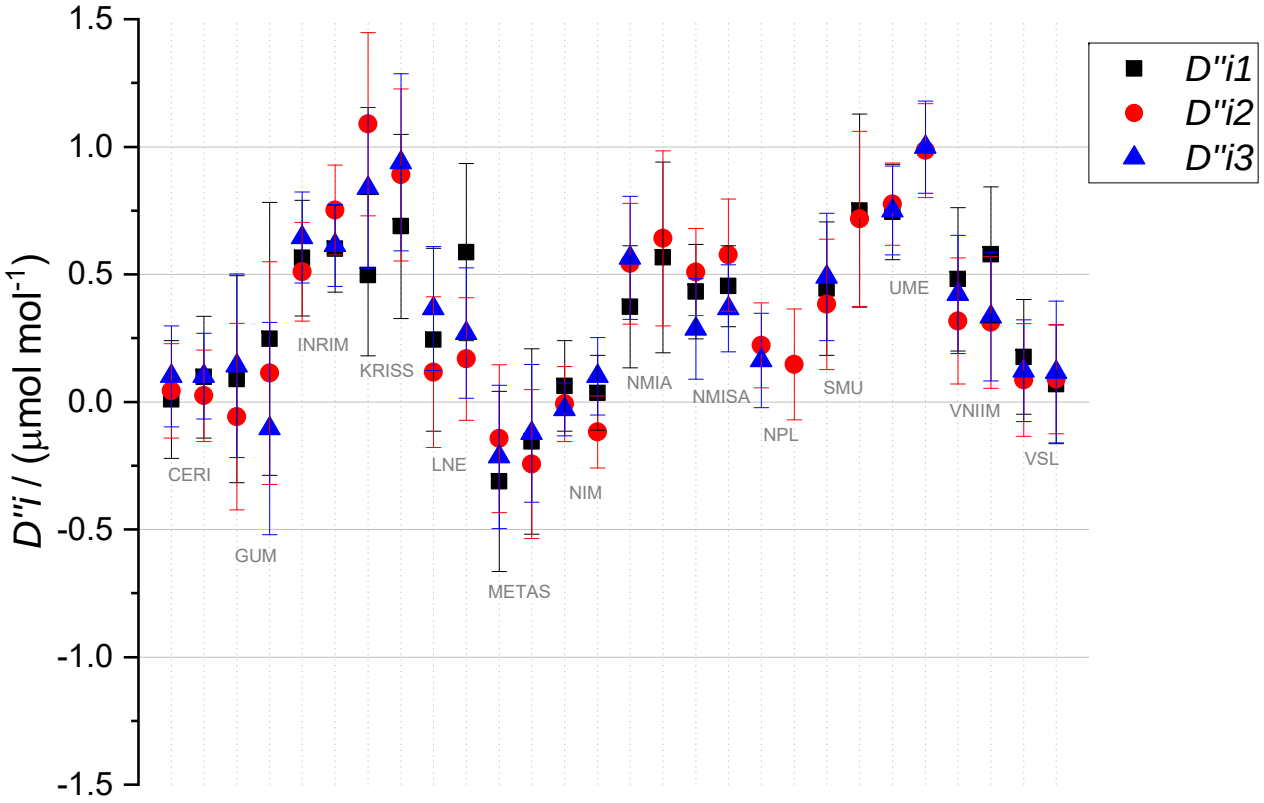

Figure 28. Difference based on the three series of measurements performed at the BIPM based on LIMAS UV results: blue diamonds – series 1 , violet diamonds – series 2, cyan diamonds – series 3. The error bar represents the expanded uncertainty at a 95 % level of confidence. Results of the first measurements for NPL were removed as already explained in the Draft A2 report.

CCQM-K74.2018: Nitrogen dioxide, 10 µmol mol^{-1}

Table 20. Results interpolated from participants' measurements $x_{NMIPred}$.and LIMAS UV values x_{BIPM_UV} and the difference from reference value D'_i calculated accordingly the criteria of section 6.2. All values are expressed in µmol mol-1 . are the mixtures without decay.*

NMI	Cylinder	D''_{i1} (µmol mol^{-1})	$U(D''_{i1})$ (µmol mol^{-1})	D''_{i2} (µmol mol^{-1})	$U(D''_{i2})$ (µmol mol^{-1})	D''_{i3} (µmol mol^{-1})	$U(D''_{i3})$ (µmol mol^{-1})
CERI	CPB 25961	0.010	0.231	0.043	0.184	0.101	0.198
CERI	CPB 18969	0.097	0.239	0.024	0.179	0.100	0.168
GUM	No D298386_1	0.089	0.406	-0.058	0.366	0.141	0.360
GUM	No D298387_1	0.247	0.535	0.113	0.436	-0.104	0.416
D247448	D247448	0.564	0.227	0.510	0.193	0.645	0.178
P27787/D247449	P27787/D247449*	0.601	0.170	0.752	0.176	0.614	0.160
KRISS	D59 6882*	0.496	0.316	1.088	0.359	0.838	0.315
KRISS	D59 6920*	0.688	0.361	0.890	0.336	0.939	0.347
LNE	1191	0.244	0.358	0.117	0.295	0.366	0.243
LNE	1183	0.587	0.347	0.168	0.240	0.269	0.256
METAS	10918	-0.311	0.353	-0.144	0.289	-0.216	0.280
METAS	10919	-0.155	0.363	-0.244	0.292	-0.123	0.269
NIM	L62804125	0.062	0.178	-0.008	0.146	-0.030	0.104
NIM	L62804135	0.035	0.147	-0.118	0.141	0.101	0.152
NMIA	MK0806*	0.373	0.239	0.542	0.237	0.564	0.241
NMIA	MK0807	0.567	0.374	0.641	0.343	10.057	0.312
NMISA	D62 6618*	0.432	0.186	0.509	0.171	0.286	0.197
NMISA	D62 6554*	0.454	0.158	0.576	0.220	0.367	0.171
NPL	2448	-	-	0.221	0.166	0.162	0.185
NPL	S357	-	-	0.147	0.217	9.844	0.142
SMU	MY9742*	0.444	0.262	0.383	0.256	0.490	0.250
SMU	MY9728	0.749	0.379	0.717	0.343	9.879	0.288
UME	PSM499791	0.744	0.187	0.775	0.162	0.750	0.174
UME	PSM499783	9.773	0.157	0.985	0.184	0.999	0.180
VNIIM	614632	0.481	0.281	0.317	0.247	0.422	0.232
VNIIM	5603778	0.577	0.266	0.312	0.258	0.334	0.251
VSL	VSL105804	0.176	0.225	0.085	0.221	0.122	0.200
VSL	VSL105806	0.069	0.232	0.089	0.214	0.117	0.277

Table 21. Measurements by the ABB Limas 11 analyzer.

NMI	Cylinder	x_{UV1} (µmol mol^{-1})	$u(x_{UV1})$ (µmol mol^{-1})	x_{UV2} (µmol mol^{-1})	$u(x_{UV2})$ (µmol mol^{-1})	x_{UV3} (µmol mol^{-1})	$u(x_{UV3})$ (µmol mol^{-1})
CERI	CPB 25961	9.863	0.057	9.790	0.050	9.716	0.072
CERI	CPB 18969	9.767	0.059	9.794	0.046	9.699	0.052
GUM	No D298386_1	10.410	0.044	10.515	0.056	10.297	0.076
GUM	No D298387_1	10.036	0.099	10.084	0.090	10.266	0.107
INRIM	D247448	9.633	0.072	9.670	0.057	9.527	0.051
INRIM	P27787/D247449	9.391	0.055	9.240	0.059	9.378	0.047
KRISS	D59 6882	9.537	0.049	8.945	0.099	9.195	0.048
KRISS	D59 6920	9.359	0.100	9.157	0.076	9.108	0.087
LNE	1191	9.516	0.073	9.579	0.076	9.293	0.060
LNE	1183	9.240	0.107	9.609	0.052	9.486	0.085
METAS	10918	9.898	0.051	9.673	0.050	9.724	0.066
METAS	10919	9.738	0.051	9.760	0.053	9.617	0.055
NIM	L62804125	9.747	0.070	9.793	0.061	9.806	0.038
NIM	L62804135	9.794	0.059	9.930	0.062	9.704	0.070
NMIA	MK0806	9.547	0.047	9.378	0.044	9.356	0.049
NMIA	MK0807	9.535	0.043	9.428	0.054	0.000	0.000
NMISA	D62 6618	9.562	0.066	9.485	0.055	9.708	0.074
NMISA	D62 6554	9.501	0.048	9.379	0.090	9.588	0.058
NPL	2448	5.866	0.517	9.639	0.041	9.683	0.067
NPL	S357	8.395	0.480	9.711	0.074	0.000	0.000
SMU	MY9742	9.693	0.071	9.754	0.065	9.647	0.059
SMU	MY9728	9.174	0.085	9.174	0.082	0.000	0.000
UME	PSM499791	9.299	0.061	9.260	0.047	9.281	0.059
UME	PSM499783	0.000	0.000	8.773	0.060	8.752	0.062
VNIIM	614632	9.343	0.076	9.488	0.061	9.375	0.054
VNIIM	5603778	9.255	0.044	9.494	0.067	9.461	0.071
VSL	VSL105804	9.666	0.065	9.750	0.067	9.710	0.051
VSL	VSL105806	9.735	0.064	9.703	0.058	9.670	0.108

ANNEX V- ABB LIMAS analyser results and offset vs BIPM reference values

In Figure 29 the BIPM measured values based on the measurements of the AAB LIMAS analyzer and HNO_3 were added to obtain $x_{UV+HNO3}$. As result in a number of cases, there is a better agreement between the values using this treatment, however it is observed once more that the underlying assumptions may not hold for all cases, and this would require further analysis of sources of potential bias.

In this case the difference is defined as:

$$D''' = x_{\mathrm{NMI}} - x_{\mathrm{UV+HNO3}} \quad (12)$$

where x_{NMI} denotes the estimation of the NO_2 amount fraction in the participants' standards at the date of the KCRVs (see sections 6.2.1 and 6.2.2) and $x_{\mathrm{UV+HNO3}}$ that is the reference value given by the BIPM on that date based on the ABB Limas 11 analyzer measurements with the addition of the HNO_3 values found in each cylinder listed previously in Table 5.

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

$$u(D''') = \sqrt{u(x_{\mathrm{NMI}})^2 + u(x_{\mathrm{UV+HNO3}})^2} \quad (13)$$

and the expanded uncertainty, at 95 % confidence level

$$U(D''') = k \cdot u(D''') \quad (14)$$

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

The proposed difference from reference value are listed in Table 22 where:

NMI	is the acronym of the participating national metrology institute;
Cylinder	the identification code of the cylinder received by the participating laboratory;
D'''	is the difference; and
$U(D''')$	the expanded uncertainty of that difference;

The graph of equivalence, based on the difference in nitrogen dioxide between participating laboratories and the BIPM are plotted in Figure 29.

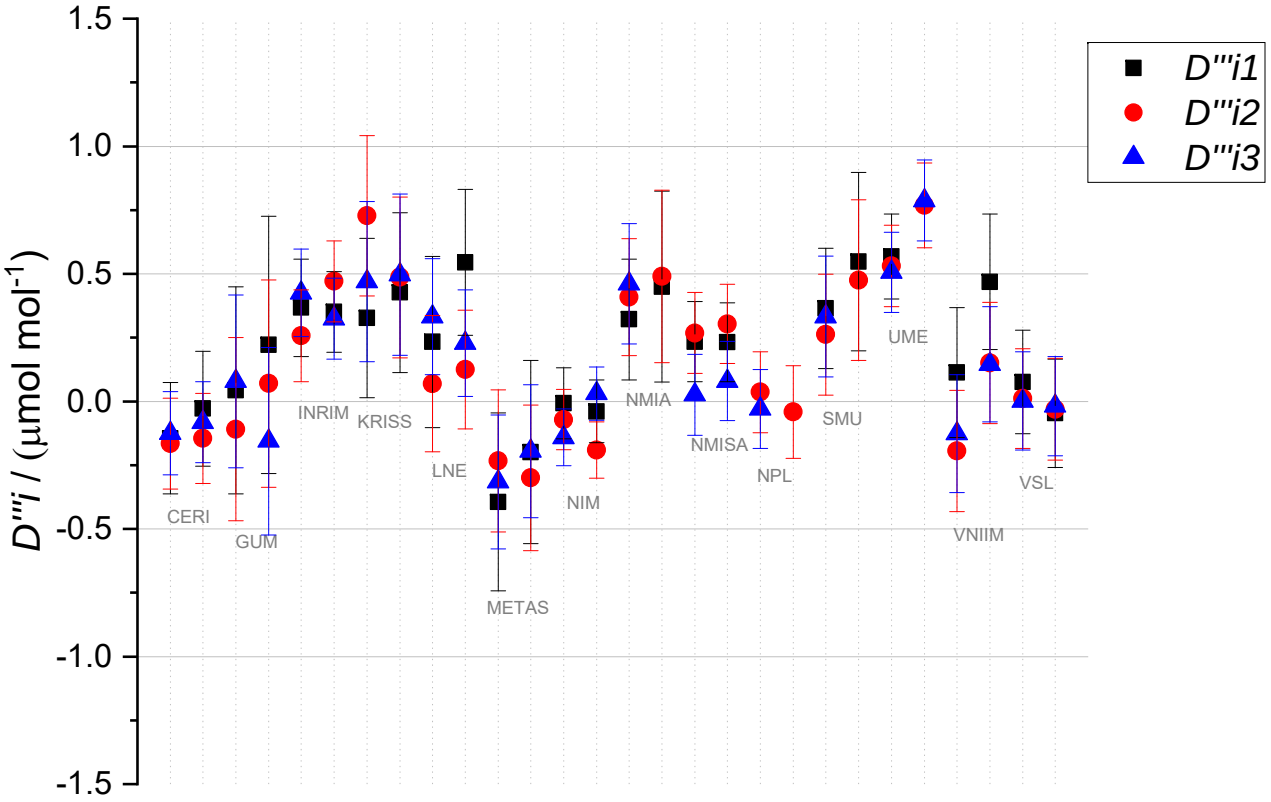

Figure 29. Difference based on the three series of measurements performed at the BIPM based on LIMAS UV results adding the HNO_3 amount of fraction found in each gas mixture (see results in Figure 18): blue diamonds – series 1 , violet diamonds – series 2, cyan diamonds – series 3. The error bar represents the expanded uncertainty at a 95 % level of confidence. Results of the first measurements for NPL were removed as already explained in the Draft A2 report.

Table 22. Results interpolated from participants' measurements $x_{NMIPred}$ and calibrated values of the AAB LIMAS UV analyzer $x_{\mathrm{BIPM\_UV}j}$ adding the HNO_3 amount of fraction found in each mixture calculated accordingly section 6.2. All values are expressed in µmol mol^{-1} . are the mixtures without decay.*

NMI	Cylinder	D'''_{i1} µmol mol^{-1}	$U(D'''_{i1})$ µmol mol^{-1}	D'''_{i2} µmol mol^{-1}	$U(D'''_{i2})$ µmol mol^{-1}	D'''_{i3} µmol mol^{-1}	$U(D'''_{i3})$ µmol mol^{-1}
CERI	CPB 25961	-0.144	0.219	-0.166	0.179	-0.125	0.163
CERI	CPB 18969	-0.029	0.225	-0.145	0.177	-0.082	0.159
GUM	No D298386_1	0.043	0.406	-0.109	0.359	0.078	0.338
GUM	No D298387_1	0.221	0.505	0.070	0.407	-0.156	0.367
INRIM	P27787/D247449*	0.367	0.191	0.257	0.180	0.426	0.171
INRIM	D247448	0.351	0.158	0.471	0.159	0.324	0.159
KRISS	D59 6920*	0.326	0.313	0.727	0.314	0.469	0.314
KRISS	D59 6882*	0.427	0.313	0.486	0.315	0.497	0.316
LNE	1191	0.233	0.335	0.069	0.268	0.332	0.228
LNE	1183	0.545	0.287	0.124	0.233	0.228	0.209
METAS	10918	-0.394	0.349	-0.233	0.278	-0.316	0.263
METAS	10919	-0.199	0.359	-0.300	0.285	-0.195	0.261
NIM	L62804125	-0.008	0.139	-0.071	0.118	-0.141	0.112
NIM	L62804135	-0.040	0.123	-0.191	0.110	0.031	0.105
NMIA	MK0806*	0.321	0.236	0.408	0.229	0.461	0.236
NMIA	MK0807	0.450	0.374	0.490	0.337	10.057	0.312
NMISA	D62 6618*	0.234	0.158	0.268	0.158	0.026	0.159
NMISA	D62 6554*	0.232	0.154	0.304	0.155	0.080	0.155
NPL	2448	-	-	0.036	0.159	-0.030	0.155
NPL	S357	-	-	-0.042	0.182	9.844	0.142
SMU	MY9742*	0.365	0.236	0.262	0.237	0.333	0.237
SMU	MY9728	0.547	0.350	0.475	0.314	9.879	0.288
UME	PSM499791	0.567	0.167	0.531	0.159	0.506	0.157
UME	PSM499783	9.773	0.157	0.768	0.166	0.788	0.159
VNIIM	614632	0.113	0.255	-0.195	0.238	-0.126	0.230
VNIIM	5603778	0.468	0.266	0.150	0.237	0.145	0.226
VSL	VSL105804	0.076	0.203	0.011	0.196	0.001	0.193
VSL	VSL105806	-0.047	0.212	-0.031	0.199	-0.018	0.194

ANNEX VI – Characteristic spectra of the analysed mixtures

In the graphs below 3 spectra have been chosen as examples of types of spectra observed in the comparison exercise including: dry cylinder type; BIPM permeation system ones; 'wet' cylinder ones.

Figure 30 plots the absorbance spectrum of the mixture 2705804 from VSL obtained on January 17, 2019. The spectrum shows a clear NO_2 signal in the region 1500 cm^{-1} to 1660 cm^{-1} and in the region 2860 cm^{-1} to 2930 cm^{-1} (not used for quantification in this work). The NO_2 amount fraction was quantified to be 9.710 ± 0.038 µmol mol^{-1} (see Table 4). The spectrum also shows a clear signal for HNO_3 that according Table 5 corresponds to an amount fraction of 100 ± 21 nmol mol^{-1}. Finally H_2O can also be observed in the regions 1200 cm^{-1} to 1950 cm^{-1} and 3500 cm^{-1} to 4000 cm^{-1}. The H_2O amount fraction according to Table 15 in this case 231 ± 102 nmol mol^{-1}.

Figure 31 plots the absorbance spectrum of a gas mixture generated by the BIPM permeation facility. The NO_2 amount fraction corresponding to this spectrum is 10.450 ± 0.038 µmol mol^{-1} containing also 176 ± 21 nmol mol^{-1} of HNO_3 and 658 ± 107 nmol mol^{-1} of H_2O.

Figure 32 plots the absorbance spectrum of the VNIIM 614632 mixture. The NO_2 amount fraction correspondent to this spectrum is 9.324 ± 0.038 µmol mol^{-1}. In this occasion the HNO_3 impurity amount fraction is 368 ± 21 nmol mol^{-1} and around 12080 ± 0.646 nmol mol^{-1} of H_2O.

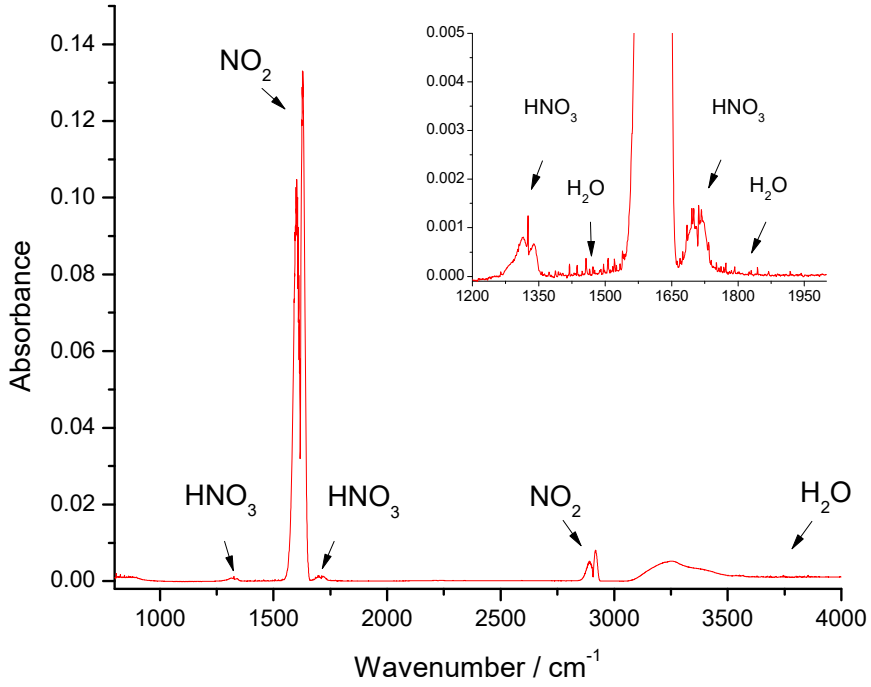

Figure 30. Infrared absorbance spectrum of VSL 105804 mixture with a NO_2 amount fraction of 9.851 µmol mol^{-1}.

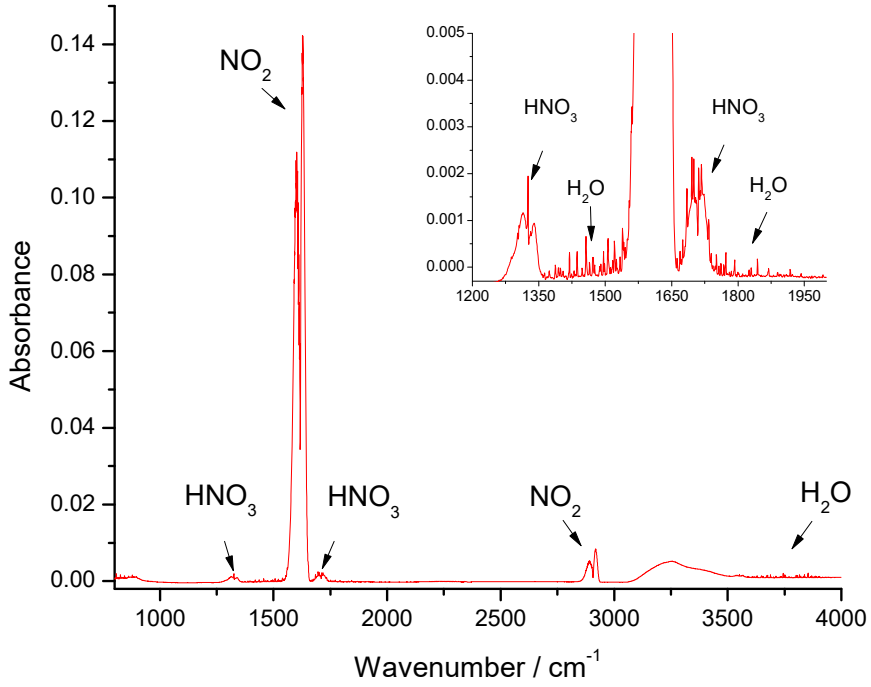

Figure 31. Infrared absorbance spectrum of a dynamic mixture generated by the BIPM permeation facility with a NO_2 amount fraction of 10.450 µmol mol^{-1} .

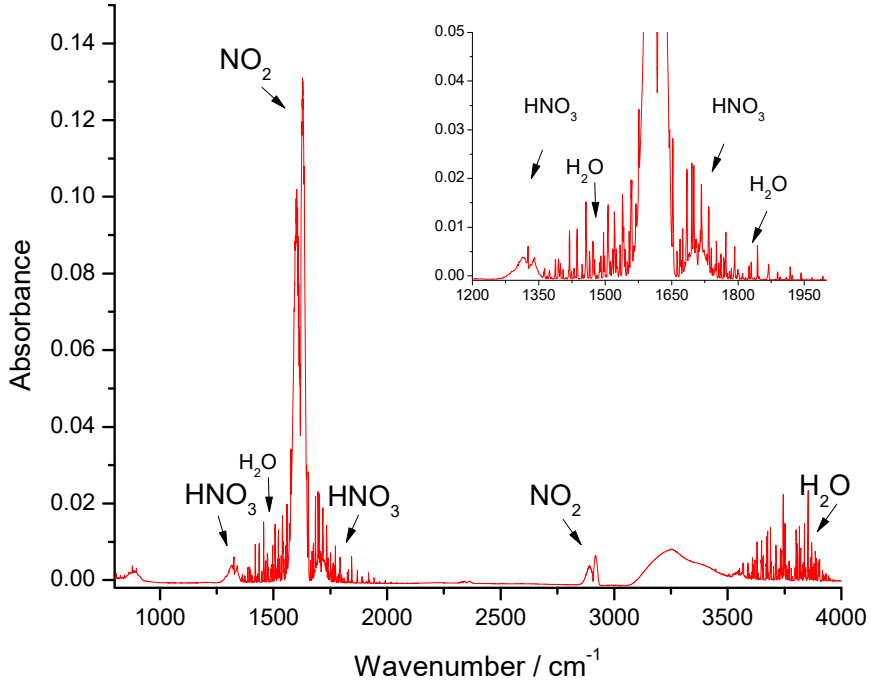

Figure 32. Infrared absorbance spectrum of VNIIM 614632 mixture with a NO_2 amount fraction of 9.324 µmol mol^{-1}.

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ANNEX VII - Measurement reports of participants

(see next pages – PDF version only)

ANNEX VII - Measurement reports of participants

Table of Contents

CERI

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).
Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.
Proposed dates: 2018.

Coordinating laboratory:
Bureau International des Poids et Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92 Fax: +33 (0)1 45 34 20 21 email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

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	CPB 25961, CPB 18969		
Cylinder pressure as received	10 MPa		

A2. Results

Cylinder 1 (CPB 25961) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	15/12/2017	10.215		
(Stability 1)	15/1/2018	10.098	0.081	*k*=2
(Stability 2)	16/2/2018	10.052	0.080	*k*=2
(Stability 3)	12/3/2018	10.022	0.080	*k*=2

Cylinder 2 (CPB 18969) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} /	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor

		μmol/mol		
(Preparation)	15/12/2017	10.194		
(Stability 1)	15/1/2018	10.088	0.081	*k*=2
(Stability 2)	16/2/2018	10.074	0.081	*k*=2
(Stability 3)	12/3/2018	10.044	0.080	*k*=2

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / μmol/mol	Expanded uncertainty $U(x_{NO2})$ / μmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

Cylinder 2- Post BIPM measurements

		Nitrogen dioxide mole fraction	Expanded uncertainty	Coverage factor

Description of measurement	Date of measurement	x_{NO2} / µmol/mol	$U(x_{NO2})$ / µmol/mol	
(Stability 4)				
(Stability 5)				
(Stability 6)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[1].

A5. Complementary information on the cylinder

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

Cylinder 1 10 MPa
Cylinder 2 10 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:

Cylinder 1

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
23/3/2018	NO	20	3 nmol/mol	*k*=2	Chemiluminescence analyzer (NO mode)

[1] 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.

Cylinder 2

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
23/3/2018	NO	20	3 nmol/mol	*k*=2	Chemiluminescence analyzer (NO mode)

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).
Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.
Proposed dates: 2018.

Coordinating laboratory:
Bureau International des Poids et Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92 Fax: +33 (0)1 45 34 20 21 email: edgar.flores@bipm.org

Return of the form:

Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

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	CPB 25961, CPB 18969		
Cylinder pressure as received	10 MPa		

A2. Results

	Nitrogen dioxide mole fraction x_{NO2} / μmol/mol	Expanded uncertainty $U(x_{NO2})$ / μmol/mol	Coverage factor
Cylinder 1 (CPB 25961)	9.90	0.16	*k*=2
Cylinder 2 (CPB 18969)	9.90	0.18	*k*=2

"Nitrogen dioxide mole fraction" were calculated as follows:

$$\frac{1}{2}\left\{S_3 + \frac{1}{3}(S_4 + S_5 + S_6)\right\}$$

where

S_3 : Nitrogen dioxide mole fraction of “Stability 3”
S_4 : Nitrogen dioxide mole fraction of “Stability 4”
S_5 : Nitrogen dioxide mole fraction of “Stability 5”
S_6 : Nitrogen dioxide mole fraction of “Stability 6”

These are the average values of the measured values just before shipping to the BIPM and post BIPM measurements. The measured values of post BIPM measurements are the average value of Stability 4, 5 and 6, because there aren’t obvious difference.

Cylinder 1 (CPB 25961) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / μmol/mol	Expanded uncertainty $U(x_{NO2})$ / μmol/mol	Coverage factor
(Preparation)	15/12/2017	10.215		
(Stability 1)	15/1/2018	10.098	0.081	*k*=2
(Stability 2)	16/2/2018	10.052	0.080	*k*=2
(Stability 3)	12/3/2018	10.022	0.080	*k*=2

Cylinder 2 (CPB 18969) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / μmol/mol	Expanded uncertainty $U(x_{NO2})$ / μmol/mol	Coverage factor
(Preparation)	15/12/2017	10.194		
(Stability 1)	15/1/2018	10.088	0.081	*k*=2
(Stability 2)	16/2/2018	10.074	0.081	*k*=2
(Stability 3)	12/3/2018	10.044	0.080	*k*=2

Cylinder 1 (CPB 25961) - Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	10/4/2019	9.798	0.078	*k*=2
(Stability 5)	23/5/2019	9.742	0.078	*k*=2
(Stability 6)	12/7/2019	9.792	0.078	*k*=2

Cylinder 2 (CPB 18969) - Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	10/4/2019	9.770	0.078	*k*=2
(Stability 5)	23/5/2019	9.748	0.078	*k*=2
(Stability 6)	12/7/2019	9.772	0.078	*k*=2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Cylinder 1 (CPB 25961)

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty	Contribution to standard uncertainty
	$u(x_i)$		$U(x_i)$	$u(y_i)$
Gas standards for measurements	0.001386	Normal	0.001386	0.001386
Stability*	0.1225 µmol/mol	Rectangle	0.07073 µmol/mol	0.007144
Measurement	0.0038	Normal	0.0038	0.0038

Combined uncertainty (Relative): 0.008210

Expanded uncertainty (Relative) (*k*=2): 0.01642

Expanded uncertainty: 0.16 µmol/mol

*Uncertainty of stability was estimated as half of 0.245 µmol/mol, the difference between the measured value just before shipping to the BIPM (Stability 3) and post BIPM measurements (the average value of Stability 4, 5 and 6).

Cylinder 2 (CPB 18969)

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty	Contribution to standard uncertainty
	$u(x_i)$		$U(x_i)$	$u(y_i)$
Gas standards for measurements	0.001386	Normal	0.001386	0.001386
Stability*	0.1405 µmol/mol	Rectangle	0.08112 µmol/mol	0.008194
Measurement	0.0038	Normal	0.0038	0.0038

Combined uncertainty (Relative): 0.009138

Expanded uncertainty (Relative) (*k*=2): 0.01828

Expanded uncertainty: 0.18 µmol/mol

*Uncertainty of stability was estimated as half of 0.281 μmol/mol, the difference between the measured value just before shipping to the BIPM (Stability 3) and post BIPM measurements (the average value of Stability 4, 5 and 6).

A4. Description of the procedure used during the gas analysis

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

Instrument: Chemiluminescence analyzer made in 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 can't be analyzed 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 observed value of NO is bigger than accurate one in this mode. Therefore uncertainty becomes bigger. So "Manual NOx" mode was selected.

Configuration of analysis system:
Gas cylinder → Regulator → Manual 4-way valve → Instrument (Converter → Detector)

Chemiluminescence analyzer was calibrated using one gas standard prepared by gravimetric method. A new gas standard was prepared for each stability measurement,

A5. Complementary information on the cylinder

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

Cylinder 1	10 MPa
Cylinder 2	10 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:

[2] 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.

Cylinder 1 (CPB 25961)

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
23/3/2018	NO	20	3 nmol/mol	*k*=2	Chemiluminescence analyzer (NO mode)

Cylinder 2 (CPB 18969)

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
23/3/2018	NO	20	3 nmol/mol	*k*=2	Chemiluminescence analyzer (NO mode)

Author ship:

Ms. Midori Kobayashi, Mr. Dai Akima, Mr. Shinji Uehara

GUM

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:
Bureau International des Poids et Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org
This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	Central Office of Measures (Główny Urząd Miar)		
Address	Elektoralna 2; 00-139 Warsaw; Poland		
Contact person	Dariusz Cieciora		
Telephone	(48) 22 581 94 39	Fax	(48) 22 581 93 95
Email*	dariusz.cieciora@gum.gov.pl; gas@gum.gov.pl		
Serial number of cylinder received	Cylinder 1: D298386 Cylinder 2: D298387		
Cylinder pressure as received			

A2. Results

Cylinder 1 (No D298386_1) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded Uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	01.02.2018	10,783	0,079	2
(Stability 1)	06.02.2018	10,526	0,234	2
(Stability 2)	07.03.2018	10,619	0,214	2
(Stability 3)	10.04.2018	10,906	0,236	2

Cylinder 2 (No D298387_1) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded Uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	01.02.2018	10,989	0,092	2
(Stability 1)	06.02.2018	10,535	0,234	2
(Stability 2)	07.03.2018	10,604	0,216	2
(Stability 3)	10.04.2018	10,827	0,234	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

A4. Description of the procedure used during the gas analysis

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

The mixtures were prepared according ISO 6142: the cylinders evacuated on turbo molecular pump, filled up an weighted on the verification balance. The mixtures were prepared in aluminium (with coated layers) cylinders. The mixtures were prepared with used pure nitrogen and three steps premixture of nitrogen dioxide.
The analytical method according to ISO 6143. The measurements were repeated 10 times for the standards and the sample. The curve was calculated from ratios by the software B_least.exe (linear case).
The standards were prepared by gravimetric method according to ISO 6142 and were diluted according ISO 6145-9.

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 cylinders:
Cylinder D298386_1: 150 bar
Cylinder D298387_1: 150 bar

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:
Bureau International des Poids et Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org
This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	Central Office of Measures (Główny Urząd Miar)		
Address	Elektoralna 2; 00-139 Warsaw; Poland		
Contact person	Dariusz Cieciora		
Telephone	(48) 22 581 94 39	Fax	(48) 22 581 93 95
Email*	dariusz.cieciora@gum.gov.pl; gas@gum.gov.pl		
Serial number of cylinder received	Cylinder 1: D298386 Cylinder 2: D298387		
Cylinder pressure as received			

A2. Results

Cylinder 1 (No D298386_1) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded Uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	01.02.2018	10,783	0,079	2
(Stability 1)	06.02.2018	10,526	0,234	2
(Stability 2)	07.03.2018	10,619	0,214	2
(Stability 3)	10.04.2018	10,906	0,236	2

Cylinder 2 (No D298387_1) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded Uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	01.02.2018	10,989	0,092	2
(Stability 1)	06.02.2018	10,535	0,234	2
(Stability 2)	07.03.2018	10,604	0,216	2
(Stability 3)	10.04.2018	10,827	0,234	2

Cylinder 1 (No D298386_1) – Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded Uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	04.04.2019	10,446	0,238	2
(Stability 5)	16.05.2019	10,355	0,252	2
(Stability 6)	10.07.2019	10,399	0,286	2

Cylinder 2 (No D298387_1) – Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded Uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	04.04.2019	10,159	0,233	2
(Stability 5)	16.05.2019	10,134	0,248	2
(Stability 6)	10.07.2019	9,989	0,283	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

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

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

A4. Description of the procedure used during the gas analysis

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

The mixtures were prepared according ISO 6142: the cylinders evacuated on turbo molecular pump, filled up an weighted on the verification balance. The mixtures were prepared in aluminium (with coated layers) cylinders. The mixtures were prepared with used pure nitrogen and three steps premixture of nitrogen dioxide.
The analytical method according to ISO 6143. The measurements were repeated 10 times for the standards and the sample. The curve was calculated from ratios by the software B_least.exe (linear case).
The standards were prepared by gravimetric method according to ISO 6142 and were diluted according ISO 6145-9.

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 cylinders:
Cylinder D298386_1: 150 bar
Cylinder D298387_1: 150 bar

INRIM

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen **(10 µmol/mol)**

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).
Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.
Proposed dates: 2018.

Coordinating laboratory:
Bureau International des Poids et Mesures Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol.
Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	INRIM – Istituto Nazionale di Ricerca Metrologica		
Address	Strada delle Cacce 9, 10135 Torino, Italy		
Contact person	Michela Sega, Francesca Rolle		
Telephone	+39 011 3919948	Fax	+39 011 3919937
Email*	m.sega@inrim.it		
Serial number of cylinder received			
Cylinder pressure as received			

A2. Results

Cylinder 1 – Before shipping to the BIPM (Cylinder number: P27787/D247449)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	17/11/2017	9.92	0.06	2
(Stability 1)	01/12/2017	10.09	0.13	2
(Stability 2)	29/01/2918	9.90	0.13	2
(Stability 3)	26/04/2018	9.84	0.13	2

Cylinder 2– Before shipping to the BIPM (Cylinder number: P27787/D247448)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	24/11/2017	10.16	0.06	2
(Stability 1)	01/12/2017	10.36	0.13	2
(Stability 2)	29/01/2918	10.24	0.13	2
(Stability 3)	26/04/2018	10.21	0.13	2

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

Cylinder 2- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The model equation used to calculate the mole fraction of NO_2 in the final mixtures is taken from the International Standard ISO 6142-1:2015:

$$x_{NO_2,\ prep} = \frac{\sum_{j=1}^{r}\left(\frac{x_{NO_2,\ j}\cdot m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)}{\sum_{j=1}^{r}\left(\frac{m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)}$$

where the index *i* refers to the various components, while *j* refers to the different parent mixtures.

The uncertainty budget was evaluated according to the guidelines prescribed in ISO 6142-1:2015.
The uncertainty budget for the gravimetric preparation of the Cylinder n. 1 at 9.92 µmol/mol of NO_2, which takes into account the weighted masses of the parent mixtures, the molar masses of gases and their purity, is reported in the following table:

Uncertainty component $u(x_i)$	**Uncertainty source**	**Standard uncertainty, $u(x_i)$**	**$\Delta x_{NO2,prep}/\delta x_i$**	**Contribution to $u(x_{NO2,\ prep})$ $\lvert\delta x_{NO2,prep}/\delta x_i\rvert \cdot u(x_i)$**
$u(m_{NO2})$	Weighed mass of the parent mixture of NO_2	$1.2\cdot10^{-3}$ g	$8.93\cdot10^{-8}$ mol·mol^{-1}·g^{-1}	$1.0\cdot10^{-10}$ mol·mol^{-1}
$u(m_{N2})$	Weighed mass of the balance gas N_2	$8.2\cdot10^{-4}$ g	$-1.58\cdot10^{-8}$ mol·mol^{-1}·g^{-1}	$1.3\cdot10^{-11}$ mol·mol^{-1}
$u(M_{NO2})$	Molar mass of NO_2	$3.0\cdot10^{-4}$ g·mol^{-1}	$-1.99\cdot10^{-11}$ mol^2·mol^{-1}·g^{-1}	$5.9\cdot10^{-15}$ mol·mol^{-1}
$u(M_{N2})$	Molar mass of N_2	$2.0\cdot10^{-4}$ g·mol^{-1}	$2.35\cdot10^{-9}$ mol^2·mol^{-1}·g^{-1}	$4.7\cdot10^{-13}$ mol·mol^{-1}
$u(M_{O2})$	Molar mass of O_2	$2.8\cdot10^{-4}$ g·mol^{-1}	$-2.03\cdot10^{-9}$ mol^2·mol^{-1}·g^{-1}	$5.7\cdot10^{-13}$ mol·mol^{-1}
$u(x_{N2inNO2})$	Mole fraction of N_2 in the parent mixture of NO_2	$4.1\cdot10^{-7}$ mol·mol^{-1}	$-8.42\cdot10^{-6}$	$3.4\cdot10^{-12}$ mol·mol^{-1}
$u(x_{N2inN2})$	Mole fraction of N_2 in balance gas (purity)	$8.7\cdot10^{-7}$ mol·mol^{-1}	$8.43\cdot10^{-6}$	$7.3\cdot10^{-12}$ mol·mol^{-1}
$u(x_{O2inNO2})$	Mole fraction of O_2 in the parent mixture of NO_2	$4.2\cdot10^{-7}$ mol·mol^{-1}	$-9.62\cdot10^{-6}$	$4.1\cdot10^{-12}$ mol·mol^{-1}

$u(x_{O2inN2})$	Mole fraction of O_2 in balance gas (impurity)	$1.4 \cdot 10^{-7}$ mol·mol^{-1}	$9.63 \cdot 10^{-6}$	$1.4 \cdot 10^{-12}$ mol·mol^{-1}
$u(x_{NO2inNO2})$	Mole fraction of NO_2 in the parent mixture of NO_2	$2.0 \cdot 10^{-7}$ mol·mol^{-1}	$1.50 \cdot 10^{-1}$	$3.0 \cdot 10^{-8}$ mol·mol^{-1}

Uncertainty budget for the gravimetric preparation of the Cylinder n. 1 at 9.92 µmol/mol of NO_2

The following table reports the uncertainty budget for the gravimetric preparation of the Cylinder n. 2 at 10.16 µmol/mol of NO_2.

Uncertainty component $u(x_i)$	**Uncertainty source**	**Standard uncertainty, $u(x_i)$**	**$\Delta x_{NO2,prep}/\delta x_i$**	**Contribution to $u(x_{NO2,\,prep})$ $\lvert\delta x_{NO2,prep}/\delta x_i\rvert \cdot u(x_i)$**
$u(m_{NO2})$	Weighed mass of the parent mixture of NO_2	$1.2 \cdot 10^{-3}$ g	$8.90 \cdot 10^{-8}$ mol·mol^{-1}·g^{-1}	$1.0 \cdot 10^{-10}$ mol·mol^{-1}
$u(m_{N2})$	Weighed mass of the balance gas N_2	$8.2 \cdot 10^{-4}$ g	$-1.61 \cdot 10^{-8}$ mol·mol^{-1}·g^{-1}	$1.3 \cdot 10^{-11}$ mol·mol^{-1}
$u(M_{NO2})$	Molar mass of NO_2	$3.0 \cdot 10^{-4}$ g·mol^{-1}	$-2.03 \cdot 10^{-11}$ mol^2·mol^{-1}·g^{-1}	$6.0 \cdot 10^{-15}$ mol·mol^{-1}
$u(M_{N2})$	Molar mass of N_2	$2.0 \cdot 10^{-4}$ g·mol^{-1}	$2.39 \cdot 10^{-9}$ mol^2·mol^{-1}·g^{-1}	$4.8 \cdot 10^{-13}$ mol·mol^{-1}
$u(M_{O2})$	Molar mass of O_2	$2.8 \cdot 10^{-4}$ g·mol^{-1}	$-2.06 \cdot 10^{-9}$ mol^2·mol^{-1}·g^{-1}	$5.8 \cdot 10^{-13}$ mol·mol^{-1}
$u(x_{N2inNO2})$	Mole fraction of N_2 in the parent mixture of NO_2	$4.0 \cdot 10^{-7}$ mol·mol^{-1}	$-8.59 \cdot 10^{-6}$	$3.5 \cdot 10^{-12}$ mol·mol^{-1}
$u(x_{N2inN2})$	Mole fraction of N_2 in balance gas (purity)	$8.7 \cdot 10^{-7}$ mol·mol^{-1}	$8.60 \cdot 10^{-6}$	$7.4 \cdot 10^{-12}$ mol·mol^{-1}
$u(x_{O2inNO2})$	Mole fraction of O_2 in the parent mixture of NO_2	$4.2 \cdot 10^{-7}$ mol·mol^{-1}	$-9.81 \cdot 10^{-6}$	$4.2 \cdot 10^{-12}$ mol·mol^{-1}
$u(x_{O2inN2})$	Mole fraction of O_2 in balance gas (impurity)	$1.4 \cdot 10^{-7}$ mol·mol^{-1}	$9.82 \cdot 10^{-6}$	$1.4 \cdot 10^{-12}$ mol·mol^{-1}
$u(x_{NO2inNO2})$	Mole fraction of NO_2 in the parent mixture of NO_2	$2.0 \cdot 10^{-7}$ mol·mol^{-1}	$1.53 \cdot 10^{-1}$	$3.0 \cdot 10^{-8}$ mol·mol^{-1}

Uncertainty budget for the gravimetric preparation of the Cylinder n. 2 at 10.16 µmol/mol of NO_2

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[1].

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 N2 6.0 a pre-mixture of NO at 100.0 μmol/mol (U=0.60 μmol/mol, k=2) in N2 purchased from NPL (UK). In order to oxidise NO into NO2, about 33 g of a mixture containing O2 at 0.0200 mol/mol in N2, were added to the mixtures. All the mixtures were gravimetrically prepared following the weighing scheme A-B-B-A. The mole fractions and the associated uncertainties of the mixtures were calculated according to section A3. The following table reports the characteristics of the calibration gas mixtures:

Mixture number	Cylinder number	NO_2 molar fraction χ μmol/mol	$U(\chi)$ (k=2) μmol/mol
INRIM 072	D56 6402	7.99	0.05
INRIM 073	D69 6430	10.04	0.06
INRIM 075	D56 6405	11.99	0.07

The calibration curves were validated using both a mixture of NO_2 at 10.05 μmol/mol (U=0.06 μmol/mol, k=2) in N_2 (INRIM 074) gravimetrically prepared at INRIM and by dynamic dilution. A further independent mixture of NO_2 at 10.01 μmol/mol (U=0.20 μmol/mol, k=2) in synthetic air (QC), purchased from NPL, was used as a quality control standard to monitor the stability of the instrumental set up during the entire period of the stability study.
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.
1 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.

No correction for environmental conditions (pressure, temperature, relative humidity) was made because the instrument was calibrated every day in which measurements were carried out.
The calibration curves were calculated using the WTLS algorithm, by means of the CCC Software developed at INRIM.

A5. Complementary information on the cylinder

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

Both the cylinders 1 and 2 were filled at 100 bar when shipped to 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:

Cylinder 1

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

Cylinder 2

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

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen

(10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures

Chemistry Department

Pavillon de Breteuil

92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores

BIPM Chemistry Department

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Fax: +33 (0)1 45 34 20 21

email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol.

Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	INRIM – Istituto Nazionale di Ricerca Metrologica		
Address	Strada delle Cacce 9, 10135 Torino, Italy		
Contact person	Michela Sega, Francesca Rolle		
Telephone	+39 011 3919948	Fax	+39 011 3919937
Email*	m.sega@inrim.it		

Serial number of cylinder received	
Cylinder pressure as received	

A2. Results

Cylinder 1 – Before shipping to the BIPM (Cylinder number: P27787/D247449)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	17/11/2017	9.92	0.06	2
(Stability 1)	01/12/2017	10.09	0.13	2
(Stability 2)	29/01/2918	9.90	0.13	2
(Stability 3)	26/04/2018	9.84	0.13	2

Cylinder 2– Before shipping to the BIPM (Cylinder number: P27787/D247448)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	24/11/2017	10.16	0.06	2
(Stability 1)	01/12/2017	10.36	0.13	2
(Stability 2)	29/01/2918	10.24	0.13	2
(Stability 3)	26/04/2018	10.21	0.13	2

Cylinder 1- Post BIPM measurements (Cylinder number: P27787/D247449)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	18/04/2019	10.10	0.13	2
(Stability 5)	13/05/2019	9.91	0.12	2
(Stability 6)	21/06/2019	10.11	0.15	2

Cylinder 2- Post BIPM measurements (Cylinder number: P27787/D247448)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	18/04/2019	10.08	0.10	2
(Stability 5)	13/05/2019	10.15	0.10	2
(Stability 6)	21/06/2019	10.25	0.13	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The model equation used to calculate the mole fraction of NO_2 in the final mixtures is taken from the International Standard ISO 6142-1:2015:

$$x_{NO_2,\,prep} = \frac{\sum_{j=1}^{r}\left(\frac{x_{NO_2,\,j}\cdot m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)}{\sum_{j=1}^{r}\left(\frac{m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)}$$

where the index *i* refers to the various components, while *j* refers to the different parent mixtures.

The uncertainty budget was evaluated according to the guidelines prescribed in ISO 6142-1:2015.

The uncertainty budget for the gravimetric preparation of the Cylinder n. 1 at 9.92 µmol/mol of NO_2, which takes into account the weighted masses of the parent mixtures, the molar masses of gases and their purity, is reported in the following table:

Uncertainty component $u(x_i)$	**Uncertainty source**	**Standard uncertainty,** $u(x_i)$	$\Delta x_{NO2,prep}/\delta x_i$	**Contribution to** $u(x_{NO2,\,prep})$ $\lvert\delta x_{NO2,prep}/\delta x_i\rvert \cdot u(x_i)$
$u(m_{NO2})$	Weighed mass of the parent mixture of NO_2	$1.2\cdot10^{-3}$ g	$8.93\cdot10^{-8}$ $mol\cdot mol^{-1}\cdot g^{-1}$	$1.0\cdot10^{-10}$ $mol\cdot mol^{-1}$
$u(m_{N2})$	Weighed mass of the balance gas N_2	$8.2\cdot10^{-4}$ g	$-1.58\cdot10^{-8}$ $mol\cdot mol^{-1}\cdot g^{-1}$	$1.3\cdot10^{-11}$ $mol\cdot mol^{-1}$
$u(M_{NO2})$	Molar mass of NO_2	$3.0\cdot10^{-4}$ $g\cdot mol^{-1}$	$-1.99\cdot10^{-11}$ $mol^2\cdot mol^{-1}\cdot g^{-1}$	$5.9\cdot10^{-15}$ $mol\cdot mol^{-1}$
$u(M_{N2})$	Molar mass of N_2	$2.0\cdot10^{-4}$ $g\cdot mol^{-1}$	$2.35\cdot10^{-9}$ $mol^2\cdot mol^{-1}\cdot g^{-1}$	$4.7\cdot10^{-13}$ $mol\cdot mol^{-1}$
$u(M_{O2})$	Molar mass of	$2.8\cdot10^{-4}$ $g\cdot mol^{-1}$	$-2.03\cdot10^{-9}$	$5.7\cdot10^{-13}$ $mol\cdot mol^{-1}$

	O_2		$mol^2 \cdot mol^{-1} \cdot g^{-1}$	
$u(x_{N2inNO2})$	Mole fraction of N_2 in the parent mixture of NO_2	$4.1 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$-8.42 \cdot 10^{-6}$	$3.4 \cdot 10^{-12}$ $mol \cdot mol^{-1}$
$u(x_{N2inN2})$	Mole fraction of N_2 in balance gas (purity)	$8.7 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$8.43 \cdot 10^{-6}$	$7.3 \cdot 10^{-12}$ $mol \cdot mol^{-1}$
$u(x_{O2inNO2})$	Mole fraction of O_2 in the parent mixture of NO_2	$4.2 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$-9.62 \cdot 10^{-6}$	$4.1 \cdot 10^{-12}$ $mol \cdot mol^{-1}$
$u(x_{O2inN2})$	Mole fraction of O_2 in balance gas (impurity)	$1.4 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$9.63 \cdot 10^{-6}$	$1.4 \cdot 10^{-12}$ $mol \cdot mol^{-1}$
$u(x_{NO2inNO2})$	Mole fraction of NO_2 in the parent mixture of NO_2	$2.0 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$1.50 \cdot 10^{-1}$	$3.0 \cdot 10^{-8}$ $mol \cdot mol^{-1}$

Uncertainty budget for the gravimetric preparation of the Cylinder n. 1 at 9.92 µmol/mol of NO_2

The following table reports the uncertainty budget for the gravimetric preparation of the Cylinder n. 2 at 10.16 µmol/mol of NO_2.

Uncertainty component $u(x_i)$	**Uncertainty source**	**Standard uncertainty,** $u(x_i)$	$\Delta x_{NO2,prep}/\delta x_i$	**Contribution to** $u(x_{NO2,\ prep})$ $\lvert \delta x_{NO2,prep}/\delta x_i \rvert \cdot u(x_i)$
$u(m_{NO2})$	Weighed mass of the parent mixture of NO_2	$1.2 \cdot 10^{-3}$ g	$8.90 \cdot 10^{-8}$ $mol \cdot mol^{-1} \cdot g^{-1}$	$1.0 \cdot 10^{-10}$ $mol \cdot mol^{-1}$

$u(m_{N2})$	Weighed mass of the balance gas N_2	$8.2 \cdot 10^{-4}$ g	$-1.61 \cdot 10^{-8}$ $mol \cdot mol^{-1} \cdot g^{-1}$	$1.3 \cdot 10^{-11}$ $mol \cdot mol^{-1}$
$u(M_{NO2})$	Molar mass of NO_2	$3.0 \cdot 10^{-4}$ $g \cdot mol^{-1}$	$-2.03 \cdot 10^{-11}$ $mol^2 \cdot mol^{-1} \cdot g^{-1}$	$6.0 \cdot 10^{-15}$ $mol \cdot mol^{-1}$
$u(M_{N2})$	Molar mass of N_2	$2.0 \cdot 10^{-4}$ $g \cdot mol^{-1}$	$2.39 \cdot 10^{-9}$ $mol^2 \cdot mol^{-1} \cdot g^{-1}$	$4.8 \cdot 10^{-13}$ $mol \cdot mol^{-1}$
$u(M_{O2})$	Molar mass of O_2	$2.8 \cdot 10^{-4}$ $g \cdot mol^{-1}$	$-2.06 \cdot 10^{-9}$ $mol^2 \cdot mol^{-1} \cdot g^{-1}$	$5.8 \cdot 10^{-13}$ $mol \cdot mol^{-1}$
$u(x_{N2inNO2})$	Mole fraction of N_2 in the parent mixture of NO_2	$4.0 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$-8.59 \cdot 10^{-6}$	$3.5 \cdot 10^{-12}$ $mol \cdot mol^{-1}$
$u(x_{N2inN2})$	Mole fraction of N_2 in balance gas (purity)	$8.7 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$8.60 \cdot 10^{-6}$	$7.4 \cdot 10^{-12}$ $mol \cdot mol^{-1}$
$u(x_{O2inNO2})$	Mole fraction of O_2 in the parent mixture of NO_2	$4.2 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$-9.81 \cdot 10^{-6}$	$4.2 \cdot 10^{-12}$ $mol \cdot mol^{-1}$
$u(x_{O2inN2})$	Mole fraction of O_2 in balance gas (impurity)	$1.4 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$9.82 \cdot 10^{-6}$	$1.4 \cdot 10^{-12}$ $mol \cdot mol^{-1}$
$u(x_{NO2inNO2})$	Mole fraction of NO_2 in the parent mixture of NO_2	$2.0 \cdot 10^{-7}$ $mol \cdot mol^{-1}$	$1.53 \cdot 10^{-1}$	$3.0 \cdot 10^{-8}$ $mol \cdot mol^{-1}$

Uncertainty budget for the gravimetric preparation of the Cylinder n. 2 at 10.16 µmol/mol of NO_2

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[3].

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 N_2 6.0 a pre-mixture of NO at 100.0 µmol/mol (U=0.60 µmol/mol, k=2) in N_2 purchased from NPL (UK). In order to oxidise NO into NO_2, about 33 g of a mixture containing O_2 at 0.0200 mol/mol in N_2, were added to the mixtures. All the mixtures were gravimetrically prepared following the weighing scheme A-B-B-A. The mole fractions and the associated uncertainties of the mixtures were calculated according to section A3.

The following table reports the characteristics of the calibration gas mixtures:

Mixture number	Cylinder number	NO_2 molar fraction χ µmol/mol	$U(\chi)$ (k=2) µmol/mol
INRIM 072	D56 6402	7.99	0.05
INRIM 073	D69 6430	10.04	0.06
INRIM 075	D56 6405	11.99	0.07

The calibration curves were validated using both a mixture of NO_2 at 10.05 µmol/mol (U=0.06 µmol/mol, k=2) in N_2 (INRIM 074) gravimetrically prepared at INRIM and by dynamic dilution. A further independent mixture of NO_2 at 10.01 µmol/mol (U=0.20 µmol/mol, k=2) in synthetic air (QC), purchased from NPL, was used as a quality control standard to monitor the stability of the instrumental set up during the entire period of the stability study. An additional independent mixture of NO_2 at 10.07 µmol/mol (U=0.15 µmol/mol, k=2) in N_2 (QC2), purchased from NPL, was used as a quality control standard to monitor the stability of the instrumental set up and to validate the calibration curves of the chemiluminescence analyser during the stability study carried out after the return of the cylinders to INRIM ("Post BIPM measurements").

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.

[3] 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.

No correction for environmental conditions (pressure, temperature, relative humidity) was made because the instrument was calibrated every day in which measurements were carried out.

The calibration curves were calculated using the WTLS algorithm, by means of the CCC Software developed at INRIM.

A5. Complementary information on the cylinder

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

Both the cylinders 1 and 2 were filled at 100 bar when shipped to 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:

Cylinder 1

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

Cylinder 2

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

KRISS

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures

Chemistry Department

Pavillon de Breteuil

92312 Sèvres Cedex, France.

Study Coordinator:

Edgar Flores

BIPM Chemistry Department

Phone: +33 (0)1 45 07 70 92

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email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol.

Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	KRISS		
Address	Center for Gas Analysis (Chemistry Building 230 Office 209) Division of Chemical and Medical Metrology Korea Research Institute of Standards and Science(KRISS) 267 Gajeong-ro, Yuseong-gu, Daejeon 34113 REPUBLIC of KOREA		
Contact person	Sang-Hyub Oh		
Telephone	+82 42 868 5341	Fax	+82 42 868 5042
Email*	shoh@kriss.re.kr		
Serial number of cylinder	D59 6920, D59 6882		
Cylinder pressure	8 MPa		

A2. Results

Cylinder 1(D59 6920) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	May 15, 2018	10.04	0.30	2.0
(Stability 1)	May 16, 2018	10.03	0.30	2.0
(Stability 2)	May 17, 2018	10.03	0.30	2.0
(Stability 3)	May 18, 2018	10.05	0.30	2.0
(Stability 4)	May 19, 2018	10.04	0.30	2.0

Cylinder 2(D59 6882)– Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	May 15, 2018	10.03	0.30	2.0
(Stability 1)	May 16, 2018	10.04	0.30	2.0
(Stability 2)	May 17, 2018	10.03	0.30	2.0
(Stability 3)	May 18, 2018	10.02	0.30	2.0
(Stability 4)	May 19, 2018	10.03	0.30	2.0

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

Cylinder 2- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Purity table for NO_2 source gas

Component	Mole fraction μ mol/mol	Uncertainty μ mol/mol
NO	645	64.5
HNO_3	1 130	150
O_2	1.0	0.05
N_2	3 340	167
CO	8.6	0.4
CO_2	75.9	3.8
H_2O	22.8	2.3
NO_2	**994 777**	**234**

Uncertainty budget for final mixture

Analyte	Relative standard uncertainties / %			Expanded uncertainty / %	Coverage factor
	Gravimetry	Analysis	Stability		
NO_2	0.08	0.48	1.39	2.95	2

- Concentration for final mixture.

Cylinder 1(D59 6920) : 10.04 µmol/mol (*U* = 0.30 µmol/mol)

Cylinder 2(D59 6882) : 10.03 µmol/mol(*U* = 0.30 µmol/mol)

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[4].

- NO_2 analyser : Chemiluminescent NO/NOx analyser (Thermo 42i-HL)
- Samples : 4 PRMs (~10 µmol/mol)
- Gas feeding system: Gas feeding system was used to control the flow rate, gas feeding time and to get data. This system is composed of MFC (Bronkhorst), 5 multi-position valves (Valco), regulator, and vacuum pump. This system was controlled by LabVIEW program.
  In this work, flow rate was 400 ml/min, and feeding time of sample and zero gas were 20 minutes and 1 minutes, respectively. Feeding tube line was evacuated after each measurement, and sample was analysed 4 times in succession as follow.

S1 - Zero - S1 - Zero - S1 - Zero - S1 - Zero - S2- Zero - S2 - Zero - S2 - Zero - S2 …

A5. Complementary information on the cylinder

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

- 8MPa

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:

- ~1000 μ mol/mol Oxygen
-

[4] 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.

Cylinder 1

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

Cylinder 2

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

Post BIPM measurements

Cylinder 1- Post BIPM measurements(D59 6920)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	2019.08.20	10.05	0.30	2.0
(Stability 5)	2019.08.22	10.05	0.30	2.0
(Stability 6)	2019.09.18	10.06	0.30	2.0

Cylinder 2- Post BIPM measurements(D59 6882)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	2019.08.20	10.03	0.30	2.0
(Stability 5)	2019.08.22	10.04	0.30	2.0
(Stability 6)	2019.09.18	10.05	0.30	2.0

LNE

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).
Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.
Proposed dates: 2018.

Coordinating laboratory:
Bureau International des Poids et Mesures Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol.
Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	LNE		
Address	1, rue Gaston Boissier 75724 Paris Cedex 15 France		
Contact person	Tatiana Macé		
Telephone	01 40 43 38 53	Fax	
Email*	tatiana.mace@lne.fr		
Serial number of cylinder received			
Cylinder pressure as received			

A2. Results

Cylinder 1191-NO2/N2 0001 – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / μmol/mol	Expanded uncertainty $U(x_{NO2})$ / μmol/mol	Coverage factor
(Preparation)	19/02/2018	10.035	0.046	2
(Stability 1)	28/02/2018	10.10	0.13	2
(Stability 2)	28/03/2018	10.02	0.13	2
(Stability 3)	27/04/2018	9.96	0.12	2

Cylinder 1183-NO/N2 0002– Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / μmol/mol	Expanded uncertainty $U(x_{NO2})$ / μmol/mol	Coverage factor
(Preparation)	22/02/2018	10.015	0.046	2
(Stability 1)	28/02/2018	10.09	0.13	2
(Stability 2)	28/03/2018	10.01	0.13	2
(Stability 3)	27/04/2018	9.97	0.12	2

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / μmol/mol	Expanded uncertainty $U(x_{NO2})$ / μmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

Cylinder 2- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / μmol/mol	Expanded uncertainty $U(x_{NO2})$ / μmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Uncertainty budget of the NO_2/N_2 0001

Uncertainty source	Unit	Value Xi	u(Xi)	Contribution to the uncertainty %
Molar mass of N_2	g/mol	28.01348	$9.9\ 10^{-5}$	0.00
Molar mass of O_2	g/mol	31.99880	$4.2\ 10^{-4}$	0.00
Molar mass of NO	g/mol	30.00614	$3.1\ 10^{-4}$	0.00

Mass of NO/N_2 premix	g	65.9087	$1.60\ 10^{-2}$	1.05
Mole fraction of NO/N_2 premix	mol/mol	$2.36221\ 10^{-4}$	$6.12\ 10^{-8}$	1.30
Mass of O_2/N_2 premix	g	50.84073	$1.50\ 10^{-2}$	0.00
Mole fraction of O_2/N_2 premix	mol/mol	$2.92403\ 10^{-2}$	$6.66\ 10^{-6}$	0.00
Mass of N_2	g	1434.992	$2.0\ 10^{-2}$	0.00
N_2 purity	mol/mol	0.99999991	$2.37\ 10^{-8}$	0.00
NO_2 in NO/N_2 premix	µmol/mol	$8.43\ 10^{-4}$	$2.6\ 10^{-5}$	0.00
H_2O reaction	µmol/mol	0.0	$1.0\ 10^{-2}$	20.75
Stability	µmol/mol	0.0	$2\ 10^{-2}$	76.9

C_{NO2}=10.035 ± 0.046 µmol/mol

Uncertainty budget of the NO_2/N_2 0002

Uncertainty source	Unit	Value Xi	u(Xi)	Contribution to the uncertainty %
Molar mass of N_2	g/mol	28.01348	$9.9\ 10^{-5}$	0.00
Molar mass of O_2	g/mol	31.99880	$4.2\ 10^{-4}$	0.00
Molar mass of NO	g/mol	30.00614	$3.1\ 10^{-4}$	0.00
Mass of NO/N_2 premix	g	65.10994	$1.3\ 10^{-2}$	0.7
Mole fraction of NO/N_2 premix	mol/mol	$2.36221\ 10^{-4}$	$6.12\ 10^{-8}$	1.3
Mass of O_2/N_2 premix	g	50.75351	$1.2\ 10^{-2}$	0.00
Mole fraction of O_2/N_2 premix	mol/mol	$2.92403\ 10^{-2}$	$6.66\ 10^{-6}$	0.00
Mass of N_2	g	1420.224	$1.7\ 10^{-2}$	0.00
N_2 purity	mol/mol	0.99999991	$2.37\ 10^{-8}$	0.00
NO_2 in NO/N_2 premix	µmol/mol	$8.4164\ 10^{-4}$	$2.6\ 10^{-5}$	0.00
H_2O reaction	µmol/mol	0.0	$1.0\ 10^{-2}$	20.8
Stability	µmol/mol	0.0	$2\ 10^{-2}$	77.2

C_{NO2}=10.015 ± 0.046 µmol/mol

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[1].

The analytical method used for the gas analysis is based on spectroscopy with a Bruker FTIR coupled with a 5,522 m gas cell. The measurement is performing by MALT (HITRAN) with BFOS interface software. The quantification of the mole fraction of NO_2 is given by the calibration of the system with a dynamic dilution (Molbloc) of a high mole fraction gravimetric mixture. The gas mixtures are analysed during 90 min each other.

A5. Complementary information on the cylinder

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

- Cylinder N°1191, pressure 70 bars
- Cylinder N°1183, pressure 80 bars

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:

Cylinder 1191 NO_2/N_2 0001

Date	Component	Mole fraction / µmol/mol	Expanded uncertainty %	Coverage factor	Measurement technique
28/02/2018	HNO_3	0.009	10	2	FTIR
28/03/2018	HNO_3	0.032	10	2	FTIR
27/04/2018	HNO_3	0.041	10	2	FTIR

Cylinder 1183 NO_2/N_2 0002

Date	Component	Mole fraction / µmol/mol	Expanded uncertainty %	Coverage factor	Measurement technique
28/02/2018	HNO_3	0.004	10	2	FTIR
28/03/2018	HNO_3	0.039	10	2	FTIR
27/04/2018	HNO_3	0.052	10	2	FTIR

[1] 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.

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures

Chemistry Department

Pavillon de Breteuil

92312 Sèvres Cedex, France.

Study Coordinator:

Edgar Flores

BIPM Chemistry Department

Phone: +33 (0)1 45 07 70 92

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Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol.

Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	LNE		
Address	1, rue Gaston Boissier 75724 Paris Cedex 15 France		
Contact person	Tatiana Macé		
Telephone	01 40 43 38 53	Fax	
Email*	tatiana.mace@lne.fr		
Serial number of cylinder received			
Cylinder pressure as received			

A2. Results

Cylinder 1191-NO2/N2 0001 – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	19/02/2018	10.035	0.046	2
(Stability 1)	28/02/2018	10.10	0.13	2
(Stability 2)	28/03/2018	10.02	0.13	2
(Stability 3)	27/04/2018	9.96	0.12	2

Cylinder 1183-NO/N2 0002– Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	22/02/2018	10.015	0.046	2
(Stability 1)	28/02/2018	10.09	0.13	2
(Stability 2)	28/03/2018	10.01	0.13	2
(Stability 3)	27/04/2018	9.97	0.12	2

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	14/05/2019	9.60	0.12	2
(Stability 5)	20/06/2019	9.57	0.12	2
(Stability 6)	12/07/2019	9.62	0.12	2

Cylinder 2- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	14/05/2019	9.70	0.12	2
(Stability 5)	20/06/2019	9.69	0.12	2
(Stability 6)	12/07/2019	9.74	0.12	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Uncertainty budget of the NO_2/N_2 0001

Uncertainty source	Unit	Value Xi	u(Xi)	Contribution to the uncertainty %
Molar mass of N_2	g/mol	28.01348	$9.9\ 10^{-5}$	0.00
Molar mass of O_2	g/mol	31.99880	$4.2\ 10^{-4}$	0.00
Molar mass of NO	g/mol	30.00614	$3.1\ 10^{-4}$	0.00
Mass of NO/N_2 premix	g	65.9087	$1.60\ 10^{-2}$	1.05
Mole fraction of NO/N_2 premix	mol/mol	$2.36221\ 10^{-4}$	$6.12\ 10^{-8}$	1.30
Mass of O_2/N_2 premix	g	50.84073	$1.50\ 10^{-2}$	0.00
Mole fraction of O_2/N_2 premix	mol/mol	$2.92403\ 10^{-2}$	$6.66\ 10^{-6}$	0.00
Mass of N_2	g	1434.992	$2.0\ 10^{-2}$	0.00
N_2 purity	mol/mol	0.99999991	$2.37\ 10^{-8}$	0.00

NO_2 in NO/N_2 premix	µmol/mol	$8.43\ 10^{-4}$	$2.6\ 10^{-5}$	0.00
H_2O reaction	µmol/mol	0.0	$1.0\ 10^{-2}$	20.75
Stability	µmol/mol	0.0	$2\ 10^{-2}$	76.9

C_{NO2}=10.035 ± 0.046 µmol/mol

<u>Uncertainty budget of the NO_2/N_2 0002</u>

Uncertainty source	Unit	Value Xi	u(Xi)	Contribution to the uncertainty %
Molar mass of N_2	g/mol	28.01348	$9.9\ 10^{-5}$	0.00
Molar mass of O_2	g/mol	31.99880	$4.2\ 10^{-4}$	0.00
Molar mass of NO	g/mol	30.00614	$3.1\ 10^{-4}$	0.00
Mass of NO/N_2 premix	g	65.10994	$1.3\ 10^{-2}$	0.7
Mole fraction of NO/N_2 premix	mol/mol	$2.36221\ 10^{-4}$	$6.12\ 10^{-8}$	1.3
Mass of O_2/N_2 premix	g	50.75351	$1.2\ 10^{-2}$	0.00
Mole fraction of O_2/N_2 premix	mol/mol	$2.92403\ 10^{-2}$	$6.66\ 10^{-6}$	0.00
Mass of N_2	g	1420.224	$1.7\ 10^{-2}$	0.00
N_2 purity	mol/mol	0.99999991	$2.37\ 10^{-8}$	0.00
NO_2 in NO/N_2 premix	µmol/mol	$8.4164\ 10^{-4}$	$2.6\ 10^{-5}$	0.00
H_2O reaction	µmol/mol	0.0	$1.0\ 10^{-2}$	20.8
Stability	µmol/mol	0.0	$2\ 10^{-2}$	77.2

C_{NO2}=10.015 ± 0.046 µmol/mol

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[5].

The analytical method used for the gas analysis is based on spectroscopy with a Bruker FTIR coupled with a 5,522 m gas cell. The measurement is performing by MALT (HITRAN) with BFOS interface software. The quantification of the mole fraction of NO_2 is given by the calibration of the system with a dynamic dilution (Molbloc) of a high mole fraction gravimetric mixture. The gas mixtures are analysed during 90 min each other.

A5. Complementary information on the cylinder

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

- Cylinder N°1191, pressure 70 bars

- Cylinder N°1183, pressure 80 bars

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:

Cylinder 1191 NO_2/N_2 0001

Date	Component	Mole fraction / µmol/mol	Expanded uncertainty %	Coverage factor	Measurement technique
28/02/2018	HNO_3	0.009	10	2	FTIR
28/03/2018	HNO_3	0.032	10	2	FTIR
27/04/2018	HNO_3	0.041	10	2	FTIR

Cylinder 1183 NO_2/N_2 0002

Date	Component	Mole fraction / µmol/mol	Expanded uncertainty %	Coverage factor	Measurement technique
28/02/2018	HNO_3	0.004	10	2	FTIR
28/03/2018	HNO_3	0.039	10	2	FTIR
27/04/2018	HNO_3	0.052	10	2	FTIR

[5] 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.

- After BIPM measurements

Cylinder 1191 NO_2/N_2 0001

Date	Component	Mole fraction / µmol/mol	Expanded uncertainty %	Coverage factor	Measurement technique
14/05/19	HNO_3	0.070	10	2	FTIR
20/06/19	HNO_3	0.066	10	2	FTIR
12/07/19	HNO_3	0.043	10	2	FTIR

Cylinder 1183 NO_2/N_2 0002

Date	Component	Mole fraction / µmol/mol	Expanded uncertainty %	Coverage factor	Measurement technique
14/05/19	HNO_3	0.102	10	2	FTIR
20/06/19	HNO_3	0.107	10	2	FTIR
12/07/19	HNO3	0.095	10	2	FTIR

METAS

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:
Bureau International des Poids et Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org
This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute: Federal Institute of Metrology METAS

Address : Lindenweg 50, 3003 Bern-Wabern

Contact person : Celine Pascale

Telephone : 0041.58.38.70.381

Email*: celine.pascale@metas.ch

Serial number of cylinder received: 10918, 10919

Cylinder pressure as received: 10918 : 124 bar. 10919 : 127 bars

A2. Results

Cylinder 1 – 10918 Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide x_{NO2} µmol/mol	Expanded Uncertainty U µmol/mol	Coverage factor
(Preparation) : VSL	N/A	N/A	N/A	N/A
(Stability 1)	23.03.2018	9.93	0.31	2
(Stability 2)	17.04.2018	9.67	0.26	2
(Stability 3)	23.05.2018	9.84	0.09	2

Cylinder 2– 10919 Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide x_{NO2} µmol/mol	Expanded Uncertainty U µmol/mol	Coverage factor
(Preparation) : VSL	N/A	N/A	N/A	N/A
(Stability 1)	28.03.2018	9.95	0.31	2
(Stability 2)	18.04.2018	9.69	0.26	2
(Stability 3)	18.05.2018	9.85	0.09	2

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide x_{NO2} µmol/mol	Expanded Uncertainty U µmol/mol	Coverage factor
(Preparation) : VSL	N/A	N/A	N/A	N/A
(Stability 1)				
(Stability 2)				
(Stability 3)				

Cylinder 2- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide x_{NO2} µmol/mol	Expanded Uncertainty U µmol/mol	Coverage factor
(Preparation) : VSL	N/A	N/A	N/A	N/A
(Stability 1)				

(Stability 2)				
(Stability 3)				

A3. Uncertainty Budget

Model Equation:

$X1_{NO2}=(qmC*P*VM_{null}/M_{Substanz}/q1)+X_{NO2}N;$
$X2_{NO2}=(qmC*P*VM_{null}/M_{Substanz}/q2)+X_{NO2}N;$
$X3_{NO2}=(qmC*P*VM_{null}/M_{Substanz}/q3)+X_{NO2}N;$

$M_{Substanz}=M_{Atom1}+2*M_{Atom2};$
$VM_{null}=M_{Null}/(d_{Null}*1000/1000000);$

$X_{mean}=(X1_{NO2}+X2_{NO2}+X3_{NO2})/3;$
$Anz_{mean}=(Anz1_{NO2}+Anz2_{NO2}+Anz3_{NO2})/3;$
$b=p/q;$
$p=(X1_{NO2}-X_{mean})*(Anz1_{NO2}-Anz_{mean})+(X2_{NO2}-X_{mean})*(Anz2_{NO2}-Anz_{mean})+(X3_{NO2}-X_{mean})*(Anz3_{NO2}-Anz_{mean});$
$q=(X1_{NO2}-X_{mean})^2+(X2_{NO2}-X_{mean})^2+ (X3_{NO2}-X_{mean})^2;$
$a=Anz_{mean}-b*X_{mean};$

$XRes10918_{NO2}=(AnzRes10918-a)/b;$
$XRes10919_{NO2}=(AnzRes10919-a)/b;$

$XBottle10918_{NO2}=XRes10918_{NO2}*(qv_{MFCdil}+qv_{duse})/qv_{duse}+X_{NO2}N;$
$XBottle10919_{NO2}=XRes10919_{NO2}*(qv_{MFCdil}+qv_{duse})/qv_{duse}+X_{NO2}N;$

Quantity	Unit	Definition
X1NO2	ppb	amount of Fraction NO2 1st calibration point
qmC	ng/min	permeation rate
P	no units	purity of permeator
VMnull	ml/mol	molar volume
MSubstanz	g/mol	molar mass
q1	ml/min	total flow 1st calibration point
XNO2N	ppb	residual amount of fraction NO2 in matrix gas
X2NO2	ppb	amount of Fraction NO2 2nd calibration point
q2	ml/min	total flow 2nd calibration point
X3NO2	ppb	amount of Fraction NO2 3rd calibration point
q3	ml/min	total flow 3rd calibration point
MAtom1	g/mol	molar mass nitrogen atom
MAtom2	g/mol	molar mass oxygen atom
MNull	g/mol	molar mass matrix gas
dNull	kg/m3	matrix gas density
Xmean	ppb	average amount of fraction calibration points
Anzmean	ppb	average display calibration points
Anz1NO2	ppb	display 1st calibration point
Anz2NO2	ppb	display 2nd calibration point
Anz3NO2	ppb	display 3rd calibration point
b	no units	slope calibration curve
p	ppb2	nominator for slope calibration curve
q	ppb2	denominator for slope calibration curve

Quantity	Unit	Definition
a	ppb	y-axis calibration curve
XRes10918NO2	ppb	amount of fraction cylinder 10918 after dilution
AnzRes10918	ppb	display cylinder 10918 after dilution
XRes10919NO2	ppb	amount of fraction cylinder 10919 after dilution
AnzRes10919	ppb	display cylinder 10919 after dilution
XBottle10918NO2	ppb	amount of fraction cylinder 10918
qvMFCdil	ml/min	dilution flow for dilution NO2 cylinder
qvduse	ml/min	flow from NO2 cylinder
XBottle10919NO2	ppb	amount of fraction cylinder 10919

Amount of fraction for cylinder 10918

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
qmC	498.00 ng/min	7.72 ng/min	normal	20	150 ppb	95.6 %
P	0.99500 no units	0.00204 no units	triangular	10000	20 ppb	1.7 %
MSubstanz	46.005500 g/mol	0.000316 g/mol				
q1	2136.56 ml/min	3.20 ml/min	normal	-4.3	-14 ppb	0.8 %
XNO2N	0.2000 ppb	0.0816 ppb	triangular	88	7.2 ppb	0.2 %
q2	2536.85 ml/min	3.81 ml/min	normal	-0.75	-2.9 ppb	0.0 %
q3	2837.18 ml/min	4.26 ml/min	normal	0.44	1.9 ppb	0.0 %
MAtom1	14.006700 g/mol	0.000100 g/mol	normal	-220	-0.022 ppb	0.0 %
MAtom2	15.999400 g/mol	0.000150 g/mol	normal	-430	-0.065 ppb	0.0 %
MNull	28.013400 g/mol	0.000577 g/mol	rectangular	350	0.20 ppb	0.0 %
dNull	1.2504000 kg/m3	0.0000577 kg/m3	rectangular	-7900	-0.46 ppb	0.0 %
Xmean	97.90 ppb	1.53 ppb				
Anzmean	100.7600 ppb	0.0502 ppb				
Anz1NO2	116.630 ppb	0.113 ppb	normal	-79	-8.9 ppb	0.3 %
Anz2NO2	98.0800 ppb	0.0712 ppb	normal	-19	-1.4 ppb	0.0 %
Anz3NO2	87.5700 ppb	0.0694 ppb	normal	14	0.98 ppb	0.0 %
p	415.62 ppb2	7.50 ppb2				
q	398.9 ppb2	13.9 ppb2				
XRes10918NO2	113.73 ppb	1.79 ppb				
AnzRes10918	117.2500 ppb	0.0387 ppb	normal	84	3.2 ppb	0.0 %
qvMFCdil	1800.40 ml/min	1.80 ml/min	normal	5.5	9.8 ppb	0.4 %
qvduse	20.8600 ml/min	0.0313 ml/min	normal	-470	-15 ppb	0.9 %
XBottle10918NO2	**9930 ppb**	**157 ppb**				

A4. Description of the procedure used during the gas analysis

A commercial chemiluminescence trace level NO_2-analyzer (Thermo 42i -TL) was used as comparator to measure the reference mixtures and both gas cylinders (10918, 10919). The comparator was calibrated with NO_2 reference mixtures in the range from 90 to 115 nmol/mol NO_2 in nitrogen 6.0.The nitrogen used

as matrix gas was purified with a combination of Microtorr/Microtorr (SAES Getter). The pressure at the comparator inlet was kept constant at 962±3 mbar with a pressure controller (LNI Swissgas)
The reference mixtures were produced dynamically by one of the METAS primary magnetic suspension balance (Rubotherm) and a NO_2 permeation unit with purity 99.5 % (VICI Metronics). The total matrix gas flow was measured by a calibrated mass flow meter (Vögtlin) prior to the permeation chamber.

The NO_2 permeation rate was approx. 490 ng·min^{-1} at 38 °C and 1013 mbar. This value was measured before and after each measurement. It is an average over min 3 days after a stabilization period of min 3 days.
Note: For measurement 1, the permeation rate was measured in another magnetic suspension balance as the one used for the direct generation of the reference gas mixtures. For measurement 2 and 3, the permeation rate was measured in the same magnetic suspension balance as used for the generation.

Both gas cylinders were dynamically diluted with N_2 6.0 (without further purification) in a system of critical orifices combined with 2 pressure controllers (Bronkhorst) and a mass flow controller (Vögtlin). Several dilution flowrates were tested to reach the calibrated concentration range of the analyzer (90 – 115 nmol/mol). The pressure at the comparator inlet was maintained constant at 962±3 mbar - LNI Swissgas). The critical orifice system was maintained at constant temperature (22°C) in a water bath (Variostat).

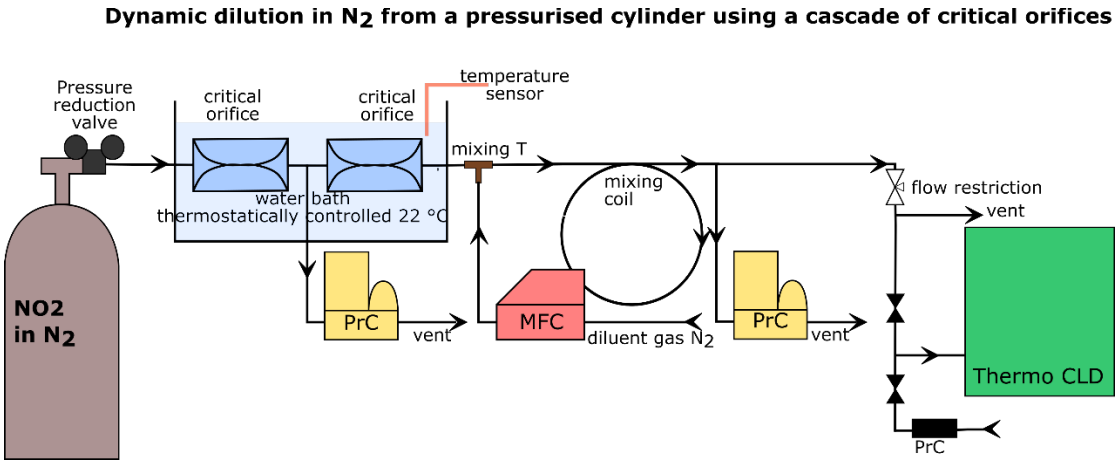


Figure 1: Dilution scheme of NO_2 cylinder

All the flows were calibrated with the primary volumeter of METAS.

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:

Cylinder 1

Date	Component	Mole fraction	Expanded Uncertainty	Coverage factor	Measurement technique
-	-	-	-	-	-

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:
Bureau International des Poids et Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org
This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute: Federal Institute of Metrology METAS

Address : Lindenweg 50, 3003 Bern-Wabern

Contact person : Celine Pascale

Telephone : 0041.58.38.70.381

Email*: celine.pascale@metas.ch

Serial number of cylinder received: 10918, 10919

Cylinder pressure as received: 10918 : 124 bar. 10919 : 127 bars

A2. Results

Cylinder 1 – 10918 Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide x_{NO2} µmol/mol	Expanded Uncertainty U µmol/mol	Coverage factor
(Preparation) : VSL	N/A	N/A	N/A	N/A
(Stability 1)	23.03.2018	9.93	0.31	2
(Stability 2)	17.04.2018	9.67	0.26	2
(Stability 3)	23.05.2018	9.84	0.09	2

Cylinder 2– 10919 Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide x_{NO2} µmol/mol	Expanded Uncertainty U µmol/mol	Coverage factor
(Preparation) : VSL	N/A	N/A	N/A	N/A
(Stability 1)	28.03.2018	9.95	0.31	2
(Stability 2)	18.04.2018	9.69	0.26	2
(Stability 3)	18.05.2018	9.85	0.09	2

Cylinder 1- 10918 Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide x_{NO2} µmol/mol	Expanded Uncertainty U µmol/mol	Coverage factor
(Preparation) : VSL	N/A	N/A	N/A	N/A
(Stability 1)	04.06.2019	9.50	0.06	2
(Stability 2)	03.07.2019	9.25	0.12	2
(Stability 3)	15.08.2019	9.56	0.21	2

Cylinder 2- 10919 Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide x_{NO2} µmol/mol	Expanded Uncertainty U µmol/mol	Coverage factor
(Preparation) : VSL	N/A	N/A	N/A	N/A
(Stability 1)	04.06.2019	9.53	0.06	2
(Stability 2)	02.07.2019	9.30	0.12	2
(Stability 3)	16.08.2019	9.44	0.21	2

A3. Uncertainty Budget

Model Equation:

$X1_{NO2}=(qmC*P*VM_{null}/M_{Substanz}/q1)+X_{NO2}N;$
$X2_{NO2}=(qmC*P*VM_{null}/M_{Substanz}/q2)+X_{NO2}N;$
$X3_{NO2}=(qmC*P*VM_{null}/M_{Substanz}/q3)+X_{NO2}N;$

$M_{Substanz}=M_{Atom1}+2*M_{Atom2};$
$VM_{null}=M_{Null}/(d_{Null}*1000/1000000);$

$X_{mean}=(X1_{NO2}+X2_{NO2}+X3_{NO2})/3;$
$Anz_{mean}=(Anz1_{NO2}+Anz2_{NO2}+Anz3_{NO2})/3;$
$b=p/q;$
$p=(X1_{NO2}-X_{mean})*(Anz1_{NO2}-Anz_{mean})+(X2_{NO2}-X_{mean})*(Anz2_{NO2}-Anz_{mean})+(X3_{NO2}-X_{mean})*(Anz3_{NO2}-Anz_{mean});$
$q=(X1_{NO2}-X_{mean})^2+(X2_{NO2}-X_{mean})^2+ (X3_{NO2}-X_{mean})^2;$
$a=Anz_{mean}-b*X_{mean};$

$XRes10918_{NO2}=(AnzRes10918-a)/b;$
$XRes10919_{NO2}=(AnzRes10919-a)/b;$

$XBottle10918_{NO2}=XRes10918_{NO2}*(qv_{MFCdil}+qv_{duse})/qv_{duse}+X_{NO2}N;$
$XBottle10919_{NO2}=XRes10919_{NO2}*(qv_{MFCdil}+qv_{duse})/qv_{duse}+X_{NO2}N;$

Quantity	**Unit**	**Definition**
X1NO2	ppb	amount of Fraction NO2 1st calibration point
qmC	ng/min	permeation rate
P	no units	purity of permeator
VMnull	ml/mol	molar volume
MSubstanz	g/mol	molar mass
q1	ml/min	total flow 1st calibration point
XNO2N	ppb	residual amount of fraction NO2 in matrix gas
X2NO2	ppb	amount of Fraction NO2 2nd calibration point
q2	ml/min	total flow 2nd calibration point
X3NO2	ppb	amount of Fraction NO2 3rd calibration point
q3	ml/min	total flow 3rd calibration point
MAtom1	g/mol	molar mass nitrogen atom
MAtom2	g/mol	molar mass oxygen atom
MNull	g/mol	molar mass matrix gas
dNull	kg/m3	matrix gas density

Quantity	Unit	Definition
Xmean	ppb	average amount of fraction calibration points
Anzmean	ppb	average display calibration points
Anz1NO2	ppb	display 1st calibration point
Anz2NO2	ppb	display 2nd calibration point
Anz3NO2	ppb	display 3rd calibration point
b	no units	slope calibration curve
p	ppb2	nominator for slope calibration curve
q	ppb2	denominator for slope calibration curve
a	ppb	y-axis calibration curve
XRes10918NO2	ppb	amount of fraction cylinder 10918 after dilution
AnzRes10918	ppb	display cylinder 10918 after dilution
XRes10919NO2	ppb	amount of fraction cylinder 10919 after dilution
AnzRes10919	ppb	display cylinder 10919 after dilution
XBottle10918NO2	ppb	amount of fraction cylinder 10918
qvMFCdil	ml/min	dilution flow for dilution NO2 cylinder
qvduse	ml/min	flow from NO2 cylinder
XBottle10919NO2	ppb	amount of fraction cylinder 10919

Amount of fraction for cylinder 10918

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
qmC	498.00 ng/min	7.72 ng/min	normal	20	150 ppb	95.6 %
P	0.99500 no units	0.00204 no units	triangular	10000	20 ppb	1.7 %
MSubstanz	46.005500 g/mol	0.000316 g/mol				
q1	2136.56 ml/min	3.20 ml/min	normal	-4.3	-14 ppb	0.8 %
XNO2N	0.2000 ppb	0.0816 ppb	triangular	88	7.2 ppb	0.2 %
q2	2536.85 ml/min	3.81 ml/min	normal	-0.75	-2.9 ppb	0.0 %
q3	2837.18 ml/min	4.26 ml/min	normal	0.44	1.9 ppb	0.0 %
MAtom1	14.006700 g/mol	0.000100 g/mol	normal	-220	-0.022 ppb	0.0 %
MAtom2	15.999400 g/mol	0.000150 g/mol	normal	-430	-0.065 ppb	0.0 %
MNull	28.013400 g/mol	0.000577 g/mol	rectangular	350	0.20 ppb	0.0 %
dNull	1.2504000 kg/m3	0.0000577 kg/m3	rectangular	-7900	-0.46 ppb	0.0 %
Xmean	97.90 ppb	1.53 ppb				
Anzmean	100.7600 ppb	0.0502 ppb				
Anz1NO2	116.630 ppb	0.113 ppb	normal	-79	-8.9 ppb	0.3 %
Anz2NO2	98.0800 ppb	0.0712 ppb	normal	-19	-1.4 ppb	0.0 %
Anz3NO2	87.5700 ppb	0.0694 ppb	normal	14	0.98 ppb	0.0 %
p	415.62 ppb2	7.50 ppb2				
q	398.9 ppb2	13.9 ppb2				
XRes10918NO2	113.73 ppb	1.79 ppb				
AnzRes10918	117.2500 ppb	0.0387 ppb	normal	84	3.2 ppb	0.0 %
qvMFCdil	1800.40 ml/min	1.80 ml/min	normal	5.5	9.8 ppb	0.4 %
qvduse	20.8600 ml/min	0.0313 ml/min	normal	-470	-15 ppb	0.9 %
XBottle10918N	**9930 ppb**	**157 ppb**				

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
O2						

A4. Description of the procedure used during the gas analysis

A commercial chemiluminescence trace level NO_2-analyzer (Thermo 42i -TL) was used as comparator to measure the reference mixtures and both gas cylinders (10918, 10919). The comparator was calibrated with NO_2 reference mixtures in the range from 58 to 121 nmol/mol NO_2 in nitrogen 6.0 (purity 99.99990%). The nitrogen used as matrix gas was purified with a combination of Microtorr/Microtorr (SAES Getter). The pressure at the comparator inlet was kept constant at 962±3 mbar with a pressure controller (LNI Swissgas).
The reference mixtures were produced dynamically by one of the METAS primary magnetic suspension balance (MSB) (Rubotherm) and different NO_2 permeation units (see Table A4.1). The total matrix gas flow was measured by a calibrated mass flow meter (Vögtlin) prior to the permeation chamber. The permeation rate was measured before and after each measurement for at least 3 days after a stabilization period (minimum 3 days).

Table A.4.1: Permeation units and conditions used for the calibration of the NO_2-analyser

Measurement	Permeation unit ID	Permeation unit purity (%)	MSB chamber temperature (°C)	MSB chamber pressure (mbar)	Permeation rate (ng/min)	Manufacturer
Before BIPM	PU1	99.5	38	1300	490	VICI Metronics
M1 after BIPM	PU2	100.0	40	2600	626	VICI Metronics
M2 after BIPM	PU3	99.0	40	2600	544	Fine Metrology
M3 after BIPM	PU4	99.0	40	2600	527	Fine Metrology

Note: For measurement 1 before BIPM, the permeation rate was measured in another magnetic suspension balance as the one used for the direct generation of the reference gas mixtures. For measurements 2 and 3 before BIPM, the permeation rate was measured in the same magnetic suspension balance as used for the generation.

Both gas cylinders were dynamically diluted with N_2 6.0 (without further purification) in a system of critical orifices combined with 2 pressure controllers (Bronkhorst) and a mass flow controller (Vögtlin) (Fig. 1). Several dilution flowrates were tested to reach the calibrated concentration range of the analyzer. As for its calibration, the pressure at the comparator inlet was maintained constant at 962±3 mbar (LNI Swissgas). The critical orifice system was maintained at constant temperature (22°C) in a water bath (Variostat). Before each measurement, the cylinders were homogenized during 2 hours.

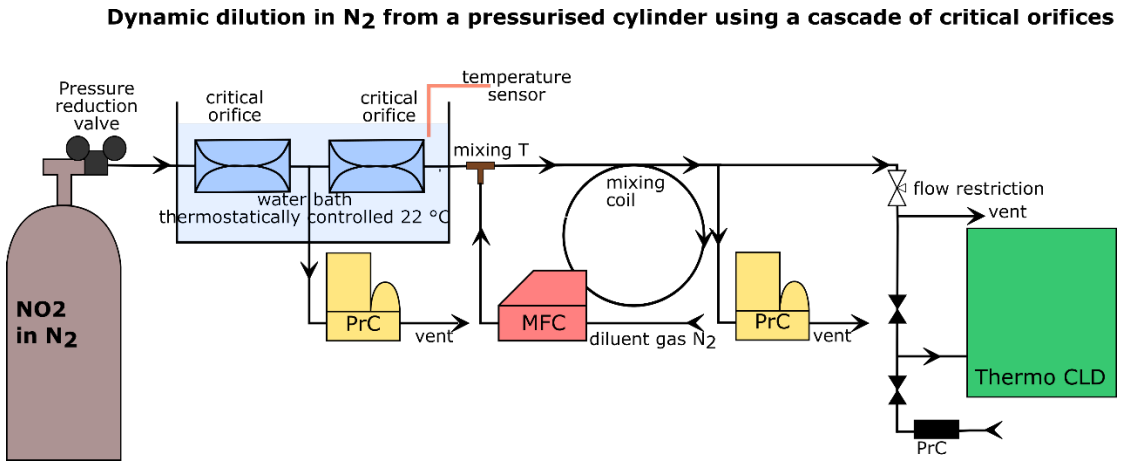


Figure 2: Dilution scheme of NO_2 cylinder

All the flows were calibrated with the primary volumeter of METAS.

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:

Cylinder 1

Date	Component	Mole fraction	Expanded Uncertainty	Coverage factor	Measurement technique
-	-	-	-	-	-

NIM

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).
Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.
Proposed dates: 2018.
Coordinating laboratory:
Bureau International des Poids et Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.
Study Coordinator:
Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org
Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	National Institute of Metrology, China(NIM)		
Address	NO. 18 Bei san huan Dong lu, Chao yang Dist., Beijing, P.R. China (100029)		
Contact person	Tiqiang Zhang, Defa Wang, Hushu Guo, Qian Han		
Telephone	+86-10-64525337	Fax	+86-10-64204601
Email*	zhangtq@nim.ac.cn		
Serial number of cylinder received	L62804135	L62804125	
Cylinder pressure as received	10MPa	10MPa	

A2. Results

Cylinder 1 (L62804135) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $(U\ x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	25/12/2017	10.001	0.010	2
(Stability 1)	26/1/2018	9.936	0.034	2
(Stability 2)	2/3/2018	9.904	0.034	2
(Stability 3)	26/3/2018	9.890	0.034	2

Cylinder 2 (L62804125) – Before shipping to the BIPM Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $(U\ x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	25/12/2017	9.998	0.010	2
(Stability 1)	26/1/2018	9.947	0.034	2
(Stability 2)	2/3/2018	9.909	0.034	2
(Stability 3)	26/3/2018	9.896	0.034	2

Cylinder 1 (L62804135) - Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $(U\ x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

Cylinder 2 (L62804125) - Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $(U\ x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

A3. Uncertainty Budget

The contributions of standard uncertainty were from preparation of gravimetric method and verification method.

$$u_{\mathrm{r}}\left(x_{NO2}\right)=\sqrt{u_{\mathrm{r,\,prep}}^{2}+u_{\mathrm{r,\,ver}}^{2}}$$

Here, x_{NO2} represents the mole fraction of NO_2 in the cylinder, u_{r} is the relative standard uncertainty, $u_{\mathrm{r,\,prep}}$ and $u_{\mathrm{r,\,ver}}$ represent uncertainty from gravimetric preparation method and from verification method, resprectively.

Source of uncertainty	$u_{\mathrm{r,\,prep}}$	$u_{\mathrm{r,\,ver}}$
Relative standard uncertainty	0.05%	0.16%
Relative expanded uncertainty*	0.34%	

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

A4. Description of the procedure used during the gas analysis

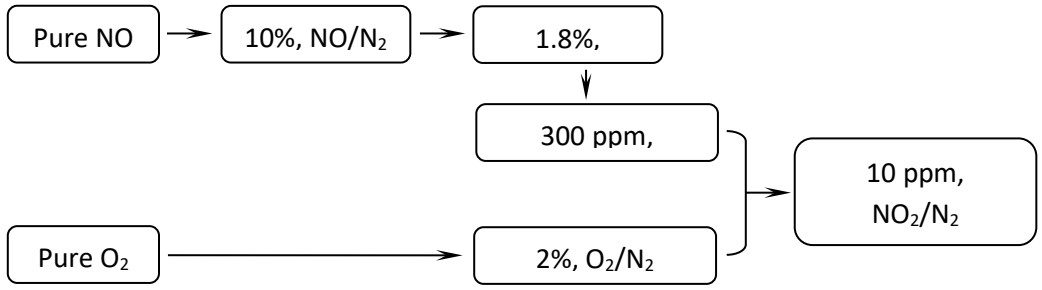
Please describe in detail the analytical method(s) used for gas analysis[6].

(1) Preparation method

1st: Pure NO was diluted by nitrogen to reach to the mole fraction of 300 μmol/mol via 2 steps.

2ed: The 2% mole fraction oxygen mixture was prepared by mixing oxygen and nitrogen.

3rd: The final standard gas (and calibration gas used for each month mearement) was prepared by adding a certain amount of 300 μmol/mol NO/N_2 and 2% mol/mol O_2/N_2 into pure nitrogen, this gas mixture aimed to contain 10 μmol/mol NO_2 and 980 μmol/mol O_2.



Specification of balance (Model No., Readability, etc.)

1) Metter XP26003L, capacity 26 kg, Readability 1 mg

2) Sartorius-ME614S, capacity 610 g, Readability 0.1 mg

[6] 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.

Weighing method (A-B-A, Substitution method, etc.)

Substitution method, reference cylinder (A-B-A)

Concentration's calculation equation is according to ISO 6142:

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

Components uncertainties are calculated with below equation:

$$u^2(x_i) = \sum_{A=1}^{P}\left(\frac{\partial x_i}{\partial m_A}\right)^2 u^2(m_A) + \sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial M_i}\right)^2 u^2(M_i) + \sum_{A=1}^{P}\sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial x_{i,A}}\right)^2 u^2(x_{i,A})$$

(2) Pre-treatment of the cylinder

The cylinders were found having an adsorption of NO_2, which leads to the negative effects for the long-term stability of NO_2 mixture. To decrease this effect, some treatments to the cylinders were carried out. First, the cylinders were heated to 50℃ and were kept for at least 15 hours when pumping to vacuum. Second, 100 μmol/mol NO_2/N_2 were used for the presaturation treatment of the cylinders' inner wall, the gas was contained in the cylinders for no less than 2 days.

(3) Purity analysis of 'pure' components

Purity table for N_2

Component	Method	Mole fraction (μmol/mol)	Distribution	Uncertainty (μmol/mol)
O_2	Oxygen Analyzer	0.05	Rectangular	0.03
Ar	GC-PDHID	45.0	Normal	0.9
H_2	GC-PDHID	0.05	Rectangular	0.03
H_2O	CRDs	0.2	Rectangular	0.12
CO	GC-PDHID	0.05	Rectangular	0.03

CO_2	GC-PDHID	0.05	Rectangular	0.03
CH_4	GC-PDHID	0.05	Rectangular	0.03
NO	APIMS	2.7×10^{-3}	Normal	1.3×10^{-3}
N_2		999954.40	-	0.92

Purity table for NO

Component	Method	Mole fraction (μmol/mol)	Distribution	Uncertainty (μmol/mol)
N_2O	FTIR	430.0	Normal	43.0
NO_2	FTIR	880.0	Normal	88.0
HNO_3	FTIR	200.0	Normal	100
N_2	GC-PDHID	100.0	Normal	20.0
NO		998390.0	-	141.4

Purity table for O_2

Component	Method	Mole fraction (μmol/mol)	Distribution	Uncertainty (μmol/mol)
N_2	GC-PDHID	2.5	Rectangular	1.4
Ar	GC-PED	1.0	Rectangular	0.6
H_2	GC-PDHID	0.25	Rectangular	0.14
H_2O	CRDs	1.0	Rectangular	0.6
CO_2	GC-PDHID	0.47	Normal	0.03
CH_4	GC-PDHID	0.25	Rectangular	0.14
O_2		999994.4	-	1.7

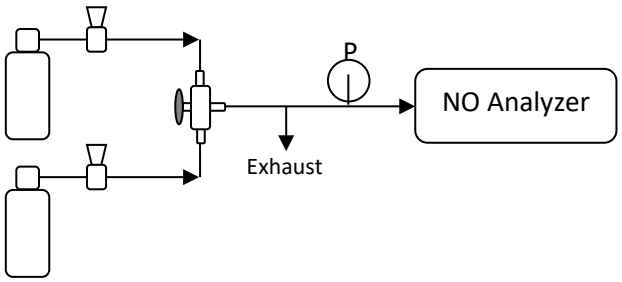
(4) Analysis method

1) Instrument

Thermo NOx analyzer (42i-HL)

2) Description of the procedure

Two standard cylinders with similar concentration were connected to pressure regulator. By using the PFA tube(1/4'), two pressure regulators and analyzer were connected to a three-way valve respectively. The sample in two standard cylinders can enter instrument respectively by changing the direction of there-way valve. The sample went through the instrument for analyzing, the inlet pressure of the analyzer was controlled at about 2.0 psi, and the flow rate of the sample was controlled at about 0.5 L/min. The analysis time of each sample was around 10 minutes and the mode was set at manual mode for analyzing only NOx. When sampling, 'A-B-A-B-A' type calibration was used.



A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM: 10Mpa for both cylinders.

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:

Cylinder 1

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

Cylinder 2

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

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).
Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.
Proposed dates: 2018.
Coordinating laboratory:
Bureau International des Poids et Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.
Study Coordinator:
Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org
Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	National Institute of Metrology, China(NIM)		
Address	NO. 18 Bei san huan Dong lu, Chao yang Dist., Beijing, P.R. China (100029)		
Contact person	Tiqiang Zhang, Defa Wang, Shuguo Hu, Qiao Han		
Telephone	+86-10-64525337	Fax	+86-10-64204601
Email*	zhangtq@nim.ac.cn		
Serial number of cylinder received	L62804135	L62804125	
Cylinder pressure as received	10MPa	10MPa	

A2. Results

Cylinder 1 (L62804135) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $(U\ x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	25/12/2017	10.001	0.010	2
(Stability 1)	26/1/2018	9.936	0.034	2
(Stability 2)	2/3/2018	9.904	0.034	2
(Stability 3)	26/3/2018	9.890	0.034	2

Cylinder 2 (L62804125) – Before shipping to the BIPM Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $(U\ x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	25/12/2017	9.998	0.010	2
(Stability 1)	26/1/2018	9.947	0.034	2
(Stability 2)	2/3/2018	9.909	0.034	2
(Stability 3)	26/3/2018	9.896	0.034	2

Cylinder 1 (L62804135) - Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $(U\ x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	24/5/2019	9.769	0.033	2
(Stability 5)	28/6/2019	9.806	0.033	2
(Stability 6)	24/7/2019	9.785	0.033	2

Cylinder 2 (L62804125) - Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $(U\ x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	29/5/2019	9.737	0.033	2
(Stability 5)	28/6/2019	9.759	0.033	2
(Stability 6)	24/7/2019	9.748	0.033	2

A3. Uncertainty Budget

The contributions of standard uncertainty were from preparation of gravimetric method and verification method.

$$u_{\mathrm{r}}\left(x_{NO2}\right)=\sqrt{u_{\mathrm{r,\,prep}}^{2}+u_{\mathrm{r,\,ver}}^{2}}$$

Here, x_{NO2} represents the mole fraction of NO_2 in the cylinder, u_{r} is the relative standard uncertainty, $u_{\mathrm{r,\,prep}}$ and $u_{\mathrm{r,\,ver}}$ represent uncertainty from gravimetric preparation method and from verification method, resprectively.

Source of uncertainty	$u_{\mathrm{r,\,prep}}$	$u_{\mathrm{r,\,ver}}$
Relative standard uncertainty	0.05%	0.16%
Relative expanded uncertainty*	0.34%	

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

A4. Description of the procedure used during the gas analysis

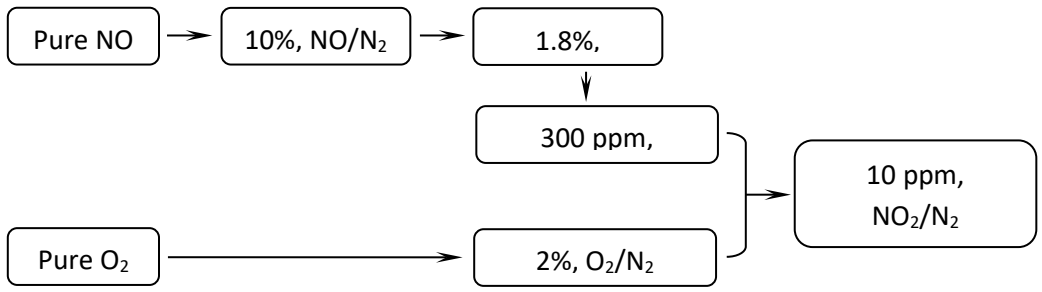
Please describe in detail the analytical method(s) used for gas analysis[7].

(1) Preparation method

1st: Pure NO was diluted by nitrogen to reach to the mole fraction of 300 µmol/mol via 2 steps.

2ed: The 2% mole fraction oxygen mixture was prepared by mixing oxygen and nitrogen.

3rd: The final standard gas (and calibration gas used for each month mearement) was prepared by adding a certain amount of 300 µmol/mol NO/N_2 and 2% mol/mol O_2/N_2 into pure nitrogen, this gas mixture aimed to contain 10 µmol/mol NO_2 and 980 µmol/mol O_2.



Specification of balance (Model No., Readability, etc.)

1) Metter XP26003L, capacity 26 kg, Readability 1 mg

[7] 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.

2) Sartorius-ME614S, capacity 610 g, Readability 0.1 mg

Weighing method (A-B-A, Substitution method, etc.)

Substitution method, reference cylinder (A-B-A)

Concentration's calculation equation is according to ISO 6142:

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

Components uncertainties are calculated with below equation:

$$u^2(x_i) = \sum_{A=1}^{P}\left(\frac{\partial x_i}{\partial m_A}\right)^2 u^2(m_A) + \sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial M_i}\right)^2 u^2(M_i) + \sum_{A=1}^{P}\sum_{i=1}^{n}\left(\frac{\partial x_i}{\partial x_{i,A}}\right)^2 u^2(x_{i,A})$$

(2) Pre-treatment of the cylinder

The cylinders were found having an adsorption of NO_2, which leads to the negative effects for the long-term stability of NO_2 mixture. To decrease this effect, some treatments to the cylinders were carried out. First, the cylinders were heated to 50℃ and were kept for at least 15 hours when pumping to vacuum. Second, 100 μmol/mol NO_2/N_2 were used for the presaturation treatment of the cylinders' inner wall, the gas was contained in the cylinders for no less than 2 days.

(3) Purity analysis of 'pure' components

Purity table for N_2

Component	Method	Mole fraction (μmol/mol)	Distribution	Uncertainty (μmol/mol)
O_2	Oxygen Analyzer	0.05	Rectangular	0.03
Ar	GC-PDHID	45.0	Normal	0.9
H_2	GC-PDHID	0.05	Rectangular	0.03
H_2O	CRDs	0.2	Rectangular	0.12

CO	GC-PDHID	0.05	Rectangular	0.03
CO_2	GC-PDHID	0.05	Rectangular	0.03
CH_4	GC-PDHID	0.05	Rectangular	0.03
NO	APIMS	2.7×10^{-3}	Normal	1.3×10^{-3}
N_2		999954.40	-	0.92

Purity table for NO

Component	Method	Mole fraction (μmol/mol)	Distribution	Uncertainty (μmol/mol)
N_2O	FTIR	430.0	Normal	43.0
NO_2	FTIR	880.0	Normal	88.0
HNO_3	FTIR	200.0	Normal	100
N_2	GC-PDHID	100.0	Normal	20.0
NO		998390.0	-	141.4

Purity table for O_2

Component	Method	Mole fraction (μmol/mol)	Distribution	Uncertainty (μmol/mol)
N_2	GC-PDHID	2.5	Rectangular	1.4
Ar	GC-PED	1.0	Rectangular	0.6
H_2	GC-PDHID	0.25	Rectangular	0.14
H_2O	CRDs	1.0	Rectangular	0.6
CO_2	GC-PDHID	0.47	Normal	0.03
CH_4	GC-PDHID	0.25	Rectangular	0.14
O_2		999994.4	-	1.7

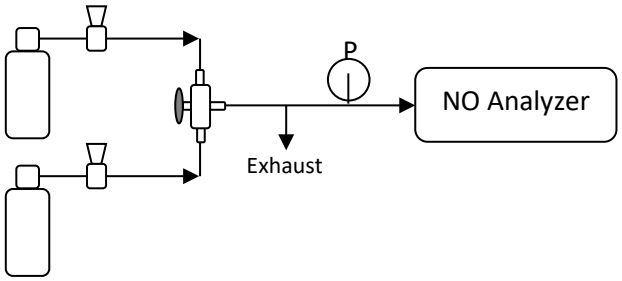
(4) Analysis method

1) Instrument

Thermo NOx analyzer (42i-HL)

2) Description of the procedure

Two standard cylinders with similar concentration were connected to pressure regulator. By using the PFA tube(1/4'), two pressure regulators and analyzer were connected to a three-way valve respectively. The sample in two standard cylinders can enter instrument respectively by changing the direction of there-way valve. The sample went through the instrument for analyzing, the inlet pressure of the analyzer was controlled at about 2.0 psi, and the flow rate of the sample was controlled at about 0.5 L/min. The analysis time of each sample was around 10 minutes and the mode was set at manual mode for analyzing only NOx. When sampling, 'A-B-A-B-A' type calibration was used.



A5. Complementary information on the cylinder

Please report the value of the pressure left in the cylinder before shipment to the BIPM: 10Mpa for both cylinders.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:

Cylinder 1

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

Cylinder 2

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

NMIA

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).
Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.
Proposed dates: 2018.

Coordinating laboratory:
Bureau International des Poids et Mesures Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	National Measurement Institute, Australia		
Address	36 BRADFIELD RD. LINDFIELD NSW 2070 Australia		
Contact person	DAMIAN SMEULDERS		
Telephone	+61 2 84673534	Fax	
Email*	gas@measurement.gov.au		
Serial number of cylinder received	MK0806 and MK0807		
Cylinder pressure as received	125 bar		

A2. Results

Cylinder 1 – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	16/03/2018 MK0806	10.015	0.028	2
(Stability 1)	5/4/18 (wet regulator)	9.74	0.32	2
(Stability 2)	5/4/18	9.97	0.09	2
(Stability 3)	6/4/18	9.95	0.17	2

Cylinder 2– Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	16/03/2018 MK0807	10.140	0.025	2
(Stability 1)	5/4/18	10.27	0.2	2
(Stability 2)	5/4/18	10.22	0.09	2
(Stability 3)	6/4/18	10.22	0.15	2

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

Cylinder 2- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Preparation: Standard uncertainty ~0.013 umol/mol.
Preparation uncertainty included uncertainty due to gravimetric processes and purity of source gases.
Verification produced a standard uncertainty of around 0.09 umol/mol
Combined expanded uncertainty was rounded to 0.20 umol/mol to cover observed variation in cylinders during testing.

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[1].

Mixtures were verified on a Nicolet FTIR with 10m gas cell. Cylinders were analysed 6 times over a three week period. The verification identified 3 mixtures that were in agreement. Initially the verification was problematic due to regulators containing moisture. Some regulators were changed and the agreement in the analysis of the cylinders improved. 2 of the 3 mixtures that were in agreement were selected to be sent to the BIPM.

A5. Complementary information on the cylinder

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

125 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:

Cylinder 1

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

Cylinder 2

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

[1] 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.

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:
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This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	National Measurement Institute, Australia		
Address	36 BRADFIELD RD. LINDFIELD NSW 2070 Australia		
Contact person	DAMIAN SMEULDERS		
Telephone	+61 2 84673534	Fax	
Email*	gas@measurement.gov.au		
Serial number of cylinder received	MK0806 and MK0807		
Cylinder pressure as received	125 bar		

A2. Results

Cylinder 1 – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	16/03/2018 MK0806	10.015	0.028	2
(Stability 1)	5/4/18 (wet regulator)	9.74	0.32	2
(Stability 2)	5/4/18	9.97	0.09	2
(Stability 3)	6/4/18	9.95	0.17	2

Cylinder 2– Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	16/03/2018 MK0807	10.140	0.025	2
(Stability 1)	5/4/18	10.27	0.2	2
(Stability 2)	5/4/18	10.22	0.09	2
(Stability 3)	6/4/18	10.22	0.15	2

Cylinder 1- Post BIPM measurements (MK0806)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	5/08/2019	9.85	0.6	2
(Stability 5)	6/08/2019	10.01	0.22	2
(Stability 6)	6/08/2019	10.00	0.22	2

Cylinder 2- Post BIPM measurements (MK0807)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	5/08/2019	10.02	0.24	2
(Stability 5)	6/08/2019	10.02	0.24	2
(Stability 6)	6/08/2019	10.01	0.24	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Preparation: Standard uncertainty ~0.013 umol/mol.
Preparation uncertainty included uncertainty due to gravimetric processes and purity of source gases.
Verification produced a standard uncertainty of around 0.09 umol/mol
Combined expanded uncertainty was rounded to 0.20 umol/mol to cover observed variation in cylinders during testing.

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[1].

Mixtures were verified on a Nicolet FTIR with 10m gas cell. Cylinders were analysed 6 times over a three week period. The verification identified 3 mixtures that were in agreement. Initially the verification was problematic due to regulators containing moisture. Some regulators were changed and the agreement in the analysis of the cylinders improved. 2 of the 3 mixtures that were in agreement were selected to be sent to the BIPM.

A5. Complementary information on the cylinder

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

125 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:

Cylinder 1 MK0806 (NMIA 1)

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

Cylinder 2

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

NMISA

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).
Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.
Proposed dates: 2018.

Coordinating laboratory:
Bureau International des Poids et Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:

Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	National Metrology Institute of South Africa		
Address	CSIR Campus Building 5 Meiring Naude Road Brummeria Pretoria 0182		
Contact person	Dr. James Tshilongo		
Telephone	+27 12 841 2589	Fax	+27 12 841 2131/4458
Email*	jtshilongo@nmisa.org		
Serial number of cylinder received	D62 6554		
Cylinder pressure as received	8.5 MPa		
Serial number of cylinder received	D62 6618		
Cylinder pressure as received	10 MPa		

A2. Results

Cylinder (D62 6554) 1 – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	07 March 2018	9,988	0,00096	k=2
(Stability 1)	08 March 2018	9,938	0,136	k=2
(Stability 2)	15 April 2018	9,943	0,168	k=2
(Stability 3)	07 May 2018	9,856	0,137	k=2

Result (Cylinder 1: D62 6554)

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
9,99	0,16	k=2

Cylinder (D62 6618) 2– Before shipping to the BIPM -

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	04 March 2018	10,0423	0,00096	k=2
(Stability 1)	12 March 2018	9,958	0,143	k=2
(Stability 2)	15 April 2018	10,029	0,144	k=2
(Stability 3)	07 May 2018	9,948	0,163	k=2

Result (Cylinder 2: D62 6618)

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
10,04	0,16	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The results for each day yielded an average mole fraction and standard uncertainty. The predicted mole fractions for the sample for the three days were averaged, and a standard deviation calculated for the three values. The uncertainties for the three different days and the verification uncertainty (ESDM) were combined as shown in Equation 1:

$$u_c^2 = \frac{u_{Day1}^2 + u_{Day2}^2 + u_{Day3}^2}{3} \ldots + (u_{ESDM})^2 + x_{grv}^2$$ Equation 1

This combined standard uncertainty was converted to an expanded uncertainty by multiplying by a coverage factor k = 2 as in Equation 2.

$U = k \times u_c$, where k = 2..... Equation 2

A4. Description of the preparation method

The NO_2 standards were gravimetrically prepared from pure nitric oxide, pure oxygen and pure nitrogen. The production diagram for the overall NO_2 standards is show in **figure 1**

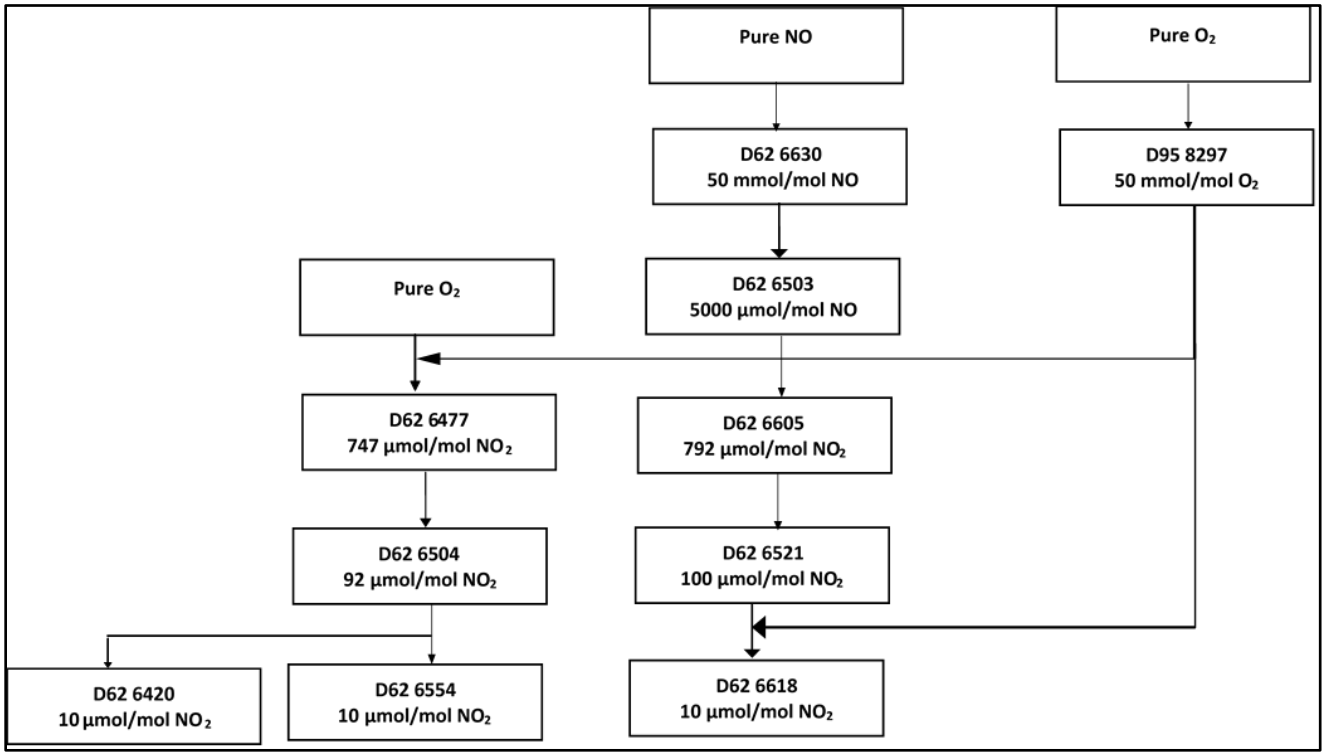

Figure 1: Production diagram for the nitrogen dioxide gas mixture

A5. Additional information for the samples

Purity tables for each of the final mixtures, including gravimetric uncertainties are shown below;

The purity table for mixture D62 6554 is shown in table 1 below:

Table 1: Purity table of D62 6554

D62 6554		
Component	**Mol/mol**	
N_2	0.9989086237999	0.0000024210390
O_2	0.0010224997119	0.0000000201507
Ar	0.0000538465723	0.0000024232565
NO_2	0.0000099888095	0.0000000004777
H_2O	0.0000000099956	0.0000000051606
CO_2	0.0000000098575	0.0000000010143
H_2	0.0000000089956	0.0000000046670
CO	0.0000000071098	0.0000000035543
C_2H_6	0.0000000062996	0.0000000032669
CH_4	0.0000000042917	0.0000000022258
N_2O	0.0000000001496	0.0000000000870
C_XH_Y	0.0000000000050	0.0000000000029

The purity table for mixture D62 6618 is shown in table 2 below:

Table 2: purity table of D62 6618

D62 6618		
Component	**Mol/mol**	
N_2	0.9993231260143	0.0000024475825
O_2	0.0006078954837	0.0000003988938
Ar	0.0000538679551	0.0000024088070
NO_2	0.0000100425992	0.0000000004811
H_2O	0.0000000099994	0.0000000051299
CO_2	0.0000000099635	0.0000000010086
H_2	0.0000000089994	0.0000000046392
CO	0.0000000070174	0.0000000035330
C_2H_6	0.0000000062998	0.0000000032474
CH_4	0.0000000042910	0.0000000022125
N_2O	0.0000000001506	0.0000000000874
C_XH_Y	0.0000000000050	0.0000000000029

A6. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[1].

The measurements were performed on the ABB Limas UV analyser using NO_2 standards from 10-100 µmol/mol. The multipoint calibration method was used for the analysis of the comparison sample. The measurements were performed over three months, with one analysis per month.

A7. 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:

Cylinder 1: D62 6554

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty nmol/mol	Coverage factor	Measurement technique
08 May 2018	HNO_3	170	12.5	k=2	Fourier transform infrared spectroscopy

Cylinder 1: D62 6618

No measurements of other components were measured in the cylinder; however, it is expected that HNO_3 will be present in the mixture between 150-300 nmol/mol.

[1] 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.

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).
Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.
Proposed dates: 2018.
Coordinating laboratory:
Bureau International des Poids et Mesures
Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department
Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:

Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	National Metrology Institute of South Africa		
Address	CSIR Campus Building 5 Meiring Naude Road Brummeria Pretoria 0182		
Contact person	Dr. James Tshilongo		
Telephone	+27 12 841 2589	Fax	+27 12 841 2131/4458
Email*	jtshilongo@nmisa.org		
Serial number of cylinder received	D62 6554		
Cylinder pressure as received	8.5 MPa		
Serial number of cylinder received	D62 6618		
Cylinder pressure as received	10 MPa		

A2. Results

Cylinder (D62 6554) 1 – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	07 March 2018	9,988	0,00096	k=2
(Stability 1)	08 March 2018	9,938	0,136	k=2
(Stability 2)	15 April 2018	9,943	0,168	k=2
(Stability 3)	07 May 2018	9,856	0,137	k=2

Result (Cylinder 1: D62 6554)

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
9,99	0,16	k=2

Cylinder (D62 6618) 2– Before shipping to the BIPM -

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	04 March 2018	10,0423	0,00096	k=2
(Stability 1)	12 March 2018	9,958	0,143	k=2
(Stability 2)	15 April 2018	10,029	0,144	k=2
(Stability 3)	07 May 2018	9,948	0,163	k=2

Result (Cylinder 2: D62 6618)

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
10,04	0,16	2

Cylinder (D62 6554) 1 – Post BIPM Measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	25 April 2019	10,007	0,092	k=2
(Stability 5)	27 May 2019	9,985	0,116	k=2
(Stability 6)	25 July 2019	9,999	0,111	k=2

Result (Cylinder 1: D62 6554) including stability measurements

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
9,99	0,16	k=2

Cylinder (D62 6618) 2 – Post BIPM Measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	25 April 2019	10,02	0,089	k=2
(Stability 5)	27 May 2019	10,01	0,118	k=2
(Stability 6)	25 July 2019	10,00	0,101	k=2

Result (Cylinder 2: D62 6618) including stability measurements

Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
10,04	0,16	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The results for each day yielded an average mole fraction and standard uncertainty. The predicted mole fractions for the sample for the three days were averaged, and a standard deviation calculated for the three values. The uncertainties for the three different days and the verification uncertainty (ESDM) were combined as shown in Equation 1:

$$u_c^2 = \frac{u_{Day1}^2+u_{Day2}^2+u_{Day3}^2}{3} \ldots + \left(u_{Stability}\right)^2 + x_{grv}^2 \qquad \text{Equation 1}$$

This combined standard uncertainty was converted to an expanded uncertainty by multiplying by a coverage factor k = 2 as in Equation 2.

$U = k \times u_c$, where k = 2 ..... Equation 2

A4. Description of the preparation method

The NO_2 standards were gravimetrically prepared from pure nitric oxide, pure oxygen and pure nitrogen. The production diagram for the overall NO_2 standards is show in **figure 1**

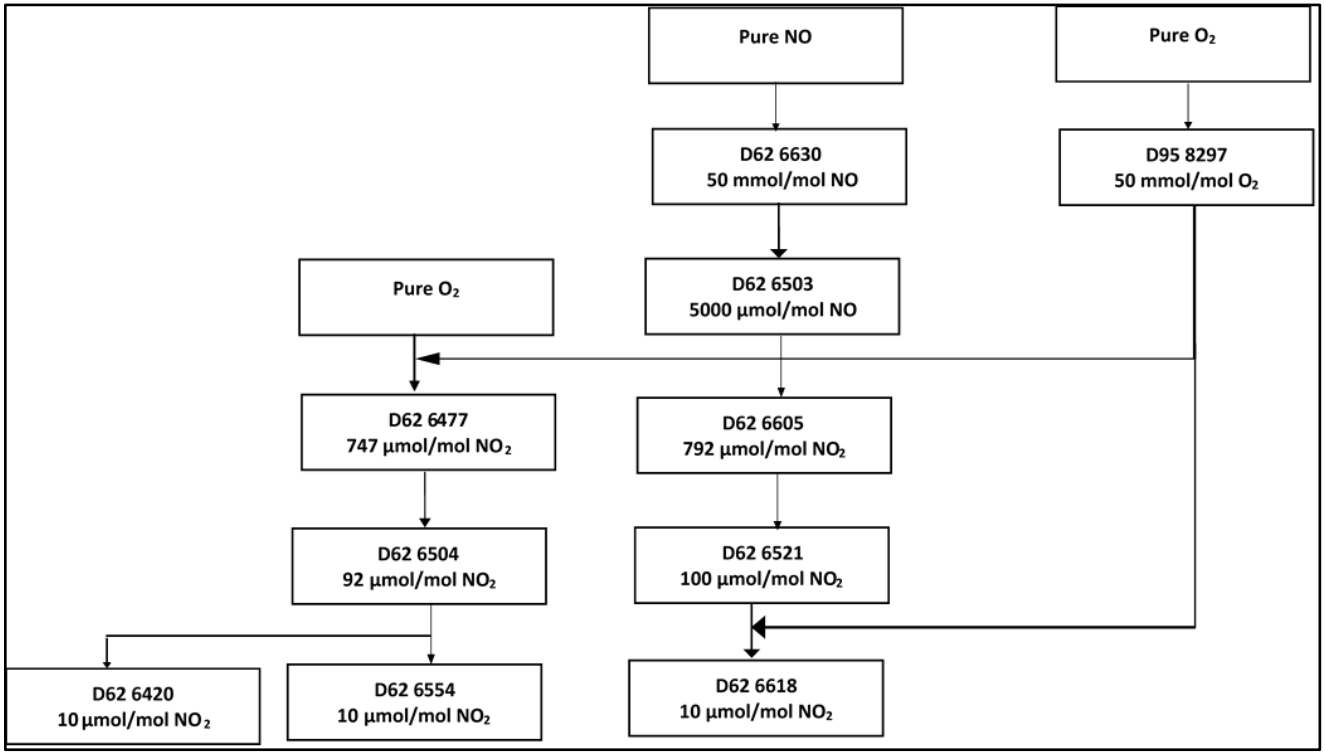

Figure 1: Production diagram for the nitrogen dioxide gas mixture

A5. Additional information for the samples

Purity tables for each of the final mixtures, including gravimetric uncertainties are shown below;

The purity table for mixture D62 6554 is shown in table 1 below:

Table 1: Purity table of D62 6554

D62 6554		
Component	**Mol/mol**	
N_2	0.9989086237999	0.0000024210390
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Ar	0.0000538465723	0.0000024232565
NO_2	0.0000099888095	0.0000000004777
H_2O	0.0000000099956	0.0000000051606
CO_2	0.0000000098575	0.0000000010143
H_2	0.0000000089956	0.0000000046670
CO	0.0000000071098	0.0000000035543
C_2H_6	0.0000000062996	0.0000000032669
CH_4	0.0000000042917	0.0000000022258
N_2O	0.0000000001496	0.0000000000870
C_XH_Y	0.0000000000050	0.0000000000029

The purity table for mixture D62 6618 is shown in table 2 below:

Table 2: purity table of D62 6618

D62 6618		
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Ar	0.0000538679551	0.0000024088070
NO_2	0.0000100425992	0.0000000004811
H_2O	0.0000000099994	0.0000000051299
CO_2	0.0000000099635	0.0000000010086
H_2	0.0000000089994	0.0000000046392
CO	0.0000000070174	0.0000000035330
C_2H_6	0.0000000062998	0.0000000032474
CH_4	0.0000000042910	0.0000000022125
N_2O	0.0000000001506	0.0000000000874
C_XH_Y	0.0000000000050	0.0000000000029

A6. Description of the procedure used during the gas analysis

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

The measurements were performed on the ABB Limas UV analyser using NO_2 standards from 10-100 µmol/mol. The multipoint calibration method was used for the analysis of the comparison sample. The measurements were performed over three months, with one analysis per month.

A7. 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:

Cylinder 1: D62 6554

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty nmol/mol	Coverage factor	Measurement technique
08 May 2018	HNO_3	Below detection limit of the FTIR	N/A	N/A	Fourier transform infrared spectroscopy

Cylinder 2: D62 6618

HNO_3 value was found to be below the detection limit of the FTIR using the 10m gas cell. The HNO_3 was not subtracted from the NO_2 value.

[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.

NPL

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen

(10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures

Chemistry Department

Pavillon de Breteuil

92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores

BIPM Chemistry Department

Phone: +33 (0)1 45 07 70 92

Fax: +33 (0)1 45 34 20 21

email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol.

Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	National Physical Laboratory		
Address	Hampton Road Teddington TW11 0LW		
Contact person	Dave Worton		
Telephone	+44 (0) 208 943 6591	Fax	
Email*	dave.worton@npl.co.uk		
Serial number of cylinder received	2448, S357		
Cylinder pressure as received	2448 – 12.0 MPa S357 – 9.0 MPa		

A2. Results

Cylinder 1 – Before shipping to the BIPM (2448)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	5th April 2018	9.99	0.07	2
(Stability 1)	19th April 2018	10.02	0.07	2
(Stability 2)	3rd May 2018	9.99	0.07	2
(Stability 3)	16th May 2018	10.02	0.07	2

Cylinder 2 – Before shipping to the BIPM (S357)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	5th April 2018	10.00	0.07	2
(Stability 1)	19th April 2018	10.04	0.07	2
(Stability 2)	3rd May 2018	10.01	0.07	2
(Stability 3)	16th May 2018	10.00	0.07	2

Cylinder 1 – Post BIPM measurements (2448)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				

Cylinder 2 – Post BIPM measurements (S357)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The estimated uncertainty for the measurement contains the following components:

- Purity analysis of NO, oxygen and nitrogen
- Gravimetric preparation (weighing and atomic weight uncertainties)
- Analytical validation

The table below details the uncertainty analysis. The preparation component includes estimated uncertainty from purity analysis, weighing and atomic weights.

		Relative Uncertainty (%)		
Identifier	Component	Preparation (*k=1*)	Validation (*k=1*)	Total (*k=2*)
2448	NO_2	0.007	0.350	0.700
S357	NO_2	0.007	0.350	0.700

To calculate the combined uncertainty, the uncertainties were combined as the square root of the sum of squares. The reported uncertainty of the result is based on standard uncertainties multiplied by a coverage factor of *k=2*, providing a level of confidence of approximately 95%.

A4. Description of the procedure used during the gas analysis

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

An ABB AO2020 LIMAS 11 UV analyser was used to validate the amount fraction of NO_2 in mixtures 2448 and S357. The analyser response to the matrix gas was recorded. The analyser response to a reference mixture was then recorded for a five minute period followed by either 2448 or S357 for the same time. This sequence was repeated four times. At the end of the experiment the analyser response to the matrix gas was recorded a second time. To minimise the effects from zero drift, a mean of the analyser response to the matrix gas before and after the experiment was used. The amount fractions of 2448 and S357 were then determined by multiplying the ratio of the analyser response to each mixture and the reference mixture (both were corrected for the analyser response to matrix gas) with the amount fraction of the reference mixture. These measurements were used to validate the gravimetric amount fractions submitted.

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

Measurements to study the stability of the mixtures were carried out over a 6 week period.

[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.

A5. Complementary information on the cylinder

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

2448 – 12.0 MPa

S357 – 9.0 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.

Cylinder 1 (2448)

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

Cylinder 2 (S357)

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

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures

Chemistry Department

Pavillon de Breteuil

92312 Sèvres Cedex, France.

Study Coordinator:

Edgar Flores

BIPM Chemistry Department

Phone: +33 (0)1 45 07 70 92

Fax: +33 (0)1 45 34 20 21

email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol.

Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	National Physical Laboratory

Address	Hampton Road Teddington TW11 0LW		
Contact person	Dave Worton		
Telephone	+44 (0) 208 943 6591	Fax	
Email*	dave.worton@npl.co.uk		
Serial number of cylinder received	2448, S357		
Cylinder pressure as received	2448 – 12.0 MPa S357 – 9.0 MPa		

A2. Results

Cylinder 1 – Before shipping to the BIPM (2448)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	5th April 2018	9.99	0.07	2
(Stability 1)	19th April 2018	10.02	0.07	2
(Stability 2)	3rd May 2018	9.99	0.07	2
(Stability 3)	16th May 2018	10.02	0.07	2

Cylinder 2 – Before shipping to the BIPM (S357)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	5th April 2018	10.00	0.07	2
(Stability 1)	19th April 2018	10.04	0.07	2
(Stability 2)	3rd May 2018	10.01	0.07	2
(Stability 3)	16th May 2018	10.00	0.07	2

Cylinder 1 – Post BIPM measurements (2448)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	8th May 2019	9.82	0.10	2
(Stability 5)*	-	-	-	-
(Stability 6)*	-	-	-	-

* We experienced difficulties to get a stable reading from this cylinder and were unable to get further stability measurements due to a lack of pressure.

Cylinder 2 – Post BIPM measurements (S357)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	8th May 2019	9.75	0.10	2
(Stability 5)	3rd June 2019	9.88	0.10	2
(Stability 6)	8th July 2019	9.81	0.10	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The estimated uncertainty for the measurement contains the following components:

- Purity analysis of NO, oxygen and nitrogen
- Gravimetric preparation (weighing and atomic weight uncertainties)
- Analytical validation

The table below details the uncertainty analysis. The preparation component includes estimated uncertainty from purity analysis, weighing and atomic weights.

		Relative Uncertainty (%)		
Identifier	Component	Preparation (*k=1*)	Validation (*k=1*)	Total (*k=2*)
2448	NO_2	0.007	0.350	0.700
S357	NO_2	0.007	0.350	0.700

To calculate the combined uncertainty, the uncertainties were combined as the square root of the sum of squares. The reported uncertainty of the result is based on standard uncertainties multiplied by a coverage factor of *k=2*, providing a level of confidence of approximately 95%.

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

Measurements to study the stability of the mixtures were carried out over a 6 week period.

A5. Complementary information on the cylinder

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

2448 – 12.0 MPa

S357 – 9.0 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.

Cylinder 1 (2448)

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

Cylinder 2 (S357)

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

[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.

SMU

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department Phone: +33 (0)1 45 07 70 92
Fax: +33 (0)1 45 34 20 21
email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	Slovak Institute of Metrology, SMU		
Address	Karloveska 63 SK-842 55 Bratislava Slovak Republic		
Contact person	Dr. Miroslava Valkova; Dr. Viliam Stovcik		
Telephone	+421 2 602 94211	Fax	
Email*	valkova@smu.gov.sk;stovcik@smu.gov.sk		
Serial number of cylinder received	Nr.1 : MY9742, Nr.2 : MY9728		
Cylinder pressure as received	13 MPa, 13MPa		

A2. Results

Cylinder 1 – Before shipping to the BIPM

MY9742

Description of measurement	**Date of measurement**	**Nitrogen dioxide mole fraction**	**Expanded uncertainty**	**Coverage factor**
(Preparation)	**4.1.2018**	**10.15**	**0.22**	**2**
(Stability 1)	**29.1.2018**	**10.18**	**0.21**	**2**
(Stability 2)	**27.2.2018**	**10.13**	**0.21**	**2**
(Stability 3)	**28.3.2018**	**10.11**	**0.21**	**2**

Cylinder 2– Before shipping to the BIPM

MY9728

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	4.1.2018	10.04	0.23	2
(Stability 1)	29.1.2018	10.05	0.23	2
(Stability 2)	27.2.2018	10.05	0.22	2
(Stability 3)	28.3.2018	10.06	0.22	2

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

Cylinder 2- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Sample cylinders for intercomparison and calibration of the instrument were prepared in SMU using static gravimetric method according to ISO 6142-1.

Purity of parent gases: Nitrogen, Oxygen and Nitrogen monoxide were measured using gas GC TCD, FID and FT-IR spectrometry.

Purity of both sample cylinders were checked using FT-IR spectrometer Varian Excalibur for the content of: N2O, HNO3, N2O4 components. No content of these componets were find - higher then 50 nmol/mol concentration (detection limit of the FT-IR instrument).

Uncertainty ugrav included weighing and purity, uanal-b least is analytical uncertainty calculated by B-least, ustab is uncertainty of the stability of NO2

and uconv is uncertainty of the conversion to NO2 after adding of Oxygen. Cylinders used for intercomparison have Aculife IV passivation of inner surface.

Table 1 Uncertainty budget

Source	Uncertainty/µmol/mol	Distribution	Sensitivity coefficient	Standard uncertainty/ µmol/mol
ugrav	0.011	Normal	1	0.011
uanal-b least	0.044	Normal	1	0.044
ustab	0.075	Normal	1	0.075
uconv	0.070	Rectangular	1	0.070
u				0.110

U(k=2)= 0.22 µmol/mol 2.2 %rel.

A4. Description of the procedure used during the gas analysis

Please describe in detail the analytical method(s) used for gas analysis[1].

Mixtures were analysed on chemiluminescence Thermo 42C NO-NO2-NOx analyser. Three standards made by SMU were used for calibration according to ISO 6143 in range (10 - 15)µmol/mol. Calibration curve was fitted using B-least software from three mesuring cycles for calibration and measured gas samples. Goodness -of -fit for each masurement cycle was under 2. The final result was the average from 3 measuring cycles.

The samples and standards with flushed gas reducers were prepared for the measurement with outlet pressure 2 bars. Cylinders were connected to the multiposition gas valve in increasing order of concentration. Mass flow controller Brooks was used for the flow controlling before gas enter measuring instrument. Stabilization of one measurement last at least 15 minutes. After stabilization, ten readings of measured values were recorded manually. After each mesurement instrument was flushed by pure nitrogen.

A5. Complementary information on the cylinder

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

Cylinders were filled to the 13 MPa. Afte validation and stability measurements, pressure decrease to the 10 MPa in MY9742 and 11 MPa in MY9728 cylinder. Both cylinders contain Oxygen in less then 1000 µmol/mol concentration.

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:

Cylinder 1

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

Cylinder 2

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

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures Chemistry Department
Pavillon de Breteuil
92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores
BIPM Chemistry Department Phone: +33 (0)1 45 07 70 92
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Telephone	+421 2 602 94211	Fax	
Email*	valkova@smu.gov.sk;stovcik@smu.gov.sk		
Serial number of cylinder received	Nr.1 : MY9742, Nr.2 : MY9728		
Cylinder pressure as received	13 MPa, 13MPa		

A2. Results

Cylinder 1 – Before shipping to the BIPM

MY9742

Description of measurement	**Date of measurement**	**Nitrogen dioxide mole fraction**	**Expanded uncertainty**	**Coverage factor**
(Preparation)	**4.1.2018**	**10.15**	**0.22**	**2**
(Stability 1)	**29.1.2018**	**10.18**	**0.21**	**2**
(Stability 2)	**27.2.2018**	**10.13**	**0.21**	**2**
(Stability 3)	**28.3.2018**	**10.11**	**0.21**	**2**

Cylinder 2– Before shipping to the BIPM

MY9728

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	4.1.2018	10.04	0.23	2
(Stability 1)	29.1.2018	10.05	0.23	2
(Stability 2)	27.2.2018	10.05	0.22	2
(Stability 3)	28.3.2018	10.06	0.22	2

Cylinder 1- Post BIPM measurements

MY 9742

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	9.4.2019	10.13	0.26	2
(Stability 5)	2.5.2019	10.14	0.23	2
(Stability 6)	5.6.2019	10.13	0.24	2

Cylinder 2- Post BIPM measurements

MY 9728

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	9.4.2019	9.87	0.23	2
(Stability 5)	2.5.2019	9.88	0.23	2
(Stability 6)	5.6.2019	9.83	0.30	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Sample cylinders for intercomparison and calibration of the instrument were prepared in SMU using static gravimetric method according to ISO 6142-1.

Purity of parent gases: Nitrogen, Oxygen and Nitrogen monoxide were measured using gas GC TCD, FID and FT-IR spectrometry.

Purity of both sample cylinders were checked using FT-IR spectrometer Varian Excalibur for the content of: N2O, HNO3, N2O4 components.

No content of these componets were find - higher then 50 nmol/mol concentration (detection limit of the FT-IR instrument).

Uncertainty ugrav included weighing and purity, uanal-b least is analytical uncertainty calculated by B-least, ustab is uncertainty of the stability of NO2

and uconv is uncertainty of the conversion to NO2 after adding of Oxygen. Cylinders used for intercomparison have Aculife IV passivation of inner surface.

Table 1.Uncertainty budget

Uncertainty source	Standard uncertainty/µmol/mol	Distribution	Sensitivity coefficient	Contribution to standard uncertainty/ µmol/mol
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ustab	0.075	Normal	1	0.075
uconv	0.070	Rectangular	1	0.070
u				0.110

U(k=2)= 0.22 µmol/mol 2.2 %rel.

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The samples and standards with flushed gas reducers were prepared for the measurement with outlet pressure 2 bars. Cylinders were connected to the multiposition gas valve in increasing order of concentration. Mass flow controller Brooks was used for the flow controlling before gas enter measuring instrument. Stabilization of one measurement last at least 15 minutes. After stabilization, ten readings of measured values were recorded manually. After each mesurement instrument was flushed by pure nitrogen.

A5. Complementary information on the cylinder

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

Cylinders were filled to the 13 MPa. Afte validation and stability measurements, pressure decrease to the 10 MPa in MY9742 and 11 MPa in MY9728 cylinder. Both cylinders contain Oxygen in less then 1000 µmol/mol concentration.

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:

Cylinder 1

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

Cylinder 2

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

UME

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures

Chemistry Department

Pavillon de Breteuil

92312 Sèvres Cedex, France.

Study Coordinator:

Edgar Flores

BIPM Chemistry Department

Phone: +33 (0)1 45 07 70 92

Fax: +33 (0)1 45 34 20 21

email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol.

Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	**UME**		
Address	**TÜBİTAK UME - Gas Metrology Laboratory** **Baris Mah. Dr. Zeki Acar Cad. No:1** **41470 Gebze / Kocaeli TURKEY**		
Contact person	**Dr. Tanıl Tarhan**		
Telephone	**+ 90 262 679 5000 / 6401**	**Fax**	**+ 90 262 679 5001**
Email*	**tanil.tarhan@tubitak.gov.tr**		
Serial number of cylinder received	**PSM499783, PSM499791**		
Cylinder pressure as received			

A2. Results

Cylinder 1: **PSM499783** – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	25.12.2017	9.851	0.007	2
(Stability 1)	17.01.2018	9.913	0.100	2
(Stability 2)	21.02.2018	9.790	0.098	2
(Stability 3)	21.03.2018	9.819	0.099	2

Cylinder 2: **PSM499791**– Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	25.12.2017	10.025	0.007	2
(Stability 1)	17.01.2018	10.028	0.101	2
(Stability 2)	21.02.2018	10.123	0.102	2
(Stability 3)	21.03.2018	10.109	0.101	2

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

Cylinder 2- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				
(Stability 5)				
(Stability 6)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The basis for the uncertainty budget is formed by the uncertainty evaluation from the gravimetric preparation and analytical measurements. Gravimetric preparation contains uncertainty sources from weighing and those from purity of the parent gases. Gravimetric preparation and its uncertainty evaluation have performed according to ISO 6142 [1]. The mole fraction of the mixtures and their measurement uncertainties were determined according to single point calibration.

The combined standard uncertainty was determined by the following equation:

$$u_c = \sqrt{u_m^2 + u_g^2}$$

where

u_m, standard uncertainty from measurements

u_g, standard uncertainty from gravimetric preparation

The expanded uncertainty was determined by multiplying the combined standard uncertainty by a coverage factor of 2 with a confidence interval of 95%.

A4. Description of the procedure used during the gas analysis

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

The nitrogen dioxide (NO_2) in nitrogen mixtures were analyzed with an analyzer, i.e., Thermo Fisher Scientific 42i Chemiluminescence NO-NO_2-NO_x Analyzer equipped with 16-Port Distribution Manifold. Verification of the mixtures was carried out by single point calibration using own gas standard.

Cylinders were equipped with low volume pressure reducers and connected to 16-port distribution manifold by means of PFA tubings. They were flushed three times before the first measurement. The standard and samples were transferred to the NO-NO_2-NO_x analyzer at a constant flow using mass flow controller. Zero flushing was performed between each measurement. Measurement results are displayed in Figure 1.

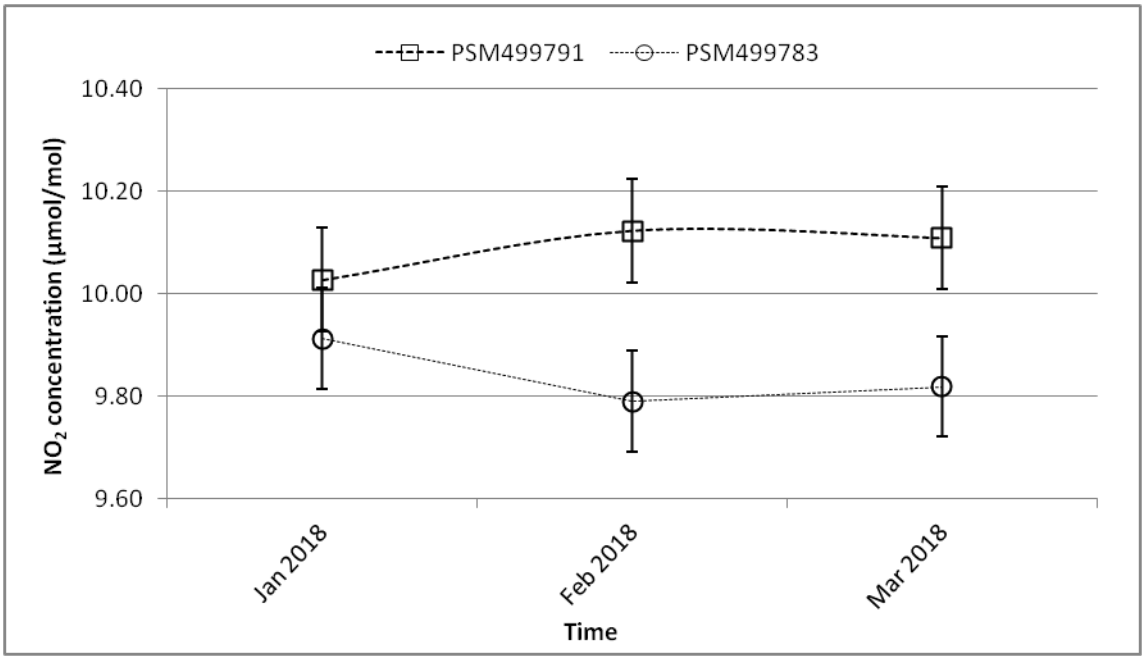

Figure 1. Measurements before sending the cylinders

A5. Complementary information on the cylinder

Mixtures were produced based on the reaction of NO with O_2 to NO_2. They were prepared from the pure components of NO, N_2, and O_2 according to the scheme displayed in Figure 2. Two different types of the pre-mixtures were prepared. These are; 3 %, 0.2 % and 0.02 % (200 µmol/mol) NO in N_2 and 4 % O_2 in N_2. Final NO in N_2 pre-mixture and 4 % O_2 in N_2 pre-mixture

[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.

were used together with pure N_2 for the final mixtures. By the reaction occurred between NO and O_2, desired final mixtures (nitrogen dioxide in nitrogen) were obtained.

Cylinder pressures before shipment to the BIPM are given below.

Cylinder Code	Pressure, bar
PSM499783	116
PSM499791	105

References:

[1] International Organization for Standardization, "ISO 6142 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods", ISO Geneva, 2001

Co-authors:
Tanıl TARHAN
Aylin BOZTEPE
Zeynep GÜLSOY

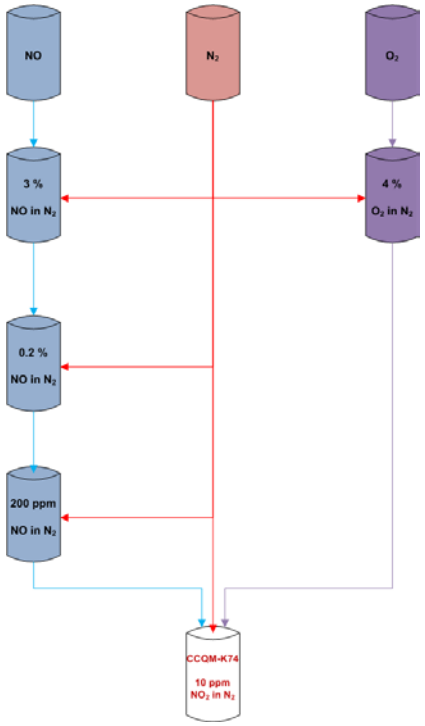

Figure 2. Preparation scheme for the mixtures

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures

Chemistry Department

Pavillon de Breteuil

92312 Sèvres Cedex, France.

Study Coordinator:

Edgar Flores

BIPM Chemistry Department

Phone: +33 (0)1 45 07 70 92

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email: edgar.flores@bipm.org

Return of the form:
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This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol.

Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	**UME**		
Address	**TÜBİTAK UME - Gas Metrology Laboratory** **Baris Mah. Dr. Zeki Acar Cad. No:1** **41470 Gebze / Kocaeli TURKEY**		
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Email*	**tanil.tarhan@tubitak.gov.tr**		
Serial number of cylinder received	**PSM499783, PSM499791**		
Cylinder pressure as received			

A2. Results

Cylinder 1: **PSM499783** – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	25.12.2017	9.851	0.007	2
(Stability 1)	17.01.2018	9.913	0.100	2
(Stability 2)	21.02.2018	9.790	0.098	2
(Stability 3)	21.03.2018	9.819	0.099	2

Cylinder 2: **PSM499791**– Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	25.12.2017	10.025	0.007	2
(Stability 1)	17.01.2018	10.028	0.101	2
(Stability 2)	21.02.2018	10.123	0.102	2
(Stability 3)	21.03.2018	10.109	0.101	2

Cylinder 1- **PSM499783**– Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	28.05.2019	9.717	0.099	2
(Stability 5)	27.06.2019	9.748	0.098	2
(Stability 6)	25.07.2019	9.745	0.098	2

Cylinder 2- **PSM499791**– Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	28.05.2019	10.003	0.102	2
(Stability 5)	27.06.2019	10.033	0.100	2
(Stability 6)	25.07.2019	10.024	0.100	2

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

The basis for the uncertainty budget is formed by the uncertainty evaluation from the gravimetric preparation and analytical measurements. Gravimetric preparation contains uncertainty sources from weighing and those from purity of the parent gases. Gravimetric preparation and its uncertainty evaluation have performed according to ISO 6142 [1]. The mole fraction of the mixtures and their measurement uncertainties were determined according to single point calibration.

The combined standard uncertainty was determined by the following equation:

$$u_c = \sqrt{u_m^2 + u_g^2}$$

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u_m, standard uncertainty from measurements

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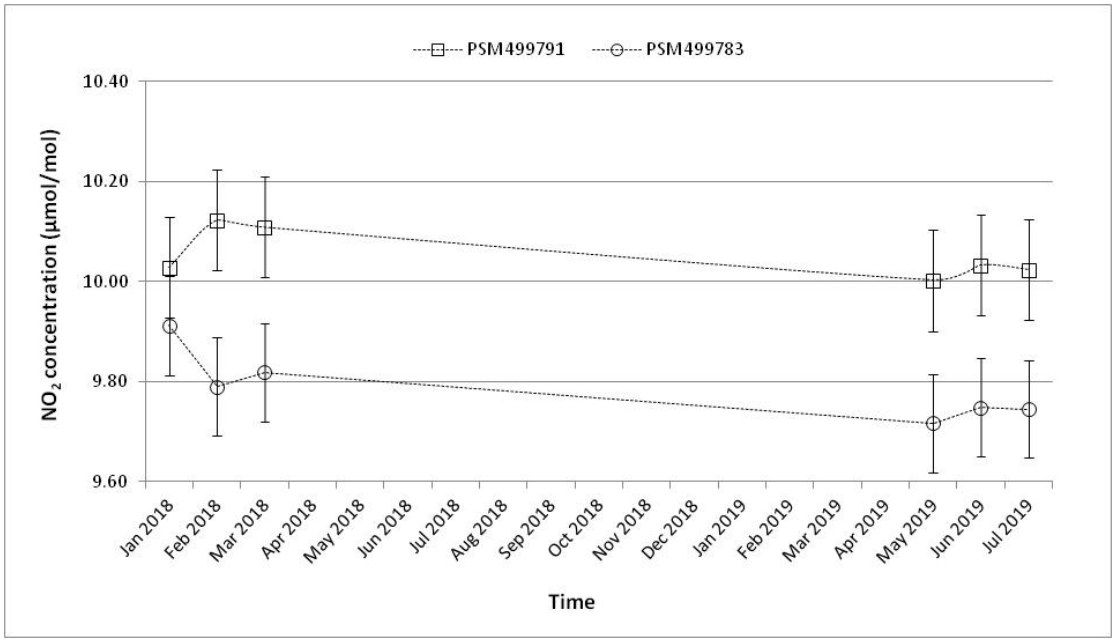

Figure 1. Measurements of the cylinders

A5. Complementary information on the cylinder

Mixtures were produced based on the reaction of NO with O_2 to NO_2. They were prepared from the pure components of NO, N_2, and O_2 according to the scheme displayed in Figure 2. Two

[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.

different types of the pre-mixtures were prepared. These are; 3 %, 0.2 % and 0.02 % (200 µmol/mol) NO in N_2 and 4 % O_2 in N_2. Final NO in N_2 pre-mixture and 4 % O_2 in N_2 pre-mixture were used together with pure N_2 for the final mixtures. By the reaction occurred between NO and O_2, desired final mixtures (nitrogen dioxide in nitrogen) were obtained.

Cylinder pressures before shipment to BIPM and after return to UME and are given below.

Cylinder Code	**Sending Pressure (bar)**	**Return Pressure (bar)**
PSM499783	116	99
PSM499791	105	90

References:

[1] International Organization for Standardization, "ISO 6142 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods", ISO Geneva, 2001

Co-authors:
Tanıl TARHAN
Aylin BOZTEPE
Zeynep GÜLSOY

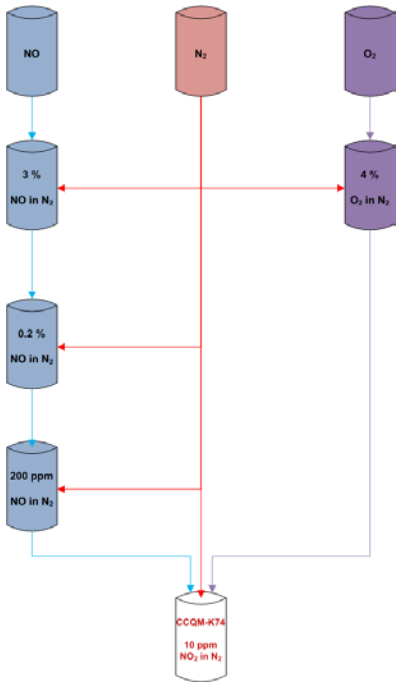

Figure 2. Preparation scheme for the mixtures

VNIIM

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures

Chemistry Department

Pavillon de Breteuil

92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores

BIPM Chemistry Department

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Return of the form:

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A1. General information

Institute	D.I. Mendeleyev Institute for Metrology (VNIIM)		
Address	19 Moskovsky pr., St. Petersburg, 190005, Russia		
Contact person	Leonid Konopelko		
Telephone	+7 812 315 11 45	Fax	+7 812 315 15 17
Email*	fhi@b10.vniim.ru		
Serial number of cylinder received	APEX 614632 (V=10 L)		5603778 (V=5L)
Cylinder pressure as received			

A2. Results

Cylinder 1 (№ APEX 614632) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
Preparation	15.03.18	9.979	0.007	2
Stability1 (Verification1)	20.03.18	9.89	0.14	2
Stability2 (Verification2)	04.04.18	9.95	0.14	2
Stability3 (Verification3)	18.04.18	9.89	0.14	2
Assigned (best) value*	20.04.18	**9.87**	0.14	2

Cylinder 2 (№ 5603778) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
Preparation	16.03.18	10.017	0.007	2
Stability1 (Verification1)	21.03.18	9.92	0.13	2
Stability2 (Verification2)	05.04.18	9.98	0.13	2
Stability3 (Verification3)	19.04.18	9.93	0.13	2
Assigned (best) value*	20.04.18	**9.97**	0.13	2

***Assigned (best) value – Gravimetric value taking into account the measured content of HNO_3**

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				

Cylinder 2- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Uncertainty budget for NO_2 mole fraction for the cylinder № APEX 614632

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Purity of N_2		999998.67 µmol/mol	B	Rectangular	0.20 µmol/mol	0.0000035	0.0000007
Purity of O_2		999997.72 µmol/mol	B	Rectangular	0.05 µmol/mol	$2.2*10^{-9}$	$1.1*10^{-10}$
Purity of NO_2		997100 µmol/mol	B	Rectangular	128 µmol/mol	0,0000128	0.00164
Weighing 1 stage premixture (≈1 %)	NO_2	7.91559621 g	A,B	Normal	0.002001 g	-1.240222	-0.002481
	N_2	478.1069511 g	A,B	Normal	0.009264 g	0.020533	0.000190
Weighing 2 stage premixture (240 µmol/mol^{-1})	1 pre-mixture	17.1116594 g	A,B	Normal	0.00225268 g	-0.568934	-0.001282
	N_2	663.7317226 g	A,B	Normal	0.0121975 g	0.014272	0.000174
	O_2	18.48796242 g	A,B	Normal	0.00230866 g	0.0141988	0.000033
Weighing final mixture	2 pre-mixture	60.8340012 g	A,B	Normal	0.00224231 g	-0.157300	-0.000353
	N_2	1413.545029 g	A,B	Normal	0.02466512 g	0.006770	0.000167
Measurement of nitric acid		0.108 µmol/mol	A	Rectangular	0.021 µmol/mol	1	0.021
Verification		9.871 µmol/mol	A	Normal	0.031 µmol/mol	1	0.031
Stability		9.871 µmol/mol	A	Normal	0.058 µmol/mol	1	0.058
Combined standard uncertainty							0.069
Expanded uncertainty k=2							0.14

Uncertainty budget for NO_2 mole fraction for the cylinder № 5603778

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ μmol/mol
Purity of N_2		999998.67 μmol/mol	B	Rectangular	0.20 μmol/mol	0.0000035	0.0000007
Purity of O_2		999997.72 μmol/mol	B	Rectangular	0.05 μmol/mol	$2.2*10^{-9}$	$1.1*10^{-10}$
Purity of NO_2		997100 μmol/mol	B	Rectangular	128 μmol/mol	0,0000128	0.00164
Weighing 1 stage premixture (≈1 %)	NO_2	7.91559621 g	A,B	Normal	0.002001 g	-1.244906	-0.002491
	N_2	478.1069511 g	A,B	Normal	0.009263 g	0.020612	0.000191
Weighing 2 stage premixture (240 $\mu mol/mol^{-1}$)	1 pre-mixture	17.8380632 g	A,B	Normal	0.00225550 g	-0.547781	-0.001236
	N_2	689.7729231 g	A,B	Normal	0.01320346 g	0.013788	0.000182
	O_2	18.97975707 g	A,B	Normal	0.00232722 g	0.013718	0.000032
Weighing final mixture	2 pre-mixture	31.4364260 g	A,B	Normal	0.00268348 g	-0.305541	-0.000820
	N_2	730.1283266 g	A,B	Normal	0.01378776 g	0.013155	0.000181
Measurement of nitric acid		0.050 μmol/mol	A	Rectangular	0.010 μmol/mol	1	0.010
Verification		9.967 μmol/mol	A	Normal	0.031	1	0.031
Stability		9.967 μmol/mol	A	Normal	0.058	1	0.058
Combined standard uncertainty							0.067
Expanded uncertainty k=2							0.13

A4. Description of the procedure used during the gas analysis

A4.1 The procedure for measuring of absorption spectra

The measurements were carried out by means of FTIR spectrometer FSM 1201 (Russia) in a multi-pass gas cell with an optical path length of 4.8 m. Spectral resolution was 1 cm^{-1}.

Prior to each measurement the cell was evacuated, then it was filled with a gas mixture and purged at a flow rate of ~ 0.8 L/min. The single beam spectrum of a sample (which included 16 scans accumulated for 1 min) was recorded after 2 minutes of purging the cell with a gas mixture.

In order to obtain the absorption spectrum of the analyzed sample relative to the vacuum, the single beam spectrum of the cell with the gas mixture was divided by a similar spectrum of the evacuated cell, measured immediately before its filling.

One measuring series included 5 measuring cycles carried out under the same environmental conditions.

6 series were carried out for APEX614632 cylinder and 5 – for cylinder № 5603778.

A4.2 Calculation of nitrogen dioxide mole fraction in stability measurements

The obtained spectra were analyzed for NO_2 content in the spectral range 1560-1650 cm^{-1} by the classic least square method. The response of the spectrometer was defined as the ratio of absorption of the sample spectrum to absorption of a standard NO_2 spectrum.

Based on the results of the analysis, the response per unit of amount of substance fraction (specific response) *a* was calculated

$$a = \frac{A}{C_{grav} \times K} \quad (1)$$

where A – response of spectrometer, a.u;

C_{grav} – NO_2 mole fraction in the gas mixture in accordance with gravimetric data, μmol/mol;

K – coefficient correcting for the difference between the measurement and standard conditions

$$K = \frac{P_m \times 293{,}15}{T_m \times 101{,}325} \quad (2)$$

where P_m and T_m – pressure and temperature of the gas mixture in the gas cell during measurements.

The mean value of the specific response $\bar{a}$ obtained within one measurement series and the corresponding value of the relative standard deviation $s_{\bar{a}}$ were calculated. The values of $s_{\bar{a}}$, typically, were in the range of 0.1-0.2 %, while the scattering of $\bar{a}$ values between different series was on the level of 1 %.

Each cylinder was tested for a correlation between the $\bar{a}$ values and the storage time of the cylinder using the F-test during the observation period – 20/03/2018 – 19/04/2018.

As a result of the test, the hypothesis of a linear relationship between the $\bar{a}$ values and the storage time of the cylinder was rejected.

Note – Later investigations (during 4 month) on the some cylinders from the same batch showed long term instability at the early stage with the rate of degradation about 40 ppb/month. This effect was not observed in 1 month period (showed above) as it was lower than scattering of the results between series.

Nitrogen dioxide mole fraction in the investigated cylinders was calculated in accordance with the equations (3) and (5)

For the assigned value C'

$$C' = C_{grav} - C_{HNO3} \quad (3)$$

The response per unit of amount of substance fraction a' taking into account detected nitric acid

$$a' = \frac{A}{C' \times K} \quad (4)$$

For the stability measurement series value of nitrogen dioxide mole fraction C_i

$$C_{i,1(2)} = \frac{\bar{A}_{i,1(2)} / K_i}{\bar{a}'_{2(1)}} \quad (5)$$

where $\bar{A}_{i,1(2)}$ – mean response of spectrometer for the cylinder 1 (2) for i measurement series, a.u.;

K_i – coefficient correcting for the difference between the measurement and standard conditions in the i series;

$\overline{\overline{a'}}_{2(1)}$ – mean specific response for all measurement series for cylinder 2 or 1, respectively, taking into account correction for HNO_3 content, a.u./(µmol/mol). (The mean specific response for all measurement series for one cylinder was used for calculations of NO2 amount fraction in the other).

A5. Complementary information on the cylinders

A5.1 Brief outline of the dilution series undertaken to produce the final mixtures
Preparation of final mixtures was carried out from pure substances in accordance with ISO 6142 in 3 stages:

1-st stage – 3 mixtures NO_2/N_2 –level 1 %;

2-nd stage –3 mixtures $NO_2/(N_2+O_2)$ – level 240 µmol/mol;

3-nd stage –5 target mixtures $NO/(N_2+O_2)$ - 10 µmol/mol.

All the mixtures were prepared in Luxfer cylinders with Quantum or Aculife III + IV coating (V= 5 L or 10 L)

Verification for all the mixtures was carried out on of FTIR spectrometer FSM 1201.

A5.2 Please report the value of the pressure left in the cylinder before shipment to the BIPM:

Serial number of cylinder	APEX 614632 (V=10 L)	5603778 (V=5L)
Cylinder pressure as sent to BIPM	80 bar	100 bar

A5.3 If any other component other than NO2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Cylinder 1 **(№ APEX 614632)**

Date	Component	Mole fraction / nmol/mol	Expanded Uncertainty/ nmol/mol	Coverage factor	Measurement technique

15.03 - 18.04.2018	HNO_3	108	36	2	FTIR

Cylinder 2 (№ 5603778)

Date	Component	Mole fraction /nmol/mol	Expanded Uncertainty nmol/mol	Coverage factor	Measurement technique
16.03 - 19.04.2018	HNO_3	50	17	2	FTIR

Analysis of the HNO3

The analysis of mixtures for nitric acid content was carried out in the range 1200-1400 cm^{-1} by the classic least squares method using the spectrometer software. Calibration curve for HNO_3 was constructed on the basis of synthetic spectra calculated using the HITRAN database. Spectra containing the results of accumulation of 160 scans within 10 minutes were used for the analysis. The standard deviation of the noise level for the baseline of these spectra was typically equal to 1.5×10^{-4} abs_{10}.

Date: 16/07/2018

Authors: L.A. Konopelko, Y.A. Kustikov, A.V. Kolobova, V.S. Ballandovich, O.V. Efremova

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures

Chemistry Department

Pavillon de Breteuil

92312 Sèvres Cedex, France.

Study Coordinator: Edgar Flores

BIPM Chemistry Department

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Return of the form:

Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol. Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	D.I. Mendeleyev Institute for Metrology (VNIIM)		
Address	19 Moskovsky pr., St. Petersburg, 190005, Russia		
Contact person	Leonid Konopelko		
Telephone	+7 812 315 11 45	Fax	+7 812 315 15 17
Email*	fhi@b10.vniim.ru		
Serial number of cylinder received	APEX 614632 (V=10 L)		5603778 (V=5L)
Cylinder pressure as received			

A2. Results

Cylinder 1 (№ APEX 614632) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
Preparation	15.03.18	9.979	0.007	2
Stability1 (Verification1)	20.03.18	9.89	0.14	2
Stability2 (Verification2)	04.04.18	9.95	0.14	2
Stability3 (Verification3)	18.04.18	9.89	0.14	2
Assigned (best) value*	20.04.18	**9.87**	0.14	2

Cylinder 2 (№ 5603778) – Before shipping to the BIPM

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
Preparation	16.03.18	10.017	0.007	2
Stability1 (Verification1)	21.03.18	9.92	0.13	2
Stability2 (Verification2)	05.04.18	9.98	0.13	2
Stability3 (Verification3)	19.04.18	9.93	0.13	2
Assigned (best) value*	20.04.18	**9.97**	0.13	2

***Assigned (best) value – Gravimetric value taking into account the measured content of HNO_3**

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	16.07.2019	9.81	0.15	2
(Stability 5)	28.08.2019	9.75	0.15	2
(Stability 6)	17.09.2019	9.74	0.15	2

Cylinder 2- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	16.07.2019	9.77	0.15	2
(Stability 5)	28.08.2019	9.76	0.15	2
(Stability 6)	17.09.2019	9.75	0.15	2

Note

The procedure for stabity 4,5,6 measurements was similar to that described in A4. Nitrogen dioxide mole fraction C_i (µmol/mol) for i measurement series was calculated in accordance with formula: $C_i = \frac{\overline{A}_i / K_i}{\overline{\overline{a'}}}$, where $\overline{A}_i$ – mean response of spectrometer for the cylinder for i measurement series, a.u.; K_i – coefficient correcting for the difference between the measurement and standard conditions; $\overline{\overline{a'}}$ – mean specific response for all measurement series before shipment to BIPM with correction for HNO_3 content, a.u./(µmol/mol).

№	Uncertainty source	Type of evaluation	Standard uncertainty, µmol/mol
1	Measurements of $\overline{A}_i$	A	0,030
2	Estimate of K	B	0,017
3	Measurements of $\overline{\overline{a'}}$	A	0,068
	Combined standard uncertainty		0,076
	Expanded uncertainty (k=2)		0,15

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

Uncertainty budget for NO_2 mole fraction for the cylinder № APEX 614632

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ μmol/mol
Purity of N_2		999998.67 μmol/mol	B	Rectangular	0.20 μmol/mol	0.0000035	0.0000007
Purity of O_2		999997.72 μmol/mol	B	Rectangular	0.05 μmol/mol	$2.2*10^{-9}$	$1.1*10^{-10}$
Purity of NO_2		997100 μmol/mol	B	Rectangular	128 μmol/mol	0,0000128	0.00164
Weighing 1 stage premixture (≈1 %)	NO_2	7.91559621 g	A,B	Normal	0.002001 g	-1.240222	-0.002481
	N_2	478.1069511 g	A,B	Normal	0.009264 g	0.020533	0.000190
Weighing 2 stage premixture (240 μmol/mol^{-1})	1 pre-mixture	17.1116594 g	A,B	Normal	0.00225268 g	-0.568934	-0.001282
	N_2	663.7317226 g	A,B	Normal	0.0121975 g	0.014272	0.000174
	O_2	18.48796242 g	A,B	Normal	0.00230866 g	0.0141988	0.000033
Weighing final mixture	2 pre-mixture	60.8340012 g	A,B	Normal	0.00224231 g	-0.157300	-0.000353
	N_2	1413.545029 g	A,B	Normal	0.02466512 g	0.006770	0.000167
Measurement of nitric acid		0.108 μmol/mol	A	Rectangular	0.021 μmol/mol	1	0.021
Verification		9.871 μmol/mol	A	Normal	0.031 μmol/mol	1	0.031
Stability		9.871 μmol/mol	A	Normal	0.058 μmol/mol	1	0.058
Combined standard uncertainty							0.069
Expanded uncertainty k=2							0.14

Uncertainty budget for NO_2 mole fraction for the cylinder № 5603778

Uncertainty source X_i		Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ μmol/mol
Purity of N_2		999998.67 μmol/mol	B	Rectangular	0.20 μmol/mol	0.0000035	0.0000007
Purity of O_2		999997.72 μmol/mol	B	Rectangular	0.05 μmol/mol	$2.2*10^{-9}$	$1.1*10^{-10}$
Purity of NO_2		997100 μmol/mol	B	Rectangular	128 μmol/mol	0,0000128	0.00164
Weighing 1 stage premixture (≈1 %)	NO_2	7.91559621 g	A,B	Normal	0.002001 g	-1.244906	-0.002491
	N_2	478.1069511 g	A,B	Normal	0.009263 g	0.020612	0.000191
Weighing 2 stage premixture (240 $\mu mol/mol^{-1}$)	1 pre-mixture	17.8380632 g	A,B	Normal	0.00225550 g	-0.547781	-0.001236
	N_2	689.7729231 g	A,B	Normal	0.01320346 g	0.013788	0.000182
	O_2	18.97975707 g	A,B	Normal	0.00232722 g	0.013718	0.000032
Weighing final mixture	2 pre-mixture	31.4364260 g	A,B	Normal	0.00268348 g	-0.305541	-0.000820
	N_2	730.1283266 g	A,B	Normal	0.01378776 g	0.013155	0.000181
Measurement of nitric acid		0.050 μmol/mol	A	Rectangular	0.010 μmol/mol	1	0.010
Verification		9.967 μmol/mol	A	Normal	0.031	1	0.031
Stability		9.967 μmol/mol	A	Normal	0.058	1	0.058
Combined standard uncertainty							0.067
Expanded uncertainty k=2							0.13

A4. Description of the procedure used during the gas analysis

A4.1 The procedure for measuring of absorption spectra

The measurements were carried out by means of FTIR spectrometer FSM 1201 (Russia) in a multi-pass gas cell with an optical path length of 4.8 m. Spectral resolution was 1 cm^{-1}.

Prior to each measurement the cell was evacuated, then it was filled with a gas mixture and purged at a flow rate of ~ 0.8 L/min. The single beam spectrum of a sample (which included 16 scans accumulated for 1 min) was recorded after 2 minutes of purging the cell with a gas mixture.

In order to obtain the absorption spectrum of the analyzed sample relative to the vacuum, the single beam spectrum of the cell with the gas mixture was divided by a similar spectrum of the evacuated cell, measured immediately before its filling.

One measuring series included 5 measuring cycles carried out under the same environmental conditions.

6 series were carried out for APEX614632 cylinder and 5 – for cylinder № 5603778.

A4.2 Calculation of nitrogen dioxide mole fraction in stability measurements

The obtained spectra were analyzed for NO_2 content in the spectral range 1560-1650 cm^{-1} by the classic least square method. The response of the spectrometer was defined as the ratio of absorption of the sample spectrum to absorption of a standard NO_2 spectrum.

Based on the results of the analysis, the response per unit of amount of substance fraction (specific response) *a* was calculated

$$a = \frac{A}{C_{grav} \times K} \quad (1)$$

where A – response of spectrometer, a.u;

C_{grav} – NO_2 mole fraction in the gas mixture in accordance with gravimetric data, μmol/mol;

K – coefficient correcting for the difference between the measurement and standard conditions

$$K = \frac{P_m \times 293{,}15}{T_m \times 101{,}325} \quad (2)$$

where P_m and T_m – pressure and temperature of the gas mixture in the gas cell during measurements.

The mean value of the specific response $\bar{a}$ obtained within one measurement series and the corresponding value of the relative standard deviation $s_{\bar{a}}$ were calculated. The values of $s_{\bar{a}}$, typically, were in the range of 0.1-0.2 %, while the scattering of $\bar{a}$ values between different series was on the level of 1 %.

Each cylinder was tested for a correlation between the $\bar{a}$ values and the storage time of the cylinder using the F-test during the observation period – 20/03/2018 – 19/04/2018.

As a result of the test, the hypothesis of a linear relationship between the $\bar{a}$ values and the storage time of the cylinder was rejected.

Note – Later investigations (during 4 month) on the some cylinders from the same batch showed long term instability at the early stage with the rate of degradation about 40 ppb/month. This effect was not observed in 1 month period (showed above) as it was lower than scattering of the results between series.

Nitrogen dioxide mole fraction in the investigated cylinders was calculated in accordance with the equations (3) and (5)

For the assigned value C'

$$C' = C_{grav} - C_{HNO3} \quad (3)$$

The response per unit of amount of substance fraction a' taking into account detected nitric acid

$$a' = \frac{A}{C' \times K} \quad (4)$$

For the stability measurement series value of nitrogen dioxide mole fraction C_i

$$C_{i,1(2)} = \frac{\bar{A}_{i,1(2)} / K_i}{\bar{\bar{a}}'_{2(1)}} \quad (5)$$

where $\bar{A}_{i,1(2)}$ – mean response of spectrometer for the cylinder 1 (2) for i measurement series, a.u.;

K_i – coefficient correcting for the difference between the measurement and standard conditions in the i series;

$\overline{\overline{a'}}_{2(1)}$ – mean specific response for all measurement series for cylinder 2 or 1, respectively, taking into account correction for HNO_3 content, a.u./(µmol/mol). (The mean specific response for all measurement series for one cylinder was used for calculations of NO2 amount fraction in the other).

A5. Complementary information on the cylinders

A5.1 Brief outline of the dilution series undertaken to produce the final mixtures
Preparation of final mixtures was carried out from pure substances in accordance with ISO 6142 in 3 stages:

1-st stage – 3 mixtures NO_2/N_2 –level 1 %;

2-nd stage –3 mixtures $NO_2/(N_2+O_2)$ – level 240 µmol/mol;

3-nd stage –5 target mixtures $NO/(N_2+O_2)$ - 10 µmol/mol.

All the mixtures were prepared in Luxfer cylinders with Quantum or Aculife III + IV coating (V= 5 L or 10 L)

Verification for all the mixtures was carried out on of FTIR spectrometer FSM 1201.

A5.2 Please report the value of the pressure left in the cylinder before shipment to the BIPM:

Serial number of cylinder	APEX 614632 (V=10 L)	5603778 (V=5L)
Cylinder pressure as sent to BIPM	80 bar	100 bar

A5.3 If any other component other than NO2, nitrogen and oxygen was detected and/or quantified please report its mole fraction in the table below:

Cylinder 1 **(№ APEX 614632)**

Date	Component	Mole fraction / nmol/mol	Expanded Uncertainty/ nmol/mol	Coverage factor	Measurement technique
15.03 - 18.04.2018	HNO_3	108	36	2	FTIR

Cylinder 2 (№ 5603778)

Date	Component	Mole fraction /nmol/mol	Expanded Uncertainty nmol/mol	Coverage factor	Measurement technique
16.03 - 19.04.2018	HNO_3	50	17	2	FTIR

Analysis of the HNO3

The analysis of mixtures for nitric acid content was carried out in the range 1200-1400 cm^{-1} by the classic least squares method using the spectrometer software. Calibration curve for HNO_3 was constructed on the basis of synthetic spectra calculated using the HITRAN database. Spectra containing the results of accumulation of 160 scans within 10 minutes were used for the analysis. The standard deviation of the noise level for the baseline of these spectra was typically equal to 1.5×10^{-4} abs_{10}.

Date: 16/07/2018

Authors: L.A. Konopelko, Y.A. Kustikov, A.V. Kolobova, V.S. Ballandovich, O.V. Efremova

VSL

Before shipping to the BIPM

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures

Chemistry Department

Pavillon de Breteuil

92312 Sèvres Cedex, France.

Study Coordinator:

Edgar Flores

BIPM Chemistry Department

Phone: +33 (0)1 45 07 70 92

Fax: +33 (0)1 45 34 20 21

email: edgar.flores@bipm.org

Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol.

Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	VSL		
Address	Thijsseweg 11 2629 JA Delft The Netherlands		
Contact person	Iris de Krom		
Telephone	0031 15 269 1754	Fax	
Email*	idekrom@vsl.nl		
Serial number of cylinder received	VSL105804 VSL105806		
Cylinder pressure as received	109 and 110 bar respectively		

A2. Results

Cylinder 1 – Before shipping to the BIPM (VSL105804)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	12-12-2017	10.005	0.0023	$k = 2$
(Stability 1)	5-1-2018	9.883	0.1	$k = 2$
(Stability 2)	1-3-2018	9.851	0.1	$k = 2$
(Stability 3)	28-3-2018	9.906	0.1	$k = 2$

Cylinder 2– Before shipping to the BIPM (VSL105806)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	12-12-2017	10.001	0.0023	$k = 2$
(Stability 1)	5-1-2018	9.883	0.1	$k = 2$
(Stability 2)	1-3-2018	9.851	0.1	$k = 2$
(Stability 3)	28-3-2018	9.847	0.1	$k = 2$

Cylinder 1- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				

Cylinder 2- Post BIPM measurements

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)				

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

A4. Description of the procedure used during the gas analysis

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

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:

Cylinder 1 (VSL105804)

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty / nmol/mol	Coverage factor	Measurement technique
17-1-2018	HNO_3	70	6	$k = 2$	CRDS
28-2-2018	HNO_3	78	7	$k = 2$	CRDS
29-3-2018	HNO_3	113	10	$k = 2$	CRDS

Cylinder 2 (VSL105806)

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
17-1-2018	HNO_3	80	7	$k = 2$	CRDS
28-2-2018	HNO_3	81	7	$k = 2$	CRDS
29-3-2018	HNO_3	113	10	$k = 2$	CRDS

[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.

Post BIPM measurements

Key comparison CCQM-K74.2018 – Nitrogen dioxide in Nitrogen (10 µmol/mol)

Result form CCQM-K74.2018-R

Project name: CCQM-K74.2018 (Nitrogen dioxide in Nitrogen 10 µmol/mol).

Comparison: Comparison of laboratories' capabilities for the measurement of the nitrogen dioxide mole fraction in nitrogen.

Proposed dates: 2018.

Coordinating laboratory:

Bureau International des Poids et Mesures

Chemistry Department

Pavillon de Breteuil

92312 Sèvres Cedex, France.

Study Coordinator:

Edgar Flores

BIPM Chemistry Department

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Return of the form:
Please complete and return the form preferably by email to edgar.flores@bipm.org

This protocol aims to evaluate the level of compatibility of NMI capabilities for value assigning nitrogen dioxide (NO_2) in nitrogen standards at a nominal mole fraction of 10 µmol/mol.

Participation in this protocol is primarily intended to underpin laboratories' CMC claims.

A1. General information

Institute	VSL		
Address	Thijsseweg 11 2629 JA Delft The Netherlands		
Contact person	Iris de Krom		
Telephone	0031 15 269 1754	Fax	
Email*	idekrom@vsl.nl		
Serial number of cylinder received	VSL105804 VSL105806		
Cylinder pressure as received	109 and 110 bar respectively		

A2. Results

Cylinder 1 – Before shipping to the BIPM (VSL105804)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	12-12-2017	x_{NOx}(grav) 10.005 x_{NO2} 9.903	0.004 0.018	$k = 2$ $k = 2$
(Stability 1)	5-1-2018	9.875	0.14	$k = 2$
(Stability 2)	1-3-2018	9.856	0.14	$k = 2$
(Stability 3)	28-3-2018	9.903	0.14	$k = 2$

Cylinder 2– Before shipping to the BIPM (VSL105806)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Preparation)	12-12-2017	x_{NOx}(grav) 10.001 x_{NO2} 9.899	0.004 0.018	k = 2 k = 2
(Stability 1)	5-1-2018	9.875	0.14	k = 2
(Stability 2)	1-3-2018	9.846	0.14	k = 2
(Stability 3)	28-3-2018	9.844	0.14	k = 2

Cylinder 1- Post BIPM measurements (VSL105804)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	21-5-2019	9.785	0.14	k = 2
(Stability 5)	25-6-2019	9.850	0.14	k = 2
(Stability 6)	25-7-2019	9.834	0.14	k = 2

Cylinder 2- Post BIPM measurements (VSL105806)

Description of measurement	Date of measurement	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol	Coverage factor
(Stability 4)	21-5-2019	9.775	0.14	k = 2
(Stability 5)	25-6-2019	9.800	0.14	k = 2
(Stability 6)	25-7-2019	9.754	0.14	k = 2

Proposal reference value

Cylinder	Nitrogen dioxide mole fraction x_{NO2} / µmol/mol	Expanded uncertainty $U(x_{NO2})$ / µmol/mol
Cylinder 1 (VSL105804)	9.851	0.14
Cylinder 1 (VSL105806)	9.816	0.14

The proposed reference value is determined from the average of the 6 stability measurements.

A3. Uncertainty Budget

Please provide a complete uncertainty budget.

$x(NO_2) = x(NO_x) – x(HNO_3) – 2\ x(N_2O_4)$

Measurand	Value	Distribution	Relative standard uncertainty (%)	Sensitivity
$x(NO_x)$	10 µmol mol^{-1}	Normal	0.023	1
$x(HNO_3)$	0.14 µmol mol^{-1}	Normal	8.7	-1
$x(N_2O_4)$	0.001 µmol mol^{-}	Normal	2.5	-2

	[1]			
Stability		Normal	0.4	1
Between cylinder effects		Normal	0.5	1
Verification		Normal	0.25	1
$x(NO_2)$	**10 µmol mol^{-1}**	Normal	**0.7**	

$x(NO_x)$ represents the gravimetric amount fraction calculated according to ISO 6142-1:2015. The gravimetric amount fraction has been corrected for the HNO_3 amount fraction ($x(HNO_3)$), according to analysis, and the N_2O_4 amount fraction ($x(N_2O_4)$), calculated based on literature*. The corrected mole fractions and the responses are used to calculate the amount fraction of the K74 gas mixtures according to ISO 6143:2001. The uncertainty of the stability has been determined using the DerSimonian-Laird model. The square root of the excess variance is taken as uncertainty contribution due to instability of the total amount fraction NO_x (and the amount fraction NO_2). Between cylinder effects have been determined based on results of four gas mixtures containing approximately 10 µmol mol^{-1} NO_x in N_2.

The expanded relative uncertainty of the 10 µmol mol^{-1} amount fraction NO_2 is 1.4% (k = 2).

* Hurtmans, D., Herman, M., & Vander Auwera, J. (1993). Integrated band intensities in N_2O_4 in the infrared range. Journal of Quantitative Spectroscopy and Radiative Transfer, 50(6), 595-602.

A4. Description of the procedure used during the gas analysis

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

For the analysis an ABB LIMAS ND-UV analyser has been used. During one measurement at least 5 static Primary Standard Materials (PSM), prepared according to ISO 6142-1:2015, have been analysed to calibrate the analyser in the range of 100 – 10 x 10^{-6} mol mol^{-1} NO_2 in N_2. A quadratic curve model has been applied. The cylinder has been equipped with a stainless steel pressure regulator and the regulator is flushed prior to use. Only a single pressure regulator is used for all cylinders, after analysis the regulator is connected to the next cylinder. The measurements are conducted manually by connecting the gas mixtures to the analyser using short pieces of PTFE tubing. A flow of 800 ml/min, controlled by a Bronkhorst mass flow controller, is led to the monitor. On the same day as the PSMs the gas mixtures for the K74 have been analysed. The response of the analyser is stabilised for 30 – 60 minutes after which the average response over the next 5 minutes is recorded.

[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.

A5. Complementary information on the cylinder

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

Cylinder 1 (VSL105804) contained 109 bar and cylinder 2 (VSL105806) 110 bar 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:

Cylinder 1 (VSL105804)

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty / nmol/mol	Coverage factor	Measurement technique
17-1-2018	HNO_3	70	12	$k = 2$	CRDS
28-2-2018	HNO_3	78	14	$k = 2$	CRDS
29-3-2018	HNO_3	113	20	$k = 2$	CRDS
31-5-2019	HNO_3	138	24	$k = 2$	CRDS
23-8-2019	HNO_3	141	25	$k = 2$	CRDS
28-8-2019	HNO_3	143	25	$k = 2$	CRDS

Cylinder 2 (VSL105806)

Date	Component	Mole fraction / nmol/mol	Expanded uncertainty	Coverage factor	Measurement technique
17-1-2018	HNO_3	80	14	$k = 2$	CRDS
28-2-2018	HNO_3	81	14	$k = 2$	CRDS
29-3-2018	HNO_3	113	20	$k = 2$	CRDS
31-5-2019	HNO_3	141	25	$k = 2$	CRDS
23-8-2019	HNO_3	151	26	$k = 2$	CRDS
28-8-2019	HNO_3	144	25	$k = 2$	CRDS